

PROTON SPIN-SPIN INTERACTIONS IN *m*-DISUBSTITUTED BENZENES

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ABSTRACT

The NMR spectra of *m*-disubstituted benzenes, in which one of the substituents is kept constant and the other varied have been analysed. It has been shown that the proton-proton interactions in these molecules are not influenced by the inductive and resonance effects of the substituent but depend on its steric effect. A measure of the relative steric effects of different substituents is thus suggested. The results have been compared with other methods of measuring steric effects.

INTRODUCTION

RECENTLY there has been substantial progress in our understanding of the mechanism and nature of the electron-coupled nuclear spin-spin interactions (Ramsey and Purcell, 1952; Ramsey, 1953; Narasimhan, 1963; Govil, 1963). Since the coupling constants are now very widely used in establishing molecular structure, it is important to have a good knowledge about the factors that may influence these values. Two major effects which should attract attention in this connection are the substitution and the solvent effects.

Banwell *et al.* (1960) have studied substitution effects on proton-proton interactions in vinyl compounds and correlated them with the electronegativity of the substituent. Dharmatti *et al.* (1962) have observed a relation between *para* proton-fluorine coupling constants in substituted fluorobenzenes and the Hammett's constant (σ_R) of the substituent. Extensive work on the substitution effects on C^{13} -H coupling constants and on C^{13} -F 19 coupling constants has also been reported (Govil, 1963; Muller and Pritchard, 1959; Malinowsky, 1961; Gutowsky *et al.*, 1962).

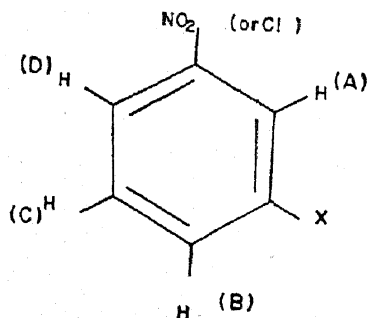
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NMR spectra of substituted benzenes have been studied extensively (Corio *et al.*, 1956; Dharmatti *et al.*, 1961; Martin *et al.*, 1962; Richards *et al.*, 1958). The substitution effects on the proton chemical shifts have been discussed in some detail by Corio and Dailey (1956). It may look strange, therefore, at first sight that no attempts have hitherto been made to correlate the proton-proton couplings in such molecules with the nature of the substituent. However, there are several reasons for this. Firstly, the spectra of monosubstituted benzenes ($A_2 B_2 C$ type) are quite complicated and difficult to analyse because of the small differences between the chemical shifts of *ortho*, *meta* and *para* protons. In fact, in some of the above papers, only the chemical shift values have been guessed from the NMR spectra. Secondly, the values of the various coupling constants are quite low (<10 c/s) (Pople *et al.*, 1959) and hence it is essential that very accurate values of the coupling constants must be obtained if one wants to study the substitution effects.

The work on disubstituted benzenes reported in this paper was undertaken with a view to find out whether substitution has any effect on the proton spin-spin interactions.

ANALYSIS OF THE SPECTRA

As has been pointed out, it is rather difficult to analyse the NMR spectra of most of the monosubstituted benzenes at the operating frequencies presently available. It is more convenient to work with disubstituted benzenes keeping one of the substituents fixed. The fixed substituent should preferably be such that it produces large chemical shifts among the various nonequivalent protons in the ring system. It is then possible to get well-resolved spectra for disubstituted benzenes. For our study, the groups $-\text{NO}_2$ and $-\text{Cl}$ were chosen as the substituents in the fixed position. The other group (X), the effect of which we wish to study, was substituted in the position *meta* to the fixed group because of some experimental conveniences and ease in assigning different transitions.



