Internal Rotation of the Dimethylamino-group in *p*-Nitrosodimethylaniline

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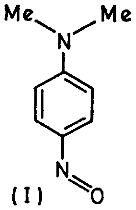
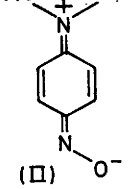
Summary A study of internal rotation in *p*-nitrosodimethylaniline (I) by ^{1}H n.m.r. spectroscopy has yielded the free energy of activation $\Delta G^\ddagger = 10{\cdot}6\ (\pm 0{\cdot}2)$ kcal./mole at 197°K, for the hitherto undetected rotation of the dimethylamino-group.

THE existence of considerable resistance to internal rotation about the Ar–NO bond in *p*-nitrosodimethyl aniline (I) is well known[1-4] and has been attributed to the appreciable contribution of the zwitterionic form (II) to the structure of (I).

I now report that an appreciable barrier hindering internal rotation of the dimethylamino-group (I) also exists and that this barrier can be measured by 100 MHz ^{1}H n.m.r. spectroscopy.† Although the rotation of the NMe_2 group is not reflected in the *aromatic* spectrum of (I),[1] the NMe_2 group (which will have a less pyramidal arrangement of bonds around the dimethylamino-nitrogen than in absence of conjugation[5]) is itself placed in an asymmetric magnetic



(I)



(II)

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† A detailed study of dialkylamino-group rotation in (I) and related molecules is being undertaken employing a n.m.r. total line shape treatment of rate.

environment by virtue of its position with respect to the nitroso-group. If one labels the methyl groups which are *syn* and *anti* with respect to the NO function in formula (I), (a) and (b) respectively, then the total rate of exchange between sites (a) and (b), $1/\tau$ (sec.$^{-1}$), is given[6] by equation (1)

$$1/\tau = 1/\tau(\mathrm{NMe_2}) + 1/\tau(\mathrm{NO}) \qquad (1)$$

where $1/\tau(\mathrm{NMe_2})$ is the rate of rotation of the NMe_2 group, and $1/\tau(\mathrm{NO})$ is the rate of rotation of the NO group.

At room temp. the 100 MHz ^1H n.m.r. spectrum of a dilute solution of (I) (*ca.* 0·1M)‡ in CD_2Cl_2 shows a sharp singlet at τ 6·85 arising from the two methyl groups which experience an averaged magnetic environment owing to rapid[6] rotation about both the Ar–NMe_2 and the Ar–NO bonds. On lowering the temperature to $-60°$, the normal changes[1-4,7] associated with the aromatic spectrum are virtually complete, corresponding to slow rotation about the Ar–NO bond. At this temperature, however, the NMe_2 resonance remains a single line, rotation of the NMe_2 group still being sufficiently rapid[6] to cause effective averaging between methyl sites (a) and (b). At $-65°$ the NMe_2 resonance is noticeably broadened, the coalescence point is $-76\ (\pm 2)°$, and at $-90°$ two peaks (a doublet with intensity ratio 1 : 1 centred at τ 6·80) separated by 4·1 Hz are observed corresponding to the "frozen" spectrum with two non-equivalent methyl groups.

At the coalescence temperature ($-76°$) one can neglect the term $1/\tau(\mathrm{NO})$ in equation (1), giving to a good approximation $1/\tau$ (the measured rate) $= 1/\tau\ (\mathrm{NMe_2})$. The rate at coalescence was estimated taking account of the finite width of the lines in absence of exchange,§ yielding $1/\tau\ (\mathrm{NMe_2}) = 7$ sec.$^{-1}$. Treating this rate in terms of absolute rate theory (with a transmission coefficient of unity) gives the free energy of activation $\Delta G^{\ddagger} = 10{\cdot}6\ (\pm 0{\cdot}2)$ kcal./mole at $-76°$ for the internal rotation of the NMe_2 group. The presence of this barrier infers that a significant delocalisation of the dimethylamino-lone-pair electrons exists in the ground state of *p*-nitrosodimethylaniline. Analogous dialkylamino-group rotations have been detected in other *p*-nitrosodialkylanilines.

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‡ A low concentration of anisole was added to the solution, the $-OCH_3$ proton signal serving as homogeneity standard. Temperatures were measured employing a thermocouple inserted directly into the spinning sample tube.

§ This estimate was made employing "Tables of NMR Exchange Broadened Multiplets," Weizmann Institute of Science, Rehovoth, Israel; A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, 1957, **27**, 1067.

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