

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXIV.¹ Quantitative Relations between Conjugation and Strain Energies and σ°_R Values: Rotational Barriers in Monosubstituted Benzenes

By T. Bruce Grindley and Alan R. Katritzky,* School of Chemical Sciences, University of East Anglia, Norwich NOR 88C

Ronald D. Topsom,* School of Physical Sciences, La Trobe University, Melbourne, Australia

Known rotational barriers for substituents in monosubstituted benzenes are correlated with ring-substituent resonance interactions and strain energies. Rotational barriers are estimated for a variety of other substituents. σ Constants are related directly to the energy scale.

THE Hammett equation and its extensions have played a major part in the correlation of rates and equilibria of aromatic compounds. Despite this they have essentially remained empirical methods of predicting properties of a series of related compounds from the properties of the base compound. Recently, we have shown² how the Hammett σ constant may be directly related to the energy scale. We now describe the application of this approach to the estimation of rotational barriers.

Rotational Barriers.—The energy barrier to rotation of a substituent about the ring-substituent bond in a substituted benzene can be equated to the difference in resonance interaction between the position of maximum energy (usually the orthogonal position of 90° twist) and that of minimum energy (usually at or near coplanarity of the substituent and ring) less the corresponding difference in strain (including rehybridisation) energy. For substituents with not more than one branch at the atom adjacent to the ring, strain is usually absent or negligible at the conformation of highest energy. Equation (1) follows, where the subscript *tw* refers to the twisted (orthogonal) conformation.

$$E = (R - R_{tw}) - S \quad (1)$$

The resonance interaction of substituent and ring in a monosubstituted benzene is proportional to the modulus of the σ°_R value of the substituent.³ In our preliminary communication² we showed that the proportionality constant connecting *R* of equation (1) with σ°_R was 33 kcal mol⁻¹. We now apply equation (2) to a wider range of substituents; the results are summarised in Table 1: for each substituent three of the four terms are

¹ Part XXXIII, T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, and R. D. Topsom, preceding paper.

² T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *Tetrahedron Letters*, 1972, 2643.

estimated from literature data and used to predict the value of the fourth term (denoted by italics and * in Table 1).

TABLE 1
Energy terms for rotational barriers in monosubstituted benzenes^a

Group	<i>E</i>	<i>R</i> = 33 σ°_R	<i>R</i> _{tw} = 33(σ°_R) _{tw}	<i>S</i>
CHO	7.9	7.9*	0	0
COMe	6.3	7.2	0	0.9*
CO ₂ Me	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	ca. 0*
CH ₂ :CH ₂	0	ca. 1	0	ca. 1*

^a For explanation see equation (2) and text.

$$E = 33[\sigma^{\circ}_R - |(\sigma^{\circ}_R)_{tw}|] - S \quad (2)$$

Rotational barriers may be determined by various direct techniques. The most commonly used for the type of molecule under study is variable temperature n.m.r. spectroscopy, where the observed changes in the spectra with temperature are directly related to the rate of the process causing the changes.⁴ ΔG^\ddagger may in general be obtained reliably; ΔH^\ddagger and ΔS^\ddagger much less so. However, for molecules where the symmetry of the transition state is the same as that of the ground state, ΔS^\ddagger should be close to 0 and $\Delta G^\ddagger = \Delta H^\ddagger$ if solvation effects are unimportant. Although n.m.r. studies of barriers in molecules in the gaseous phase are starting

³ For a summary see A. R. Katritzky and R. D. Topsom, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87; A. R. Katritzky and R. D. Topsom in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, p. 119.

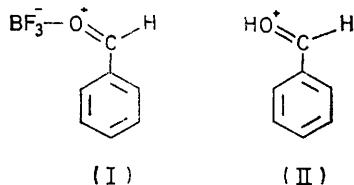
⁴ G. Binsch, *Topics Stereochem.*, 1968, **3**, 97; R. M. Lynden-Bell, *Progr. N.M.R. Spectroscopy*, 1967, **2**, ch. 4 and references therein.

to appear,⁵ for substituted benzenes only liquid-phase studies are available.

