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STRUCTURE ANALYSIS OF TRIARYL DERIVATIVES OF THE GROUP V ELEMENTS

VIII *. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLARSINE, $C_{18}H_{15}As$

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Summary

The structure of triphenylarsine, $C_{18}H_{15}As$, has been elucidated by an X-ray structure analysis. Crystals are triclinic, *a* 15.275 Å, *b* 11.193 Å, *c* 17.866 Å, α 80.12°, β 95.48°, γ 93.65°, space group $P\bar{1}$, $Z = 8$. The refinement converges at $R = 0.032$. The average value of As–C bond distances is 1.957 Å, the average value of the valence angle CAsC is 100.1°. The four symmetrically independent molecules in the crystal structure are connected in pairs by the elements of supersymmetry.

Introduction

During the course of a systematic investigation of the structures of the Group V (N, P, As, Sb, Bi) triaryl derivatives and their physico-chemical properties we have performed the full X-ray structure analysis of the arsine series precursor, $AsPh_3$ (TFAS). As it has been shown earlier [1] the *p*-substituted triphenylarsine derivatives are not influenced by the value of the valence angle CAsC; on the contrary, the presence of bulky methyl groups in the positions 2 and 6 of the phenyl rings leads to an increase of this angle by ~ 7° [2]. The analogous situation has been observed in the series of triarylphosphines [3,4,5], triarylstibines [6,7] and triarylbismuthines [8,9,10].

X-ray data collection, structure determination and refinement

Unit cell parameters and the space group of TFAS have already been determined [11] in 1952; however, the crystal structure has not been solved. Single crystals of

(Continued on p. 132)

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* For part VII see ref. 5

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TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\times 10^3$)

	Molecule A				Molecule B			
	X	Y	Z	U^a	X	Y	Z	U^a
As	2061.5(5)	604.7(6)	9117.7(4)	60(1)	2919.9(5)	4478.9(6)	742.8(4)	56(1)
C(11)	1171(4)	−676(5)	8931(3)	48(2)	3816(5)	5723(6)	965(3)	51(3)
C(12)	307(5)	−468(7)	9012(4)	67(3)	4687(5)	5493(6)	925(4)	61(3)
C(13)	−358(5)	−1341(9)	8906(5)	84(4)	5346(5)	6338(8)	1072(4)	73(3)
C(14)	−152(5)	−2402(7)	8694(4)	66(3)	5142(5)	7411(7)	1261(4)	72(3)
C(15)	701(5)	−2595(6)	8607(4)	64(3)	4292(6)	7653(6)	1313(4)	71(3)
C(16)	1361(4)	−1751(6)	8727(4)	58(3)	3628(4)	6806(6)	1165(4)	61(3)
C(21)	3095(5)	−54(6)	8826(4)	60(3)	1885(4)	5144(6)	1047(4)	55(3)
C(22)	3219(6)	80(7)	8055(4)	76(3)	1788(5)	4994(7)	1815(4)	68(3)
C(23)	3945(8)	−362(9)	7817(5)	98(4)	1058(7)	5395(9)	2076(5)	93(4)
C(24)	4589(6)	−874(9)	8322(7)	100(4)	421(6)	5924(8)	1568(6)	86(4)
C(25)	4464(6)	−1031(8)	9094(6)	92(4)	494(6)	6082(8)	799(5)	89(4)
C(26)	3720(5)	−634(7)	9338(4)	70(3)	1231(5)	5683(7)	538(4)	66(3)
C(31)	2264(4)	185(6)	10228(4)	51(3)	2734(4)	4924(6)	−368(3)	50(2)
C(32)	2751(5)	1019(6)	10613(4)	64(3)	2232(4)	4117(6)	−767(4)	60(2)
C(33)	2894(5)	793(8)	11390(5)	79(4)	2121(5)	4351(8)	−1555(5)	75(3)
C(34)	2552(6)	−232(9)	11811(4)	80(4)	2497(5)	5385(8)	−1942(4)	71(3)
C(35)	2051(5)	−1061(7)	11437(4)	73(3)	2982(5)	6206(6)	−1557(4)	70(3)
C(36)	1912(5)	−862(6)	10653(4)	59(3)	3090(5)	5967(6)	−775(4)	58(3)

