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STRUCTURE ANALYSIS OF TRIARYL DERIVATIVES OF THE GROUP V ELEMENTS. CRYSTAL AND MOLECULAR STRUCTURE OF TRI-*p*-TOLYLANTIMONY, $C_{21}H_{21}Sb$

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Summary

An X-ray structure analysis of tri-*p*-tolylantimony has been made. Crystals are rhombohedral, a 9.988 Å, α 79.77°, $Z = 2$, space group $R\bar{3}$. Final value of R is 0.024 after full-matrix least squares refinement. The valence angle C—Sb—C, 97.3°, is in good accordance with values for triaryl derivatives of other Group V elements

Introduction

The physicochemical properties (e.g. spectral) of the triaryl derivatives of Group V elements are, to a great extent, dictated by the value of the valence angle at the heteroatom. The C—Sb—C angle for triaryl derivatives of antimony, from published analyses, has very discrepant values from 113° [1] to 94° [2]. Until now the X-ray investigations of triarylantimony derivatives had not been undertaken. In order to obtain more complete and detailed data on such structures we have performed the X-ray structure analysis of tri-*p*-tolylantimony, $C_{21}H_{21}Sb$.

Results

X-ray data collection

A rhombohedral crystal with dimensions 0.16 × 0.16 × 0.13 mm was chosen for data collection. Crystals are trigonal, space group $R\bar{3}$, a 12.806(3) Å, c 20.129(6) Å, $V = 2859$ Å^3, D_c 1.38 g cm^{-3}, $Z = 6$ (for rhombohedral setting the lattice parameters are: a 9.988 Å, α 79.77°, V 953 Å^3, $Z = 2$), $F(000) = 1188$. Solution and refinement were based on 817 unique reflections ($I \geqslant 3\sigma(I)$) measured with a Syntex P$\bar{1}$ automatic four-circle diffractometer using graphite crystal monochromated Mo—K_α radiation, $\theta/2\theta$ scan technique to S_{max} 0.59 Å^{-1}.

TABLE 1

ATOMIC COORDINATES AND THERMAL PARAMETERS ($\times 10^3$). ANISOTROPIC THERMAL PARAMETERS LISTED ACCORDING FOLLOWING SCHEME: $T = exp\{-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2(hka^*b^*)U_{12} + 2(hla^*c^*)U_{13} + 2(klb^*c^*)U_{23}]\}$

Atom	X	Y	Z	U/U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0.0	0.0	0.18833(3)	81.3(3)	81.3	54.3(3)	40.6	0	0
C(1)	0.1159(3)	0.1625(3)	0.1353(2)	67(2)	67(2)	61(2)	38(2)	−7(2)	−11(2)
C(2)	0.0814(3)	0.1997(3)	0.0791(2)	68(2)	74(3)	64(2)	34(2)	−12(2)	−10(2)
C(3)	0.1576(4)	0.3075(4)	0.0486(2)	80(3)	82(3)	65(2)	49(2)	−5(2)	2(2)
C(4)	0.2725(3)	0.3833(3)	0.0728(2)	68(3)	64(2)	92(3)	38(2)	5(2)	0(2)
C(5)	0.3063(3)	0.3463(4)	0.1281(2)	61(3)	83(3)	107(4)	34(2)	−20(2)	−8(3)
C(6)	0.2310(4)	0.2386(4)	0.1591(2)	74(3)	81(3)	80(3)	43(2)	−16(2)	0(2)
C(7)	0.3583(5)	0.5022(4)	0.0406(3)	110(4)	93(4)	143(5)	49(3)	18(3)	24(3)
H(2)	0.319(6)	0.530(6)	0.011(4)	63(15)					
H(3)	0.135(3)	0.330(3)	0.009(2)	63(14)					
H(5)	0.379(4)	0.393(4)	0.145(2)	97(18)					
H(6)	0.254(4)	0.212(4)	0.198(2)	70(15)					
H(71)	0.319(6)	0.530(6)	0.011(4)	155(27)					
H(72)	0.386(5)	0.490(5)	0.007(3)	146(26)					
H(73)	0.372(6)	0.557(6)	0.071(4)	174(28)					

The data were corrected for Lorentz and polarization effects (using the program FOCAL written by us in FORTRAN IV for the EC-1022 computer) but not for absorption and extinction, as this was considered unnecessary ($\mu/\rho = 11.3$).

Structure determination and refinement

The lattice parameters obtained were very similar to those found for the previously solved structure of tri-*p*-tolylarsine [3]. Using these circumstances we brought the coordinates of Sb to conformity with a chosen H-setting on axis 3. All calculations were performed using the crystallographic programs complex "X-RAY-72" [4] adapted by us in the limits of DOS/EC, a system for use on a EC-1022 computer at the Karpov Institute. The coordinates of the carbon atoms were found by experimental Fourier synthesis, the coordinates of the hydrogen atoms were found partly geometrically (phenyl rings), partly by difference syntheses (methyl groups) after two steps of refinement. The successive refinement of the structure was performed by anisotropic full-matrix least squares method using anomalous scattering [5] of the Sb atom through the whole data set. The final *R*-value was 0.024. The scattering factors for Sb and C were taken from the literature [6], as were the values used for H [7]. Final positional and thermal parameters of atoms with their e.s.d.'s are given in Table 1.

