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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Table I. Spectral Data for meta-Substituted Phenyl Isocyanides, Azides, Isocyanates, and Isothiocyanates[a]

Subst 1	Subst 2	$\sigma_R°(2)^d$	1600-cm^{-1} region Cm^{-1}	1600-cm^{-1} region $\epsilon_A{}^b$	A^c	$(A - 340)/$ 19,000	$\bar{R}_m{}^{2\,e}$
NC	NMe_2	−0.53	1602, 1578	581, 83	9377	0.477	0.38
	F	−0.34	1608, 1596	130, 202	3577	0.171	0.19
	Me	−0.10	1600	46	1349	0.056	0.05
	Cl	−0.22	1594, 1582	136, 104	2677	0.123	0.10
N_3	NMe_2	−0.53	1596	453	9974	0.508	0.69, 0.52
	F	−0.34	1610, 1592	201, 276	8115	0.410	0.42, 0.31
	Me	−0.10	1606, 1592	107, 95	3571	0.170	0.19, 0.16
	Cl	−0.22	1594, 1580	532, 144	5767	0.286	0.29, 0.22
	NO_2	+0.17	1616, 1588	44, 68	1209	0.046	0.07, 0.13
NCO	NMe_2	−0.53	1600, 1580	486, 198	13184	0.677	0.66
	F	−0.34	1610, 1594	108, 120	8748	0.444	0.42
	Me	−0.10	1610, 1592	131, 98	3815	0.183	0.21
	Cl	−0.22	1598, 1578	556, 192	6255	0.312	0.30
	NO_2	+0.17	1616, 1586	67, 63	1360	0.054	0.12
NCS	$NMe_2{}^f$	−0.53	1596	284	7151	0.359	0.60
	F	−0.34	1606, 1588	258, 253	7693	0.388	0.36
	Me	−0.10	1606, 1584	100, 62	3391	0.161	0.15
	Cl	−0.22	1590, 1574	685, 139	5821	0.289	0.25
	NO_2	+0.17	1612, 1582	56, 115	1090	0.040	0.09

[a] Spectra run in CCl_4 except where otherwise indicated. [b] Peak extinction coefficient: $\epsilon_A = a_{max}/cl$ where a_{max} is absorbance at peak maximum, c is concentration, and l is cell length. [c] Total integrated intensity of the bands: $A = \Sigma a_{max}/cl$. [d] Values from ref 12. [e] $\bar{R}_m = [\sigma_R°(1)^2 + \sigma_R°(2)^2\ \sigma_R°(1)\sigma_R°(2)]^{1/2}$; for the azides, two values are given corresponding to the equation $\bar{R}_m{}^2 = (\sigma_R°s)^2 + (\sigma_R°as)^2 + \sigma_R°s(x \pm \sqrt{3}y)$, see eq 6 in text. [f] Spectrum run in chloroform solution.

onance electron-donor) fluorine (I) and therefore that the $^{19}F\sigma_R°$ value may by unreliable as a measure of the unperturbed interaction between the isothiocyanate group NCS and a benzene ring.

I

An analogous situation is observed for the isocyanato group ($\sigma_R° = -0.17$ from ^{19}F results,[13] −0.40 from infrared[9]). This substituent has not been extensively examined by other techniques although dipole moment studies[14] suggest that it is a weak resonance donor.

The electronic character of the azide group attached to aromatic rings has been investigated by Smith[15] who has summarized much earlier work. The group directs ortho–para in electrophilic substitution and is activating: bromination rates give $\sigma_p{}^+ = -0.54$, which is consistent with $\nu_{C=O}$ in *p*-azidoacetophenone. However, p*K* measurements on substituted benzoic acids and anilinium ions show that the azide group is acid strengthening in all cases: $\sigma_m = 0.35 \pm 0.02$, $\sigma_p = 0.09 \pm 0.01$. Ultraviolet spectral measurements give $\sigma_p - \sigma_m = 0.29$. Thus Smith[15] concluded that the azide group was an inductive acceptor and a strong resonance donor. The infrared method[9] gives a $\sigma_R°$ value of −0.366. Syrkin[16] has demonstrated strong interaction between the substituents in *p*-nitrophenyl azide by dipole moments, whereas Sheinker[17] concluded from ir intensity measurements of the NNN vibration near 2100 cm^{-1} that the azide group is a weak electron donor which can show acceptor properties when another substituent which was a strong donor was present.

