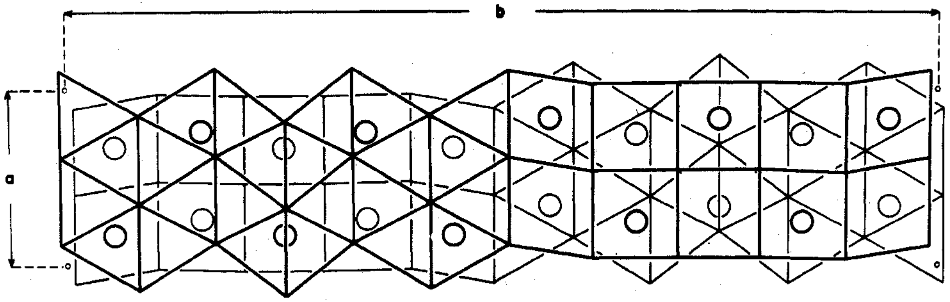

**Figure 1.** Schematic representation of the crystal structure of $Ho_5Cl_{11}$ (from ref 5). The holmium atoms are drawn as light and bold circles at $z \approx 0$ and $z \approx {}^1/_2$. The chlorine atoms are located at the intersection points of the somewhat puckered nets at $z \approx {}^3/_4$ and $z \approx {}^1/_4$.

refinement,[8] yielding the unit cell $a = 7.078$ (2) Å, $b = 34.57$ (2) Å, $c = 6.603$ (3) Å, and $\beta = 90.19$ (5)°. The numbers in parentheses are estimated errors obtained by tripling numerical standard deviations. The actual space group is $P2_1/m$ (No. 11) but to a very good approximation the structure can be described with the space group *Pnma* (No. 62) which is a minimal supergroup of $P2_1/m$. There are 4 formula units per unit cell and the calculated density is 4.994 g $cm^{-3}$. The crystal structure (Figure 1) can be understood as a one-dimensional superstructure of the fluorite type built from five basic fluorite units with four additional anions per unit cell. In order to accommodate these anions, half of the primitive cubic anion packing is transformed into a closest packing. The superimposed anion layers of these two packings lead to a vernier-like[9] picture.

The relatively large difference between the x-ray and the analytical stoichiometries, Cl/Ho = 2.20 vs. 2.14, deserves some comment since typical analyses normally give ratios which are accurate to within ±0.02 or less. Since there is no evidence in the powder diffraction patterns for a range of composition for $HoCl_{2.20}$ the low analytical results must have been caused by inclusion of a small amount of either the metal or a still lower phase. In either case, the small amount necessary to account for the difference would hardly be evident in the x-ray powder films and impossible to detect on solution of a sample for analysis since fairly strong acetic acid has to be used in order to avoid precipitation of quite stable hydrolysis products. Although sheets rather than chunks of metal were used in most equilibrations small amounts of metal could have been scraped from the substrate in an attempt to recover all of the material. Finely divided holmium might also be produced by either a disproportionation equilibrium under small temperature gradients or, better, by accidental excursions of the sample above the peritectic decomposition temperature (551 °C) since the region for effective equilibration above the eutectic is only 8° wide. Magnetic evidence for traces of finely divided metal has been found for a $GdCl_{1.5}$ sample,[10] a comparable situation where there is only a 31° wide region for equilibration below the decomposition point of the sesquichloride (632 °C).

On the other hand, very recent experiences have made it increasingly clear that many of the earlier rare earth metal–metal halide studies in which only a dihalide or less-reduced phase has been achieved during equilibration of the molten trichloride with excess metal represented only metastable equilibrium. It now appears that very small amounts of more reduced monochloride or other phases form and effectively block the surface of the metal toward further reaction, as recently demonstrated during the synthesis of ScCl.[11] Simultaneously the synthesis of GdCl, TbCl, and still others has been reported.[12] The fact that earlier equilibrations in the $HoCl_3$–Ho system with chunks of metal yielded Cl/Ho ratios around 2.18 and ratios around 2.14 were obtained only on extended equilibrations using small amounts of $HoCl_3$ and packets of holmium foil to ensure complete reduction is consistent with either contamination by metal or by monochloride, but the latter now seems more likely. Further studies of this system are necessary to show this conclusively, however.

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**Registry No.** $Ho_5Cl_{11}$, 63039-66-7.

