Structural Studies on the Phosphorus – Nitrogen Bond. VI. The Crystal Structure of Tris(morpholino)phosphine Oxide

CHRISTIAN RØMMING [a] and JON SONGSTAD [b]

[a] Department of Chemistry, University of Oslo, Oslo 3, Norway and [b] Department of Chemistry, University of Bergen, 5014 Bergen-Univ., Norway

The structure of the title compound, [O-$(CH_2CH_2)_2N]_3PO$, has been determined by X-ray methods using diffractometer data collected both at 18 °C and at −150 °C. The crystals are monoclinic, space group $P2_1/n$, with $a = 9.107(1)$ Å; $b = 11.145(1)$ Å; $c = 14.605(1)$ Å and $\beta = 97.03(1)°$ at −150 °C. Full-matrix least-squares refinement gave a final R-value of 0.045 for 4151 reflections.

The average P−N bond length is 1.66 Å and the sum of the nitrogen bond angles ranges from 349.1 to 358.6°. The lone pair of one of the nitrogen atoms has a direction essentially *anti* to the P−O bond; the lone pairs of the two remaining nitrogen atoms are approximately orthogonal to the P=O bond and to each other.

One of the morpholino groups is disordered in the crystal and the resolution of the disorder could only be achieved by the low temperature data set.

It is concluded that tris(dialkylamino)phosphine oxides represent a border case with regard to conformational preference. An increase of the donor ability of the amino groups or the presence of coordinating Lewis acids may change the conformation from the asymmetric *gauche-gauche-anti* one to the fairly symmetric propeller one. The structure of tris(dimethylamino)phosphine oxide is discussed.

In previous studies in this series various tris(dialkylamino)phosphines, $(R_2N)_3P$, together with pentacovalent species and phosphonium salts derived from these phosphines have been studied by X-ray methods; cf. Refs. 1 and 2. Generally, these compounds are highly asymmetric with regard to the N−P−N bond angles, the P−N bond lengths and the hybridization of the nitrogen atoms. One of the nitrogen atoms is essentially sp^3 hybridized and its lone pair direction is *anti* to the phosphorus lone

pair in the P^{III}-compounds, to the phosphorus − chalcogen bond in $(R_2N)_3PX$ (X = Se or Te) and to the phosphorus − carbon bond in the (Morpholine)$_3$P$^+$R-cation.[2] In 4-NO$_2$−PhP$^+$-(Piperidine)$_3$ClO$_4$, however, the piperidino groups in the cation are twisted in a propeller-like arrangement with all nitrogen atoms being essentially sp^2 hybridized. Furthermore, Cameron and co-workers[3] have recently shown that in the weak adduct between tris(dimethylamino)phosphine oxide, [(CH$_3$)$_2$N]$_3$PO, HMPA, and Ph$_2$As(S)-Me, the three NMe$_2$ groups are all planar and the HMPA part of the adduct adopts a propeller conformation with three fairly equal O−P−N−C torsion agles. Apparently, for certain substituents, the energy difference between the two conformations in compounds derived from tris(dialkylamino)phosphines, the asymmetric *gauche-gauche-anti* conformation [1,2] and the fairly symmetric propeller one, is fairly small.

Since there have been indications that the polar phosphorus − oxygen linkage in $(R_2N)_3PO$ may alter the conformational preference in favour of the propeller, we have turned to structural studies of this class of compounds in their uncomplexed state. Further knowledge of the preferred conformation may also shed some light upon the unique solvent properties of HMPA, by far the most important compound within this group.[4,5] The exceptional cation solvating properties of this compound is well documented[6] and a large number of metal complexes with HMPA have been prepared.[7,8] Several metal complexes[9] and addition compounds[3,10,11] with HMPA have been studied by X-ray methods. No studies on any uncomplexed tris(dialkylamino)phosphine oxides have so far been
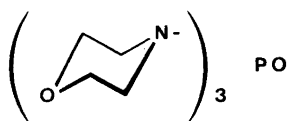
Scheme 1.

reported; HMPA itself is not easily attacked by X-ray methods, being a liquid at room temperature and a glassy substance at low temperature.

