Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XLIII.[1] Quantitative Estimation of Electronic Interactions in Mono- and Di-substituted Ethylenes and the Prediction of Rotational Barriers [1]

By **George P. Ford** and **Alan R. Katritzky,*** School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Ronald D. Topsom,* School of Physical Sciences, La Trobe University, Melbourne, Australia

Known rotational barriers in monosubstituted ethylenes are discussed in terms of substituent resonance and strain parameters. Related reasoning allows the rationalisation of known rotational barriers in 4-(dimethylamino)but-3-en-2-one in terms of substituent–ethylene and substituent–substituent interactions.

WE recently related Hammett σ constants directly to the interaction energy between the substituent and the benzene ring,[2] and have derived quantitative relationships between σ°_R values and rotational barriers for both mono-[3] and *para*-di-substituted[4] benzenes. The barrier to rotation in monosubstituted benzenes is given by equation (1) where R and R_{tw} represent the resonance interactions in the form most favourable for overlap (in general planar) and that least favourable respectively. The equivalent equation in σ°_R terms was shown to be equation (2).[3]

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

$$E = 33[\sigma^\circ_R - (\sigma^\circ_R)_{tw}] - S \qquad (2)$$

We have also shown that the intensity of the ν(C=C) band in mono-[5] and di-substituted[1] ethylenes can be related to the same σ°_R values that are applicable in the benzene series. This indicates that the interaction between the double bond and the substituent in ethylenes is proportional to that ($33\sigma^\circ_R$) between the ring and the substituent for the corresponding benzenes. We give reasons below for believing that the quantity applicable to ethylenes is $25\sigma^\circ_R$.

Monosubstituted Ethylenes.—The equation for the barrier to rotation in monosubstituted ethylenes is complicated by the existence of *s-cis-* and *s-trans-*forms where the substituent is of less than C_{2v} symmetry. In equations (3) and (4), E_t and E_c are the barriers measured from the two ground states; R_t, R_c, and R_{tw} represent the resonance interactions in the *s-trans-*, *s-cis-*, and transition states, and S_t and S_c are the steric interactions. We consider that $0.5(R_c + R_t)$ is proportional to σ°_R, and deduce equation (5) where b is the derived constant. We choose the quantity $0.5(R_c + R_t)$ on the grounds that the σ°_R values which are derived from the substituted phenyl compounds refer to substituents which are in an environment which simultaneously has the characteristics of both *s-cis-* and *s-trans-*ethylene forms.

$$E_t = (R_t - R_{tw}) - S_t \qquad (3)$$

$$E_c = (R_c - R_{tw}) - S_c \qquad (4)$$

$$0.5(E_c + E_t) = b[|\sigma^\circ_R| - |(\sigma^\circ_R)_{tw}|] - 0.5(S_c + S_t) \qquad (5)$$

The Formyl Group.—The barriers, E_c and E_t for acrylaldehyde have been determined[6] as 4.96 and 7.02 kcal mol^{-1}. The σ°_R value for the formyl group from i.r. measurements for planar benzaldehyde is[7] 0.24 and $(\sigma^\circ_R)_{tw}$, the σ°_R value for the same group in the orthogonal configuration, is believed[2] to be *ca.* 0. As before,[2] we take $S_c = S_t = 0$ and deduce the value of $b = 25$ kcal mol^{-1} $\sigma^\circ_R{}^{-1}$ from equation (5).

The Acetyl Group.—The same treatment for methyl vinyl ketone requires a knowledge of the strain energy in each conformation. We consider the *s-cis-*form to be essentially strain-free, *i.e.* $S_c =$ *ca.* 0, while the strain

---

[1] Part XLII, G. P. Ford, A. R. Katritzky, and R. D. Topsom, preceding paper.

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

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

[4] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1975, 443.

[5] A. R. Katritzky, R. F. Pinzelli, M. V. Sinnott, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6861.

[6] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.*, 1957, **A242**, 36.

[7] 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.

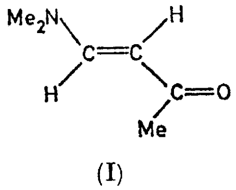
energy in the s-*trans*-form will be similar to the 0.9 kcal mol^{-1} deduced [2] for acetophenone. Introduction of this value, together with the rotational barriers $E_c = 4.79$ and $E_t = 5.25$ from the literature [8,9] and the i.r.-determined [7] value $\sigma^{\circ}_{\mathrm{R}} = 0.22[(\sigma^{\circ}_{\mathrm{R}})_{tw} = ca.\ 0]$ into equation (5), again indicates b to be 25 kcal mol^{-1} $\sigma^{\circ}_{\mathrm{R}}{}^{-1}$.