Another technique used to obtain barriers to rotation about single bonds attached to aromatic nuclei, vibrational spectroscopy, is an indirect method in that assumptions must be made regarding the shape of the potential function along a vibration which leads over the barrier being observed. The assumptions commonly made^{6,7} are reasonable when applied to the gas phase but probably less so in the case of the liquid phase. In general the results of the direct and indirect techniques cannot be compared directly since ΔH^\ddagger is a complex function of the coefficients V_1 , V_2 , and V_3 of a Fourier series of cosine terms obtained from vibrational spectroscopy. The barriers obtained by the two methods may be quite different, especially if ΔS^\ddagger is significant.

The Formyl Group.—The rotational barrier for benzaldehyde from n.m.r. studies is 7.9 kcal mol⁻¹ in vinyl chloride.⁸ Vibrational spectroscopy also has given estimates for the Ph-CHO rotational barrier; in the gas phase, 4.90⁹ and 4.66⁶ kcal mol⁻¹ from microwave and i.r., respectively, and in the liquid phase, 5.90,¹⁰ 6.69,⁶ and 6.8¹¹ from i.r. studies. An *ab initio* MO calculation gave¹² 6.6 kcal mol⁻¹.

The σ°_R for planar benzaldehyde is 0.24 from i.r. results¹³ and $(\sigma^\circ_R)_{tw}$ is estimated to be *ca.* 0 since σ°_R for both $-\text{CHCl}_2$ and $-\text{CH}(\text{OMe})_2$ is very small.¹³ Further experimental work is in progress to verify this. There is considerable evidence that benzaldehyde, which is planar in its ground state, is essentially strain-free.^{14,15} By equating $(\sigma^\circ_R)_{tw}$ and S to zero the proportionality constant (33) in equation (2) was evaluated² from the n.m.r.-determined barrier.



N.m.r. studies have been made on the rotational barriers of substituted compounds of types (I)¹⁶ and (II)¹⁷ where the formyl group is complexed. From these results barriers of 8.6 and 14.4 may be estimated for the unsubstituted complexes (I) and (II), respectively.

⁵ R. E. Carter and T. Drakenberg, *J.C.S. Chem. Comm.*, 1972, 582; R. K. Harris and R. A. Spragg, *Chem. Comm.*, 1967, 362.

⁶ W. G. Fatley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, 1965, **21**, 231.

⁷ A. V. Cunliffe, *J. Mol. Structure*, 1970, **6**, 9.

⁸ F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1964, **86**, 119.

⁹ R. K. Kakar, E. A. Rinehart, C. R. Quade, and T. Kojima, *J. Chem. Phys.*, 1970, **52**, 3803.

¹⁰ J. H. S. Green, W. Kynaston, and H. A. Gebbie, *Nature*, 1962, **195**, 595.

¹¹ G. E. Campagnaro and J. L. Wood, *J. Mol. Structure*, 1970, **6**, 117.

¹² W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

¹³ R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **90**, 1757.

The relatively low barrier for the BF_3 complex (I) probably arises because of strain in the ground state. However, strain should be small in the cation (II) and the barrier here implies σ°_R of +0.43 for the group $\text{C}^+(\text{OH})_2$.

The Acetyl Group.—The rotational barrier for acetophenone from n.m.r. studies was estimated² as 6.3 kcal mol⁻¹ at 298 K. An i.r. determination in the gas phase gave¹⁸ 3.1 kcal mol⁻¹ and an *ab initio* calculation indicated¹² 4.39 kcal mol⁻¹.