The spectra of *m*-disubstituted benzenes (Structure I) are of the ABCD type so long as the substituent (X) itself does not couple with the ring protons. This is true with the substituents which either have a zero nuclear spin or a quadrupole moment. The latter causes a rapid relaxation resulting in the collapse of spin multiplets and apparently decoupling with the ring protons (Pople, 1958). In such spectra it is easy to identify the different transitions. Since J_{AC} is very small and J_{AB} and J_{AD} are of the same order of magnitude the A spectrum will in most cases be a triplet, the separation between the various lines being about 2 c/s. In rare cases where J_{AC} has a resolvable magnitude or J_{AB} and J_{AD} have a resolvable difference, one gets finer structure for the triplet. Similarly the C group is in most cases a triplet with separation of about 8 c/s between the various lines. The B and D groups will each give six line spectrum, two triplets separated by J_{BC} or J_{CD} (~ 8 c/s) and each line in the triplet separated by about 2 cps. In case J_{AB} (or J_{AD}) differ from J_{BD} by more than 0.3 c/s, an eight-line spectrum for these protons is obtained. It is thus possible to pick up the A and C group lines because of their typical fine structure. Out of the remaining lines those due to D group are at a lower field in nitrobenzenes because its proximity to the strongly electron withdrawing $-\text{NO}_2$ group. Similar argument hold good for chlorobenzenes. In this way unambiguous assignments can be made for each transition in the spectrum of the nitro- and the chloro-benzenes.

The analysis of the ABCD type of spectrum has been reported earlier (Dharmatti *et al.*, 1962; Govil *et al.*, 1961). Trial and error calculations are made after proper assignments of the various transitions on the lines discussed above. Thus accurate values of the various chemical shifts and coupling constants are obtained. For nitrobenzene and *m*-fluoro-nitrobenzene (when X is H or F) one gets more complicated spectra of the type $A_2 B_2 C$ and ABCDX respectively. These spectra have been analysed earlier (Dharmatti *et al.*, 1962; Govil *et al.*, 1965). When X is $-\text{NO}_2$ the spectrum gets greatly simplified because of the resultant symmetry ($A B_2 C$ type). The spectrum of this molecule (*m*-dinitrobenzene) also has been analysed earlier (Abraham *et al.*, 1960).

EXPERIMENTAL

All NMR spectra were recorded at 60 Mc/s on a Varian high resolution NMR spectrometer. Eight traces of each spectrum were taken—four with the field increasing and the remaining with field decreasing. The distances between the various peaks in each trace were measured by the side band technique and a mean of the various readings was taken. The mean devia-

tion between the observations corresponding to different traces was less than ± 0.2 c/s. The spectra were also recorded with fast scanning relative to an internal standard (cyclohexane in most cases) and the shifts were measured within an accuracy of 2 c/s. In all cases chemical shifts have been finally expressed relative to tetramethylsilane.

Most of the samples used in this investigation were of high purity (Eastman Organic Chemicals). The degree of purity of each compound was checked by melting points (or boiling points of liquids). Some of the samples were prepared in our laboratory by standard methods. For the purpose of recording the spectra, liquid samples were used without dilution while the solids were dissolved in suitable solvents, *e.g.*, the sodium salt of *m*-nitrosulphonic acid was dissolved in 95% D₂O; *m*-iodonitrobenzene, *m*-bromonitrobenzene, *m*-chloronitrobenzene and *m*-nitroanisole were dissolved in carbon tetrachloride; and *m*-nitroaniline, *m*-nitroacetanilide and *m*-nitrophenol were dissolved in tetrahydrofuran. In all the cases the strength of the solution was kept just below the saturation limit. Nitrogen was bubbled through all the samples to drive away any dissolved oxygen. The values of the chemical shifts and the coupling constants determined as mentioned above are given in Table I. The use of the digital computer, TIFRAC considerably simplified the calculations involved.

DISCUSSION

Possible Substitution Effects.—The substitution effects in the benzene ring can take place through the following three different mechanisms:

(i) The Inductive Effect (I) operates through the sigma electrons in the ring system and causes a change in their densities at *ortho*, *meta* and *para* positions. Measures of this effect are the Hammett's constant σ_I and NMR chemical shifts.

(ii) The Resonance Effect (R) acts through the pi-electrons of the ring and causes a variation in the pi-electron densities at the *ortho* and *para* positions. Quantitative estimates of this effect can be had from Hammett's constant σ_R and NMR chemical shifts.

(iii) The Steric Effect arises from the overlap of the volume of influence of the substituent on that of hydrogen atom in the *ortho* position. An accurate measure of the pure steric effects of different substituents is not yet known. Some information about steric effects may be obtained from van der Waal radii of atoms and chemical reactivities.

