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EQUATORIAL PREFERENCE OF THE SULFIMIDE FUNCTIONALITY IN CYCLIC N-ARYL SULFIMIDES

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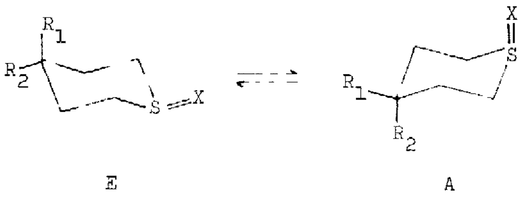
Considerable interest has recently been directed to the conformational properties of sulfoxide, sulfimide and sulfoximide functionalities incorporated into a six membered ring[1]. The preference of the conformer with axial sulfoxide group in thiane-1-oxides, 1A, seems well documented[1,2]. *Cis*-isomers of 4-substituted thiane-1-oxides have been shown to be thermodynamically more stable than the *trans*-isomers and are supposed to exist preferably in the S-O-axial conformation[3]. A smaller preference for the axial position has been found in thiane-1-(N-arylsulfonyl) imides (2), whereas thiane-1-imide (3) shows a comparably small preference for the equatorial conformation[1]. The prevalence of the axial form has been ascribed to attractive interactions between substituents on sulfur and the *syn*-axial hydrogens on C-3 and C-5[4], but additional reasons have to be considered as indicated by recent results with 1,3-dithiane- and oxathiane-1-oxides[5-7].



1 $R_1 = R_2 = H$, $X = O$
2 $R_1 = R_2 = H$, $X = N\text{-}SO_2\text{-aryl}$
3 $R_1 = R_2 = H$, $X = NH$
4 $R_1 = R_2 = H$, X = N-p-chlorophenyl
5 $R_1 = CH_3$, $R_2 = H$, X = N-p-chlorophenyl
6 $R_1 = H$, $R_2 = CH_3$, X = N-p-chlorophenyl
7 $R_1 = CH_3$, $R_2 = H$, $X = O$
8 $R_1 = H$, $R_2 = CH_3$, $X = O$

We now wish to report a considerable equatorial preference of the sulfimide functionality in thiane-1-(N-p-chlorophenyl) imide (4) and *cis*-1-thiadecalin-1ß-(N-p-chlorophenyl) imide (9ß)[8], in contrast to the observed axial preference in 2[1]. The ^{13}C-NMR spectrum of 4, recorded at +29°C, shows an averaged spectrum of 4E and 4A, due to rapid ring inversion. At -90°C two sets of signals, corresponding to conformers E and A, are clearly visible, lowering the temperature to -100°C brings no further change.

Assignment of signals rests on comparison with the spectra of cis- (5) and trans-4-methyl-thiane-1-(N-p-chlorophenyl) imides (6)[9], cis- (7) and trans-4-methyl-thiane-1-oxides (8)[9], and cis- and trans-4-tert.butyl-thiane-1-oxides[2]. C-atoms 3 and 5 in conformers A are more shielded than in the corresponding conformers E by 6.2 to 7.5 ppm because of the γ-gauche effect brought about by X, C-atoms 2 and 6 are also more shielded in A by 5 to 7 ppm because of the smaller ß-effect[10,2]. As in the case of cyclic sulfoxides[2], ^{13}C NMR spectra of N-arylsulfimides allow unambiguous configurational assignment.

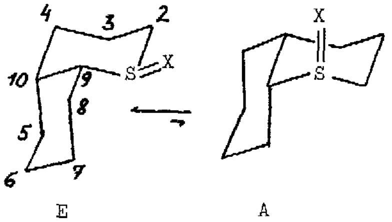
Table I. NMR Chemical Shifts[a]

Compound	^1H	^{13}C									
	δ_{ae}[b]	Heterocyclic Ring						Aromatic Ring			
		C-2	C-3	C-4	C-5	C-6	CH_3	C-1'	C-2'	C-3'	C-4'
4[c]	0.39	46.80	21.87	24.55	21.87	46.80	--	155.54	119.13	128.88	120.12
4E[c,d]		47.93	24.08	24.08	24.08	47.93	--	154.55	118.28	128.96	119.62
4A[c,d]		40.92	16.53	24.08	16.53	40.92	--	155.19	118.28	128.96	119.42
5	0.22	42.18	25.27	29.96	25.27	42.18	21.33	154.77	119.14	128.67	120.51
6	0.47	48.05	31.90	30.92	31.90	48.05	21.44	153.91	118.91	128.75	120.81
7	0.49	45.74	23.73	30.89	23.73	45.74	22.43	--	--	--	--
8	0.66	50.68	29.95	30.45	29.95	50.68	20.72	--	--	--	--
9ß[e]	0.46	47.79	19.70	30.34	25.61	27.92	--	155.82	118.87	128.61	120.33
9ß[f]		47.62	19.66	30.22	25.71	28.44	--	155.88	119.33	128.67	120.59
9ßE[g]		48.04	19.82	30.60	25.53	26.97	--	155.31	118.04	128.62	119.69
10α[h]	0.38	48.55	22.94	32.67	33.34	25.54	--	155.85	118.87	128.42	120.23

