# The Stereochemistry of Dithiolan Rings.   An X-Ray Study of 2-Chloro-1,3-dithia-2-stibacyclopentane

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Although there have been recent structural investigations of dithiolate complexes[1-3] (where the ring systems are planar due to delocalized π-bonding between the sulphur and carbon atoms, S–C–C–S), nothing has hitherto been published on the configuration of saturated systems of the type

$$X—M\Big\langle{{S—CH_2}\atop{S—CH_2}}$$
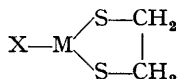
(where M represents an element from Group V and X is a univalent substituent). We have therefore undertaken a single-crystal X-ray study of 2-chloro-1,3-dithia-2-stibacyclopentane   (M = Sb; X = Cl), crystals of which were kindly supplied to us by Dr. E. W. Abel of this Department.

Crystal data: $ClSbS_2(CH_2)_2$, $M = 249\cdot4$, *monoclinic*, $a = 6\cdot94$, $b = 10\cdot05$, $c = 9\cdot27$ Å, $\beta = 100°$ $52'$, $U = 635\cdot0$ Å^3, $D_m = 2\cdot57$ g. cm.$^{-3}$, $Z = 4$, $D_c = 2\cdot61$ g. cm.$^{-3}$, space group $P2_1/a$.

The structure has been solved by the usual combination of successive Fourier syntheses and least-squares refinement based on 884 independent non-zero reflections, and refined to an R-value of $8\cdot6\%$. Crystallographic details will be published elsewhere, but of immediate interest is our finding that the ring is markedly non-planar (see Figure).

The unit cell contains four molecules, two of which are mirror-images of the other two. It may well be that the ring configuration is labile in solution, but its non-planarity is of considerable relevance to the interpretation of the n.m.r. spectra of this and similar compounds.[4] The Figure shows one molecule of each kind present in the crystal; important bond lengths and angles are:—

Sb–Cl, $2\cdot46 \pm 0\cdot01$ Å; Sb–S$_1$, $2\cdot40 \pm 0\cdot01$ Å; Sb–S$_2$, $2\cdot41 \pm 0\cdot01$ Å; S$_1$–C$_1$, $1\cdot84 \pm 0\cdot02$ Å; S$_2$–C$_2$, $1\cdot84 \pm 0\cdot02$ Å; C$_1$–C$_2$, $1\cdot49 \pm 0\cdot03$ Å; $\angle$Cl–Sb–S$_1$, $94\cdot9 \pm 0\cdot2°$; $\angle$Cl–Sb–S$_2$, $98\cdot0 \pm 0\cdot2°$; $\angle$Sb–S$_1$–C$_1$, $100\cdot3 \pm 0\cdot7°$; $\angle$Sb–S$_2$–C$_2$, $96\cdot2 \pm 0\cdot8°$ $\angle$S$_1$–C$_1$–C$_2$, $111\cdot2 \pm 1\cdot6°$; $\angle$S$_2$–C$_2$–C$_1$, $111\cdot6 \pm 1\cdot7°$.
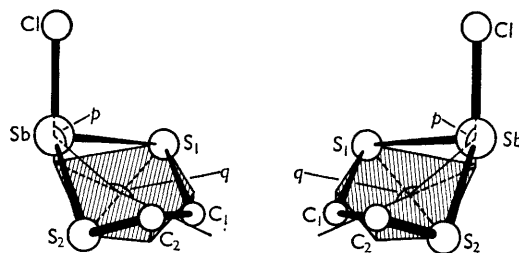
The errors quoted are estimated standard deviations from the block diagonal least-squares refinement programme.[5]

A convenient way of viewing the structure is to imagine a "hinge" along the S_1–S_2 line between the Sb–S_1–S_2 plane and the plane defined by S_1, S_2, and the mid-point of C_1–C_2; the two carbon atoms, of course, show equal and opposite deviations (of $\sim$0·4 Å) from the latter plane. The dihedral angle q between these two planes is 168°, and the angle p between the Sb–Cl bond and the line joining Sb to the midpoint of S_1–S_2 is 99°. It is interesting to note that the Sb, S_1, S_2, and C_1 atoms are nearly coplanar, the atom C_1 deviating by only 0·1 Å from the plane defined by the Sb–S bonds. The small difference between the angles Cl–Sb–S_1 and Cl–Sb–S_2 can probably be ascribed to weak dipolar interactions in the crystal between Sb–Cl bonds in different molecules, as the crystal packing is such as to make these bonds nearly antiparallel.

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