CRYSTAL STRUCTURES OF TRI(O-TOLYL)STIBINE IN TWO CRYSTAL FORMS

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Abstract

The X-ray crystal structure of tri(o-tolyl)stibine has been determined in two different crystal forms namely monoclinic and triclinic. To the best of our knowledge the work seems to be the first example showing polymorphism in organoantimony compounds. Both the molecules are chiral.

Introduction

The structure and physico-chemical properties of triaryl derivatives of Group (V) elements depend to a great extent on the phenyl ring substituents. The literature shows that the C-Sb-C angles in triaryl derivatives of antimony range from 105.3° in (Mesityl)$_3$Sb [1], 104.7°(2) in (2,6 dimethylphenyl)$_3$Sb [2], 97.3°(1) in (p-tolyl)$_3$Sb [3] to 95.0°(3) in Ph$_3$Sb [4]. In order to get more complete and detailed data on such structures, we have performed X-ray structure analysis of tri(o-tolyl)stibine $C_{21}H_{21}Sb$. X-ray crystal structure of tri(o-tolyl)stibine has been determined in two different crystal forms.

Experimental

Tri(o-tolyl)stibine was prepared according to the published procedure [5] and the product was recrystallised from hexane to get crystals (**1**) in a monoclinic form. The attempted reaction of tri(o-tolyl)stibine with a solution of cobalt chloride in methanol at 80ÚC resulted , upon concentration, crystals of tri(o-tolyl)stibine in triclinic form (2). The IR and ^{1}H NMR spectra were compared with that in literature [5].

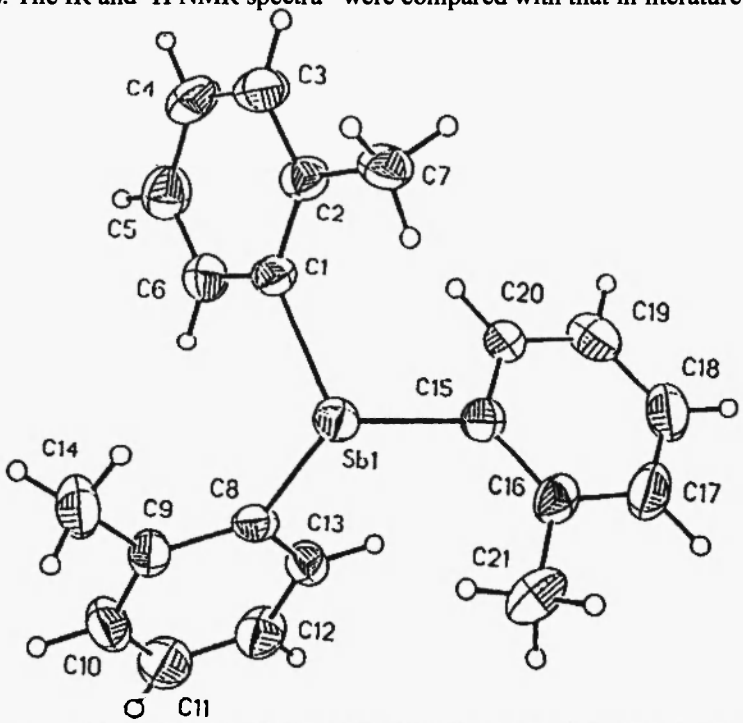

Fig. 1. Molecular structure of tri(o-tolyl)stibine in monoclinic crystal form.

X-ray Crystal structure determination: Data were collected on a Siemens P4\Pc diffractometer at 293° K, in a 2θ range of 3.0 to 50.0° using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The system used for calculations was Siemens SHLEXTL PLUS (PC Version) and structure determination by direct methods and refinement by full matrix least squares procedure. Atomic coordinates, equivalent isotropic and anisotropic displacement cofficients have been deposited. Crystal data are given in Table 1.

