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Infrared Intensities: A Guide to Intramolecular Interactions in Conjugated Systems

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Contents

I. Introduction

This review is concerned with intramolecular interactions in organic molecules and, in particular, with the use of infrared intensity measurements as a guide to such interactions in conjugated systems. The development of accurate methods of measuring infrared intensities has allowed us and some other workers to make significant contributions to the understanding of substituent interactions over the last ten years. Our concern in this review is to emphasize the evidence on the electronic interactions rather than the infrared aspects, and we write primarily for organic chemists. Further details of infrared techniques are given elsewhere.[1] As will be shown below, the use of infrared intensities is particularly valuable in assessing the extent of intramolecular interaction in ground-state π-electron systems, and we thus restrict ourselves to conjugated molecules. In particular, we limit the review to molecules containing one of the fundamental unsaturated systems such as an aromatic, heteroaromatic, or ethylenic nucleus and look at the effects of changing a directly attached substituent, effects which are considerably more profound on the *intensity* than on the *frequency* of infrared vibrational modes.[2]

A. Intramolecular Interactions

The electronic interactions that we are concerned with may alternatively be considered as substituent electronic effects on the system concerned. Such effects can be transmitted by several distinct mechanisms. A recent review[3] lists the most important as:

The I_σ effect—the inductive effect of a polar group transmitted by diminishing relay along a system of σ bonds.

The F effect—the field effect of a polar group transmitted through space to a site where it affects a measurement.

The resonance effect (R), which results from the interaction of substituent orbitals of suitable symmetry with the π orbitals of the unsaturated nucleus and can lead to charge transfer either to or from the substituent.

The π_{orb} effect—the repulsion of the filled π orbitals of the nucleus caused by substituent induced π–π^* mixing; no charge transfer is involved.

The π_F and π_σ effects—the disturbance of the π system of the nucleus by the I_σ and F effects of the substituent.

A great strength of the infrared intensity method is that it allows the measurement of resonance effects virtually uncomplicated by those arising from the other interactions.

B. Conjugation

This term has a variety of uses in the recent literature, and we therefore wish to make some clear distinctions here to avoid confusion. The term probably first referred to a system of adjacent π orbitals. In this sense one can say that the two double bonds in butadiene are conjugated or that one of the lone pair of electrons on the oxygen atom in phenol is conjugated with the benzene ring. However, the word conjugation is also used to assess the degree of interaction, in terms of either energy or charge transfer, and this can lead to confusion. Thus an ultraviolet or Raman spectroscopist might say that in going from butadiene to hexatriene, the increase in conjugation is greater than in going from ethylene to butadiene since his spectra indicate considerable changes. However, these changes result from excited orbitals, and ground-state properties, such as bond lengths, may reasonably[4] be explained without significant interaction compared to isolated double bonds. The actual amount of interaction that occurs in ground-state energy when two suitable systems are adjacent (conjugated in the original sense) is better described as the "resonance energy"; this is generally supposed to be fairly small but finite for butadiene. Again using butadiene as an example, conjugation and even a finite resonance energy does not necessarily lead to charge transfer. By contrast charge transfer would take place in ethynyl cyanide since the atoms have differing electronegativities. In the review we shall frequently refer to a resonance interaction; this may imply either an energy effect or a charge-transfer effect depending on the method of measurement and we shall endeavor to define it appropriately. Thus the measurement of the barrier to rotation of a substituent attached to a benzene ring gives an energy value while a carbon-13 NMR shift value is related to an electron density. These effects might be expected to parallel one another in related systems although this is not always true.[5]

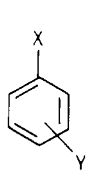
C. Separation of Polar and Resonance Effects

Work on substituent electronic effects from 1940 to 1960 was concentrated on the linear free energy relationships pioneered by Hammett.[6] The Hammett equation (1) was used to correlate

$$P - P^0 = \rho\sigma \tag{1}$$

the effect of a substituent on a particular equilibrium ($P = \log K$), rate of reaction ($p = \log k$), or physical property (P in energy units). The value of ρ varies according to the electron demand of the reaction or property measured but is a constant for a fixed set of conditions. The σ constant for a substituent Y gives a measure of its electronic effect on the reaction or measurement center from the position concerned.

The σ constant is thus rather a measure of the substituent's electronic effect at the reaction site than a measure of its effect on the benzene ring in isolation. The acidity of *m*- and *p*-Y-substituted benzoic acids (**1**, X = CO_2H) was originally taken as



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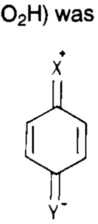

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a standard reaction and ρ arbitarily taken as unity in water at 25 °C. The σ values derived were found to be broadly applicable to some other equilibria and physical properties. However, Hammett had pointed out[6] that σ constants might vary for certain substituents depending on the electronic requirements of the reaction site in cases when X and Y could interact. This "through conjugation" (2) thus leads to different substituent constants for some para substituents, e.g., when derived from aniline–anilinium ion equilibria (σ^-) than from benzoic acid–benzoate anion equilibria (σ). New substituent constants, σ^+ and σ^-, were thus obtained for cases where the property measured placed a demand on electrons or had a surplus of them, respectively. The realization that a large part of the variation in σ values could be ascribed to direct conjugation between the substituent and the reaction site led to attempts to estimate σ^0 values for systems where 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. Fair agreement is found for σ^0 values from various sources except for strong electron donors (see section VI.A). With each scale of σ values, different values are required for each position of substitution.

Taft and his co-workers[7] pioneered attempts to split σ values into inductive and resonance contributions, citing eq 2 where

$$\bar{\sigma}_p = \bar{\sigma}_R + \sigma_I \tag{2}$$

σ_p is σ_p, σ_p^+, σ_p^-, or σ_p^0 and σ_R is the corresponding resonance parameter (σ_R, σ_R^+, σ_R^-, σ_R^0). The early approach[7] was to estimate σ_I either from aliphatic systems or by comparison of data for meta- and para-substituted benzenes, and thus obtain $\bar{\sigma}_R$ by difference. Subsequent work with aliphatic systems,[8] on the infrared intensity of C–H stretching vibrations[9] in monosubstituted benzenes, and F-19 NMR chemical shifts in meta substituted fluorobenzenes[10] has provided further confirmation for the σ_I values. Thus the σ_R^0 values are reasonably well established and represent the disturbance of the π system in a monosubstituted benzene. Unfortunately[3] the scale and the particular values will depend on the method of measurement since inductive effects on the π system (π_σ and π_F) and π_{orb} effects may or may not be included in addition to resonance effects. If, however, the values are derived by fitting data to a dual substituent parameter, eq 3,[11,12] then any π_σ and π_F effects will be

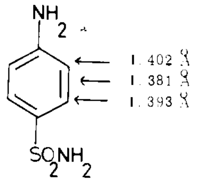
$$P - P^0 = \rho_I\sigma_I + \rho_R\sigma_R^0 \tag{3}$$

taken up in the first term as these should be proportional to the polar nature of the substituent and thus to σ_I.

D. Other Experimental Approaches

Early studies of electron disturbances in conjugated systems were mainly limited[13] to the interpretation of dipole moment measurements and ultraviolet spectra of benzene derivatives. Dipole moments give only a general guide[13] to the presence and direction of resonance interactions through the mesomeric moments obtained as differences between the moment of the substituted benzene and that of a correspondingly substituted alkyl derivative.[14] However, the dipole moment differences cannot be directly compared to resonance effects as they also depend on distance factors such as differences in the relative charge separations. Recent work on ultraviolet spectra[15] has also shown that the frequencies do not follow ground-state substituent electronic effects; this difference is expected since such spectra are a function of the overall molecular orbitals in both the ground and excited states. By contrast the intensities[15] of ultraviolet $\pi \rightarrow \pi^*$ absorptions in monosubstituted benzenes do seem to reflect resonance interactions, but the measurements are restricted by experimental difficulties.

Changes in bond length may also give an indication of resonance interactions in conjugated systems. Thus some 1,4-disubstituted benzenes having one resonance electron-donating substituent and one resonance electron-withdrawing substituent show bond lengths in accord with a contribution from the canonical form **2**; an example[16] is **3**. However, because of thermal motions it is not possible to obtain precise enough data from x-ray or neutron diffraction to allow a more quantitative interpretation while microwave and electron diffraction results are very limited for suitable molecules. Recent work[17] has demonstrated that the internal angle of the benzene ring at the position of attachment varies as the electronegativity of the substituent.



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The use of NMR shift data requires the separation of the inductive contribution to the shift and the assumption that the overall effect arises only from substituent electronic effects. It is observed empirically that the carbon-13 shift differences between the para and meta carbon atoms in monosubstituted benzenes[18] and the fluorine-19 shift differences between para- and meta-substituted fluorobenzenes[19] were proportional to chemically derived $\sigma_R{}^0$ values. More recently, dual substituent parameter analysis has shown[20] that the individual meta and para shifts do not have quite the same dependence on σ_I values, and thus the differences give only an approximate relation to $\sigma_R{}^0$. Infrared frequencies can also be related[21] to resonance effects via a dual substituent parameter treatment, but these are only occasionally on the $\sigma_R{}^0$ (as against $\sigma_R{}^+$, σ_R, or $\sigma_R{}^-$) scale.

In the light of this lack of direct data, we can see that the direct proportionality of infrared intensities (A) to the square of $\sigma_R{}^0$ values for certain vibrations in substituted benzenes, heteroaromatics, ethylenes, and acetylenes is an important advance. In the last ten years we have made extensive use of this technique,[22] and this review is to a large extent a coverage of the chemically significant evidence that we have derived. It covers related work by other authors and the literature has been consulted up to early 1976.

E. Theoretical Approaches

Theoretical approaches to the determination of resonance interactions have been rather limited. One immediate problem is whether the resonance interaction (the $\sigma_R{}^0$ substituent constant) is defined in terms of the delocalization energy involved in the interaction between the substituent and the unsaturated group or in terms of the charge transfer that occurs. It is difficult to divide the energy terms in a theoretical calculation so as to obtain the required quantity but, by contrast, charge transfer is readily obtained. Theoretical studies at both the CNDO/2[23,24] and STO-3G[20] level have shown that the values of overall π-electron transfer between substituents and an unsaturated system are closely proportional to the $\sigma_R{}^0$ values derived from chemical and physical techniques. This has led to the recent suggestion[25] that $\sigma_R{}^0$ might best be derived from such calculations so as to place them on a clear foundation. At the ab initio

$$\sigma_R{}^0 = 4.8\Sigma\Delta q_\pi \tag{4}$$

level, eq 4 was suggested for monosubstituted benzenes, and $\sigma_R{}^0$ values from other measurements have been satisfactorily compared with these theoretical figures.

It should be noted that the π-electron charges induced by a substituent at a particular position in a monosubstituted benzene are *not* simply proportional to the overall charge transfer, or, therefore, to $\sigma_R{}^0$. This is because π_F, π_σ, and π_{orb} effects are also involved. Thus for the para position in a monosubstituted benzene eq 5 applies.

$$\Delta q_{\pi(p\text{-}C)} = 0.03\sigma + 0.11\sigma_R{}^0 \tag{5}$$

The connection of the $\sigma_R{}^0$ scale with energy values is important. The relationship of these values to the barriers to rotation in substituted benzenes and ethylenes provides such a linkage. This is discussed in section VIII.

F. Infrared Aspects

1. General Considerations

The following description is intentionally brief; a more detailed coverage can be found in several[26] excellent monographs and reviews.

The intensity of an isolated infrared band is not strictly a ground-state property but is proportional to the square of the rate of change of the dipole moment with the normal coordinate $(\partial\mu/\partial Q)$ (eq 6) when c is the velocity of light, N_0 is Avogadro's

$$A = \frac{\pi N_0}{3000c^2 \times 2.303}\left(\frac{\partial\mu}{\partial Q}\right)^2 \tag{6}$$

number, and the other constants are factors resulting from the units used in the experimental measurement of intensity. From this point of view $A^{1/2}$ is the logical quantity to try to relate to electronic effects in a series of molecules of varying substituent.

Before any such correlation can be attempted, it is necessary that the band intensity can be accurately measured and that this measured value is not affected by extraneous factors. In practice this means that the absorption must be in a region of the spectrum which is relatively free from other absorptions. Recent line-fitting techniques[27] allow the estimation of intensities of overlapping bands, but if the absorptions are of the same symmetry type, then intensity sharing occurs and the values obtained are not simply interpreted. Thus it is not useful[28] to measure the intensity of the NO_2 stretching vibrations in nitrobenzenes since these are admixed with both the ν_8 and ν_{19} ring vibrations nearby.

Measurements would ideally be made in the gas phase, but a more realistic requirement for medium size organic molecules is that they be measured in dilute solution in a noninteracting, nonpolar solvent. It is also important to test for, and if necessary, allow for, concentration effects, but in our experience this is important only for vibrations such as $\nu_{C\equiv N}$ in benzonitriles[29] where specific interactions are possible.

Steric and mass sensitive vibrations must be avoided while only those vibrations ("group vibrations") in which little motion occurs in attached atoms are likely to give ready information on substituent effects.

The use of high-precision double-beam grating spectrometers nowadays allows reproducible and accurate determinations of infrared intensities within the limitations discussed above. Such values are improved by line-fitting techniques even for isolated bands since proper allowance is then made for the "wings" of each absorption. Most of our measurements have been recorded by direct integration but we have used line fitting in special cases as mentioned below. In general the $A^{1/2}$ values are estimated to be accurate to ± 1 unit (A in liter mole^{-1} centimeter^{-2} throughout) where $A^{1/2} > 15$.

2. Theoretical Calculation of Intensities

Our work has mainly concerned two characteristic ring vibrations (ν_8 and ν_{19}) of substituted benzenes, together with analogous vibrations in related heteroaromatics, and the $\nu_{C=C}$ and $\nu_{C\equiv C}$ stretching vibrations in substituted ethylenes and acetylenes. Besides relating them to resonance interactions via the $\sigma_R{}^0$ scale, we have also used[30-33] the CNDO/2 method to obtain theoretical intensities with considerable success. The intensity of an infrared absorption is directly related to the square of the dipole transition moment as shown in eq 6. If the form of the vibration is known from a normal coordinate analysis, then it is possible to calculate the dipole moment of the molecule at various stages as the atoms move. This allows the calculation of the dipole transition moment as the rate of change of dipole as the vibration goes through the equilibrium position. The intensity thereby calculated by eq 6 should really refer to an isolated molecule in the gas phase at absolute zero. Further, we have used one set of coordinates for each series. In spite of these approximations, it has been found that agreement between theory and experiment is usually within 20% and better if gas-phase results are used.

The correlation found between $A^{1/2}$ and σ_R^0 therefore suggests that $\partial\mu/\partial Q$ is proportional to the ground-state property σ_R^0. This seems strange at first sight since the dipole transition moments must follow the change in overall, rather than just π, dipole moment during the vibration. We have examined[34] calculations at the CNDO/2 level, but it is not clear why this happens. However, simple resonance pictures are in accord as shown for example in section II.A below. We believe that changes during a vibrational mode are far greater in the π- than in the σ-dipole moment.

II. Substituted Benzenes

A. Monosubstituted Benzenes

1. Infrared Aspects

The correlation of infrared intensity data with substituent effects is now becoming clear following the recent work of Schmid and his co-workers and of ourselves on substituted benzenes.

