Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. XIII.[1,2] Molecular Orbital Calculations of the Intensities of Ring-Stretching Bands of Substituted Benzenes

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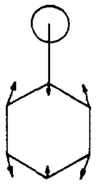
Abstract: Intensity values are calculated for the infrared ν_{16} vibrations near 1600 cm^{-1} of monosubstituted benzenes by the SHMO, the ω, and the CNDO/2 techniques. They all predict well the qualitative trends in the observed infrared intensities and the CNDO/2 method shows fair quantitative agreement. Calculated values are also presented and discussed for meta- and para-disubstituted benzenes.

Previous papers in this series have shown that the intensities of the ν_{16} and ν_{13} ring-stretching vibrations[7] of mono- and disubstituted benzenes are determined by the $\sigma_R{}^\circ$ values of the substituents. Thus eq 1[8] and 2[9] were found to be applicable to mono- and para-disubstituted benzenes for the ν_{16} vibrations

$$A_{\text{mono}} = 17{,}600(\sigma_R{}^\circ)^2 + 100 \quad (1)$$

$$A_{\text{para}} = 11{,}800(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2 + \alpha)^2 + 170 \quad (2)$$

near 1600 cm^{-1} (*cf.* diagrams I and II). The measured A values were expressed in IUPAC practical units.[10] The constant increments of 100 and 170 represent[8,9] overtone corrections while α is a term representing[9] mutual interaction between the two substituents. For benzene and symmetrically para-disubstituted benzenes, the equations show that the bands are inactive as required by symmetry considerations.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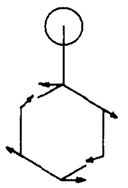
II

The Hammett $\sigma_R{}^\circ$ values a measure of a substituent's effect on the π-electron density of the ring and is related[11] to other properties of the π-electron density such as C-13 and F-19 shielding parameters. The good correlations obtained by eq 1 and 2 and by similar expressions for ortho- and meta-disubstituted benzenes,[12] substituted durenes,[8] and monosubstituted pyridines and pyridine 1-oxides[13] support the postulate that the intensities of the ν_{16} (and also of the ν_{13})[14] bands are governed largely by π-electron density changes during the vibration.

This suggested that molecular orbital calculations involving consideration only of π-electron densities might be successful in predicting the infrared intensities. Since the intensities are more correctly a function of the total electron density changes during the vibration, it seemed worthwhile to also carry out an all valence electron calculation. The method adopted is considerably simpler both in conception and in practice than usual methods for infrared intensity calculations.[15,16] Successful calculations of these types would be important both for their own sakes and because they could establish a direct connection between MO and Hammett equation parameters, thus linking the two most important contemporary methods for rationalizing the chemical and physicochemico properties of aromatic species. Since the inception of this work, a direct link between $\sigma_R{}^\circ$ parameters and CNDO electron densities has been demonstrated;[17] several earlier treatments of the Hammett equation in

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(2) Preliminary communications of part of this work: R. T. C. Brownlee, A. R. Katritzky, M. V. Sinnott, M. Szafran, R. D. Topsom, and L. Yakhontov, *Tetrahedron Lett.*, 5773 (1968).

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(10) Expressed in IUPAC practical units; *C. R. Vingtieme Conf., Munich*, 187 (1959). The A values are $1/cl\int \log (I_0/I)d\nu$ integrated over the whole band; some authors employ the symbols B or E for this quantity and use A for the quantity $1/cl\int \ln (I_0/I)d\nu$, that is, values 2.303 greater than those given in papers in the present series. The 2.303 factor was inadvertently omitted in ref 2.

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(16) L. A. Gribov, *ibid.*, **25**, 26 (1968). Gribov writes "...the development of the parametric theory of intensities in IR spectra has reached a known limit. Within the scope of such ideas it is difficult to expect any serious progress forward. It is even more doubtful that playing with the coordinates can lead to useful, physical improvements in the theory."

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terms of MO parameters are available[18,19] but such work has been of an empirical or semiempirical nature and has had only limited success.

