Organic and Biological Chemistry

Distortions of the π-Electron System in Monosubstituted Benzenes[1]

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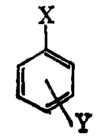
Abstract: The various factors causing electronic disturbances when a group is substituted in an aromatic nucleus are considered. A simple infrared method is described which allows the estimation of the distortions of the π-electron system resulting from such substitution and the values obtained are compared with those previously reported by other methods. The use, limitations, and future extensions of the method are discussed. The results give further information on the relative importance of the possible factors contributing to such π-electron displacements.

The determination of electronic interactions in aromatic molecules has long been the aim of many chemists. Sure knowledge of the mechanisms and magnitudes of such interactions would allow the prediction of many physical properties, reaction rates, and position of equilibria, as well as aid the correlation of the large accumulation of existing data.

Over the last 15 years the major approaches to the effect of a substituent on the electron density in the benzene ring have centered on the Hammett equation,[4] $\log k/k_0 = \rho\sigma$. The σ constant for a substituent Y in the *meta* or *para* position (*ortho* positions could be complicated by steric interactions) gives a measure of its electronic effect on the reaction center X.



Most σ values differ from the *meta* and *para* positions and can also vary according to the electronic requirements of the reaction. This latter variation led to the proposal of σ^- [4,5] and σ^+ [6] constants and, later, to the suggestion of continuously variable values.[7] The realization that a large part of this variation could be ascribed to direct conjugation between the substituent and the reaction site was followed by the estimation[8,9] of σ^0 values for systems in which such interactions were precluded or minimized. The σ^0 values should thus be a measure only of the interaction of the substituent with the benzene ring as felt at the reaction site.

The total electronic disturbance can be considered as arising from various discrete factors although such separations are subject to argument.[7,10] Taft and his co-workers[9] have divided the over-all effects into inductive and resonance contributions. We will follow them in considering inductive effects as the electrical disturbances in the σ bonds of the molecule arising from the polarity of the Ar–Y bond, and resonance effects as the disturbance in the π-electron system of the molecule. A measure of the inductive effects of substituents, expressed as σ_I values, has been obtained[11] from aliphatic reactivities and extended when such values were found[12] to correlate well with the F^{19} shielding parameters for *meta*-substituted fluorobenzenes. The resonance contributions can then be obtained from the formulas

$$\sigma_R = \sigma - \sigma_I$$

$$\sigma^0{}_R = \sigma^0 - \sigma_I$$

The σ_R values vary from reaction to reaction but $\sigma^0{}_R$ values are constant for a particular solvent, expressing the resonance interactions between a substituent and the nucleus.

Various attempts[7,9,13] have to be made to assess the relative contributions made to σ_I and σ_R values by the various possible mechanisms of electronic transmission. Although the inductive effect is usually considered to arise by the progressive and diminishing relay of a bond polarity through a system of σ bonds, some authors[13,14] have considered that the major part may be ascribed to field effects. Similarly resonance effects, as defined above, may arise from (a) a distortion of the π system of the nucleus caused by the polarity of the Ar–Y

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[1] A preliminary account of part of this work has appeared previously: R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Am. Chem. Soc.*, **87**, 3260 (1965).

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[3] Nuffield Visiting Fellow, University of East Anglia, 1964–1965.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[5] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[6] C. W. McGary, Y. Okamoto, and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 3037 (1955).

[7] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964), and references given therein.

[8] H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

[9] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[10] S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

[11] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, and references given therein.

[12] R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis., *J. Am. Chem. Soc.*, **85**, 709 (1963).

[13] M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539 (1962).

[14] M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3548 (1962).

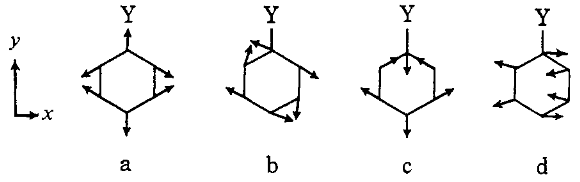
σ bond, the so-called π-inductive[15] or inductoelectromeric[16] effect; (b) resonance interactions of the π electrons of the ring either with electrons or a vacant orbital on the α atom of the substituent; (c) a repulsion of the ring π electrons by nonbonded electrons on a substituent such as fluorine;[17] and (d) direct conjugation of the substituent with the reaction site. The various magnitudes of these effects are also controversial. For example, while nitro and cyano groups are commonly thought of as having a resonance-withdrawing effect arising from factor b, it has been alternatively suggested[18] that most of the effect arises from factor a. Other more sophisticated theories have been proposed in particular cases involving, for example, C–H, C–C, and carbon–halogen bond hyperconjugation,[19] substituent d-orbital participation,[20] or interactions of the free electrons on the β substituent atoms (such as in $ArCF_3$) with the nucleus.[21]

Any such treatment of interactions in terms of component parts needs reliable values for the various constants. Apart from the variability of factor d, solvent effects can also alter resonance disturbances.[22] Recent nmr work[23] has shown that $\sigma^0{}_R$ values correlate well with the difference in fluorine nmr shielding parameters for corresponding *para*- and *meta*-substituted fluorobenzenes. Unfortunately the fluorine atom can still conjugate with electron-withdrawing substituents such as a nitro group and measured values in such cases are denoted $\bar{\sigma}_R$ to indicate that they may be enhanced by factor d mentioned above.