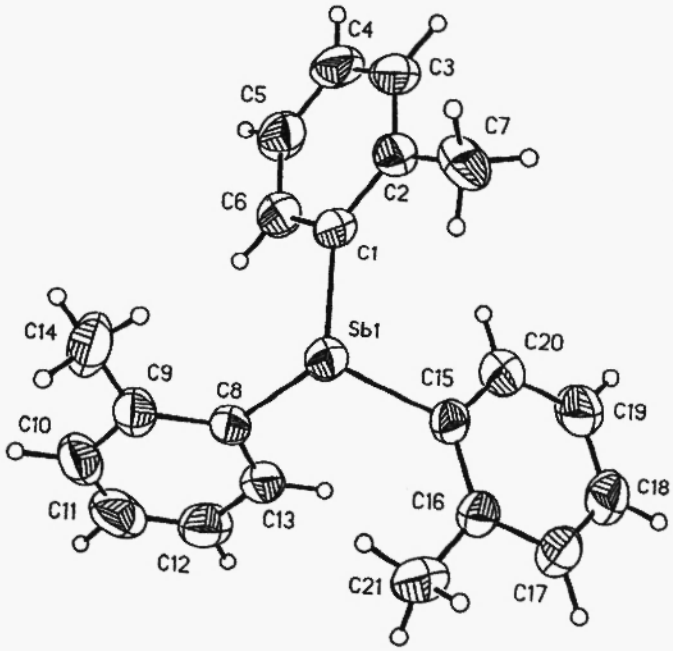

Fig. 2. Molecular structure of tri(o-tolyl)stibine in triclinic crystal form

Table 1. Crystal data for tri(o-tolyl)stibine (**1**) and (**2**)

Compound	$[(o\text{-}Me)C_6H_4]_3Sb$	$[(o\text{-}Me)C_6H_4]_3Sb$
Molecular Wt.	395.1	395.1
Empirical Formula	$C_{21}H_{21}Sb$	$C_{21}H_{21}Sb$
Crystal System	Monoclinic	Triclinic
Space Group	C2/c	P1
a, Å	38.330(4)	5.319(1)
b, Å	5.267(1)	10.190(1)
c, Å	20.324(2)	16.437(2)
α,°		91.53(1)
β, °	120.59(1)	95.56(1)
γ,°		94.93(1)
Z	8	2
D_C, g cm^{-3}	1.486	1.486
Crystal size, mm	0.32 x 0.16 x 0.16	0.44 x 0.28 x 0.16
V, Å^3	3531.8(7)	882.9(2)
F(000)	1584	396
μ, cm^{-1}	15.57	15.57
Scan type	ω	ω
Scan speed	Variable; 8.0 to 100.0°/min	Variable; 4.0 to 100.0°/min
Independent reflections	4656 (R_{int}= 0.0245)	3115 (R_{int}= 0.0285)
R	0.049	0.046
No. of unique reflections	2944 [F>4.0σ(F)]	2788 [F> 3.0σ(F)]
$\Delta_{\rho\ max}$, $\Delta_{\rho\ min}$ e Å^{-3}	0.769, -0.803	0.702, -0.886
R_w	0.053	0.055
GOF	1.15	1.25

Results and discussion

The molecular structure of (**1**) and (**2**) and the atom numbering systems are shown in Fig.1 and Fig. 2, respectively. Selected bond lengths and bond angles for both the crystal forms are reported in Table 2 while the atomic coordinates for monoclinic crystal form (**1**) and triclinic crystal from(**2**) are reported in Table 3 and 4, respectively.

Table 2. Selected bond lengths (Å) and bond angles (°) for tri(o-tolyl)stibine in monoclinic (**1**) and triclinic forms (**2**)

	(1)			(2)	
(1) (2)					
Sb(1)-C(1)	2.166 (8)	2.170(6)	Sb(1)-C(8)	2.167(6)	2.154(6)
Sb(1)-C(15)	2.165(8)	2.163(6)	C(1)-C(2)	1.402 (8)	1.402(8)
C(1)-C(6)	1.38 (1)	1.40(9)	C(2)-C(3)	1.371 (1)	1.40 (1)
C(2)-C(7)	1.52 (1)	1.50(1)	C(3)-C(4)	1.387 (1)	1.38 (1)
C(4)-C(5)	1.38 (1)	1.38 (1)	C(5)-C(6)	1.375 (1)	1.39 (1)
C(8)-C(9)	1.41(1)	1.410 (8)	C(8)-C(13)	1.373 (1)	1.394 (9)
C(9)-C(10)	1.364 (9)	1.39 (1)	C(9)-C(14)	1.524 (1)	1.51(1)
C(10)-C(11)	1.37(1)	1.38(1)	C(11)-C(12)	1.352 (1)	1.39 (1)
C(1)-Sb(1)-C(8)	97.7 (3)	97.1(2)	C(1)-Sb(1)-C(15)	97.5 (3)	97.0(2)
C(8)-Sb(1)-C(15)	97.0 (3)	96.7(2)	Sb(1)-C(1)-C(2)	119.0 (6)	119.4(4)
Sb(1)-C(1)-C(6)	122.3 (5)	120.5(4)	C(2)-C(1)-C(6)	118.6 (7)	119.9(5)
			C(1)-C(2)-C(7)	120.8 (7)	
Sb(1)-C(8)-C(13)	121.2 (5)	122.1(4)	Sb(1)-C(8)-C(9)	119.7 (5)	119.4(4)
Sb(1)-C(15)-C(20)	120.5 (6)	120.6(4)	Sb(1)-C(15)-C(6)	119.8 (5)	120.2(5)

