A packing diagram is shown in Fig. 2. The molecules form a dimer around the inversion center at $(\frac{1}{2},0,\frac{1}{2})$ through $N(9)-H(9)\cdots N(3)$ hydrogen bonds $[N(9)\cdots N(3^i) = 2\cdot972\ (5)$, $H(9)\cdots N(3^i) = 2\cdot047$ Å, $\angle N(9)-H(9)\cdots N(3^i) = 161\cdot9°$, symmetry code (i) $1-x$, $-y$, $1-z]$. An intermolecular distance of $2\cdot445$ Å between $O(8)$ and $H(4^{ii})$ [symmetry code (ii) $-x$, $-y$, $-z$] stabilizes the crystal structure in the **a** direction. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

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Structural Investigation of the Triaryl Derivatives of the Group V Elements. IX.* Structure of Triphenylamine, $C_{18}H_{15}N$

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Abstract. $M_r = 245\cdot2$, monoclinic, Bb, $a = 15\cdot655\ (5)$, $b = 22\cdot257\ (7)$, $c = 15\cdot807\ (5)$ Å, $\gamma = 91\cdot04\ (2)°$, $V = 5507\ (3)$ Å^3, $Z = 16$, $D_m = 1\cdot18$, $D_x = 1\cdot18$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot64$ cm^{-1}, $F(000) = 2080$, $T = 297$ K, $R = 0\cdot036$ for 2902 reflections. The mean values for N—C bonds and CNC angles are $1\cdot419\ (6)$ Å and $119\cdot6\ (7)°$, respectively. Four independent molecules in the crystal are related pairwise by the supersymmetry elements. The structural parameters of triphenylamine (TPHA) molecules are compared with those of a series of triaryl derivatives of the Group V elements.

Introduction. The structural investigation of the triaryl derivatives of N subgroup elements Ar_3X, where $X = N,P,As,Sb$ and Bi, is of special interest for the solution of the problem of the possibility of the interaction between the lone electron pair (l.e.p.) of the hetero-atom X and π electrons of adjoining aromatic systems ($p\pi$ conjugation).

The character of the l.e.p. in Ar_3X is mostly influenced by the molecular conformation and also by the value of the bond angle CXC. These values in Ar_3X compounds can vary significantly (according to the state of the valence electrons s^2p^3 of the Group V elements) from $\sim90°$ (σ bonds C—X are formed by the p orbitals of X) to $\sim120°$ (σ bonds are formed by sp^2 orbitals of X), and the character of the l.e.p. can vary from s^2 to p^2. The greater the contribution of the p state in the l.e.p. orbital the more probable is an overlapping of this orbital with π orbitals of aromatic rings or its donation to the highest occupied molecular orbital (HOMO) of the corresponding compound.

Therefore, structural investigations of such compounds are important for both prediction and estimation of the intramolecular electronic interactions and for the calculation of different molecular parameters.

In continuation of a series of structural investigations of the triaryl derivatives of the Group V elements (Sobolev, Chetkina, Romm & Guryanova, 1976; Sobolev, Romm, Belsky & Guryanova, 1979,1980; Sobolev & Belsky, 1981; Sobolev, Romm, Belsky, Syutkina & Guryanova, 1981; Sobolev, Romm, Chernikova, Belsky & Guryanova, 1981; Sobolev, Belsky, Chernikova & Akhmadulina, 1983; Sobolev, Belsky & Romm, 1983; Sobolev, Belsky, Romm & Guryanova, 1983) we report here the crystal and molecular structure of triphenylamine and summarize some results on the structures Ar_3X from the point of view of the steric influence on molecular conformation. [The

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* Part VIII: Sobolev, Belsky, Chernikova & Akhmadulina (1983).

unit-cell parameters and possible space group for TPHA were reported earlier (Iveronova & Roitburd, 1952) but the crystal structure has not previously been determined.]

