Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXV.[1] Conjugation in *para*-Substituted Benzenes and its Relation to Strain Energies and σ Values

By **T. Bruce Grindley** and **Alan R. Katritzky,*** School of Chemical Sciences, University of East Anglia, Norwich
Ronald D. Topsom,* Department of Organic Chemistry, La Trobe University, Victoria, Australia

$\Delta G^{\ddagger}$ Values for the rotational barriers of a variety of *para*-disubstituted benzenes are determined by the n.m.r. coalescence method: for two compounds $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are found by complete line shape matching. These and other available barriers are compared with barriers determined by the i.r. intensity method. The work supports the previous conclusion that σ values can be related directly to the energy scale and points to a method for predicting substituent–substituent interactions in such compounds from i.r. derived parameters.

THE availability of variable temperature n.m.r. methods has allowed [2,3] direct determination of the free energy barriers to rotation around some bonds. While $\Delta G^{\ddagger}$ may often be obtained reliably, particularly from complete line shape analyses, values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are less accurate. However, for molecules where the symmetry of the transition state is the same as that of the ground state, then $\Delta S^{\ddagger}$ should be close to zero and $\Delta G^{\ddagger}$ equal to $\Delta H^{\ddagger}$ if solvation effects are unimportant; experimental evidence is available [3] to support this.

We are particularly interested [1,4] in barriers to rotation in substituted benzenes since these should be related [5] to the conjugation between the substituent and the benzene ring. Although n.m.r. studies of barriers in molecules in the gaseous phase are starting to appear,[6] for substituted benzenes only liquid phase studies are available.

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[1] Part XXXIV, T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 289.

[2] R. M. Lynden-Bell in 'Progress in Nuclear Magnetic Resonance Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, Oxford, 1967, vol. 2, ch. 4 and references therein.

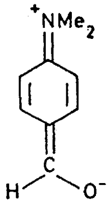
[3] G. Binsch, *Topics Stereochem.*, 1968, **3**, 97; H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219; T. B. Grindley and A. R. Katritzky, unpublished results.

[4] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *Tetrahedron Letters*, 1972, 2643.

[5] R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J.C.S. Perkin II*, 1974, 247.

[6] R. E. Carter and T. Drakenberg, *J.C.S. Chem. Comm.*, 1972, 582; R. K. Harris and R. A. Spragg, *Chem. Comm.*, 1967, 362.

The barrier to rotation of a group in a monosubstituted benzene can be significantly altered in some cases by a second substituent attached to a ring even in the absence of steric effects. Thus the barrier to rotation of the formyl group about the C_{Ar}–C bond in benzaldehyde is [7] 7·9 kcal mol^{-1} but in *p*-dimethylaminobenzaldehyde rises * to 10·7 kcal mol^{-1}. This increase in barrier can be ascribed to 'through conjugation' involving the substituents as shown in valence-bond terminology by contributions of form (A). In the same way the barrier to the dimethylamino-group is also greater [5] here than in *NN*-dimethylaniline.



(A)

Some other physical evidence is available for such through conjugation. Thus *X*-ray studies have shown [8,9] the expected changes in bond lengths in *para*-disubstituted benzenes containing one strong electron-donating and one strong electron-withdrawing substituent. Dipole moment studies [10] have also provided evidence for such compounds. However, neither type of study leads to an accurate assessment of the mutual substituent interaction. Studies on rotational barriers provide the most direct measurement but not many examples are available and experimental difficulties limit their extension.

We have, by contrast, made extensive measurements of the i.r. intensities of certain ring stretching modes of both mono- [9,11] and *para*-di-substituted [5,9,12] benzenes. The i.r. intensity of the ν_8 ring stretching modes near 1600 cm^{-1} in *para*-disubstituted benzenes in which one substituent is a donor and one an acceptor is given [5] by equation (1), and this equation is in general agreement

$$A_{(para\text{-}YZ)} = 15{,}000[\sigma_R{}^0\mathrm{Y} - \sigma_R{}^0\mathrm{Z} + 2\delta(\mathrm{YZ})]^2 + 170 \qquad (1)$$

with rotational barrier results processed by equations (5) and (7). We further generalized i.r. results for *para*-disubstituted benzenes in terms of equations (2) and (3)

$$2\delta_{(\text{donor Y, }\pi\text{-acceptor Z})} = K_{\mathrm{A}}(\sigma^+\mathrm{Y} - \sigma^0\mathrm{Y}) \qquad (2)$$

$$2\delta_{(\text{donor Y, }d\text{-orbital acceptor Z})} = K_{\mathrm{XZ}}\sigma_R{}^0\mathrm{Y} \qquad (3)$$

where equation (2) applies to compounds having an electron donor paired with a π-electron acceptor while equation (3) applies where the acceptance is into *d*-orbitals. Analysis of the data has allowed us to assess the π-electron conjugation between substituents and the benzene ring. In Part XXXIV [1] we compared our i.r. results with rotational barrier evidence for monosubstituted benzenes. The object of the present paper is to make a similar comparison for *para*-disubstituted benzenes with particular reference to establishing a more general basis for the discussion of through conjugation.

