Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A comparison of 2,7-dihydro-2,2,7,7-tetramethyl-3,6-diphenyl-1,4,5-thiadiazepine and the corresponding 1,1-dioxide

Eric Cuthbertson,[a] Christopher S. Frampton[b]* and David D. MacNicol[a]

[a]Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, and [b]Department of Chemistry, Roche Discovery Welwyn, Welwyn Garden City, Hertfordshire AL7 3AY, England
Correspondence e-mail: christopher.frampton@roche.com

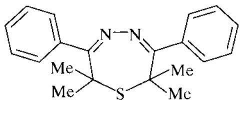
Received 27 November 2000
Accepted 19 December 2000

The structures of the highly substituted title heterocycles, $C_{20}H_{22}N_2S$ and $C_{20}H_{22}N_2O_2S$, have been determined at 123 (1) K. Both molecules possess exact C_2 symmetry and the seven-membered rings have very similar twist-boat conformations. The magnitudes of the C—S—C bond angles, 107.13 (6) and 108.27 (7)°, respectively, are influenced significantly by the four substituent methyl groups on the seven-membered rings.

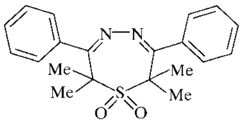
Comment

The preparation of heterocycle (I) by reaction of 2,2″-thiodiisobutyrophenone with anhydrous hydrazine and the subsequent oxidation of (I) to sulfone (II) have been described previously (Cuthbertson *et al.*, 1975). The present communication gives the first structural details concerning the related molecules (I) and (II), which exhibit directly analogous packing in common space group *Pbcn*.

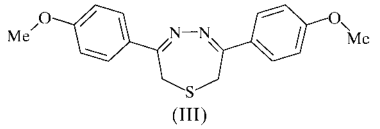
Both molecules (I) and (II) possess exact C_2 symmetry, the twofold rotation axis passing through the S atom and bisecting the N—N bond in each case, as is illustrated in Fig. 1. The molecular conformations, extending to the orientation of the phenyl substituents, are remarkably similar with the seven-membered rings having twist-boat conformations characterized by pairs of respective endocyclic torsion angles: C7—N1—N1′—C7′ −68.75 (17) and −66.6 (2)°, N1—C7—C8—S1 68.79 (12) and 68.78 (13)°, and C7—C8—S1—C8′ −37.69 (5) and −37.62 (6)°. Interestingly, the imine components of the azine moieties in (I) and (II) are significantly non-planar and the corresponding values of the N1′—N1—C7—C8 torsion angle are 4.96 (16) and 3.39 (19)°, respectively. A close correspondence between bond lengths and between bond angles is also found for (I) and (II). For example, the N1—N1′ and N1—C7 bond lengths for (I), 1.3977 (18) and 1.2818 (14) Å, may be compared with the values of 1.3882 (19) and 1.2850 (15) Å for (II), whilst respective C7—N1—N1′ bond angles are 119.75 (8) and 120.88 (9)°. Oxidation of cyclic sulfide (I) to sulfone (II) is accompanied by only minor changes in the C8—S1 bond length and C8—S1—C8′ bond angle, the former decreasing slightly from 1.8515 (11) to 1.8429 (12) Å and the latter increasing from 107.13 (6) to 108.27 (7)°. Sulfone (II) has an O═S═O angle of 118.29 (8)°.



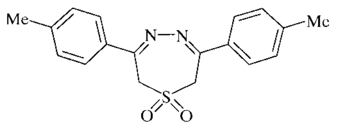
(I)



(II)



(III)



(IV)

The isomorphous molecular packing for (I) and (II) can best be described as van der Waals and although there are no unusually close intermolecular contacts in (I), there is one C—H⋯O contact in (II) of 2.44 Å that is slightly less than the sum of the van der Waals radii of 2.50 Å, as defined by Pauling (1960). This contact originates from the methyl C9 atom of one molecule to an O atom of a centrosymmetrically related molecule [HC9⋯O1^{ii}; symmetry code: (ii) $1-x$, $1-y$, $-z$].

The effect of substitution of the heterocyclic ring by four methyl groups may be assessed by reference to the less substituted analogues (III) and (IV). Sulfone (IV) (Cuthbertson *et al.*, 1980) has been found to adopt a twist-boat conformation (close to C_2-symmetric) resembling that of (II), the magnitude of the C—N—N—C torsion angle being 66.8 (8)° in (IV) and 66.6 (2)° in (II). The two crystallographically independent C—C ring bonds in (IV), lengths 1.507 (8) and 1.490 (10) Å, and the C—S bonds of (IV), lengths 1.777 (7) and 1.799 (7) Å, are significantly less than the corresponding bond lengths in highly substituted (II), which are 1.5313 (16) and 1.8429 (12) Å. The C—S—C bond angle in (IV), 101.1 (3)°, is increased to 108.27 (7)° for the C8—S—C8′ angle in (II). This increase may be ascribed to the high increase of substitution of the α-C atoms of sulfone (II), each of which features *gem*-dimethyl substituents. The *gem*-dimethyl effect (Eliel & Wilen, 1994) reduces the C7—C8—S1 angle in (II) to 107.31 (8)°, from corresponding values of 109.3 (5) and 109.9 (5)° for its model counterpart (IV). Since (II) and (IV) have similar conformations, a decrease in the above angle (occurring twice) may be expected, owing to geometric ring constraints, to result in an increase in the C—S—C angle. However, part of the increase in C—S—C angle in (II) may arise from the moderately short contacts of 3.2053 (17), 3.0829 (16) and 2.9191 (16) Å between C10 and C7′, N1 and N1′, respectively. An acyclic parallel to this second factor, attributed to steric effects, is found between $(CH_3)_2SO_2$ and bulky $(CCl_3)_2SO_2$, which have C—S—C angles of

102.6 (9) and 109.8 (4)°, respectively (Hargittai & Hargittai, 1974; Hargittai *et al.*, 1983).