In this paper we have attempted to predict the intensity of a series of mono- and disubstituted benzenes by calculating the rate of change of the dipole moment with the normal coordinate ($\partial\mu/\partial Q$). This quantity (in electrostatic units) is related to the measured intensity (in l. mol^{-1} cm^{-2} = cm mmol^{-1}) by eq 3,[20] where N_0 is Avogadro's number, c is the velocity of light in cm sec^{-1}, and the factor 2.303 is required to obtain A in terms of the experimental units employed.[10]

$$A_{\text{calcd}} = \frac{N_0\pi}{3 \times 2.303 \times 10^3 c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2 = 0.305\left(\frac{\partial\mu}{\partial Q}\right)^2 \tag{3}$$

We have determined $\partial\mu/\partial Q$ by calculating the dipole moment at various points along the normal coordinate and obtaining the gradient graphically.

For the reasons discussed above we believed that the changes in intensity in the ν_{16} modes with substituent are a result of changed electronic distribution within the molecule, and do not arise as a result of changes in the form of the normal coordinate. Thus we have used the forms and the displacements derived by Scherer[21] for chlorobenzene for all the calculations on monosubstituted benzenes. Further, Scherer[22] has suggested that the form of the vibration changes little with substituents of moderate size and bond energy. We earlier found[8] that the frequency is constant except for very heavy substituents.

At the time of our first calculations[23] no similar work had been published although the method was foreshadowed by Brown[24] (*cf.* also ref 25) and has since been developed independently by Segal and Klein in the calculation of dipole derivatives with respect to symmetry coordinates in di-, tri-, and tetraatomic molecules.[26] Chandra has recently discussed our correlations between $\sigma_R{}^\circ$ and infrared intensities in terms of a simple molecular orbital model but no quantitative correlation was derived.[27]

Calculations

The procedure for determining $\partial\mu/\partial Q$ in the correct units and with the correct normalization was as follows.

At the extremes of a vibration the kinetic energy of vibration is transformed into potential energy V, which is defined by eq 4 for a particular vibration of harmonic frequency λ.

$$2V = \lambda Q^2 \tag{4}$$

The potential energy V was equated to $^1/_2\, hc\nu$ (where c is the velocity of light in cm sec^{-1}, ν is the frequency of the vibration in wave numbers (1600 cm^{-1})), and the harmonic frequency λ equated to $4\pi^2c^2\nu^2$ leading to eq 5 for the change in the normal coordinate equivalent to a vibration having this energy (ΔQ in units of g$^{1/2}$ cm, *i.e.*, mass$^{1/2}$ × length).

$$\Delta Q = {}^1/_2\pi\sqrt{h/c\nu} = 1.87 \times 10^{-21} \tag{5}$$

The determination of the atomic displacements corresponding to this vibrational energy is obtained from eq 6 where L_i are the L matrix elements and ΔR_i are the displacements in centimeters and N_0 is Avogadro's number.

$$\Delta R_i = L_i \Delta Q N_0{}^{1/2} = L_i(1.462 \times 10^{-9}) \tag{6}$$

Scherer's Cartesian displacements, ΔR_i, for the 1600- and 1585-cm^{-1} bands for chlorobenzene (Table I) were calculated from the Cartesian L matrix elements L_i[28] using eq 6. The chlorine atom remains stationary[21,28] and equilibrium bond lengths of 1.397 and 1.700 Å were used for C–C and C–Cl, respectively.

Table I. Cartesian Displacements for the 1600- and 1585-cm^{-1} Bands in Chlorobenzene

	1600 band, Å		1585 band, Å	
Atom[a]	x	y	x	y
1	0.0000	0.0094	−0.0170	0.0000
2	0.0051	−0.0178	0.0111	−0.0073
3	0.0057	0.0184	−0.0129	−0.0043
4	0.0000	−0.0091	0.0241	0.0000
5	−0.0057	0.0184	−0.0129	0.0043
6	−0.0051	−0.0178	0.0111	0.0073

[a] Carbon atom to which chlorine is attached is 1, the y axis being along the carbon–chlorine bond.