The electronic character of vinyl isocyanide has recently been studied by Matterson and Bailey;[18] they conclude from proton magnetic resonance and from MO calculations that the isocyanide groups interact as a resonance donor with the vinyl group. Earlier, Ugi and Meyr[19] had studied the uv and ir absorption of aryl isonitriles and concluded that resonance interaction occurred with para electron acceptor substituents. The infrared method[9] gives a $\sigma_R°$ value of −0.146 for the substituent attached to a benzene ring.

To gain a quantitative measure of the resonance interaction we have investigated all these substituents under conditions of varying demand for electron acceptance and donation. The integrated area, *A*, of the ν_{16} band near 1600 cm^{-1} for monosubstituted benzenes is related to $\sigma_R°$ by eq 1.[9] We have shown that for para-[20] and meta-[21]disubstituted benzenes equations of the form 2 and 3 are expected to, and do, hold. In eq 2, the term λ represents mutual interaction between the substituents. It is thus possible to determine the direction and magnitude of the mesomeric effect of the substituents mentioned above in the pres-

$$A_{mono} = 17{,}600(\sigma_R°)^2 + 100 \qquad (1)$$

$$A_{para} = 11{,}800[\sigma_R°1 - \sigma_R°2 + \lambda]^2 + 170 \qquad (2)$$

$$A_{meta} = 19{,}000[(\sigma_R°1)^2 + (\sigma_R°2)^2 + \sigma_R°1\sigma_R°2] + 340 \qquad (3)$$

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Table II. Spectral Data for para-Substituted Phenyl Isocyanides, Azides, Isocyanates, Isothiocyanates, and Nitrosobenzenes[a]

Subst			1600-cm^{-1} region						
1	2	$\sigma_R°(2)$[d]	Cm^{-1}	$\epsilon°$[b]	A[c]	$\left(\frac{A - 170}{11,800}\right)^{1/2}$	$\sigma_R°(1) - \sigma_R°(2)$[e]	λ[f]	$\bar{R}_p$[g,e]
NC	NMe$_2$	−0.53	1610	420	4585	0.612	0.39	0.22	0.61
	F	−0.34	1604	55	580	0.186	0.19	0.05	0.24
	Me	−0.10	1582	17	325	0.115	0.05	0.02	0.17
	Cl	−0.22	1644, 1620, 1594	7, 4, 16	370	0.130	0.07	−0.05	0.02
NO	NMe$_2$	−0.53	1605	850	13410	1.060	0.60	+0.54	1.14
	OMe	−0.43	1599, 1585	265, 150	5410	0.665	0.50	+0.28	0.78
	F	−0.34	1598	360	2835	0.475	0.41	+0.10	0.51
	Me	−0.10	1603	88	1139	0.287	0.17	−0.07	0.24
	Cl	−0.22	1601	130	1000	0.265	0.29		0.29
	Br	−0.23	1590, 1582	64, 53	1163	0.290	0.30		0.30
	NO$_2$[h]	+0.17	1610	52	719	0.216	0.10		0.10
	COMe[h]	+0.22	1600, 1585	*Ca.* 20, 20	374	0.131	0.15		0.15
	CO$_2$Me[h]	+0.18	1605, 1585	*Ca.* 12, 12	290	0.101	0.11		0.11
	CN[h]	+0.09	1600	*Ca.* 4	60	0.0	0.02		0.02
N$_3$	NMe$_2$	−0.53	1612	102	4147	0.581	0.21	+0.40	0.58
	F	−0.34	1598	16	398	0.139	0.10	+0.08	0.11
	Me	−0.10	1614, 1582	35, 30	780	0.227	0.27	+0.05	0.22
	Cl	−0.22	1594	88	684	0.208	0.17	−0.12	0.28
	NO$_2$	+0.17	1608, 1594	538, 361	6260	0.718	0.54	−0.15	0.69
NCO	NMe$_2$	−0.53	1614	106	3980	0.568	0.13	+0.45	0.58
	F	−0.34	1600	17	337	0.119	0.06	+0.09	0.03
	Me	−0.10	1616, 1580	39, 45	913	0.241	0.30	+0.06	0.25
	Cl	−0.22	1598	113	967	0.260	0.19	−0.13	0.32
	NO$_2$	+0.17	1608, 1598	624, 391	7030	0.763	0.58	−0.18	0.76
NCS	NMe$_2$	−0.53	1608	303	4527	0.608	0.18	+0.44	0.62
	F	−0.34	1694	20	412	0.143	0.01	+0.08	0.07
	Me	−0.10	1610	28	516	0.172	0.25	+0.06	0.20
	Cl	−0.22	1592	50	579	0.186	0.13	−0.11	0.25
	NO$_2$	+0.17	1606, 1592	598, 187	6639	0.740	0.52	−0.14	0.66

