# Conformational Preferences of Sulfimides

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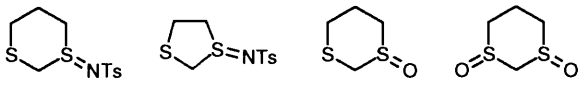
The X-ray crystal structures of sulfimides **11**, **15** and **16** are reported. Analysis of these and literature data suggests that the conformational preferences of sulfimides of six-membered cyclic sulfides can be rationalised by attractive and repulsive special *gauche* effects. Such effects may also affect the conformations of sulfimides of five-membered cyclic sulfides, but it is necessary, in addition, to invoke other interactions.

Sulfimides **1** (*Chem. Abstr.* name sulfilimines) are the nitrogen analogues of sulfoxides **2**.[1] Despite the fact that they are easy to

**1** **2**

prepare and that their chemistry parallels closely that of sulfoxides, which have many synthetic applications, sulfimides remain a relatively poorly studied class of compounds. Our particular interest is in the application of sulfimides to problems in asymmetric synthesis where, again, chiral sulfoxides are prominent.[2]

We are currently investigating the potential of the tosylimides of 1,3-dithiane and 1,3-dithiolane, **3** and **4**, respectively, as chiral



**3** **4** **5** ***trans*-6**

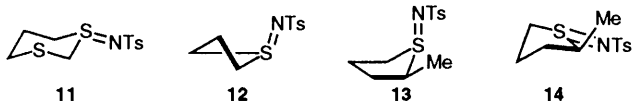
acyl anion equivalents, inspired by the work of the groups of Page and of Aggarwal on sulfoxides **5** and **6**.[3] It became apparent that prediction of (*a*) the conformations of compounds such as **3** and **4** and (*b*) the structures of the anions derived from them, is extremely difficult from literature precedent. Indeed, similar confusion is evident in the sulfoxide series.[4] We decided, therefore, to address these questions. Our observations on the conformational preferences of sulfimidyl groups, are presented here.

The sulfimidyl bond in thiane 1-tosylimide **7** has a clear

**7** **8** **9** **10**

preference for the axial position as judged by NMR studies and confirmed by X-ray crystallography.[5] This is consistent with the axial preference of the sulfinyl bond in thiane 1-oxide **8**.[5c-g,6] The energy difference between the axial and equatorial conformers must, however, be small as competition from even a sterically undemanding alkyl group desiring its preferred equatorial position is sufficient to force the sulfimide to adopt the equatorial conformation.[5a] Hence, for example, *cis*-2-methylthiane 1-tosylimide **9** has the methyl group in its preferred equatorial position and the sulfimide bond in its preferred axial position, whereas the *trans* isomer **10** has both substituents equatorial, *i.e.* with the methyl group in its favoured equatorial position and the sulfimide bond, uncharacteristically, also equatorial.[5a]

Other changes also reduce the axial preference. Examples with less electron withdrawing substituents on nitrogen (*e.g.* aryl) show a clear preference for the equatorial form[7] as does the tosylimide group in the 1,3-dithiane derivative **11**,[5g,8] these



**11** **12** **13** **14**

results being deduced from NMR data alone. It should be noted that equilibria (equatorial–axial) are observed usually by NMR spectroscopy but, in all cases where crystallographic data are also available, the dominant conformer in solution is that found in the solid state.[5-9]

The thiolane analogues exhibit similar trends, although conformational distinctions are less marked in the more flexible five-membered rings. For example, the sulfimidyl bond has been shown, by NMR and X-ray analysis, to be pseudoaxial in thiolane 1-tosylimide **12**, axial in the *cis* 2-methyl compound **13** and *endo-isoclinal* in the *trans* 2-methyl analogue **14**, where the methyl group is also *endo-isoclinal*.[9] The conformational preferences of *N*-aryl and 1,3-dithiolane derivatives have not been examined.

We reasoned that confirmation of the NMR studies on the dithiane imide **11** by X-ray crystallography along with parallel investigations of 1,3,5-trithiane 1-tosylimide **15** and 1,3-dithiolane 1-tosylimide **16** would help to clarify the continuing

**15** **16**

uncertainty regarding the reasons for the various conformational preferences.

