The molecular and crystal structures of the tris(dimethylamino)-phosphoranes (Me$_2$N)$_3$P–X (X = BH$_3$, CH$_2$, NH or O)

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Single crystal X-ray diffraction studies and *ab initio* calculations up to the MP2/6-31G* level of theory were carried out for the isoelectronic compounds (Me$_2$N)$_3$PBH$_3$, (Me$_2$N)$_3$PNH and (Me$_2$N)$_3$PO. The calculations predict all three compounds to adopt C_s symmetry in the ground state. The alternative geometries with local or total C_3 symmetry also correspond to local minima on the potential hypersurface. In the solid state (Me$_2$N)$_3$PBH$_3$ and (Me$_2$N)$_3$PNH do not obey exact C_s symmetry, but are close to it, while (Me$_2$N)$_3$PO shows crystallographic mirror symmetry. The structural data are compared with earlier studies on (Me$_2$N)$_3$PCH$_2$ and the free phosphine P(NMe$_2$)$_3$, which both are also almost C_s symmetric. In the series (Me$_2$N)$_3$P–X (X = BH$_3$, CH$_2$, NH or O) the P–X bond lengths decrease, the P–N (pseudo) in plane distances are 1.683(1), 1.698(4), 1.677(1) and 1.659(1) Å, the (pseudo) out of plane P–N distances are (av. = average) 1.654(av.), 1.668(av.), 1.656(av.) and 1.649(1) Å. The (pseudo) in plane angles X–P–N are 114.9(1), 122.4(4), 120.2(1) and 118.7(1)°, while the (pseudo) out of plane angles X–P–N are 112.3(av.), 110.0(av.), 110.4(av.) and 110.0(av.)°. In all structures the NMe$_2$ groups in the (pseudo) plane of symmetry are steeply pyramidal at nitrogen, while the (pseudo) out of plane NMe$_2$ groups are markedly flattened. The other structural parameters are also discussed in comparison. *Ab initio* calculations (MP2/6-31G*) on the isoelectronic (Me$_2$N)$_3$PF$^+$ predict this system to favour C_3 over C_s symmetry. In contrast, the parent system (H$_2$N)$_3$PF$^+$ is predicted to prefer C_s symmetry.

Introduction

Compounds containing the tris(dialkylamino)phosphine unit, P(NR$_2$)$_3$, are important reagents in synthetic organic and inorganic chemistry: (Me$_2$N)$_3$PO (HMPA) used to be a widely employed solvent until its carcinogenic potential was recognised; (Me$_2$N)$_3$PNH is used as a building block for phosphazene bases;[1] (Me$_2$N)$_3$PCH$_2$ is an important reagent which has the advantage of being turned into water-soluble HMPA in Wittig reactions for olefin synthesis;[2] (Me$_2$N)$_3$P is a popular ligand in transition metal chemistry.

The P(NR$_2$)$_3$ units in phosphoranes and the three-valent phosphines prefer geometrical arrangements in C_s symmetry. Recently we have demonstrated this to be an inherent phenomenon in this class of compounds by establishing the crystal structure of the parent compound P(NMe$_2$)$_3$ and the solid-state and gas-phase structures of the ylide (Me$_2$N)$_3$PCH$_2$, which were found to reveal intriguingly similar geometries of their P(NMe$_2$)$_3$ units, *i.e.* the geometry in (Me$_2$N)$_3$PCH$_2$ is not much affected by the different oxidation state of phosphorus or the presence of the CH$_2$ group. Moreover, the experimental data from the gas phase and solid state were in almost perfect agreement with *ab initio* calculations,[3] which shows theory to be a very helpful tool for this class of compounds for providing realistic estimates of properties not easily accessible by experiments.

C_s Symmetry as a preferred geometry is not unique for P(NMe$_2$)$_3$ compounds, but is also found in structures of the heavier congeners As and Sb, *i.e.* in the molecules As(NMe$_2$)$_3$ and Sb(NMe$_2$)$_3$,[4] and most recently even for the simplest phosphorus ylide Me$_3$PCH$_2$.[5] The barriers to conversion of C_s symmetrical structures into those with local C_3 symmetry are generally low, but sufficient to dominate the molecular geometries in the ground state and to result in experimentally observable effects. Less pronounced than in the amides of Group 15 is this effect in triamides of Group 14 elements, *i.e.* in compounds like HSi(NMe$_2$)$_3$,[6] whereas other compounds of Group 15 are

less well established and only a few examples of structurally elucidated cases are known, *e.g.* N(SbMe$_2$)$_3$, which, however, has a completely planar structure of C_3 symmetry.[7] *iso*-Tetrazene, N(NH$_2$)$_3$, a non-existent compound, has been predicted by *ab initio* calculations to be steeply pyramidal and to adopt also C_3 symmetry.[3] This means that nitrogen as a central element behaves completely different as compared with the heavier elements of Group 15 in this respect.