[a] Spectra run in CCl$_4$ except where otherwise indicated. [b] Peak extinction coefficient: $\epsilon_A = a_{max}/cl$. [c] Measured intensity $A = \Sigma a_{max}/cl$. [d] Values from ref 12. [e] For the azides the appropriate correction for asymmetry has been incorporated. [f] λ is defined by eq 8, 9, and 10 as appropriate, see text. [g] $\bar{R}_p = {}^c\sigma_R°(1) - \delta_R°(2) + \lambda$. [h] Spectra run in benzene–carbon tetrachloride solution.

ence of a second substituent of varying electronic requirements.

Experimental Section

Compounds were obtained commercially or prepared by known methods. Purities were checked by gas chromatography or melting point. Spectra were obtained on either a Perkin-Elmer 125 or 225 spectrophotometer under conditions similar to those previously specified.[21] Solvents were purified as before. Intensity area A values quoted are averages of four readings usually on two separate solutions; reproducibility of $A^{1/2}$ was ±2 units. The extinction coefficients ϵ were determined from the formula $\epsilon = a_{max}\Delta\nu_{1/2}/cl$. These are less accurate because of the finite slit width and since not all peaks have Lorentzian shape. The A values contained the entire absorption with the principal band as any combination bands may share intensity with the ring vibration and their intrinsic intensity is allowed for in the formulas employed. The values for the meta-disubstituted compounds are given in Table I and those for para-disubstituted compounds in Table II. Carbon tetrachloride was employed as the solvent except where the low solubility of the aromatic compound necessitated otherwise (see footnotes to tables).

Discussion

Orientation of the Substituents Relative to the Ring. It is necessary to consider the geometry of the substituted aromatic compounds before the results can be fully interpreted. This is required because electronic interactions are more complicated than indicated in eq 2 and 3 if the overall symmetry is below C_{2v}. The NC, NO, N$_3$, NCS, and NCO substituents are all linear. Such a linear group can either lie on the C$_1$–C$_4$ ring axis, or can be bent away from this axis either in the plane of the ring, perpendicularly to the plane, or at some intermediate angle.

All available evidence, including electron diffraction and dipole moment results, suggests[5,6] that the RNC angle for isocyanides is 180°; *i.e.*, the NC group is colinear with C$_1$C$_4$. This is not the case for aryl nitroso compounds; although the NO group lies in the plane of aromatic ring, the ArNO angle in *p*-iodonitrosobenzene has been shown[22] to be 125° by X-ray studies.

