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## 2-*exo*-Chloro-3-*endo*-(2-nitrophenylthio)-7,7-dimethylbicyclo[2.2.1]heptane, C<sub>15</sub>H<sub>18</sub>ClNO<sub>2</sub>S

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**Abstract.**  $M_r = 311.83$ , triclinic,  $P\bar{1}$ ,  $a = 7.3039$  (9),  $b = 7.9432$  (9),  $c = 13.4552$  (8) Å,  $\alpha = 95.92$  (1),  $\beta = 98.66$  (1),  $\gamma = 99.74$  (1)°,  $V = 753.9$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.374$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 3.90$  cm<sup>-1</sup>,  $F(000) = 328$ , room temperature,  $R = 0.037$  for 2430 observed reflections. The Cl atom is in an *exo* and the arylthio group in an *endo* orientation with respect to the norbornane framework, which has a synchro-twist conformation. Rather high twist angles are probably due to the additivity of the effects of substituents. The short intramolecular S...O distance of 2.643 (2) Å corresponds to a secondary interaction and the C—S...O unit is nearly linear.

**Introduction.** Interaction of sulfenyl chlorides with norbornene in solvents of low polarity usually proceeds as a *trans*-addition reaction *via* the *exo* attack of the electrophile. It is known, however, that the addition of C<sub>6</sub>H<sub>5</sub>SCl to 7,7-dimethyl-8,9,10-trinorbornene gives a product with an *endo* position for the C<sub>6</sub>H<sub>5</sub>S group (Brown & Liew, 1970). We have studied the addition of 2-nitrophenylsulfenyl chloride to 7,7-dimethyl-8,9,10-trinorbornene in various solvents and found several products with different configurations for the substituents. The structure of one such adduct [compound (I), obtained in hexane, m.p. 384–385 K] has been determined.

**Experimental.**  $D_m$  not measured. Crystal 0.3 × 0.3 × 0.2 mm. Unit cell: 24 reflections, 14 <  $\theta$  < 16°. Automatic four-circle Hilger & Watts diffractometer (Mo  $K\alpha$ , graphite monochromator,  $\theta/2\theta$  scan,  $\theta \leq 30^\circ$ ,  $h -10$  to 11,  $k -10$  to 11,  $l 0$  to 17). No absorption correction. Two standards, variation  $\pm 3\%$ . 3211 reflections measured, 2993 unique, 2430 independent with  $I \geq 2\sigma(I)$ , 530 unobserved.  $R_{int} \sim 3\%$ . Positions of Cl and S atoms from three-dimensional Patterson function. All other non-hydrogen atoms located in subsequent Fourier syntheses. Structure refined on  $F$  by full-matrix least-squares technique with anisotropic temperature factors. H atoms located in a difference

Fourier map and included in the refinement with isotropic temperature factors. Final  $R = 0.037$  and  $R_w = 0.036$ ;  $w = 1/\sigma^2(F)$ .  $(\Delta/\sigma)_{max} = 0.07$ . Max. and min. peaks on final  $\Delta\rho$  map 0.35 and 0.27 e Å<sup>-3</sup>. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations carried out with an Eclipse S/200 computer using the modified EXTL program package (Gerr, Yanovsky & Struchkov, 1983).

**Discussion.** The molecular geometry of (I) is shown in Fig. 1. Atomic coordinates and their equivalent isotropic temperature factors are listed in Table 1, and bond angles in Table 2; some characteristics of the planar parts of the molecule are given in Table 3.\*

According to the present structural investigation compound (I) may be unequivocally formulated as in the title. The Cl and S atoms in a molecule of (I) are

\* Lists of structure factors, anisotropic thermal parameters and Tables 3 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39476 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

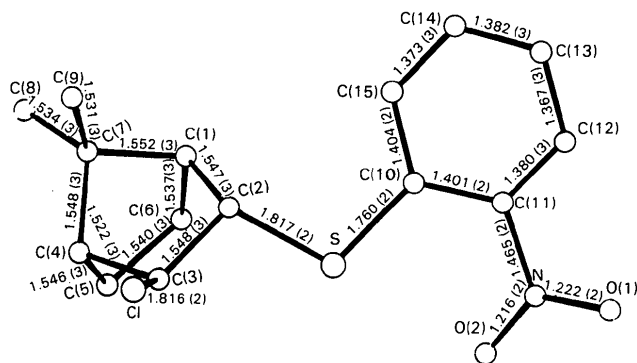


Fig. 1. The molecular structure of the title compound. (Distances in Å.)

