The nitrogen atom of the β-lactam, N(5), is displaced by 0·204 (2) Å from the plane of C(4), C(6) and C(8), similar to displacements in the cephalosporins (Sweet & Dahl, 1970). The out-of-plane distortions of an amide group can be partitioned among out-of-plane bending at the nitrogen (χ_N) and the carbonyl carbon (χ_C) and twisting around the N—CO bond (τ) (Winkler & Dunitz, 1971). The appropriate parameters here are χ_N −29·5, χ_C 0·6 and τ 186·9° [*i.e.* a twist of 6·9°], conforming to earlier observations that out-of-plane bending in strained amides is greater at nitrogen than at the carbonyl carbon (Winkler & Dunitz, 1971; Buchanan, Kitson, Mallinson, Sim, White & Cox, 1983). The torsion angles within the non-planar four-membered ring are 6·6 (2)–7·6 (2), mean 7·2°.

The nitrogen atom has pyramidal geometry in several biologically active β-lactams (Sweet & Dahl, 1970). The present results show that pyramidal geometry can also be associated with the absence of antibiotic activity. A recent review has reported that pyramidal geometry at the β-lactam nitrogen is not necessary for antibiotic activity (Page, 1984).

The N—CO bond in the β-lactam, 1·361 (4) Å, is rather longer than N(12)—C(23) in the side-chain amide, 1·320 (4) Å, and, conversely, the β-lactam C(8)—O(11) distance of 1·206 (4) Å is shorter than the C(23)—O(24) distance of 1·233 (4) Å. These results indicate less $p\pi$ overlap in the β-lactam than in the normal side-chain amide.

There are two hydrogen-bonded intermolecular contacts in the crystal: O(13)H···O(24) ($\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$) 2·85 (1) Å and O(11)···HN(12) ($1-x, y, \frac{1}{2}-z$) 2·85 (1) Å.

I am grateful to Dr E. W. Colvin for excellent crystals of the title compound.

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Structure of an *N*-Sulphinylaniline Cycloadduct

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Abstract. (8a*RS*,9*RS*,10a*SR*)-10-Phenyl-1,2,3,4,5,6,7,8,8a,10a-decahydro-10*H*-9-thia-10-azaphenanthrene 9-oxide, $C_{18}H_{23}NOS$, $M_r = 301·45$, monoclinic, $P2_1$, $a = 5·661\ (2)$, $b = 18·071\ (5)$, $c = 8·178\ (4)$ Å, $\beta = 103·74\ (3)$°, $V = 812·67$ Å^3, $Z = 2$, $D_x = 1·23$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 1·64$ mm^{-1}, $F(000) = 324$, $T = 290\ (1)$ K, $R = 0·062$ for 1112 observed reflections. In the title compound the S—O bond is *trans* to the two C—H bonds of the ring junctions. The heterocyclic ring adopts a conformation such that S and N are displaced by −0·65 (1) and 0·18 (1) Å from the mean plane of the other four atoms. The S—O, S—N and S—C bond lengths are 1·475 (5), 1·680 (6) and 1·779 (8) Å, respectively.

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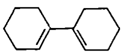
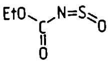
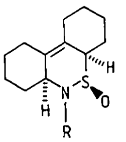
Introduction. It has recently been shown that the cycloadduct of 1,1′-bicyclohexenyl (I) and ethyl *N*-sulphinylcarbamate (II) is (8a*RS*,9*RS*,10a*RS*)-10-ethoxycarbonyl-1,2,3,4,5,6,7,8,8a,10a-decahydro-10*H*-9-thia-10-azaphenanthrene 9-oxide (III*a*) (Dauter, Hanson, Reynolds & Stockburn, 1984) and that its formation is by pericyclic reaction (Hanson & Stockburn, 1985). The stereochemistry found for (III*a*) requires that (II) enters the transition state for cycloaddition in the *Z* configuration about the N=S bond, *i.e.* the normal ground-state geometry for sulphinylamino compounds (van Woerden & Bijl-Vlieger, 1974). *N*-Sulphinylaniline (IV) fails to react with (I) at ambient temperatures [when (II) reacts] and also on heating. However, in the presence of the Lewis acid, $BF_3.Et_2O$, (IV) and (I) do react, producing (III*b*). The structure determination of (III*b*) was undertaken to determine whether or not the catalysed pathway follows a similar stereochemical course to that of the simple thermal reaction.