In isocyanates, isothiocyanates, and azides (RXYZ), all the XYZ angles are 180°. Thus the crystal-structure determination of cyanuric triazide[23,24] and the electron-diffraction work of Pauling[25] on methylazide finally demonstrated this for the azido group. This feature of the structure of the –NCO and –NCS groups was not a subject of controversy in the same way as for the azido group, and the accepted linearity is confirmed by X-ray studies.[26]

The orientation of the NCO, NCS, and NNN groups relative to the benzene ring has been less clear. Vibrational spectroscopy can distinguish between structures of type II (C_{2v} symmetry) and those of type III (C_s symmetry). Although structures of type IV are strictly of C_s symmetry, the ring vibrations should approximate to C_{2v}. Detailed vibrational studies[27,28] do indicate structures of type IV for both phenyl

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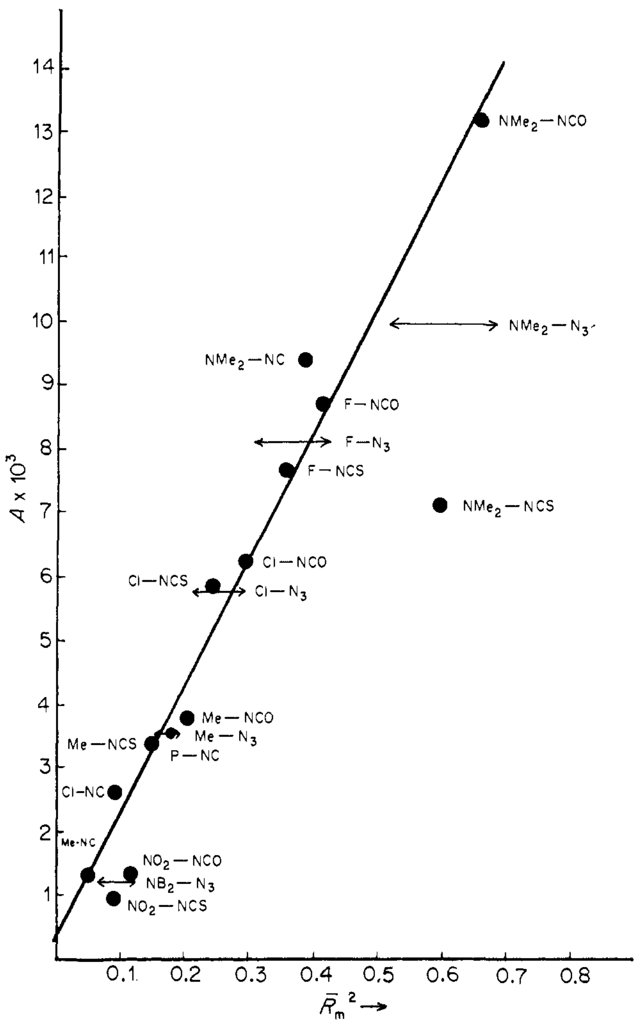


Figure 1. Plots of A_{obsd} against $\bar{R}_m{}^2 = [(\sigma_R{}^\circ 1)^2 + (\sigma_R{}^\circ 2)^2 + \sigma_R{}^\circ 1 \sigma_R{}^\circ 2]$ for meta-substituted isocyanates, isothiocyanates, and isocyanides. For the meta-substituted azides the range shown corresponds to $[(\sigma_R{}^\circ N_3)^2 + (\sigma_R{}^\circ 3)^2 + \sigma_R{}^\circ 3\ (x \pm \sqrt{3},y)]$, *cf.* text. The line shown is that of ref 13.

isocyanate and phenyl isothiocyanate. Dipole moment studies of meta- and para-substituted derivatives are also capable in principle of distinguishing between coaxial and nonlinear arrangement, and indeed of affording an estimate of the angle of deviation. However, such deductions are fallible, especially for distinguishing between low and zero deviation from linearity. Sidgwick and Sutton[29] in early work calculated the CNN angle in phenylazides to be 180° to within 12° from measurements on the *p*-bromo and nitro derivatives. Kristián and coworkers[30] find zero values for the dipole moment of *p*-bisisothiocyanatobenzene and small deviation only from additivity for other para-substituted derivatives and conclude that angle CNC = 180°. Ulicky[26] has found from X-ray work on *p*-iodo- and *p*-bromophenyl isothiocyanate that NCS is inclined to the plane of the ring in the plane of the C_1–C_4 axis.

