pounds, and the structure determination is first to demonstrate the ability of Hg_2^{2+} to coordinate covalently nitrogen donor ligands to both mercury atoms.

The mercury–nitrogen (Hg–N_1) bond distance of 2.16 (3) Å in this complex indicates that the mercurous ion, Hg_2^{2+}, is capable of forming strong coordinate bonds. The distance is only slightly greater than the normal mercury(II)–nitrogen bond lengths,[22] despite the reduced nuclear charge for the lower oxidation state of mercury and the weak σ-donor ability of the ligand. However, the inductive effect of the substituent in 4-cyanopyridine is expected to make the pyridine nucleus a good π acceptor. Therefore, in the absence of appreciable $N \rightarrow Hg$ σ bonding, it is possible that π bonding $(d\pi \rightarrow \pi^*)$ stabilizes the mercury–nitrogen bond, resulting in a normal bond distance. (Wong and Brewer have employed a similar argument to explain the strength of the coordination bond in the zinc(II)–4-cyanopyridine complex.[30])

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The Crystal and Molecular Structure of Tris(dimethylhydrazino)bis(phosphine oxide), $OP(NCH_3NCH_3)_3PO$

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The structure of tris(dimethylhydrazino)bis(phosphine oxide), $OP(NCH_3NCH_3)_3PO$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $C2/c$ or Cc with four molecules in a unit cell of dimensions $a = 9.757$, $b = 10.068$, $c = 13.175$ Å, and $\beta = 104.98°$. Full-matrix, least-squares refinement has led to a final value of the unweighted R index (on structure factors in group $C2/c$) of 0.056 for the 1781 reflections for which the observed intensity $I > 3\sigma(I)$. The structure is fully disordered so that the molecular symmetry, which is 32, appears to be $\bar{3}m$. All P, O, and C atoms in one molecule are nearly at the same positions as the corresponding atoms in the inverse molecule at the same lattice site; accordingly only average positions for these atoms have been determined. Each molecule consists of two OP units joined by three NCH_3NCH_3 bridges. The P–N bond length (1.66 Å) and the geometry about the nitrogen are discussed in terms of dπ–pπ bonding. The 2.82-Å separation of the two phosphorus atoms may indicate a weak bond between them.

Introduction

The stereochemistry of phosphorus–nitrogen compounds is of current interest[1–3] because of the possible formation of pπ–dπ bonds between these two atoms. Structures of several cyclic P^V–N compounds[4–7] have been published and while only a few compounds containing the P^{III}–N unit have been examined,[2,3,8–11] the number is growing rapidly. Unfortunately, with the single exception of the $F_2PN(CH_3)_2$[9] and $B_4H_8F_2PN(CH_3)_2$[8] pair there are no data available which permit structural comparisons between similar compounds in which the effect of oxidation state, lone-pair electrons, and neighboring groups on the P–N linkage can be detected.

Recently, $P(NCH_3NCH_3)_3P$ was studied by X-ray diffraction.[2] Since we had already begun a structural investigation of its crystalline dioxide, $OP(NCH_3NCH_3)_3PO$, first reported by Payne, Noth, and Henniger,[12] the opportunity presented itself to examine the effects of increasing oxidation state and of coordination of the phosphorus lone pair on the structure of a P–N unit incorporated in a sterically constrained cage. $OP(NCH_3NCH_3)_3PO$ was of further interest in view of the current theoretical studies on the PO bond[13–15] and because of the suggestion that in similar S–N compounds, coordination of the nonbonding pairs on sulfur eliminates the influence of these lone pairs on physical properties, allowing effects arising from d-orbital participation to be more easily observed.[16]

Experimental Section

$OP(NCH_3NCH_3)_3PO$[12] was prepared by air oxidation of $P(NCH_3NCH_3)_3P$ in pyridine solution. Pale yellow prismatic crystals were obtained by recrystallization from the same solvent by Dr. E. Putkey. An equant prismatic crystal approximately 0.040 cm on a side was sealed in a capillary tube with a wall thickness of 0.001 cm. Preliminary investigations using a Syntex $P\bar{1}$ autodiffractometer indicated that the crystals were monoclinic and had systematic absences corresponding to the space groups Cc and $C2/c$. Cell dimensions at 22° were found