Experimental. Crystals of TPHA were grown from ethanol solution at room temperature. Colourless single crystal $0.32 \times 0.39 \times 0.50$ mm. Automatic Syntex $P\bar{1}$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Unit-cell parameters determined using the diffractometer setting angles of 14 general reflections with $20 < 2\theta < 30°$. No absorption correction. $\theta{-}2\theta$ scan technique, variable scan speed, $\theta_{max} = 25°$. h,k,l $\overline{16},0,0$ to $16,26,16$. Three standard reflections monitored after every 100 reflections showed no significant systematic variation. Out of 3582 unique reflections collected, 2902 with $I > 3\sigma(I)$ were used for the structure solution and refinement. The systematic absences (hkl $h + l = 2n$, $hk0$ $k = 2n$) indicated space groups Bb (No. 9) and $B2/b$ (No. 15). The noncentrosymmetric group was chosen according to the Harker sections. Structure solved using the direct method by $RANT$ procedure (373 normalized structure amplitudes with $E_{min} > 1.6$). The usual sequence of isotropic and anisotropic refinements (on F) was

performed. H-atom positions were calculated and refined isotropically. Refinement converged to $R = 0.036$ (unit weights, $wR = 0.036$). $(\Delta/\sigma)_{max} = 0.29$. Final zero Fourier synthesis revealed only minor peaks possibly attributable to bonding electrons $(\Delta\rho = 0.18 \text{ e Å}^{-3})$. No secondary-extinction correction. All calculations performed using $SHELXTL$ (Sheldrick, 1981) with a NOVA-3 computer incorporated in the Nicolet $R3$ crystallographic system. Atomic scattering factors for N and C from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965).

Discussion. The atomic coordinates are listed in Table 1,* interatomic distances and bond angles are presented in Table 2. The value of the bond angle CNC in the four independent TPHA molecules varies from 118.5 to $120.8°$ [mean value $119.6 (7)°$]; the N—C bond

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Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\times 10^3)$ *with their e.s.d.'s*

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	Molecule A				Molecule B			
	x	y	z	$U_{eq}(\text{Å}^2)$	x	y	z	$U_{eq}(\text{Å}^2)$
N	2008 (3)	2259 (2)	458 (3)	63 (2)	365 (3)	195 (2)	7006 (3)	61 (2)
C(11)	1816 (3)	1681 (2)	800 (3)	50 (2)	529 (3)	780 (2)	6667 (3)	46 (2)
C(12)	981 (3)	1496 (2)	913 (4)	74 (2)	1352 (3)	976 (2)	6522 (4)	68 (2)
C(13)	811 (4)	930 (3)	1273 (4)	84 (3)	1498 (3)	1544 (2)	6169 (4)	82 (2)
C(14)	1466 (5)	565 (2)	1499 (4)	76 (2)	827 (5)	1905 (2)	5969 (4)	76 (2)
C(15)	2291 (4)	755 (2)	1370 (3)	67 (2)	21 (4)	1711 (3)	6127 (4)	73 (2)
C(16)	2467 (3)	1307 (2)	1031 (3)	58 (2)	−128 (3)	1150 (2)	6469 (3)	58 (2)
C(21)	2666 (3)	2611 (2)	838 (3)	50 (1)	−347 (3)	−145 (2)	6715 (3)	50 (2)
C(22)	2687 (3)	2663 (2)	1715 (3)	61 (2)	−504 (3)	−174 (2)	5851 (3)	58 (2)
C(23)	3339 (4)	2989 (2)	2095 (3)	68 (2)	−1202 (3)	−496 (2)	5545 (3)	67 (2)
C(24)	3958 (3)	3269 (2)	1615 (4)	72 (2)	−1746 (3)	−798 (2)	6100 (4)	74 (2)
C(25)	3937 (3)	3224 (2)	746 (3)	63 (2)	−1581 (3)	−775 (2)	6952 (4)	67 (2)
C(26)	3289 (3)	2893 (2)	356 (3)	55 (2)	−887 (3)	−444 (2)	7270 (3)	57 (2)
C(31)	1663 (3)	2427 (2)	−335 (3)	50 (2)	788 (3)	18 (2)	7755 (3)	51 (2)
C(32)	1538 (3)	2012 (2)	−970 (3)	60 (3)	871 (3)	407 (2)	8439 (3)	60 (2)
C(33)	1195 (4)	2182 (3)	−1732 (4)	72 (2)	1286 (3)	227 (3)	9164 (3)	67 (2)
C(34)	989 (3)	2771 (3)	−1886 (3)	72 (2)	1617 (3)	−340 (3)	9212 (3)	74 (2)
C(35)	1122 (4)	3189 (2)	−1255 (4)	71 (2)	1532 (3)	−726 (2)	8539 (4)	73 (2)
C(36)	1448 (3)	3022 (2)	−481 (3)	62 (2)	1123 (3)	−550 (2)	7814 (3)	64 (2)

