of acetic anhydride. Formic acid solvent was prepared by storing practical grade formic acid (Eastman Kodak Co., 97%) over boric anhydride for several days, decanting, and distilling from fresh anhydride. Absolute ethanol was prepared according to the method of Fieser.[23] 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled just prior to use.

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions in formic acid were 0.02 M. In all other solvents the solutions were 0.03 M. In a typical kinetic run, the requisite amount of ester was accurately weighed into a 25-mL volumetric flask and then sufficient solvent was added rapidly to give a 25-mL reaction solution volume. Reaction time commenced with the addition of the solvent.[24] The solvent used for each kinetic run and the flask containing the ester were thermostated in a constant-temperature bath held to ±0.05 °C at least 20 min prior to a run. At appropriate times, 2-mL aliquots were analyzed for liberated pentamethylbenzenesulfonic acid. In acetic acid and ethanol, aliquots were titrated directly. The aliquots taken from the trifluoroethanol and aqueous ethanol solvents were quenched with 5-mL of cold ethanol before titration, while those taken from formic acid were quenched with 8 mL of cold, purified dioxane[26] before titration. The titrating solutions were for acetolysis and formolysis 0.050 N sodium acetate in acetic acid and for the alcoholyses 0.020 N sodium methoxide in anhydrous methanol. The indicators used were the following: for acetolysis, bromophenol blue (in acetic acid); for formolysis, bromocresol green (in acetic acid); for trifluoroethanolysis, bromophenol blue (in 20% aqueous EtOH); for alcoholyses, bromothymol blue (in water).

Registry No. 3-OPms, 70561-86-3; cyclopropylcarbinol, 2516-33-8; pentamethylbenzenesulfonyl chloride, 52499-94-2.

(23) L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed., D. C. Heath, Boston, Mass., 1957, p 285.

(24) The ester dissolved rapidly—within a few seconds— in all solvents except formic acid. To effect rapid dissolution in this solvent, the ester was fluidized with 15 drops of ethyl acetate before addition of the formic acid. As measured in our laboratory,[25] this quantity of ethyl acetate has no effect on the observed rate of such formolysis reactions.

(25) D. D. Roberts, unpublished data.

(26) Purified by percolation through chromatographic grade alumina (Aluminum Co. of America, F-20 grade).

Conformational Preference of the Sulfimide Functionality in Cyclic Sulfimides

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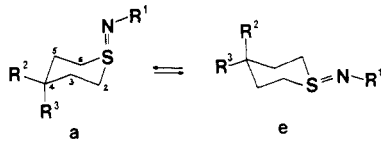
Received April 4, 1979

Conformational equilibria of various >S=N—R derivatives (R = C_6H_4X, SO_2Ar, COAr, COOEt, COMe) of thiane and of some oxa- and dithianes were determined by low-temperature ^{13}C NMR spectroscopy. The conformational preference of the thiane 1-(*N*-aryl)imides was found to depend on the electron-withdrawing capacity of the substituents on the aromatic ring. Replacement of the aromatic ortho hydrogens by methyl or fluorine did not greatly change the equilibrium. A nearly constant difference in conformational free energy was found between 1-[*N*-(*p*-chlorophenyl)]imides and 1-oxides for the various heterocyclic ring systems investigated.

Recently we reported a pronounced preference of the S=N bond in thiane 1-[*N*-(*p*-chlorophenyl)]imide (**1**) for the equatorial conformation,[1] in contrast to the *N*-H (**2**),[2] the *N*-benzoyl (**3**),[3] and the *N*-tosyl (**4**)[2,3] analogues and to the S=O bond in thiane 1-oxide.[2,4] In 1,3-dithiane 1-*N*-imides only the N-equatorial form could be observed[3,5] at low temperature, regardless of the substituent on nitrogen, similar to the situation in 1,3-dithiane 1-oxide.[6]

In an attempt to explain the preference for the axial position of oxygen in thiane 1-oxides, Johnson[7] originally suggested that attractive London interactions might outweigh van der Waals repulsions. This was subsequently confirmed in Westheimer-type calculations by Allinger[8] and has been used to explain the conformational equilibria

Scheme I



a e

1, R^1 = *p*-C_6H_4Cl, R^2 = R^3 = H
2, R^1 = R^2 = R^3 = H
3, R^1 = COC_6H_5, R^2 = R^3 = H
4, R^1 = $SO_2C_6H_4CH_3$, R^2 = R^3 = H
5, R^1 = $COOC_2H_5$, R^2 = R^3 = H
6, R^1 = $COCH_3$, R^2 = R^3 = H
7, R^1 = *p*-C_6H_4Cl, R^2 = CH_3, R^3 = H
8, R^1 = *p*-C_6H_4Cl, R^2 = H, R^3 = CH_3
9, R^1 = *p*-C_6H_4Cl, R^2 = R^3 = CH_3
10, R^1 = COC_6H_5, R^2 = R^3 = CH_3
11, R^1 = $SO_2C_6H_4CH_3$, R^2 = R^3 = CH_3
12, R^1 = *p*-C_6H_4Cl, R^2 = Cl, R^3 = H
13, R^1 = *p*-C_6H_4Cl, R^2 = H, R^3 = Cl

(1) P. K. Claus, W. Rieder, F. W. Vierhapper, and R. L. Willer, *Tetrahedron Lett.*, 119 (1976).

(2) (a) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, 31, 3429 (1966); (b) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Am. Chem. Soc.*, 94, 208 (1972); (c) J. B. Lambert, C. E. Mixan, and D. H. Johnson, *ibid.*, 95, 4634 (1973); (d) J. B. Lambert and S. I. Featherman, *Chem. Rev.*, 75, 611 (1975).

(3) P. K. Claus, F. W. Vierhapper, and R. L. Willer, *J. Chem. Soc., Chem. Commun.*, 1002 (1976).

(4) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975).

(5) R. B. Greenwald, D. H. Evans, and J. R. DeMember, *Tetrahedron Lett.*, 3885 (1975); J. R. DeMember, R. B. Greenwald, and D. H. Evans, *J. Org. Chem.*, 42, 3518 (1977).

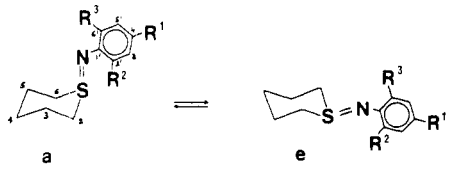
(6) (a) L. Van Acker and M. Anteunis, *Tetrahedron Lett.*, 225 (1974); (b) M. J. Cook and A. P. Tonge, *J. Chem. Soc., Perkin Trans. 2*, 767 (1974); (c) S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, 97, 1468 (1975).

(7) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, 86, 2935 (1964); 87, 1109 (1965).

(8) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Am. Chem. Soc.*, 91, 337 (1969).

0022-3263/79/1944-2863$01.00/0

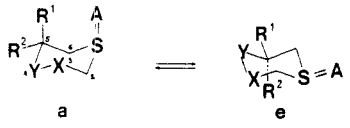
Scheme II



a e

1, R^1 = Cl, R^2 = R^3 = H
14, R^1 = R^2 = R^3 = H
15, R^1 = OCH_3, R^2 = R^3 = H
16, R^1 = CH_3, R^2 = R^3 = H
17, R^1 = F, R^2 = R^3 = H
18, R^1 = CN, R^2 = R^3 = H
19, R^1 = NO_2, R^2 = R^3 = H
20, R^1 = H, R^2 = CH_3, R^3 = H
21, R^1 = H, R^2 = R^3 = CH_3
22, R^1 = Cl, R^2 = R^3 = CH_3
23, R^1 = H, R^2 = F, R^3 = H
24, R^1 = H, R^2 = R^3 = F

Scheme III



a e

X, Y = CH_2, R = H unless otherwise indicated

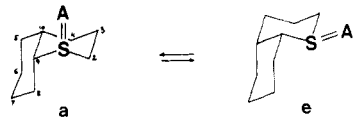
25, A = *N*-*p*-C_6H_4Cl, X = S
26, A = *N*-*p*-C_6H_4Cl, X = S, R^1 = CH_3
27, A = *N*-*p*-C_6H_4Cl, X = S, R^2 = CH_3
28, A = *N*-COC_6H_5, X = S
29, A = *N*-$SO_2C_6H_4CH_3$, X = S
30, A = *N*-*p*-C_6H_4Cl, Y = S
31, A = *N*-*p*-C_6H_4Cl, Y = O

in thiane 1-imides as well.[2] More recently, however, in new force field calculations Allinger has rationalized the preference for axial oxygen in thiane 1-oxide by the gauche interactions with the vicinal α hydrogens:[9] while there are four such interactions in the equatorial conformation, there are only two in the axial form. The interaction with the syn-axial hydrogens in the S–O axial conformation was found to be repulsive by this new calculation.[9a]

Polarities of substituents and exocyclic bond lengths have been discussed as major contributing factors to conformational equilibria. The significance of the increase in axial conformation with increasing polarity of substituents, for instance, in hetero-substituted cyclohexanes,[9b,c] has been uncertain because of different atomic radii and bond lengths. An increase in bond length has been used to rationalize the higher proportion of axial 1-oxide in selenane 1-oxide compared to that in thiane 1-oxide;[2d] the potential function has a repulsive part at very short distances between oxygen and the syn-axial hydrogens, followed by an attractive region at longer distances. In a recent communication[10] an alternative explanation for the preference of thiane 1-oxide for the S–O axial conformation has been suggested, based on a nonfavorable dipolar structure in the equatorial form.