	Molecule C				Molecule D			
	X	Y	Z	U^a	X	Y	Z	U^a
As	3499.0(5)	8544.3(7)	5255.6(4)	61(1)	1673.1(6)	3600.2(7)	5142.5(4)	66(1)
C(11)	4411(5)	7935(6)	6052(4)	55(7)	1494(4)	2371(6)	4473(4)	55(3)
C(12)	5244(5)	8487(7)	6010(4)	72(3)	1694(5)	2754(7)	3727(4)	73(3)
C(13)	5914(5)	8083(9)	6544(6)	90(4)	1586(6)	1962(10)	3221(4)	90(4)
C(14)	5783(7)	7152(9)	7126(5)	87(4)	1249(6)	816(10)	3417(5)	95(4)
C(15)	4968(7)	6612(8)	7170(4)	85(4)	1051(6)	427(7)	4159(6)	97(4)
C(16)	4279(5)	6998(7)	6652(4)	71(3)	1157(6)	1200(7)	4683(4)	81(4)
C(21)	2441(4)	8000(6)	5785(4)	55(3)	837(5)	2944(6)	5898(4)	61(3)
C(22)	2144(6)	8763(7)	6217(4)	75(3)	0(6)	3332(7)	5775(5)	84(4)
C(23)	1399(7)	8456(9)	6589(5)	103(5)	−588(7)	2937(12)	6302(8)	124(6)
C(24)	934(5)	7386(10)	6534(5)	83(4)	−365(10)	2149(12)	6951(8)	131(7)
C(25)	1233(6)	6602(8)	6111(5)	87(4)	474(9)	1779(10)	7074(5)	118(5)
C(26)	1982(5)	6910(7)	5726(4)	68(3)	1071(5)	2160(8)	6559(5)	92(4)
C(31)	3493(4)	7326(6)	4585(4)	56(3)	2780(5)	3083(6)	5711(4)	63(3)
C(32)	3137(5)	7651(7)	3850(4)	73(3)	3089(6)	3676(7)	6312(5)	87(4)
C(33)	3115(6)	6832(10)	3344(5)	94(4)	3861(8)	3394(8)	6731(5)	101(5)
C(34)	3487(6)	5740(10)	3562(5)	89(4)	4375(6)	2542(10)	6546(6)	99(5)
C(35)	3857(5)	5412(7)	4281(5)	78(4)	4073(6)	1936(9)	5963(5)	96(4)
C(36)	3860(5)	6206(7)	4799(4)	70(3)	3283(5)	2210(7)	5539(4)	69(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2

BOND LENGTHS (*d* Å) WITH STANDARD DEVIATIONS IN PARENTHESES

Bond	A	B	C	D
As–C(11)	1.961(6)	1.953(7)	1.959(7)	1.963(7)
As–C(21)	1.935(7)	1.950(7)	1.961(7)	1.966(7)
As–C(31)	1.958(7)	1.959(7)	1.963(7)	1.955(7)
C(11)–C(12)	1.38(1)	1.38(1)	1.38(1)	1.39(1)
C(12)–C(13)	1.39(1)	1.37(1)	1.37(1)	1.36(1)
C(13)–C(14)	1.37(1)	1.37(1)	1.36(1)	1.35(2)
C(14)–C(15)	1.36(1)	1.36(1)	1.35(1)	1.38(1)
C(15)–C(16)	1.36(1)	1.38(1)	1.37(1)	1.37(1)
C(16)–C(11)	1.37(1)	1.38(1)	1.39(1)	1.38(1)
C(21)–C(22)	1.39(1)	1.38(1)	1.37(1)	1.36(1)
C(22)–C(23)	1.37(1)	1.38(1)	1.37(1)	1.36(2)
C(23)–C(24)	1.36(2)	1.36(1)	1.37(2)	1.36(2)
C(24)–C(25)	1.39(2)	1.37(1)	1.38(1)	1.36(2)
C(25)–C(26)	1.38(1)	1.39(1)	1.39(1)	1.36(1)
C(26)–C(21)	1.37(1)	1.38(1)	1.38(1)	1.38(1)
C(31)–C(32)	1.39(1)	1.39(1)	1.37(1)	1.39(1)
C(32)–C(33)	1.37(1)	1.38(1)	1.39(1)	1.36(1)
C(33)–C(34)	1.36(1)	1.37(1)	1.36(2)	1.37(2)
C(34)–C(35)	1.38(1)	1.38(1)	1.35(1)	1.37(1)
C(35)–C(36)	1.38(1)	1.37(1)	1.39(1)	1.38(1)
C(36)–C(31)	1.39(1)	1.38(1)	1.39(1)	1.37(1)