## Results and Discussion

The conformations of compounds **11**, **15** and **16**, as determined by X-ray crystallography, are shown in Fig. 1, with the previously determined structures of **7** and **12** for comparison.[5a,9] The result for the dithiane derivative **11** confirms the equatorial preference indicated by the NMR studies.[8] The trithiane imide **15** also shows the equatorial preference but the dithiolane imide **16** clearly has an axial sulfimidyl bond. The envelope conformation of the latter example is different to the half-chair adopted by the simple thiolane analogue **12**, but similar to some more substituted examples (*e.g.* **13**).[9]

It has been demonstrated that the conformational preference of sulfinyl and sulfimidyl bonds depends on the relative magnitudes of the entropic contribution, which favours equatorial, and the thermochemical factor which favours

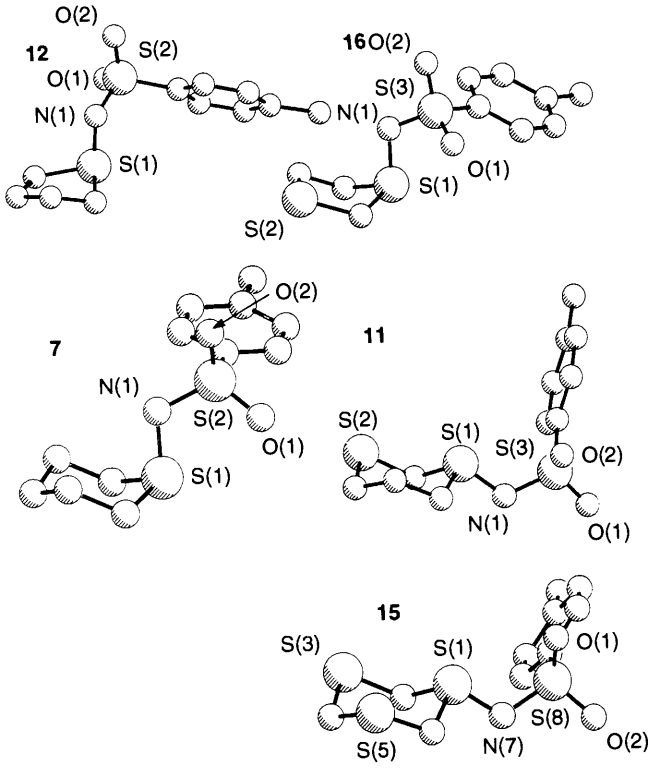



Fig. 1

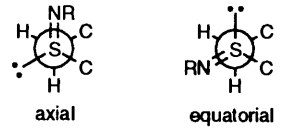



Fig. 2

axial.[10] Three classes of interaction have been invoked to explain the thermochemical preference for the axial position: (*i*) *gauche* effects; (*ii*) 1,3-*syn* attractive interactions; (*iii*) long range molecular orbital interactions. These effects will be discussed in turn below.

Gauche *Effects*.—It has been suggested on a number of occasions that the axial preference of both sulfinyl and sulfimidyl bonds is due to unfavourable *gauche* interactions with vicinal C–H bonds (Fig. 2).[11] Claus pointed out, however, that, should this effect be important, all examples should show the axial preference.[5b] His results showed clearly that this was not the case as there are many examples of equatorial sulfimidyl bonds, this being confirmed by our structures of **11** and **15**. In addition, Claus demonstrated that steric interactions with the sulfimide bond are unimportant, as significant increases in the bulk of the *N*-substituent (*e.g.* phenyl to 2,6-dimethylphenyl) produced no noticeable change in conformational preference.[5b]

Having shown that the unfavourable *gauche* effects described above were not responsible for the axial preference, Claus proposed an attractive *gauche* effect between the highly polarised S–N bond and the *gauche* C–C bonds, which he suggested would be more polarisable than the C–H bonds.[5b] This explanation seemed plausible, as increasing the polarisation of the sulfimide bond by increasing the electronegativity of the *N*-substituent (*e.g.* aryl to tosyl) increases the proportion of the axial conformer.[5b] We sought to investigate this effect by replacing the vicinal C–C bonds by C–S bonds, which should be rather more polarisable. Compounds **11** and **15** would be expected to have axial sulfimide bonds, maximising the *gauche* interactions with C–S bonds. In fact, in both **11** and **15** the