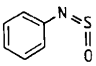

(I)



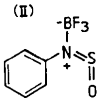
(II)



(III)(a) R = CO_2Et
(b) R = Ph



(IV)



(V)

Experimental. *N*-Sulphinylaniline was reacted with 1,1′-bicyclohexenyl in diethyl ether at ambient temperature in the presence of three mole equivalents of $BF_3.Et_2O$. The resultant precipitate, which contained BF_3, was dissolved in aqueous alcohol and the solution extracted with diethyl ether. After drying, the extract was evaporated to give the title compound (III*b*) which was recrystallized first from cyclohexane and then from methanol to give colourless plates, elongated along **a**. A crystal of size 0·50 × 0·20 × 0·20 mm was used for data collection. Preliminary unit-cell and space-group data from Weissenberg photographs. Accurate cell dimensions from least-squares refinement of θ for 20 reflections. Hilger & Watts Y290 four-circle diffractometer controlled by an LSI-11 microcomputer, Cu $K\alpha$ radiation, $\omega/2\theta$ scanning mode, 28 steps of 0·02°, count time per step 1 s, $\theta_{max} = 62°$. Index range h −6 to 6, k 0 to 20, l 0 to 9 for 1580 reflections measured, 1343 unique reflections, $R_{int} = 0·043$, 223 with $I \le 2\sigma(I)$ classified as unobserved. Periodic checks on three reference reflections (19$\bar{3}$, 154, 1$\bar{5}$4) revealed no decrease in intensity. No absorption correction. Structure solved by direct methods using *MULTAN*80 (Main *et al.*, 1980). Structure refined by full-matrix least squares on *F* with *SHELX*76 (Sheldrick, 1976). Atomic scattering factors and f' and f'' from *International Tables for X-ray Crystallography* (1974). All non-H atoms refined anisotropically. 19 of 23 H atoms located in difference map; these not refined but all H atoms included at their calculated positions. Eight reflections affected by extinction omitted. Refinement converged at $R = 0·062$, $wR = 0·087$ for 1112 observed reflections; weighting scheme, $w = 0·6316/[\sigma^2(F) + 0·002F^2]$. Final calculated shifts $\le 0·1\sigma$; residual electron density in final difference map: $-0·42 \le \Delta\rho \le 0·24$ e Å^{-3}. Figures drawn with *PLUTO* (Motherwell, 1972).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (×10^4) (*with e.s.d.'s in parentheses*)

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	U_{eq}(Å^2)
C(1)	258 (12)	1257 (4)	156 (8)	535
C(2)	−2515 (12)	1387 (5)	−315 (10)	641
C(3)	−3408 (14)	1418 (6)	−2221 (10)	710
C(4)	−2694 (14)	719 (5)	−3040 (8)	693
C(5)	15 (13)	596 (6)	−2548 (8)	655
C(6)	952 (11)	575 (5)	−657 (7)	518
C(7)	2256 (13)	14 (4)	204 (8)	519
C(8)	3327 (18)	−613 (5)	−616 (10)	703
C(9)	3162 (22)	−1363 (5)	164 (11)	844
C(10)	4359 (18)	−1345 (5)	2024 (11)	741
C(11)	3036 (16)	−787 (4)	2855 (9)	640
C(12)	3095 (13)	−2 (4)	2124 (8)	515
S(13)	1398 (3)	567 (1)	3204 (2)	515
O(14)	−1019 (8)	223 (3)	2990 (7)	604
N(15)	1307 (10)	1315 (8)	1970 (6)	521
C(16)	1127 (11)	2018 (4)	2760 (7)	521
C(17)	2676 (13)	2583 (4)	2463 (10)	696
C(18)	2513 (17)	3276 (5)	3248 (12)	840
C(19)	974 (14)	3382 (5)	4276 (10)	675
C(20)	−460 (16)	2832 (5)	4506 (10)	777
C(21)	−395 (14)	2134 (4)	3767 (9)	643

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)–C(6)	1·497 (11)	C(12)–S(13)	1·779 (8)
C(1)–N(15)	1·465 (8)	S(13)–O(14)	1·475 (5)
C(6)–C(7)	1·351 (10)	S(13)–N(15)	1·680 (6)
C(7)–C(12)	1·529 (9)	N(15)–C(16)	1·439 (9)

Ring *A*: 1·497–1·544; average 1·518 (10)
Ring *B*: 1·510–1·542; average 1·520 (11)
Ring *C*: 1·326–1·419; average 1·376 (12)

C(2)–C(1)–N(15)	112·7 (6)	C(12)–S(13)–O(14)	107·0 (3)
C(6)–C(1)–N(15)	115·0 (6)	C(12)–S(13)–N(15)	96·4 (3)
C(1)–C(6)–C(7)	123·7 (5)	O(14)–S(13)–N(15)	111·9 (3)
C(5)–C(6)–C(7)	124·6 (7)	C(1)–N(15)–S(13)	119·9 (5)
C(6)–C(7)–C(8)	123·9 (6)	C(1)–N(15)–C(16)	117·5 (5)
C(6)–C(7)–C(12)	112·4 (6)	S(13)–N(15)–C(16)	115·8 (4)
C(7)–C(12)–S(13)	115·2 (5)	N(15)–C(16)–C(17)	116·8 (6)
C(11)–C(12)–S(13)	106·0 (6)	N(15)–C(16)–C(21)	122·5 (6)

