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Structural Studies on the Phosphorus–Nitrogen Bond. IV. The Crystal Structure of Tris(morpholino)arsine. A Comparison with the Crystal Structure of Tris(morpholino)phosphine

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The structure of the title compound, $[O(CH_2CH_2)N]_3As$, has been determined from X-ray data. Full-matrix least-squares refinement led to a conventional R-value of 0.047 for 2132 reflections.

The crystals are orthorhombic, space group $Cmc2_1$, with cell dimensions (at −150 °C): a= 16.493(2) Å; b=8.352(1) Å; c=21.376(3) Å. With Z=8 there are two half molecules connected by pseudo symmetry per asymmetric unit.

The structure of the molecule is quite analogous to that of the corresponding phosphorus compound: (*i*) Two small NAsN bond angles of 94.1° and one large of 109.9°; (*ii*) two short As–N bond lengths of 1.853(3) Å, while the third is probably significantly longer, 1.866(4) Å; (*iii*) one of the nitrogen atoms is essentially sp^3 hybridized and its lone pair is strictly *anti* to the arsenic lone pair; (*iv*) the remaining two nitrogen atoms have lower *p*-character, and their lone pairs are roughly normal to the arsenic lone pair and to each other; (*v*) the two morpholino groups linked through short bonds to the arsenic atom are twisted in opposite directions.

The major differences are the following: (*i*) The presence of a mirror symmetry plane in tris(morpholino)arsine; (*ii*) the sum of the NAsN bond angles is 298.1° as compared to 306.6° in the phosphorus compound; (*iii*) the slightly higher average *p*-character of the nitrogen atoms in the arsenic compound than in the phosphorus compound.

The difference in As–N and P–N bond lengths, ~0.15 Å, as compared to 0.11 Å as calculated from the sum of the covalent radii, suggests that the double bond character of the P–N bond in tris(dialkylamino)phosphines is responsible for a shortening of the P–N bond length of at least 0.04 Å.

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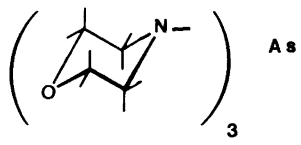
In Part 1 of this series the crystal and molecular structure of two tris(dialkylamino)phosphines, tris(morpholino)phosphine, Mor_3P, and tris(piperidino)phosphine, Pip_3P, was described.[1] It was shown that these compounds do not possess C_3 local symmetry, but are highly asymmetric species. In subsequent studies on pentacovalent species derived from tris(dialkylamino)phosphines, this asymmetric orientation of the three groups linked to the central phosphorus atom has also been observed.[2,3] Apparently, the structure of these compounds is governed by the demand of the lone pair of the nitrogen atoms to be not only orthogonal to each other, but also to the phosphorus lone pair in the tervalent compounds and to the phosphorus–chalcogen bond in the pentacovalent species.

The question arises, however, whether this structural arrangement of three dialkylamino substituents linked to a phosphorus atom in both tervalent and pentacovalent species is due to special bonding phenomena in the phosphorus compounds, or wther it is general for compounds with a central atom from the fifth main group linked to three nitrogen atoms, each holding a lone pair of electrons. In the present study we want to report the crystal and molecular structure of tris(morpholino)arsine, Mor_3As. (Scheme 1).



Scheme 1.

Tris(morpholino)arsine was found to be the compound of choice since suitable crystals were readily obtained[4] and the fairly low rate of reaction with carbon dioxide and water allowed crystallographic data to be collected at liquid nitrogen temperature. The nicely crystalline tris(piperidino)-arsine, Pip_3As,[5] was found to be too unstable to be included in the present study.

EXPERIMENTAL

Material. Tris(morpholino)arsine, Mor_3As, was made as described in Ref. 4. The compound was twice crystallized from benzene and finally twice from acetonitrile, m.p. 115–116 °C (113–114 °C[4]). All operations with this compound were carefully performed in an atmosphere of dry argon. The crystal used for the X-ray study was grown in acetonitrile and had approximate dimensions $0.1 \times 0.2 \times 0.4$ mm.

X-Ray data. Data were collected on a SYNTEX $P\bar{1}$ diffractometer with a temperature of −150° at the crystal site using graphite crystal monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Cell parameters were determined by a least-squares fit to the diffractometer settings of 15 general reflections with $30° < 2\theta < 40°$. Intensity data were collected by the $\theta - 2\theta$ scan technique, scan speed 3° min^{-1}, scan width ±1.2°; background counts were taken for 0.35 times the scan time at each of the scan limits. All reflections within an octant of reciprocal space out to a sin θ/λ value of 0.7 Å^{-1} were measured. Three standard reflections were measured at regular intervals during the data collection; a mean decrease in intensity of 17 % was observed and the data were accordingly adjusted. Out of 2281 unique reflections, 2132 with $I > 2.5\sigma(I)$ were retained for the structure analysis. Standard deviations for the intensities were calculated by $\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N is the scan count minus background count. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Description of the computer programs applied for the structure analysis is given in Ref. 6. In the full-matrix least-squares program the quantity minimized was $\Sigma w \Delta F^2$, where w is the inverse of the variance of the observed structure factors; for reflections with sin $\theta/\lambda < 0.45$ Å^{-1} w was multiplied with a function of sin θ/λ to give less weight to low-order reflections. Atomic form factors were those of Doyle and Turner[7] for As, O, N and C and of Stewart, Davidson and Simpson[8] for H.