EXPERIMENTAL

All compounds were commercial samples, purified by recrystallization or distillation, or were prepared by literature methods as in Table 1. Solvents were dried over molecular sieves except for vinyl chloride which was distilled directly from a gas cylinder through a vacuum system into the n.m.r. tube. All samples were degassed in n.m.r. tubes and sealed under vacuum. Concentrations of samples ranged from 4 to 10% v/v.

TABLE 1

Physical properties of *para*-substituted dimethylanilines made by literature methods

Substituent	M.p. (°C)	Lit. m.p. (°C)	Ref.
COEt	101—103	103	*a*
COPr^i	50—52	46—49	*b*
COBu^t	90—92	86—87	*c*

[a] A. W. Nineham, *J. Chem. Soc.*, 1952, 635. [b] H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Ber.*, 1963, **96**, 2671. [c] P. A. Barrett and D. E. Bays, B.P. 911,342/1962 (*Chem. Abs.*, 1963, **58**, 8980).

100 MHz N.m.r. spectra were recorded using a Varian HA-100 spectrometer with a V-4333 probe and V-4343 variable temperature unit for samples with coalescence temperatures of −95°. Sample temperatures using this probe were measured using a standard methanol sample containing tetramethylsilane and the Varian calibration chart. Samples with coalescence points below −100° were measured on a probe [13] containing a platinum resistance thermometer in the nitrogen stream below the sample. This thermometer was calibrated against a second platinum resistance thermometer in an open spinning sample tube containing $CFCl_3$–CF_2BrCF_2Br (1 : 1 v/v). The probe did not contain a heater and temperatures were adjusted by changing the nitrogen flow rate.

Calculations.—All computer calculations were carried out on an ICL 1905E computer.

The n.m.r. spectra for the aromatic protons of all compounds examined except *p*-fluorobenzaldehyde showed

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* Our results in methylene chloride from coalescence measurements at 100 MHz. Previous workers have found 10·8 kcal mol^{-1} in methylene chloride,[7] 10·2 kcal mol^{-1} in vinyl chloride,[8] and 10·5 kcal mol^{-1} in toluene.[8]

[7] F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1964, **86**, 119.

[8] See, for example, J. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68; T. F. Lai and R. E. Marsh, *ibid.*, 1967, **22**, 885; A. M. O'Connell and E. N. Maslen, *ibid.*, p. 134.

[9] A. R. Katritzky and R. D. Topsom, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87.

[10] See, for example, M. T. Rogers, *J. Amer. Chem. Soc.*, 1955, **77**, 3681 and references therein.

[11] R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1757.

[12] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.

[13] For a detailed description of this probe see K. Price, Ph.D. Thesis, University of East Anglia, 1969; A. Purdie, M.Sc. Thesis, University of East Anglia, 1970.

AA'BB' patterns at high rates of rotation and ABCD patterns at low rates. For all compounds except those considered below, $\Delta G^{\ddagger}$ was obtained from coalescence temperatures by treatment of the change in the spectra as the coalescence of two isolated AB quartets using equation (4) of Kurland *et al.*[14]