Table 1. Fractional atomic coordinates ( $\times 10^5$  for Cl and S,  $\times 10^4$  for C, N, O,  $\times 10^3$  for H) and isotropic thermal parameters

$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$  for non-hydrogen atoms and  $B_{\text{iso}}$  for H atoms.

	x	y	z	$B_{\text{eq}}$ or $B_{\text{iso}}(\text{\AA}^2)$
Cl	-14973 (8)	58764 (9)	11537 (4)	5.51 (2)
S	25601 (7)	54104 (6)	31989 (4)	3.72 (1)
O(1)	2409 (3)	1952 (2)	5465 (2)	7.40 (7)
O(2)	3099 (2)	2635 (2)	4045 (1)	5.65 (5)
N	2692 (2)	2999 (2)	4874 (1)	4.40 (5)
C(1)	3203 (3)	8806 (2)	2536 (1)	3.39 (5)
C(2)	1767 (3)	7161 (2)	2591 (1)	3.19 (5)
C(3)	1055 (3)	6473 (3)	1455 (1)	3.90 (5)
C(4)	1924 (3)	7904 (3)	903 (1)	4.37 (6)
C(5)	3994 (3)	7672 (3)	958 (2)	5.20 (7)
C(6)	4857 (3)	8263 (3)	2082 (2)	4.48 (6)
C(7)	2138 (3)	9567 (3)	1654 (1)	4.11 (6)
C(8)	3307 (4)	11167 (3)	1352 (2)	5.96 (8)
C(9)	291 (3)	10083 (3)	1863 (2)	5.03 (7)
C(10)	2471 (2)	5967 (2)	4489 (1)	3.03 (4)
C(11)	2527 (2)	4780 (2)	5189 (1)	3.30 (5)
C(12)	2402 (3)	5204 (3)	6197 (2)	3.93 (5)
C(13)	2241 (3)	6834 (3)	6550 (1)	4.07 (6)
C(14)	2187 (3)	8044 (2)	5883 (1)	3.74 (5)
C(15)	2309 (3)	7632 (2)	4882 (1)	3.33 (5)
H(1)	358 (2)	955 (2)	317 (1)	3.2 (4)
H(2)	75 (2)	744 (2)	292 (1)	3.2 (4)
H(3)	146 (3)	538 (2)	127 (1)	3.9 (4)
H(4)	130 (3)	789 (2)	21 (2)	4.4 (4)
H(5.1)	404 (3)	649 (3)	79 (2)	5.9 (5)
H(5.2)	462 (3)	839 (3)	49 (2)	6.0 (5)
H(6.1)	590 (3)	926 (3)	213 (2)	5.4 (5)
H(6.2)	522 (3)	734 (3)	241 (1)	4.5 (4)
H(8.1)	445 (3)	1091 (3)	124 (2)	5.8 (5)
H(8.2)	274 (3)	1142 (3)	73 (2)	6.9 (6)
H(8.3)	368 (4)	1202 (3)	192 (2)	8.1 (7)
H(9.1)	-35 (4)	1036 (3)	123 (2)	7.7 (7)
H(9.2)	-58 (3)	919 (3)	209 (2)	6.3 (6)
H(9.3)	55 (4)	1106 (3)	240 (2)	7.8 (7)
H(12)	248 (3)	434 (2)	662 (1)	4.3 (4)
H(13)	213 (3)	709 (3)	724 (1)	4.3 (4)
H(14)	203 (3)	922 (3)	615 (2)	5.1 (5)
H(15)	225 (3)	847 (2)	442 (1)	3.8 (4)

displaced from the mean plane C(1)C(2)C(3)C(4) by  $-1.198$  (1) and  $1.251$  (1)  $\text{\AA}$  respectively, so that the Cl atom has an *exo* and the arylthio group an *endo* orientation with respect to the norbornane framework.

Owing to the steric strain caused by the presence of the substituents the norbornane framework acquires a somewhat twisted conformation, which according to the commonly used nomenclature (Altona & Sundaralingam, 1970) should be designated as synchro-twist  $S(+,+)$ . Such a conformation is evident from a comparison of the torsion angles in Table 4 (deposited):  $|\text{C}(7)-\text{C}(1)-\text{C}(2)-\text{C}(3)| > |\text{C}(7)-\text{C}(4)-\text{C}(3)-\text{C}(2)|$ ;  $|\text{C}(7)-\text{C}(1)-\text{C}(6)-\text{C}(5)| < |\text{C}(6)-\text{C}(5)-\text{C}(4)-\text{C}(7)|$ . The difference between torsion angles  $|\text{C}(7)-\text{C}(1)-\text{C}(2)-\text{C}(3)|$  and  $|\text{C}(7)-\text{C}(4)-\text{C}(3)-\text{C}(2)|$  in molecule (I) is  $13.0$  (2) $^\circ$ ; although its average value in a number of similar structures studied earlier [see, for example, Newton, Pantaleo, Kirbawy & Allinger (1978) and Ferrier, Prasit, Gainsford & Le Page (1983)] is  $\approx 5^\circ$ . It should be noted, however, that in the structure of 3-[(*N*-methyl)benzylaminomethyl]-8,9,10-trinorbornan-2-ol, analogous to (I) and having one *exo* and one *endo* substituent (Fratini, Britts & Karle, 1967), the difference in the torsion angles is as large as

