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STRUCTURE ANALYSIS OF TRIARYL DERIVATIVES OF THE GROUP V ELEMENTS

III *. MOLECULAR STRUCTURE AND SPECTRA OF TRIS(2,6-DIMETHYLPHENYL)STIBINE, $C_{24}H_{27}Sb$

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Summary

X-Ray structure analysis, dipole moment measurement and electronic spectra investigation have been carried out on tris(2,6-dimethylphenyl)stibine. Crystals are monoclinic, a 15.873 Å, b 16.204 Å, c 8.246 Å, γ 103.29°, $Z = 4$, space group $P2_1/b$. The mean value of valence angle C—Sb—C is 104.7°; that of the Sb—C bonds 2.190 Å. The molecular conformation is governed by steric effects due to the methyl groups. The dipole moment is 0.62 D.

Introduction

The structure and physico-chemical properties of triaryl derivatives of the Group V elements depend, to a great extent, on the phenyl ring substituents. The introduction of two methyl groups in *ortho* positions on each phenyl ring of, e.g., triphenylphosphine results in a significant increase of the P atoms valence angle (C—P—C): 103° in triphenylphosphine [1], and 109.5° in tris-(2,6-dimethylphenyl)phosphine (TDPP) [2] and trimesitylphosphine (TMP) [3]. Corresponding significant variations may be seen in the electronic spectra [4] and dipole moments [5] of such molecules. It was of interest to find out whether this situation is valid for triaryl derivatives of other Group V elements. In this paper the complete X-ray structure analysis and the measurement of electronic spectra and dipole moment of tris(2,6-dimethylphenyl)stibine (TDPS) are reported.

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* Part I see ref. 12; Part II see ref. 13.

TABLE 1

FINAL ATOMIC COORDINATES WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	*X*	*Y*	*Z*
Sb	0.69949(2)	0.28473(2)	0.44646(4)
C(11)	0.7793(3)	0.3845(3)	0.2966(6)
C(12)	0.8295(3)	0.3527(3)	0.1838(6)
C(13)	0.8824(4)	0.4072(4)	0.0802(7)
C(14)	0.8861(4)	0.4928(4)	0.0822(8)
C(15)	0.8352(4)	0.5239(3)	0.1894(8)
C(16)	0.7815(3)	0.4709(3)	0.2992(6)
C(17)	0.8279(4)	0.2593(4)	0.1706(8)
C(18)	0.7324(4)	0.5129(3)	0.4173(8)
C(21)	0.8008(3)	0.2593(3)	0.6057(6)
C(22)	0.7881(4)	0.1739(3)	0.6542(7)
C(23)	0.8560(4)	0.1476(4)	0.7293(7)
C(24)	0.9341(4)	0.2014(4)	0.7579(8)
C(25)	0.9449(4)	0.2847(4)	0.7151(8)
C(26)	0.8806(3)	0.3155(3)	0.6408(7)
C(27)	0.7041(4)	0.1100(4)	0.6277(9)
C(28)	0.8977(4)	0.4094(4)	0.6063(8)
C(31)	0.6134(3)	0.3462(3)	0.5858(7)
C(32)	0.5457(4)	0.3633(3)	0.4921(7)
C(33)	0.4810(4)	0.3931(4)	0.5679(9)
C(34)	0.4829(4)	0.4064(4)	0.7319(9)
C(35)	0.5484(4)	0.3896(4)	0.8236(7)
C(36)	0.6146(4)	0.3580(3)	0.7531(7)
C(37)	0.5407(4)	0.3509(4)	0.3106(8)
C(38)	0.6833(5)	0.3391(5)	0.8618(8)
H(13)	0.912(3)	0.391(3)	0.013(7)
H(14)	0.917(3)	0.530(3)	0.008(7)
H(15)	0.837(4)	0.576(3)	0.193(7)
H(171)	0.867(4)	0.253(4)	0.088(9)
H(172)	0.775(4)	0.229(4)	0.134(8)
H(173)	0.840(4)	0.238(4)	0.263(9)
H(181)	0.763(4)	0.561(4)	0.442(9)
H(182)	0.677(4)	0.511(4)	0.385(8)
H(183)	0.735(4)	0.488(4)	0.519(9)
H(23)	0.850(4)	0.099(3)	0.758(7)
H(24)	0.977(4)	0.177(4)	0.808(7)
H(25)	0.988(3)	0.314(3)	0.743(7)
H(271)	0.710(5)	0.070(4)	0.691(9)
H(272)	0.702(4)	0.092(4)	0.529(9)
H(273)	0.658(4)	0.132(4)	0.651(9)
H(281)	0.938(5)	0.433(4)	0.672(9)
H(282)	0.923(4)	0.421(4)	0.507(9)
H(283)	0.847(4)	0.434(4)	0.614(8)
H(33)	0.440(3)	0.405(3)	0.508(7)
H(34)	0.443(4)	0.430(4)	0.775(7)
H(35)	0.550(3)	0.398(3)	0.924(7)
H(371)	0.495(5)	0.366(4)	0.269(8)
H(372)	0.531(4)	0.297(4)	0.287(8)
H(373)	0.588(5)	0.384(4)	0.260(8)
H(381)	0.688(4)	0.361(4)	0.955(9)
H(382)	0.672(4)	0.287(5)	0.882(8)
H(383)	0.738(4)	0.374(4)	0.814(9)