The geometry around the Sb(1) atoms is distorted tetrahedral in both structures (**1**) and (**2**) with minor differences in distances and bond angles, most of these are within the experimental error. In both the structures, the presence of the o-tolyl rings make the molecules asymmetric, as long as it is possible to have a right and left helix. The molecules are situated on the axis 3 and these have pyramidal shape.

Table 3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$) for tri(o-tolyl)stibine in monoclinic crystal form (**1**)

	x	*y*	*z*	*U*
Sb(1)	3749(1)	3997(1)	1818(1)	40(1)
C(1)	3269(2)	2054(14)	1884(4)	42(3)
C(2)	2866(2)	2776(14)	1386(4)	45(3)
C(3)	2561(2)	1660(16)	1450(5)	58(4)
C(4)	2645(3)	-199(16)	1994(5)	60(4)
C(5)	3041(3)	-925(18)	2480(4)	61(4)
C(6)	3347(2)	199(14)	2421(4)	50(3)
C(7)	2763(2)	4843(16)	795(4)	54(3)
C(8)	4256(2)	1949(14)	2727(4)	42(3)
C(9)	4415(2)	2711(14)	3490(3)	45(3)
C(10)	4759(2)	1545(17)	4040(4)	61(4)
C(11)	4951(2)	-332(19)	3880(5)	66(4)
C(12)	4798(2)	-1077(19)	3147(4)	62(4)
C(13)	4449(2)	63(14)	2569(4)	48(3)
C(14)	4209(3)	4768(18)	3699(4)	67(4)
C(15)	3710(2)	1852(13)	875(3)	40(3)
C(16)	3961(2)	2474(14)	589(4)	50(3)
C(17)	3908(3)	1138(20)	-52(4)	65(4)
C(18)	3614(3)	-680(20)	-409(4)	68(4)
C(19)	3365(2)	-1280(18)	-120(4)	63(3)
C(20)	3417(2)	-26(14)	516(4)	45(3)
C(21)	4288(3)	4439(17)	963(5)	67(5)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

The average value of Sb-C distances, 2.164 (6)Å falls within the limits 2.032-2.216Å found in related organoantimony structures [6-8]. The methyl atom C(7) practically lies up in the direction of the Sb(1) atom, which is the less hindered position. The antimony atom is in between the planes formed by C(1)-C(8)-C(15), the C atoms bonded to Sb(1) and C(7)-C(14)-C(21) plane out of it in both the crystal forms. Both the crystals present the same stereochemistry and in both the crystal forms molecule is chiral. The angle between the planes of phenyl rings is 0.7(3) ° in both the cases.

