Halogen-exchange Reactions and Barriers to Torsion Around N–S Bonds in Halogeno-sulphinamides

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Summary The n.m.r. spectra of a series of halogeno-sulphinamides are described at varying temperatures and concentrations; the spectra are intepreted in terms of restricted torsion around the N–S bond ($\Delta G^{\ddagger}$ 35—60 kJ mol^{-1}) and rapid halogen-exchange reactions in the case of the chloro- and bromo-compounds.

THE sulphur atom in sulphinamides shows configurational stability.[1] Thus the sulphur atom in a series of *NN*-dialkylhalogenosulphinamides, R_2NSOX (**1**) is apparently chiral and if the substituents R contain a prochiral centre (*e.g.* CH_2 or CMe_2) the geminal substituents should be anisochronous.[2] The methylene protons in di-isobutylaminosulphinyl fluoride (**1h**) and the methyl groups in the corresponding di-isopropyl compound (**1i**) showed the expected geminal non-equivalence ($\Delta\nu$ = 1·0 and 1·4 Hz for spectra in CH_2Cl_2). However geminal non-equivalence was not observed for any of the chloro-compounds (**1b**—**e**) in a wide variety of solvents nor in spectra at lower temperatures, where torsion around the S–N bond is slow (*vide infra*). The sulphur atom thus does not constitute a chiral centre. The loss of configurational stability, is unlikely to be associated with a rapid 'umbrella' inversion at sulphur[1] and an alternative explanation, that a rapid intermolecular halogen exchange is occurring with loss of configuration at sulphur, must be considered.

TABLE. *Torsional barriers in aminosulphinamides* R_2NSOX[a]

Compound	R	X	Δν(Hz)	T_c/°C	Δ$G^‡$/kJ mol^{-1}
(**1a**)	Me	Cl	3·8	−44	50·6[e]
(**1b**)	Et	Cl	5·5[b]	−37	52·4
(**1c**)	Bz	Cl	10·0[c]	−29	53·1[e]
(**1d**)	Bu^t	Cl	7·35[c]	−19	56·0[e]
(**1e**)	Pr^i	Cl	1·8[b]	−14	61·5[e]
(**1f**)	Me	F	d	d	d
(**1g**)	Et	F	d	−105	*ca.* 35
(**1h**)	Bu^t	F	d	−102	*ca.* 35
(**1i**)	Pr^i	F	7·0[b]	−82	41·8[e]
(**1j**)	Me	Br	3·5[b]	−27	56·5[e]

[a] Measured for solutions in CH_2Cl_2 at 60 MHz. [b] Methyl signal. [c] Methylene signal. [d] Not measured. [e] Calculated from full line shape analysis.

Evidence for rapid halogen exchange came from a study of fluoro- and chloro-*NN*-dimethylsulphinamides [(**1a**) and (**1f**)]. Dilute mixed solutions (each 0·1 M in CH_2Cl_2) at ambient temperature showed spectra composed of the spectra of the individual compounds, *i.e.* a singlet at τ 7·12 for (**1a**) and a doublet, τ 7·20, $^3J_{H,F}$ 2·75 Hz for (**1f**). As the concentration of the mixture was increased the absorptions broadened and a solution (1·0M in each)showed a single absorption at τ 7·16. Similar rapid intermolecular halogen exchange with loss of stereochemistry at the exchanging site has previously been observed for some chlorophosphines[3] and chlorostannanes.[4] Halogen exchange between the chloro- and bromo-compounds (**1a**) and (**1j**) was more rapid. Mixed solutions showed a single absorption for spectra at ambient temperature even for 0·001M solutions.

The spectra of the chloro- and bromo-compounds [(**1a**) and (**1j**)] were however temperature dependent. At low temperatures the alkyl groups became anisochronous. In the absence of an effective chiral centre at sulphur the methyl groups can only become diastereotopic if torsion around the S–N bond is slow on the n.m.r. time scale; slow inversion at nitrogen is not a sufficient condition to render the methyl groups diastereotopic. This result is in agreement with very low barrier to nitrogen inversion in *N*-sulphinyl amines which is probably even lower[5] than the barrier of *ca.* 30 kJ mol^{-1} shown by simple, open-chain amines.[6] Additionally the observed barriers increased with increasing size of the substituent R (see Table) suggesting a torsional rather than inversion barrier. The barriers in the Table for the chloro- and bromo-compounds are of the same order of magnitude as the value Δ$G^‡$ 50·3 kJ mol^{-1}, previously reported for torsion around the N–S bond in *NN*-dimethyltrichloromethylsulphinamide (**1**; X = CCl_3, R = Me).[7]

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[1] R. M. Moriaty, *J. Org. Chem.*, 1965, **30**, 600.
[2] See K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1 for terminology.
[3] B. Fontal and H. Goldwhite, *Tetrahedron*, 1966, **22**, 3275; D. Imberg and H. Friebolin, *Z. Naturforsch.*, 1968, **23b**, 759.
[4] D. V. Stynes and A. L. Allred, *J. Amer. Chem. Soc.*, 1971, **93**, 2666.
[5] C. H. Bushweller and J. W. O'Neill, *J. Amer. Chem. Soc.*, 1970, **92**, 2159; M. J. S. Dewar and W. B. Jennings, *ibid.*, 1971, **93**, 401.
[6] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357; A. T. Bottini and J. D. Roberts, *ibid.*, 1958, **80**, 5203.
[7] H. J. Jakobsen and A. Senning, *Chem. Comm.*, 1967, **617**.