The use[24] of carbon-13 nmr shielding parameters to measure electron densities provides the first method of determining such values without the introduction of a second group to act as a probe. Once again the *para* shift, when corrected by the corresponding *meta* value, correlates well with $\sigma^0{}_R$ values and some quantitative justification[25] of the use of such a method has been given. The consistency of certain $\sigma^0{}_R$ values obtained from reactivity and fluorine or carbon-13 nmr measurements suggests the validity of separating inductive and resonance effects. The first two methods are not extendable to more complex aromatic molecules and necessary compounds may not be easy to synthesize. The last method also seems unlikely to be useful for more complex systems.[24,26]

The use of infrared spectroscopy in the determination of σ constants has previously been limited to correlations between substituent parameters and the effect of a *meta* or *para* substituent on the frequency or intensity of a mode arising from a second fixed substituent.[27] No correlation has been attempted between aromatic ring vibrations and substituent constants for substituted benzenes. However, it has been shown[28] that the intensities of certain ring vibrations in the 1600–1400-cm^{-1} region are markedly altered by substitution. Thus the band at 1600 cm^{-1} is very intense in dimethylaniline or phenol but weak in cyanobenzene. A rough correlation was shown at that time between apparent extinction coefficients and mesomeric moments.

The four ring vibrations in the 1600–1400-cm^{-1} region in monosubstituted benzenes arise from two doubly degenerate modes (ν_{16} and ν_{13} in Herzberg's notation) in benzene itself. The degeneracy is lifted because a monosubstituted benzene has at the most C_{2v} symmetry, and this only if the substituent is of sufficient symmetry. These four bands form two pairs: those at approximately 1600 (a) and 1585 cm^{-1} (b) arise from the infrared-forbidden ν_{16} benzene vibration at 1585 cm^{-1}, while those at 1500 (c) and 1440 cm^{-1} (d) arise from the infrared-allowed ν_{13} benzene vibration at 1485 cm^{-1}. For monosubstituted benzenes of C_{2v} symmetry, vibrations a and c are A_1 (symmetrical with respect to a plane perpendicular to the ring) while b and d are B_1 (asymmetrical with regard to that plane).



The intensity of the A_1 vibrations should vary with any resultant charge disturbance produced in the direction of the y axis during the vibration. The B_1 vibrations should similarly reflect any resultant change in the x axis. When the over-all symmetry is lowered to C_s by a less symmetrical substituent, all these vibrations become of symmetry type A'. As a result, intensities may be shared between a and b, and any correlations made with the intensity of only one of the pair would be of doubtful validity.

We investigated the integrated areas of these pairs of ring vibrations as a possible measure of electronic disturbance in a substituted benzene ring and we recently reported[1] preliminary results which demonstrated this. Because of the symmetry argument above and also because the two ν_{16} bands are not invariably completely resolved at the slit width used, we decided to integrate a and b together. A similar procedure is not possible with c and d since, as will be discussed below, other absorptions occur nearby. The similar use of other ring modes, such as those in the 600-cm^{-1} region,[29] is currently being investigated.

Experimental Section

Chemicals and Solvents. The compounds used were commercial samples purified by standard methods and checked by vapor phase chromatography. Spectroscopic grade carbon tetrachloride and

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[15] H. H. Jaffe, *J. Am. Chem. Soc.*, 77, 274 (1955), and previous papers in the series.

[16] D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 2406 (1953).

[17] J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapters 9 and 10.

[18] A. Talvik, P. Zuman, and O. Exner, *Collection Czech. Chem. Commun.*, 29, 1266 (1964).

[19] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[20] L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, 87, 1012 (1965).

[21] W. A. Sheppard, *ibid.*, 87, 2410 (1965).

[22] R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, 81, 5352 (1959).

[23] R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, 85, 3146 (1963).

[24] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, 42, 2427 (1965), and references given therein.

[25] T. K. Wu and B. P. Dailey, *ibid.*, 41, 2796 (1964).

[26] G. B. Savitsky, *J. Phys. Chem.*, 67, 2723 (1963).

[27] See C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, pp 568–577, and references given therein.

[28] A. R. Katritzky, *J. Chem. Soc.*, 4162 (1958).

[29] D. H. Brown, A. Mohammed, and D. W. A. Sharp, *Spectrochim. Acta*, 21, 659 (1965).

cyclohexane were stored over molecular sieve. No aromatic impurities could be detected in the solvent spectra run at 1-mm path length.

Spectroscopy. The spectra were recorded on a Perkin-Elmer 125 spectrometer in sodium chloride cells using carbon tetrachloride or cyclohexane as solvents. The cell path length was determined by the interference method.[30] The solvent absorptions were balanced using a variable path length cell. Most of the compounds used did not absorb close to 1549 cm^{-1} and balance was therefore obtained using this $\nu_{\text{C-Cl}}$ overtone peak in carbon tetrachloride. Other samples were balanced by the experience thus gained in the appropriate settings of the variable cell for differing molarities and by comparison of the resultant spectra with those of thin films of the pure compounds. The concentrations of the solutions (0.15–1.5 *M*) were adjusted to give peak heights between 20 and 70% transmission.

