$\overline{\mu_{II}} = 13.8 \times 10^{-18}$. It appears that the most probable values lie between the last two pairs of values. Calculations similar to those outlined above, when carried out on the non-polar forms, yielded the values 2.4×10^{-18} and 1.5×10^{-18} for compounds I and II, respectively. From these results it is evident that a full charge separation must exist in the molecule of II and a nearly full separation in that of I.

The reason why compound II should have an experimental moment 3.5 higher than that of I is not evident. The extinction coefficients of solutions of the two compounds were found to be identical within our experimental error with no indication of a second absorption peak corresponding to a non-polar form. Of course, unequal contributions from the various possible configurations can account for the observed difference but quantitative treatment is impossible.

Although the moments of these two compounds are high, they are not as high as the value 17.7×10^{-18} found previously for a very polar merocyanine[3] and the smaller of the two is of the same magnitude as the moments of three other dye molecules[4] previously investigated. The striking aspect of these values is that the moment of compound II is indistinguishable from the value calculated on the basis of a completely heteropolar structure and that for compound I is only 26% lower, while contributions from resonating non-polar structures normally lower the resultant moment[4] much more than 26%. In coördinate bonds, the moment is only 0.36 to 0.65 of the calculated value[16] and, for the almost pure ionic structures of salt molecules, the moments are reduced from 20 to 50% by mutual induction between the ions.[16] The good agreement between the moment value observed for compound II and that calculated for an undistorted heteropolar structure is like that obtained in the case of dipolar ions,[17] such as those of amino acids.

Acknowledgments.—The authors are indebted to Dr. R. C. Miller of the Frick Laboratory for assistance and advice during the course of this work.

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[16] C. P. Smyth, ref. 4, pp. 248–250.

[17] C. P. Smyth, ref. 4, p. 394.

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Relative Electron Densities in Substituted Benzenes[1]

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The proton magnetic resonance spectra of a number of monosubstituted benzenes have been studied in an attempt to derive values of the relative electron density from observations of the chemical shifts of the ring protons, and to study the effect of various functional groups on these shifts. Shifts are assigned to the protons at different ring positions, and these indicate differences in the electron distribution at the *ortho*, *meta* and *para* positions. The observed shifts are compared with data from other experimental sources, with theoretical calculations of electron densities in substituted benzenes and with the electronic theory of orientation effects in benzene substitutions. In particular, the importance of polarization effects in aromatic substitution reactions is emphasized.

Introduction

The position taken by an entering group in a substituted benzene appears to be intimately connected with the value of the electron density at the *ortho*, *meta* and *para* positions. Both problems have been the subject of numerous theoretical and experimental investigations.[2–5] A number of effects have been postulated (such as the ± I-effect, the ± E-effect, etc.), and these form the basis of the so-called "electronic theory of aromatic substitution." The success of this theory lends importance to any experimental method which will help to evaluate relative electron densities in these molecules.

It is now a well established fact that the chemical shifts observed in proton resonances reflect differences in the electron distribution about chemically non-equivalent protons.[6,7] These shifts arise from the small magnetic fields set up by the electrons which oppose the applied field and are directly proportional to it. This is commonly called a diamagnetic shielding of the protons by the electrons. The result of these shielding effects on the proton resonance is a set of absorption lines which correspond to the number of non-equivalent protons contained in the molecule. Ethanol for example, shows three principal groups of absorption lines which correspond to the non-equivalent CH_3, CH_2 and OH protons.

The conclusion that the chemical shifts can be taken as an approximate measure of electron density is subject to the restriction that no important changes in bond hybridization occur. Studies[8] of the proton shifts in aliphatic molecules containing single, double and triple bonds, show that the proton shift for an acetylenic proton has a value which is intermediate between the observed values for protons attached to carbon atoms using single and double bonds; thus chemical shifts are not simply related to changes in bond hybridization. Careful structural studies have shown no appreciable changes in C–H bond distances or

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] (a) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934); (b) C. C. Price, *ibid.*, **29**, 3 (1941).

[3] L. N. Ferguson, *ibid.*, **50**, 47 (1952).