A lot of earlier work on related subjects has been carried out, but referring to all would be beyond the scope of this paper: the gas-phase structure of P(NMe$_2$)$_3$, for which probably too high symmetry (C_3) was assumed;[8] various attempts to extract the correct symmetry for P(NMe$_2$)$_3$ on the basis of photoelectron spectroscopy (PES), which finally Cowley *et al.* got right;[9] the structure determination of metal complexes[10] and other derivatives[11] of this ligand showing preference for a C_s arrangement of the P(NMe$_2$)$_3$ unit.

An interesting consequence of the low symmetry of P(NMe$_2$)$_3$ is the occurrence of two different P–N bond lengths and two different modes of nitrogen co-ordination in these systems: one long in the plane of symmetry binding a pyramidal NMe$_2$ group, and one short connecting two almost planar NMe$_2$ groups to the phosphorus centre. In a recent contribution on a related problem, Cl$_2$PNMe$_2$, it was shown that the barrier to inversion at nitrogen is generally low, such that different methods of structure determination give different answers, which lead to controversially discussed molecular geometries.[12]

In this paper we aim to show the differences in the structures of the P(NMe$_2$)$_3$ units in the series of isoelectronic compounds (Me$_2$N)$_3$PBH$_3$, (Me$_2$N)$_3$PCH$_2$, (Me$_2$N)$_3$PNH, (Me$_2$N)$_3$PO and the ion (Me$_2$N)$_3$PF$^+$, *i.e.* by systematic variation of the fourth substituent at P through the first period of the Periodic Table. These compounds might be seen as phosphine adducts of the unstable molecules monoborane BH$_3$, carbene CH$_2$, nitrene NH, "oxene" O and F$^+$ although they would usually be classified as phosphoranes probably with the exception of (Me$_2$N)$_3$PBH$_3$.
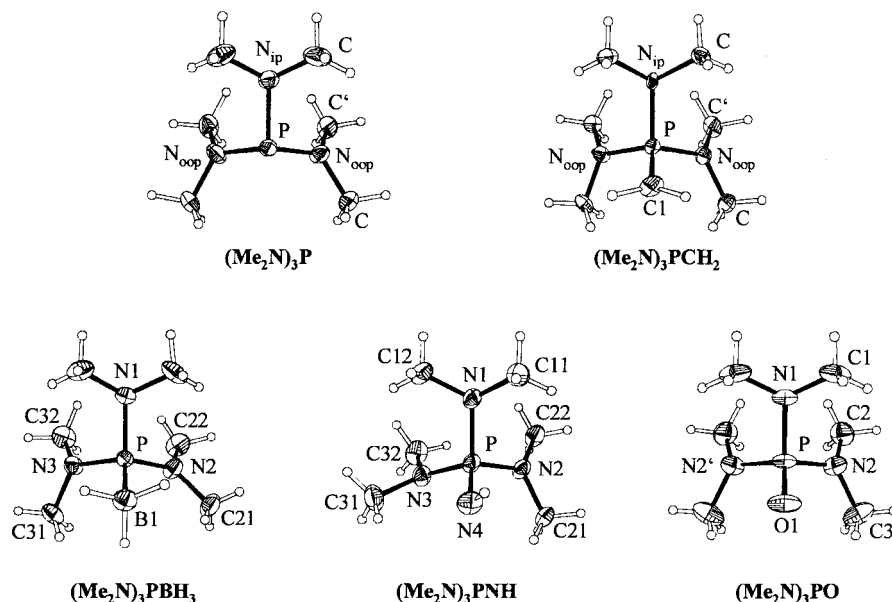
Fig. 1 Low-temperature crystal structures of $(Me_2N)_3P–X$ compounds. The structures of $(Me_2N)_3P$ and $(Me_2N)_3PCH_2$ determined in an earlier contribution and are displayed for comparison and to illustrate the general atom labelling in Table 1. The structures of $(Me_2N)_3PBH_3$, $(Me_2N)_3PNH$ and $(Me_2N)_3PO$ are shown with their atomic labelling. The molecules are oriented such that the (pseudo) mirror plane is perpendicular and vertical to the plotting plane.

