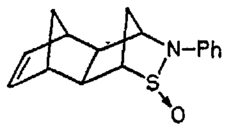
Crystal and Molecular Structure of *exo*-7,11-methano-5,6a,7,7a,10,11,11a-octahydrobenz[*c*]indeno[5,6-*e*]thiazine 6-Oxide

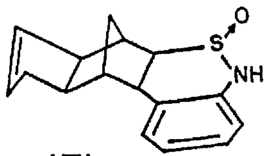
By **D. J. Pointer** and **J. B. Wilford**,* Department of Chemistry, Teesside Polytechnic, Borough Road, Middlesbrough, Teesside TS1 3BA
K. M. Chui, Department of Chemical Crystallography, South Parks Road, Oxford

The structure of the title compound has been determined by a three-dimensional *X*-ray analysis. The monoclinic unit cell (space group $P2_1/c$) has dimensions $a = 7{\cdot}02$ $b = 12{\cdot}86$ $c = 14{\cdot}35$ Å and $\beta = 92{\cdot}04°$ for $Z = 4$. The structure was solved by centrosymmetric symbolic addition and refined by least-squares calculations to R 0·103 for 2201 reflections. The molecule has *exo*-stereochemistry and is a racemic compound, with enantiomeric molecules forming centrosymmetric dimers through pairs of N–H · · · O=S hydrogen bonds.

THE $(4\pi + 2\pi)$ cycloaddition reactions involving cyclopentadiene usually give predominantly the thermodynamically more stable *endo*-stereomers as adducts,[1] although a recent *X*-ray study [2] has suggested that the *exo*-stereomer is favoured with a quinone as the dienophile. With *N*-sulphinylaniline, cyclopentadiene has been reported [3] to give the 1 : 2-adduct (I) shown later [4]



(I)



(II)

to be the 1 : 2-adduct (II) in which *N*-sulphinylaniline has acted as the diene, and to be identical with the 1 : 1-adduct obtained using the dimer dicyclopentadiene. An assignment of the stereochemistry might be deduced as *exo* by n.m.r. evidence of comparison with the norbornene adduct.[5] That the orientation of the unsymmetrical diene system, *N*-sulphinylaniline also influences the stereochemistry, is shown by the present *X*-ray study which finds the principle product to be a racemic compound [6] having the *exo*-configuration.

EXPERIMENTAL

exo-7,11-*Methano*-5,6a,7,7a,10,11,11a-*octahydrobenz*[c]-*indeno*[5,6-e]*thiazine* 6-*Oxide*.—Recrystallisation from methanol of material prepared as in ref. 4 gave aciculiform crystals, m.p. 254 °C (decomp.) (Found: C, 70·72; H, 6·52; N, 5·30; S, 12·00. Calc. for $C_{16}H_{17}NOS$: C, 70·81; H, 6·31; N, 5·16; S, 11·81%); $\nu_{max.}$ (KBr disc): 3185 (N–H), 1615 (aliph. C=C, weak), 1600 (arom. C=C), and 1037 (S=O) cm^{-1}; $\lambda_{max.}$ (EtOH): 241 (ε, 6400), and 280 nm (ε, 1120); n.m.r. data (τ units measured on a Perkin-Elmer R 12A spectrometer at 60 MHz for a solution in trifluoroacetic acid with tetramethylsilane as reference): 2·9 (3H, s, t, C-1, C-2, C-3), 3·2 (1H, q, C-4), 4·1, 4·4 (2H, 2d, C-8, C-9), 6·6 (1H, s, N-5 removed by deuteriation), 8·5 (2H, d, C-12). No *endo*-stereomer was obtained.

Crystal Data.—$C_{16}H_{17}NOS$, $M = 271{\cdot}4$, Monoclinic, $a = 7{\cdot}018(5)$, $b = 12{\cdot}86(1)$, $c = 14{\cdot}35(1)$ Å, $\beta = 92{\cdot}04(2)°$, $U = 1293$ Å^3, $D_c = 1{\cdot}39$, $Z = 4$, $D_m = 1{\cdot}39$ (by flotation), $F(000) = 576$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 20·7 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, No. 14).

A needle-shaped crystal of cross-section smaller than the optimum size (1 mm) was used to obtain intensity data on a Hilger and Watts four-circle diffractometer. The ω–2θ scan method,[7] with balanced filters for $\theta < 30°$, and a β-filter only for $30° < \theta < 70°$ was used to obtain 2295 reflections having $I > 3\sigma(I)$. Corrections were made for Lorentz and polarisation effects, and for absorption [8] using the experimentally determined variation in intensity with crystal orientation for the $\bar{4}00$ reflection.

