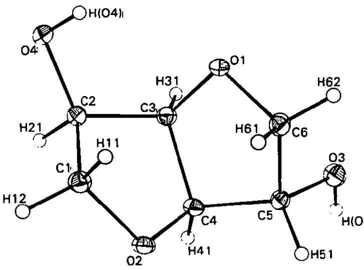

Fig. 1. Atom numbering and thermal ellipsoids (50% probability level) of the non-H atoms. The H atoms were given an arbitrary 0·07 Å radius.

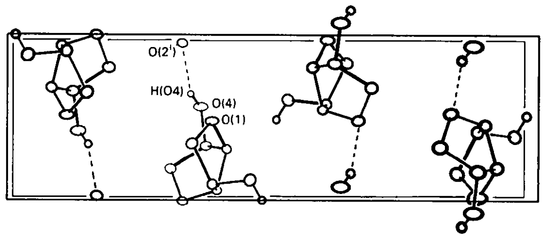

Fig. 2. Unit-cell content viewed down **b**. The intermolecular hydrogen bond is indicated by a broken line. For the sake of clarity the intramolecular hydrogen bond [H(O4)···O(1)] is not indicated.

DIAN consists of two planes [defined by C(1)O(2)C(4)C(3) and by C(4)C(3)O(1)C(6) respectively] nearly perpendicular (87·0°) to each other. The maximum deviation from the mean planes is 0·004 Å [O(2)] and 0·006 Å [O(1)] respectively; atom O(4) is in the *endo* and atom O(3) in the *exo* position (see Table 2). Atoms C(2) and C(5) are displaced from the planes concerned by 0·58 and 0·59 Å respectively, while in BrDIAN C(1) and C(6) are displaced from the planes through the remaining four atoms. Therefore, in interpreting ^{1}H NMR data one must keep in mind that the conformation of the ring system is rather flexible and dependent on the steric demands and electronic properties of the substituents.

The packing of the molecules is illustrated in Fig. 2. There are two O···O contacts shorter than 2·85 Å, which can be interpreted as belonging to a bifurcated hydrogen bond between O(4) and O(1) in the same molecule and between O(4) and O(2) in a symmetry-related molecule (see Table 3). This observation supports the conclusion drawn from IR spectral studies (Brimacombe *et al.*, 1958) that, in dilute solution, there exists an intramolecular hydrogen bond. In the crystal this intramolecular interaction is much weaker than the intermolecular one. It may be noted that the configuration of the O(2)—C(4)—C(5)—O(3) part of the molecule does not allow an intramolecular hydrogen bond.

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Structure of (8a*RS*,9*RS*,10a*SR*)-10-Ethoxycarbonyl-1,2,3,4,5,6,7,8,8a,10a-decahydro-10*H*-9-thia-10-azaphenanthrene 9-Oxide, $C_{15}H_{23}NO_3S$

By Zbigniew Dauter,* Peter Hanson, Colin D. Reynolds and William A. Stockburn

Department of Chemistry, University of York, York YO1 5DD, England

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Abstract. $M_r = 297·42$, monoclinic, $P2_1/c$, $a = 5·264$ (2), $b = 11·598$ (3), $c = 25·694$ (5) Å, $\beta = 104·36$ (1)°, $V = 1519·66$ Å^3, $F(000) = 640$, $T = 290$ (1) K, $Z = 4$, $D_x = 1·30$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 1·84 mm^{-1}, $R = 0·064$ for 1518 observed reflections. The relative configuration at S in the title compound has been determined: the S—O bond is *trans* to the two C—H bonds on the heterocyclic ring.

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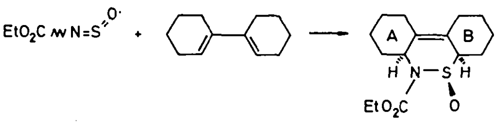
* Permanent address: Department of Biochemistry, Technical University of Gdansk, Gdansk, Poland.

Introduction. Cycloaddition reactions play a key role in the strategies of the synthetic chemist. They serve an obvious function in the creation of cyclic structures but also provide stereochemical control. Certain sulphinylamino compounds, *R*N=S=O, may cycloadd across their N—S double bonds to dienes yielding 1,2-thiazine *S*-oxides (Kresze & Wucherpfennig, 1967). During this reaction a chiral centre is created at S. In the cycloadducts, various diastereoisomers may arise from the coupling of this chirality with that existent or created at other centres.

As part of a study of the use of sulphinylamino compounds we have investigated the mechanism of the reaction of *N*-sulphinylurethane (I) with 1,1-bicyclohexenyl (II) (Hanson & Stockburn, unpublished work). This cycloaddition yields the title compound (III) as the sole product. Since the relative configuration at S is not easily deduced from spectroscopic observations the crystal and molecular structure determination was undertaken.