A further criteria for distinction between a structure of type III and one of type II or IV is available from ir

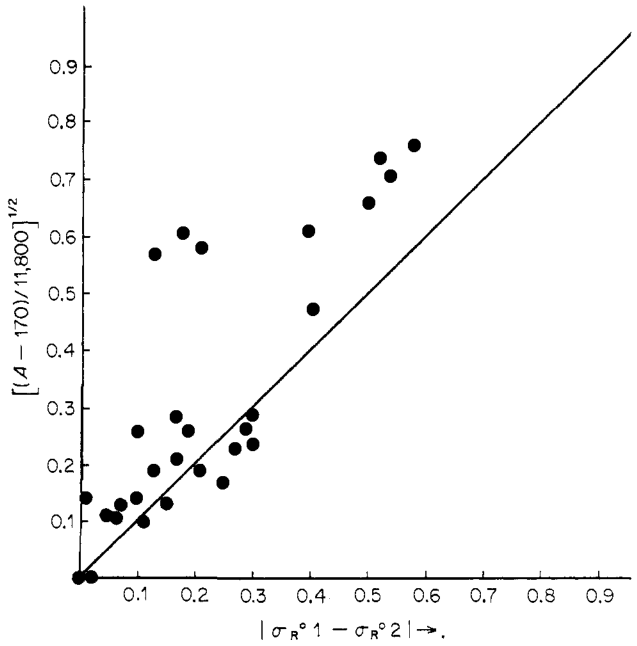
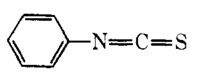


Figure 2. Plot of $[(A_{\text{obsd}} - 170)/11{,}800]^{1/2}$ against $|\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2|$ for para-substituted isocyanate, isothiocyanates, and isocyanides. For the para-substituted azide, the abscissa is $[(\sigma_R{}^\circ N_3 - \sigma_R{}^\circ 2)^2 + 2(\sigma_R{}^\circ 2)(\sigma_R{}^\circ N_3 - \sigma_R{}^\circ x)]$. The line shown is that expected from eq with $\lambda = 0$.

intensity measurements on the 1600-cm^{-1} band of symmetrically para-disubstituted benzenes. Previous work[20] has shown that for asymmetrical groups of type III the para-disubstituted derivative, which exists as a mixture of cis V and trans VI forms in solution, has an allowed band due to V. No absorption other than the overtone is expected either for a type II or for a type IV structure: VII is centrosymmetric, and VIII the dipole components which do not cancel out are at right angles to the ring plane and should not interact with the in-plane ring vibration. Whereas the bisisothiocyanate showed only a broad overtone at 1566 cm^{-1} and the bisisocyanate a broad overtone at 1540 cm^{-1} (with a shoulder at 1578 cm^{-1}), the bisazide gave a distinct band at 1582 cm^{-1} with shoulders at 1608 and 1632 cm^{-1}. The bisnitroso compound is very unstable and was not measured. The absorption



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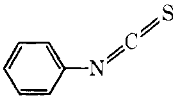

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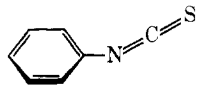

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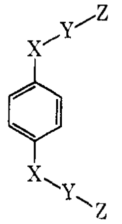

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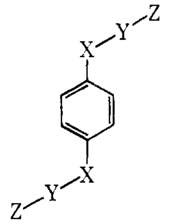

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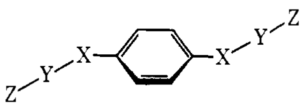

