

APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE
IN
THE STUDY OF CONJUGATED SYSTEMS

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by

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P R E F A C E

The importance of conjugation and hyperconjugation in unsaturated systems like butadiene and propylene, for which only one unexcited resonance structure can be written, is now a controversial matter. This thesis describes investigations that have been made in an effort to obtain further evidence which might help resolve this controversy. The development of the concepts of conjugation and hyperconjugation and the evidence in favour of and against the latter are briefly reviewed to furnish the necessary background for the work described. The technique of employing proton chemical shifts in a special type of sterically hindered system for the study of resonance interactions between donor and acceptor groups across the benzene ring is described and the significance of the results obtained for a series of derivatives is discussed. The effort that has been made to evaluate the substituent constants of the NH_3^+ and NMe_3^+ groups which can help evaluation of steric effects in this study is described next. In a parallel study of the derivatives employed in the investigation mentioned and other related derivatives, the IR vibrational band intensities have been measured to get supporting evidence although the title of the thesis mentions only NMR methods. The methyl band width data are

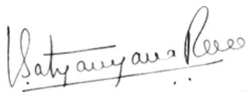
considered next and their usefulness for the study of changes in π -electron distribution in donor-acceptor systems. The NMR spectra of a number of boron fluoride adducts of some substituted benzaldehydes are described and the information that can be obtained from these on substituent effects is evaluated.

I take this opportunity to express my deep sense of gratitude to Dr. P. Madhavan Nair, Scientist, National Chemical Laboratory, Poona, for suggesting this problem and for his inspiring guidance and supervision during the course of these investigations.

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(V. Satyanarayana Rao)

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CHAPTER I

CONJUGATION AND HYPERCONJUGATION - A REVIEW

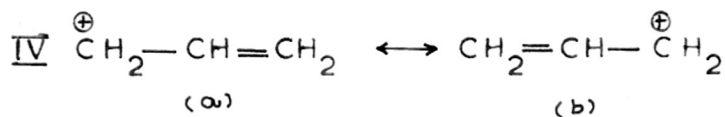
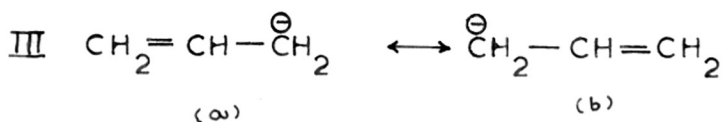
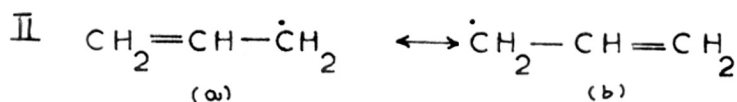
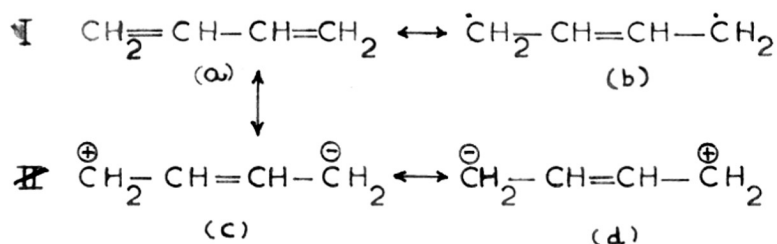
CONJUGATION AND HYPERCONJUGATION

The concept of conjugation in unsaturated organic compounds was introduced many years ago to account for the special properties shown by systems like butadiene, hexatriene, acrylonitrile or vinyl acetylene in which multiple bonds alternate with single bonds. Although this concept can be traced back to the work of Michael¹, Thiele², Flurscheim^{3,4} and others, it was clearly formulated in electronic terms for the first time by Robinson⁵, Ingold^{6,7} and their co-workers. Later, with the advent of quantum chemistry, this notion was laid on a firm theoretical foundation. It became apparent that the special properties of conjugated systems were attributable to the presence of "delocalized" π -electrons in "Molecular orbitals"; or speaking in terms of valence bond description of molecules, these were traceable to resonance between various canonical structures, that may be written for these systems⁸.

The accepted position in the nineteen thirties regarding the concept of conjugation and effects of polar groups in conjugated systems may be stated as follows:

When the principal classical structure contains single bonds, each interposed between two multiple bonds,

or one side having a π -electron, a π -electron pair or quartet or at least a π -electron vacancy and a multiple bond on the other, the species is said to be conjugated⁹. This can be illustrated with the help of the following species which are stabilized by resonance between various structures as shown in I, II, III and IV.

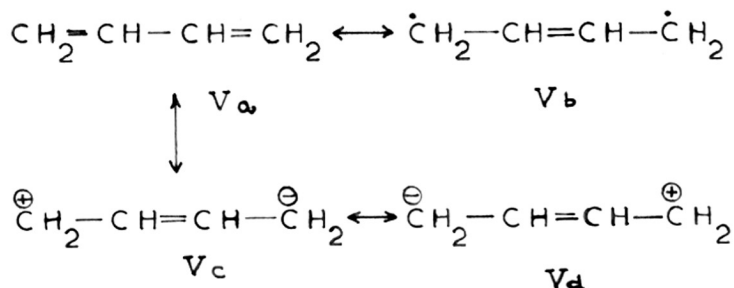


The difficulties that conjugated systems always presented when their properties were considered from the

view point of the classical valence theory, disappeared in the light of this formulation. These properties could not be uniquely represented by a conventional valency structure, in which each carbon atom forms two single bonds and one double bond. But when all the valence structures were taken into account, the physical and chemical behaviours of these systems could be readily rationalized. In the ordinary double bond, the overlap between the orbitals of the π -electrons on the adjacent carbon atoms provides both the extra strength of the double bond and also its resistance to free rotation. In a conjugated system, since the smearing out or "delocalization" of π -electrons would result in bonds of intermediate character, barriers to rotation about bonds, which are single in the classical formulation could be explained readily⁸.

In the flush of the success of the resonance theory, its application was grossly oversimplified. The number of resonance structures that one could write for a system was often used without any clear reference to their contributions as a measure of resonance energy. Actually resonance theory requires that, in order for resonance stabilization to be appreciable, the contributing structures should not differ very much from one another in

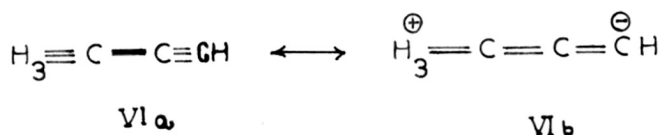
energy. Also, it was often difficult to guess correctly the relative magnitudes of the energies of the contributing structures, so that inferences on resonance stabilization did not have proper foundations. For example, in the case of butadiene, the shortening of the C₂-C₃ bond was attributed to resonance between structures like (Va to Vd).



It was not until the end of nineteen forties that doubts were raised on the validity of such naive interpretations. The work of Hans Kuhn¹⁰ and others¹¹ on the absorption spectra of polyenes during the period showed the necessity for the alternation of single and double bonds in polyenes. The importance of conjugation thus seemed to be less than that assumed from empirical considerations.

In the nineteen thirties some important observations

were made on the influence of alkyl groups in conjugated systems. Herzberg¹², Badger¹³ and their collaborators found that the C-C bond length in methylacetylene is 1.46 Å only, which is shorter than the normal C-C bond length of 1.54 Å in ethane. Pauling and co-workers¹⁴ suggested that the decrease from the normal value of 1.54 Å for a single bond in methylacetylene and methylcyanide (1.49 Å) is partly due to change in the single bond radius and mainly due to the partial double bond character of the single bond, arising from resonance of the type indicated below:

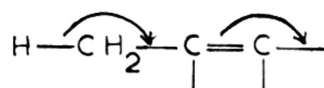


But in the case of propylene, no significant shortening was apparent for the CH₃-C bond. The shortening being only 0.03 Å, was considered to be well within the experimental error¹⁵. In this connection Walsh¹⁶ pointed out the fact that shortening is marked and abrupt in passing from HC₂ to H-C₂ in the series methane, ethylene and acetylene, in which there is no conjugation. It could be marked even in the passage from CH₃-C = to CH₃-C ≡ for similar reasons.

The introduction of alkyl substituents in place of hydrogen normally affects the rates and equilibria of chemical reactions and in a number of cases the relative effects of different alkyl groups follow the inductive order ($\text{CH}_3 < \text{C}_2\text{H}_5 < \text{CH}(\text{CH}_3)_2 < \text{C}(\text{CH}_3)_3$). In 1935, Baker and Nathan¹⁷ found that in the reaction of p-alkylbenzylbromides with pyridine in dry acetone, the relative effects of alkyl groups ~~was~~^{were} almost in the opposite order. It appeared that an alternative mode of electron release was operating in this reaction, the donor action decreasing in the order $\text{Me} > \text{Et} > \text{i-Pr} > \text{t-Bu}$. The mechanism of electron release in this case was later recognized to be electromeric in nature and the reactivity order mentioned is called the Baker-Nathan order. Mulliken¹⁸ studied the absorption spectra of cyclopentadiene and a number of related compounds and found that there is a displacement of the absorption towards longer wavelengths in the case of cyclopentadiene as compared to the open-chain conjugated dienes. He found that the abnormal behaviour can be satisfactorily accounted for, if the methylene group can be treated as a system having one σ -bond and one quasi π -bond in the molecular orbital description of these systems. In the context of his own observations and those of the others mentioned above, Mulliken designated such interactions

of methyl and methylene groups as "hyperconjugation" following a suggestion from Brown (W.G.).

Hyperconjugation can be defined in a rather simple way as the power of alkyl groups to conjugate with multiple bonds. Considering the Baker-Nathan order in the light of this definition, the methyl group attached to an unsaturated system, permits electron release by what is essentially a type of electromeric effect.



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Such electron release will facilitate or retard a reaction depending on whether it is electron accession to or electron recession from the reaction centre that facilitates the reaction. It was considered that although the inductive effect of the t-butyl group is more than that of the methyl group, the new mode of electron release would not be possible in the former because the tertiary carbon atom would prevent the additional methyl groups from being part of the conjugated system¹⁹. The assumption here is that C-C bonds would not be effective in hyperconjugation. If the Baker-Nathan order predominates over the inductive

effect, the relative stabilities of *p*-alkyl benzaldehydes in relation to their cyanohydrins would be expected to diminish in the order $\text{Me} > \text{Et} > \text{i-Pr} > \text{t-Bu}$, because in the free aldehydes, conjugation extends to the sidechain carbonyl group so that the new effect stabilizes the free aldehyde to a greater extent than it would the cyanohydrin²⁰.

The application of the notion of hyperconjugation to a variety of chemical problems was discussed by Mulliken, Reike and Brown²¹. Ordinary conjugation causes shortening of single bonds and hyperconjugation should also change the length of C-C bonds that attach the alkyl groups to the unsaturated system. But since hyperconjugation is weaker than ordinary conjugation, appreciable changes are not likely to be produced. Benzene is the simplest case of bond shortening due to conjugation, in which all bonds are identical in length (1.39 Å). The shortening of bonds due to hyperconjugation may be well within the limits of experimental error, because electron delocalization occurs to a small extent only. Since conjugation as well as hyperconjugation alter the electron distribution in a molecule it would also affect its dipole moment. Whether the moment is increased or decreased depends on whether the conjugation or resonance moment is in the same or opposite direction to the normal moment. In *t*-butyl benzene the observed dipole

moment has been regarded as arising largely from the inductive effect of the t-butyl group, which has been assumed to exhibit no hyperconjugation²². Hyperconjugation is probably less in olefins than in aldehydes, because of the smaller polarization of the ethylenic bonds.

Alkyl groups on unsaturated carbon atoms reduce the heat of hydrogenation of an olefin. Delocalization, whenever it occurs, stabilizes the system and hence less heat will be evolved in the hydrogenation process than in the corresponding system which is not stabilized by conjugation. The observed progressive diminution of the heat of hydrogenation would, therefore, be consistent with the notion of hyperconjugation. As may be expected, the heat of hydrogenation of cyclopentadiene was found to be lower than that of butadiene¹⁸. Similarly small variations were noticed in the heats of hydrogenation of alkylbenzenes.

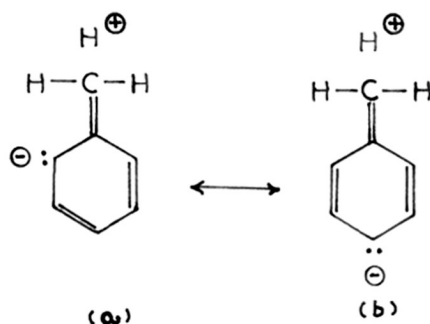
Ordinary conjugation is expected to result in displacement of absorption bands in electronic spectra towards longer wavelengths and so also hyperconjugation. Effects of hyperconjugation, though small in the ground state may be expected to be much more pronounced in the excited state of a molecule or in the transition state of a reaction^{19,23}. Mulliken suggested that about 0.14 ev of the total of 0.8 ev decrease in the ionization potential in passing from ethylene

to propylene is attributable to hyperconjugation.

The concept of hyperconjugation was found to be useful in discussing a large number of physical and chemical properties of alkyl substituted aromatic and unsaturated systems.

In toluene, the length of the C-H bonds of methyl group is increased by 0.001 Å, while the length of the C-Me bond is decreased appreciably (1.51 Å) compared to the normal C-C bond length of 1.54 Å. It was considered that at least half of the bond shortenings in toluene, methyl acetylene and acetonitrile were due to hyperconjugation²⁴.

The dipole moment of toluene is 0.4 D and the methyl group is positive with respect to the benzene ring²³. So, it was assumed that the electrons released by the alkyl groups are delocalized and that resonance between structures like VIIIa and VIIIb stabilizes the molecule²⁵.



VIII

Mayrot et al.²⁶ assumed the larger value for the dipole moment of methyl chloroform, compared to chloroform is due to hyperconjugation. In the case of trans-croton-aldehyde, there is an increase in the dipole moment (0.6 D), compared to acrolein (2.88 D)^{27,28}. Crawford²⁵ cited the case of methyl butadiene as further evidence of the polarity resulting from hyperconjugation.

The ionization potential of ethylene was reduced by the introduction of methyl substituents and the same effect was seen in other²⁹ unsaturated and aromatic compounds. This was taken as evidence for hyperconjugation in the positive ion formed by loss of an electron from a hydrocarbon. The argument^{was} based on the idea that hyperconjugation should be more important in the positive ion than in the neutral molecule from which it is derived; hyperconjugation would then reduce the energy of the positive ion more than that of the parent molecule so that the energy difference between the two (i.e. the ionization potential) would be decreased. The data show that the ionization potentials of radicals are consistent with the resonance interactions of hyperconjugative type. Ionization potentials, absorption spectra and chemical reactivity deal both with the ground and excited states of molecules.

A modification of the simple molecular orbital theory has been successfully applied to the treatment of ionization potentials of methyl substituted unsaturated molecules by Streitwieser and Nair³⁰. The calculations employed the hetero-atom model for the methyl group and it was found that the best agreement between calculated and experimental values were obtained when both inductive and hyperconjugative effects were allowed for. These calculations were indeed of a very approximate type and their shortcomings have been pointed out by Dewar. However, more sophisticated and recent all valence electron molecular orbital calculations indicate that hyperconjugation is significant in such systems.

Conjugated molecules such as butadiene absorb at much lower frequencies than simple olefins. With increasing conjugation the first $\pi \rightarrow \pi^*$ transition shifts progressively to lower frequencies so that long polyenes may absorb in the visible region and be coloured (e.g. the carotenoid pigments). This striking phenomena has been taken as an evidence³¹ for resonance interaction in conjugated polyenes, resonance being more important in the excited state than in the ground state.

The near ultraviolet absorption spectra of a series

of benzocyclo-alkenes were studied. A minimum frequency for the absorption bands in the series was observed at 270 m μ for benzocycloheptene. It appears significant that this same inflexion occurs in the solvolysis rates for the related benzhydryl halides. The data indicate that hyperconjugation³² plays an important role and an explanation has been offered in terms of Franck-Condon principle. Similarly, methyl substitution in benzene causes a shift of its absorption band towards longer wavelengths and an enhancement of its intensity. Molecular orbital calculations have led to the conclusion that the bathochromic shift of the 0,0 band results from hyperconjugation³³. The intensification of the transition by alkyl groups is associated with a transition moment produced by a migration of charge into the benzenoid ring^{34,35}. According to Mulliken³⁶ "the migration of unsaturation-electron charge implies hyperconjugation". Furthermore, the wavelengths as well as intensities of this band in alkyl benzenes decrease in the following order: toluene, ethylbenzene, isopropylbenzene, and t-butylbenzene. This order can be explained by a decrease in the contribution by hyperconjugation³⁷, although an alternative explanation has been proposed³⁸. Substituents capable of donating electrons to a conjugated system by resonance interaction shift the $n \rightarrow \pi^*$ transition to shorter wavelengths^{39,40}. In aliphatic

carbonyl compounds of the type $RCOR'$, Rao *et al.*⁴¹ found a large decrease in the wavelength in going from $R'=H$ to $R'=CH_3$. But a progressive increase in the wavelength was observed in the series Me, Et, i-Pr, t-Bu, suggesting electron release in the Baker-Nathan order and by implication hyperconjugation.

McCauley and Lein studied⁴² the protonation of 1,3,5-trialkylbenzenes in BF_3 -HF solution and concluded that C-H hyperconjugation is an important mode of electron release in the cation produced.

The Baker-Nathan order was found in a number of reactions¹⁹. Among the explanations offered for this, hyperconjugation was generally preferred to the others. Berliner⁴³ discussed the present status of the Baker-Nathan order in terms of current interpretations and suggested that hyperconjugation of C-H bonds provides the most consistent and satisfactory explanation for the behaviour of alkyl groups on benzene ring. Brown *et al.*⁴⁴ point out the importance of C-C hyperconjugation in the solvolysis of *p*-*t*-butylbenzylhalides. The relative importance of C-C and C-H hyperconjugation in the aliphatic and aromatic series was studied by Taft *et al.*^{45,46}.

The method of comparing secondary deuterium isotope effects on the rate of a number of different reactions was

applied by Shiner⁴⁷ for studying hyperconjugation with considerable success. Lewis's⁴⁸ observation on the isotope effect in the decomposition of 2-pentyl-chloro-sulfite led to the suggestion that the isotope effect measured the increase in hyperconjugation accompanying activation.

The evidence for the validity of conjugation and hyperconjugation from IR comes from the fact that the IR frequencies characteristic of stretching vibrations of C=O and C=C bonds are lowered by conjugation with phenyl or vinyl groups. This would be expected if resonance interactions should weaken double bonds. One would, on this basis, expect hyperconjugation to lead to a similar lowering of vibration frequencies in compounds with alkyl groups adjacent to a multiple bond. The evidence in this regard has been reviewed by Dewar⁶⁹ who has pointed out that it is not favourable. He has also pointed out that consideration of the evidence from IR is complicated by factors other than resonance. Vibration frequencies are sensitive to the inductive effects of substituents. The frequencies of IR bands correspond to frequencies of vibration of the whole molecule, not of individual bonds in it. Even if a given vibration is largely centered on a given bond, its frequency may still depend on the size,

shape and mass of adjacent groups.

One of the clearest pieces of evidence for hyperconjugation came from the hyperfine splittings observed in the electron spin resonance spectra of radicals⁴⁹. For the ethyl radical, for example, the hyperfine coupling constant for the β -protons were found to be of the same magnitude as for the α -protons. A similar effect was seen in other more complex radicals whenever methyl groups are attached at points where the odd electron density is appreciable⁵⁰⁻⁵⁴. This result is consistent with the "no bond" type of resonance as postulated by Wheland⁵⁵. Symons⁵⁶ recently reviewed the ESR evidence for hyperconjugation and expressed the opinion that hyperconjugation involving bonds other than C-H is also important. But, as will be seen later it will be unwise to generalize the importance of hyperconjugation on the strength of evidence pertaining to radicals alone.

A related piece of evidence is the observation of long range spin-spin coupling between vinylic (or aromatic) protons and protons of vinylic (or aromatic) methyl groups. In 1958, Hoffman⁵⁷ reported that the methyl groups of m-xylene and mesitylene are coupled to the ring protons with $J = 0.45$ and 0.62 cps respectively and suggested that

this long range spin-spin coupling is due to hyperconjugation between the π -orbitals of the benzene ring and the C-H bond orbitals of the methyl group. However, he could not satisfactorily account for the relatively large coupling constant for m-xylene. Gronowitz studied the long-range spin-spin coupling in methylthiophenes and thiophene thiols⁵⁸. He has argued that hyperconjugation is more in methylthiophenes than in the benzene analogues. This statement is apparently made on the basis of the magnitudes of the long-range coupling constants and is misleading. It is not clear at all why hyperconjugation energy - the stabilization resulting from hyperconjugation - is greater for methylthiophene than for toluene. Long range coupling of the S-H group of thiophene thiols with the ring protons was found to vary as expected from a conjugative mechanism⁵⁸. Kowalewski and Kowalewski^{59,60} proposed that a significant part of the long range coupling (0.4 to 0.9 cps) in N-methyl⁶¹ and N,N-dimethyl formamides⁶⁰ involves hyperconjugation since the long range spin-spin coupling in the N-methyl and N,N-dimethyl acetamides is not much smaller, having a value of 0.4 cps. In view of the approximate equality of the hyperfine coupling constants for the fragments C-H and C-CH₃ and also the molecular orbital⁶⁵⁻⁶⁸ description of the coupling in systems such as

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those studied by these workers, this result is only to be expected. Hyperconjugation for N-methyl groups was also studied by McLachlan⁶². Whipple et al.⁶³ studied the long-range couplings in haloallenes and found that both the non-equivalence of the protons and non-planar structure of the molecules should favour hyperconjugation in these systems. Pritchard and Gummer⁶⁴ considered that hyperconjugation is quite appreciable in allene.

Nuclear Quadrupole Resonance spectroscopic studies in benzylchlorides seem to indicate the existence of halide hyperconjugation in ground states of molecules.

Until about a decade ago the concept of hyperconjugation was rather well accepted. However, even during the period of its greatest popularity, it was not universally accepted⁶⁹. With the passage of time it became increasingly apparent that the phenomena that were explained earlier on the basis of hyperconjugation could be rationalized equally well by alternative postulates. We may consider a few of such alternative theories put forward.

In methyl acetylene⁷⁰ and derivatives of acetonitrile^{71,72} the C-C single bonds show a length of 1.46 Å, which is not dependent on the substituents on the sp³ carbon atom, even though simple electronegativity considerations would predict a variation of the bond lengths with the

substituent. In malononitrile⁷³ the C-C bond length is 1.46 Å and if the π -bonding caused by hyperconjugation were important, each C-C single bond should possess considerably less double bond character than in acetonitrile. So, the observed shortening of carbon sp-sp³ bond may not be the result of any kind of conjugation. Coulson^{74,75} suggested that about half of the shortening in bond lengths can be ascribed to changes in bond lengths with hybridization. Molecular orbital calculations⁷⁶ support the conclusions of Coulson. In cyclo-octa-tetraene, the non-planarity of any two double bonds largely prevents an extended conjugation and thus the resonance contribution⁷⁷ in the ground state is negligible. The lengths of the double bonds (1.337 Å) are in fact identical with the length of the C-C bond in ethylene, while the lengths of the single bonds (1.460 Å) are actually less than the length of the central bond in butadiene (1.483 Å). This evidence would appear to indicate that the central bond in butadiene is essentially a pure single bond without being conjugated to the rest of the molecule.

In a recent reconsideration of the importance of conjugation and hyperconjugation, Dewar and Schmeising⁷⁸ came to the conclusion that they are insignificant in the ground states of molecules, for which only one classical

(unexcited) resonance structure can be written. They showed that the C-C bond lengths in these systems are determined by the state of hybridization of the carbon atoms. The observed stabilization of such molecules is attributable to changes in bond energy associated with hybridization changes rather than to resonance. They also found that resonance stabilization plays a less important role than is generally believed even in benzene. If the π -electron resonance is unimportant in ordinary conjugation (as in butadiene) it should be much more so in hyperconjugation.

Bartell⁷⁹ has considered the effects of non-bonded interactions (repulsions) in systems for which hyperconjugation has been generally invoked for interpretation of properties.

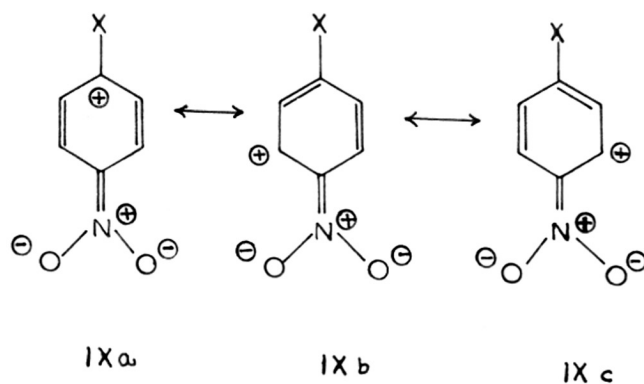
Dewar pointed^{69,80} out that the arguments in favour of conjugation and hyperconjugation from dipole moments study rests on the very dubious assumption that the dipole moments of C-C and C-H bonds are unaffected by changes in the hybridization of carbon. In fact Walsh⁸¹ has put forward the argument that single bonds between carbon atoms of different hybridization should be polar. The polarity of C-H bonds also should vary with the hybridization of

carbon. The hydrogen atoms should become more positive when the s-character in the carbon orbital used to form the bond is larger. This is indicated by the large increase in acidity of the C-H groups in the series ethane < ethylene < acetylene. The dipole moment of toluene can arise on the basis of this view, from the electronegativity differences between the methyl and aromatic carbons. Petro⁸² showed that hyperconjugated structures do not explain the non-zero dipole moment of toluene.

Dewar and Schmeising⁸³ have pointed out that the current interpretations of the thermochemical data in organic chemistry have rested on the assumption that bond energies are constant and independent of environment. This cannot be correct in view of the variation of bond lengths with the changes in hybridization of carbon. Bond energies must vary likewise, increasing with decreasing bond length. Dewar and Schmeising⁶⁹ have shown that the energy changes involved are very large indeed. Turner⁸⁴ has reviewed the thermochemical evidence pertinent to the question of hyperconjugation.

It was mentioned earlier that the electronic
adsorption spectra of alkyl benzenes seemed to indicate
that the electron donor action of alkyl groups decreases in

the order $\text{Me} > \text{Et} > \text{i-Pr} > \text{t-Bu}$. The trend was the same for *p*-alkylnitrobenzenes and acetophenones, the spectra in these cases being obtained in basic solvents. However, when the solvent employed was changed to carbon tetrachloride or when the spectra were obtained in the vapour phase, the electron release was no longer in the Baker-Nathan order and an inductive order was seen instead. Thus, for *p*-alkylnitrobenzenes it was shown by Schubert and Sweeny^{85,86} that there was a progressive increase in the bathochromic shift for the series of substituents Me, Et, i-Pr and t-Bu. The reversal of inductive order in basic solvents was explained by Schubert and Sweeny in terms of steric hindrance to solvation in the excited state which is a charge transfer state described by the canonical structures IXa, IXb, IXc.



Similarly in electronic transitions of the type in which a substituent is called upon strongly to accept negative charge (e.g. the "principal" transition of *p*-substituted phenols⁸⁶ in the gas phase) it has been found that alkyl groups are apparently better electron acceptors than hydrogen and order is $t\text{-Bu} > i\text{-Pr} > \text{Et} > \text{Me}$.

Dewar⁶⁹ has disagreed with McCaulay and Lein's⁴² view that hyperconjugation is an important factor in determining the stability of positive ions obtained by protonation of 1,3,5-trialkylbenzenes. The Baker-Nathan order shown by the uncorrected equilibrium constants for the protonation reaction disappears when proper allowance is made for the differences in the activity of the neutral hydrocarbons in the hydrogen fluoride and heptane solutions involved in the study.

Dewar has pointed out that even the strongest piece of evidence so far produced for hyperconjugation, namely, hyperfine coupling in ESR spectra, does not have any significance for "even" systems⁶⁹. Radicals are systems for which the equivalent orbital representation does not hold and hyperconjugation is expected to be significant in such species. Dewar also expressed doubts about the admissibility of long-range spin-spin coupling between protons, as evidence

for hyperconjugation since the coupling arises by interaction of molecules with the applied magnetic field. We may state here the nature of this objection a little more explicitly. The coupling with which we are concerned, proceeds through π -electrons and is dependent on the mixing of triplet configurations into the ground state electronic configuration as a result of the interaction with the magnetic field. In other words the coupling is due to the radical character induced. The manifestation of long range coupling would therefore prove only induced radical character and it cannot be taken as evidence for hyperconjugation in the normal molecule.

Eabor and Taylor⁸⁷ from the investigation of tritium exchange concluded that the variable influences of the alkyl groups cannot be reconciled with interpretations for Baker-Nathan effect that stress either hyperconjugation or steric hindrance to solvation and they suggested that both factors are significant.

If all the properties for which hyperconjugation is invoked can be understood entirely in terms of hybridization changes one would expect that it should have general validity. However, it is hard to explain some observations entirely on the basis of hybridization changes. For example,

the lengths of C-Si bonds in methylsilane (1.867 Å), vinyl silane (1.853 Å) and silylcyanide (1.850 Å) are very similar. Here there is apparently no large change in the effective covalent radius of carbon with unsaturation. This data on C-Si bond lengths⁸⁸⁻⁹¹ could support Bartell's interpretation in terms of non-bonded interactions. Brown⁹² and Sutton⁹³ have pointed out that available evidence is consistent with this theory.

In view of the present controversy over the concept of conjugation and hyperconjugation, Mulliken⁹ and Muller and Mulliken⁹⁴ have suggested that it would be desirable to classify them into three types: isovalent, sacrificial (ordinary) and plivalent. Isovalent conjugation and hyperconjugation can be divided further into three sub-types: dative, non-dative, and homodative in order of increasing conjugative stabilization. Sacrificial conjugation has been suggested to be more important than ordinary (sacrificial) hyperconjugation and the Baker-Nathan order has been described as differential hyperconjugation. Ordinary conjugation and hyperconjugation are sacrificial in the sense that π -electron stabilization is effected only by structures in which one π -bond is lost, as compared with classical valence bond structures. When the secondary structure involved in resonance has one more bond

than the main valence bond structure, the conjugation we have is of the plivalent type. Plivalent conjugation and hyperconjugation are of course, always dative. However, electron release is not an essential or important feature of the delocalization theory of ordinary hyperconjugation and so it (ordinary hyperconjugation) is quite different from dative conjugation and hyperconjugation where electron release is essential.

Even though most of the effects attributed to hyperconjugation can be explained in alternative terms, "most of the effects claimed for hyperconjugation seem to exist"⁹⁵ for carbonium ions and carbanions. Coulson⁹⁵ has pointed out that part of the confusion regarding hyperconjugation is probably semantic in nature. The steric repulsion theory has been ruled out by Bright Wilson⁹⁶, because it cannot account for the barriers to rotation well known for unsaturated systems like butadiene⁹⁷. The hybridization theory cannot be ruled out, but it is not possible to find any testable predictions from it as far as rotational barriers are concerned. These may have their origin in dispersion and other van der Waal's forces or in conjugation.

Mulliken⁹⁸ has expressed the opinion that an important reason why it is difficult to decide experimentally between

hybridization and electron delocalization as causes of bond shortening is the fact that the two effects largely operate in parallel (wherever there is double bond conjugation there is change in hybridization). Under these circumstances it becomes rather necessary, and proper to place considerable reliance on theory, provided it is reliable theory. In any event it is the same delocalization theory that seems clearly necessary to explain the observed bond shortenings in dative iso-valent conjugation which is used in estimating the effects of electron delocalization in conjugation and hyperconjugation in general. He also expressed his opinion that the Baker-Nathan effect in harmony with other evidence, does seem to support the idea that C-H hyperconjugation is a stronger effect than C-C hyperconjugation. However, it appears also that the evidence is not very conclusive because of the possibility of other small masking and (or) simulating effects. Mulliken⁹⁹ concedes that Dewar's challenge has in any event made clear the importance of a careful re-examination of the theoretical basis of conjugation, hyperconjugation and related phenomena.

After the conference on Hyperconjugation in 1959 and the "epistologue" of 1962 on Carbon-Carbon bonds, only a few investigations have been made in connection with the

problem of conjugation and hyperconjugation. Some of them are mentioned below:

The relative rates of nitration¹⁰⁰ (in aq. acetic acid) and mercuration¹⁰¹ (both in acetic acid and tri-fluoroacetic acid) have been found to follow the inductive and Baker-Nathan orders respectively despite the fact that both are electrophilic substitution reactions.

Sorensen¹⁰² has reported an elegant study of isomerization equilibria for several series of tri- and tetra-alkyl cyclo-pentadienylcations in conc. H_2SO_4 . He found that when placed in open competition for stabilizing allylic carbonium ions of this type, a methyl group is more favoured thermodynamically over a t-butyl group by about 1.8 K.cal/mole in terms of free energy and by about the same amount in enthalpy. The effect of ethyl and isopropyl groups fell in between these limits in the proper Baker-Nathan order.

Recently Schubert¹⁰³ and Gurka studied the behaviour of the relative rates of bromination of monoalkyl benzenes in aqueous-trifluoroacetic acid and found that it is in contradiction to the Baker-Nathan hypothesis and serves to illustrate once again the important role of solvation (solvent effects) in governing the relative kinetic parameters

of alkyl substituted compounds. The role of solvents in the interpretation of the Baker-Nathan order of reactivity has also been stressed recently by Stock and Himoe¹⁰⁴ from their study of the relative rates of chlorination of mono alkylbenzenes in carboxylic acid solvents.

Very recently the heats of formation for a number of alkyl and polyalkyl benzenonium ions with Me, i-Pr and t-Bu substituents have been computed by Arnett and Larsen¹⁰⁵ from calorimetric measurements of the heats of protonation of the corresponding hydrocarbon in the solvent system $\text{SbF}_5\text{-HSO}_3\text{F}$ which is a "super acid". Large heats of formation have been found which increase in size as a function of the number of groups in the benzene ring. Within experimental error all results in a given series fell in the Baker-Nathan order, the effect being many-fold larger than those observed previously for series of this type. It remains to be seen however, if free energy differences in this system really correspond to enthalpy differences.

It is also of interest here to note that some recent all valence electron molecular orbital calculations^{106,107} for systems like propylene, methyl acetylene, acetaldehyde, acetone and acetonitrile indicate that hyperconjugation is

not negligible. However, it must be admitted that these calculations, although they are considerably more sophisticated than those made earlier, still involve approximations.

It can be seen from the foregoing review that hyperconjugation and to a smaller extent conjugation have remained controversial despite the tremendous effort that has been made over the past three decades. In most of the attempts made to demonstrate the existence or evaluate the importance of conjugation and hyperconjugation, it is found that other masking effects often complicate the analysis of the data obtained. In view of the unsettled nature of the problem it is desirable to make further efforts to resolve it and the work reported in this thesis was undertaken in this context.

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CHAPTER II

**PROTON CHEMICAL SHIFTS IN SOME
SUBSTITUTED PHTHALIC ESTERS**

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It was noted earlier that the main NMR spectroscopic evidence for hyperconjugation is the observation of long range spin-spin coupling between protons in alkyl substituted unsaturated systems^{1a}. A related piece of evidence is the enhancement of geminal coupling in the presence of adjacent multiple bonds. This has been interpreted in terms of hyperconjugation^{1b,c,d}. As noted earlier, Dewar has taken exception to this type of evidence and maintained that it does not truly prove anything for unperturbed even systems, since the coupling concerned arises entirely as a consequence of the mixing of excited triplet configurations with the ground state (singlet) configuration². The same difficulty would, of course, be present in the consideration of chemical shift evidence, although there is the difference that both diamagnetic and paramagnetic terms are involved. Nevertheless, in the case of chemical shift evidence the magnitudes involved are usually larger and the possibility that observed trends may be correlated with other data, unrelated to singlet-triplet configuration

interaction, are better. Although there has been no serious effort to study hyperconjugation with the aid of chemical shifts, a few observations have indeed been made in this regard.

Corio and Weinberg³, who studied the methyl resonances of some substituted thiophenes, found that the signals of 2- and 3-methylthiophenes are at lower field than that of 2,3-dimethylthiophene. They suggested that if hyperconjugation is important in these systems, one might expect the methyl groups to be shifted to lower fields, as the electron release per methyl group would be smaller in the dimethyl derivative than in the monomethyl derivatives. But this low field shift may not be genuine, since the data have not been corrected for bulk susceptibility. Even if it turns out to be genuine, it can readily be accounted for on the basis of the inductive effect of the methyl group and the anisotropy of the C-Me bond.

Reddy and Goldstein⁴ studied the effect of methyl substitution on the chemical shift of substituted ethylenes. The effect of methyl substitution is ascribed to hyperconjugation, since the α -proton shift is a long range effect and also since it is roughly independent of the variations in the polarity of other substituent.

This interpretation is quite uncertain, since the inductive effect of the methyl group has been ignored.

