Fig. 1. A perspective view of the centrosymmetric di-μ-chloro-bis[chloro(1,2-cyclohexanedione dioxime)copper(II)] complex with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, H atoms as small spheres with a radius of 0·1 Å.

Table 3. *Comparison of geometries of the* Cu_2X_2 *cores in di-μ-halo-bis[halo(α,β-dione dioxime)copper(II)] dimers (lengths in Å, angles in deg)*

Ligand	X	(1)	(2)	(3)	(4)	X–X'
a	Cl	2·24	2·70	88	3·445	3·57
a	Br	2·387	2·883	85·59	3·599	3·881
b	Br	2·358	3·427	78·1	3·737	4·544
c	Cl	2·252	2·822	87·4	3·530	3·690

Ligands and references: (a) 2,3-Butanedione dioxime. X = Cl: Svedung (1969). X = Br: Endres (1978). (b) Diphenylethanedione dioxime: Endres, Andoseh & Mégnamisi-Bélombé (1981). (c) 1,2-Cyclohexanedione dioxime: this work.

distorted square pyramid. The two halide ions and the two oxime N atoms form the base, whilst a halide ion of the adjacent monomer occupies the apical position. In the title compound the cyclohexane ring of the dioxime ligand adopts a twisted conformation.

Interdimer H bonding occurs with distances H(2)–O''(1) = 2·51 (3), O(2)–O''(1) = 3·032 (4) Å, where O''(1) is generated from the O(1) position of Table 1 by the symmetry operation x,y,z − 1.

Possible magnetic interactions are primarily determined by the geometry of the structural core Cu_2X_2 in which the angle Cu—X—Cu is of crucial importance. For the four [CuX₂(α,β-Hdodo)]₂ structures determined so far, data characteristic of this core are compared in Table 3. The connection between magnetic properties and this structural feature has recently been discussed by Marsh, Hatfield & Hodgson (1982).

The CuBr₂ adduct of nioxime, however, has a different structure where dimerization occurs via bridging O atoms (Mégnamisi-Bélombé & Endres, 1983).

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10-Chlorophenothiantimonin, C₁₂H₈ClSSb

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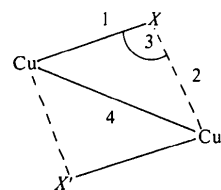
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Abstract. $M_r = 341·5$, orthorhombic, *Pnma*, $a = 9·973$ (2), $b = 10·833$ (2), $c = 11·144$ (3) Å, $V = 1204·03$ (3) Å³, $Z = 4$, $D_x = 1·88$ g cm⁻³, λ(Mo Kα) = 0·71073 Å, $\mu = 26·6$ cm⁻¹, $F(000) = 656$, $T = 294$ K. Final $R = 0·025$ for 969 observed reflections. This is the first structure report of a heterocyclic molecule

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involving antimony in the disubstituted-anthracene system. The exocyclic Cl atom is in a quasi-equatorial position, in contrast to the corresponding arsenic heterocycles. The Sb—Cl distance is 2·390 (2) Å, the Sb—C and S—C distances are 2·141 (4) and 1·775 (5) Å and the C—Sb—C, C—Sb—Cl and C—S—C bond angles are 89·8 (2), 94·6 (1) and 100·2 (2)°, respectively. The folded molecule is bisected by a lattice-imposed mirror plane, and the dihedral angle between the C_6H_4SbS planes is 112·14 (6)°.

Introduction. Structural reports of heterocyclic molecules involving a Group VI element (X) and a Group V element (Y) of template (I) (Fig. 1a) have included a number of substituted phenothiazines ($X = $ S, $Y-Z = $ N—R) which are of interest because of their chemotherapeutic activity [see Chu & van der Helm (1975) and Malmstrom & Cordes (1972) and references therein], and several arsenic compounds: $X = $ O, $Y-Z = $ As—Cl (Stuckey, Cordes, Handy, Perry & Fair, 1972), $X = $ O, $Y-Z = $ As—S— (Grindstaff, Cordes, Fair, Perry & Handy, 1972), and $X = $ S, $Y-Z = $ As—Cl (Pennington, Cordes, Graham & Jung, 1983). Structural data for a variety of heterocyclic molecules of template (I) allow conclusions on the extent of the bonding of the X and Y atoms with the π system of the phenylene groups, as well as information on the isomer stereochemistry at the Y atom (the two possible isomers are shown in Fig. 1b and c). The subject of this report provides the first structural data for a molecule of type (I) which contains an Sb atom ($Y-Z = $ Sb—Cl), and the first example of a template (I) molecule in the isomeric form shown in Fig. 1(c).