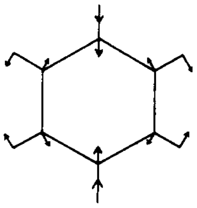
Schmid[9,35] measured the intensity of the ν_{CH} vibrations in many mono- and disubstituted benzenes, azabenzenes, and polycyclic analogues. The results for various positions can be obtained separately by partial deuteration. The results show that the intensities follow the σ_I values of the substituents leading to equations such as (7), where a, *b*, and *c* are constants for a

$$A = a\sigma_I^2 - b\sigma_I + c \tag{7}$$

particular substituent pattern. They also showed that the dipole transition moment was to a considerable extent isolated in the CH bond and was a function of the bond polarity and hence of σ_I. The work does not, however, directly appertain to our subject of resonance interactions except in so far as it shows that polar substituent effects in aromatic molecules seem to be the same as in aliphatic cases.

In our own work, we have made extensive use of ν_8 and ν_{19} ring vibrations of substituted benzenes.[88] These vibrations occur in a region of the spectrum which is relatively free of other absorptions for most substituted benzenes and careful integration, either manually or by line fitting methods, leads to highly reproducible results. The vibrations have some complexities, in infrared terms, and a brief description[36] is therefore given.

The 1600-cm^{-1} (ν_{8a}) and 1585-cm^{-1} (ν_{8b}) bands in monosubstituted benzenes arise from the IR forbidden in-plane ν_8 benzene vibration at 1585 cm^{-1}. The direction of the atomic displacements in the degenerate pair in benzene itself is shown in **4** and **5**.



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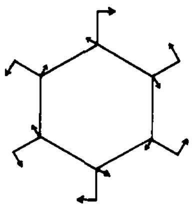

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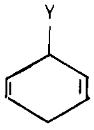
Such diagrams of the forms of the normal modes result from force-field calculations and a comparison of calculated and observed frequencies for halogenated and deuterated benzenes. The degeneracy is lifted when the symmetry is reduced by attaching even one symmetrical substituent, and two infrared active vibrations are obtained. Calculations show that the forms of the normal coordinates for mono- or disubstituted benzenes are very similar to benzene itself.

A considerable amount of the potential energy of the vibration of these modes is involved in C–H bending. Most of the intensity, however, arises from the ν_{8a} vibration, and it can be seen here that the C–H bending modes are symmetrical and any contributions they may make to the dipole moment will cancel out. The intensity here thus derives from C–C stretching modes since the contribution to the potential energy from the C–H and C–X stretching modes has been shown to be negligible in monosubstituted benzenes.

There is thus some point[31] to trying to integrate the intensity of the ν_{8a} vibration separately from the ν_{8b} intensity since the former might reflect resonance interactions more closely. This can be visualized[37] in terms of a valence-bond treatment. In a monosubstituted benzene, during the vibration ν_{8a} there is a distortion of the molecule in the sense of **6** $\rightleftharpoons$ **7** (where the effect is much exaggerated).



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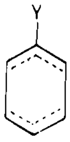

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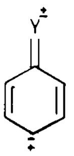

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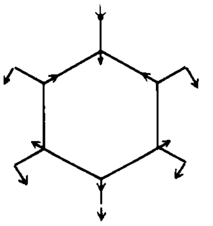
The shorter bonds will have greater double-bond character and the longer bonds greater single bond character. Thus if the substituent Y is capable of resonance interaction with the ring, then canonical forms of type **8** will be of more importance for **6** than **7** and lead to an oscillating dipole during the vibration.

It is theoretically possible to separate ν_{8a} and ν_{8b} intensities for substituents of C_{2v} or higher symmetry since the two vibrations are of different symmetry species. We have made such separations[31] using line-fitting programs (see below). However, when the molecule is of less than C_{2v} symmetry, then both vibrations belong to the same symmetry species and intensity sharing can occur between the two measured absorptions. In general, therefore, we have to integrate both vibrations together, and any C–H bending contribution to the ν_{8b} mode will reduce the precision of relationships to substituent-ring resonance interactions.

One should note that either a resonance-donating or resonance-accepting substituent will lead to an intensity, and thus from its consideration no direction can be ascribed to the charge transfer. The situation with ν_{19} vibrations[38] does not parallel this since the vibration is active in benzene itself and the substituent will increase or decrease the intensity according to the direction of the effect. The directions of the atomic displacements in the ν_{19a} and ν_{19b} vibrations in benzene itself are shown in **9** and **10**, respectively.



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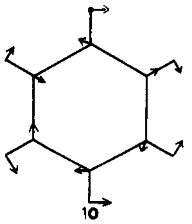

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The C–H bending vibrations lead to the intensity in ν_{19a} for benzene itself and contribute to the intensity in monosubstituted benzenes. This can be estimated, but uncertainty here together with the presence nearby of other strong vibrations has made use of this absorption less attractive.

2. Theoretical Calculations

We have made quite intensive calculations of the dipole moment derivatives (and hence intensities) of ν_8 and ν_{19} vibrations in monosubstituted benzenes[30,31] using the CNDO/2 method. These have been compared to measured intensities (using line-fitting methods) including separate[31] values for ν_{8a} and ν_{8b} and for ν_{19a} and ν_{19b} for compounds where this is permissible, measured both in nonpolar solvents and in the gas phase where volatility allows. We find that the method gives remarkable agreement, Figure 1 being for calculated and measured (in solution) overall ν_8 intensities. Least-squares analysis gives eq 8 with a correlation coefficient of 0.989. The

$$A = 1.16A_{\text{calcd}} + 48 \tag{8}$$

corresponding equations for the ν_{8a} and ν_{19a} vibrations are eq 9 and 10. Fewer results were available for gas-phase mea-

$$A = 1.29A_{\text{calcd}} + 54,\ r = 0.992 \tag{9}$$

$$A = 1.23A_{\text{calcd}} + 398,\ r = 0.960 \tag{10}$$

surements, but here eq 11 was the best fit for the overall ν_8 intensity.

$$A_{\text{gas}} = 1.14A_{\text{calcd}} - 14,\ r = 0.999 \tag{11}$$

Clearly there is good proportionality between measured and calculated values and the absolute values are surprisingly good. This adds much to the overall confidence with which we can use CNDO/2 calculations in describing substituent effects.

A dual substituent parameter analysis of the calculated figures clearly shows the paramount importance of resonance interaction. For the overall ν_8 intensity, eq 12 represents the best fit.

$$A^{1/2}{}_{\text{calcd}} = 7.6\sigma_{\text{I}} - 128.5\sigma_{\text{R}}{}^0 \tag{12}$$

One additional advantage of the calculations is that the direction of the charge displacement is also obtained. These[31] are in line with normal expectation.

3. ν_8 *Intensities of Monosubstituted Benzenes*

A limited number of such intensities have been measured by the line-fitting methods. For these results eq 13 applies[31] for the

$$A^{1/2} = 3.7\sigma_{\text{I}} - 141.2\sigma_{\text{R}}{}^0 \tag{13}$$

overall ν_8 intensity and eq 14 for the ν_{8a} intensity in compounds

$$A^{1/2} = 0.5\sigma_{\text{I}} - 140.4\sigma_{\text{R}}{}^0 \tag{14}$$

of C_{2v} symmetry. The fit was excellent in both cases and clearly shows the overriding importance of the resonance interaction in determining these intensities. For most cases, however, the two absorptions should not be separately integrated (see section II.A.2), and the overall intensity was obtained by manual integration. For this procedure the appropriate DSP analysis for compounds where the substituent constants were already established gave[12] eq 15. The lower resonance transmission

$$A^{1/2} = 4.2\sigma_{\text{I}} - 133.2\sigma_{\text{R}}{}^0 \tag{15}$$

constant arises because the A values do not include the wings and are thus of smaller magnitude than the values for the line fitted integration.

The obvious close linear relationship between $A^{1/2}$, $\Sigma\Delta q_\pi$, and $\sigma_{\text{R}}{}^0$ allows us to use the intensities here to calculate the other two quantities for a wide range of substituents. The appropriate working equation for $\sigma_{\text{R}}{}^0$ values for the usual case of manual integration and combined ν_8 intensities is[37] eq 16, where

$$A = 17\,600(\sigma_{\text{R}}{}^0)^2 + 100 \tag{16}$$

the units of A are in L mol^{-1} cm^{-2} (IUPAC standard units of intensity) and the 100 unit constant refers to an overtone in the region. Thus eq 17 can be used to obtain $\sigma_{\text{R}}{}^0$ values.

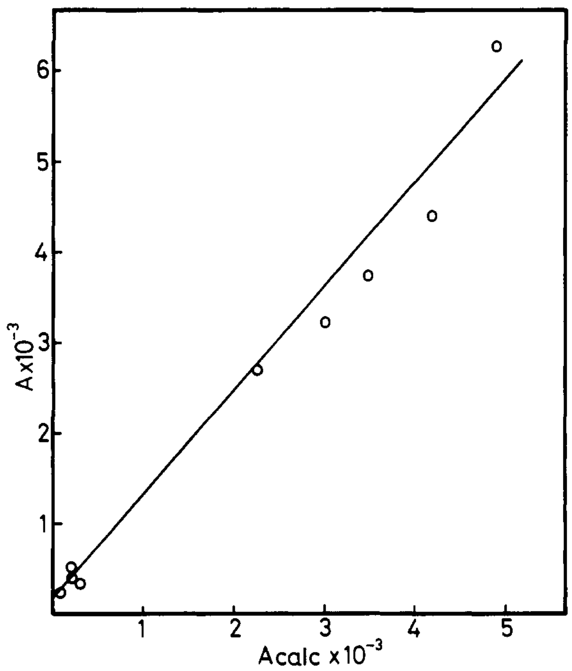
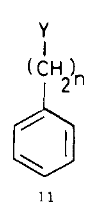


Figure 1. Plot of observed (A) vs. calculated (A_{calcd}) intensities for the combined ν_8 vibrations of monosubstituted benzenes (line of best fit is $A = 1.16A_{\text{calcd}} + 48$; correlation coefficient, 0.989; standard deviation, 300).

$$|\sigma_{\text{R}}{}^0| = 0.0075(A - 100)^{1/2} \tag{17}$$

We have thus obtained $\sigma_{\text{R}}{}^0$ values for almost 200 substituents (see later in Table VI), and these are usually in good agreement with those obtained by other methods where available. Our method has (i) considerable experimental convenience requiring only that the required benzene can be synthesized, dissolves in an inert solvent, and does not have any other strong absorptions close to 1600 cm^{-1}; (ii) the advantage that it utilizes the monosubstituted benzene rather than adding a second group such as a fluorine atom or carboxylic acid group to act as a probe (such a second group may influence the resonance interaction of the first substituent with the ring); and (iii) measures the overall π-electron interaction between the substituent and the ring rather than the effect felt at some particular carbon atom in the ring.

One particular aspect of point iii is seen in the behavior of ω-substituted alkylbenzenes **11**. A change in substituent Y where



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n = 2 or 3, disturbs[39] the π-electron distribution in the ring as shown by carbon-13 NMR shifts or ultraviolet spectra. This has been explained[39] in terms of a π_{F} effect. However, the intensity of the ν_8 vibrations is substantially the same as in the corresponding alkylbenzenes (**11**, Y = H) showing that the relatively remote Y group does not alter the hyperconjugation between the side chain and the ring. The method thus allows the separation of the various substituent effects that lead to π disturbance in substituted benzenes (see also section IX).

Values of $\sigma_{\text{R}}{}^0$ less than 0.1 are not well determined by eq 17 both because of uncertainties in the overtone correction term and because low intensities are more difficult to measure. More accurate values can be obtained from work on substituted ethylenes (section IV) or on meta-disubstituted benzenes (see

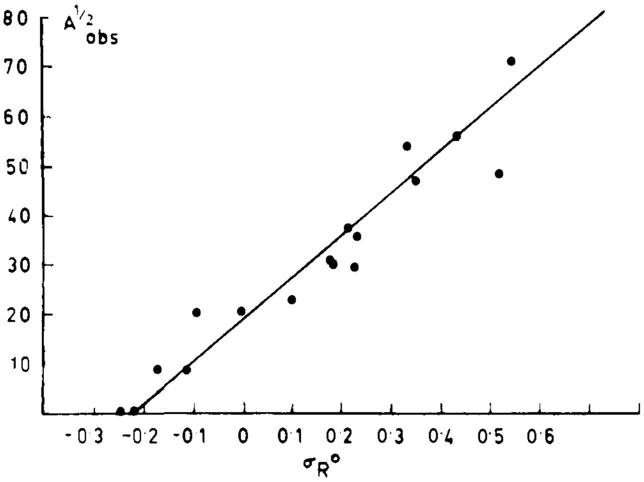


Figure 2. Plot of $A^{1/2}$ for ν_{19a} band of monosubstituted benzenes against σ_R^0 values.

section II.C). The direction (sign) of the resonance interaction is not given by eq 17 as explained above but is usually readily assigned from intensity measurements on disubstituted benzenes or, in some cases, from measurements on the ν_{19} absorption.

Discussion of the findings as they affect the varying resonance interaction of various classes of substituent is reserved to section VI.

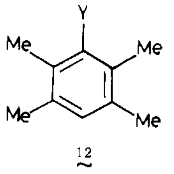
4. *The ν_{19} Vibration in Monosubstituted Benzenes*

The ν_{19a} bands are usually separated from the ν_{19b} absorptions; the latter are of low intensity and often obscured by other vibrations. We have measured the extinction coefficients ϵ (based on peak height and band half-width) of the ν_{19a} absorptions for a large number of monosubstituted benzenes. The integrated intensities cannot be measured for all compounds because of nearby vibrations. Nevertheless, there is a general relationship between $A^{1/2}$ or $\epsilon^{1/2}$ and σ_R^0 values (see Figure 2). Since the identity is only approximate, we prefer not to propose a formal equation. The relationship in Figure 2 does allow a sign to be given to σ_R^0 values, but this would still be uncertain for values of low magnitude.

B. Steric and Mass Effects

1. *Steric Effects in Monosubstituted Durenes*

The idea of the reduction of resonance interaction between the ring and substituent by twisting is fundamental to theories on conjugation. We have used substituted durenes **12** to test the effect of steric hindrance on the infrared intensities of ν_8 absorption. This vibration is forbidden in durene itself (**12**, Y = H) because of the symmetry of the molecule. Steric hindrance in durenes has been the subject of much work, and a decrease in resonance interaction of substituents compared to that in monosubstituted benzenes has been demonstrated by UV, dipole moment, and NMR measurements and from reactivity studies.[40]



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Extension of our ideas[37] of the origin of the predominant resonance contributions to the intensities of ν_8 vibrations suggests that for symmetrical substituents the durene values[37] should parallel those for monosubstituted benzenes; the effects of the four methyl groups should cancel out. A plot of durene intensities for such substituents is indeed linear against benzene results or against $(\sigma_R^0)^2$ (Figure 3). The correlation is described by eq 18; the difference in the slope from that for monosubstituted benzenes doubtless arises from changes in the form of the mode. However, substituents of lower symmetry such as NMe_2, OMe, NO_2, exhibit lower effective σ_R^0 than found in monosubstituted benzenes. These $(\sigma_R^0)_{durene}$ values show considerable steric inhibition of conjugation; thus σ_R^0 and $(\sigma_R^0)_{durene}$ values for various substituents are respectively: NMe_2, 0.54, 0.23; OMe, 0.42, 0.28; NO_2, 0.17, 0.10. We can estimate the angle of twist, θ, here if we know the $(\sigma_R^0)_{twist}$ value, that is the conjugation still remaining at 90° rotation. Equation 19 has been derived[41] assuming a $\cos^2 \theta$ resonance dependence.

$$A_{durene} = 11\,300(\sigma_R^0)^2 - 30 \qquad (18)$$

$$(\sigma_R^0)\theta = (\sigma_R^0)_{tw} + [\sigma_R^0 - (\sigma_R^0)_{tw}] \cos^2 \theta \qquad (19)$$

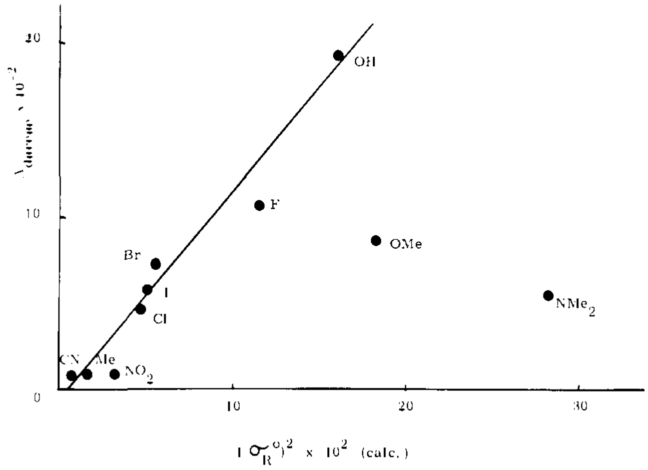


Figure 3. Plot of *A* for durenes against the squares of the σ_R^0 values for the corresponding monosubstituted benzenes.