**Supplementary Material Available:** Table I, the observed and calculated distances and intensities for $Ho_5Cl_{11}$ (1 page). Ordering information is given on any current masthead page.

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# Unusual Phosphorus Basicity of $P(OCH_2CH_2)_3N$ and the Molecular Structure of $H_3BP(OCH_2CH_2)_3N$

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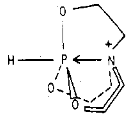
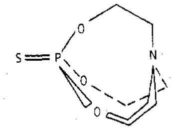
In two recent communications we showed that spectral (NMR and IR) and chemical properties of the new polycyclic species **1**[2a] and **2**[2b] were consistent with a tricyclic and bicyclic



**1**



**2**

configuration, respectively, and these structures were confirmed

**Table I.** Fractional Coordinates[a] and Anisotropic Thermal Parameters[b] for $H_3BP(OCH_2CH_2)_3N$

| Atom[c] | $x$ | $y$ | $z$ | $\beta_{11}$[d] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| P(1) | 0.3063 (1) | 0.5848 (1) | 0.0496 (1) | 0.0052 (1) | 0.0048 (1) | 0.0047 (1) | 0.0001 (1) | −0.0010 (1) | −0.0002 (1) |
| O(2) | 0.2474 (4) | 0.6905 (4) | 0.0894 (4) | 0.0064 (3) | 0.0103 (4) | 0.0090 (3) | 0.0019 (3) | −0.0015 (3) | −0.0034 (3) |
| C(3) | 0.2564 (6) | 0.7430 (7) | 0.1862 (6) | 0.0076 (6) | 0.0088 (6) | 0.0091 (6) | 0.0021 (6) | 0.0007 (5) | −0.0038 (5) |
| C(4) | 0.3652 (7) | 0.7887 (7) | 0.2124 (7) | 0.0091 (7) | 0.0106 (7) | 0.0082 (6) | 0.0008 (6) | −0.0006 (5) | −0.0051 (6) |
| N(5) | 0.4553 (4) | 0.7165 (4) | 0.1972 (4) | 0.0071 (5) | 0.0076 (4) | 0.0054 (3) | −0.0005 (3) | 0.0007 (3) | −0.0001 (3) |
| C(6) | 0.4648 (7) | 0.6183 (6) | 0.2564 (6) | 0.0089 (7) | 0.0098 (6) | 0.0060 (5) | −0.0019 (5) | −0.0036 (5) | 0.0011 (5) |
| C(7) | 0.4373 (7) | 0.5156 (6) | 0.2022 (6) | 0.0090 (6) | 0.0080 (6) | 0.0051 (4) | 0.0006 (5) | −0.0027 (5) | 0.0016 (5) |
| O(8) | 0.3365 (4) | 0.5174 (4) | 0.1487 (4) | 0.0109 (5) | 0.0070 (3) | 0.0087 (4) | −0.0023 (3) | −0.0037 (3) | 0.0020 (3) |
| O(9) | 0.4139 (4) | 0.6194 (4) | −0.0039 (3) | 0.0088 (4) | 0.0125 (5) | 0.0045 (3) | −0.0031 (3) | 0.0013 (3) | −0.0009 (3) |
| C(10) | 0.4757 (7) | 0.7169 (7) | 0.0076 (5) | 0.0090 (6) | 0.0099 (7) | 0.0057 (5) | −0.0036 (6) | 0.0020 (5) | 0.0010 (5) |
| C(11) | 0.5248 (7) | 0.7341 (8) | 0.1105 (5) | 0.0088 (6) | 0.0116 (8) | 0.0060 (5) | −0.0064 (6) | 0.0002 (5) | 0.0003 (5) |
| B(12) | 0.2157 (8) | 0.5061 (8) | −0.0414 (8) | 0.0097 (9) | 0.0079 (7) | 0.0088 (7) | 0.0004 (6) | −0.0048 (7) | −0.0012 (6) |

| Atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | Atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| H(3A)[e] | 0.240 (7) | 0.675 (8) | 0.238 (6) | 4.4 (19)[f] | H(10A) | 0.400 (11) | 0.778 (11) | −0.005 (9) | 11.9 (34) |
| H(3B) | 0.194 (8) | 0.791 (7) | 0.193 (6) | 3.1 (17) | H(10B) | 0.530 (7) | 0.724 (6) | −0.042 (6) | 3.4 (16) |
| H(4A) | 0.361 (8) | 0.832 (8) | 0.275 (8) | 5.7 (22) | H(11A) | 0.581 (9) | 0.771 (10) | 0.117 (8) | 4.4 (26) |
| H(4B) | 0.379 (8) | 0.852 (8) | 0.153 (8) | 6.7 (24) | H(11B) | 0.542 (9) | 0.819 (9) | 0.107 (7) | 4.6 (23) |
| H(6A) | 0.401 (6) | 0.630 (6) | 0.333 (6) | 3.3 (15) | H(12A) | 0.203 (7) | 0.561 (7) | −0.106 (7) | 4.4 (18) |
| H(6B) | 0.534 (9) | 0.602 (7) | 0.284 (7) | 4.5 (22) | H(12B) | 0.251 (9) | 0.448 (9) | −0.052 (8) | 4.9 (25) |
| H(7A) | 0.438 (6) | 0.452 (5) | 0.240 (6) | 1.2 (13) | H(12C) | 0.132 (7) | 0.492 (6) | 0.000 (6) | 3.8 (16) |
| H(7B) | 0.492 (7) | 0.490 (6) | 0.145 (6) | 3.4 (17) | | | | | |

[a] Standard deviations are given in parentheses. [b] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Numbering of the atoms corresponds to that in Figure 1. [d] All $\beta$ values are $\beta \times 10^3$. [e] Hydrogen atoms are labeled with the number of the carbon atoms to which they are bonded. Where more than one hydrogen is bonded to a carbon atom the hydrogens are labeled with a number and a letter. [f] Hydrogen atom temperature factors are isotropic.

by x-ray crystallographic means. Here we show that spectral and chemical studies do not permit a clear conclusion to be drawn regarding the question of a tricyclic vs. a bicyclic structure for the title borane compound **3**. We also show that the unusual basicity of $P(OCH_2CH_2)_3N$ in **3** is not the result of the formation of a P←N transannular bond.

Compound **3**, formed upon reaction of a toluene solution of unstable $P(OCH_2CH_2)_3N$ with $H_3B{\cdot}THF$ at room temperature,[3] is a stable solid which can be purified by sublimation. The downfield $^{31}P$ chemical shift of this adduct with respect to 85% $H_3PO_4$ (97.6 ppm) is nearly the same as that of $H_3BP(OCH_2)_3CMe$ (97 ppm)[4] wherein phosphorus is tetracoordinate. The spin–spin coupling $^1J(PB)$ in **3** (120.3 Hz) is, however, substantially larger than that of $H_3BP(OCH_2)_3CEt$ (91.4 Hz).[4] A feature in the $^{13}C$ NMR spectra of **1** and **2** which might be tentatively taken as indicative of their respective structures is the coupling of the $NCH_2$ carbon to the phosphorus. Thus this coupling is 12.8 Hz in **1** and undetectable in **2**. The corresponding value of 2.0 Hz in **3** renders any structural assignment on this criterion ambiguous, however. Increasing Lewis basicity in a series of phosphite esters has been found to cause a decrease in the symmetric and asymmetric BH stretching frequencies in their $BH_3$ adducts, as well as a decline in the weighted average of these modes.[5] Such a basicity trend is suggested by the BH modes of $H_3BP(OCH_2)_3CMe$ (2420, 2361 cm$^{-1}$), $H_3BP(OMe)_3$ (2398, 2352 cm$^{-1}$) and **3** (2385, 2355 cm$^{-1}$) observed in solution, and their weighted averages are confirmatory of this trend (2400, 2383, 2375 cm$^{-1}$, respectively). Solution equilibrium studies monitored by $^1H$ NMR spectroscopy in toluene and $Me_2SO$ also show that the order of basicity is $P(OCH_2CH_2)_3N > P(OMe)_3 > P(OCH_2)_3CMe$. While it would be tempting to postulate the existence of a transannular P←N interaction in **3** to account for the position of the parent phosphatrane $P(OCH_2CH_2)_3N$ in the basicity order indicated by the infrared and equilibrium investigations, the $^{31}P$ chemical shift of **3** is consistent with a bicyclic structure rather than with the tricyclic structure required by the presence of a P←N bond.