In the present study, which will be discussed shortly an attempt has been made to correlate the proton chemical shifts in a specially chosen series of substituted benzenes, with the Hammett σ_R parameter and compare the effects of the methyl and t-butyl groups in order to estimate the importance of hyperconjugation. In order to put the present study in perspective it is useful to review briefly the attempts made by earlier workers to relate chemical shifts and coupling constants of protons and other nuclei to chemical reactivity parameters which are measures of changes in electron distribution in aromatic systems.

In a couple of early investigations proton chemical shifts of ortho, meta and para monosubstituted benzenes were studied by Corio and Dailey⁵ and Bothner-By and Glick⁶. It was found that para proton shifts at infinite dilution could be correlated with the Hammett σ -values⁶. The measurements of Spiesecke and Schneider⁷ further confirmed this correlation. They also measured ^{13}C chemical shifts which will be dealt with later.

Some workers^{8,9} have established a linear relationship

between amino group proton chemical shifts and Hammett substituent constant (σ) for meta- and para-substituted anilines. Schaefer et al.⁹ found that amino proton shifts of ortho-substituted anilines were linearly related to Taft's σ_o values, but the intercept differs from that observed for the meta and para compounds, and they concluded that the amino proton shifts are primarily dependent upon the π -electron density at the amino nitrogen atom. Recent studies on similar lines by McDonald and co-workers¹⁰ have shown an excellent linear correlation between appropriate Hammett substituent constants and chemical shifts of amino protons in a number of substituted anilines, other carbocyclic aromatic amines and heteroaromatic amines in DMSO solvent. Hückel molecular orbital (HMO) calculations of the π -electron densities at the exocyclic atom have been made for a series of carbocyclic aromatic amines and heteroaromatic amines. The electron densities are linearly related to the chemical shifts observed for each series, although the slopes differ for the carbocyclic and heteroaromatic amines. They have suggested that it is possible to relate Hammett substituent constants linearly with HMO electron densities although the parameters of such relationships will be a function

of the assumptions made in the HMO calculations.

Recently Yoder et al.¹¹ have studied the methyl chemical shifts in a series of substituted toluenes, t-butylbenzenes, N,N-dimethylanilines and anisoles. Methyl chemical shifts have been found to exhibit a linear correspondence to the Hammett σ constants with an order of relative slopes toluenes > anisoles > dimethyl anilines > t-butylbenzenes. However, the total range of variation of methyl shifts is only 13.2 Hz and 6.7 Hz for substituted N,N-dimethylanilines and t-butylbenzenes respectively at 60 Mc.

Besides studies on proton chemical shifts considerable amount of effort has been made to correlate ^{19}F chemical shifts and coupling constants in aromatic systems with Hammett constants.

The effect of substitution on the fluorine resonance of fluorobenzenes was first studied by Gutowsky et al.¹² The plot of the δ values against σ constants yielded separate straight lines for the meta and para substituted compounds and the lines are fitted by the following equations.

$$\delta_m = -5.92 \sigma_m$$

$$\delta_p = -17.9 \sigma_p + 4.84$$

The different slopes for the lines may be interpreted as a manifestation of the differences in the characters of the electronic effects arising from the meta and para substitution. The ^{19}F chemical shifts in a number of polysubstituted fluorobenzenes were found to demonstrate an approximate validity of the additivity principle. Meyer and Gutowsky¹³ suggested the use of fluorine δ values of substituted benzenes for predicting Hammett σ constants.

Taft¹⁴ has directly related the two fluorine NMR shielding parameters for m-substituted fluorobenzenes and p-substituted fluorobenzenes to σ_{I} and $\sigma_{\text{R}}^{\text{O}}$ parameters respectively. A linear relationship between these two shielding parameters has also been reported.

Lawrenson¹⁵ has determined the ^{19}F chemical shifts and coupling constants in pentafluorophenyl derivatives. The chemical shifts of the fluorine nuclei meta and para to the substituent 'X' have been related to the reactivity parameters of the substituents. The chemical shifts of fluorines meta and para to the substituent have shown a considerable resemblance to the fluorine chemical shifts in para and meta-substituted monofluorobenzenes^{16,24}. An empirical relationship has been developed relating para and meta fluorine chemical shifts with both σ_{I} and $\sigma_{\text{R}}^{\text{O}}$ parameters.

More recently Hogben et al.¹⁷ have re-examined the ^{19}F NMR spectra of pentafluorophenyl derivatives along with pentafluorophenyl phosphine derivatives and their complexes. They have established a linear relationship between the chemical shifts of the *p*-fluorine (δ_p) and the coupling between *ortho* and *para* fluorines ($J_{2,4}$). Since $J_{2,4}$ is found to be linearly related to δ_p , they have argued that this coupling constant is also a measure of π -interactions. Two lines of opposite slopes have been obtained for electron-donating and electron-withdrawing substituents. In the case of phosphines coupling between the phosphorus and *p*-fluorine ($J_{1,4}$) parallels $J_{2,4}$. They have suggested that the coupling constants $J_{2,4}$ and $J_{1,4}$ might have the advantage of being less sensitive to inductive effects than δ_p .

Very recently Hogben and coworkers¹⁸ have examined the fluorine chemical shifts and coupling constants of pentafluorophenyl derivatives with widely varied substituents. It has been found that two of the *meta* coupling constants ($J_{2,4}$ and $J_{2,6}$) form good straight line relationships with the chemical shifts of *p*-fluorine and it is argued that these relationships are mainly dependent upon the π -electron donor or acceptor character of the substituent. They have also examined the

π -interactions within molecules using the $J_{2,4} - \delta_p$ relationship in pentafluorophenyl derivatives, pentafluorophenyl phosphine derivatives and compounds of the type $C_6F_5-X-MR_3$. They have given the estimates of (p $\rightarrow$ d) π bonding between group IV elements and oxygen, sulfur and nitrogen. The influence of σ -bond polarity upon back-donation by halogen has also been considered.

Studies on ^{13}C chemical shifts and coupling constants in aromatic systems have also received the attention of many workers because they are also indirectly related to the changes in electron densities in these systems. Spiess and Schneider⁷ measured ^{13}C chemical shifts along with 1H resonance shifts in a variety of aryl-X compounds. They observed a very close correspondence between ^{13}C and 1H resonances at para position, where the primary contribution to the relative shifts arises from resonance effects of 'X'. They considered that the proton resonance responds to the π -electron density on the carbon atom to which it is bonded, and under favourable conditions both 1H and ^{13}C resonance shifts might be employed to obtain information about the π -electron density distribution in aromatic systems. An approximate correlation of these shifts with Hammett σ -values was seen.

At the meta position they found that the ^{13}C resonance shifts were surprisingly small and uniform, indicating small or negligible inductive effects due to X, and there was no evident correlation with the meta proton shifts. For meta-carbon or meta-hydrogen shifts no correlation with σ -values could be found. This observation is rather odd and it would tend to cast doubts on the validity of relating aromatic proton chemical shifts to π -electron densities. It might be recalled that in Taft's correlation m-proton shifts are attributed entirely to σ_I effects.

Lauterbur¹⁹ studied the ^{13}C NMR spectra of a variety of compounds and concluded that the range of ^{13}C chemical shifts in non-alternant hydrocarbons are much larger than those observed in alternants, suggesting that variations in π -electron densities are primarily responsible for such shifts in aromatic rings.

The additivity relations of ^{13}C chemical shifts in polysubstituted benzenes established by Lauterbur²⁰ for two electron releasing groups (CH_3 , OCH_3) were also found²¹ to hold for three other mesomerically electron releasing groups (Cl , Br , F) and one electron-withdrawing group (COCH_3) in a series of para-disubstituted benzenes of the type $\text{p-C}_6\text{H}_4\text{X}_2$. It was concluded that additivity

relations should be helpful in the assignment of ^{13}C NMR spectra of polysubstituted benzenes. However, Savitsky²¹ has recently expressed the opinion that it is doubtful that the interpretation of small deviations from the additivity relation can be used as a tool for the study of π -electron density distribution in the benzene ring before solvent effects are better understood and techniques of higher precision for measuring ^{13}C chemical shifts are developed.

Maciel and Natterstad²² have determined the ^{13}C chemical shifts of several monosubstituted benzenes and para-substituted fluorobenzenes. The shifts of the para carbons in monosubstituted benzenes have been found to correlate with Taft's resonance parameters, especially when the shifts have been corrected by the amount of the meta shift. A much less precise correlation has been found between the ^{19}F chemical shifts in the para-substituted fluorobenzenes and the ^{13}C -F chemical shifts in the same set of compounds than between these ^{19}F shifts and the para ^{13}C shifts in monosubstituted benzenes. The relationship between the ^{13}C and ^{19}F shifts has been considered in terms of the available theories. They have concluded that both ^{13}C shifts in monosubstituted benzenes and ^{19}F shifts in para-substituted fluorobenzenes

would be useful indices of the π -electron densities in para-positions.

Mention may be made in this connection about the importance of Dhami and Stothers's²³ work on carbonyl ^{13}C chemical shifts in substituted acetophenones. No correlation with σ -parameter was evident. In contrast to the chemical shifts of the aromatic para carbon nuclei, carbonyl shielding in substituted acetophenones are relatively insensitive to polar effects of the substituent. They suggested the possibility of correlating the carbonyl ^{13}C chemical shifts with the interplanar angle between the groups in ortho-disubstituted acetophenones.

Very recently Yoder and his collaborators¹¹ have measured the methyl ^{13}C -H coupling constants for series of substituted toluenes, t-butylbenzenes, N,N-dimethylanilines and anisoles. Although the total variation of the constants is small, a linear relationship between coupling constants and Hammett σ -constants of substituents has been found, and the relative slopes of these lines (toluenes > dimethylanilines > anisoles > t-butylbenzenes) have been interpreted in terms of the mode of transmission of substituent effects to the methyl site. The relative magnitudes of the slopes for the second and third series have been rationalized in terms of the overlap of lone pair

orbitals of nitrogen and oxygen with the π -orbitals of the phenyl group. The chemical shifts follow slightly different order of relative slopes (toluenes > anisoles > N,N-dimethylanilines > t-butylbenzenes) as mentioned earlier. The greater transmission of substituent effects in the series of toluenes has been easily rationalized by the inductive or field effects; the methyl group in toluenes is one atom closer to the benzene ring than it is in the other series. The total range of variation is, however, quite small.

^{15}N -H and ^{15}N - ^{13}C coupling constants have also been correlated with substituent effects. Binsch *et al.*²⁵ have shown that ^{15}N -H coupling is proportional to the s-character of the N-H bond and Axenrod *et al.*²⁶ have used this relation to study the effect of substituents on the benzene ring. They have reported a linear correlation between the magnitude of the directly bonded ^{15}N -H coupling constants and the appropriate Hammett σ -constants in a series of aniline- ^{15}N derivatives. They have found that the observed ^{15}N -H coupling constant in aniline is intermediate between those observed for typical systems containing sp^3 and sp^2 hybridized nitrogen. They have pointed out that this might be attributed to delocalization of the nitrogen lone pair by orbital overlap with

the π -system of the aromatic ring resulting in enhanced "s" character in the N-H bond compared to a normal sp^3 hybridized ammonium ion. It has been observed that the ^{15}N -H coupling is increased by the introduction of electron-withdrawing substituents, whereas electron-donating substituents can be seen to have the reverse effect.

The foregoing review of NMR studies of substituent effects thus shows that no observable parameter or property has so far been directly correlated solely with mesomeric effects (σ_R values). In all the studies mentioned above the substituent effects have been correlated with Hammett σ constant which is composed of σ_I and σ_R terms. What has been possible is a demonstration of linear correlations between $(\delta_p - \delta_m)$ and σ_R . The precision of these correlations is apparently not good enough for it to be used profitably in the evaluation of the strength of hyperconjugative interaction, because no such attempt seems to have been made so far. It is of interest here to note that while Taft and coworkers have reported that m -fluorine chemical shifts are related to σ_I only, in Lawrenson's work the same shifts are related to both σ_I and σ_R parameters. We might also recall here Dewar's objections to Taft's analytical procedure. Perhaps the difficulty here arises from the

neglect of inductive-mesomeric effects.

In the present investigation it is intended to study resonance interactions, including hyperconjugation, between donor and acceptor groups in substituted benzenes. One might, in principle, expect that conjugative interaction between substituents in *p*-disubstituted benzenes would be detectable in aromatic proton chemical shifts themselves. However, even in strongly interacting systems like *p*-nitroaniline, it has been shown that the rule of additivity of substituent effects holds to a good approximation. A special effort²⁷ has been made to see if there is any trend in the small departures of observed shifts from the additivity rule. In this connection a fairly large number of para- and meta-disubstituted benzene derivatives have been studied in addition to those of Smith²⁸. The results were negative. Thus it was quite clear that aromatic proton chemical shifts in derivatives of this type are of no use at all for the study of conjugative interaction between groups across the benzene ring. In order to circumvent the difficulty an ~~as~~ ingenious method has been suggested by Nair and Fairwell²⁹. They have pointed out that systems like methyl *o*-nitro benzoate, dimethylphthalate or *o*-dinitrobenzene in which the substituent groups are rotated out

of the plane of the benzene ring due to steric interaction may be employed with advantage for the study of donor-acceptor interaction. In these systems the protons at positions (C_3 and C_6) ortho to the substituent groups do not show the normal downfield shift observed for similar protons of carboxyl and nitro derivatives of benzene. The upfield shift is ascribed partly to the reduction of conjugative interaction and partly to the changes in the anisotropic contribution to shielding accompanying the rotation of the acceptor groups from the preferred conformation coplanar with the aromatic ring. They suggested that if a donor group is put para to one of the acceptor groups in this system, the acceptor group would tend to interact mesomerically with the donor and come closer to the aromatic plane. This rotation was expected in turn to affect the conformation of the second acceptor group and push it more out of the plane of the ring. According to theory, therefore, interaction between donor and acceptor groups in this system should be reflected in the chemical shifts of the protons ortho to the acceptor groups. They examined 4- and 5-methyl as well as 4- and 5- t-butyl derivatives of o-nitro benzoic ester and found that the methyl group appeared to be a stronger donor than the t-butyl group in

this system. If the postulate regarding the behaviour of the system is correct, the reported results would indeed imply that hyperconjugative interaction is quite significant and the data seemed to be consistent with the notion that carbon-carbon hyperconjugation is weaker than C-H hyperconjugation. The present study has been undertaken in order to put these qualitative ideas regarding the effects of donor-acceptor interaction on sterically hindered systems of the type suggested on firm experimental basis. The system chosen is a series of 4-substituted dimethyl phthalates, including amino, methoxy, hydroxy, fluoro, chloro, bromo, iodo, methyl, t-butyl and nitro derivatives.

RESULTS AND DISCUSSION

Dimethyl 4-aminophthalate was prepared via the nitro derivative starting from phthalic anhydride which was nitrated to yield a mixture of 3- and 4-nitrophthalic acids. On esterification with dry hydrogen chloride in methanol the latter gave the diester which could be easily separated from the mono-ester.

The 4-methyl derivative was prepared by Diels-Alder addition of isoprene and maleic anhydride to give 4-methyl 1,2,3,6-tetrahydro phthalic anhydride. The

tetrahydrophthalic anhydride was then dehydrogenated with bromine to get 4-methylphthalic anhydride, which was later esterified with methanol to give dimethyl 4-methylphthalate.

The t-butyl compound was prepared starting from naphthalene. Naphthalene was alkylated with t-butylchloride to give 2,6-di-t-butyl naphthalene which was oxidized to the corresponding 1,4-quinone with chromic anhydride. The 2,6-di-t-butyl 1,4-naphthaquinone was then oxidized successively with KMnO_4 and H_2O_2 to yield 4- t-butylphthalic acid which was esterified to obtain the required dimethyl 4- t-butylphthalate.

All the spectra except the one for the fluoro derivative were recorded on a Varian A-60 NMR spectrometer. The aromatic proton region was recorded on an expanded scale with sweep width of 100 Hz and employing a sweep rate of 0.2 Hz/sec. The reading accuracy was therefore easily better than 0.1 Hz. The spectrum of the fluoro derivative for which resolution was not very good at 60 Mc was obtained at 220 Mc through the courtesy of Varian Associates, Palo Alto, California, USA. The samples were all scanned wherever possible in carbon tetrachloride solution after checking for any dilution effect since some of the derivatives (e.g. t-butyl compound) showed some

change with dilution. Tetramethylsilane (TMS) was used as internal reference, unless otherwise stated. Chemical shifts (δ) are expressed in cps downfield from TMS. Most of the spectra were analyzed wherever possible, first in the ABX approximation and later refined by the iterative procedure of LAOCN 3* using a CDC 3600 computer. The matching that was obtained between calculated and experimental spectra was either good or excellent. The rms errors were about 0.1 for two derivatives, 0.065 for one, 0.05 for two, 0.04 for three, 0.01 for another two and 0.000 for the last. All possible combinations of signs of the meta and para coupling constants have been tried. Good frequency matching could be obtained in a number of cases for more than one combination of signs. In these instances the values chosen are those that gave both intensity and frequency matching. Wherever both signs for a spin-coupling constant gave equally good fits the ambiguity is indicated. However, this did not cause any difficulty in the choice of parameter sets for discussion,

*We are indebted to Dr. A.A. Bothner-By and the Quantum Chemistry Exchange Programme, Indiana University for a copy of LAOCN-3. The programme was used with minor modifications.

since one sign could be eliminated by comparison with another set where no ambiguity exists. The consideration in making this choice is that coupling between protons at specified positions will have the same sign in analogous derivatives. In the analysis of the spectrum of the methyl derivative, the aromatic protons were first regarded as an isolated three-spin system i.e. ignoring their weak coupling with the methyl protons. The signals of the 3- and 5-protons showed some fine structure arising from the coupling to the methyl protons and an attempt was made to analyze the spectrum as a six-spin system. The resolution obtained is not good enough to claim significant success in this attempt. However, the analysis is at least a partial success since it was able to produce the groups of absorptions actually recorded. The programme could adjust the benzylic coupling constants of the C₃- and C₅-protons to -0.495 Hz and -0.583 Hz with probable errors of 0.022 Hz. and 0.027 Hz. Since the spectrum of the bromo derivative (dimethyl 4-bromophthalate) consisted of two groups of unresolved multiplets, no refinement could be attempted and only chemical shifts could be obtained. The best spectral parameters obtained by LAOCN-3 for the various cases are shown in Table 1. Preliminary analysis of methyl and fluoro derivatives were made also by the method of moments described by Anderson

TABLE 1 - BEST SPECTRAL PARAMETERS OBTAINED BY LAOCN 3 FOR 4-SUBSTITUTED DIMETHYL PHTHALATES (IN H₂ DOWNFIELD FROM INTERNAL TMS)

Sub- st- tuent	Proton Chemical Shifts			Coupling Constants			RMS error
	C ₃ -proton	C ₆ -proton	C ₅ -proton	J _{3,5}	J _{3,6}	J _{5,6}	
NH ₂	403.083 ± 0.193	461.548 ± 0.054	399.336 ± 0.255	2.468 ± 0.158	1.129 ± 0.373	7.869 ± 0.375	0.103
	402.771 ± 0.212	461.512 ± 0.052	399.683 ± 0.193	-2.479 ± 0.146	0.574 ± 0.373	8.439 ± 0.377	0.096
	402.491 ± 0.055	461.493 ± 0.037	399.711 ± 0.060	-2.312 ± 0.063	0.256 ± 0.112	8.656 ± 0.113	0.100
	402.512 ±	461.500 ±	399.698 ±	2.309 ±	-0.263 ±	8.628 ±	0.100
	0.00.064	0.038	0.070	0.063	0.131	0.128	
OH	420.735 ± 0.046	462.807 ± 0.024	415.330 ± 0.041	2.662 ± 0.049	0.203 ± 0.050	8.664 ± 0.056	0.040
	420.748 ± 0.046	462.811 ± 0.024	415.313 ± 0.041	-2.665 ± 0.049	0.285 ± 0.056	8.623 ± 0.058	0.040
	420.960 ± 0.054	462.831 ± 0.044	415.109 ± 0.057	2.415 ± 0.062	0.274 ± 0.074	8.411 ± 0.076	0.091
	420.970 ±	462.834 ±	415.096 ±	-2.419 ±	0.345 ±	8.375 ±	0.091
	0.054	0.044	0.057	0.062	0.080	0.077	

.....contd.

TABLE 1 (Contd.)

Sub- sti- tuent	Proton Chemical Shifts			Coupling Constants			RMS error
	C ₃ -proton	C ₆ -proton	C ₅ -proton	J _{3,5}	J _{3,6}	J _{5,6}	
OMe	420.659 ± 0.257	462.489 ± 0.054	415.353 ± 0.223	2.717 ± 0.132	0.373 ± 0.306	8.810 ± 0.303	0.050
	420.420 ± 0.093	462.438 ± 0.023	416.242 ± 0.122	-2.727 ± 0.013	-0.049 ± 0.212	9.276 ± 0.213	0.005
	420.511 ± 0.087	462.495 ± 0.042	415.869 ± 0.093	2.695 ± 0.070	0.236 ± 0.148	8.719 ± 0.149	0.107
	420.544 ± 0.088	462.503 ± 0.042	415.828 ± 0.100	-2.639 ± 0.068	0.365 ± 0.164	8.633 ± 0.160	0.107
F*	437.335 ± 0.013	463.376 ± 0.013	429.604 ± 0.018	2.628 ± 0.021	-0.022 ± 0.018	8.644 ± 0.025	0.039
Cl	458.173 ± 0.000	459.458 ± 0.000	448.469 ± 0.000	2.037 ± 0.000	0.347 ± 0.000	8.216 ± 0.000	0.000
	458.362 ± 0.000	459.225 ± 0.000	448.514 ± 0.000	-1.818 ± 0.000	0.880 ± 0.000	8.338 ± 0.000	0.000
I	480.697 ± 0.017	446.354 ± 0.007	471.874 ± 0.008	1.814 ± 0.013	0.321 ± 0.015	7.932 ± 0.011	0.010
	480.688 ± 0.017	446.358 ± 0.007	471.879 ± 0.008	-1.831 ± 0.013	0.374 ± 0.014	7.957 ± 0.011	0.010

*The values obtained for coupling between ring protons and fluorine are:

$$J_{H_6,F}(\text{meta}) = 5.372 \pm 0.025; J_{H_5,F}(\text{ortho}) = 7.751 \pm 0.044;$$

$$J_{H_3,F}(\text{ortho}) = 8.377 \pm 0.025.$$

.....contd.

TABLE 1 (contd.)

Sub- sti- tuent	Proton Chemical Shifts			Coupling Constants			RMS error
	C ₃ -proton	C ₆ -proton	C ₅ -proton	J _{2,5}	J _{3,6}	J _{5,6}	
CH ₃	445.076 ± 0.039	456.031 ± 0.035	436.375 ± 0.036	1.941 ± 0.054	0.462 ± 0.054	7.873 ± 0.047	0.065
	445.073 ± 0.031	456.045 ± 0.032	436.358 ± 0.033	-1.980 ± 0.043	0.653 ± 0.046	7.796 ± 0.043	0.062
	445.077 ± 0.039	456.036 ± 0.035	436.368 ± 0.036	2.025 ± 0.054	-0.732 ± 0.051	7.804 ± 0.046	0.065
	445.071 ± 0.039	456.002 ± 0.036	436.408 ± 0.037	-1.936 ± 0.054	-0.720 ± 0.057	7.941 ± 0.049	0.065
CH ₃ [*]	445.327 ± 0.017	456.032 ± 0.016	436.400 ± 0.018	1.972 ± 0.023	0.680 ± 0.023	7.897 ± 0.023	0.150
	445.306 ± 0.017	456.013 ± 0.016	436.414 ± 0.018	1.966 ± 0.023	0.644 ± 0.022	7.875 ± 0.023	0.143
t-Bu	457.782 ± 0.056	456.939 ± 0.084	449.579 ± 0.080	2.026 ± 0.105	0.425 ± 0.086	8.299 ± 0.073	0.106
	457.952 ± 0.052	456.808 ± 0.079	449.540 ± 0.078	-1.984 ± 0.086	1.408 ± 0.095	8.126 ± 0.071	0.106
	458.020 ± 0.057	456.753 ± 0.083	449.522 ± 0.076	2.758 ± 0.165	-1.459 ± 0.093	7.851 ± 0.091	0.106
	457.807 ± 0.053	456.919 ± 0.080	449.574 ± 0.081	-1.624 ± 0.091	-0.778 ± 0.101	8.352 ± 0.074	0.106

* and ** indicate that these values have been obtained from six spin analysis by taking into account the benzylic coupling also. The coupling constants of methyl protons to ring protons have been adjusted to:

$$^*J_{H_3,CH_3} = 0.454 \pm ; J_{H_5,CH_3} = 0.534 \pm ; J_{H_6,CH_3} = -0.014 \pm$$

$$^{**}J_{H_3,CH_3} = -0.435 \pm 0.022; J_{H_5,CH_3} = -0.583 \pm 0.027; J_{H_6,CH_3} = 0.018 \pm 0.021.$$

...contd.

TABLE 1 (Contd.)

Sub- sti- tuent	Proton Chemical Shifts			Coupling Constants			RMS error
	C ₃ -proton	C ₆ -proton	C ₅ -proton	J _{3,5}	J _{3,6}	J _{5,6}	
NO ₂	514.242 ± 0.027	470.052 ± 0.027	502.631 ± 0.028	2.301 ± 0.038	0.430 ± 0.040	8.533 ± 0.038	0.055
	514.235 ± 0.027	470.056 ± 0.027	502.635 ± 0.028	-2.313 ± 0.038	0.534 ± 0.037	8.559 ± 0.038	0.055
	514.222 ± 0.027	470.062 ± 0.027	502.641 ± 0.028	2.332 ± 0.038	-0.736 ± 0.040	8.589 ± 0.038	0.055
	514.236 ± 0.027	470.055 ± 0.027	502.634 ± 0.028	-2.307 ± 0.038	-0.667 ± 0.037	8.549 ± 0.038	0.055
+ NMe ₃	503.123 ± 0.036	485.560 ± 0.033	436.076 ± 0.041	3.027 ± 0.047	-0.305 ± 0.305	9.487 ± 0.236	0.042
	503.288 ± 0.125	485.322 ± 0.132	435.844 ± 0.122	-2.802 ± 0.165	0.639 ± 0.154	8.396 ± 0.206	0.134
	503.447 ± 0.130	485.194 ± 0.130	435.811 ± 0.120	2.637 ± 0.200	0.384 ± 0.215	8.578 ± 0.216	0.134
	503.354 ± 0.130	485.269 ± 0.130	435.830 ± 0.123	-2.638 ± 0.170	-1.291 ± 0.165	8.722 ± 0.203	0.134
	467.458 ± 0.013	471.728 ± 0.013	461.518 ± 0.014	2.290 ± 0.017	0.554 ± 0.018	8.370 ± 0.017	0.014
+ NH ₃	467.406 ± 0.015	471.305 ± 0.018	461.389 ± 0.019	-2.528 ± 0.021	1.251 ± 0.026	7.978 ± 0.020	0.023
	467.429 ± 0.016	471.780 ± 0.019	461.491 ± 0.020	2.271 ± 0.020	0.505 ± 0.024	8.324 ± 0.022	0.023

and McConnell³⁰. The relative intensities were estimated by measurement of the areas of the absorption signals using a planimeter. The centres of the absorption peaks were read on a frequency scale relative to an arbitrary origin. The first moment gives the mean frequency or centre of gravity of the multiplet signals. The second and third moments were calculated in the usual way with the mean frequency as the origin. For the analysis of spectrum containing one basic multiplet with three non-equivalent groups of nuclei (N_1, N_2, N_3), the relations between chemical shifts ($\Delta\nu_i$) and the moments are as follows:

$$N_1 \Delta\nu_1 + N_2 \Delta\nu_2 + N_3 \Delta\nu_3 = 0 \quad \dots 1$$

$$N_1 (\Delta\nu_1)^2 + N_2 (\Delta\nu_2)^2 + N_3 (\Delta\nu_3)^2 = N \langle (\Delta\nu)^2 \rangle \dots 2$$

$$N_1 (\Delta\nu_1)^3 + N_2 (\Delta\nu_2)^3 + N_3 (\Delta\nu_3)^3 = N \langle (\Delta\nu)^3 \rangle \dots 3$$

It has been shown that if a reduced moment is defined as in equation (4) $R = \langle (\Delta\nu)^3 \rangle \langle (\Delta\nu)^2 \rangle^{-3/2} \dots 4$

and reduced chemical shift (Ω) as in equation (5)

$$\Omega_i = \Delta\nu_i \langle (\Delta\nu)^2 \rangle^{-1/2} \dots 5$$

the set of equations (1), (2) and (3) can be solved graphically. The plot of ' Ω ' against ' R ' gives an 's' shaped curve and for any value of ' R ', three values of ' Ω ' can be read off from it. The latter correspond to the

chemical shifts of the three sets of nuclei. For the present analysis the plot was made on an expanded scale (X-axis: $H = 0.1 = 3$ cms; Y-axis: $\Omega = 0.1 = 10$ cms). The spectrum of dimethyl 4-methylphthalate was analysed by this method and the chemical shifts obtained are given below:

C_3 -proton	=	444.570 Hz
C_5 -proton	=	435.286 Hz
C_6 -proton	=	455.140 Hz

The spectrum of the fluorine derivative was also analysed by a modification of the same method. When there is more than one basic multiplet (arising from two nuclear species or well-separated signals), an extended version of the above theory can be applied to the moments of each multiplet separately. If the nuclei giving rise to the basic multiplet under consideration are also coupled to other groups, the formulae for the first three moments become

$$\langle (\Delta \nu) \rangle = N^{-1} \sum_i \Delta \nu_i = 0 \quad \dots \quad 6$$

$$\langle (\Delta \nu)^2 \rangle = N^{-1} \left[\sum_i (\Delta \nu_i)^2 + \frac{1}{3} \sum_i \sum_m^* I_m (I_m + 1) J_{im}^2 \right] \quad \dots \quad 7$$

$$\langle (\Delta \nu^3) \rangle = N^{-1} \left[\sum_i (\Delta \nu_i)^3 + \sum_i \sum_m^* I_m (I_m + 1) \Delta \nu_i J_{im}^2 \right] \quad \dots \quad 8$$

where $\sum_m^*$ indicates summation over all nuclei which give rise to other basic multiplets. ' I_m ' is the spin of nuclei 'm'. The summation over 'i' is still over the nuclei belonging to the basic group under consideration. These formulae show that the second and third moments are not only determined by chemical shifts within the basic group, but also have contributions from the spin coupling constants with other basic groups. It can be seen that if equations (7) and (8) are rewritten in the form of (2) and (3), $\sum N_i (\Delta \nu_i)^2$ is no longer equal to $N \langle (\Delta \nu)^2 \rangle$ and $\sum N_i (\Delta \nu_i)^3$ is no longer equal to $N \langle (\Delta \nu)^3 \rangle$. The second and third moment terms have to be appropriately corrected and the 'effective' moments used. Since the correction for the third moment involves the chemical shifts which are not known, one has to resort to a method of successive approximations to get the correct solution. Reasonable values for J_{HF} are assumed from those established for other fluorine derivatives and the second moment was corrected accordingly. In the first calculation the reduced moment was computed ignoring the correction for the third moment. A set of Ω and $\Delta \nu_i$ values obtained from this was used for computation of the correction for third moment and a new reduced moment was calculated. The corresponding Ω and $\Delta \nu_i$

were calculated and, the process repeated until convergence was obtained. The $\Delta\nu_i$ values obtained after each refinement are given below:

	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$
Initial values	18.650	-3.990	-14.640
First refinement	18.910	-4.888	-14.040
Second refinement	18.920	-4.903	-14.030
Third refinement	18.920	-4.903	-14.030

The final chemical shifts obtained for dimethyl 4-fluorophthalate are given below:

C ₆ -proton	..	463.920 Hz
C ₅ -proton	..	430.970 Hz
C ₃ -proton	..	440.097 Hz

It was gratifying to find that the differences between the chemical shifts obtained by moment method and by the iterative procedure were only slight.

Aromatic Proton Chemical Shifts

The aromatic region of the NMR spectrum of dimethylphthalate is shown in Fig.1. The C₃ and C₆-protons which are ortho to the carbomethoxy groups do not show the usual downfield shifts observed for similar protons of carboxyl derivatives. Steric hindrance and electrical interaction between the COOMe groups would make it impossible

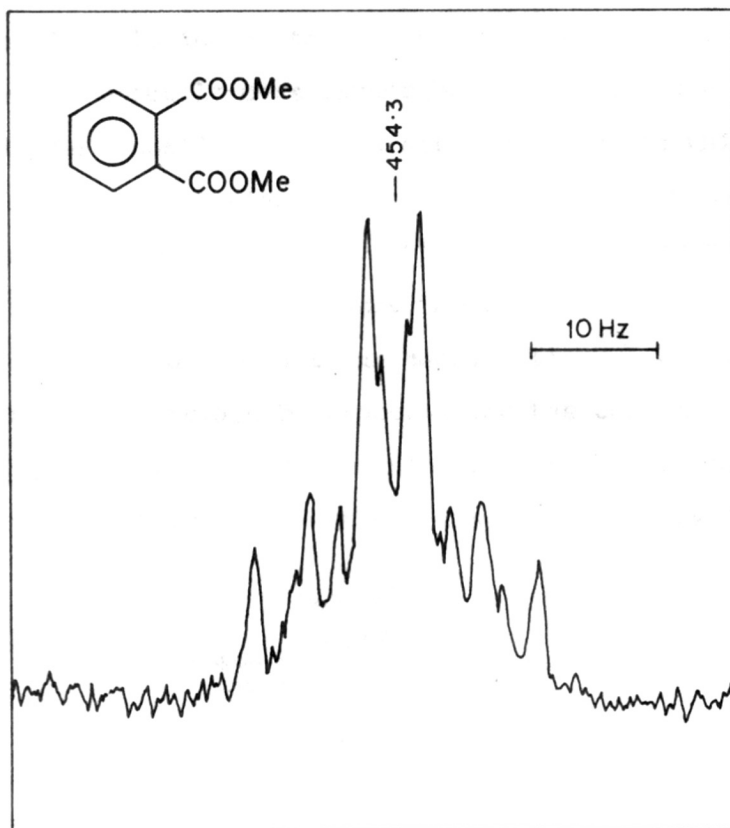
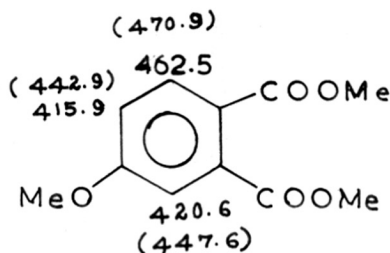


FIG. 1. AROMATIC REGION OF THE NMR SPECTRUM OF DIMETHYL-PHTHALATE

for them to be coplanar with the aromatic ring. The absence of the normal paramagnetic shift clearly arises from the rotation of the COOMe groups in this system from the normally more favourable conformation coplanar with the aromatic ring. As noted earlier, in this type of system, if an electron donating substituent that can enter into resonance interaction with the carboxyl group is introduced, we may expect the latter to rotate and come nearer to the coplanar conformation*. A downfield shift may therefore be expected for the corresponding ortho proton. This expectation is realized in the NMR spectrum (Fig.2) of 4-methoxy dimethylphthalate (I).



I

*It is not suggested here or in parent ester itself that the COOMe groups are remaining fixed in a definite conformation. They are presumably oscillating around minimum energy conformations which are different in the various derivatives.