TABLE I
Chemical shifts and coupling constants of *m*-nitro and *m*-chlorobenzenes

No.	Compound	X	Chemical shift relative to tetramethylsilane				Coupling constants cps					
			δ_A	δ_B	δ_C	δ_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
<i>m</i> -Nitrobenzenes												
1	<i>m</i> -Nitrosulphonic acid (Na Salt)	-SO ₃ H	PPM -8.80	PPM -8.43	PPM -7.97	PPM -8.52	1.7	0.0	2.4	7.8	1.1	8.3
2	<i>m</i> -Iodonitrobenzene	-I	-8.47	-8.21	-7.38	-8.04	2.2	0.2	1.5	8.0	1.0	8.3
3	<i>m</i> -Bromonitrobenzene	-Br	-8.26	-7.83	-7.48	-8.14	2.0	0.6	2.2	8.2	1.2	8.3
4	<i>m</i> -Dinitrobenzene	-NO ₂	-8.94	-8.60	-7.91	-8.60	2.2	0.5	2.2	8.2	..	8.2
5	<i>m</i> -Nitroaniline	-NH ₂	-7.44	-6.92	-7.19	-7.40	1.7	0.2	1.6	8.3	1.3	8.3
6	<i>m</i> -Nitroacetanilide	-NHCOCH ₃	-8.50	-7.99	-7.44	-7.84	2.7	0.0	2.2	8.5	1.5	8.3
7	<i>m</i> -Chloronitrobenzene	-Cl	-8.11	-7.68	-7.56	-8.11	1.8	0.3	1.9	8.5	1.7	8.4
8	<i>m</i> -Nitrobenzoic Acid	-COOH	-8.74	-8.36	-7.73	-8.43	2.0	0.0	2.2	8.5	1.6	8.3
9	<i>m</i> -Nitrophenol	-OH	-7.61	-7.17	-7.38	-7.69	2.0	0.2	1.7	8.6	1.6	8.4
10	<i>m</i> -Nitroanisole	-OCH ₃	-7.56	-7.13	-7.36	-7.69	2.6	0.5	2.0	8.6	1.6	8.3
11	<i>m</i> -Fluoronitrobenzene	-F	-7.82	-7.48	-7.64	-8.02	1.9	0.6	1.7	8.7	1.9	8.1
12	Nitrobenzene	-H	-8.18	-7.69	-7.54	-8.18	2.0	0.0	2.0	8.7	2.0	8.4
<i>m</i> -Chlorobenzenes												
1	<i>m</i> -Iodochlorobenzene	-I	-7.59	-7.43	-6.83	-7.16	1.5	0.3	2.0	7.8	1.0	8.3
2	<i>m</i> -Bromochlorobenzene	-Br	-7.34	-7.19	-6.93	-7.08	1.9	0.4	2.0	8.0	1.1	8.4
3	<i>m</i> -Chloroaniline	-HN ₂	-6.40	-6.24	-6.86	-6.62	2.2	0.4	2.0	7.9	1.1	8.3

It is clear from the above discussion that the position D (Structure I) is influenced by both the inductive and the resonance effects of the substituent X, the position C by only the inductive effect and the positions A and B by all the three (inductive, resonance and steric effects). Variations in the proton-proton couplings ($J^{\text{H-H}}$) in different positions can occur through any of the above effects.

The coupling constant in aromatic compounds can be written as

$$J^{\text{H-H}} = J_{\sigma}^{\text{H-H}} + J_{\pi}^{\text{H-H}}$$

where $J_{\sigma}^{\text{H-H}}$ and $J_{\pi}^{\text{H-H}}$ are the contributions of the sigma and pi-electrons to the coupling constants. In benzene $J_{\pi}^{\text{H-H}}$ is negligible (McConnell, 1956), which indicates that the coupling constants are likely to be independent of resonance effects. The last column of Table I shows that the values of J_{CD} remain constant within experimental error for both the series of compounds (8.3 ± 0.1 c/s), irrespective of the substituent X. Thus the proton-proton coupling constants are not only independent of the resonance effects but are also surprisingly insensitive to variations in the inductive effect.

