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THE STRUCTURE ANALYSIS OF TRIARYL DERIVATIVES OF THE GROUP V ELEMENTS

V *. SPECTRA, CRYSTAL AND MOLECULAR STRUCTURE OF TRIMESITYLARSINE, $C_{27}H_{33}As$

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Summary

The complete X-ray structure analysis of trimesitylarsine (TMAS), $C_{27}H_{33}As$, has been performed. The crystals are triclinic, a 18.718, b 16.418, c 8.204 Å, α 99.99, β 97.85, γ 104.56°, $Z = 4$, space group $P\bar{1}$ (two independent molecules in the asymmetric unit); the final value of the R-factor is 0.038. In the electronic spectrum of TMAS the long-wave band has the maximum at 276 nm which differs significantly from that of triphenylarsine (TPAS) at 249 nm. The bathochromic spectral shift and the molecular conformation are caused by the steric effects as a result of bulky methyl groups in the positions 2,4 and 6 in the phenyl rings. Two independent molecules are connected by a pseudo-axis of symmetry.

Introduction

As a part of the program to investigate the influence of steric effects upon the structure and physico-chemical properties of the compounds Ar_3X (X = Group V element) we have performed the complete X-ray structure analysis of trimesitylarsine (TMAS), as has been done previously for phosphines [1,2], stibines [3,13] and bismuthines [4,5]. As has been previously noted, the introduction of the methyl groups in the 2- and 6-positions of each phenyl ring increases substantially the valence angle CXC. This was confirmed also by the dipole moments measurements [6].

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* For part IV see ref. 11.

Experimental part

A single crystal of TMAS with the size 0.18 × 0.17 × 0.20 mm was chosen for the X-ray experiment. The unit cell parameters were determined by using a SYNTEX P$\bar{1}$ automatic diffractometer: a 18.718(3), b 16.418(3), c 8.204(2) Å, α 99.99(2), β 97.85(2), γ 104.56(2)°, D_x 1.22 g cm^{-3}, $Z = 4$, space group $P\bar{1}$, $F(000)$ 912. The 6491 experimental intensities were collected on the same diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ collection method, $s_{max} = 0.64$). After the correction for Lorentz and polarization effects, 6422 reflections with $I \geqslant 3\sigma(I)$ were considered as observed and were used in further calculations. The correction for absorption was not applied ($\mu_{Mo} = 15.3$ cm^{-1}).

Structure determination and refinement

Comparison of the unit cell parameters of TMAS and those of the previously published trimesitylphosphine (TMP) [1] showed a rather good resemblance. Thus the atomic coordinates of TMP were first used as a starting model for TMAS, the R-factor at this stage was 0.38. The subsequent Fourier synthesis revealed more accurate atomic coordinates for TMAS. The structure was refined by full matrix least-squares using anisotropic (As, C atoms) and isotropic (H atoms) thermal parameters. The scattering factors for As, C and H were taken from ref. 7. All calculations were performed using the XRAY-72 set of crystallographic programs [8] on a EC-1033 computer. The atomic coordinates of As and C atoms with their e.s.d.'s are given in Table 1 *.

Discussion

The general view of the molecules and their mutual orientation are shown in the Fig. 1 Bond lengths and valence angles with their e.s.d.'s are given in Tables 2 and 3. The mean CAsC angle and As—C bond length are 107.6° and 1.976 Å, respectively. These values are significantly higher than those of tri-*p*-tolylarsine (99.8° and 1.954 Å), tri-*p*-chlorophenylarsine (99.5° and 1.958 Å), tri-*p*-methoxyphenylarsine (98.3° and 1.963 Å) found in the previous works [10,11]. Such increase of the valence angle and bond length along with the loss of the molecule's C_{3v} symmetry can be explained by the presence of the methyl substituents in the positions 2 and 6 of the phenyl rings. This effect is also responsible for the difference in rotation angles of phenyl rings in respect to the C(11) C(21) C(31) plane (Table 4). Such an increase of the valence angle CAsC compared to *p*-substituted triarylarsines is typical for the whole series of Ar_3X compounds. This was noted earlier for triarylphosphines [1,2,12], triarylstibines [3,13] and triarylbismuthines [4,5]. It must be mentioned that there is a good resemblance between TMAS and TMP, both in respect to the unit cell parameters and the value of the CXC angle (107.6 and 109.5°, respectively) and in respect to the dipole moments (DM) of these compounds. The DM of TMAS (0.70 D) is less than of triphenylarsine by 0.44 D [6], while the DM of TMP (0.98 D) is less than of triphenylphosphine by 0.54 D [14]. This resemblance in the behaviour of aromatic phosphines

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* Lists of F_0 and F_c, tables of anisotropic thermal parameters of As and C atoms and positional parameters of H atoms may be received upon request from the authors.