Results and discussion

Application of *in situ* methods for crystal growth directly on the diffractometer allowed the determination of the solid-state structures of $(Me_2N)_3PNH$ and $(Me_2N)_3PO$ by X-ray diffraction of single crystals. A suitable specimen of $(Me_2N)_3PBH_3$ was grown from solution in hexane. The data of $(Me_2N)_3PCH_2$ and $(Me_2N)_3P$ stem from our earlier investigations[3] and will be used for comparison. Despite a gas-phase structure of $(Me_2N)_3PCH_2$ having been described in this earlier contribution,[3] we refer here to the solid-state structure only for the sake of consistency.

All three compounds crystallise in the monoclinic system, but in different space groups: $(Me_2N)_3PO$ crystallises in the space group $P2_1/m$ with a crystallographic mirror plane passing through the O, P and N1 atoms, similar to $(Me_2N)_3PCH_2$ which also crystallises with crystallographic mirror symmetry; the molecules of $(Me_2N)_3PBH_3$ and $(Me_2N)_3PNH$ show no crystallographic symmetry. The structures are displayed in Fig. 1. Table 1 contains the relevant experimentally determined structural parameters, as well as the geometry results of *ab initio* calculations up to the electron correlated level of theory MP2/6-31G* and the corresponding data of $(Me_2N)_3PCH_2$ and $(Me_2N)_3P$ for comparison.

Aspects concerning all $(Me_2N)_3PX$ compounds

All three compounds, $(Me_2N)_3PBH_3$, $(Me_2N)_3NH$ and $(Me_2N)_3PO$, are incorporated into the crystal lattices as monomers with no intermolecular contacts, which would normally be regarded as significant. As *ab initio* calculations consistently predict the ground state to have C_s symmetry for all three compounds, this lower symmetry of $(Me_2N)_3PBH_3$ and $(Me_2N)_3$-PNH is surprising at first glance. However, according to theory there are only very small energy differences between slightly different geometries. The occurrence of distorted geometries of $(Me_2N)_3PBH_3$ and $(Me_2N)_3PNH$ in the crystals indicates that in particular the twist about the P–N bonds is energetically not demanding.

For $(Me_2N)_3PBH_3$ and $(Me_2N)_3PO$, which both are in principal capable of adopting perfect C_3 geometries, full structure optimisations under these symmetry constraints have also been carried out. Although these geometries do correspond to minima on the potential hypersurfaces, they are 6.7 kJ mol^{-1}

$[(Me_2N)_3PBH_3]$ and 17.3 kJ mol^{-1} $[(Me_2N)_3PO]$ higher in energy than the C_s ground states (MP2/6-31G*). For the three-valent phosphine $(Me_2N)_3P$ the difference between C_s and C_3 geometries is 28.4 kJ mol^{-1}.[1] The substituents X at the phosphorus centre thus decrease these energy barriers to the C_s–C_3 interconversion, but it is difficult to rationalise why X = BH_3 and X = O behave so differently. These results show the driving force for the adoption of C_s symmetry to be high enough to explain the strong preference of compounds containing $(Me_2N)_3P$ units for C_s rather than local C_3 symmetric arrangements, on the other hand low enough to be overridden by the sum of weak lattice forces in crystals, which then lead to the observed deviations.

As expected the bond length P–X decreases in the series of compounds $(Me_2N)_3P–X$ (X = BH_3, CH_2, NH, O), due to the increasing importance of an ylidic contribution, *i.e.* charge separation between P and X in the form P$^+$–X$^-$. For the following discussion of other parameters we focus on the differences occurring in the series $(Me_2N)_3P–X$, while we neglect the deviations from C_s symmetry in $(Me_2N)_3PBH_3$ and $(Me_2N)_3PNH$ and rather compare average values of these compounds as far as possible. Thus we refer to the molecular plane of symmetry in all compounds, even if there is no exact one present.

There are two types of nitrogen centres in the molecules, one with a longer distance to the phosphorus atom, which is pyramidally co-ordinated, and two almost planar, with shorter P–N bond lengths. Both types of P–N bonds get shorter along the series $(Me_2N)_3PX$ with X = CH_2, NH, O. These values seem consistent with chemical intuition, as more electronegative substituents lead to more positively charged P atoms, which strengthens the ionic contribution of the P–N bond. The compound $(Me_2N)_3PBH_3$, however, has shorter P–N bonds than $(Me_2N)_3PCH_2$. This series of parameter values is satisfactorily reproduced by the *ab initio* calculations.