[4] G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2806 (1935).

[5] H. H. Jaffe. *J. Chem. Phys.*, **20**, 279, 778 (1952).

[6] H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

[7] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **76**, 243 (1952).

[8] L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

TABLE I[a,b]

NMR DATA AND SUBSTITUENT CONSTANTS FOR MONO-SUBSTITUTED BENZENES

Substituent	δ_o^B	δ_m^B	δ_p^B	Δ_o	Δ_m	Δ_p	σ_m	σ_p
$-NO_2$	+0.97	+0.30	+0.42	−0.56	+0.33	+1.08	+0.710	+1.270
$-CHO$	+ .73	+ .23	+ .37	− .96	+ .10	+ .98	+ .382	+1.126
$-COCl$	+ .90	+ .23	+ .30	....	....	....	.....	.....
$-COOCH_3$	+ .93	+ .20	+ .27	....	....	....	+ .315	+0.636
$-COCH_3$	+ .63	+ .27	+ .27	....	....	....	+ .306	+ .874
$-CN$	+ .30	+ .30	+ .30	+ .52	+ .30	+ .96	+ .678	+1.000
$-COOH$	+ .63	+ .10	+ .17	+ .35	+ .05	+ .69	+ .355	+0.728
$-CCl_3$	+ .80	+ .17	+ .23	....	....	+ .26	.....	.....
$-CHCl_2$	+ .13	+ .13	+ .13	− .51	+ .14	+ .25	.....	.....
$-CH_2Cl$	.00	.00	.00	− .54	+ .02	− .07	.....	+ .184
$-CH_3$	− .10	− .10	− .10	− .50	− .09	− .55	− .069	− .170
$-CH_2CH_3$	− .07	− .07	− .07	....	....	....	− .043	− .151
$-CH_2OH$	− .07	− .07	− .07	....	....	....	.....	.....
$-CH_2NH_2$	− .03	− .03	− .03	....	....	....	.....	.....
$-Cl$	.00	.00	.00	− .27	+ .21	− .24	+ .373	+ .227
$-Br$[c]	.0	.0	.0	+ .55	+ .24	− .23	+ .391	+ .232
$-I$	+ .30	− .17	− .10	+1.93	+ .26	− .12	+ .352	+ .276
$-OCH_3$[c]	− .23	− .23	− .23	−2.24	....	−1 14	+ .115	− .268
$-OH$[d]	− .37	− .37	− .37	−2.50	+ .09	−1.06	− .002	− .357
$-NH_2$	− .77	− .13	− .40	−2.31	− .02	−1.46	− .161	− .660
$-NH(CH_3)$	− .80	− .30	− .57	....	....	....	− .302	− .592
$-N(CH_3)_2$	− .50	− .20	− .50	....	....	....	− .211	− .600

[a] σ constants taken from H. H. Jaffe, *Chem. Revs.*, **53,** 191 (1952). [b] Δ values referred to fluorobenzene (ref. 12). [c] Anisole and bromobenzene show an incipient fine structure, which has not yet been resolved. [d] The line width in the phenol resonance is somewhat broader (2–3 cycles) than the line width observed for benzene, and present resolving power fails to disclose any fine structure. The broadening is most probably caused by the –OH proton whose resonant frequency is in the immediate neighborhood of the resonant frequency required for the ring protons.

angles with substitution in the benzene ring, so that the assumption made in this study that there is no significant change in the hybridization of the carbon bonding orbital in the C–H bonds studied is probably a safe one.

A monosubstituted benzene contains five protons, of which three types are chemically distinguishable. Current theories predict differences in the electron distribution at the *ortho*, *meta* and *para* positions. This suggests that under conditions of high resolution differences in chemical shifts may be observable. This resolution has been obtained in a number of cases

Experimental

The measurements were made with a high resolution nuclear magnetic resonance spectrometer similar in design to the Varian model 4300 using a 12″ Varian magnet. The spectrometer was operated at a frequency of 30 Mc. and a magnetic field of approximately 7050 gauss. The samples were contained in cylindrical glass tubes having an inside diameter of 3 mm. The sample tubes were filled to a height of approximately 5 cm., corresponding to a total volume of about 0.4 cc. The actual volume contained within the receiver coil was only 0.07 cc. The samples were rotated at a speed of 500–1000 r.p.m. in order to obtain better effective field homogeneity. The resolution of the spectrometer was sufficient to resolve well defined resonance lines whose frequency separation was 3 cycles.