	Molecule C				Molecule D			
N	2817 (3)	301 (2)	4561 (3)	60 (1)	4425 (2)	2345 (2)	7931 (2)	57 (1)
C(11)	3224 (3)	−70 (2)	5158 (3)	47 (2)	4155 (3)	2675 (2)	7216 (3)	46 (2)
C(12)	4098 (3)	−128 (2)	5139 (3)	71 (2)	3283 (3)	2695 (2)	7024 (3)	66 (2)
C(13)	4504 (3)	−484 (2)	5720 (4)	83 (2)	3013 (3)	3015 (2)	6327 (3)	83 (2)
C(14)	4041 (4)	−791 (2)	6325 (3)	77 (2)	3589 (3)	3320 (2)	5818 (3)	76 (2)
C(15)	3164 (3)	−734 (2)	6355 (3)	72 (2)	4452 (3)	3311 (2)	6021 (3)	69 (2)
C(16)	2755 (3)	−374 (2)	5774 (3)	60 (2)	4733 (3)	2988 (2)	6713 (3)	57 (2)
C(21)	3202 (3)	868 (2)	4363 (3)	49 (2)	4082 (3)	1758 (2)	8077 (3)	48 (2)
C(22)	3294 (4)	1050 (2)	3529 (3)	58 (2)	3919 (4)	1559 (2)	8882 (3)	57 (2)
C(23)	3687 (4)	1608 (3)	3357 (4)	66 (2)	3565 (4)	980 (3)	9000 (4)	59 (2)
C(24)	3960 (3)	1971 (2)	4006 (5)	70 (2)	3384 (3)	620 (2)	8319 (4)	62 (2)
C(25)	3859 (3)	1787 (2)	4825 (4)	63 (2)	3559 (4)	817 (2)	7529 (4)	64 (2)
C(26)	3483 (3)	1240 (2)	5003 (3)	56 (2)	3895 (3)	1376 (2)	7404 (3)	56 (2)
C(31)	2036 (3)	121 (2)	4190 (3)	54 (2)	5180 (3)	2530 (2)	8367 (3)	48 (1)
C(32)	1393 (3)	526 (2)	4075 (3)	61 (2)	5859 (3)	2145 (2)	8463 (3)	62 (2)
C(33)	631 (3)	352 (3)	3704 (4)	71 (2)	6588 (3)	2339 (3)	8876 (4)	74 (2)
C(34)	498 (3)	−230 (2)	3456 (4)	77 (2)	6646 (3)	2920 (3)	9189 (3)	79 (2)
C(35)	1130 (4)	−637 (2)	3578 (4)	90 (3)	5974 (4)	3301 (2)	9097 (3)	74 (2)
C(36)	1905 (3)	−466 (2)	3936 (4)	76 (2)	5233 (3)	3109 (2)	8690 (3)	60 (2)

lengths are in the range 1·408–1·427 Å [mean value 1·419 (6) Å]. The N atom deviates from the plane of the bonded C atoms (Table 3, deposited) by 0·085, 0·104, 0·013 and 0·116 Å in the four molecules [mean deviation 0·08 (4) Å]. The phenyl rings are planar; their geometry is unexceptional. The dihedral angles between phenyl-ring planes and the plane of the N-bonded C atoms vary from 37·0 to 50·5° [mean value 44 (5)°]. These results for TPHA are in a good agreement with those for tri-p-tolylamine (Reynolds & Scaringe, 1982).

Table 2. *Bond lengths* (Å) *and angles* (°) *with standard deviations in parentheses*