CRYSTAL DATA

Tris(morpholino)arsine, $C_{12}H_{24}O_3N_3As$, m.p. 115–116 °C. Orthorhombic, $a = 16.493(2)$ Å; $b = 8.352(1)$ Å; $c = 21.376(3)$ Å; $V = 2944.5$ Å^3; ($t = -150$ °C); $M = 333.26$; $Z = 8$; $F(000) = 1488$; μ(Mo$K\alpha$) = 24.5 cm^{-1}; $D_x = 1.503$ gcm^{-3}. Absent reflections: (hkl) for $h + k$ odd, ($h0l$) for l odd. Space group $Cmc2_1$ (No. 36).

STRUCTURE DETERMINATION

From the systematically absent reflections the space group may be $Cmc2_1$ (No. 36), $C2cm$ (No. 40) or $Cmcm$ (No. 63). Intensity statistics gave strong evidence for an acentric structure, thus excluding $Cmcm$, statistics on the zone data pointed to a centric (001) projection and acentric (010) and (100) projections. The most probable space group was thus $Cmc2_1$, and the structure was refined assuming this symmetry.

The structure was solved by the use of the program assembly MULTAN.[9] Refinements were performed in the way described in Ref. 1 with the exception that hydrogen parameters were not refined.

There are two half molecules of the compound per asymmetric unit; each are related to the rest of the molecule by a mirror plane. By inspection of coordinates and the covariance matrix it was found that the two half molecules were related by a pseudo centre of symmetry. The structure was refined according to the initial model (two half molecules) to a conventional R-factor of 0.044, $R_w = 0.048$, $S = [\Sigma w \Delta F^2/(n-m)]^{\frac{1}{2}} = 2.32$, overdetermination ratio 10.8. Constrained refinements assuming a centre of symmetry in (1/4, 0.4449, 1/4) lead to an R-factor of 0.047, $R_w = 0.052$, $S = 2.47$; the overdetermination ratio was 16.5. The molecular geometries obtained from the two ways of refinement did not exhibit any significant differences. The following discussion is based on the figures obtained from the constrained refinement.

Final atomic parameters from both refinements are listed in Table 1. Tables of observed and calculated structure factors are available from the authors.