TFAS were obtained from ethanol and CCl_4 solution by evaporation. A crystal with size of 0.17 × 0.17 × 0.16 mm was chosen for the X-ray experiment. All experimental data were collected using a Syntex $P\bar{1}$ automatic four-circled diffractometer. The unit cell parameters are as follows: a 15.275(4) Å, b 11.193(3) Å, c 17.866(3) Å, α 80.12(2)°, β 95.48(2)°, γ 93.65(2)°, V 2992(1) Å^3, D_c 1.36 g cm^{-3}, $Z = 8$, space group $P\bar{1}$, $F(000)$ 1248e. 4713 experimental intensities were collected (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan technique to $\sin\theta/\lambda_{max} = 0.57$ Å^{-1}). The data were corrected for Lorentz and polarization effects but not for absorption (μ(Mo) = 23.8 cm^{-1}). For further calculations 4325 reflections with $I > 3\sigma(I)$ were used.

To determine coordinates of the four As atoms we used the program MULTAN-78 [12]. During the structure determination 362 normalized reflections with $E_{min} = 1.6$ were used. All further calculations were performed on the NOVA-3 minicomputer using the SHELXTL system written by G.M. Sheldrick. The coordinates of the carbon atoms were found by experimental Fourier synthesis and the coordinates of the hydrogen atoms were calculated from geometric considerations. The whole structure was refined by the full-matrix least-squares method using anisotropic (As and C atoms) and isotropic (H atoms) thermal parameters *. The final R value is 0.032. The atomic coordinates of As and C atoms, bond lengths, valence angles, mean planes equations and angles between least-squares planes are given in Tables 1, 2, 3 and 4.

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* Tables of anisotropic thermal parameters of As and C atoms, parameters of H atoms and lists of F_0 and F_c may be obtained upon request from the authors.

TABLE 3

BOND ANGLES (ω°) WITH STANDARD DEVIATIONS IN PARENTHESES

Angle	A	B	C	D
C(11)–As–C(21)	100.4(3)	100.1(3)	100.1(3)	99.8(3)
C(11)–As–C(31)	99.2(3)	100.1(3)	100.5(3)	99.7(3)
C(21)–As–C(31)	99.6(3)	100.3(3)	100.6(3)	100.8(3)
As–C(11)–C(12)	117.3(5)	117.9(5)	117.3(5)	115.8(5)
As–C(11)–C(16)	123.8(5)	123.7(5)	124.8(5)	125.1(5)
C(12)–C(11)–C(16)	118.9(6)	118.4(6)	117.9(7)	119.1(7)
C(11)–C(12)–C(13)	120.7(7)	120.5(7)	119.9(7)	119.8(7)
C(12)–C(13)–C(14)	119.2(8)	120.0(7)	121.8(9)	121.7(8)
C(13)–C(14)–C(15)	119.8(7)	120.7(7)	118.4(9)	118.8(9)
C(14)–C(15)–C(16)	121.3(7)	119.5(7)	121.5(8)	120.8(8)
C(15)–C(16)–C(11)	120.1(6)	120.9(7)	120.4(7)	119.7(7)
As–C(21)–C(22)	118.5(6)	117.0(5)	117.3(5)	118.1(6)
As–C(21)–C(26)	123.7(6)	123.9(5)	123.2(5)	123.0(6)
C(22)–C(21)–C(26)	117.9(7)	119.0(7)	119.5(7)	118.9(7)
C(21)–C(22)–C(23)	120.8(8)	120.7(7)	120.6(8)	119.8(9)
C(22)–C(23)–C(24)	121.5(9)	119.5(9)	120.7(9)	122(1)
C(23)–C(24)–C(25)	118.1(9)	121.3(9)	119.3(9)	118(1)
C(24)–C(25)–C(26)	120.8(9)	119.0(8)	120.3(8)	121(1)
C(25)–C(26)–C(21)	120.8(8)	120.4(7)	119.5(7)	120.3(9)
As–C(31)–C(32)	117.6(5)	117.8(5)	116.6(5)	117.2(6)
As–C(31)–C(36)	123.8(5)	123.8(5)	124.2(5)	124.6(6)
C(32)–C(31)–C(36)	118.5(6)	118.4(6)	119.1(7)	118.2(7)
C(31)–C(32)–C(33)	120.3(7)	120.3(6)	119.6(7)	121.4(8)
C(32)–C(33)–C(34)	121.6(8)	119.8(7)	120.5(9)	120.3(9)
C(33)–C(34)–C(35)	118.8(8)	120.8(7)	120.9(9)	118.9(9)
C(34)–C(35)–C(36)	120.6(7)	119.1(7)	119.4(8)	121.0(9)
C(35)–C(36)–C(31)	120.2(7)	121.6(6)	120.7(7)	120.1(7)