The dipole moment change $\Delta\mu$ associated with this displacement for a vibration with this energy allows

$$\frac{\partial\mu}{\partial Q} \simeq \frac{\Delta\mu}{\Delta Q} = \frac{\Delta\mu(10^3)}{1.87} \tag{7}$$

us to determine $\partial\mu/\partial Q$ where $\Delta\mu$ is in Debye units.

Since in the experimentally measured intensities the 1600- and 1585-cm^{-1} bands overlap and were integrated together, the calculations of the intensities were made for both bands and then added together for comparison with the experimental value. The same frequency (1600 cm^{-1}) was used for both bands in eq 5 resulting in the same normalization for Q. The error in the intensity as a result of this approximation is small as can be seen from eq 5.

Calculations of π-Dipole Moments by the Simple HMO Method. For carbocyclic aromatic compounds, the Coulomb integrals for ring carbon atoms and the bond integrals for the ring C–C bonds are all equated to unity. Various values have been suggested for α and β for heteroatoms attached to the ring; we have used those recommended by Streitwieser[29] (see Table II). A FORTRAN program[30] was written to calculate π-dipole moments from the secular determinant (*via* π-electron densities and atomic coordinates). To find the change

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(30) Details will be supplied on request.

Table II. Simple HMO Calculations of $\partial\mu/\partial Q$ for Monosubstituted Benzenes

Subst	k^a	h^a	μ,[b] D	$\Delta\mu$,[c] D	$\Delta\mu$,[d] D	$\partial\mu/\partial Q_a$	$\partial\mu/\partial Q_b$	$A_{calcd}^{1/2}$	$A_{obsd}^{1/2}$
Me	0.23	1.2	0.1418	0.017	0.005	9.0	2.6	5.2	13.2
Cl	0.4	2.0	0.2817	0.030	0.009	16.0	5.0	9.3	28.8
Br	0.3	1.5	0.2201	0.024	0.007	12.6	3.7	7.3	30.4
F	0.7	3.0	0.5094	0.057	0.020	30.5	10.5	17.9	45.3
OH	0.8	2.0	1.0047	0.113	0.037	60.2	19.8	35.1	53.3
OMe	0.8	2.0	1.0047	0.113	0.037	60.2	19.8	35.1	56.8
NH_2	0.8	1.5	1.3304	0.150	0.047	80.1	25.1	46.4	62.0

[a] Molecular orbital parameters taken from ref 29. [b] Calculated permanent dipole moment. [c] Difference between calculated values of the permanent dipole and the dipole at maximum amplitude of vibration for the ν_{16a} vibration. [d] Difference as *c* for the ν_{16b} vibration.

in the π-dipole moment during the vibration, the π-dipole moment for displacements either side of the equilibrium position of magnitude corresponding to those in Table II, and those twice as great, were then plotted against displacement, and $\partial\mu/\partial Q$ was calculated from the slope at zero displacement. During the vibration, the carbon–carbon bond lengths, and hence the bond integrals β_{rs}, vary considerably. Values of β_{rs} corresponding to the various bond lengths[29a] were calculated using eq 8[31] and inserted into the secular determinant. The modified π-charge densities thus obtained, together with the displaced atomic coordinates, enabled a π-dipole moment for the distorted molecule to be calculated.