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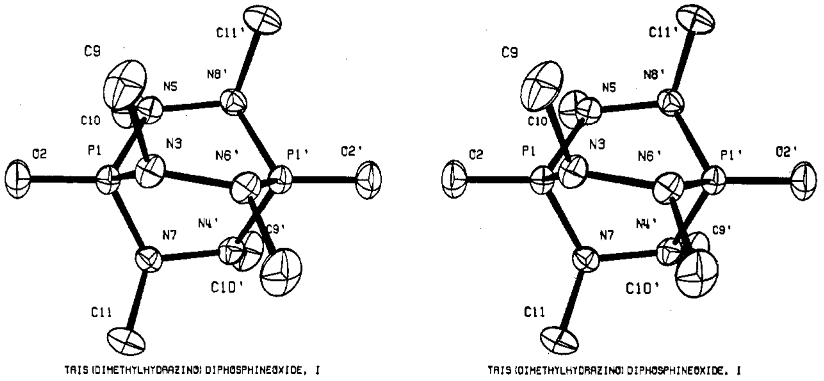

Figure 1.—A stereodrawing of molecule I showing ellipsoids of 30% probability. (C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.)

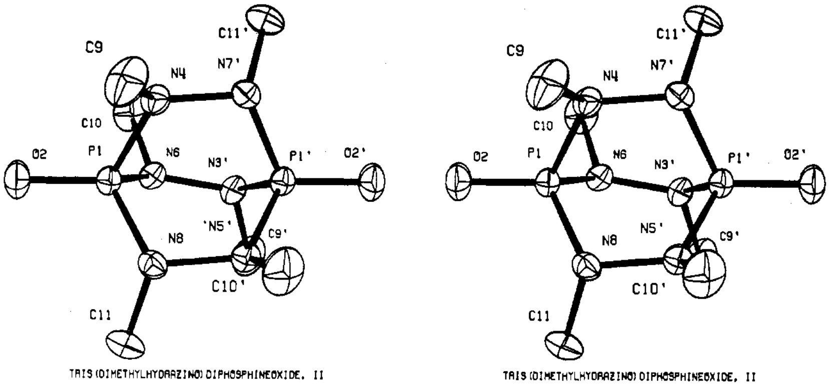

Figure 2.—A stereodrawing of molecule II showing ellipsoids of 30% probability. The view is the same as that in Figure 1, so that P, O, and C positions are superimposable, demonstrating the disorder.

to be a = 9.757 (2), b = 10.068 (2), c = 13.175 (2) Å, and β = 104.98 (2)° by a least-squares fit of 13 high-angle 2θ values. The density is calculated to be 1.434 g cm^{-3} using a formula weight of 268.2 amu with four such units per unit cell. Because the compound is very soluble in organic solvents and is extremely sensitive to moisture, the crystal density was not measured.

Intensities were measured on the Syntex four-circle autodiffractometer using graphite-monochromatized Mo Kα radiation (Mo Kα_1, λ 0.70926 Å; Mo Kα_2, λ 0.71354 Å) and a pulse-height analyzer. The θ–2θ scan technique was employed, at a scan rate which varied from 2 to 24°/min (in 2θ) in such a way that weaker reflections were examined most slowly to minimize counting errors. The scan range varied from 2.02° at 2θ = 3° to 2.49° at 2θ = 70°. All reciprocal lattice points for which $2\theta < 70°$ and many for which $70° < 2\theta < 80°$ were examined. A time equal to half of the scan time for each reflection was spent counting background at each end of the scan range. Three check reflections which were measured periodically during the data collection showed no significant trend in intensity. The recorded counts were corrected for background and for Lorentz and polarization effects but not for absorption; the value of μr is approximately 0.07, so that this correction is negligible. Observational variances $\sigma^2(I)$ were computed from counting statistics alone. All reflections for which the net counts exceeded 3 times the standard deviation were used throughout.

Determination and Refinement of the Structure.—An approximate absolute scale factor and an average isotropic thermal parameter (2.0 Å^2) were found by Wilson's method.[17a] Normalized structure factors (E's) were calculated whose distribution indicated[17b] that the space group was noncentric and therefore Cc instead of $C2/c$. (Initial structure solution and refinement was done in Cc; only when the resulting structure nearly showed $C2/c$ symmetry was the latter group adopted and used for final refinements.) The coordinates of the phosphorus and oxygen atoms were deduced from a three-dimensional Patterson synthesis, and the carbon and nitrogen atoms were all found in a single step of Fourier refinement. Each molecular site contains either molecule I or, with equal probability, its inverse (II) (see Figures 1 and 2). Least-squares refinement using isotropic thermal parameters reduced the R_1 index ($R_1 = \Sigma|F_o - |F_c||/\Sigma F_o$) to 0.09 assuming single atomic positions for all P, O, and C atoms; these positions must all be averages of two disordered positions (one from each enantiomer) which are close together. A Fourier synthesis of the region around each carbon atom did not indicate that these peaks might be resolved further. The introduction of anisotropic thermal parameters and subsequent full-matrix least-squares refinement reduced R_1 to 0.0556 and R_2 to 0.0560. Observed and calculated structure factors are presented in Table I,[18] and the final parameters are given in Tables II and III. The goodness of fit, $(\Sigma w(F_o - F_c)^2/(m - s))^{1/2}$, is 2.2. A final