The 0 and 100% transmission settings were adjusted at 1600 cm^{-1} and the slit program employed gave an effective slit width of about 2 cm^{-1} at this frequency. The spectra were scanned slowly with maximum suppression. Most spectra were measured at a chart scale of 1 mm per two wave numbers but, for weak absorptions, were also expanded to 1 cm per two wave numbers.

Integration. The transmission values obtained were converted to absorbance values every two wave numbers (every cm^{-1} for expanded spectra). The integrated intensity (*A*, l. mole^{-1} cm^{-2}) was then obtained from the formula

$$A = \Sigma a/Cl$$

where *C* was the concentration of the compound in moles per liter, *l* the path length in centimeters, and *a* the absorbance value each wavenumber corrected for any base line. Such *A* values were found to be highly reproducible, variation in $A^{1/2}$ values (which, as is discussed below, are used to measure resonance interactions) being less than one unit in each case.

The major errors in intensity measurements are usually the correct assignment of the base line and the presence of interfering vibrations. Nearly all the samples used gave clean absorptions at 1600 and 1585 cm^{-1} with transmission values close to 100% on either side. Only for benzoic acid, styrene, and nitrobenzene was there any significant ambiguity in integration and only for the last compound was this important. Even here the $A^{1/2}$ value quoted is considered to be reliable to well within three units while for the great majority of substituents, the accuracy of the $A^{1/2}$ values is probably as good as their reproducibility.

Values of the extinction coefficient, ϵ, where

$$\epsilon = a_{\max}\Delta\nu_{1/2}/Cl$$

were also determined for the 1600 and 1500 cm^{-1} bands. These will be less accurate because of the relatively wide slit width employed and since not all the peaks have Lorentzian shape. These values should be related to the appropriate *A* values by the formula

$$A = k\epsilon$$

where *k* is approximately $\pi/2$ but includes a factor[31] for finite slit width.

Results and Discussion

Use of Intensities to Give σ^0_R Values. The square roots of the integrated intensities of the ν_{16} bands are shown in Tables I and II. The intensity (*A*) of an absorption is related to the rate of change of dipole moment with the normal coordinate at the equilibrium position ($\partial\mu/\partial Q$) by the formula

$$A = \frac{N\pi}{3c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2$$

Thus $A^{1/2}$ is proportional to $\partial\mu/\partial Q$ and is the logical quantity[32] to relate to other physical properties of the substituent.

Table I. Correlation of σ^0_R Values with the Square Roots of the Integrated Intensities of the ν_{16} Bands in a Select Number of Monosubstituted Benzenes

Substituent	$A^{1/2}$	$-\sigma^0_R$ (nmr)[b]	$-\sigma^0_R$ (reactivity)[b]
NMe$_2$	71.4	0.54	0.52
OMe	57.7	0.43	0.41
OH	54.2	0.43	0.40
F	46.4	0.32	0.35
Cl	30.5	0.18	0.20
Et	17.0	0.14	0.09
Me	16.6	0.146	0.10
Ph	16.1[a]	0.093	0.10

[a] Value is $(A/2)^{1/2}$ to allow for two phenyl groups. [b] Reference 23.

Table II. Calculation of σ^0_R Values from the Integrated Intensities (*A*) of the ν_{16} Bands in Monosubstituted Benzenes

Substituent	$A^{1/2}$	$\pm\sigma^0_R$ (calcd)	$-\sigma^0_R$ (nmr)[b]	$-\sigma^0_R$ (reactivity)[b]	$\bar{\sigma}_R$ (nmr)[d]	$\bar{\sigma}_R$ (reactivity)[e]
NMe$_2$	71.4	0.535	0.54	0.52	...	...
NHMe	70.0	0.525	...	...	...	...
OMe	57.7	0.43	0.43	0.41	...	...
OH	54.2	0.40	0.43	0.40	...	...
OPh	49.2[a]	0.36	0.312	...	...	...
F	46.4	0.34	0.32	0.35	...	...
CO$_2$H	35.3	0.25	...	...	...	...
SMe	34.5	0.245	0.173	0.24[c]	...	...
CHO	33.9	0.24	...	...	0.265	...
OCOMe	32.7	0.23	0.21	...	...	...
Br	32.3	0.23	0.163	0.19	...	...
I	31.0	0.215	0.14	0.12	...	...
COMe	30.7	0.215	...	...	0.19	0.12
Cl	30.5	0.215	0.18	0.20	...	...
SH	27.6	0.19	0.15	...	...	...
CO$_2$Et	25.9	0.175	...	...	0.195	0.08
NO$_2$	25.2	0.17	...	...	0.19	0.14
t-Bu	19.3	0.125	...	...	...	(0.08)[e]
Bu	18.5	0.12	...	...	...	...
Pr	18.1	0.115	...	...	...	...
i-Pr	17.9	0.115	...	...	...	(0.09)[e]
sec-Bu	17.9	0.115	...	...	...	...
CF$_3$	17.8	0.115	...	...	0.10	0.02
Et	17.0	0.105	0.14	0.09	...	...
Me	16.6	0.105	0.146	0.10	...	...
Ph	16.1[a]	0.10	0.093	0.10	...	...
CH$_2$CN	15.5	0.095	0.08	...	...	...
SO$_3$Me	15.2	0.095	...	...	0.18	...
CN	15.1	0.09	...	...	0.21	0.08
CH$_2$OH	9.7	0.05	...	...	...	...
CH$_2$Cl	9.5	0.05	0.03	...	...	...
CH=CH$_2$	7.6	0.035	0.03	...	...	...
CCl$_3$	0	...	...	...	...	...