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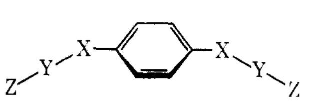

VIII

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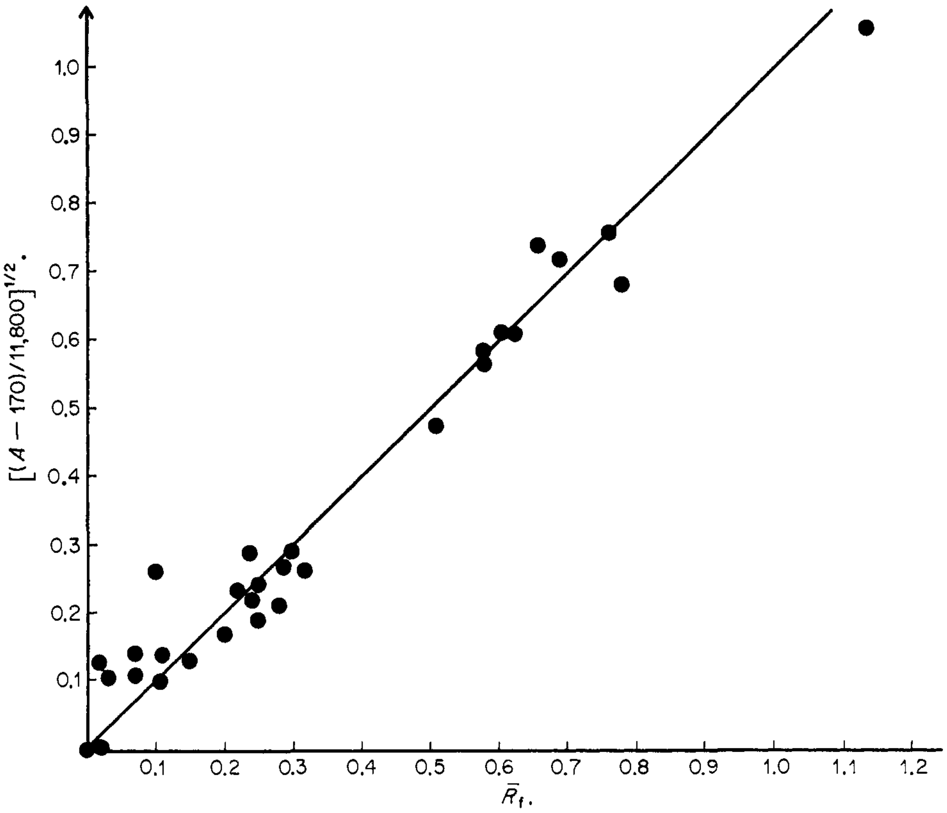
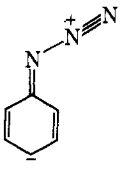
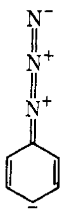


Figure 3. Plot of $[(A_{obsd} - 170)/11{,}880]^{1/2}$ against $|\sigma_R°1 - \sigma_R°2 + \lambda|$ for para-substituted isocyanates, isothiocyanates, isocyanides, and (incorporating asymmetry correction) for azides. The line shown is that of eq 2 and λ is calculated from eq 5, 6, or 7 as appropriate.

would, in any case, be of very low intensity since that of nitrosobenzene itself is very weak.

Hence, we conclude, both from the literature data and from our own ir measurements, that the geometrical arrangement of phenyl isocyanate and isothiocyanate are as in IV, whereas that of phenyl azide is analogous to III. Such a difference in orientation is expected on electronic grounds, as demonstrated by a VB treatment: canonical form IX is more important than X for phenyl azide, but XII is more important than XI for phenyl isocyanate. Hence overlap between the ring and the substituent π systems is preferred for the azide, but overlap between the ring π system and the sp^2-hybridized lone pair on nitrogen for the isocyanate (and isothiocyanate).