A similar situation exists for (I) and (III), though the structure of the latter was determined using only a limited data set (Hundal *et al.*, 1988); nonetheless, the C8—S1—C8′ angle in sulfide (I), 107.13 (6)°, is significantly opened compared with the C—S—C angle of 100 (1)° in (III). The molecule of (I) has a *gem*-dimethyl-influenced C7—C8—S1 angle of 107.53 (7)°, and transannular contacts between C10 and C7′, N1, N1′ of 3.2282 (15), 3.0939 (14) and 2.9210 (14) Å, respectively.

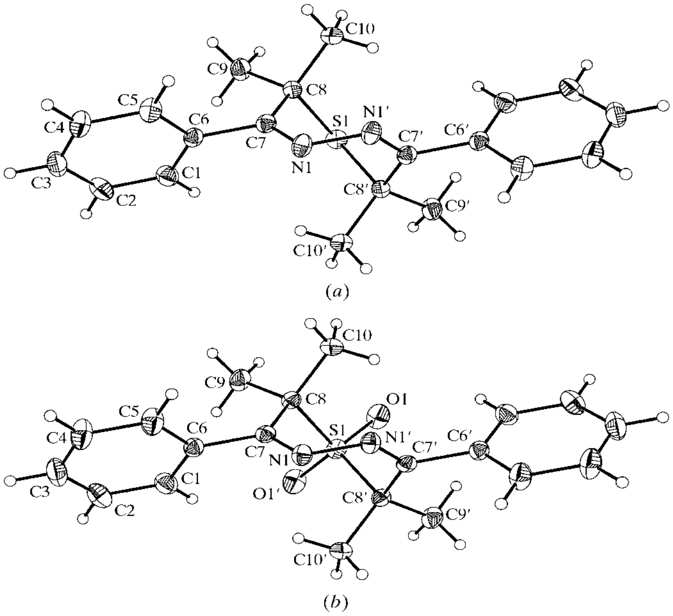


Figure 1
Comparative views of the molecules of (*a*) (I) and (*b*) (II), illustrating the exact C_2 symmetry in each case. The common atomic numbering scheme is shown and displacement ellipsoids are drawn at 50% probability.

Experimental

Compounds (I) and (II) were prepared as described previously (Cuthbertson *et al.*, 1975). (I) was recrystallized from benzene–light petroleum giving colourless needles (m.p. 480–481 K), whilst recrystallization of sulfone (II) from benzene gave colourless plates [m.p. 470–472 K (decomposition)].

Compound (I)

Crystal data

$C_{20}H_{22}N_2S$
$M_r = 322.46$
Orthorhombic, *Pbcn*
$a = 19.4661$ (7) Å
$b = 10.7312$ (4) Å
$c = 8.3000$ (3) Å
$V = 1733.83$ (11) Å^3
$Z = 4$
$D_x = 1.235$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4415 reflections
$\theta = 3.275$–29.252°
$\mu = 0.188$ mm^{-1}
$T = 123$ (1) K
Prism, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker AXS 1K CCD area-detector diffractometer
Narrow-frame ω scans
15326 measured reflections
2138 independent reflections
1856 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.28°$
$h = -25 \rightarrow 25$
$k = -13 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.122$
$S = 1.007$
2138 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.101P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Compound (II)

Crystal data

$C_{20}H_{22}N_2O_2S$
$M_r = 354.46$
Orthorhombic, *Pbcn*
$a = 18.9551$ (11) Å
$b = 11.4905$ (7) Å
$c = 8.1745$ (4) Å
$V = 1780.43$ (17) Å^3
$Z = 4$
$D_x = 1.322$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 904 reflections
$\theta = 3.242$–28.848°
$\mu = 0.198$ mm^{-1}
$T = 123$ (1) K
Prism, colourless
0.30 × 0.25 × 0.10 mm

Data collection

Bruker AXS 1K CCD area-detector diffractometer
Narrow-frame ω scans
16286 measured reflections
2214 independent reflections
1815 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 28.28°$
$h = -25 \rightarrow 25$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.093$
$S = 1.006$
2214 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.500P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with $U_{\rm iso}$ free to refine.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART* and *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1607). Packing diagrams for both structures are also available. Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (1999). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cuthbertson, E., Hardy, A. D. U. & MacNicol, D. D. (1975). *J. Chem. Soc. Perkin Trans.* 1, pp. 254–262.
Cuthbertson, E., MacKenzie, R. K., MacNicol, D. D., Mills, H. H., Wilson, F. B., Ghouse, K. M. & Williamson, D. G. (1980). *Spectrochim. Acta Part A*, **36**, 333–335.
Eliel, E. L. & Wilen, S. H. (1994). *Stereochemistry of Organic Compounds*, pp. 682–684. New York: Wiley.
Hargittai, M. & Hargittai, I. (1974). *J. Mol. Struct.* **20**, 283–292.
Hargittai, M., Vajda, E., Nielsen, K., Klaeboe, P., Seip, R. & Brunvoll, J. (1983). *Acta Chem. Scand. Ser. A*, **37**, 341–352.
Hundal, M. S., Sood, G., Kapoor, P. & Tandon, S. S. (1988). *J. Crystallogr. Spectrosc. Res.* **18**, 601–607.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.