[a] Values are $(A/2)^{1/2}$. [b] Reference 23. [c] Values are $2.0\sigma^m$: R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959). [d] Reference 23; calculated from figures for dilute solutions in cyclohexane using the formula given therein. [e] Reference 40; values are σ_R.

The relative values of $A^{1/2}$ found for dimethylaniline, fluorobenzene, and nitrobenzene are in proportion to the known values for σ^0_R for these substituents. They cannot, on the other hand, be linearly related to the respective σ, σ^0, σ^+, σ^-, or σ_R values.[7] A recent paper[23] gave σ^0_R values for 13 substituents where they were available from both reactivity and fluorine nmr investigations. We have measured $A^{1/2}$ values for ten[33] of these to test the validity of a correlation with σ^0_R.

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(30) W. J. Potts, "Chemical Infrared Spectroscopy," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1963, p 117.

(31) W. Brügel, "An Introduction to Infrared Spectroscopy," Methuen and Co., Ltd., London, 1962, p 292.

(32) T. L. Brown, *J. Phys. Chem.*, **64**, 1798 (1960).

(33) The other three possible compounds were aniline (the NH$_2$ scissoring vibration of *ca.* 1615 cm^{-1} prevents a determination here), trifluoroanisole, and the phenoxide ion (not soluble in our solvents).

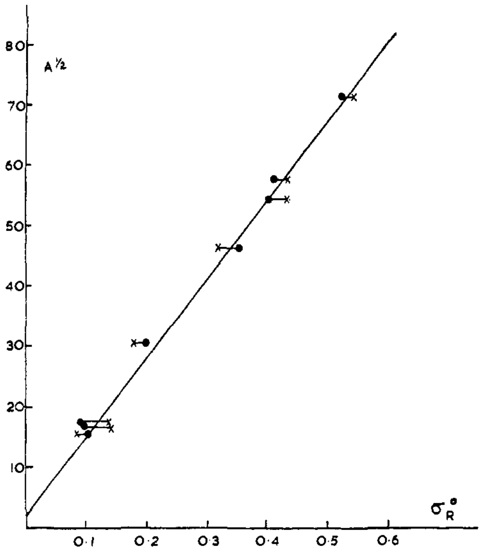

Figure 1. Plot of $A^{1/2}$ (A in l. mole^{-1} cm^{-2}) *vs.* σ^0_R values: ●, reactivity; ×, fluorine nmr.

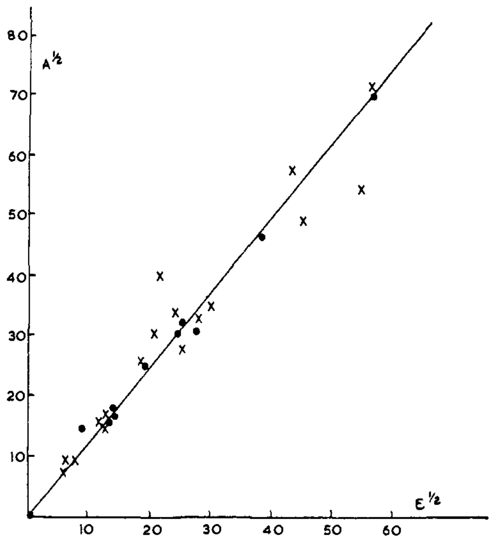

Figure 2. Plot of $A^{1/2}$ for combined ν_{16} bands against $\epsilon^{1/2}$ for ν_{16a}: ●, symmetrical substituents; ×, others.

The values for bromo- and iodobenzene have been omitted since a frequency shift was observed here which may indicate a change in vibrational interaction (see below). The correlation for the other eight substituents (Table I) is shown in Figure 1.

The correlation is seen to be excellent and the equation obtained by the least-squares procedure, using the mean of the reactivity and nmr values of σ^0_R for each substituent, was

$$\sigma^0_R = 0.0079A^{1/2} - 0.027 \qquad (1)$$

The correlation coefficient was 0.984. The intercept at $\sigma^0_R = 0$ has a positive value of $A^{1/2}$ compared to the identity $\sigma^0_R = 0.0074A^{1/2}$ used in our earlier communication[1] where the intercept was deliberately taken at the origin. We consider that the present statistically derived formula is more reliable. A summation band arising from C_{Ar}–H wagging vibrations occurs[34] at about 1600 cm^{-1} and will make a small contribution to the measured intensities, thus explaining a positive intercept. Further refinement of the equation is not likely to be useful since this summation band will be of variable frequency and magnitude as shown in the 1620–1570-cm^{-1} range in benzotrichloride ($A^{1/2} < 2$) and monodeuteriobenzene ($A^{1/2} = 5.5$).

Equation 1 allows the calculation of σ^0_R values for the 33 compounds investigated and these are shown, together with literature figures, in Table II.

