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Low Symmetry in $P(NR_2)_3$ Skeletons and Related Fragments: An Inherent Phenomenon

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Abstract: A single-crystal X-ray diffraction study at 110 K and *ab initio* calculations up to the MP2/6-31G* level of theory showed that the ground state of $P(NMe_2)_3$ has C_s symmetry, with two different coordination geometries at the nitrogen atoms (pyramidal and planar). The calculated and experimentally determined geometries are in good agreement. Steric strain could be ruled out as the predominant factor causing the deviation from the expected C_3 symmetry, because *ab initio* calculations on the model system $P(NH_2)_3$ (up to MP2/6-311G**) also indicate C_s symmetry for the ground-state structure, whereas calculations on $N(NH_2)_3$ have predicted this molecule to have C_3 symmetry. The structure of the phosphorane $H_2C{=}P(NMe_2)_3$ has been elucidated by X-ray diffraction in the solid state (110 K) and by electron diffraction in the gas phase augmented by restraints derived from *ab initio* calculations up to the MP2/6-31G* level of theory. Solid-state and gas-phase structures are in good agreement showing again the C_s arrangement to be the ground-state structure of the molecule. *Ab initio* calculations (MP2/6-311G**) indicate that $H_2C{=}P(NH_2)_3$ also has C_s symmetry. The reasons for the preference for C_s rather than C_3 symmetry adopted by the $P(NR_2)_3$ units are discussed in terms of steric repulsion, lone pair, and other electronic interactions. Literature reports of structures of derivatives containing $P(NMe_2)_3$ units are discussed in the light of the new results. Selected structural results include: $P(NMe_2)_3$ (XRD, average values); P−N(1/2) 1.687, P−N(3) 1.731 Å, N(1)−P−N(2) 110.8, N(3)−P−N(1/2) 97.7°, $\sum\angle$ at N(1/2) 355.9, at N(3) 337.6°; $H_2C{=}P(NMe_2)_3$ (GED/XRD average without esd); P−C(1) 1.620(5)/1.655(6), P−N(1/2) 1.684(3)/1.668, PN(3) 1.718(6)/1.698(4) Å, N(1)−P−N(2) 115.2(13)/114.7(2), N(1/2)−P−N(3) 97.0(5)/99.6, C(1)−P−N(1/2) 110.0(5)/110.0, C(1)−P−N(3), 127.1(8)/122.4(4)°, $\sum\angle$ at N(1/2) 359.5(11)/353.4, at N(3) 332.9(13)/337.3(6)°.

Phosphorus−nitrogen compounds form a well-known class of compounds, which has attracted considerable interest in the past and found a wide application in organic synthesis and technical processes.[2] The most intriguing structural features of P/N compounds are the short P−N bonds, which cannot be classified as normal single bonds. First attempts to explain the strength of these bonds referred to $(p_\pi{-}d_\pi)$ interactions, but later on it turned out that contributions of electrostatic effects in the heteropolar P−N bonds and negative hyperconjugation involving the nitrogen lone pairs of electrons are superior explanations.[3] The molecular structures of a large number of phosphorus−nitrogen compounds have been studied. One notable result is the finding of a planar nitrogen atom and an extremely short P−N bond in $F_2P{-}NMe_2$ in the solid state,[4] which is at variance with gas-phase data but probably the result of a very flat potential minimum of the nitrogen inversion.[5]

The structures of a number of compounds containing a PN_3 skeleton have been elucidated in the past and many different arrangements and conformations have been found, which include nitrogen environments in many variations between the extremes of planar and steeply pyramidal arrangements. The simplest compound in this context, $P(NH_2)_3$, is only known in complexed form. However, the gas-phase structure of $P(NMe_2)_3$, for which C_3 symmetry was assumed,[6] was determined by Vilkov *et al.* in 1969 by electron diffraction and was often seen as a reference for the undistorted molecule. In 1973 Cowley *et al.* postulated $P(NMe_2)_3$ to adopt C_s symmetry on the basis of photoelectron spectra (PES).[7] Later, Lappert *et al.* favored a C_{3v} structure as an alternative interpretation,[8] which caused some controversy followed by reinvestigations of the PE spectra by Hargis and Worley, who again assigned them in terms of a C_s geometry.[9] This was supported by the structure determination of a few complexes of this ligand showing preference for a C_s arrangement of the $P(NMe_2)_3$ unit.[10,11] These results have again been doubted by semiempirical MO calculations on $P(NH_2)_3$[11] and $P(NMe_2)_3$[12] both favoring C_3 structures as the global energy minima, which, however, are only slightly lower in energy than the C_s symmetric ones.

In the present paper we will show that the C_s symmetry is an *inherent structural property* of compounds containing $P(NR_2)_3$ skeletons and related $E(NR_2)_3$ units, which contain a 3p or higher row element E of groups 14 and 15. For this purpose we

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determined the crystal structures of $P(NMe_2)_3$ and $H_2C{=}P(NMe_2)_3$ and compared them with *ab initio* calculations of these systems and corresponding model systems without organic substituents. We also studied the structure of $H_2C{=}P(NMe_2)_3$ in the gas phase and are thus able to confirm the reliability of the calculated predictions.

Experimental Section

Materials. A sample of $P(NMe_2)_3$ was prepared by the ammonolysis of PCl_3 with $HNMe_2$ according to a literature procedure.[13] $H_2C{=}P(NMe_2)_3$ was synthesized by deprotonation of the corresponding phosphonium salt (prepared from $P(NMe_2)_3$ and CH_3I) with potassium hydride in THF.[14] The samples were purified by repeated distillation.

Electron Diffraction. Electron scattering intensity data for $H_2C{=}P(NMe_2)_3$ were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[15] The sample of $H_2C{=}P(NMe_2)_3$ was held at 120 °C and the inlet nozzle at 140 °C during the experiments. Scattering data for benzene were recorded concurrently and used to calibrate the camera distance and electron wavelength, which were 260.08 mm and 0.05631 Å for the long camera distance and 94.76 mm and 0.05632 Å for the short camera distance, respectively. Three plates were taken at each camera distance. Data were obtained in digital form using the Joyce Loebl MDM6 microdensitometer[16] at the EPSRC Daresbury Laboratory. The data analysis followed standard procedures, using established data reduction[17] and least-squares refinement programs[17] and the scattering factors established by Fink and co-workers.[18] The following data range, interval, and weighting points (trapezoidal weighting function) were used in the refinement: $s_{min} = 2.0$, $s_{max} = 16.4$, $\Delta s = 0.2$, $sw_1 = 4.0$, $sw_2 = 14.0$ $Å^{-1}$ for the long camera data; $s_{min} = 9.6$, $s_{max} = 35.6$, $\Delta s = 0.4$, $sw_1 = 11.6$, $sw_2 = 30.4$ $Å^{-1}$ for the short camera data. The scale factors refined to 0.805(7) and 0.644(11) for long and short camera data, respectively. Elements of the least-squares correlation matrix (×100) with absolute values >50 (for numbering of p and u see Tables 7 and 8, k_1 and k_2 are scaling factors for long and short camera distance, respectively): p_2/p_3 −76, p_2/u_1 83, p_3/p_4 52, p_3/u_1 74, p_4/p_{10} −54, p_4/p_{11} 55, p_4/u_1 −57, p_6/p_{10} −53, p_6/p_{11} 52, p_6/u_{14} 51, p_7/p_8 −80, p_7/p_{14} −62, p_9/p_{14} 52, p_9/p_{15} −74, p_9/p_{17} −66, p_{10}/p_{11} −96, p_{10}/p_{12} 54, p_{11}/p_{12} −66, p_{12}/p_{13} −69, p_{15}/p_{17} 64, p_{16}/k_1 −75, u_4/k_2 60.