ORTEP drawing of the molecule is shown in Fig. 1, where the numbering of the atoms is also indicated.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. Normal refinement (a) and constrained refinement (b). The anisotropic temperature factor is given by $\exp[-2\pi^2(U11a^{*2}h^2+\ldots+2U12a^*b^*hk+\ldots)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(a) Normal refinement									
AS1	.00000	.21254(2)	.06944	.0108(3)	.0144(3)	.0188(4)	.0000	.0000	.0020(3)
AS2	.50000	.67728(8)	.43056(4)	.0107(3)	.0111(3)	.0163(4)	.0000	.0000	.0018(3)
O1	.2234(3)	−.0662(5)	.1489(2)	.0154(19)	.0205(19)	.0367(24)	.0074(15)	−.0019(18)	.0027(17)
O2	.0000	.7053(6)	.1711(4)	.0219(38)	.0125(27)	.0373(46)	.0000	.0000	.0023(23)
O3	.2786(3)	.9612(5)	.3511(2)	.0175(19)	.0187(19)	.0347(24)	.0065(15)	−.0000(18)	.0003(17)
O4	.5000	.1880(7)	.3270(4)	.0149(33)	.0192(28)	.0330(43)	.0000	.0000	−.0009(24)
N1	.0921(3)	.1178(6)	.1025(2)	.0150(21)	.0189(23)	.0260(25)	.0051(18)	−.0021(18)	−.0039(19)
N2	.0000	.3818(8)	.1267(3)	.0125(27)	.0112(26)	.0258(34)	.0000	.0000	−.0010(25)
N3	.4082(3)	.7721(5)	.3971(2)	.0162(21)	.0139(20)	.0243(23)	.0055(17)	.0012(18)	−.0041(18)
N4	.5000	.5087(8)	.3735(3)	.0104(25)	.0105(26)	.0243(32)	.0000	.0000	−.0018(23)
N4	.5000	.5087(8)	.3735(3)	.0104(25)	.0105(26)	.0243(32)	.0000	.0000	−.0018(23)
C11	.1003(3)	.0850(7)	.1693(3)	.0134(22)	.0151(23)	.0267(28)	.0021(19)	−.0014(20)	.0022(21)
C12	.1898(3)	.0628(7)	.1851(3)	.0156(23)	.0206(24)	.0308(30)	.0017(21)	−.0029(21)	.0020(23)
C13	.2154(4)	−.0329(7)	.0837(3)	.0176(23)	.0244(28)	.0325(35)	.0060(20)	.0019(22)	−.0026(23)
C14	.1265(3)	−.0125(6)	.0656(3)	.0180(21)	.0213(23)	.0243(26)	.0031(19)	−.0013(25)	−.0065(25)
C21	.0726(3)	.4822(6)	.1224(3)	.0142(22)	.0150(24)	.0285(28)	−.0014(19)	.0029(22)	−.0002(21)
C22	.0708(3)	.6047(7)	.1753(3)	.0153(23)	.0175(26)	.0330(31)	−.0007(19)	−.0041(21)	.0017(23)
C31	.3994(3)	.8037(6)	.3301(3)	.0143(21)	.0173(24)	.0226(25)	.0056(19)	−.0007(19)	.0003(20)
C32	.3102(3)	.8295(7)	.3154(3)	.0174(22)	.0185(25)	.0274(28)	.0035(21)	−.0068(21)	.0010(23)
C33	.2872(4)	.9315(8)	.4169(3)	.0191(25)	.0264(28)	.0320(36)	.0093(21)	.0056(22)	.0004(23)
C34	.3763(3)	.9073(6)	.4341(3)	.0218(23)	.0252(25)	.0214(25)	.0077(19)	.0028(26)	−.0078(27)
C41	.4274(3)	.4056(6)	.3771(3)	.0114(21)	.0138(23)	.0260(27)	−.0023(18)	.0036(20)	.0030(20)
C42	.4291(3)	.2863(6)	.3240(3)	.0143(21)	.0131(24)	.0314(29)	−.0023(18)	−.0015(20)	−.0012(21)
(b) Constrained refinement									
AS	.00000	.21267(5)	.06944(2)	.0107(2)	.0126(2)	.0175(2)	.0000	.0000	.0019(2)
O1	.2224(2)	−.0688(3)	.1489(1)	.0166(10)	.0205(12)	.0353(14)	.0072(9)	−.0008(10)	.0012(10)
O2	.0000	.7036(4)	.1720(2)	.0184(14)	.0156(16)	.0359(18)	.0000	.0000	.0005(15)
N1	.0920(2)	.1180(3)	.1027(1)	.0157(13)	.0157(12)	.0252(14)	.0051(10)	−.0002(11)	−.0039(11)
N2	.000	.3816(5)	.1266(2)	.0119(16)	.0111(16)	.0250(19)	.0000	.0000	−.0012(14)
C11	.1005(2)	.0855(4)	.1696(2)	.0140(14)	.0169(15)	.0240(16)	.0042(11)	−.0012(12)	.0015(12)
C12	.1897(2)	.0616(4)	.1849(2)	.0164(14)	.0195(15)	.0284(17)	.0023(12)	−.0047(13)	.0010(13)
C13	.2141(2)	−.0369(5)	.0834(2)	.0188(15)	.0269(17)	.0324(20)	.0085(13)	.0041(14)	−.0006(14)
C14	.1252(2)	−.0148(4)	.0657(2)	.0202(14)	.0239(15)	.0225(15)	.0062(12)	.0012(14)	−.0073(14)
C21	.0726(2)	.4831(4)	.1226(2)	.0127(13)	.0149(13)	.0270(15)	−.0020(11)	.0033(12)	.0015(12)
C22	.0709(2)	.6041(4)	.1756(2)	.0148(14)	.0162(14)	.0322(18)	−.0015(12)	−.0028(13)	.0004(13)

Atom	x	y	z	B	Atom	x	y	z	B
(a) Normal refinement									
H111	.069	−.014	.180	1.3	H112	.078	.178	.193	1.3
H121	.196	.038	.230	1.3	H122	.220	.163	.175	1.3
H131	.239	−.124	.059	1.3	H132	.245	.068	.074	1.3
H141	.096	−.114	.075	1.3	H142	.122	.013	.020	1.3
H211	.073	.540	.081	1.3	H212	.122	.415	.126	1.3
H221	.121	.672	.173	1.3	H222	.070	.546	.216	1.3
H311	.421	.711	.306	1.3	H312	.431	.903	.319	1.3
H321	.279	.730	.326	1.3	H322	.304	.853	.270	1.3
H331	.256	.833	.428	1.3	H332	.265	1.025	.441	1.3
H341	.381	.882	.480	1.3	H342	.408	1.006	.425	1.3
H411	.377	.473	.374	1.3	H412	.427	.348	.418	1.3
H421	.428	.345	.284	1.3	H422	.380	.217	.328	1.3

Table 1. Continued.

(b) Constrained refinement

H111	.070	−.014	.181	1.3	H112	.079	.178	.194	1.3
H121	.196	.037	.230	1.3	H122	.220	.162	.175	1.3
H131	.237	−.129	.050	1.3	H132	.245	.063	.073	1.3
H141	.004	−.115	.075	1.3	H142	.121	.011	.020	1.3
H211	.073	.541	.082	1.3	H212	.122	.415	.126	1.3
H221	.120	.673	.173	1.3	H222	.071	.546	.216	1.3

Table 2. Structural data.