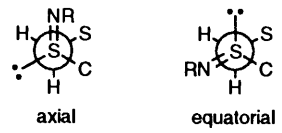



Fig. 3

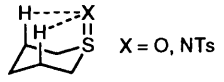



Fig. 4

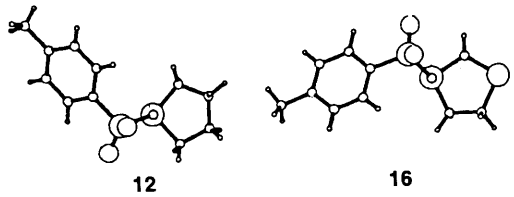



Fig. 5

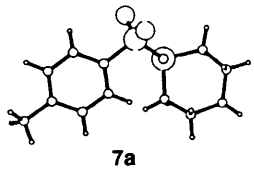



Fig. 6

equatorial sulfimide bond is *anti* to the C–S bond or bonds (Fig. 3). There seems little evidence, therefore, for an attractive *gauche* effect based on bond polarisability.

Although we believe the *gauche* effects thus far used to explain the conformational preferences of sulfimides to be unimportant, other *gauche* effects can be used to rationalise our results. These are discussed later.

1,3-Syn *Attractive Interactions*.—Another popular explanation for the axial preference of some sulfoxides and sulfimides is an attractive interaction between the oxygen or nitrogen, respectively, and the axial hydrogen on C–3 (Fig. 4).[11,12] Our results seem, at first sight, to support this idea. The thiolane compounds **12** and **16**, which both have the possibility of 1,3-interactions, both have axial sulfimidyl bonds. In addition, examination of the orientation of the lone pair on nitrogen shows that it is correctly disposed for such an interaction in both cases (Fig. 5), clearly pointing towards a C-3 hydrogen.

The behaviour of the thiane series **7**, **11** and **15** cannot, however, be rationalised in this manner. Although removing all possibility of 1,3-*syn* attractive interactions, as in **15**, does result in the sulfimide adopting the equatorial form, the dithiane derivative **11**, which does offer an opportunity for 1,3-interactions, also has an equatorial preference. More convincingly, examination of the crystal structure of the thiane derivative **7** suggests that N–H interactions cannot be responsible for its axial preference. Two geometries are found for **7**,[5a] one is shown in Fig. 6, neither of which has the nitrogen lone pair oriented for an attractive 1,3-interaction.

We propose, therefore, that, although attractive *syn* 1,3-interactions may be responsible for the axial preference of the sulfimidyl bond in the thiolane series, this effect is not of significance in the thiane series.

*Long Range Molecular Orbital Interactions*.—In a 1975 paper by Zefirov a quantum mechanical rationalisation for the axial preference of the sulfinyl bond in thiane 1-oxide **8** was

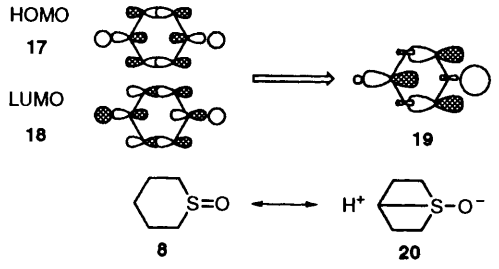


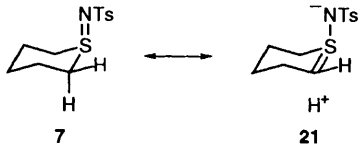

Fig. 7

presented.[13] HOMO **17** is the highest occupied in-plane molecular orbital of cyclohexane and its analogues. An equatorial electronegative substituent will significantly perturb this orbital, as would be the case for equatorial thiane 1-oxide. A conventional perturbation treatment of the problem mixes the HOMO **17** with the LUMO of the same symmetry **18** (Fig. 7), which is also in the plane. This treatment is reportedly valid for both chair and boat conformations.[13] For thiane 1-oxide the resulting polarised orbital **19** has an increased coefficient on the oxygen and a decreased coefficient on the equatorial C(4) hydrogen. This effect can also be visualised as being due to a contribution from the dipolar structure **20**. This unfavourable dipolar form would be avoided by placing the electronegative substituent (*i.e.* oxygen) axial, where it is orthogonal to both the HOMO and LUMO and has, therefore, no polarising effect on them.