(I) (II) (III)

Experimental. Title compound prepared by the reaction of *N*-sulphinylurethane with 1,1-bicyclohexenyl. Recrystallization of product from ethanol gave colourless needles, elongated along **a**. Unit-cell and space-group data from Weissenberg photographs. Lattice parameters from 24 reflections by least squares. Systematic absences *h*0*l* *l* odd and 0*k*0 *k* odd confirm space group $P2_1/c$. Hilger & Watts Y290 computer-controlled four-circle diffractometer, ω–2θ scanning technique, crystal 1·1 × 0·25 × 0·10 mm, count time per step 1 s, range of each scan 0·52°, $\theta_{\max} = 51°$ ($-5 \leq h \leq 5$, $0 \leq k \leq 11$, $0 \leq l \leq 25$). $R_{\rm int} = 0{\cdot}054$ for 2251 reflections; 697 of which [$I \leq 2\sigma(I)$] classified as unobserved. Standard reflections (165, $\bar{1}6\bar{5}$, 237) monitored periodically showed no crystal decomposition. No absorption correction. Structure determined by direct methods using *MULTAN*80 (Main *et al.*, 1980). *E* map revealed the positions of all non-hydrogen atoms. Full-matrix least-squares refinement on *F* (*SHELX*; Sheldrick, 1976). Atomic scattering factors and f' and f'' from *International Tables for X-ray Crystallography* (1974). Anisotropic thermal parameters for non-hydrogen atoms included in final cycles. All 23 H atoms located from a difference map and refined. Refinement converged at $R = 0{\cdot}064$, $R_w = 0{\cdot}074$ for 1518 observed reflections; $w = 3{\cdot}7486/|\sigma^2(F_o) + 0{\cdot}001|F_o|^2|$. $\Delta/\sigma \leq 0{\cdot}15$ for coordinates, $\leq 0{\cdot}30$ for thermal parameters for the non-hydrogen atoms. $-0{\cdot}35 \leq \Delta\rho \leq 0{\cdot}38$ e Å^{-3} in final difference map.

Discussion. The final atomic coordinates are listed in Table 1 and selected bond distances and angles in Table 2.*

The molecular structure of (III) is shown in Fig. 1 (Vallely, 1983), with the arbitrary atom-numbering scheme used in the structure analysis. A diagram of the packing is given in Fig. 2 (Motherwell, 1972). The structure determination has shown that the S—O bond

Table 1. *Final atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10⁴) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

	x	*y*	*z*	$U_{\rm eq}$ (Å²)
C(1)	−1263 (7)	1792 (3)	8258 (1)	466
C(2)	−4207 (8)	1492 (4)	8144 (2)	567
C(3)	−5496 (9)	1754 (4)	7569 (2)	625
C(4)	−5122 (8)	2989 (4)	7433 (2)	635
C(5)	−2171 (8)	3310 (4)	7560 (2)	568
C(6)	−863 (7)	3044 (3)	8139 (1)	465
C(7)	525 (7)	3786 (3)	8493 (1)	490
C(8)	1284 (11)	4979 (4)	8340 (2)	675
C(9)	817 (12)	5928 (4)	8713 (2)	815
C(10)	2208 (16)	5655 (4)	9287 (2)	872
C(11)	1322 (14)	4508 (4)	9448 (2)	712
C(12)	1654 (8)	3514 (3)	9078 (2)	522
S(13)	459 (2)	2246 (1)	9338 (1)	529
O(14)	−2254 (6)	2496 (3)	9381 (1)	689
N(15)	280 (6)	1415 (2)	8790 (1)	472
C(16)	1028 (7)	282 (3)	8843 (2)	499
O(17)	663 (5)	−396 (2)	8481 (1)	656
O(18)	2312 (5)	29 (2)	9352 (1)	589
C(19)	3305 (9)	−1146 (4)	9450 (2)	636
C(20)	5884 (11)	−1269 (5)	9299 (2)	823

Table 2. *Selected distances* (Å) *and angles* (°)

C(1)—C(6)	1·510 (5)	S(13)—N(15)	1·689 (3)
C(1)—N(15)	1·474 (4)	N(15)—C(16)	1·368 (5)
C(6)—C(7)	1·332 (5)	C(16)—O(17)	1·198 (4)
C(7)—C(12)	1·506 (5)	C(16)—O(18)	1·347 (5)
C(12)—S(13)	1·792 (4)	O(18)—C(19)	1·459 (5)
S(13)—O(14)	1·489 (3)	C(19)—C(20)	1·509 (7)