Bond lengths (Å)

As	N1	1.853(3)
As	N2	1.866(4)
N1	C11	1.461(5)
C11	C12	1.522(5)
C12	O1	1.437(5)
O1	C13	1.432(5)
C13	C14	1.527(5)
C14	N1	1.467(4)
N2	C21	1.470(4)
C21	C22	1.519(5)
C22	O2	1.436(4)

Torsion angles (°)

C11	N1	As	N2	50.4(3)
C14	N1	As	N2	−171.0(3)
C11	N1	As	N1[a]	−45.4(3)
C14	N1	As	N1[a]	93.1(3)
N1	As	N2	C21	62.2(3)
N1	As	N2	C21[a]	−172.5(3)

Bond angles (°)

N1	As	N2	94.1(1)	(2×)
N1	As	N1[a]	109.9(2)	
As	Ni	C11	122.3(2)	
As	N1	C14	114.9(2)	
N1	C11	C12	109.1(3)	
C11	C12	O1	110.3(3)	
C12	O1	C13	110.3(3)	
O1	C13	C14	110.8(3)	
C13	C14	N1	108.5(3)	
C14	N1	C11	110.5(3)	
As	N2	C21	113.5(2)	(2×)
N2	C21	C22	109.0(3)	
C21	C22	O2	111.1(3)	
C22	O2	C22[a]	109.0(4)	
C21	N2	C21[a]	109.1(4)	

Short intramolecular contacts (Å)

As	C11	2.91	C11	C11[a]	3.21
As	C14	2.81	H111	H111[a]	2.29
As	C21	2.80			

Various derived and averaged data

	N1	N2
Nx		
N−C (Å)	1.464	1.470
C−C (Å)	1.524	1.519
C−O (Å)	1.435	1.436
Deviation of Nx from plane AsCC (Å)	0.32	0.46
Sum of N bond angles (°)	347.7	336.1
Torsion angle lone pair(As)−As−N-lone pair(N)	±71.8	180.0
Sum of As bond angles (°)	298.1	

[a] Across the mirror plane.

RESULTS AND DISCUSSION

In Table 2 bond lengths, bond angles, torsion angles and various other structural data are given. Estimated standard deviations are calculated from the correlation matrix. In Fig. 2 are shown the Newman projections of the As−N bond; the broken lines indicating the torsion angles which are defined as outlined in Ref. 1. In Table 3 a comparison is made between the most relevant structural parameters in tris(morpholino)arsine, Mor_3As, determined in the present study, and in tris(morpholino)-phine, Mor_3P, from Ref. 1.

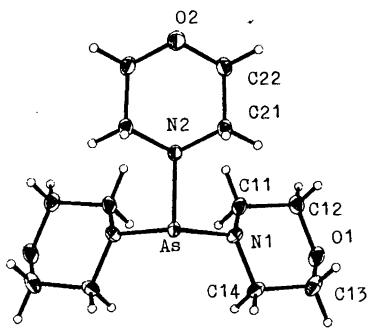


Fig. 1. ORTEP drawing of tris(morpholino)arsine.

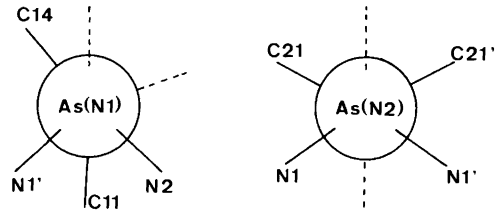


Fig. 2. Newman projections along the As – N bonds.

Conformational considerations. The structure of Mor_3As, as is particularly evident from the data in Table 3, is in principle similar to the structure of the corresponding phosphorus compound. Two of the nitrogen lone pairs are partly orthogonal to the hetero atom lone pair, to each other and to the lone pair of the third nitrogen atom. The latter atom is essentially sp^3 hybridized and its lone pair is strictly *anti* to the arsenic lone pair. The bond angle between the two twisted morpholino groups is considerably larger than the two remaining NAsN bond angles, presumably of steric reasons. In several pentacovalent species derived from tris(dialkylamino)phosphines, $(R_2N)_3PX$, the three dialkylamino substituents are accommodated in a similar way.[2,3] Apparently the preference for orthogonal lone pairs combined with the steric demands of the substituents is governing the structure of this class of compounds.[1] However, the P – X bonds, the lone pair of the rather small phosphorus atom with considerable directional properties owing to its significant *p*-character and the rather diffuse lone pair of the larger arsenic atom of significantly higher *s*-character (see below) appear to exert the same conformational influence in $(R_2N)_3PX$, $(R_2N)_3P$ and $(R_2N)_3As$, respectively. One may thus conclude that the orthogonalization of the nitrogen lone pairs relative to each other is the determining factor with regard to the structure of these compounds, while the effect of the lone pair of or bonds from the heteroatom is of less importance.

Table 3. Comparison of some structural parameters in tris(morpholino)arsine, Mor_3As, and tris(morpholino)phosphine, Mor_3P.