With the exception of benzoic acid, all samples were studied in 50% solutions of cyclohexane using the sharp methylene resonance of the cyclohexane as a reference in measuring chemical shifts. The benzoic acid was observed in acetone using the methyl resonance of the acetone as a reference. Measurements were made by superimposing an audio frequency signal, from a Hewlett–Packard interpolation oscillator, upon the sawtooth sweep voltage applied to the field modulation coils. This produced side bands on the observed resonances whose frequency separation from the central resonance corresponded to the frequency of the signal from the oscillator. The oscillator was then adjusted until the side band of the reference was superimposed on the resonance being measured, using visual observation on the oscilloscope. The frequency differences, which were of the order of 170 cycles, could usually be measured with a precision of ±1 cycle.

The purpose of making these measurements in cyclohexane solutions rather than using the pure compound, was to eliminate bulk diamagnetic susceptibility corrections which can be quite large.[9] However, the possibility exists that complications due to molecular association are present in the cyclohexane solutions. These effects appear to be negligible from a consideration of a series of measurements made on solutions varying in composition from 10 to 90% cyclohexane.

The samples were obtained from the various organic laboratories at Columbia University and from commercial sources. The purity of samples was quite high, although interference from small amounts of impurities is usually negligible, especially for studies of C–H bonds.

Results

The chemical shifts, relative to the benzene resonance, of the *ortho*, *meta* and *para* protons are given in the first three columns of Table I. Where the same value is given for each of the proton types, no resolution in the ring spectrum was observable. The shifts are reported in terms of the δ^B parameter in parts per million; δ^B being defined as

$$\delta^B = 10^6 \times (H_r - H_s)/H_r = \Delta\omega/30$$

where H_s is the field in gauss required for resonance absorption in the sample, H_r the field necessary for the reference, and $\Delta\omega$ is the shift in cycles from the reference compound. Since δ-values are ordinarily referred to the proton resonance in H_2O, the δ^B-values of this study have been given the superscript "B" to emphasize that the shifts reported here are referred to benzene. Particular protons are distinguished by an appropriate subscript.

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(9) B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77,** 3977 (1955).

The sign convention adopted for the chemical shifts is such that a positive shift for a proton indicates that it is less diamagnetically shielded than the protons in benzene (that is, the density of the electron cloud in the neighborhood of the proton is smaller than the electron density about the protons in benzene), and negative shifts correspond to protons which are more diamagnetically shielded than the protons in benzene.

Tracings of the observed spectra are shown in the accompanying figures. The scale is in cycles of shift from the cyclohexane resonance and may be converted to δ^B-values by subtracting 172 and dividing by 30. In all cases the applied magnetic field increases linearly from left to right.

The spectrum of nitrobenzene (Fig. 1) is analogous, in its general characteristics, to the spectra obtained from other monosubstituted benzenes which have a resolvable fine structure (*cf.* Figs. 5, 6, 10 and 12). In a monosubstituted benzene the adjacent *ortho* and *meta* protons undergo a mutual spin–spin coupling which splits their resonance lines into a pair of doublets. Baker[10] has proposed that in nitrobenzene the *para* line is superimposed on the *meta* doublet (corresponding to the intense resonance in Fig. 1). Since the nitro group is electron withdrawing, the *ortho* doublet would be expected to be on the low field (high frequency relative to cyclohexane) side of the spectrum. Evidence supporting the hypothesis of Baker has been obtained from an examination of the ring proton spectrum of 2,5-dimethylnitrobenzene (Fig. 2), and 2,6-dimethylnitrobenzene (Fig. 3). In the first of these, each *ortho* and *meta* proton is adjacent not to another proton but to one of the methyl groups, and this precludes spin-spin coupling between the *ortho* and *meta* protons.[11] In this case resonance absorption is observed at 171 and 187 cycles. (The ratio of the areas under the resonance curves is 2:1.) The spectrum of 2,6-dimethylnitrobenzene in which there are no protons *ortho* to the nitro group, shows a single resonance at 171 cycles. In these cases, the *para* line is indeed superimposed on the *meta* resonance, and being nearly identical chemically, there is no observable spin-spin interaction between them.