This equation can be used to derive $(\sigma_R^0)_{tw}$ values if θ is known from other work or to derive θ if $(\sigma_R^0)_{tw}$ is known. Thus $(\sigma_R^0)_{tw}$ for OMe has been estimated[41] as −0.23 from the known geometry of methoxydurene, the comparatively large value arising as overlap is possible of both the oxygen p orbitals with the benzene π system in the twisted, sp^3-hybridized, anisole. Other $(\sigma_R^0)_{tw}$ values can be derived from model compounds of known geometry; thus the $(\sigma_R^0)_{tw}$ value[42] of −0.13 for NMe_2 allows us to estimate θ as 61° for dimethylaminodurene.

2. *Deuterio Compounds and Mass Effects*

We have found[28] that the ν_8 intensities of para-deuterio- and pentadeuterio monosubstituted benzenes are generally almost identical with those of simple monosubstituted compounds. This shows that the hydrogens either individually make no contribution or that they all cancel out, resulting in zero resultant contribution. It further suggests little mass effect on the vibration, and this is supported by the fairly constant frequency values for the monosubstituted benzenes; however, the vibration does seem to be altered by particularly heavy attached atoms such as Br and I, and we must therefore be somewhat cautious with σ_R^0 values derived for such substituents.

C. Meta-Disubstituted Benzenes

We have studied the intensities of a considerable number of meta-disubstituted benzenes. Since our full paper in 1969,[43] we have recorded many other results for various further classes of substituent and so have reanalyzed the results for this review.

The dipole transition moment $\partial\mu/\partial Q$, and hence the resulting intensity, is a vector quantity, and the relationship of its size in

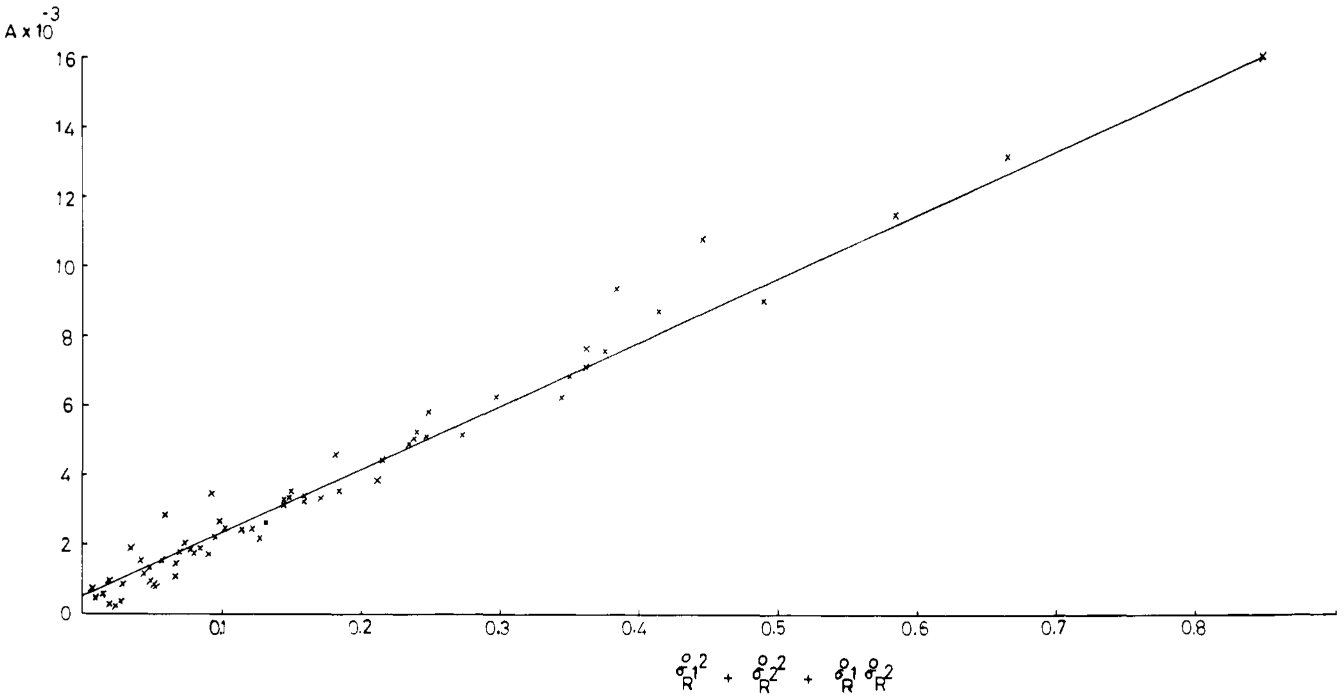


Figure 4. Plot of $A \times 10^{-3}$ vs. $\sigma_R{}^0 1^2 + \sigma_R{}^0 2^2 + \sigma_R{}^0 1 \sigma_R{}^0 2$ for meta-disubstituted benzenes with symmetrical (C_{2v}) substituents.

the disubstituted compounds to those in the monosubstituted series must be treated vectorially. It has been shown[43] that in the absence of substituent–substituent interaction, for a compound containing two substituents in symmetrically equivalent positions, eq 20 holds, where $\sigma_R{}^0 1$ and $\sigma_R{}^0 2$ are the $\sigma_R{}^0$ values for the two respective substituents, and θ is the angle between their dipole transition moments.

$$A = b[(\sigma_R{}^0 1)^2 + (\sigma_R{}^0 2)^2 + 2\sigma_R{}^0 1 \sigma_R{}^0 2 \cos \theta] + C \quad (20)$$

1. Substituents of C_{2v} Symmetry

Where both substituents are of C_{2v} symmetry, the analysis of results follows eq 20. It can be shown[43] that only one of the two possible modes is important here and eq 21 is thereby derived corresponding to vector addition of $\sigma_R{}^0 1$ and $\sigma_R{}^0 2$ at 60 °C.

$$A_{\text{meta}} = b[(\sigma_R{}^0 1)^2 + (\sigma_R{}^0 2)^2 + \sigma_R{}^0 1 \sigma_R{}^0 2]^2 + C \quad (21)$$

We have analyzed the intensity values for some 65 meta-disubstituted benzenes of suitable symmetry against $[(\sigma_R{}^0 1)^2 + (\sigma_R{}^0 2)^2 + \sigma_R{}^0 1 \sigma_R{}^0 2]$, and the results are shown in Figure 4. The agreement is excellent and gives rise to eq 22. This compares well with our earlier report[42] of $b = 19\,000$, $c = 340$ based on far less data. The small difference in b from the value found for monosubstituted benzenes (eq 16) doubtless arises from a small change in the mode of the vibration.

$$A_{\text{meta}} = 18\,230[(\sigma_R{}^0 1)^2 + (\sigma_R{}^0 2)^2 + \sigma_R{}^0 1 \sigma_R{}^0 2] + 500 \quad (22)$$

The success of the equation in terms of our concepts allows us to make further comments about substituent effects. Thus, the absence of any significant or systematic deviation suggests little effect of one substituent on the conjugation of the other. (For a discussion of possible field effects of an electronegative group inducing a greater resonance effect in a donor, see section IV.D.)

Another important use of eq 22 is to measure $\sigma_R{}^0$ values and directions for weakly resonance interacting substituents. The term in $\sigma_R{}^0 1 \sigma_R{}^0 2$ is positive for two substituents of the same type but otherwise negative. Thus if the substituent whose $\sigma_R{}^0$ value is required is paired with a substituent of known and moderately strong resonance interaction, then significant differences in intensity are expected. Thus taking fluorine as a fixed substituent, for example, gives eq 23 where $\sigma_R{}^0$ is the value required for the second substituent. The usefulness and sensitivity of this approach can be seen in the predicted A values below:

$$A = 18\,230[0.1156 + (\sigma_R{}^0)^2 - 0.34\sigma_R{}^0] + 500 \quad (23)$$

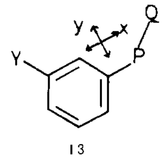
$\sigma_R{}^0$	A_{calcd}	$\sigma_R{}^0$	A_{calcd}
−0.10	3640	+0.05	2350
−0.05	2970	+0.10	2170
0.00	2610		

We have used this approach to derive $\sigma_R{}^0$ values for many weakly resonance interacting substituents.[45]

2. Substituents of Lower Symmetry

The analysis is more complicated when one or both substituents are of less than C_{2v} symmetry since both the modes have to be taken into account in the overall ν_8 intensity. For cases where one substituent is of C_{2v} symmetry (substituent 1) and one not, we have derived[43] eq 24, where $\sigma_R{}^0 x$ and $\sigma_R{}^0 y$ are the components of $\sigma_R{}^0 2$ along and perpendicular to the ring-substituent bond, respectively (**13**).[89]

$$A_{\text{meta (as/s)}} = 18\,250[(\sigma_R{}^0 1)^2 + (\sigma_R{}^0 2)^2 + \sigma_R{}^0 1(\sigma_R{}^0 x \pm \sqrt{3}\sigma_R{}^0 y)] + 500 \quad (24)$$



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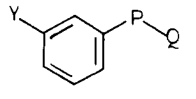

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The deviations shown by meta-disubstituted compounds containing one unsymmetrical substituent from eq 22 and also independent evidence from NMR coupling constants, torsional frequencies, and dipole moment or Kerr effect measurements indicate that the populations of conformer pairs **13** and **14** are far from equal.[43]

It would be very desirable to have a reliable method of estimating their relative populations, but unfortunately it is not possible to get more than a general indication from eq 24. This is mainly because of the difficulty of obtaining $\sigma_R{}^0 x$ and $\sigma_R{}^0 y$ values. We have obtained the figures in Table II on the as-

TABLE I. Values of $\sigma_R{}^0$, $\sigma_R{}^0x$, and $\sigma_R{}^0y$ for Substituents of Less than C_{2v} Symmetry

	$\sigma_R{}^0$	$\sigma_R{}^0x$	$\sigma_R{}^0y$
OMe	−0.428	−0.425	0.062
SMe	−0.250	−0.241	0.068
COMe	0.219	0.216	0.036
CO_2Me	0.155	0.140	0.066
CO_2Et	0.180	0.173	0.045
CHO	0.244	0.233	0.073
SO_2Me	0.06	0.06	0.000

TABLE II. Integrated Intensities (A_{obsd}) Compared with A_{cis} and A_{trans} Values Calculated by Eq 25 for Meta-Disubstituted Benzenes with One Substituent of at Least C_{2v} Symmetry and One of Lower Symmetry

Substituent					
Asym	Sym	A_{obsd}	A_{trans}	A_{cis}	% trans
CHO	F	2670	1465	3035	23
	Cl	1820	1026	2040	22
	Br	1770	1042	2104	31
COMe	Me	1260	1050	1277	7
	F	2660	1759	2532	0
CO_2Me	Me	920	656	1074	37
	F	2990	1469	2889	0
	Cl	1610	801	1718	12
	Br	1580	836	1796	22
	CF_3	660	1585	1167	0
OMe	Me	4730	4606	4998	68
	F	9020	7924	9256	17
	Cl	6400	6002	6864	54
	Br	6620	6141	7044	47
	$SiMe_3$	3650	3686	3568	69

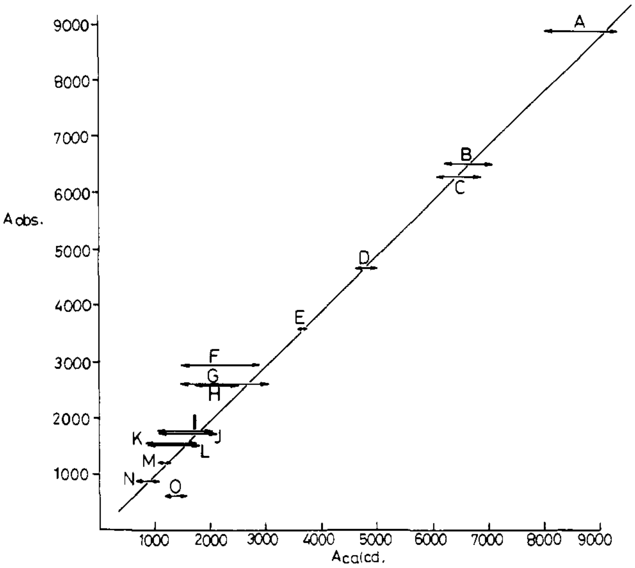


Figure 5. Plots of A_{obsd} against A_{calcd} for the alternative conformations of meta-disubstituted benzenes containing one substituent of at least C_{2v} symmetry and one of lower symmetry: (A) OMe and F; (B) OMe and Br; (C) OMe and Cl; (D) OMe and Me; (E) OMe and $SiMe_3$; (F) CO_2Me and F; (G) CHO and F; (H) COMe and F; (I) CHO and Cl; (J) CHO and Br; (K) CO_2Me and Cl; (L) CO_2Me and Br; (M) COMe and Me; (N) CO_2Me and Me; (O) CO_2Me and CF_3.

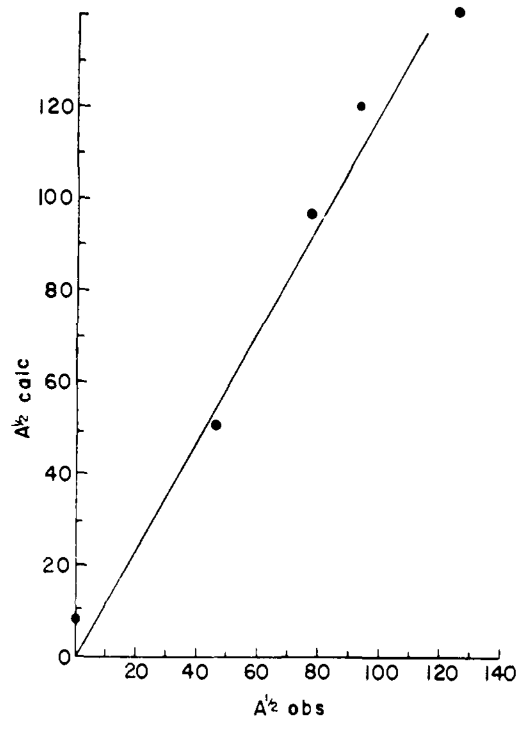


Figure 6. Plot of $A^{1/2}$ calculated by CNDO/2 against observed $A^{1/2}$ values for the ν_8 vibrations of meta-disubstituted benzenes.

sumption that the populations of cis and trans forms in symmetrically para-disubstituted benzenes are equal (see section II.E). Because of inductive effects, we have further omitted cases where one substituent is a strong donor and the other has a strong polar effect. With these in mind we have used eq 24 and the data in Table I to calculate the results in Table II and show it diagrammatically in Figure 5. (Data for nitro-containing compounds are not included since the ν_{NO_2} vibration is mixed[28] with the ν_8 modes.) The line shown in Figure 5 has unit slope. If the mole fraction existing in the cis conformation is n, then eq 25

$$n = \frac{A_{obsd} - A_{trans}}{A_{cis} - A_{trans}} \tag{25}$$

follows,[43] and the resulting percentage of cis and trans forms is given in Table II.