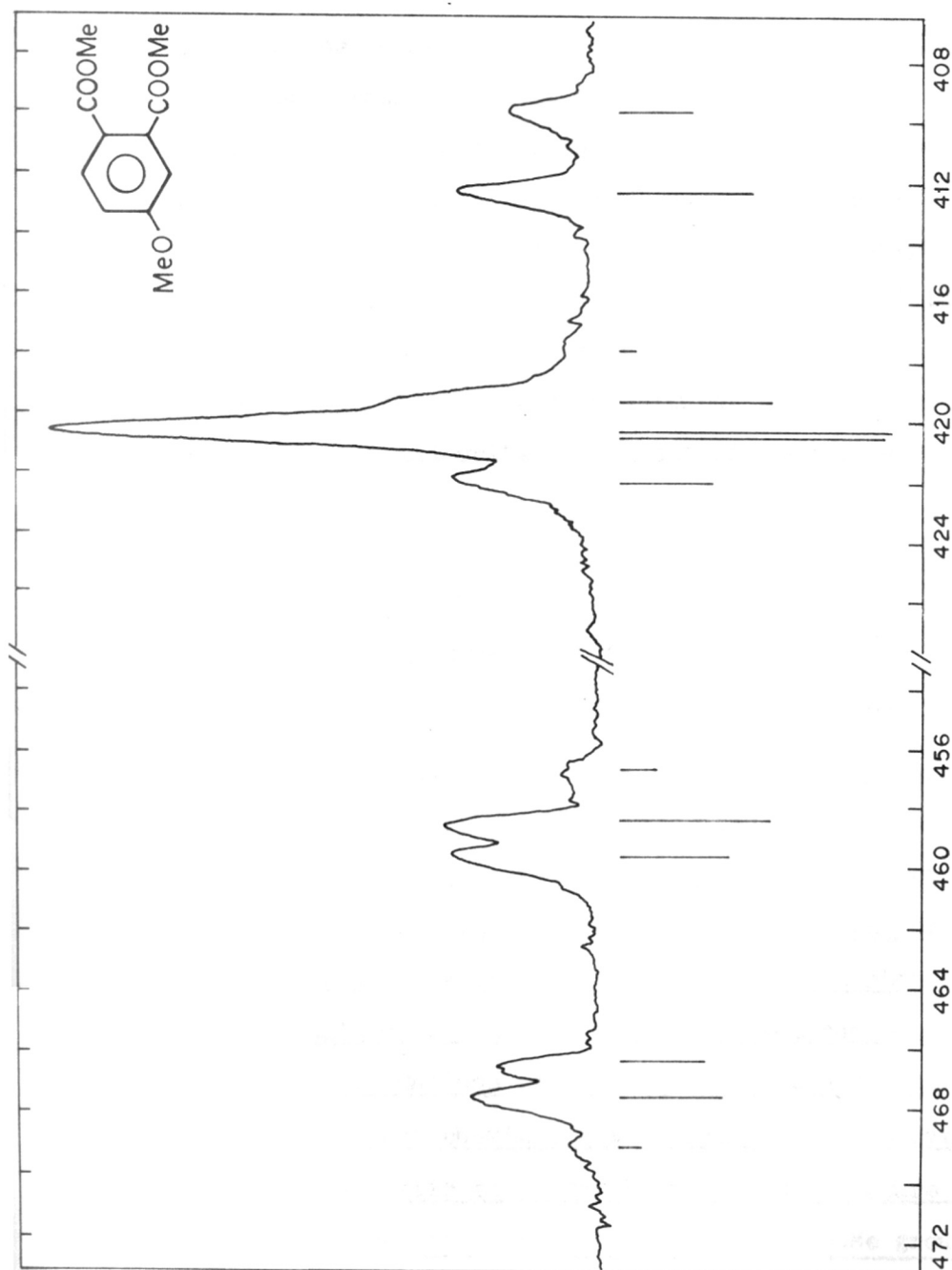


FIG. 2. OBSERVED AND CALCULATED SPECTRA OF DIMETHYL
4-METHOXY PHTHALATE

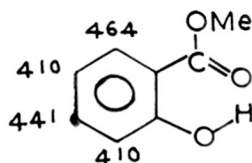
Since the substituent effects of the methoxyl group are diamagnetic at all positions of the benzene ring, it is very remarkable that the C_6 proton is showing a shift downfield (opposite in direction to the expected shift on the basis of the normal substituent effect) as compared with similarly placed proton of dimethylphthalate. In order to estimate the magnitude of this downfield shift as well as other associated shifts we may make allowance for the "normal" substituent effect of the methoxyl group and write down a set of "corrected" chemical shifts as follows:

$$\begin{aligned}\delta_{H_6}^{cor} &= \delta_{H_6}^{obs} - S_{m, OMe} &= 462.489 + 8.400 = 470.889 \text{ Hz.} \\ \delta_{H_3}^{cor} &= \delta_{H_3}^{obs} - S_{O, OMe} &= 420.659 + 27.000 = 447.659 \text{ Hz.} \\ \delta_{H_5}^{cor} &= \delta_{H_5}^{obs} - S_{O, OMe} &= 415.953 + 27.000 = 442.953 \text{ Hz.}\end{aligned}$$

S_O and S_m are substituent constants for the ortho and meta positions respectively; the values used being those of Smith³¹. According to the additivity rule these corrected shifts should coincide with the observed shifts for the unsubstituted ester if the conformations of carbomethoxy groups remain unaltered in the substituted compound. In fact the conformations are altered and the deviations of these "corrected" chemical shifts from those observed for the parent phthalic ester may be taken as a measure of the resonance interaction between the OMe and COOMe group para

to each other. We find that the C_6 -proton is shifted downfield by about 11.4 Hz from the expected position, i.e. relative to the C_6 (or C_3) proton of dimethyl-phthalate. The associated shifts for the C_3 - and C_5 -protons are 11.84 Hz and 6.00 Hz upfield. This is consistent with expectations. As the COOMe group at C_1 tends to come into the plane of the aromatic ring, the COOMe group at C_2 goes away from it and the expected chemical shift changes for the ortho (C_3) and para (C_5) protons are upfield. The upfield shift for the ortho proton should be larger than for the other since there would be an appreciable contribution from the anisotropic effects of the COOMe group at the former in addition to the effect of a decrease in mesomeric electron withdrawal. It is thus clear that the abnormal chemical shifts observed in the system may be traced to the interaction between donor and acceptor groups in this system and that the actual physical changes visualized for the system are substantially correct. When the substituent is an amino group instead of a methoxy group, the effects are larger (C_6 : 16.45 Hz downfield; C_3 : 14.42 Hz, C_5 : 7.61 Hz upfield). There is no necessity at this stage to consider the dispositions of the C=O and C-OMe bonds about the C_1 - C_4 axis, since both these components of COOMe group

have paramagnetic effects on the ortho proton in a planar conformation. The effect of the C-OMe group may be illustrated with the help of the spectrum of methylsalicylate (II) whose C_6 -proton absorbs at 28 Hz.



II

downfield from the absorption of benzene. Hydrogen bonding between the OH and C=O groups holds the COOMe groups in this compound in the required configuration.

The observed and computed spectra for the other derivatives are shown in figures 7 → 14 (towards the end of this Chapter). The observed and corrected shifts for the entire series are shown in Table 2. The behaviour just described is found in varying extents in the other derivatives studied. For instance, in the fluoro derivative paramagnetic and diamagnetic shifts are observed for the C_6 - and C_3 -protons respectively, although S_0 and S_m values for fluorine are both diamagnetic. Again, with the methyl derivative the observed diamagnetic shift for the C_6 -proton is not as much as would be expected on the basis of the S_m value for the methyl group. Similarly the

TABLE 2 - OBSERVED AND CORRECTED PROTON CHEMICAL SHIFTS IN 4-SUBSTITUTED DIMETHYL PHTHALATES (IN HZ DOWNFIELD FROM TMS)

Sub- sti- tuent and solvent.	C ₃ -Proton		C ₆ -Proton		C ₅ -Proton	
	Observed	Corrected	Observed	Corrected	Observed	Corrected
NH ₂ b	403.083	445.083 ± 4.800	461.548	475.948 ± 4.800	399.336	441.336 ± 4.800
OH b	420.735	449.535	462.807	470.607	415.330	444.130
OCH ₃ a	420.659	447.659 ± 1.200	462.489	470.889 ± 0.600	415.953	442.953 ± 1.200
F a	437.335	451.135 ± 1.800	463.376	465.176 ± 1.800	429.604	443.404 ± 1.800
Cl a	458.173	454.573 ± 0.600	459.458	463.058 ± 1.200	448.469	444.869 ± 0.600
Br a	467.000	455.000 ± 1.200	457.000	464.200 ± 1.200	457.000	445.000 ± 1.200
I a	480.697	457.897 ± 0.600	446.354	460.154 ± 0.600	471.874	449.074 ± 0.600
CH ₃ a	445.076	455.276 ± 2.400	456.031	464.431 ± 1.8	436.375	446.575 ± 2.400
t-Bu a	457.782	452.982	456.939	459.939	449.579	444.779
NO ₂ b	514.242	459.042	470.052	459.252	502.631	447.431
NMe ₃ c	503.123		485.560		496.076	
NH ₃ c	467.458		471.728		461.518	

a. Solvent CCl₄;

b. Solvent CCl₃;

c. Solvent D₂O

observed diamagnetic shift for the C_3 -proton is much larger than expected. The observed trend of deviations from the additivity rule is thus consistent although the magnitude involved is different. It would appear from this that the mesomeric interaction is the one that is important in determining deviations from the rule of additivity of chemical shifts in this system. If it were the inductive effect alone or a combination of inductive and mesomeric effects that are responsible for the deviations, the pattern of shifts should have been different. In this connection it is useful to compare the effects of substitution of fluoro and methyl groups. The Hammett σ constant of fluorine as calculated from reactivity and NMR data is 0.062, which represents the sum of a fairly large inductive electron withdrawing effect ($\sigma_I = +0.502$) and a comparable mesomeric electron donor effect ($\sigma_R = -0.44$). Similarly the Hammett σ constant for methyl group is -0.17, the σ_I and σ_R terms being -0.05 and -0.12 respectively. Thus it is clear that the effects of fluoro and methyl groups to be expected on the basis of Hammett σ -constants should be opposite in direction. However, the observed paramagnetic and diamagnetic deviations (for the C_6 - and C_3 -protons respectively) in 4-fluoro and 4-methyl derivatives are

in the same direction, more pronounced in the former. In other words, the C_6 -protons of both compounds show paramagnetic deviations and the C_3 -protons diamagnetic deviations. This behaviour would suggest - in agreement with theoretical expectations - that the mesomeric effect is the most important and, perhaps, the only factor that we have to take into account in order to rationalize the data. The deviations from the additivity rule might therefore show good correlation with σ_R parameters.

The "corrected" chemical shifts of C_3 and C_6 protons are plotted against Taft's σ_R parameters. A good correlation is obtained (Fig.3). A small scatter of some of the points from the straight line graph might perhaps be due to uncertainties associated with the substituent constants used. When allowance is made for the uncertainties in the additivity constants, the scatter that is seen cannot be regarded as significant. Thus the correlation is probably better than what is apparent from the present plot which is made on the basis of available estimates of (NMR) substituent constants (S_0 and S_m). The increasing paramagnetic shift seen for the C_6 -proton with increasing mesomeric donor action of the 4-substituent is in agreement with theoretical considerations already put forward. When C_1 -carbomethoxy group

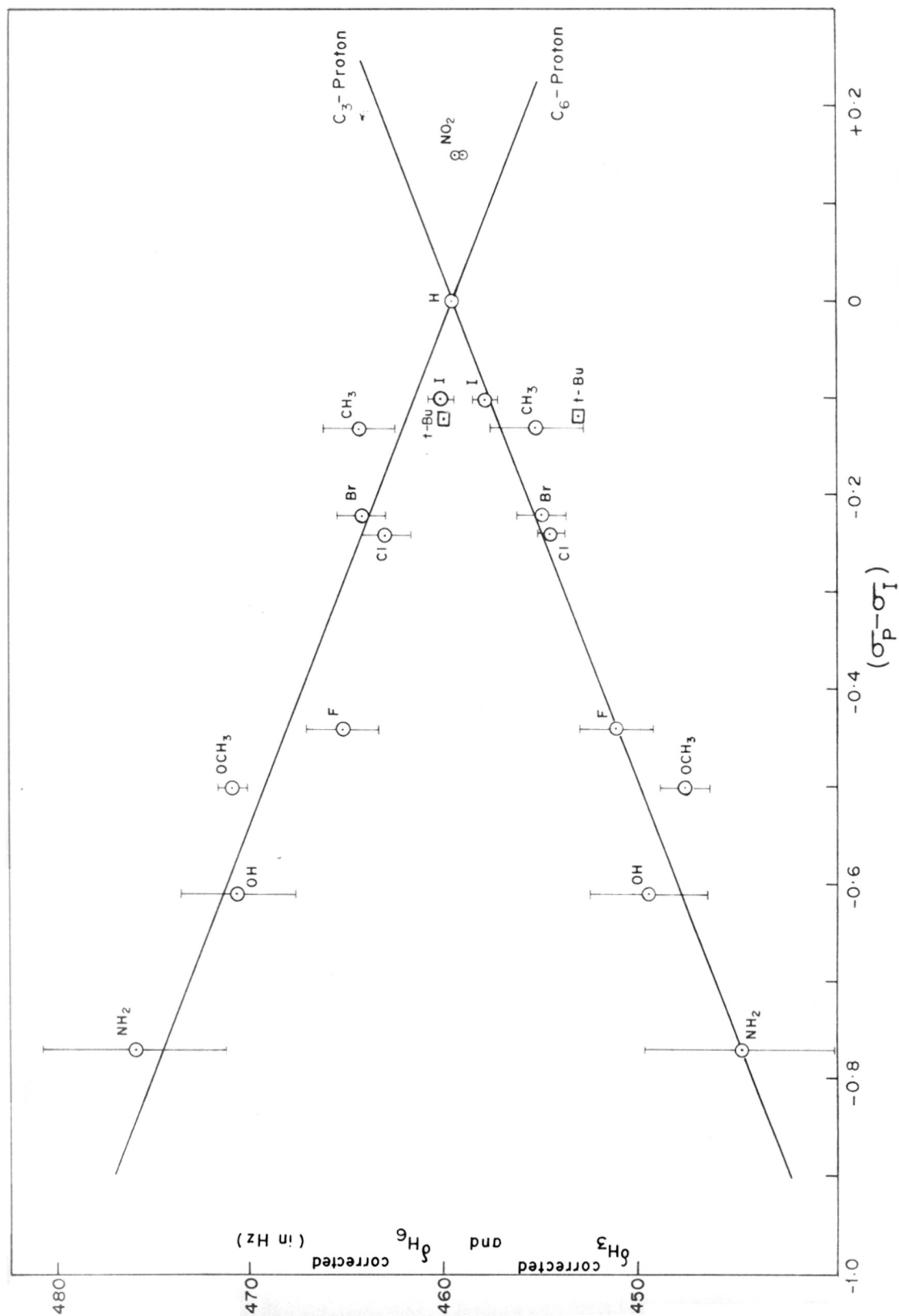


FIG.3 PLOT OF CORRECTED CHEMICAL SHIFTS OF C₃- AND C₆-PROTONS ($\delta_{H_3}^{cor.}$, $\delta_{H_6}^{cor.}$) VS. $(\sigma_P - \sigma_I)$

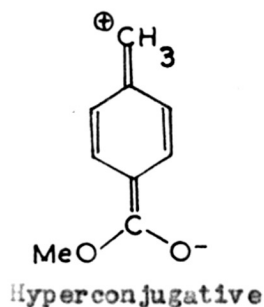
rotates and comes closer to the coplanar conformation it would push the C_2 -carbomethoxy group more out of the plane of the aromatic ring. As a consequence of this steric interaction and the accompanying change in conformation of the C_2 -carbomethoxy group a diamagnetic shift was expected for the C_3 proton. It is of considerable interest that deviation observed for the C_3 -proton is not only in the expected direction, i.e. diamagnetic, but also that its magnitude is roughly the same as that of the paramagnetic deviation for the C_6 -proton. This indicates that the rotations of the carbomethoxy groups of the system are tightly linked. It would appear that the angles through which the COOMe groups are rotated in opposite directions are equal. This means that in the absence of complicating features we might take the difference between the corrected C_6 and C_3 -proton chemical shifts, i.e. the sum of the paramagnetic and diamagnetic deviations, as a measure of donor-acceptor interaction. These would do just as well as the C_6 -proton paramagnetic shifts.

It is of interest to note that the "corrected" chemical shifts of C_3 and C_6 protons in dimethyl 4-nitrophthalate (459.042 Hz and 459.252 Hz) are approximately equal to the C_3 (or C_6) proton chemical shift (459.653 Hz)

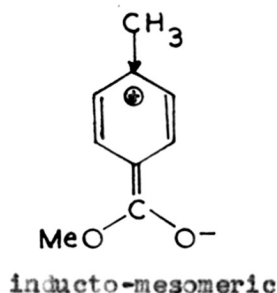
in the parent phthalic ester. The "corrected" C_5 -proton chemical shift (447.431 Hz) in the nitro derivative (dimethyl 4-nitrophthalate) is also close to the corresponding proton shift in the unsubstituted phthalic ester (448.947 Hz). This is consistent with the expectation because nitro is not a donor group. In the absence of mesomeric interaction between donor and acceptor groups the average conformations of the carboxyls would be very much the same as in phthalic ester and the chemical shifts follow the additivity rule as in other systems.

Thus the deviations from the additivity rule in this system are systematic and a correlation between "corrected" C_6 - and C_3 -proton chemical shifts with σ_R parameter indicates that in this selected system the mesomeric interactions can be studied separately unhampered by admixture with inductive effects.

The nature of the interaction of the alkyl groups in the methyl and t-butyl derivatives may be of either the hyperconjugative (III) or inducto-mesomeric type (IV). In the latter type of interaction, the resonance of the carbomethoxy group with the aromatic ring is enhanced by the inductive electron donor action by the alkyl group which by definition takes place along the $C_{Me}-C_{Ar}$ bond. If the interaction is of this type one should expect the



III



IV

observed effect to be enhanced when the methyl group is replaced by t-butyl group, since the inductive effect of the latter is much larger.

The spectra of the dimethyl 4-t-butylphthalate and the methyl analogue are shown in Figs.5 and 4. It may be recalled that the analysis for these are excellent as seen from the perfect match between theoretical and experimental spectra. The corrected C_6 proton chemical shift for the t-butyl derivative (Table 2) is hardly different from the C_6 (or C_3) proton chemical shift of parent dimethylphthalate. In the background of the variation observed in the paramagnetic shift of C_6 -protons with change in the electron-donating strength of different donor

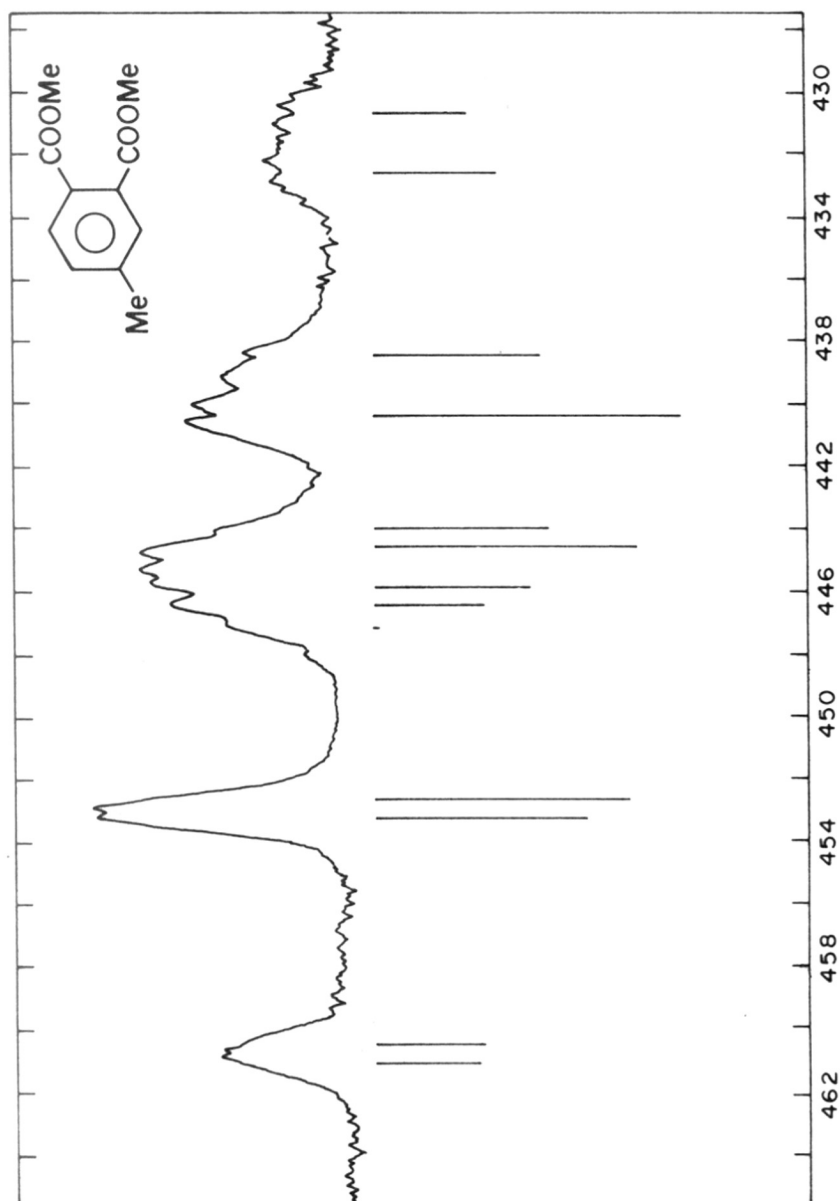


FIG. 4 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-METHYLPHTHALATE

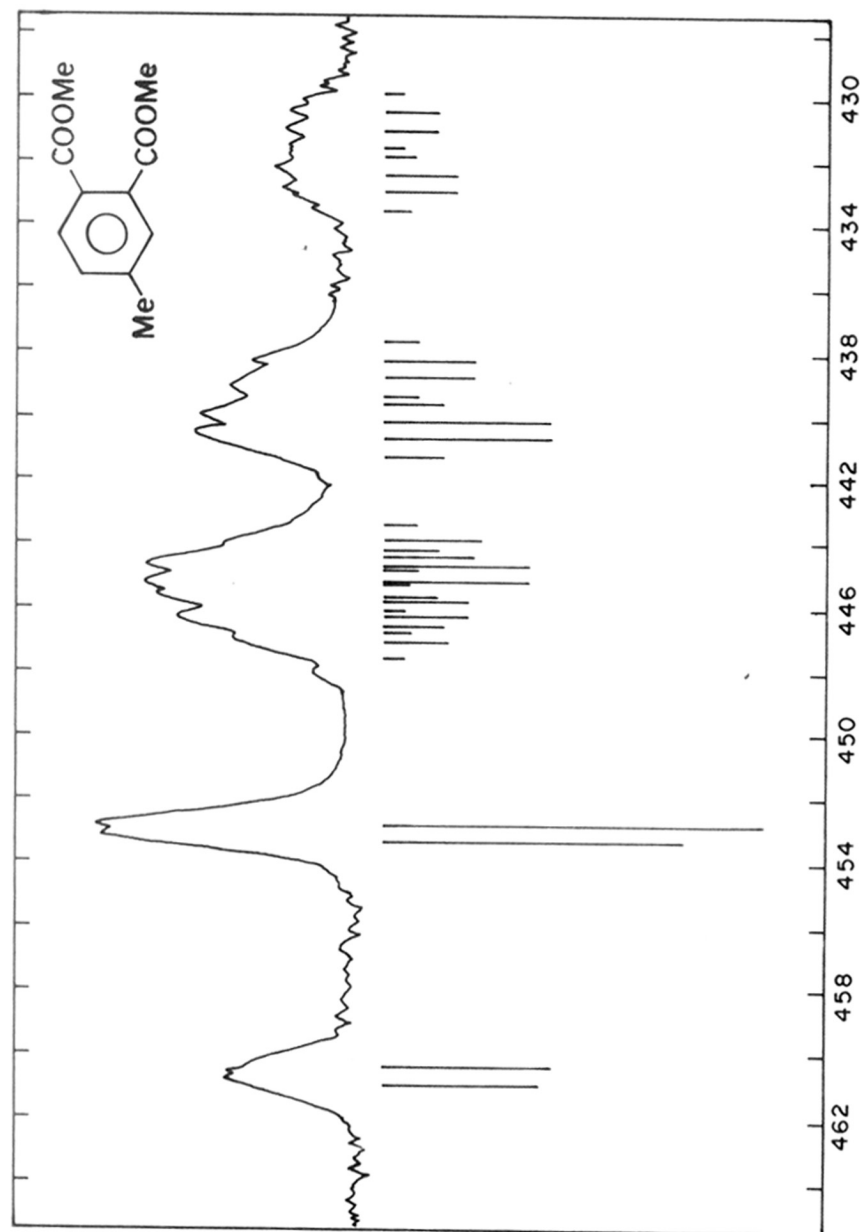


FIG.4 (a) OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-METHYL PHTHALATE
(SIX SPIN ANALYSIS INCLUDING BENZYLIC COUPLING)

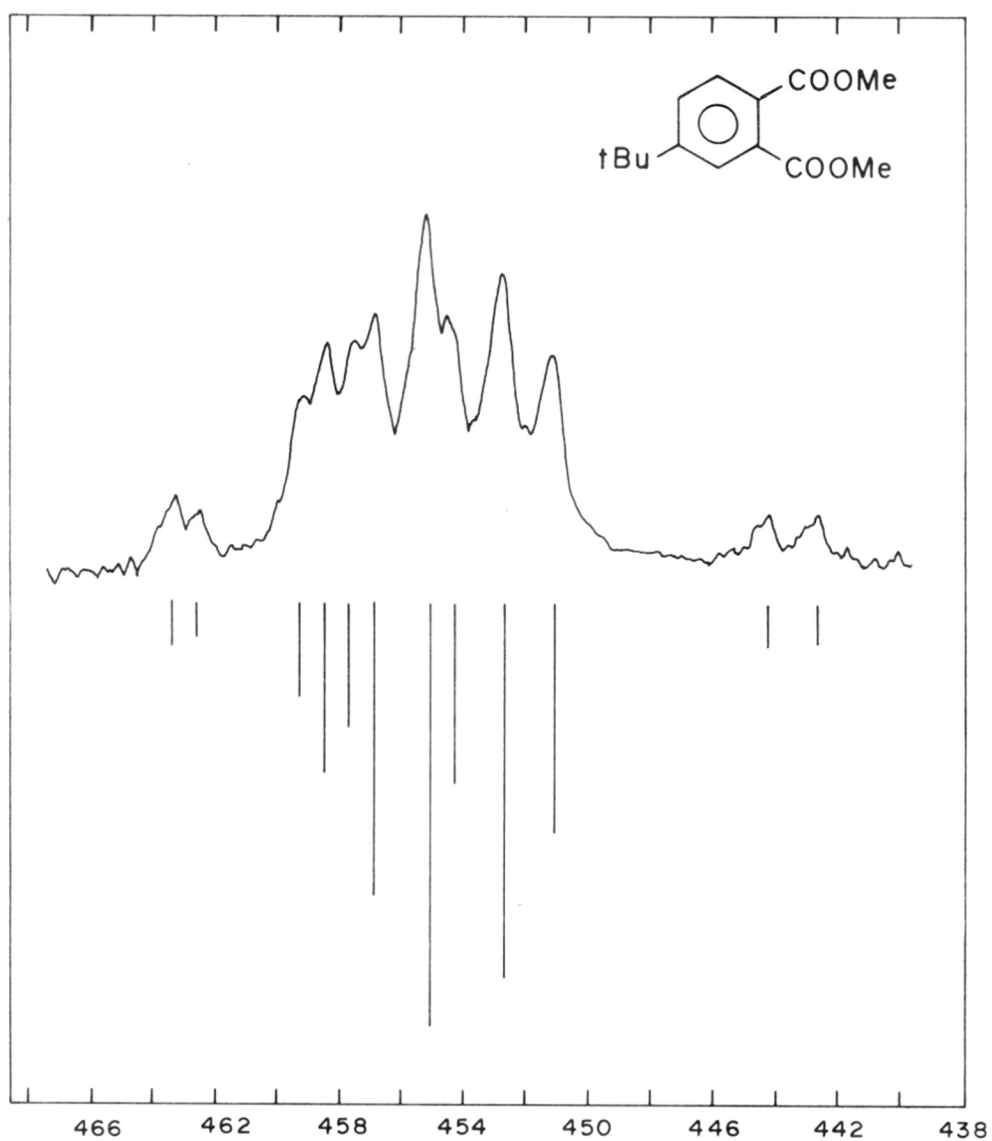


FIG.5 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL
4-*tert*-BUTYL PHTHALATE

groups, the conclusion that may be drawn is that the mesomeric interaction between the t-butyl and C₁-carbo-methoxy group as well as inductomesomeric interaction between them is weak in this system. In this situation one would expect that the diamagnetic shift experienced by the C₃-proton would also be negligible since the paramagnetic effect for C₆-H and diamagnetic effect for C₃-H are roughly equivalent for most other derivatives. The corrected chemical shift of C₃-proton shows an upfield deviation of about 6.5 Hz from additivity rule. This indicates that there might be steric interaction between the t-butyl group and the carbomethoxy group at position-2 communicated through the intervening proton. If there is an appreciable steric effect one might in turn wonder whether the conclusion drawn from the C₆-proton chemical shift is correct. Consideration of the details of the steric interaction shows that the conclusion is not only not vitiated but is in fact reinforced. In m-t-butyl-benzoic ester there is no chemical shift evidence for steric interaction between the substituent groups. The van der Waals radii for t-butyl group and hydrogen indicate that there should be very appreciable interaction between the C₃-H and the C₄-t-butyl groups. An in-plane deformation of the C-H bond will be communicated to the COOMe group

at the meta-position which likes normally to retain its mesomeric interaction with benzene ring. In m-t-butyl benzoic ester, therefore, any steric pressure felt by the COOMe group would be accommodated preferably by an in-plane deformation of the C_{ar} -COOMe bond. However, in 4-t-butyl phthalic ester there is a buttressing group (C_1 -COOMe) behind, and in-plane deformation is no longer possible. Steric pressure felt by C_2 -COOMe group of dimethyl 4-t-butylphthalate would therefore tend to rotate it out of the plane and would make it more easy for the C_1 -COOMe group to move closer to the aromatic plane. In other words, for a given mesomeric donor strength of 4-substituent the rotation of the COOMe group para to it towards the conformation coplanar with the benzene ring is made more facile by the steric effect. Thus the paramagnetic shift experienced by the C_6 -proton will be enhanced by the steric interaction and the conclusion that the mesomeric donor action of the t-butyl group is very weak and definitely less than that of the methyl group is reinforced. The diamagnetic shift felt by the C_3 -proton is also exaggerated due to the steric effect of the t-butyl group. The difference between the "corrected" C_3 and C_6 -proton chemical shifts is thus really enhanced by the steric interaction and it is not a true measure of donor-acceptor interaction. However, a comparison

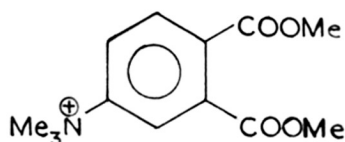
of these differences for the methyl and t-butyl derivatives is useful. The differences are as follows:

$$\begin{aligned}\delta_{H_6}^{cor} - \delta_{H_3}^{cor} &= 9.155 \text{ Hz (Methyl)} \\ \delta_{H_6}^{cor} - \delta_{H_3}^{cor} &= 6.957 \text{ Hz (t-butyl)}\end{aligned}$$

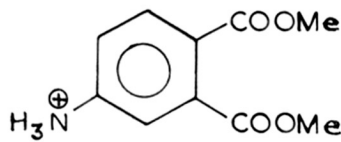
It can be seen that the difference between the "corrected" C_3 - and C_6 -proton chemical shifts in methyl derivative is slightly larger (by about 2.2 Hz) than the corresponding difference in the t-butyl derivative inspite of the fact that the effects of steric interaction are included for the latter. This again reinforces the conclusion drawn from C_6 -H shifts namely that the methyl group is a stronger donor than the t-butyl group in the interaction studied. In other words, hyperconjugation is significant and C-H hyperconjugation is apparently stronger than C-C hyperconjugation.

Although the effect of steric interaction invoked to explain the abnormal diamagnetic shift for the C_3 -proton is theoretically convincing, it would be desirable to demonstrate the effect separately in other derivatives in which the substituent group is nearly as bulky as t-butyl group but does not interact with the acceptor group (C_1 -COOMe) mesomerically. In this connection, the derivatives

(3,4-dicarbomethoxyphenyl) trimethyl ammonium sulphate (V) and (3,4-dicarbomethoxyphenyl) ammonium sulphate (VI) have been examined and their spectra and chemical shifts are presented along with other derivatives of the series.



V



VI

Unfortunately no reliable substituent constants for NMe_3^+ and NH_3^+ groups are available. An attempt to determine these ran into difficulties. The efforts made in this connection to estimate the substituent constants and the relevant data are discussed separately in the next Chapter.

Moreover, a rough correlation between "corrected" C_5 -proton chemical shifts of all the derivatives in the series and σ_R parameter is also observed (Fig.6). With the increase of σ_R , the C_5 -proton shifts move upfield. This trend is expected in view of the conformational change in COOMe group at position 2. With increasing donor-acceptor interaction (or conjugation of COOMe group

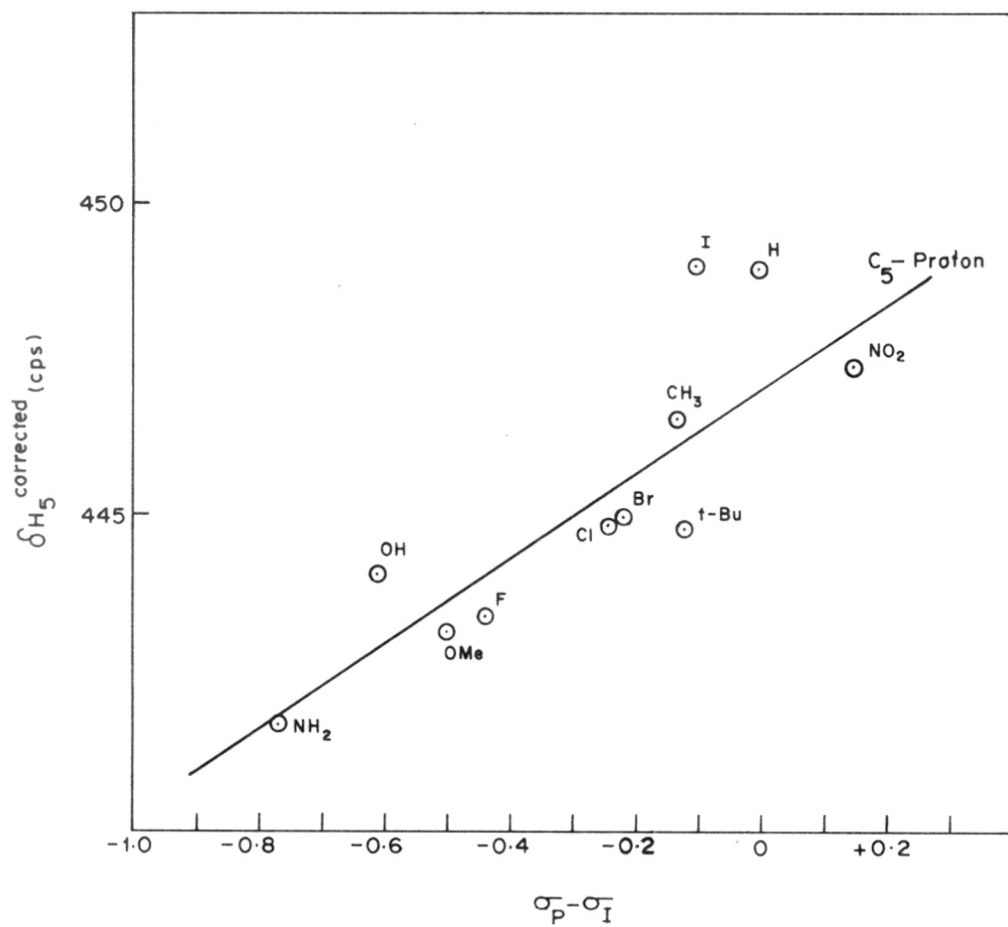


FIG. 6. PLOT OF CORRECTED CHEMICAL SHIFTS OF C_5 -PROTON
 $(\delta_{H_5}^{cor.})$ vs. $(\sigma_P - \sigma_I)$

at position 1 with the ring) the COOMe group at position 2 is expected to be pushed more and more out of the plane of the benzene ring, or, in other words, more out of conjugation with the ring resulting in an increase in electron density at the para position (C_5) (relative to that of phthalic ester) which is reflected in an upfield shift of the proton attached to that particular carbon (C_5 -proton). Thus all departures from additivity rule clearly arise from the same source. It is of considerable interest to note that t-butyl group shows significant deviation from this correlation i.e. the upfield shift is larger than may be expected from donor-acceptor interaction and it again indicates a larger rotation of the C_2 -COOMe group away from the aromatic plane because of steric interaction.

Splitting of carbomethoxy absorptions

In dimethylphthalate the methyl proton resonances in both the COOMe groups occur at the same place showing that they are magnetically equivalent. When once the 4-position is substituted by an electron-donating group, the methyl protons in COOMe groups are no longer equivalent and they absorb at slightly different fields. A measurement of this non-equivalence was undertaken since it appeared that it would give results that may be related to

those found in the study of aromatic proton chemical shifts. The results obtained are presented in Table 3 and shown diagrammatically in Fig.15.

