

Internal Rotation in Dimethylaniline and *para*-Substituted Derivatives

By R. K. MACKENZIE and D. D. MACNICOL*

(Department of Chemistry, University of Glasgow, Glasgow, W.2)

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 ΔG^\ddagger (at 133°K) = $5.1 (\pm 1.0)$ kcal mol $^{-1}$ for rotation in the parent compound dimethylaniline itself.

A RECENT study¹ using the kinetic n.m.r. technique² 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 described¹ 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-NMe₂ 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 NMe₂

and (V) indicates a diminishing tendency for delocalisation of the NMe₂ lone pair into the π -electron system of the

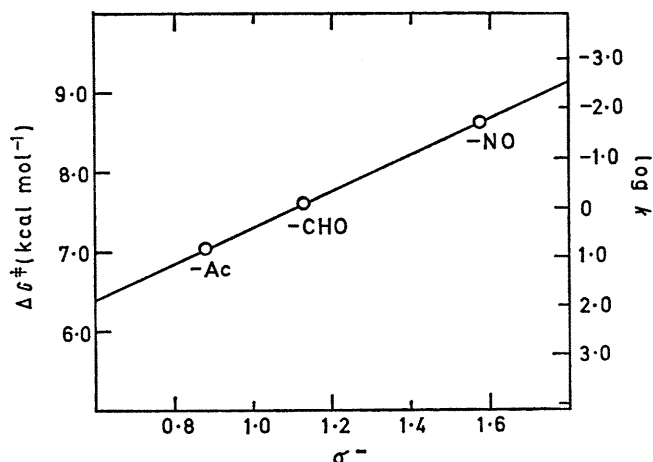


FIGURE. Linear free energy relationship for internal rotation of the NMe₂ group in *para*-substituted dimethylanilines (ca. 0.05 M) in a mixture of $[\text{D}_8]\text{toluene}$ and vinyl chloride (ca. 1:1 v/v) as solvent.

TABLE

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

| Compound | $ \delta\nu ^a$ (Hz) | T_c^b (°) | $\Delta G_e^{\ddagger c}$ (kcal mol $^{-1}$) | $\Delta G^{\ddagger e}$ (133°K) (kcal mol $^{-1}$) | $\log k^d$ (at 133°K) | σ^- |
|--|----------------------|-------------|--|--|---|--------------------|
| <i>p</i> -Nitrosodimethylaniline (I) .. | 7.1 | -87.5 | 9.9 (± 0.1) | 8.6 (± 0.2) | -1.66 | 1.57 ^e |
| <i>p</i> -Formyldimethylaniline (III) .. | 5.4 | -125 | 7.8 (± 0.1) | 7.6 (± 0.2) | 0.01 | 1.126 ^f |
| <i>p</i> -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) |
| <i>p</i> -Nitrodimeethylaniline .. | .. | .. | .. | 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 $[\text{D}_8]\text{toluene}$ and vinyl chloride (ca. 1:1, v/v) as solvent. These shifts are sensitive to the proportion of solvent components.

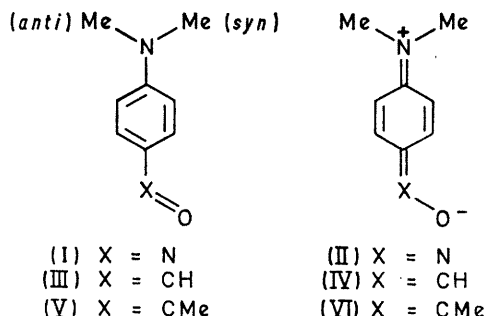
^b The coalescence temperature ($\pm 2^\circ$).

^c Evaluated with a transmission coefficient of unity.

^d Obtained for (I) and (III) by extrapolation of higher-temperature kinetic data: rates of NMe₂ 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 NMe₂ rotations have been found, cf. ref. 8.

^e Value from ref. 5.

^f Value from ref. 3.



rotation in (I), (III), and (V) show a marked dependence upon the *para*-substituent. The decreasing resistance to internal rotation of the NMe₂ group found for (I), (III),

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.

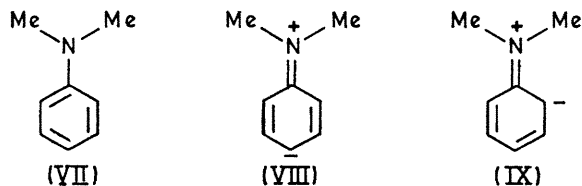
Further, when, as shown in the Figure, these free energies (or $\log k$ at 133°K) are plotted against the Hammett substituent parameter³⁻⁵ σ^- a straight line is obtained corresponding to equation (1)^{3,4} with $\log k_0 = 4.09$

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

and $\rho = -3.7$. Since $\log k_0$ relates to internal rotation of the NMe₂ group in the dimethylaniline (VII) itself, one obtains, using absolute rate theory, ΔG^\ddagger (at 133°K) = $5.1 (\pm 1.0)$ 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*-nitrodimeylaniline which are inaccessible to the n.m.r. method because of symmetry considerations. For example,



taking the value³ of 1.27 for σ^- of the nitro-group gives, ΔG^\ddagger (at 133°K) = 7.9 (± 0.4) kcal mol⁻¹ for internal rotation of the dimethylamino-group of *p*-nitrodimeylaniline. Interestingly, the results of an X-ray crystallographic investigation⁶ suggest that a quinonoid form [analogous to, for example, (II)] makes a significant contribution to the structure of *p*-nitrodimeylaniline in the crystal, while the increased rotational barrier of this molecule, compared with that of dimethylaniline, indicates⁷ that the quinonoid form also contributes to the structure of the molecule in solution.

We thank the S.R.C. for a research studentship (to R.K.M.).

(Received, August 3rd, 1970; Com. 1274.)

¹ D. D. MacNicol, *Chem. Comm.*, 1969, 1516.

² J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, ch. 10; C. S. Johnson, jun., in "Advances in Magnetic Resonance," ed. J. S. Waugh, Academic Press, New York, 1965, vol. 1, p. 33; G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.

³ H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

⁴ P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

⁵ I. D. Rae and L. K. Dyll, *Austral. J. Chem.*, 1966, **19**, 835.

⁶ T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965, **18**, 68.

⁷ R. W. Taft, jun., in "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

⁸ R. E. Klinck, D. H. Marr, and J. B. Stothers, *Chem. Comm.*, 1967, 409.