	[a]	Mor_3As		[a]	Mor_3P	
∠NAsN°, ∠NPN°	109.9(2)	94.1(1)	94.1(1)	110.7(1)	97.9(1)	98.0(1)
Σ∠NAsN°, Σ∠NPN°		298.1(4)			306.6(3)	
Σ∠N°	336.1(8)	347.7(7)	347.7(7)	337.6(6)	353.2(6)	350.5(6)
Σ∠N°		343.8(8)			347.1(6)	
As–N Å, P–N Å	1.866(4)	1.853(3)	0.853(3)	1.726(3)	1.691(3)	1.696(3)
As–N_{sp3} Å, P–N_{sp3} Å		~1.88 [b]			1.74(1) [b]	
As–N_{sp2} Å, P–N_{sp2} Å		~1.84 [b]			1.69(1) [b]	
∠AsNC°, ∠PNC°	113.5(2)	114.9(2)	114.9(2)	114.4(2)	125.9(2)	124.3(2)
	113.5(2)	122.3(2)	122.3(2)	115.0(2)	116.7(2)	115.6(2)
Torsion angles,° [c]	180	−71.8	71.8	170.6	−70.9	73.2
N–C, Å	1.470(4)	1.467(5)	1.464(4)	1.470(4)	1.463(4)	1.460(4)
C–C, Å	1.518(5)	1.525(5)	1.525(5)	1.498(6)	1.497(5)	1.505(5)
C–O, Å	1.436(4)	1.436(5)	1.436(5)	1.421(5)	1.423(5)	1.417(5)

[a] The nitrogen atom with its lone pair *anti* to the lone pair of the hetero atom. [b] Extrapolated values. [c] Torsion angles between nitrogen lone pair and hetero atom lone pair as defined in Ref. 1.

It is apparent that Mor_3As, similar to Mor_3P, does not possess any local C_{3v} symmetry with regard to the AsN_3 moiety. The arsenic compound, however, is of higher symmetry than the phosphorus compound since a symmetry plane is present as required by the space group $Cmc2_1$. This symmetry plane, formed by the central arsenic atom and the nitrogen and oxygen atoms in the morpholino group in the *trans* position, causes Mor_3As to possess C_s symmetry. In Mor_3P (space group $P\bar{1}$) no such mirror plane exists, since the nitrogen atom being essentially sp^2 hybridized is not strictly in *anti* position and the two remaining nitrogen atoms have slightly but significantly different hybridization as viewed by the sum of the nitrogen bond angles. Tris(piperidino)phosphine, Pip_3P, is even further from C_s symmetry since two of the piperidino groups are twisted in the same direction.[1]

The question arises whether this difference in symmetry is due to packing effects or whether more subtle considerations are necessary, *i.e.* this size of the central atom, the hybridization of the hetero atom lone pair *etc.* Since very few crystallographic studies on corresponding tervalent phosphorus and arsenic species have appeared, it is obviously premature to conclude that this difference in symmetry as observed in the present study is to be general. It is known, however, that triphenyl phosphine, Ph_3P, possesses no symmetry owing to the unequal rotation of the benzene rings about the P–C bonds;[10] triphenyl arsine, Ph_3As, has escaped a structure determination due to its "complex crystal structure".[11] In tris(4-methylphenyl)arsine a fairly symmetrical arrangement of the 4-methylphenyl groups has been observed.[12] One may thus recommend that when IR and Raman spectra of corresponding tervalent phosphorus and arsenic species in their solid state are to be compared and assigned, this possible difference in symmetry is to be taken into account. It is interesting to note that in pentacovalent species and in tetrahedrally coordinated tervalent species, *i.e.* in onium cations and in metal complexes, no difference in symmetry for phosphorus and arsenic species appears to be present.[13,14]

Bond angles around the arsenic atom. As in Mor_3P, there is one large bond angle and two smaller ones, 109.9° and 94.1°, respectively. The larger bond is between bonds to the twisted morpholino groups.

The sum of the NAsN bond angles is 298.1° as compared to 306.1 for the sum of the NPN bond angles in Mor_3P.[1] A number of microwave and electron diffraction studies on AsX_3 and PX_3(X = Hal. R. SiF_3 *etc.*) have appeared; for a survey of XAsX and XPX bond angles, *cf.* Refs. 15–17. The reduction in XMX bond angles in MX_3 molecules on descending the fifth row is generally believed to be due to increasing *p*-character of the bond between the M and X atoms and thus to increasing *s*-character of the hetero atom lone pair. Since the average difference between the NAsN and NPN bond angles in Mor_3As and Mor_3P is 2.7° and compares favourably with other atoms linked to the arsenic and the phosphorus atom,[15–17] it is tempting to conclude that As–N bonds and P–N bonds in tris(dialkylamino)arsines and in tris(dialkylamino)phosphines are as different as are most other As–X and P–X bonds in tervalent species. It is thus to be assumed that the *s*-character of the arsenic lone pair in Mor_3As is somewhat higher than that of the phosphorus lone pair in Mor_3P than for other tervalent arsenic and phosphorus species.