Structure Determination and Refinement.—An overall temperature factor of 3·2 Å^2 was obtained from a Wilson plot and used to calculate normalised structure factors.[9] The structure was solved by symbolic addition by use of a programme for centrosymmetric structures.[10] The signs of 431 reflections with $|E| > 1{\cdot}1$ were determined in terms of one symbol, and a Fourier synthesis using the least probable solution based on these reflections revealed all the non-hydrogen atoms in the asymmetric unit. Full matrix least-squares refinement with isotropic temperature factors gave R 0·14. When all atoms were given anisotropic temperature factors, R decreased to 0·12. A difference Fourier map then clearly revealed all the hydrogen atom positions, and these were included with isotropic temperature factors in the calculation of structure factors. Alternate rounds of refinement of positional parameters for all atoms except hydrogen, and temperature factors for all atoms were carried out. The hydrogen atom positions were then adjusted from a difference Fourier map and final cycles of least-squares refinement were then continued until convergence without further adjustment of hydrogen atom positions and temperature factors. A weighting scheme of the form: $1/w = 1 + [F_o - a/b]^2$ with $a = 463$ and $b = 741$ was included in all but the initial cycle of refinement, and 94 reflections having calculated structure factors $<0{\cdot}6$ on the absolute scale were not included in the final cycles, after which R was 0·103.

1 J. Sauer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 211; 1967, **6**, 16.
2 D. J. Pointer, J. B. Wilford, and O. J. R. Hodder, *J. Chem. Soc.* (*B*), 1971, 2009.
3 E. G. Kataev, V. V. Plemenkov, *Zhur. obshchei. Khim.*, 1962, **32**, 3817 (*Chem. Abs.*, 1963, **58**, 12544*f*).
4 G. R. Collins, *J. Org. Chem.*, 1964, **29**, 1688.
5 A. Macaluso and J. Hamer, *J. Org. Chem.*, 1967, **32**, 506.
6 E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 44.
7 U. W. Arndl and B. J. M. Willis, 'Single Crystal Diffractometry,' Cambridge University Press, Cambridge, 1966, p. 265.
8 DR4C3 Data reduction programme with absorption corrections, Oxford University Chemical Crystallography Laboratory, 1970.
9 Autocode structure analysis programme (November tape), O. J. R. Hodder and J. S. Rollett, Oxford University, 1968.
10 Centro-symmetric symbolic addition programme, O. J. R. Hodder, C. K. Prout, and J. S. Rollett, 1968.

RESULTS AND DISCUSSION

The Diels–Alder reaction, now considered to be a concerted $(4\pi + 2\pi)$ cycloaddition,[11] usually shows a preference for *endo*-addition for which several explanations have been advanced,[11,12] usually involving interactions between atoms not bonded in the adduct. The *endo*-preference has recently [13] been interpreted in terms of extending conjugation in the 2π system. Cyclopentadiene, usually the 4π system, becomes the 2π system in the reaction with *N*-sulphinylaniline where presumably it first dimerises and reacts as an alkene having no extending conjugation. *N*-Sulphinylaniline, partly utilising the aromatic ring, acts as the diene which with two possible orientations in the transition state can give a racemic product having the *exo*-stereochemistry presently reported.

The conformation of the molecule is depicted in Figure 1, which gives the atomic numbering system, and Tables 1 and 2 list the final atom parameters with

TABLE 1

Fractional atomic co-ordinates and isotropic vibrational amplitudes (Å²) with their estimated standard deviations in parentheses