Good agreement is found between our values and those available from either fluorine nmr or reactivity studies for such diverse substituents as vinyl, trifluoromethyl, nitro, formyl, and chloromethyl groups. The values for bromo- and iodobenzene, and probably thiophenol and thioanisole, suggest that there may be some mass effect possibly involving nonbonded electrons on the α-substituent atom. It seems unlikely that this results from a decrease in vibrational interactions between the ring mode and one involving the Ar–Y bond. Thus, although the observed decrease in frequency of the ν_{16a} vibration[35] in the series ArX where X is F (1598 cm^{-1}), Cl (1585 cm^{-1}), Br (1580 cm^{-1}), I (1574 cm^{-1}) would be expected as the Ar–X mode decreased in frequency, a calculation made assuming σ^0_R for iodobenzene to be 0.13 and there to be little vibrational interaction gives a corrected A value for fluorobenzene of three times that actually measured. We hope in a later paper in this series to report an investigation of such mass effects utilizing series of monosubstituted benzenes.

Use of Extinction Coefficients to Calculate σ^0_R Values. The reproducibility and probable accuracy of the $A^{1/2}$ values given has been estimated to be generally better than one unit leading to a possible accuracy in σ^0_R values of better than 0.01 unit. The extinction coefficients ($\epsilon = a_{\max}\Delta\nu_{1/2}/Cl$) are more readily calculated although arguments against using these have been given in the introduction. Such $\epsilon^{1/2}$ values for the ν_{16a} vibration are listed in Table III and are plotted in Figure 2 against $A^{1/2}$ values obtained for the combined ν_{16} absorptions. Values for propyl and butyl substituents are not shown to avoid confusion.

The correlation is seen to be good for compounds of C_{2v} symmetry and the equation derived (least-squares procedure) was $A^{1/2} = 1.23\epsilon^{1/2} - 1.37$, with a correlation coefficient of 0.996. This gives the equation

$$\sigma^0_R = 0.0097\epsilon^{1/2} - 0.038 \qquad (2)$$

The figure shows that, as expected, the correlation is much less precise for compounds having only C_s symmetry.

For monosubstituted benzenes, it is not possible to integrate the ν_{13} bands as a pair since the lower frequency peak occurs in a region of moderate spectral activity; for example, CH_2 scissoring and C–H bending modes appear nearby and may interact with the ring mode. The extinction coefficient of the 1500-cm^{-1} peak can be measured in most cases and is given in Table III. Figure 3 shows values of $\epsilon^{1/2}$ for this absorption plotted against the calculated (Table II) σ^0_R values. The line was fitted by inspection. The linear correlation is not very precise even for compounds of C_{2v} symmetry and shows only a general trend for the others. This probably reflects the deviation from

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[34] D. H. Whiffen, *Spectrochim. Acta*, 7, 253 (1955).

[35] The ν_{16a} bands for the other compounds used were in the 1610–1595-cm^{-1} range.

Table III. Comparision of $A^{1/2}$ values (ν_{16}) with $\epsilon^{1/2}$ Values for the 1600- (ν_{16a}) and 1500-cm^{-1} (ν_{13a}) Bands in Monosubstituted Benzenes. Mesomeric Moments Are Also Listed

Substituent	$A^{1/2}$	$\epsilon^{1/2}{}_{16a}{}^{a}$	$\epsilon^{1/2}{}_{13a}{}^{a}$	D.[b]	D./d[c]
NMe_2	71.4	56.9	50.0	1.66	0.59
NHMe	70.0	56.7	63.5	...	...
OMe	57.7	43.4	44.4	0.96	0.24
OH	54.2	55.0	38.8	...	...
OPh	49.2	45.3	47.9	...	...
F	46.4	38.6	43.2	...	...
CO_2H	40.0	21.6	11.6	...	...
SMe	34.5	29.9	26.8	...	...
CHO	33.9	24.0	3.0	...	...
OCOMe	32.7	28.0	37.6	...	...
Br	32.3	25.3	32.3	...	...
I	31.0	27.7	27.7	...	...
COMe	30.7	20.6	5.1	0.56	0.13
Cl	30.5	24.8	33.7	0.41	0.13
SH	27.6	25.3	27.6	...	...
CO_2Et	25.9	18.4	8.1	0.50	0.07
NO_2	25.2	18.8	...	0.76	0.22
t-Bu	19.3	15.2	21.4	...	...
Bu	18.5	14.8	20.6	...	...
Pr	18.1	13.0	19.5	...	...
i-Pr	17.9	15.6	22.0	...	...
sec-Bu	17.9	15.0	22.0	...	...
CF_3	17.8	13.7	21.3	...	...
Et	17.0	13.0	19.5	...	...
Me	16.6	13.6	19.6	0.35	0.10
Ph	16.1	13.0	20.4	...	...
CH_2CN	15.5	11.9	18.4	...	...
SO_3Me	15.2	12.2	10.9	...	...
CN	15.1	8.9	...	0.45	0.11
CH_2OH	9.7	6.3	14.0	...	...
CH_2Cl	9.5	7.6	14.3	...	...
$CH{=}CH_2$	7.6	6.1	16.2	...	...
CCl_3	0	0	...	...	...
H	0	0	17.7	0	0

[a] A and ϵ in l. mole^{-1} cm^{-2}. [b] K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 2818 (1951); A. R. Katritzky, E. W. Randall, and L. E. Sutton, *ibid.*, 1769 (1957). [c] Reference 37.