Among the factors we may consider in connection with this differentiation of the methoxyls are the inductive and mesomeric effects as well as the effects of the electric field of the substituent and its magnetic anisotropy. The inductive effect of a substituent is generally considered to be roughly equal at the meta and para positions so that both carbomethoxyl groups of a 4-substituted dimethyl phthalate would be equally affected by the 4-substituent. Small differences in the environments of the methoxyls can also result from the third and fourth factors mentioned. Unlike these, the mesomeric interaction tends to differentiate the methoxyl groups. We have already obtained evidence which shows that the mesomeric effect of the substituent would push the C-1 carbomethoxy more towards the plane of the aromatic ring and C-2 carbomethoxy group away from the same plane. On account of the magnetic anisotropy of benzene ring, this conformational change will result in a shielding of the C-2 carbomethoxy group with respect to the C-1 carbomethoxy group. The displacement of electrons to the C-1 carbomethoxy group will, of course, tend to shield the methoxyl and

TABLE 3 - METHYL PROTON CHEMICAL SHIFTS OF COOMe GROUPS
IN 4-SUBSTITUTED PHTHALIC ESTERS (in Hz)

Substituent	Me Absorption positions	Splitting order	
NH ₂	229.75	233.50	3.75
OMe	228.60	230.00	1.40
OH	231.50	233.50	2.00
t-Bu	230.15	231.00	0.85
Me	229.25	229.75	0.50
F	230.75	231.65	0.90
Cl	231.25	231.75	0.50
Br	231.20	231.75	0.55
I	231.15	231.75	0.60
NO ₂	235.90	236.50	0.60
H	231.00	-	-

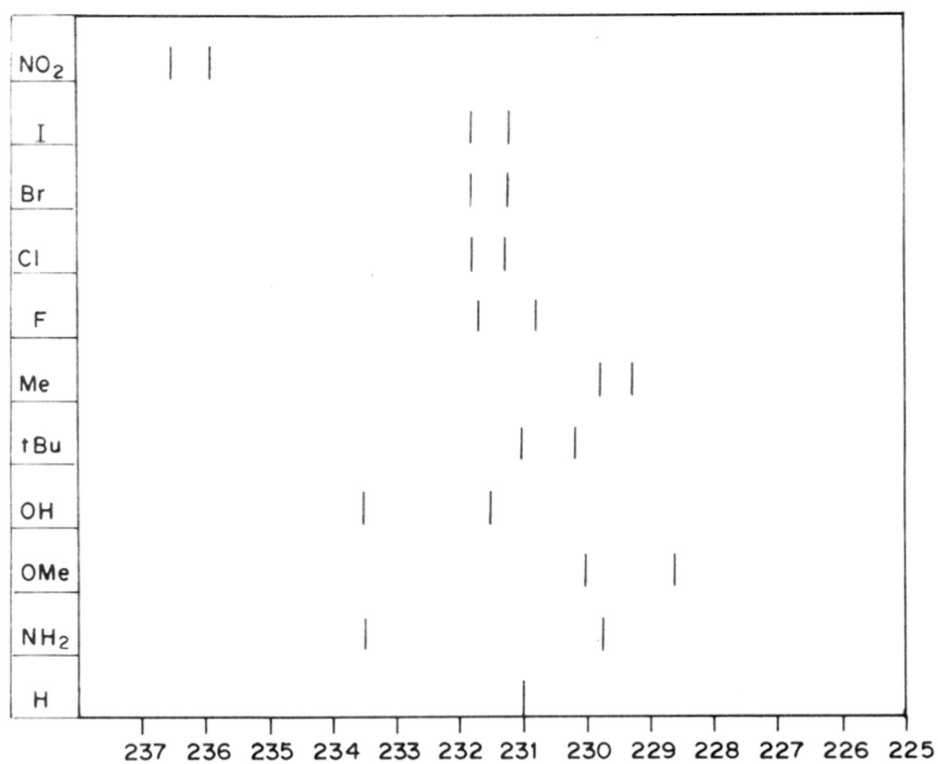


FIG. 15 PROTON CHEMICAL SHIFTS OF -COOMe GROUPS IN
4-SUBSTITUTED DIMETHYLPHTHALATES

the decrease of conjugation of the C-2 methoxyl should in principle cause a decrease in shielding. These effects should, however, be minor as compared to the differentiation caused by the magnetic anisotropy of the aromatic ring. The results in Table 3 and which are illustrated diagrammatically in Fig.15 show that the data may be qualitatively rationalized in terms of inductive and mesomeric effects. It is seen that both methoxyl signals move downfield under the influence of electron-withdrawing inductive effect, and upfield with enhanced splitting as a result of electron donating mesomeric effect. The spectra of the amino and hydroxyl derivatives have been obtained in chloroform because of insolubility in carbon tetrachloride and they are not quantitatively comparable with the other spectra. However, the expectation that methoxyl splitting would be large in the presence of a large mesomeric interaction seems generally valid, the amino derivative giving the largest splitting. Coming now to the methyl and t-butyl derivatives, the splitting is apparently larger for the latter. In the consideration of the aromatic proton chemical shifts for these derivatives we have obtained indication of the presence of a steric factor which would affect the C-2 carboxyl orientation. It therefore looks reasonable

to attribute the larger splitting for t-butyl derivative as compared with that for the methyl derivative to steric interaction whose nature has already been discussed. The methoxyls of the nitro derivative are appreciably deshielded evidently because of the strong inductive effect. The small difference in methoxyl environments is probably to be traced in this case to the effects of electric field, the magnetic anisotropy of the nitro group and the mesomeric effect which may still have an influence although all three substituents are strong acceptors in this case.

The small variations observed for the methoxyl absorption positions are thus consistent with the general picture of the nature of the 4-substituted phthalic ester system that has emerged from this study.

Coupling constants

It is interesting to see what additional information can be obtained for the system under study from a consideration of the coupling constants which are presented in Table 4. It may be recalled that these have been obtained from analyses that are very good and ambiguities of sign have been eliminated by consideration of consistency in the series of derivatives. The probable errors in these parameters range from 0.1 to 0.00 Hz. When the

TABLE 4 - COUPLING CONSTANTS IN 4-SUBSTITUTED DIMETHYL
 PHTHALATES (in Hz)

Substituent	$J_{3,5}$ (meta)	$J_{2,6}$ (para)	$J_{5,6}$ (ortho)
NH ₂	2.468	1.129	7.869
OH	2.662	0.203	8.664
OCH ₃	2.717	0.373	8.810
F	2.628	-0.022	8.644
Cl	2.037	0.347	8.216
Br	-	-	-
I	1.814	0.321	7.932
CH ₃	1.941	0.462	7.873
t-Bu	2.026	0.425	8.299
NO ₂	2.301	0.490	8.533
⁺ NMe ₃	3.027	-0.305	9.487
⁺ NH ₃	2.290	0.554	8.370

substituent is changed, the vicinal constants, $J_{5,6}$, decrease in the order $^+\text{NMe}_3 > \text{OMe} > \text{OH} > \text{F} > ^+\text{NH}_3 > \text{t-Bu} > \text{Cl} > \text{I} > \text{Me} \approx \text{NH}_2$. The values for OMe, OH and NH_2 derivatives used in this comparison are those obtained when $J_{3,5}$ is taken to be positive. The spectra in these cases approach those of true ABX systems and it becomes difficult to ascertain the true sign of J_{AB} . Very good fits are obtained with negative values for $J_{3,5}$. These analyses are not included in the comparison above since the negative sign cannot be considered for any of the other derivatives. The observed variation for $J_{5,6}$ is complex and can be understood only as a superposition of several effects.

Several attempts have been made in recent years to correlate variations in vicinal coupling constants with the changes in hybridization³²⁻³⁴, π -bond order³⁵⁻³⁷, charge polarization⁴² etc. The first of these failed to account for the variations of $J_{13\text{C,H}}$ for vinyl fluorides³⁸ and monosubstituted benzenes. Similarly the second failed to account for the C-C bond distances in vinyl fluoride³⁹ and other monosubstituted^{40,41} ethylenes.

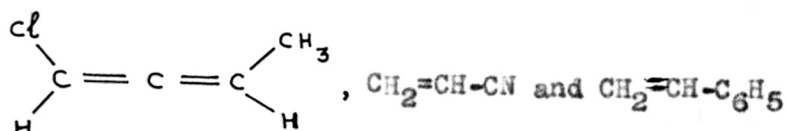
In the fragment $\text{XHC}_1\text{-HC}_2$ it has been observed experimentally that the size of vicinal coupling constant

(J^V) decreases as the electronegativity (E_X) of the atom 'X' increases. This decrease is most marked in ethylenic systems^{43,54}, less so in cyclopropanes, epoxides or norbornenes and least in simple acyclic molecules like ethanes^{44,45}. This trend is also expected theoretically³². The dependence of J^V on E_X is thought to be largely due to the rehybridization of carbon atoms with a small contribution from the inductive effect³². Now, in the fragment $XHC_1-HC_2-HC_3-HC_4$ both these effects fall off monotonically as we go away from 'X' down the fragment. Therefore, any observable variation in the size of $J_{2,3}^V$ and $J_{3,4}^V$ with E_X (electronegativity of X) should parallel that of $J_{1,2}^V$, although, of course, it would be considerably attenuated. However, it has been shown that in 1-substituted propanes⁴⁶ and propenes⁴⁷ $J_{1,2}^V$ decreases and $J_{2,3}^V$ increases as the E_X of the substituent increases. The same behaviour is observed in monosubstituted cyclopropanes⁴⁸.

A number of workers have noted that in some aromatic systems ortho coupling ($J_{2,3}^V$) can be related to the sum of electronegativities of two groups e.g. some 2-substituted pyridines⁴⁹, furanes⁵⁰ and ortho-disubstituted benzenes⁵¹. The same behaviour was also noticed by Cox⁵² in aromatic compounds studied by him.

Recently in monosubstituted benzenes a pronounced increasing trend of $J_{2,3}$ with electronegativity has been observed⁵³. Of the remaining coupling constants, only the ones connecting the ortho protons to the other protons in the ring have shown definite trends with electronegativity. The couplings $J_{2,4}$ ($= J_{4,6}$), $J_{2,5}$ and $J_{3,6}$ have displayed, instead, decreasing trends. A less definite and more scattered behaviour has been shown by the plot of $J_{3,5}$ against electronegativity. The vicinal coupling constants $J_{3,4}$ ($= J_{4,5}$) have remained almost stationary, with maximum variation of ± 0.2 cps randomly distributed over the whole range of electronegativity.

The reason for the enhancement of $J_{2,3}^V$ with increase in electronegativity of the substituent at C_1 remains obscure. Cohen and Schaefer⁴⁷ have suggested the possibility of "hyperconjugation" having a role in determining the vicinal coupling in



and its effect is opposite to that observed for geminal coupling. The significance of this statement is not clear. Very recently Castellano⁵⁵ has suggested that there might

be some connection between the observed pattern of variation of spin coupling and alternation of charge densities indicated by sophisticated all valence electron molecular orbital calculations⁵⁶ for compounds with electronegative substituents.

In the compounds examined in this study, if we consider the halogen and methoxyl derivatives as a group separately the electronegativity order $\text{OMe} > \text{F} > \text{Cl} > \text{I}$ is indeed found for $J_{5,6}$ as may be expected. The meta coupling constant $J_{3,5}$ also follows the same order. A close comparison of ortho and meta coupling constants in 4-methyl and 4-t-butyl dimethyl phthalic esters, reveals the fact that the coupling constant is larger in the case of t-butyl derivative. If this is to be understood in terms of the electronegativity correlation just discussed, it would imply that t-butyl group is more electronegative than the methyl group. However, this is contrary to the well known fact that the t-butyl group is inductively a stronger donor of electrons than the methyl group, more particularly when the origin of the inductive effect is traced to the polarity of the C-H bond ($\text{C} \leftrightarrow \text{H}$) and the non-polarity of C-C bond. The possibility that the relatively larger $J_{5,6}$ for t-butyl derivative may be attributable to a steric effect cannot be ruled out. The

relative values for $^+\text{-NMe}_3$ and $^+\text{-NH}_3$ derivatives also suggest the same thing. The value of 7.869 Hz for the amino derivative which has been obtained under the assumption that $J_{3,5}$ is positive, is difficult to understand. Perhaps the assumption made is not really justifiable and a reconsideration of the data may become necessary when more definite determinations of the signs of $J_{3,5}$ are made.

Conclusions

The expectation that proton chemical shifts in 4-substituted phthalic esters would be a convenient system for the study of mesomeric electron donor strength of substituents has been neatly demonstrated. The departures of the aromatic proton chemical shifts from the additivity rule are related to the conformational change in COOMe groups that accompanies donor-acceptor interaction. The methyl splittings confirm the soundness of the analysis. Methyl group appears to be a stronger donor than the t-butyl group in this system. Although evidence for a steric interaction is indicated for the t-butyl derivative, it is shown that this does not vitiate the conclusion regarding donor strength, but only reinforces it. The spin coupling constants obtained, although interesting by themselves, do not furnish any useful information regarding donor-acceptor interaction.

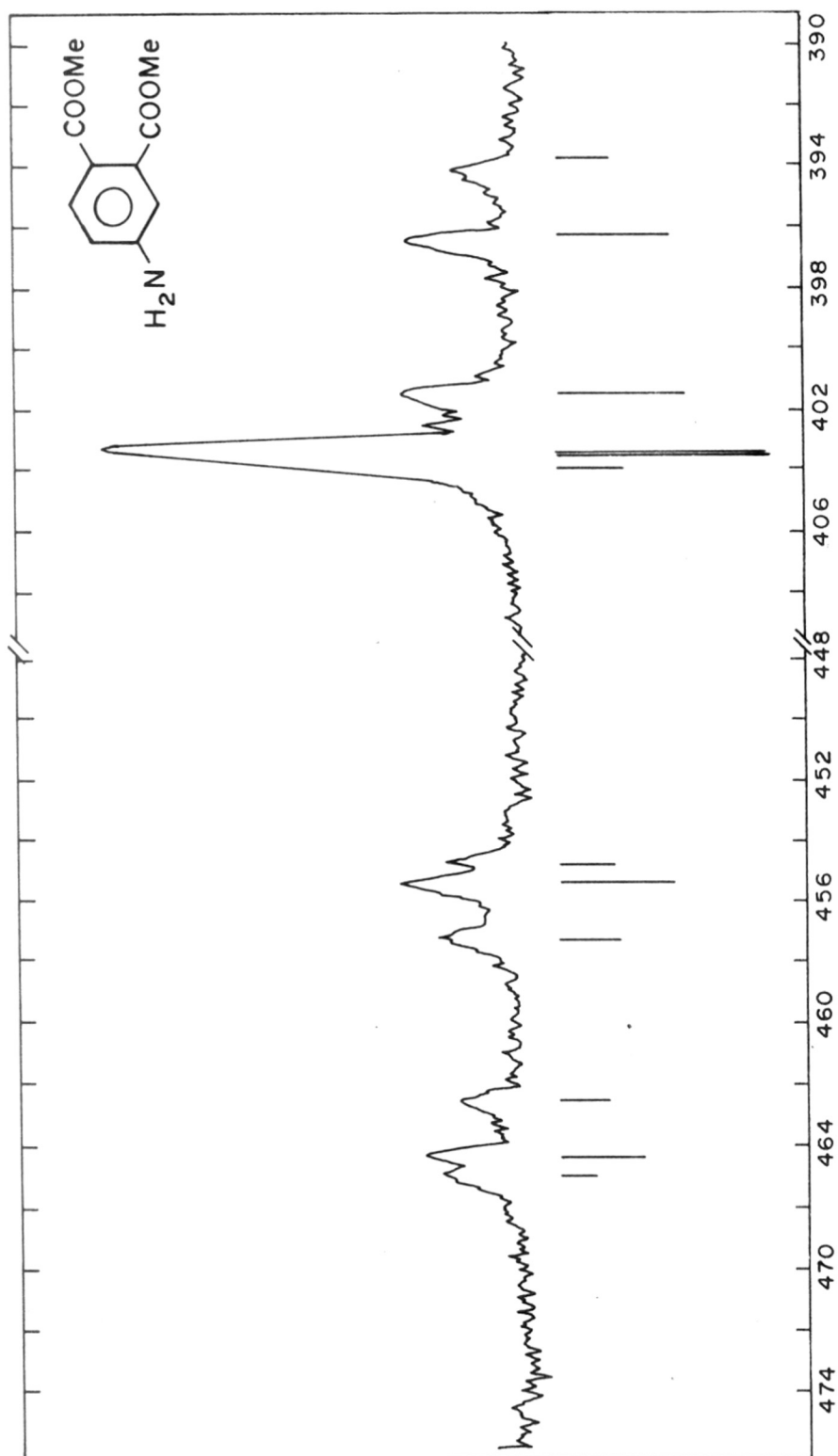


FIG. 7 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-AMINOPHTHALATE

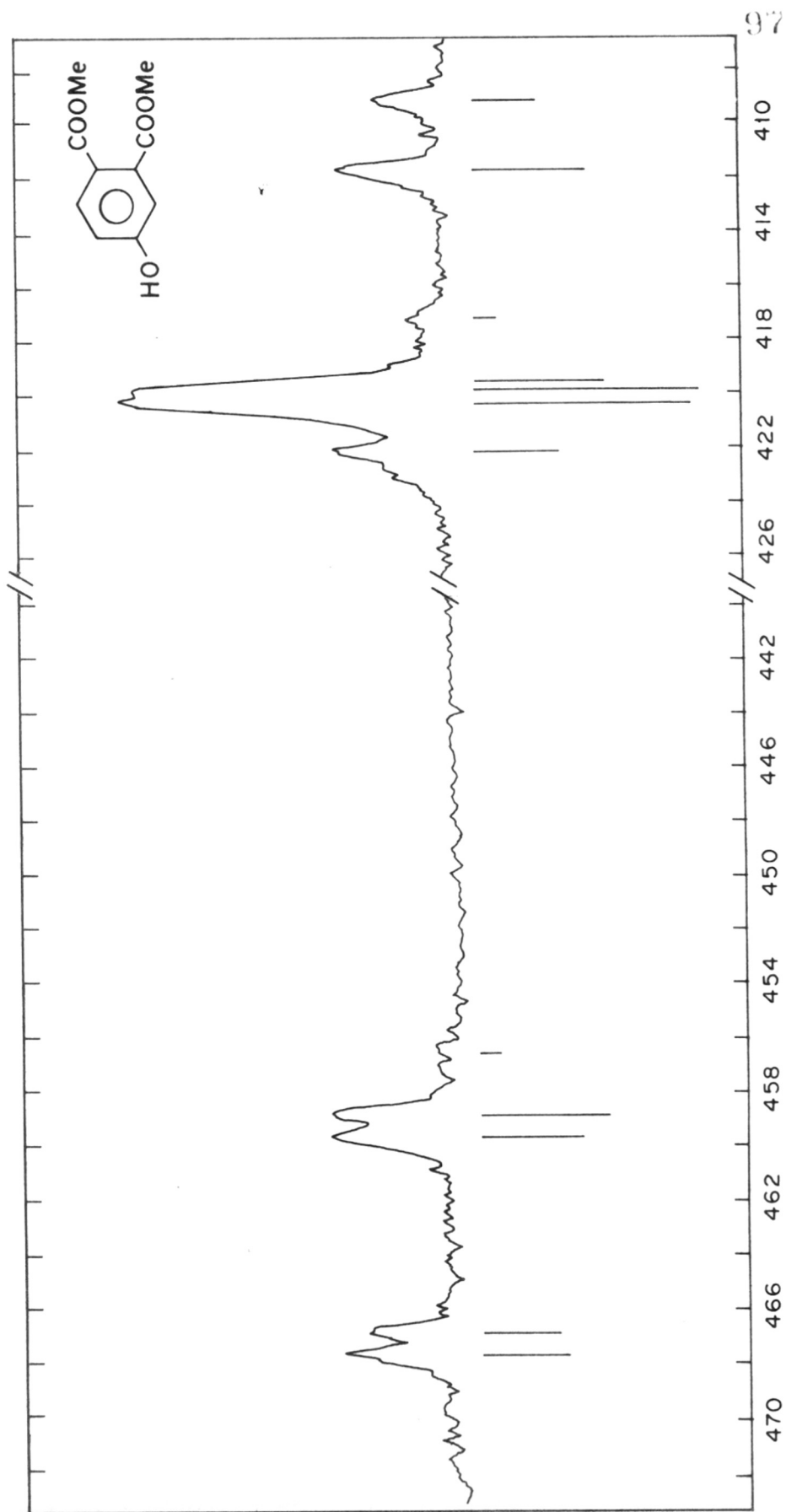


FIG.8 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4 - HYDROXYPHTHALATE

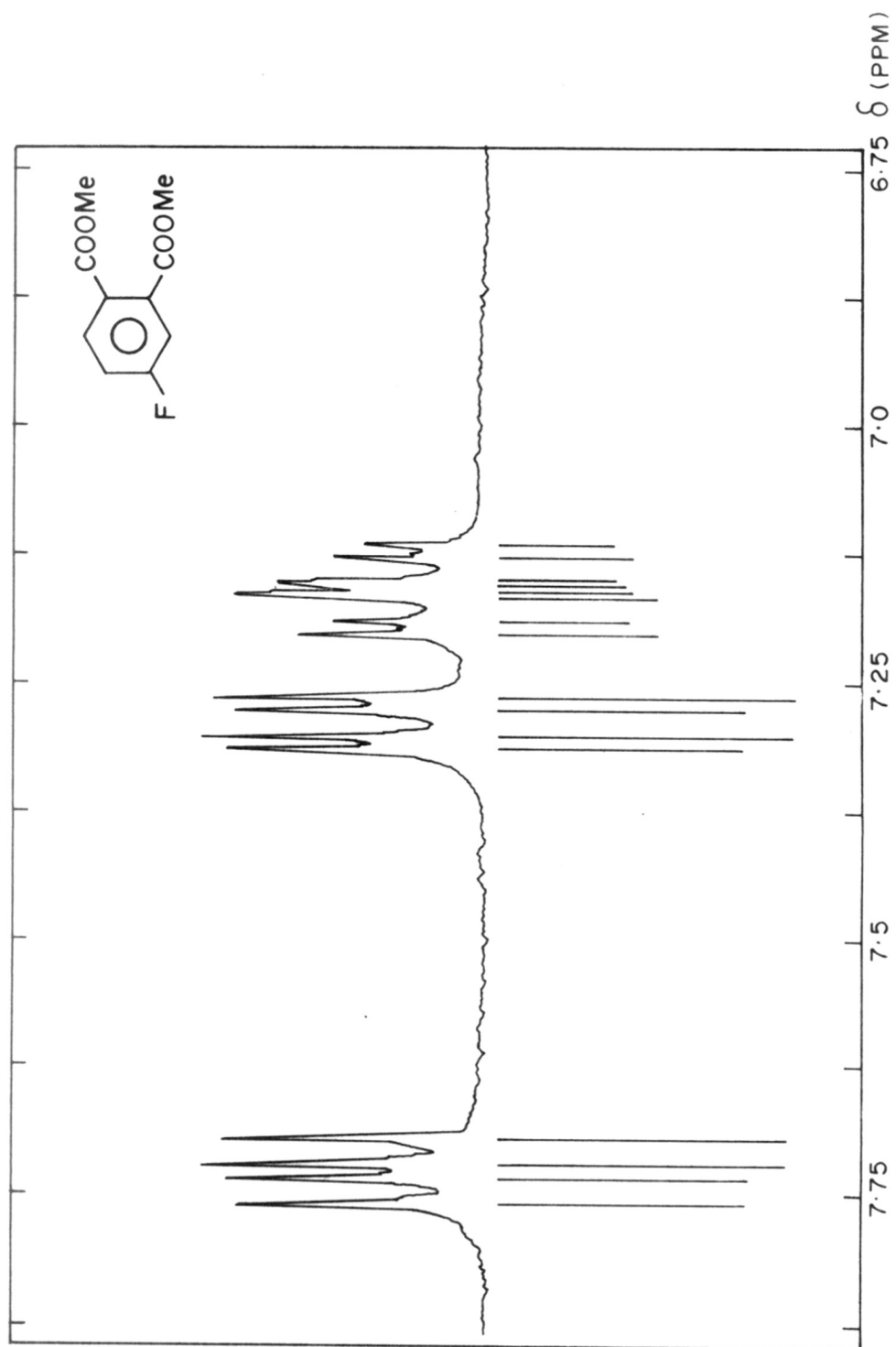


FIG.9 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-FLUOROPHTHALATE

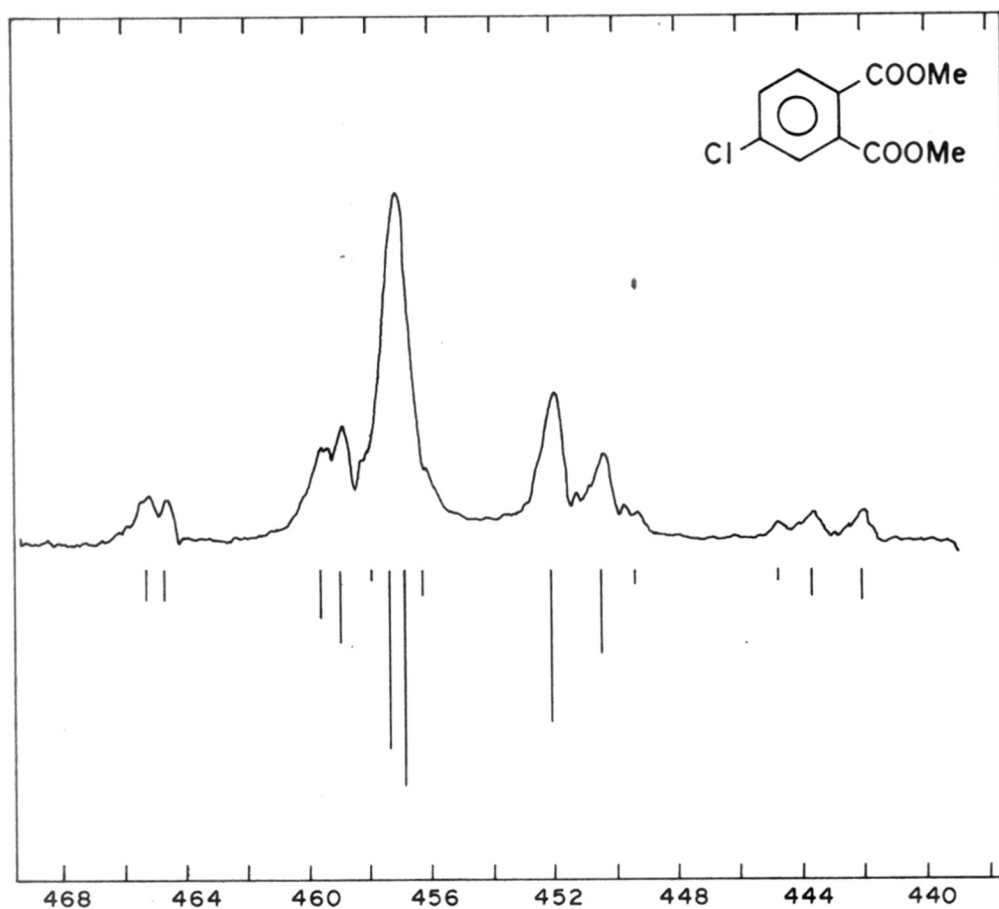


FIG. 10 OBSERVED AND CALCULATED SPECTRA OF DIMETHYL
4-CHLOROPHTHALATE

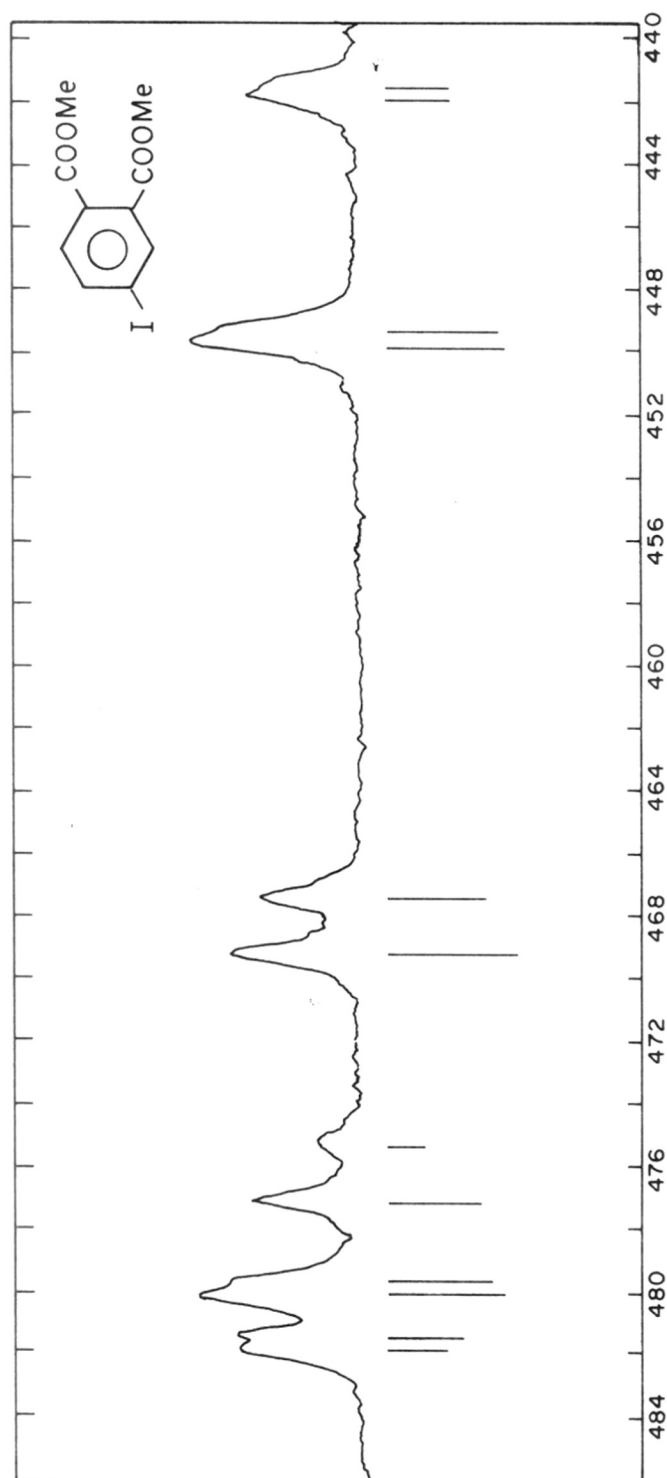


FIG. 11. OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-IODOPHTHALATE

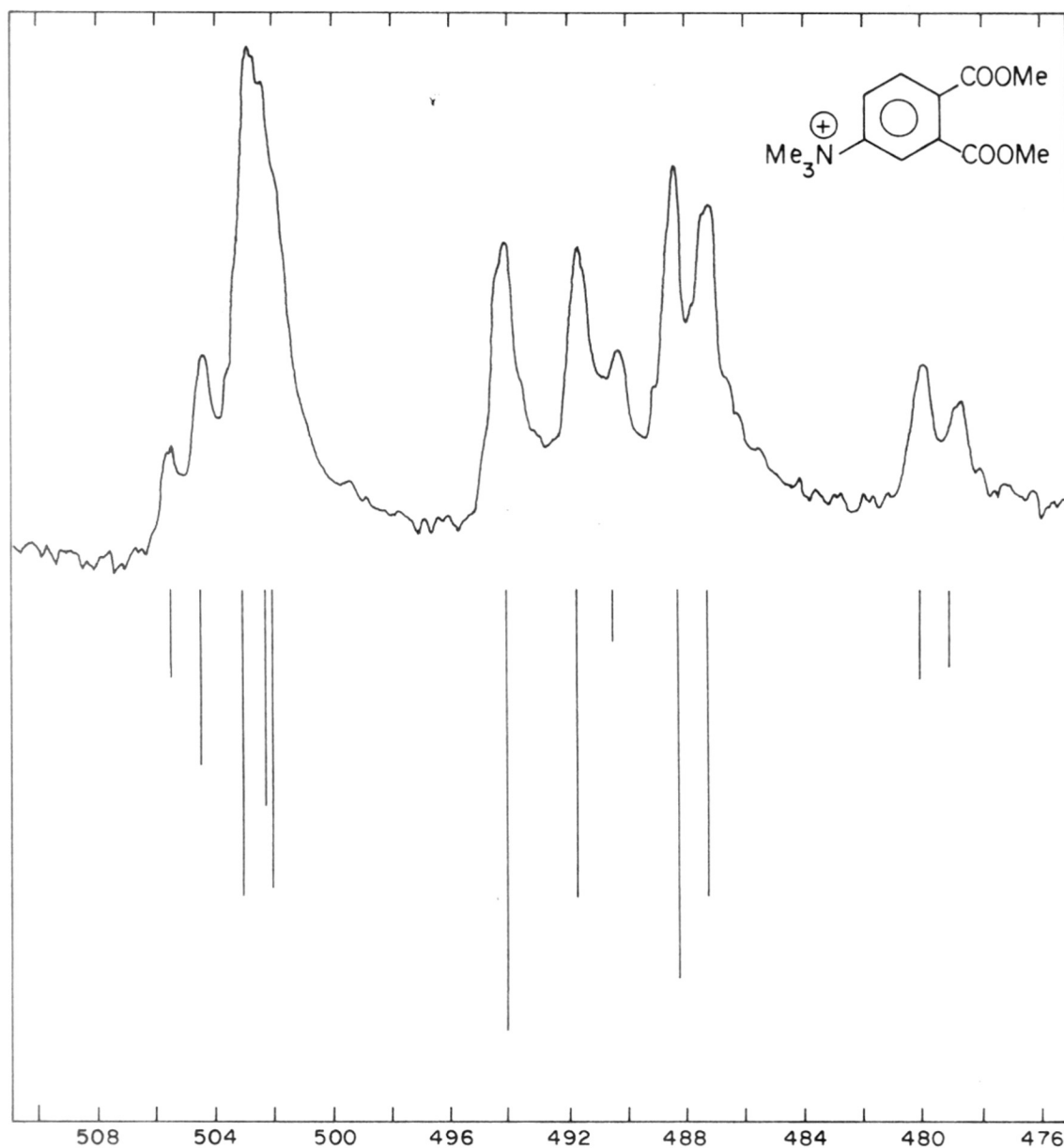


FIG. 12. OBSERVED AND CALCULATED SPECTRA OF DIMETHYL 4-
TRIMETHYL AMINOPHTHALATE
(3,4-DICARBOMETHOXYPHENYLTRIMETHYLAMMONIUM SULPHATE)

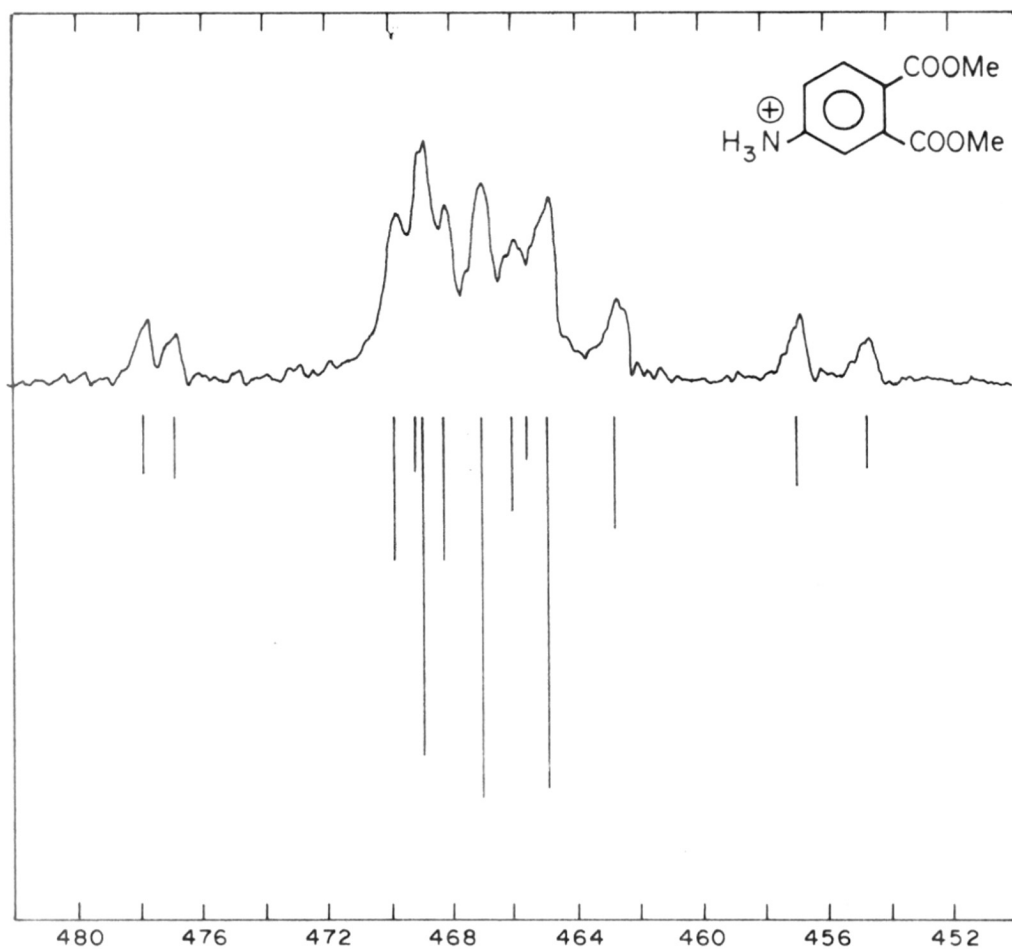


FIG. 13. OBSERVED AND CALCULATED SPECTRA OF DIMETHYL-4-AMMONIUM PHTHALATE
(3,4-DICARBOMETHOXYANILINIUM SULPHATE)

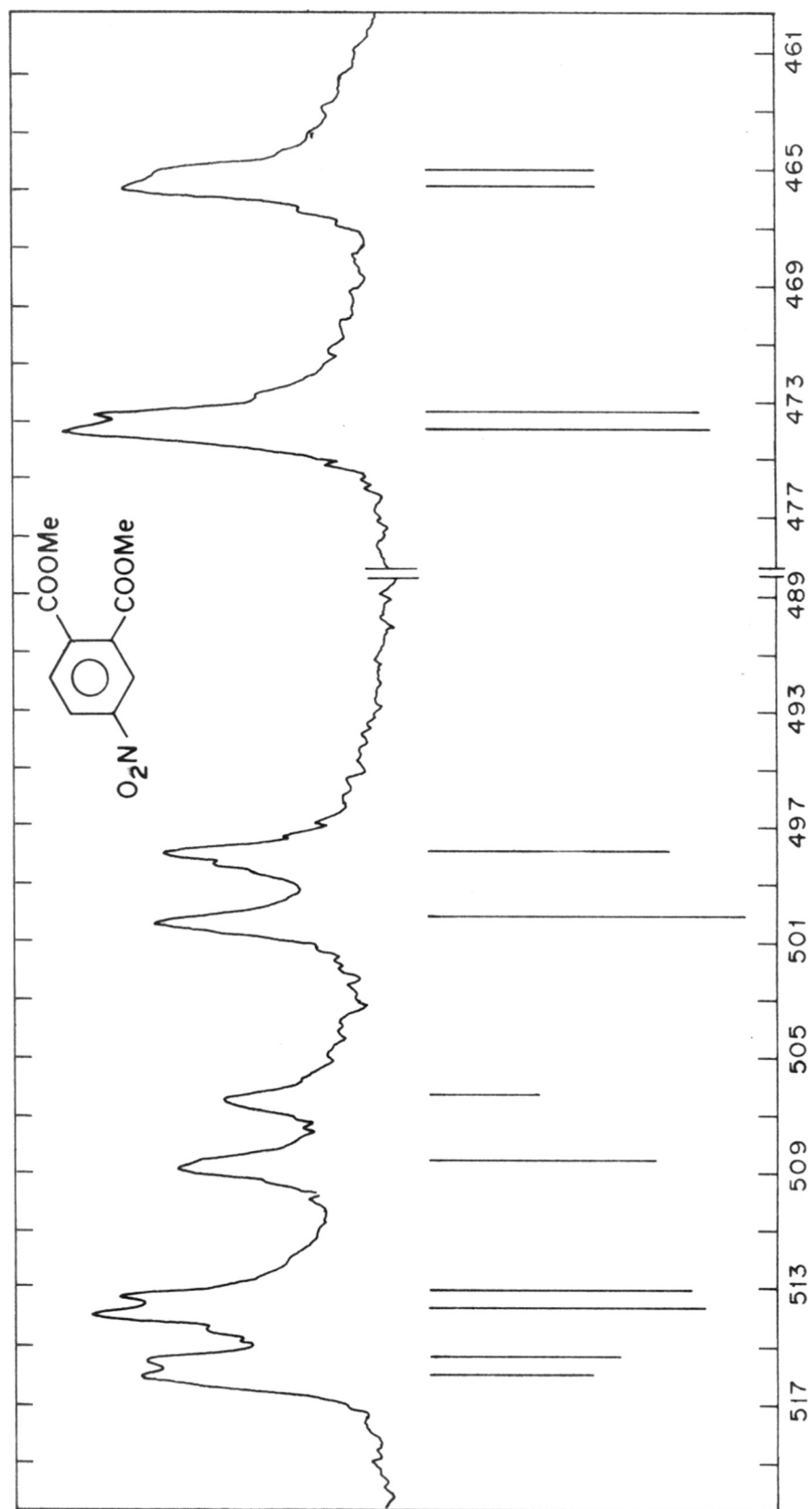


FIG. 14. OBSERVED AND CALCULATED SPECTRA OF DIMETHYL-4-NITROPHTHALATE

E X P E R I M E N T A L

Dimethyl 4-aminophthalate⁵⁷:

Commercial phthalic acid was nitrated to get a mixture of 3- and 4-nitrophthalic acids in almost equal amounts. The 3-nitro acid, being very less soluble in water, was separated as far as possible by recrystallisation from water. Even after four recrystallisations, the product obtained was found to be impure, but it contained mainly the 4-nitro acid. This was then esterified with methanol saturated with hydrogen chloride gas. The separation of the isomeric acids through their esters uses the fact that the 3-nitro acid forms a monomethyl ester, while the 4-nitro acid forms a ^{di}dimethyl ester. The monomethyl ester of 3-nitrophthalic acid was separated by treating with a strong solution of sodium bicarbonate. The dimethyl ester of 4-nitrophthalic acid was obtained as a heavy liquid, which was allowed to crystallise. The ester obtained as pale yellow crystals, melted at 111-112°C.