$$K = \pi[(\Delta\nu^2 + 6J^2_{AB})/2]^{\frac{1}{2}} \qquad (4)$$

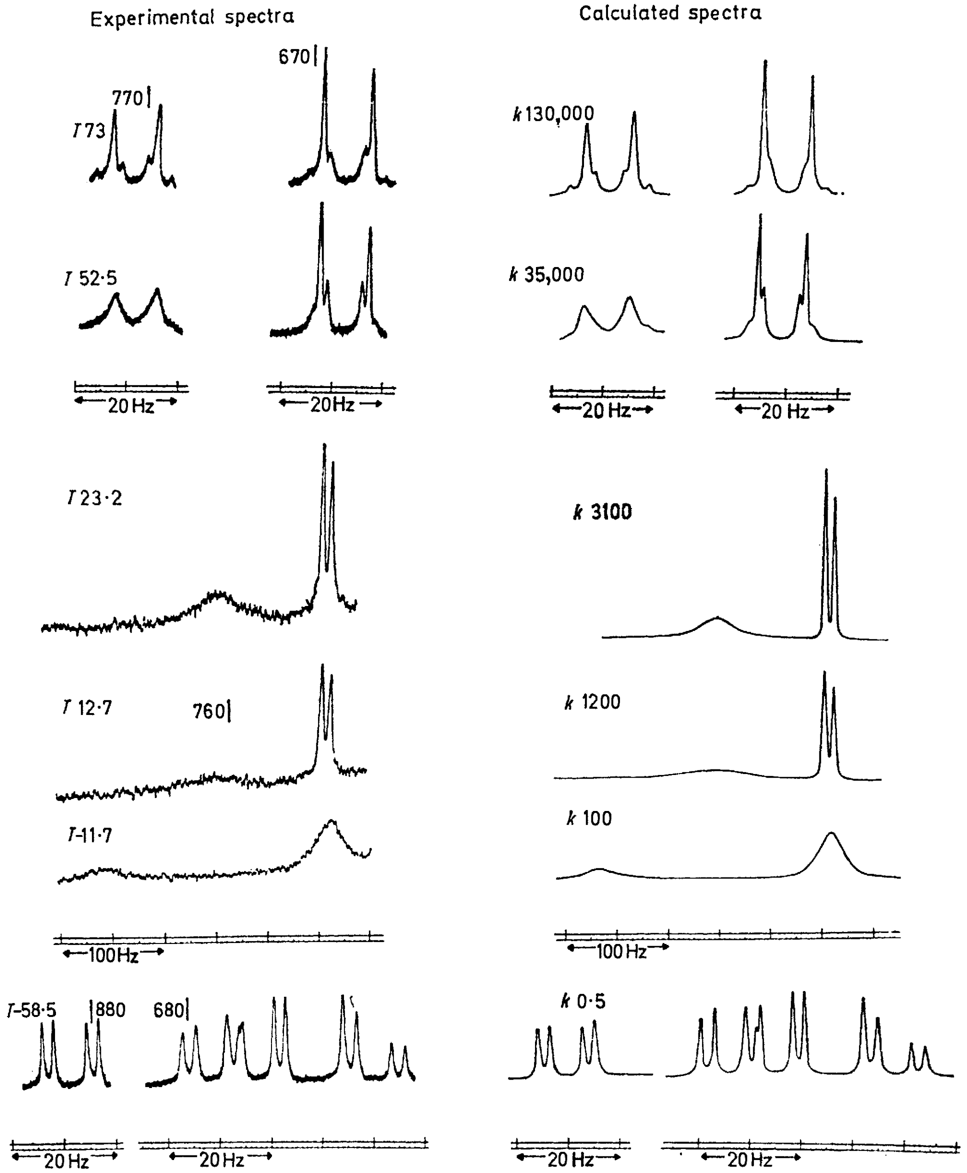

FIGURE 1 Comparison of experimental and calculated 100 MHz n.m.r. spectra of the aromatic protons of 4-dimethylaminonitrosobenzene in CH_2Cl_2 at different temperatures [indicated by T (°C)]. Rate constants for the simulated spectra are indicated by k. Marker lines in Hz from internal Me_4Si are shown on the experimental spectra

For two compounds, *NN*-dimethyl-4-nitrosoaniline (I) and 4-dimethylaminobenzaldehyde (II) a complete line shape analysis was carried out using the DNMR 3 program of Kleier and Binsch.[15] For (I) in CH_2Cl_2 rate effects were observable from the highest temperature studied, 73°, to −35°. Eight spectra from −45 to −90° were analysed using the LAOCOON 3 program[16] (root mean square deviation ranged from 0·058 to 0·092) and the temperature dependence of the chemical shift differences over this range were obtained and individual chemical shifts were extrapolated to higher temperatures. For compound (II) spectra

p-$RC_6H_4NMe_2$
(I) R = NO
(II) R = CHO

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[14] R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

[15] D. A. Kleier and G. Binsch, *J. Magnetic Resonance*, 1970, **3**, 146; Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970.

[16] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

were analysed using the LAOCOON 3 program under conditions of slow rotation and it was assumed that chemical shifts were temperature independent. Line widths were assumed to change linearly from the slow to fast exchange limits. Line shape matching for both compounds was carried out by visual matching of experimental spectra and computer calculated simulations as shown in Figure 1.

Activation parameters were obtained from plots of ln $(kh/\kappa k_BT)$ against $1/T$ as shown in Figure 2, where k is the rate constant determined as above, h is Planck's constant, κ is the transmission constant assumed to be 1, and k_B is Boltzmann's constant. The intercept was $\Delta S^‡/R$ and the slope was $-\Delta H^‡/R$ where R is the gas constant. Because of the wide variation in rates observed, 130,000—10, the values obtained for (I) will be more accurate than those for (II).