To reach a better understanding of the exceptional conformational behavior of 1, we have now systematically investigated the change of a number of variables in the system. The compounds prepared and investigated are shown in Schemes I–IV. In addition to the imides already

Scheme IV



a e

32, A = O
33, A = *N*-*p*-C_6H_4Cl
34, A = *N*-C_6H_5

investigated by us[1,3] or by others,[2,5] the 1-*N*-$COOC_2H_5$ and the 1-*N*-$COCH_3$ derivatives of thiane (**5**, **6**) and a number of 1-(*N*-aryl)imides of thiane bearing substituents of varying electron-withdrawing capacity in the ortho or para position of the aromatic ring (**14**–**24**) were prepared. We also investigated the 1-imides of 4,4-dimethylthiane (**9**–**11**), 4-chlorothiane (**12**, **13**), 5-methyl-1,3-dithiane (**26**, **27**), 1,4-oxathiane (**31**), and 1,4-dithiane (**30**). Finally the bicyclic *cis*-1-thiadecalin 1β-oxide (**32**) was prepared for comparison with the corresponding 1β-[*N*-(*p*-chlorophenyl)]imide (**33**)[1] and 1β-(*N*-phenyl)imide (**34**).

Results

Assignment of Configuration and Conformation. The conformational equilibria were measured by low-temperature ^{13}C NMR spectroscopy in dichloromethane (with 20% deuterioacetone added as a lock substance). Assignments of the signals both in the room-temperature spectra (averaged conformations **a** and **e**) and of the individual conformers at low temperature (−80 to −100 °C) were accomplished with the aid of shift parameters obtained from conformationally homogeneous cyclic sulfimides[11] and the parent sulfides.[12,13] Carbon atoms next to S-1 are strongly deshielded, with the effect of an equatorial S=N being larger than an axial one ($\beta_e > \beta_a$). Carbon atoms γ to the substituent on sulfur are shielded, the axial imide functionality having a larger effect than the equatorial one ($\gamma_a > \gamma_e$). Thus the signals of C-2,6 and C-3,5, averaged in the room-temperature spectra, each separated into two well-resolved signals, respectively, at −80 °C, with the more upfield ones due to conformation **a**. C atoms "doubly δ" (i.e., C-4) to an axial or equatorial imide nitrogen show only small shift differences in anancomeric thiane sulfimides.[11] Therefore in the low-temperature spectra of the thiane 1-imides investigated in this work the signals of C-4 of the two conformers were not resolved.

In the case of the sulfimides derived from 4-methylthiane (**7**, **8**)[1] and 4-chlorothiane (**12**, **13**), configurational assignments were made on the same principles. Differentiation between C-4 and C-2,6, C-3,5 was obvious from the signal intensities and the off-resonance decoupled spectra. The effects of an axial or equatorial 4-methyl group on thiane had been reported,[12] and we determined the corresponding effects of axial or equatorial 4-chlorine (see Table III). Use of these shift effects on the low-temperature shift values of **1e** and **1a** for calculation of shifts of the 4-methyl compounds **7** and **8** and of the 4-chloro compounds **12** and **13** gave four sets of data, respectively (**7e**, **7a**, **8e**, **8a**; **12e**, **12a**, **13e**, **13a**). Comparison of these calculated spectra with the room-temperature spectra of the (nearly anancomeric) compounds **7** and **8** and with the −80 °C spectra of **12** and **13** allowed un-

(9) (a) N. L. Allinger and J. Kao, *Tetrahedron*, **32**, 529 (1976); (b) D. H. Wertz and N. L. Allinger, *ibid.*, **30**, 1579 (1974). (c) There seems to be an error in ref 9b, p 1585: the preference for the *equatorial* position of X for the compounds in Table 3 decreases with increasing polarity of C–X.

(10) N. S. Zefirov, *Tetrahedron Lett.*, 1087 (1975).

(11) (a) P. K. Claus, W. Rieder, and F. W. Vierhapper, *Monatsh. Chem.*, **109**, 609 (1978); (b) *ibid.*, **109**, 631 (1978); (c) P. K. Claus, W. Rieder, F. W. Vierhapper, and J. Bailer, *Tetrahedron*, in press.

(12) R. L. Willer and E. L. Eliel, *J. Am. Chem. Soc.*, **99**, 1925 (1977).

(13) F. W. Vierhapper and R. L. Willer, *J. Org. Chem.*, **42**, 4024 (1977); P. K. Claus, F. W. Vierhapper, and R. L. Willer, *ibid.*, **42**, 4016 (1977).

ambiguous assignment of both configuration and conformation. Agreement between calculated and experimental shift values was passable; substituent effects on thiane and on thiane-1-(*N*-aryl)imide would be expected to vary for reasons of different ring geometry and electron density in the various positions.[14]

The chemical shifts for C-2 and C-6 and for C-4 and C-5 in **25**, **28**, and **29** are very close. Assignments were made possible by comparison with the spectrum of **25**-2-d_2,[15] in which C-2 is no longer seen (loss of NOE, split into a quintet) and C-4 and C-6 are shifted slightly upfield. Configurational and (for **27**) conformational assignments of the sulfimides derived from 5-methyl-1,3-dithiane (**26**, **27**) were based on comparison of the data for (nearly anancomeric) **25** and a methyl shift parameter,[16] in an exactly analogous way and also with palpable deviations between calculated and found chemical shifts as outlined above for **7**, **8**, **12**, and **13**. Signals in the conformers of **30** and **31** were assigned from the shift data of the parent sulfides on the principle outlined for the thiane imides.

Assignments in **33** and **34**, both overwhelmingly in conformation **e**, were based on comparison with assignments made for methyl-substituted analogues.[11] The signals of conformer **e** in the sulfoxide **32** (at −50 °C) were easily assigned by the close similarity to those of **33** and **34**, an exception being C-2, where the absence of the shielding benzene ring causes the signal to appear significantly downfield. The situation was more complicated for **32a**, since no *cis*-1-thiadecalin 1-(*N*-aryl)imides with an axial S–N bond were available for comparison. The various signals were assigned with the aid of shift parameters derived from thiane 1-oxides[4] and the corresponding thianes[12] and by calculating approximate shift values from the signals of **32e** and the averaged room-temperature spectrum, where most signals were rather broad, indicating slow ring inversion on the NMR time scale.

The ^{13}C chemical shifts of the compounds investigated are collected in Tables I–III.

Determination of Equilibrium Constants. Determination of ratios of conformers by variable-temperature ^{13}C NMR is well established; the application of this technique on heterocyclic compounds has recently been extensively reviewed.[17] One can measure the areas of corresponding signals in the two conformers; it has been shown that nuclear Overhauser enhancements and relaxation times for such carbon atoms are nearly identical.[18] If the chemical shifts of matching signals are sufficiently different, the Eliel equation[19] may be used; since ^{13}C signals are palpably temperature dependent, only qualitatively correct results can be expected. Similarly, the use of the averaged room-temperature spectrum and of anancomeric model compounds suffers from the difficulty of correctly estimating the shift effects of the holding groups.