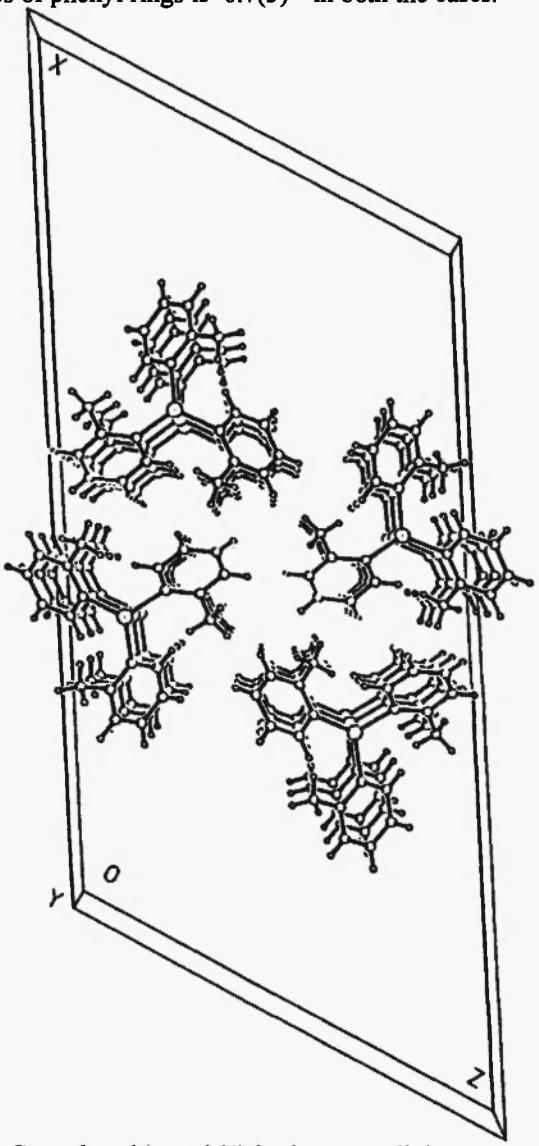

Fig.3. Crystal packing of (**1**) in the monoclinic system

It is noteworthy that the mean value of the angle C-Sb-C in (**1**) is 97.4(3)°and 96.66(2)° in (**2**) is much similar 97.3(1)° found in tri(p-tolyl)stibine [3] but significantly smaller than the angles 105.3°, 104.7(2)° found in 2,4,6-trimesitylstibine and tris- (2,6-dimethylphenyl)stibine respectively [1,2].

This difference, along with the somewhat smaller C-Sb bond length (2.164 Å) in (**1**) and (**2**) in comparison to 2.190 Å for tris(2,6-dimethylphenyl)stibine is due to the steric hindrance from the two methyl groups in the ortho positions, which affects the whole shape of the molecule [2].

Intermolecular distances are greater than normal van der Waals interactions. The packing of the molecules in (**1**) and (**2**) are shown in Figures 3 and 4, respectively. In both the cases the molecules are arranged forming columns along the X- axis in (**1**) and along the Y axis in (**2**). The difference between them may be understand considering a different closed packing of the columns, as long as there are no significant intermolecular interactions. There is a inequality of valence angles Sb-C-C at the carbons C(1), C(8) and C(15). The structural parameters of the phenyl ring are as expected.

Table 4. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$) for tri(o-tolyl)stibine in trilinic crystal form (**2**).

	x	*y*	*z*	*U*
Sb(1)	4122(1)	8781(1)	7517(1)	39(1)
C(1)	6439(11)	7946(6)	8497(3)	40(2)
C(2)	5731(13)	6679(6)	8752(4)	47(2)
C(3)	7187(16)	6187(7)	9409(4)	58(2)
C(4)	9231(17)	6937(8)	9818(4)	65(3)
C(5)	9910(16)	8192(8)	9569(4)	61(2)
C(6)	8514(13)	8697(7)	8913(4)	49(2)
C(7)	3502(16)	5845(7)	8332(5)	61(2)
C(8)	5560(11)	7770(5)	6517(3)	40(2)
C(9)	4581(12)	7984(6)	5708(4)	45(2)
C(10)	5403(16)	7281(7)	5063(4)	59(2)
C(11)	7167(19)	6379(8)	5208(5)	68(3)
C(12)	8182(18)	6163(8)	5997(5)	66(3)
C(13)	7364(14)	6863(6)	6643(4)	51(2)
C(14)	2660(16)	8971(8)	5529(4)	60(2)
C(15)	6463(12)	10614(6)	7461(3)	42(2)
C(16)	6152(13)	11688(6)	7980(4)	51(2)
C(17)	7586(18)	12844(7)	7883(5)	66(3)
C(18)	9244(20)	13015(8)	7302(6)	77(3)
C(19)	9566(17)	11976(8)	6801(5)	66(3)
C(20)	8168(13)	10770(6)	6878(4)	50(2)
C(21)	4343(18)	11567(9)	8632(5)	71(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