Lorentzian shape of some of the bands for compounds of C_{2v} symmetry and the greater difficulty in assigning the base line. Nevertheless the presence of a ν_{13a} vibration in benzene itself allows a sign to be given to $\sigma^0{}_R$ unless the value is so low as to introduce ambiguity.

The intensities of both pairs of ring modes thus seem to be a function of the π-electron distortion in the ring. Correlation of other ring modes is currently being investigated.

Vibrational Interactions. It is possible that interactions could affect the measured intensities for particular substituents. Certainly compounds containing a primary amino group have a scissoring mode close to 1600 cm^{-1} which excludes them from the present study. The only other compounds having strong absorptions in the vicinity, which could enhance the ν_{16} bands, are those having carbonyl groups. This enhancement would be expected to be greater in compounds like benzaldehyde and acetophenone than in phenyl acetate where the carbonyl absorption occurs at a higher frequency. The σ value obtained for this latter compound is indeed close to that obtained by fluorine nmr experiments. It is hard to get an independent measure of possible enhancements for compounds having an α-carbonyl group since fluorine nmr results may also be exhanced by resonance between the fluorine atom and the substituent.[23]

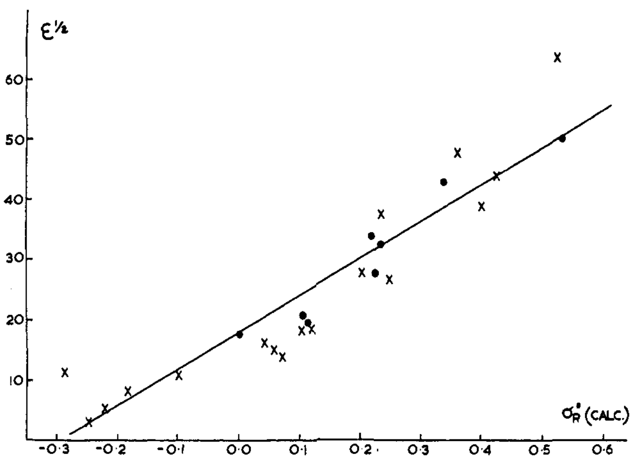
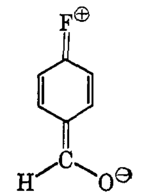


Figure 3. Plot of $\epsilon^{1/2}$ for ν_{13a} band against $\sigma^0{}_R$ values: ●, symmetrical substituents; ×, others.



Our results on *para*-disubstituted compounds[36] indicate that such resonance is of little importance in nonpolar solvents and therefore the σ_R values as determined by fluorine nmr experiments in cyclohexane (Table II) are close to $\sigma^0{}_R$ values. A comparison of these values with ours for benzaldehyde and acetophenone suggests that vibrational interaction is also of little consequence here.

Intermolecular Interactions. We have demonstrated that no significant part of the observed π-electron disturbances arises as a result of specific solute–solvent interactions. Table IV shows that intensity measurements made in cyclohexane, for a representative selection as substituents, do not differ markedly from those in carbon tetrachloride.

Table IV. Comparison of $A^{1/2}$ Values Measured for Solutions in Carbon Tetrachloride and Cyclohexane

Substituents	$A^{1/2}$ (CCl_4)	$A^{1/2}$ (C_6H_{12})	Substituent	$A^{1/2}$ (CCl_4)	$A^{1/2}$ (C_6H_{12})
NMe_2	71.4	69.0	Cl	30.5	29.5
OMe	57.7	58.3	NO_2	25.2	22.2
OH	54.2	52.3	Me	16.6	16.0
F	46.4	47.4	CN	15.1	13.9
Br	32.3	31.7			

We have also shown (Table V) that the intensity values for benzotrifluoride, phenol, and benzoic acid are virtually independent of concentration. It seems likely, however, that the relatively high value observed for benzoic acid should be ascribed to the dimer rather than unassociated molecules. A decrease in the accuracy of intensity measurements prevents studies being made at lower concentrations.

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(36) P. J. Q. English, A. R. Katritzky, and R. D. Topsom, to be published.

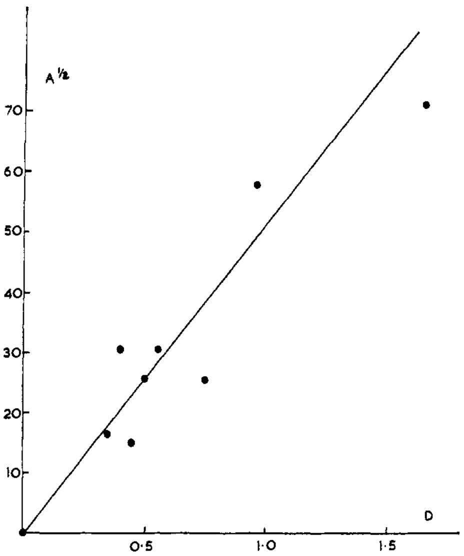

Figure 4. Plot of $A^{1/2}$ against D.