Results

X-ray data collection

A single crystal of TDPS with dimensions 0.15 × 0.15 × 0.15 mm was obtained from ethanol solution by evaporation. The unit cell parameters, determined using a Syntex P$\bar{1}$ automatic four-circle diffractometer, are: a 15.873(5) Å, b 16.204(3) Å, c 8.246(2) Å, γ 103.29(1)°, V 2065 Å^3, D_c 1.41 g cm^{-3}, $Z = 4$, space group $P2_1/b$ (C_{2h}^5), $F(000)$ 888 e. Solution and refinement were based on 1940 independent reflections, 1747 of which had $I \geqslant 3\sigma(I)$, measured with the same diffractometer using a graphite monochromator, Mo-K_α radiation, $\theta/2\theta$ scan technique to $(\sin\theta/\lambda)_{max} = 0.54$ Å^{-1}. The data were corrected for Lorentz and polarization effects but not for absorption (μ = 13.6 cm^{-1}).

Structure determination and refinement

To determine the Sb atom coordinates we used the structural program MULTAN-78 [6] adapted by us for the EC-1033 computer at the Karpov Institute. During the structure determination we considered 201 normalized reflections with $E_{min} = 1.48$ which gave us 3749 SIGMA2 relationships. The set with

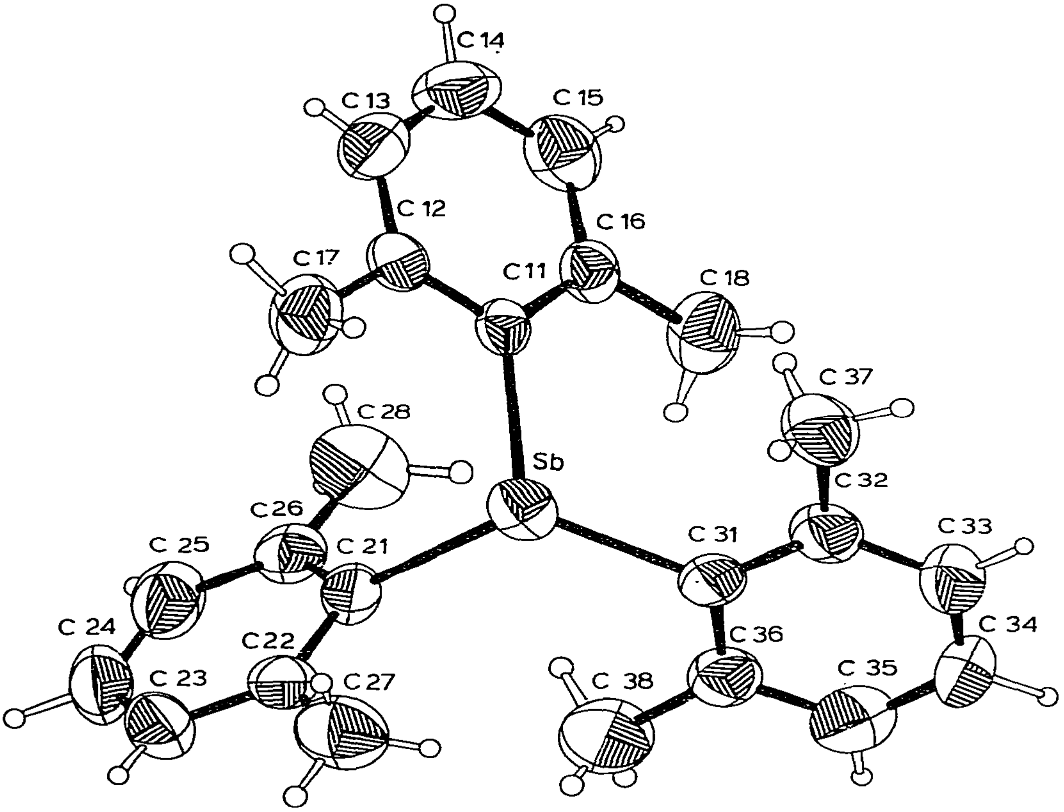

Fig. 1. Structure of the molecule.

the best combined FOM * gave us the coordinates of the Sb atom. Those of C atoms were found from Fourier synthesis. After two steps of refinement by block-diagonal least squares techniques, using a Nicolet P3/R3 crystallographic system, the coordinates of the hydrogens were found partly experimentally from difference Fourier synthesis, and partly from geometric considerations. All subsequent steps, including full-matrix least squares refinement, were performed using the crystallographic program XRAY-72 [7]. The carbon and anti-