TABLE 2

Rotational barriers in *para*-disubstituted benzenes determined by n.m.r. methods

Substituents	Solvent	T_c (°C)	$\Delta\nu$	$\Delta G^‡$ [a]/ kcal mol^{-1}	$\Delta H^‡$/ kcal mol^{-1}	Ref.
CHO, NMe_2	CH_2Cl_2 [b]	−60·5 [e]	18·4	10·7	11·1	*j*
		−68·0 [f]	5·7	10·7		
	CH_2Cl_2 [c]	−71·0	*g*	10·8		*k*
	$PhCD_3$ [c]	−56	71	10·5		*l*
	$CH_2{=}CHCl$ [c]	−73·0	14	10·2		*l*
CHO, OMe	$CH_2Cl_2 - C_2F_4Br_2$ [b] (2 : 1)	−89 [e]	14	9·3		*j*
	$PhCD_3$ [c]	−75	80	9·4		*l*
	$CH_2Cl_2 - C_2F_4Br_2$ [b] (1 : 1)	−87 [e]	14	9·4		*j*
	$CH_2{=}CHCl$ [c]	−99	*g*	9·2		*k*
CHO, F	*d*	−110	6·3	8·4		*j*
CHO, Me	*d*	107·5 [e]	9·0	8·5		*j*
		−115 [f]	6·2	8·2		*j*
COMe, NMe_2	*d*	−110·5	9·2	8·3		*j*
	$PhCD_3$ [c]	−92	80	8·5		*l*
COMe, OMe	*d*	−144	8	6·6		*j*
	$PhCD_3$ [c]	−116	*h*	⩽7·3 [h]		*l*
	$CH_2{=}CHCl$ [c]	−142	*h*	~6·5 [h]		*l*
COEt, NMe_2	*d*					*j*
$COPr^i$, NMe_2	*d*	−122	6·5	7·8		*j*
$COBu^t$, NMe_2	*d*	—145	6	6·6		*j*
NO, NMe_2	CH_2Cl_2 [b]	2·5 [e]	230·0	12·7	14·1	*j*
	CH_2Cl_2 [b]	−12·5	33·5	12·9		*j*
	$CDCl_3$ [c]			*h*	14·9	*m*
	Me_2CO [c]			12·1 [h]	11·2	*n*
	Me_2CO [b]	2·5 [e]	233·4	12·7		*j*
	Me_2CO	−13·5 [f]	37·6	12·8		*j*
	$(CD_3)_2CO$	−3	232	12·4		*o*
NO, NEt_2	$(CD_3)_2CO$	4	226	12·8		*o*
NO, NHMe	$(CD_3)_2CO$	−3	232	12·4		*o*
NO, NHEt	$(CD_3)_2CO$	5	230	12·8		*o*
NO, NHPh	$(CD_3)_2CO$	−6	256	11·7		*o*
NO, NH_2	$(CD_3)_2CO$	−4	230	12·4		*o*
NO, ONa	$(CD_3)_2CO$	80	67	17·3		*o*
NMe_2, NO	$PhCD_3 - CH_2{=}CHCl$ (1 : 1)	−87·5	*h*	9·9 [i]	8·6	*p*
NMe_2, CHO	$PhCD_3 - CH_2{=}CHCl$ (1 : 1)	−125	*h*	7·8 [i]	7·6	*p*
NMe_2, COMe	$PhCD_3 - CH_2{=}CHCl$ (1 : 1)	−134	*h*	7·2 [i]	7·0	*p*
CHO^+H, Pr^i	$FSO_3H - D_2O$ (9 : 1)	+29	61·0	16·1		*q*
CHO^+H, OMe	$FSO_3H - D_2O$ (9 : 1)	+60	*g*	17·9		*q*
CHO^+H, Me	$FSO_3H - D_2O$ (9 : 1)	+36	12·9	16·4		*q*
CHO^+H, F	$FSO_3H - D_2O$ (9 : 1)	−17	*g*	13·6		*q*
CHO^+H, Cl	$FSO_3H - D_2O$ (9 : 1)	−11	54·0	13·9		*q*
CHO^+H, Br	$FSO_3H - D_2O$ (9 : 1)	−9	33·2	14·0		*q*
CHO^+H, Me	$SbF_5 - FSO_3H - SO_2$	*g*	*g*	16·3		*r*
CHO^+H, Cl	$SbF_5 - FSO_3H - SO_2$	*g*	*g*	14·8		*r*
CHO^+H, Br	$SbF_5 - FSO_3H - SO_2$	*g*	*g*	14·8		*r*
$\overset{+}{C}HO\overset{-}{B}F_3$, OMe	CH_2Cl_2	−17	*g*	14·2		*s*
$\overset{+}{C}HO\overset{-}{B}F_3$, Me	CH_2Cl_2	−41	*g*	?		*s*