X-ray Structure Analyses. $P(NMe_2)_3$. A cylindrical crystal (>0.8 mm long, 0.3 mm diameter) was grown from the melt in a capillary mounted on a Stoe Stadi-4 diffractometer with an Oxford Cryosystems low-temperature device,[19] by cooling the sample from 121 to 120 K at a rate of 10 K h^{-1} after growing a seed crystal. $C_6H_{18}N_3P$: $M_r = 163.20$, triclinic, space group $P\bar{1}$, $a = 6.184(2)$, $b = 11.471(4)$, $c = 14.676(5)$ Å, $V = 1003.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.080$ mg m^{-3}, $2\theta_{max} = 50.0°$; Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å, μ(Mo K$_\alpha$) = 0.219 mm^{-1}, $T = 110.0$ K; scan mode $\omega - \theta$ (width $1.2 + 0.35 \tan \theta$), 4130 reflections, 3545 independent, $R_{int} = 0.046$; no absorption correction; solution by direct methods,[20] refinement of 326 parameters on F^2,[21] all H atom positions were located in difference Fourier maps and isotropically refined. $R = 0.063$ for 2607 reflections with $F_o^2 > 4\sigma(F_o^2)$, $R_{w2} = 0.227$ for all 3545 data; extrema of residual electron density +0.78 and −0.59 e Å^{-3}; final weighting scheme: $w = [\sigma^2(F_o^2) + (0.1412P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

$H_2C{=}P(NMe_2)_3$. A crystal was grown from the melt in a capillary mounted on a Stoe Stadi-4 diffractometer with an Oxford Cryosystems low-temperature device.[19] After growing a seed crystal, the sample was cooled from 231 to 228 K at a rate of 20 K h^{-1} to obtain a cylindrical crystal (>0.5 mm long, 0.3 mm diameter). $C_7H_{20}N_3P$: $M_r = 177.23$, orthorhombic, space group $Pna2_1$, $a = 11.593(2)$, $b = 12.446(3)$, $c = 7.297(3)$ Å, $V = 1052.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.118$ mg m^{-3}, $2\theta_{max} = 50.0°$; Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å, μ(Mo K$_\alpha$) = 0.213 mm^{-1}, $T = 110.0$ K; scan mode $\omega - \theta$ (width $1.2 + 0.35 \tan \theta$), 1496 reflections, 1338 independent, $R_{int} = 0.037$; empirical absorption correction by ψ scans, min/max transmission 0.813 and 0.916; solution by direct methods,[20] refinement of 121 parameters on F^2.[21] The ylidic H atoms were located in difference Fourier maps and isotropically refined; all other hydrogen position were calculated in idealized positions with fixed tetrahedral angles and one common CH distance was refined for each CH_3 group; their isotropic thermal parameters were tied to that of the adjacent C atom by a factor of 1.5. The absolute structure was determined with the Flack parameter being 0.35(24). $R = 0.048$ for 936 reflections with $F_o^2 > 4\sigma(F_o^2)$, $R_{w2} = 0.111$ for all 1336 data; extrema of residual electron density +0.39 and −0.23 e Å^{-3}; final weighting scheme: $w = [\sigma^2(F_o^2) + (0.0508\,P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

***Ab Initio* Calculations.** *Ab initio* molecular orbital calculations were carried out for the parent systems [$P(NMe_2)_3$ and $H_2C{=}P(NMe_2)_3$] and for the model systems $P(NH_2)_3$, $N(NH_2)_3$, and $H_2C{=}P(NH_2)_3$ using the Gaussian 92 program.[22] Geometry optimizations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Calculations on model compounds were undertaken at the SCF level using the standard 3-21G*,[17-19] 6-31G*,[26-28] and 6-311G**[29,30] basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. A single additional geometry optimization was performed at the QCISD/6-31G* level to test the effects of a more complete description of electron correlation.

Size considerations restricted the highest level calculations on the parent system MP2/6-31G*. Vibrational frequency calculations were performed at the SCF/3-21G* and SCF/6-31G* levels for the parent systems.

For both parent and model phosphine systems and for $N(NH_2)_3$ structures of C_{3v}, C_3, and C_s symmetry were considered, while calculations were undertaken for two ylide structures (both C_s symmetry). Molecular geometries, absolute energies, and the energy separation between isomers are reported in the tables and the Supporting Information.

Results and Discussion

Crystal Structure of $P(NMe_2)_3$. Although earlier experiments suggested that $P(NMe_2)_3$, which is a liquid at ambient temperature, always solidifies glassy upon cooling,[11] a single crystal could be grown *in situ* on the diffractometer. The crystal belonged to the triclinic system, space group $P\bar{1}$. It contained two independent molecules in the asymmetric unit, which both

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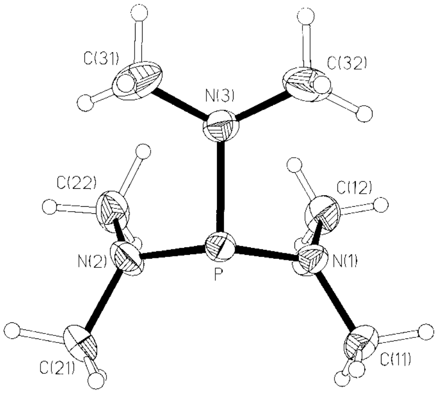

Figure 1. Low-temperature crystal structure of $P(NMe_2)_3$. Only one of the two independent molecules in the asymmetric unit is shown.

Table 1. Molecular Geometries of Two Independent Molecules of $P(NMe_2)_3$ as Determined by X-ray Crystallography (distances in Å, angles in deg)

	molecule 1	molecule 2
P−N(1/2)	1.681(3)/1.684(3)	1.682(3)/1.699(3)
P−N(3)	1.732(3)	1.729(3)
N(1)−C(11/12)	1.458(5)/1.458(5)	1.458(5)/1.453(5)
N(2)−C(21/22)	1.459(5)/1.458(5)	1.451(5)/1.444(5)
N(3)−C(31/32)	1.455(5)/1.461(5)	1.464(5)/1.468(5)
N(1)−P−N(2)	111.3(2)	110.2(2)
N(3)−P−N(1/2)	97.5(2)/97.3(2)	98.4(2)/97.4(2)
P−N(1/2)−C(11/21)	117.8(3)/117.0(3)	117.8(3)/116.4(3)
P−N(1/2)−C(12/22)	125.7(3)/125.3(3)	126.7(3)/124.0(2)
P−N(3)−C(31/32)	112.8(2)/113.5(3)	114.4(2)/113.9(2)
C(11/12)−N(1/2)−C(12/22)	113.2(3)/113.0(4)	114.2(3)/112.5(3)
C(31)−N(3)−C(31)	110.4(4)	110.1(3)
Sums of angles at		
N(1)/N(2)	356.7/355.3	358.7/352.9
N(3)	336.7	338.4

Table 2. Molecular Geometries and Absolute and Relative Energies of the C_s and C_3 Structures of $P(NMe_2)_3$[a]

parameter	3-21G*/SCF	6-31G*/SCF	6-31G*/MP2
		C_s	
P−N(1/2)	1.688	1.702	1.719
P−N(3)	1.724	1.737	1.755
N(1)−C(11)	1.467	1.448	1.456
N(1)−C(12)	1.468	1.448	1.457
N(3)−C	1.475	1.456	1.467
C−H[b]	1.086	1.087	1.095
N(1)−P−N(2)	109.2	110.1	112.0
N(1)−P−N(3)	98.6	98.7	96.5
P−N(1)−C(11)	125.7	125.1	123.8
P−N(1)−C(12)	119.2	117.5	116.5
P−N(3)−C	117.6	114.6	112.9
H−C−N[b]	110.4	110.8	110.5
$\sum$<N(1)	358.6	356.1	353.4
$\sum$<N(3)	346.3	339.5	335.2
abs energy	−737.925466	−741.726043	−743.122048
		C_3	
P−N	1.697	1.707	1.722
C(1)−N	1.467	1.446	1.453
C(2)−N	1.462	1.443	1.450
C−H[b]	1.085	1.086	1.097
N−P−N	103.4	104.3	103.5
P−N−C(1)	118.6	117.2	116.8
P−N−C(2)	127.4	127.9	126.5
H−C−N[b]	110.7	111.1	110.8
$\sum$<N(1)	360.0	359.2	358.0
abs energy	−737.920493	−741.717711	−743.111229
$\Delta E(C_3-C_s)$	13.5	21.8	28.4
$\Delta E(C_{3v}-C_s)$	253.9	211.9	195.3

[a] Bond distances in Å; angles in degrees, absolute energies in E_h, energy differences in kJ mol^{-1}. [b] Average.

have very similar geometries (see Table 1 and Figure 1). Although both molecules have almost exact C_s symmetry, this is not crystallographically imposed.