The decrease in the As cone angle in Mor_3As, relative to the P cone angle in Mor_3P, does not seem to alter than structure of the molecules significantly. Owing to the longer As–N bonds, ~0.15 Å. it appears equally difficult to accomodate the three morpholino substituents in the two compounds.

Bond angles around the nitrogen atoms. The sum of the bond angles at the nitrogen atoms, $\Sigma\angle N$, are all significantly less than 360°. The one nitrogen atom with its lone pair *anti* to the arsenic lone pair is essentially sp^3 hybridized, $\Sigma\angle N$ is 336.1°, (337.6° in Mor_3P[1]), while the remaining nitrogen atoms have lower *p* character, $\Sigma\angle N$ are 347.7°. The average sum of the nitrogen bond angles in Mor_3As is 343.8° as compared to 347.1° in Mor_3P. The AsNC bond angles in Mor_3As are about the same as the PNC bond angles in Mor_3P.

The arsenic-nitrogen bond. The two twisted morpholino groups are linked to the central arsenic atom by bonds As–N1 of 1.853 Å. The third As–N bond, the bond to the essentially sp^3 hybridized nitrogen atom N2, is probably significantly longer, 1.866 Å. In tris(dialkylamino)phosphines, $(R_2N)_3P$, the dependence of the P–N bond upon the hybridization of the nitrogen atom is considerable allowing one to determine by a quite reliable extrapolation the $P-N_{sp3}$ and $P-N_{sp2}$ bond lengths,[1] *cf.* Table 3.

Due to the lower accuracy in the As–N bond length determination a similar extrapolation for

As–N_{sp3} and As–N_{sp2} is uncertain, but the data obtained in the present study may suggest As–N_{sp3} and As–N_{sp2} bond lengths to be ~1.87–1.88 and ~1.84 Å, respectively. It seems thus that the dependence of the As–N bond length upon the sum of the nitrogen bond angles is somewhat less than for the P–N bond length, *cf.* Table 3. This observation may serve as a criterion for the difference in back-bonding from the nitrogen atom to the arsenic atom and to the phosphorus atom in $(R_2N)_3As$ and $(R_2N)_3P$, respectively. Owing to the lower efficiency of the arsenic 4*d*-orbitals than the phosphorus 3*d*-orbitals to act as acceptor orbitals,[18] the attachment of strongly electronegative substituents to the hetroatom in amino-substituted arsines and phosphines may influence the geometry of the nitrogen atoms differently. In dihalodimethylaminophosphines, X_2PNMe_2, the nitrogen atom generally adopts a planar geometry,[19] while in the corresponding arsenic compounds the nitrogen atom is apparently pyramidal.[20]

The As–N and P–N bond lengths in Mor_3As and Mor_3P seem to confirm a difference in back-bonding from the nitrogen atom to the two hetero-atoms. The average bond length difference is ~0.15 Å as compared to the difference in single bond radii of 0.11 Å.[21] One may thus conclude that back-bonding in aminophosphines causes a shortening of the P–N bond of at least 0.04 Å.

However, the observed As–N bond lengths are still significantly shorter than estimated from the single bond radii, 1.91 Å, [21] which may indicate that even the As–N bonds in aminoarsines have a bond order slightly different from unity. The results from various NMR studies seem to indicate that the As–N bond in tervalent arsines containing a dialkylamino group has some restricted rotation, but less than the P–N bond in similarly substituted aminophosphines.[22–25] Magnetic susceptibility measurements seem also to be in accord with the idea of some contribution from double bond in the arsenic–nitrogen bond in aminoarsines.[26] It should be emphasized, however, that all studies of aminoarsines which suggest some multiple bonding in this class of compounds have been performed on compounds which contain one or two highly electronegative substituents, *i.e.* Cl, F, Ph *etc.* These substituents may then augment the N→As back-bonding due to contraction of the arsenic *d*-orbitals similar to what has been proposed in phosphorus compounds. No detailed low temperature NMR studies on tris(dialkylamino)arsines seem to have been performed.

There appear to be no estimates in the literature for the bond energy of the arsenic–nitrogen bond. However, the C–X bond length difference in Me_3X (X=As and P) is about 0.14 Å[27] and is thus approximately of the same magnitude as that observed in the present study for the N–X bond length difference in Mor_3As and Mor_3P. Since the C–As bond energy in Me_3As is only slightly less than the C–P bond energy in Me_3P,[28] one may conclude that the As–N bond energy may be rather similar to the bond energy of the P–N bond, 275–300 kJ/mol.