Dimethyl 4-nitrophthalate (30 g) was taken in a 3-necked round bottomed flask equipped with a mechanical stirrer and a dropping funnel. Zinc dust (20 g) and water (100 ml) were added to it and 50% acetic acid (150 g) was added slowly from a dropping funnel, while the mixture

was kept stirred. The temperature was not allowed to rise above 25°C . After the addition was over, the mixture was stirred for another hour. The amino ester was precipitated by neutralizing the acid present with ammonia, the reaction mixture being kept cold by addition of excess of crushed ice. The precipitate was separated by filtration. The precipitate was treated with ethyl acetate for removal of zinc salts which were insoluble in the solvent. The filtered ethyl acetate extract was treated with dil. H_2SO_4 (15%) in a separating funnel, whereby all the amino compound passed into the aqueous acid, leaving any unreacted nitro compound in the ethylacetate layer. The free amino ester was liberated with excess ammonia. On cooling the solution with crushed ice, dimethyl 4-aminophthalate crystallised out and was separated by filtration. The colourless crystals were further purified by recrystallising from alcohol. The amino ester obtained, melted at 83°C . Yield 19.2 g (73%).

Dimethyl 4-fluorophthalate⁵⁸

Dimethyl 4-aminophthalate (10.5 g) was dissolved in a mixture of conc. HCl (20 ml) and water (10 ml). The solution was cooled to 0°C and then diazotized with

sodium nitrite (3.5 g) dissolved in water (15 ml). To the cold diazotized solution was added a saturated solution of sodium fluoborate (17 g). The mixture was stirred rapidly, whereupon, the diazonium fluoborate of dimethylphthalate precipitated in crystalline form. The latter was filtered and washed with absolute alcohol and then absolute ether. The diazonium compound was dried in vacuum desiccator over sulfuric acid for 24 hours. The dry diazonium compound (10 g) was placed in a round bottomed flask (500 ml) connected to a wash bottle containing a 10% solution of sodium hydroxide through an empty trap. The flask was heated slowly to 125°C in an oil-bath. When the evolution of gases had abated, the temperature of the bath was raised to 140°C and maintained there for one hour. The oily residue was dissolved in carbontetrachloride, the solution washed with 10% aqueous sodium hydroxide, separated and dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled. The product, dimethyl 4-fluorophthalate, was obtained in a yield of 33 % (3.5 g).

Dimethyl 4-chlorophthalate⁵⁸

A solution of 21 g of crystallised copper sulfate

and 5.4 g of sodium chloride in 65 ml of hot water was prepared in a 500 ml three necked flask. The flask was fitted with a mechanical stirrer and an alkaline solution of sodium sulfite (4.4 g of NaHSO_3 and 3 g of NaOH in 30 ml water) was added during a period of 5 to 10 minutes. The mixture was allowed to cool to room temperature and washed by decantation. The cuprous chloride obtained as a white powder was suspended in a mixture of 100 ml of water and 25 ml of conc. HCl . Dimethyl 4-aminophthalate (10.5 g) was dissolved in a mixture of 20 ml of conc. HCl and 10 ml of water and diazotized with 3.5 g of sodium nitrite dissolved in 15 ml of water. The diazotized solution was introduced slowly and with rapid stirring below the surface of the suspension of cuprous chloride already prepared. The mixture was then heated on a steam-bath for sometime. The oily layer was extracted with carbontetrachloride, the solution washed with dil. HCl , aqueous sodium-hydroxide and finally washed with water repeatedly. The CCl_4 solution was dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled under reduced pressure, m.p. 37°C .

Dimethyl 4-bromophthalate⁵⁸

The cuprous bromide was prepared just as cuprous chloride using 10.5 g of copper sulfate, 5.5 g of sodium

bromide, 2.2 g of sodium sulfite and 1.5 g of sodium hydroxide. The cuprous bromide obtained was suspended in 100 ml of water and 15 ml of 48% hydrobromic acid. 10.5 g of 4-amino ester was dissolved in a mixture of 20 ml of 48% HBr with 3.5 g of sodium nitrite in 15 ml of water. The diazotized solution was introduced slowly below the surface of the suspension of cuprous bromide in water and HBr, with rapid stirring. The mixture was then heated on a steam-bath and the oily layer was extracted with CCl_4 , washed with dil. HCl, aq. NaOH and finally with water. The CCl_4 solution was dried over anhydrous sodium sulfate and the solvent removed. The residue was purified by distilling under reduced pressure, m.p. 40°C , b.p. $303-306^\circ\text{C}$.

Dimethyl 4-iodophthalate⁵⁸

10.5 g of the 4-amino ester was dissolved in a mixture of 4 ml of conc. H_2SO_4 and 30 ml of water and diazotized with 3.5 g of sodium nitrite dissolved in 15 ml of water. The diazotized solution was treated with 12 g of potassium iodide in 100 ml of water. The iodide ester was obtained in the form of a red oil. The product was purified by distillation under reduced pressure, b.p. 219°C .

Dimethyl 4-hydroxyphthalate

The 4-amino ester was diazotized as usual in conc. H_2SO_4 . The clear diazonium sulfate solution was poured slowly into a large volume of water with stirring. The mixture was heated on a steam-bath for several hours. The solution was extracted with ether after it was cooled. The ether solution was dried over anhydrous sodium sulfate. Ether was removed and the solid left was purified by recrystallization from toluene. The pure dimethyl 4-hydroxyphthalate melted at $107-8^\circ\text{C}$.

Dimethyl 4-methoxyphthalate

The 4-hydroxy ester was converted into its methyl ether by refluxing the compound with dimethyl sulfate, anhydrous potassium carbonate in dry acetone. The 4-methoxy compound was purified by distillation under reduced pressure (b.p. $195-7^\circ\text{C}/20\text{ mm}$).

Dimethyl 4-methylphthalate⁵⁹

In a one litre round bottomed flask fitted with a reflux condenser were placed maleic anhydride (37.5 g), freshly distilled isoprene (25 g), picric acid (100 mg) and benzene (130 ml). The mixture was heated to start the reaction, which then proceeded with evolution of heat. When the initial reaction subsided, the mixture was

heated under gentle reflux for 20 hours. The benzene and isoprene were removed by distillation under reduced pressure. The residue was treated with pet. ether (80-120°C) and enough benzene to dissolve the material. The solution was treated with a little charcoal and allowed to crystallize. The 4-methyl-1,2,3,6-tetrahydrophthalic anhydride (40 g), which separated as colourless needle-shaped crystals, was quite pure and melted at 64°C.

The above anhydride (19 g) was dissolved in glacial acetic acid (40 ml) and a solution of bromine (50 g) in glacial acetic acid (44 ml) was added to it slowly keeping the temperature of the mixture at 60°C. The addition of bromine was completed in an hour. The first third of the bromine solution was decolorized immediately and some hydrogen bromide evolved. The mixture was then refluxed for 16 hours and the solution concentrated under reduced pressure. The residue was then heated at 210-220°C for 9 hours, during which time considerable amount of hydrogen bromide evolved and the material became dark. This residue was distilled under reduced pressure (20 mm). A colorless liquid was obtained, which crystallized immediately. The crude 4-methylphthalic anhydride was further purified

by recrystallizing it from benzene-pet. ether mixture. The yield of the pure material melting at 93°C was 12 g (68%). The pure 4-methylphthalic anhydride (5 g) was refluxed with absolute methanol (50 ml) and a little sulfuric acid as catalyst, for one hour. The mixture was poured into cold water from which the dimethyl ester was separated by extraction with ether and the unreacted 4-methylphthalic acid was removed by washing the ether extract with dilute sodium carbonate solution. The ether solution was dried over anhydrous sodium sulfate and ether removed. The resulting oil was distilled under reduced pressure. The dimethyl 4-methylphthalate came off at $120-2^{\circ}\text{C}/3.5\text{ mm.}$

Dimethyl 4-tert-butylphthalic acid⁶⁰

In a 2 litre separatory funnel were placed 296 g (380 ml, 4 moles) of t-butyl alcohol and 988 ml (12 moles) of C.P. conc. HCl (sp. gr. 1.19). After shaking, the layers were allowed to separate (15-20 minutes) and the upper layer was drawn off and washed first with a 5% sodium bicarbonate solution, then with water until neutral to moist litmus paper. The t-butyl chloride was treated with 40 g of calcium chloride

and shaken thoroughly, then distilled while passing cold water through the condenser. The fraction boiling at 50-52°C weighed 320 g (80%).

One mole of naphthalene (128 g) was dissolved in two moles of (185 g) of t-butyl chloride with warming and mechanical stirring. As soon as the solid had dissolved the heating was discontinued and anhydrous AlCl_3 (1 g) was added. When the vigorous reaction that had set in subsided, another lot of AlCl_3 (1 g) was added. The solution soon turned dark and after the addition of a further amount of AlCl_3 (2 to 4 g) solidified to a cream coloured mass. After about 20 minutes the evolution of HCl stopped and the solid was dissolved in the minimum amount of hot methanol and the solvent allowed to cool. The di-t-butyl derivative separated out in an yield of about 74 g. Distillation of methanol solution gave 45 g of 2-t-butyl naphthalene (b.p. 280-290°C) and 52 g of the disubstituted compound (b.p. 320-340°C) m.p. 80-82°C. Recrystallization of this from methanol gave more of the less soluble 2,6-di-t-butyl naphthalene (I).

Half a mole (50 g) of chromium trioxide dissolved in a mixture of 80 ml of glacial acetic acid

and 40 ml of water was added slowly to a hot solution of 0.1 mole (24 g) of (I) in 200 ml of glacial acetic acid and the solution was refluxed for 15 minutes. The hot solution was poured onto ice and the solid obtained was crystallized from ethanol. Yield of the pale yellow 2,6-di-t-butyl-1,4-naphthaquinone (II) was 46-57%, m.p. 86-87°C. A mixture of (II) (13.5 g), KMnO_4 (27 g) and water (500 ml) was refluxed for 3 hours. Cooled and filtered. The manganese dioxide was extracted with 75 ml of 7% sodium hydroxide solution and this solution was combined with the original filtrate. After adding about 100 ml of 3% H_2O_2 the mixture was allowed to stand overnight. The alkaline solution was extracted with ether and the ether layer discarded. Acidification of the alkaline layer, extraction with ether and evaporation of ether gave 4 g of 4-t-butylphthalic acid. Recrystallization from xylene removed the yellow contaminating material and the acid separated in white, odourless crystals which melted with decomposition at 155-157°C. The acid was then esterified with methanol and catalytic amounts of conc. H_2SO_4 to give the dimethyl 4-t-butylphthalate.

Dimethylphthalate

Pure o-phthalic acid was esterified with methanol

in the traditional way and the ester isolated.

The pale yellow liquid obtained was further purified by distillation to get a colorless liquid b.p. $161^{\circ}\text{C}/3\text{ mm.}$

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CHAPTER III

**PROTON CHEMICAL SHIFTS IN SUBSTITUTED
ARYL AMMONIUM AND ARYL TRIMETHYLAMMONIUM SALTS**

PROTON CHEMICAL SHIFTS IN SUBSTITUTED
ARYL AMMONIUM AND ARYL TRIMETHYL AMMONIUM SALTS

It may be recalled that in an attempt to explain the apparent deviation of the $C_{(3)}$ -proton chemical shift in dimethyl 4-t-butylphthalate from the correlation observed the effect of steric interaction (of the butteressing type) has been invoked. That is, the diamagnetic shift for the $C_{(3)}$ -proton which is larger than expected has been rationalized on the basis of the larger rotation of the $C_{(2)}$ -COOMe group out of the plane of the benzene ring due to the butteressing action of the $C_{(1)}$ -COOMe group in the presence of a steric interaction between the 4-t-butyl group and the $C_{(3)}$ -proton which is communicated to the $C_{(2)}$ -COOMe group. If this rationalization is correct, it should be possible to demonstrate the effect separately by choosing a group which is nearly as bulky as t-butyl group but does not interact with the acceptor group (COOMe) at $C_{(1)}$ -position mesomerically. A pair of substituents that would correspond in size to methyl and t-butyl groups are NH_3^+ and NMe_3^+ respectively. In order to estimate the effect of steric interaction, their 'normal' substituent effects on

aromatic protons in a benzene ring should first be estimated. In other words, an effective substituent constant should be evaluated. For this purpose a number of di-substituted, mostly *p*-disubstituted, quaternary anilinium salts and trimethyl anilinium salts have been prepared and their aromatic proton chemical shifts determined.

RESULTS AND DISCUSSION

The relevant data obtained are presented in Table 1. If the rule of additivity¹ holds good, for the cations concerned, it should be possible to evaluate the ortho and meta substituent constants ($s_o^{+NMe_3}$, $s_m^{+NMe_3}$) for the NMe_3^+ group employing the usual procedure. These are given by the expressions,

$$\begin{aligned} s_o^{+NMe_3} &= \delta_o^{obs} - s_m^X - \delta^B \\ s_m^{+NMe_3} &= \delta_m^{obs} - s_o^X - \delta^B, \end{aligned}$$

where δ_o^{obs} and δ_m^{obs} are observed chemical shifts from TMS for protons ortho and meta to the NMe_3^+ group. s_o^X and s_m^X are the ortho and meta substituent constants of the group 'X' and δ^B is the line position of benzene

TABLE 1 - PROTON CHEMICAL SHIFTS IN 4-SUBSTITUTED PHENYL-
TRIMETHYLAMMONIUM SULPHATES (in Hz)

Substituent	Solvent	Proton Chemical Shifts			Calculated substituent constants for -NMe ₃ group	
		C _{2,6} -protons	C _{3,5} -protons	Ortho	Meta	
COOMe	D ₂ O	477.000	497.00	34.000		9.600
"	MeOH	485.300	494.700	42.300		7.300
Me	D ₂ O	458.365	441.635	21.365 ± 1.2		7.035 ± 1.2
"	MeOH	468.500	448.500	21.500 ± 1.2		13.900 ± 1.2
CHO	D ₂ O	488.000	488.000	34.800 ± 1.8		10.200 ± 2.4
"	MeOH	490.000	490.000	36.800 ± 1.8		12.200 ± 2.4
H	MeOH	477.000	457.000	37.000		17.000

PROTON CHEMICAL SHIFTS IN 3-SUBSTITUTED PHENYLTRIMETHYLAMMONIUM
SULPHATES (in Hz)

Substituent	Solvent	Proton Chemical Shifts		Calculated substituent constants for NMe ₃ group	
		C ₂ -proton	C ₅ -proton	Ortho	Meta
COOMe	D ₂ O	506.000	466.000	18.600	23.000
"	MeOH	510.000	467.000	22.600	24.000

in methanol with TMS as internal reference. For spectra obtained in aqueous solutions, a theoretical line position for benzene in water may be calculated by obtaining the spectrum of a water soluble p-disubstituted aromatic compound (p-cresol) using TMS as external reference. Assuming that the rule of additivity holds and using the substituent constants (polar solvent) for Me and OH groups, the theoretical benzene line position (internal reference) may be calculated which may be used for obtaining substituent constants from other water soluble p-disubstituted benzene derivatives. The position of this 'theoretical' absorption position is 440 Hz downfield from an external TMS standard. In methanol solution benzene is 440 Hz downfield from TMS (internal standard). The calculated substituent constants are presented in Table 1. Unfortunately the calculated 'constants' show large variations. The value of the ortho constant varies from 18.6 Hz to 42.3 Hz and the meta constant varies from 7.3 Hz to 24 Hz, the lower and upper limits for the ortho and meta constants being obtained from 3-carbomethoxyphenyl-trimethylammonium sulphate and 4-carbomethoxyphenyl trimethylammonium sulphate. In m-t-butylbenzoic ester, it is seen that

the rule of additivity holds good despite the steric interaction that is undoubtedly present in the molecule². These discrepancies in the trimethyl ammonium derivatives might be traced to the ionic character of the molecules. The effects of solvation are apparently dependent on structure.

It is of interest to note that the spectrum of $\text{p-NMe}_3^+-\text{C}_6\text{H}_4-\text{CHO}$ in D_2O shows a single peak (488 Hz) for all the four ring protons, the aldehydic proton absorption coming at the expected place (602 Hz). The signal of $-\text{NMe}_3^+$ group appears at 224 Hz. But when the spectrum of the same sample is obtained in methanol solution, it shows not only this two line spectrum for the aromatic and aldehyde protons but also an extra quartet with another absorption superposed on it. The singlet absorptions at 606 Hz and 490 Hz are in the intensity ratio 1:4 and this clearly indicates that these signals are indeed due to the quaternary ammonium salt of the aldehyde. The quartet apparently arises from another species which is generated from the ammonium salt. When the methanolic solution is warmed the signals due to the second species (the quartet) became more and more intense at the expense of those of the trimethyl ammonium salt. On repeated warming the

transformation of the quaternary compound goes to completion as indicated by the complete disappearance of the aldehyde absorption and the singlet aromatic proton absorption at 430 Hz. The final spectrum is of the new species. The changing pattern of the spectrum is presented in Fig.1. The possibilities we might consider for the reaction that is apparently taking place are (i) methyl migration from the quaternary nitrogen atom to the carbonyl oxygen and (ii) solvolysis of the quaternary ammonium ion and accompanying conversion of the aldehyde into its acetal catalyzed by the acid produced in the solvolysis. In the final spectrum the absorption of the benzylic proton is at 459 Hz. This is at too high a field to be due to α -methoxy-*p*-N,N-dimethylaminobenzyl cation. The reaction that takes place is probably the second of the two possibilities. The final product can, of course, be obtained through the first path by subsequent co-ordination of methanol with the carbonium ion. The transformation and the equilibria involved are shown in Chart 1.

When conc. H_2SO_4 (one or two drops) is added to a methanolic solution of *p*-aminobenzaldehyde and the spectrum is recorded, it is noted that the aldehyde

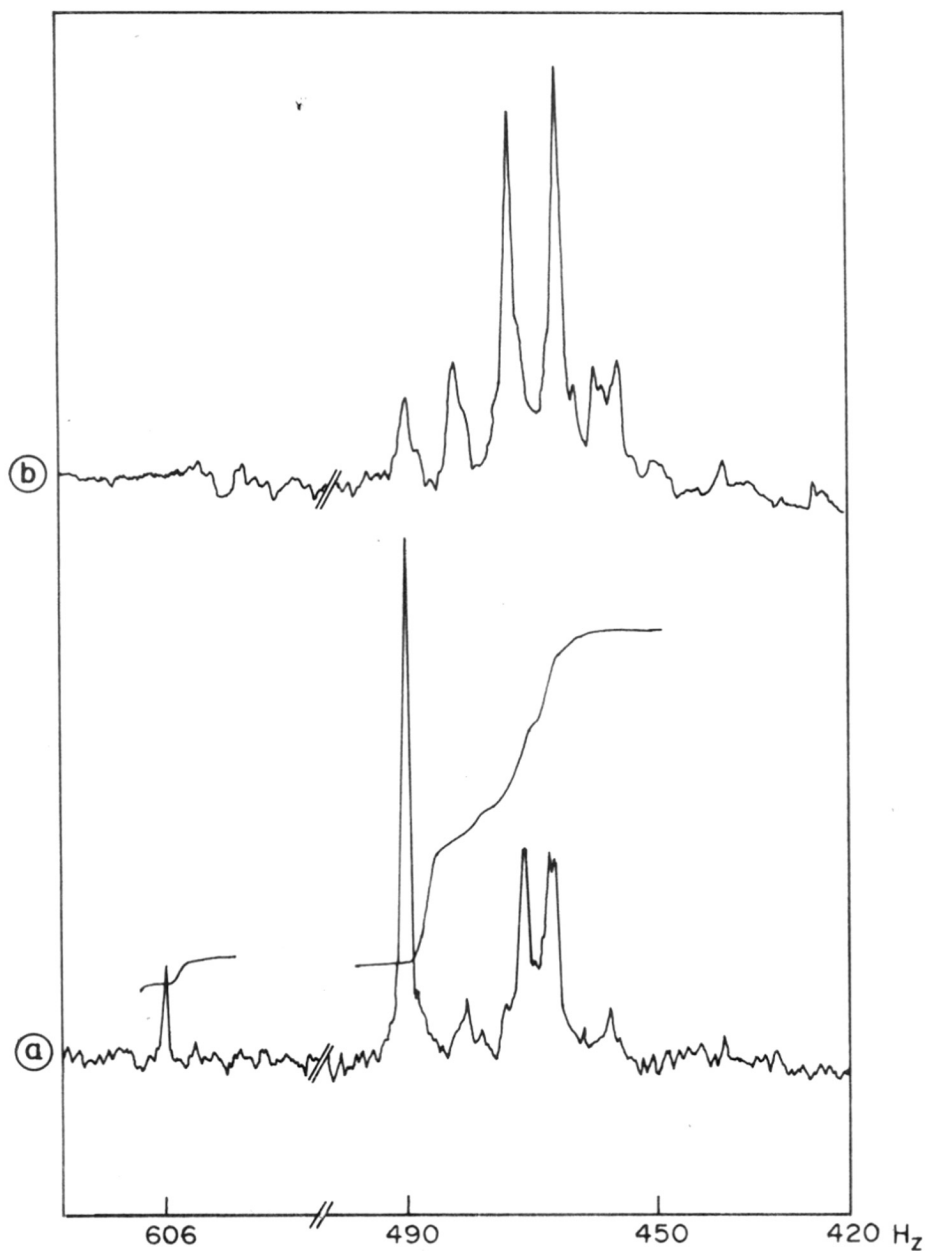
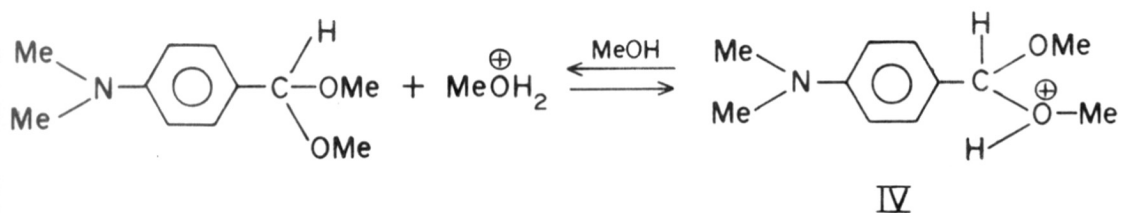
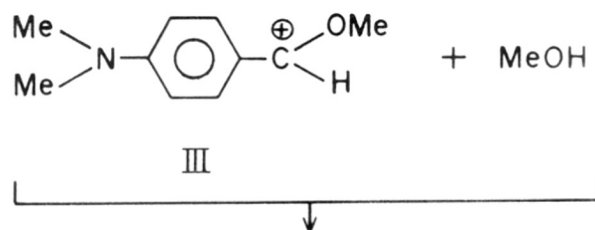
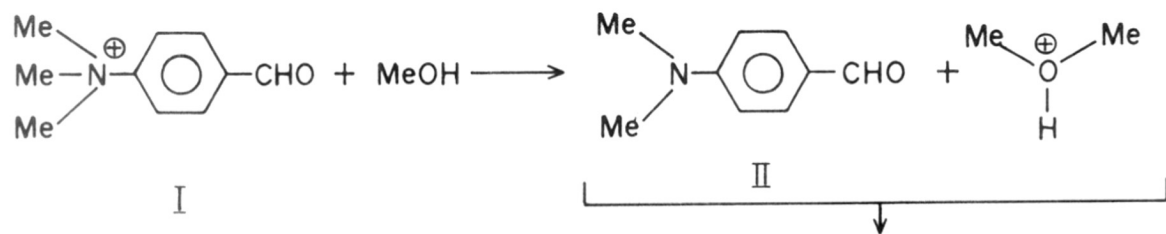


FIG.1 AROMATIC REGION OF THE SPECTRA OF:-

(a) 4-FORMYLPHENYLTRIMETHYLAMMONIUM SULPHATE IN METHANOL
 (b) " " " " " " "
 ON WARMING

CHART 1

proton in the original aldehyde comes along with the aromatic protons at 459 Hz (Fig.2). In view of the foregoing discussion the species that is produced in predominant amount is apparently the acetal of the aldehyde.

The anilinium salts of some other *p*-substituted anilines devoid of basic sites except for the amino nitrogen are prepared by adding conc. H_2SO_4 (one or two drops) to a methanolic solution of the compound. The chemical shifts are presented in Table 2. The ortho and meta substituent constants ($S_o^{\text{NH}_3^+}$, $S_m^{\text{NH}_3^+}$) are evaluated by the same procedure followed in the case of quaternary ammonium salts. Here again the NMR substituent effects measured as $S_o^{\text{NH}_3^+}$, $S_m^{\text{NH}_3^+}$ are not constant when the *p*-substituents are altered. The reason for failure of the additivity rule is presumably the same as in the case of the trimethyl ammonium salts.

In order to answer the question posed with regard to phthalic esters we might, in this unfortunate circumstance, consider the use of S_o and S_m values obtained from carbomethoxy derivatives in place of average values. The derivatives concerned are

TABLE 2 - PROTON CHEMICAL SHIFTS IN 4-SUBSTITUTED
ANILINIUM SULPHATES (in Hz)

Substituent	Proton Chemical Shifts		Calculated substituent constants for $-\text{NH}_3^+$ group	
	C _{2,6} -protons	C _{3,5} -protons	Ortho	Meta
OMe	441.925	423.075	5.600 $\pm$ 1.800	5.200 $\pm$ 2.400
F	453.000	435.000	14.800 $\pm$ 3.600	10.000 $\pm$ 1.800
Cl	450.000	450.000	13.000 $\pm$ 2.400	7.600 $\pm$ 1.200
Br	444.385	461.115	11.500 $\pm$ 1.200	11.000 $\pm$ 0.600
I	437.030	470.970	5.400	6.370
Me	440.000	440.000	3.000 $\pm$ 1.200	5.400 $\pm$ 1.200
t-Bu	445.300	453.700	8.300	8.300
COOMe	456.340	488.660	13.340	1.260

p-carbomethoxy-trimethyl anilinium and p-carbomethoxy anilium salts. Unfortunately the deviations observed are maximum in these derivatives and it does not look advisable to utilize the substituent constants obtained from these derivatives to estimate the effect of steric interaction in 4-NMe₃⁺ substituted dimethylphthalates by comparison with the corresponding -NH₃⁺ derivative. The spectrum of p-carbomethoxytrimethylanilinium sulphate obtained in D₂O shows that the NMe₃⁺ group remains stable in this solution. The difficulty encountered in this present attempt at evaluation of the substituent constants must therefore be attributed to solvent effects.

EXPERIMENTAL

p-Substituted anilines

p-Anisidine, p-toluidine, and all the four p-haloanilines were obtained from commercially available samples which were further purified by either crystallization or distillation depending upon whether they were solids or liquids. Commercial p-aminobenzoic acid was converted to its methyl ester with methanol and catalytic amounts of conc. H_2SO_4 m.p. 112°C .

p-t-Butylaniline was obtained in the course of the preparation of p-t-butylbenzoic acid which is described in Chapter III. Commercial m-aminobenzoic acid was purified by recrystallization and esterified to get the methyl ester m.p. 37°C .

p-Aminobenzaldehyde³

Crystalline sodium sulfide (3 g, 0.125 mole) nonahydrate, flowers of sulfur (15 g, 0.47 g atom) and sodium hydroxide pellets (27 g, 0.67 mole) were added to distilled water (600 ml) in a 1-litre beaker. The mixture was heated on a steam-bath for 15-20 minutes with occasional stirring and then poured into a 2-litre round-bottomed flask containing a hot solution of

p-nitrotoluene (50 g, 0.36 mole) in 95% ethanol (300 ml). A reflux condenser was attached and the mixture heated under reflux for 3 hours. The resulting clear but deep red solution was rapidly steam-distilled until about 1.5 - 2 litres of condensate had been collected. The distillate was clear when the distillation was stopped. The residue in the flask had a volume of 500-600 ml as required. This solution was rapidly chilled in an ice-bath with occasional vigorous shaking and stirring to induce crystallization. After 2 hours in the ice-bath, the golden yellow crystals of p-amino benzaldehyde were collected on a Buchner funnel and washed with 500 ml of ice water to remove sodium hydroxide. The product was immediately placed in a vacuum desiccator over solid potassium hydroxide pellets for 24 hours. The yield of the pure p-aminobenzaldehyde, m.p. 68-70°C, amounted to 18-22 g (40-50%).

There was no indication of the formation of oily tar (polymeric condensation products of p-aminobenzaldehyde with itself) which can sometimes be obtained in this preparation.

p-Dimethylaminobenzaldehyde⁴

In a 3-necked two litre flask equipped with a

mercury seal stirrer, a dropping funnel and a reflux condenser carrying CaCl_2 guard tube, was placed dimethyl formamide (44.2 ml, 0.6 mole). The flask was cooled in an ice-salt mixture and phosphorus oxychloride (25.3 g, 0.165 mole) was added dropwise with stirring. A vigorous reaction occurred with the formation of a $\text{DMF} \cdot \text{POCl}_3$ complex. After all the oxychloride was added, dimethylaniline (20 g, 0.165 mole) was added slowly, with stirring. At the end of the addition, a greenish yellow precipitate began to form. The reaction mixture was heated on a water-bath and stirring continued for another two hours. The precipitate redissolved and the mixture was then cooled and poured onto crushed ice (500 g). The solution was made nearly neutral by adding a solution of sodium hydroxide, while the temperature was kept below 20°C by adding crushed ice. The solution was finally neutralized to pH 6-8 by adding aqueous sodium acetate solution (150 ml) with vigorous stirring. *p*-Dimethylaminobenzaldehyde began to separate and the mixture was kept overnight in a frigidaire. The precipitate was separated by filtration and greenish colour was removed by washing with water. The required aldehyde was obtained as a

pale yellow solid (20 g) after drying in air.

The pure product, after recrystallization from alcohol melted at 72°C (lit. 73°C).

Quaternary ammonium salts

Quaternary ammonium salts of the following anilines were prepared:

- 1) Aniline
- 2) *p*-Toluidine
- 3) methyl *p*-aminobenzoate
- 4) methyl *m*-aminobenzoate
- 5) *p*-aminobenzaldehyde
- 6) dimethyl 4-aminophthalate

As a typical example for this series, the preparation of the quaternary ammonium salt of methyl *p*-aminobenzoate is described below.

A large excess of dimethyl sulfate (6 g) was added to methyl *p*-aminobenzoate (1 g) in small portions at a time with simultaneous addition of sodium methoxide solution. Finally the mixture was made alkaline to phenolphthalein by adding sodium methoxide solution. The mixture was kept overnight and 30% sodium hydroxide solution (20-25 ml) was added. The oily layer separated was allowed to solidify. The solid was separated and

crystallized from a mixture of acetone and methanol.

The quaternary salts of aniline and *p*-amino-benzaldehyde were obtained starting from the dimethyl amino derivatives instead of the amino compounds. The procedure followed to get the salt was same as that described above.

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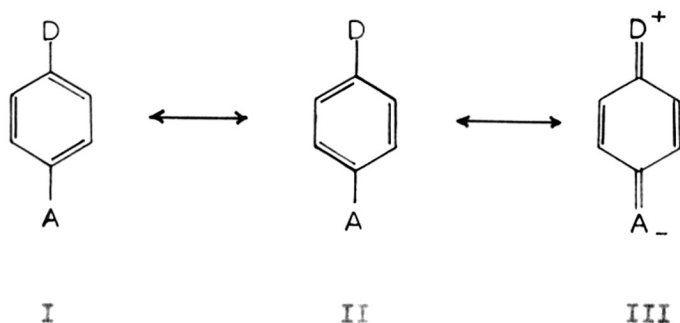
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CHAPTER IV

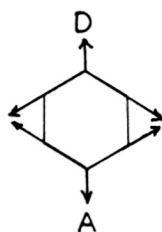
**INFRARED BAND INTENSITIES OF SOME
DI - AND TRI - SUBSTITUTED BENZENES**

INFRARED BAND INTENSITIES OF SOME DI- AND TRI-SUBSTITUTED BENZENES

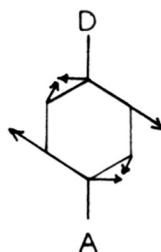
In the background of the results obtained in the previous Chapter, it appeared likely that a study of IR vibrational band intensities and frequencies in 4-substituted phthalic esters and necessary allied derivatives would furnish results that may be related to the interaction between donor and acceptor groups. The band chosen for this purpose is the C=C stretching mode (ν_{16a} and ν_{16b}). When there is an interaction between the donor and acceptor groups para to each other on a benzene ring, it would normally be expected that the extent of localization of the double bond in the ring as in structure (III) varies with the strength of the interaction. If the



acceptor group is fixed and the donor group is varied along a series, then the degree of localization of the double bonds as indicated and the associated charge separation will vary with donor strength. In a vibrational mode in which nuclear coordinate changes favour structure (III) there will be strong interaction between electronic and nuclear motions and the strength of the mesomeric interaction will be manifested in the intensity of this mode since the rate of change of dipole moment during any vibration determines its intensity. The vibration parallel to the direction of charge separation ν_{16} , is indicated in IV and V. The compounds studied



IV



V

are a series of *p*-substituted benzoic esters and the series of 4-substituted phthalic esters covered by the NMR study. The intensities of NO_2 sym. stretching band and $\text{C}\equiv\text{N}$ stretching band have also been studied for a close comparison of the effects of methyl and *t*-butyl

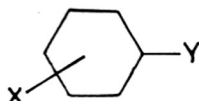
groups. In order to put the present study in perspective, the applications of measurements of vibrational band intensities in general and, in particular, with regard to substituent effects in benzene derivatives are reviewed briefly below.