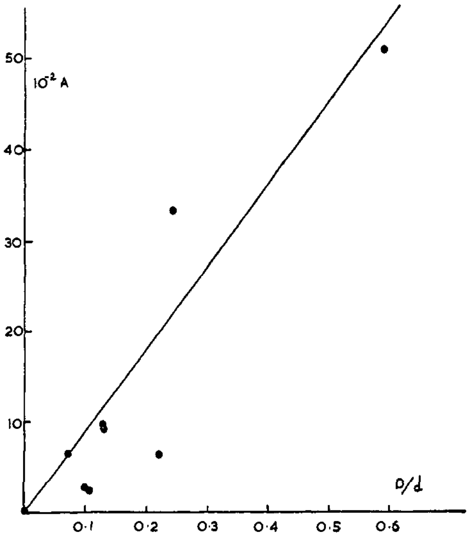

Figure 5. Plot of A against D/d.

Mesomeric Moments. If has been shown[28] that the mesomeric moments (D.) of the substituent were approximately proportional to the apparent extinction coefficients ($a_{\max}/Cl$) of the 1600-cm^{-1} band in some monosubstituted benzenes. Figure 4 shows a plot of D., for substituents where such values are well established, against the square root of the integrated intensity. It is seen that no precise relationship exists.

Table V. Variation of $A^{1/2}$ Values with Concentration of Benzotrifluoride, Phenol, and Benzoic Acid

	A. Benzotrifluoride			
Molarity	0.52	1.04	1.50	
$A^{1/2}$	17.8	17.9	17.6	
	B. Phenol			
Molarity	0.08	0.15	0.22	0.42
$A^{1/2}$	53.1	53.3	54.2	53.0
	C. Benzoic Acid			
Molarity	0.10	0.21	0.30	0.39
$A^{1/2}$	36.2	34.3	35.3	36.4

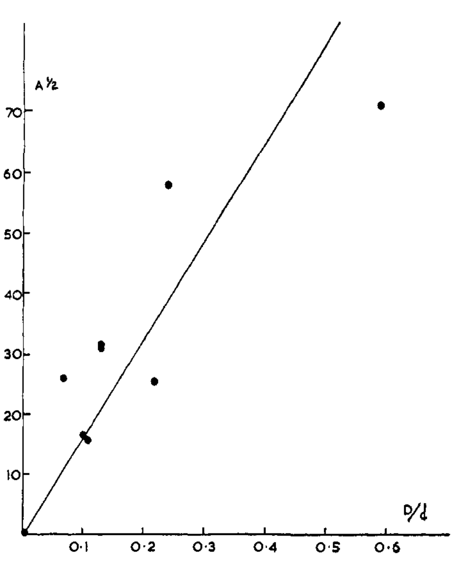

Figure 6. Plot of $A^{1/2}$ against D/d.

Exner[37] has pointed out that the mesomeric moment divided by the effective charge separation (d) in such compounds is more meaningful than the mesomeric moment itself. He obtained good correlations between such D./d and σ_R values. However, Figures 5 and 6 show that no better correlation exists between D./d values and either A or $A^{1/2}$.

Factors Contributing to σ^0_R Values. The consistency of σ^0_R values found from reactivity, fluorine, and carbon-13 nmr experiments and the present work greatly strengthens the idea that π-electron distortions can be discussed as a discrete property of these systems, and it therefore seems reasonable to consider possible contributing factors. We can recognize three important influences, namely, the π-inductive effect, mesomeric interactions including hyperconjugation, and ring π-electron repulsions resulting from interactions with nonbonded electrons on the substituent.

The π-inductive effect has variously been considered as the major cause of π-electron distortions,[15] as being a possible explanation for alkyl group hyperconjugation,[14] and as causing the total disturbance observed for electron-withdrawing substituents such as NO_2, CN, CF_3, SO_2R, and possibly CO_2Et.[18] We believe, however, that it accounts for no more than a negligible proportion of the disturbance in monosubstituted benzenes. Thus any such π-inductive effect would be proportional to the inductive effect in the A–Y bond. The σ values for benzonitrile ($\sigma^0_R = 0.09$, $\sigma_I = 0.53$[12]) give a limit of about 0.02 unit in σ^0_R as arising per 0.1 unit in σ_I. This would leave a considerable amount of unexplained disturbance even in nitrobenzene ($\sigma^0_R = 0.17$, $\sigma_I = 0.60$[12]) and ethyl benzoate ($\sigma^0_R = 0.18$, $\sigma_I = 0.21$[12]). However, the trichloromethyl group causes no apparent π-electron disturbance in spite of having a considerable inductive effect.[11,38] Further, fluorine nmr results have shown that the $CH_2NH_3^+$ substituent ($\sigma_I = 0.25$[12]) also has $\sigma^0_R = 0$. The NMe_3^+ group ($\sigma_I = 0.93$[12]) likewise has been esti-

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(37) O. Exner, *Collection Czech. Chem. Commun.*, **25**, 642 (1960).