Experimental. Title crystal prepared by reaction of $SbCl_3$ with corresponding dimethyltin heterocycle according to general procedure described by Meinema, Romao & Noltes (1973), suitable crystals obtained by slow cooling of a CCl_4 solution; colorless parallelepiped crystal used for data collection had dimensions 0·19 × 0·22 × 0·32 mm, mounted with epoxy on a glass fiber; all data collected using an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 25 reflections with 2θ between 22 and 27° used for a least-squares determination of cell constants given above; a total of 1252 unique reflections measured using θ–2θ scans for 2θ from 2 to 50° ($h = 0$ to -11, $k = 0$ to 12, $l = 0$ to 13), scan range (0·8° + 0·35° tan θ), scan speeds varied from 2 to

20°min^{-1}; intensities of four reflections ($\overline{2}6\overline{1}$, $3\overline{3}5$, $\overline{4}3\overline{3}$ and $6\overline{2}2$) measured periodically during data collection varied less than 2·6% and thus indicated crystal and electronic stability; 277 reflections had $I \le 3 \sigma (I)$ and considered unobserved; systematic absences of $0kl$ for $k + l$ odd and $hk0$ for h odd indicate space group $Pna2_1$ or space group $Pnma$; statistical tests of intensity distribution of data set indicated a centrosymmetric space group, and subsequent successful refinement in $Pnma$ confirmed centrosymmetric choice; structure solved by direct methods using $MULTAN78$ (Main, Hull, Lessinger, Declercq, Germain & Woolfson, 1978) followed by Fourier and least-squares techniques; the asymmetric unit consists of one half of one molecule: the molecule is located on a crystallographic mirror plane which includes the S, Sb and Cl atoms; final full-matrix least-squares refinement based on $(|F_o| - |F_c|)^2$ included 89 parameters (positional and anisotropic thermal parameters for all non-H atoms and positional and isotropic thermal parameters for all H atoms) for a parameter/reflection ratio of 1:10·9; no absorption or secondary-extinction corrections made; six reflections (004, 001, -221, 020, 031, 040) removed because of strong evidence of extinction problems; final $wR = 0·027$, $S = 1·19$, weighting scheme of unit weights gave no systematic variation of $\Delta F/\sigma (F)$ as a function of either F or sin θ; in final cycle of refinement maximum shift/error 0·66; final difference map had a maximum value of $0·50 e \text{ Å}^{-3}$; atomic scattering factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs used were those of Enraf–Nonius (1979) SDP program package.

Discussion. Table 1 gives atom coordinates and B values for the atoms, and Table 2 gives derived distances and angles. Fig. 2 presents a general view of the molecule showing the atom-numbering scheme used as well as two special views of the molecule, and Fig. 3 is a stereoview showing the crystal packing.*

The structure of 10-chlorophenothiantimonin is not only the first structure of a heterocyclic molecule of template (I) containing an Sb atom, but is the first type (I) molecule which has the exocyclic atom in the 'equatorial' position, *i.e.* inside the fold angle of the molecule (Fig. 1c). The three arsenic-containing heterocyclic molecules described and referenced in the *Introduction* all were found to have the exocyclic atom in the 'axial' position, or outside the fold angle (Fig. 1b). There are significant differences in the structural features of the present antimony compound with its equatorial chlorine and the arsenic axial molecules: The antimony molecule has a dihedral angle between the
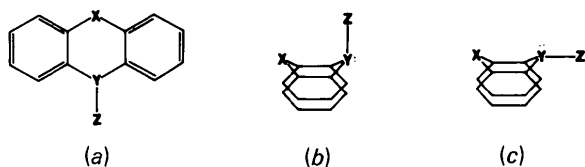
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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38402 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. (a) Template (I). (b) Axial isomer. (c) Equatorial isomer.

Table 1. *Final fractional coordinates and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}*/B_{iso}(\text{Å}^2)$
Sb	0·89793 (4)	0·25	0·22921 (4)	3·705 (8)
S	1·0248 (2)	0·25	0·4885 (2)	5·07 (4)
Cl	0·9682 (2)	0·25	0·0241 (2)	5·24 (4)
C(1)	1·0374 (4)	0·3894 (4)	0·2835 (4)	3·45 (8)
C(2)	1·0830 (4)	0·3757 (4)	0·4006 (4)	3·76 (8)
C(3)	1·1719 (5)	0·4630 (5)	0·4486 (4)	5·0 (1)
C(4)	1·2151 (5)	0·5584 (5)	0·3796 (5)	6·0 (1)
C(5)	1·1716 (6)	0·5713 (4)	0·2624 (5)	5·9 (1)
C(6)	1·0821 (5)	0·4880 (4)	0·2148 (4)	4·6 (1)
H(C3)	1·192 (4)	0·446 (4)	0·527 (3)	4·2 (9)
H(C4)	1·270 (5)	0·629 (5)	0·415 (5)	8 (1)
H(C5)	1·213 (5)	0·649 (5)	0·213 (5)	8 (1)
H(C6)	1·047 (4)	0·501 (5)	0·126 (4)	6 (1)

