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INTERNAL ROTATION IN N,N-DIMETHYL-2,4-DINITROANILINE

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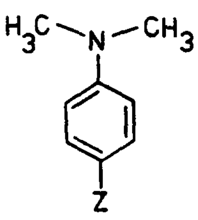
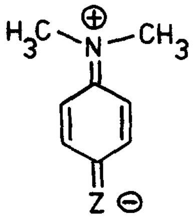
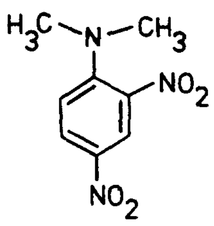
A study by the dynamic n.m.r. method has established[1] that appreciable barriers to internal rotation of the dimethylamino-group around the N-aryl bond exist in _para_-substituted N,N-dimethylanilines (I), a barrier dependence being found reflecting the contribution of the zwitterionic resonance form (II), where Z denotes a group capable of strong electron-accepting resonance.



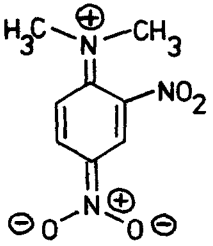
(I)



(II)



(III)



(IV)

While mesomerism-dependent barriers occurring in molecules of this type have received attention, there has been no report to date of a corresponding barrier for any N,N-dialkylaniline possessing an _ortho_-substituent.[2] In order to study the effect of the introduction of such a substituent close to the dialkylamino-function, dynamic n.m.r. measurements on N,N-dimethyl-2,4-dinitroaniline[5] (III) and related compounds have been undertaken.

The 100 MHz ^1H n.m.r. spectrum of the title compound (III) was studied as a function of temperature employing as solvent a _ca_. 1:1, v/v, mixture of $CHCl_2F/CHClF_2$. Consistent with earlier reported measurements,[6] a single sharp peak is observed for the $-N(CH_3)_2$ protons at -60°C; however, below _ca_. -100°C a marked broadening is evident, and, on further cooling, one observes the "frozen" spectrum at _ca_. -150°C with distinct resonances 34 Hz apart arising from the non-equivalent methyl groups of the dimethylamino-function, slow rotation about the N-aryl bond now allowing methyl environments _syn_ and _anti_ to the _ortho_-nitro group to be detected separately. From the doublet coalescence, at -127°C (±2°), one obtains[7] a free energy of activation $\Delta G^{\neq}$ for the dimethylamino-group rotation of 7.1 (±0.2) kcal./mole.

A recent independent study[8] of the electronic spectrum of compound (III) indicates that the ortho-nitro group is very markedly rotated out of plane with the benzene ring, so that nitrogen lone-pair delocalisation reflects much more strongly the contribution of resonance from (IV) involving the para-nitro group, rather than the contribution, which may be expected to be at most only minor, of a corresponding resonance form (not shown) involving the ortho-nitro group.

It is noteworthy that the rotational barrier for (III) is not greatly different from that predicted[9] for p-nitrodimethylaniline itself, namely 7.9 (±0.4) kcal./mole, and it is interesting that introduction of an ortho-nitro group into 2-dimethylamino-5-nitro-pyridine, which is isoelectronic with p-nitro-dimethylaniline, to give 2-dimethylamino-3,5-dinitropyridine, produces no marked change in barrier height.[10]

^{1}H n.m.r. measurements on N,N-dimethyl-2-nitro-4-methylsulphonylaniline reveal kinetic effects for the $-N(CH_3)_2$ protons at temperatures lower than for (III), these being consistent with a reduced barrier reflecting the lower mesomeric electron accepting power[11] of the $-SO_2CH_3$ group ($p\pi \rightarrow d\pi$ conjugation), compared to the 4-nitro group which it formally replaces.

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