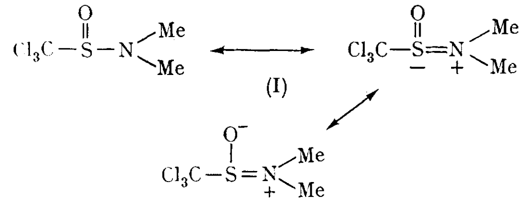
Hindered Internal Rotation about the N–S Bond in *NN*-Dimethyltrichloromethanesulphinamide

By H. J. JAKOBSEN* and A. SENNING

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

THE use of n.m.r. techniques in the study of rate processes associated with hindered rotation about different types of bonds is well known[1] and has gained special interest in the case of *NN*-dialkylamides.[2] Restricted rotation about the N–S bond in *NN*-dimethylsulphinamides due to *pπ–dπ* delocalization would be associated with nonequivalence of the two methyl groups. However, to our knowledge the available evidence concerning *NN*-dimethylsulphinamides indicates extremely rapid reorientation about the N–S bond as only a single *N*-methyl signal is observed even at low temperatures.[3]

In connection with other studies on sulphinic acid derivatives, *NN*-dimethyltrichloromethanesulphinamide (I) b.p. 76—77°/0·5 mm., n_D^{24} 1·5267, was prepared and the temperature dependence of its ¹H n.m.r. spectrum investigated.† At 35° the n.m.r. spectrum consists of a sharp singlet at τ 7·05. Below −46° this signal separates into two peaks due to the nonequivalence of the *N*-methyl groups and at temperatures below −80° the two sharp singlets have reached their maximum separation of 0·33 p.p.m. Peak separation measurements in the temperature range between complete separation and coalescence were used to calculate the Arrhenius parameters for the barrier to rotation about the N–S bond according to Gutowsky and Holm.[4] From the plot of $\log_{10} 1/\tau\delta\omega$ against $1/T$ (Figure) the activation energy



(I)

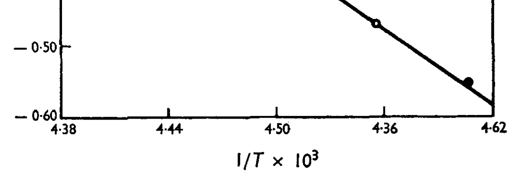


FIGURE. *Temperature dependence of the rate constant (1/2τ) for the hindered internal rotation in* NN-*dimethyltrichloromethanesulphinamide.*

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† ¹H n.m.r. spectra were recorded at 60 Mc./sec. on a Varian A-60 spectrometer equipped with a Varian V-6057 variable-temperature accessory unit using 11% (v/v) solutions in CS_2 with Me_4Si as internal standard.

TABLE

Nuclear magnetic resonance data and activation parameters for NN-*dimethyltrichloromethanesulphinamide*

T_c (°C)	$\Delta\nu_{AB}$[a] (c./sec.)	E_a (kcal./.mole)	$\log_{10}A$	ΔF‡ (kcal./mole)	ΔH‡ (kcal./mole)	ΔS‡ (e.u.)
-46 ± 2°	$19{\cdot}5\pm0{\cdot}2(-82°)$	$8{\cdot}1\pm1{\cdot}0$	$9{\cdot}4\pm0{\cdot}9$	$11{\cdot}9\pm0{\cdot}1$	$7{\cdot}6\pm1{\cdot}0$	-19 ± 5

[a] $\Delta\nu_{AB}$ is the separation of the *N*-methyl signals in c./sec. at the indicated temperature.

E_a was calculated to be 8·1 kcal./mole with a frequency factor, *A*, equal to $2{\cdot}4 \times 10^9$ sec.$^{-1}$ (Table).

Values for the free energy, enthalpy, and entropy of activation were calculated using Eyring's rate equation and a transmission coefficient of 1. The values obtained for $\Delta F^‡$, $\Delta H^‡$, and $\Delta S^‡$ at the coalescence temperature T_c are given in the Table. The negative $\Delta S^‡$ value suggests a transition state with a greater degree of order than the ground state and it is tempting to suggest that the barrier form probably involves a planar or near-planar sp^2 configuration at nitrogen and a pyramidal configuration at sulphur.

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[1] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon, Oxford, 1965.

[2] For a recent study see: M. Hammaker and B. A. Gugler, *J. Mol. Spectroscopy*, 1965, **17**, 356.

[3] R. M. Moriarty, *J. Org. Chem.*, 1965, **30**, 600.

[4] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.