TABLE II

FINAL POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	x	y	z
P(1)	2377 (1)	1412 (1)	−690 (1)
O(2)	2257 (2)	279 (2)	−1405 (1)
N(3)	2596 (4)	2845 (3)	−1218 (2)
N(4)	3780 (4)	2414 (3)	−627 (2)
N(5)	3713 (4)	1303 (3)	372 (2)
N(6)	2547 (4)	1033 (3)	566 (2)
N(7)	966 (4)	1635 (3)	−221 (3)
N(8)	1020 (4)	2479 (4)	−967 (2)
C(9)	3882 (4)	2989 (3)	−1681 (3)
C(10)	3790 (4)	94 (3)	1067 (2)
C(11)	−456 (3)	1868 (4)	−1033 (3)

[a] Values are given ×10^4. See Figures 1 and 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

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(18) Table I will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1643. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III

THERMAL VIBRATION PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P(1)	89 (1)	64 (1)	37 (1)	4 (1)	30 (1)	−10 (1)
O(2)	157 (3)	88 (2)	60 (1)	2 (3)	43 (3)	−55 (2)
N(3)	104 (4)	74 (3)	36 (1)	14 (5)	48 (4)	10 (3)
N(4)	89 (3)	75 (3)	42 (2)	−3 (5)	56 (4)	0 (3)
N(5)	90 (3)	69 (3)	39 (1)	24 (5)	22 (3)	7 (3)
N(6)	94 (3)	62 (2)	45 (2)	21 (5)	37 (4)	18 (3)
N(7)	78 (3)	73 (3)	48 (2)	−21 (5)	27 (4)	−10 (3)
N(8)	80 (3)	80 (3)	40 (2)	−4 (5)	6 (4)	−8 (4)
C(9)	221 (5)	117 (3)	79 (2)	−6 (6)	190 (6)	18 (4)
C(10)	201 (5)	84 (2)	72 (2)	85 (5)	17 (5)	46 (3)
C(11)	77 (2)	174 (4)	110 (3)	−26 (5)	−15 (4)	−84 (6)

[a] The b are $\times 10^4$. See Figures 1 and 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter. The temperature factor is $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

TABLE IV

MOLECULAR DIMENSIONS

I. Bond Lengths, Å

P(1)–O(2)	1.464 (2)	N(3)–N(6)′	1.448 (5)
		N(4)–N(7)′	1.444 (5)
P(1)–N(3)	1.640 (3)	N(5)–N(8)′	1.442 (5)
P(1)–N(4)	1.685 (3)		
P(1)–N(5)	1.651 (3)	N(3)–C(9)	1.538 (5)
P(1)–N(6)	1.664 (3)	N(4)–C(9)	1.532 (5)
P(1)–N(7)	1.663 (3)	N(5)–C(10)	1.514 (4)
P(1)–N(8)	1.670 (4)	N(6)–C(10)	1.545 (5)
		N(7)–C(11)	1.535 (5)
		N(8)–C(11)	1.548 (5)