Fig. 1

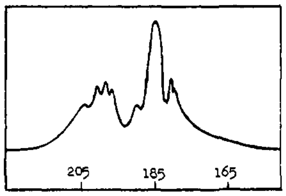
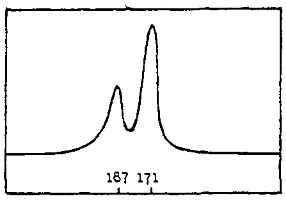


Fig. 2



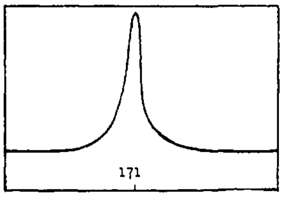


Fig. 3

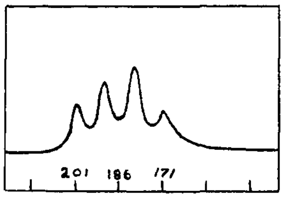


Fig. 4

Fig. 1.—Ring spectrum of nitrobenzene; reference C_6H_{12}.

Fig. 2.—Ring proton spectrum of 1,4-dimethylnitrobenzene; reference C_6H_{12}.

Fig. 3.—Ring proton spectrum of 1,3-dimethyl-2-nitrobenzene; reference C_6H_{12}.

Fig. 4.—Ring spectrum of *p*-chloronitrobenzene.

Figure 4 shows the ring spectrum of *p*-chloronitrobenzene in which *ortho–meta* coupling is possible. The spectral pattern is a simple quartet as expected. The greater apparent intensity of the two central peaks results from the fact that the chemical shift and the spin–spin interaction constant are of nearly comparable size.[12] Hence, the *ortho* and *meta* shifts can be obtained approximately by determining the center of the corresponding doublet.[13] For nitrobenzene these are, 201 cycles for the *ortho* protons and 183 cycles for *meta* (relative to cyclohexane). The previous discussion indicates that the *para* resonance is closer to *meta* than to *ortho*, and that the *para* line is superimposed on the *meta* doublet. It seems reasonable to take as a measure of the *para* shift the position of the most intense line in the pattern. For nitrobenzene, this line occurs at 185 cycles. It should be noted that the left-hand component of the *meta* doublet in *p*-chloronitrobenzene is somewhat more intense than the right-hand member of the *ortho* doublet. The spin–spin theory for two-proton systems[12] shows that these components should have equal intensities. The only possible difficulty here is the ambiguity which may be encountered in determining the strongest resonance in the pattern. However, when the *para* proton is present, as in nitrobenzene, the intensity of the

Fig. 5

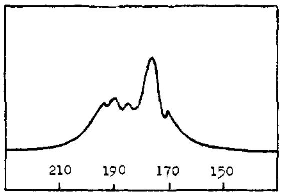
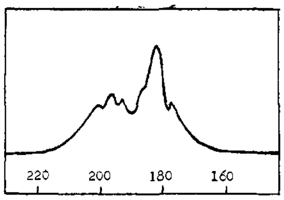


Fig. 6



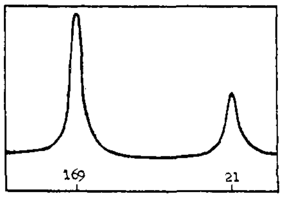


Fig. 7

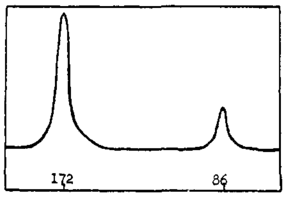


Fig. 8

Fig. 5.—Ring proton spectrum of benzoic acid; reference C_6H_{12}.

Fig. 6.—Ring spectrum of benzoyl chloride; reference C_6H_{12}.