TABLE 2

INTERATOMIC DISTANCES AND VALENCE ANGLES

Bond	d(Å)	Angle	ω(°)
Sb—C(11)	2.191(4)	C(11)SbC(21)	98.7(2)
Sb—C(21)	2.188(5)	C(21)SbC(31)	109.5(2)
Sb—C(31)	2.192(6)	C(31)SbC(11)	106.0(2)
C(11)—C(12)	1.398(7)	SbC(11)C(12)	112.7(3)
C(12)—C(13)	1.369(7)	SbC(11)C(16)	127.6(4)
C(13)—C(14)	1.375(9)	C(12)C(11)C(16)	119.7(4)
C(14)—C(15)	1.370(9)	C(11)C(12)C(13)	119.6(5)
C(15)—C(16)	1.395(7)	C(11)C(12)C(17)	122.5(4)
C(16)—C(11)	1.393(7)	C(13)C(12)C(17)	117.9(5)
C(12)—C(17)	1.510(8)	C(12)C(13)C(14)	121.4(5)
C(16)—C(18)	1.505(8)	C(13)C(14)C(15)	119.2(5)
		C(14)C(15)C(16)	121.4(5)
		C(11)C(16)C(15)	118.7(5)
		C(11)C(16)C(18)	124.6(4)
		C(15)C(16)C(18)	116.6(5)
C(21)—C(22)	1.410(7)	SbC(21)C(22)	114.2(3)
C(22)—C(23)	1.392(9)	SbC(21)C(26)	126.4(4)
C(23)—C(24)	1.362(8)	C(22)C(21)C(26)	118.8(5)
C(24)—C(25)	1.367(9)	C(21)C(22)C(23)	118.8(5)
C(25)—C(26)	1.380(9)	C(21)C(22)C(27)	122.5(5)
C(26)—C(11)	1.410(7)	C(23)C(22)C(27)	118.7(5)
C(22)—C(27)	1.505(8)	C(22)C(23)C(24)	122.4(6)
C(26)—C(28)	1.509(8)	C(23)C(24)C(25)	118.5(6)
		C(24)C(25)C(26)	122.4(5)
		C(21)C(26)C(25)	119.1(5)
		C(21)C(26)C(28)	122.7(5)
		C(25)C(26)C(28)	118.1(5)
C(31)—C(32)	1.403(8)	SbC(31)C(32)	112.8(4)
C(32)—C(33)	1.380(9)	SbC(31)C(36)	126.2(4)
C(33)—C(34)	1.369(11)	C(32)C(31)C(36)	120.4(5)
C(34)—C(35)	1.362(10)	C(31)C(32)C(33)	119.1(5)
C(35)—C(36)	1.393(9)	C(31)C(32)C(37)	122.6(5)
C(36)—C(31)	1.392(8)	C(33)C(32)C(37)	118.3(6)
C(32)—C(37)	1.510(8)	C(32)C(33)C(34)	120.7(6)
C(36)—C(38)	1.469(9)	C(33)C(34)C(35)	120.4(7)
		C(34)C(35)C(36)	121.1(6)
		C(31)C(36)C(35)	118.3(5)
		C(31)C(36)C(38)	123.6(5)
		C(35)C(36)C(38)	118.1(5)