$$\beta_{rs} = \beta_0 \exp[-1.7(R_{rs} - 1.397)] \qquad (8)$$

Thus for chlorobenzene, using the parameters[29a] $k = 0.4$, and $h = 2.0$, the π-dipole moment was calculated in the equilibrium position, and at the maximum amplitude of the vibration (and at twice this amplitude) on either side of the equilibrium position using the data of Table I. These π-dipole moments (Table II) were plotted against the displacement for both the A_1 and B_1 bands giving changes in dipole moment of 0.026D and 0.010D, respectively, corresponding to vibrational energies of $^1/_2\, h\nu c$. These graphical values are slightly superior to the actual displacement values of 0.030D and 0.009D (Table II). Use of eq 7 gives $\partial\mu/\partial Q$ values of 16.0 esu for the A_1 band and 5.0 esu for the B_1 band. The corresponding intensities (A_{calcd}) can be obtained from eq 3 and their total compared with the observed value (A_{obsd}). For numerical convenience and to aid comparison with $\sigma_R{}^\circ$ values, Table II lists $A_{obsd}^{1/2}$ (28.8 for chlorobenzene) and $A_{calcd}^{1/2}$ (9.3). The $A_{obsd}^{1/2}$ values have been corrected for the overtone contribution.

Calculation of π-Dipole Moments by the ω Technique. Extended Hückel methods involving the ω technique to obtain self-consistency were applied using a modified version of QCPE program No. 110.[32] The same values for α and β for ring carbon atoms and heteroatoms as in the simple HMO method were used. The self-consistent α^{i+1} values were calculated using eq 9 and $\omega = 1.4$[29c] (n_r is the number of electrons). Values

$$\alpha_r^{i+1} = \alpha_r = (n_r - q_r^i)\omega\beta_0 \qquad (9)$$

of $A_{calcd}^{1/2}$ for the A_1 band calculated by the ω technique are given in Table III.

Table III. Values of $A^{1/2}$ for Monosubstituted Benzenes

Subst	$\partial\mu/\partial Q_a$ ω	$\partial\mu/\partial Q_a$ CNDO	$\partial\mu/\partial Q_b$ CNDO	$A_{calcd}^{1/2}$ CNDO	$A_{obsd}^{1/2}$	$(A_{calcd}^{1/2})_\pi$ CNDO
CN		16.8	6.0	9.8	11.3	
Me		26.6	14.5	16.8	13.2	17.0
CF_3		27.6	7.9	15.8	14.7	18.6
NO_2		31.4	7.8	18.0	23.1	28.9
Cl	12.1				28.8	
Br	9.9				30.8	
CHO		38.0	8.4	21.5	32.4	25.1
F		73.2	46.4	48.0	45.3	25.9
OH	43.7	95.2	46.7	58.6	53.3	51.1
NH_2	77.2	118.8	44.4	70.2	62.0	57.5

Calculation of Dipole Moments by the CNDO/2 Method. The CNDO/2 method of Pople, *et al.*,[33] in contrast to the HMO methods, considers explicitly all valence electrons, and does not (in its normal form) involve adjustable parameters. It enables a calculation of atom charge densities merely from a knowledge of the geometry of a molecule. The method has given good results for the dipole moments of aromatic molecules[34,35] and has previously been used to calculate the infrared intensities with respect to symmetry coordinates of simple molecules of high symmetry such as carbon dioxide and methane.

The imput data consist of molecular dimensions; the benzene rings in the vibrational ground state were considered to be regular hexagons with C–C bond distances of 1.397 Å,[36] and C–H bond distances of 1.08 Å.[36] Bond distances and angles used for the substituents are summarized in Table IV; they were

Table IV. Molecular Dimensions[a] Used for Substituents Attached to Benzene Rings

Subst	Bond lengths, Å		Bond angles
F	C–F = 1.3315		(linear)
NO_2	C–N = 1.48	N–O = 1.21	CNO = 120°
OH	C–O = 1.36	O–H = 0.97	COH = 109° 28′
NH_2[b]	C–N = 1.43	N–N = 1.01	CNH = 120°
Me	C–C = 1.51	C–H = 1.10	CCH = 109° 28′
CN	C–C = 1.42	C–N = 1.16	(linear)
CF_3	C–C = 1.50	C–F = 1.33	CCF = 109° 28′
CHO	C–C = 1.48	C–O = 1.21	CHO = 120°
		C–H = 1.08	

[a] Taken from ref 37. [b] The NH_2 group is assumed to lie in the plane of the benzene ring.