Discussion

The molecule is situated on the axis 3, it has pyramidal shape (Fig. 1) and as a whole it loses its own pseudosymmetry C_{3v}. The bond distances and valence angles determined are given in Table 2. The value of Sb—C, 2.141 Å, falls within the limits 2.032—2.216 Å found in organoantimony structures [e.g. 8—11].

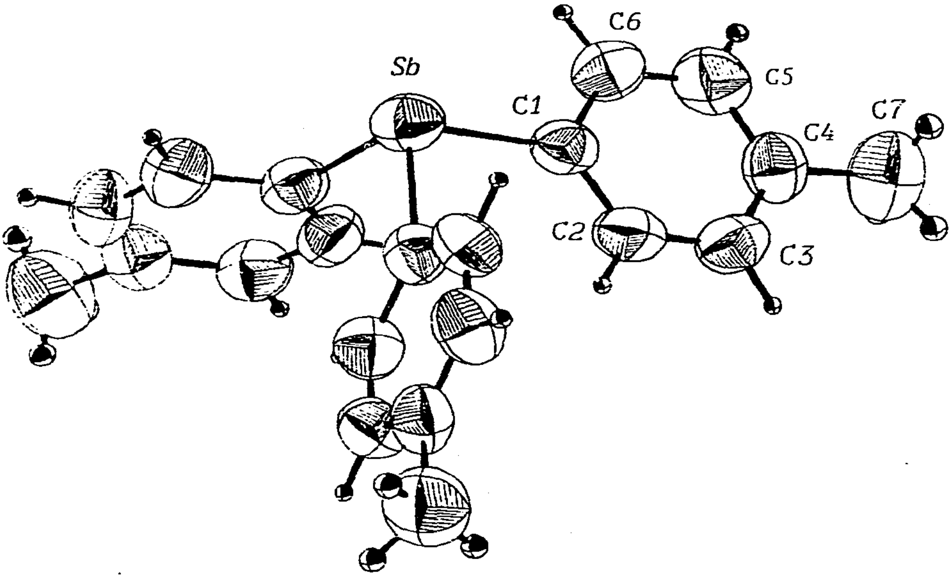

Fig. 1. ORTEP diagram of $C_{21}H_{21}Sb$

TABLE 2

INTERATOMIC DISTANCES (d) AND VALENCE ANGLES (ω)

Bond	d (Å)	Angle	ω (°)
Sb—C(1)	2.141(3)	C(1)SbC(1')	97.3(1)
C(1)—C(2)	1.383(5)	C(6)C(1)C(2)	116.9(3)
C(2)—C(3)	1.374(6)	C(1)C(2)C(3)	121.6(3)
C(3)—C(4)	1.384(5)	C(2)C(3)C(4)	121.3(3)
C(4)—C(5)	1.362(5)	C(3)C(4)C(5)	117.1(3)
C(5)—C(6)	1.375(6)	C(4)C(5)C(6)	122.3(3)
C(6)—C(1)	1.384(5)	C(5)C(6)C(1)	120.1(3)
C(4)—C(7)	1.508(6)	SbC(1)C(2)	123.9(2)
C(2)—H(2)	0.87(4)	SbC(1)C(6)	119.2(3)
C(3)—H(3)	0.94(4)	C(3)C(4)C(7)	122.6(3)
C(5)—H(5)	0.88(4)	C(5)C(4)C(7)	120.3(3)
C(6)—H(6)	0.96(4)		
C(7)—H(71)	0.95(6)		
C(7)—H(72)	0.81(6)		
C(7)—H(73)	0.88(7)		

The structural parameters of the phenyl ring correspond to the normal ones. The methyl atom C(7) practically lies in the plane of the phenyl ring whereas the Sb atom is significantly out of it (Table 3). The angle between the planes of phenyl rings is 90.08°, each of these planes forms an angle of 54.8° with the C(1)—C(1')—C(1") plane. Intermolecular distances correspond to normal Van der Waals interactions.

The value of valence angle C—Sb—C found in this investigation is in good accordance with the values determined for other triphenyl derivatives of Group V elements. Together with the increase in the covalent radius of the hetero-atom: N(0.70), P(1.10), As(1.21), Sb(1.41), Bi(1.47) Å [12], the value of this angle decreases in the same sequence: 116, 109, 102, 97, 94° [3,13—16]. Simultaneously, the long wavelength band in the UV spectra of the compounds XPh_3 [where X = N(297 nm), P(261 nm), As(248 nm), Sb(256 nm), Bi(248—250 nm)] is shifted to a shorter wavelength. We suggest that this is connected with the less favourable conditions for π-overlapping and a decrease in valence

TABLE 3

ATOMIC DEVIATIONS FROM LEAST-SQUARES PLANE THROUGH BENZENE RING (C(1)—C(6))

Plane equation: $-0.6761X + 0.4558Y + 0.5765Z = 2.0950$

Atom	Deviation (Å)
Sb	—0.090
C(1)	0.001 [a]
C(2)	0.001 [a]
C(3)	0.000 [a]
C(4)	0.000 [a]
C(5)	0.000 [a]
C(6)	0.001 [a]
C(7)	—0.003

[a] Atoms used for plane calculation.

angle and an increase in *s*-character in the undivided electron pair orbital of the heteroatom.

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