For the COMe group, σ°_R is 0.22, and $(\sigma^\circ_R)_{tw}$ should be very small for the reasons given previously for the formyl group. For acetophenone some strain is expected from repulsion between the methyl group and the *ortho*-hydrogen atoms; however, available physical evidence regarding the conformation of acetophenone (*cf.* discussion in ref. 14) from Kerr constants indicates that it is near planar,¹⁵ and thus the strain energy should be small.¹⁴ Substitution of the above values in equation (2) yields $S = 0.9$ kcal mol⁻¹, in agreement with this reasoning.

The CO₂H and CO₂R Groups.—For these groups there are no experimental determinations of rotational barriers, although an *ab initio* calculation has derived 5.76 kcal mol⁻¹ for the barrier in benzoic acid.¹² Benzoic acid itself has been found to be planar in the crystal.¹⁹

The σ°_R value for the CO₂H group is reported as 0.29;¹³ however, this probably refers to the dimeric acid; *cf.* σ°_R for CO₂Me of 0.16.¹³ For both these groups $(\sigma^\circ_R)_{tw}$ will be *ca.* zero since the value for $-\text{C}(\text{OMe})_3$ is 0.0.¹³ The strain energy here is expected to be small; indeed there may be attractive interactions between the oxygen atoms and the *ortho*-hydrogen atoms.²⁰ Equation (1) allows calculation of barriers to rotation of 5.3 and 5.9 kcal mol⁻¹ for the CO₂Me and CO₂Et groups, respectively, assuming $S = 0$ and $(\sigma^\circ_R)_{tw} = 0$.

Dialkylamino-groups.—N.m.r. studies of *p*-substituted dimethylanilines allow estimation²¹ of the rotational barrier for dimethylaniline as 5.1 kcal mol⁻¹ at 133 K. Recent Kerr constant and dipole moment results²² suggest that the angle between the NMe₂ plane and the benzene-N plane is less than 20°, in contrast to earlier work which had suggested θ of 29.5°. An electron diffraction study of vapour phase (III) gives a CNC

¹⁴ A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, 3449.

¹⁵ C. L. Cheng, R. J. W. Le Fèvre, G. L. D. Ritchie, P. A. Goodman, and P. H. Gore, *J. Chem. Soc. (B)*, 1971, 1198.

¹⁶ A. Greenvald and M. Rabinovitz, *Chem. Comm.*, 1969, 642.

¹⁷ M. Rabinovitz and A. Ellenweig, *Tetrahedron Letters*, 1971, 4439; R. Jost, P. Rimmelin, and J. M. Sommer, *Chem. Comm.*, 1971, 879.

¹⁸ F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta*, 1967, **23A**, 891.

¹⁹ G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Cryst.*, 1955, **8**, 157.

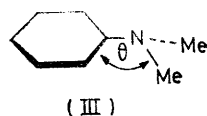
²⁰ W. L. Jorgensen and L. C. Allen, *J. Amer. Chem. Soc.*, 1971, **93**, 567.

²¹ R. K. Mackenzie and D. D. MacNicol, *Chem. Comm.*, 1970, 1299.

²² M. J. Aroney, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1968, 507.

²³ J. W. Smith, *J. Chem. Soc.*, 1961, 81.

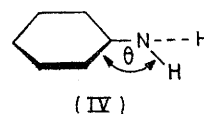
angle of 116° and suggests little deviation from planarity.²⁴ From X-ray studies of dimethylaminoaromatic compounds, the dimethylamino-group is, in general, close to planarity with the aromatic ring.²⁵



For the NMe_2 group, σ°_{R} is -0.53 ,¹³ and $(\sigma^\circ_{\text{R}})_{\text{tw}}$ has been determined²⁶ for the NR_2 group in benzoquinuclidine as -0.13 . Strain in near-planar dimethylaniline is likely to be considerable, owing mainly to the rehybridisation which accompanies the change from sp^3 to a situation close to sp^2 hybridisation in ground-state dimethylaniline and to a lesser extent to classical steric strain between the *ortho*-hydrogen atoms and the methyl groups. Substituting values for σ°_{R} and $(\sigma^\circ_{\text{R}})_{\text{tw}}$ in equation (2) gives S_{NMe_2} as $8.1 \text{ kcal mol}^{-1}$, a reasonable value since inversion barriers in trialkylamines have been estimated as 6.0 – $6.7 \text{ kcal mol}^{-1}$ by n.m.r.²⁷ and $7.46 \text{ kcal mol}^{-1}$ by vibrational spectroscopy.²⁸

