Hindered Nitrogen Inversion and Restricted Rotation about the N–S Bond in Sulphenamides

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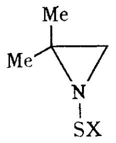
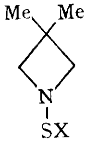
HETEROATOMS (O, N, halogens, *etc.*) directly bonded to nitrogen are known to increase markedly the nitrogen inversion barrier.[1,2] Some cyclic[3,4] and acyclic[5] sulphenamides, where sulphur is directly linked to nitrogen, have been studied recently and the changes observed in the n.m.r. spectrum as a function of temperature have been interpreted as originating from a hindered nitrogen inversion rate process.

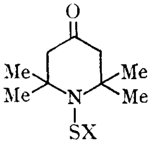
We now report our results on some sulphenamides (I)—(XIII)‡ and show that hindered N–S bond rotation rather than hindered nitrogen inversion is the operating rate process in some[4,5] of the reported cases.[6] The n.m.r. spectra of compounds (I)—(V) and (VIII)—(XI) are temperature dependent. The methylene group of compounds (I)—(IV) shows a singlet at high temperature and a doublet [small unresolved *J*(*gem*)] at low temperature, whereas the methyl singlet splits [(III) and (IV)] or does not split [(I) and (II)] into a doublet on lowering of the temperature. The methylene and methyl groups of (V), (VIII), and (IX) both give a singlet at high temperature and, respectively, an AB pattern and a doublet at low temperature. The methylene proton signal of (X)[5] and (XI) changes from a singlet to an AB pattern on lowering of the temperature. For (VI), (VII), (XII), and (XIII) no coalescence is observed, indicating that the rate process is too fast down to −100° for (VI), (XII), and (XIII) (it being assumed that the signals do not coincide accidentally) and too slow up to 160° for (VII). The coalescence temperature (T_c) of the various signals and the free energies of activation at coalescence $\Delta G_c^{\ddagger}$, calculated for the various compounds by the usual method, are listed in the Table.



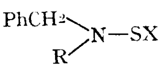
(I) $X{=}CCl_3$
(II) $X{=}Bu^t$
(III) $X{=}Ph$
(IV) $X{=}Me$



(V) $X{=}CCl_3$
(VI) $X{=}Ph$



(VII) $X{=}CCl_3$
(VIII) $X{=}Ph$
(IX) $X{=}Me$



	R	X
(X)	$PhCH_2$	CCl_3
(XI)	Pr^i	CCl_3
(XII)	Pr^i	Ph
(XIII)	$PhCH_2$	Me

Two major facts are apparent from the results listed in the Table:

(1) For the same substituent X on sulphur the activation energy is always much *lower* for the ethyleneimine derivative than for the other less-strained sulphenamides.

(2) On changing X along the series CCl_3, Bu^t, Ph, Me, the activation energy *increases* markedly with compounds (I)—(IV) and *decreases* markedly with (V)—(VI), and (VII)—(XIII).

As the barrier to nitrogen inversion should be much higher for the strained system (I) than for (VII) for instance (and even more so if steric effects are taken into account), result (1) leads to the conclusion that the rate process observed for compounds (V) and (VII)—(XI) cannot be nitrogen inversion. Furthermore, the processes operating in (I)—(IV) and in (V) and (VIII)—(XI) must be different as they show an inverse dependence on the nature of X [Result (2) above].

All these results can be rationalized by considering that two rate processes[7] are operating in sulphenamides: hindered nitrogen inversion (NI) and hindered rotation about the N–S bond (BR: bond rotation). In addition, the stable conformation about the N–S bond must be chiral as for instance in A or in B[8] in order to explain the observed spectral patterns [for instance the non-equivalence of the methylene protons in (X) and (XI)].

The series of interconversions $A \rightleftharpoons B \rightleftharpoons A' \rightleftharpoons B' \rightleftharpoons A$ involves two transition states (one for NI and one for BR) whose relative height will determine which rate process will operate and lead to spectral changes.§

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‡ These compounds have usually been obtained by treating the corresponding amines with the different substituted sulphur chlorides RSCl. Purification of these compounds was difficult and the analytical data for (II), (IV), and (VII) were less satisfactory than for the other compounds, but their spectra are in agreement with the suggested structures.

§ At a temperature where both processes are slow on the n.m.r. time scale, both forms A and B should be observable if they are of not too different energies.