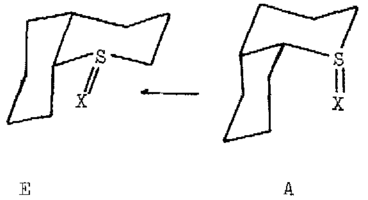
[a] In ppm, solvent $CDCl_3$+ 5% TMS, at +29°C, if not otherwise indicated. Spectra were recorded on a Varian XL-100, 100 MHz ^1H-spectra in the CW mode, ^{13}C-spectra at 25.16 MHz in the FT mode. [b] Shift difference of axial and equatorial protons at C-2. [c] ^{13}C-spectrum in CH_2Cl_2 + 20% CD_3COCD_3 + 2% TMS, signals of C-2, C-1' and C-4' were used for integration. [d] At -90°C. [e] C-7: 21.81, C-8: 25.61, C-9: 63.25, C-10: 37.44. [f] At +55°C, C-7 22.17, C-8: 25.50, C-9 63.15, C-10: 37.12. [g] At -69°C, C-7 21.16, C-8 25.79, C-9 63.84, C-10. 38.05. [h] C-7 25.28, C-8 27.62, C-9 66.55, C-10: 40.03.

Integration[11] of signals in the -90°C ^{13}C-spectrum of 4 gives a ratio of 80±5 % E to 20±5 % A, an equilibrium constant $K \approx 4$ and $-\Delta G^o_{183} \approx 0.5$ kcal/mol. Since ^{13}C-NMR shifts are temperature dependent, use of Eliel's equation $K = \frac{\delta_e - \delta}{\delta - \delta_a}$[12] can only give very approximate results : 71 % or 84 % E at +29°C, using signals of C-3,5 or C-2,6, respectively.

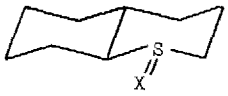
The equatorial preference of the sulfimide functionality is also shown by the ^{13}C-NMR spectrum of cis-1-thiadecalin-1β-(N-p-chlorophenyl) imide (**9β**)[13]. Reacting cis-1-thiadecalin with N-chloro-succinimide and 4-chloroaniline afforded only one of the two configurational isomers **9α** and **9β**. Assignment of the structure of **9β** is based on the following observations. conformation A in **9α** is excluded because of severe N/CH$_2$ syn-axial interactions. In the ^{13}C-NMR spectrum of the remaining conformer **9α**E C-2 must resonate at comparatively high field because of the γ-gauche interaction with C-8. The room temperature spectrum shows C-2 at 47.79 ppm, very close to the signal of C-2 in trans-1-thiadecalin-1α-(N-p-chlorophenyl) imide (**10α**)(the equatorial configuration of which has been rigorously established by X-ray analysis[14]), thus **9α**E and therefore **9α** has to be excluded, and for the same reason (γ-gauche C-2/C-8) **9β** must exist predominantly in conformation E[15]. Signals at +29°C are slightly broadened due to ring inversion, at +55°C inversion is fast and all signals are sharp. At -69°C the signals are again sharp, only one set of signals, corresponding to conformer E, is clearly seen. Since 10% of a second isomer are easily detected it is concluded that **9β**, at -69°C, exists to $\geq$90% in conformation E, $K \geq 9$, $-\Delta G^{o}_{204} \geq 0.9$ kcal/mol.



9β



9α



10α

X = N-p-chlorophenyl

Additional qualitative evidence for the conclusions drawn comes from comparison of the δ_{ae}-values[1] of the α-protons in the ^{1}H-NMR spectra, also listed in Table 1.

Possible reasons for the preference of the aryl sulfimide functionality for the equatorial conformation will be discussed in the full paper.

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8. Compounds investigated were prepared by reaction of the parent cyclic sulfides with N-chlorosuccinimide and 4-chloroaniline by a procedure recently reported : P K. Claus, W. Rieder, P. Hofbauer and E. Vilsmaier, *Tetrahedron* **31**, 505 (1975). An exception was **5**, which could only be obtained from **8** in moderate yields in a manner analogous the one reported P. Claus and W. Vycudilik, *Mh. Chem.*, **101**, 396 (1970). All new compounds gave satisfactory elemental analysis.
9. Because of the comparatively large $-\Delta G^{o}$ (1.6 to 1.8 kcal/mol) in favour of equatorial CH_3, these compounds are supposed to be $\geq$90% in the CH_3-equatorial conformation.
10. D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94**, 5318 (1972), for other leading references see G. J. Martin, M. L. Martin and S. Odiot, *Org. Mag. Res.*, **7**, 2 (1975).
11. Since NCE's and T_1's of C-atoms of a given compound may differ, only corresponding signals in **4**E and **4**A were compared (cf. H. Booth and D. V. Griffiths, *J. C. S. Perkin II*, 111 (1975)).
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13. "β" means "on the same side of the ring as the hydrogen on C-10", "α" means " on the side opposite to this hydrogen"
14. A. McPhail, P. K. Claus and F. W. Vierhapper, in preparation.
15. The equilibrium in *cis*-1-thiadecalin was determined to be slightly in favour of the conformation with 2-equatorially-3-axially methylene substituted thiane ring (**9**βE or **9**αA, no X) : $K_{205} = 1.4$, $-\Delta G^{o}_{205} = 0.14$ kcal/mol : F. W. Vierhapper and R. L. Willer, in preparation.