The Amino-group.—The non-planarity of aniline in the vapour phase was demonstrated by a microwave study²⁹ and confirmed by u.v., which indicated a barrier³⁰ to inversion at the nitrogen atom of $1.6 \text{ kcal mol}^{-1}$ and an angle θ between the ring–N plane and the HNH plane of 46° . Estimates of θ for aniline in the liquid phase from Kerr constants and dipole moments have ranged from 39 to 48.5° ,^{22,23} with later work emphasising the lower value. Similar work on substituted anilines indicates that θ is large with electron-donating substituents and near 0° in *p*-nitroaniline.³¹ Other evidence in support of these conclusions is that in the gas phase, *p*-fluoroaniline has a value of θ of 46.4° ,³² whereas in crystalline *p*-nitroaniline, the amino-group is planar.³³

Comparison of the inversion barrier³⁰ for (IV), $1.6 \text{ kcal mol}^{-1}$, with that of methylamine,³⁴ $4.8 \text{ kcal mol}^{-1}$, indicates that the rehybridisation strain in aniline is *ca.* $3.2 \text{ kcal mol}^{-1}$. Classical steric strain is probably small. The σ°_{R} value for NH_2 is -0.47 ,¹³ and $(\sigma^\circ_{\text{R}})_{\text{tw}}$ is



presumably approximately the same as for NMe_2 . If these terms are substituted in equation (2) the barrier to rotation in aniline can be estimated as $8.0 \text{ kcal mol}^{-1}$.

The NHR Group.—Direct experimental evidence is sparse. The low temperature n.m.r. spectrum of *N*-ethyl-*p*-nitrosoaniline indicates that NHEt rotation becomes slow simultaneously with the slowing of NO rotation,³⁵ which suggests that the NHEt rotational barrier is larger than for the NMe_2 group. Thus, $12 \pm 2 \text{ kcal mol}^{-1}$ (T_c of -40°C) can be estimated for NHEt rotation from published spectra for *p*-nitroso-*N*-ethylaniline in acetone;³⁵ *cf.* $11.1 \text{ kcal mol}^{-1}$ for NMe_2 rotation in *p*-nitrosodimethylaniline at -40° in toluene-vinyl chloride (1:1).²¹ The corresponding barriers in the monosubstituted benzenes will be less.

N-Methylaniline is non-planar, and the angle between the ring and NCH plane is estimated²³ as 38.5° from dipole moments. The σ°_{R} value for NHMe is 0.52 ,¹³ and $(\sigma^\circ_{\text{R}})_{\text{tw}}$ is taken as that of the NMe_2 group (0.13). The classical steric strain energy in *N*-methylaniline should be roughly half that in *N,N*-dimethylaniline but the rehybridisation strain will remain roughly the same as in aniline since the barriers to inversion of methylamine³⁴ and dimethylamine³⁶ are similar. The total strain is estimated as $5.5 \text{ kcal mol}^{-1}$, the average of those for NH_2 and NMe_2 . The barrier to rotation of the NHMe group can now be estimated as $7.4 \text{ kcal mol}^{-1}$ by substitution into equation (2).

The Methoxy-group.—No generally accepted experimental value is available for the barrier to OMe rotation in anisole. The dielectric relaxation of anisole was interpreted³⁷ in terms of ΔH° $1.5 \text{ kcal mol}^{-1}$ for OMe rotation (see however, refs. 38 and 39), whereas vibrational spectra indicated⁴⁰ $6.0 \text{ kcal mol}^{-1}$. Crystal structure determinations of many methoxybenzenes show that the molecules are planar or close to planar (Ph-O-CH_3 angle $<5^\circ$).⁴¹ The barrier was calculated by

²⁴ L. V. Vilkov and T. P. Timasheva, *Doklady Akad. Nauk S.S.S.R.*, 1965, **161**, 351.

