Acta Cryst. (1983). C**39**, 889–890

exo-2-Chloro-*anti*-[7](4-chlorophenylthio)benzo[8,9,10]trinorbornene,* $C_{17}H_{14}Cl_2S$

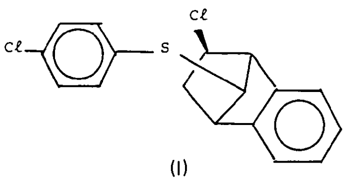
By George H. Schmid, Barry Toyonaga, Pik Yuen Siew and Stanley C. Nyburg

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

(*Received* 26 *July* 1982; *accepted* 22 *February* 1983)

Abstract. $M_r = 321{\cdot}8$, monoclinic, $C2/c$, $a = 16{\cdot}63$ (5), $b = 10{\cdot}53$ (3), $c = 18{\cdot}72$ (5) Å, $\beta = 112{\cdot}6$ (1)°, $U = 3026$ (13) Å^3, $Z = 8$, $D_x = 1{\cdot}41$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}494$ mm^{-1}, $F(000) = 1328$, $T = 298$ K. Final $R = 0{\cdot}076$ using 1439 observed reflections. The two C atoms attached to the benzene ring are slightly out of plane with it in a direction (*syn*) towards the bridge C atom. This is opposite to the (*anti*) direction predicted by molecular orbital theory. However, other known benzo[8,9,10]trinorbornene structures show that the direction of slight noncoplanarity is variable and is probably controlled in the crystal by whether or not the 8,9,10-trinorbornene system carries bulky substituents.

Introduction. The title compound (I) is a rare example of a rearranged product from the addition of an arenesulfenyl halide to an alkene.



(I)

Experimental. Material obtained in 30% yield by addition of 4-chlorobenzenesulfenyl chloride to benzo[8,9,10]trinorbornadiene in methylene dichloride [the only other adduct was shown by ^{1}H NMR to be *endo*-2-chloro-*exo*-3-(4-chlorophenylthio)benzo[8,9,10]-trinorbornene], off-white and well formed crystals deposited from initially oily reaction product, one such *ca* $0{\cdot}25 \times 0{\cdot}17 \times 0{\cdot}083$ mm used for structure analysis; cell dimensions obtained from nine angle settings on a Picker four-circle diffractometer; systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$, space group Cc or $C2/c$ (latter confirmed); no absorption corrections made; data collected in θ–2θ scan mode to $\theta = 25°$ in quadrant $h = 0$ to 18, $k = 0$ to 10, $l = -20$ to 16; intensity of a standard reflection monitored every 400 reflections, e.s.d. 1·5%; 1439 reflections out of 2625 considered significant by criterion $F > 2\sigma(F)$ where $\sigma(F) = \{[\sigma(I).\mathrm{Lp}]^2 + 0{\cdot}02F^4\}^{1/2}/2F$, $\sigma(I) = (\text{scan} + \sum\text{background})^{1/2}$; merging consistency for $0kl$ 0·093; structure solved by direct methods and refined using *SHELX* (Sheldrick, 1976), which also provided the atomic scattering factors; H atoms placed in theoretical positions and their isotropic temperature factors refined; final $R = 0{\cdot}076$, $R_w = 0{\cdot}087$, refinement of $w = k/[\sigma^2(F) + |G|F^2]$ gave $k = 0{\cdot}9819$ and $G = 0{\cdot}03482$; in final refinement cycle maximum shift-to-error for hydrogen temperature factors 0·213.

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1,† bond distances and angles in Table 2. Fig. 1 shows a perspective view of the molecule with the atomic-numbering scheme.