To resolve this question a molecular structure determination was undertaken. Suitable crystals of **3** were obtained by sublimation in a sealed tube. Preliminary examination showed the crystals to be orthorhombic with $a = 12.219$ (3), $b = 12.236$ (2), and $c = 13.006$ (2) Å and eight units of $H_3BP(OCH_2CH_2)_3N$ per unit cell. The space group was unambiguously assigned as *Pbca* by the systematic extinctions ($0kl$ absent if $k = 2n + 1$, $h0l$ absent if $l = 2n + 1$, and $hk0$ absent if $h = 2n + 1$).

The unique intensities of 1535 reflections with $2\theta \le 114°$ were measured using a computer-controlled four-circle diffractometer and Cu K$\alpha$ radiation (1.5418 Å). Of these, 957 were judged to be observed after correction for Lorentz, polarization, and background effects ($F_o \ge 3\sigma(F_o)$).

Routine application of direct methods, MULTAN,[6] in the centrosymetric space group *Pbca* located the phosphorus atom in the first phased $E$ synthesis.[7] The rest of the nonhydrogen atoms were found in succeeding electron density calculations and the hydrogen atoms were located in difference $F$ syntheses.[7] Full-matrix least-squares refinements including anisotropic temperature factors proceeded uneventfully to final crystallographic agreement factors of $R = 0.072$ and $R_w = 0.070$. Table I contains the fractional coordinates and anisotropic thermal parameters, and the bond distances and angles are collected in Table II.

The almost tetrahedral geometry around phosphorus (av OPO angle = 107.3°) and the very nearly trigonal-planar nitrogen geomtry (av CNC angle = 119.7°) in **3** (Figure 1) result in a structure very similar to that of **2**.[2b] Thus in contrast to a proton, the polarizing power of a sulfur atom and a $BH_3$ group appears to be insufficient to engage the nitrogen lone pair in the formation of a P←N bond in the phosphatrane polycycle. As discussed earlier, the planar geometry around nitrogen appears to be primarily induced by steric constraints imposed by the hydrogens in the $(CH_2CH_2)_3N$ moiety.[2b]

While the structure of **3** is consistent with NMR data, it remains to rationalize the position of $P(OCH_2CH_2)_3N$ in the basicity order $P(OCH_2CH_2)_3N > P(OMe)_3 > P(OCH_2)_3CMe$ indicated by the infrared and equilibrium experiments. From the available information on stereoelectronic factors in phosphorus ester basicities,[8] two potential sources of basicity enhancement in $P(OCH_2CH_2)_3N$ merit comment: phosphorus orbital interactions with oxygen orbitals and with a nitrogen orbital. Earlier we proposed that the reduction of phosphorus basicity from $P(OMe)_3$ to $P(OCH_2)_3CMe$ stems from lone pair

**Table II.** Intramolecular Bond Distances and Angles of $H_3BP(OCH_2CH_2)_3N^a$

| Distances (A) | | Angles (deg) | |
|---|---|---|---|
| P(1)-O(2) | 1.568 (5) | O(2)-P(1)-O(8) | 105.6 (3) |
| P(1)-O(8) | 1.575 (5) | O(2)-P(1)-O(9) | 108.3 (3) |
| P(1)-O(9) | 1.547 (5) | O(2)-P(1)-B(12) | 111.1 (4) |
| P(1)-B(12) | 1.884 (11) | O(8)-P(1)-O(9) | 108.2 (3) |
| O(2)-C(3) | 1.417 (10) | O(8)-P(1)-B(12) | 112.6 (4) |
| C(3)-C(4) | 1.482 (12) | O(9)-P(1)-B(12) | 110.9 (4) |
| C(4)-N(5) | 1.425 (10) | P(1)-O(2)-C(3) | 129.2 (5) |
| N(5)-C(6) | 1.431 (9) | O(2)-C(3)-C(4) | 116.4 (7) |
| N(5)-C(11) | 1.429 (9) | C(3)-C(4)-N(5) | 115.3 (7) |
| C(6)-C(7) | 1.480 (11) | C(4)-N(5)-C(6) | 120.6 (6) |
| C(7)-O(8) | 1.414 (10) | C(4)-N(5)-C(11) | 118.4 (6) |
| O(9)-C(10) | 1.420 (10) | C(6)-N(5)-C(11) | 120.1 (6) |
| C(10)-C(11) | 1.481 (10) | N(5)-C(6)-C(7) | 116.0 (6) |
| | | C(6)-C(7)-O(8) | 114.8 (6) |
| | | P(1)-O(8)-C(7) | 127.9 (5) |
| | | P(1)-O(9)-C(10) | 129.3 (5) |
| | | O(9)-C(10)-C(11) | 115.5 (6) |
| | | N(5)-C(11)-C(10) | 116.8 (7) |

[a] Numbering of atoms corresponds to that in Figure 1.