²⁵ M. van Meerssche and G. Leroy, *Bull. Soc. chim. belges*, 1960, **69**, 204; M. van Meerssche and A. Cruceq, *ibid.*, 1959, **68**, 559; T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68.

²⁶ N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. V. Sinnott, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 2255.

²⁷ M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, 1971, **93**, 401; C. H. Bushweller and J. W. O'Neil, *ibid.*, 1970, **92**, 2159; C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, 1970, **92**, 6349; 1971, **93**, 542.

²⁸ G. W. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 3396.

²⁹ D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152.

³⁰ J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectroscopy*, 1966, **20**, 359.

³¹ C. W. N. Cumper and A. Singleton, *J. Chem. Soc. (B)*, 1967, 1096, 1100; M. J. Aroney, K. E. Calderbank, R. J. W. Le Fèvre, and R. K. Pierens, *ibid.*, 1968, 561.

³² A. Hastie, D. G. Lister, R. L. McNeil, and J. K. Tyler, *Chem. Comm.*, 1970, 108.

³³ K. N. Trueblood, E. Goldish, and J. Donohue, *Acta Cryst.*, 1961, **14**, 1009.

³⁴ M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectroscopy*, 1967, **22**, 272.

³⁵ I. C. Calder and P. J. Garratt, *Tetrahedron*, 1969, **25**, 4023.

³⁶ J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1968, **48**, 5058.

³⁷ S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, 1967, **46**, 373.

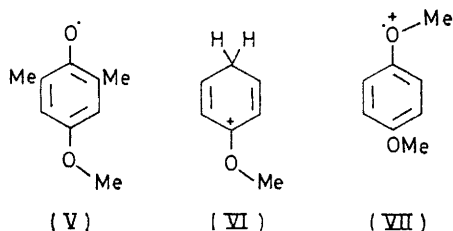
³⁸ D. B. Farmer and S. Walker, *Canad. J. Chem.*, 1969, **47**, 4645.

³⁹ R. J. W. Le Fèvre, D. V. Radford, and E. P. A. Sullivan, *Austral. J. Chem.*, 1967, **20**, 623.

⁴⁰ N. L. Owen and R. E. Hester, *Spectrochim. Acta*, 1969, **25A**, 343.

⁴¹ T. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Cryst.*, 1950, **3**, 279; G. W. R. Bartindale, M. M. Crowder, and K. A. Morley, *ibid.*, 1959, **12**, 111; H. G. Normant and I. L. Karle, *ibid.*, 1962, **15**, 873; C. Romers and B. Hesper, *ibid.*, 1966, **20**, 162; J. L. Galigné and J. Falguieriettes, *ibid.*, 1968, **B24**, 1523; M. Sax. R. Desiderato, and T. W. Dakin, *ibid.*, 1969, **B25**, 362.

CNDO/2⁴² as 1.8 kcal mol⁻¹ but by Allinger *et al.*⁴³ and Pople *et al.*¹² as essentially zero.



Barriers have been calculated, or can be estimated from the literature data, for methoxy-group rotation in the radical (V),⁴⁴ the cation (VI),⁴⁵ and the radical cation (VII)⁴⁶ as 7.8, 12.7,* and 10.7,† respectively. The barrier for anisole should be considerably lower than these values (*cf.* also ref. 47).

I.r. intensities indicate¹³ that the methoxy-group in durene has an effective σ°_R value of -0.28 ; *cf.* -0.43 for OMe in anisole. If we assume that the angle of twist in methoxydurene is 61° , similar to that for dimethylaminodurene (see below), then $(\sigma^{\circ}_R)_{tw}$ for OMe is 0.23 . A comparatively large value for $(\sigma^{\circ}_R)_{tw}$ for OMe is expected, as overlap is possible of both the oxygen *p*-orbitals with the benzene π -system in the twisted, *sp*²-hybridised anisole.