In the −80 °C ^{13}C spectra of the thiane 1-imides the signals for C-4 partly overlapped with the signals of C-3,5 of conformer **e**; only the signals of C-2,6 were used for integration. In the case of the 4-substituted thiane derivatives and in case of the oxa- and dithiane derivatives additional pairs of signals could be evaluated, and the agreement was very good. When the temperature was lowered to −100 °C (which caused solubility problems), the two signals of the aromatic C-1′ carbons of **a** and **e** in the thiane 1-(*N*-aryl)imides became resolved, and their areas also showed the same ratio. The conformational free energy differences thus determined are collected in Table IV.

If the probe temperature was lowered still further (<−100 °C), the signals of the aromatic C-2′,6′ carbons of conformations **a** and **e** became resolved in addition to the C-1's. In the case of the thiane 1-[*N*-(*p*-nitrophenyl)]imide (**19**), and also for *cis*-4-methylthiane 1-[*N*-(*p*-nitrophenyl)]imide, a very considerable broadening of C-2′,6′ was observed at −80 °C. This is likely to be due to restricted rotation around the C-1′–N bond. Solubility problems prevented further lowering of the temperature to investigate this phenomenon, which was only observed in the *p*-nitro compounds.

As in the case of conformationally homogeneous thiane 1-(*N*-aryl)imides,[11] no indication of diastereotopism of C-3,5 and of C-2,6 was observed. In the crystal the C–S bond orientated *anti*periplanar to the N–C-1′ bond is generally found shorter than the gauche-orientated one, both in axially and equatorially 1-(*N*-substituted)thianes.[20] Rotation or oscillation around the S–N bond must thus be still fast on the NMR time scale at −80 to −100 °C.

The results collected in Table IV can be condensed as follows:

1. The proportion of conformation **e** in 1-*N*-R substituted thianes increases in the order R = COC_6H_5 < $COOC_2H_5$ < $SO_2C_6H_4CH_3$ < $COCH_3$ < H < C_6H_4X.

Within the series of 1-*N*-C_6H_4X substituted thianes the percentage of conformation **e** increases, less pronouncedly, in the order X = NO_2 < CN < F ≲ CH_3 ≲ Cl ≲ H < OCH_3.

The observed order in both series suggests an increase of proportion of conformation **e** with decreasing electron-withdrawing capacity of the 1-*N* substituent although some deviations from the expected order are observed in both series.

2. Replacement of the aromatic ortho hydrogens in thiane 1-(*N*-phenyl)imide by bulkier methyl groups has a negligible effect on the conformational equilibrium. Replacement by fluorine leads to a small increase of conformation **e**.

3. A comparison with corresponding sulfoxides (literature data collected in Table V) shows that for all six-membered sulfur-containing rings investigated the *N*-(*p*-chlorophenyl) group favors the equatorial position by ~0.65 ± 0.5 kcal/mol more than the oxygen.

4. Changes of solvents (in the narrow limits imposed by the low solubility of the sulfimides at low temperature, the instability of the compounds,[11,15] and the need of a deuterium lock signal) show that the conformational equilibria of the 1-(*N*-aryl)imides do not vary significantly in 80% CH_2Cl_2/20% CD_3COCD_3, in CD_2Cl_2, in 50% CH_2Cl_2/50% toluene-d_8, and in 50% CH_2Cl_2/50% CD_3OD.

Discussion

An attempt to match our results with the earlier explanations for the preference of oxygen in thiane 1-oxide (and of nitrogen in some thiane 1-imides) for the axial position shows that a "squeezing" of the substituent on sulfur by the four vicinal hydrogens in conformation **e** (which was recently calculated[9] to be the predominant cause for the S–O axial preference in thiane 1-oxide) is of

(14) E. L. Eliel and R. L. Willer, *J. Am. Chem. Soc.*, **99**, 1936 (1977).
(15) J. Bailer, P. K. Claus, and F. W. Vierhapper, *Tetrahedron*, in press.
(16) E. L. Eliel, V. S. Rao, and F. G. Ridell, *J. Am. Chem. Soc.*, **98**, 3583 (1976).
(17) E. L. Eliel and K. M. Pietrusiewics, *Top. Carbon 13 NMR Spectrosc.*, **3**, 171 (1979).
(18) H. Booth and M. L. Jozefowicz, *J. Chem. Soc., Perkin Trans. 2*, 895 (1976).
(19) E. L. Eliel, *Chem. Ind. (London)*, 568 (1959); see also E. L. Eliel and F. W. Vierhapper, *J. Am. Chem. Soc.*, **97**, 2424 (1975).
(20) A. T. McPhail, K. Hargrave, P. K. Claus, and F. W. Vierhapper, manuscript in preparation.

Table I. ^{13}C Chemical Shifts[a]