Application of this description to sulfimides is unsatisfactory. Imides of five-membered sulfides, where such long range MO interactions cannot be invoked, often show a pseudo-axial preference nevertheless, whereas imides of six-membered analogues rarely show the predicted axial preference. We acknowledge, however, that long range MO effects cannot be completely discounted in the six-membered series as both a highly electron demanding *N*-substituent and a short cross-ring distance might be required. Claus' *N*-arylthiane 1-imides would be excepted on the former account and the *N*-tosyl imides of dithiane and trithiane **11** and **15** on the latter.

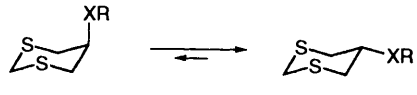
*Special* Gauche *Effects*. There is substantial evidence for the existence of two special *gauche* effects, namely (*a*) the attractive *gauche* effect and (*b*) the repulsive *gauche* effect.[14] We feel that most of the observations on conformational preferences of sulfimides can be rationalised by invoking these two effects as explained below.

*The attractive* gauche *effect*. It has been calculated that, when bond–bond interactions (either steric or electrostatic) are not too large, bond–antibond interactions can exert an effect on conformational preference.[15] The result is a tendency for polarised A–X bonds (where X is strongly electronegative) to lie *trans* to the best donor bonds (in this case C–H) to maximise the $\sigma_{CH}$–$\sigma^*_{AX}$ interaction. In the case of cyclic sulfimides this would result in an axial sulfimidyl bond, as the equatorial example would have the polar A–X bond *trans* to a C–C bond. This effect can be represented by considering a contribution from the resonance form **21**.




The existence of an attractive *gauche* effect is an appealing explanation for the axial preference of sulfimidyl bonds, especially if the results from the group of Claus[5b] are reexamined. As mentioned earlier there is an increasing tendency for the sulfimidyl bond to be axial as the electron demand of the *N*-substituent increases. This is consistent with the literature observations and calculations which show that the attractive *gauche* effect only applies when X in the A–X bond is highly electronegative. We conclude that increasing the electron demand of the *N*-substituent renders the nitrogen sufficiently electronegative for bond–antibond interactions to be important in determining the conformation.

*The repulsive* gauche *effect*. The repulsive *gauche* effect is observed when one or both *gauche* substituents have lone pairs in diffuse orbitals and is probably due, therefore, to repulsive overlap of these orbitals.[14] This effect has most frequently been measured in compounds which have sulfur containing substituents in vicinal sites, *e.g.* **22**, or a sulfur vicinal to another heteroatom, usually oxygen, *e.g.* **23**.[16] In these cases the




**22** X = S
**23** X = O

preference for the equatorial conformer is much greater than would be predicted from conventional steric and electrostatic considerations.

It is not surprising, then, to observe that the sulfimidyl bond has a strong equatorial preference in compounds **11** and **15**, as an axial orientation would place it *gauche* to one or two sulfur atoms, respectively. The apparent lack of a repulsive *gauche* effect in the dithiolane derivative **16** is, however, puzzling. It may be that *syn* 1,3-attractive interactions, as discussed previously, are more important in this case, but we cannot exclude a perturbation due to crystal packing forces.

## Conclusion

The unusual conformational preferences of sulfimides of six-membered cyclic sulfides can be satisfactorily explained by invoking so-called special *gauche* effects. The attractive *gauche* effect favours the axial conformer and becomes important with strongly electron demanding groups on nitrogen. Otherwise, conventional steric and electrostatic interactions, which favour the equatorial conformer, prevail. Even with strongly electron demanding groups on nitrogen, 3-thia analogues show a marked equatorial preference. This is a manifestation of the repulsive *gauche* effect which is due to interactions with the diffuse filled 3p orbitals on sulfur.

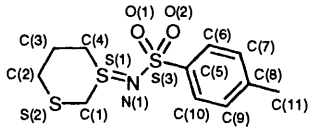
The conformational preferences of sulfimides of five-membered cyclic sulfides require further investigation. Although the attractive *gauche* effect can be used to explain the axial preference, the reason for the apparent absence of a repulsive *gauche* effect in the dithiolane derivative **16** remains unclear.

Finally, we remark that caution is required in extrapolating these conclusions to sulfoxide analogues where other combinations of interactions may be important.

## Experimental

*General*.—IR spectra were recorded using a Perkin–Elmer 1720X FT IR spectrometer. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker ACF 250 MHz instrument. Mass spectra were recorded on a Kratos MS 90 instrument. Reactions were monitored by TLC on silica gel plates ($G_{254}$). Column chromatography was performed using Merck silica gel 60.