The Methoxy-group.—A value of 3.69 kcal mol^{-1} for the barrier E_t in methyl vinyl ether has been determined [8] by the ultrasonic absorption method while the enthalpy difference between the *s-cis*- and *s-trans*-forms is found [10] to be 0.66 kcal mol^{-1} in favour of the *s-cis*-form. The barrier E_c is thus 4.35 kcal mol^{-1}. The $\sigma^{\circ}_{\mathrm{R}}$ value for the methoxy-group in anisole is determined [7] by the i.r. method to be 0.43. Since oxygen has two lone pairs the residual resonance interaction in the twisted configuration is expected to be substantial. Thus, the residual resonance electron transfer in this configuration of methyl vinyl ether was predicted [11] in a CNDO/2 molecular orbital calculation to be 68%, and in an *ab initio* calculation to be 47% of that in the planar *s-cis*-conformation. These results are broadly consistent with the value of $(\sigma^{\circ}_{\mathrm{R}})_{tw}$ (0.23) deduced [3] previously. The strain energies are somewhat troublesome to estimate In an admittedly approximate manner we previously [3] suggested a value of *ca.* 4 kcal mol^{-1} for the release of steric strain accompanying the rotation of the methoxy-group in anisole. In addition to the 'classical' strain there will be a contribution from the rehybridisation of the oxygen atom. It is probably reasonable to neglect the classical strain in the *s-trans*-form, although not in the *s-cis*-form, and the rehybridisation component will be important in both planar conformations. Further, since the resonance interaction persists in the transition state so also will presumably part of the hybridisation strain. In the absence of more specific knowledge relating to these contributions we simply note that an average strain contribution of *ca.* 1—2 kcal mol^{-1} is consistent with a value of b in the range 25—30 kcal mol^{-1} $\sigma^{\circ}_{\mathrm{R}}{}^{-1}$.

Other Substituents.—The i.r.-determined [12] barrier in nitroethylene is 6.5 kcal mol^{-1} although the reliability of this value has been questioned.[13] The present theory indicates that, with $S_c = S_t = 0$, $\sigma^{\circ}_{\mathrm{R}} = 0.17$,[7] and $(\sigma^{\circ}_{\mathrm{R}})_{tw} = 0$,[3] the barrier should be approximately 4.2 kcal mol^{-1}.

The barrier E_t in methyl vinyl sulphide from the ultrasonic absorption method is [8] *ca.* 1.9 kcal mol^{-1} and the *s-cis*-form is determined [14] from variable temperature i.r. spectroscopy to be the more stable (gas phase) by 1.4 kcal mol^{-1}. I.r. intensities indicate [7] that $\sigma^{\circ}_{\mathrm{R}} = -0.25$ in thioanisole and a value $(\sigma^{\circ}_{\mathrm{R}})_{tw} = -0.05$ has been estimated.[15] These data lead to the prediction of an average strain energy of 4.4 kcal mol^{-1}. The rehybridisation component for sulphur, unlike that for oxygen, is not expected to be large. However, the smaller CSC bond angle of 95°,[14] as compared with the 120° [16] for methyl vinyl ether is in agreement with a significantly larger classical strain component in the sulphide.

trans-1,2-*Disubstituted Ethylenes*.—There is unfortunately insufficient information for a full treatment of these compounds. Nevertheless, it is of interest to consider the available data for *trans*-4-(dimethylamino)but-3-en-2-one (I) within the framework of the ideas developed above.



(I)

From the coalescence temperature technique the free energy of activation for rotation of the NMe$_2$ group was [17] 13.34 kcal mol^{-1}, and the barrier opposing the rotation of the acetyl group was [18] 11.6 kcal mol^{-1}. Both the reported barriers were averaged with respect to the *s-cis,s-trans*-isomerism of the acetyl group. On the other hand, the activation parameters, $\Delta H^{\ddagger} = 13.6 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 5.4 \pm 2$ cal mol^{-1} K^{-1}, were deduced [19] from the line-shape method for the acetyl rotation.

The enthalpy of activation for the acetyl rotation in (I) can be compared with the average value, $\Delta H^{\ddagger} = 5.0$ kcal mol^{-1}, in methyl vinyl ketone itself.[8,9] Thus the additional barrier of 8.6 kcal mol^{-1} in the enamino-ketone must be due largely to the additional resonance stabilisation in the ground state associated with the through-conjugation interaction.

The barrier to rotation of the dimethylamino-group in the parent ethylene is not known although it may be estimated by the method described above. The $\sigma^{\circ}_{\mathrm{R}}$ and $(\sigma^{\circ}_{\mathrm{R}})_{tw}$ values for NMe$_2$ are respectively -0.53 [7] and -0.13 [3] and hence the electronic contribution to the barrier is deduced from equation (5), with $b = 25$, to be 10.0 kcal mol^{-1}. To obtain the actual barrier the strain energy released during the rotation must be deducted. This we consider to be adequately approximated by that deduced for the analogous rotation in the benzene series. However, the analogous strain energy is not that associated with the rotation of the NMe$_2$ group in *NN*-dimethylaniline, but that associated with the rotation of

---

[8] E. Wyn-Jones, K. R. Crook, and W. J. Orville-Thomas, *Adv. Mol. Relaxation Processes*, 1972, **4**, 193.