(38) The value $\sigma = 0.42$ (O. Korver, J. V. Veenland, and Th. J. De Boer, *Rec. Trav. Chim.*, **84**, 289 (1965)) has been determined for this substituent in cyclohexane.

mated[39] from reactivity measurements to have a negligible σ_R value. It is difficult to escape the conclusion, also argued recently by Sheppard,[21] that the π-inductive effect is, at most, very small. Our present evidence does not allow any general conclusions to be made as to the relative contributions of the other two factors.

The values reported here for alkylbenzenes show a slight increase in disturbance in the series Me < Et < *i*-Pr < *t*-Bu. This order is in contrast to that obtained[40] for σ_R values, but a larger value of σ^0_R has been found[23] for ethylbenzene than methylbenzene by fluorine-19 nmr experiments. We are investigating a series of alkylbenzenes and *p*-nitroalkylbenzenes in both carbon tetrachloride and more polar solvents and defer further discussion on hyperconjugation until we report these results.

Other current investigations include measurements on cycloalkyl- and cycloheteroalkyl-substituted benzenes, on the solvent and temperature dependence of π-electron disturbances in mono- and disubstituted benzenes, and on monosubstituted pyridines. We are also studying the use of the method as a tool to investigate hydrogen bonding and complex formation between aromatic and aliphatic molecules.

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[39] C. F. Wilcox, Jr., and J. S. McIntyre, *J. Org. Chem.*, 30, 777 (1965).

[40] R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, 5, 210 (1959).

The Absolute Configuration of an Axially Dissymmetric Compound. (*S*)-(+)-1-Benzylidene-4-methylcyclohexane[1]

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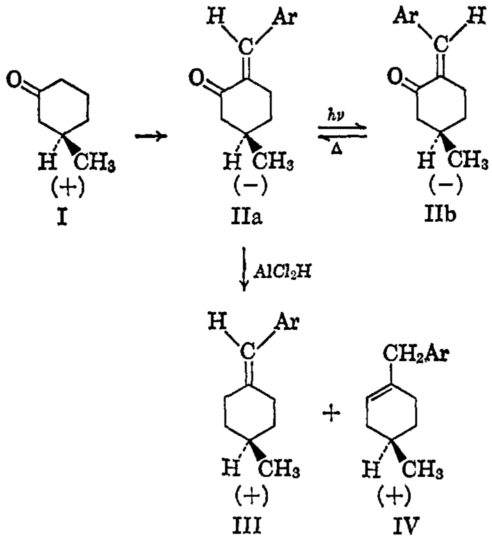
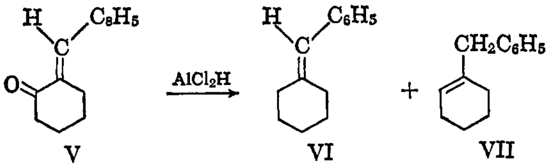
Abstract: (*R*)-(+)-3-Methylcyclohexanone was converted to the (*R*)-(−)-5-benzal derivative and this was reduced by use of aluminum chloride–lithium aluminum hydride to a separable mixture of (*S*)-(+)-1-benzylidene-4-methylcyclohexane and (*R*)-(+)-4-methyl-1-benzylcyclohexene. The benzalketone and the benzylidenecyclohexane show strong negative Cotton effects, indicating that their chromophores are twisted. The relationship of these results to several models of optical activity is discussed, and configurations of several additional cyclohexylidene compounds are predicted.

Dissymmetric spiranes, cycloalkylidene compounds, and allenes[2] are of interest because some of them cannot show either "atomic"[3] or "conformational"[3] dissymmetry and so must owe their optical rotatory properties to longer range, or "permolecular,"[3] dissymmetry effects. As one step in a program aimed at defining more sharply the concept of "permolecular" dissymmetry,[4] we have now determined the absolute configurations of a series of 1-benzylidene-4-methylcyclohexanes (III) and measured their optical rotatory dispersion curves (see Figure 1 and Table V).

Our starting material, (+)-3-methylcyclohexanone (I), is available, without need for resolution, by hydrolysis of (+)-pulegone,[5] the major constituent of oil of pennyroyal.[6] Its absolute configuration (*R*)[7] has been established in several ways.[8–10] Condensation with





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[1] A Useful Model of Optical Activity, part VI; for part V see Hydrogenolyses with Chloroaluminum Hydrides, J. H. Brewster, *Tetrahedron*, 13, 106 (1961); for part IV see J. H. Brewster, S. F. Osman, H. O. Bayer, and H. B. Hopps, *J. Org. Chem.*, 29, 121 (1964).

[2] For a review see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 307–317.

[3] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

[4] For useful criticisms of our failure to develop this aspect of our work in more detail see: (a) W. Kauzmann, F. B. Clough, and I. Tobias, *Tetrahedron*, 13, 57 (1961); (b) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961). (c) A paper dealing with this matter at more length is in preparation.

[5] O. Wallach, *Ann.*, 289, 337 (1895).

[6] E. Guenther, "The Essential Oils," Vol. III, D. van Nostrand Co., Inc., New York, N. Y., 1949, p 575.

[7] Notation of R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 12, 81 (1956).

[8] A. Fredga, *Arkiv Kemi Mineral. Geol.*, 14B, No. 27 (1941); **15B**, No. 23 (1942); A. Fredga and E. Leskinen, *ibid.*, **19B**, No. 1 (1944).