TABLE 1

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	*X*	*Y*	*Z*
As	0.72534(3)	0.75802(3)	0.00152(5)
As'	0.26225(2)	0.64731(3)	0.73380(5)
C(11)	0.6289(3)	0.7116(3)	0.0707(5)
C(12)	0.5698(3)	0.6700(3)	−0.0651(6)
C(13)	0.5016(3)	0.6238(3)	−0.0368(7)
C(14)	0.4893(3)	0.6168(3)	0.1237(7)
C(15)	0.5476(3)	0.6595(3)	0.2549(6)
C(16)	0.6168(3)	0.7070(3)	0.2354(6)
C(17)	0.5756(3)	0.6739(4)	−0.2461(6)
C(18)	0.4147(4)	0.5645(4)	0.1480(9)
C(19)	0.6742(3)	0.7520(4)	0.3916(6)
C(21)	0.7215(3)	0.8684(3)	−0.0612(5)
C(22)	0.7656(3)	0.8904(3)	−0.1775(6)
C(23)	0.7591(3)	0.9585(3)	−0.2542(6)
C(24)	0.7097(3)	1.0058(3)	−0.2144(6)
C(25)	0.6690(3)	0.9863(3)	−0.0930(6)
C(26)	0.6732(3)	0.9183(3)	−0.0138(6)
C(27)	0.8241(3)	0.8457(4)	−0.2230(7)
C(28)	0.7028(4)	1.0789(4)	−0.3004(8)
C(29)	0.6285(3)	0.9058(3)	0.1240(7)
C(31)	0.8069(2)	0.7812(3)	0.1973(6)
C(32)	0.8227(3)	0.7058(3)	0.2358(6)
C(33)	0.8846(3)	0.7131(3)	0.3558(7)
C(34)	0.9336(3)	0.7912(4)	0.4406(6)
C(35)	0.9181(3)	0.8644(3)	0.4010(6)
C(36)	0.8558(3)	0.8611(3)	0.2846(6)
C(37)	0.7714(3)	0.6175(3)	0.1505(8)
C(38)	1.0009(4)	0.7981(4)	0.5690(8)
C(39)	0.8437(4)	0.9471(3)	0.2624(7)
C(11)'	0.3363(2)	0.7272(3)	0.6435(5)
C(12)'	0.3969(3)	0.7813(3)	0.7669(5)
C(13)'	0.4580(3)	0.8320(3)	0.7190(6)
C(14)'	0.4623(3)	0.8301(3)	0.5505(6)
C(15)'	0.4020(3)	0.7781(3)	0.4335(6)
C(16)'	0.3385(3)	0.7281(3)	0.4729(5)
C(17)'	0.3977(3)	0.7883(4)	0.9533(6)
C(18)'	0.5304(3)	0.8841(4)	0.5012(8)
C(19)'	0.2743(3)	0.6802(3)	0.3295(6)
C(21)'	0.1943(2)	0.7105(3)	0.8273(5)
C(22)'	0.1529(3)	0.6693(3)	0.9325(6)
C(23)'	0.1125(3)	0.7123(3)	1.0306(6)
C(24)'	0.1127(3)	0.7966(3)	1.0245(6)
C(25)'	0.1519(3)	0.8352(3)	0.9154(6)
C(26)'	0.1925(3)	0.7946(3)	0.8148(6)
C(27)'	0.1471(3)	0.5765(3)	0.9436(7)
C(28)'	0.0691(4)	0.8435(4)	1.1319(8)
C(29)'	0.2297(3)	0.8427(3)	0.6952(7)
C(31)'	0.2025(2)	0.5574(3)	0.5373(5)
C(32)'	0.2404(3)	0.4957(3)	0.4829(6)
C(33)'	0.2029(3)	0.4262(3)	0.3517(7)
C(34)'	0.1307(3)	0.4140(3)	0.2716(7)
C(35)'	0.0941(3)	0.4748(3)	0.3261(6)
C(36)'	0.1291(3)	0.5463(3)	0.4557(6)
C(37)'	0.3202(3)	0.5044(3)	0.5564(7)
C(38)'	0.0899(3)	0.3385(4)	0.1284(8)
C(39)'	0.0846(3)	0.6108(3)	0.4941(7)