TABLE 4

LEAST-SQUARES PLANES[a]

Plane No.	Atoms defining the plane	*P*	*Q*	*R*	*D*
I(A)	C(11)A, C(21)A, C(31)A	−0.2283	0.8925	−0.3889	−4.4748
II(A)	C(11)A–C(16)A	−0.0623	0.2559	−0.9647	−14.6413
III(A)	C(21)A–C(26)A	−0.4184	−0.9071	−0.0451	−4.3528
IV(A)	C(31)A–C(36)A	0.8701	−0.4890	−0.0626	−1.2317
I(B)	C(11)B, C(21)B, C(31)B	−0.2106	0.9032	−0.3741	4.2919
II(B)	C(11)B–C(16)B	−0.0055	0.2588	−0.9659	0.0598
III(B)	C(21)B–C(26)B	−0.4085	−0.9121	−0.0335	−6.5347
IV(B)	C(31)B–C(36)B	0.8671	−0.4959	−0.0464	0.7167
I(C)	C(11)C, C(21)C, C(31)C	0.0643	0.9051	−0.4203	5.5160
II(C)	C(11)C–C(16)C	0.3256	−0.7558	−0.5682	−12.4100
III(C)	C(21)C–C(26)C	−0.5061	0.3161	−0.8025	−5.8746
IV(C)	C(31)C–C(36)C	0.8894	0.3589	−0.2832	4.7407
I(D)	C(11)D, C(21)D, C(31)D	−0.0766	0.9028	−0.4231	0.1650
II(D)	C(11)D–C(16)D	−0.9286	0.2629	−0.2583	−2.2302
III(D)	C(21)D–C(26)D	−0.1858	−0.8658	−0.4646	−9.1808
IV(D)	C(31)D–C(36)D	0.4930	0.6012	−0.6288	−1.7071

TABLE 4 (continued)

Angles between least-squares planes(°)

	A	*B*	*C*	*D*
I–II	51.8	53.4	64.9	65.3
I–III	45.8	43.5	53.8	55.2
I–IV	52.4	52.2	59.9	39.5
II–III	80.6	78.4	87.0	86.3
II–IV	83.2	84.9	79.7	82.1
III–IV	85.3	84.3	83.7	71.3

[a] The plane equation has the form $PX + QY + RZ = D$.

Atomic deviations from least-squares planes (Å)

Plane	Atom	A	B	C	D
I	As [b]	0.917	−0.907	0.905	0.917
	C(11)	0.0	0.0	0.0	0.0
	C(21)	0.0	0.0	0.0	0.0
	C(31)	0.0	0.0	0.0	0.0
II	As [b]	−0.015	0.012	0.042	0.038
	C(11)	−0.002	0.006	0.008	−0.006
	C(12)	0.010	−0.003	−0.003	0.009
	C(13)	−0.010	−0.002	0.0	−0.012
	C(14)	0.003	0.005	−0.001	0.011
	C(15)	0.005	−0.002	0.006	−0.008
	C(16)	−0.005	−0.003	−0.010	0.005
III	As [b]	−0.080	0.087	0.045	−0.074
	C(21)	−0.012	−0.005	0.002	0.004
	C(22)	−0.010	0.005	−0.003	−0.001
	C(23)	0.025	−0.004	−0.002	−0.006
	C(24)	−0.021	0.002	0.008	0.008
	C(25)	−0.007	−0.001	−0.009	−0.005
	C(26)	0.017	0.002	0.004	−0.001
IV	As [b]	−0.071	0.114	0.048	0.071
	C(31)	0.006	0.010	−0.008	0.002
	C(32)	−0.010	−0.007	0.017	0.006
	C(33)	0.005	−0.001	−0.015	−0.012
	C(34)	0.004	0.006	0.004	0.016
	C(35)	−0.007	−0.002	0.005	−0.008
	C(36)	0.002	−0.006	−0.003	0.005

[b] Atoms not used for plane calculations.