Ring *A*: 1·497–1·552; average 1·519 (6)
Ring *B*: 1·502–1·531; average 1·514 (7)
C—H: 0·90–1·11; average 0·99 (5)

C(2)—C(1)—N(15)	113·9 (3)	C(1)—N(15)—S(13)	120·5 (2)
C(6)—C(1)—N(15)	113·6 (3)	C(1)—N(15)—C(16)	117·2 (3)
C(6)—C(7)—C(8)	123·1 (4)	S(13)—N(15)—C(16)	120·7 (2)
C(6)—C(7)—C(12)	124·1 (3)	N(15)—C(16)—O(17)	124·6 (3)
C(7)—C(12)—S(13)	117·1 (3)	N(15)—C(16)—O(18)	111·7 (3)
C(11)—C(12)—S(13)	106·4 (3)	O(17)—C(16)—O(18)	123·7 (3)
C(12)—S(13)—O(14)	107·5 (2)	C(16)—O(18)—C(19)	116·3 (3)
C(12)—S(13)—N(15)	96·4 (2)	O(18)—C(19)—C(20)	110·5 (4)
O(14)—S(13)—N(15)	108·5 (2)		

Ring *A*: 109·2–111·8; average 110·7 (3)
Ring *B*: 110·3–113·8; average 112·3 (4)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all bond distances and angles, torsion angles and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39050 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is *trans* to the C—H bonds on C(1) and C(12). This is consistent with a suprafacial–suprafacial approach of the N—S π system to that of the diene and agrees with the activation parameters found from kinetic measurements which imply pericyclic reaction of Diels–Alder type.

In their ground states sulphinylamino compounds are thought to exist in a *Z* configuration about the N—S double bond (van Woerden & Bijl-Vlieger, 1974). If the dienophile entered the transition state with this stereochemistry, the present finding requires both the S—O and N—CO_2Et moieties to overlap the carbocycles of the diene in the transition state. Subsequent ready and expected configurational inversion at N but retention at S would yield (III). Alternatively, the *N*-sulphinylurethane could convert to the *E* configuration on passage to a transition state where overlap of one carbocycle of the diene with the S—O bond is greatly preferred to comparable overlap with the N—CO_2Et fragment. The stereospecificity observed in the product would then derive from the degree of this preference.

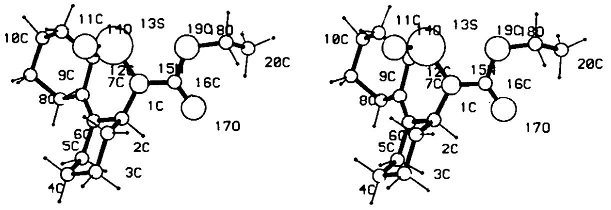

Fig. 1. The molecular structure of (III) with the atom-numbering scheme.

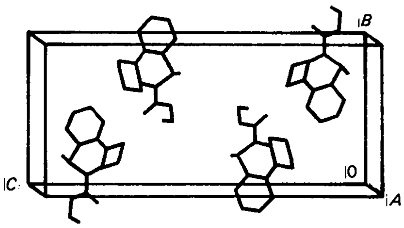

Fig. 2. Packing diagram.

The average C—C bond lengths in rings *A* and *B* are 1·519 (6) and 1·514 (7) Å respectively, in good agreement with the values tabulated by Sutton (1965). The average C—C—C angles are 110·7 (3) and 112·3 (4)°. Both rings *A* and *B* are in the chair conformation with C(1) and C(4) 0·69 and −0·67 Å out of the mean plane through C(2), C(3), C(5) and C(6) (ring *A*) and C(7) and C(10) 0·57 and −0·66 Å from the mean plane defined by C(8), C(9), C(11) and C(12) (ring *B*).

The heterocyclic ring adopts a half-chair conformation with S(13) and N(15) −0·50 and 0·35 Å out of the mean plane through C(1), C(5), C(6), C(7), C(8) and C(12). The S—N and C—S bond lengths are within the range of values observed for other S—N and C—S single bonds (Acheson, Bryce, Das, Dauter, Rees & Reynolds, 1983; Chivers, Codding & Oakley, 1981; Ferrari, Gasparri Fava & Pelizzi, 1981). The torsion angles C(1)—N(15)—S(13)—O(14), C(1)—N(15)—S(13)—C(12), C(7)—C(12)—S(13)—O(14), C(7)—C(12)—S(13)—N(15) are −55·0, 55·8, 72·8 and −38·9°, respectively.

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