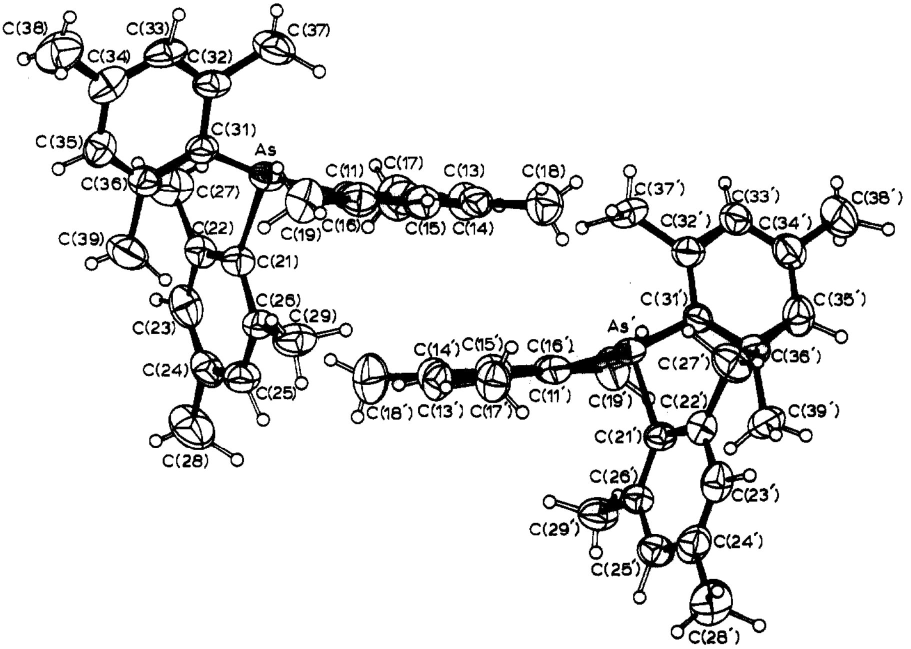

Fig. 1. An ORTEP [9] drawing of two independent molecules projected onto the best plane.

and arsines is connected with the fact that the dipole moments of these compounds depend mainly on the state of the unshared electrone pair (UEP) of the heteroatom, i.e. on the geometric configuration of such molecules. It should be noted that mesomeric moments connected with $p\pi$ and $p\pi$—$d\pi$ conjugation in aromatic arsines and phosphines are supposed to be small compared to the atomic DM of heteroatoms UEP. The differences between aromatic arsines and phosphines are seen in their physico-chemical properties depending both on the ground and excited state of the molecules. The long wave band in the electronic spectrum of triphenylarsine has the maximum at 249 nm and in that of TMAS at 276 nm. Thus the bathochromic shift is 27 nm. Such a shift can be to a great extent explained by the presence of methyl groups in positions 2, 4, 6 of each phenyl ring of TMAS, since the long wave band of mesitylene (λ_{max} = 266 nm) is shifted relative to that of benzene (λ_{max} = 255 nm). The same situation is found in the spectra of triphenylphosphine (λ_{max} = 262 nm) and TMP (λ_{max} = 314 nm). The strong bathochromic shift (52 nm) in this case is connected with the increasing π-conjugation in 2,6-disubstituted triarylphosphines because of the CPC angle and the π-conjugation in the hybrid orbital of UEP. It is evident that the ability of the 3p orbital of phosphorus to π-overlap with the 2p orbital of carbon is much higher than that of the 4p orbital of arsenic.

Molecular packing

As has been previously shown [15], the structures of organic and organometallic homomolecular crystals, where the chemically identical molecules occupy symmetrically independent positions, are encountered rather rarely. The ana-