In the present study we report the crystal and molecular structure of tris(morpholino)phosphine oxide, Mor$_3$PO, a nicely crystalline and non-hygroscopic compound. By choosing morpholino groups as substituents a direct comparison could be made with previous results from studies of Mor$_3$P,[12] Mor$_3$PSe[1] and Mor$_3$PTe.[13] Similar to HMPA, Mor$_3$PO is a powerful ligand toward hard metal cations and a number of complexes have been prepared.[14-18] No structural reports on metal complexes with coordinated Mor$_3$PO molecules have so far been published.

EXPERIMENTAL

Material. Tris(morpholino)phosphine oxide was prepared as described by Malatesta and Tarantino[19] from POCl$_3$ and morpholine. The compound was repeatedly recrystallized from benzene and ethanol to remove traces of morpholinium hydrochloride, m.p. 187−188 °C

(183−185 °C[19]). Crystals suitable for the X-ray study were grown from acetonitrile at room temperature.

X-Ray data. A crystal with dimensions 0.3 × 0.3 × 0.4 mm was used for the X-ray experiments. Data for the measurements of cell dimensions and intensity data were collected on a SYNTEX P1̄ diffractometer. Data sets were obtained both at room temperature and with −150 °C at the crystal site using graphite crystal monochromated MoKα radiation ($\lambda = 0.71069$ Å). Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were collected with the $\theta - 2\theta$ scan technique, scan speed 2−4° min^{-1}, scan width 2.2° (2θ). Intensity data in a quadrant of reciprocal space within $\sin \theta / \lambda = 0.75$ Å^{-1} were measured. The number of observed reflections [$I \geq 2.5\sigma(I)$] were 2786 for the room temperature data set and 4151 for the low temperature set. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The refinement procedure followed was as described in Ref. 2.

CRYSTAL DATA

Tris(morpholino)phosphine oxide, C$_{12}$H$_{24}$N$_3$O$_4$P, m.p. 187−188 °C. Monoclinic. $t = 18$ °C: $a = 9.172(1)$ Å; $b = 11.255(2)$ Å; $c = 14.785(2)$ Å; $\beta = 96.73(2)°$; $V = 1515.8$ Å.^{3} $t = -150$ °C: $a = 9.107(1)$ Å; $b = 11.145(1)$ Å; $c = 14.605(1)$ Å; $\beta = 97.03(1)°$; $V = 1471.3$ Å^3. $M = 305.31$; $Z = 4$;
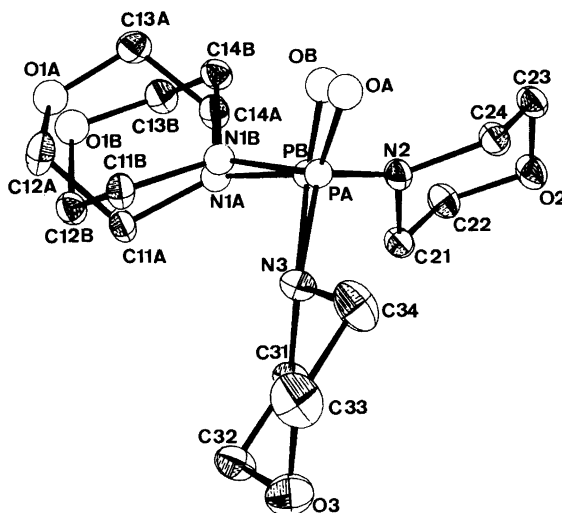