Of the four configurations theoretically possible, the one adopted has Cl(1) towards the 8,9,10-trinorbornene bridge and has sulfur attached to C(7) on the side away from the phenylene ring. The best least-mean-squares planes of C(1), C(6), C(5), C(2) and of

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
Cl(1)	3419 (2)	10357 (3)	1135 (2)	4·4 (1)
Cl(2)	3859 (2)	1864 (3)	3130 (2)	5·0 (1)
S	3496 (2)	7401 (2)	1741 (1)	2·9 (1)
C(1)	4089 (5)	7241 (8)	458 (4)	2·3 (2)
C(2)	4815 (5)	8736 (8)	1372 (4)	2·2 (2)
C(3)	4110 (6)	9503 (9)	741 (5)	2·7 (2)
C(4)	3588 (5)	8489 (9)	140 (5)	3·0 (3)
C(5)	5445 (5)	8301 (8)	987 (4)	2·3 (2)
C(6)	4988 (5)	7377 (7)	437 (4)	2·2 (2)
C(7)	4360 (5)	7421 (8)	1343 (5)	2·5 (2)
C(8)	6306 (5)	8609 (8)	1126 (5)	2·7 (3)
C(9)	6688 (7)	7963 (11)	670 (6)	3·9 (3)
C(10)	6259 (6)	7079 (10)	135 (5)	3·4 (3)
C(11)	5399 (6)	6769 (10)	1 (5)	3·2 (3)
C(12)	3597 (5)	5819 (8)	2095 (5)	2·6 (3)
C(13)	3854 (6)	4794 (8)	1758 (5)	3·1 (3)
C(14)	3940 (7)	3570 (9)	2076 (5)	3·4 (3)
C(15)	3727 (6)	3387 (8)	2720 (5)	2·9 (3)
C(16)	3443 (7)	4359 (10)	3046 (6)	3·9 (4)
C(17)	3374 (6)	5588 (9)	2746 (5)	3·2 (3)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

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* Alternative nomenclature: (1R*,4S*,9S*)-2-chloro-9-(4-chlorophenylthio)-1,2,3,4-tetrahydro-1,4-methanonaphthalene.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38445 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the benzene ring are 2·0 (9)° out of coplanarity, the bending being towards the bridge C atom. This bending (*syn*) is in the opposite sense to that (*anti*), 3·4°, calculated for the two H atoms of 8,9,10-trinorbornene using an STO-3G basis set (Rondan, Paddon-Row, Caramella & Houk, 1981). Table 3 compares the present molecule with four others containing a benzo[8,9,10]trinorbornene system. The table shows the direction of displacement of the two atoms attached to the benzene ring away from the latter's best least-squares plane. The angular deviation from coplanarity of the two fused ring systems is also given. The only generalization which can be made about such a small sample is that where there are no bulky substituents [examples (ii) and (iii)] the sense of displacement is in accord with the theoretical calculations. Where there are bulky substituents [present case and example (v)] one or both displacements are *syn*. Lastly, where the 8,9,10-trinorbornene system is further bridged, [example (iv)] the displacement from coplanarity is exceptionally large.

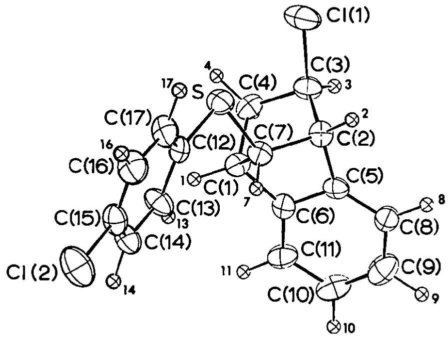

Fig. 1. *ORTEP* plot (Johnson, 1965) of molecule showing atomic numbering and 50% probability ellipsoids.