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Table V. Permanent Dipole Moments (D) for Monosubstituted Benzenes

Subst	μ_{calcd} (CNDO/2 method) a	b	c	μ_{obsd}[d]	$\Delta\mu$[e]	$\Delta\mu$[f]
Me	0.22	0.20	0.21	0.37	0.0497	0.0272
F	1.67	1.62	1.67	1.60	0.1369	0.0868
OH[g]	1.76	1.72	1.66	1.41	0.1782	0.0872
NO_2	4.95	4.94	5.20	4.28	0.0340	0.0146
CN	3.23	3.23	3.22	4.20	0.0315	0.0113
CHO	2.50	2.52	2.54	2.78[h]	0.0717	0.0157
CF_3	2.73	2.59	2.66	2.87	0.0516	0.0147
NH_2[g]			0.98	1.49	0.2221	0.0830

[a] From ref 34. [b] From ref 17. [c] Present work. [d] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. Values are gas phase unless otherwise stated. [e] Difference between calculated permanent dipole and dipole at maximum amplitude for the ν_{16a} vibration, calculated by CNDO/2 method. [f] Difference as in footnote *e* for the ν_{16b} vibration. [g] Groups assumed to lie in plane of ring. [h] Benzene solution value.

obtained from X-ray crystallographic data.[37] Calculations of the dipole moments for the equilibrium position and vibrationally distorted molecules were carried out using QCPE program No. 91.[38] The calculated dipole moments are recorded in Table V, which also gives measured values, and values calculated by the CNDO technique by previous workers. Agreement is quite good in most cases.

The values of $\partial\mu/\partial Q$ and thus $A_{\mathrm{calcd}}^{1/2}$ were obtained from the dipole moments as described above for the HMO calculations. They are given in Table III, which also includes the observed values and those calculated by the ω technique.

Separation of π and σ Components of the Dipole Changes. The output from the CNDO program also lists the π-electron densities. From these and the geometry of the molecule, the π-dipole moments at the equilibria and stretched positions were calculated. The infrared dipole derivatives $\partial\mu_\pi/\partial Q$, arising solely from changes in the π-dipole moment were then calculated using the procedures above and are shown in Table III.

Disubstituted Benzenes. The CNDO/2 calculations were extended to meta- and para-disubstituted benzenes, using the atomic displacements given by Scherer[22] for *m*- and *p*-dichlorobenzene. The results are given in Table VI (meta) and Table VII (para compounds) together with observed intensity values.

Table VI. Values of $\partial\mu/\partial$ for Meta-disubstituted Benzenes

Subst		$\partial\mu/\partial Q_a$	$\partial\mu/\partial Q_b$	$A_{\mathrm{calcd}}^{1/2}$	$A_{\mathrm{obsd}}^{1/2}$
F	F	106.2	136.5	95.9	76.8
F	NH_2	179.0	117.9	118.4	92.3[a]
F	CN	67.2	60.5	50.0	56.1
F	NO_2	67.9	65.6	52.2	20.0
NH_2	NH_2	221.2	112.2	140.0	125.5[b]
NH_2	CN	57.5	78.8	53.8	
NH_2	NO_2	118.2	84.5	80.5	63.2
CN	CN	13.9	4.0	7.9	0.0
CN	NO_2	17.9	11.5	11.8	20.0
NO_2	NO_2	12.4	16.7	11.5	44.8

[a] Observed intensity is for F, ND_2. [b] Observed intensity is for NMe_2, NMe_2.