Fig. 7.—Proton spectrum of toluene. The intense line at the left is from the ring protons. Reference C_6H_{12}.

Fig. 8.—Proton spectrum of benzyl chloride; reference C_6H_{12}.

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[10] E. B. Baker, *J. Chem. Phys.*, **23**, 984 (1955).

[11] It is assumed that coupling of the *ortho* and *meta* protons on opposite sides of the ring, leading to observable effects, is negligible.

[12] E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

[13] More exact relations are given in ref. 12. However, for the cases considered here, the correction is less than one cycle.

strongest line is so much greater than the other lines there can be little doubt as to its position. Shifts for substances having a ring proton spectrum analogous to nitrobenzene were determined similarly.

In those cases where a full ring spectrum is obtained, the *ortho* and *para* shifts have a probable error of ±1 cycle or ±0.03 δ^B unit. The *meta* shift, being obscured by the *para* resonance, is less precisely known; the probable error is about ±2 cycles or ±0.07 δ^B unit. Where a single shift is given in Table I for all protons, the probable error is ±0.03 δ^B unit in each case.

The spectra obtained from the chlorotoluenes are shown in Figs. 7–10. Toluene shows resonance absorption at 169 and 21 cycles; these absorption frequencies correspond to the chemically nonequivalent ring and methyl group protons. The introduction of one chlorine atom to form benzyl chloride, shows the expected I-effect but it is felt almost entirely by the α-carbon protons; these being shifted 65 cycles toward lower magnetic field, while the ring protons are shifted 3 cycles in the same direction. In benzal chloride, the second chlorine atom has much the same effect as the first. The α-carbon proton is shifted 68 cycles toward lower field, the ring protons shifting only 4 cycles in the same direction. However, in trichlorotoluene, the three chlorine atoms exert a strong I-effect on the ring protons which results in a full spectrum resembling nitrobenzene. These results correlate well with the change in directive influence that is observed in this series. In the case of toluene, $\delta^B = -0.10$ and the methyl group is activating and *ortho-para* directing. For benzyl chloride, $\delta^B = 0.00$. The $-CH_2Cl$ group is neither activating nor deactivating, and can direct to *meta* as well as *ortho* and *para*. In benzal chloride, $\delta^B = +0.13$. The $-CHCl_2$ group is somewhat deactivating and shows an increase in *meta* directing ability. Finally, trichlorotoluene, in which the entire spectrum is shifted toward lower field, is deactivating and predominantly *meta* directing.

Fig. 9

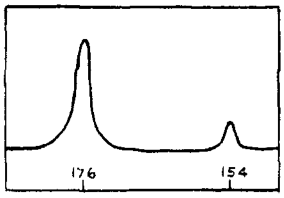
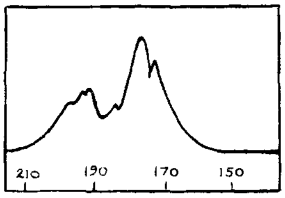


Fig. 10



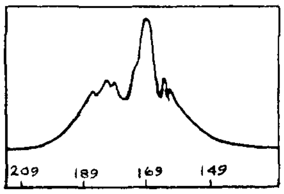


Fig. 12

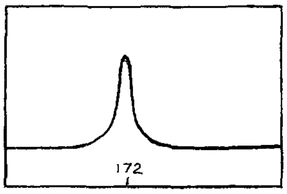


Fig. 11

Fig. 9.—Proton spectrum of benzal chloride; reference C_6H_{12}.

Fig. 10.—Proton spectrum of trichlorotoluene; reference C_6H_{12}.

Fig. 11.—Proton spectrum of chlorobenzene; reference C_6H_{12}.

Fig. 12.—Proton spectrum of iodobenzene; reference C_6H_{12}.