The true intensities of both fundamental and overtone vibration bands have been used in structural diagnosis for differentiation and estimation of functional groups. The significance of vibrational band intensities has been discussed by Thompson¹. Integrated band intensities have been determined for the fundamentals of CH_3 , CH_2 and CH group vibrations in aliphatic hydrocarbons, ketones and esters by Francis² and the mean values per group have been estimated. The results show clearly that if carbonyl groups or oxygen atoms are adjacent to the alkyl groups, the vibrational intensities of the latter are much affected, mainly through electronic effects. Much work has been done on carbonyl groups. Results of Barrow³, Francis² and unpublished work of Thompson show that in aliphatic groups, the intensity varies markedly with the type-ketone, ester, amide, etc. and Barrow has tried to correlate this variation with the molecular resonance energy. The position of carbonyl groups in a steroid

skeleton or in a side chain can sometimes be decided⁴ from intensity values and Burer and Gunthard⁵ have found an interesting variation of intensity for the carbonyl group in saturated ring ketones of different size. The various types of NH group in aliphatic or aromatic secondary amines⁶, amides or heterocyclic bases differ considerably as regards vibrational band intensity, which can be used for type identification. Rough intensity data for the olefinic C=C group stretching vibration may also discriminate between classes in which the nature of the attached groups is different⁷. Moccia⁸ and Thompson observed that the fundamental OH group vibration in simple phenols is about three times more intense than the same vibration in simple alcohols.

Vibrational frequencies and intensities are, respectively, controlled essentially by the bond force constants and $\partial\mu/\partial Q_i$, the variation of molecular dipole moment with normal co-ordinate. Change of a substituent group may effect either, neither, or both of frequency and intensity for the chromophoric group. Sometimes the frequency shift is very small but the change of band intensity is large. Along the series CHX_3 where X = Cl, Br, I, for example⁹ there is little change in the C-H bond stretching frequency, but its

intensity increases some fourfold. It should be possible to interpret the experimental data in terms of inductive, mesomeric or resonance and steric influences of substituent groups. Some attempts have been made to correlate frequencies and band intensities of key groups with electronegativity of attached groups¹⁰ or with the molecular resonance energy. Disubstituted benzenes (VI)



VI

are a class of compounds for which several attempts have been made to relate spectral parameters (frequencies and intensities) to inductive, mesomeric and steric effects of substituents. Most frequently the practice has been to study the effects of substituents "X" on a vibration which is almost localized in group Y. The effect of Hammett σ constant¹¹ upon the vibration frequency ν of the group Y has been measured for a number of series including phenols¹², anilines^{13, 14}, benzoic acids¹⁵, nitrobenzenes^{15, 39} and aryl ketones¹⁶. Fairly regular trends have been found between ν and σ .

Electron donating groups with positive σ values sometimes raise ν , but may act in the reverse sense, and the frequency shifts are as a rule fairly small. It was found, however, that the effect of substituents upon the intensity of the $C\equiv N$ group in substituted benzonitriles is large¹⁷⁻¹⁹. Thompson et al.^{17,20} found that the data on substituted benzonitriles fit a linear relation between $\log A$ and σ despite the work of Brown²¹ which could not justify this empirical linear relation and they found that the slope of this $\log A$ vs. σ plot is about the same in different solvents. Similar measurements were also made with substituted anilines and N-methylanilines, for the N-H bond stretching vibrations^{22,23}. It was found that the slopes of $\log A$ vs. σ plots for antisymmetric and symmetric stretching vibrations are different. Krueger found that some ortho substituted anilines fall into line if Taft²⁴ substituent constants are used and that it may be possible to separate σ_I and σ_R factors. The corresponding studies of the OH vibration band in substituted phenols have led to similar conclusions.

The effect of nuclear substituents on the $C=O$ group frequency and intensity in compounds of the type

-COR has also been measured^{25,31}. The compounds

include benzaldehyde benzoic esters, acetophenones and benzophenones. In these molecules, the substituent effects the frequency, but the band intensity is hardly influenced at all. In substituted acetanilides, nuclear substituents appear to have almost no effect upon either the frequency or intensity of the NH group²⁶. The important general conclusion to be drawn from these results is that the influence of nuclear substituents can operate in different ways. The fact that with a pair of series such as the benzonitriles and anilines, the introduction of electron-donating substituents decreases both the $C\equiv N$ and NH_2 group frequencies, does not imply that the vibrational intensities will be effected in the same sense, they are in fact changed in opposite directions. The interplay of inductive and resonance effects is evident in such cases.

Katritzky²⁷ has predicted previously that the intensities of the ring stretching (skeletal modes) bands in six-membered aromatic rings which appear at about 1600 and 1585 cm^{-1} (ν_{16a} and ν_{16b}) should be a function of the charge distribution in the ring. An approximate relationship between the apparent extinction coefficient of these bands for monosubstituted benzenes and the mesomeric moments of the substituent was shown.

It was found²⁸ that the square roots of the total integrated areas of these absorption bands correlate closely with reported σ_R^0 values and the negligible influence of inductive effect is confirmed by the low intensity ($A < 2$) of the vibration for benzotrichloride, which has a relatively high dipole moment. It has been shown²⁹ that the intensities of certain ring vibrations in the region $1600\text{--}1400\text{ cm}^{-1}$ arising from two doubly degenerate modes (ν_{16} and ν_{13}) are markedly altered by substitution. Thus, the band at 1600 cm^{-1} is very intense in dimethylaniline or phenol but weak in benzonitrile. A rough correlation was shown between apparent extinction coefficients and mesomeric moments. It is to be noted that a summation band arising from $C_{Ar}\text{--}H$ wagging vibration occurs³⁰ at about 1600 cm^{-1} and will make a small contribution to the measured intensities, thus explaining a positive intercept at $\sigma_R^0 = 0$, when σ_R^0 is plotted against $A^{1/2}$. Katritzky²⁸ has taken the intercept deliberately at the origin. Other similar ring modes, such as those in the 600 cm^{-1} region³² have been investigated.

Compounds containing a primary amino group have a scissoring mode close to 1600 cm^{-1} which excludes them from the study of intensity correlation. The other compounds

having strong absorption in the vicinity, which could enhance the ν_{16} band, are those having carbonyl groups. This enhancement would be expected to be greater in compounds like benzaldehyde and acetophenone than in phenylacetate where the C=O absorption occurs at a higher frequency.

It has been shown²⁷ by Katritzky that the mesomeric moment (D) of the substituent is approximately proportional to the apparent extinction coefficients ($a_{\max}/Cl$) of the 1600 cm^{-1} band in some monosubstituted benzenes. No precise relationship exists when $\sqrt{A}$ is plotted against D.³³ Exner³⁴ has pointed out that the mesomeric moment divided by the effective charge separation (d) in such compounds is more meaningful. He obtained good correlation between D/d and σ_R values. However, no better correlation has been reported³³ between D/d values and either A or $A^{1/2}$. Recently some workers have studied the intensities of other vibrations in monosubstituted benzenes. The intensity of the C-H aromatic stretching modes is directly related^{35(a)} to the σ_I values of the substituent. However, the intensities of the C-H out-of-plane bonding modes for monosubstituted alkyl^{35(b)} and halobenzenes^{35(c)} show no simple variation with the usual substituent parameters

although a limited correlation with dipole moments has been reported^{35(d)}. Exner and Bocek^{35(e)} have studied a large number of meta and para substituted benzonitriles. A reasonable linear correlation between the frequencies and intensities of the C≡N stretching mode and σ^+ has been reported despite the considerable experimental errors.

Brownlee et al.^{35(f)} have very recently studied the intensities of several monosubstituted benzenes for the ν_{16} mode. The correlation formulated earlier by them, i.e.

$$\sigma_R^0 = 0.0079 A^{1/2} - 0.027,$$

has been further refined to

$$A_{\text{mono}} = 17,600 (\sigma_R^0)^2 + 100.$$

A new set of σ_R^0 values have been calculated based on the above correlation and the discrepancies could be explained. It is to be noted that the measured integrated intensities of alkylbenzenes for this mode are in agreement (within 5%) with those values obtained by Wexler^{35(b)} except for the t-butyl derivative. These relative intensities cannot be accounted for on the basis of a correlation with σ_R^0 . The σ_R^0 values decrease in the order Me > Et > i-Pr > t-Bu while the ν_{16} intensities apparently increase. In a further extension of this work

English et al.^{35(g)} have measured the ν_{16} intensities of many p-disubstituted benzenes and correlated them by the relation

$$A_{\text{para}} = 11,800 (\sigma_{R1}^0 - \sigma_{R2}^0)^2 + 170.$$

For donor-acceptor (D-A) type of combination of substituents substantial deviations from the correlation are seen apparently because the interaction between the groups is no longer a function of σ_R^0 . An effort has been made to explain the deviations by introducing a correction term ($K_A K_D$) for the direct interaction between the substituents which becomes important in this type. The term K_D is set equal to $(\sigma_D^+ - \sigma_D^-)$ and values of K_A that would be required to get agreement with observed 'A' values have been computed. This analysis is rather involved and the interpretation of the correction factor leaves much to be desired.

It is clear from the foregoing review that measurements of integrated intensities are of considerable use in the study of substituent effects in the benzene ring, although the frequency variations are hard to explain as they are complicated by a number of factors³⁶. It can be seen that no effort has been made to study hyperconjugation with the help of intensity data.

In most of the earlier studies of substituent effects, *t*-butyl derivatives have been omitted. The reported data for alkyl derivatives are not consistent with the notion that conjugative interaction of these groups is the chief determinant of intensity. It is necessary, therefore, to clarify and confirm the behaviour of alkyl groups in relation to that of others. In the present investigation it was proposed to study the donor-acceptor interaction across benzene ring with the help of infrared band intensities and see if the data would be helpful for the evaluation of the importance of hyperconjugation. The measurements undertaken in this study were already completed by the time the work of English *et al.*^{35(g)} appeared and there has been some overlap in the selection of compounds. The present study was planned as a complete parallel to the one described in the previous Chapter and the derivatives chosen were *p*-substituted benzoic esters and 4-substituted phthalic esters with various substituents namely, OMe, F, Cl, Br, I, Me, *t*-Bu and NO₂. The NH₂ derivative was not included because of its poor solubility in CCl₄.

Intensity Measurements

In general band intensities can be obtained by the various methods described below. The absorbance

($\log I_0/I$) of a band peak is very sensitive to a number of possible errors. The conditions under which this can be used as a safe measure of band intensity have been discussed by Thompson³⁷. The difficulties arising from the finite slit width might be removed by the use of integrated band areas. Wilson and Wells³⁸ developed a method to obtain the true integrated band intensities by extrapolating the plot of apparent intensity (B), given by expression (1),

$$B = \frac{1}{c\ell} \int \ln \left(\frac{T_0}{T} \right)_{\nu} d\nu \quad \dots (1)$$

against apparent absorbance $\log (T_0/T)_{\max}$ to zero absorbance in accordance with Ramsay's equation

$B = A + A_0 \ln (T_0/T)_{\max}$. For computation of 'A' Ramsay⁴ proposed another equation (2) in which "K" has a value

$$A = K \cdot \frac{1}{c\ell} \ln \left(\frac{T_0}{T} \right)_{\max} \cdot \Delta \nu_{1/2}^a \quad \dots (2)$$

determined by the ratio $S_{\text{eff}}/\Delta \nu_{1/2}^t$ and is usually about 1.5 (S_{eff} is the effective spectral slit width and $\Delta \nu_{1/2}^t$ is the true half band width). This method of getting "A" is suspect because of the difficulties in getting the values of "K" and $\Delta \nu_{1/2}^a$, the latter because of the unsymmetrical contour of a band. Thompson and Steel¹⁷ determined the band area

$$B' = \int \ln \left(\frac{T_0}{T} \right)_{\nu} \cdot d\nu$$

by graphical integration and plotted against c.l.

Recently Katritzky and coworkers³³ obtained the integrated intensity (A , l. mole⁻¹ cm⁻²) from the formula $A = \sum a/c.l$ where "C" is the concentration of the compound in moles per litre, "l" is the path length in centimeters and "a" the absorbance value for each wave number corrected for any base line. Some workers⁴⁰ have used $\epsilon_{\max}$ (extinction coefficient) as a measure of the true intensity of a vibration band which assumes that the half band width is invariant. But this condition is not always obtained.

In the present investigation the true band intensities have been obtained by the procedure analogous to that employed by Thompson and Steel. All the spectra were recorded on a Perkin-Elmer model 221 IR spectrophotometer fitted with grating and sodium chloride prism. Carbontetrachloride (dried over P₂O₅ and distilled) was used as solvent for recording the spectra. All the spectra were recorded under similar set of conditions. Several solutions of different concentrations were made up independently for each substance and measurements were made in two pairs of absorption cells with different path lengths (0.1 and 0.5 mm). The spectra were recorded at the maximum possible scale expansion on the instrument

(P.E. 221). The absorbance value "a" at each wave number was corrected for the base line in the usual way and the a-values thus obtained were re-plotted against ν on a linear scale. From the curve thus obtained the area of the peak was measured by means of a planimeter. Following the procedure of Thompson and Steel, the integrated areas obtained at different concentrations and path lengths were plotted against c.l. In all the compounds studied, good straight lines passing through the origin were obtained. Beer's law was quite well obeyed. The slopes of the curves gave numbers proportional to the absolute intensities.

RESULTS AND DISCUSSION

(i) Intensities: The relative intensities thus obtained for the ν_{16} bands of p-substituted benzoic esters and 4-substituted phthalic esters are presented in Tables 1 and 2. English et al.^{35(g)} had made "corrections" for asymmetry effects in the work that has been referred to earlier. The procedure for correction involves decomposition of σ_R^O values into $\sigma_{R\ x}^O$ and $\sigma_{R\ y}^O$ terms (x and y components). The physical significance of this resolution and its justification is not clear. The relative intensities in Tables 1 and 2 are uncorrected.

TABLE 1 - RELATIVE INTENSITIES OF ν_{16}
BANDS OF p-SUBSTITUTED BENZOIC ESTERS

Substituent	Relative Intensity
OMe	10.3850
F	5.6850
Cl	3.6535
Br	4.3270
I	4.5315
Me	2.1620
t-Bu	1.9175
NO ₂	2.2825
H	1.0000

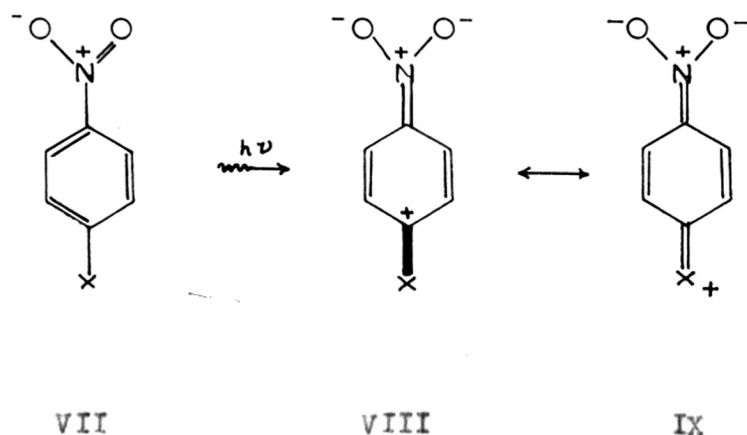
TABLE 2 - RELATIVE INTENSITIES OF ν_{16} BANDS
OF 4-SUBSTITUTED PHTHALIC ESTERS

Substituent	Relative Intensity
OMe	7.257
F	4.103
Cl	2.562
Br	2.976
I	3.036
Me	1.946
t-Bu	1.663
H	1.000

A correction for the asymmetry of the COOMe group is not, in any case, needed here because this factor remains constant in the series studied. Among the other substituents the only case where asymmetry comes in is for the OMe group. Whatever correction is required for this is apparently small^{35(g)} and no inconvenience is encountered by its neglect in the considerations made below. It is apparent that the general trend of variations of intensities is the same in both series of compounds. In both the series the methoxyl derivatives are found to give maximum intensity as may be expected from the pronounced resonance interaction that is present in the molecule. But in the halogen derivatives the intensities are found to decrease in the order $F > I > Br > Cl$. The inductive effect is one of electron-withdrawal and is given by the electronegativity order $F > Cl > Br > I$. The mesomeric effect is also in the same order $F > Cl > Br > I$, but in opposition to the inductive effect since it is electron releasing. This order is substantiated not only by reactivity data but also by NMR shielding parameters⁴¹ and half-wave potentials⁴² in polarographic reduction of substituted benzenes. The calculated⁴³ double bond character of the B-X bonds in boron trihalides indicate that the $p - \pi$

donor resonance decreases in the order $F > Cl > Br > I$ ⁴⁴. The same order is indicated from the force constants⁴⁵, K , of the C-X and C $\equiv$ N bonds in the cyanogen halides X-C $\equiv$ N. The order of ν_{16} band intensities cannot therefore be understood in terms of inductive and mesomeric effects.

The ultraviolet absorption behaviour of benzene derivatives containing donor and acceptor groups para to each other is of special interest here. The first transition for this type of compounds, e.g. nitrobenzenes and acetophenones, may be expected to be dominated by the electron withdrawing action of the acceptor group (nitro or carbonyl group) as represented by the resonance between structures like VII, VIII and IX.



However, in both series of compounds (*p*-substituted nitrobenzenes and acetophenones) the apparent electron release is in the order $I > Br > Cl > F > H$ (i.e. the order of decreasing wavelength for the first transition^{46(b)}). If it is assumed that the predominant mode of electron release in these transitions is electro-
meric (i.e. mesomeric), then the observed order must be taken as the order of electromeric release! This conclusion would be strange since we have seen that the other data do not support it. Nevertheless, this is the conclusion reached by Forbes and Ralph^{46a}, who suggested that the generally accepted order of electro-
meric release $F > Cl > Br > I$ is incorrect. On the other hand, if it is assumed that the generally accepted order of electromeric release is correct, then it must be concluded that electromeric release is not the pre-
dominant mode of electron release by the halogens in the principal electronic transitions of the *p*-halonitro-
benzenes and acetophenones. The inductive effect need not be considered since its direct effect is to oppose the resonance which releases electrons to the nitro group.

Schubert et al.^{46b} studied the vapour spectra of *p*-haloanisoles also. They found that the shift to longer

wavelengths of the first electronic transition was in the order $I > Br > Cl > F$. In *p*-haloanisoles the group para to the halogen is a strong electron donor while in *p*-halonitrobenzenes it is a strong acceptor. The fact that the order of net electron acceptance in the anisoles corresponds to the order of net electron release in the nitrobenzenes was rationalized by Burawoy and Thompson⁴⁷ in terms of the polarizability of the substituent. Jaffe and Orchin⁴⁸ have agreed with the view that polarizability is the controlling factor in light absorption of these derivatives. Molar refraction is a property which depends on the polarizability of electrons and an excellent correlation between the frequency shift and the molar refraction of the halo compounds was observed^{46b}. It may be noted in passing that $d-\pi$ -acceptor resonance of Cl, Br and I has been invoked to explain the trend in acidities of halophenols ($Cl < Br < I$) and basicities of *p*-haloanilines^{49,50}. However, this is a factor that is not relevant in the consideration of the behaviours of *p*-halobenzoic esters, *p*-halonitrobenzenes or *p*-haloacetophenones. The data on dipole moments are of no help, since two different orders have been reported for the resonance moments for the halogens by two groups of workers^{51,52}.

Coming now back to the intensity data obtained in this study it is obviously impossible to correlate the data with any one of the various possible effects, namely, inductive, mesomeric and polarizability effects. It is apparent that more than one effect has to be considered. The results can be rationalized by considering both polarizability and mesomerism. It is very likely that the inductive effect is also one of the determinants of intensity; but it is difficult to make out a case for it on the basis of the present results. The variation of intensities for the halogen derivatives is diagrammatically shown in Fig.1(a). The figure suggests that two factors determine the intensities for these compounds. One has an effect that decreases in the series while the other has an effect which increases. The high intensity in the case of fluoro derivative may be ascribed to the mesomeric electron-releasing capacity of fluorine. The fall in intensity in the transition from F to Cl can be understood as arising from a decrease in mesomeric effect. However, in order to understand the intensity change for the transition from chlorine to iodine through bromine, it is necessary to invoke the polarizability effect which is naturally expected to play a more important role in the heavier substituents. For these derivatives the

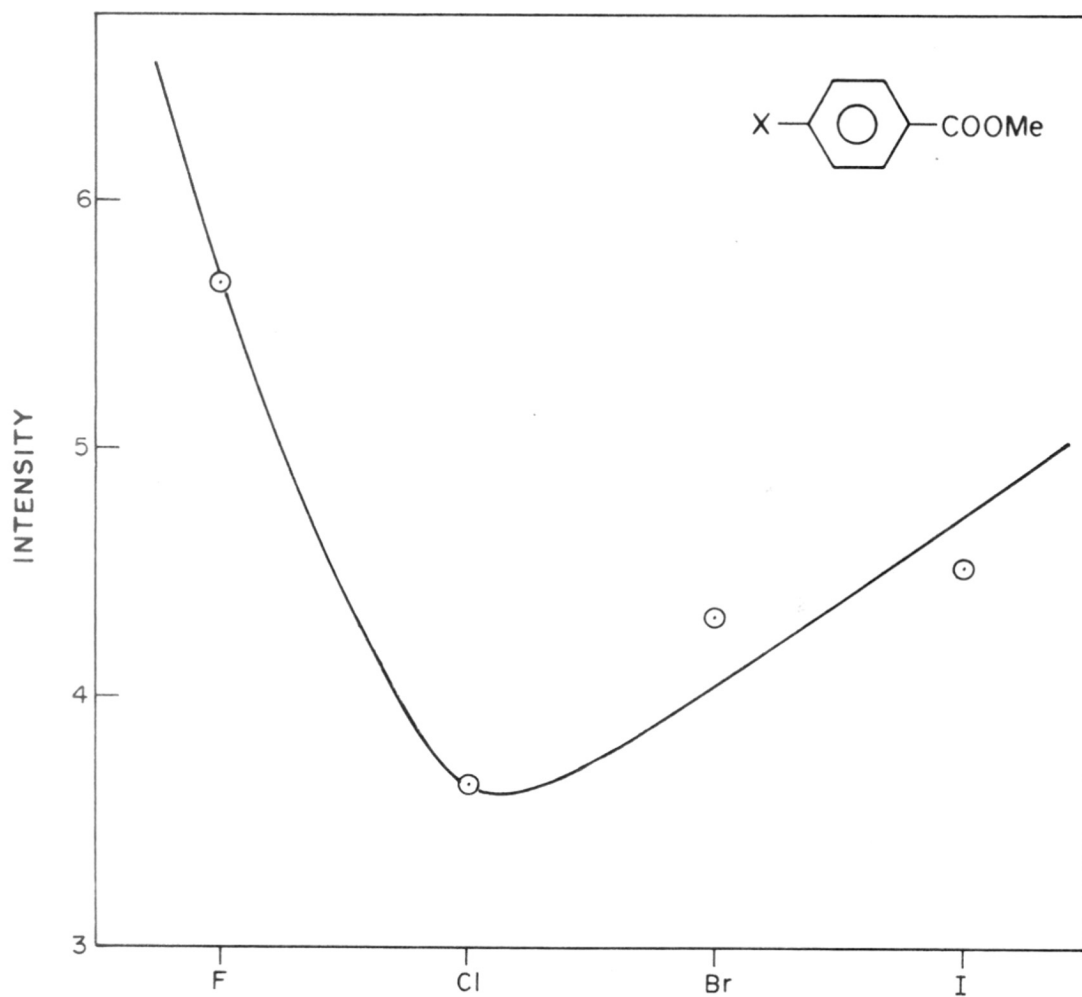


FIG. 1(a) SCHEMATIC REPRESENTATION OF ν_{16} BAND INTENSITIES OF $\underline{p}$ -HALOBENZOIC ESTERS

effect of mesomeric interaction is apparently smaller than that of polarizability. The polarizability effect would be weak or non-existent in the fluoro derivative. The plot of "log A" against Taft's resonance parameters (σ^-_R) shows a reasonable correlation except for the large deviation in the case of iodine derivative (Figs. 1b and 2). It can be seen that the intensities follow the general trend of variation with the degree of resonance interaction i.e. increasing with the increasing donor strength of the substituent. The large deviation of iodine derivative can be understood on the basis of the polarizability effect as pointed out above.

A comparison of the relative intensities of the ν_{16} modes of methyl and t-butyl derivatives in both the series (i.e. p-substituted benzoic esters and 4-substituted phthalic esters) suggests that electron release is in the order Me > t-Bu. According to estimates of Taft⁵³, the inductive electron-releasing effect of the t-butyl group is greater than that of methyl group and the reverse order occurs for mesomeric electron release. The validity of these estimates has, however, been questioned by Dewar³⁶. The intensity order (Me > t-Bu) clearly indicates that it is the contribution of the mesomeric electron release that is larger than that of

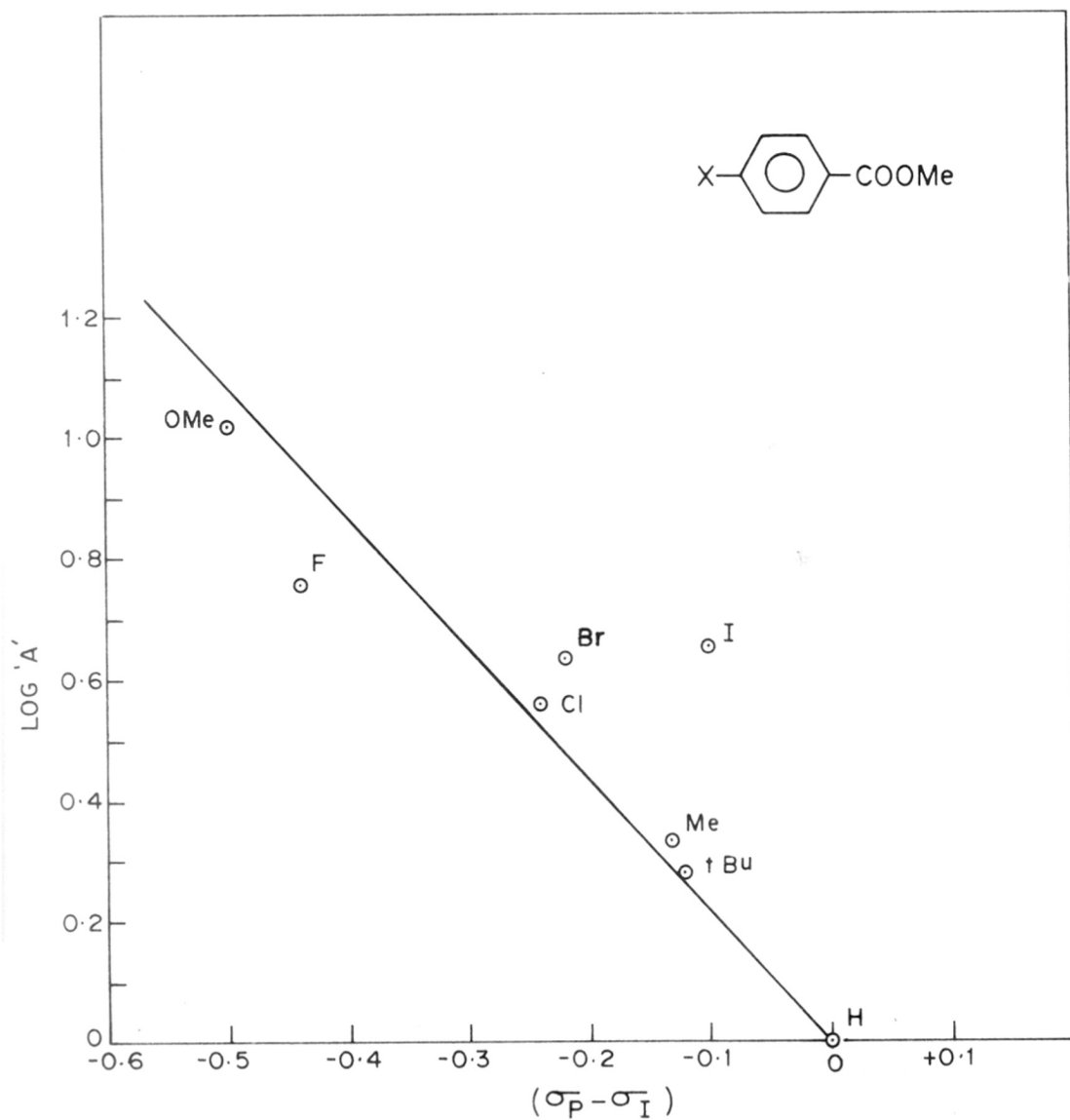


FIG.1b. PLOT OF LOG 'A' VS. TAFT'S RESONANCE
PARAMETER $(\sigma_P - \sigma_I)$

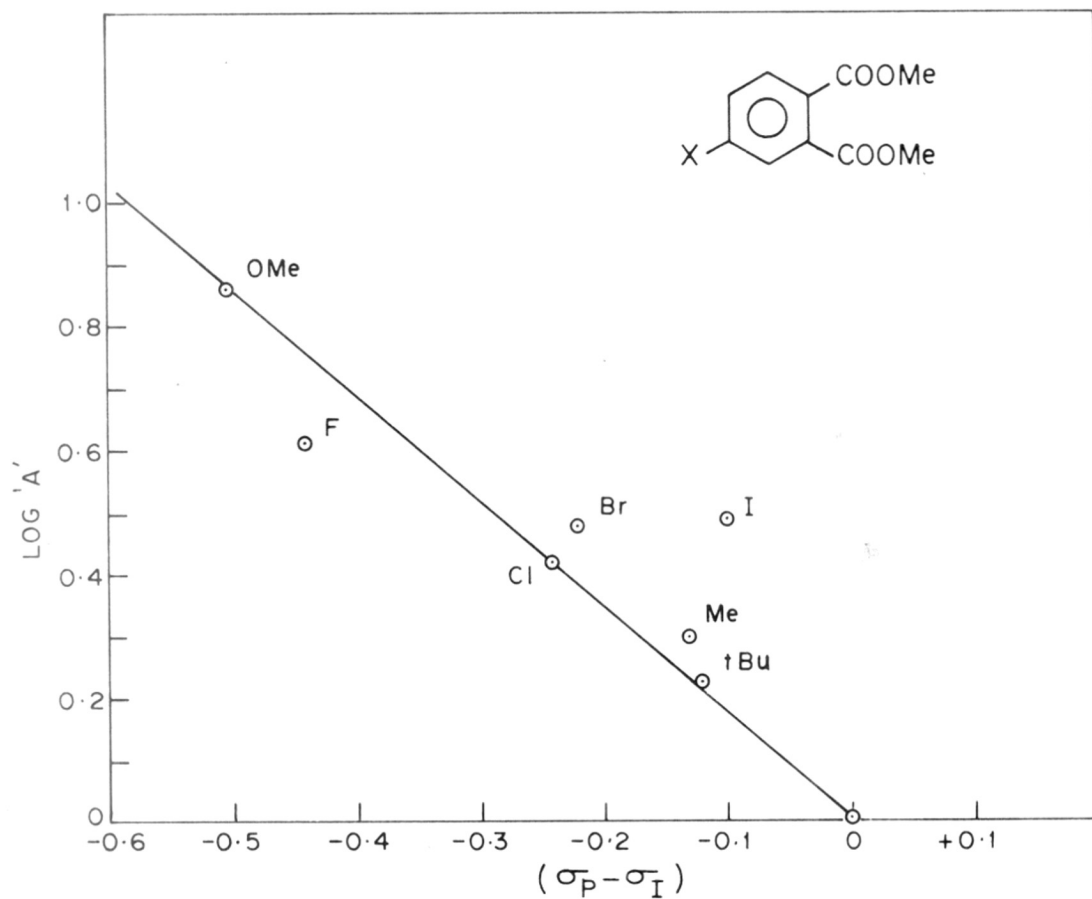
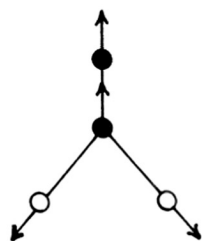


FIG. 2 PLOT OF LOG 'A' VS. TAFT'S RESONANCE
PARAMETER $(\sigma_P - \sigma_I)$

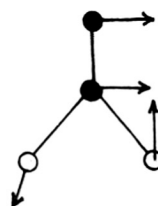
either the inductive effect or the polarizability effect. The latter effects are larger in the t-butyl derivatives and it is in spite of this that methyl derivatives have the higher intensity. The conclusion therefore is that hyperconjugation is important and that C-H hyperconjugation is stronger than C-C hyperconjugation.

It was noted earlier that for disubstituted benzenes intensities of characteristic vibrational bands of groups like CN and NO₂ have been studied as a function of the nature of the second substituent. However, since t-butyl derivatives have been left out of these studies, they are not helpful in relation to the problem of hyperconjugation. It was, therefore, decided to include methyl and t-butyl derivatives of nitrobenzene and benzonitrile in this study. It has been pointed out³⁹ that when a nitro group of a nitrobenzene is conjugated with an electron-releasing group at the para-position, resonance permits greatly increased charge separation. In such compounds it would, therefore, be normally expected that the NO₂ sym. stretching (vibration parallel to the direction of charge separation) mode would become more intense, while the NO₂ asym. stretching bands (vibrations perpendicular to the charge separation)

need not be affected. The NO_2 sym. stretching bands



NO_2 sym. str.



NO_2 asym. str.

of both *p*-nitrotoluene and *p*-*t*-butylnitrobenzene have been recorded and the relative intensities have been estimated as described earlier. The relative intensities of NO_2 sym. stretching band (1348.5 cm^{-1}) of methyl and *t*-butyl derivatives are shown in Table 3. The intensity of the methyl derivative is found to be more than that of the corresponding *t*-butyl derivative even though the difference is not marked (Me 1.21, *t*-butyl 1.00). Similarly the $\text{C}\equiv\text{N}$ stretching band (2230 cm^{-1}) intensities of *p*-methyl benzonitrile and *p*-*t*-butylbenzonitrile have been estimated and are presented in Table 4. Here again the band intensities fall in the order Me > *t*-Bu (Me 1.42, *t*-Bu 1.31, H 1.00). In all the systems studied the effect of methyl group on the selected vibrational band intensities

TABLE 3 - RELATIVE INTENSITIES FOR NO₂ SYM. STR. BAND
(1348.5 cm⁻¹) in p-SUBSTITUTED NITROBENZENES

Substituent	Relative Intensity
Me	1.205
t-Bu	1.000

TABLE 4 - RELATIVE INTENSITIES FOR C≡N STRETCHING
(2230 cm⁻¹) BAND IN p-SUBSTITUTED BENZONITRILES

Substituent	Relative Intensity
Me	1.4166
t-Bu	1.3125
H	1.0000

is found to be stronger than that of t-butyl group which would be suggestive of mesomeric type of electron-release from C-H bonds i.e. hyperconjugation. The results of IR band intensity measurements are thus consistent with the results obtained from the PMR chemical shift study described earlier in so far as the effects of methyl and t-butyl groups are concerned and the conclusions drawn earlier are indeed reinforced by this study.