TABLE 2

BOND LENGTHS (d) WITH STANDARD DEVIATIONS IN PARENTHESES

Bond	d(Å)	d'(Å)
As—C(11)	1.974(5)	1.973(4)
As—C(21)	1.983(5)	1.985(5)
As—C(31)	1.970(4)	1.970(4)
C(11)—C(12)	1.398(6)	1.403(5)
C(11)—C(16)	1.412(7)	1.408(6)
C(12)—C(13)	1.383(7)	1.383(7)
C(12)—C(17)	1.514(7)	1.511(7)
C(13)—C(14)	1.387(8)	1.391(7)
C(14)—C(15)	1.368(6)	1.364(6)
C(14)—C(18)	1.503(8)	1.507(8)
C(15)—C(16)	1.381(7)	1.378(7)
C(16)—C(19)	1.495(6)	1.505(6)
C(21)—C(22)	1.380(7)	1.387(7)
C(21)—C(26)	1.415(7)	1.411(7)
C(22)—C(23)	1.397(8)	1.398(8)
C(22)—C(27)	1.517(9)	1.519(7)
C(23)—C(24)	1.387(8)	1.392(8)
C(24)—C(25)	1.367(8)	1.372(8)
C(24)—C(28)	1.517(9)	1.522(9)
C(25)—C(26)	1.398(7)	1.392(7)
C(26)—C(29)	1.508(8)	1.499(8)
C(31)—C(32)	1.419(7)	1.420(7)
C(31)—C(36)	1.402(5)	1.397(6)
C(32)—C(33)	1.380(7)	1.385(6)
C(32)—C(37)	1.510(6)	1.495(7)
C(33)—C(34)	1.376(7)	1.368(7)
C(34)—C(35)	1.386(9)	1.391(8)
C(34)—C(38)	1.495(9)	1.508(7)
C(35)—C(36)	1.386(7)	1.388(6)
C(36)—C(39)	1.521(8)	1.521(8)

lysis of the molecular packing in such crystals is of special interest since in these cases non-Fedorov symmetry can be found [16,17]. Using the special program and the procedure described in ref. 18 we carried out the quantitative comparison of the symmetrically unrelated molecules TMAS and TMAS′. The geometric resemblance of the molecules can be described with the aid of the inconsistency criterion $s = (\Sigma w_i R_i^2 / \Sigma w_i)^{1/2}$, where R_i is a distance between the same atoms in different molecules at their closest matching; w_i is a weight factor. The closest superposition of the molecules occurs when their centers of gravity coincide with the subsequent minimization of the function $U = \Sigma_{i=1} w_i r_i^2$ (r_i is a distance between atoms).

The calculations showed that the symmetrically independent molecules TMAS and TMAS′ are rather similar but not identical, the criterion $s = 0.193$ Å*. At their closest concurrance atoms C(29), C(37) and C(18) have maximum inconsistencies (0.401, 0.320 and 0.311 Å, respectively). If we ignore the methyl atoms (their w's are set at 0), the criterion s diminishes to 0.146 Å. The analysis of the calculated results revealed that the main difference

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* The H atoms were ignored for this comparison.

TABLE 3

BOND ANGLES (ω) WITH STANDARD DEVIATIONS IN PARENTHESES

Angle	$\omega(^\circ)$	$\omega'(^\circ)$
C(11)—As—C(21)	106.4(2)	108.3(2)
C(11)—As—C(31)	108.2(2)	105.5(2)
C(21)—As—C(31)	109.2(2)	107.9(2)
As—C(11)—C(12)	113.4(3)	113.6(3)
As—C(11)—C(16)	127.4(3)	127.3(3)
C(12)—C(11)—C(16)	118.7(4)	118.6(4)
C(11)—C(12)—C(13)	119.9(5)	119.7(4)
C(11)—C(12)—C(17)	123.1(4)	122.4(4)
C(13)—C(12)—C(17)	117.0(4)	117.8(4)
C(12)—C(13)—C(14)	122.2(4)	122.0(4)
C(13)—C(14)—C(15)	116.8(5)	116.9(4)
C(13)—C(14)—C(18)	120.3(4)	121.1(4)
C(15)—C(14)—C(18)	122.9(6)	122.0(5)
C(14)—C(15)—C(16)	123.9(5)	123.9(4)
C(11)—C(16)—C(15)	118.4(4)	118.6(3)
C(11)—C(16)—C(19)	123.9(4)	124.1(4)
C(15)—C(16)—C(19)	117.6(4)	117.3(4)
As—C(21)—C(22)	113.6(4)	113.5(4)
As—C(21)—C(26)	122.8(5)	126.5(4)
C(22)—C(21)—C(26)	119.4(4)	119.4(4)
C(21)—C(22)—C(23)	120.0(5)	120.1(5)
C(21)—C(22)—C(27)	122.8(5)	122.7(5)
C(23)—C(22)—C(27)	117.1(5)	117.1(5)
C(22)—C(23)—C(24)	121.3(5)	121.0(5)
C(23)—C(24)—C(25)	118.3(5)	117.9(5)
C(23)—C(24)—C(28)	120.5(5)	120.0(5)
C(25)—C(24)—C(28)	121.1(5)	121.0(5)
C(24)—C(25)—C(26)	122.4(5)	122.9(5)
C(21)—C(26)—C(25)	118.5(5)	118.5(4)
C(21)—C(26)—C(29)	124.0(5)	124.1(4)
C(25)—C(26)—C(29)	117.4(5)	117.4(4)
As—C(31)—C(32)	113.8(3)	113.0(3)
As—C(31)—C(36)	127.8(4)	128.1(3)
C(32)—C(31)—C(36)	117.7(4)	118.9(3)
C(31)—C(32)—C(33)	119.8(4)	118.7(4)
C(31)—C(32)—C(37)	120.8(4)	122.8(4)
C(33)—C(32)—C(37)	119.3(5)	118.3(5)
C(32)—C(33)—C(34)	123.0(6)	123.0(5)
C(33)—C(34)—C(35)	116.8(5)	117.7(4)
C(33)—C(34)—C(38)	122.4(6)	123.0(5)
C(35)—C(34)—C(38)	120.8(5)	119.3(5)
C(34)—C(35)—C(36)	122.8(4)	121.9(4)
C(31)—C(36)—C(35)	119.9(5)	119.6(5)
C(31)—C(36)—C(39)	123.4(4)	123.8(4)
C(35)—C(36)—C(39)	116.7(4)	116.4(4)