[a] Except where otherwise noted $\Delta G^‡$ is at T_c. The barrier refers to the first named substituent. [b] At 100 MHz. [c] At 60 MHz. [d] At 100 MHz in $CH_2Cl - CH_2{=}CHCl$ (1 : 1). [e] From H-2 and -6. [f] From H-3 and -5. [g] Not quoted. [h] Energy parameters determined by approximate equations other than the coalescence equations. [i] $\Delta G^‡$ at 133 K. [j] This work. [k] Ref. 7. [l] R. E. Klinck, D. H. Marr, and J. B. Stothers, *Chem. Comm.*, 1967, 409. [m] P. K. Korver, P. J. Van der Haak, and Th. J. de Boer, *Tetrahedron*, 1966, **22**, 3157. [n] D. D. MacNicol, R. Wallace, and J. C. D. Brand, *Trans. Faraday Soc.*, 1965, **61**, 1. [o] I. C. Calder and P. J. Garratt, *Tetrahedron*, 1969, **25**, 4023. [p] Ref. 12. [q] M. Rabinovitz and A. Ellencweig, *Tetrahedron Letters*, 1971, 4439. [r] R. Jost, P. Rimmelin, and J. M. Sommer, *Chem. Comm.*, 1971, 879. [s] A. Greenvald and M. Rabinovitz, *Chem. Comm.*, 1969, 642.

Errors.—The errors in $\Delta G^‡$ determined by the coalescence method, which depend on the precision of measurement of T_c, $\Delta\nu$, and J, are likely to be small: an error of 2° in T_c involves an error of 0·1—0·2 kcal mol^{-1} in $\Delta G^‡$.

RESULTS

Results of barriers determined in the present work, together with other n.m.r. determined rotational barriers are collected in Table 2. Agreement for barriers determined by different workers by the n.m.r. method is good, when allowance is made for solvent differences.

DISCUSSION

Entropies of Rotation.—For *NN*-dimethyl-4-nitrosoaniline (I) and 4-dimethylaminobenzaldehyde (II) complete line shape analyses of spectra in CH_2Cl_2 gave $\Delta S^{\ddagger}$ values for rotation of 5·0 and 2·5 cal mol^{-1} K^{-1} for the nitroso and formyl substituents respectively. These values are probably typical for rotation about single bonds attached to aromatic rings in the absence of symmetry effects or strong solvent interactions.

Clearly for these compounds, $\Delta G^{\ddagger}$ will only be slightly temperature dependent. For a change from 100 to 300 K the changes in $\Delta G^{\ddagger}$ are 1·0 and 0·5 kcal mol^{-1} for (I) and (II) respectively. The larger entropy for (I) may reflect greater interaction of (I) with the solvent in the ground state. As we are dealing with differences of $\Delta H^{\ddagger}$, we consider that it is reasonable to assume that the small entropy terms in the rotation energy difference between mono and disubstituted compounds, $E(Y, \text{mono}) - E(Y, \textit{para}\text{-YZ})$, will cancel.

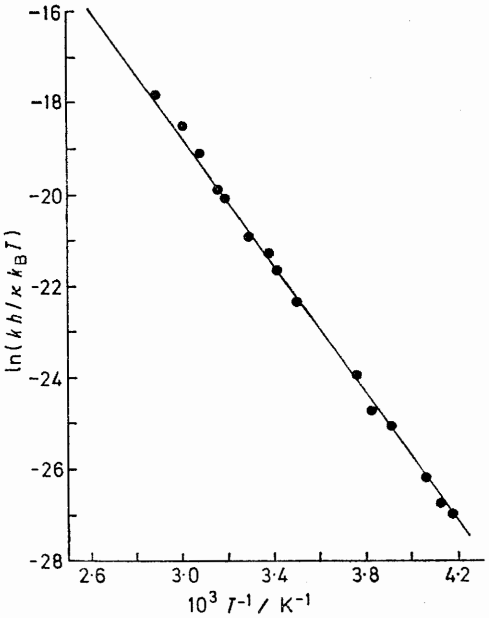

FIGURE 2 Plot of ln $(kh/\kappa k_B T)$ against $1/T$ where h is Planck's constant, κ is the transmission constant assumed to be 1, k_B is Boltzmann's constant, k is the rate constant, and T is the temperature in K