	Molecule A	Molecule B	Molecule C	Molecule D
N–C(11)	1·423 (6)	1·427 (6)	1·413 (7)	1·417 (6)
N–C(21)	1·416 (7)	1·413 (7)	1·423 (6)	1·422 (6)
N–C(31)	1·418 (7)	1·416 (7)	1·408 (7)	1·423 (6)
C(11)–C(12)	1·375 (7)	1·372 (7)	1·377 (7)	1·400 (7)
C(12)–C(13)	1·403 (8)	1·397 (7)	1·376 (7)	1·382 (7)
C(13)–C(14)	1·367 (9)	1·371 (8)	1·374 (8)	1·378 (7)
C(14)–C(15)	1·37 (1)	1·35 (1)	1·382 (8)	1·389 (7)
C(15)–C(16)	1·364 (6)	1·377 (8)	1·383 (7)	1·385 (7)
C(16)–C(11)	1·377 (7)	1·366 (7)	1·388 (7)	1·383 (7)
C(21)–C(22)	1·391 (7)	1·389 (7)	1·386 (7)	1·370 (7)
C(22)–C(23)	1·379 (7)	1·383 (7)	1·403 (8)	1·406 (8)
C(23)–C(24)	1·372 (8)	1·388 (7)	1·369 (9)	1·369 (9)
C(24)–C(25)	1·378 (8)	1·372 (9)	1·37 (1)	1·350 (9)
C(25)–C(26)	1·387 (7)	1·395 (7)	1·372 (6)	1·356 (7)
C(26)–C(21)	1·380 (7)	1·381 (7)	1·374 (7)	1·390 (7)
C(31)–C(32)	1·376 (7)	1·390 (7)	1·375 (6)	1·386 (7)
C(32)–C(33)	1·375 (8)	1·380 (7)	1·378 (7)	1·377 (7)
C(33)–C(34)	1·377 (9)	1·375 (9)	1·366 (8)	1·386 (9)
C(34)–C(35)	1·377 (8)	1·372 (8)	1·367 (7)	1·371 (8)
C(35)–C(36)	1·379 (8)	1·373 (8)	1·386 (8)	1·387 (7)
C(36)–C(31)	1·392 (6)	1·381 (6)	1·379 (6)	1·387 (6)
C(11)–N–C(21)	118·6 (4)	119·6 (4)	118·5 (4)	119·6 (4)
C(11)–N–C(31)	120·0 (4)	119·4 (4)	120·7 (4)	119·4 (4)
C(21)–N–C(31)	120·4 (4)	119·5 (4)	120·8 (4)	119·0 (4)
N–C(11)–C(12)	120·3 (4)	120·4 (4)	120·0 (4)	119·3 (4)
N–C(11)–C(16)	120·1 (4)	120·8 (4)	120·9 (4)	121·4 (4)
C(12)–C(11)–C(16)	119·6 (4)	118·9 (4)	119·2 (4)	119·3 (4)
C(11)–C(12)–C(13)	119·0 (5)	119·5 (5)	120·6 (4)	119·8 (4)
C(12)–C(13)–C(14)	120·5 (6)	120·5 (5)	120·4 (5)	121·0 (4)
C(13)–C(14)–C(15)	119·5 (5)	119·5 (6)	119·6 (5)	119·1 (4)
C(14)–C(15)–C(16)	120·8 (5)	120·3 (6)	120·1 (4)	120·5 (4)
C(15)–C(16)–C(11)	120·6 (5)	121·3 (6)	120·1 (4)	120·3 (4)
N–C(21)–C(22)	119·0 (4)	118·8 (4)	120·6 (4)	120·9 (4)
N–C(21)–C(26)	121·2 (4)	121·4 (4)	119·9 (4)	120·6 (4)
C(22)–C(21)–C(26)	119·8 (4)	119·7 (4)	119·6 (4)	118·5 (4)
C(21)–C(22)–C(23)	119·6 (4)	120·4 (4)	119·0 (5)	119·2 (5)
C(22)–C(23)–C(24)	120·5 (5)	120·1 (4)	120·3 (6)	120·4 (6)
C(23)–C(24)–C(25)	120·2 (5)	119·3 (5)	120·0 (6)	119·9 (5)
C(24)–C(25)–C(26)	119·9 (4)	121·2 (5)	120·4 (5)	120·4 (5)
C(25)–C(26)–C(21)	120·0 (4)	119·3 (4)	120·7 (4)	121·6 (5)
N–C(31)–C(32)	121·2 (4)	121·1 (4)	120·7 (4)	121·1 (4)
N–C(31)–C(36)	119·8 (4)	119·9 (4)	120·3 (4)	118·9 (4)
C(32)–C(31)–C(36)	119·0 (4)	119·0 (4)	119·0 (4)	120·0 (4)
C(31)–C(32)–C(33)	120·4 (5)	120·3 (5)	120·8 (5)	119·9 (5)
C(32)–C(33)–C(34)	121·1 (6)	120·0 (5)	120·3 (5)	120·1 (5)
C(33)–C(34)–C(35)	118·7 (5)	119·9 (5)	119·2 (5)	120·1 (5)
C(34)–C(35)–C(36)	120·8 (5)	120·6 (5)	121·1 (5)	120·4 (5)
C(35)–C(36)–C(31)	120·0 (5)	120·3 (4)	119·6 (5)	119·5 (4)