		heterocycle[c]			aromatic ring[c]				
compd[b]	t, °C	C-2	C-3	C-4	C-1′	C-2′	C-3′	C-4′	others
1	29	46.80	21.87	24.55	155.54	119.13	128.88	120.12	
1e	−90	47.93	24.08	24.08	154.55	118.28	128.96	119.62	
1a	−90	40.92	16.53	24.08	155.19	118.28	128.96	119.62	
3	29	40.93	19.95	24.53	137.74	127.98	128.83	130.59	CO 176.03
3e	−72	43.60	23.35	24.09	137.03	128.23	128.57	130.91	
3a	−72	37.45	17.14	24.09	137.03	128.23	128.57	130.91	
4	29	44.76	19.64	23.70	142.83	126.49	129.63	141.89	CH_3 21.42
4e	−85	47.62	23.77	23.20	142.57	126.83	129.89	141.81	CH_3 21.61
4a	−85	41.25	16.29	23.20	142.57	126.83	129.89	141.81	CH_3 21.61
5	29	42.45	20.16	24.38					CO 165.05, CH_2 61.23, CH_3 15.08
5e	−80	45.56	23.52	23.89					CO 165.36, CH_2 61.33, CH_3 14.95
5a	−80	38.67	16.71	23.89					CO 165.36, CH_2 61.33, CH_3 14.95
6	29	41.24	20.48	24.33					CO 181.37, CH_3 24.69
6e	−80	43.48	23.42	24.16					CO 181.49, CH_3 24.49
6a	−80	37.19	17.19	24.16					CO 181.49, CH_3 24.49
7	29	42.48	25.24	30.81	155.74	119.36	128.87	120.03	CH_3 22.09
7a	−85	41.22	24.57	30.91	155.12	118.69	128.88	119.42	CH_3 22.83
9	29	42.13	33.51	29.08	155.50	119.23	128.92	120.28	CH_3(*trans*) 28.50, CH_3(*cis*) 27.25
9e	−80	43.30	35.92	29.01	154.51	118.24	128.87	119.58	CH_3(*trans*) 31.80, CH_3(*cis*), 23.32
9a	−80	37.34	28.34	29.01	154.51	118.24	128.87	119.58	CH_3(*trans*) 23.03, CH_3(*cis*) 32.46
10	29	36.61	31.71	29.01	137.73	127.95	128.80	130.56	CH_3(*trans*) 26.16, CH_3(*cis*) 29.48, CO 176.25
10e	−80	39.15	35.20	29.06	136.80	128.15	128.52	130.88	CH_3(*trans*) 31.67, CH_3(*cis*) 23.30, CO 175.70
10a	−80	33.91	28.86	29.06	136.80	128.15	128.52	130.88	CH_3(*trans*) 22.88, CH_3(*cis*) 32.54, CO 175.70
11	29	40.56	31.19	28.60	142.69	126.46	129.60	141.93	CH_3(*trans*) 26.01, CH_3(*cis*) 29.38, CH_3 21.43
12	29	42.86	29.61	55.46	155.06	119.58	128.98	120.86	
12e	−80	41.91	31.78	55.37	154.41	118.47	128.97	120.08	
12a	−80	41.91	26.71	55.37	154.61	118.99	128.97	119.98	
13	29	38.72	26.05	56.65	155.03	119.67	129.00	121.30	
13e	−80	47.37	33.95	57.08	(154.15)	118.87	129.02	119.93	
13a	−80	35.62	24.09	57.08	154.63	118.87	129.02	119.93	
14	29	47.04	21.80	24.73	156.74	118.24	129.17	116.10	
14e	−100	48.15	24.15	24.15	155.79	116.91	129.48	115.83	
14a	−100	40.95	16.23	24.15	156.30	117.38	129.48	115.83	
15	29	47.73	22.30	24.73	151.92	119.27	115.00	149.92	OCH_3 56.00
15e	−80	48.66	24.22	24.22	150.74	117.82	114.14	148.90	OCH_3 55.35
15a	−80	41.69	16.65	24.22	150.74	117.82	114.14	148.90	OCH_3 55.35
16	29	47.25	22.05	24.66	153.62	118.20	129.72	125.24	CH_3 20.43
16e	−80	48.30	24.13	24.13	152.81	116.91	129.78	124.78	CH_3 20.53
16a	−80	41.00	16.36	24.13	152.81	116.91	129.78	124.78	CH_3 20.53
17	29	47.36	21.97	24.67	152.84	118.73	115.35	155.58	
17e	−80	48.56	24.17	24.17	152.08	117.41	115.57	154.75	
17a	−80	41.45	16.30	24.17	152.08	117.41	115.57	154.75	
18	29	45.76	21.30	24.35	161.66	117.98	133.39	96.63	CN 121.35
18e	−80	47.32	23.84	23.84	161.04	117.35	133.61	95.83	CN 121.74
18a	−80	40.28	16.54	23.84	161.04	117.35	133.61	95.83	CN 121.74
19	29	45.26	21.10	24.25	164.87	116.78	126.27	136.72	
19e	−80	46.95	23.80	23.80	164.67	116.38	126.51	135.63	
19a	−80	40.12	16.54	23.80	164.67	116.38	126.51	135.63	
20	29	46.92	21.26	24.83	154.76	129.73	130.12	114.36	C-5′ 126.58, C-6′ 115.97, CH_3 18.63
20e	−80	48.55	24.23	24.23	154.38	128.53	130.08	113.51	C-5′ 126.67, C-6′ 115.77, CH_3 19.21
20a	−80	41.19	16.23	24.23	154.38	128.53	130.08	113.51	C-5′ 126.67, C-6′ 115.77, CH_3 19.21
21	29	50.34	22.13	24.92	153.25	133.84	128.22	120.22	CH_3 20.43
21e	−80	51.93	25.03	24.21	152.93	133.64	128.14	120.22	CH_3 20.36
21a	−80	45.25	16.28	24.21	154.06	134.21	128.14	120.22	CH_3 20.36
22	29	50.34	22.14	24.87	152.07	135.65	127.65	124.25	CH_3 20.01
22e	−80	51.76	25.01	24.09	151.61	135.50	127.45	123.85	CH_3 20.29
22a	−80	45.33	16.31	24.09	152.77	136.10	127.45	123.85	CH_3 20.29
23	29	47.71	21.96	24.62	144.53	156.21	115.42	116.15	C-5′ 124.46, C-6′ 119.53
23e	−80	48.34	24.12	24.12	144.11	155.09	115.13	115.67	C-5′ 124.59, C-6′ 116.55
23a	−80	40.94	16.30	14.12	144.11	155.09	115.13	115.67	C-5′ 124.59, C-6′ 116.55
24	29	49.46	22.17	24.70	133.12	157.94	111.30	115.64	
24e	−80	50.73	24.37	24.15	132.53	156.70	111.42	114.94	
24a	−80	43.90	16.09	24.15	132.53	156.70	111.42	114.94	
25	29	49.06		28.44	154.22	119.40	129.03	121.43	C-5 29.09, C-6 49.55
25e	−95	48.25		28.05	153.43	118.42	129.06	120.66	C-5 29.47, C-6 48.25
26	29	48.38		35.17	154.40	119.57	129.02	121.40	C-5 36.96, C-6 56.48, CH_3 22.29
27	29	48.45		34.93	154.71	119.66	129.00	121.30	C-5 30.12, C-6 54.48, CH_3 19.14
27e	−80	49.13		34.41	153.99	118.55	128.98	120.52	C-5 32.94, C-6 55[d], CH_3 17.63
27a	−80	42.70		34.07	153.99	119.12	128.98	120.52	C-5 21.39, C-6 47.45, CH_3 22.59
28	29	45.33		28.92	*e*	128.11	128.92	130.95	C-5 26.31, C-6 44.26
28e	−82	45.08		28.73	135.99	128.42	128.59	131.32	C-5 27.64, C-6 43.84, CO 176.27
29[f]	29[f]	48.96		28.05	142.26	126.51	129.75	140.78	C-5 28.05, C-6 48.62, CH_3 21.46
30	29	45.12	20.94		154.65	119.78	128.99	120.97	
30e	−80	49.19	27.34		154.09	118.41	128.99	120.12	

Table I (*Continued*)

compd[b]	t, °C	heterocycle[c] C-2	C-3	C-4	aromatic ring[c] C-1′	C-2′	C-3′	C-4′	others
30a	−80	41.23	17.60		154.22	119.00	128.99	120.12	
31	29	44.48	61.70		154.88	119.74	128.99	121.05	
31e	−80	47.75	65.63		154.18	118.73	129.00	120.21	
31a	−80	39.89	58.62		154.18	118.73	129.00	120.21	

[a] In parts per million from Me_4Si. Solvent CH_2Cl_2 + 20% acetone-d_6. [b] For formulas see Schemes I–IV. [c] C-2 and C-3 of the heterocyclic ring are identical with C-6 and C-5, respectively, unless shifts for C-6 and C-5 are reported under "others". The same applies for C-5′ and C-6′ of the aromatic ring (identical with C-3′ and C-2′, respectively, unless otherwise indicated). [d] Overlaid with signal of CH_2Cl_2. [e] Not seen. [f] The compound proved too insoluble in our solvent system for recording at low temperature. See however ref 5.

Table II. ^{13}C Chemical Shifts of *cis*-1-Thiadecalin Derivatives[a]

compd	t, °C	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1′	C-2′	C-3′	C-4′
32	+55	47.60	17.86	29.71	28.52	24.03	23.25	24.03	62.03	34.0[b]				
32	+29	47.5[b]	17.78	29.57	28.30	23.90	23.11	23.90	61.9[b]	33.8[b]				
32e	−50	51.48	19.09	31.22	25.25	27.36	20.63	26.20	64.65	38.72				
32a	−50	40.25	15.68	25.90	32.11	20.46	27.36	21.48	56.22	23.40				
33[c]	+29	47.79	19.70	30.34	25.61	27.97	21.81	25.61	63.25	37.44	155.65	118.83	128.67	120.49
33e[c]	−69	48.04	19.82	30.60	(25.53)	26.97	21.16	(25.79)	63.84	38.05	155.31	118.04	128.62	119.69
34	+29	47.93	19.82	30.46	25.64	27.92	21.79	25.64	62.99	37.64	156.65	117.90	128.94	116.35
34e	−45	48.44	19.95	30.80	(25.54)	27.13	21.19	(25.96)	63.57	38.23	156.50	117.18	129.02	115.91

[a] In parts per million from Me_4Si. Solvent $CDCl_3$. For numbering see Scheme IV and footnote *c* of Table I. Parentheses indicate that assignments are not unambiguous. [b] Signal was very broad. [c] From ref 11b.

Table III. ^{13}C Chemical Shifts of Starting Sulfides[a]

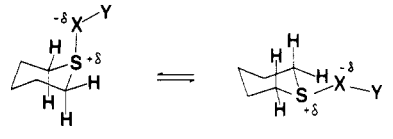
compd	t, °C	C-2	C-3	C-4	C-5	C-6
1,4-oxathiane	+29	69.15	27.44		27.44	69.15
1,4-dithiane	+29	29.61	29.61		29.61	29.61
4-chlorothiane	+29	26.32	37.12	58.99	37.12	26.32
	−100[b,c]	29.02	38.26	59.38	38.26	29.02
		0.0	+10.5	+32.9	+10.5	0.0
		22.02	34.34	59.38	34.34	22.02
		−7.0	+6.6	+32.9	+6.6	−7.0

[a] In 80% CH_2Cl_2 + 20% acetone-d_6; in parts per million from Me_4Si. [b] First line of figures, Cl-equatorial conformer; third line of figures, Cl-axial conformer. Second and fourth line of figures, shift differences to parent thiane (shift values from ref 12; solvent $CDCl_3$). [c] Ratio of conformers: 61% equatorial, 39% axial; ΔG° = 0.15 kcal/mol. The literature value is 0.2 ± 0.15 kcal/mol from ^1H NMR measurements (R. Borsdorf, P. F. Matzen, H. Remane, and A. Zschunke, *Z. Chem.*, 11, 21 (1971)).

no great consequence in the thiane 1-imides: if the steric constraint brought about by the gauche hydrogens were the main reason for an axial preference, one would expect all thiane 1-imides to prefer the axial form; the observed change in conformational equilibrium with the character of the substituent on nitrogen (substantial preference of the equatorial S–N orientation in the case of *N*-arylimides) could hardly be rationalized.