Substituent Effects on Rotational Barriers.—We earlier demonstrated [1] that for a monosubstituted benzene the barrier to rotation (E, in kcal mol^{-1}) about the single bond attaching the substituent to the benzene ring is given by equation (5) where $\sigma_R{}^0$Y and $(\sigma_R{}^0\text{Y})_{\text{tw}}$ are the resonance

$$E_{(\text{Y,mono})} = 33[\sigma_R{}^0\text{Y} - (\sigma_R{}^0\text{Y})_{\text{tw}}] - S_{(\text{Y})} \quad (5)$$

parameters [9] when the substituent is in the conformations of lowest and highest energy respectively and S is the strain energy in the lowest energy state. The quantity $(\sigma_R{}^0)_{\text{tw}}$ was introduced to allow for the fact that some substituents (*e.g.* NMe_2) continue to interact by resonance with the ring even when twisted 90° out of plane.

To extend this treatment to *para*-disubstituted benzenes we must allow for the additional resonance interaction between the two substituents, such as typified in structure (A). This interaction per substituent is denoted [5] δ (in units of $\sigma_R{}^0$) when the two substituents are in their lowest energy conformation. If substituent Y is twisted into the position of maximum energy then the additional resonance due to interaction between the two substituents is reduced to $\delta(\sigma_R{}^0\text{Y})_{\text{tw}}/\sigma_R{}^0\text{Y}$. Thus for a *para*-disubstituted benzene, the barrier to rotation about the substituent Y is described by equation (6).

$$E_{(\text{Y,para-YZ})} = 33[|\sigma_R{}^0\text{Y}| - |\sigma_R{}^0\text{Y}|_{\text{tw}} + \delta(1 - |\sigma_R{}^0\text{Y}|_{\text{tw}}/|\sigma_R{}^0\text{Y}|)] - S_{(\text{Y})} \quad (6)$$

Subtraction of equations (5) and (6) gives (7) from which the magnitude in kcal mol^{-1}, $33\delta(\text{YZ})$, of the additional interaction per substituent, Y or Z, in a *para*-disubstituted benzene may be calculated. This procedure may be checked in three ways. (i) Where the barriers to rotation of substituents Y and Z in a *para*-disubstituted benzene can be measured independently, then $33\sigma(\text{YZ})$ can be calculated both from equation (7) and from the corresponding equation in which Y and Z are interchanged. (ii) The i.r. intensity of the ν_8 ring stretching modes near 1600 cm^{-1} in *para*-disubstituted benzenes in which one substituent is a donor and one an acceptor is given by equation (1), in which δ measures the interaction between the two substituents, *i.e.* the amount by which $\sigma_R{}^0$ donor is decreased and $\sigma_R{}^0$ acceptor is increased. Hence equation (8) gives another method of calculating the interaction in kcal mol^{-1}. (iii) The empirical relations given in equations (2) and (3) for the direct interaction between substituents in *para*-disubstituted benzenes where $\lambda = 2\delta$ can be used with the known values of K_A and K_X.[6] Equations (9) and (10) follow from which the interaction between the substituents can again be calculated.

$$33\delta(\text{YZ})[1 - |(\sigma_R{}^0\text{Y})_{\text{tw}}/\sigma_R{}^0\text{Y}|] = E(\text{Y}, \textit{para}\text{-YZ}) - E(\text{Y,mono}) \quad (7)$$

$$33\delta(\text{YZ}) = 16{\cdot}5\{([A(\textit{para}\text{-YZ}) - 170]/15{,}000)^{\frac{1}{2}} - \sigma_R{}^0\text{Y} + \sigma_R{}^0\text{Z}\} \quad (8)$$

$$33\delta(\text{YZ}) = 16{\cdot}5K_A(\text{Z})[\sigma^+\text{Y} - \sigma^0\text{Y}] \text{ for } \pi\text{-acceptors} \quad (9)$$

$$33\delta(\text{YZ}) = 16{\cdot}5K_X\sigma_R{}^0\text{Y} \text{ for } d\text{-orbital acceptors} \quad (10)$$

Method (i) which requires the independent measurement of the barriers to rotation of substituents Y and Z can be applied using the data in Table 2 for *p*-dimethylamino-benzaldehyde and -acetophenone. The values obtained by direct use of σ values are 2·6 and 2·9 kcal mol^{-1} for the former and 2·4 and 2·1 kcal mol^{-1} for the acetophenone $\{|\sigma_R{}^0(\mathrm{NMe_2})| = 0{\cdot}53$, $|\sigma_R{}^0(\mathrm{NMe_2})|_{\mathrm{tw}} = 0{\cdot}13$, $|\sigma_R{}^0(\mathrm{CHO})| = 0{\cdot}24$, $|\sigma_R{}^0(\mathrm{CHO})|_{\mathrm{tw}} = 0$, $|\sigma_R{}^0(\mathrm{COMe})|_{\mathrm{tw}} = 0$, $|\sigma_R{}^0(\mathrm{COMe})| = 0{\cdot}22\}$.