Table 4. *Supersymmetrical relationships in TPHA*

Molecules	Operation of supersymmetry	Δ_{mean}	Shift components (fractions of unit-cell edges)
A' and B	2_q	0·14	0 0 $\frac{1}{4}$
A' and D	$4_q (q \approx 2)$	0·17	0 $\frac{1}{4}$ 0
C' and C	$4_q (q \approx 2)$	0·16	0 $\frac{1}{2}$ 0
A and C	2_q	0·07	$\frac{1}{4}$ 0 $\frac{1}{4}$
B and D	2_q	0·07	$\frac{1}{4}$ 0 $\frac{1}{4}$
C and D	2_q	0·20	0 0 $\frac{1}{4}$

Symmetry code: (') $x, \frac{1}{2} + y, 1 - z$.

The TPHA structure is the first example of an organic molecular crystal with space group Bb and four molecules per asymmetric unit. The quantitative comparison of these molecules has shown that geometrically they are very similar. The discrepancy criterion $s = (\sum R_i^2/N)^{1/2}$ (where R_i is the distance between corresponding atoms in the different molecules at the closest coincidence, and N is the number of atoms) for all possible pairs of TPHA molecules is in the range $0·03 < s < 0·13$ Å.

In the crystal the molecules which are not equivalent by space-group symmetry are related pairwise by supersymmetry elements (Zorkii & Koptsik, 1980). These elements are characterized in Table 4: 2_q – rotation by 180° in combination with a shift along the axis of rotation, 4_q – rotation by 90° in combination with a shift along the axis of rotation, m_p – mirror reflection and a shift parallel to the mirror plane, $\bar{1}_s$ – inversion. The deviations from fine supersymmetrical transformations Δ_{mean} are calculated as $\Delta_{mean} = \frac{1}{2}(\sum \Delta_i^2/N)^{1/2}$, where Δ_i is the distance between the corresponding atoms of two independent molecules compared after fulfillment of the corresponding supersymmetrical transformation. All calculations were performed using the *SUSY* program (Kukina & Zorkii, 1981). The axes and planes of supersymmetry have special orientations: the axes 2_q and 4_q are parallel to [101], and the planes m_p are perpendicular to [10$\bar{1}$]. Fig. 1 shows the independent elements of supersymmetry which relate the pairs of molecules A and B (C_1), A and C (L_1), A and D (M_1), B and C (M_2), B and D (L_2), C and D (C_2).

According to general considerations the Ar_3X molecules should have C_3 symmetry. Such symmetry was found by an X-ray analysis for molecules of tri-p-tolylstibine (Sobolev, Romm, Belsky & Guryanova, 1979), tri-p-tolylarsine (Sobolev & Belsky, 1981), and tri-p-tolylphosphine (Sobolev, Belsky, Romm & Guryanova, 1983). However, it turned out that the C_3 symmetry of Ar_3X molecules is the
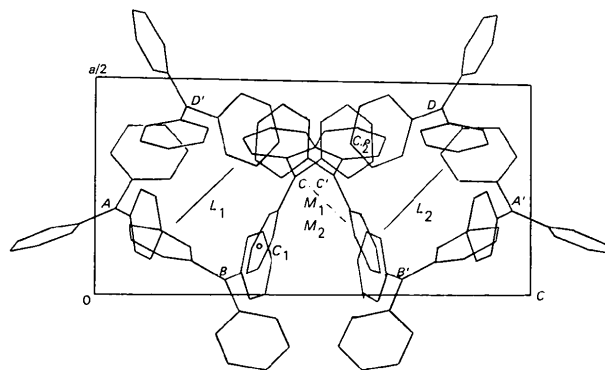

Fig. 1. Projection into the (010) plane (primed molecules are related to unprimed ones by symmetry $x, \frac{1}{2} + y, 1 - z$).