Fig. 1. ORTEP plot of Mor$_3$PO. Open circles are atoms refined with isotropic thermal parameters.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by exp $-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}
O2	.4910(1)	.3227(1)	1.0068(1)	.0358(6)	.0236(5)	.0243(5)	−.0008(4)	.0138(4)
O3	1.1930(1)	.1737(1)	.8160(1)	.0165(5)	.0437(7)	.0354(6)	.0025(5)	−.0008(4)
N2	.6281(1)	.1828(1)	.8792(1)	.0245(5)	.0208(5)	.0173(5)	−.0024(4)	.0075(4)
N3	.8865(1)	.1252(1)	.8042(1)	.0189(5)	.0185(5)	.0235(5)	−.0013(4)	.0047(4)
C21	.6323(2)	.3142(1)	.8758(1)	.0235(6)	.0210(6)	.0210(6)	−.0012(5)	.0067(5)
C22	.4977(2)	.3648(2)	.9149(1)	.0269(7)	.0261(7)	.0263(7)	.0037(5)	.0084(5)
C23	.4806(2)	.1944(1)	1.0064(1)	.0292(7)	.0241(7)	.0222(6)	−.0042(5)	.0116(5)
C24	.6162(2)	.1390(1)	.9725(1)	.0275(6)	.0205(6)	.0202(6)	−.0017(5)	.0071(5)
C31	.9401(2)	.2478(1)	.7926(1)	.0176(5)	.0185(6)	.0241(6)	−.0012(4)	.0036(4)
C32	1.0885(2)	.2403(2)	.7554(1)	.0189(6)	.0296(7)	.0297(7)	−.0019(5)	.0060(5)
C33	1.1410(2)	.0554(2)	.8265(1)	.0287(8)	.0368(9)	.0394(9)	.0139(7)	.0054(7)
C34	.9940(2)	.0558(2)	.8659(1)	.0348(8)	.0299(8)	.0320(8)	.0096(6)	.0096(6)
C11A	.7001(3)	.1779(4)	.6178(2)	.0204(13)	.0277(18)	.0153(12)	.0003(12)	.0059(9)
C12A	.6213(4)	.1052(3)	.5386(2)	.0251(13)	.0385(17)	.0180(11)	.0068(12)	.0004(10)
C13A	.4002(3)	.1075(3)	.6037(2)	.0195(11)	0.309(16)	.0251(13)	−.0019(10)	−.0020(10)
C14A	.4667(3)	.1844(4)	.6839(2)	.0147(11)	.0367(20)	.0201(13)	.0025(11)	.0026(9)
C11B	.6997(3)	.1133(4)	.6242(2)	.0184(12)	.0266(18)	.0156(12)	.0033(11)	.0026(8)
C12B	.6300(3)	.2047(3)	.5551(2)	.0200(12)	.0308(15)	.0183(11)	−.0013(10)	.0021(9)
C13B	.4070(3)	.1983(3)	.6218(2)	.0181(11)	.0326(16)	.0240(13)	.0031(11)	.0016(10)
C14B	.4729(3)	.1097(4)	.6940(2)	.0167(11)	.0278(17)	.0206(12)	−.0018(10)	.0019(9)

Atom	X	Y	Z	B	Atom	X	Y	Z
O1A	.4676(3)	.1350(3)	.5234(2)	2.1(0)	O1B	.4720(3)	.1897(3)	.5375(2)
OA	.7068(3)	−.0386(2)	.8439(2)	1.7(0)	OB	.6726(3)	−.0241(2)	.8209(2)
N1A	.6278(3)	.1640(2)	.7025(2)	1.5(0)	N1B	.6335(3)	.1271(3)	.7097(2)
PA	.71738(9)	.08810(7)	.81318(5)	1.2(0)	PB	.69906(9)	.10445(7)	.80046(5)
H211	.631	.341	.810	3.0	H212	.724	.344	.913
H221	.406	.339	.875	3.0	H222	.504	.454	.916
H231	.391	.169	.965	3.0	H232	.474	.166	1.071
H241	.605	.050	.971	3.0	H242	.706	.162	1.014
H311	.952	.290	.853	3.0	H312	.868	.293	.748
H321	1.127	.323	.749	3.0	H322	1.074	.200	.694
H331	1.215	.010	.869	3.0	H332	1.127	.015	.765
H341	1.008	.093	.928	3.0	H342	.958	−.028	.871
A111	.804	.149	.631	3.0	A112	.699	.264	.599
A121	.634	.018	.554	3.0	A122	.668	.124	.482
A131	.416	.021	.620	3.0	A132	.291	.124	.592
A141	.420	.163	.740	3.0	A142	.447	.271	.668
B111	.680	.031	.599	3.0	B112	.809	.128	.636
B121	.674	.194	.495	3.0	B122	.653	.286	.580
B131	.299	.182	.608	3.0	B132	.423	.281	.647
B141	.451	.026	.672	3.0	B142	.429	.124	.752