IX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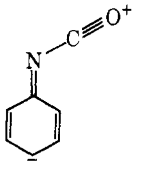
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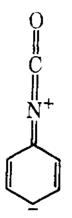
XII

Asymmetry Correction for Phenyl Azides and Nitrosobenzenes. We previously deduced that if the components of $\sigma_R°$ for an asymmetric substituent are denoted by $\sigma_R°x$ in the C_1–C_4 direction of the benzene ring and $\sigma_R°y$ perpendicular to this, eq 4 and 5 hold. This enables the calculation of $\sigma_R°x$ and $\sigma_R°y$ components for the azide group as −0.351 and 0.092, respectively. An asymmetry correction should also be made for the nitrosobenzenes but calculations indicate that these would be less than 0.005 σ unit and thus insignificant.

$$A_{\text{mono-as}} = 17{,}600[(\sigma_R°x)^2 + (\sigma_R°y)^2] + 100 \quad (4)$$

$$A_{\text{para-as/as}} = 11{,}800[2(\sigma_R°y)^2] + 170 \quad (5)$$

Infrared Intensities of meta-Substituted Derivatives. Spectral data for the meta-substituted isocyanides, isocyanates, isothiocyanates, and azides are presented in Table I. The published[9] values of $\sigma_R°$ for the corresponding monosubstituted benzenes are used to calculate values of $[(\sigma_R°1)^2 + (\sigma_R°2)^2 + \sigma_R°1\sigma_R°2]$. A_{obsd} has been plotted against this quantity in Figure 1; the line shown is that found previously,[21] and corresponds to eq 3. For the meta-substituted phenyl azides, two calculated points are shown which correspond to those calculated using the + and − signs in eq 6,[21] with the values of x and y which were derived in the preceding section of this paper.

$$A_{\text{meta-as/s}} = 19{,}000[(\sigma_R°s)^2 + (\sigma_R°as)^2 + \sigma_R°s(x \pm \sqrt{3}y)] + 340 \quad (6)$$

The satisfactory fit of the points to the previously deduced line in Figure 1, and the agreement of the $(A - 340/19{,}000)$ value with $\bar{R}_m^{-2}$) in Table I, confirms the magnitudes of the $\sigma_R°$ values deduced for the NCO, NCS, N_3, and NC groups from the intensities of the corresponding monosubstituted benzenes and, further shows that each of these groups is an electron donor.

Infrared Intensities of para-Substituted Derivatives. Spectral data are presented in Table II. In the absence of mutual interaction between the substituents, eq 2 should apply (with $\lambda = 0$), except that for the azides an asymmetry correction factor must be included as shown in eq 7.[20] The wide discrepancies shown in Figure 2 indicate that strong substituent–substituent interactions are indeed found. The results indicate that each of the substituents NCO, NCS, N_3, and NC can act as either resonance donors or as resonance acceptors according to whether they are placed para to an acceptor or donor substituent. The nitroso substituent appears to act as an electron acceptor in all cases; the magnitude of this acceptance increases if paired with a strong electron donor, and nitroso thus acts analogously to substituents such as cyano.

$$A_{\text{para-as/s}} = 11{,}800[(\sigma_R{}^\circ\text{s} - \sigma_R{}^\circ\text{as})^2 + 2\sigma_R{}^\circ\text{s}(\sigma_R{}^\circ\text{as} - \sigma_R{}^\circ x)] + 170 \qquad (7)$$

$$\lambda = K_A[\sigma^+ - \sigma^\circ] \qquad (8)$$

The deviations can be treated quantitatively. Interactions with para-donor groups in which the substituents NCO, etc. act as electron acceptors relative to their normal behavior should be correlated by the factor λ of eq 8[20] where K_A is a constant characteristic of the acceptor and σ^+ and σ° refer to the donor substituent. Using the data of Table III, we calculate by least squares K_A values of 0.36, 0.35, 0.32, 0.43, and 0.17 for the groups NCO, NCS, N_3, NO, and NC, respectively. For interactions with the d-orbital acceptors chlorine or bromine in which the groups NCO, etc. act as electron donors, the λ should be given by eq 9 in which $\sigma_R{}^\circ$D refers to substituent NCO, etc. and K_x = 0.32 for chloro and 0.42 for bromo[20] characteristic for the d-orbital acceptor. Finally, for interactions with the π-acceptor NO_2, λ should be given by eq 10 which is one of two alternative methods given in ref 20.