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

Cl(1)–C(3)	1·82 (1)	C(5)–C(8)	1·39 (1)
Cl(2)–C(15)	1·755 (9)	C(6)–C(11)	1·40 (1)
S–C(12)	1·776 (9)	C(8)–C(9)	1·42 (1)
C(1)–C(4)	1·55 (1)	C(9)–C(10)	1·35 (1)
C(1)–C(6)	1·52 (1)	C(10)–C(11)	1·39 (2)
C(1)–C(7)	1·55 (1)	C(12)–C(13)	1·40 (1)
C(2)–C(3)	1·54 (1)	C(12)–C(17)	1·42 (1)
C(2)–C(5)	1·55 (1)	C(13)–C(14)	1·40 (1)
C(2)–C(7)	1·57 (1)	C(14)–C(15)	1·40 (1)
C(3)–C(4)	1·55 (1)	C(15)–C(16)	1·37 (1)
C(5)–C(6)	1·41 (1)	C(16)–C(17)	1·40 (1)

C(4)–C(1)–C(6)	107·5 (7)	C(1)–C(7)–C(2)	94·8 (6)
C(4)–C(1)–C(7)	101·5 (7)	C(5)–C(8)–C(9)	116·3 (9)
C(6)–C(1)–C(7)	97·5 (7)	C(8)–C(9)–C(10)	123 (1)
C(3)–C(2)–C(5)	104·5 (7)	C(9)–C(10)–C(11)	120 (1)
C(3)–C(2)–C(7)	102·8 (7)	C(6)–C(11)–C(10)	119·0 (9)
C(5)–C(2)–C(7)	97·2 (6)	S–C(12)–C(13)	123·9 (7)
Cl(1)–C(3)–C(2)	111·2 (6)	S–C(12)–C(17)	117·4 (7)
Cl(1)–C(3)–C(4)	111·6 (6)	C(13)–C(12)–C(17)	118·6 (9)
C(2)–C(3)–C(4)	104·2 (7)	C(12)–C(13)–C(14)	121·1 (9)
C(1)–C(4)–C(3)	103·7 (7)	C(13)–C(14)–C(15)	118·4 (9)
C(2)–C(5)–C(6)	105·8 (7)	Cl(2)–C(15)–C(14)	118·3 (7)
C(2)–C(5)–C(8)	132·4 (8)	Cl(2)–C(15)–C(16)	119·7 (8)
C(6)–C(5)–C(8)	121·7 (8)	C(14)–C(15)–C(16)	122·0 (9)
C(1)–C(6)–C(5)	107·8 (7)	C(15)–C(16)–C(17)	120 (1)
C(1)–C(6)–C(11)	132·5 (8)	C(12)–C(17)–C(16)	119·7 (8)
C(5)–C(6)–C(11)	119·6 (8)		

Table 3. *Comparison of present molecule with four others containing a benzo*[8,9,10]*trinorbornene system*

See text for explanation. Starred atoms have numbering assigned in the Cambridge Crystallographic Data Centre (1982) files. (Positional e.s.d.'s for these crystal structures are not listed in the file.)

				Reference
(i) Present compound	C(1) *syn*	C(2) *syn*	2·0 (7)°	
(ii) 5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene	C(5) *anti*	C(8) *anti*	1·1 (7)°	(*a*)
(iii) π-(*exo*-2-Acetoxybenzo[8,9,10]-trinorbornenyl)-*exo*-tricarbonylchromium	C(4) *anti*	C(5) *anti*	2·9 (9)°	(*b*)
(iv) 5-(*p*-Bromophenyl)-7-oxo-1,4-diphenyl[2,3-*l*]phenanthrobicyclo[2.2.1]hept-2-ene benzene methanol solvate	C(11)* *syn*	C(14)* *anti*	7·8°	(*c*)
(v) 11-Fluorosulfonyl-7,8,12-trimethyltetracyclo[$7.4.0.0.^{2,7}.0^{4,8}$]-trideca-1(9),10,12-triene	C(1)* *anti*	C(7)* *syn*	2·1°	(*d*)

References: (*a*) Brown & Mason (1978). (*b*) Taylor, Griffith & Amma (1976). (*c*) Yasuda, Harano & Kanematsu (1980). (*d*) Coxon, Pojer, Robinson & Steel (1978).

Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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