II. Bond Angles, Deg

O(2)–P(1)–N(3)	114.2 (2)	C(9)–N(3)–N(6)′	112.1 (3)
O(2)–P(1)–N(4)	115.3 (2)	C(9)–N(4)–N(7)′	114.4 (3)
O(2)–P(1)–N(5)	114.1 (1)	C(10)–N(5)–N(8)′	112.4 (3)
O(2)–P(1)–N(6)	115.6 (2)	C(10)–N(6)–N(3)′	114.1 (3)
O(2)–P(1)–N(7)	114.1 (2)	C(11)–N(7)–N(4)′	112.4 (3)
O(2)–P(1)–N(8)	115.7 (2)	C(11)–N(8)–N(5)′	113.7 (3)
P(1)–N(3)–N(6)′	113.1 (3)	C(9)–N(3)–P(1)	117.4 (2)
P(1)–N(4)–N(7)′	114.2 (3)	C(9)–N(4)–P(1)	115.1 (2)
P(1)–N(5)–N(8)′	113.3 (3)	C(10)–N(5)–P(1)	118.1 (2)
P(1)–N(6)–N(3)′	114.3 (3)	C(10)–N(6)–P(1)	115.6 (3)
P(1)–N(7)–N(4)′	112.6 (2)	C(11)–N(7)–P(1)	116.6 (2)
P(1)–N(8)–N(5)′	114.0 (2)	C(11)–N(8)–P(1)	115.5 (2)
N(3)–P(1)–N(5)	104.9 (2)		
N(4)–P(1)–N(6)	102.6 (2)		
N(5)–P(1)–N(7)	104.0 (2)		
N(6)–P(1)–N(8)	103.6 (2)		
N(7)–P(1)–N(3)	104.5 (2)		
N(8)–P(1)–N(4)	102.3 (2)		

III. Some Dihedral Angles, Deg

P(1)–N(3)–N(6)′–P(1)′	18.7 (4)
P(1)–N(4)–N(7)′–P(1)′	18.7 (4)
P(1)–N(5)–N(8)′–P(1)′	18.3 (4)

difference Fourier synthesis did not reveal the positions of the disordered hydrogen atoms. The refined anisotropic thermal ellipsoids (see Figures 1 and 2) do not appear to be artificially large due to disorder, although this effect must be present to some extent.

The effects of the unresolved disorder are apparent in the variations in bond lengths and angles given in Table IV. Average values of these, however, except where carbon positions are involved, should not be appreciably affected.

The full-matrix least-squares program used[19] minimizes $\Sigma w(\Delta|F|)^2$; the weights were the reciprocal squares of σ, the standard deviation of each observation. Atomic scattering factors[20] for P^0, O^0, N^0, and C^0 (valence) were used. The values for phosphorus were increased by 0.10 electron to take account of the real component of anomalous dispersion.[21] In the last cycle of least-squares refinement all shifts were less than 1% of their corresponding esd's.

The final unweighted R_1 index for the similar structure refined in space group Cc is 0.0513 (R_2 = 0.0513 also). The $\mathcal{R}$ significance test of Hamilton,[22] if applied to the weighted R_2 ratio of 1.09, gives the result that the centric group can be handily rejected at the 0.005 confidence level. The average values of the chemically unique molecular parameters are, however, identical except for the N–N bond, which is 0.02 Å longer in Cc. The discrepancies between chemically equivalent features of the molecule are much more unreasonable for the acentric structure. For these reasons, the results are presented in the centric space group. Other workers[23] have encountered similar situations.

Discussion

The $OP(NCH_3NCH_3)_3PO$ molecule (Figures 1–3, Table IV) consists of two PO groups linked by three NCH_3NCH_3 bridges. The arrangement of the outer atoms (the oxygen atoms and methyl groups) of a molecule of $OP(NCH_3NCH_3)_3PO$ is invariant (or nearly so) to the crystallographic inversion operation at the molecular center of gravity. For this reason either conformer may be accommodated at a lattice site and the structure is disordered. Very similar disorder is found[2] in $P(NCH_3NCH_3)_3P$.

The normal P–N single-bond length is usually considered to be 1.77 Å (the P–N distance[24] in $H_3NPO_3^{2-}$) or 1.80 Å (the sum of Pauling covalent radii[25]). The value of 1.66 Å observed in $OP(NCH_3NCH_3)_3PO$ is considerably less than this, being closer to the 1.641-Å double-bond length in $(C_6H_5)_2FP{=}NCH_3$[5] and to other seemingly short P–N bonds as in H_2NPF_2 (1.650 Å),[3] $F_2PN(CH_3)_2$ (1.628 Å),[9] $(H_2N)_3PBH_3$ (1.65 Å),[10] $\{NP[N(CH_3)_2]_2\}_3$ (1.68 Å for the exocyclic bond),[7] and $(Cl_3PNCH_3)_2$ (1.629 Å for the equatorial bond)[6] which have all been explained by attributing $d\pi$–$p\pi$ character to the bond. However, $d\pi$–$p\pi$ bonding was discounted[2] in the closely related $P(NCH_3NCH_3)_3P$ because nitrogen's pyramidal configuration places its lone-pair electrons in the wrong spatial orientation to overlap phosphorus 3d orbitals effectively according to the rules proposed by Cruickshank.[26] On the other hand, the d orbitals which Cruickshank thought to be unimportant in π-bond formation (the t_2 orbitals in T_d systems) have recently been shown[27] to contribute heavily to such bonds. Hence, since planarity (*e.g.*, sp^2 hybridization) of the nitrogen is not required for π-bond formation,[28] P–N $d\pi$–$p\pi$ bonding cannot be eliminated in either $P(NCH_3NCH_3)_3P$ or $OP(NCH_3NCH_3)_3PO$ on steric grounds alone. Indeed, since the nitrogen pyramid in $P(NCH_3NCH_3)_3P$ and $OP(NCH_3NCH_3)_3PO$ has been flattened considerably from sp^3 hybridization (the sum of the bond angles about nitrogen is 345.6° in the former compound[2] and 343° in the latter one) toward the planar (sp^2) configuration which is most favorable for