The values of J_{BC} and J_{BD} are found to vary with the change in the substituents. The results indicate a general decrease in these values with heavier substituents. The variations can be explained only in terms of the steric effect present at proton B. The steric effect can bring about a distortion of the C-H bond and hence a change in the inter-atomic angles. Consequently, the *s* character of the carbon orbitals and hence the coupling constants are likely to change. Using valence bond theory, Karplus (1959) has shown that nuclear spin-spin interactions are very sensitive to inter-atomic angles. Gutowsky and Poite (1961) who have extended the calculations of Karplus to ethylenic systems have shown that a change of the H-C-C angle from 120-125° causes the calculated value of $J_{\sigma}^{\text{H-H}}$ to decrease from 6.1-4.0 cps. Thus in the compounds under discussion, distortions of less than 3° are sufficient to explain the observed variations. It may be pointed out that it is difficult to observe such small distortions by direct physical methods for the determination of bond angles. However, the relative magnitudes of the steric effects of different substituents can well be estimated from values of coupling constants. In Table I, the different compounds have been arranged in the order of increasing values of J_{BC} and J_{BD} . This, therefore, is also the order in which the steric effects of different substituents decrease.

We shall now compare the information regarding steric effects as given by coupling constants with that available from (1) van der Waal radii and (2) chemical reactivity.

(1) *The van der Waal Radii.*—Since the steric effects arise because of the repulsive forces between the atoms (proton B or A and substituent X in our case) from interpenetration of their electron shells (Newman) the overlap of van der Waal surface of the substituent with proton B can be taken as a measure of steric effect (Pauling, 1960; Coulson *et al.*, 1959). For mono-atomic substituents such overlaps can be calculated trigonometrically from known values of bond lengths, bond angles and van der Waal radii of atoms in a straightforward manner. These values are given in Table II. For substituents like hydrogen and fluorine there is no overlap and hence no steric

TABLE II
Measures of relative steric effects of different substituents

Substituent	Overlap of van der Waal surfaces of B and X calculated from standard values of covalent and van der Waal radii in Å	σ_s	J_{nc} cps	J_{nd} cps	
—SO ₃ Na	with S	0.15	..	7.8	1.1
	„ O	0.02			
—I		0.25	...	8.0	1.0
—Br		0.18	1.15	8.2	1.2
—NO ₂	„ N	0.02	1.27	8.2	..
	„ O	0.07			
—NH ₂	„ N	0.02	..	8.3	1.3
	„ H	Nil			
—NHCOCH ₃	„ N	0.02	..	8.5	1.5
—Cl		0.13			
—COOH	„ C	0.08	1.05	8.5	1.7
	„ O	0.06	..	8.5	1.6
—OH	„ O	Nil	1.60	8.6	1.6
	„ H	0.12			
—OCH ₃	„ O	Nil			
	„ C	0.04	0.38	8.6	1.6
	„ H	0.07			
—F	..	Nil	0.87	8.7	1.9
—H	...	Nil	..	8.7	2.0

effect. In such cases, the maximum values for the couplings J_{BC} and J_{BD} are obtained. A linear behaviour is observed when the values of J_{BC} are plotted against the overlap for monoatomic substituents (Fig. 1). For polyatomic substituents, the situation is complex since the overlap of the substituent as a whole has to be considered, while the van der Waal radii of only individual atoms are known. In such cases, values of the overlap with individual atoms of the substituent were calculated (Table II). Even for the maximum values of the overlaps, the points in Fig. 1 for polyatomic substituents generally fall much below the line for monoatomic substituents; thus showing that the actual steric effects in these cases are larger than those estimated from van der Waal radii of individual atoms. SO_3Na seems to have the maximum steric effects among the various substituents studied, although the overlap with individual atoms S and O with H are not as much as in some of the monoatomic substituents.

(2) *The Chemical Reactivities.*—Holleman (1925) compared the *ortho* to *para* substitution in several substituted benzenes when the entering group