Spectral data and free energies of activation $\Delta G_c^{\ddagger a}$

Compound	Solvent	Protons	Δν (Hz) (at *T*°)	*J* (Hz) (at T°)	T_c	$\Delta G_c^\ddagger$ (kcal./mole)
(I)	CH_2Cl_2–$CFCl_3$	CH_3	—	—	< −100°	—
		CH_2	30·7 (−100°)	<1 (−100°)	−87±3°	9·1±0·3
(II)	$CDCl_3$	CH_3	—	—	—	—
		CH_2	40·0 (−70°)	<1 (−70°)	−25±3°	12·2±0·3
(III)	CH_2Cl_2	CH_3	3·0 (−80°)	—	−58±3°	11·9±0·3
		CH_2	30·0 (−80°)	<1 (−80°)	−23±2°	12·4±0·2
(IV)	$CDCl_3$	CH_3	9·0 (−60°)	—	−21±3°	13·2±0·3
		CH_2	35·0 (−60°)	<1 (−60°)	−3±3°	13·4±0·3
(V)	CH_2Cl_2	CH_3	5·9 (−75°)	—	−45±2°	12·0±0·2
		CH_2	27·2 (−75°)	6·25 (−75°)	−30±2°	12·1±0·2
(VI)	CH_2Cl_2	CH_3	—	—	< −100°	—
		CH_2	—	—	< −100°	<9[c]
(VII)	HCB[b]	CH_3	7·75 (33°)	—	>160°	>23
		CH_2	9·8 (33°)	15·7 (33°)	>160°	—
(VIII)	TCE[b]	CH_3	4·6 (33°)	—	62±2°	18·1±0·2
		CH_2	22·3 (33°)	12·4 (33°)	90±2°	18·1±0·2
(IX)	$CDCl_3$	CH_3	19·2 (−10°)	—	39±2	15·9±0·2
		CH_2	22·6 (−10°)	12·1 (−10°)	44±2	15·8±0·2
(X)	$CDCl_3$	CH_2	8·3 (−5°)	14·4 (−5°)	28±2	15·0±0·2
(XI)	TCE[b]	CH_2	8·9 (0°)	15·1 (0°)	47±2	15·9±0·2
(XII)	$CDCl_3$	CH_2	—	—	< −100°	<9[c]
(XIII)	$CDCl_3$	CH_2	—	—	< −100°	<9[c]

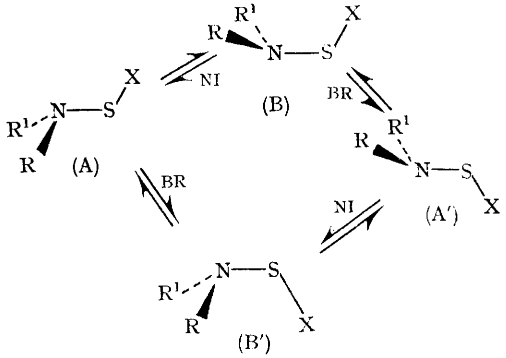
[a] Measurements at 60 MHz; Varian A-60 spectrometer;
[b] HCB = Hexachlorobutadiene; TCE = Tetrachloroethylene;
[c] Estimated values, Δν and *J* values being taken from related compounds.

From the results obtained for our compounds and from the above discussion it then follows that:

(*a*) the rate process observed for compounds (I)—(IV) is hindered nitrogen inversion;

(*b*) the rate process leading to the spectral changes observed for compounds (V) and (VII)—(XI), is hindered rotation around the N–S bond, nitrogen inversion being faster.[9]

Several effects[3] may be invoked to rationalize the low activation energies of nitrogen inversion in (I)—(IV) and the high barriers to N–S bond rotation in the other compounds: steric interactions, electronic lone pair repulsions, $(p–d)\pi$ bonding, *etc.* Simultaneous operation of several of these effects can be considered.



(*Received, June* 17*th*, 1968; *Com.* 794.)

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[1] J. M. Lehn and J. Wagner*m. Chem. Com*,, 1968, 148.
[2] D. Felix and A. Eschenmoser, *Angew. Chem.*, 1968, **80**, 197; S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 506.
[3] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.
[4] K. Murayama and T. Yoshioka, *Tetrahedron Letters*, 1968, 1363.
[5] M. Raban, *Chem. Comm.*, 1967, 1017.
[6] Independent evidence leading to the same conclusion has been obtained by M. Raban, F. B. Jones, jun., and G. W. J. Kenney, jun. (personal communication).
[7] In compounds (V)—(IX) a ring puckering or ring inversion process is also present. However, the activation energies for such processes are expected to be much lower than those reported here (see *e.g.* ref. 1; J. T. Gerig, *J. Amer. Chem. Soc.*, 1968, **90**, 1065; F. R. Jensen and B. H. Beck, *ibid.*, 1066).
[8] Such conformations are well known for the disulphides RSSR. See also Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, 1965, **30**, 2692.
[9] The shape of the potential curve for rotation may be quite complex; libration may be possible but complete rotation is hindered. This also should hold for the sulphinamide described by H. J. Jacobsen and A. Senning (*Chem. Comm.*, 1967, 617). For the shape of the potential barrier to rotation in a related system see: S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1967, **89**, 5710.