The most intriguing structural result is the appearence of two different coordination geometries at nitrogen in the three NMe_2 groups in each molecule of $P(NMe_2)_3$. This was unexpected, as an earlier gas-phase structure determination of this compound implied it to have C_3 symmetry.[6] In stark contrast to flattened PNC_2 skeletons which include the nitrogen atoms N(1) and N(2) (sums of angles between 352.9 and 358.7°), the $PN(3)C_2$ units are clearly pyramidally coordinated (sums of angles at N: 336.7 and 338.4°). According to their formally different hybridizations, the nitrogen atoms form P−N bonds with two different lengths. In one of the two crystallographically independent molecules the sp^3-type nitrogen atom N(3) is 1.732 Å from the phosphorus center, whereas the nitrogen atoms N(1) and N(2), which are almost of the sp^2 type, have an average distance to the phosphorus atom of only 1.684 Å. The uncertainties for the N−C distances and their individual values do not allow similar conclusions to be drawn for these parameters.

The PNC angles which include the flattened N(1) and N(2) atoms indicate a considerable amount of steric repulsion between the NMe_2 groups. The observed effect is a widening of the PN(1)C(12) and PN(2)C(22) angles which include the methyl groups which are closest to the $N(3)Me_2$ groups. Simultaneously the corresponding PN(1)C(11) and PN(2)C(21) angles are compressed by about the same amount. The average difference between the PNC angles belonging to the flattened and the pyramidal nitrogen geometries is as large as 8.2°.

The geometry at the phosphorus atom is far from being an ideal pyramid with equal NPN angles. The NPN angles enclosed by the two flattened nitrogen atoms N(1) and N(2) are markedly wider [111.3(2) and 110.2(2)°] than those including the pyramidal N(3) atom [range from 97.3(2) to 98.4(2)°].

***Ab Initio* Calculations on $P(NMe_2)_3$.** In order to test if the structural results can be reproduced by theory for a single molecule or whether they are imposed by packing forces in the crystal, we performed a graded series of *ab initio* calculations on this molecule with the highest level of theory applied being MP2/6-31G*. The C_{3v} structure of $P(NMe_2)_3$ was found to correspond to a high energy saddle point, while the C_3 and C_s symmetric model structures were always predicted to be local minima on the potential energy hypersurface. The C_s structure was found to be the lowest energy arrangement, and the C_3 structure was 28.4 kJ mol^{-1} higher in energy (MP2/6-31G*). This is clearly at variance with earlier MNDO calculations, which favored the C_3 conformation by more than 12 kJ mol^{-1}.[12] Our results show that only the lowest energy conformer is present in the crystal structure. Other energy differences between the three calculated structures obtained at different levels of theory are included in Table 2.

Values of geometric parameters for the two local minima on the potential energy surface are presented in Table 2 (C_s and C_3 structure). The bond lengths and angles were found to be fairly insensitive to the theoretical method adopted, and as expected, the introduction of electron correlation leads to a slight lengthening of the bonds. In general, there is a good agreement in most of the bond lengths and angles between the calculated C_s geometry and the experimental structure. The lengths of the two symmetrically nonequivalent P−N bonds are predicted to be greater by theory (1.755 and 1.719 Å) than determined experimentally (1.732 and 1.684 Å), as are the N−C bond lengths. The sum of angles about the phosphorus atom is calculated to be 304.9° and found experimentally to be 306.1° (average of the two independent molecules). The calculated NPN angles are very similar to the experimental values,

Table 3. Molecular Geometries and Absolute and Relative Energies of the Molecular Structures of $P(NH_2)_3$, $N(NH_2)_3$ and $H_2C{=}P(NH_2)_3$ Calculated at the MP2/6-311G** Level of Theory[a]

	$P(NH_2)_3$	$N(NH_2)_3$	$H_2C{=}P(NH_2)_3$
		C_s	
P/N−N(1)	1.704	1.414	1.675
P/N−N(3)	1.736	1.478	1.717
P−C/P−C−H			1.654/118.2
N(1)−P/N−N(2)	112.0	106.7	132.2
N(1)−P/N−N(3)	93.0	106.9	107.5
$\sum$<N(1)	346.1	322.7	346.6
$\sum$<N(3)	330.2	312.4	331.2
abs energy	−508.33128	−221.96680	−507.49375
		C_3	
P/N−N	1.716	1.424	
N−P/N−N	101.8	109.4	
$\sum$<N(1)	336.9	318.9	
abs energy	−508.32735	−221.97291	
ΔE	(C_3-C_s) 10.3	(C_s-C_3) 16.0	$(C_s-C_{s'})$ 27.1
ΔE	$(C_{3v}-C_s)$ 100.2	$(C_{3v}-C_3)$ 78.7	

[a] Bond distances in Å; angles in degrees; absolute energies in E_h; energy differences in kJ mol^{-1}; a more complete set of data is given in the Supporting Information. [b] Average.

providing strong evidence for the distortion of the coordination geometry of the phosphorus atom being caused by intramolecular forces rather than by packing of the molecules in the crystal. The two symmetry-equivalent nitrogen environments are characterized by a sum of angles of 358.6°, which is also very close to the highest value found experimentally (range from 352.9 to 358.7°). These differences between the two molecules in the asymmetric unit and between the two halves of each of these provide a good indication of packing effects in the crystal. It can be assumed that despite the large difference in these sums of angles, the changes in energy corresponding to these distortions are quite small.

In the light of these theoretical results, the energy difference between the C_3 and C_s structure could be attributed to the steric repulsion between the NMe_2 groups, which appears to be more important in the C_3 model than in the C_s structure, the closest H−H distances being 2.14 and 2.36 Å, respectively, which are both smaller than the generally accepted value for the sum of two hydrogen van der Waals radii (2.4 Å).[31] However, in the next paragraph we will show that even in the absence of steric repulsion, the C_s structure is still preferred, although the energy difference is much smaller.

***Ab Initio* Calculations on $P(NH_2)_3$.** In order to determine whether steric repulsion of the NMe_2 groups or an electronic effect is the main reason for the structural anomalies described above, we performed a carefully graded series of calculations on the simplest possible model system, $P(NH_2)_3$. The results are shown in Table 3, and a perspective view of the calculated structures is given in Figure 2.

Three different conformational isomers were considered. Vibrational frequency calculations excluded the C_{3v} structure from being a stable minimum (MP2/6-31G*), whereas both C_3 and C_s arrangements were predicted to be local minima on the potential energy hypersurface, with the C_s arrangement being lower in energy. Our best estimate favors the C_s structure by 10.3 kJ mol^{-1} (MP2/6-311G**), whereas earlier computations (SCF/STO-3G*) favored the C_3 arrangement by only 1.2 kJ mol^{-1}.[11] Most values of geometrical parameters proved to be insensitive to improvements in the theoretical treatment.

As found for $P(NMe_2)_3$, the two nonequivalent P−N bonds in the C_s structure were predicted to be substantially different.