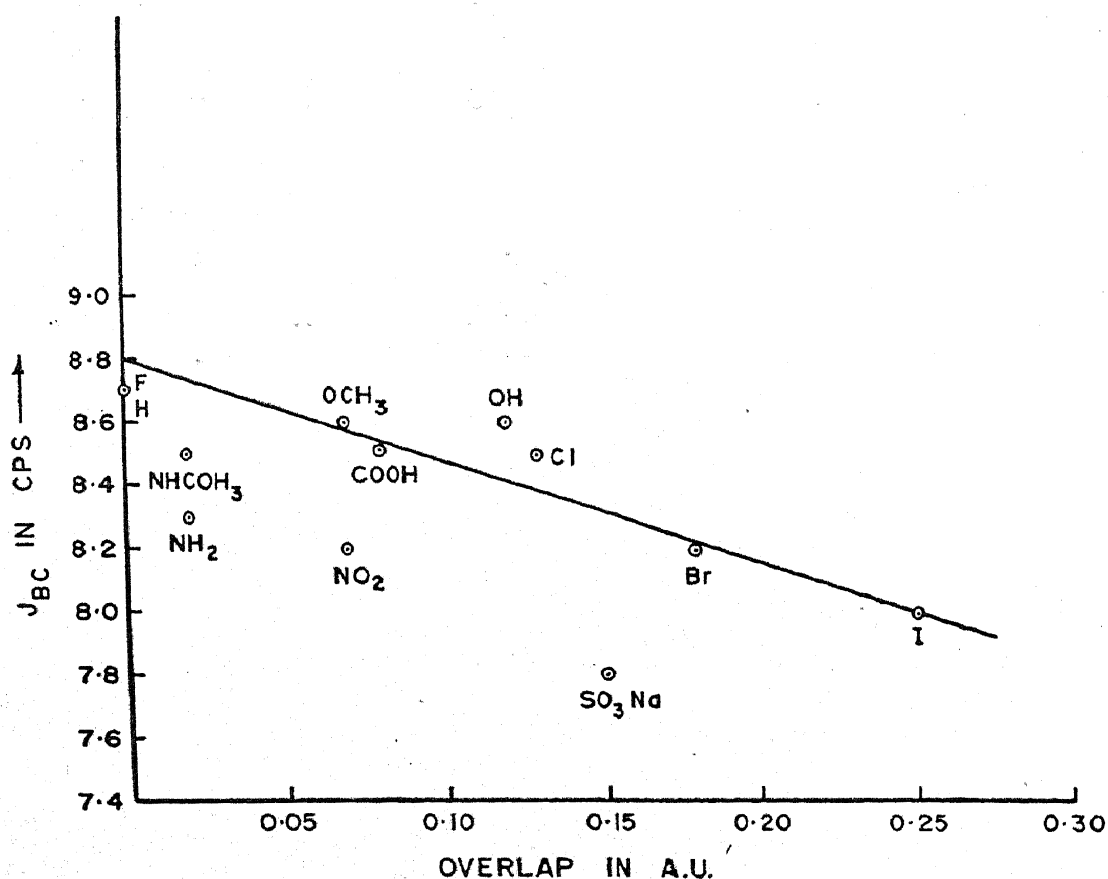


Fig. 1. Relation between overlap of Van der Waal surfaces and J_{BC}

was Cl, NO₂, Br and SO₃H and showed that the steric effects of the different entering groups increase in the order Cl < NO₂ < Br < SO₃H. This order is confirmed from data on coupling constants discussed in this paper. Because of the several complicating factors, not much useful information regarding steric effect could be obtained from reaction kinetics after Holleman's work. Recently, Farthing and Nam (1958) developed a Hammett type equation for *ortho* substituents. They expressed the Hammett's constant σ_0 for *ortho* substituents as a sum of two factors, the electric substituent constant σ_E and the steric substituent constant σ_S .

$$\sigma_0 = \sigma_S + \sigma_E.$$

They further assumed that σ_E is the same both for *ortho* and *para* substitutions and hence the value of σ_E is equal to the Hammett's constant σ_P . Knowing σ_E , the values of σ_S were calculated by these workers for several substituents which are reproduced in Table II. It is seen that the steric effects as determined by van der Waal radii and coupling constants do not correlate with σ_S values. The assumption made by Farthing *et al.* that the electronic effects at both *ortho* and *para* positions are equal, does not therefore seem to be justified.

In the compounds studied in this investigation the proton at position A will be influenced by the steric effects of both the substituents —NO₂ (or Cl) and X. The actual geometry in which this proton will find itself will, therefore, depend on the combined steric influence and the geometry of the two substituents. The values of the coupling constants J_{AB} , J_{AC} , J_{AD} do not decrease systematically with the increasing steric effects of substituent X. The values are, however, in the expected ranges.

CONCLUSION

It is shown that the NMR measurements are likely to lead to a better understanding of the relative magnitudes of the steric effects of different substituents which play an important part in several spheres of organic chemistry.

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