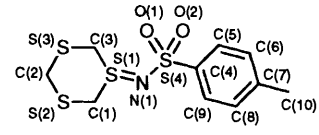
N-[1,3]*Dithian-1-ylidene-4-methylbenzenesulfonamide*[17,18] **11**. To a 100 cm$^3$ round-bottomed flask equipped with a condenser and magnetic stirrer were added dichloromethane




**11**

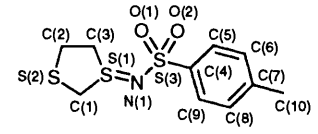
(50 $cm^3$), 1,3-dithiane (0.5 g, 4.2 mmol) and hexadecyltributylphosphonium bromide (≈0.2 mmol). Solid Chloramine-T (1.02 g, 4.5 mmol) was added slowly with stirring and cooling with a water bath. After addition was complete the water bath was removed and stirring was continued for 2 h. The reaction mixture was washed with cold aqueous sodium hydroxide (5%, 100 $cm^3$) followed by two washes with water (100 $cm^3$). The dichloromethane layer was dried over anhydrous magnesium sulfate, filtered and concentrated. The crude product was recrystallised from chloroform–diethyl ether (2:1); yield: 0.95 g (78%). M.p. 164–165 °C (Found: C, 45.5; H, 5.2; N, 4.7. $C_{11}H_{15}NO_2S_3$ requires: C, 45.65; H, 5.22; N, 4.84%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1279, 1139, 1090 and 969; $\delta_H$(250 MHz; [$^2H_6$]$Me_2SO$) 7.63 (2 H, m, Ar), 7.30 (2 H, m, Ar), 4.29 (1 H, br ABq, *J* 12.6, 18.7 Hz, 2a-H), 4.24 (1 H, ABq, *J* 12.4, 18.7 Hz, 2e-H), 3.27 (1 H, m, 6e-H), 3.14 (1 H, dt, *J* 2.9, 12.3 Hz, 6a-H), 2.75 (1 H, ddd, *J* 2.6, 11.3, 12.5 Hz, 4a-H), 2.60 (1 H, br dt, *J* 4.0, 14.0 Hz, 4e-H), 2.41 (1 H, m, 5e-H), 2.05 (1 H, dddt, *J* 3.1, 11.7, 11.7, 14.9 Hz, 5a-H) and 2.35 (3 H, s, Me); $\delta_C$(62.9 MHz; [$^2H_6$]$Me_2SO$) 142.2, 141.3, 129.4, 125.8 (4 × Ar), 46.7 (C-4), 46.6 (C-1), 26.8 (C-2), 26.4 (C-3) and 21.0 ($CH_3$); *m*/*z*(CI/$NH_3$) 290 ($MH^+$).

N-[1,3,5]*Trithian*-1-*ylidene*-4-*methylbenzenesulfonamide*[18] **15**. A suspension of 1,3,5-trithiane (1.0 g, 7.24 mmol) in a solution of Chloramine-T (2.0 g, 8.76 mmol) in dimethylformamide (30 $cm^3$) was stirred at room temp. for 1 h to give a clear solution, which was then poured into cold water. The resultant precipitate was isolated by filtration and recrystallised from acetonitrile; yield: 1.78 g (80%). M.p. 196–199 °C; $R_f$ 0.45 (EtOAc) (Found: C, 38.9; H, 4.2; N, 4.4. $C_{10}H_{13}NO_2S_4$ requires: C, 39.06; H, 4.26; N, 4.56%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1280, 1136, 1090 and 986; $\delta_H$(400 MHz; [$^2H_6$]$Me_2SO$) 7.46 (4 H, m, Ar), 4.63 (4 H, ABq, *J* 12.4 Hz, $CH_2S$(=NTs)), 4.05 (2 H, ABq, *J* 14.0 Hz, $SCH_2S$) and 2.35 (3 H, s, Me); $\delta_C$(62.9 MHz; [$^2H_6$]$Me_2SO$) 141.9, 141.5, 129.5, 125.9 (4 × Ar), 49.1 (C-1/C-3), 30.5 (C-2) and 21.0 ($CH_3$); *m*/*z*(CI/$NH_3$) 308 ($MH^+$).