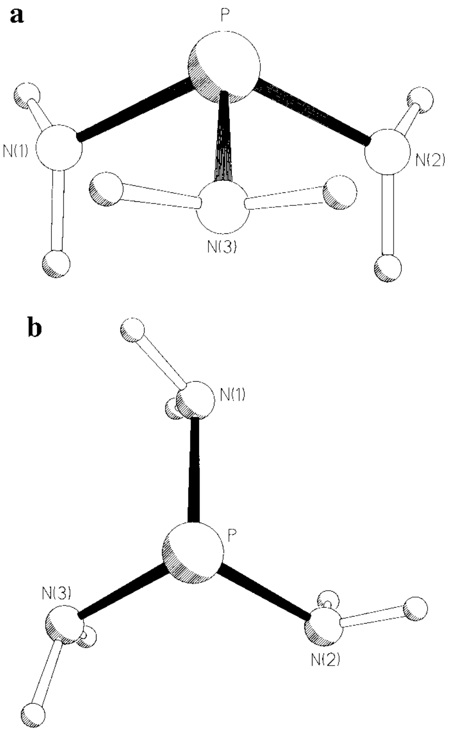

Figure 2. Ab initio calculated molecular geometries of the two local minima (C_s and C_3 structures) of $P(NH_2)_3$.

Table 4. Angles (deg) between Vectors Defined by the Ideal Lone Pairs Position and the Adjacent Atom in the Calculated Structures of $P(NH_2)_3$ and $P(NMe_2)_3$ (MP2/6-31G* level)

	multiplicity	$P(NH_2)_3$	$P(NMe_2)_3$
	C_s		
P-lp/N(1)-lp	2	108.4	107.6
P-lp/N(3)-lp	1	170.9	170.9
N(1)-lp/N(2)-lp	1	93.7	101.2
N(1)-lp/N(3)-lp	2	114.6	114.3
	C_3		
P-lp/N(1)-lp	3	85.4	58.3
N(1)-lp/N(2)-lp	3	119.4	85.0

Like in the *per*methylated system $P(NMe_2)_3$, the C_s structure for $P(NH_2)_3$ is lower in energy than the C_3 arrangement. It is obvious that the reasons for this cannot be steric in nature. The H···H distances on neighboring NH_2 groups are much further apart than 2.4 Å (2.86 in the C_s and 2.71 Å in the C_3 structure at MP2/6-311G**). Consequently, this argument should also not be solely used to explain the anomalies in the $P(NMe_2)_3$ system.

Another explanation to probe is the repulsion of nitrogen and phosphorus lone pairs of electrons. There are four lone pairs in tervalent PN_3 systems, which makes an all-orthogonal arrangement generally impossible, although this would be the hypothetical optimum energy arrangement. A compromise could consist of an orthogonal arrangement of three lone pairs with the fourth one oriented antiparallel to one of the latter.

Table 4 shows the angles which are enclosed by each pair of vectors defined by the ideal lone pair position (equal angles lp−E−X to the three geminal atoms X) and the adjacent atom. These values are rather uncharacteristic and when all the deviations from the assumed minimum energy orientations are considered for the C_s and C_3 structure, the C_3 rather than the C_s arrangement would be preferred even if larger weight is applied to the contributions of vicinal lone pairs. With respect to these data, lone pair repulsions can be ruled out as the major contribution to the observed preference of C_s structures.

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Comparison with Homologous and Isoelectronic Sytems. Another way of checking whether the orientation of lone pairs is the predominant cause of the observed structural anomalies is to explore the structures of other triamidopnictogen species. The simplest of these is isotetrazane, $N(NH_2)_3$, which is an unknown compound. We studied this structure by using the same theoretical methods as employed for $P(NH_2)_3$. The results of the calculations are shown in Table 3.

Surprisingly, the structure with C_3 symmetry is the most stable for $N(NH_2)_3$. It lies as much as 16.0 kJ mol^{-1} (MP2/6-311G**) below a C_s model, which is also a local minimum on the potential energy hypersurface. (A further local minimum with C_s symmetry lies 51.8 kJ mol^{-1} in energy above the C_3 structure; a C_{3v} model does not correspond to a local minimum and is 78.7 kJ mol^{-1} above the C_3 structure.) The length of the three equivalent N−N bonds is 1.424 Å at the MP2/6-311G** level of theory and 1.431 Å at MP2/6-31G*, which is of the same order as observed for hydrazine (1.439 Å at MP2/6-31G* and 1.449 Å, experimentally),[32] and thus there is no hint for any extraordinarily strong lone pair repulsion.

The difference between the minimum energy structures of $P(NH_2)_3$ and its homolog $N(NH_2)_3$ gives strong indication that the reason for the energetic preference for the C_s structure of $P(NH_2)_3$ could be attributed to the same type of interaction as also causes the difference between the planar geometries of nitrogen centers bound to second-row elements and the pyramidal ones of nitrogen centers bound to first-row elements. Probably the best explanation which has been found for these effects so far is that of negative hyperconjugation including the nitrogen lone pairs of electrons.[33] However, this explanation is still not sufficient to describe why there are two different nitrogen environments in the same molecule. Various other factors have been discussed in the literature to rationalize those effects for related compounds,[33] but none of those seems to have a major effect which would be helpful to be discussed in this context.

The same structural motif as found in $P(NH_2)_3$ should appear in other $E(NR_2)_3$ compounds where E is a fragment containing a binding site which is a second or higher row element. First indications for a similar behavior of compounds with E = As and Sb have recently been presented.[35] Only few experimental structural data of valence isoelectronic compounds to $P(NH_2)_3$ and $P(NMe_2)_3$ or closely related compounds are available in the literature.

A molecule which is also isoelectronic to $P(NMe_2)_3$ but does not have a lone pair of electrons on the central atom E is triaminosilane, $HSi(NH_2)_3$. We have recently shown that there is also a preference for the C_s-type arrangement in the class of compounds containing SiN_3 units.[36] The energy differences between the C_s and the C_3 structures of the silicon compounds are in the same range as those for the corresponding phosphorus compounds (13.5 kJ mol^{-1} for the $HSi(NH_2)_3$ molecule at MP2/6-311G**). With respect to these results, any contribution of the lone pair of electrons at the phosphorus atom in $P(NH_2)_3$ can be ruled out as an explanation. As compared to the isoelectronic $P(NH_2)_3$, $HSi(NH_2)_3$ has quite different angles at the central atom (P and Si). Both the N(1)EN(2) angle between the symmetry-equivalent nitrogen atoms and the one including the nitrogen atom lying on the plane of symmetry, N(1)EN(3), are more acute in the phosphorus compound (112.0 and 93.0°, respectively) than in the silicon compound (123.6 and 103.8°, respectively at MP2/6-311G**). This can be rationalized by the qualitative VSEPR concept[37] in terms of a larger requirement of the lone pair domain in the phosphine as compared to the hydrogen atom in the silicon compound.

The geometries at the nitrogen atoms in $P(NH_2)_3$ and $HSi(NH_2)_3$ are also markedly different. Whereas $P(NH_2)_3$ has much steeper pyramids defining the nitrogen environments [sum of angles at N(1) 346.1°, at N(3) 330.3°], both non-symmetry-related nitrogen centers in $HSi(NH_2)_3$ are only shallow pyramids [N(1) 350.2, N(3) 351.4°, respectively]. These results are at variance with a single crystal X-ray diffraction study of $(2,4,6\text{-}Ph_3C_6H_2)Si(NH_2)_3$, which indicated the presence of three different nitrogen environments in the NH_2 groups[38] reliant on the determination of hydrogen positions, which are generally not well determined by X-ray crystallography.

So far we have shown that $E(NR_3)_3$ systems exhibit inherent structural asymmetry, which seems to be a valid generalization for E being a heavier element of group 14 and 15, whereas C_3 structures seem to be preferred for the 2p elements, as indicated by calculations on $N(NH_2)_3$. The question arises whether these observations can be transferred to pentavalent group 15 compounds containing $E(NR_3)_3$ as a structural unit. We therefore started investigating the structures of such compounds.

