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STRUCTURE ANALYSIS OF TRIARYL DERIVATIVES OF THE GROUP V ELEMENTS

IV *. MOLECULAR STRUCTURES OF TRI-*p*-CHLOROPHENYLARSINE, TRI-*p*-METHOXYPHENYLARSINE AND TRI-*p*-TOLYLARSINE

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Summary

An X-ray structure analysis of three *p*-substituted triphenylarsines has been carried out: tri-*p*-chlorophenylarsine (TPCPA), orthorhombic, space group *Pbca*, $Z = 8$, $R = 0.032$; tri-*p*-methoxyphenylarsine (TPMPA), trigonal, space group $R\bar{3}$, $Z = 2$, $R = 0.032$; tri-*p*-tolylarsine (TPTA), trigonal, space group $R\bar{3}$, $Z = 2$, $R = 0.022$. The most important interatomic distances and bond angles are: As—C 1.958 (mean for TPCPA), 1.963 (TPMPA), 1.954 Å (TPTA); CAsC 99.5 (TPCPA), 98.3 (TPMPA), 99.3° (TPTA).

Introduction

During a systematic investigation of the structures of triarylderivatives of the Group V elements it was considered to be of interest to see how the *para* substituents influenced the conformation of the molecules Ar_3M. For this study we chose the compounds of type $(p\text{-}XC_6H_4)_3As$, where X = CH_3 (TPTA), Cl (TPCPA), OCH_3 (TPMPA) (see Fig. 1). The structure of TPTA had already been studied by X-ray diffraction [1]; however the value of the bond angle CAsC 102° did not agree with our observations [5]. Considering that the previous investigation had been performed in 1963 by the photo-method, it seemed desirable to redetermine the structure of TPTA using a more accurate method.

X-ray data collection, structure determination and refinement

All the experimental data were obtained using a Syntex $P\bar{1}$ automatic four-circled diffractometer, λ Mo-K_α, graphite monochromator, $\theta/2\theta$ scan method.

* For Part III see ref. 7.

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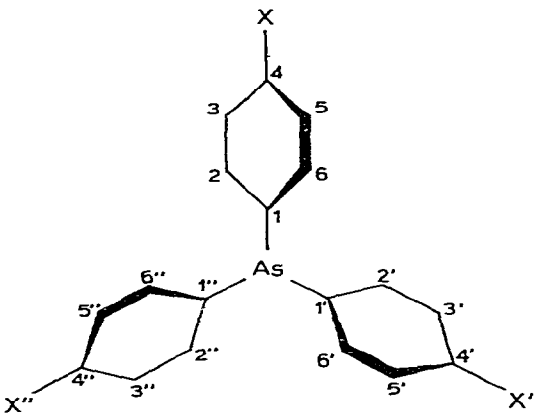

1, X = Cl (TPCPA)

2, X = OCH_3 (TPMPA)

3, X = CH_3 (TPTA)

Fig. 1. Atom numbering scheme in TPTA, TPCPA and TPMPA.

The general experimental features and lattice parameters are given in Table 1. The integral intensities were corrected for Lorenz and polarization effects but not for absorption.

The coordinates of the As atoms were found using heavy atom technique; those of non-hydrogen atoms were obtained after subsequent Fourier syntheses. For the TPTA structure initial coordinates were taken from ref. 1 after being converted into the H-setting of the rhombohedral space group $R\bar{3}$ chosen by us. The coordinates of H atoms were partly calculated using geometric considerations and partly localized from difference syntheses. The structure deter-

TABLE 1

GENERAL CRYSTALLOGRAPHIC DATA

	TPCPA	TPMPA	TPTA
Empirical formula	$C_{18}H_{12}AsCl_3$	$C_{21}H_{21}AsO_3$	$C_{21}H_{21}As$
a (Å)	14.584(3)	13.288(2)	12.697(2)
b (Å)	15.855(5)	13.288	12.697
c (Å)	14.711(3)	18.905(3)	19.746(5)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	120	120
V (Å^3)	3402(1)	2830(1)	2757(1)
D_c (g cm^{-3})	1.60	1.40	1.26
Space group	*Pbca*	$R\bar{3}$	$R\bar{3}$
Z	8	6	6
F(000)	1632	1224	1080
μ (cm^{-1})	25.7	19.2	19.5
S_{max}	0.595	0.57	0.57
λ (Å)	0.71069	0.71069	0.71069
Number of reflections	1600	667	388
M.W.	409.57	396.32	348.32