	x/a	y/b	z/c	U_{iso}
C(1)	0·4202(8)	0·1677(4)	0·1548(4)	
C(2)	0·5273(9)	0·1149(5)	0·0906(5)	
C(3)	0·5550(9)	0·1587(5)	0·0038(5)	
C(4)	0·4810(8)	0·2552(5)	−0·0182(4)	
C(4a)	0·3719(7)	0·3083(4)	0·0468(4)	
N(5)	0·2924(7)	0·4070(4)	0·0225(3)	
S(6)	0·3022(2)	0·5006(1)	0·1030(1)	
O(6)	0·5025(5)	0·5143(3)	0·1411(3)	
C(6a)	0·1817(7)	0·4342(4)	0·1946(4)	
C(7)	−0·0381(8)	0·4456(5)	0·1844(4)	
C(7a)	−0·1245(8)	0·4163(5)	0·2794(4)	
C(8)	−0·0218(9)	0·4531(5)	0·3671(4)	
C(9)	0·0455(9)	0·3725(5)	0·4182(4)	
C(10)	−0·0065(9)	0·2697(5)	0·3778(4)	
C(10a)	−0·1048(8)	0·2957(5)	0·2836(4)	
C(11)	0·0042(8)	0·2718(5)	0·1950(4)	
C(11a)	0·2123(7)	0·3142(4)	0·2035(3)	
C(11b)	0·3387(7)	0·2646(4)	0·1335(4)	
C(12)	−0·0909(8)	0·3488(6)	0·1259(4)	
H(1) *	0·400	0·120	0·222	0·048
H(2)	0·600	0·040	0·111	0·059
H(3)	0·643	0·120	−0·042	0·059
H(4)	0·473	0·296	−0·083	0·050
H(5)	0·323	0·434	−0·050	0·044
H(6a)	0·223	0·474	0·258	0·039
H(7)	−0·090	0·520	0·161	0·044
H(7a)	−0·267	0·450	0·275	0·045
H(8)	0·007	0·534	0·383	0·052
H(9)	0·100	0·380	0·487	0·053
H(101)	−0·100	0·220	0·425	0·057
H(102)	0·117	0·210	0·361	0·057
H(10a)	−0·243	0·250	0·275	0·046
H(11)	0·000	0·180	0·183	0·047
H(11a)	0·277	0·290	0·272	0·038
H(121)	−0·050	0·360	0·050	0·053
H(122)	−0·233	0·330	0·128	0·053

* Hydrogen atoms are numbered according to the atom to which they are bonded.

[11] R. B. Woodward, R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395, 2046, 2511, 4388.
[12] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543; W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 1967, 3095.
[13] K. N. Houk, *Tetrahedron Letters*, 1970, 2621.

TABLE 2

Anisotropic temperature factors (Å²)

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	$2\times10^3U_{12}$	$2\times10^3U_{13}$	$2\times10^3U_{23}$
C(1)	43(3)	38(3)	68(3)	10(5)	0(6)	−3(5)
C(2)	44(4)	49(3)	85(3)	14(5)	1(6)	−20(6)
C(3)	43(4)	59(4)	80(5)	−2(6)	23(6)	−35(7)
C(4)	42(3)	54(3)	58(4)	−5(5)	12(5)	−25(6)
C(4a)	34(3)	44(3)	44(3)	−1(4)	1(4)	−10(4)
N(5)	48(3)	46(2)	39(2)	1(4)	7(4)	−9(3)
S(6)	40(1)	39(1)	41(1)	−2(1)	0(1)	5(1)
O(6)	39(3)	63(2)	52(2)	−26(4)	−12(3)	−2(4)
C(6a)	38(3)	38(3)	42(3)	5(5)	−5(4)	−6(4)
C(7)	36(3)	50(3)	49(3)	14(5)	−4(5)	8(5)
C(7a)	37(3)	53(3)	46(3)	5(5)	12(5)	7(5)
C(8)	54(4)	59(4)	51(4)	−3(6)	15(5)	−11(6)
C(9)	54(4)	68(4)	40(3)	11(6)	7(5)	−1(5)
C(10)	61(4)	55(4)	55(3)	15(6)	17(5)	15(6)
C(10a)	41(3)	53(3)	48(3)	−16(5)	8(5)	−5(5)
C(11)	39(3)	54(3)	52(3)	−28(5)	9(5)	−18(5)
C(11a)	34(3)	38(3)	41(3)	3(4)	−2(4)	10(4)
C(11b)	36(3)	42(3)	43(3)	1(4)	−1(4)	−11(4)
C(12)	35(3)	79(4)	47(3)	−20(6)	−13(5)	−1(6)

The anisotropic temperature factor is of the form $-\log T = 2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}hla^*c^* + 2U_{12}hka^*b^*]$.

TABLE 3

Interatomic distances (Å) angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances not involving hydrogen

C(1)–C(2)	1·387(9)	C(7)–C(7a)	1·558(8)
C(1)–C(11b)	1·400(8)	C(7)–C(12)	1·539(8)
C(2)–C(3)	1·388(10)	C(7a)–C(8)	1·505(9)
C(3)–C(4)	1·376(9)	C(7a)–C(10a)	1·558(8)
C(4)–C(4a)	1·406(8)	C(8)–C(9)	1·346(9)
C(4a)–N(5)	1·424(7)		
C(4a)–C(11b)	1·392(7)	C(9)–C(10)	1·483(9)
N(5)–S(6)	1·668(5)	C(10)–C(10a)	1·532(9)
S(6)–O(6)	1·501(4)	C(10a)–C(11)	1·539(8)
S(6)–C(6a)	1·803(5)	C(11)–C(11a)	1·560(8)
C(6a)–C(7)	1·552(8)	C(11)–C(12)	1·536(9)
C(6a)–C(11a)	1·562(7)	C(11a)–C(11b)	1·506(7)