The values obtained must be appreciated to be only approximate. However, our values are in general agreement with those reported from other methods; thus 53% cis has been given[44] for *m*-fluoro-, 42% cis for *m*-chloro-, and 44% cis for *m*-bromobenzaldehydes from dipole moment studies, while rough calculations[46] have suggested that the trans conformers should be stabilized by ΔG values of the order of 400 cal mol^{-1}.

The analysis is complex where both substituents are of less than C_{2v} symmetry although some general conformational conclusions have been thereby derived.[43]

We have also reported[30] CNDO/2 calculations of the intensities for meta-disubstituted benzenes. These values plot well against observed values as shown in Figure 6 which has a slope of 1.15. The original paper[30] reported values for meta-substituted nitrobenzenes which deviated more from the best fit; this is now appreciated[28] to be a result of intermixing of the ν_{NO_2} and ν_8 absorptions.

The ν_{19a} vibration of meta-disubstituted benzenes occurs at about 1405 cm^{-1} and is frequently obscured by other absorptions. We have, however, measured[38] the intensities of the ν_{19b} vibration near 1470 cm^{-1} for a considerable number of compounds and plotted the results using eq 21 to obtain $b = 9870$, $c = 210$. However, there is considerable scatter even for compounds with both substituents of at least C_{2v} symmetry, and this further points to the limited use of ν_{19} absorptions in the estimation of resonance interactions.

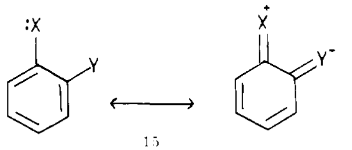
D. Ortho-Disubstituted Benzenes

The ortho-disubstituted benzenes can be treated in an analogous fashion to the meta-disubstituted compounds although here the probability of both steric and electronic interactions must be appreciated. For compounds having both substituents

$$A_{\text{ortho}} = b[(\sigma_R{}^01)^2 + (\sigma_R{}^02)^2 - \sigma_R{}^01\sigma_R{}^02] + c \qquad (26)$$

of at least C_{2v} symmetry, we have derived[43] eq 26.

An additional complication here is that while substituents such as NO_2 and NMe_2 have such symmetry, their resonance interaction will be affected by twisting resulting from the nearby ortho substituent. This is in addition to the mutual substituent conjugation (**15**) where one substituent is a resonance donor and one a resonance acceptor. Thus it is not surprising that eq 26 is of only moderate utility for the restricted class of substituents with cylindrical symmetry. The values of *b* and *c* derived here are 15 900 and −80, respectively. In an early paper[43] we used these values together with a similar analysis to that for meta-disubstituted benzenes (section II.C) to assess the likely intensities of the cis (**16**) and trans (**17**) forms where one substituent was of cylindrical symmetry and one was asymmetric. Such results were intended to be very tentative, but both since our actual values have subsequently been criticized[44] without this being realized and because we do not think that further advances can be made by our method, we suggest that the method not be used for such studies.



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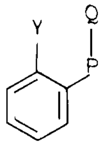

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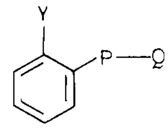

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E. Para-Disubstituted Benzenes

We have made extensive investigations of the infrared intensities of para-disubstituted benzenes which we have found to provide evidence for substituent–substituent interactions such as through-conjugation, d-orbital effects, and effects on rotational barriers.

1. Noninteracting Substituents

For noninteracting substituents, both of at least C_{2v} symmetry, eq 27 applies.[48]

$$A = b(\sigma_R{}^01 - \sigma_R{}^02)^2 + c \qquad (27)$$

Analysis[28] of a large number of intensities of para-disubstituted benzenes containing two resonance-donating or two resonance-accepting substituents suggests that *b* is 15 150. The value of *c* has been estimated to average 170 from intensities of similar compounds with two identical substituents (of at least C_{2v} symmetry) since the ν_8 absorption is forbidden here. The actual value of *b* for the working eq 28 was chosen[28] also on the

$$A_{\text{para}} = 15\,000(\sigma_R{}^01 - \sigma_R{}^02)^2 + 170 \qquad (28)$$

basis of comparison with ^{19}F studies on para-substituted fluorobenzenes, with theoretical studies and with rotational barriers (all discussed below).

We have also made[28] a general analysis of all results for para-disubstituted benzenes which takes into account both possible resonance and inductive effects of one substituent on the resonance interaction of the other. However, the approach above is more directly applicable since appropriate interaction constants for this alternative method are only available for a restricted number of substituents.

The somewhat lower value of *b* than that found for monosubstituted benzenes is confirmed[28] by theoretical calculations. We have found that while the difference between the carbon skeletal displacements would actually lead to a small increase in *b* in para-disubstituted benzenes as compared with the monosubstituted ones, the para hydrogen atom makes a considerable contribution to the intensity in the latter. If this is allowed for in the calculations, a gradient of 15 000 seems suitable.

The results obtained do not show any systematic deviations. They provide no firm support either for the concept of "saturation",[49] namely, that if two like resonance substituents (both donors or both acceptors) are para substituted then their resonance effects will be diminished or for the idea that the field effect of one substituent will alter the resonance interaction of the other. It must be appreciated, however, that one is measuring relatively small differences here.

2. Asymmetry Effects

Where at least one of the substituents is of less than C_{2v} symmetry, asymmetry corrections are required. Equation 29

$$A = 15\,000[(\sigma_R{}^0\text{s} - \sigma_R{}^0\text{as})^2 + 2\sigma_R{}^0\text{s}(\sigma_R{}^0\text{as} - \sigma_R{}^0\text{x})] + 170 \qquad (29)$$

applies to a compound containing one substituent s of at least C_{2v} symmetry. The constant term $2(\sigma_R{}^0\text{ as} - \sigma_R{}^0\text{x})$ can be determined for asymmetric substituents if $\sigma_R{}^0\text{x}$ (see Table I) is known. This can be derived from eq 30 and 31, where $A_{\text{para-as/as}}$

$$A_{\text{mono-as}} = 17\,600[(\sigma_R{}^0\text{x})^2 + (\sigma_R{}^0\text{y})^2] + 100 \qquad (30)$$

$$A_{\text{para-as/as}} = 30\,000(\sigma_R{}^0\text{y})^2 + 170 \qquad (31)$$

refers to the para-substituted benzene having two identical asymmetric substituents. Values of $\sigma_R{}^0\text{x}$ and $\sigma_R{}^0\text{y}$ are listed in Table I for some common substituents. Values of the constant term in the correction factor vary from zero to 0.030 (CO_2Me). Some other values are: OMe, −0.006; COMe, 0.006; CO_2Et, 0.014, and CHO, 0.022. Even in the presence of a second strongly resonance-interacting group the asymmetry correction factor is small; for example, for *p*-fluorobenzaldehyde it is only 0.0075 and contributes only 103 units to the overall intensity (calculated as 2900 L mol^{-1} cm^{-2}). The correction can therefore normally be neglected.

3. Substituent–Substituent Interactions

When one substituent is a resonance donor and one an acceptor (p or d orbital), additional resonance interaction can occur as shown in **2**. We take this into account by introducing an additional term λ into eq 28, thus deriving eq 32.

$$A_{\text{para}} = 15\,000[\sigma_R{}^01 - \sigma_R{}^02 + \lambda]^2 + 170 \qquad (32)$$

The interaction term λ can thus be measured and, indeed, it is found[28,48] that λ increases with the donating ability of the donor or accepting ability of the resonance withdrawing group. We have further found[28,48] empirically that λ can be described by eq 33 and 34. Equation 33 applies to *p*-orbital acceptors, such

$$\lambda = K_A(\sigma^+\text{D} - \sigma^0\text{D}) \qquad (33)$$

$$\lambda = K_X\sigma_R{}^0\text{D} \qquad (34)$$

as cyanide or carbonyl group substituents, and eq 34 to d-orbital acceptors such as chlorine or bromine atoms. We find empirically[48] that eq 35 can be used in the place of eq 33 for donor substituents where σ^+D is unknown.

$$\lambda = 6.5\sigma_R{}^0A(\sigma_R{}^0\text{D})^2 \qquad (35)$$

The σ^+D, σ^0D, and $\sigma_R{}^0$D refer to the donor substituent while K_A and K_X are constants characteristic of a particular p- or d-

TABLE III. Electronic Constants for Some Common Substituents

	σ_R^0	$\sigma^+ - \sigma^0$	K_A	K_X
NMe_2	−0.53	−1.26		
ND_2	−0.47	−0.92		
OMe	−0.43	−0.66		
OH	−0.40	−0.79		
F	−0.40	−0.24		
SMe	−0.25	−0.57		0.51
Cl	−0.22	−0.11		0.22
Br	−0.23	−0.16		0.32
I	−0.22	−0.14		0.43
Me	−0.10	−0.16		
t-Bu	−0.13	−0.06		
NMe_3^+	−0.15	−0.40	0.13	
CN	0.09		0.13	
CF_3	0.11		0.08	
CO_2Et	0.18		0.14	
COMe	0.22		0.16	
CHO	0.24		0.25	
$SiMe_3$	0.02			0.43
SO_2Me	0.06			0.49

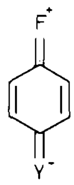
orbital acceptor. We have treated[28] a large amount of data by a combination of eq 32 and eq 33 or eq 34 and find remarkable consistency in derived K_A and K_X values. These are tabulated for some common substituents together with σ_R^0 and $\sigma^+ - \sigma^0$ values in Table III.

The values of K_A and K_X thus provide quantitative estimates of the ability of acceptor groups to enter into through-conjugation with donors. They really refer only to the solvent employed but will be almost constant for the relatively nonpolar solvents mostly used.

In Figure 7 we show a graph of $[(A - 170)/15\,000]^{1/2}$ against $[\sigma_R{}^0 1 - \sigma_R{}^0 2 + \lambda]$ for all para-disubstituted benzenes for which data are available. The λ values were zero or calculated from eq 33 or 34 as appropriate. The excellent correlation provides strong evidence for the utility of the approach adopted.

4. Para-Substituted Fluorobenzenes

The successful application of eq 32–34 includes para-substituted fluorobenzenes. Thus clearly contributions from **18** are



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important in the overall structure. This indicates that the fluorine-19 shifts in such compounds will not only measure the resonance interaction of the substituent as felt at the para position, but also some contribution from through-conjugation. Thus σ_R^0 values derived as differences in the shifts of correspondingly substituted para- and meta-substituted fluorobenzenes, on the assumption of cancellation of resonance effects, will be enhanced to this extent. A careful analysis[28] vs. infrared derived figures leads to eq 36 and gives extra support for the value of

$$(A - 170)^{1/2} = b^{1/2}[\sigma_R{}^0(\text{NMR}) - 0.34] \qquad (36)$$

b used in deriving eq 28 and 32. For cases where no interaction is possible, the ^{19}F and IR derived values are almost identical.

5. ν_{19} Vibrations

We have also reported[38] ν_{19a} intensities for a considerable number of para-disubstituted benzenes. The intensities in $A^{1/2}$ units are linear against the sum of the corresponding values for the corresponding monosubstituted benzenes, the intercept corresponding to the CH bonding contribution of the four aromatic CH groups. The appropriate equation is (37). For the ν_{19}

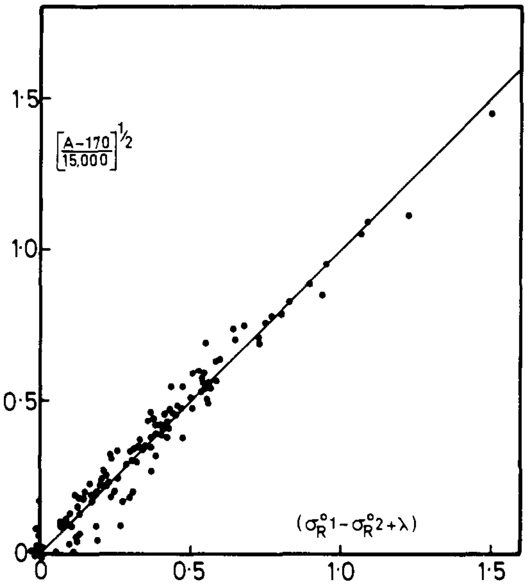


Figure 7. Plot of $[(A - 170)/15\,000]^{1/2}$ against $[\sigma_R{}^0 1 - \sigma_R{}^0 2 + \lambda]$ for para-disubstituted benzenes.

$$A_{\text{para}} = 1.02(A_X{}^{1/2} + A_Y{}^{1/2}) - 15.8 \qquad (37)$$

vibration the intensity is always increased by para substitution whether the second group is of the same or opposite resonance interaction as the first, and this can be demonstrated[38] to be reasonable in terms of the antisymmetric nature of the vibration.

Another interesting feature is that there is no enhancement in the intensities compared to the corresponding monosubstituted compounds where one substituent is a strong donor and one is a strong acceptor. This again arises because of the nature of the vibration; through-conjugated forms can be shown to introduce no extra dipole transition moment. However, if the polar effect of one group caused an increase in the resonance interaction of the other (the field-induced resonance effect, section IV.D), then an enhancement would be expected; the present results thus argue against other than a fairly small field-induced resonance effect in such compounds.

III. Heteroaromatic Molecules

Certain heteroaromatic molecules such as pyridine, thiophene, and furan have ring-breathing modes analogous to the ν_8 and ν_{19} absorptions of benzene. We have investigated the use of such vibrations which provide useful information on resonance interactions. However, certain limitations arise since the ring heteroatom can itself act as a pseudo-substituent and be involved in specific interactions with added substituents.

A. Substituted Pyridines and Pyridine *N*-Oxides

We have measured[50] the intensities of the ring breathing modes near 1600 cm^{-1} for several N-substituted pyridines and for series of 2-, 3-, and 4-substituted pyridines and 4-substituted pyridine *N*-oxides. The intensities for pyridine and N-substituted derivatives have been used to obtain effective σ_R^0 values for the ring nitrogen or N-substituted nitrogen treated as pseudo substituents. The ring nitrogen is a moderately strong electron-withdrawing substituent ($\sigma_R^0 = 0.24$) in these terms while the *N*-oxide group is a "donor" ($\sigma_R^0 = -0.21$). There is little increase in resonance withdrawal in the *N*-methylpyridinium cation compared to pyridine in agreement with other evidence.

The 4-substituted pyridines may be considered as a special type of para-disubstituted benzene using the $\sigma_R{}^0$ values for the ring nitrogen derived above.[50] Resonance electron-donating substituents lead to enhancement indicative of mutual interaction, and a K_A value of 0.12 has been derived.[28] In 4-substituted pyridine 1-oxides, the *N*-oxide group can behave both as a donor with a ($\sigma^+ - \sigma^0$) value of 0.60, or as an electron acceptor, depending on the nature of the substituent.

The intensities for 2- and 3-substituted pyridines can also be treated as for ortho- and meta-disubstituted benzenes. However the agreement is not precise, and it would be unwise to use the method to predict the preferred conformers of substituents such as acetyl which can lead to cis and trans forms.