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THEIR e.s.d.'s

Atom	TPCPA			TPMPA			TPTA		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
As	3798.1(4)	819.8(4)	1771.8(3)	0	0	1974.8(4)	0	0	1828.7(4)
C(1)	3488(3)	1829(3)	2470(4)	920(4)	1475(4)	1458(2)	1051(3)	1529(3)	1359(2)
C(2)	3966(4)	2584(4)	2468(4)	2050(4)	2233(4)	1674(2)	723(3)	1937(3)	801(2)
C(3)	3697(4)	3258(4)	2994(4)	2756(4)	3263(4)	1325(2)	1482(3)	3037(3)	504(2)
C(4)	2957(4)	3185(4)	3552(4)	2326(4)	3565(4)	743(2)	2640(3)	3776(3)	756(2)
C(5)	2468(4)	2454(5)	3580(4)	1199(4)	2837(4)	519(2)	2976(3)	3371(4)	1318(2)
C(6)	2738(4)	1783(4)	3033(4)	523(4)	1814(4)	873(2)	2207(4)	2272(4)	1616(2)
C(7)	—	—	—	4064(5)	5406(5)	581(3)	3493(4)	4982(4)	429(2)
O	—	—	—	2941(3)	4558(3)	341(2)	—	—	—
Cl(1)	2630(1)	4019(1)	4248(1)	—	—	—	—	—	—
C(1′)	4636(4)	328(3)	2672(4)						
C(2′)	5419(4)	731(4)	2979(4)						
C(3′)	5952(4)	381(4)	3657(4)						
C(4′)	5694(4)	−361(3)	4033(4)						
C(5′)	4912(4)	−771(4)	3750(4)						
C(6′)	4393(4)	−420(4)	3056(4)						
Cl(1′)	6351(1)	−812(1)	4897(1)						
C(1″)	4685(4)	1265(3)	897(3)						
C(2″)	5461(4)	798(4)	865(4)						
C(3″)	6039(4)	1056(4)	−11(4)						
C(4″)	5848(4)	1775(4)	−480(4)						
C(5″)	5080(4)	2249(4)	−286(4)						
C(6″)	4504(4)	1982(4)	403(4)						
Cl(1″)	6589(1)	2116(1)	−1333(1)						

TABLE 3

BOND LENGTHS (Å) AND THEIR e.s.d.'s

	TPCPA	TPMPA	TPTA
As—C(1)	1.954(5)	1.963(4)	1.954(4)
C(1)—C(2)	1.386(8)	1.385(6)	1.368(5)
C(2)—C(3)	1.377(8)	1.373(6)	1.371(5)
C(3)—C(4)	1.360(8)	1.371(7)	1.383(6)
C(4)—C(5)	1.361(9)	1.379(6)	1.376(6)
C(5)—C(6)	1.392(9)	1.365(6)	1.373(6)
C(6)—C(1)	1.373(8)	1.375(7)	1.385(6)
C(4)—Cl	1.739(6)	—	—
C(4)—O	—	1.371(5)	—
C(4)—C(7)	—	—	1.509(6)
C(7)—O	—	1.418(6)	—
As—C(1′)	1.963(5)		
C(1′)—C(2′)	1.384(8)		
C(2′)—C(3′)	1.381(8)		
C(3′)—C(4′)	1.355(8)		
C(4′)—C(5′)	1.378(8)		
C(5′)—C(6′)	1.388(8)		
C(6′)—C(1′)	1.360(8)		
C(4′)—Cl′	1.743(6)		
As—C(1″)	1.957(5)		
C(1″)—C(2″)	1.388(8)		
C(2″)—C(3″)	1.387(8)		
C(3″)—C(4″)	1.362(8)		
C(4″)—C(5″)	1.379(8)		
C(5″)—C(6″)	1.384(8)		
C(6″)—C(1″)	1.374(8)		
C(4″)—Cl″	1.742(6)		

mination and the first steps of the refinement were performed using the programs of the NICOLET R3 crystallographic system. All further steps of refinement were made using the XRAY-72 complex of crystallographic programs [2]. The refinement proceeded with full matrix-least squares using anisotropic (As, Cl, O, C) and isotropic (H) thermal parameters. The final R values are: 0.032 (TPCPA and TPMPA) and 0.022 (TPTA). The positional parameters of non-hydrogen atoms with their e.s.d.'s are given in Table 2. * Fig. 1 also gives the atomic numbering scheme.