Table VII. Values of $\partial\mu/\partial Q$ for Para-disubstituted Benzenes

Subst		$\partial\mu/\partial Q_a$	$\partial\mu/\partial Q_b$	$A_{\mathrm{cacld}}^{1/2}$	$A_{\mathrm{obsd}}^{1/2}$
F	Me	51.7	34.3	34.6	24.1
F	OH	21.7	2.1	12.1	8.5[a]
F	NH_2	35.9	2.6	19.9	15.8[b]
F	CF_3	113.1	58.1	70.4	55.8
F	NO_2	109.8	40.5	64.6	65.5
F	CHO	129.6	55.3	78.0	73.1
NH_2	Me	111.9	29.8	64.7	41.1[b]
NH_2	OH	15.7	3.2	8.8	0.0[d]
NH_2	CN	161.4	39.7	91.8	97.9[c]
NH_2	CF_3	173.7	54.1	100.8	91.3[c]
NH_2	NO_2	173.5	36.9	97.7	134.4[c]
NH_2	CHO	197.1	51.4	114.0	133.2[c]
Me	CN	50.3	10.4	28.4	26.8
Me	OH	81.8	32.9	48.8	36.0
NO_2	OH	143.9	19.8	80.4	84.8[a]
CF_3	OH	142.3	57.3	84.8	69.8[a]

[a] Observed intensity is for OMe. [b] Observed intensity is for ND_2. [c] Observed intensity is for NMe_2. [d] Observed intensity is for OMe/NH_2 substituent.

Discussion

Monosubstituted Benzenes. The $A_{\mathrm{calcd}}^{1/2}$ values obtained by the SHMO method (Table II) are plotted against the observed values in Figure 1 and the corresponding quantities calculated by the CNDO/2 (Table III) are similarly plotted in Figure 2. These graphs and tables allow the following conclusions: (i) the calculated values are in the correct order of relative effect of the substituents; (ii) the contribution of ν_{16b} to the total intensity is significant but usually considerably less than that of ν_{16a}; (iii) the intensity values calculated by the SHMO method are less than the actual values, the discrepancy being greatest for the weakly interacting substituents; (iv) the use of the ω technique probably has little advantage over SHMO, in view of the problem of adjustable parameters; (v) the intensity values calculated by the CNDO/2 method are generally in remarkably good agreement with the observed values and show a satisfactory linear relationship with them. The straight line plot in Figure 2 has a slope of 1.15.

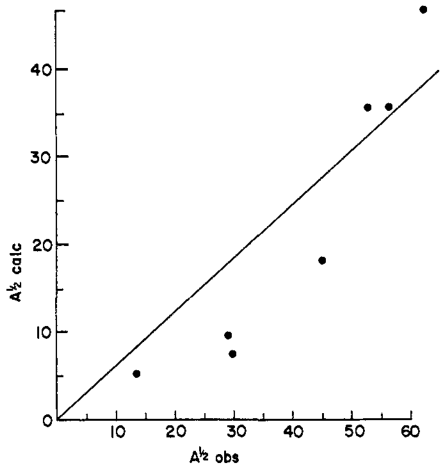

Figure 1. Plot of calculated $A^{1/2}$ by SHMO against observed $A^{1/2}$ values for the ν_{16} vibrations of monosubstituted benzenes.

Calculations by the CNDO/2 method give the individual π and σ components to $\partial\mu/\partial Q$. The intensity

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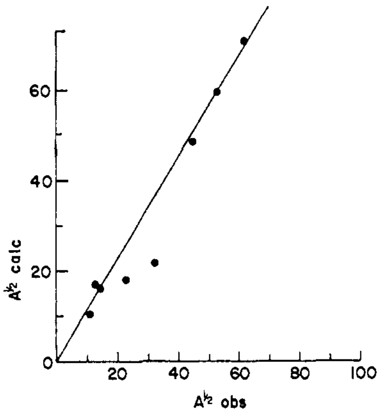

Figure 2. Plot of $A^{1/2}$ calculated by CNDO/2 against observed $A^{1/2}$ values for the ν_{16} vibrations of monosubstituted benzenes.