The spectra in this series can be interpreted as a competition between the inductive effect of the chlorine atoms, and hyperconjugation. The inductive effect increases with the number of chlorine atoms added to the α-carbon, while the effect of hyperconjugation decreases with increase in the number of chlorine atoms. In toluene, the effect of hyperconjugation is a maximum and, as a result, the ring protons experience a small negative shift. In benzyl chloride the effects of hyperconjugation and induction are of about equal size but oppose one another, resulting in zero shift of the ring protons. The effect of hyperconjugation becomes quite small in benzal chloride and the predominant I-effect of the chlorine atoms produces a positive shift of the ring protons. In trichlorotoluene, there is little possibility for hyperconjugation, for the center of charge in the C–Cl bonds is closer to the chlorine atom, and the center of charge in the substituent group as a whole lies within the tetrahedron formed by the chlorine atoms and the α-carbon. The possibility of overlapping is therefore quite small, and the chlorine atoms exert an inductive effect only.

The halogen-benzenes (Figs. 11–12) may be interpreted as a competition of inductive and conjugation effects. Chlorobenzene (Fig. 11) shows only a single resonance with chemical shift $\delta^B = 0.00$. The I-effect causes negative charge to be withdrawn from the ring, while the effect of conjugation donates charge to the ring. The superposition of these effects virtually annuls one another and the result is an essentially equal distribution of charge at all ring positions.

Bromobenzene (not shown) shows indications of fine structure but this has not been fully resolved. The situation here is probably a predominance of the I-effect over that of conjugation. Thus the charge distribution at ring positions are of the same order of magnitude.

Assuming that the effect of conjugation decreases more rapidly than the I-effect, it would be predicted that iodobenzene should resemble nitrobenzene. Reference to Fig. 12 shows that this is verified by experiment. Although the I-effect is operating in iodobenzene, it is not powerful enough to shift the entire spectrum to the low field side of benzene. Instead, the *ortho* protons have a positive shift (being closer to the electron-withdrawing iodine atom), while the *meta* and *para* protons have small negative shifts.

If the symbol q is used to represent electron density, then for the halogen-benzenes we have: chlorobenzene, $q_o = q_m = q_p$; bromobenzene, $q_o \cong q_m \cong q_p$; and iodobenzene, $q_o < q_m \cong q_p$.

Discussion

I. Comparison with Other Data.—There are several other possible sources of information on electron densities in substituted benzenes: among them, the predictions of the electronic theory of directive influences in benzene substitution, the Hammett sigma constants, and the nuclear magnetic resonance study of fluorine resonances in substituted fluorobenzenes as carried out by Gutowsky and co-workers.[14] In the present section, σ constants and fluorine resonance data will be considered. The data are presented in Table I, in which the data of Gutowsky, *et al.*, are designated by the symbol Δ in order to avoid confusion with the δ^B-values of this study.

There is rough agreement between the relative electron densities obtained for strong *ortho-para* directing and strong *meta* directing substituents from δ^B-values and those obtained from values of σ or Δ. However, the halogen derivatives of benzenes and those substituted benzenes whose protons show only a single resonance have values of the relative electron density derived from δ^B differing very markedly from those inferred from σ- and Δ-values. In most cases, these differences are much too large to be attributed to experimental errors. They arise instead, from the important differences which exist between the δ^B-values and the σ- and Δ-parameters. The σ-constant is a measure of the electron density at a position which is *meta* or *para* to a given substituent; moreover, at this position there is a $-COOH$ group. The Δ-values have a similar interpretation, except that at the position in question there is a fluorine atom. The δ^B-values, however, measure the electron density at a position which is *ortho*, *meta* or *para* to the substituent in the isolated monosubstituted benzene molecule. The other cases closely approximate the isolated molecule which has just been polarized by an attacking group (F or COOH). The σ- and Δ-parameters, referring to physically similar situations, show a correspondence which is generally good.[14] The results of this study which give values of the electron density differing markedly from those indicated by Δ- and σ-values, are generally obtained from those molecules for which orientation effects suggest that polarization, by an attacking group, induces large changes in the electron distribution. The electron densities measured by δ^B-values differ from those measured by σ- and Δ-values, because they are obtained using molecules which correspond to quite different physical situations. The effect of additional substituents on the electron distribution in a monosubstituted benzene is shown quite markedly by the ring proton spectrum of 2,5-dimethylnitrobenzene, and 2,6-dimethylnitrobenzene. Here, the introduction of the two electron donating methyl groups shifts the nitrobenzene pattern 14 cycles (0.47 δ^B unit) toward benzene. Only in this study of the mono-substituted benzenes are we dealing with electron densities in the isolated molecule. In terms of theoretical organic chemistry, only inductive and mesomeric effects are present. Complications arising from the polarizing effects of additional substituents, or of reacting species, are entirely absent.