B. Five-Membered Heteroaromatics

1. Furan

In collaboration with Professor Chaillet we have used[51] the CNDO/2 theoretical method developed for the benzenes to calculate the intensities and frequencies of the three ring-breathing modes (ν_5, ν_6, ν_{15}) of furan and some 2-substituted furans. The method gave intensities of the right order for many of the substituents and vibrations.

In a more empirical study we had previously measured[52] the intensities of these three vibrations for a considerable number of 2-substituted furans. From the form of the vibration and valence-bond representations we empirically derived equations to link the intensities with the $\sigma_R{}^0$ value of the substituent, an effective $\sigma_R{}^0$ value for the furan oxygen, and a term for mutual interaction. The possibility of rotational isomerism with unsymmetrical substituents such as acetyl further complicates the analysis. Nevertheless, the approach is fairly successful in explaining intensities for the ν_{15} and ν_6 vibrations and leads to an effective $\sigma_R{}^0$ value of -0.13 for furan. The success of the method is shown in Figure 8 where the line is drawn to follow eq 38. The values of λ were calculated from eq 34 and 35 using

$$A_{\nu 15(\text{furan})} = 38\,400(\sigma_R{}^0 + \lambda)^2 + 110 \qquad (38)$$

$\sigma_R{}^0$(furan) as -0.13. Thus, the K_A and K_X values derived from benzenes are seen to be also applicable here.

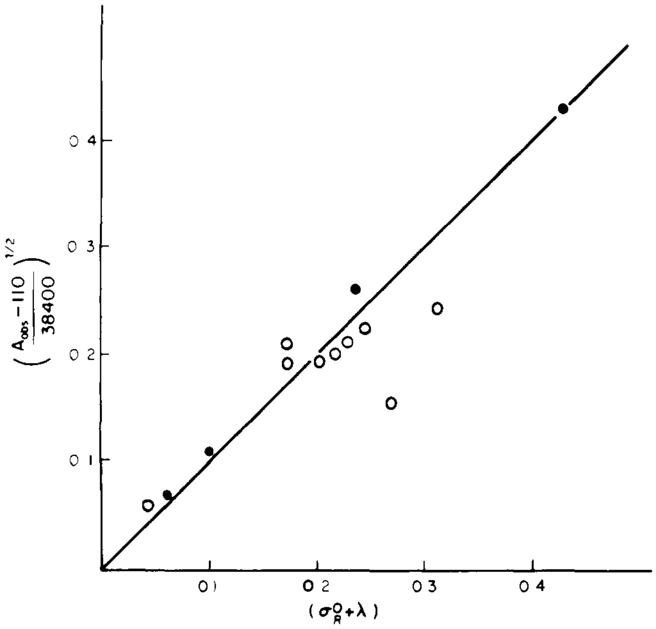


Figure 8. Plot of $[(A_{\text{obsd}} - 110)/38\,400]^{1/2}$ against $[\sigma_R{}^0 + \lambda]$ for ν_{15} for 2-substituted furans: ●, donor substituents; ○, π-acceptors.

2. 2-Substituted Thiophenes and Selenophenes

The corresponding intensities of an extensive series of 2-substituted thiophenes have been successfully treated[52] in an analogous fashion to that used for the 2-substituted furans. Rotational isomerism is more important here, particularly for compounds with a carbonyl group attached to the ring. A value of $\sigma_R{}^0 = -0.14$ was derived for the effect of the S-atom in the thiophene ring. Recent work[53] has shown that the method is also applicable to 2- and 3-substituted selenophenes. The integrated intensities of the ν_{15} and ν_5 vibration of both series and the ν_6 vibration of the 2-substituted compounds can be accounted for in terms of additive contributions with directional properties estimated from resonance theory or treated as regressional parameters. While direct interactions between the selenium and the substituent almost certainly occur, they do not seem generally important. Thus the main conclusion from the application of our method to these compounds is to show that resonance interactions here are analogous to those in benzenes and can be reasonably predicted.

IV. Ethylenes

Much of the work on substituent effects in general and on resonance interactions in particular has centered on benzene derivatives. Nevertheless results for substituted ethylenes further illustrate and develop certain important concepts. Furthermore the equations and concepts are much simpler in this series.

The very limited contributions made by physical and chemical methods, other than infrared spectroscopy, to the study of resonance interactions in substituted ethylenes have recently been summarized elsewhere.[54]

At the theoretical level, surprisingly few ab initio calculations are available for substituted ethylenes. However, a series of CNDO/2 calculations have been performed,[24] and these should be meaningful as far as charge density effects are concerned since such calculations on benzenes[24] closely parallel results[20,55] at the ab initio level. The overall π-electron transfer between the substituent and the ethylene group closely parallels $\sigma_R{}^0$ values; in fact, DSP treatment gives[54] eq 39, demonstrating

$$\Sigma\Delta q_\pi = -0.05\sigma_I + 1.57\sigma_R{}^0 \qquad (39)$$

the small and probably nonsignificant dependence on σ_I. Clearly then it appears reasonable to interpret $\sigma_R{}^0$ here in terms of ground-state π charge transfer as was found for benzene derivatives. The change in π-electron population at the α or β atoms with substituent is considerably dependent on σ_I as well as $\sigma_R{}^0$ as has also been found[20] for individual positions in substituted benzenes.

Within this framework we now consider the results of infrared intensity investigations. The vibration employed is the C=C stretching mode (ν_2) that occurs near 1640 cm^{-1} in substituted ethylenes. This is a planar vibration[32] involving motion of the π-bonded carbon atoms with little motion associated with the substituent; it is fairly similar in mono- and disubstituted compounds.

A. Monosubstituted Ethylenes

The measured intensities of the ν_2 vibrations of an extensive series of monosubstituted ethylenes[56] were shown to generally follow $(\sigma_R{}^0)^2$ (see Figure 9), eq 40 being appropriate, correlation coefficient 0.998 (18 points).

$$A_{\text{eth}} = 27\,100(\sigma_R{}^0)^2 + 80 \qquad (40)$$

The 80 L mol^{-1} cm^{-2} constant was ascribed to an overtone vibration. Possible variation in this would restrict the use of eq 40 to estimate $\sigma_R{}^0$ values for low intensities; such uncertainty has been estimated[56] at 7% in $\sigma_R{}^0$ values of 0.10 rising to 30% at 0.05. This apart, however, the relationship both shows that

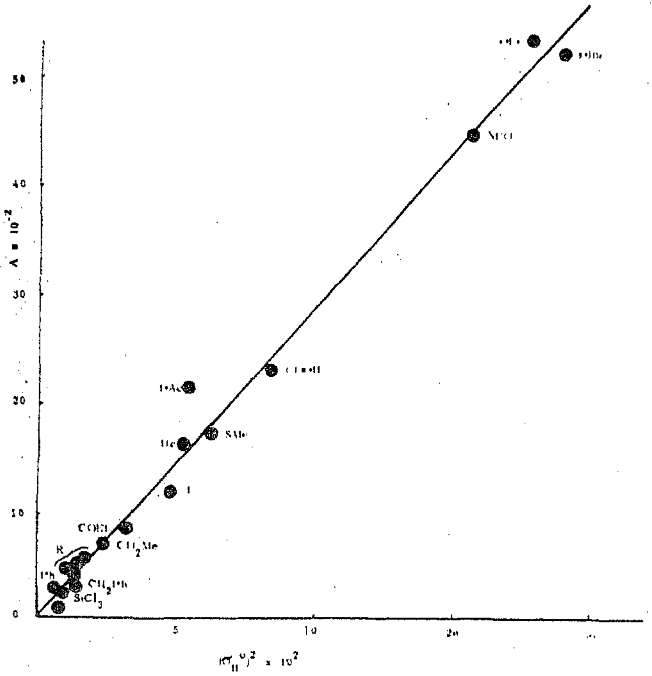
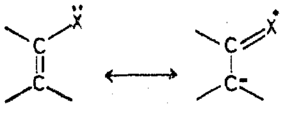


Figure 9. Integrated intensity of the IR C═C stretching vibration for monosubstitued ethylenes plotted against $(\sigma_R^0)^2$.

resonance interactions in ethylenes closely parallel those in benzenes and provides a convenient way of determining or checking σ_R^0 values.

The only substituents for which significant deviations are found are COH and COR where rotational isomerism significantly intervenes as is covered in section VI.B.

The intensities thus seem to depend solely on π-electron charge transfer, and this can be visualized in simple resonance concepts. Thus as the vibration occurs the CC bond expands and contracts leading to a change in π transfer. For the extended form, the contribution of canonical form **20** to the overall structure should be greater than at the other extreme since the CC distance is greater. Thus one expects the change in dipole during the vibration to be affected by the resonance interactions and, if σ electron and atomic polarizability terms are either small or cancel, to be proportional to such interactions. Indeed one would not expect any great change in dipole from σ effects here since the CX bond is not greatly altered in the vibration.



19 20

The method, together with results for corresponding vibrations in substituted benzenes, allows the ready estimation of σ_R^0 for a wide variety of substituents although results from monosubstituted ethylenes do not give the direction, as against the magnitude, of the charge transfer.

Intensity studies on systems when the substituent Y is removed from the double bond by one or more methylene groups provide further information. A substituent CH_2X can have "resonance" interactions with a π system since the orbitals in the two CH and the CX bonds are not orthogonal to the π system unless the bonds are coplanar with the plane of the ethylene group. This "hyperconjugation" leads to charge transfer between the π system of the ethylene group and the σ system of the CH_2Y group. The σ_R^0 figures in Table IV are derived from the intensity studies using eq 40 and show significant variation with change in Y. The interaction of such CH_2X groups has also been studied in benzene derivatives and is more fully discussed in section VI.B.

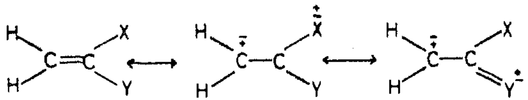
TABLE IV. σ_R^0 Values for Substituents of Type $(CH_2)_nX$

X	$n = 1$	$n = 2$[a]	$n = 3$[a]
n-Pr	−0.12		
NMe_2	−0.10		
OCOMe	−0.08		
Cl	−0.04	−0.10	−0.13
Br	−0.02		−0.12
I	−0.05		
OH	−0.06	−0.16	−0.13
OMe	−0.04		
OEt	−0.06		
SMe	−0.10		
SBu	−0.05[a]	−0.13	−0.15
SO_2Bu	−0.09[a]	−0.23	−0.14
NCO	−0.06		
NCS	−0.07		
CN	−0.09	−0.11	−0.12
Ph	−0.10		

[a] Calculated from intensity data of M. Podzimková, M. Procházka, and M. Paleček, *Collect. Czech. Chem. Commun.*, **34**, 2101 (1969).

B. 1,1-Disubstituted Ethylenes

The form of the $\nu_{C=C}$ vibration in 1,1-disubstituted ethylenes is very similar[57] to that in monosubstituted ethylenes. Thus in the 1,1-disubstituted ethylenes, the intensity arises as a consequence of the changing weights of contributing canonical forms **22** to **23** during the vibration resulting in an oscillating dipole moment. This dipole moment results from the superposition of two vectors, one associated with the interaction of each of the substituents and the double bond. Equation 20 applies here but it is not possible to obtain the angle θ for each compound, and it was therefore assumed that an average angle could be found applicable to the entire series. A regression analysis showed[57] that this angle was close to 90°, meaning that the cosine terms could be neglected. The best fit gave rise to eq 41.



21 22 23

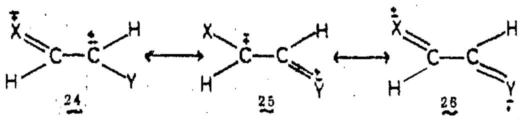
$$A = 24\,100[(\sigma_R^0 1)^2 + (\sigma_R^0 2)^2] + 60 \qquad (41)$$

The plot obtained of A vs. $(\sigma_R^0 1)^2 + (\sigma_R^0 2)^2$ is very good, suggesting little systematic substituent–substituent interaction. The difference in slope to eq 40 probably arises from small changes in the form of the vibration.

C. 1,2-Disubstituted Ethylenes

The motion of the heavy skeleton in 1,2-disubstituted ethylenes is again found[58] to be essentially identical with that of the monosubstituted compounds. Intensity data have been reported[58] by us for several cis-1,2-disubstituted ethylenes, but, although a correlation with σ_R^0 constants was obtained according to a somewhat complex equation, insufficient data were available to carry out any complete treatment.

By contrast we were able to measure[58] the intensities of quite an extensive series of trans-1,2-disubstituted ethylenes. The intensities can be understood in terms of the changing significance of the polar resonance structures **24–26** during the vibration, including the "through-resonance" structure **26** which



24 25 26

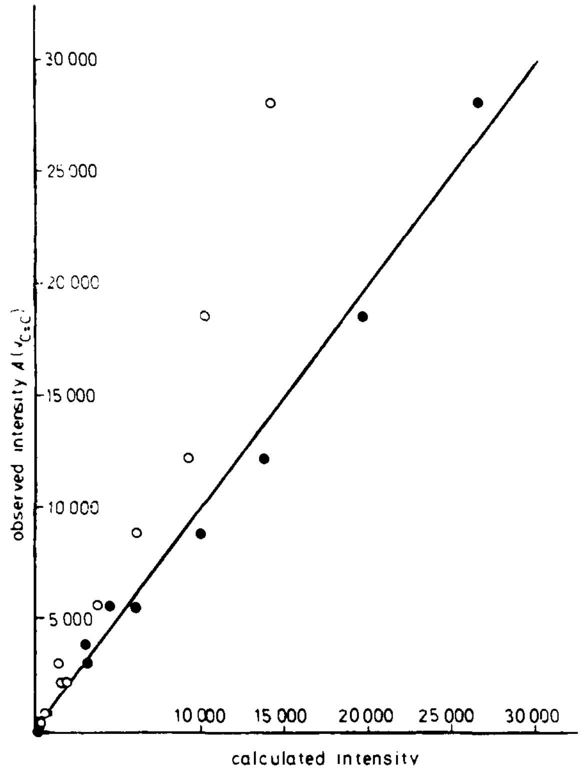


Figure 10. Plot of observed intensities in trans-1,2-disubstituted ethylenes against those calculated from the equation $A = 26\,500(\sigma_R{}^01 - \sigma_R{}^02 + 1.5\lambda)^2 - 7$ with λ deduced from para-disubstituted benzenes (●) and λ = 0 (○). The line is that of unit slope.

has no analogy in the 1,1-disubstituted ethylene series. When the two substituents are identical and symmetrical, the molecule has C_{2h} symmetry, and the vectors describing the interaction of each substituent with the double bond add at 180°. In the general case the angle θ (eq 20) may differ somewhat from 180° although large deviations are not expected.

The structure characteristic of mutual interaction **26** will also contribute varying weight during the vibration and thus affect the overall intensity. In order to account for this, an interaction term δ is included in the description, leading to eq 42 where θ is assumed to be 180°. Here δ is an interaction constant in the units of $\sigma_R{}^0$ and characteristic of a given pair of substituents. We derived a similar interaction term (λ) from our work on para-disubstituted benzenes (section II.E), and it has been shown empirically[58] that the intensities for the trans-1,2-disubstituted ethylenes fit eq 43, thus $\delta = 1.5\lambda$. Figure 10 shows a plot of

$$A = a[\sigma_R{}^01 - \sigma_R{}^02 + \delta]^2 + C \qquad (42)$$

$$A = 26\,500[\sigma_R{}^01 - \sigma_R{}^02 + 1.5\lambda]^2 \qquad (43)$$

these data together with values calculated with λ = 0. The displacement of the points for a given compound thus illustrates the contribution made by the mutual conjugation term. In the extreme case studied, the mutual interaction of the strong donor NMe_2 with the strong acceptor CO_2Me accounts for half of the observed intensity. The λ values thus provide a good guide to such interactions as discussed in section II.E. The greater importance of such mutual interactions in ethylenes compared to para-disubstituted benzenes is in accord with theoretical calculations which show greater substituent induced π-charge changes at the β position to a substituent in ethylenes than at the para position in benzenes.