Discussion

All three molecules have an identical pyramidal shape and in the crystal lose their own C_{3v} symmetry. However, TPMPA and TPTA keep the 3 fold axis given in Table 3. The value of bond angle CAsC in TPTA turned out to be significantly less (99.3°) than was reported in ref. 1 (102°) and is in a good agreement with those of the related compounds TPCPA and TPMPA (99.5 and 98.3°). The As—C (mean 1.961 Å) and C—C distances in the planar benzene rings correspond to

* Tables of F_o and F_c, anisotropic and isotropic thermal parameters, coordinates of H atoms, tables of least squares planes and drawings of molecules may be obtained upon request from the authors.

TABLE 4

BOND ANGLES (°) AND THEIR e.s.d.'s

	TPCPA	TPMPA	TPTA
C(1)AsC(1′)	96.6(2)	98.3(2)	99.3(2)
C(1)AsC(1″)	101.1(2)	98.3	99.3
C(1′)AsC(1″)	101.7(2)	98.3	99.3
AsC(1)C(2)	126.1(4)	119.6(4)	124.9(3)
AsC(1)C(6)	117.3(4)	124.1(3)	117.9(3)
C(2)C(1)C(6)	116.6(5)	116.3(4)	117.2(4)
C(1)C(2)C(3)	121.8(5)	122.8(5)	122.6(4)
C(2)C(3)C(4)	119.9(6)	119.0(4)	120.2(4)
C(3)C(4)C(5)	120.4(6)	119.7(5)	117.4(4)
C(4)C(5)C(6)	119.0(6)	119.9(4)	122.0(4)
C(5)C(6)C(1)	122.3(6)	122.4(4)	121.7(4)
C(3)C(4)Cl	120.6(5)	—	—
C(5)C(4)Cl	119.0(5)	—	—
C(4)OC(7)	—	118.6(4)	—
C(3)C(4)O	—	125.0(4)	—
C(5)C(4)O	—	115.4(4)	—
C(3)C(4)C(7)	—	—	120.9(4)
C(5)C(4)C(7)	—	—	121.7(4)
AsC(1′)C(2′)	123.4(4)		
AsC(1′)C(6′)	117.6(4)		
C(2′)C(1′)C(6′)	118.8(5)		
C(1′)C(2′)C(3′)	121.0(5)		
C(2′)C(3′)C(4′)	119.2(5)		
C(3′)C(4′)C(5′)	121.1(5)		
C(4′)C(5′)C(6′)	119.0(5)		
C(5′)C(6′)C(1′)	120.9(5)		
C(3′)C(4′)Cl′	120.1(4)		
C(5′)C(4′)Cl′	118.8(4)		
AsC(1″)C(2″)	119.6(4)		
AsC(1″)C(6″)	121.3(4)		
C(2″)C(1″)C(6″)	118.7(5)		
C(1″)C(2″)C(3″)	120.2(5)		
C(2″)C(3″)C(4″)	119.8(5)		
C(3″)C(4″)C(5″)	121.2(5)		
C(4″)C(5″)C(6″)	118.5(5)		
C(5″)C(6″)C(1″)	121.6(5)		
C(3″)C(4″)Cl″	119.9(4)		
C(5″)C(4″)Cl″	118.9(4)		

normal values. The configuration of the C_3As pyramid may be described using the distance of the As atom to the C(1)C(1′)C(1″) plane: TPTA 0.928, TPCPA 0.925, TPMPA 0.956 Å, i.e. very close in all three molecules. The As atoms are in the planes of phenyl rings within limits of 0.05 Å. The orientation of latter relative to the C(1)C(1′)C(1″) plane are characterized by the values of the dihedral angles φ(°):

	TPTA	TPMPA	TPCPA
φ(1—6)	53.4	52.4	59.9
φ(1′—6′)	53.4	52.4	83.6
φ(1″—6″)	53.4	52.4	22.1

The angles between the planes of the phenyl rings are as follows (TPTA, TPMPA,

TPCPA, respectively):

	1—6	1′—6′	1″—6″
1—6	—	88.2, 86.6, 88.6	88.2, 86.6, 51.9
1′—6′	—	—	88.2, 86.6, 64.7

As it can be seen from the analysis of geometric features of the molecules, the change of substituents in the *para*-position of the phenyl ring has practically no effect on the conformation of the molecule Ar_3As. The mean value of the valence angle CAsC (99°) for the 3 molecules is in good agreement with those of other members of the P—As—Sb—Bi series [3—6].

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