II. Comparison with Theoretical Values of Electron Densities.—The relative electron densities obtained in the present study of mono-substituted benzenes are in serious disagreement with those calculated by Jaffe.[5] Jaffe's work was based on the assumption that polarization effects are negligible and that the σ constants are a measure of the electron density in the isolated monosubstituted benzene molecule. This assumption is contradicted by the conclusions which have been drawn from the results of this study, and it is also in disagreement with the earlier theoretical work of Wheland and Pauling.[4] The two theoretical studies make different assumptions about the nature and strength of the inductive effect of the substituent. Jaffe used a considerably larger value of the inductive constant ϵ in order to obtain agreement between his calculated electron densities and the σ-constants. Wheland and Pauling obtained results in rough agreement with those of this study, in particular finding little difference in the *ortho*, *meta* and *para* electron densities in the halogen benzene derivatives and suggesting that orientation in these molecules depends on polarization.

III. Classification of Substituents.—The results of this study show that substituents may influence the electron density at the *ortho*, *meta* and *para* positions in three distinct ways. These differences suggest a classification of the substituents as follows: *Class A:* $-NO_2$, $-CHO$, $-COCl$, $-COOCH_3$, $-COCH_3$, $-COOH$ and $-CCl_3$. These substituents are all *meta*-directing, deactivating and have large positive shifts for all ring protons. Furthermore, a mono-substituted benzene having a substituent belonging to this class has a ring spectrum analogous to the ring spectrum obtained from nitrobenzene. Now previous arguments have shown that the shifts for the *meta* and *para* protons are nearly equal. Indeed, the analysis of the ring proton spectra of the dimethylnitrobenzenes indicates that these shifts are nearly identical. The difficulties encountered in determining the *meta* shifts, however, are such that this latter conclusion cannot be made in general. The present data do allow the conclusion that the shifts for the *meta* and *para* protons are of the same order of magnitude, and these are considerably smaller than the *ortho* shift. For all the substituents in Class A then, it follows that $q_o < q_m \simeq q_p$. *Class B:* $-NH_2$, $-NH(CH_3)$ and $-N(CH_3)_2$. These substituents are *ortho-para* directors, activate the ring, and have large negative shifts for all ring protons. At the present time, there is insufficient data for any general remarks concerning electron densities in these molecules. *Class C:* $-CHCl_2$, $-CH_2Cl$, $-CH_3$, $-CH_2CH_3$, $-CH_2OH$, $-CH_2NH_2$, $-Cl$, $-Br$[15], $-OCH_3$,[15] $-OH$, and $-CN$. The substituents of this class show resonance absorption at only one frequency which is different for different substituents. This indicates that for these substituents, the ring protons are "chemically equivalent" in the sense that the electron densities at the *ortho*, *meta* and *para* positions are the same, that is, $q_o = q_m = q_p$. It is conceivable that the natural line widths of these resonances are greater than the chemical shifts of the ring protons. The line widths observed in these resonances were about 6–7.5 cycles,[15] as compared with the value of 7 cycles observed for benzene. So that if these

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[14] H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

[15] See Table I, notes *c* and *d*.

shifts exist at all, they are quite small and the conclusions drawn here should remain valid.

The mesomeric forms (that is, the resonating structural formulas) for monosubstituted benzenes having as substituent a member of Class A or Class C always predict that $q_o = q_p \neq q_m$. This suggests that the inductive effect is normally of greater importance than the mesomeric effect (in the isolated molecule).

IV. The Importance of Polarization.—It was shown in Section III that substituents in Class C induce equal charge densities at all ring positions. Furthermore, directive substituents of all types are included in this class. In particular, this class includes –OH, which is a strong *ortho-para* director, and –CN, which is strongly *meta* directing.

