Internal Rotation in Dimethylaniline and *para*-Substituted Derivatives

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Summary A study of internal rotation in *para*-substituted dimethylanilines by ^1H n.m.r. spectroscopy shows that the barrier to internal rotation of the dimethylamino-group is markedly dependent upon the nature of the *para*-substituent, and a Hammett correlation gives $\Delta G^\ddagger$ (at 133° K) = 5·1 (±1·0) kcal mol^{-1} for rotation in the parent compound dimethylaniline itself.

A RECENT study[1] using the kinetic n.m.r. technique[2] has shown that there is an appreciable barrier hindering internal rotation of the dimethylamino-group in *p*-nitrosodimethylaniline (I). We now report preliminary results of 100 MHz variable-temperature measurements which were made on *p*-formyldimethylaniline (III), *p*-acetyldimethylaniline (V), and (I) in order to ascertain how the barrier is affected by the nature of the *para*-substituent.

The ^1H n.m.r. spectra of compounds (I), (III), and (V) all show temperature-dependent behaviour analogous to that already described[1] for (I), the *syn* and *anti* methyl groups giving rise to separate signals at sufficiently low temperatures when rotation about both the Ar–XO bond and the Ar–NMe_2 bond is appropriately slow.[1,2]

Results are summarised in the Table. As can be seen, the free energies of activation given at 133°K for NMe_2 rotation in (I), (III), and (V) show a marked dependence upon the *para*-substituent. The decreasing resistance to internal rotation of the NMe_2 group found for (I), (III), and (V) indicates a diminishing tendency for delocalisation of the NMe_2 lone pair into the π-electron system of the aromatic ring in this order, and is consistent with progressively decreasing contributions of the quinonoid forms (II), (IV), and (VI) to the actual electronic structures of (I), (III), and (V), respectively.

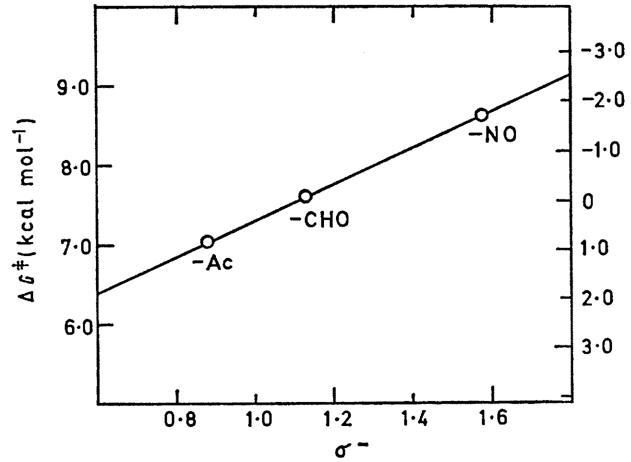


FIGURE. *Linear free energy relationship for internal rotation of the* NMe_2 *group in* para-*substituted dimethylanilines* (ca. 0·05 M) *in a mixture of* [$^2H_8$]*toluene and vinyl chloride* (ca. 1 : 1 v/v) *as solvent.*

TABLE

N.m.r. parameters for internal rotation of the dimethylamino-group in dimethylanilines

Compound	$\lvert\delta\nu\rvert$[a] (Hz)	T_c[b] (°)	$\Delta G_c^{\ddagger c}$ (kcal mol^{-1})	$\Delta G^{\ddagger c}$ (133°K) (kcal mol^{-1})	log k[d] (at 133° K)	σ^-
p-Nitrosodimethylaniline (I) ..	7·1	−87·5	9·9 (±0·1)	8·6 (±0·2)	−1·66	1·57[e]
p-Formyldimethylaniline (III) ..	5·4	−125	7·8 (±0·1)	7·6 (±0·2)	0·01	1·126[f]
p-Acetyldimethylaniline (V) ..	8·2	−134	7·2 (±0·1)	7·0 (±0·2)	0·93	0·874[f]
Dimethylaniline (VII)				5·1 (±1·0)	4·09	(0)
p-Nitrodimethylaniline				7·9 (±0·4)	−0·50	1·27[f]

[a] The 100 MHz "frozen" shift separation for *syn* and *anti* methyl groups measured at low temperature with a mixture of [$^2H_8$]toluene and vinyl chloride (*ca.* 1 : 1, v/v) as solvent. These shifts are sensitive to the proportion of solvent components.

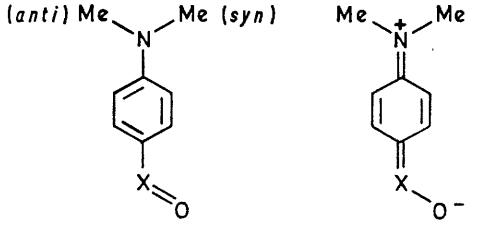
[b] The coalescence temperature (±2°).

[c] Evaluated with a transmission coefficient of unity.

[d] Obtained for (I) and (III) by extrapolation of higher-temperature kinetic data: rates of NMe_2 rotation (k in s^{-1}) were measured by matching experimental and computer-calculated spectra, the former being recorded when the rate of X = O rotation is negligible —refs. 1 and 2 (details will be given in a full paper). Negative entropies of activation for NMe_2 rotations have been found, *cf.* ref.8.

[e] Value from ref. 5.

[f] Value from ref. 3.



(I) X = N
(III) X = CH
(V) X = CMe

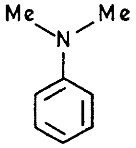
(II) X = N
(IV) X = CH
(VI) X = CMe

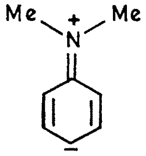
Further, when, as shown in the Figure, these free energies (or log k at 133°K) are plotted against the Hammett substituent parameter[3–5] σ^- a straight line is obtained corresponding to equation (1)[3,4] with log k_0 = 4·09

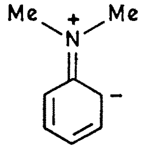
$$\log (k/k_0) = \rho\sigma^- \qquad (1)$$

and ρ = −3·7. Since log k_0 relates to internal rotation of the NMe_2 group in the dimethylaniline (VII) itself, one obtains, using absolute rate theory, $\Delta G^\ddagger$ (at 133°K) = 5·1 (±1·0) kcal mol^{-1} for internal rotation in the parent compound. The magnitude of this barrier implies considerable lone pair delocalisation in the ground state, corresponding to significant contributions of zwitterionic forms such as (VIII) and (IX) to the structure of (VII).

The above correlation is also of interest in that it allows evaluation of rotational barriers in molecules, such as *p*-nitrodimethylaniline which are inaccessible to the n.m.r. method because of symmetry considerations. For example, taking the value[3] of 1·27 for σ^- of the nitro-group gives, $\Delta G^{\ddagger}$ (at 133°K) = 7·9 (±0·4) kcal mol^{-1} for internal rotation of the dimethylamino-group of *p*-nitrodimethylaniline. Interestingly, the results of an *X*-ray crystallographic investigation[6] suggest that a quinonoid form [analogous to, for example, (II)] makes a significant contribution to the structure of *p*-nitrodimethylaniline in the crystal, while the increased rotational barrier of this molecule, compared with that of dimethylaniline, indicates[7] that the quinonoid form also contributes to the structure of the molecule in solution.


(VII)


(VIII)


(IX)

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