The overall slope of the correlation line (eq 43) is extremely close to that correlating the monosubstituted compounds (eq 40) which is indicative of an almost exactly additive π-electron perturbation by the substituents. Thus the substituents appear to exert their normal resonance effect as far as the double bond is concerned even where considerable mutual interaction occurs. This is in accord[54] with the additivity of ^{13}C chemical shifts at the ethylenic carbon atoms in such compounds. In other words π-charge changes at ethylenic carbon atoms seem to be unaffected by any additional mutual interaction between substituents. We return to this subject in section IV.D.

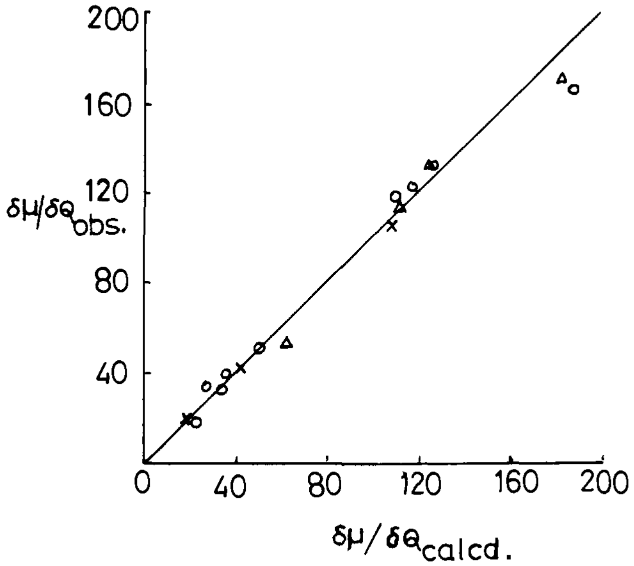
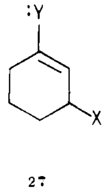


Figure 11. Comparison of observed and calculated values of $\partial\mu/\partial Q$ (esu) for mono- (●), 1,1-di- (○), trans-1,2-di- (△), and cis-1,2-disubstituted (X) ethylenes.

One other aspect of this work concerns the reliability of theoretical calculations as far as charge density effects are concerned. The calculations are usually referred to measured dipole moments, but such values are not numerous for ethylenes, particularly disubstituted compounds. However, we have shown that for both mono-[32] and disubstituted[57,58] ethylenes, one can calculate dipole transition moments by the CNDO/2 method that are in good agreement with experimental values; this is shown in Figure 11. This suggests that the CNDO/2 charge distributions are reliable. (The slope in Figure 11 is the theoretical one of unit slope, not the best fit. Points for C═C—C═O compounds where coupling may affect infrared intensities are the only data not included.)

D. Substituted Cyclohexenes

Compounds of type **27** and **28** provide[59] a good test of the influence of one reasonably remote substituent X on the resonance interaction of another (Y) with an ethylenic π system. Thus a highly polar X group, such as cyano, might increase the interaction of an electron resonance donating substituent Y by increasing the importance of the canonical form **29.** This would be expected to result in an increase in infrared intensity over that for the unsubstituted compound **30** (other work[59] shows that the



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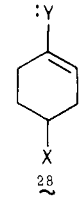

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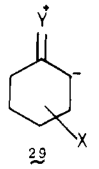

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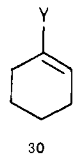

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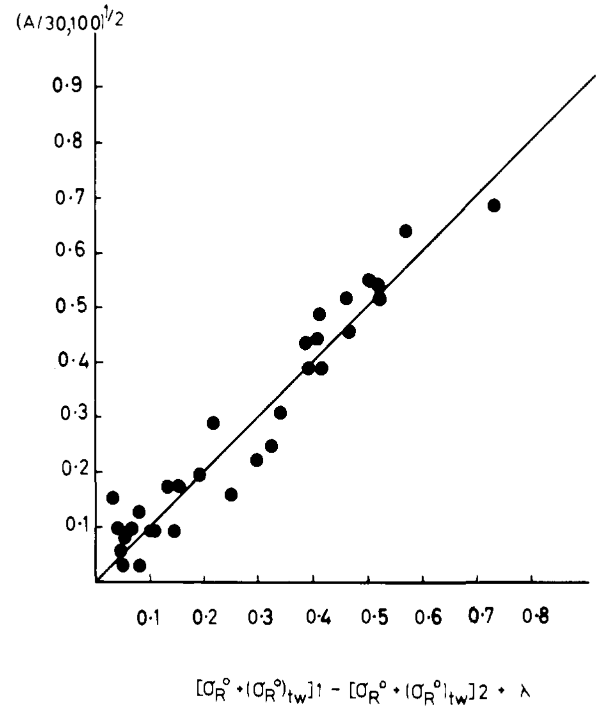


Figure 12. Plot of $(A/30\ 000)^{1/2}$ for all disubstituted acetylenes against $[\sigma_R{}^0 1 + (\sigma_R{}^0 1)_{tw} - \sigma_R{}^0 2 - (\sigma_R{}^0 2)_{tw} + \lambda]$.

intensity of the $\nu_{C{=}C}$ vibration in cyclohexene itself is little affected by a 3- or 4-substituent).

We have studied[59] compounds where Y = OMe and Cl and X = CN, H, or Me and find evidence for such *field-induced resonance effects*; however, the apparent absence of significant contribution from field-induced resonance to overall electronic effects in disubstituted benzenes argues for caution in interpretation of the cyclohexene results. Indeed carbon-13 study[60] of the substituted cyclohexenes does not confirm the results although one must be very careful in relating such shifts directly to electron densities. Initial results of a Raman investigation[61] currently in progress, however, appear to support field-induced resonance in substituted cyclohexenes.

V. Acetylenes

Much less information is available[33] from other work concerning resonance interactions in substituted acetylenes than in the corresponding benzenes or even ethylenes. The $\nu_{C\equiv C}$ absorption is in a region of the spectrum fairly isolated from other bands and within a series of mono-[33] or disubstituted acetylenes[62] has been shown to be relatively free from mass effect or Fermi resonance problems. However, the form of the vibration is somewhat different between acetylene itself, a monosubstituted derivative, and a disubstituted derivative.

The $\nu_{C\equiv C}$ absorption is analogous to the ethylene and benzene vibrations previously described in that it should be mainly affected by the resonance interactions of the substituents with the triple bond. We have shown[33] that, as with the other systems, theoretical calculations of the CNDO/2 type can reasonably assess the intensities. The calculations also show that the intensities are fairly independent of small changes in the form of the vibration. As far as the empirical approach is concerned, however, an additional feature here is the presence of two orbitals for the substituent to interact with. If we consider only the one that interacts to give the best resultant energy, then $\sigma_R{}^0$ is the appropriate term since the substituent orbital will be at the preferred geometry for maximum interaction. However, at the same time, there will be a second 2p orbital on the acetylenic carbon at 90° to this; here the $(\sigma_R{}^0)_{tw}$ values (section II.B) will be appropriate. Thus a more accurate empirical description here will include both $\sigma_R{}^0$ and $(\sigma_R{}^0)_{tw}$. For monosubstituted acetylenes there turns out[33] to be little to choose empirically between using $\sigma_R{}^0$ alone or both $\sigma_R{}^0$ and $(\sigma_R{}^0)_{tw}$, but for the disubstituted acetylenes[62] the latter approach is better.

A. Monosubstituted Acetylenes

We have measured[33] the intensities of the $\nu_{C\equiv C}$ vibration for some 20 monosubstituted acetylenes. Approximate treatment using $\sigma_R{}^0$ alone gave eq 44. The constant 0.05 is presumably

$$A^{1/2} = 217(\sigma_R{}^0 + 0.05) \qquad (44)$$

required because of the variation in the form of the normal vibration compared to acetylene itself: the correlation coefficient was 0.992 for 18 points. Concurrent use of $\sigma_R{}^0$ and $(\sigma_R{}^0)_{tw}$ gave eq 45, correlation coefficient 0.989, and thereby eq 46 which

$$A^{1/2} = 162[\sigma_R{}^0 + (\sigma_R{}^0)_{tw} + 0.14] \qquad (45)$$

$$A = 26\ 250[\sigma_R{}^0 + (\sigma_R{}^0)_{tw} + 0.15]^2 \qquad (46)$$

we regard as the appropriate working equation. The equations are particularly useful to derive $\sigma_R{}^0$ values for substituents having other vibrations close to 1600 cm^{-1} and thus not being determinable from benzene or ethylene data. Thus we have derived a $\sigma_R{}^0$ value of 0.14 for the $CONH_2$ substituent. We have also shown that literature data can be similarly treated although these figures may be less reliable in terms of procedures used for the integration.

B. Disubstituted Acetylenes

We have made[62] similar measurements for series of 2-substituted *tert*-butylacetylenes and phenylacetylenes. Here it is clearly preferable to use both $\sigma_R{}^0$ and $(\sigma_R{}^0)_{tw}$; the equation derived with $\sigma_R{}^0$ alone predicts an intensity for a symmetrically disubstituted acetylene. Analysis leads to eq 47 and 48 for the

$$A^{1/2} = 181\{[\sigma_R{}^0 + (\sigma_R{}^0)_{tw}] - [\sigma_R{}^0 + (\sigma_R{}^0)_{tw}]\mathrm{Bu}^t + 0.01\} \qquad (47)$$

$$A^{1/2} = 233\{[\sigma_R{}^0 + (\sigma_R{}^0)_{tw}] - [\sigma_R{}^0 - 0.06]\mathrm{Ph}\} \qquad (48)$$

tert-butyl and phenyl series, respectively, with correlation coefficients of 0.992 and 0.983, respectively.

The two equations can be combined in terms of mutual interaction between substituent and phenyl group in the second series by use of eq 49. A graph of eq 49 for points in both series is shown in Figure 12.

$$A = 30\ 000\{[\sigma_R{}^0 + (\sigma_R{}^0)_{tw}]1 - [\sigma_R{}^0 + (\sigma_R{}^0)_{tw}]2 + \lambda\}^2 \qquad (49)$$

VI. Substituent Effects

A. Values of $\sigma_R{}^0$

We intend to discuss substituent resonance interactions in terms of their ground-state magnitude, as measured by $\sigma_R{}^0$ values, and in terms of their changed response under conditions of π-electron demand or surplus as measured by K_A, K_X, and $\sigma^+ - \sigma^0$ values. We therefore first need to look at the various scales of $\sigma_R{}^0$ to establish the individual values that we then discuss.

The four basic methods of obtaining $\sigma_R{}^0$ values are the following.

(i) The analysis of reactivity or equilibrium data for reaction series of aromatic molecules where enhanced resonance effects are not anticipated. A typical example is the analysis[12] of data for the acidity of substituted phenylacetic acids. The $\sigma_R{}^0$ scale can be obtained[12] from a statistical analysis of several sets of such data using the DSP equation[11,12] (50), where P is the data in energy units (log K or log k), the values of σ_I are taken from

$$P - P^0 = \rho_I\sigma_I + \rho_R\sigma_R{}^0 \qquad (50)$$

other work, and the values of σ_R^0 are assumed for a few substituents of low polarizability to be the same as σ_R (BA).

(ii) The σ_R^0 values can be derived empirically[19] from the difference in the ^{19}F chemical shifts of correspondingly substituted meta- and para-substituted fluorobenzenes using eq 51.

$$\sigma_R^0 = -0.34\left(\int_H^{p-X} - \int_H^{m-X}\right) \qquad (51)$$

(iii) As discussed above, the σ_R^0 values can be derived from infrared intensity data from mono- or meta-disubstituted benzenes, or from substituted ethylenes or acetylenes.

(iv) It has been shown[20] that σ_R^0 values are proportional to ab initio calculated overall π-electron transfer between a substituent and the ring in monosubstituted benzene. It has recently[25] been proposed that such values might provide the most basic definition of σ_R^0 and would be put on the correct scale by using eq 4.

The substituents whose σ_R^0 values have been established by methods i and iv are limited to the common groups; considerably more have been determined by method ii, while σ_R^0 values for nearly 200 substituents are available from method iii.

We first compare σ_R^0 values for some common substituents in Table V. Values for $(\sigma_R^0)_{lw}$ are also listed here for convenience. It can be seen that the infrared determined values are in good general agreement with those determined by other methods. Furthermore, the significant differences found for the ^{19}F figures for acceptor groups (p or d orbital) such as iodine or cyanide can be explained in terms of contributions of type **18**. Thus, until a theoretically derived scale is established it is preferable to use our infrared derived values as standard. In Table VI we list such values for 187 substituents; they are derived from substituted benzenes, ethylenes, or acetylenes as shown. The values in this table are used in the discussion below.

B. C-Linked Substituents

1. Alkyl and Substituted-Alkyl Groups

Here we consider intramolecular resonance interactions between π systems and alkyl groups including all substituted-alkyl groups except where the β substituent is linked by a metal atom (section VI.D).

The data in Table VI show that simple alkyl groups are all weak resonance donors. The effect is somewhat greater in longer chain alkyl groups such as octyl and in secondary or more so in tertiary alkyl groups. The bridgehead substituents 1-bicyclo[2.2.2]octyl and adamantan-1-yl are particularly enhanced as is cyclopropyl. These findings are in agreement with other work, but we have found[63,64] further from results in para-disubstituted benzenes that resonance interactions of the larger alkyl groups are also more sensitive to the electron demand of the π system than the smaller groups such as methyl. Thus the response of the adamantan-1-yl substituent is quite sensitive to the para substituent; in other words it is quite polarizable. These results are supported by recent gas-phase studies of the effect of alkyl substituents on the stabilities of some anions and cations. This evidence shows[64] that the reversed order of polarizability found in reactions such as the ionization of substituted-phenyl dimethylcarbinyl chlorides, where a *p*-methyl substituent aids the reaction more than a *p-tert*-butyl group, must arise because of steric inhibition of solvation. This is further supported[65] by the negligible extra effect in such a reaction given by a bridgehead alkyl group compared to the effect in a less electron-demanding situation.

The resonance effect of the neopentyl substituent remains anomalous. It is the weakest donor of all unsubstituted alkyl groups, and its effect is not greatly enhanced in situations of electron demand.

TABLE V. σ_R^0 Values for Some Common Substituents[a]

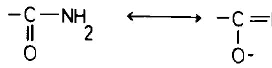
	Reactivity	^{19}F	IR Ph	IR Et	Theor	$(\sigma_R^0)_{lw}$
NMe_2	−0.52	−0.54	−0.53			−0.13
NH_2	−0.48	−0.48	−0.47		−0.48[b]	−0.13
OMe	−0.41	−0.43	−0.43		−0.45	−0.23
OH	−0.40	−0.43	−0.40		−0.44	−0.26
F	−0.35	−0.32	−0.34		−0.34	−0.34
Cl	−0.20	−0.18	−0.22			−0.22
Br	−0.19	−0.16	−0.23	−0.24		−0.23
I	−0.12	−0.14	−0.22	−0.20		−0.22
SMe	−0.24	−0.17	−0.25	−0.24		−0.05
t-Bu		−0.17	−0.13	−0.13		−0.13
Me	−0.10	−0.15	−0.10		−0.03	−0.10
CF_3	0.08	0.10	0.11		0.05	0.11
CN	0.10	0.21	0.09	0.04	0.10	0.10
CHO		0.27	0.24	(0.06[c])	0.14	0.0
COMe	0.18	0.19	0.22	(0.15[c])	0.12	0.0
CO_2Et	0.12	0.19	0.18			0.0
NO_2	0.16	0.19	0.17	0.17	0.13	0.0
$CONH_2$				0.14[d]	0.10	

[a] Appropriate for inert solvent. [b] Estimated from actual geometry. [c] Affected by rotational isomerism. [d] From acetylene data.