As the δ values are also available from i.r. measurements [method (ii)] then barrier and S values could be inter-related by equation (6). Equally the use of equation (6) for cases where E and S values are known provides a test for such alternative values.

Table 3 compares some values of these interaction terms obtained from rotational barriers and i.r. measurements [methods (ii) and (iii)]. The values show broad agreement only presumably because of errors in taking small differences in larger quantities in both the n.m.r. and i.r. methods, the approximations [5] in the i.r. method and the errors inherent in the n.m.r. determination of barriers. The n.m.r. results suggest that the i.r. method leads to too high values for the interaction energies. Other evidence is limited but Taft [17] estimated the interaction energies in certain *para*-substituted ethyl benzoates in aqueous organic solvents as $\mathrm{NMe_2}$, 0·95; $\mathrm{NH_2}$, 0·90; OMe, 0·45; F, 0·15 in kcal mol^{-1}. Use of equation (2), however, gives 2·9, 2·1, 1·5, 0·55 kcal mol^{-1} respectively, again suggesting that the i.r. method leads to high values.

TABLE 3

Substituent–substituent interactions in *para*-disubstituted benzenes $\mathrm{C_6H_4YZ}$ (kcal mol^{-1})

Substituents		33δ (YZ) from n.m.r.		33δ (YZ) from i.r. intensity	
		Y Barrier	Z Barrier	Obs.	Calc.
Y	Z	*a*	*a*	*b*	*c*
CHO	$\mathrm{NMe_2}$	2·8	3·6	5·1	5·2
CHO	OMe	1·4		2·8	2·7
CHO	F	0·5		0·1	1·0
CHO	Me	0·4		2·2	0·7
COMe	$\mathrm{NMe_2}$	2·0	2·8		3·3
COMe	OMe	0·3		1·6	1·7

[a] Calculated from equation (7). [b] Calculated from equation (1). [c] Calculated from equation (8).

Through Conjugation in para-*Disubstituted Benzenes*.—The overall qualitative agreement between the n.m.r. and i.r. figures in Table 3 is encouraging and gives expectation that the method may be general. The same relative order of interactions is indicated from both series and Tables 2 and 3 both indicate that as expected the magnitude of the interaction follows the donor $(\sigma^+ - \sigma)$ value [2,5] for a fixed acceptor substituent such as CHO, COMe, and $\mathrm{CHOH^+}$. We now look at the results for some series of compounds where sufficient values are available to allow discussion. For convenience we summarise the relevant values of E, S, $\sigma_R{}^0$, $(\sigma_R{}^0)_{\mathrm{tw}}$, and 33δ in Table 4.

TABLE 4

Substituent–substituent interaction energies (kcal mol^{-1})

Substituents		Barriers		S		$\sigma_R{}^0$		$(\sigma_R{}^0)$tw		33δ	
R-1	R-2	1	2	1	2	1	2	1	2	1	2
CHO	$\mathrm{NMe_2}$	10·7	7·6	0	7·8	0·24	0·53	0	0·134	2·7	3·0
	OMe	9·3	3·8 [a]	0	3 [b]	0·24	0·43	0	0·24 [b]	1·3	
	F	8·4	*c*	0		0·24	0·34	0	*c*	0·4	
	Me	8·3	*c*	0		0·24	0·10	0	*c*	0·3	
	H	7·9	*c*	0		0·24	0·0	0	*c*	−0·1	
COMe	$\mathrm{NMe_2}$	8·3	7·2	0·9	7·8	0·22	0·53	0	0·134	2·0 [d]	2·4 [d]
COEt	$\mathrm{NMe_2}$	8·1	*e*	?	7·8	0·21	0·53	0	0·134	1·3 + S	
COPr^{i}	$\mathrm{NMe_2}$	7·8	*e*	?	7·8	0·19	0·53	0		1·4 + S	
COBu^{t}	$\mathrm{NMe_2}$	6·6	*e*	?	7·8	0·15	0·53	0		1·5 + S	
NO	$\mathrm{NMe_2}$	12·4	8·6	0	7·8	0·245 [f]	0·53	0	0·134	4·31	4·31
	$\mathrm{NEt_2}$	12·8		0		0·245 [f]	0·57	0	0·14 [b]	4·7	
	NHMe	12·4		0		0·245 [f]	0·52	0	0·12 [b]	4·3	
	NHEt	12·8		0		0·245 [f]	0·52	0	0·13 [b]	4·7	
	NHPh	11·7		0		0·245 [f]	0·50	0	*e*	3·6	
	$\mathrm{NH_2}$	12·4		0		0·245 [f]	0·47	0	0·12 [b]	4·3	
	ONa	17·3		0		0·245 [f]	0·59	0	*c*	9·2	