The difference between these two types of P–N bonds is most pronounced for the unsubstituted phosphine $(Me_2N)_3P$ ($\Delta = 0.044$ Å), almost the same for $(Me_2N)_3PBH_3$ and $(Me_2N)_3PCH_2$ ($\Delta = 0.029$ and 0.030 Å) and least for the most electronegative X in $(Me_2N)_3PO$ ($\Delta = 0.010$ Å). The calculations do not reproduce these observations: as $(Me_2N)_3P$, 0.036, $(Me_2N)_3PBH_3$, 0.016, $(Me_2N)_3PCH_2$, 0.046, $(Me_2N)_3PNH$, 0.003, $(Me_2N)_3PO$, -0.001 Å. In particular the last value is a surprise, as the two flattened nitrogen centres are best described by an sp^2 hybrid,

Table 1 Selected geometrical parameter values for $(Me_2N)_3P$, $(Me_2N)_3PBH_3$, $(Me_2N)_3PCH_2$, $(Me_2N)_3PNH$ and $(Me_2N)_3PO$ from low temperature crystallography (XRD) and *ab initio* calculations (MP2/6-31G*). The identifier "ip" denotes in plane, "oop" out of plane with respect to the mirror planes of molecular symmetry or the best approximate mirror plane. Distances are given in Å, angles in °; av. represents the average of all available values

	$(Me_2N)_3P$		$(Me_2N)_3PBH_3$		$(Me_2N)_3PCH_2$		$(Me_2N)_3PNH$		$(Me_2N)_3PO$	
	XRD	MP2/6-31G*	XRD	MP2/6-31G*	XRD	MP2/6-31G*	XRD	MP2/6-31G*	XRD	MP2/6-31G*
$r(P–X)$			1.913(1)	1.942	1.655(6)	1.663	1.557(1)	1.567	1.477(1)	1.498
$r(P–N_{ip})$	1.731(av.)	1.755	1.683(1)	1.712	1.698(4)	1.740	1.677(1)	1.699	1.659(1)	1.687
$r(P–N_{oop})$	1.687(av.)	1.719	N2 1.650(1), N3 1.658(1)	1.696	1.668(av.)	1.694	N2 1.659(1), N3 1.652(1)	1.696	1.649(1)	1.688
$r(N_{ip}–C)$	1.462(av.)	1.467	C11 1.468(2), C12 1.463(1)	1.471	1.472(av.)	1.472	C11 1.766(1), C12 1.769(1)	1.464	1.466(2)	1.467
$r(N_{oop}–C)$	1.453(av.)	1.456	C21 1.452(2), C31 1.459(2)	1.462	1.455(av.)	1.461	C21 1.455(2), C31 1.458(2)	1.457	1.463(2)	1.457
$r(N_{oop}–C')$	1.462(av.)	1.457	C22 1.452(2), C32 1.459(2)	1.463	1.460(av.)	1.462	C31 1.455(2), C32 1.453(2)	1.460	1.459(2)	1.460
$r(X–H_{ip})$			1.10(2)	1.213				1.015		
$r(X–H_{oop})$			1.15(av.)	1.206	0.89(2)	1.083	0.77(2)			
$X–P–N_{ip}$			114.9(1)	114.6	122.4(4)	124.8	120.2(1)	124.7	118.7(1)	120.9
$X–P–N_{oop}$			N2 112.7(1), N3 111.8(1)	113.8	110.0(av.)	109.4	N2 113.9(1), N3 106.8(1)	109.7	110.0(1)	110.2
$N_{ip}–P–N_{oop}$	97.7(av.)	96.5	N2 103.0(1), N3 100.6(1)	99.7	99.7(av.)	98.5	99.7(1), 106.8(1)	99.9	102.3(1)	100.6
$N_{oop}–P–N_{oop}$	110.8(av.)	112.0	113.0(1)	113.7	114.7(2)	116.5	109.2(1)	112.4	113.3(1)	114.2
$P–N_{ip}–C$	113.7(av.)	112.9	C11 115.4(1), C12 116.9(1)	114.3	114.1(av.)	111.8	C11 115.6(1), C12 116.4(1)	117.2	117.5(1)	116.7
$P–N_{oop}–C$	125.4(av.)	123.8	C21 123.3(1), C31 117.0(1)	118.5	121.6(av.)	120.9	C22 119.2(1), C32 121.9(1)	122.5	122.1(1)	122.3
$P–N_{oop}–C'$	117.3(av.)	116.5	C22 122.6(1), C32 123.1(1)	121.1	119.5(av.)	119.1	C21 126.1(1), C31 121.9(1)	118.4	119.3(1)	117.8
$C–N_{ip}–C$	110.3(av.)	109.4	110.8(1)	109.9	109.1(4)	108.7	111.5(1)	111.6	112.2(2)	111.0
$C–N_{oop}–C'$	113.2(av.)	113.1	N2 113.9(1), N3 113.2(1)	112.2	111.1(av.)	111.8	N2 113.0(1), N3 113.2(1)	113.0	112.4(1)	113.5
$P–X–H_{ip}$			110.1(11)	100.9			115(2)	116.2		
$P–X–H_{oop}$			103.6(10), 106.8(13)	109.1	116(av.)	118.1				
$\Sigma\angle (N_{ip})$	337.7(av.)	335.2	343.1	338.5	337.3	323.3	343.5	346.9	347.2	344.4
$\Sigma\angle (N_{oop})$	355.9(av.)	353.4	N2 359.8, N3 353.3	351.8	353.4	351.8	N2 358.3, N3 357.0	353.8	353.8	353.6