**15**

N-[1,3]-*Dithiolan*-1-*ylidene*-4-*methylbenzenesulfonamide*[18] **16**. To a 100 $cm^3$ round-bottomed flask equipped with a condenser and magnetic stirrer were added dichloromethane (50 $cm^3$), 1,3-dithiolane (4.2 mmol) and hexadecyltributylphosphonium bromide (~0.2 mmol). Solid Chloramine-T (1.02 g, 4.5 mmol) was added slowly with stirring and cooling with a water bath. After addition was complete the water bath was removed and stirring was continued for 2 h. The reaction mixture was washed with cold aqueous sodium hydroxide (5%, 100 $cm^3$) followed by two washes with water (100 $cm^3$). The dichloromethane layer was dried over anhydrous magnesium sulfate, filtered and concentrated. The crude product was




**16**

**Table 1** Crystal data and structure refinement for **11**, **15** and **16**

| | **11** | **15** | **16** |
|---|---|---|---|
| Formula | $C_{11}H_{15}NO_2S_3$ | $C_{10}H_{13}NO_2S_4$ | $C_{10}H_{13}NO_2S_3$ |
| *M* | 289.42 | 307.45 | 275.39 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| *a*/Å | 6.168(6) | 6.159(3) | 6.428(4) |
| *b*/Å | 12.909(8) | 9.709(4) | 20.216(12) |
| *c*/Å | 17.608(9) | 12.417(4) | 9.515(5) |
| α/° | 110.79(4) | 110.92(3) | 90(0) |
| β/° | 96.92(6) | 93.47(3) | 100.21(4) |
| γ/° | 94.42(7) | 104.52(3) | 90(0) |
| *U*/Å$^3$ | 1290(2) | 662.1(5) | 1216.9(12) |
| *T*/K | 230 | 230 | 220 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2(1)/c$ |
| *Z* | 4 | 2 | 4 |
| $D_x$/g cm$^{-3}$ | 1.490 | 1.542 | 1.503 |
| Crystal size/mm | 0.39, 0.23, 0.10 | 0.51, 0.38, 0.29 | 0.25, 0.23, 0.16 |
| $\mu$/mm$^{-1}$ | 0.563 | 0.706 | 0.593 |
| *F*(000) | 608 | 320 | 576 |
| $\theta_{min}$,$\theta_{max}$/° | 1.7, 25.0 | 1.7, 25.0 | 2.0, 25.0 |
| Index ranges | 7, ±15, ±20 | 7, ±11, ±14 | 7, ±23, ±11 |
| No. data collected | 5030 | 2591 | 2977 |
| Independent reflections | 4568 | 2350 | 2012 |
| *R*(int) | 0.0203 | 0.0277 | 0.0361 |
| Weighting parameters: | | | |
| *a* | 0.0546 | 0.0661 | 0.0455 |
| *b* | 0.6111 | 0.3021 | 0.7059 |
| $R(F)$ [$I > 2\sigma(I)$] | 0.0396 | 0.0323 | 0.0386 |
| $R_w(F^2)$ (all data) | 0.1110 | 0.0949 | 0.1013 |
| Goodness of fit on $F^2$ | 1.007 | 0.987 | 1.068 |
| Max. diff. peak and hole/e Å$^{-3}$ | 0.30, −0.34 | 0.36, −0.36 | 0.23, −0.34 |
| Data, restraints, parameters | 4566, 0, 309 | 2350, 0, 156 | 2012, 0, 146 |

**Table 2** Selected bond lengths (Å) and angles (°) for **11** (data for one of the two molecules in the asymmetric unit)

| | |
|---|---|
| S(1)–N(1) | 1.636(3) |
| S(1)–C(4) | 1.796(3) |
| S(1)–C(1) | 1.799(4) |
| S(2)–C(1) | 1.787(3) |
| S(2)–C(2) | 1.800(3) |
| S(3)–O(1) | 1.433(2) |
| | |
| N(1)–S(1)–C(4) | 103.52(14) |
| N(1)–S(1)–C(1) | 101.4(2) |
| C(4)–S(1)–C(1) | 98.4(2) |
| C(1)–S(2)–C(2) | 98.7(2) |
| S(2)–C(1)–S(1) | 109.6(2) |
| C(3)–C(2)–S(2) | 113.3(2) |
| C(2)–C(3)–C(4) | 112.1(3) |
| C(3)–C(4)–S(1) | 111.9(2) |