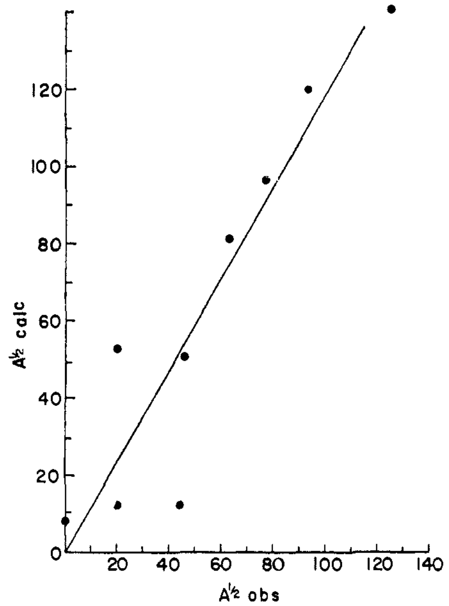

Figure 3. Plot of $A^{1/2}$ calculated by CNDO/2 against observed $A^{1/2}$ values for the ν_{16} vibrations of meta-disubstituted benzenes.

values observed should depend on the change in the overall dipole moment of the molecules rather than the change in the π-dipole moment and, in accord with this, no improvement in correlation is found when $A_{\mathrm{obsd}}^{1/2}$ values are plotted against $(A_{\mathrm{calcd}}^{1/2})_\pi$ values (Table III) instead of against $A_{\mathrm{calcd}}^{1/2}$. It has been shown that $\sigma_R{}^\circ$ values are proportional to the π-electron transfer between the ring and the substituent in a monosubstituted benzene[17] and also to both the π and total electron changes occurring at the para position.[39] It is somewhat surprising that the intensity variations here correlate so well with $\sigma_R{}^\circ$ values. It would seem likely that the correlation is predominantly determined by the intensity of the ν_{16a} vibration but values of the dipole derivatives here are not sufficiently different from proportionately $A_{\mathrm{calcd}}^{1/2}$ (for the total ν_{16a} plus ν_{16b}) to establish this point.

It would thus seem that the calculations employed offer very satisfactory correlations with the observed intensities. The additional correlation found with $\sigma_R{}^\circ$ values is probably still best treated at this stage in the development of the theory in terms of the simplified valence-bond picture, previously advanced,[8] which suggests varying overlap between the π systems of the substituent and the ring during the vibration.

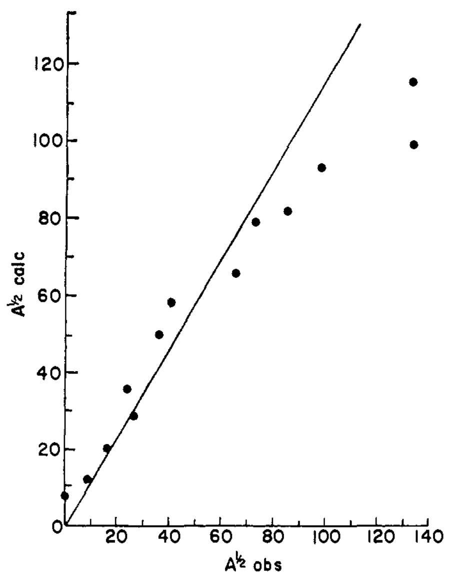

Figure 4. Plot of $A^{1/2}$ calculated by CNDO/2 against observed $A^{1/2}$ values for the ν_{16} vibrations of para-disubstituted benzenes.

Disubstituted Benzenes. Values of $A_{\mathrm{calcd}}^{1/2}$ for meta-disubstituted benzenes (Table VI) are plotted against the observed values in Figure 3. The correlation is seen to be reasonably satisfactory and the slope of the best straight line through the points again has a slope of 1.15. The corresponding values for the para-disubstituted compounds (Table VII) are shown in Figure 4. The $A_{\mathrm{calcd}}^{1/2}$ values for compounds where both substituents are donors once again give a satisfactory linear plot against $A_{\mathrm{obsd}}^{1/2}$. When a line of slope 1.15 is employed, it can be seen that para-disubstituted benzenes having one π-donating and one π-accepting substituent show greater observed intensities than expected from the calculation. These are the compounds in which direct resonance interaction is expected between the substituents. It is known that considerable changes in bond lengths, both between the substituent and the ring and within the ring, occur in such compounds as p-nitroaniline[40] and p-aminobenzoic acid.[41] Unfortunately there do not appear to be any accurate crystallographic bond lengths for the compounds under discussion here and hence the calculations were made on the undistorted geometry and do not mirror the observed intensities. Nevertheless it does suggest that our treatment of these effects in terms of a substituent interaction (the α term in eq 2) is correct.