If substitution on the benzene nucleus takes place by electrophilic (or nucleophilic) attack, then the attacking species can have no *a priori* initial preference for the *ortho*, *meta* or *para* positions; the electron density is the same at all ring positions. However, experiment shows that selective attack does occur. The most straightforward way out of this difficulty is to assume that the attacking reagent polarizes the molecule in such a way as to permit selective attack at the different ring positions.

In the process of polarization, it is assumed that when the polarizing reagent is at an effectively infinite distance from the molecule undergoing substitution, there are equal charges at all ring positions. As the attacking species makes its approach, the charge distribution in the isolated molecule begins to change, and when in near juxtaposition, polarization is complete. At this moment, the reactants have reached the transition state and reaction follows with selective attack. The charge must be distributed to certain "preferred" ring positions. This is a necessary consequence of the assumption of electrophilic or nucleophilic attack. The mechanism by which charge is accepted from, or donated to, the ring is not revealed by the data of this study. However, as was pointed in Section I, the σ- and Δ-values are a close approximation to the electron densities at the ring positions when the substitution process takes place; the δ^B-values measure the electron densities in the isolated molecules before substitution.

The electron densities in the halobenzenes indicate that polarization effects are especially important here. Chlorobenzene and bromobenzene have already been placed in Class C. In iodobenzene, the *ortho* protons are more positive than the *para* proton which has about the same shift as the *meta* protons. However, iodobenzene shows negligible *meta* substitution, and directs almost exclusively *ortho-para*. It thus appears that the halogens require a rather large degree of polarization to account for their directive influence. The importance of polarization in the halogen-benzenes was first suggested by Ingold.[16]

In connection with polarization, there is one more point worthy of mention. If, say, toluene is nitrated and chlorinated, the relative amounts of disubstituted products are different, that is, the ratio of *ortho* to *para* substitution does not remain constant. On the basis of polarizing influences this may be the result of a difference in the polarizing ability of different attacking species.

V. The para–ortho Ratio.—Lapworth and Robinson[17] have obtained data on the ratio of *para* to *ortho* substitution in the nitration of chlorotoluenes and halogen derivatives of benzene which they have explained on the basis of the inductive effect of the substituent group. This explanation is inconsistent with the values of the relative electron density obtained in this study. Certainly for the halogen derivatives of benzene there is insufficient difference in the *para* and *ortho* electron densities in the isolated monosubstituted molecules (or the difference is in the wrong direction) to account for the *para-ortho* ratios.

In order to reconcile the data on the *para-ortho* ratio with the values of the relative electron density obtained in this study it is necessary to assume that polarization of the molecule by a reacting molecule approaching the *para* position is much more effective than at the *ortho* position.

Conclusions

The most significant conclusion to be drawn from the results of the present study is the importance of polarization effects in determining the directive influence of the halogens and substituents in Class C. Furthermore, its importance seems not to be confined to these substituents. For example, the shifts of the *meta* and *para* protons in nitrobenzene are very nearly the same. However, the introduction of a second substituent yields chiefly the *meta* isomer and only trace amounts of the *para* derivative. In certain cases, measurable amounts of the *ortho* isomer are formed, yet in the isolated molecule the *ortho* protons have a much larger positive shift than the *meta* protons. These results are difficult to explain unless it is assumed that some degree of polarization of the nitrobenzene molecule takes place during the course of reaction. This result appears to be true for all the substituents of Class A, but this conclusion must await a more accurate determination of the meta shifts for these molecules.

Differences in the relative electron densities obtained from δ^B-values and σ- and Δ-parameters have been attributed to the perturbing influence of additional substituents. In fact, a di-substituted benzene has been interpreted as a close approximation to the monosubstituted molecule which is being polarized by an attacking reagent. This suggests that the proton resonances in disubstituted benzenes may reveal information about the importance of polarization effects. A study of disubstituted benzene molecules is already in progress.

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[16] C. K. Ingold *Ann. Rep. Chem. Soc.*, **23**, 134 (1926).

[17] A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1927).