The conclusion from our data is that the polarity of the S–X group (Scheme V) must be one of the deciding factors for the conformational equilibrium: the more polarized the bond between sulfur and its substituent, the higher is the proportion of axial conformer. While it remains difficult to compare systems with different S–X bonds (for instance S–O in sulfoxides and S–N in sulfimides) because of different atomic radii and bond lengths, a comparison of compounds with different S–X group polarity but with the same size of atom bonded directly to sulfur and with similar S–X bond lengths and the same number of substituents Y attached to X (although with different steric requirements) as in the sulfimides is more conclusive. The differences in bond length in the series of thiane 1-imides are rather small (1.61–1.67 Å[20,21]) to explain satisfactorily the observed differences in conformational equilibrium,

Scheme V



Y strongly electron withdrawing: increased importance of canonical form $>S^{+}-\bar{X}-$

Y mildly electron withdrawing or electron releasing: increased importance of canonical form $>S=\bar{X}-$

solely on the basis of the influence of bond length;[2d] to the contrary, we note a very similar S–N bond length (1.62–1.636 Å[21] vs. 1.615–1.638 Å[20]) but different conformational behavior (31% **e** vs. 72–86% **e**) for *N*-tosyl- and *N*-arylsulfimides, respectively.

Electron-withdrawing substituents on nitrogen are assumed to increase the polarization or "ionic character" of the S–N bond and the magnitude of the group moment vector in the direction of the S–N bond. An increase of the percentage of "ionic character" with increasing electron-withdrawing capacity of para substituents in *S,S*-dimethyl-*N*-arylsulfimides has recently been demonstrated by the determination of S–N bond lengths[20] and S–N bond moments.[21] In the series of thiane 1-imides the preference for axial S–N orientation obviously increases with in-

(21) E. L. Eliel, J. Koskimies, A. T. McPhail, and D. Swern, *J. Org. Chem.*, 41, 2137 (1976), and literature cited therein.

Table IV. Conformational Equilibria of Cyclic Sulfimides[a]

compd	t, °C	% e	ΔG°, kcal/mol
1	−90	82	0.55
14	−80	80	0.53
15	−80	85	0.66
	−80	85[b]	0.66
	−80	86[c]	0.70
16	−80	80	0.53
17	−80	80	0.53
18	−80	76	0.44
19	−80	72	0.36
20	−80	82	0.58
21	−80	80	0.53
22	−80	80	0.53
23	−80	86.5	0.71
24	−80	85	0.66
2[d]	−85[d]	55[d]	0.07[d]
3	−72	40	−0.16
4	−85	31	−0.30[e]
5	−80	42	−0.12
6	−80	51	0.01$_5$
7	−85	<5	<−0.9
9	−80	72	0.36
10	−80	29	−0.34
12	−80	63	0.20
13	−80	15	−0.66
25	−90	>95	>1.1
27	−80	69	0.3
28	−82	⩾95	⩾1.1
29[f]	−80	>95	>1.1[f]
30	−80	40	−0.16
31	−80	46	−0.06
34[g]	−45	>95	>1.3[g]
33[g]	−69	>95	>1.3[g]

[a] Determined by integration of ^{13}C NMR signals (in 80% CH_2Cl_2 + 20% acetone-d_6 unless otherwise indicated). Signals in the low-temperature spectra were expanded to a width of 1 Hz mm^{-1} and the areas were determined by (a) plotting the integral curve, (b) calculating areas by multiplying signal height with half-height width, and (c) counting squares on the graph paper. Possible errors in area determination (by comparison of these three methods, comparison of spectra of 1 recorded at different times, and comparison of signal ratios if more than one pair of C atoms could be integrated) are ±2% (for $K \approx 1$) to ±10% (for $K \approx 20$). Possible errors in ΔG° are ±0.1 kcal/mol. [b] In CD_2Cl_2. [c] In 50% CH_2Cl_2 + 50% toluene-d_8. [d] From ref 2. [e] Reference 2 reports 40% e, $\Delta G^\circ = -0.15$ kcal/mol at −89 °C by ^1H NMR of 4-3,3,5,5-d_4. [f] Determined by ^1H NMR in CD_2Cl_2, since compound was too insoluble for low-temperature ^{13}C NMR.[5] [g] In $CDCl_3$.

Table V. Conformational Equilibria of S-Oxides

compd	t, °C	% e	ΔG°[a]	ref
thiane 1-oxide[b]	−90	38	−0.17$_5$	2
4,4-dimethylthiane 1-oxide[b]	−90	30	−0.30$_5$	2
1,3-dithiane 1-oxide[b]	−92	84.6	+0.63	6a
	−81.5	84	+0.63	6c
1,4-oxathiane 4-oxide[b]	−80	15	−0.68	25
1,4-dithiane 1-oxide[b]	c	12	−0.8	26
cis-4-chlorothiane 1-oxide[b]	−75	26	−0.4	24
trans-4-chlorothiane 1-oxide[b]	−65	⩽4	⩽−1.3	24
cis-1-thiadecalin 1β-oxide, **32**	−50	65	0.27	*d*

[a] In kcal/mol. [b] Taken from the literature. [c] Not reported. [d] This work.

creasing electron-withdrawing capacity of the 1-substituent. We observe rather large differences in conformational free energy ΔG° between *S*-imides with strongly electron-withdrawing substituents (Y = COR, COOR, SO_2-aryl) and *N*-arylimides. The dependence of the conformational equilibria on the electron-donor or -acceptor properties of para substituents is—not unexpectedly—much smaller, but the difference between the *p*-nitro (28% **a**) and the *p*-methoxy (15% **a**) group is well outside the experimental margin of error. When a comparison of *S*-imides with different N substituents is made, there seems to be some minor inconsistencies in the concept of S–X group polarity, most notably the position of ΔG° of **2** (Y = H) relative to the other thiane 1-imides.[36] But this position of **2** (between the *N*-tosyl and *N*-aryl derivatives) is also one of the arguments against the assumption that the bulk of the substituent Y on nitrogen might be a deciding factor to the conformational preference, an assumption which already previously has been rejected.[2] In solution, Y doubtlessly orientates itself away from the six-membered ring, as it does in the crystal.[20] The insensitivity to exchange of the ortho hydrogens on the *N*-phenyl ring against the more space-demanding methyl groups (see below) is additional proof that the bulk of the aryl ring is not the deciding factor for the equatorial preference in the 1-(*N*-aryl)imides.[36]

Unfortunately, thiane imides with electron-releasing substituents on nitrogen (e.g., alkyl) can not yet be investigated because of their low stability. The determination of the conformational equilibria of such compounds might help to explain the position of **2** (determined by ^1H NMR spectroscopy[2]) in the series of 1-*N*-R substituted thianes (vide supra). Simple qualitative considerations of polar substituent effects are inadequate: ^{13}C NMR investigations on *S,S*-dimethyl-*N*-arylsulfimides[22] indicate that the ortho- and para-carbon atoms of the aromatic ring experience substantial shielding through resonance with the sulfimide group. This shows the *N*-aryl substituent in *N*-arylsulfimides is also a fairly strong electron acceptor. If these results can be transferred to the thiane 1-(*N*-aryl)imides (which seems likely because of the near identity of the aromatic ^{13}C shifts), then the position of ΔG° of **2** between the *N*-acyl and the *N*-aryl derivatives suggests that the electron-donor or -acceptor properties of the 1-*N* substituent represents only one of the major contributing factors. No information on the S–N bond polarity of *N*–H-substituted sulfimides is as yet available, and we are unable to compare magnitude and direction of the group moment of S=NH with that of S=N—acyl or S=N—aryl. It has been suggested[2] that hydrogen bonds might be responsible for the conformational behavior of **2**; while this explanation cannot apply to the even higher equatorial preference in *N*-arylimides, it may still be correct in the case of **2**.