Crystal Structure of $H_2C{=}P(NMe_2)_3$. One of the simplest pentavalent compounds containing a linkage of the $P(NMe_2)_3$ fragment to carbon is tris(dimethylamino)methylenephosphorane, $H_2C{=}P(NMe_2)_3$. This simple phosphorus ylide and its derivatives have attracted much interest in Wittig-type reactions.[39]

We carried out a detailed structural investigation of this compound, because the structures of some of its derivatives, silylated at the ylidic carbon atom, showed different geometric arrangements of the $P(NMe_2)_3$ groups in their crystals, and it was not clear which structures are close to the ground state and which are distorted by packing forces.

A crystal of $H_2C{=}P(NMe_2)_3$, which was grown *in situ*, belonged to the orthorhombic system, space group $Pna2_1$. Although there is no crystallographic symmetry imposed on the structure of the monomeric molecules, their geometry is close to C_s symmetry (see Table 5 and Figure 3).

Despite the different formal oxidation state, the geometry of the $P(NMe_2)_3$ part of the $H_2C{=}P(NMe_2)_3$ molecule is very similar to the free molecule $P(NMe_2)_3$ (see Table 1). As expected the P−N bond lengths are shorter in the pentavalent compound than in the tervalent one and the difference between the symmetry-nonequivalent P−N bond distances in the two structures is greater in the trivalent $P(NMe_2)_3$ (0.048, *cf.* 0.012 Å). The environments of the nitrogen centers in $H_2C{=}P(NMe_2)_3$ are characterized by their sum of angles being 355.6(7) and 351.6(6)° for the two flattened nitrogen atoms and 337.3(7)° for the pyramidal one, which compares very well to the arrangement in $P(NMe_2)_3$ (355.9 and 337.6°, on average). It should be noted that the isopropyl groups in the phosphonium ylide $Me_2C{=}P(i\text{-}Pr)_3$, which are isoelectronic to the dimethyl-

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Table 5. Experimentally Determined (GED, XRD) and Calculated Geometry of $H_2C=P(NMe_2)_3$ (esd's in parentheses)

	GED (r_a, $<_a$)	XRD(r, $<$)	MP2/6-31G*(r_e, $<_e$)
distances, r, (Å)			
P−C(1)	1.620(5)	1.655(6)	1.663
P−N(1/2)	1.684(3)	1.666(4)/1.669(4)	1.694
P−N(3)	1.718(6)	1.698(4)	1.740
N(1/2)−C(11/21)	1.457(3)	1.453(6)/1.456(5)	1.462
N(1/2)−C(12/22)		1.458(7)/1.462(6)	1.461
N(3)−C(31/32)	1.461(6)	1.484(5)/1.456(5)	1.472
angles, < (deg)			
N(1)−P−N(2)	115.2(13)	114.7(2)	116.5
N(1/2)−P−N(3)	97.0(5)	100.3(2)/99.0(2)	98.5
C(1)−P−N(1/2)	110.0(5)	110.6(3)/109.4(3)	109.4
C(1)−P−N(3)	127.1(8)	122.4(4)	124.8
P−N(1/2)−C(11/21)	121.9(7)	120.4(4)/118.6(3)	119.1
P−N(1/2)−C(12/22)	122.6(7)	122.4(4)/121.1(3)	120.9
P−N(3)−C(31/32)	111.4(5)	113.9(3)/114.3(3)	111.8
C(11/21)−N(1/2)−C(12/22)	115.0(5)	112.8(4)/111.4(4)	111.8
C(31)−N(3)−C(32)	110.1(10)	109.1(4)	108.7
N−C−H (average)	111.1(3)	109.4 (fixed)	110.2
P−C(1)−H(11/12)	118.1	117(4)/115(4)	118.1
H(11)−C(1)−H(12)	117.6	128(5)	117.6
sums of angles (deg) at			
N(1)/N(2)	359.5(11)	355.6(7)/351.1(6)	351.8
N(3)	332.9(13)	337.3(6)	332.3
dihedral angles, τ (deg)			
C(1)−P−N(1/2)−C(11/21)	±1.5(18)	31.3(5)/−44.0(5)	±38.2
C(1)−P−N(1/2)−C(12/22)	±178.4(21)	−174.0(4)/171.5(4)	±175.8

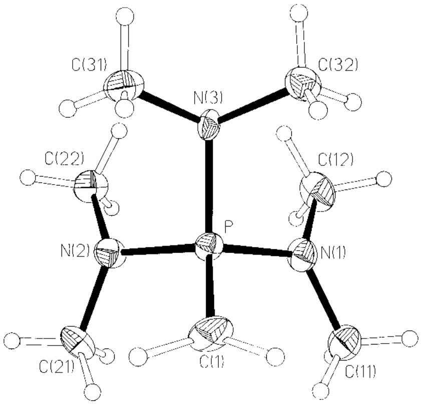

Figure 3. Molecular structure of $H_2C=P(NMe_2)_3$ as determined by low-temperature crystallography.

amino groups in $H_2C=P(NMe_2)_3$, show an analogous C_s arrangement in a crystal structure analysis.[40]

Asymmetry of this type was also reported earlier for some phosphorus ylides bearing silyl substituents at the ylidic carbon atom.[41,42] One of them is the ylide (naphsi)$C=P(NMe_2)_3$ (naphsi = 1,8-disilylnaphthalene), which shows almost perfect agreement of the geometry of the $C=P(NMe_2)_3$ unit with that of $H_2C=P(NMe_2)_3$. However, in some other silylated compounds $[(Me_2N)_3P=C(SiMe_3)_2$ and $(Me_2N)_3P=C(SiMe_2Ph)_2]$ the geometry of the $P(NMe_2)_3$ unit deviates somewhat from that in $H_2C=P(NMe_2)_3$.[43] In the sections below, we will show that the geometry of $H_2C=P(NMe_2)_3$ described here agrees very well with that of the undistorted free molecule, which indicates that those deviations in the silicon derivatives can probably be attributed to crystal packing effects.

The space requirement of the carbanionic group CH_2 leads to a sum of angles NPN of 314.0°, whereas the lone pair of electrons at the phosphorus center in $P(NMe_2)_3$ is more sterically demanding, which causes the sum of NPN angles to be 306.1° in this compound. The individual angles are all compressed by about the same amount.

The P−C bond length in $H_2C=P(NMe_2)_3$ is well in the established range for ylidic P−C linkages and may be compared to those of other methylenephosphoranes such as $H_2C=PMe_3$ [1.640(6) Å in the gas phase][44] and $[(Me_2N)_3P=CH]_2Si$-(O*i*Pr)$_2$41 [1.658(2) and 1.656(2) Å, respectively]. The positions of the ylidic hydrogen atoms in $H_2C=P(NMe_2)_3$ indicate a planar PCH_2 unit [sum of angles 360(8)°], although these hydrogen positions are not well determined.

***Ab Initio* Calculations for $H_2C=P(NMe_2)_3$.** In order to compare the structural findings in the solid state with the geometry of a free molecule we performed *ab initio* calculations on two isomers of $H_2C=P(NMe_2)_3$ (both C_s symmetry) with the CH_2 group being either perpendicular or parallel to the mirror plane of symmetry. Only the perpendicular model was predicted to lie in a potential well, while the parallel arrangement corresponds to the transition state for rotation about the P−C bond. The rotational barrier was estimated in this way to be 18.8 kJ mol^{-1} on the MP2/6-31G* level of theory and 15.2 kJ mol^{-1} when corrected for zero point energy (from SCF/6-31G* frequency calculations).

The calculated geometries of the stable isomer listed in Table 6 agree well with the crystal structure. The environment of the ylidic carbon atom is calculated to be clearly flattened, but not planar. The sum of angles at this carbon atom is predicted to be 353.8°, which is well within one esd of the crystallographic results.