(*b*) Bonded distances involving hydrogen (all estimated standard deviations *ca.* 0·03 Å)

C(1)–H(1)	1·16	C(8)–H(8)	1·08
C(2)–H(2)	1·12	C(9)–H(9)	1·05
C(3)–H(3)	1·04	C(10)–H(101)	1·15
C(4)–H(4)	1·07	C(10)–H(102)	1·19
N(5)–H(5)	1·12	C(10a)–H(10a)	1·14
C(6a)–H(6a)	1·08	C(11)–H(11)	1·19
C(7)–H(7)	1·07	C(11a)–H(11a)	1·11
C(7a)–H(7a)	1·09	C(12)–H(121)	1·15
		C(12)–H(122)	1·03

(*c*) Interbond angles

C(2)–C(1)–C(11b)	121·1(5)	C(7)–C(7a)–C(10a)	103·8(4)
C(1)–C(2)–C(3)	119·6(6)	C(8)–C(7a)–C(10a)	104·0(5)
C(2)–C(3)–C(4)	120·5(6)	C(7a)–C(8)–C(9)	111·2(5)
C(3)–C(4)–C(4a)	119·7(6)	C(8)–C(9)–C(10)	113·4(6)
C(4)–C(4a)–C(11b)	120·6(5)	C(9)–C(10)–C(10a)	104·4(5)
C(4)–C(4a)–N(5)	119·2(5)	C(7a)–C(10)–C(10a)	106·7(5)
N(5)–C(4a)–C(11b)	120·1(5)	C(7a)–C(10a)–C(11)	102·2(4)
C(4a)–N(5)–S(6)	117·8(3)	C(10)–C(10a)–C(11)	117·7(5)
N(5)–S(6)–O(6)	110·6(2)	C(10a)–C(11)–C(11a)	110·9(4)
N(5)–S(6)–C(6a)	98·9(2)	C(10a)–C(11)–C(12)	100·8(5)
O(6)–S(6)–C(6a)	104·4(2)	C(11a)–C(11)–C(12)	102·1(4)
S(6)–C(6a)–C(7)	112·1(4)	C(6a)–C(11a)–C(11b)	116·5(4)
S(6)–C(6a)–C(11a)	117·4(4)	C(11)–C(11a)–C(11b)	111·8(5)
C(7)–C(6a)–C(11a)	103·6(4)	C(11a)–C(11b)–C(4a)	123·1(5)
C(6a)–C(7)–C(7a)	108·1(4)	C(11a)–C(11b)–C(1)	118·4(5)
C(6a)–C(7)–C(12)	101·2(4)	C(4a)–C(11b)–C(1)	118·3(5)
C(7a)–C(7)–C(12)	100·8(4)	C(7)–C(12)–C(11)	94·5(5)
C(7)–C(7a)–C(8)	117·8(5)		

TABLE 3 (*Continued*)

(*d*) Intermolecular non-bonded distances $< 4{\cdot}5$ Å

$C(1) \cdots O(6^{II})$	3·557(7)	$N(5^{I}) \cdots O(6^{II})$	2·975(6)
$C(1) \cdots C(12^{III})$	4·180(9)	$H(5^{I}) \cdots O(6^{II})$	1·94(3)
$C(2) \cdots O(6^{II})$	4·075(8)	$O(6) \cdots C(7^{III})$	3·379(7)
$C(2) \cdots C(12^{III})$	4·047(9)		
$C(3) \cdots C(12^{III})$	3·862(9)		

Roman numerals as superscripts refer to the equivalent positions relative to the reference molecule at x, y, z:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$ II $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
III $1 + x, y, z$

estimated standard deviations and anisotropic temperature factors.*

Interatomic distances and angles (Table 3) are significantly less accurate for hydrogen atoms than all others, since no refinement of hydrogen atom co-ordinates was carried out, and hence no reliable estimates of the errors are available. The S(6)–O(6) bond length [1·501(4) Å] is longer than the mean values of 1·45 Å