The torsion angles. The torsion angle of the As–N bond for the essentially sp^3 hybridized nitrogen atom N2 is strictly 180°; the remaining two torsion angles are of symmetry reasons equal but of opposite sign, 71.8° and −71.8°. As for the corresponding phosphorus compound an average value of ~70° seems to be the optimum compromise between steric repulsion of the atomic cores and the electronic energy.[1]

The structure of the substituents. The morpholino substituents are all in the expected chair conformation and are linked to the hetero atom in an approximately equatorial direction. The bond angles and the bond lengths in the two types of morpholino substituents in the molecule are equal as may be seen from the data in Table 2. The data in Table 3 may suggest that the C–C and C–O bond lengths are somewhat longer in Mor_3As than in Mor_3P, but it is doubtful whether this elongation is significant. However, ^{13}C NMR on Mor_3As and Mor_3P and a number of other tris(dialkylamino)-arsines and tris(dialkylamino)phosphines in deuteriobenzene at room temperature, in which all dialkylamino substituents are equal on the NMR time scale, have shown that all carbon atoms, especially the α-carbon atoms in the arsines are without exception at lower field, 1–2 ppm, than in the corresponding phosphorus compounds.[29]

Intramolecular contacts. The eight molecules in the unit cell are tightly packed and the volume per molecule is 368 $Å^3$ as compared to 375 $Å^3$ for the phosphorus compound.[1] Not surprisingly there are several short intramolecular contacts as shown in Table 2. Some As–C contacts are only 2.80 Å and the two H111 protons are only 2.3 Å apart.

Comments on the reaction pattern of tris(dialkylamino)arsines. Tris(dialkylamino)arsines, and also the corresponding stibines,[30] have been extensively studied in recent years owing to their exceptional

reactivity toward a number of electrophilic species (for extensive reviews, Refs. 31 – 33). A number of compounds, CO_2, CS_2, RNCO, RNCS *etc.* are known to be inserted between the arsenic and the nitrogen atom according to eqn. (1).[34]

$$(R_2N)_3As + >C=X \rightarrow (R_2N)_2As-X-C-N\begin{matrix}R\\R\end{matrix} \quad (1)$$

The aminoarsines are also valuable reagents in a number of organic syntheses, *i.e.* in the facile preparation in high yield at low temperature of enamines and *gem*-diamines according to eqns. (2) and (3).[35]

$$(R_2N)_3As + R^1CH_2CHO \rightarrow R^1CH=CHNR_2 \quad (2)$$

$$(R_2N)_3As + R^1{}_2CO \rightarrow R^1{}_2C(NR_2)_2 \quad (3)$$

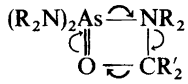
With the corresponding aminophosphines the reactions take place only slowly at elevated temperatures.[36]

The cause for the high reactivity of the aminoarsines appears to be due to an exceptional nucleophilicity of the nitrogen atoms, especially toward hard carbon centra, but even toward alkyl halides these compounds act solely as nitrogen nucleophiles.[37-38] Only toward some metalcarbonyl complexes are these compounds arsenic donors,[39-41] and they may therefore better be classified as bis(dialkylamino)arseno dialkylamines; the corresponding phosphines are reputed to act almost entirely as phosphorus donors.[1]

The presence of one essentially sp^3 hybridized nitrogen atom in Mor_3As is in accord with the amine functions of these compounds, and the generally low nucleophilicity of tervalent arsenic compounds[42] explains why the arsenic atom only with difficulty can compete with the nitrogen atom for electrophilic centra. The difficult question to answer, however, is why the aminoarsines act as exceptionally powerful nitrogen nucleophiles, especially toward carbonyl and thiocarbonyl carbon atoms, which is generally supposed to be the first step in the reactions depicted by eqns. (1) to (3), and why aminophosphines are poor nitrogen nucleophiles toward similar substracts.

Since the *p*-character of the essentially sp^3 hybridized nitrogen atom and also the average *p*-character of the nitrogen atoms in Mor_3As and Mor_3P are about the same, *cf.* Table 3, it is to be assumed that the ground state of the nitrogen atoms can hardly be the cause for the significant difference in reactivity. Furthermore, arguments based upon greatly different As – N and P – N bond energies are probably incorrect as outlined above. Since arsenic and phosphorus exhibit approximately the same electronegativity,[43] it is doubtful whether mechanisms based upon a significantly more electropositive arsenic atom than a phosphorus atom in the ground state or somewhere along the reaction coordinate can be the cause of the reactivity difference. Actually, it has been suggested that the first step in the reaction between $(R_2N)_3As$ and mineral acids, HX, is protonation of the arsenic atom[44] which is also a possible first step in the reaction between $(R_2N)_3P$ and HX.[45] Mechanisms based upon an electrophilic arsenic atom in the ground state of tris(dialkylamino)arsines[35] seem, therefore, highly inconceivable.

At the present stage one is thus left with a cyclic transition state as the best explanation for the exceptional reactivity of aminoarsines toward carbonyl compounds and related species as shown in Scheme 2.



Scheme 2.