Ring *A*: 109·5–111·9; average 111·2 (7)
Ring *B*: 108·4–114·4; average 111·8 (7)
Ring *C*: 116·9–122·3; average 120·0 (8)

C(1)–C(6)–C(7)–C(12)	2·4*	C(6)–C(1)–N(15)–C(16)	167·5
C(6)–C(7)–C(12)–S(13)	21·9	C(1)–N(15)–S(13)–O(14)	53·7
C(7)–C(12)–S(13)–O(14)	70·4	C(1)–N(15)–C(16)–C(17)	−74·4
C(7)–C(12)–S(13)–N(15)	−44·9	S(13)–N(15)–C(16)–C(21)	−44·2
C(12)–S(13)–N(15)–C(1)	57·6	S(13)–N(15)–C(1)–C(6)	−42·4
C(12)–S(13)–N(15)–C(16)	−151·9	N(15)–C(1)–C(6)–C(7)	6·0

* E.s.d.'s ~0·5°.

Discussion. Final atomic parameters are listed in Table 1* and selected bond lengths, bond angles and torsion angles in Table 2.

The molecular structure of (III*b*) is shown in Fig. 1, with the arbitrary atom-numbering scheme used in the structure analysis. The crystal packing is shown in Fig. 2.

The structure determination has confirmed that the catalysed cycloaddition of (IV) to (I) follows the same stereochemical course as the uncatalysed addition of (II): a pericyclic transition state involving suprafacial–suprafacial addition of the diene to the *Z* configuration of the dienophile results in the S—O bond of the product being *trans* to the C—H bonds of the ring junctions, C(1) and C(12). It has been argued (Hanson & Stockburn, 1985) that for the reaction of (I) and (II) the transition state occurs early in the reaction coordinate so that the forces which constrain sulphinylamino compounds to the *Z* configuration in the ground state are still present to some degree. This obviously must hold true in the present case also. It seems improbable, therefore, that the complex of PhNSO and BF_3 should involve an O—B bond; some conformations of such a complex would significantly increase the steric interaction already present between the O moiety and the *ortho* position of the phenyl ring (van Woerden & Bijl-Vlieger, 1974). Kresze & Rössert (1978) have noted that alkyl *N*-sulphinylamines, *R*NSO, which are unreactive in cycloaddition reactions with dienes, are converted into reactive dienophiles by further alkylation with trialkyloxonium salts. The products ultimately isolated are dialkylated at N, indicative of an initial methylation there also. It appears, therefore, that the kinetically active complex of BF_3 and (II) involves a coordination of the Lewis acid through N. This should lead to a comparable increase in dienophilic character of (II) and indeed enhance the probability that the Ph and O moieties remain *cis* about the N—S bond in the transition state which the structure of (III*b*) requires [see (V)].

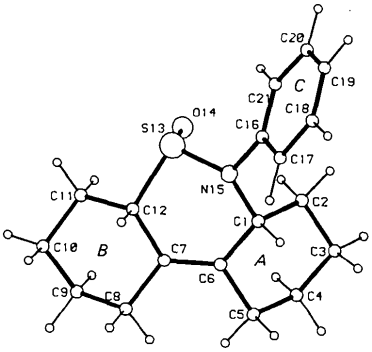


Fig. 1. The molecular structure of (III*b*) with the atom-numbering scheme.

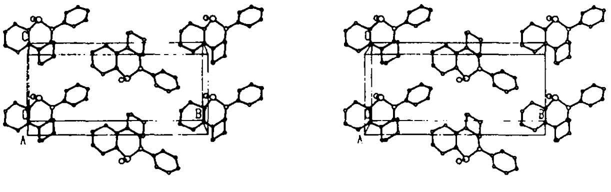


Fig. 2. Packing diagram.

The heterocyclic ring adopts a conformation such that S(13) and N(15) are displaced by −0·65 (1) and 0·18 (1) Å out of the mean plane through C(1), C(6), C(7) and C(12). The S—O, S—N and C—S bond lengths agree well with the values observed in (III*a*) (Dauter *et al.*, 1984).

The average C—C bond lengths in rings *A* and *B* are 1·518 (10) and 1·520 (11) Å respectively and the average C—C—C angles are 111·2 (7) and 111·8 (7)° respectively. These values agree with those tabulated by Sutton (1965). Ring *A* has a regular chair conformation with endocyclic torsion angles in the range ± 55·0 to 56·5°, and atoms C(2) and C(5) −0·68 and 0·65 Å out of the mean plane through C(1), C(3), C(4) and C(6). Ring *B* adopts a distorted chair conformation with atoms C(7) and C(10) −0·55 and 0·71 Å from the plane defined by C(8), C(9), C(11) and C(12). The internal torsion angles for ring *B* vary from ± 43·8 to 61·0°.

The phenyl ring is essentially planar with a maximum deviation from the mean least-squares plane of 0·009 (6) Å.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, and bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42345 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.