Discussion

The mean As–C bond length, 1.957(8) Å, and CAsC angle, 100.1(4)°, are close to those in the *p*-substituted triarylarsines: 1.964 Å and 99.3° in tri-*p*-tolylarsine (TPTA), 1.958 Å and 99.8° in tri-*p*-chlorophenylarsine (TPCPA) and 1.963 Å and 98.3° in tri-*p*-methoxyphenylarsine (TPMPA) [1]. But when considered in detail, the

TABLE 5

THE RESULTS OF QUANTITATIVE COMPARISON OF SYMMETRICALLY UNRELATED MOLECULES OF TFAS

Atoms	R_i(Å)					
	A and B	A and C	A and D	B and C	B and D	C and D
As	0.03	0.04	0.06	0.01	0.07	0.05
C(11)–C(16)	0.01–0.09	0.02–0.34	0.04–0.24	0.01–0.29	0.08–0.33	0.06–0.29
C(21)–C(26)	0.03–0.07	0.02–0.22	0.05–0.21	0.02–0.25	0.06–0.35	0.05–0.34
C(31)–C(36)	0.03–0.05	0.03–0.21	0.06–0.32	0.02–0.22	0.04–0.40	0.04–0.12
s	0.05	0.19	0.17	0.19	0.24	0.20

geometrical characteristics of the four symmetrically independent molecules are certainly different. We performed the quantitative comparison of symmetrically unrelated molecules in the crystal structure. The geometrical resemblance of the molecules may be described with the aid of the inconsistency criterion $s = \sqrt{\sum_{i=1}^{N} R_i^2/N}$, R_i being the distance between the same atoms in the different molecules at their closest matching and N the number of atoms in the molecule. Calculations were performed using the program SUSY [13]. Results of the comparison of the symmetrically independent molecules of TFAS (molecules A, B, C and D) are given in Table 5.

The calculations * showed that only two molecules A and B are rather similar (the criterion $s = 0.05$ Å). The pairs of molecules A and C, A and D, B and C, B and D, C and D have noticeable differences in their geometrical characteristics (the values of s are in the range of 0.17–0.20 Å). These differences are the result of the different orientation of the mutual phenyl groups. The molecular packing of TFAS is shown

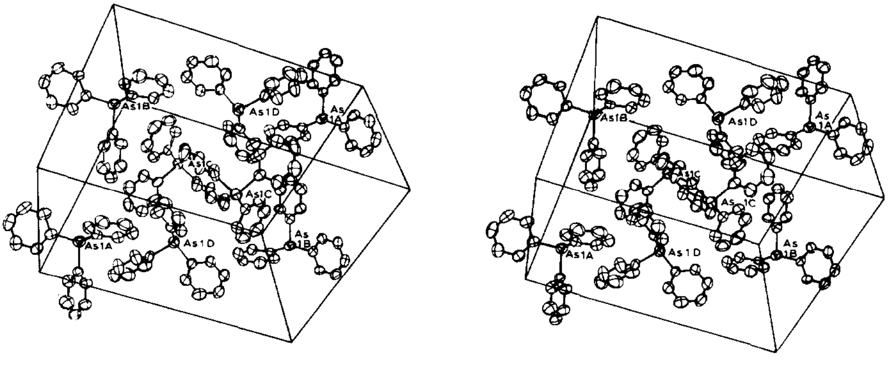

Fig. 1. An ORTEP drawing of the packing of stereopairs of TFAS molecules.

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* The H atoms were ignored for the comparison.

in Fig. 1. Analysis of the molecular packing and comparison of the molecules revealed that the pairs of molecules can be transformed into one another by a supersymmetrical operations [14]. The independent molecules A and B are connected by a center of supersymmetry. The other pairs of molecules can be transformed into one another by a rotation by 180° and a shift along the axis of rotation (operations 2_q) or by a reflection in the plane and a shift along this plane (operation m_p), this is a result of interaction $2q$ with center of symmetry.

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