(ii) Frequencies: The frequencies of the ν_{16} bands are presented in Table 5. According to theory, with increasing donor-acceptor interaction localization of double bonds as in structure III would be favoured. Although the ν_{16} mode involves the simultaneous motion of several nuclei, the increased localization of bonds may be expected to make the mode more stiff. It would therefore be expected that the frequencies of the ν_{16} band would decrease as the donor-acceptor interaction decreases. In the p-substituted benzoic ester series the frequency of the methoxyl derivative is the highest as expected and in the halogen derivatives the frequencies decrease in the order $F > Cl > Br > I$ which is consistent with the order of mesomeric electron-release. A plot of frequencies against σ_R values (Fig.3) of the

TABLE 5 - MEASURED FREQUENCIES OF PEAK MAXIMA NEAR 1600
AND 1700 cm^{-1} FOR p-SUBSTITUTED BENZOIC ESTERS

Substituent	C=C stretching frequency (ν_{16})	C=O stretching frequency
OMe	1578.75(w) 1606.25(s)	1720.00
F	1602.00(s) 1622.50(w)	1727.50 - 1730.00
Cl	1579.50(w) 1596.00(s)	1727.50 - 1730.00
Br	1572.5(w) 1591.00(s)	1730.00
I	1575.00(w) 1586.00(s)	1730.00
Me	1572.50(w) 1612.50(s)	1725.00
t-Bu	1569.00(w) 1607.50(s)	1726.30
NO ₂	1601.00(w) 1608.25(s)	1733.75
H	1581.25(w) 1601.25(s)	1726.25

w = weak; s = strong

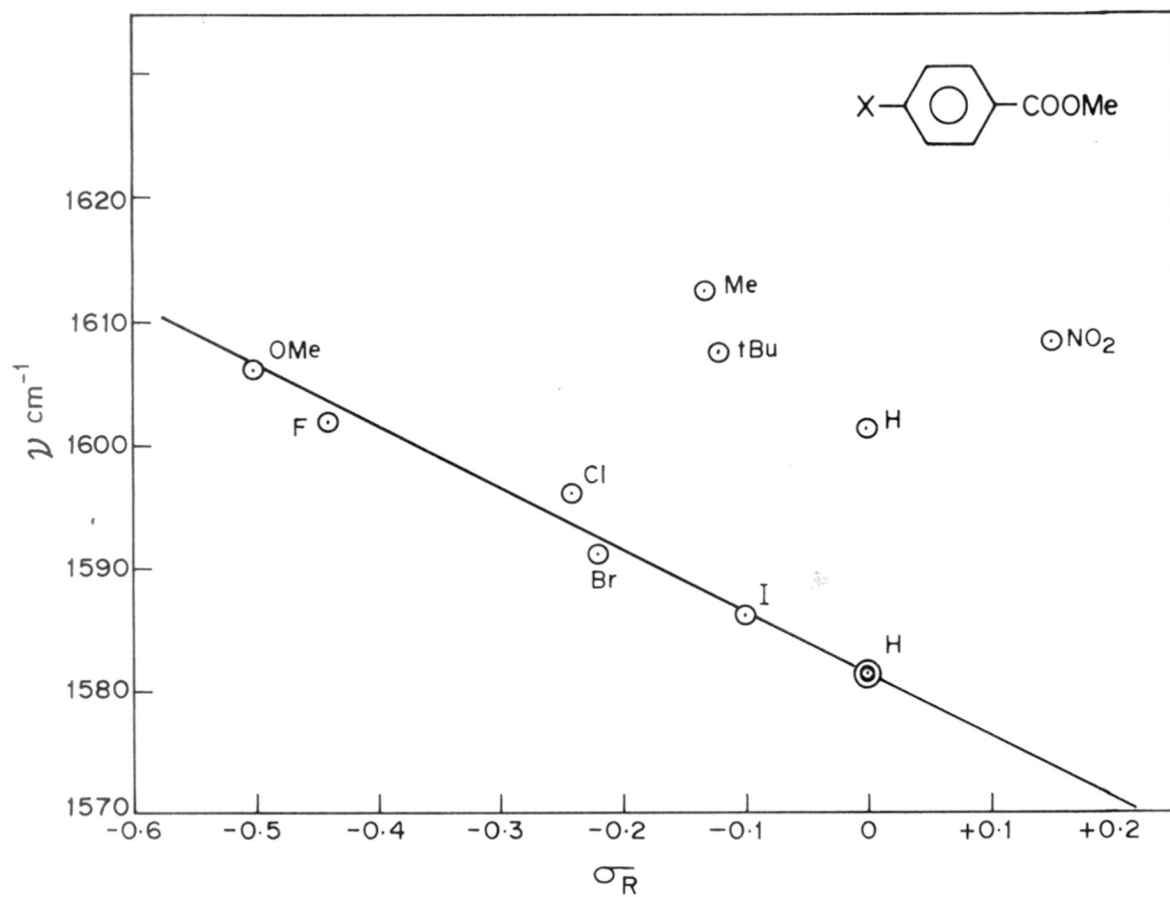


FIG. 3 PLOT OF FREQUENCIES VS. TAFT'S RESONANCE PARAMETER

substituents shows a linear relationship for the methoxyl and halogen derivatives. The frequencies of methyl and t-butyl derivatives could not be fitted into the same line and this clearly indicates that it is difficult to understand the gradation of frequencies on the basis of a single variable only. It is gratifying to note that the frequencies of electronegative substituents namely F, Cl, Br, I and also OMe show a regular variation with the resonance parameter. The frequencies of methyl and t-butyl derivatives do not fall on this line presumably because the inductive effect has also to be considered. In the electronegative series this effect is not manifested apparently because of the relation between mesomeric and inductive effects. The stronger mesomeric donor is also the stronger inductive acceptor in this case. The mesomeric effect thus would merely appear uniformly reduced along the series. On the other hand in the methyl and t-butyl derivatives, the situation is different. The inductive and mesomeric effects are in the same direction and these form a different set. The frequencies are 1612.5 and 1607.5 cm^{-1} respectively for the methyl and t-butyl groups. The methyl group is apparently a stronger donor than the t-butyl. The relative frequencies for the methyl and t-butyl derivatives

again indicate that the mesomeric interaction has the pronounced effect on this vibrational mode.

The frequencies of ν_{16} band in 4-substituted phthalic esters are shown in Table 6. In this series the frequency of methoxyl derivative is found to be less than that of the fluoro derivative and the order is $F > OMe > Cl > Br > I$ unlike in the case of *p*-substituted benzoic esters ($OMe > F > Cl > Br > I$). However, in the halogen group of derivatives the variation of frequencies is consistent in both series. A linear relationship is obtained when the frequencies are plotted against the Taft resonance parameters of these substituents (Fig.4). The departure of the OMe derivative from the correlation may be understood on the basis of a possible additional interaction of the $C_{Ar}-O^{Me}$ dipole with the dipole of the C(2) COOMe group. The methoxyl at position-4 may have a preferred conformation in this system (away from the C(2) COOMe group) and the interaction mentioned might complicate the consideration of atomic motion in the normal mode of interest. Such an interaction would not be present with the other substituents (F, Cl, Br, I, Me, *t*-Bu) since they are axially symmetric. The relative frequencies of the methyl and *t*-butyl ($Me\ 1610\ cm^{-1}$, *t*-butyl $1606\ cm^{-1}$)

TABLE 6 - MEASURED FREQUENCIES OF PEAK MAXIMA NEAR 1600
and 1700 cm^{-1} FOR 4-SUBSTITUTED DIMETHYLPHthalATES

Substituent	C=C stretching frequency (ν_{16})	C=O stretching frequency
OMe	1575.00 1603.75	1731.50
F	1590.00 1610.00	1737.50
Cl	1566.25 1592.50	1737.50
Br	1560.00 1587.50	1737.50
I	1557.50 1581.25	1737.50
Me	1575.00 1610.00	1735.00
t-Bu	1567.50 1606.00	1735.00
H	1580.00 1600.00	1736.25

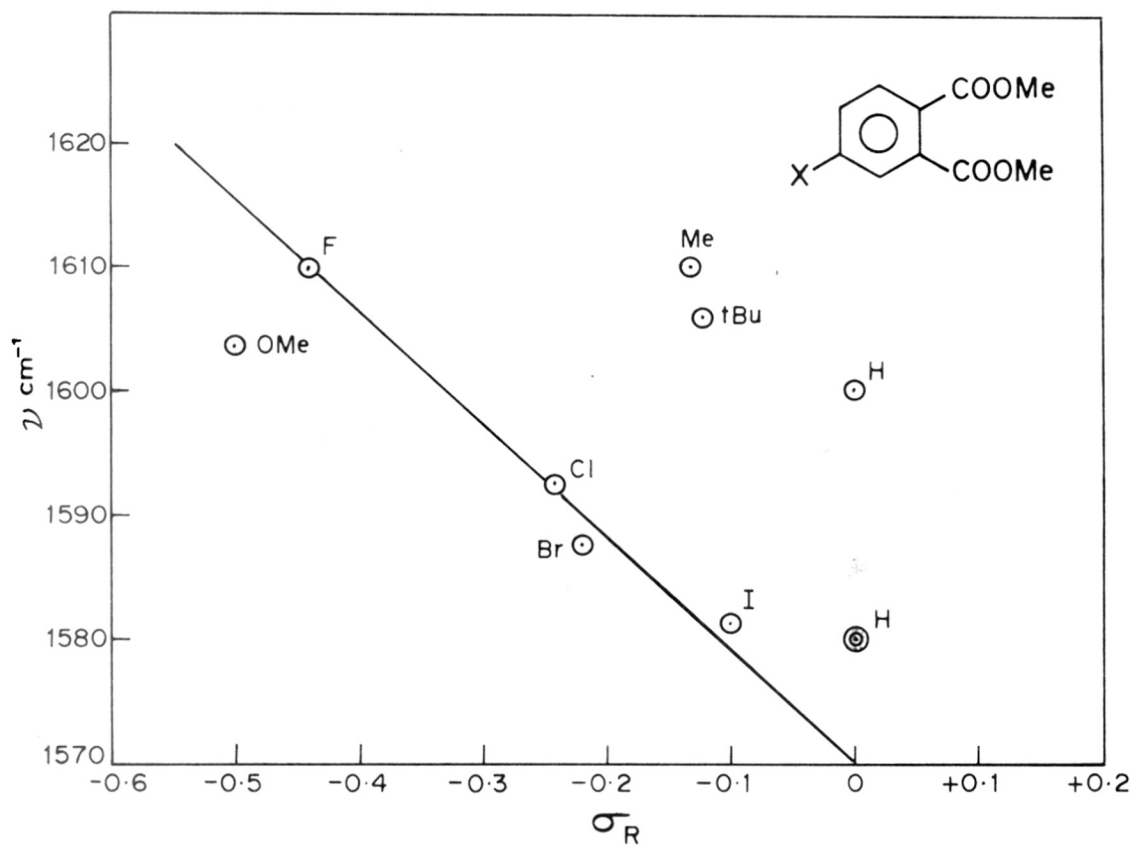
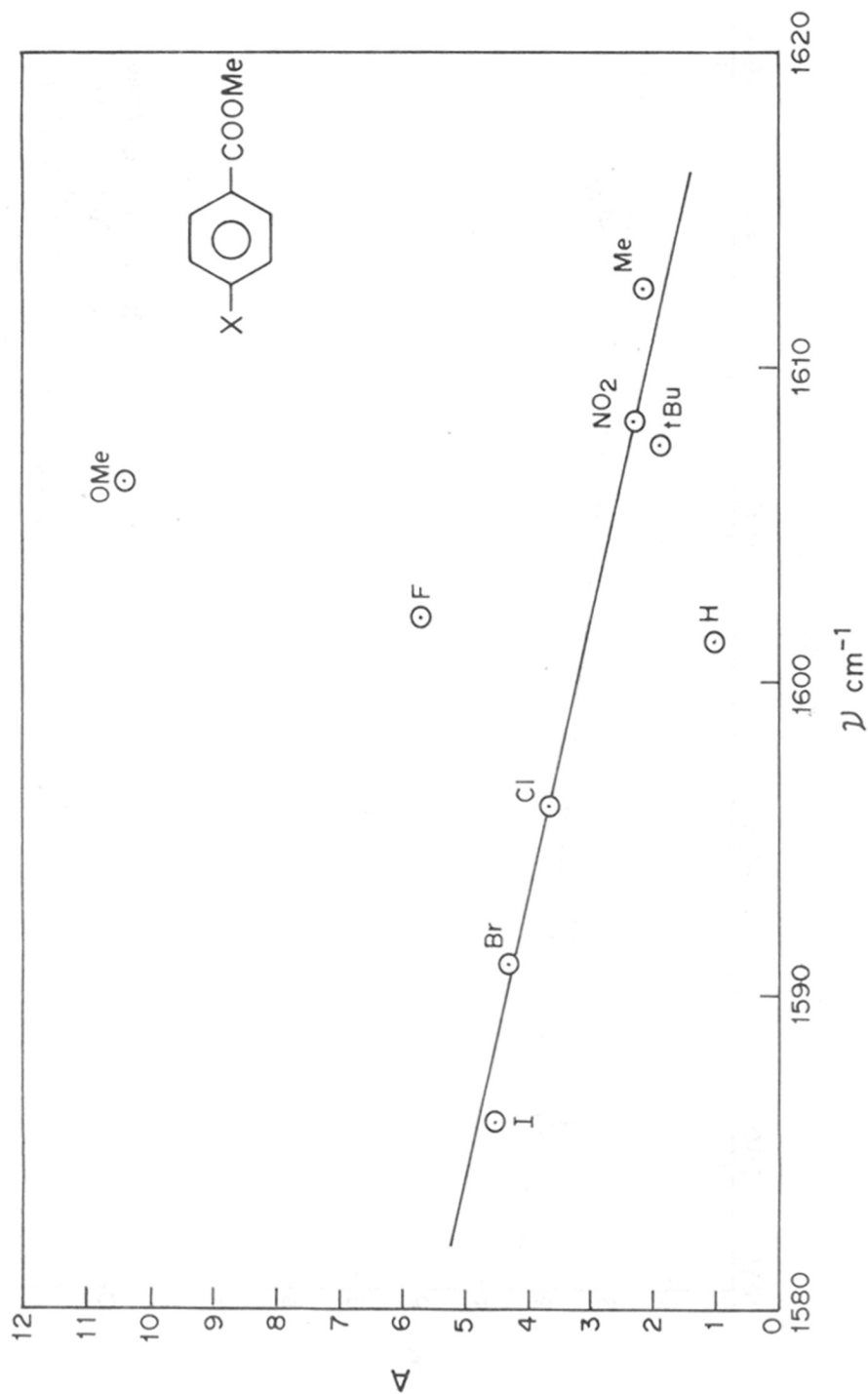
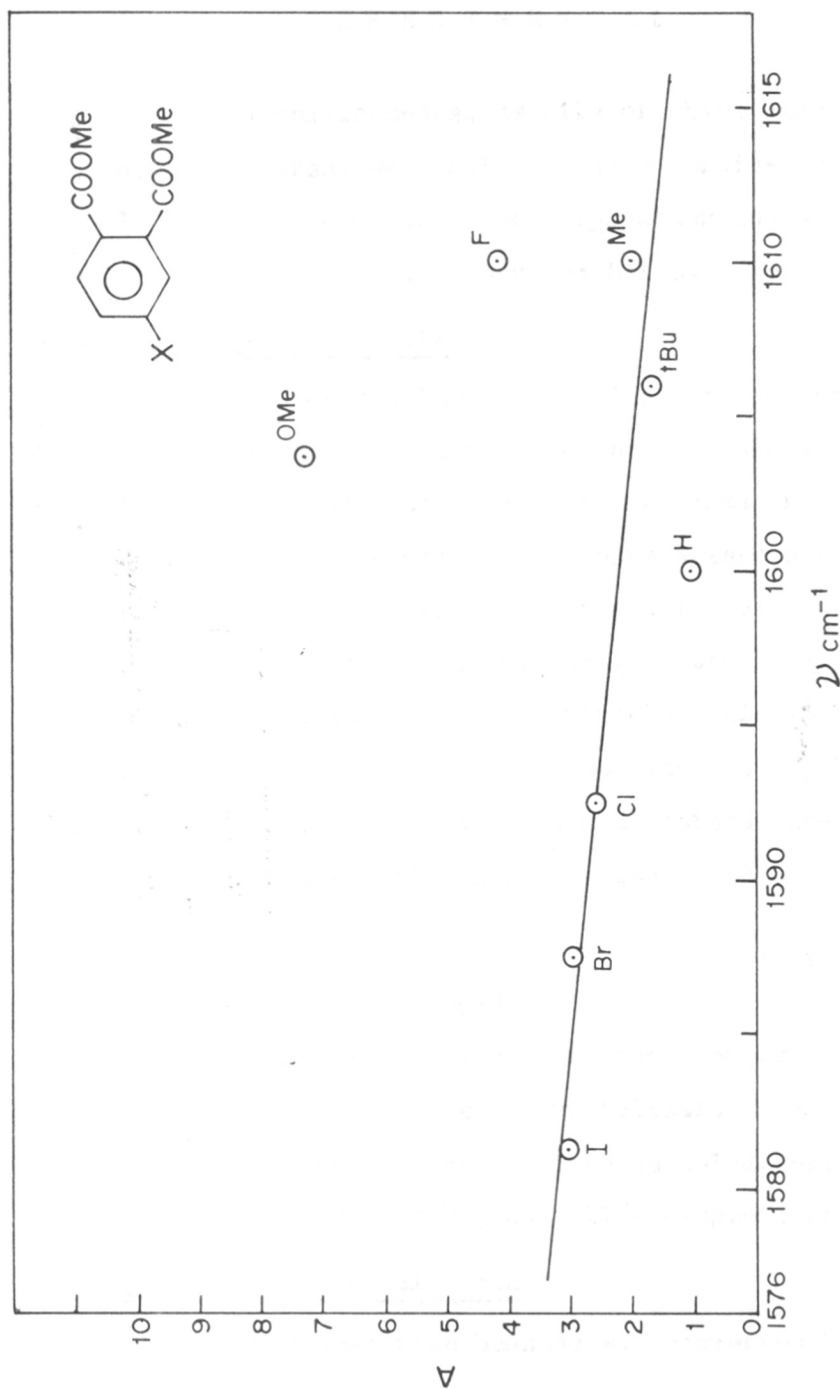


FIG. 4 PLOT OF FREQUENCIES VS. TAFT'S RESONANCE PARAMETER

derivatives again indicate that methyl is the stronger donor.

It is of interest to see whether any correlation exists between the intensities and frequencies themselves. In fact the plot of frequencies against intensities (Figs.5 and 6) for both the series of compounds (i.e. *p*-substituted benzoic esters and 4-substituted phthalic esters) shows a linear relationship except for the deviations in the case of OMe and F derivatives in both the series. This relationship suggests that the factor (factors) that is (are) responsible for the variations in the frequencies is (are) also mostly responsible for the variations in the intensities.

FIG. 5 PLOT OF FREQUENCIES (ν) VS. RELATIVE INTENSITIES (A)

FIG. 6 PLOT OF FREQUENCIES (ν) VS. RELATIVE INTENSITIES (A)

E X P E R I M E N T A L

IR measurements, details of which have already been presented, were all made on a Perkin-Elmer Model 221 IR Spectrophotometer. The preparation and purification of materials used is described below.

Methyl p-halobenzoates⁵⁴

All the p-halobenzoic acids were prepared from the corresponding halotoluenes by permanganate oxidation. The halotoluenes themselves are prepared from p-toluidine by Sandmeyer's reaction. The esters were obtained by subsequent esterification of the acids with methanol and catalytic amounts of conc. H_2SO_4 . Methyl p-fluorobenzoate was obtained as a colourless liquid boiling at $198^\circ C$. The chloro ester was obtained as a solid melting at $44^\circ C$, while the bromo and iodo esters were obtained as crystalline solids which melted at $80^\circ C$ and $114^\circ C$ respectively.

p-Toluic and Anisic acids

Commercial samples were used for esterification to get the esters after recrystallising from hot water. The methyl esters were obtained as colourless liquids boiling at $160^\circ C/20$ mm, and $217^\circ C$ respectively.

p-tert-butyl benzoic acid

Thiophene free benzene was converted to t-butyl-

benzene⁵⁵ in 65-70% yield by the Friedel-Craft's alkylation method using anhydrous aluminium chloride and t-butyl alcohol. The pure t-butylbenzene, which distilled over at 163-164°C was collected.

Tert-butylbenzene was then converted to the 4-nitro-t-butylbenzene⁵⁶. Fuming nitric acid (216 g, d 1.5) was added drop by drop to mechanically stirred t-butyl benzene (217 g) at ordinary temperature. The mixture was stirred for one hour more after the addition was over and then poured into an ice-water mixture. The yellow oil, which separated was collected and washed with water several times to remove the excess nitric acid. Again it was washed with sodium carbonate solution followed by water. The yellow oil obtained was dried over anhydrous sodium sulfate and fractionated. 4-Nitro-t-butylbenzene distilled over at 88°/2 mm. yield: 198 g (66-70%).

4-Nitro-t-butylbenzene was reduced to the corresponding amine with iron and hydrochloric acid⁵⁷. 4-Nitro-t-butylbenzene (180 g) and water (200 ml) were taken in a 3-necked round bottomed flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel. The mixture was heated on a waterbath at 100°C while conc. HCl (120 ml) was added slowly and the mixture

stirred vigorously. After the addition was over, the mixture was stirred for another two hours, while the temperature was maintained at 100°C . The free amine was liberated from the hydrochloride with excess sodium hydroxide solution and separated by steam distillation. The unreacted nitro compound, being not steam-volatile remained in the flask. The free amine, which is slightly soluble in water was separated by extracting it with ether. The ether solution was dried with KOH pellets and the solvent removed. The residue was distilled under reduced pressure and the fraction distilling at $78-79^{\circ}\text{C}/2\text{ mm}$ as a colourless liquid was collected.

The amine was converted into its acetyl derivative by digesting with a mixture of acetic anhydride and acetic acid. The product was isolated by pouring into crushed ice and separating the solid material. This acetyl derivative was recrystallized from ethanol repeatedly until it was free from other contaminating isomers as evidenced by the NMR spectrum.

The acetamino-derivative was hydrolyzed back to the corresponding amine with 70% sulfuric acid by refluxing for about 2 hours. The solution was cooled and the free amine was liberated by treating with excess alkali. The

amine was extracted with ether, dried over anhydrous sodium sulfate. The amine was purified by distillation.

4-Amino-t-butylbenzene was converted to its nitrile by the method analogous to that employed for the preparation of benzonitrile⁵⁸ using cuprous cyanide. The nitrile was isolated by steam distillation. It was then hydrolyzed to the acid with 10% sodium hydroxide solution. The acid was isolated and purified by recrystallizing from alcohol. Pure 4-t-butylbenzoic acid was obtained as snow-white glistening crystals, which melted at 143°C. This acid was then converted to its methyl ester in the usual way. Pure methyl 4-t-butylbenzoate was obtained as a colourless liquid, which distilled over at 117°C/2.5 mm.

Benzonitrile⁵⁸

Benzonitrile was prepared from aniline by Sandmeyer's reaction using cuprous cyanide. The compound was obtained as a colourless liquid which boiled at 189-190°C.

p-Tolunitrile

p-Toluidine was converted to its nitrile by a method analogous to that employed for the preparation of benzonitrile⁵⁸ using cuprous cyanide. p-Tolunitrile was obtained as a colourless liquid boiling at 90-91°C/11 mm.

p-t-butylbenzonitrile

The procedure for the preparation of this nitrile is given under the preparation of p-t-butylbenzoic acid.

p-Nitrotoluene

Commercial p-nitrotoluene was used after recrystallizing it from alcohol. The compound melted at 53°C.

Methyl p-nitrobenzoate:

p-Nitrotoluene was oxidized with alkaline potassium permanganate and the resulting acid isolated. The p-nitrobenzoic acid thus obtained was converted into its methyl ester by refluxing with methanol and little sulfuric acid as catalyst. Pure methyl p-nitrobenzoate was obtained as fine pale yellow needles, which melted at 95-96°C.

p-Nitro-t-butylbenzene

This compound was obtained during the preparation of p-t-butylbenzoic acid. It was fractionated several times using a long column. The compound was quite pure as shown by the NMR spectrum.

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CHAPTER V

**NMR METHYL BAND WIDTHS OF SOME
SUBSTITUTED AROMATIC COMPOUNDS**

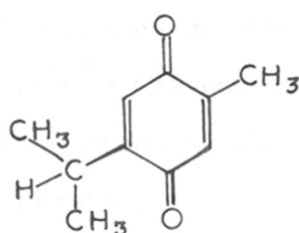
NMR METHYL BAND WIDTHS OF SOME SUBSTITUTED AROMATIC COMPOUNDS

It has been shown recently that measurements of long range spin-spin coupling between sp^3 benzylic and aromatic protons, which has been called "benzylic" coupling, can be of considerable help in the study of π -electron distribution in aromatic compounds¹. This coupling proceeds mostly through π -electrons and it has been pointed out that it is proportional to the square of the mobile bond order between aromatic carbon atoms involved. This was demonstrated qualitatively for sets of closely related methyl substituted compounds. The methyl group has also been employed as an element for probing π -electron distribution in indane for a re-examination of the Mills-Nixon effect^{1a}. The present study is concerned with the application of the same technique for sensing the changes in π -electron distribution caused by strong donor-acceptor interaction across the benzene ring. In order to set the present investigation in the perspective, the literature on benzylic and allylic coupling is briefly reviewed below:

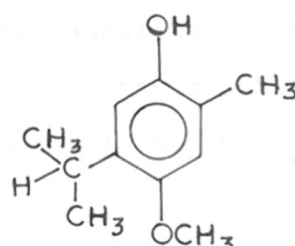
Long range spin-spin interactions between methyl

protons and aromatic or olefinic protons were first reported by Hoffman^{2,3} in a number of aromatic, olefinic and heterocyclic compounds. He observed in mesitylene a distinct quartet for the methyl protons and a multiplet for the aromatic ring protons and interpreted his data on the basis of hyperconjugation between the C-H bond orbitals of the methyl group and π -electron orbitals of the unsaturated systems. In the case of ortho substituted toluenes the long range coupling was found to depend on the nature of the substituent. The multiplicity of the methyl signals in the NMR spectrum of 2,2'-dimethyldiphenyl ether, which was explained by Shimizu and Fujiwara⁴ as arising from the non-equivalence of the methyl groups, was later shown by Tiers et al.⁵ to be the result of long range spin-spin coupling of the methyl protons with the aromatic protons. It was found that this separation between the two signals of the methyl groups is temperature independent and also that the gross peak half-width does not change as the radio frequency of the spectrometer is varied from 40 to 60 MHz. From a systematic study of the para substituted alkylbenzenes, it was shown by Rottendorf and Sternhell⁶ that in these compounds the benzylic protons are coupled to the ring protons in the ortho positions.

The coupling constant for this kind of interaction through four bonds was shown to be dependent on the type of double bond involved, through the example of thymolquinone (I) and the monomethyl ether (II) of the corresponding quinol^{7,8}. In (I) the



(I)



(II)

C_2-O_3 bond is very much like an ethylenic double bond and there is observable splitting of the methyl whereas in (II) the ring is fully aromatic in nature and there is no observable interaction between the aromatic protons and the side chain protons. Considerable amount of work has been done on benzylic and other types of long range coupling³ and reviews on these have appeared⁹⁻¹¹.

Theoretical treatments of long range spin-spin coupling through π -electrons in aromatic and open chain unsaturated systems were first made by McConnell and Karplus¹²⁻¹⁴ and later by others¹⁵. In the case of aromatic compounds, the linear relationship ($a_H = \rho^2$)

observed between the magnitude of hyperfine splittings (a_H) in the paramagnetic resonance spectra of aromatic free radicals and the spin densities (ρ) at the carbon atoms involved was used by McConnell to formulate an effective spin Hamiltonian for the coupling between π -electron spin and proton spin. Using molecular orbital wave functions the π contribution^{14a} to the coupling between protons attached to carbon atoms N and N' was shown to be given by the expression,

$$J_{NN'}^{\pi} = (\beta Q)^2 P_{NN'}^2 / h \Delta E$$

where $P_{NN'}$ is the mobile bond order between the carbon atoms, Q is the effective isotropic hyperfine splitting constant, β is the Bohr magneton and ΔE is an average electronic (singlet-triplet) excitation energy. Corresponding valence bond treatments have been made by McConnell himself for aromatic compounds and by Karplus for ethylenic systems which could be applied for cases involving coupling through four or five bonds. These treatments are modifications of the generally theory of electron-coupled nuclear spin-spin interaction.

It was pointed out that the proportionality of hyperfine splitting to spin density would be true for

not only aromatic protons but methyl protons as well¹⁶ and that the expression derived by McConnell could be made applicable to benzylic coupling also if one of the Q 's is replaced by the hyperfine splitting constant (Q') for the C-X fragment where X is the benzylic carbon atom bearing protons^{1a,b}. Making allowance for a possible σ -contribution, benzylic coupling may therefore be expected to be linearly related to the square of the mobile bond order (P). Adequate evidence has been provided for the P^2 dependence of benzylic coupling from a study of a series of closely related methyl substituted aromatic compounds for which ΔE could be assumed to be roughly constant^{1c}.

Since substitution of strongly interacting groups alter the π -electron distribution of aromatic ring quite appreciably, the substitution method for isolating spin-spin interactions for purposes of their measurement has serious limitations, particularly when multiple substitution is involved. In this connection, we may recall the efforts made by Rottendorf and Sternhell^{17a} to see if long range coupling in benzene derivatives could be related to electronic structure by the substitution technique. They prepared all the three isomeric tetrachlorotoluenes and measured

the benzylic coupling in each. The ortho and para couplings were found to be the same (0.63 ± 0.01 Hz) and $J_{\text{CH}_3-\text{H}}$ (meta) was 0.36 Hz. The equality of methyl coupling to the ortho and para protons indicated that it is difficult to relate these data to π -electron distribution in toluene itself which was what was desired. Any inference regarding relative magnitudes of bond orders from benzylic coupling constants can be made, only if one can be sure that the other parameters that determine J^{π} , more particularly the ΔE values, are comparable*. These factors have clearly conspired to make any deduction from measurements on the tetrachloro-toluenes impossible.

In spite of the limitations of the method, it is still of considerable value, since convenient and reliable methods available for the determination of relative magnitudes of π -bond orders, other than X-ray crystallographic analysis, are very limited. A technique that has been employed by Hunsberger et al.^{18,19} estimates

*The Q's are also affected by changes in π -electron distribution. They have been shown to be a function of π -electron density^{17b}.

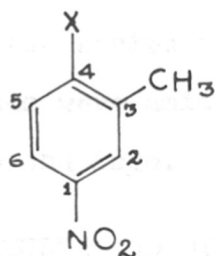
bond orders from the lowering of carbonyl stretching frequency that results from hydrogen bonding with OH groups when these groups (C=O and O-H) are connected through the bonds of interest. The method uses a standard curve which describes the variation of the hydrogen bonded carbonyl frequency in a set of compounds for which bond orders are known. Practical applications of this relationship are, however, often attended by serious difficulties and uncertainties since they are complicated by steric²⁰ and other factors which are difficult to estimate precisely. The PMR absorption of the chelated hydroxyl of the same system has also been used in a similar way with considerable success²¹. Jonathan et al.²² have shown that the vicinal coupling constant in aromatic systems is linearly related to the mobile bond order. But vicinal coupling proceeds mostly through σ bonds, the π -contribution being very small. The margin of uncertainty for the large component is so high when compared to the magnitude of the smaller part, that it is difficult to use vicinal coupling constants for comparison of bond orders²³ whose relative magnitudes are quite uncertain.

As pointed out at the outset, benzylic coupling constants can be of considerable importance in the study of

π -electron distribution in aromatic compounds. It has been shown²⁴ recently from the methyl bandwidth data for toluic esters that the relative bond order magnitudes in these are about the same as in benzoic acid itself. This indicates that the methyl group may be used as a sensing element to measure qualitatively the relative bond orders even when the coupling cannot be measured explicitly provided that the effects of the interaction of the methyl group with the other substituents can be ignored.

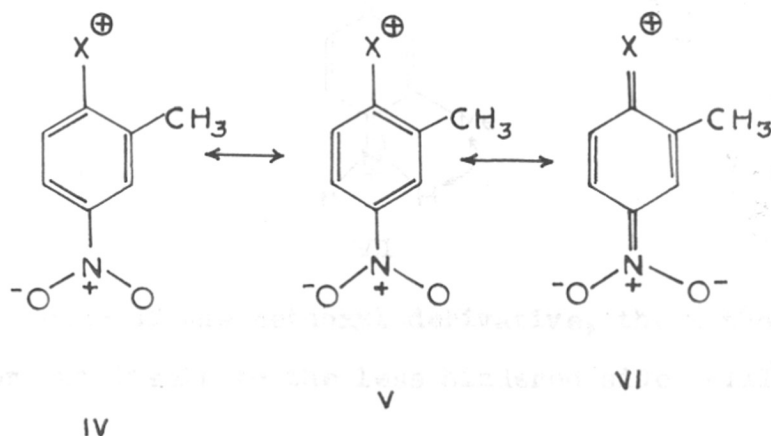
In the present investigation it is intended to study donor-acceptor interaction between substituent groups in aromatic compounds using the technique mentioned above i.e. using methyl group as a sensing element. The systems chosen for this study are nitrobenzenes with donor substituents in the *p*-position. The methyl group is introduced into this system either ortho to the donor group or ortho to the acceptor nitro group. If a methyl group is introduced ortho to the donor group in systems like *p*-nitroaniline and if the methyl group is assumed to function merely as a sensing element, then the methyl bandwidth would be expected to be determined predominantly by the coupling to the ortho-proton i.e. by *p*-value

(bond order) for the C_2-C_3 bond as in the case of



III

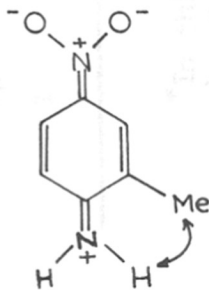
p-substituted toluenes in which the methyl group is coupled more strongly to the ortho protons than to the meta or para protons. Thus in 4-substituted 3-methyl nitrobenzenes, the coupling of the aromatic methyl to the C_2 -proton should contribute most to the bandwidth of the methyl group and this may be expected to vary with the extent of conjugation of the 4-substituent (X) with the NO_2 group across the aromatic ring. With increasing mesomeric donor strength of 'X' the contribution of structure VI to the resonance of the system ($IV \leftrightarrow V \leftrightarrow VI$ etc)



should increase and this in turn result in an increase in methyl bandwidth. It was with this expectation that the present study on the series mentioned was undertaken. The substituents chosen were amino, methoxyl, hydroxyl, fluoro, chloro, bromo and iodo.

RESULTS AND DISCUSSION

The methyl bandwidth data for 4-substituted 3-methyl nitrobenzenes are presented in Table 1. The bandwidths change with substituent in the order $\text{OMe} > \text{NH}_2 > \text{F} > \text{OH} > \text{Cl} > \text{Br} > \text{I}$. The methoxyl derivative should normally be expected to have a smaller bandwidth than the amino. The apparent inversion that is obtained may be understood on the basis of steric hindrance of the conjugation of the nitrogen lone pair with the aromatic ring and the nitro group by the ortho methyl group (as indicated in VII).



VII

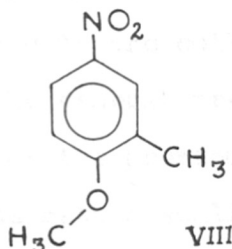
In the case of the methoxyl derivative, the methoxyl methyl can orient itself to the less hindered side (VIII) so that

TABLE 1 - NMR METHYL BAND WIDTH DATA FOR
4-SUBSTITUTED-3-METHYL-NITROBENZENES (in Hz)

Substituent	Methyl band width
NH ₂	1.95
OMe	2.20
OH	1.75
F	1.90*
Cl	1.85
Br	1.75
I	1.70

*In this case Me signal splits into two because of coupling with ortho fluorine (2.10 Hz). The value shown in the table has been obtained by subtracting the Me-F coupling from the total band width (4.00 Hz).

it may be free from steric interaction with the ortho



methyl group and can interact mesomerically with the para substituent. The lower band width of the hydroxyl derivative, as compared to that of the methoxyl may be attributed to be an effect of intermolecular hydrogen bonding. When the hydroxyls are involved in hydrogen bonding between themselves the lone pair electrons on oxygen are less available for delocalization into the benzene ring. The halogen derivatives fall in the expected electron-releasing order namely $F > Cl > Br > I$. The expectation band width data would reflect the variation of the strength of donor-acceptor interaction is thus realized.

Having established that it is possible to study donor-acceptor interaction in aromatic ring systems through methyl group as sensing element, it looked interesting to see whether there will be any advantage by shifting the methyl group from the position ortho to the donor group to the position ortho to the nitro group. A parallel set of derivatives with the same donor-substituents (amino,

methoxy, fluoro, chloro, bromo and iodo) have been prepared with methyl group in the alternative position.

The methyl band width data are collected in Table 2.

It can be seen that the general trend of variation is consistent with that of the previous system even though the total variation is rather small indicating that the system is not very sensitive for this type of study.

This lack of sensitivity may be understood on the basis of two major factors. Firstly, the nitro group under the influence of steric interaction by the methyl group may be rotated through an appreciable angle away from the plane of the benzene ring. This would make the nitro group to be less conjugated with the donor group across the ring as compared to the previous system.

Secondly, the methyl group itself being a donor group through hyperconjugation may interact with the adjacent (ortho) nitro group. These two factors decrease the interaction of the nitro group with the *p*-substituent and make the methyl band width relatively less sensitive to variations of donor strength in the *p*-substituent.

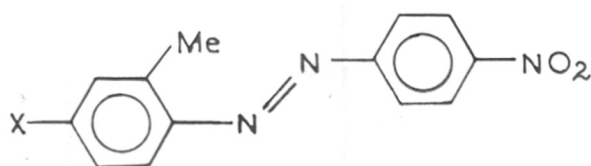
It is, however, gratifying to note that there are indications of the same trend as in the previous case even though the total range of variation is small. The band widths follow the electron-releasing order for the amino, methoxyl, fluorine and chloro derivatives. The

TABLE 2 - NMR METHYL BAND WIDTH DATA FOR
4-SUBSTITUTED-2-METHYL NITROBENZENES
(in Hz)

Substituent	Methyl Band width
NH ₂	1.80
OMe	1.60
F	1.50
Cl	1.30
Br	1.30
I	1.30

change from chloro to iodo through bromo does not produce any measurable decrease in the band widths apparently because of the small differences in donor strength.