In the series of thiane 1-(*N*-aryl)imides (Scheme II), the compounds with para substituents Cl, H, CH_3, and F (**1**, **14**, **16**, **17**) show percentages of conformer **e** in a narrow range (79–82%), close to the experimental margin of error. The *p*-nitro- and *p*-cyano-substituted compounds (**19**, **18**) show a slightly, but significantly decreased S–N-equatorial proportion while the *p*-methoxy-substituted compound (**15**) shows an increased S–N-equatorial proportion, indicating a dependence of the conformational equilibrium on the electron-donor or -acceptor properties of the substituents on the aryl ring.

The behavior of the ortho mono- and disubstituted *N*-arylimides requires some discussion. The influence of the bulkier methyl groups in both ortho positions of the aromatic ring is remarkably small. X-ray analysis of ortho-H-substituted thiane 1-(*N*-aryl)imides[20] (and also of 4-nitrophenyl-*S,S*-dimethylsulfimide) shows that the XC_6H_4NS moiety is almost planar. The exocyclic N–C(1′)–C(ortho) angles are invariably rather different, pointing to an appreciable nonbonded 1,5 interaction

(22) G. Kresze, M. Berger, P. K. Claus, and W. Rieder, *Org. Magn. Reson.*, 8, 170 (1976).

between one ortho hydrogen and the sulfur. It is reasonable to expect that an even larger interaction occurs when both ortho hydrogens are replaced by methyl groups and that coplanar orientation of aromatic ring and S–N group must then become difficult. This does not influence the conformational equilibrium at all, although it is reflected in an enhanced deshielding of C-2,6 of the thiane ring (~+22.8 ppm in **21e** and **22e** against normally ~+19 ppm for conformers **e**; ~+16.2 ppm in **21a** and **22a** against normally ~+12 ppm for conformers **a**) in the sulfimide. The nonadditivity of shift effects in the case of ortho substitution does not allow us to decide, on the basis of the aromatic ^{13}C shifts, if a change in the geometry of the phenylsulfimide moiety takes place upon ortho disubstitution. If such a distortion occurs, it probably has little bearing on the S–N bond polarity and hence on the conformational equilibrium, as the data indicate.

Both the mono- and the difluoro derivatives show a significantly increased preference for the equatorial conformation (**23**, 86.5%; **24**, 85%). An argument against an attractive interaction of an *o*-fluoro atom with the hydrogens at C-2,6 of the thiane ring in conformation **e** is the chemical shifts of C-2,6: as in case of the *o*-methyl compounds only the *o,o'*-disubstituted derivative shows a palpably increased deshielding, which makes orientation of the fluorine in **23** away from the thiane ring more likely. Alternatively one may again consider the polarization of the S–N bond. The mesomeric effect of the fluorine should lead to a high electron density at C-1'. The very considerable shielding[23] of C-1' (and C-3') in **23** may be considered an indication for this localization of electrons; we note a smaller, but also rather noticeable, shielding of C-1' in the *p*-methoxy compound, which has the highest preference for conformation **e** in the para-substituted series. High shielding of C-1' may thus be an indication for a high percentage of conformation **e** in the *N*-arylsulfimides; a large deshielding (as in the *p*-CN and the *p*-NO_2 derivatives) could indicate a diminished amount of **e**. In the *o,o'*-difluoro compound **24** C-1' is still further shielded, although the percentage of **e** is slightly smaller than in **23**. The shift effect at C-2,6 (vide supra) points to a steric strain, which might be relieved by a change in geometry of the phenylsulfimide moiety, which then diminishes the chance of delocalization of the negative charge at C-1' into the N–S bond.

In 4,4-dimethylthiane 1-oxide the proportion of axial conformer is larger than in the parent thiane oxide ($\Delta\Delta G°$ = ~0.15 kcal/mol). This was ascribed[2] to a narrowing of the C(3)–C(4)–C(5) bond angle and a consequently greater distance of the axial oxygen to the syn-axial hydrogens at C(3) and C(5). Alternatively, the increase has been explained[14] by a flattening of the C(2)–S–C(6) region leading to a splaying outward of H-2a and H-6a and a reduction in interaction with CH_3-4a. A similar increase of conformation **a** is seen in 4,4-dimethylthiane 1-[*N*-(*p*-chlorophenyl)]imide **9** (vs. **1**, $\Delta\Delta G°$ = −0.19 kcal/mol) and in the corresponding *N*-benzoyl derivative **10** (vs. **3**, $\Delta\Delta G°$ = −0.18 kcal/mol). The 4,4-dimethyl moiety in 1-X-substituted thianes (X = O, NR) thus contributes a constant −0.15 to −0.20 kcal/mol to the conformational energy.

The differences in $\Delta G°$'s between sulfoxides (Table V) and (*p*-chlorophenyl)imides (Table IV) of six-membered heterocycles are nearly constant, irrespective of the presence of a polar substituent in position 4 or of a second heteroatom in position 3 or 4: the *N*-(*p*-chlorophenyl)-imide group favors the equatorial position by 0.65 ± 0.05 kcal/mol more than the oxygen. Introduction of a 4-chloro substituent in thiane 1-oxide led to an increase in axial conformer,[24] very pronounced for the trans isomer because of a 1,4-dipolar effect ($\Delta\Delta G° \leq -1.13$ kcal/mol) and only slightly for the cis compound ($\Delta\Delta G°$ = −0.23 kcal/mol). Nearly identical differences in conformational energy are found between the 1-(*N*-aryl)imide **1** and the trans 4-chloro compound **13** ($\Delta\Delta G°$ = −1.21 kcal/mol) and the cis isomer **12** ($\Delta\Delta G°$ = −0.35 kcal/mol), respectively. Very similar results are found in the 4-heterothiane series. Introduction of a 4-heteroatom (O, S) into the thiane 1-oxide led also to a pronounced increase in axial conformation;[25,26] the 1-[*N*-(*p*-chlorophenyl)]imide group once more reduces this preference for the axial S–X orientation by 0.62–0.64 kcal/mol to a very small preference for the axial conformers of **31** ($\Delta G°$ = −0.06 kcal/mol) and **30** (−0.16 kcal/mol).

$\Delta G°$ for **25** is too large to be measured directly,[3] but the difference from 1,3-dithiane 1-oxide[6] is at least as large as in the other cases mentioned above: the ^{13}C chemical shifts of **25** change only very slightly upon lowering the temperature from +30 to −90 °C, and no indication of signals of **25a** is detected at this temperature, which makes $\Delta G°$ > 1.1 kcal/mol. The $\Delta G°$ for *trans*-5-methyl-1,3-dithiane 1-[*N*-(*p*-chlorophenyl)]imide (**27**) is 0.3 kcal/mol; the preference for the equatorial position of the methyl group in the parent 5-methyl-1,3-dithiane has been determined as 1.16 kcal/mol.[12,27] Assuming as an approximation that changes of ring geometry upon formation of the sulfimide are only slight, a $\Delta G°$ of 1.4–1.5 kcal/mol is calculated for **25**, which again leads to a difference of 0.7–0.8 kcal/mol (vs. 0.65 kcal/mol in the other six-membered ring systems) between sulfoxide and sulfimide.

An increase in conformer **e** is also seen in the *cis*-1-thiadecalin 1β-(*N*-aryl)imides **33**[1,11] and **34** compared to the case for sulfoxide **32**. Here the sulfoxide already favors the equatorial conformation. A plausible explanation is that C-2 and C-8 come into closer proximity upon substitution of S-1 in conformation **a**, thereby increasing the preference for conformation **e**; in the parent *cis*-1-thiadecalin (Scheme IV, no A) **e** is in only slight excess ($\Delta G°$ = 0.14 kcal/mol[13]). A repulsive character of the interaction between the substituents on sulfur and the syn-axial hydrogens of the thiane ring[9] should lead to an increase in **a**, since a corresponding interaction with H-8e in conformation **e** is avoided.

Conclusions

It is obvious that a number of effects overlap to produce the conformational equilibria observed. While our data show no great importance of the steric interaction with the gauche α hydrogens,[9] they indicate a considerable importance of the polarization of the bond between sulfur and its substituent. This is in accord with an explanation[10] for the preference of thiane 1-oxide for the S–O axial form based on nonfavorable dipolar structures for the equatorial form derived by resonance theory. The consequence of stronger polarization may also be an enhancement of attractive interactions to the axial hydrogens at C-3,5 in the axial conformations. In addition, or alternatively to these explanations, we note that in the axial conformation S–X (X = O or NR) is gauche to two C–C and two C–H

(23) See also J. B. Stothers, "Carbon 13 NMR Spectroscopy", Academic Press, New York, 1972, p 197.