The presence of electronegative groups, Y, in substituents CH_2Y, CHY_2, and CY_3 reduces and then reverses the resonance effect; thus for CH_2Cl, $\sigma_R^0 = -0.03$; $CHCl_2$, +0.02; CCl_3, +0.07. There are sufficient such results to allow the determination of a K_A value of 0.08 for the CF_3 substituent. Such groups also show[64] variable resonance interaction depending on the electron demand of the system; indeed the CF_3 and CCl_3 groups can act as electron donors in conditions of sufficiently high electron demand. We have argued elsewhere[64] that this is strong evidence that the major effect is on the charge transfer between the π system produced and the CF_3 group (hyperconjugation) although there is evidence[64] from other sources that the polarity of such groups may affect the resonance interaction of the second substituent with the ring (field-induced substituent effect).

2. Acyl Substituents

Substituents of type COY and CO_2R are all weak to moderate electron acceptors by resonance. The $CONH_2$ substituent is a weaker acceptor than say COMe as expected because of contribution of the canonical form **32** which lessens the resonance accepting capabilities of the group.

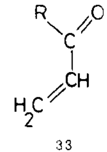


$$\underset{\substack{\| \\ O}}{-C}-NH_2 \longleftrightarrow \underset{\substack{| \\ O^-}}{-C}=\overset{+}{N}H_2$$

31 **32**

Steric effects diminish the resonance interaction in substituents COR when R is large. Thus we have used[66] the reduction in σ_R^0 values in this series to estimate the twisting out of the plane of the benzene ring of groups such as COEt, COPr-*i* and COBu-*t* assuming that CHO or alternatively COMe is in the plane. Thus the COBu-*t* is estimated to be 33–37° out of plane. The values obtained are in agreement with figures derived from other methods.[66,67]

The results from such studies on acylbenzenes have been used[66] to investigate the relative amounts of s-trans (**33**) and s-cis (**34**) conformations in vinyl ketones. The results from in-



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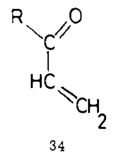

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TABLE VI. Infrared Derived $\sigma_R{}^0$ Values[a]

Subst	$\sigma_R{}^0$	Subst	$\sigma_R{}^0$	Subst	$\sigma_R{}^0$
		SMe_2^+	−0.09	NPh_2	−0.44
H	0.00	SCF_3	0.00	$N(CF_3)_2$	±0.13
D	0.00	SCOMe	±0.08	$NHNH_2$	−0.49
F	−0.34	S^-Na^+	−0.033[c]	$(NH)_2Ph$	−0.44
Cl	−0.22	$SO_2^-Na^+$	0.00[c]	NHOH	−0.22
Br	−0.23	$SO_3^-Na^+$	0.00[c]	NMeCOMe	−0.42
I	−0.22	SOMe	−0.07[e]	NHCOMe	−0.42
ICl_2^+	+0.12	SO_2Me	+0.06[e]	NO	+0.25[f]
IPh_2^+	+0.28[b]	SO_3Me	+0.07[d]	$N{=}NPh$	±0.06
OH	−0.40, −0.42[c]	SOPh	±0.07	NCO	−0.40
OMe	−0.43	SOBu-*t*	0.0	NCS	−0.35
OEt	−0.43, −0.43[d]	SO_2Bu-*t*	+0.10	NSO	−0.09
OPr-*n*	−0.43	SO_2Ph	+0.06	NCNPh	−0.46
OPr-*i*	−0.43, −0.43[d]	SO_2Cl	+0.11	NO_2	+0.17
OBu-*n*	−0.43, −0.44[d]	SO_2CHCH_2	+0.03[d]	$N_2^+BF_4$	+0.29[c,e]
OBu-*t*	−0.34, −0.43[d]	SePh	−0.19	$ND_3^+Cl^-$	−0.19[c,e]
OPh	−0.36	ND_2	−0.47	$ND_2Me^+Cl^-$	−0.15[c]
OCOMe	−0.24	NHMe	−0.52	$NDMe_2^+Cl^-$	−0.14[c]
$OCOCF_3$	−0.23	NDMe	−0.52	$NMe_3^+Cl^-$	−0.14[c,e]
OCF_3	−0.25	NMe_2	−0.53	$NDCMeNDPh^+Cl^-$	−0.59[c]
OSO_2Me	−0.26	NHEt	−0.52	PH_2	−0.05[e]
O^-Na^+	−0.59[c]	NHBu-*n*	−0.54	PMe_2	−0.08[e]
SH	−0.19[e]	NHPr-*i*	−0.53	PEt_2	−0.08[e]
SMe	−0.25,[e] −0.24[d]	NEt_2	−0.57	PPH_2	−0.08[e]
SEt	−0.19, −0.22[d]	$N(CH_2)_2$	−0.38	PCl_2	+0.07[e]
SPr-*i*	−0.16, −0.21[d]	$N(CH_2)_3$	−0.55	$P(OEt)_2$	+0.06[e]
SBu-*t*	−0.07,[e] −0.19[d]	$N(CH_2)_4$	−0.63	PPh_2O	+0.07[e]
SPh	−0.19	$N(CH_2)_5$	−0.47	PPh_2S	+0.06[e]
$PMe_3^+Cl^-$	±0.08[c]	CH_2CHO	±0.11	$C(OH)(CF_3)_2$	±0.11
$PPH_3^+Br^-$	0.00[e]	CH_2CN	±0.09	$CH{=}CH_2$	±0.05
$PO(OH)SiMe_3$	±0.09	CH_2OH	±0.06[d]	$CH{=}CHCO_2Et$	±0.10
$PO(OH)_2$	±0.08[c]	CH_2OMe	±0.04[d]	$CH{=}CHNO_2$	±0.13
$PO(OH)GeMe_3$	±0.08	CH_2OEt	±0.06[d]	$CH{=}CHNEt_2$	−0.31
PPh_4	±0.03	CH_2OCOMe	±0.08[d]	$C{\equiv}CH$	−0.09[e]
$AsPh_2$	±0.07	CH_3NMe_2	±0.10[d]	$C{\equiv}CPh$	±0.15
$AsPh_4$	±0.04	CH_2SMe	±0.10[d]	CHO	+0.24
$SbPh_2$	±0.07	CH_2SiMe_3	±0.20[e]	COMe	+0.22
$SbPh_4$	±0.06	CH_2SnMe_3	−0.26[e]	COEt	+0.21
$BiPh_2$	±0.10	CH_2Cl	−0.03[e]	COPr-*i*	+0.19
Me	−0.10	CH_2Br	−0.02[d]	COBu-*t*	+0.15
Et	−0.10	CH_2I	−0.05[d]	$COCMe_2Et$	+0.15
n-Pr	−0.11	CH_2NCO	−0.06[d]	$COCMeEt_2$	+0.14
i-Pr	−0.12	CH_2NCS	−0.07[d]	COPh	+0.19
n-Bu	−0.12, −0.12[d]	$CH_2ND_3^+Cl^-$	0.00	COCl	+0.21
sec-Bu	−0.12	C_6H_5	−0.10	$CONH_2$	+0.13[g]
i-Bu	−0.12	*p*-C_6H_4Cl	−0.14	CO_2H	+0.29
t-Bu	−0.13	*p*-C_6H_4Br	−0.14	CO_2Me	+0.16
Pentyl	−0.12, −0.14[d]	*p*-C_6H_4Me	−0.14	CO_2Et	+0.18
Neopentyl	−0.09	*p*-C_6H_4OMe	−0.15	$SiMe_3$	+0.03[e]
Octyl	−0.14	$CH(OMe)_2$	0.00	$SiCl_3$	+0.09
1-Bicyoctyl	−0.17	$CH(SiMe_3)_2$	−0.24	$Si(OEt)_3$	+0.08
1-Adamantyl	−0.15	$CHCl_2$	+0.02[e]	$SiMe_2SiMe_3$	+0.04[d]
$CH(CH_2)_2$	−0.18	$CHBr_2$	0.00	$SiMe(SiMe_3)_2$	+0.06
$CH(CH_2)_3$	−0.12	$C(OMe)_3$	0.00	$SiPh_3$	−0.04[e]
$CH(CH_2)_4$	−0.14	$C(SiMe_3)_3$	−0.24	$GeMe_3$	−0.08[e]
$CH(CH_2)_5$	−0.13	CF_3	+0.10[e]	$GePh_3$	−0.08[e]
$CH_2CH(CH_2)_2$	−0.12	CCl_3	+0.07[e]	$SnPh_3$	−0.10[e]
CH_2Ph	±0.10[d]	CBr_3	0.00	$SnEt_3$	−0.13[e]
$CHPh_2$	−0.11	C_2F_5	+0.08	$SnMe_3$	−0.10[e]
CPh_3	−0.13	$CF(CF_3)_3$	+0.02	$PbPh_3$	0.00
BCl_2	+0.30	$AlPh_2$	±0.11	Li	±0.14
$B(OH)_2$	+0.23[b]	ZnPh	±0.11	2-Furyl	−0.14
BPh^-Na^+	−0.13[b]	CdPh	±0.10	2-Thienyl	−0.13
BPh_2	+0.22	HgPh	±0.03		

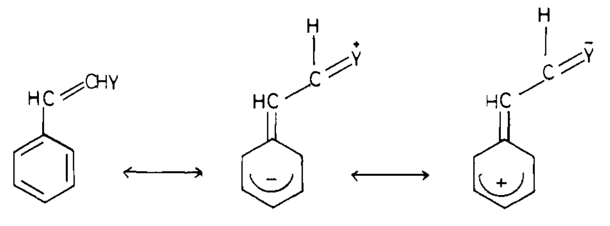
[a] For nonpolar solvents unless otherwise indicated. Derived from monosubstituted benzenes unless otherwise indicated. [b] In DMSO. [c] In D_2O. [d] Derived from ethylenes. [e] Derived from meta-disubstituted benzenes. [f] See ref 86. [g] Derived from acetylenes.

tensity studies on both the $\nu_{C=C}$ and $\nu_{C=O}$ vibrations show that the s-trans form strongly predominates for R = H but as R increases the amount diminishes and is estimated to be only about 10% for R = *t*-Bu.

3. *Other C-Linked Substituents*

The cyano substituent is a weak resonance acceptor, whereas the vinyl and ethynyl groups are weak resonance donors. The

C=C system does act as a moderately efficient transmission system for resonance interactions as expected from possible contributions from canonical forms of type **36** and **37** depending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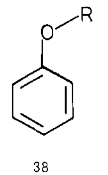
on the nature of Y. Thus for various Y groups the $\sigma_R{}^0$ values are NMe_2, −0.31; H, ±0.05; NO_2, 0.13. The effect of transmission through a benzene ring can also be studied by looking at the effect of substituents, attached to the benzene ring, on the $\nu_{C=C}$ vibration in substituted styrenes. The apparent $\sigma_R{}^0$ for para-substituted phenyl groups are[56] OMe, −0.15; Me, −0.14; Cl, −0.14; H, −0.10. It must be realized that the ν_8 absorption in the benzene ring and the $\nu_{C=C}$ one in the double bond occur close together, and thus the intensities and hence these $\sigma_R{}^0$ values may be affected by intensity sharing.

The ethynyl group is a weak resonance donor when attached to a benzene ring ($\sigma_R{}^0 = -0.09$). In para-substituted phenylacetylenes,[68] the substituents can interact with the triple bond as found for styrenes above. This can be treated as a change in $\sigma_R{}^0$ value with substituent of the YC_6H_4 group or alternatively treated in terms of through-conjugation as for other para-disubstituted benzenes. In the second approach, study of the ν_8 intensities allows us to determine a K_A value of 0.21 for the ethynyl group. Thus it is readily polarizable and can be compared with K_A values of 0.16 for COMe and 0.30 for the highly polarizable NCO group.

C. O-, S-, and N-Linked Substituents

1. Alkyloxy Substituents

As the alkyl group R increases in size in **38**, one might expect increasing repulsion between it and the neighboring ortho hydrogen which could lead to loss of planarity between the RO atoms and the ring. The $\sigma_R{}^0$ values show that this does indeed occur (R, $\sigma_R{}^0$: Me, −0.43; Et, −0.44; *i*-Pr, −0.43; *t*-Bu, −0.34) but only significantly for the *tert*-butyl phenyl ether. This is in agreement[69] with molecular models and with UV and reactivity studies. The small asymmetry correction found for the methoxy group (see section III.C) and the small difference in ν_8 intensity calculated for the alternative conformations of meta-substituted anisoles suggest[69] that conjugation is almost the same in s-trans **39** and s-cis **40** alkyl vinyl ethers. Thus any dependence on the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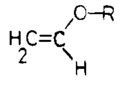
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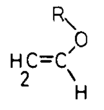
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nature of R here should reflect steric effects. Models again suggest that these should be significant for the s-cis form of *tert*-butyl vinyl ether. Other physical evidence suggests[69] that the s-cis form predominates for R = Me, and Et but that the proportion of s-trans conformer increases markedly for R = *i*-Pr and becomes dominant for the *tert*-butyl vinyl ethers. The virtually constant $\nu_{C=C}$ intensities[69] and hence derived $\sigma_R{}^0$ values for OMe → OBu-*t* in $CH_2{=}CHOR$ show that the conjugation in **39** and **40** must indeed be almost identical.

2. S-Linked Substituents

Similar arguments to that in the previous section can be made for thioalkoxy groups,[69,70] SR. Although the CSC bond angle is significantly smaller than the COC angle, steric effects should dominate only for the phenyl and vinyl *s-cis-tert*-butyl thioethers. The considerable and progressive changes in $\sigma_R{}^0$ found for the phenyl SR compounds (R, $\sigma_R{}^0$: Me, −0.25; Et, −0.19; *i*-Pr, −0.16; *t*-Bu, −0.08) have been explained[69] in terms of the twisting of the SR group being of less energetical importance because of the reverse delocalization into the sulfur d orbitals which is almost independent of rotation. Much less decrease in the effective $\sigma_R{}^0$ is found[69] in the corresponding series of alkyl vinyl thioethers as might be expected since the s-trans form has considerably less steric hindrance, and rotation is not therefore preferred.

We have also studied[71] the resonance interaction of SOY groups such as SOMe and SO_2Me. Other studies have indicated preferred conformations with the S=O group out of the plane of the benzene ring; π-electron interaction should thus reflect mainly transfer from the ring into the d orbitals of the S ($\sigma_R{}^0$ = 0.06 for SO_2Me) and, in the case of MeSO, possible S lone pair donation into the ring explaining the $\sigma_R{}^0$ value of −0.07 observed. Both groups, however, can become strong acceptors when the phenyl system is substituted para by a strong resonance donor.

The $SMe_2{}^+$ substituent is a weak resonance *donor;* a similar result has been shown for $NR_3{}^+$ and is discussed in the next section.