Since two factors have been mentioned in explanation of the unsuitability of 4-substituted 2-methylnitrobenzenes for studying donor-acceptor interaction by the methyl sensing technique, it would be of interest to consider the behaviour of some 4-substituted 2-methyl-4'-nitro-azobenzenes (IX) which have also been examined.



IX

In the latter system, unlike in the former, steric interaction between the methyl group and the adjoining group (azo in the latter case) would not be a major factor. From the point of view of acceptor strength, this system should be excellent because the group involved is *p*-nitrophenylazo. The data in Table 3 show that the methyl band width is not altered when substituent is changed from methoxyl to hydroxyl or iodo. The conclusion apparently is that methyl is an interacting group in this

TABLE 3 - NMR METHYL BAND WIDTH DATA FOR
4-SUBSTITUTED-2-METHYL-4'-NITRO-
AZOBENZENES (in Hz).

Substituent	Methyl Band width
OMe	1.70
NH ₂	1.70
I	1.70

system, not a mere sensing element which probes the resultant distribution of electrons arising from the interaction of the *p*-nitrophenyl azo group with the 4-substituent exclusively. The behaviour of the methyl group is consistent with the conclusions of the earlier studies in this thesis.

It is of interest to look at the aromatic proton chemical shifts in all the three series of compounds since they have become available in the band-widths study. It may be recalled that the rule of additivity has been found to hold good not only for di-substituted benzenes but also for tri-substituted²⁴ benzenes as well. The chemical shift data for the first series of this study namely 4-substituted-3-methylnitrobenzenes, are presented in Table 4. One would normally expect the chemical shifts of C₂- and C₆-protons to be nearly the same because methyl substituent effects at ortho and meta positions in a benzene ring are roughly the same. It is apparent that the chemical shifts of C₂- and C₆-protons are different and in the halogen series the deviations from the additivity rule decrease in the order I > Br > Cl > F. However, the data in Table 5 for the second series of compounds (4-substituted-2-methyl-nitrobenzenes)

TABLE 5 - PROTON CHEMICAL SHIFTS IN 4-SUBSTITUTED-
2-METHYL-NITROBENZENES (in Hz).

Substituent	C ₃ -proton	C ₅ -proton	C ₆ -proton	Other groups (Me protons)
NH ₂	384.00	385.50	464.50	149.00
OMe	404.00	405.00	477.50	153.50
OH	407.00	407.00	485.00	157.00
F	421.00 ± 2.50	421.00 ± 2.50	481.50	158.00
Cl	442.00	439.00	476.50	156.50
Br	451.50	447.50	471.00	155.75
I	461.50	461.50	461.50	154.00

TABLE 6 - PROTON CHEMICAL SHIFTS IN 4-SUBSTITUTED-2-METHYL-4'-NITRO-AZO BENZENES (in Hz).

Substituent	C ₃ -proton	C ₅ -proton	C ₆ -proton	C _{2,6} -protons	C _{3,5} -protons
OMe	414.00	410.00	468.00	479.00	502.50
OH	411.00	407.00	468.50	479.50	503.50
NH ₂	403.00	399.00	467.00	479.00	504.00
I	467.50	462.00	444.50	481.88	504.13

indicate that the C_3 - and C_5 -proton chemical shifts are roughly the same as may be expected on the basis of the additivity rule. In the last series namely the substituted azobenzenes, the departures of the C_3 - and C_5 -proton shifts from the additivity rule are small (Table 6). The reason for the deviations from the additivity rule in the case of first series of compounds is not apparent and a detailed analysis would be required in order to trace the origin.

EXPERIMENTAL

NMR Measurements

All spectra were recorded on a Varian A-60 NMR spectrometer operating at 60 MHz. Solutions (10-20%) were prepared in pure and dry carbon tetrachloride or deuteriochloroform for recording the spectra. Tetramethylsilane was used as a standard in all band width measurements i.e. comparison of band widths were made at identical spectrometer conditions, which gave the same band width for TMS reference signal. Calibration of the chart was made by using TMS in deuterated chloroform (436 Hz).

All methyl signals were recorded at 100 Hz sweep width at 500 seconds sweep time, so that the sweep rates were 0.2 Hz/sec. The band widths reported are averages obtained from minimum five independent scanings of the methyl signal in each case. rf and filter band widths were adjusted so as to obtain optimum conditions i.e. best resolution and sufficiently low noise level.

4-Nitro-*o*-toluidine (2-amino-5-nitrotoluene)²⁵

o-Toluidine was converted into its acetyl derivative by digesting with a mixture of equal volumes of acetic anhydride and acetic acid. The product was isolated by pouring onto crushed ice and separating the solid material.

The dried, finely powdered o-acetaminotoluene (22.25 g) was added to the nitration mixture (HNO_3 30.6 ml, d. 1.32; H_2SO_4 32.4 ml) maintained at 50°C . The addition was made 0.2 g at a time over a period of one hour, the contents of the flask being rapidly stirred mechanically. The substance was exposed to the mixture for another 2 hours at 50°C . The nitration product was precipitated by pouring the reaction mixture into an ice-brine mixture (2 litres) with vigorous stirring. The precipitated nitro derivatives were filtered very rapidly using a large area Buchner funnel and rapidly washed free from acid with ice-cold water. After rough drying over porous tiles, the material was spread thinly on clock glasses and exposed in vacuo to P_2O_5 for 7 days.

The dried, finely powdered mixture of acetyl derivative was dissolved in conc. H_2SO_4 with mechanical stirring. An equal volume of water was slowly added and the solution heated on the waterbath for 4 hours to ensure complete hydrolysis. On cooling to 0°C and diluting with an equal volume of ice-cold water, the greater proportion of the free bases was precipitated. After filtration, the filtrate was made alkaline at 0°C with aqueous ammonia, when a further small quantity of free base was collected by ether extraction. Separation of the required

compound from their isomers was accomplished by fractional crystallization from carbon tetrachloride. 4-Nitro-*o*-toluidine thus obtained was recrystallized from alcohol, m.p. 129°C.

2-Chloro, 2-Bromo, 2-Iodo, 2-Fluoro, 2-hydroxy,

2-Methoxy-5-nitrotoluenes

The amino group of 2-amino-5-nitrotoluene was replaced by Cl, Br, I, F, OH and OMe by Sandmeyer's reaction as described in Chapter II. All the derivatives were found to be pure from their NMR spectra and the physical properties reported in literature.

2-Nitro-5-aminotoluene

m-Toluidine was converted into its acetyl derivative just as described under *o*-toluidine.

The finely powdered dry acetyl derivative (25 g) was added to glacial acetic acid (25 ml) contained in a 3-necked round bottomed flask fitted with a mechanical stirrer and a separatory funnel. Conc. H_2SO_4 (50 ml, 92 g) were introduced into the well stirred mixture. The flask was surrounded with a freezing mixture of ice and salt. A cold mixture of conc. HNO_3 (15.5 g, 11 ml) and conc. H_2SO_4 (12.5 g, 7 ml) was added gradually from the dropping funnel while the temperature was maintained below 10°C. After all the acid had been added, the flask

was removed from the freezing mixture and allowed to stand at room temperature for 1 hour. The reaction mixture was poured onto crushed ice (250 g) whereby the crude nitro derivative was at once precipitated. After allowing to stand for 15 minutes the precipitate was filtered under suction on a Buchner funnel, washed thoroughly with cold water until free from acids and drained well. The pale yellow product was dried well. The mixture of nitro-acetamino derivatives was hydrolyzed to the amines using 70% H_2SO_4 . The mixture of isomers of free bases were separated by steam-distillation, until the required compound in the flask was free from other contaminating isomers which are steam-volatile. The free base was recrystallized from alcohol. It was found to be quite pure from its m.p. (134°C) and NMR spectrum.

5-Chloro, 5-bromo, 5-Iodo, 5-fluoro, 5-hydroxy, 5-methoxy-2-nitro-toluene

The amino group of 2-nitro-5-aminotoluene was replaced by Cl, Br, I, F, OH and OMe by Sandmeyer's reaction described in the previous Chapter. The derivatives were found to be quite pure from their NMR spectra and physical properties as reported in literature.

2-Methyl-4-amino-4'-nitroazobenzene²⁶

m-Toluidine hydrochloride 3.45 g (0.025 mole) in

water (30 ml) was added slowly to a sodium acetate-acetic acid solution (3.3N NaOAc, 0.33N HOAc; 25 ml) with stirring at 0°C (external ice-cooling).

p-Nitroaniline hydrochloride (4.36 g, 0.025 mole) dissolved in water (20 ml) and conc. HCl (1.369 g or 3.318 ml, *d*, 1.18) was diazotized in the usual way with sodium nitrite (1.725 g) in water (10 ml). The diazonium solution was thus obtained was added dropwise during 0.5 hour to the stirred ice-cold solution (or suspension) of *m*-toluidine and stirring continued overnight at 0-2°C. 2N Sodium hydroxide solution was added to the suspension until it was alkaline to clayton-yellow (Titan yellow). The azo compound was filtered off, washed thoroughly with water and vacuum dried. The recrystallized product from alcohol was found to be a mixture of ortho- and para-coupled compounds, the former being the main isomer,

A number of solvents were tried to separate the components of the mixture by fractional crystallization; but all the attempts failed. Finally the separation of the isomers was achieved by column chromatography using silica gel as the adsorbant and benzene as the eluent, the ratio between the compound and the adsorbant being 1:300. The compound was slightly soluble in benzene in cold. Hence, a mixture of silica gel and compound in dry

ether was prepared (or the compound was adsorbed on silica gel) and the solid was dried in vacuum after removing the ether carefully. This was spread on the top of the column after it was packed with the required amount of silica gel. The compound was separated from the mixture by eluting with benzene. The more strongly adsorbed compound was found to be the required one and the less strongly adsorbed was shown (as expected) to be the hydrogen bonded ortho-coupled product. The compound was further purified by recrystallization from benzene, m.p. 153°C.

2-Methyl-4-hydroxy-4'-nitroazobenzene²⁷

m-Nitroaniline (13.8 g) was dissolved in hot water (150 ml) containing conc. HCl (55 ml). The solution was poured over ice (375 g) and when the temperature had fallen below 10°C, sodium nitrite (7.3 g) in 15 ml of water was added slowly with stirring. After fifteen minutes the remaining ice and a small amount of flocculent yellow solid were filtered off rapidly, and the filtrate was added slowly and with stirring to a cooled (ice-salt) solution of m-cresol (10 g) in 250 ml of water containing sodium hydroxide (22.5 g). The dark brown pasty mass of the sodium salt of the coupling product was allowed to

stand overnight at room temperature after which it was acidified with hydrochloric acid. The orange solid was filtered off, washed thoroughly with water and dried at 100°C for six hours. The yield of crude product appeared quantitative (24.5 g). The product was dissolved in boiling alcohol (200 ml) and the hot solution was filtered. The filtrate when cooled and diluted with water deposited an orange fibrous mass of the azo compound which sintered at 157°C and melted at 162-163°C with decomposition. The product when chromatographed on silica gel as described above gave a deep reddish orange zone. The middle 2/3 of this zone was collected by elution. After removal of solvent the product was further purified by recrystallization from benzene in deep red needles which melted at 163-164°C.

2-Methyl-4-methoxy-4'-nitro azobenzene

The pure chromatographed sample of 2-Me-4-(OH)-4'-NO₂ azobenzene was converted into its methyl ether by the usual method described earlier using dimethyl sulphate, potassium carbonate in dry acetone. The product obtained melted at 138°C after recrystallization from benzene-pet. ether mixture.

4-Iodo-2-methyl-4'-nitro azobenzene

4-Amino-2-methyl-4'-nitro azobenzene was diazotized

as usual and the clear diazonium salt was treated with potassium iodide solution. The iodo derivative was separated and recrystallized from benzene-pet. ether mixture. The yield was very poor apparently because of very slow diazotization and accompanying difficulties.

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CHAPTER VI

PROTON CHEMICAL SHIFTS IN BF_3 - ADDUCTS
OF SOME p - SUBSTITUTED BENZALDEHYDES

PROTON CHEMICAL SHIFTS IN BF_3 -ADDUCTS
OF SOME *p*-SUBSTITUTED BENZALDEHYDES

In connection with the separation of the inductive and mesomeric effects of substituent groups in benzene ring, it was considered that measurements of barriers to internal rotation would give valuable information. It appeared that oxy-carbonium salts that can conceivably be obtained from a series of *para*-substituted benzaldehydes would furnish a suitable system, for which the temperature range for experimental measurements would be more convenient and more easily accessible than in the case of aldehydes themselves. By dissolution of these aldehydes in reagents like conc. H_2SO_4 we can, of course, obtain the corresponding hydroxy carbonium ions. But these could not be expected to permit the observation of molecular properties unhampered by interactions with the solvent. The relevant literature on the subject is briefly reviewed below.

The barriers to rotation in benzaldehyde and its *p*-methoxy and *p*-*N,N*-dimethylamino derivatives were estimated from the temperature dependence of their NMR spectra by Anet and Ahmad¹. The method depends on the non-equivalence that develops between the two protons ortho to the aldehyde

group when its rotation with respect to the phenyl group is slowed down, and it can in principle be used for the estimation of the relative strengths of electron donor groups in the para position. However, the estimated differences between the barriers for p-methoxy and p-N,N-dimethyl-amino derivatives on the one hand and parent aldehyde on the other are only 1.3 and 2.8 K cal. respectively. Similarly the barriers to rotation in some 2,4,6-tri-*t*-butyl benzophenones reported recently by Lauer and Staab² do not show much variation with changes in substitution at the 4'-position. The values measured for the 3',5'-dimethyl, 2',4',6'-trimethyl and 3',4',5'-trimethoxy derivatives are 17.2, 17.3 and 18.5 K cal. respectively. The change from -H to -OMe at the 4'-position results in a change of the barrier by 1.3 Kcal only. The system is thus unsuitable for measurements of small, but important, differences in donor strength, e.g. between the methyl and *t*-butyl group. In the oxy-phenyl carbonium salts the barriers to rotation may be expected to be larger. While the conjugation in the cation is isovalent, that of the neutral aldehyde is only sacrificial. The π -bond order for the $C_\alpha-C_1$ bond would therefore be larger in the former species than it is in the latter.

The literature on oxy-carbonium ions has been

reviewed recently^{3,4}. Several stable dialkoxy- and trialkoxy carbonium salts were prepared by Meerwein⁵ a decade ago. The NMR spectra of a number of these have been studied⁶. Although Meerwein mentioned the formation of mono-oxy-phenyl carbonium salts, experimental details have not been described and the salts do not seem to have been isolated. α -Acetoxy-isopropyl cation⁷ has been observed as one of the species present in a solution of isopropenyl acetate in sulphuric acid. A number of NMR spectroscopic studies of mono-oxy carbonium ions⁸ have appeared more recently. Although the basicities of aromatic aldehydes were earlier regarded⁹ to be too low to permit isolation of oxy-carbonium salts derived from them such salts have been obtained¹⁰. Very recently the behaviour of *p*-substituted benzaldehydes and benzylidene diacetates in pure acetic anhydride in presence of perchloric acid has been investigated and α -acetoxy phenyl carbonium salts have been isolated from these solutions¹⁰. The apparent order of donor strength of the *p*-substituent as indicated by the α -proton absorption positions is $\text{Me} > \text{F} > \text{I} > \text{Br} > \text{Cl}$ which is practically the same as the Hammett order $\text{Me} > \text{F} > \text{I} > \text{Cl} > \text{Br}$ except for the inversion with regard to bromine and chlorine which has been considered as not serious in view of the very small differences in donor strength.

In the study of α -acetoxy-*p*-substituted benzyl perchlorates just referred to, the *t*-butyl derivative has not been covered. In the background of our interest in the comparison of the properties of methyl and *t*-butyl derivatives, attempts were made to obtain α -acetoxy-*p*-*t*-butylbenzyl perchlorate. All these attempts proved futile for reasons which are not clear yet. Hence it was decided to try a variation of the earlier procedure and see whether the acetyl cation, that would be liberated in solution from the reaction of acetyl chloride with anhydrous silver fluoborate, can be transferred directly on to the carbonyl oxygen of the *p*-substituted aldehyde (e.g. *p*-tolualdehyde) to get the corresponding carbonium fluoborate. The reagents were mixed in molecular proportions using ethylene dichloride as solvent and species in solution studied by NMR spectroscopy. A number of experiments of this type seemed to indicate that the species obtained is something other than the expected α -acetoxy carbonium fluoborate. Although the aromatic proton shifts and α -proton shifts for the species were comparable to that of α -acetoxy *p*-xylyl perchlorate there was no indication of lone acetyl group (i.e. more than one acetyl signal was obtained in most experiments). The absorptions of aromatic protons at the 2,6 and 3,5 positions did indicate that

the conversion of the aldehyde into an oxy-carbonium salt. It appeared likely that the acetyl cation produced in solution instead of being transferred on to the carbonyl oxygen might be pulling fluorine from the BF_4^- to give acetyl fluoride and free BF_3 . The BF_3 that is liberated might co-ordinate with the carbonyl group of the aldehyde to give an adduct. The correctness of the surmise was demonstrated by a spectrum of the BF_3 adduct prepared separately.

In view of the comparable shifts obtained for ring protons and C- α protons in the BF_3 -adduct of *p*-tolualdehyde and α -acetoxy *p*-xylyl perchlorate it was thought that the BF_3 -adducts of various *p*-substituted aldehydes themselves might be a set of compounds that may be employed in place of the acetoxy carbonium salts for the purpose we had in mind. The adducts have the advantage that they are very readily obtained and their spectra do not seem to have been studied earlier. The following study of these adducts was, therefore, undertaken.

RESULTS AND DISCUSSION

The BF_3 -adducts of *p*-methoxy, fluoro, chloro, bromo, iodo, methyl and *t*-butyl benzaldehydes were prepared by adding excess BF_3 -etherate to the aldehyde and removing cautiously the excess BF_3 -etherate under reduced pressure.

(1-2 mm). Molecular weight determination by the Mechrolab Inc. model 301A Vapour Pressure Osmometer showed that these were 1:1 adducts. The NMR spectra (60 MHz) of the colourless solids were recorded both in dry BF_3 -etherate and ethylene dichloride. The spectral data* for the adducts and the aldehydes are given in Tables 1,2 and 3. The absorptions of the α -protons of these adducts are in the region 565.5 - 587.0 Hz and those of the ring protons show an A_2B_2 pattern typical of the *p*-phenylene group. The latter appear at positions quite different from those of the corresponding aldehydes. In the case of *p*-bromobenzaldehyde the ring protons come almost together in one group whereas in the adduct the ring protons show a clear A_2B_2 absorption pattern with a 10 Hz shift between the A_2 and B_2 pairs. In the aldehyde the aldehydic proton absorbs at 601.5 Hz whereas in the BF_3 -adduct it moves upfield by a considerable amount (15.5 Hz). This behaviour is also consistent with the assumption of delocalization of charge on α -carbon atom into the benzene ring and *p*-substituent. The lower field part of the A_2B_2 pattern is

*All chemical shifts are expressed as Hz downfield from TMS (internal standard).

TABLE 1 - PROTON CHEMICAL SHIFTS IN P-SUBSTITUTED
BENZALDEHYDES IN ETHYLENEDICHLORIDE
(in Hz downfield from TMS).

Substituent	C _{2,6} -protons	C _{3,5} -protons	Aldehydic proton
OMe	473.085	424.415	597.000
F	477.500	436.500	601.500
Cl	472.365	455.635	602.500
Br	466.500	456.500	601.500
I	479.915	459.085	602.000
Me	467.560	442.440	599.500
t-Bu	470.165	456.335	601.000
H	476.500		603.000

TABLE 2 - PROTON CHEMICAL SHIFTS IN BF₃-ADDUCTS OF
p-SUBSTITUTED BENZALDEHYDES IN BF₃-ETHERATE
(in Hz downfield from TMS).

Substituent	C _{2,6} -protons	C _{3,5} -protons	H _α
OMe	497.170	435.830	563.000
F	491.500	443.000	589.000
Cl	488.230	462.770	589.000
Br	483.535	473.465	589.500
I	488.185	472.315	586.500
Me	489.220	455.280	577.500
t-Bu	492.990	470.010	578.700
H	489.500		593.000

TABLE 3 - PROTON CHEMICAL SHIFTS IN BF_3 -ADDUCTS OF 2-SUBSTITUTED BENZALDEHYDES IN ETHYLENE DICHLORIDE (in Hz).

Substituent	$\text{C}_{2,6}$ -protons		$\text{C}_{3,5}$ -protons		H_α
	Observed	Corrected	Observed	Corrected	
OMe	494.175	497.775 $\pm$ 1.800	432.325	454.525 $\pm$ 2.400	565.500
F	501.250	503.050 $\pm$ 3.600	447.000	462.000 $\pm$ 1.800	580.500
Cl	491.760	494.760 $\pm$ 2.4	465.240	462.840 $\pm$ 1.200	587.000
Br	486.285	492.885 $\pm$ 1.200	476.215	466.615 $\pm$ 0.600	586.000
I	486.720	495.120	470.280	445.680	586.000
Me	488.230	491.230 $\pm$ 1.200	453.770	459.170 $\pm$ 1.200	576.500
t-Bu	493.035	496.035	468.465	463.665	580.500
H	498.500				585.500

apparently produced by the protons in the 2- and 6-positions which are electron deficient. In all the cases, the lower half of the *p*-phenylene A_2B_2 type of absorption is assigned to the 2- and 6-protons and the correctness of this assignment is further substantiated by the spectra of other derivatives (e.g. OMe, F, Me etc.). No correlation is seen between the observed $H_3(5)$ or $H_2(6)$ chemical shifts and any of the reactivity parameters namely σ_p , σ_m and σ_R . However, the variations in the α -proton absorption positions indicate that they are determined by the nature of the *p*-substituent, the absorption being at the highest field in the methoxyl derivative. Electron-donor substituents seem to shift the α -proton signal upfield. This is apparently due to the reduction in positive charge at the α -carbon atom as a result of electron release from the substituent. This feature cannot be explained on the basis of a π -complex or C-1 σ -complex structure for these derivatives. The apparent order of donor strength indicated by the α -proton signals is $OMe > Me > t-Bu = F > I = Br > Cl$, which resembles the Hammett order ($OMe > t-Bu > Me > F > I > Cl > Br$). Since the difference in σ -values for Cl and Br is very small, the inversion of the order with regard to bromine and chlorine derivatives need not be regarded as a serious discrepancy. A contribution from the polarizability factor can easily

account for the obtained order. However, the inverted order for methyl and t-butyl derivatives cannot be ignored and it is consistent with other results reported in this thesis. The polarizability factor should be much larger for the t-butyl group. It is in spite of this that methyl is found to be a stronger donor than the t-butyl group. Since the inductive effect is also larger for the t-butyl group, the observed order of donor strengths for the methyl and t-butyl groups cannot be understood unless the importance of hyperconjugation is conceded. C-H hyperconjugation is apparently more important than the C-C hyperconjugation.

As mentioned earlier, no systematic variation is detectable in the C₂, C₆ and C₃, C₅-proton shifts. It would be of interest to see if these absorptions follow the additivity rule^{11,12}. The corrected chemical shifts obtained by subtracting the effects of the C₄-substituents are shown along side the experimental shifts in Table 3. The ortho and meta substituent constants (S_o and S_m) obtained by Smith¹² have been used to get the 'corrected' shifts for both groups of protons. The difference between the 'corrected' shifts and the chemical shift of benzene protons should represent the substituent constants of the $\text{-}\overset{+}{\text{C}}\begin{array}{l} \text{H} \\ \text{OBF}_3 \end{array}$ group if the rule of additivity holds.

The 'corrected' shifts are not constant for the species studied. An attempt has been made to see whether the deviations from additivity rule follow any regular trend. No such trend is obvious.

The NMR spectra of the adducts of the Me and t-Bu derivatives have been studied below room temperature going down to -40°C . This is not adequate to cause any splitting of the C_2 - and C_6 -proton signals. Since arrangements for working at lower temperatures are yet to be made, further experiments have been postponed.

EXPERIMENTAL

Benzaldehyde

Commercial benzaldehyde was distilled under reduced pressure, after removing the acid present by treating with a solution of sodium bicarbonate, and the fraction boiling at $49^{\circ}/1.5$ mm was collected.

p-Tolualdehyde

Commercial p-tolualdehyde (Fluka AG grade) was taken in ether and vigorously shaken up with saturated sodium bisulfite solution and the solid formed was filtered off. The filtrate was again shaken with bisulfite solution and the solid obtained was mixed with the main bulk. This bisulfite addition product was washed with ether and dried. The dry solid was decomposed with dil. H_2SO_4 and the free aldehyde isolated. This was further purified by distillation.

p-t-butylbenzaldehyde

Because of side reactions involved in the synthesis of this material from p-t-butylbromobenzene and ethyl orthoformate, it was decided to obtain it by the Etard's reaction.

A solution 150 g of chromium (VI) oxide (C.P.) in 100 ml of water was placed in a 1500 ml 3-necked flask

fitted with a mechanical stirrer, a dropping funnel, a thermometer and a tube to carry away the vapors of chromyl chloride and hydrogen chloride. 330 ml of conc. HCl was added and the solution cooled to 0°C by an ice-salt mixture. While the solution being stirred, 450 ml of conc. H_2SO_4 was added drop by drop from the dropping funnel. Ice was added to the cooling-bath as needed, and the temperature maintained such that it did not rise above 15 to 20°C . When all the H_2SO_4 was added, the reaction mixture was transferred to a separatory funnel and the lower layer of chromyl chloride¹³ was drawn off into a glass-stoppered container. Yield 189 g (81%). The dark-red product was distilled through an 18 inch Vigreux column using calcium chloride guard tube. The fraction boiling between 115 and 116°C at 735 mm amounted to 65% of the crude product.

Toluene (50 g, 0.543 mole) dried over calcium hydride was placed in a dry one litre-flask fitted with thermometer and t-butyl chloride (50 g, 0.540 mole) was added. To this mixture was added 0.30 g (0.0019 mole) of sublimed anhydrous ferric chloride in one portion and a reflux condenser was attached. Vigorous gas evolution occurred immediately, the temperature rose from 25°C to 28°C in 10 seconds and then dropped to 18°C after one minute.

at which time the reaction was almost complete. Three minutes after the addition of the catalyst, 200 ml of water was added and the mixture shaken. The product (p-t-butyl toluene)¹⁴ was steam-distilled, separated from the distillate and dried over anhydrous potassium carbonate. It was then fractionated using a long column and the fraction distilling over at 192-193°C/760 mm was found to be free from the other isomers.

A solution of p-t-butyl toluene (20 g, 0.135 mole) in carbon disulphide (150 ml) was added over 30 minutes period to a stirred solution of chromyl chloride (42 g, 0.27 mole) in the same solvent (100 ml). The whole system was protected from moisture using a P₂O₅ guard tube. After keeping the mixture for 48 hours at room temperature, the dark coloured crystalline intermediate was collected and washed with carbon disulphide and dried in vacuum for 15 minutes. The complex was decomposed with ^{water} (1 litre) and the aqueous mixture was extracted with ether immediately so as to avoid the contact of the aldehyde for a long time with chromic acid and chromic chloride which are formed in the hydrolysis. The ether extract was first washed with NaHCO₃ solution and subsequently with water. After drying the extract over anhydrous sodium sulfate, the solvent was removed and the residue distilled under reduced pressure. Pure p-t-butylbenzaldehyde distilled

over at $126^{\circ}\text{C}/2.5 - 3 \text{ mm}$.

p-Anisaldehyde

Commercial p-anisaldehyde was used after distilling without any further purification and the compound distilled at $111-112^{\circ}\text{C}/4 \text{ mm}$.

p-Halobenzaldehydes

All the p-halobenzaldehydes were prepared from the corresponding halotoluenes by chromic anhydride oxidation, in acetic anhydride-acetic acid solution and hydrolysing the benzylidene diacetate to the aldehyde. The halotoluenes were prepared from p-toluidine by Sandmeyer's reaction.

p-Chlorobenzaldehyde was obtained in a yield of 86% which melted at $45-46^{\circ}\text{C}$. p-Fluorobenzaldehyde was obtained as a colourless liquid boiling at $57^{\circ}\text{C}/2 \text{ mm}$ in a yield of 28-29%. p-Bromobenzaldehyde was obtained in a yield of 36% as a fine crystalline solid which melted at 55°C , while the p-iodobenzaldehyde was obtained as needle shaped crystals melting at $75-76^{\circ}\text{C}$ in a yield of 32%.

Preparation of the BF_3 -adducts

The aldehyde was mixed with excess BF_3 -etherate and the excess BF_3 -etherate was removed under reduced pressure (1-2 mm) cautiously. The solid obtained was crystalline and almost colourless in all the cases. These solids are moisture sensitive and decompose to the corresponding aldehyde.

Molecular weights of these adducts were determined in ethylene dichloride solution using the Mechrolab Inc., model 301A Vapour Pressure Osmometer and it was found that these were 1:1 adducts. For instance, a molecular weight of 177.78 was found for the adduct of *p*-tolualdehyde as against the expected value of 187.8. Considering the sensitivity of the adduct to moisture, the agreement that is obtained may be considered fair.

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SUMMARY

S U M M A R Y

The development of the concepts of conjugation and hyperconjugation and the evidence in favour of the latter have been briefly reviewed. The alternative explanations that have been offered in place of hyperconjugation have also been considered. The ambiguity in this regard, which was first highlighted by Dewar about a decade ago, has remained unresolved. The studies reported in this thesis have been made in an attempt to resolve this ambiguity.

In an effort to find a new and sufficiently sensitive nuclear magnetic resonance method for the study of hyperconjugation a new series of benzene derivatives has been studied. Quantitative studies of substituent effects in benzene derivatives by nuclear magnetic resonance have so far used mostly fluorine chemical shifts although other spectral parameters have also been investigated. The question of hyperconjugation has not been studied with the aid of ^{19}F shifts. Moreover, the validity of the interpretation of ^{19}F shifts, advanced by Taft and co-workers has been questioned recently. Aromatic proton chemical shifts in monosubstituted benzenes are much less sensitive to substituent effects than ^{19}F shifts. The study of disubstituted benzenes is of little help for detection of conjugation between substituent groups across the aromatic ring because

chemical shifts in these obey the additivity rule. It has been pointed out recently that the difficulties in the use of ^1H chemical shifts for study of resonance interaction between substituents may be overcome by the choice of sterically hindered systems of a special type. As part of a programme for the systematic investigation of this technique, the NMR spectra of a series of 4-substituted phthalic esters involving a total of eleven derivatives have been studied. The paramagnetic shifts that are usually associated with the ortho protons of aromatic carbomethoxy derivatives are not seen in dimethylphthalate in which the substituent groups are rotated from the plane of the aromatic ring. The upfield shift is ascribed partly to the reduction of conjugative interaction and partly to the changes in the anisotropic contribution to the shielding accompanying the rotation of the acceptor groups from the preferred conformation coplanar with the aromatic ring. It has been suggested that in this system if a donor group is put para to one of the acceptor groups, the acceptor group would tend to interact mesomerically with the donor and come closer to the aromatic plane. This conformational change should be reflected in a downfield shift of the absorption of the ortho protons (at C_6 -position). This expectation is shown to be correct by the results obtained.

The rotation of the C_1 -COOMe group would normally be expected to affect the conformation of the second acceptor group (C_2 -COOMe) and push it more out of the plane of the benzene ring due to the inherent nature of the system. This expectation has also been realized in the upfield shift of the C_3 -proton ortho to the C_2 -COOMe group. In order to estimate these downfield and upfield shifts allowance has been made for the effect of substituent and a set of 'corrected' shifts have been obtained. If the conformations of the carboxyls remain unaltered on substitution, the additivity rule may be expected to hold for these derivatives, and the 'corrected' shifts (for the C_6 - and C_3 -protons) should be expected to be equal to the C_3 (or C_6) proton shift for the parent compound, i.e. dimethylphthalate. The deviations of these 'corrected' chemical shifts from the corresponding value for the parent phthalic ester have been found to be a measure of resonance interaction between donor and acceptor groups para to each other. These deviations have been shown to be correlated well with Taft's σ_R parameters of the substituents. It has also been shown that the interaction between the COOMe and methyl group is predominantly of the "hyperconjugative" type and not of the "inducto-mesomeric" type. The paramagnetic shift that has been found for the C_3 -proton is larger in the methyl derivative

than in the t-butyl derivative showing that the methyl group is a stronger donor than t-butyl in this system. If the "inducto-mesomeric" interaction were more important than direct mesomeric interaction, the order of the relative shifts would have been reversed (i.e. the paramagnetic shift associated with the C_3 -proton in the t-butyl derivative would have been much larger than the corresponding shift in the methyl analogue). The larger diamagnetic shift associated with C_3 -proton in the t-butyl derivative as compared to the methyl derivative has been explained by invoking steric interaction between the t-butyl group and the C_3 -proton which is communicated to the C_2 -COOMe group and made manifest by the buttressing action of the C_1 -COOMe. It is shown that this steric interaction cannot vitiate the conclusion regarding the relative donor strengths of the methyl and t-butyl groups. It has been concluded that the mesomeric interactions can be studied in isolation in this system (unhampered by admixture with inductive effect) and that C-H hyperconjugation is stronger than C-C hyperconjugation.

With a view to demonstrate the effect of steric interaction which has been invoked in order to explain the apparent deviation of the C_3 -proton shift in dimethyl 4-t-butylphthalate, a number of p-substituted anilinium and phenyltrimethylammonium salts have been examined. In order to ascertain the effect of

steric interaction it was proposed to determine the normal NMR substituent constants of the NH_3^+ and NMe_3^+ groups and apply these to the spectra of the corresponding phthalic esters. However, this attempt was not successful since the required substituent constants could not be pinned down with sufficient precision. In the ionic derivatives involved the solvation characteristics themselves changes with substitution and they also have apparently a significant effect on chemical shifts and it does not seem possible to define substituent constants that are useful.

In the background of the results obtained from NMR studies a parallel study of IR vibrational band intensities has been undertaken. The band chosen for this purpose was that of ring mode (ν_{16a} and ν_{16b}). The compounds studied are p-substituted benzoic esters (with substituents OMe, F, Cl, Br, I, Me, t-Bu and NO_2) and 4-substituted phthalic esters (with substituents OMe, F, Cl, Br, I, Me and t-Bu). The maximum intensity in the series was obtained for the OMe derivative and has been understood on the basis of its strong electron-donating action whereas the variations of the intensities among the halogen family have been rationalized by considering both mesomerism and the polarizability factor. The fall of intensity in the transition from F to Cl has been understood as arising from a decrease in mesomeric effect.

However, the intensity change for the transition from chlorine to iodine through bromine has been rationalized on the basis of the polarizability effect which is naturally expected to play a more important role in the heavier substituents. The relative intensities of methyl derivatives have been found to be more than that of the t-butyl derivatives in both the series indicating that methyl group is a stronger donor than t-butyl group. The same conclusion has been reached from a study of the intensities of NO_2 symmetric stretching and $\text{C}\equiv\text{N}$ stretching bands in p-Me and ^p-t-butyl substituted nitrobenzenes and benzonitriles respectively.

The technique of using methyl group as a sensing element has been extended to study donor-acceptor interaction across benzene ring. It is to be noted that the changes in π -electron distribution in donor-acceptor systems can be followed only to the extent they are reflected in the mobile bond orders. The systems chosen for this purpose were nitrobenzenes with donor-substituents in the para position. The methyl group was introduced either ortho to the donor group or ortho to the acceptor group. In 4-substituted 3-methyl nitrobenzenes the expectation that PMR methyl band width data would reflect the variation of the strength of donor-acceptor interaction has been realized. In a parallel set of derivatives namely 4-substituted 2-methyl nitrobenzenes it has been

found that the general trend of variation of methyl band width is consistent with that of the previous system even though the total variation is rather small indicating that the system is not very sensitive for this type of study. The factors that are responsible for this lack of sensitivity may be (a) steric interaction between methyl and NO_2 groups in which case the NO_2 group being rotated through an appreciable angle away from the plane of the benzene ring would be less conjugated with the para donor group across the ring and (b) direct interaction of methyl group with the adjacent NO_2 group. In order to circumvent the former difficulty some 4-substituted 2-methyl-4'-nitroazobenzenes have been examined. Here again the methyl band width data revealed that in these type of systems the methyl group is an interacting group, not a mere sensing element. This may be regarded as evidence in favour of hyperconjugation.

A number of BF_3 -adducts of *p*-substituted benzaldehydes have been prepared and their NMR spectra discussed. The variations in the α -proton absorption positions have indicated that the apparent order of donor-strength resembles Hammett order except for the inversion of the order with regard to bromine and chlorine. The observed order with regard to methyl and *t*-butyl derivatives cannot be

understood unless the importance of hyperconjugation is conceded. This again reinforces the notion that C-H hyperconjugation is important and stronger than C-C hyperconjugation.

All the studies on conjugative interaction between donor and acceptor groups made in this thesis have given a consistent answer to the problem of hyperconjugation. Hyperconjugation appears to be important even in the ground states of molecules.