Table III. σ Values[a] for Donor Groups

	σ^+	σ°	$\sigma^+ - \sigma^\circ$
NMe_2	−1.7	−0.44	−1.26
OMe	−0.78	−0.12	−0.66
F	−0.07	0.17	−0.24
Me	−0.31	−0.15	−0.16

[a] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964).

$$\lambda = K_X\sigma_R{}^\circ\text{D} \qquad (9)$$

$$\lambda = 6.5[\sigma_R{}^\circ(NO_2)][\sigma_R{}^\circ(\text{D})]^2 \qquad (10)$$

Table III includes values of λ calculated by eq 8, 9, and 10 and also of $\bar{R}_p$ defined by eq 11 (together with the appropriate correction for asymmetry for the azides). There is satisfactory agreement between $\bar{R}_p$ and $[(A - 170)/11{,}800]^{1/2}$, as shown in Figure 3.

$$\bar{R}_p = |\sigma_R{}^\circ(1) - \sigma_R{}^\circ(2) + \lambda| \qquad (11)$$

The results thus clearly indicate that the resonance properties of the NCO, NCS, and N_3 substituents are very sensitive to the system to which they are attached, and can in fact be reversed from donation to acceptance. The nitroso substituent however, is apparently loathe to act as an electron donor and this must be related to the electronegativity of the oxygen atom making contributions of the form $Ar{=}N^+{=}O$ energetically unlikely. In the isocyanate group the oxygen atom is isolated from the nitrogen atom by the intermediate carbon atom and the form $Ar{=}N^+{=}C{=}O$ would have more significance to the overall structure. The results obtained for the nitroso substituent are in agreement with dipole moment[31] and nmr[32] measurements of para-substituted derivatives.

The Nitroso Stretching Frequency (ν_{NO}). There has been considerable discussion[5,31] in the past about the position of the nitroso stretching absorption. It has been suggested to occur about 1600 cm^{-1} in aliphatic nitroso compounds and 1490–1530 cm^{-1} in nitrosobenzenes. Some of the early confusion arose because of the tendency of the nitroso compounds to form dimers. It is worth pointing out[5,31] that while nitrosobenzenes containing a para-resonance donor such as iodo or dimethylamino are monomeric even in the solid state, other nitrosobenzenes exist as colorless or yellow dimeric forms in the solid but give green monomeric solutions. Absorptions at 1500–1530 cm^{-1} were indeed observed with all the nitrosobenzene solutions employed, but the ν_{13a} benzene mode is also expected to occur at about this frequency. However the intensity of the band observed was found to be much greater than expected for the ν_{13a} band. Thus the ν_{13a} absorption for *p*-cyanotoluene occurs at 1510 cm^{-1} and has an intensity of 610 l. mol^{-1} cm^{-2}. The ν_{13a} absorption of *p*-nitrosotoluene would be expected to be of similar magnitude since the resonance effects of the nitroso and cyano substituents are comparable. However an absorption of 3920 l. mol^{-1} cm^{-2} is actually observed with a maximum at 1511 cm^{-1} and a shoulder at 1517 cm^{-1}. It thus seems clear that the ν_{NO} absorption does appear at approximately 1510 cm^{-1} and no interference with the 1600 cm^{-1} values seems to occur.

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(31) B. G. Gowenlock and W. Luttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1968).

(32) I. C. Calder and P. J. Garratt, *Tetrahedron*, **25**, 4023 (1969).