Conformational Preference of the S–N Bond in Thian and 1,3-Dithian 1-Imides

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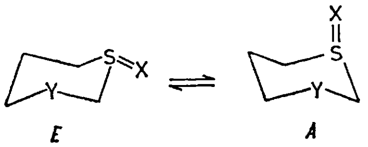
Summary The conformational properties of thian and 1,3-dithian 1-imides with tosyl, benzoyl, and *p*-chlorophenyl substituents on nitrogen have been investigated by low-temperature ^{13}C and ^{1}H n.m.r. spectroscopy.

SULPHOXIDE and *N*-arylsulphonylsulphimide groups in the thian systems (**1a**) and (**1b**) have been found to show a preference for the axial position of the S–X bond (Scheme),[1] but equatorial preference has been reported for other thian imides (**1c**)[1] and (**1d**).[2] In the 1,3-dithian series a pronounced preference for equatorial S–O in the 1-oxide (**2a**) has recently been reported,[3] and an equatorial position of the *N*-tosyl group in (**2b**) has been suggested.[4]

In order to determine the influence of different substituents on nitrogen on the conformational behaviour of cyclic sulphimides, a number of thian and 1,3-dithian 1-imides were prepared and investigated by low-temperature ^{13}C and ^{1}H n.m.r. spectroscopy. The conformational preferences of the compounds are in the Table.

At room temperature compounds (**1**) and (**2**) showed averaged ^{13}C n.m.r. spectra, owing to rapid ring inversion. At low temperatures two sets of signals, corresponding to conformers *E* and *A*, could be observed in the case of (**1b**), (**1d**), and (**1e**); only one conformer could be detected in the case of (**2d**) and (**2e**).† Assignment of signals was based on comparison with the spectra of other known thian and 1,3-dithian 1-imides,[2,5] and from known β- and γ-substituent effects, which have been confirmed for cyclic sulphimides with axial or equatorial S–N bonds.[2,5] Integration of corresponding signals‡ in the low-temperature ^{13}C n.m.r. spectra of (**1b**), (**1d**), and (**1e**) gave the isomer ratios and free energy differences in the Table. The only conformer of compounds (**2**) detectable in the low-temperature ^{13}C n.m.r. spectra is assigned the equatorial form *E*. Assuming γ-shift effects of S–N bonds in the 1,3-dithian derivatives (**2**) to be of similar magnitude as observed in the case of the conformationally homogeneous 1-*N*-*p*-chlorophenylimides of 4,6-*cis*-dimethyl-1,3-dithian[5] ($\gamma_{anti} - \gamma_{gauche}$ *ca.* 13 p.p.m.) and considering the small (< 1 p.p.m.) temperature effect on ^{13}C chemical shifts, a population of 10% of conformer *A* at room temperature should result in a 1—2 p.p.m. upfield shift of the C-5 signal in the averaged spectrum. The results indicate that for compound (**2d**) the population of conformer *A* is < 10% at room temperature and <5% (and thus below detectability) at −90 °C. Although signals for *A* are not seen in the low-temperature spectrum of (**2e**),§ the temperature dependence of the C-5 signal is relatively pronounced (1·3 p.p.m. change from room temp. to −90 °C), indicating a population of conformer *A* of perhaps slightly more than 10% at room temperature.



(**1**) Y = CH_2
(**2**) Y = S

a; X = O
b; X = $NSO_2C_6H_4$-*p*
c; X = NH
d; X = NC_6H_4Cl-*p*
e; X = NCOPh

Scheme

These results were confirmed by the ^{1}H n.m.r. spectra of (**2**) [the spectra of (**1**) were too tightly coupled for unambiguous interpretation]. Very little change was observed in the AB pattern of the C-2 protons for (**2b**) and (**2d**) upon lowering the temperature from +30 to −90 °C; no signals due to *A* could be detected. On the other hand, the changes seen for the corresponding protons in (**2e**) are sizeable, and at −85 °C part of the low-field half of the AB system (due to the equatorial proton) of *A* could be seen (the high-field halves of *A* and *E* are superimposed), but was too small for integration.