The breaking of the arsenic nitrogen bond may thus be facilitated through interaction between the arsenic atom and the heteroatom, either synchronously or through a two-step mechanism. Even though the P – O and P – S bond energies are superior to the As – O and As – S bond energies, this mechanism may not be possible for the corresponding aminophosphines since the higher rotational energy and possibly the higher inversion energy of the phosphorus atom will prevent the lone pair of the phosphorus atom to attain a suitable position for interaction with the orbitals of the heteroatom. Furthermore, the shorter P – N bond will cause an increased steric difficulty for the formation of a cyclic transition state as shown above. It is apparent that only accurate kinetic studies can clarify the mechanisms for the reaction depicted by eqns. (1) to (3).

REFERENCES

1. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 32* (1978) 689.
2. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 33* (1979) 187.
3. Rømming, C., Iversen, A. J. and Songstad, J. *Acta Chem. Scand. A 34* (1980) 333.
4. Funk, H. and Køhler, H. *J. Prakt. Chem. 14* (1961) 226.
5. Vetter, H.-J., Nöth, H. and Hayduk, U. *Z. Anorg. Allg. Chem. 331* (1964) 35.
6. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.
7. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A 24* (1968) 390.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
9. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A 27* (1971) 368.
10. Daly, J. J. *J. Chem. Soc.* (1964) 3799.
11. Trotter, J. *Can. J. Chem. 40* (1962) 1878.
12. Trotter, J. *Can. J. Chem. 41* (1963) 14.
13. Boorman, P. M., Codding, P. W. and Kerr, K. A. *J. Chem. Soc. Dalton Trans.* (1979) 1482.
14. Gilli, G., Sacerdoti, M. and Domiano, P. *Acta Crystallogr. B 30* (1974) 1485.
15. Sutton, L. E. *Table of Interatomic Distances*, The Chemical Society, London 1958.
16. Wells, F. A. *Structural Inorganic Chemistry*, 4th Ed., Clarendon Press, Oxford 1975, pp. 679, 703.
17. Claeys, E. G., Van der Kelen, G. P. and De Ketelaere, R. F. *J. Mol. Struct. 40* (1977) 89.
18. Cowley, A. H. and Schweiger, J. R. *J. Am. Chem. Soc. 95* (1973) 4179.
19. Morris, E. D. and Nordman, C. E. *Inorg. Chem. 8* (1969) 1673.
20. Durig, J. R. and Casper, J. M. *J. Mol. Struct. 10* (1971) 427.
21. Pauling, L. *The Nature of the Chemical Bond*, 2nd Ed., Oxford University Press, London 1940, p. 164.
22. Yoder, C. H., Griffith, D. R. and Schaeffer, C. D., Jr. *J. Inorg. Nucl. Chem. 32* (1970) 3689.
23. Cowley, A. H., Dewar, M. J. S., Jackson, W. R. and Jennings, W. B. *J. Am. Chem. Soc. 92* (1970) 5206.
24. Dewar, M. J. S., Lucken, E. A. C. and Whitehead, M. A. *J. Chem. Soc.* (1960) 2423.
25. Scherer, O. J. and Janssen, W. *Chem. Ber. 103* (1970) 2784.
26. Durand, M. and Laurent, J.-P. *Bull. Soc. Chim. Fr.* (1973) 2169.
27. Beagley, B. and Medwid, A. R. *J. Mol. Struct. 38* (1977) 229.
28. Price, S. J. W. and Richard, J. R. *Can. J. Chem. 48* (1970) 3209.
29. *Unpublished observations.*
30. Kiennemann, A. and Kieffer, R. *J. Organomet. Chem. 60* (1973) 255.
31. Doak, G. O. and Freedman, L. D. *J. Organomet. Chem. 89* (1975) 81; *106* (1976) 115.
32. Zingaro, R. A. and Irgolic, K. J. *J. Organomet. Chem. 138* (1977) 125; *176* (1979) 245.
33. Kober, F. *Chem. Ztg. 100* (1976) 313.
34. Manoussakis, G. and Karayannidis, P. *J. Inorg. Nucl. Chem. 31* (1969) 2978.
35. Manoussakis, G. *J. Inorg. Nucl. Chem. 30* (1968) 3100.
36. Burgada, R. and Roussel, J. *Bull. Soc. Chim. Fr.* (1970) 192.
37. Nöth, H. and Vetter, H.-J. *Naturwissenschaften 16* (1963) 553.
38. Fluck, E. and Jakobson, G. *Z. Anorg. Allg. Chem. 369* (1969) 178.
39. Bouquet, G. and Bigorgne, M. *Bull. Soc. Chim. Fr.* (1962) 433.
40. King, R. B. and Korenowski, T. F. *Inorg. Chem. 10* (1971) 1188.
41. Barbeau, C. and Turcotte, J. *Can. J. Chem. 54* (1976) 1603.
42. Pearson, R. G., Sobel, H. and Songstad, J. *J. Am. Chem. Soc. 90* (1968) 319.
43. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd Ed., Interscience, New York 1972, p. 115.
44. Yambushev, F. D., Tenisheva, N. Kh. and Khusainov, Kh. *Z. Zh. Obshch. Khim. 47* (1977) 418.
45. Lafaille, L., Mathis, F. and Barrans, J. *C. R. Acad. Sci. Ser. C 285* (1977) 575.

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