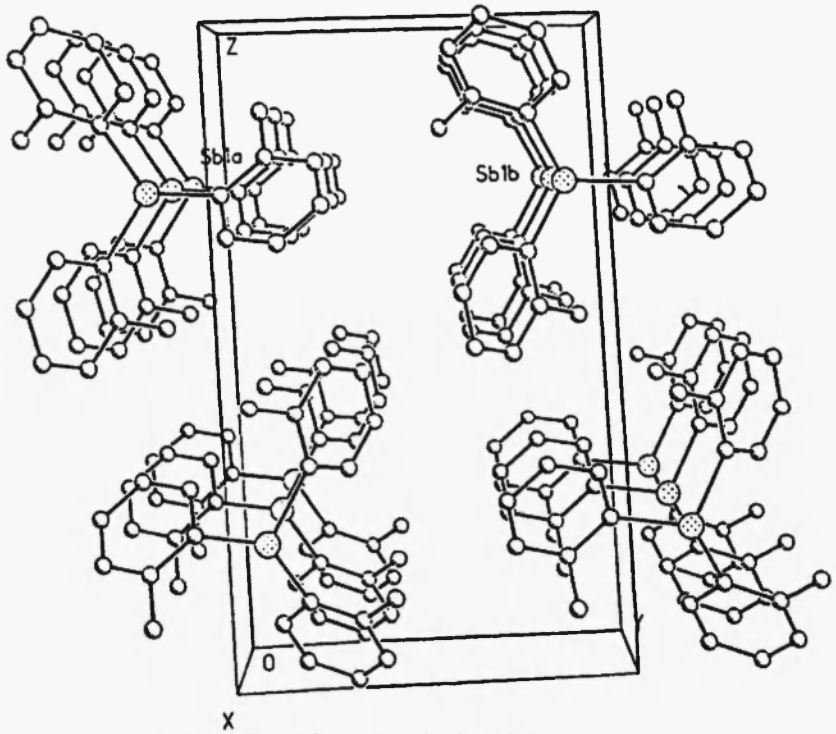

Fig.4. Crystal packing of (**2**) in the triclinic system

In summary, as it has been reported earlier, the p-substituted triphenylarsine and p-substituted triphenylstibine derivatives are not influenced by the value of the valence angle C-As-C or C-Sb-C [3,9] .On the contrary, the presence of two methyl groups in the 2- and 6- positions of the phenyl rings leads to

an increase of these angles [2,10]. But the presence of only one methyl group in the ortho position is not able to influence the C-Sb-C angle as it is found in both the crystal forms. To the best of our knowledge this report seems to be the first example showing polymorphism in organoantimony compounds. Both the molecules are chiral

References

1. M.Ates, H.J. Breunig, K.H. Ebert, R. Kaller, M. Drager and U. Behrens, *Z. Naturforsch B Chem. Sci.*, **47** 503 (1992).
2. A.N.Sobolev, I.P. Romm, V.K. Belsky, O.P.Syukina and E.N. Guryanova, *J. Organomet. Chem.*, **209** 49 (1979).
3. A.N.Sobolev, I.P. Romm, V.K. Belsky and E.N. Guryanova, *J. Organomet. Chem.*, **179** 153 (1979).
4. E.A. Adams, J.W. Collis and W.T. Pennington, *Acta Cryst. C* ,**C46** 917 (1990).
5. V.P.Glushkova, T.V.Talalaeva, Z.P.Tazmanova, G.S. Zhdanov and K.A. Kocheshkov, *Sbornik Statei Obshch. Khim.*, **2** 992 (1953) ; C.A. **49**, 6859 (1955).
6. E.A. Adams, J.W. Kolis and W.T. Pennigton, *Acta Crystalllogr. C*, **C46** 917 (1990).
7. P. Sharma, N. Rosas, Rama Shankar, A. Toscano, S. Hernandez and A. Cabrera, *Main Group Met. Chem.*, **19** 21 (1996).
8. P. Sharma, N. Rosas, G. Espinosa and A. Cabrera, *Acta Crystallogr.C*, **C52** 889 (1996).
9. A.N. Sobolev, V.K. Belsky and E.N. Guryanova, *J. Organomet. Chem.*, **214** 41 (1981).
10. A.N. Sobolev, I.P. Romm, N.Y. Chernikova, V.K. Belsky and E.N. Gryanova, *J. Organomet. Chem.*, **219** 35 (1981).

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