$F(000) = 656$; $D_x(18\,°C) = 1.338$ gcm^{-3}; $D_x(-150\,°C)$ $= 1.378$ gcm^{-3}; $\mu(MoK\alpha) = 2.0$ cm^{-1}. Space group $P2_1/n$ (No. 14).

STRUCTURE DETERMINATION

The structure was determined by direct methods using the program assembly MULTAN and refined by Fourier and least-squares methods. Positions were calculated for hydrogen atoms and these were included as fixed contributors in the least-squares calculations.

One of the morpholino rings turned out to be disordered in a way similar to that found in 4-nitrobenzyl tris(morpholino)phosphonium perchlorate.[2] The two disordered components

correspond to an inversion of the ring and the disorder affects also the P − O part of the molecule. The resolution of the disordered atoms was not possible by means of the room temperature data set; therefore the low temperature data set was collected. The disorder was treated in the way described in Ref. 2 with the splitting of the atoms of the one morpholino ring and also the phosphorus atom with the attached oxygen atom. The two remaining morpholino groups seem to be unaffected by the disorder.

The situation is illustrated in Fig. 1 where the atoms drawn as open cricles had to be treated isotropically whereas the atoms drawn as ellipsoids were given anisotropic thermal parameters. The refinements converged to a conventional R factor of 0.045, $R_w = 0.051$ and the standard deviation of an observation of unit weight, $S = |\Sigma w \Delta F^2/(m-n)|^{\frac{1}{2}}$, was 3.3.

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

An ORTEP drawing of the molecule is shown in Fig. 1 where the numbering of the atoms is also indicated. In Table 2 are listed the most important structural parameters for the $(C_2N)_3PO$ part of the molecule; sites A and B refer to the two positions of the one disordered morpholino group. The values in the parentheses are the average for the two sites. Also in Table 2 the corresponding structural parameters for the selenide, Mor_3PSe,[1] are given. As mentioned above, it was not possible to resolve the disordered atoms by means of the room temperature data set. However, the refinement based upon this data set (2786 reflections) converged to R and R_w factors of 0.051 and 0.056, respectively, and an S value of 1.81. The calculated torsion angles O − P − N1-lone pair(N1), O − P − N2-lone pair (N2) and O − P − N3-lone pair(N3), 168, − 78 and 79°, respectively, are in fair agreement with the torsion angles from the low temperature data set, cf. entry 3 in Table 2.

DISCUSSION

As mentioned above, one of the morpholino groups was found to be disordered. In order to obtain a satisfactory resolution, the atoms of this ring together with the phosphorus atom and the attached oxygen atom had to be split. The two "half" morpholino rings are actually inversion forms and are oriented in such a way that the direction of the nitrogen lone pair is approximately retained after the inversion. Thus, this splitting causes only a negligible error in the torsion angle about the P − N bond, cf. entry 3 in Table 2. However, since some of

Table 2. A comparison between some structural parameters in tris(monopholino)phosphine, Mor_3PO, and in the corresponding selenide, Mor_3PSe.[1]

