Conformational Interchange in Acyclic Sulphonamides: Evidence for Directional p_π–d_π Bonding in N–S Bonds

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Summary The low temperature n.m.r. spectra of dialkylsulphamoyl chlorides indicate a considerable barrier (*ca.* 11·5 kcal mol^{-1}) to rotation around the N–S bond; the ground-state conformation is similar to that predicted for an α-sulphonyl carbanion.

REPULSIVE interactions between vicinal lone pairs of electrons have been generally cited as an origin of the enhanced barriers to rotation around bonds connecting a nitrogen atom to another atom possessing non-bonding electrons.[1,2] However, we now report the existence of substantial barriers to rotation around the N–S bonds in a series of dialkylsulphonamides, even though the sulphur atom in each of these compounds possesses no lone pair of electrons.

$R_2N\text{–}SO_2X$

(**1**; R = Et, X = Cl), (**2**; R = PhCH$_2$, X = Cl), (**3**; R = Bu^i, X = Cl), (**4**; R = Et, X = Me), (**5**; R = Et, X = Ph), (**6**; R = Et, X = NEt).

The n.m.r. spectrum of diethylsulphamoyl chloride (**1**) in CHCl$_2$F solution showed the normal methylene quartet of an A_2M_3 system at ambient temperature. The quartet collapsed at $-40°$ to a partly overlapping multiplet of 16 lines (Figure) which can be attributed to the AB portion of an ABM_3 system. The observed chemical shift nonequivalence of the geminal methylene protons at low temperature indicates a molecular dissymmetry† on the n.m.r. time-scale that may be interpreted in terms of either slow nitrogen inversion or slow rotation around the N–S bond. The dibenzyl (**2**) and di-isobutyl (**3**) compounds exhibit similar temperature dependent spectra as the methylene proton signals collapse below $-50°$ to an AB quartet and an ABM multiplet, respectively. The free energies of activation for the conformational interchange were determined by the dynamic n.m.r. method[3] (Table).

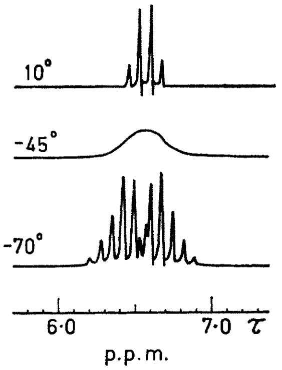


FIGURE. *Methylene proton signals of* Et$_2$N–SO$_2$Cl (**1**) *at* 100*MHz in* CHCl$_2$F *solution.*

N.m.r. data (at 100 *MHz in* CHCl$_2$F *solution) and free energy barriers* (ΔG‡) *for conformational interchange in dialkylsulphamoyl chlorides*

Compound	Δν[a] (Hz)	J_{AB} (Hz)	T_c (°)	k[b] (s^{-1})	ΔG‡ at T_c (kcal mol^{-1})
(**1**)[c]	28·7	14·1	−43	69	11·4±0·2
(**2**)	26·1	14·8	−51	76	11·0±0·1
(**3**)	58·2[d]	13·8	−36	*ca.* 150[d]	11·4±0·3

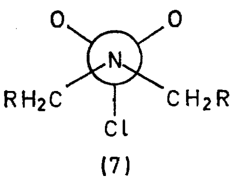
[a] Chemical shift nonequivalence of the methylene protons at the coalescence temperature (T_c) determined by adjusting the pre-exchange value to afford the optimum fit between experimental and theoretical spectra.

[b] Exchange rates at coalescence of the AB quartet were computed using a programme which extracts the exchange rate directly from the digitised experimental spectrum; see J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 3396.

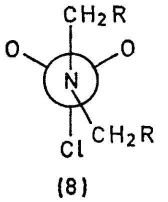
[c] Spectra observed with decoupling of the methyl signal.

[d] Approximate analysis.

The measured barriers can probably be assigned to torsion around the N–S bond rather than to nitrogen inversion as the latter is considered to be a much lower energy process for the following reasons: (i) the barrier to nitrogen inversion in an acyclic amine is only *ca.* 6·5 kcal mol^{-1},[2b,4] and even in acyclic hydrazines where the barrier is augmented by lone-pair interactions the inversion barrier is only 8 kcal mol^{-1};[2] (ii) p_π–d_π bonding between the nitrogen lone pair and vacant sulphur orbitals should decrease the inversion barrier below that in a simple amine, and indeed this effect has been observed in *N*-sulphonylaziridines.[5] Additionally, an *X*-ray investigation[6] of (Me$_2$N)$_2$SO$_2$ and an electron diffraction study[7] of Me$_2$NSO$_2$Cl indicate flattening of the nitrogen pyramid.



(7)



(8)

The observation of diastereotopic methylene protons in the low temperature spectra of (**1**), (**2**), and (**3**) is consistent with (**7**) as the ground-state conformation, but inconsistent with (**8**).‡ It is interesting that (Me$_2$N)$_2$SO$_2$ adopts a type (**7**) conformation in the solid state and extended Hückel MO calculations indicate that the type (**7**) conformation of (F$_2$N)$_2$SO$_2$ is more stable than type (**8**) by *ca.* 9·5 kcal mol^{-1}.[6]

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† Specifically, the observation of nonequivalent CH$_2$ protons shows that the molecule does not possess a σ-plane (on the n.m.r. time-scale) containing the methylene carbon atoms.

‡ In (**8**) the alkyl groups are nonequivalent but the methylene protons within each alkyl group are enantiotopic and hence isochronous in achiral solvents, see K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1; the nitrogen atom is drawn planar to represent rapid nitrogen inversion.

Sulphonamides are isoelectronic with α-sulphonyl carbanions and recent SCF–MO calculations[8] on a model system have suggested that the most stable conformation is (**7**; N = C^-, Cl = H).

The chlorine substituent seems to increase the barrier as the n.m.r. spectra of (**4**), (**5**), and (**6**) in CH_2Cl_2 solution remain unchanged down to −90°. The results are best interpreted in terms of a directional dependent p_π–d_π bond which is enhanced by the electronegative chlorine substituent on the sulphur atom in (**1**), (**2**), and (**3**). Although an isolated set of *d*-orbitals should not result in directional p_π–d_π bonding,[9] the *d*-orbitals in sulphonamides may mix strongly in the S–O and S–Cl bonds and thus lead to asymmetry in the S–N π-bond.

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