The calculations made should really be contrasted with gas-phase intensity values. There is no general theory that allows one to estimate the change in intensity of a particular vibration in going from the gas phase to a solution in a given solvent, but since the form of the ν_{16} vibration does not change greatly with substituent it seems reasonable to suppose that the relative effect will be approximately the same for each compound. We

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have already shown[8,42] that the intensities are not generally sensitive to changes in concentration and solvent and intend to measure the gas-phase values of some substituted benzenes.

Conclusions

The method employed for these calculations makes several major assumptions apart from those in the CNDO/2 or SHMO schemes themselves. These include the use of normal coordinates derived for chlorobenzenes for a whole series of substituted benzenes, the ignoring of solvent effects on the intensities, and the assumption that the substituent does not move relative to the center of mass. The validity of making such assumptions is well supported by the results, particularly the agreement between observed intensities and those calculated by the CNDO/2 method.

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Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. XIV.[1] Groups with Donor–Acceptor Character

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Abstract: In the corresponding monosubstituted benzenes, the isocyanate, isothiocyanate, and azide groups act as moderate resonance donors, but these groups can each interact strongly with a para substituent either to donate or to accept electrons. The isocyanide group is also an electron donor and interacts moderately with para substituents. The nitroso group is a weak electron acceptor; this acceptance is enhanced when the group is situated para to a strong electron donor but no evidence was found for donor ability. Further evidence is adduced for the position of the nitroso stretching frequency.

Certain substituent groups appear to be capable of either acceptance or donation of electrons when attached to aromatic systems. Such variation in resonance character could lead to confusion since the effect observed might depend on the particular experiment used as a probe. Thus for a hypothetical substituent $-X{=}Y$ capable of either resonance donation $({=}X^{+}{=}Y)$ or acceptance $({=}X{-}Y)$, one could observe the donor properties in electrophilic aromatic substitution or the acceptor ones in nucleophilic aromatic substitution. As an example, some textbooks[3] still suggest that the nitroso substituent can act in this way since bromination of nitrosobenzene gives predominantly *p*-bromonitrosobenzene while the nitroso substituent also aids nucleophilic aromatic substitution when placed ortho or para to a suitable leaving group. While it has been shown[4] that bromination of nitrosobenzene actually proceeds *via* an *N*-bromohydroxylamine intermediate thereby nullifying this evidence,[5,6] it is still unclear whether the nitroso substituent is able to donate electrons if called upon to do so by virtue of attachment to an electron-deficient aromatic system. Its observed accepting properties when attached to an electron-rich system such as 4-pyrazolyl[7] cannot be used as evidence of lack of electron-donating ability under opposite circumstances. Previous quantitative estimates of its resonance effect have not been in agreement (^{19}F nmr[8] $\sigma_R{}^{\circ}$ +0.33; ir[9] +0.07).

Considerable confusion has also existed[10] concerning the electronic effect of the isothiocyanate group, and the considerable researches of Kristián have not completely cleared this up.[10] The inductive effect of isothiocyanate is to withdraw electrons but calculations,[11] ^{19}F nmr,[8] dipole moment,[10] chemical,[10] and spectral[10,12] evidence all suggest that it behaves as a resonance donor. However, the situation is not as simple as this combination of results may suggest. Although the ^{19}F results[8] yield a $\sigma_R{}^{\circ}$ value of only -0.06, we found the considerably higher value of -0.35 by an infrared study[9] of isothiocyanatobenzene. This suggests that the isothiocyanato substituent may interact as a resonance acceptor when situated para to the (res-

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