| | Mor₃PO | | | | | | | Mor₃PSe | | |
| | Site A | | | | Site B | | | | | |
	N1[a]	N2[b]	N3		N1[a,b]	N2	N3	N1[b]	N2[a]	N3
$\Sigma\angle N(°)$	351.6	352.1	349.1		358.6	355.2	350.8	354.9	340.1	349.7
$\Sigma\angle N(°)$		350.9		(352.9)[c]		354.9			348.2	
Tors.angle (°)	167.6	−90.6	82.5		167.4	−74.6	76.2	−77.6	178.9	65.8
	(167.5)[c]	(−83.4)[c]	(79.8)[c]							
P−N (Å)	1.665(3)	1.701(1)	1.616(1)		1.683(3)	1.633(2)	1.717(1)	1.661(2)	1.684(2)	1.670(2)
P−N (Å)		1.66				1.66			1.672	
ΣP−N (Å)		4.982		(4.985)[c]		4.988			5.015	
$\angle$XPN(°)	118.3(1)	114.1(1)	111.4(1)		120.6(1)	106.6(1)	107.9(1)	112.0(1)	115.1(1)	111.4(1)
$\Sigma\angle$XPN(°)		341.1		(338.1)[c]		335.1			338.5	
$\angle$NPN(°)[d]	114.4(1)	101.3(1)	98.9(1)		112.5(1)	105.0(1)	104.5(1)	101.2(1)	114.1(1)	102.4(1)
$\Sigma\angle$NPN(°)		314.6		(319.8)[c]		325.0			317.7	
P−X (Å)		1.483(3)		(1.486)[c]		1.489(3)			2.106(1)	

[a] The nitrogen atom with its lone pair *anti* to the P − X bond (X = O,Se). [b] The nitrogen atom with the lowest *p*-character. [c] Values in parenthesis are average values for sites A and B. [d] The bond angle between bonds to nitrogen atoms other than the one heading the column.

the atoms in the two sites, A and B, *cf.* Fig. 1, are fairly close to each other (less than 0.5 Å), their positions could not be determined with satisfactory accuracy. As a result, the calculated P−N bond distances and the bond angles around the phosphorus atom are probably subjected to considerably larger errors than the estimated standard deviations listed in Table 2. The listed values for these parameters, the P−N and the P−O bond lengths and the NPN and the OPN angles are therefore not real and merit no further discussion. The average values for the two sites have been calculated and are the basis for the discussion. They are listed in parenthesis in Table 2.

Compared with Mor$_3$PSe, the average bond angles around the nitrogen atoms are significantly larger as shown by the sum of the nitrogen bond angles, $\Sigma \angle N$; the average being 348.2° in Mor$_3$PSe and 352.9° in Mor$_3$PO. This increment in the *s*-character of the nitrogen atoms is accompanied by a slight but significant decrease in the P−N bond lengths, the average sum being 4.985 Å in the oxide as compared to 5.015 Å in the selenide. The coordination at the phosphorus is in principle tetrahedral but significantly distorted with considerably larger OPN bond angles than NPN bond angles. The average values for the sum of the XPN and NPN bond angles are quite comparable in the oxide and in the selenide. Apparently, the size of the chalcogen atom, X, has negligible influence upon the geometry of the phosphorus atom in $(R_2N)_3PX$.

The morpholino substituents in Mor$_3$PO are all in the expected chair conformation and are linked to the phosphorus atom approximately equatorially. A survey of the bond lengths and bond angles in these substituents is given in Table 3. All structural parameters, even for the disordered morpholino ring, are as expected.

In the crystal there are no especially short intra- or intermolecular contacts and the crystal packing is apparently dominated by van der Waals' forces. Newman diagrams of the conformation about the P−N bonds are shown in Fig. 2. Regardless the difficulties encountered during the structure determination and hence the uncertainties in some of the structural parameters, there is no doubt that the lone pair of one of the nitrogen atoms, N1A and N1B, is essentially *anti* to the oxygen atom with respect to the phosphorus − nitrogen bond (torsion angle 167.5°). The two remaining morpholino groups are twisted in opposite directions with O−P−N-lone pair (N) torsion agles of approximately −80 and 80°, respectively. The arrangement of the amino substituents in Mor$_3$PO is thus quite analogous to what has previously been observed in Mor$_3$PSe,[1] *cf.* Table 2, in the parent aminophosphine, Mor$_3$P,[12] and its telluride.[13] Owing to the uncertainties in the present structure, no relationship between the *p*-character of the nitrogen atoms and the corresponding P−N bond length could be established, *cf.* the first four entries in Table 2.