Other nonvalent distances (Å) less then 4 Å

C(11)—C(21)	3.324(7)	C(11)—C(31)	3.501(7)	C(21)—C(31)	3.577(8)
C(11)—C(17)	2.550(8)	C(21)—C(27)	2.556(7)	C(31)—C(37)	2.556(8)
C(11)—C(18)	2.567(8)	C(21)—C(28)	2.563(7)	C(31)—C(38)	2.546(9)
C(17)—C(21)	3.613(8)	C(38)—C(11)	3.142(8)	C(37)—C(11)	3.703(8)
C(18)—C(31)	3.233(7)	C(28)—C(18)	3.769(9)	C(38)—C(21)	3.276(9)
C(18)—C(37)	3.641(8)	C(28)—C(38)	3.943(9)		

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* Figures of merit.

mony atoms were refined in anisotropic approximation using anomalous scattering [8] of the Sb atom. The isotropic B values of hydrogens were attributed as $B_i + 1$, where B_i is the corresponding isotropic temperature factor for the corresponding C atoms. Atomic scattering factors were taken from ref. 9 for Sb and C's and from ref. 10 for H's. The atomic coordinates with their e.s.d.'s are given in Table 1. The final R-value is 0.023 for 1747 reflections.

Discussion

The ORTEP [11] diagram of the molecule is shown in Fig. 1. Atomic bonds and valence angles are given in Table 2. It is noteworthy that the mean value of the angle C—Sb—C in TDPS (104.7°) is significantly larger than that of tri-*p*-tolylstibine (TPTS) (97.3°) [12]. This difference, along with the somewhat longer C—Sb bond (2.190 Å in TDPS and 2.141 Å in TPTS) is due to the steric hindrance from methyl groups in *ortho* positions, which affects the whole shape of the molecule. There is a inequality of valence angles Sb—C—C at the "basic" carbons C(11), C(21) and C(31) (the mean values are 113.3 and 126.6°). The same distortion is present in other triphenyl-substituted compounds of the Group V elements with substituents in *ortho* positions, e.g. 113.5 and 127° in TDPP [2], 114.2 and 127.3° in TMP [3], 115 and 126° in trimesitylbismuth [13], 118.6 and 122.4° in tri-*o*-tolylphosphine [14]. The inequality of dihedral angles (Table 3) between the plane C(11)—C(21)—C(31) and the planes of phenyl rings is also due to the steric effects. The deviations of methyl groups

TABLE 3

LEAST-SQUARES PLANES

Plane I. Atoms C(11), C(21), C(31)
Plane equation: $0.3053X + 0.7972Y + 0.5208Z = 9.4472$
Plane II. Atoms C(11)—C(16)
Plane equation: $0.7314X + 0.1374Y + 0.6679Z = 10.460$
Plane III. Atoms C(21)—C(26)
Plane equation: $-0.3965X + 0.2121Y + 0.8932Z = 0.6874$
Plane IV. Atoms C(31)—C(36)
Plane equation: $0.3195X + 0.9380Y - 0.1344Z = 7.1630$