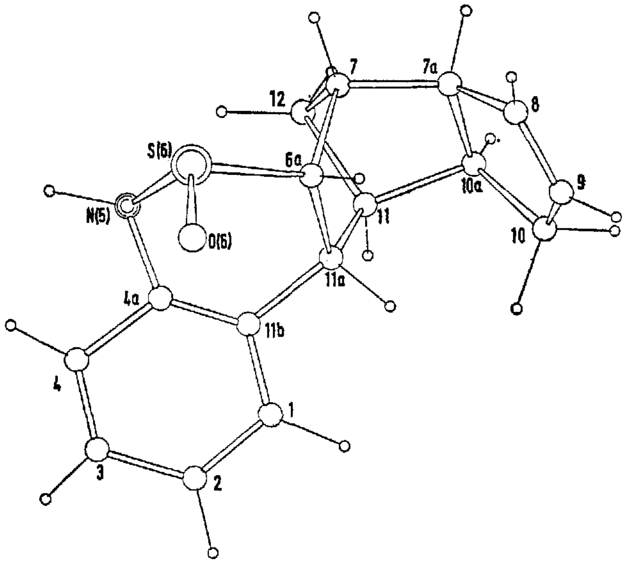


FIGURE 1 Molecular structure projected on the unit-cell plane (of equation $-0{\cdot}578X - 0{\cdot}744Y - 0{\cdot}336Z + 3{\cdot}16 = 0$), showing the atomic numbering system

quoted [14] for 5,5-dimethyl-*N*-methylsulphonylsulphilimine and the values 1·425 and 1·443 Å for methanesulphonanilide,[15] both of which have adjacent nitrogen atoms, but agrees closely with the value of 1·502(9) found [16] for the extensively hydrogen-bonded methanesulphinic acid. All bond lengths in the cyclopentadiene dimer part of the molecule conform closely to the

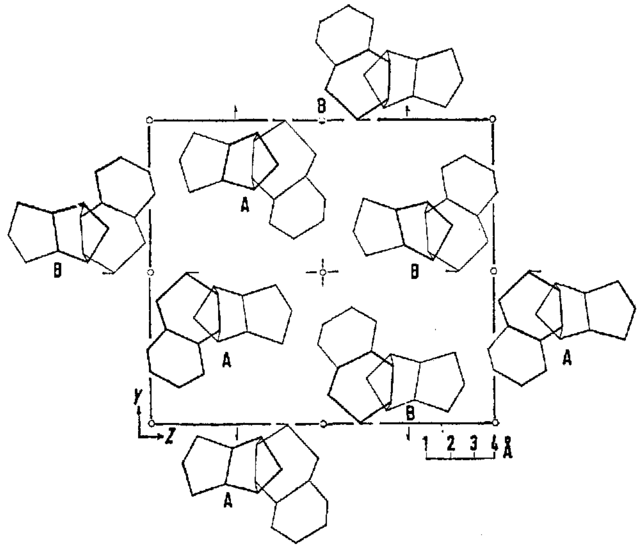


FIGURE 2 The molecular packing viewed down the *a* axis. Molecules designated A and B are enantiomeric

reported [17] dimensions for α-3-bromobenzoyloxy-(cyclopentadiene dimer), and the bridgehead angle C(7)–C(12)–C(11) of 94·5(5)° is similar (92·7°) in that molecule. The carbon atoms of the benzene ring are close to their least-squares best plane † and bond lengths and valency angles are acceptably similar to literature values.

The molecular packing within the crystal cell is shown in Figure 2. Two enantiomeric molecules form a centrosymmetric dimer through a symmetrical pair of N–H ··· O hydrogen bonds. The total N–H ··· O distance is 2·975(6), the N–H bond is 1·12(3), and the H ··· O distance is 1·94(3) Å, with the angle at the hydrogen atom 151°; all comparable with the corresponding values given for methanesulphonanilide (ref. **15** and refs. therein).

We thank Professor H. M. Powell for the use of the diffractometer, and the Oxford University Computing Laboratory for computer time.

[2/122 *Received*, 20*th January*, 1972]

* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20388 (16 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), **1970**, Issue No. 20.

† The equation of the plane is $-0{\cdot}816x - 0{\cdot}444y - 0{\cdot}370z + 4{\cdot}143 = 0$ where x, y, and z in Å are related to the unit-cell directions a, b, and c respectively.

[14] A. Kalman, *Acta Cryst.*, 1967, **22**, 501.
[15] H. P. Klug, *Acta Cryst.*, 1968, *B*, **24**, 792.
[16] K. Seff, E. G. Heidner, M. Meyers, and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, **25**, 350.
[17] R. Destro, C. M. Gramaccioli, and M. Simonetta, *Chem. Comm.*, 1968, 568.