In a previous paper¹³ we calculated the angle of twist of substituents in durenes using equation (3). This is now known to be inadequate both because $(\sigma^{\circ}_R)_{tw}$ ($\theta = 90^\circ$) can differ significantly from zero, and because $(\sigma^{\circ}_R)_\theta$ and terms proportional to $(\sigma^{\circ}_R)_\theta$ are now accepted as having a $\cos^2 \theta$ relationship^{14,48,49} to the angle of twist. Thus we now write equation (4). For the NMe₂ group in dimethylaminodurene, $(\sigma^{\circ}_R)_{tw}$ is 0.13 , σ°_R is 0.53 , and $(\sigma^{\circ}_R)_\theta$ is 0.23 ; therefore θ is 61° as opposed to the 65° calculated previously.¹³

$$(\sigma^{\circ}_R)_\theta = \sigma^{\circ}_R \cos \theta \quad (3)$$

$$(\sigma^{\circ}_R)_\theta = (\sigma^{\circ}_R)_{tw} + [\sigma^{\circ}_R - (\sigma^{\circ}_R)_{tw}] \cos^2 \theta \quad (4)$$

It is difficult to estimate the strain energy in anisole. The total strain will be comprised of Me/H repulsions and of rehybridisation-at-oxygen components; it could be in the region of 50% of that for dimethylaniline. Substitution of $(\sigma^{\circ}_R)_{tw} = 0.23$ and $S_{OMe} = 4$ kcal mol⁻¹ into equation (2) indicates a rotational barrier of 2.6 kcal mol⁻¹ for methoxy-rotation, which would be reasonable in view of the preceding discussion.

* Calculated assuming $h = 10^2$ s⁻¹ at $T_0 = 15^\circ$ C.⁴⁵

† Calculated assuming a coalescence point of 54° where $\tau = 10^{-6}$ s.

⁴² E. Helgstrand, *Acta Chem. Scand.*, 1970, **24**, 3687.

⁴³ N. L. Allinger, J. J. Maul, and M. J. Hickey, *J. Org. Chem.*, 1971, **36**, 2747.

⁴⁴ W. J. van den Hoek, W. G. B. Huysmans, and M. J. C. van Gemert, *J. Magnetic Res.*, 1970, **3**, 137.

⁴⁵ D. M. Brouwer, E. L. Mackor, and C. Maclean, *Rec. Trav. chim.*, 1966, **85**, 114.

⁴⁶ W. F. Forbes and P. D. Sullivan, *Canad. J. Chem.*, 1966, **44**, 1501.

⁴⁷ M. Horak, E. R. Lippincott, and R. K. Khanna, *Spectrochim. Acta*, 1967, **23A**, 1111.

The Hydroxy-group.—Microwave spectra indicate a barrier of 3.29⁵⁰ to 3.36⁵¹ kcal mol⁻¹ for the rotation of the OH group in phenol, whereas i.r. values are 3.48⁵² and 3.56.⁵³ Classical strain in the coplanar conformation will be small¹³ but there will be some rehybridisation strain. Consideration of equation (2) indicates that $(\sigma^{\circ}_R)_{tw}$ must be large for the OH group. In view of the results for OMe, this is to be expected, for in the orthogonal conformation the O-H bond will overlap with the π -system and act as a slightly better donor than the O-Me bonds. If $S_{OH} = ca. 2$ kcal mol⁻¹ then $(\sigma^{\circ}_R)_{tw}$ for OH is -0.26 , consistent with the above reasoning.

The Nitro-group.—The barrier to rotation about the C-N bond in nitrobenzene has been estimated from the microwave spectrum⁵⁴ to be $3 (\pm 1.5)$ kcal mol⁻¹ and calculated¹² to be 5.74 kcal mol⁻¹.