between TMAS and TMAS′ exists in the relative orientation of the phenyl groups with respect to the plane C(11) C(21) C(31). The differences in the inclination of planes II, III and IV (Table 4) to this plane are 0.1, 8.8 and —7.8°, respectively.

In the crystal the symmetrically unrelated (meaning the classical space group symmetry) molecules can be transformed into one another by a supersymmetrical operation [17] which comprises a rotation of 180° around the axis l and a shift δ, parallel to this axis. The accuracy of this operation is 0.15 Å. The axis

TABLE 4

LEAST-SQUARES PLANES

The plane equation has a form: $AX + BY + CZ = D$

No.	Atoms defining the plane	A	B	C	D
I	C(11), C(21), C(31)	−0.4139	0.6396	0.6478	2.2214
II	C(11)—C(16)	−0.5643	0.8187	−0.1064	4.3084
III	C(21)—C(26)	0.4996	0.6273	0.5974	11.3789
IV	C(31)—C(36)	0.6861	−0.0269	−0.7270	8.4599
I′	C(11)′, C(21)′, C(31)′	−0.4745	0.3869	−0.7907	0.9890
II′	C(11)′—C(16)′	−0.6525	0.7469	−0.1281	6.4159
III′	C(21)′—C(26)′	0.6477	0.3592	0.6716	6.6685
IV′	C(31)′—C(36)′	0.3166	0.5247	−0.7902	2.8894

Atomic deviations (Å) from least-squares planes

Atom	I	II	III	IV	I′	II′	III′	IV′
As [a]	−0.707	−0.299	−0.336	0.280	−0.728	−0.317	0.364	−0.123
C(1)		−0.011	−0.022	0.003		−0.018	0.019	−0.004
C(2)		0.004	0.014	0.005		0.000	−0.008	0.000
C(3)		0.006	0.006	−0.006		0.015	−0.008	0.002
C(4)		0.009	−0.019	−0.001		−0.012	0.014	0.001
C(5)		0.003	0.011	0.010		−0.006	−0.004	−0.005
C(6)		0.007	0.010	−0.011		0.021	−0.013	0.007
C(7) [a]		0.044	0.115	−0.018		0.036	−0.080	0.057
C(8) [a]		−0.032	−0.043	0.000		−0.035	0.021	0.008
C(9) [a]		0.057	0.144	−0.083		0.144	−0.100	0.100

Angles (degrees) between least-squares planes

	I	II	III	IV	I′	II′	III′	IV′
I		46.5	54.4	39.5	86.1			
II			80.3	70.6				
III				83.8				
I′						45.6	45.6	47.3
II′							76.1	73.4
III′								82.1

[a] Atoms not used for plane calculation.

l is parallel to the plane XY, is 0.29 Å from it and has the orientation cosines 0.619, −0.785, 0.000. The shift δ is equal to 3.61 Å.

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