It has previously been argued that the *anti*-conformation for one phosphorus − nitrogen bond, and thus a *gauche-gauche-anti* (*g-g-a*) conformation when three nitrogen atoms are linked to a phosphorus atom is only to be anticipated when the nitrogen atoms display a slight or distinct pyramidal configuration.[1,20] The argument is based upon the assumption that the antibonding *sp* hybrid orbital on the phosphorus atom *anti* to the most electronegative substituent may interact with the nitrogen lone pair provided the latter has some *p*-character.[21] Additionally, the *anti* conformation will satisfy the basic assumption of the VSEPR model.[22] By a sufficient drain of electron density from the

Table 3. A survey of some bond lengths and bond angles and various averaged data for the morpholino groups in Mor$_3$PO.

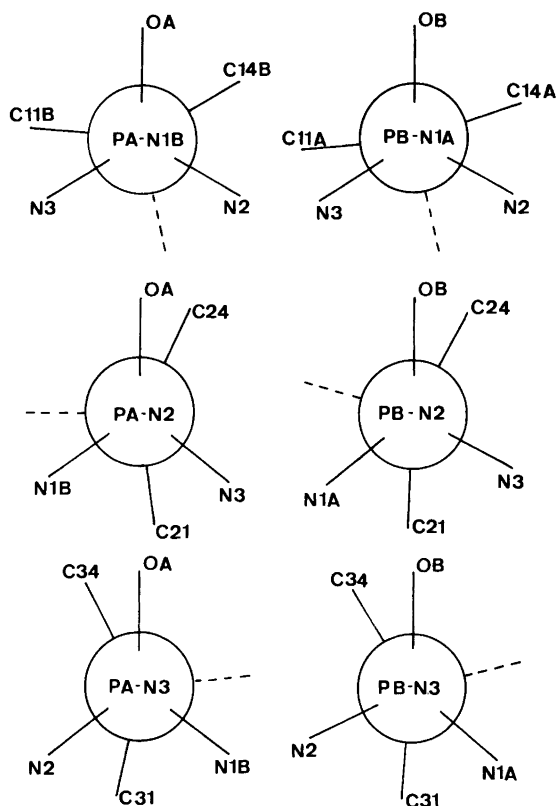|	N1(A)	N1(B)	N2	N3
$\angle$ CNC(°)	111.5(3)	111.1(2)	111.7(1)	110.8(1)
$\angle$ COC(°)	109.5(2)	110.3(2)	109.5(1)	110.2(1)
$\angle$ PNC1(°)	123.9(2)	127.2(2)	110.6(1)	117.7(1)
$\angle$ PNC4(°)	116.5(2)	120.1(2)	123.8(1)	122.3(1)
$\overline{N−C}$ (Å)	1.479	1.463	1.465	1.465
$\overline{C−C}$ (Å)	1.517	1.516	1.520	1.521
$\overline{C−O}$ (Å)	1.426	1.437	1.422	1.421

Fig. 2. Newman diagrams of the P−N bonds in Mor₃PO.

nitrogen atoms, either by the substituents as in tris(anilino)phosphine [23] and in tris(pyrazolo)-phosphine [24] or by the phosphorus atom as in the 4-nitrobenzyltris(piperidino)phosphonium cation,[2] the nitrogen atoms will attain an essentially planar coordination and the fairly symmetrical propeller conformation is favoured. An increase in the electronegativity of the chalcogen atom or, alternatively, an increase in the polarity of the P−X bond in $(R_2N)_3PX$ will similarly cause an electron transfer from the nitrogen atoms to the chalcogen atom, cf. the average sum of nitrogen bond angles in Mor₃PO and Mor₃PSe in Table 2, second entry. This transfer will be aided by increased donor ability of the dialkylamino group in $(R_2N)_3PX$ and in related compounds. In Mor₃PSe, Pip₃PSe and $(Me_2N)_3PSe$ the average sum of the nitrogen bond angles are 348.2, 353.0 and 352.9°, respectively.[1] The slightly but probably significantly longer P−Se bond length in the two latter compounds substantiates this conclusion. Actually, in

phosphonium cations derived from $(R_2N)_3P$, this difference in donor ability of the amino groups may cause the shift from the g-g-a conformation in Mor₃P⁺R to the propeller one in Pip₃P⁺R.[2]