[9] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc.* (*B*), 1969, 810.

[10] N. L. Owen and N. Sheppard, *Trans. Faraday Soc.*, 1964, **60**, 634.

[11] G. P. Ford, Ph.D. Thesis, University of East Anglia, 1974.

[12] K. R. Loos and Hs. H. Günthard, *J. Chem. Phys.*, 1967, **46**, 1201.

[13] R. Meyer, A. Gammeter, P. Smith, H. Kühne, P. Nösberger, and Hs. Günthard, *J. Mol. Spectroscopy*, 1973, **46**, 397.

[14] J. Fabian, H. Kröber, and R. Mayer, *Spectrochim. Acta*, 1968, **24A**, 727.

[15] T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, R. T. C. Brownlee, J. A. Munday, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 276.

[16] N. L. Owen and N. Sheppard, *Spectrochim. Acta*, 1966, **22**, 1101.

[17] J. Dabrowski and L. J. Kozerski, *Org. Magnetic Resonance*, 1972, **4**, 137.

[18] J. Dabrowski and L. J. Kozerski, *Org. Magnetic Resonance*, 1973, **5**, 469.

[19] M.-L. Filleux-Blanchard, H. Durand, and G. J. Martin, *Org. Magnetic Resonance*, 1970, **2**, 539.

the NHMe group in *N*-methylaniline, which involves only one NMe–H interaction—the situation in the ethylenic compound. This we deduced [3] previously to be 5.5 kcal mol^{-1}. Our estimate of the barrier hindering the rotation of the NMe_2 group in *NN*-dimethylaminoethylene is therefore 4.5 kcal mol^{-1}.

Unfortunately, only $\Delta G^{\ddagger}$ for this rotation in (I) is known (see above) which differs from the estimated enthalpy of activation for the rotation in the vinyl compound by 8.8 kcal mol^{-1}. The additional enthalpy of activation due to the through-conjugation is however expected to be near this value, which is not incompatible with our expectation that it should be identical with the additional enthalpy of activation of *ca.* 8.6 kcal mol^{-1} deduced above for the rotation of the acetyl group.

The through-conjugation contribution to the enthalpy of activation for the rotation of the substituents is rather larger than the 2—3 kcal mol^{-1} found [4] in the analogous *p-NN*-dimethylaminoacetophenone. This is in accord with the analogous but larger interaction constant required to correlate the i.r. band intensity of the ν(C=C) vibration in *trans*-1,2-disubstituted ethylenes compared with the similar interaction in *para*-disubstituted benzenes. Thus we have found [1] the intensity of this vibration in *trans*-1,2-disubstituted ethylenes to be correlated by equation (6), where $\sigma^{\circ}_{R}D$ and $\sigma^{\circ}_{R}A$ refer to the donor and acceptor groups respectively and λ is an interaction constant derived [20] from i.r. studies of *para*-disubstituted benzenes and generalised in terms of equation (7) and published [20] values of K_A and $[\sigma^{+}(D) - \sigma^{\circ}(D)]$. We believe that λ represents the additional stabilisation of the ground state associated with the through conjugation. If it is assumed that the constant 25 kcal mol^{-1} $\sigma^{\circ}{}_{R}{}^{-1}$ also applies to λ, the contribution to the barrier to rotation due to the through-conjugation is deduced to be *ca.* 7.6 kcal mol^{-1}, which may be compared with the 8.6 kcal mol^{-1} deduced above directly. However, the values of λ appropriate to the i.r. measurements depend on both the molecular geometry and the form of the normal vibration somewhat differently from the σ°_{R} constants and further work is necessary to clarify this point.

$$A = 26\,500[\sigma^{\circ}_{R}(D) - \sigma^{\circ}_{R}(A) + 1.5\lambda]^2 + 19 \qquad (6)$$

$$\lambda = K_A[\sigma^{+}(D) - \sigma^{\circ}(D)] \qquad (7)$$

There is little literature work with which to compare the present results. Thus *X*-ray-determined bond lengths in many cases may not be a sensitive enough guide, *e.g.* it was recently [21] concluded that the benzene ring, the C=C, and the NO_2 group show little mutual interaction in 1-(2-chloro-4-dimethylaminophenyl)-2-nitro-ethylene.

Conclusions.—Although reliable data for the rotational barriers in simple ethylenic compounds are few, the general theory described in this paper forms a promising framework for the quantitative discussion of these barriers.

We thank the S.R.C. for a studentship (to G. P. F.).

[5/117 *Received*, 20*th January*, 1975]

---

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

[21] T. S. Cameron, D. J. Cowley, and J. E. Thompson, *J.C.S. Perkin II*, 1974, 774.