Hindered Internal Rotation in 5-(*NN*-Dimethylamino)-1,3,4-oxathiazole 3,3-Dioxide

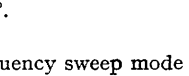
By H. J. JAKOBSEN* and A. SENNING

(*Department of Organic Chemistry, Chemical Institute, University of Aarhus,* 8000 *Århus C, Denmark*)

NUMEROUS examples of n.m.r. studies on hindered rotation of a dimethylamino-group attached to a double bond, as in amides,[1] vinylogous amides,[2] and thioamides[3] are known. Inductive, resonance, and steric effects influence the barrier to rotation about the C–N bond. However, only a few examples have been published of high rotational barriers of a dimethylamino-group attached to a heterocyclic ring, We now report the activation parameters for such an example.

In a study of some *N*-sulphonylamidines it was observed that the ^{1}H n.m.r. signal† for the dimethylamino-protons in 5-(*NN*-dimethylamino)-1,3,4-oxathiazole 3,3-dioxide (I)‡ appears as an exchange-broadened doublet (δ 3·16 p.p.m.) at ambient temperature. In the temperature range 30—70° the line shape for this signal shows the well-known behaviour for interchange between two uncoupled sites, with a coalescence temperature of +53°. At the various temperatures above and below coalescence the rate constants, $k = (2\tau)^{-1}$, were obtained by comparing experimental and calculated line shapes. The activation parameters (see Table) for the hindered rotation of the dimethylamino-group were obtained by fitting the rate constants by least squares to an Arrhenius plot.

The steric influences on the rotational barrier



(I)

Activation parameters for internal rotation in (I)

T_c	$\Delta\nu^a$	E_a	$\log_{10}A$	ΔF_{T_c}‡	ΔH_{T_c}‡	ΔS_{T_c}‡
(°K)	(Hz)	(kcal./mole)		(kcal./mole)	(kcal./mole)	(e.u.)
326 ± 2°	5·0 ± 0·1	17·9 ± 0·7	13·0 ± 0·5	17·6 ± 0·2	17·3 ± 0·8	−1·1 ± 3·3

[a] $\Delta\nu$ is the separation of the *N*-methyl signals in Hz (at 100 MHz) at 0°.

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† ^{1}H n.m.r. spectra were recorded at 100 MHz (Varian HA-100) in the frequency sweep mode using a 6·5% w/w solution in $CHBr_3$ and tetramethylsilane as internal reference. Chemical shifts, in the absence of interchange, were measured using the audio-sideband technique. Temperatures were measured using Varian precalibrated methanol and ethylene glycol samples and are believed to be correct within ±2°. At each temperature T_2 was calculated from the full line width at half maximum intensity of an internal reference line (acetonitrile) after comparison with the line widths of one of the doublet lines and the reference line obtained in the absence of interchange.

‡ 5-(*NN*-Dimethylamino)-1,3,4-oxathiozole 3,3-dioxide, m.p. 136—138·5°, was obtained by heating triethyl *NN*-dimethylorthocarbamate (H. Bredereck, F. Effenberger, and H.-P. Beyerlin, *Chem. Ber.* 1964, **97**, 1834) and chloromethanesulphonamide under reflux. In a personal communication, Dr. K. Dickoré, Farbenfabriken Bayer AG, Leverkusen, Germany, has informed us that he independently prepared the same compound *via* different routes.

are reduced to a minimum in (I), thus the observed barrier indicates the presence of a partial double bond between the ring and the dimethylamino-group, presumably due mainly to the electronegativity of the ring SO_2 group. Such a partial double bond is usually invoked to explain the rotational barriers in amides[1] and thioamides[3] which are generally of the same order of magnitude as observed for (I).

The barrier in (I), a cyclic *N*-sulphonylamidine, may be deduced from our results on other sulphonylamidines and from the work of Sandström on thioamides.[3] From earlier work on *NN*-dimethylamidines, the barrier to rotation is dependent on the electronegativity of the *N′*-substituent (at least in compounds with no severe steric interaction) since no barrier could be obtained for *NN*-dimethylacetamidine[4] while *NN*-dimethyl-*N′*-*p*-tolyl- and *p*-nitrophenyl-formamidine[5] gave $\Delta F^{\ddagger}$ values of 14·1 and 15·9 kcal./mole, respectively. For *NN*-dimethyl-*N′*-chloromethanesulphonylformamidine (II), in which steric interactions of the dimethylamino-group with other groups are insignificant,§ we have obtained $\Delta F_{T_c} = 23{\cdot}3 \pm 0{\cdot}4$ kcal./mole ($\Delta\nu = 2{\cdot}6$ Hz, solvent *o*-dichlorobenzene, $T_c = 145 \pm 2°$) which is the highest barrier observed so far in any amidine system. From this value for (II) a $\Delta F^{\ddagger}$ value of 17 kcal./mole may be estimated for (I) by using the $\Delta F^{\ddagger}$ values of 24·0 and 17·7 kcal./mole for dimethylthioformamide [$RCNSMe_2$ (III; R = H)] and *O*-methyl *NN*-dimethylthiocarbamate (III; R = MeO), respectively, where steric interactions are also negligible.[3] This estimate is in agreement with the experimentally observed value of 17·6 kcal./mole (see Table).

This Communication was partly prompted by the work of Schwenker and Rosswag[6] on some benzamidines in which it was stated that the influence of a SO_2 group on the rotational barriers in these systems is negligible since it was observed that the barrier in *NN*-dimethyl-*N′*-benzenesulphonylbenzamidine (IV) is about 10% lower than in *NN*-dimethylbenzamidine. However, since it has been shown (ref. 3 and 6) that with substituents like phenyl considerable steric effects are operative, we believe that crowding in the planar state, which will raise its energy, diminishes the barrier in (IV). Furthermore, we have recently obtained evidence for this belief in other *NN*-dimethyl-*N′*-benzenesulphonylamidines for which no splitting of the dimethylamino-signal was observed at ambient temperature.

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§ This statement is based upon the fact that the *cis*-rotamer of *N*-methyl-*N′*-chloromethanesulphonylformamidine predominates strongly in solution (see ref. 3).

[1] R. C. Neuman, jun., and V. Jonas, *J. Amer. Chem. Soc.*, 1968, **90**, 1970 and references cited.
[2] H. E. Kramer, *Annalen*, 1966, **696**, 28.
[3] J. Sandström, *J. Phys. Chem.*, 1967, **71**, 2318.
[4] R. C. Neuman, jun. and L. B. Young, *J. Phys. Chem.*, 1965, **69**, 2570.
[5] O. J. Bertelli and J. T. Gerig, *Tetrahedron Letters*, 1967, 2481.
[6] G. Schwenker and H. Rosswag, *Tetrahedron Letters*, 1968, 2691.