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A DIRECT RELATION OF SIGMA CONSTANTS TO THE ENERGY SCALE[1]

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Despite widespread use and investigation, sigma constants have remained essentially empirical proportionality constants, providing measures of the difference in stabilisation, for example of the product and reactant, by the substituent in question. We now show that the resonance σ_R^o constants may be directly related to the energy scale using 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 the energy of resonance interaction between the position of maximum energy (usually the orthogonal position of 90° twist) and the position of lowest energy (usually at or near co-planarity of substituent and ring) less the corresponding difference in strain energy. In this publication we consider barriers to rotation about substituents in which the strain energy at the conformation of highest energy can be neglected; this is usually the case for substituents with not more than one branch at the atom adjacent to the ring. Further, we can assume that the inductive interaction is not significantly affected by twisting. Equation 1 then follows, where the subscript tw refers to the twisted (orthogonal) position. The resonance interaction of a substituent and a benzene ring is proportional to the modulus of the σ_R^o value,[2] Eq. 2; substitution of Eq. 2 in Eq. 1 yields Eq. 3.

$$\underline{E} = \left\{\underline{R} - \underline{R}_{\underline{tw}}\right\} - \underline{S} \quad\text{.......}\quad (1)$$

$$\underline{R} = \underline{a}.\left|\sigma_R^o\right| \quad\text{.......}\quad (2)$$

$$\underline{E} = \underline{a}\left\{\left|\sigma_R^o\right| - \left|(\sigma_R^o)_{\underline{tw}}\right|\right\} - \underline{S} \quad\text{.......}\quad (3)$$

For the substituents CHO, COMe, and NMe_2, the σ_R^o values are +0.244, +0.219, and -0.533, respectively.[3] The value of $(\sigma_R^o)_{\underline{tw}}$ for NMe_2 is -0.134;[4] for CHO and COMe we put $(\sigma_R^o)_{tw} = 0$ in view of the very small values found experimentally[3] for such groups as $CHCl_2$, $\bar{C}H(OMe)_2$. The strain energy in dimethylaniline is considerable, arising both from the rehybridisation of nitrogen atom (note that for planarity at the nitrogen atom this would be expected to be 6.0 - 6.7 kcal mole^{-1}, values which have recently been reported[5] for the inversion barriers of trialkylamines) and from steric repulsions between the methyl groups and the *ortho* hydrogen atoms. By contrast there is considerable evidence that benzaldehyde, which is planar in its equilibrium state, is essentially strain free,[6] and the strain in acetophenone is expected to be small ($\leqq$ 1.5 kcal mole^{-1} *cf.* Ref. 6).

The rotation barrier* is known for benzaldehyde[8] (7.9 kcal mole^{-1}) and has been estimated for dimethylaniline[9] (5.1 kcal mole^{-1}). The barrier for acetophenone itself can be estimated from those given[10] for substituted derivatives as 6.3 kcal mole^{-1}. Successive substitution of these data into Eq. 3 yields Equations 4, 5, and 6, respectively, from which the following values are found: $\underline{a}$ = 32.4 kcal mole^{-1}, $\underline{S}_{NMe_2}$ = 7.8 kcal mole^{-1}, and $\underline{S}_{COMe}$ = 0.9 kcal mole^{-1}.

$$7.9 = 0.244\,\underline{a} \ldots\ldots\ldots \tag{4}$$

$$5.1 = (0.533 - 0.134)\,\underline{a} - \underline{S}_{NMe_2} \ldots\ldots\ldots \tag{5}$$

$$6.3 = 0.219\,\underline{a} - \underline{S}_{COMe} \ldots\ldots\ldots \tag{6}$$

Confirmatory evidence for the magnitude of $\underline{a}$, the constant relating $\sigma_R^{\,o}$ to energy, can be obtained from *para*-disubstituted benzenes in which the barriers to rotation of both substituents are known. In such compounds which carry an electron donor substituent opposite an electron acceptor, there is an important interaction term, λ , which represents the direct conjugation between the two substituents:[11] if one substituent is twisted then λ will disappear if $(\sigma_R^{\,o})_{\underline{tw}}$ = 0 and otherwise λ will be reduced in the proportion $(\sigma_R^{\,o})_{\underline{tw}}/\sigma_R^{\,o}$.

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*Footnote

The entropy term $\Delta S^{\ddagger}$ is expected to be small in these systems in the absence of specific solvation since the transition and ground state structures are identical in symmetry and experimental evidence is available to support this.[7] Thus $\Delta G^{\ddagger}$ should be a good measure of the potential energy of the barriers in these cases.

In the treatment which follows we use the values of S already deduced, but obtain independent estimates of the constant a and, incidentally, values for λ.

p-Dimethylaminobenzaldehyde. The barrier for rotation of the CHO group[12] is 10.7 kcal mole^{-1} and that for NMe_2[9] is 7.6 kcal mole^{-1}. Equations 7 and 8 follow, from which $\underline{a} = 34.0$ and $\underline{a}\,\lambda_{NMe_2/CHO} = 2.5$ kcal mole^{-1}.

$$10.7 = \underline{a}\,(0.244 + \lambda) \qquad (7)$$

$$7.6 = \underline{a}\,(0.533 + \lambda - 0.134 - 0.25\lambda) - 7.8 \qquad (8)$$

p-Dimethylaminoacetophenone. Here, the barrier for COMe rotation[10] is 8.5 kcal mole^{-1} and that for NMe_2 rotation[9] is 7.0 kcal mole^{-1}. From the resulting Eq. 9 and 10 we find $\underline{a} = 31.7$ and $\underline{a}\,\lambda_{NMe_2/COMe} = 3.7$ kcal mole^{-1}.

$$8.5 = \underline{a}\,(0.219 + \lambda) - 1.2 \qquad (9)$$

$$7.0 = \underline{a}\,(0.533 + \lambda - 0.134 - 0.25\lambda) - 7.8 \qquad (10)$$

Conclusions. The agreement between the values of a calculated by the three methods ($\underline{a} = 32.7 \pm 1.3$) justifies the treatment given. We suggest the rounded figure of 33 kcal mole^{-1} per $\sigma_R^{\,o}$ unit as the standard figure to obtain values of ring-substituent resonance interaction energies in monosubstituted benzenes. The method points clearly to further extensions to calculate strain values for other substituents, and to substituent-substituent interaction energies in polysubstituted benzenes. Such work is in hand.

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