Table. Conformational preferences of thian and 1,3-dithian 1-imides

Compound[a]	°C	%*E*	*K*	$-\Delta G^{\circ}$[b]	Method[c]
(**1b**)[d,e]	−85	31	0·45	−1·26 (−0·3)	^{13}C[d]
(**1d**)[f]	−90	80	4·0	2·09 (0·5)	^{13}C
(**1e**)[a,g]	−72	40	0·67	−0·67 (−0·16)	^{13}C
(**2b**)[h]	−80	>95	>19	>4·6 (>1·1)	^{1}H
(**2d**)[f]	−90	>95	>19	>4·2 (>1·0)	^{13}C, ^{1}H
(**2e**)[a,g]	−82	⩾95	⩾19	⩾4·6 (⩾1·1)	^{13}C, ^{1}H

[a] All new compounds gave satisfactory elemental analysis. [b] In kJ mol^{-1} (kcal mol^{-1} in parentheses). [c] ^{13}C n.m.r. spectra were recorded in CH_2Cl_2 + 20% CD_3COCD_3 + 2% Me_4Si, at 25.16 MHz in the Fourier transform mode, and ^{1}H-spectra in CD_2Cl_2 + 2% Me_4Si, at 100·1 MHz in the Fourier transform mode, on a Varian XL-100 spectrometer. [d] Lambert *et al.* (ref. 1) report 40% *E*, $-\Delta G^{\circ}$ 0·15 kcal mol^{-1} at −89 °C, ^{1}H n.m.r. spectroscopy for [3,3,5,5-$^{2}H_4$]-(**1b**). [e] Prepared by reaction of (**1a**) with tosyl amide, P_2O_5, and Et_3N, analogous to the synthesis of *N*-arylsulphimides (P. Claus and W. Vycudilik, *Monatsh.*, 1970, **101**, 396). For preparation see also ref. 1. [f] Prepared by reaction of the parent cyclic sulphide with *N*-chlorosuccinimide and 4-chloroaniline by a method recently reported (P. K. Claus, W. Rieder, P. Hofbauer, and E. Vilsmaier, *Tetrahedron*, 1975, **31**, 505). [g] From the parent cyclic sulphide and *N*-bromobenzamide by a modification of a procedure (H. Kise, G. F. Whitfield, and D. Swern, *Tetrahedron Letters*, 1971, 1761) for synthesis of *N*-acyldimethylsulphimides. [h] Prepared according to the method in ref. 4.

Lambert *et al.*[1] suggested that the small preference for the equatorial position of the S–N bond in (**1c**) might arise from greater ease of intermolecular hydrogen bonding, but this explanation fails at least in the case of (**1d**) which shows a much higher preference for conformation *E*. The dependence of the conformational equilibria in thian 1-imides on the substituent on nitrogen might be due to the variation in polarization of the S–N bond. While the strongly electron-withdrawing substituents in (**1b**) and (**1e**) bring about a situation resembling (**1a**) (with attractive interactions between N and the *syn*-axial protons at C-3 and C-5 in conformer *A*), the less electron-attracting phenyl ring leaves only the steric repulsion between *syn*-axial substituents and, hence, a predominance of conformation *E*. This explanation (although not the only one conceivable) is substantiated by experiments with thian 1-*N*-arylimides bearing *para*-substituents of different electron-donating or -withdrawing properties.

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† ^{13}C n.m.r. shifts for (**2b**) in CD_2Cl_2 have been reported to be 'relatively constant' from +35 to −90 °C (ref. 4). The compound proved too insoluble for low-temperature ^{13}C n.m.r. investigation in the solvent mixture which we used.

‡ Nuclear Overhauser effects and relaxation times of such carbon atoms have been shown to be nearly equal: see H. Booth and M. L. Josefowicz, *J.C.S. Perkin II*, 1976, 895.

§ Detection of small amounts of conformers *A* is difficult because of low solubility of compounds (**2**) at low temperatures.

[1] J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.*, 1972, **37**, 377; *J. Amer. Chem. Soc.*, 1972, **94**, 208.

[2] P. K. Claus, W. Rieder, F. W. Vierhapper, and R. L. Willer, *Tetrahedron Letters*, 1976, 119.

[3] L. Van Acker and M. Anteunis, *Tetrahedron Letters*, 1974, 225; M. J. Cook and A. P. Tonge, *J.C.S. Perkin II*, 1974, 767; S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Amer. Chem. Soc.*, 1975, **97**, 1468.

[4] R. B. Greenwald, D. H. Evans, and J. R. DeMember, *Tetrahedron Letters*, 1975, 3885.

[5] P. K. Claus, W. Rieder, and F. W. Vierhapper, *Tetrahedron Letters*, 1976, 1335.