Table 5. *Valence angles CXC (°) and bond lengths X—C (Å) for Ar₃X compounds*

Ar X		Phenyl	p-Tolyl	2,6-Xylyl	Mesityl
N	CNC	119·6	119·9		
	N–C	1·419	1·419		
		(a)	(b)		
P	CPC	103·0	101·7	109·5	109·7
	P–C	1·828	1·832	1·84	1·837
		(c)	(d)	(e)	(f)
As	CAsC	100·0	99·3		107·6
	As–C	1·957	1·954		1·976
		(g)	(h)		(i)
Sb	CSbC		97·3	104·7	
	Sb–C		2·141	2·190	
			(j)	(k)	
Bi	CBiC	94·0	94·7		102·0
	Bi–C	2·240	2·248		2·290
		(l)	(m)		(n)

References: (a) present work; (b) Reynolds & Scaringe (1982); (c) Daly (1964); (d) Sobolev, Belsky, Romm & Guryanova (1983); (e) Sobolev *et al.* (1976); (f) Blount, Maryanoff & Mislow (1975); (g) Sobolev, Belsky, Chernikova & Akhmadulina (1983); (h) Sobolev & Belsky (1981); (i) Sobolev, Romm, Chernikova, Belsky & Guryanova (1981); (j) Sobolev *et al.* (1979); (k) Sobolev, Romm, Belsky, Syutkina & Guryanova (1981); (l) Howley & Ferguson (1968); (m) Sobolev, Belsky & Romm (1983); (n) Sobolev *et al.* (1980).

exception rather than the rule. In most cases the packing of Ar₃X molecules is accompanied by a substantial distortion of their ideal symmetry. The differences of bond angles CXC can be as large as 5–12°; significant differences are also shown by the dihedral angles between phenyl-ring planes. Table 5 lists the mean values of CXC angles and X—C bond lengths in Ar₃X molecules whose structures have been determined by X-ray analysis [Ar = C_6H_5, 4-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$; X = N,P,As, Sb,Bi]. It can be seen clearly that regardless of structural features of aromatic fragments the CXC bond angles in each series of analogous Ar₃X compounds decrease with an increase of the covalent radius of the X atom: Ar₃N (0·70 Å) > Ar₃P (1·10 Å) > Ar₃As (1·21 Å) > Ar₃Sb (1·41 Å) > Ar₃Bi (1·47 Å).

Introduction of a methyl group in the position 4 of each phenyl ring does not, in fact, influence the conformation of the central fragment of the molecule. Bond angles CXC and bond lengths X—C in triphenyl- and tri-p-tolyl derivatives are very similar.

Introduction of two methyl groups in the *ortho* positions 2 and 6 of the phenyl rings results in a substantial increase of the CXC angle due mainly to steric factors. This increase in 2,6-disubstituted derivatives is approximately the same (7–8°) with respect to the non-substituted ones for all elements X considered. Additional introduction of a methyl group in the position 4 of a 2,6-disubstituted ring does not influence the molecular conformation: the angles CXC and bond lengths X—C of the 2,6-xylyl and mesityl derivatives are very similar.

The bond angles CNC in the molecules of triphenyl- and also tri-p-tolylamine (Reynolds & Scaringe, 1982) are close to 120°, which corresponds to the sp^2 hybridization of the N bonding orbitals. Therefore, this shows that the l.e.p. of the N atom in triarylamines occupies the p orbital which favours the realization of the intramolecular pπ interaction.

The analysis of the structural parameters of triaryl-phosphines allows the conclusion that a l.e.p. state of the P atom can vary from sp (CPC angle 101–103°) to sp^3 (CPC angle 109·5°). Accordingly, conditions of the pπ conjugation in triarylphosphines can also vary (Romm, Guryanova, Romanov, Sherbakova, Stepanova & Pudovick, 1980). The energy of pπ conjugation of triphenylphosphine is 30 kJ mol⁻¹. The corresponding energy of 2,6-disubstituted compounds should be considerably higher, which is in accordance with a large bathochromic shift (ca 50 nm) of the long waveband in electronic spectra on introduction of CH_3 groups in the positions 2 and 6 of each phenyl ring of triphenylphosphine (Romm & Guryanova, 1977).