Tervalent compounds derived from simple secondary aliphatic compounds as $(R_2N)_3P$ [12] and their selenated or tellurated [13] pentacovalent compounds exclusively prefer the g-g-a conformations regardless of the donor ability of the amino groups. However, in the corresponding oxides, $(R_2N)_3PO$, the propeller shaped conformation may be the preferred one with amino groups of better donor ability than the morpholino group. In addition compounds and in metal complexes in which the dipolar nature of the P−O bond is increased and hence the p-character of the nitrogen atoms is further decreased, the propeller shaped conformation may be the energetically favoured one.[3] In the majority of the metal complexes with tris(dimethylamino)phosphine oxide, HMPA, as ligand the propeller conformation of the HMPA

molecules is the preferred one. However, in some compounds like the monoclinic form of dioxodichlorobis(HMPA)Mo^{VI}[25] and in the adduct between HMPA and barbital[11] the *g-g-a* conformation of the HMPA molecules is observed. Apparently, weakly coordinated HMPA is a border case with regard to the conformational preference and the crystal lattice forces may be the determining factor for the conformation of HMPA.

REFERENCES

1. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 33* (1979) 187.
2. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 34* (1980) 631.
3. Brown, D. H., Cameron, A. F., Cross, R. J. and McLaren, M. *J. Chem. Soc. Dalton Trans.* (1981) 1459.
4. Normant, H. *Angew. Chem. 79* (1967) 1029.
5. Parker, A. J. *Chem. Rev. 69* (1969) 1.
6. Parker, A. J., Mayer, V., Schmid, R. and Gutmann, V. *J. Org. Chem. 43* (1978) 1843.
7. Schaefer, M. and Curran, C. *Inorg. Chem. 4* (1965) 623.
8. De Bolster, M. W. G. and Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas. 90* (1971) 477.
9. Sinha, S. P., Pakkanen, T. T., Pakkanen, T. A. and Niinistö, L. *Polyhedron 1* (1982). *In press.*
10. Steudel, R., Rose, F. and Pichardt, J. *Z. Anorg. Allg. Chem. 434* (1977) 99.
11. I-Nan Hsu and Craven, B. M. *Acta Crystallogr. B 30* (1974) 1299.
12. Rømming, C. and Songstad, J. *Acta Chem. Scand. A 32* (1978) 689.
13. Rømming, C., Iversen, A. J. and Songstad, J. *Acta Chem. Scand. A 34* (1980) 333.
14. Donoghue, J. T., Fernandez, E. and Peters, D. A. *Inorg. Chem. 8* (1969) 1191.
15. De Bolster, M. W. G., Kortram, I. E. and Groeneveld, W. L. *J. Inorg. Nucl. Chem. 35* (1973) 1843.
16. De Bolster, M. W. G. *Z. Anorg. Allg. Chem. 404* (1977) 78.
17. Dunstan, P. O. and Matos, F. A. P. *An. Acad. Bras. Cienc. 51* (1979) 211.
18. Schvetz, A. A., Amarskii, E. G. and Moiseeva, O. A. *Koord. Khim. 5* (1979) 1510.
19. Malatesta, P. and Tarantino, B. *Il Farmaco (Pavia) Ed. Sci. 10* (1955) 15.
20. Maartmann-Moe, K., Rømming, C. and Songstad, J. *Acta Chem. Scand. To be published.*
21. Burdon, J., Hotchkiss, J. C. and Jennings, W. B. *J. Chem. Soc. Perkin Trans. 2* (1976) 1052.
22. Gillespie, R. J. *J. Chem. Educ. 47* (1970) 18.
23. Tarassoli, A., Haltiwanger, R. C. and Norman, A. D. *Inorg. Nucl. Chem. Lett. 16* (1980) 27.
24. Cobbledick, R. E. and Einstein, F. W. B. *Acta Crystallogr. B 31* (1975) 2731.
25. Viossat, B., Khodadad, P. and Rodier, N. *Acta Crystallogr. B 33* (1977) 2523, 3793.