**Table 3** Selected bond lengths (Å) and angles (°) for **15**

| | |
|---|---|
| S(1)–N(1) | 1.631(2) |
| S(1)–C(3) | 1.796(2) |
| S(1)–C(1) | 1.799(2) |
| S(2)–C(1) | 1.783(2) |
| S(2)–C(2) | 1.794(3) |
| S(3)–C(3) | 1.785(2) |
| S(3)–C(2) | 1.791(3) |
| S(4)–N(1) | 1.601(2) |
| | |
| N(1)–S(1)–C(3) | 100.66(10) |
| N(1)–S(1)–C(1) | 102.09(10) |
| C(3)–S(1)–C(1) | 97.16(11) |
| C(1)–S(2)–C(2) | 98.90(11) |
| C(3)–S(3)–C(2) | 99.68(11) |
| N(1)–S(4)–C(4) | 107.79(10) |
| S(4)–N(1)–S(1) | 114.84(11) |
| S(2)–C(1)–S(1) | 112.00(13) |
| S(3)–C(2)–S(2) | 115.45(14) |
| S(3)–C(3)–S(1) | 112.65(11) |

recrystallised from chloroform–diethyl ether (3:1); yield: 0.6 g (52%). M.p. 159–161 °C (Found: C, 43.6; H, 4.8; N, 5.1. $C_{10}H_{13}NO_2S_3$ requires: C, 43.46; H, 4.62; N, 4.91%); $\nu_{max}(CDCl_3)/cm^{-1}$ 1274, 1138, 1087 and 979; $\delta_H$(250 MHz; $CDCl_3$) 7.64 (2 H, ABq, Ar), 7.33 (2 H, ABq, Ar), 4.38 (1 H, ABq, *J* 12.1 Hz, $SCH_2S$), 3.90 (1 H, ABq, *J* 12.1 Hz, $SCH_2S$) and 3.4 (4 H, m, $SCH_2CH_2S$); $\delta_C$(62.9 MHz; $CDCl_3$), 141.7, 141.4, 129.5, 125.9 (4 × Ar), 53.3 (C-3), 51.8 (C-1), 32.1 (C-2) and 21.0 ($CH_3$); *m/z* (CI/$NH_3$) 276 ($MH^+$).

*X-Ray Crystallography.*—All measurements were made using a Siemens P3R3 four-circle diffractometer equipped with an Oxford Cryosystems Cryostream Cooler (version 2.4). Graphite monochromated Mo-Kα radiation ($\lambda$ = 0.710 73 Å) was used to collect the intensity data in the $\omega$–$2\theta$ mode. Unit cell parameters and orientation matrices were obtained by least-squares refinement of the setting angles of 20 high angle reflections.

The crystallographic program system was SHELXTL PLUS[19] and SHELXL-93;[20] the refinement program uses atomic scattering factors taken from International Tables for Crystallography.[21] The structures were solved by direct methods and refined using full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were inserted using a riding model and given isotropic thermal parameters equal to 1.2 (or 1.5 for methyl groups) times the equivalent isotropic displacement parameter of the atom to which it is attached. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = [\text{max. } (F_o^2, 0) + 2F_c^2]/3$. The *R* factors are defined as $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

**Table 4** Selected bond lengths (Å) and angles (°) for **16**

| | |
|---|---|
| S(1)–N(1) | 1.634(3) |
| S(1)–C(3) | 1.772(3) |
| S(1)–C(1) | 1.788(3) |
| S(2)–C(2) | 1.786(3) |
| S(2)–C(1) | 1.790(4) |
| C(2)–C(3) | 1.520(4) |
| | |
| N(1)–S(1)–C(3) | 100.4(2) |
| N(1)–S(1)–C(1) | 105.4(2) |
| C(3)–S(1)–C(1) | 93.1(2) |
| C(2)–S(2)–C(1) | 97.7(2) |
| S(3)–N(1)–S(1) | 112.0(2) |
| S(1)–C(1)–S(2) | 109.6(2) |
| C(3)–C(2)–S(2) | 109.7(2) |
| C(2)–C(3)–S(1) | 108.8(2) |

A summary of the crystal data and refinement details is given in Table 1; selected bond lengths and angles are given in Tables 2–4. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Instructions to Authors, 1994.

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