(24) J. C. Martin and J. J. Uebel, *J. Am. Chem. Soc.*, **86**, 2936 (1964); G. Wood, C. C. Baker, and A. Klingerman, *Can. J. Chem.*, **51**, 3329 (1973).
(25) D. M. Frieze and S. A. Evans, *J. Org. Chem.*, **40**, 2690 (1975).
(26) Reference 9a, personal communication by M. Anteunis.
(27) E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc.*, **91**, 2703 (1969).

bonds, whereas in the equatorial form it is gauche to four C–H bonds. Dipole moments induced into these bonds by the S–X dipole should lead to an increase in the axial conformation with increasing polarization of S–X because of the higher C–C polarizability. While we find this last possibility most convincing, the data allow no decision as to which explanation is correct.

Experimental Section

^{13}C NMR spectra were recorded on a Varian XL-100-12 pulsed Fourier transform NMR spectrometer at 25.16 MHz, at the temperature and in the solvents indicated in Tables I–III. The probe temperature was measured by the insertion of a thermometer into the 10-mm tube. Digital resolution was 0.6 Hz (0.025 ppm) at 16K data points and 5000-Hz spectral width.

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Microanalyses were carried out at the Institute of Physical Chemistry, Universität Wien, by Dr. J. Zak.

Starting Materials. The syntheses of thiane,[7] 4-methylthiane,[7] 4,4-dimethylthiane,[12] 4-chlorothiane,[28] 5-methyl-1,3-dithiane,[15,16,27] 1,4-dithiane,[29a] and *cis*-1-thiadecalin[13] have been described elsewhere. 1,3-Dithiane, 1,4-oxathiane, aniline, 4-chloroaniline, 2- and 4-fluoroaniline, *o*- and *p*-toluidine, 4-cyanoaniline, *p*-anisidine, 2,6-dimethylaniline, and chloramine-T were obtained commercially. 2,6-Difluoroaniline was synthesized[30] from commercial 1,3-difluorobenzene, and 2,6-dimethyl-4-chloroaniline was synthesized from 2,6-dimethylaniline with sulfuryl chloride.[31] *tert*-Butyl hypochlorite,[29b] *N*-bromobenzamide,[32] *N*-bromoacetamide,[29c] and *N*-chlorourethane[33] were prepared according to the literature.

Compounds Investigated. The syntheses of the *N*-(*p*-chlorophenyl)imides **1**, **7**, **8**, **9**, and **33** by the reaction of sulfide, *p*-chloroaniline, and *tert*-butyl hypochlorite have been reported in detail.[11a] 1-(*N*-Aryl)imides **14**–**24** and **34** were prepared in an analogous manner from sulfide, aniline, and *tert*-butyl hypochlorite. Yields of products after repeated recrystallization from ether, ether–hexane (for more soluble compounds), chloroform–ether, or chloroform (for sparingly soluble compounds) were between 40 and 60%. Melting points, solvents used for recrystallization, and results of elemental analysis follow.

14: mp 119–120 °C (chloroform–ether). Anal. Calcd for $C_{11}H_{15}NS$: C, 68.35; H, 7.82. Found: C, 68.27; H, 7.73.

15: mp 60–61 °C (ether at low temperatures, after purification of the crude material via the picrate (mp 145–147 °C)). The compound darkens at room temperature; no elemental analysis was performed.

16: mp 123–125 °C (ether–*n*-hexane). Anal. Calcd for $C_{12}H_{17}NS$: C, 69.52; H, 8.26. Found: C, 69.48; H, 8.38.

17: mp 116–118.5 °C (ether). Anal. Calcd for $C_{11}H_{14}FNS$: C, 62.53; H, 6.68. Found: C, 62.37; H, 6.55.

18: mp 122–123.5 °C (chloroform–ether). Anal. Calcd for $C_{12}H_{14}N_2S$: C, 66.02; H, 6.46. Found: C, 65.98; H, 6.35.

19: mp 130–134 °C (benzene–hexane). Anal. Calcd for $C_{12}H_{14}N_2O_2S$: C, 55.44; H, 5.92. Found: C, 55.34; H, 6.01.

20: mp 72–73 °C (ether–petroleum ether). Anal. Calcd for $C_{12}H_{17}NS$: C, 69.52; H, 8.26. Found: C, 69.49; H, 8.20.

21: mp 25–32 °C (ether–petroleum ether at low temperature). Because of the difficulty of removing residues of solvent from the low-melting compound, no elemental analysis was performed.

22: mp 44–46.5 °C (ether–*n*-hexane). Anal. Calcd for $C_{13}H_{18}ClNS$: C, 61.04; H, 7.09. Found: C, 61.00; H, 7.01.

23: mp 108.5–110 °C (ether). Anal. Calcd for $C_{11}H_{14}FNS$: C, 62.53; H, 6.68. Found: C, 62.39; H, 6.51.

24: mp 62–63 °C (ether). Anal. Calcd for $C_{11}H_{13}F_2NS$: C, 57.62; H, 5.72. Found: C, 57.55; H, 5.64.

34: mp 116.5–117.5 °C (ether) [after separation from *cis*-1-thiadecalin 1α-(*N*-phenyl)imide by column chromatography (Al_2O_3, $CHCl_3$)]. Anal. Calcd for $C_{15}H_{21}SN$: C, 72.82; H, 8.56. Found: C, 72.75; H, 8.50.

trans-4-Chlorothiane 1-[*N*-(*p*-chlorophenyl)]imide (**13**) was the only imide isolated from the reaction of 4-chlorothiane, *p*-chloroaniline, and *tert*-butyl hypochlorite: yield 62%; mp 129–131.5 °C (ether–*n*-hexane). Anal. Calcd for $C_{11}H_{13}Cl_2NS$: C, 50.39; H, 5.00; Cl, 27.04. Found: C, 50.46; H, 4.95; Cl, 27.24.

Reaction of 1,3-dithiane, 1,4-dithiane, and 1,4-oxathiane, respectively, with *p*-chloroaniline and *tert*-butyl hypochlorite gave **25**,[3,15] **30**, and **31**. Reaction of 5-methyl-1,3-dithiane gave **26** and **27** in a ratio of 2:1; the isomers were separated by fractional crystallization.[15]

30: yield 45.4%, mp 135–140 °C (chloroform–ether). Anal. Calcd for $C_{10}H_{12}ClNS_2$: C, 48,87; H, 4.92. Found: C, 48.49; H, 4.76.

31: yield 75%; mp 132–134 °C (chloroform–ether). Anal. Calcd for $C_{10}H_{12}ClNOS$: C, 52.28; H, 5.27. Found: C, 52.16; H, 5.18.

Compounds **4**,[2] **11**,[2] and **29**[3,5] were prepared from the sulfides and chloramine-T as previously described.

cis-4-Chlorothiane 1-[*N*-(*p*-chlorophenyl)]imide (**12**) was synthesized from *trans*-4-chlorothiane 1-oxide[24] and 4-chloroaniline with P_2O_5–triethylamine analogous to the synthesis of **7** from *trans*-4-methylthiane 1-oxide ("method C" in ref 11a). **12** was isolated as the picrate from the reaction mixture: yield after cleavage of the picrate and recrystallization from ether–*n*-hexane 18%; mp 112–113 °C. Anal. Calcd for $C_{11}H_{13}Cl_2NS$: C, 50.39; H, 5.00. Found: C, 50.44; H, 4.93.

1-(*N*-Benzoyl)imides **3**,[3] **10**, and **28** were prepared[34] from the appropriate sulfides and *N*-bromobenzamide by a modified literature procedure:[35]

Sulfide (10 mmol) was dissolved in CH_2Cl_2 (distilled from P_2O_5). The stirred solution was cooled to −70 °C and a solution of *N*-bromobenzamide (10 mmol) in CH_2Cl_2 was added gradually. *N*-Bromobenzamide precipitated but redissolved with proceeding reaction. After addition was complete (30 min) stirring was continued for 2 h. The mixture was shaken with 30 mL of 5% aqueous NaOH, the organic layer was separated and washed with water, the solution was dried over Na_2SO_4, and the solvent was distilled off. Separation from the side products sulfoxide and benzamide was accomplished by column chromatography (Al_2O_3, $CHCl_3$). Purification of the imides from residual sulfoxide by crystallization proved difficult.