As for As, Sb and Bi derivatives, the values of the CXC angles indicate that the p component of the l.e.p. state decreases in the series As > Sb > Bi.

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Structure of (*trans*-2-Hydroxycyclohexyl)dimethylphosphine Oxide, C8H17O2P

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Abstract. $M_r = 176\cdot20$, monoclinic, $P2_1/c$, $a = 8\cdot674$ (2), $b = 11\cdot532$ (3), $c = 10\cdot050$ (2) Å, $\beta = 106\cdot32$ (2)°, $V = 964\cdot7$ (4) Å^3, $Z = 4$, $D_x = 1\cdot211$, $D_m = 1\cdot19$ Mg m^{-3}, $\lambda(\text{Cu }K\alpha) = 1\cdot5418$ Å, $\mu = 2\cdot17$ mm^{-1}, $F(000) = 384$, $T = 298$ K, $R = 0\cdot049$ for 1581 observed reflections. The cyclohexyl ring is in a chair conformation and the 2-hydroxyl and dimethylphosphine groups are both in the equatorial conformation. The bonding around the phosphorus has a slightly distorted tetrahedral configuration. There is an intermolecular hydrogen bond which links the hydroxy group to the phosphine oxide.

Introduction. Trialkylphosphines deoxygenate epoxides at high temperatures to produce olefins of inverted configuration and the corresponding trialkylphosphine oxide. For example, (*E*)-2-butene oxide on treatment with tributylphosphine at 423 K produces a 4:1 mixture of (*Z*)- and (*E*)-2-butene (Boskin & Denney, 1959). The mechanism is believed to involve a nucleophilic ring opening of the epoxide by the phosphine with inversion of configuration at carbon, a rotation about the carbon–carbon single bond to place the phosphorus and oxygen in close proximity, and a *syn* elimination of the phosphine oxide. It has been demonstrated recently (Buynak, McKenzie-Graff & Jadhav, 1984) that this reaction is catalyzed by zinc bromide and that when it is performed with phosphines containing an Si–N–P linkage, the silicon can be transferred to the oxygen after the initial ring-opening to produce air- and moisture-sensitive β-trimethylsiloxyiminophosphoranes. These compounds can be hydrolyzed to the more stable β-hydroxyphosphine oxides. Previously, no intermediates have been isolated from the reaction of neutral phosphines (Vedejs & Fuchs, 1973) and epoxides. It is mechanistically important to demonstrate that this

process does occur with inversion of configuration, even in the presence of Lewis acids and with the rather unusual silylaminophosphines. The crystal structure of a β-hydroxyphosphine oxide (I) is reported in this paper. (I) was prepared by the reaction of [bis-(trimethylsilyl)amino]dimethylphosphine with cyclohexane oxide and subsequent hydrolysis of the iminophosphorane as shown in the reactions in Fig. 1.

Experimental. Chemical formula established by NMR data, single crystals obtained by crystallization from toluene in the form of transparent colorless cubic prisms, unit-cell parameters by least-squares analysis of 15 reflections with 2θ from 15 to 79°, space group $P2_1/c$ determined from systematic absences ($h0l$ absent with l odd, $0k0$ absent with k odd), D_m by flotation in a mixture of chlorocyclohexane and bromocyclohexane, automatic diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, crystal $0\cdot22 \times 0\cdot22 \times 0\cdot22$ mm, c axis of the crystal approximately along the φ axis of the diffractometer, $\theta/2\theta$ scanning mode, 1615 independent reflections with $2\theta < 130°$, range of hkl: $-10{\rightarrow}9$, $0{\rightarrow}13$, $0{\rightarrow}11$, 1585 observed, $I > 3\sigma(I)$; three standard reflections measured after every 50 reflections showed a
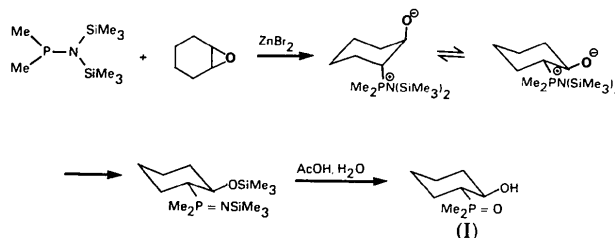

Fig. 1. Proposed reaction scheme for the preparation of (I).