***Ab Initio* Calculations for $H_2C=P(NH_2)_3$.** For a more rigorous theoretical treatment of the CPN_3 core of $H_2C=P(NMe_2)_3$, we performed calculations on the model system $H_2C=P(NH_2)_3$. As for $H_2C=P(NMe_2)_3$, two isomers of $H_2C=P(NH_2)_3$ were considered. As in the parent compound, the isomer with the CH_2 unit oriented perpendicular to the C_s mirror plane turned out to be lower in energy than the transition state with

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Table 6. Molecular Geometries and Absolute Energies of $H_2C{=}P(NMe_2)_3$[a]

parameter	3-21G*/SCF	6-31G*/SCF	6-31G*/MP2
P−C	1.647	1.657	1.663
P−N(1)	1.664	1.679	1.694
P−N(3)	1.699	1.714	1.740
C−H[b]	1.083	1.084	1.094
C−H$_{ylide}$	1.073	1.074	1.083
N(1)−C(11)	1.473	1.454	1.461
N(1)−C(12)	1.474	1.455	1.462
N(3)−C	1.484	1.460	1.472
C−P−N(1)	111.1	111.3	109.4
C−P−N(3)	120.5	122.0	124.8
N(1)−P−N(2)	100.4	100.1	98.5
N(1)−P−N(3)	112.8	113.7	116.2
P−C−H	120.8	119.2	118.1
P−N(1)−C(11)	121.8	120.6	119.1
P−N(1)−C(12)	123.2	122.2	120.9
P−N(3)−C	115.9	114.6	111.8
H−C−N[b]	110.1	110.6	110.2
$\sum$<N(1)	341.8	338.6	332.4
$\sum$<N(2)	357.5	354.6	351.8
abs energy	−776.708377	−780.708309	−782.234116
$\Delta E(C_s'-C_s)$	5.9	11.6	18.8

[a] Bond distances in Å; angles in degrees; absolute energies in E$_h$; energy differences in kJ mol^{-1}. [b] Average values.

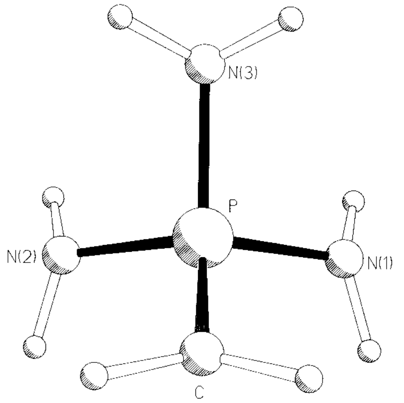

Figure 4. *Ab initio* calculated molecular geometry of $H_2C{=}P(NH_2)_3$. The minimum energy structure is shown.

parallel CH$_2$ orientation. The barriers to rotation about the P−C bond were predicted to have similar magnitudes as those for $H_2C{=}P(NMe_2)_3$, which is 19.9 kJ mol^{-1} for $H_2C{=}P(NH_2)_3$ at the MP2/6-311G** level of theory (corrected by the ZPE calculated at the MP2/6-31G* level).

The geometric parameter values obtained for the stable isomer of $H_2C{=}P(NH_2)_3$ are presented in Table 3, and a view of the geometry is given in Figure 4. In general, improvements in the theoretical method were found to have only a slight effect on geometric parameter values. If the results from the smallest basis set are excluded, the P−C bond length varied between 1.684 and 1.656 Å and the highest level calculation yielded a value of 1.654 Å (MP2/6-311G**). Estimates of P−N distances proved slightly more sensitive to the adopted theoretical method. In particular, the introduction of electron correlation led to increases of about 0.02 Å. Values for the P−N distances in pentavalent $H_2C{=}P(NH_2)_3$ were generally slightly shorter than in the tervalent phosphine $P(NH_2)_3$. The corresponding comparison of $H_2C{=}P(NH_2)_3$ with the *N*-permethylated $H_2C{=}P(NMe_2)_3$ shows these bonds to be slightly shorter in the model compound.

As was found for $P(NH_2)_3$, the geometries of the nitrogen atoms in $H_2C{=}P(NH_2)_3$ proved to be sensitive to the adopted theoretical method. At the SCF/3-21G* level the two symmetry-equivalent nitrogen environments were calculated to be almost planar ($\sum\angle$ at N: 359.3°), while they became more pyramidal with increased sophistication of theoretical treatment (346.4° at MP2/6-311G**). In the same sense the NH$_2$ group, which is intersected by the plane of symmetry, is predicted to be more pyramidal at higher levels of theory (342.1° at SCF/3-21G* and 331.2° at MP2/6-311G**), but at all levels it was more steeply pyramidal than the other two groups.

A notable difference between the structures of $H_2C{=}P(NH_2)_3$ and $H_2C{=}P(NMe_2)_3$ is the magnitude of the CPN angles. The one including one of the symmetry equivalent nitrogen atoms N(1) and N(2) is 107.5° in $H_2C{=}P(NH_2)_3$ and 109.4° in $H_2C{=}P(NMe_2)_3$, both at the MP2/6-31G* level of theory, thus lying close together. At the same theory level the angles CPN(3) including the nitrogen atom on the plane of symmetry were calculated to be as large as 133.1° in $H_2C{=}P(NH_2)_3$, but only 124.8° in $H_2C{=}P(NMe_2)_3$, which is close to the value of 122.4(4)° determined for this compound by crystallography. This difference can be explained by a greater mutual repulsion of the methylated amino groups in $H_2C{=}P(NMe_2)_3$ as compared with the model compound.

Gas-Phase Structure of $H_2C{=}P(NMe_2)_3$. Finally, as we wanted to gain definitive *experimental* evidence for the C_s geometry of the undistorted molecule of $H_2C{=}P(NMe_2)_3$ we performed a gas-phase structure determination by analysis of electron diffraction data. We recently introduced a refinement procedure which enables us to cope even with molecules of this size and complexity, as will be shown in the following paragraphs. This analysis procedure[45] (SARACEN)[46] differs from the conventional way of gas-phase structure analysis in so far, as almost all of the parameters are refined and those which do not refine satisfactorily under conventional circumstances become subject to flexible restraints derived from theoretical calculations with an assigned uncertainty for this value, which is based on the estimated reliability of the calculated parameter. In addition it is possible to apply those restraints also to dependent parameters. As compared to the use of rigid constraints of unknown reliability, which until now has been the normal method, our new approach provides us with the best structures of free molecules by combining the advantages of electron diffraction and computational methods. For a detailed description of the procedure we refer to our recent papers.[45,46]

Numerous models have been tested to fit the experimental molecular scattering intensities (Figure 5), including those with local C_3 symmetry for the $P(NMe_2)_3$ group and various conformations of overall C_s symmetry. The best fit to the data was achieved with a geometry which is very close to the one determined in the crystal and predicted by *ab initio* calculations. The finally refined parameter values are given in Table 5 together with the theoretical and crystallographic results for comparison.

Despite the progress achieved with our SARACEN procedure for relatively large systems, the large number of geometric parameters necessary for the definition of this system required the adoption of some assumptions to simplify the problem. These were overall C_s symmetry, local C_2 symmetry of the NMe$_2$ groups, and local C_{3v} symmetry for the NCH$_3$ units as well as equal lengths for all C−H distances in the molecule. The model was then defined by 18 parameters, which are described in Table 7 and discussed below.

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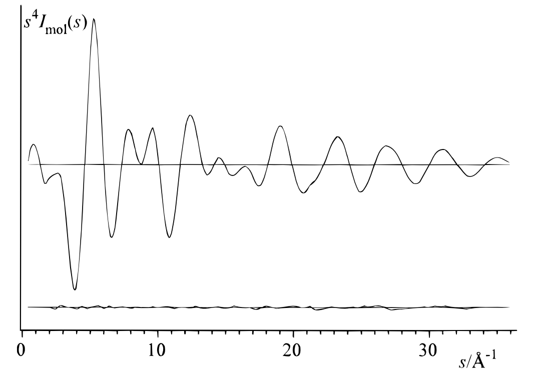

Figure 5. Observed and final weighted difference combined molecular-scattering intensity curves for the GED study of $H_2C{=}P(NMe_2)_3$. Theoretical data are shown for the region 0−2 Å^{-1}, for which no experimental data are available.