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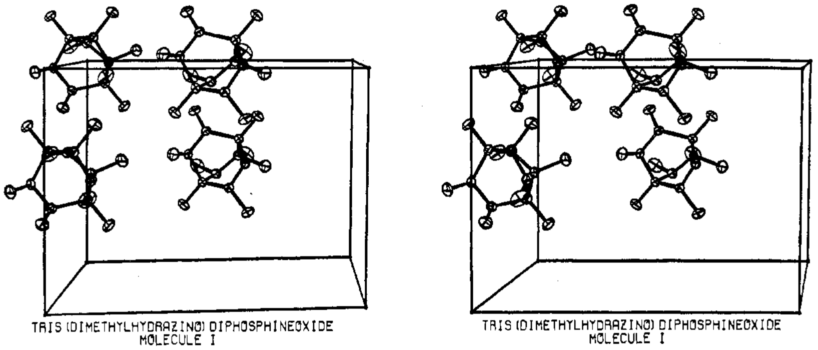

Figure 3.—A stereodrawing showing the packing of molecules I only. Ellipsoids of 30% probability are shown. The unit cell is shown with +*c* horizontal to the right, +*b* vertical downward, and +*a* upward out of the page toward the reader.

π bonding, it is actually attractive to postulate a $d\pi$–$p\pi$ interaction to explain nitrogen's stereochemistry. Ring strain[29] and perhaps crystal effects may account for the nonplanar conformation around the nitrogen.

In addition to $d\pi$–$p\pi$ P–N bonding more extensive delocalization is possible within these molecules. Direct spin–spin coupling of the two phosphorus nuclei has already been proposed[30] to account for features of the nmr spectrum of $P(NCH_3NCH_3)_3P$; this, along with the actual phosphorus–phosphorus separation, could be the result of a weak bond between the two atoms. Both the P–P distances in $OP(NCH_3NCH_3)_3PO$ (2.82 Å) and in $P(NCH_3NCH_3)_3P$ (2.99 Å—calculated from data in ref 2) are significantly less than twice the van der Waals radius of phosphorus (3.8 Å)[25] and at the same time much longer than the normal P–P single-bond length (2.3 Å).[25]

The P–N bond in $OP(NCH_3NCH_3)_3PO$ (1.66 Å) is about 0.02 Å shorter and the NPN angle (103.6°) is 2.5° greater than the corresponding values in $P(NCH_3NCH_3)_3P$. Similar behavior was also noted between $F_2PN(CH_3)_2$[9] and $B_4H_8F_2PN(CH_3)_2$[8] where the P–N and P–F bonds decrease by about 0.03 Å and the FPF angle increases by 4.9° going from three- to four-coordinate phosphorus. Neither the N–N bond lengths nor the structures of the PNNP bridges are the same between the two compounds. In $P(NCH_3NCH_3)_3P$ the bond distance is 1.46 Å and the four atoms are coplanar, while in the dioxide the bond has shortened by 0.02 Å and twisting about P–P axes has occurred with the two PNN planes intersecting at an 18.6° dihedral angle. This conformational difference between the PNNP groups is particularly interesting in light of the controversy which has surrounded the ground-state conformation of structurally related bicyclo[2.2.2]octane derivatives, where both the D_3 and D_{3h} configurations of the cage have been recently observed and where the energy difference between conformers now appears to be slight.[31,32] In the phosphorus–nitrogen analogs the stable conformation also seems to be determined by subtle crystal or substituent effects, probably indicating small energy differences in this case as well.

The P–O bond length, 1.46 Å, is within the normal range expected in X_3PO type compounds.[33] Previous calculations[27] indicate that at this distance the P–O bond also has significant phosphorus 3d character.

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