3: yield 45%; mp 138.5–139.5 °C (chloroform–ether). Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83. Found: C, 64.88; H, 6.73.

10: Separation from the sulfoxide by crystallization proved impossible. The sulfoxide was distilled off at 10^{-3} torr at a Kugelrohr distillation unit; the residual imide was recrystallized: yield 13%; mp 101–104 °C (ether). Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68. Found: C, 67.14; H, 7.51.

28: yield 30%; mp 133–143 °C dec (dichloromethane–ether). Anal. Calcd for $C_{11}H_{13}NOS_2$: C, 55.20; H, 5.47. Found: C, 55.05; H, 5.38.

Thiane 1-[*N*-(ethoxycarbonyl)]imide (**5**)[34] was prepared as follows. Thiane (10 mmol) was dissolved in 40 mL of anhydrous

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(36) One referee has pointed out that in our discussion we neglect atomic inversion at sulfur and variations of the S–N–X bond angle. Our investigations on conformationally homogeneous sulfimides[11] allow us to exclude the possibility of S inversion at ≤−80 °C. S–N–X bond angles, determined for a number of sulfimides by X-ray crystallography,[20,21,37] were between 112.6 and 116.2° for such different compounds as $Cl_2CHCONS(C_2H_5)_2$[37a] and $CH_3SO_2NS(CH_3)_2$,[37b] and there is no consistency between these changes and the changes in conformational equilibria. Thus, while these variations may be a cause for inconsistencies in our series (as the referee suggested), they can hardly be a main reason for the observed changes in conformational behavior.

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dichloromethane, and 11 mmol of *N*-chlorourethane in 30 mL of CH_2Cl_2 was gradually added at −50 °C. The mixture was stirred at −50 to −70 °C for 2 h. The solvent was distilled off, the residue was dissolved in ether, and the inorganic salts were filtered off. The mixture of products was separated by column chromatography (Al_2O_3, $CHCl_3$): yield of **5** 53%; mp 50–53 °C (ether-*n*-hexane). Anal. Calcd for $C_8H_{15}NO_2S$: C, 50.77; H, 7.40. Found: C, 50.46; H, 7.25.

Thiane 1-(*N*-acetyl)imide (**6**)[34] was prepared by the following method. Thiane (50 mmol) was dissolved in 200 mL of anhydrous CH_2Cl_2. To the stirred solution a suspension of 55 mmol of *N*-bromoacetamide in 100 mL of CH_2Cl_2 was gradually added at −70 °C. After addition was complete stirring was continued for 2 h and the equivalent amount of triethylamine was then slowly added. The mixture was gradually brought to room temperature, and the solvent and unreacted triethylamine were distilled off at 10^{-3} torr, keeping the temperature as low as possible (20 °C). The residue was suspended in ether, and the ether was dried and concentrated. The remaining oil was fractionated by column chromatography (Al_2O_3, $CHCl_3$) and the product was recrystallized repeatedly from ether: yield 4%; mp 98–101 °C. Anal. Calcd for $C_7H_{13}NO_2$: C, 52.80; H, 8.23. Found: C, 52.76; H, 8.41.

cis-1-Thiadecalin 1β-oxide (**32**) was prepared as follows. To a solution of 60 mmol of *cis*-1-thiadecalin in 100 mL of anhydrous CH_2Cl_2 was added 57 mmol of *m*-chloroperbenzoic acid in 120 mL of CH_2Cl_2 at 0 °C. When addition was complete the mixture was stirred at room temperature overnight. The solution was extracted with dilute aqueous NaOH, and the extract was washed with CH_2Cl_2. The dichloromethane solutions were united and the solvent was distilled off. The residue was distributed between petroleum ether and water. The aqueous phase was extracted with CH_2Cl_2, and the extract was dried and the solvent distilled off. The residue was distilled in a Kugelrohr distillation unit (150 °C (3 torr)). The distillate crystallized. GC analysis showed two compounds in a ratio of 79:21. The product was recrystallized from ether–petroleum ether and the major component was obtained in pure form. NMR analysis showed it to be **32**; the mother liquor contained **32** and *cis*-1-thiadecalin 1α-oxide in equal amounts: yield of **32** 56%; mp 60–62 °C. Anal. Calcd for $C_9H_{16}SO$: C, 62.74; H, 9.36. Found: C, 62.60; H, 9.41.

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Registry No. **1**, 59335-75-0; **3**, 62936-65-6; **4**, 13553-73-6; **5**, 70528-34-6; **6**, 70528-35-7; **7**, 59335-79-4; **9**, 67512-77-0; **10**, 70528-36-8; **11**, 31815-16-4; **12**, 70528-37-9; **12** picrate, 70528-38-0; **13**, 70528-39-1; **14**, 70528-40-4; **15**, 70528-41-5; **15** picrate, 70528-42-6; **16**, 70528-43-7; **17**, 70528-44-8; **18**, 70528-45-9; **19**, 70528-46-0; **20**, 70528-47-1; **21**, 70528-48-2; **22**, 70528-49-3; **23**, 70528-50-6; **24**, 70528-51-7; **25**, 56158-05-5; **26**, 70528-52-8; **27**, 70528-53-9; **28**, 62936-66-7; **29**, 58484-97-2; **30**, 70528-54-0; **31**, 70562-06-0; **32**, 59335-76-1; **33**, 67530-04-5; **34**, 70528-55-1; *cis*-1-thiadecalin 1α-oxide, 70561-54-5; *cis*-1-thiadecalin-1α-(*N*-phenyl)imide, 70561-55-6; *cis*-1-thiadecalin, 57259-80-0; thiane, 1613-51-0; aniline, 62-53-3; *p*-anisidine, 104-94-9; *p*-toluidine, 106-49-0; 4-fluoroaniline, 371-40-4; 4-cyanoaniline, 873-74-5; 4-nitroaniline, 100-01-6; *o*-toluidine, 95-53-4; 2,6-dimethylaniline, 87-62-7; 2,6-dimethyl-4-chloroaniline, 24596-18-7; *o*-fluoroaniline, 348-54-9; 2,6-difluoroaniline, 5509-65-9; *p*-chloroaniline, 106-47-8; 4-chlorothiane, 32358-87-5; 1,4-dithiane, 505-29-3; 1,4-oxathiane, 15980-15-1; 5-methyl-1,3-dithiane, 38761-25-0; *N*-bromobenzamide, 19964-97-7; 4,4-dimethylthiane, 40324-30-9; 1,3-dithiane, 505-23-7; *N*-chlorourethane, 16844-21-6; *N*-bromoacetamide, 79-15-2.

Quantitative Separation of Electronic and Steric Substituent Effects in Reactions between Aliphatic Amines and Electron Acceptors[1]

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The effects of three N substituents on reactivities of aliphatic amines were analyzed by means of free-energy-related substituent constants and regression analysis. In hydrogen-bond formation with $CHCl_3$ and charge-transfer-complex formation with I_2, electronic and steric effects of three N substituents were quantitatively separated by means of the equation $\log K = \rho^*\sum\sigma^* + a_1E_s^c(R_1) + a_2E_s^c(R_2) + a_3E_s^c(R_3) + c$, where K is the equilibrium constant, ρ^*, a_1, a_2, and a_3 are susceptibility constants, and c is the intercept. $\sum\sigma^*$ is the sum of the Taft σ^* values of three N substituents. $E_s^c(R_1)$, $E_s^c(R_2)$, and $E_s^c(R_3)$ are, respectively, the Hancock corrected steric constants of N-substituents R_1, R_2, and R_3, where $E_s^c(R_1) \geq E_s^c(R_2) \geq E_s^c(R_3)$. Examination of literature data seems to suggest a general applicability of the present procedure to various reactivities of aliphatic amines.

Aliphatic amines react with various lone pair electron acceptors. The reactivities are generally governed by polar and steric factors of three N substituents. Free-energy-related substituent parameters have been used to carry out a number of analyses for such reaction systems as the acid dissociation of ammonium ions,[2] gas-phase association with BMe_3,[3] Menschutkin reaction with EtI,[4] and others.[5-9] However, these works primarily correlated the reactivity with the total polar effect of three N substituents by using $\sum\sigma^*$, the summation of the Taft σ^* values, for sterically "unhindered" amines. The deviation of the data for the "hindered" amines from the apparent correlation for the "unhindered" compounds was only qualitatively attributed to the steric effect of bulky N substituents.

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