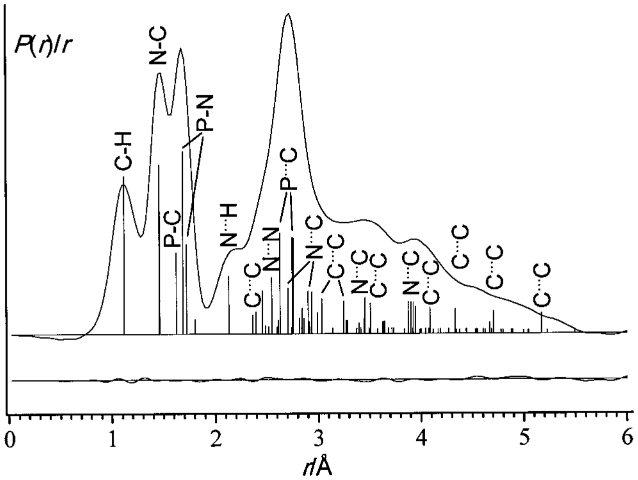

Figure 6. Observed and final weighted difference radial distribution curves for $H_2C{=}P(NMe_2)_3$. Before Fourier inversion the data were multiplied by $s\cdot\exp[(-0.002s^2)/(Z_P - f_P)/(Z_N - f_N)]$. Contributions of individual interatomic distances are shown as vertical lines (see Table 8).

Table 7. Definition of Parameters and Restraints used in the GED Refinement (distances in Å; angles in deg, esd's in parentheses)

no.	description	refined to	restraint (uncertainty)
p_1	r[CH(mean)]	1.115(1)	
p_2	Δr[PC(1) − PN(mean)]	−0.075(6)	−0.047(10)
p_3	r[PN(mean)]	1.695(1)	
p_4	Δq[PN(3) − PN(1)]	0.034(9)	0.046(10)
p_5	r[NC(mean)]	1.458(1)	
p_6	Δr[N(1)C(11,12) − N(3)C(31)]	0.004(9)	0.010(10)
p_7	∠[C(1)PN(1)]	110.0(5)	
p_8	Δ∠[C(1)PN(1) − C(1)PN(3)]	17.1(11)	15.4(15)
p_9	∠[N(1)PN(2)]	115.2(13)	
p_{10}	∠[PN(3)C(31)]	111.4(5)	
p_{11}	Δ∠[PN(1)C(11,12)(mean) − PN(3)C(31)]	10.8(6)	8.2(15)
p_{12}	∠[C(11)N(1)C(12)]	115.0(5)	
p_{13}	Δ∠[C(32)N(3)C(31) − C(11)N(1)C(12)]	−4.9(13)	−3.1(15)
p_{14}	∠[wag N(1)C(11,12) about N(1)][a]	−0.4(6)	−0.9(10)
p_{15}	τ[PN(1)]	241.7(14)	
p_{16}	∠[NCH(mean)]	111.1(3)	
p_{17}	τ[N(1)C(11)]	20.3(24)	
p_{18}	τ[PN(3)C(31)]	8.6(55)	

[a] Defines the angle by which the methyl groups are twisted about an axis perpendicular to the PNC_2 plane before both methyl groups are moved out of this plane.

Table 8. Selected Distances (r_a, Å) and Vibrational Amplitudes u (Å) as Obtained by the GED Refinement of $H_2C{=}P(NMe_2)_3$ (esd's in parentheses)

no.	description	distance	amplitude	comment
d_1	P−N(1)	1.684(3)	0.041(3)	
d_2	P−N(3)	1.718(6)	0.041	tied to u_1
d_3	P−C(1)	1.620(5)	0.038	tied to u_1
d_4	N(1)−C(12)	1.457(3)	0.044(1)	
d_5	N(3)−C(31)	1.461(6)	0.044	tied to u_4
d_6	C−H(mean)	1.115(1)	0.086(1)	
d_7	P⋯C(12)	2.757(7)	0.064(3)	
d_8	P⋯C(11)	2.746(9)	0.064	tied to u_7
d_9	P⋯C(31)	2.630(3)	0.059	tied to u_7
d_{10}	N(1)⋯C(1)	2.707(8)	0.063	refined then fixed
d_{11}	N(1)⋯N(3)	2.549(9)	0.100	fixed
d_{12}	N(1)⋯N(2)	2.844(21)	0.110	fixed
d_{13}	N(3)⋯C(1)	2.989(12)	0.110	fixed
d_{14}	C(11)⋯C(12)	2.457(9)	0.071(8)	
d_{15}	C(31)⋯C(32)	2.395(18)	0.071	tied to u_{14}
d_{16}	N(1)⋯C(22)	3.452(10)	0.105	refined then fixed
d_{17}	N(1)⋯C(21)	3.923(25)	0.187(4)	
d_{18}	N(1)⋯C(32)	2.900(17)	0.230	fixed
d_{19}	N(1)⋯C(31)	3.901(8)	0.187	tied to u_{17}
d_{20}	N(3)⋯C(12)	2.934(16)	0.170	fixed
d_{21}	N(3)⋯C(11)	3.873(10)	0.187	tied to u_{17}
d_{22}	C(1)⋯C(12)	4.086(8)	0.120	fixed
d_{23}	C(1)⋯C(11)	3.031(13)	0.180	fixed
d_{24}	C(1)⋯C(32)	3.503(17)	0.109	refined then fixed
d_{25}	C(12)⋯C(22)	3.445(26)	0.154	refined then fixed
d_{26}	C(12)⋯C(21)	4.702(11)	0.222(19)	
d_{27}	C(12)⋯C(32)	3.245(19)	0.110	fixed
d_{28}	C(12)⋯C(31)	4.333(12)	0.130	fixed
d_{29}	C(11)⋯C(22)	3.945(18)	0.138	tied to u_{17}
d_{30}	C(11)⋯C(31)	5.171(9)	0.164(17)	
d_{31}	C(11)⋯C(21)	4.667(42)	0.222	tied to u_{26}

Table 7 also contains a description of the flexible restraints (mostly applied to differences between related parameters) and their uncertainties. The values for the restraints were adopted from the highest level *ab initio* calculation (MP2/6-31G*). The uncertainties for differences in bond lengths (parameters p_2, p_4, and p_6) were assigned to be 0.01 Å, which seems to be realistic with respect to the almost complete convergence of the calculated values achieved with the high level of theory. The uncertainties for most of the parameters describing differences in angles (p_8, p_{11}, and p_{13}) were assumed to be 1.5°, taking into account the fact that these restraints are applied to parameters including different nitrogen environments. Only the parameter p_{14}, which describes the deviation of the $PN(1/2)Me_2$ groups from local C_s symmetry by twisting the NMe_2 groups about the nitrogen atoms, was given a lower uncertainty of 1.0°, as it describes differences between very similar parameters. It was tried to refine the geometry of the PCH_2 group, but it turned out that there is too little information contained in the molecular intensity data to give reliable results. Consequently, the geometry of this group was fixed at the calculated values.

The amplitudes of vibration were fixed at values derived from the experience with related compounds, unless refinement was possible. The fixed ratio between amplitudes which were refined in groups were based on known comparable values. The structure was then refined without taking perpendicular amplitude corrections into account (shrinkage effect).

The radial distribution curve is presented in Figure 6. The overall geometry is in good accordance with both the calculated geometry and that derived from the crystal structure, showing that the C_s symmetry of the molecule does indeed correspond to the minimum energy structure.