[a] Calculated using an estimated value of S. [b] Estimated; see ref. 1. [c] No barrier to rotation. [d] This value had been calculated by error in the preliminary communication (ref. 3) by a slightly different method to be 3·7 kcal mol^{-1}. The correct value using that method is 2·2 kcal mol^{-1}. We thank Dr. D. D. MacNicol for pointing this error out to us. [e] Not known. [f] See text.

Substituted Benzaldehydes and Acetophenones.—The magnitude of the interaction decreases as expected as the donor $(\sigma^+ - \sigma)$ value [2,5] decreases. Dipole moment studies indicate [18] that except for 4-methoxy- (and presumably 4-dimethylamino-) benzaldehyde the measured moments are not larger than the sum of the segments, indicating that these direct interaction terms are small, in agreement with the above result (see Table 3). The size of the interaction term in *p*-dimethylaminobenzaldehyde calculated from the rotation of the $\mathrm{NMe_2}$ group is somewhat larger, probably due to interaction with the solvent toluene in the determination of the latter barrier.[19]

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Similar comments may be made about the interaction terms derived from the acetophenones.

Substituted Dimethylamino-compounds.—Relatively few dimethylanilines have been studied with respect to the NMe_2 barrier. For *p*-acyl-dimethylanilines in which the acyl group varies from HCO to Bu^tCO, the substituent–substituent interaction should decrease as the acyl group increases in size on both steric and electronic grounds.[20] This is true for the first two members of the series, HCO and COMe. However, for the last three members of the series, the interpretation is hindered because the values of *S*, the strain in the ground state, are unknown (*cf*. Table 4).

Table 5

Substituent–substituent interactions (kcal mol^{-1}) in *p*-acyldimethylanilines

p-Substituent	CHO	COMe	COEt	$COPr^i$	$COBu^t$
Interaction − strain	2·7	1·1	1·3	1·4	1·5
Strain	0	0·9	?	?	?
Interaction	2·7	2·0			

For the interaction to decrease across the series would indicate that the strain in the ground state should also diminish, *e.g*. as 0·6, 0·4, and 0·2 kcal mol^{-1} for COEt, $COPr^i$, and $COBu^t$ respectively. Although this seems at first sight unlikely, it could occur if *S* decreases much more rapidly with the angle of twist than does the resonance interaction. However, attempted calculations based on evaluation of non-bonded interactions did not appear to support this view. Similar calculations [21] on 2-acetylfuran also fail [22] to explain steric interactions.

Nitroso-compounds.—For *NN*-dimethyl-4-nitrosoaniline (I), both barriers are known. Application of equation (3) to the barrier about the NMe_2 group gives 4·3 kcal mol^{-1} for 33δ. This value can now be applied with equation (3) to the barrier for NO rotation. If *S* and $(\sigma_R^0)_{tw}$ for NO are each assumed to be zero, then σ_R^0 for NO is +0·25. The previous σ_R^0 values for NO were 0·07 [11] as determined by the i.r. method [9] in CCl_4 and 0·30 [23] in cyclohexane or 0·32 [24] in trichlorofluoromethane as determined by the ^{19}F n.m.r. method. The ^{19}F n.m.r. result is distorted by through resonance between the *para*-F and -NO groups; [12] the previous i.r. result is probably affected by dimerization in CCl_4. We believe that $\sigma_R^0(NO) = +0·25$ is the best available value. Applying this value of σ_R^0 to the other nitroso-compounds gives the interaction values of Table 4.

General Conclusions.—The general agreement found between the n.m.r. and i.r. results is encouraging and supports the basic theory underlying the work. An important consequence is that substituent–substituent interactions in energy terms may now be assessed for most *para*-disubstituted benzenes using equation (5). Furthermore the use of equation (6) allows the calculation of the analogous interactions where a *d*-orbital acceptor is attached in the *para*-position to a π-electron donor.

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