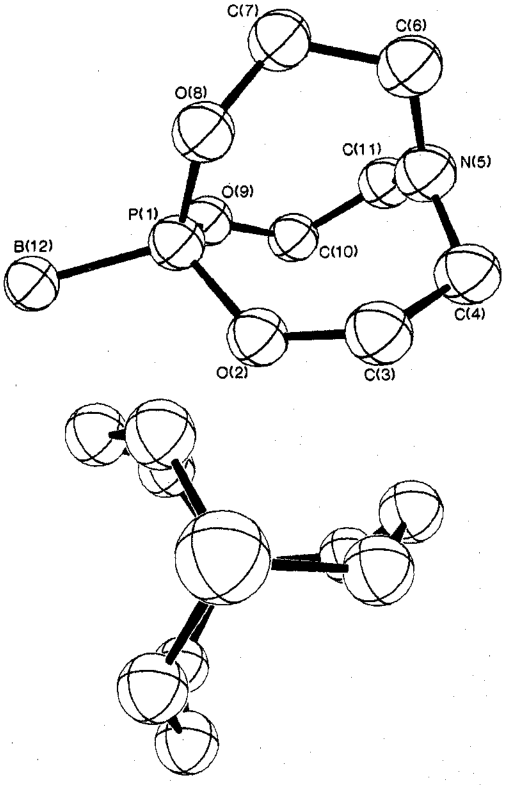
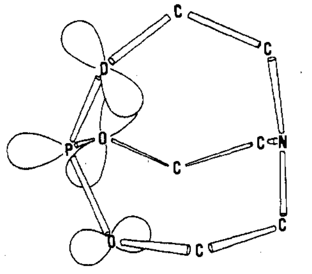


**Figure 1.** Computer drawing of 1-borano-2,8,9-trioxa-1-phospha-5-azabicyclo[3.3.3]undecane (**2**). The stereochemistries of nitrogen and phosphorus are emphasized in perspective in the top figure while the conformation of the bridging moieties is revealed in the bottom figure as viewed down the BPN axis.

orbital repulsion effects[9] and oxygen rehybridization (a "hinge effect")[10] associated with increased molecular constraint in the cage ester. Because the "hinge effect" is believed to operate only when the POC angle is below 120°,[10] it appears that this influence is not important in **3** (av POC angle = 128.8°). On the basis of the nonpolarizing character of the phosphorus lone pair in $P(OCH_2CH_2)_3N$ and the downfield $\delta^{31}P$ value (115.2 ppm) which is typical of $P(OR)_3$ compounds, it is reasonable to suppose that the free polycyclic base possesses a structure like that of **2** and **3** except for relatively minor bond angle and length changes associated with the presence of tervalent phosphorus. Because of the twisting of the $OCH_2CH_2$ bridges with respect to the P–N axis (as found in **2** and **3**), the largely unhybridized 2p lone pair orbital on each oxygen in $P(OCH_2CH_2)_3N$ is in a position to interact repulsively with the phosphorus lone pair in this preferred molecular conformation. Although the average conformation of $P(OMe)_3$ is not known, it is very probably one in which lone pair overlaps similar to those in $P(OCH_2CH_2)_3N$ are present. The greater basicity of $P(OCH_2CH_2)_3N$ would suggest that the average of these interactions in $P(OMe)_3$ may be less effective (i.e., the interacting orbitals may be closer to an orthogonal relationship with one another) in the absence of other influences. Although the PN distance in **3** (3.098 (0.005) Å) is well beyond the sum of the covalent radii (1.80 Å) it is within the sum of the van der Waals radii (3.4 Å). To what extent this structural feature may influence the basicity of phosphorus also remains an open question.



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**Registry No.** **3**, 62973-70-0.

**Supplementary Material Available:** A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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