3. N- and P-Linked Substituents

The NR_2 substituents are the strongest resonance donors in the list in Table VI, the $N(CH_2)_4$ substituent with $\sigma_R{}^0 = -0.63$ being the most negative individual value. The relative order of conjugation of the cyclic imines is confirmed by UV and carbon-13 spectra. The increase in interaction in *N*-phenylpyrrolidine over *N,N*-diethylaniline may result[37] from a steric enhancement in that interaction between the α-hydrogens on the imine ring and ortho hydrogens leads to a preferred conformation favorable for delocalization.

The charged ammonio substituents such as $ND_3{}^+$ and $NMe_3{}^+$ have been conclusively shown[42] to be resonance electron donors by studies on meta- and para-substituted phenylammonium salts. This conclusion has now been accepted to be in accord with other evidence.[72] The mechanism of electron donation is similar to that operating in alkyl groups such as CH_3 and CMe_3. Interestingly, ab initio calculations[20] at the STO-3G level do not indicate such an effect even though these calculations agree well with results for other noncharged monosubstituted benzenes. It is possible that solvent effects have some part in the effect.

The charged diazo substituent, $N_2{}^+$, is[42] a strong acceptor substituent ($\sigma_R{}^0$ = 0.29) and has a high K_A value of 0.50[28] indicating its great tendency to mutual interaction with resonance electron-donating substituents.

The PY_2 substituents[73,74] are generally weak in their resonance interactions, PH_2, PR_2, and PPh_2 being donors while PCl_2 and $P(OEt)_2$ are acceptors as shown by work on meta-disubstituted benzenes. The low resonance donation of PMe_2 compared to NMe_2, OMe, and even SMe shows the combined effect of the more diffuse p orbitals of the phosphorus atom, tending to lower donation of electrons into the ring π orbitals compared to nitrogen and the back-donation into the phosphorus d orbitals. Once again the resonance donating power of a group such as PPh_2 is so low that its effect can be reversed[73] to electron acceptance when conjugated with a strong resonance donor.

D. Metalloid Substituents

Our studies[75] have shown that $\sigma_R{}^0$ values are generally small for substituents having a metal atom directly joined to the unsaturated system; thus $\sigma_R{}^0$ is only +0.14 even for PhLi. Higher values are, however, found for boron; thus $\sigma_R{}^0$ is +0.30 for BCl_2. Substituents YMe_3,[76] where Y is Ge, or Sn, are weak donors while $SiMe_3$ is a weak acceptor. The substituents CH_2SiMe_3 and CH_2SnMe_3 are,[77] by contrast, quite significant resonance donors ($\sigma_R{}^0 = -0.20$ and -0.26, respectively) supporting a hyperconjugative mechanism of interaction for these substituents. The alternative suggestion that they cause a significant polarization of the benzene π system (a π-inductive effect) can be discarded since this would not lead to enhanced $\sigma_R{}^0$ values as obtained by our infrared method. The values also show that reverse p-d overlap is not important in contradiction to earlier suggestions (see discussion in ref 77).

E. Substituents with Donor–Acceptor Character

It has been seen that many, indeed most, substituents show a resonance interaction whose magnitude is dependent on the electron demand of the π system to which they are attached. Thus electron-withdrawing substituents such as cyanide or donating ones such as NMe_2 show greater interaction when placed in electron-rich or electron-deficient π systems, respectively. If a substituent has only a small resonance interaction with an otherwise unsubstituted hydrocarbon π system ($\sigma_R{}^0$ low magnitude), then it is possible that the actual donation or acceptance can be reversed in a suitable system. Thus, for example, we have shown[73] above that PPh_2 is a weak donor in triphenylphosphine but becomes an acceptor in an electron-rich system, while CF_3 is an example[64] of the opposite effect. Obviously the measured effect of such substituents will depend on the system. Some substituents, discussed in this section, are so readily polarizable that in the past there have been arguments as to their electronic effect since this varied according to the electronic environment in each experiment.

Examples of very polarizable substituents are[78,79] NO, NC, NSO, NCO, N_3, and NCS. The NSO substituent[79] has the highest K_A that we have measured (0.50 also found for $N_2{}^+$). The last five substituents above can change from donor to acceptor or near acceptor behavior under conditions of strong electron excess. On the other hand, they show increased donor behavior when placed para to electron acceptors or d-orbital acceptors. Thus for NSO the effective $\sigma_R{}^0$ value is +0.68 when para to a dimethylamino group but −0.12 when para to cyano. We choose to treat this in terms of mutual interaction (K_A values, etc.), but we emphasize again that the substituent effect measured by such methods as acidity of substituted benzoic acids or basicity of substituted anilines would be different depending on the method used.

VII. *Evidence from Substituent Vibrations*

Most of our work has been on the vibrations of the hydrocarbon π system rather than those of the substituent. The latter approach has been the subject of much earlier and also some recent work both as far as frequencies and intensities are concerned. Both aspects have been discussed recently,[21,80–82] and we cover only the most important points of the use of substituent intensities here.

The first point is that there have been very few high precision studies of such intensities for a series of compounds with a reasonable number of different substituents. The substituent vibration, for example $\nu_{C{\equiv}N}$ in substituted benzonitriles,[29] is invariably affected by both the inductive and resonance effects of the second substituent. This is reasonable since the inductive effect of a substituent may polarize the π system of the ring which in turn will lead to a different interaction with the vibrating probe, for example, cyanide. Evidence on substituent resonance interactions must therefore be obtained by analysis of the data into inductive and resonance components, and this is best done using the DSP treatment. An effective separation into such components requires[80] a basic set of at least eight substituents (NMe_2, OMe, F, Cl, or Br, Me, H, and two electron-withdrawing groups) for spectroscopic work. This is done using already derived σ values and measuring any special effects in terms of the σ_R scale needed for good fit ($\sigma_R{}^-$, $\sigma_R{}^0$, σ_R, and $\sigma_R{}^+$).

The interesting result found from frequency studies[21] is that the particular resonance scale followed is a predictable function of the vibrating group. Where there is direct conjugation with the ring, it is found that resonance electron-withdrawing groups such as ν_{CN} in para-substituted benzonitriles and ν_{CO} in para-substituted benzoates show ν values dependent on substituent $\sigma_R{}^+$ values; for further removed groups such as ν_{OH} in para-substituted benzoic acids, the values depend on σ_R(BA) while for ν_{OH} in phenols the values depend on substituent $\sigma_R{}^-$ values. We are currently studying $A^{1/2}$ values in similar series; values for ν_{CN} of para-substituted benzonitriles[29] and ν_{CO} in para-substituted methyl benzoates[83] follow $\sigma_R{}^+$ with better precision than the frequencies and provide a simple method of determining such $\sigma_R{}^+$ values. In the case of ν_{NN} of para-substituted benzenediazonium salts[42] the $\sigma_R{}^+$ scale is not enhanced enough to reproduce the results, and a scale such as ($\sigma_R{}^+ - \sigma_R{}^0$) has to be used.

VIII. *Rotational Barriers and the Relationship of $\sigma_R{}^0$ to the Energy Scale*

The resonance interaction of a substituent attached to an olefinic or aromatic system increases the barrier to rotation about the substituent–carbon bond. Measurement of these barriers should provide an energy estimation of the resonance interaction in contrast to the charge transfer basis used above.

A. Monosubstituted Benzenes

We have found[41,84] that the rotational barrier about the substituent-ring bond in monosubstituted benzenes can be related to the resonance interaction provided allowance is made for any strain and rehybridization changes in the rotation. In general, rotation reduces conjugative interactions (leading to higher energy) but relieves strain which partly compensates for this. In eq 52 R is the resonance interaction in the preferred (usually

$$E = (R - R_{tw}) - S \qquad (52)$$

at or near coplanarity of the substituent and the ring) conformation and R_{tw} at the position of maximum energy (usually the orthogonal position of 90° twist). The strain energy (S) includes any rehybridization term. We have further established[84] that for monosubstituted benzenes the resonance terms can be replaced by $33\sigma_R{}^0$ giving eq 53. Use of this equation allows the estimation

$$E = 33(|\sigma_R{}^0| - |\sigma_R{}^0|_{tw}) - S \qquad (53)$$

of any one quantity of the four provided that the other three are known or can be estimated satisfactorily. The $(\sigma_R{}^0)_{tw}$ values can be estimated[41] from infrared results in substituted durenes and related compounds (see section II.B). Available results are summarized in Table VII (taken from ref 41). Apart from its use in determining barriers or strain energies eq 53 directly relates $\sigma_R{}^0$ values to the energy scale.

B. Monosubstituted Ethylenes

In the case of monosubstituted ethylene,[85] s-cis (c) and s-trans (t) forms are possible if the substituent is of less than C_{2v} symmetry.[90] The energy barriers to rotation of a substituent about the carbon–substituent bond in either can be described similarly by eq 54.

TABLE VII. Energy Terms (kcal mol^{-1}) for Rotational Barriers in Monosubstituted Benzenes[a]

Group	E	$R = 33\sigma_R{}^0$	$R_{tw} = 33(\sigma_R{}^0)_{tw}$	S
CHO	7.9	7.9*	0	0
COMe	6.3	7.2	0	0.9*
CO_2Me	5.3*	5.3	0	0
NMe_2	5.1	17.5	4.3	8.1*
NH_2	8.0*	15.5	4.3	3.2
NHMe	7.4*	17.2	4.3	5.5
OMe	2.6*	14.2	7.6	4
OH	3.4	13.9	8.5*	2
NO_2	5.8	5.6	0	~0*
$CH{=\!=}CH_2$	0	~1	0	~1*

[a] In each case three of the values are from the literature (see ref 41 for details): the fourth quantity thus deduced is asterisked.

TABLE VIII. $\sigma_R{}^0$ Values for Substituent MPh_x[a]

M	MPh	MPh_2	MPh_3	MPh_2	MPh	M
Li	Be	B	C	N	O	F
+0.14		+0.22	−0.13	−0.44	−0.36	−0.34
	Mg	Al	Si	P	S	Cl
		0.11	~0.0	−0.08	−0.19	−0.22
	Zn		Ge	As	Se	Br
	+0.11		~0.0	−0.07[b]	−0.19	−0.23
	Cd		Sn	Sb		I
	+0.10		~0.0	−0.08[b]		−0.22

[a] From ref 75 except PPh_3 (ref 73). [b] Signs are tentative for $AsPh_3$ and $SbPh_3$.

$$E_{t,c} = (R_{t,c} - R_{tw}) - S_{t,c} \tag{54}$$

We believe that $0.5(R_t + R_c)$ is directly related to $\sigma_R{}^0$; the latter is derived from substituted benzenes in which a substituent is in an electronic environment which simultaneously resembles both the s-cis and s-trans ethylene. Thus we have derived[85] eq 55. The use of known energy barriers has allowed us to determine b as 25 kcal mol^{-1} $(\sigma_R{}^0)^{-1}$. This equation allows the determination of previously unknown barriers from tabulated $\sigma_R{}^0$ values, and we can again relate $\sigma_R{}^0$ values directly to the energy scale.

$$0.5[E_c + E_t] = b[\sigma_R{}^0 - (\sigma_R{}^0)_{tw} - 0.5(S_c + S_t)] \tag{55}$$

The constant b found for substituted ethylenes is somewhat lower than the 33 kcal mol^{-1} $(\sigma_R{}^0)^{-1}$ found for the substituted benzenes. This is in accord[54] with theoretical calculations which suggest a slightly lower overall π charge transfer in substituted ethylenes compared to substituted benzenes.

C. Para-Disubstituted Benzenes

The method can be extended[86] to rotational barriers about the substituent–ring bonds in disubstituted benzenes. We must allow for the additional resonance interaction between the two substituents (λ). This interaction is denoted δ per substituent (where $\lambda = 2\delta$), where the two substituents are in their lowest energy conformation (see section II.E). If one substituent (Y) is twisted into the position of maximum energy, then the additional resonance due to interaction between the two substituents is reduced to $\delta(\sigma_R{}^0Y)_{tw}/\sigma_R{}^0Y$. Thus for a para-disubstituted benzene, the barrier to rotation about the substituent is described by eq 56.

$$E_{(Y,p\text{-}XY)} = 33[|\sigma_R{}^0Y| - |\sigma_R{}^0Y|_{tw} + \delta(1 - |\sigma_R{}^0Y|_{tw}/|\sigma_R{}^0Y|)] - S_Y \tag{56}$$

After subtraction of eq 53 for the monosubstituted compound PhY, eq 57 results from which the magnitude of the additional interaction, 33δ, can be calculated (in kcal mol^{-1}). We have checked these results by comparison with λ values obtained by eq 32 and from eq 33 or eq 34. For example, combination with eq 33 would give eq 58 for p-orbital acceptors.

$$33\delta[1 - |(\sigma_R{}^0Y)_{tw}/\sigma_R{}^0Y|] = E_{(Y,p\text{-}XY)} - E_{Y;\,mono} \tag{57}$$

$$33\delta = 16.5K_A(X)(\sigma^+Y - \sigma^0Y) \tag{58}$$

Thus infrared intensities of para-disubstituted benzenes or tabulated K_A and K_X values can be used to derive the additional energy barriers caused by through-conjugation. This then gives the magnitude of such mutual substituent interactions in energy units. The infrared derived figures[86] give satisfactory agreement in view of the errors inherent in taking small differences in both the NMR method used for barrier determination and in the IR method and also the experimental error in the actual NMR determination of the barrier. While the infrared method[86] gives interaction energies somewhat higher than expected, the figures are relatively in the correct order: for substituted benzaldehydes, for example, the magnitudes decrease as expected with decrease in donor $(\sigma^+ - \sigma)$ value.

Very recently, ^{13}C-determined barriers for a series of para-substituted acetophenones have become available;[87] the excellent agreement with eq 58 is shown below:

Substituent	NMe_2	OMe	Me	F	Cl	Br
ΔE (NMR)	2.9	1.3	0.5	0.5	0.1	0.1
ΔE (eq 58)	3.3	1.7	0.4	0.6	0.2	0.4

D. Trans 1,2-Disubstituted Ethylenes

The method is equally applicable to disubstituted ethylenes. While little experimental data are available for a full test, results for *trans*-4-(dimethylamino)but-3-en-2-one[85] show considerable promise for the future.

IX. General Conclusions

It can be seen that infrared intensities have led to a great expansion of our knowledge about substituent resonance interaction both with hydrocarbon π systems and with other conjugated substituents. In addition the work has helped our understanding of preferred substituent conformations, steric effects on conjugation, substituent to π-system rotational barriers, and the potential of various theoretical methods to reproduce charge distribution in unsaturated organic molecules. Some of the particular successes have been the ready measurement of substituent $\sigma_R{}^0$ values, the obtaining of relative substituent–substituent interactions including d-orbital ones, and their definition in terms of values such as K_A and K_X and also the clear demonstration that for many substituents their electronic effect will vary from system to system. These investigations have also aided the general understanding of the possible mechanisms of substituent effects on π systems since they measure only the resonance contribution while other methods give the overall effect.

In Table VIII we give a general summary of trends in a periodic form for various directly attached atoms. It is seen that resonance donors lie to the right in general and that their effect diminishes for heavier elements.

For the future we see firstly a greater understanding of the importance of $\sigma_R{}^0$, K_A, and K_X, and $(\sigma_R{}^+ - \sigma^0)$ values as a basic measure of substituent resonance effects. At the same time we feel that this will diminish the feeling that there are so many σ scales that it is better to ignore them. What we need in physical organic chemistry at the moment is to understand better the nature of substituent electronic interactions and provide numerical values here rather than to have empirical scales hopefully applicable to just certain types of reactions.

For ourselves, we have enjoyed the collaboration of the past ten years which has resulted in some 50 articles. This particular collaboration has now come to its end in terms of our current interests, and we sincerely thank those co-workers, referees, and others who have provided so much helpful work and comment.

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