

## Internal Rotation in 2-Dimethylaminopyridine

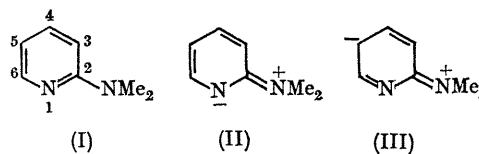
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**Summary** A study of internal rotation in 2-dimethylaminopyridine by  $^1\text{H}$  n.m.r. spectroscopy has yielded the activation parameters,  $\Delta H^\ddagger = 7.6 (\pm 1.0)$  kcal./mole and  $\Delta S^\ddagger = 0.1 (\pm 6)$  e.u., for the rotation of the dimethylamino-group.

THE kinetic n.m.r. technique<sup>1,2</sup> has been used to investigate internal rotation in aromatic molecules Ar-X when X is an unsaturated group or has lone-pair electrons.<sup>3,4</sup> This method is now applied to 2-dimethylaminopyridine (I) in which a significant delocalisation of the dimethylamino-lone-pair has been inferred<sup>†</sup> from dipole moment studies.<sup>5</sup>

The contribution of zwitterionic resonance forms such as (II) and (III) to the actual electronic structure of (I) will tend to produce a less pyramidal arrangement of bonds round the dimethylamino-nitrogen than in absence of conjugation,<sup>6</sup> and the  $\text{NMe}_2$ -substituent is placed in an



<sup>†</sup> The conjugative electron release of the dimethylamino-substituent has also its reflection in activation of the ring of (I) towards electrophilic attack. For example (I), in contrast to pyridine itself, brominates readily (see "The Chemistry of Heterocyclic Compounds," Pyridine and its Derivatives, ed. E. Klingsberg, Interscience, 1962, Part 3, p. 36).

asymmetric magnetic environment with one methyl group situated closer to the ring nitrogen than the other.

At room temperature, the 100 MHz. spectrum of a dilute solution (*ca.* 0.2M) of (I)† in vinyl chloride shows an extremely sharp line ( $\Delta\nu_{1/2} < 0.5$  Hz.) at  $\tau$  6.99 arising from the protons of the dimethylamino group, rapid rotation<sup>1</sup> around the Ar-NMe<sub>2</sub> bond causing magnetic averaging between the two methyl sites. Below  $-100^\circ$  this line

( $\pm 1.0$ ) kcal./mole and  $\Delta S^\ddagger = 0.1$  ( $\pm 6$ ) e.u., have been found for the internal rotation of the dimethylamino group of (I).

A comparison of the above parameters with those obtained recently<sup>7</sup> for isoelectronic 4-dimethylaminopyrimidine (IV) [which may be considered as a resonance hybrid involving appreciable contributions from zwitterionic forms such as (V) and (VI)] is given in the Table.

Compound	Solvent	$\Delta H^\ddagger$ <sup>a</sup>	$\Delta S^\ddagger$ <sup>b</sup>	$\Delta G^\ddagger$ <sup>a</sup>	ref.
2-Dimethylaminopyridine .. ..	Vinyl chloride	$7.6 \pm 1.0$	$0.1 \pm 6$	$7.6 \pm 0.2$	—
4-Dimethylaminopyrimidine .. ..	CHCl <sub>3</sub>	$10.7 \pm 0.4$	$-5 \pm 1$	—	7
4-Dimethylaminopyrimidine .. ..	Bu <sup>n</sup> NH <sub>2</sub>	$11.7 \pm 0.6$	$11 \pm 1.5$	—	7

<sup>a</sup> In kcal./mole.  $\Delta G^\ddagger$  is the free energy of activation at the coalescence temperature which is  $-120(\pm 2)^\circ$  for (I), the corresponding rate being calculated (see ref. 1) using the expression  $k(\text{sec.}^{-1}) = \pi(\nu_A - \nu_B)/\sqrt{2}$ .

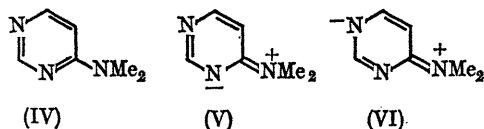
<sup>b</sup> In e.u.

starts to broaden markedly, the coalescence point is  $-120(\pm 2)^\circ$ , and at  $-137^\circ$  two well-resolved peaks (a doublet with intensity ratio 1:1 centred at  $\tau$  7.00) separated by 19.5 Hz. are observed corresponding to the "frozen" spectrum with two non-equivalent methyl groups. From the changes in line shape as a function of temperature,<sup>§</sup> and using absolute rate theory (with a transmission coefficient of unity), the activation parameters,  $\Delta H^\ddagger = 7.6$

On passing from 2-dimethylaminopyridine to 4-dimethylaminopyrimidine, which may be considered formally as the replacement of C(5)-H of (I) by a ring nitrogen, the barrier height increases markedly. This is almost certainly a reflection of the greater contribution of the resonance form (VI) (with the negative charge on an electronegative ring nitrogen) to 4-dimethylaminopyrimidine compared with that of the zwitterionic counterpart (III) to the electronic structure of 2-dimethylaminopyridine.

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† The 2-dimethylaminopyridine (supplied by Aldrich) was carefully purified before use, the final step being preparative v.p.c. A low concentration of anisole was added to the solution, the -OCH<sub>3</sub> proton signal serving as homogeneity standard for the kinetic measurements.

§ Rates were measured below the coalescent temperature employing as the spectral characteristic the ratio of maximum to central minimum of the curves ("Tables of NMR Exchange Broadened Multiplets," Weizmann Institute of Science, Rehovoth, Israel; A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, 1957, 27, 1067). Above coalescence rates were measured using eg. 12 of ref. 2.

<sup>1</sup> 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. by J. S. Waugh, Academic Press, New York, 1965, vol. 1, p. 33; L. W. Reeves in "Advances in Phys. Org. Chem.," ed. V. Gold, Academic Press, London, 1965, vol. 3, p. 187.

<sup>2</sup> A. Allerhand, H. S. Gutowsky, J. Jonas, and Meinzer, *J. Amer. Chem. Soc.*, 1966, 88, 3185.

<sup>3</sup> For references involving the use of n.m.r. in the study of internal rotation in aromatic molecules see ref. 7; J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, 1964, 41, 1033.

<sup>4</sup> A more general review of the study of internal rotation is given by J. P. Lowe in "Progr. in Phys. Org. Chem.," ed. A. Streitwieser, jun., and R. W. Tatt, Interscience, New York, 1968, vol. 6, p. 1.

<sup>5</sup> H. Lumbroso and J. Barassin, *Bull. Soc. chim. France.*, 1965, 3143.

<sup>6</sup> B. M. Wepster in "Progr. in Stereochemistry," ed. W. Klyne and P. B. D. de la Mare, Butterworths, 1958, vol. 2, p. 99.

<sup>7</sup> A. R. Katritzky and G. J. T. Tiddy, *Org. Magnetic Resonance*, 1969, 1, 57.