ATOMIC DEVIATIONS FROM LEAST-SQUARES PLANES

Atom	Dev. (Å)	Atom	Dev. (Å)	Atom	Dev. (Å)	Atom	Dev. (Å)
Sb	—0.884	Sb	—0.036	Sb	—0.429	Sb	—0.237
C(11) [a]		C(11) [a]	0.010	C(21) [a]	—0.017	C(31) [a]	0.008
C(21) [a]		C(12) [a]	—0.011	C(22) [a]	0.008	C(32) [a]	0.001
C(31) [a]		C(13) [a]	0.002	C(23) [a]	0.008	C(33) [a]	—0.006
		C(14) [a]	0.008	C(24) [a]	—0.014	C(34) [a]	0.004
		C(15) [a]	—0.010	C(25) [a]	0.005	C(35) [a]	0.005
		C(16) [a]	0.001	C(26) [a]	0.011	C(36) [a]	—0.011
		C(17)	—0.050	C(27)	0.034	C(37)	0.008
		C(18)	0.058	C(28)	0.101	C(38)	—0.040

ANGLES BETWEEN THE NORMALS TO THE PLANES

I—II	47.1°	I—III	59.1°	I—IV	39.2°
II—III	70.4°	II—IV	74.2°	III—IV	87.3°

[a] Atoms used for plane calculation.

TABLE 4

UV SPECTRA

Stibine	λ_{max}	$\lg \epsilon_{max}$	λ_{max}	$\lg \epsilon_{max}$
$[C_6H_3(CH_3)_2]_3Sb$	204	4.98	282	4.04
$[C_6H_2(CH_3)_3]_3Sb$	208	5.04	284	4.11
$(C_6H_5)_3Sb$	195	4.96	254	4.08

from the mean planes of corresponding rings are from —0.05 to 0.10 Å. The shortest non-valence distances in the molecule are given in Table 2. All intermolecular contacts correspond to normal Van der Waals interactions (the shortest one is 3.60 Å). Therefore, it is clear that the molecular geometry loses its own C_3 pseudosymmetry because of intramolecular steric effects.

It was interesting to compare the physico-chemical properties of TDPS with those of trimesitylstibine (TMS) and triphenylstibine (TPS). In the TMS molecule there are also two methyl groups in *ortho*-position on each ring and the angle C—Sb—C should be close to that in TDPS. The electronic spectra of TDPS, TMS and TPS were measured in n-hexane using a Perkin-Elmer 450 spectrophotometer. The spectra contain two absorption maxima in the near UV region (Table 4).

The spectra of TDPS and TMS resemble each other. The absorption maxima in these spectra are strongly shifted to the long-wave region compared with those of TPS. The dipole moment of TDPS (benzene, 25°C) is 0.62 D (P_∞ = 136.96, R_D = 122.90 cm^3), for TMS the dipole moment is 1.10 D (P_∞ = 173.01, R_D = 141.14 cm^3). This difference is connected with the presence of methyl groups in *para* positions in TMS and their absence in TDPS. The contribution of these groups to the dipole moment of stibine, calculated using the equation $\mu = \mu(CH_3) \times \sqrt{3 + 6 \cos \theta}$, is equal to 0.45 D ($\theta$(CSbC) = 104.7°, $\mu(CH_3)$ = 0.37 D). This value corresponds well to the difference of dipole moments of TDPS and TMS.

It is interesting that the dipole moment of TMS (1.10 D) is bigger than that of TPS (0.85 D [5]). In both compounds the dipole moment has the direction $\overrightarrow{Ar_3Sb}$ and, to a great extent, is governed by the atomic dipole moment of the Sb atom unshared electron pair. The latter should be bigger in TMS because of the greater π-character of the hybrid orbital of the Sb atom unshared electron pair (61% instead of 31% in TPS).

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