Table 2. Bond angles ( $^\circ$ )

Cl-C(3)-C(2)	112.5 (1)	C(2)-C(1)-C(6)	108.3 (2)
Cl-C(3)-C(4)	115.0 (1)	C(2)-C(1)-C(7)	101.3 (1)
C(2)-C(3)-C(4)	103.9 (2)	C(6)-C(1)-C(7)	102.7 (2)
S-C(2)-C(1)	119.7 (1)	C(1)-C(6)-C(5)	103.1 (2)
S-C(2)-C(3)	107.3 (1)	C(3)-C(4)-C(5)	103.8 (2)
C(1)-C(2)-C(3)	102.0 (1)	C(4)-C(5)-C(6)	103.4 (2)
C(2)-S-C(10)	104.1 (1)	C(3)-C(4)-C(5)	103.9 (2)
S-C(10)-C(11)	122.5 (1)	C(3)-C(4)-C(7)	104.3 (2)
S-C(10)-C(15)	122.0 (1)	C(5)-C(4)-C(7)	101.8 (2)
C(11)-C(10)-C(15)	115.5 (2)	C(1)-C(7)-C(4)	92.9 (3)
C(10)-C(11)-C(12)	122.7 (2)	C(1)-C(7)-C(8)	113.6 (2)
C(10)-C(11)-N	120.8 (2)	C(4)-C(7)-C(8)	114.4 (2)
C(12)-C(11)-N	116.5 (2)	C(1)-C(7)-C(9)	114.4 (2)
C(11)-C(12)-C(13)	120.2 (2)	C(4)-C(7)-C(9)	115.6 (2)
C(12)-C(13)-C(14)	118.8 (2)	C(8)-C(7)-C(9)	106.1 (2)
C(13)-C(14)-C(15)	121.1 (2)	O(1)-N-O(2)	123.4 (2)
C(10)-C(15)-C(14)	121.7 (2)	O(1)-N-C(11)	117.8 (2)
		O(2)-N-C(11)	118.8 (2)

$14$  (1) $^\circ$ . As was suggested (Altona & Sundaralingam, 1970) such strong twisting can be accounted for by additivity of the twisting effects of the substituents.

The intramolecular non-bonded S...O(2) distance of  $2.643$  (2)  $\text{\AA}$  is significantly shorter than the sum ( $3.30$   $\text{\AA}$ ) of the van der Waals radii (Bondi, 1964) and evidently corresponds to a secondary interaction. The C(2)-S...O(2) unit is nearly linear; the relevant 'pseudo' bond angle is  $170.3$  (1) $^\circ$ . Although, in general, the distances typical for S...O secondary bonds vary within a wide range of  $2.03$ – $2.80$   $\text{\AA}$ , in compounds similar to (I) the analogous distances do not differ significantly, *viz.*  $2.694$  (2)  $\text{\AA}$  in 3-*exo*-methoxy-5-*exo*-(2-nitrophenylthio)tricyclo[2.2.1.0<sup>2,6</sup>]heptane (Garratt, Przybylska & Cygler, 1983) and  $2.739$  (2)  $\text{\AA}$  in 1-chloromethyl-3-*endo*-(2,4-dinitrophenylthio)tricyclo[2.2.1.0<sup>2,6</sup>]heptane (Przybylska & Garratt, 1981) and are close to that found in (I).

The benzene ring is almost exactly planar [ $\Delta_{\text{max}}$  C(15) =  $-0.005$  (2)  $\text{\AA}$ ]; the deviations of the S and N atoms from its mean plane are  $0.043$  (1) and  $0.010$  (2)  $\text{\AA}$ . The C(2)SC(10) plane forms dihedral angles of  $15.3$  and  $119.7^\circ$  with the benzene ring and the C(1)C(2)C(3)C(4) plane respectively.

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