$$* B_{eq} = \tfrac{8}{3} \pi^2 (U_{11} + U_{22} + U_{33}).$$

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

|			
Sb—Cl	2·390 (2)	C(5)—C(6)	1·376 (7)
Sb—C(1)	2·141 (4)	C(1)—C(6)	1·388 (6)
S—C(2)	1·775 (5)	C(3)—H(C3)	0·92 (3)
C(1)—C(2)	1·390 (6)	C(4)—H(C4)	1·02 (5)
C(2)—C(3)	1·402 (7)	C(5)—H(C5)	1·09 (5)
C(3)—C(4)	1·358 (7)	C(6)—H(C6)	1·07 (4)
C(4)—C(5)	1·383 (8)	Sb···S	3·154 (2)
Cl—Sb—C(1)	94·6 (1)	C(4)—C(5)—C(6)	120·1 (5)
C(1)—Sb—C(1')	89·8 (2)	C(1)—C(6)—C(5)	120·0 (4)
C(2)—S—C(2')	100·2 (2)	C(2)—C(3)—H(C3)	111 (2)
Sb—C(1)—C(2)	113·7 (3)	C(4)—C(3)—H(C3)	129 (2)
Sb—C(1)—C(6)	126·5 (3)	C(3)—C(4)—H(C4)	121 (3)
C(2)—C(1)—C(6)	119·7 (4)	C(5)—C(4)—H(C4)	117 (3)
S—C(2)—C(1)	119·5 (3)	C(4)—C(5)—H(C5)	116 (3)
S—C(2)—C(3)	120·9 (3)	C(6)—C(5)—H(C5)	124 (3)
C(1)—C(2)—C(3)	119·5 (4)	C(1)—C(6)—H(C6)	121 (3)
C(2)—C(3)—C(4)	119·8 (5)	C(5)—C(6)—H(C6)	119 (3)
C(3)—C(4)—C(5)	120·8 (5)	S···Sb—Cl	139·31 (4)
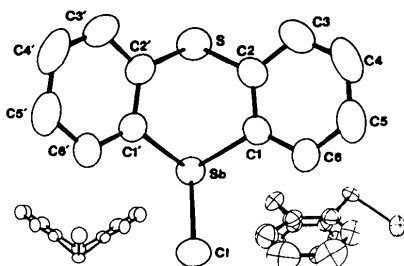
Fig. 2. Atom numbering and special views of the title compound.
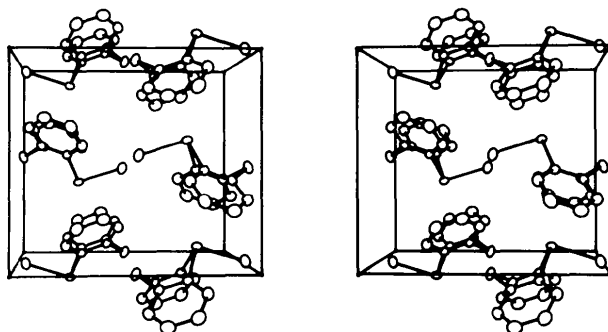
Fig. 3. Stereoview of the molecular packing. The x axis is vertical, the z axis horizontal, and the origin is in the rear, lower, left-hand corner.

two C_6H_4SbS planes (planar to within 0·03 Å) of 112·14 (6)° while the arsenic molecules are much less folded with dihedral angles of 152–178°; the cross-ring S···Sb distance is 3·154 (2) Å compared to the S···As distances of 3·4–3·5 Å; the X—C—C internal angles of the central ring are 113·7 and 119·5° for the antimony molecule while they are consistently larger than 120° (120–126°) for the arsenic molecules; and, the C—S bonds are somewhat longer and the C—S—C bond angle is 7° smaller for the antimony compound compared to the $X = S$, Y—Z = As—Cl molecule.

Some, but certainly not all, of these significant differences are due to the smaller (89·8 vs 94–100°) C—Y—C angles formed by the Sb atom. It appears, however, the bulk of the changes in the central-ring parameters for the antimonin vs the arsenins is associated with the different position for the exocyclic atom (Fig. 1b and c). The only other structure report of a type (I) molecule for a Group V heterocycle with an equatorial exocyclic substituent is a preliminary communication on a molecule with two As—Me groups (Kennard, Mann, Watson, Fawcett & Kerr, 1968). This latter molecule, like the antimony molecule and in contrast to the other arsenic molecules, also possesses short As···As cross-ring distances, central ring As—C—C angles of less than 120°, and a small dihedral angle of 117°. Future structures of other molecules of template (I) containing antimony and (especially) phosphorus will be of interest to provide more data on these interesting structural differences for the two isomeric forms.

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