The values obtained for the two different P−N distances are in the range between the values of solid-state structure and the theoretically predicted one, whereas the P−C distance refined to a value as low as 1.620(5) Å, which is significantly lower than the crystallographic one. Comparable values of other methylene phosphoranes have been discussed with the crystal structure above, but this value comes close to that of a carbodiphosphorane, $Me_3P{=}C{=}PMe_3$, the P−C distance of which was determined to be 1.594(3) Å in the gas phase.[47]

The NPN angles obtained by all three independent methods are very close thus adding support to the reliability of the structure of the PN_3 core. The largest difference between the angle values appears to be for the CPN(3) angle. This refines to 127.1(8)° in the GED analysis, is calculated to be 124.8°, and is determined in the crystal to be 122.4(4)°. As discussed above, this parameter was predicted to be even larger in the model compound $H_2C{=}P(NH_2)_3$.

The geometries of the NMe_2 groups compare well with those of the crystal structure and of theory. $H_2C{=}P(NMe_2)_3$ has the most planar environments for the atoms N(1) and N(2) in the gas phase as described by the sums of angles at the nitrogen atom which are 359.5(11)°.

The parameters describing the conformation of the molecule refined unexpectedly well for a system of this complexity. The orientation of the methyl groups including the carbon atoms C(12) and C(22), which come closest to the $N(3)Me_2$ group is very much the same for the free molecule in the gas phase and for the molecule embedded in the crystal lattice, as indicated by the similarity of the torsion angles C(1)PN(1)C(12) and C(1)-PN(2)C(22) (see Table 4).

Comparison with Structural Data from the Literature. There are a few structural studies reported on systems containing PN_3 units. Most of them deal with complicated molecules including ring systems and have been carried out in the solid state. Here we want to consider only simple structures, which are accessible to rational arguments explaining these structures. In the complicated cases there are too many possible contributions, which can force the molecules to adopt the observed geometries. In particular we want to discuss the systems $O{=}P(NMe_2)_3$, $Se{=}P(NMe_2)_3$, $(Me_2N)_3P{=}C{=}P(NMe_2)_3$, and $(Me_2N)_3P{=}NSiMe_3$ and focus on the overall conformations and symmetry of the molecules and the influence of the substituents at the $P(NMe_2)_3$ unit on the coordination geometries of the nitrogen atoms.

Despite the wide use of hexamethylphosphoric acid triamide (HMPA), no structural data for the pure system have been reported, but there is some information available about the uncoordinated system from at least three crystal structure determinations.[48−51] For the related system $O{=}P(NH_2)_3$ structural data show that the molecular conformation in the crystal is largely dominated by hydrogen bridges.[52]

The most intriguing difference to the systems dicussed above is that in all these structures the $O{=}P(NMe_2)_3$ molecules contain three almost planar nitrogen environments. The magnitudes of the sums of angles about the nitrogen atoms in these structures range from 352.8 to 360.0°, and there is no hint of any preference for a C_s arrangement of the whole $O{=}P(NMe_2)_3$ molecule. The difference to the geometries of the molecules $P(NMe_2)_3$ and $H_2C{=}P(NMe_2)_3$ can be rationalized by the high effective nuclear charge of oxygen as compared to the methylene unit in the ylide or the absence of any ligand in the tervalent triaminophosphane. The oxygen substituent withdraws electron density from the phosphorus center leading to a stronger interaction of this with the NMe_2 ligands and resulting in an almost planar geometry of *all* three NMe_2 groups, which can then no longer be accommodated in a C_s-type conformation as realized for $H_2C{=}P(NMe_2)_3$. The effect of electron-withdrawing ligands at the phosphorus atom on NMe_2 groups bound to it has been demonstrated earlier with the gas-phase structure of the difluoro compound $F_2P(NMe_2)_3$, which contains three virtually planar $PNMe_2$ units.[53]

As a consequence of the contribution of electronegative substituents at the phosphorus atom outlined above one should expect systems of the type $E{=}P(NMe_2)_3$, with E being a less electron-withdrawing ligand, to exhibit the same conformation as found for $H_2C{=}P(NMe_2)_3$. In fact this has been shown for $Se{=}P(NMe_2)_3$ in a crystal structure study.[54] Although this molecule is isovalence-electronic to $O{=}P(NMe_2)_3$, its geometry is very similar to the structures of the ylide and the triaminophosphane discussed above. It almost has C_s symmetry and shows two markedly different nitrogen environments, characterized by their different sums of angles at the nitrogen atoms, two being 358.2° and one being 341.9°.

A similar conformation has also been found in the carbodiphosphorane $(Me_2N)_3P{=}C{=}P(NMe_2)_3$, which has been structurally characterized in the solid state.[55] This compound consists of two $P(NMe_2)_3$ groups, which are related by crystallographic symmetry, each having almost C_s symmetry and containing two planar NMe_2 ligands ($\sum\angle$ 358.2 and 358.6°) and one pyramidal one ($\sum\angle$ 343.8°).

The same structural behavior was found for $(Me_2N)_3PAuCl$[56] and for other transition metal complexes of $(Me_2N)_3P$ in the solid state. Recently we could also show that $(Me_2N)_3P{=}NSiMe_3$ has almost local C_s symmetry in its $(Me_2N)_3P$ unit.[56] This compound may be seen as a borderline case in which the electronegativity of the nitrogen atom is not quite sufficient to lead to the same structural observations as for $O{=}P(NMe_2)_3$.

Conclusions

We have shown that the unexpected C_s symmetry of the molecule $P(NMe_2)_3$ with its two different nitrogen environments is an inherent structural feature of $P(NR_2)_3$ skeletons. As theoretical studies on the model compound $P(NH_2)_3$ show, this is caused by electronic effects and not imposed by steric strain or packing forces in the crystal. By comparative theoretical studies of isoelectronic compounds we obtained strong evidence for a similar behavior of other $E(NR_2)_3$ compounds, where E is a fragment containing a second or higher row element of groups 14 and 15, whereas the first row compound $N(NH_2)_3$ shows the expected behavior with the propeller-like C_3 stucture being the only stable form. We are aware of other studies of $E(NMe_2)_3$ compounds with E = As, Sb, and Bi, which are presently under way,[35] and agree with our findings for the phosphorus homologous compounds. Lone pair repulsion could be ruled out as the major contribution to the observed effects, but the precise origin is still not clear and an even more thorough theoretical treatment will be necessary to generalize these findings for the group 14 and 15 nitrogen compounds. We understand that a revision of the structure of $P(NMe_2)_3$ in the gas phase has now been started by the Moscow electron diffraction group, which also carried out the first refinements on this structure.

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The structural findings for tervalent group 15 compounds are consistent with other molecules containing the $P(NR_2)_3$ unit in pentavalent phosphorus compounds of the type $X{=}P(NR_2)_3$. We have shown this by structural studies in the solid state and in the gas phase for $X = CH_2$ and are now in a position to explain a number of related structural studies in the literature, *e.g.* with $X = Se$. Only the most electron-withdrawing phosphorus substituent X (*i.e.* oxygen) in pentavalent compounds is able to override the conformational preference for the C_s geometry discussed here, leading to structures with all nitrogen environments being almost planar. Related phosphorus compounds with three equivalent substituents, such as alkoxy groups, could also be subject to geometry distortions as decribed in this work and should be investigated with these new findings taken into account.

We are presently trying to get experimental structural results for the free $HN{=}P(NMe_2)_3$ and $O{=}P(NMe_2)_3$ systems to resolve the problem with the observed structural differences of $O{=}P(NMe_2)_3$.

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Supporting Information Available: A full listing of data to the crystal structure determination, including atomic coordinates and isotropic and anisotropic displacement parameters, a complete set of results of the *ab initio* calculated geometries of $P(NH_2)_3$, $N(NH_2)_3$, and $H_2CP(NH_2)_3$ at different levels of theory, and a complete correlation matrix for the ED refinement (12 pages). See any current masthead page for ordering and Internet access instructions.

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