The σ°_R value is 0.17 ,¹³ and $(\sigma^{\circ}_R)_{tw}$ should be small. It is difficult to estimate the strain for this group but equation (2) indicates that *S* is essentially zero if the calculated value of the barrier is used. This is in agreement with the known planar structure of nitrobenzene.⁵⁴

The Vinyl Group.—Little indication is available of the size of the rotational barrier in styrene: a theoretical study¹² indicated a barrier of 4.42 kcal mol⁻¹, but no torsional bands were observed in the far-i.r. spectrum of styrene.¹⁸

The σ°_R value is small as obtained by both i.r. and ¹⁹F n.m.r. methods (0.05 and -0.03 , respectively). The barrier predicted by equation (2) is *ca.* 1 kcal mol⁻¹ when the strain and $(\sigma^{\circ}_R)_{tw}$ are both taken to be zero. A very small barrier accords with the negative result of the far-i.r. experiment.

p- π -Conjugation Energies Determined by Complexation.—Russian workers⁵⁵ estimated conjugation energies in monosubstituted benzenes (PhX) by comparing the heats of complexation of PhX and MeX with Lewis acids, *e.g.* AlBr₃ and GaCl₃. The difference between the two heats, assuming that the bond energies of complexation are identical (as supported by dipole moment studies) is given by the difference between *R* (as defined by us) and a strain factor, probably mainly *S*, but also including strain energy terms from the compound MeX and both the complexes.

Table 2 shows the $\Delta\Delta H$ values for complexation, and also $R = 33\sigma^{\circ}_R$. Subtracting these values gives the

⁴⁸ E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 1955, 3754.

⁴⁹ K. S. Dhama and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 479.

⁵⁰ H. Forest and B. P. Dailey, *J. Chem. Phys.*, 1966, **45**, 1736.

⁵¹ T. Pedersen, N. W. Larsen, and L. Nygaard, *J. Mol. Structure*, 1969, **4**, 59.

⁵² H. D. Bist and D. R. Williams, *Bull. Amer. Phys. Soc.*, 1966, **11**, 326.

⁵³ L. Radom, W. J. Hehre, J. A. Pople, G. L. Carlson, and W. G. Fateley, *J.C.S. Chem. Comm.*, 1972, 308.

⁵⁴ J. H. Hög, L. Nygaard, and G. O. Sørensen, *J. Mol. Structure*, 1970, **7**, 111.

⁵⁵ I. P. Romm, E. N. Guryanova, and K. A. Kocheshkov, *Tetrahedron*, 1969, **25**, 2455.

TABLE 2

Strain energies from complexation studies							
Group	NMe ₂	OMe	OEt	OPh	SMe	SEt	SPh
$\Delta\Delta H$ complexation	8.1	7.8	6.5	11.3	4.4	3.2	7.3
AlBr ₃							
$\Delta\Delta H$ complexation	9.0	6.5	5.7	10.9	5.2	3.8	7.8
GaCl ₃							
$33\sigma^{\circ}_R$	17.6	14.1	14.5	24.0 ^a	8.3	6.3	6.2
Σ strain factor	9.5	6.3	8.0	12.7	3.9	3.1	-0.9
AlBr ₃							
Σ strain factor	8.6	7.6	8.8	13.1	3.1	2.5	-1.6
GaCl ₃							
S	7	4					

^a $66\sigma^{\circ}_R$, assuming that both rings lose their resonance with the oxygen atom.

total strain factors involved. For the two cases where comparison with S is possible, the results are consistent with the above reasoning.

Conclusions.—Our overall knowledge of rotational barriers, while fragmentary, is consistent with their being determined by a combination of resonance and strain energies, as expressed by equation (1), and with resonance energies being directly proportional to σ°_R constants as expressed by equation (2). The quantitative energy barriers predicted in this paper should provide a basis for further work in this area.

[3/1202 Received, 8th June, 1973]