which should bind more strongly to the P atom than a pyramidal sp³ N atom. However, the distinction between pyramidal and planar nitrogen co-ordination is not always that clear. The ideal sum of angles for a pyramidal N atom would be 328° (three times the tetrahedral angle) but all values listed in Table 1 for the "in plane" nitrogen atoms, $\Sigma \angle$ (N_{ip}), are substantially bigger, whereas the sum of angles for the "out of plane" nitrogen atoms, $\Sigma \angle$ (N_{oop}), never reach exactly 360°. The difference between more flat and more pyramidal nitrogen atoms is smallest for $(Me_2N)_3PO$, which is consistent with the observation of a slight difference in the P–N bond lengths.

The most intriguing structural parameters in $(Me_2N)_3PX$ compounds are the X–P–N angles. They are largely different with respect to the two distinct types of nitrogen centres. There is always one large angle to the nitrogen atom in the (approximate) molecular symmetry plane, and two small angles enclosed by X and the two flattened nitrogen centres. The largest variance is observed in the ylide $(Me_2N)_3PCH_2$, $\Delta = 12.4°$, it is slightly less in the imine ($\Delta = 9.9°$, note the large deviations from ideal C_s symmetry in this case) and even less in the oxide, $\Delta = 8.7°$. Again the borane adduct cannot be seen as a simple extension of the series O, NH, CH_2, as the difference in this case is only 2.5° on average.

$(Me_2N)_3PBH_3$

In a paper from 1960 describing the synthesis and chemical properties of $(Me_2N)_3PBH_3$ its high stability even to steam is attributed to stabilisation of the B–H bonds by interaction with empty d orbitals at phosphorus.[13] If such an interaction took place, one should expect a compressed P–B–H angle, and indeed the in plane P–B–H angle is only 100.9° (the other two 109.1) according to the calculations (note that the crystal structure values are different, but their significance can be doubted). This value is similar to those of $H_3P–BH_3$ [103.6(2)°] and $MeH_2P–BH_3$ [102.9(6) and 104.2(10)°]. However, the relatively long P–B distances [$(Me_2N)_3PBH_3$: 1.913(3), $H_3P–BH_3$[14] P–B 1.937(5) and $MeH_2P–BH_3$[15] 1.906(6) Å] do not allow the BH_3 unit to become more pyramidal, and the N–B–H angle in $H_3N–BH_3$ is only slightly larger [104.69(11)°][16] than in $H_3P–BH_3$, while the N–B [1.6722(5) Å] bond is much shorter than the P–B bond. Thus there is no reason to quote d-orbital participation on this basis.

The crystal structure of non-methylated $(H_2N)_3PBH_3$, determined in 1960 by Nordman,[17] shows that this simpler model compound also adopts almost C_s symmetry. The hydrogen positions in this case do not allow for an unambiguous determination of the geometry at the nitrogen centres, and the P–N distances do not reflect the inherent differences. At 123.3(6)° as a large B–P–N angle and 108.4(4) and 109.0(5)° as small B–P–N angles the distortion from C_3 symmetry is substantially larger than in the methylated analogue $(Me_2N)_3PBH_3$ [114.9(1)/112.7(1) and 111.8(1)°].

$(Me_2N)_3PNH$

The crystal structure of the *N*-trimethylsilyl derivative of $(Me_2N)_3PNH$ has recently been determined and allows one to assess the effect of silylation at the imino centre.[8] The Si atom in $(Me_2N)_3PNSiMe_3$ and the imino hydrogen atom in $(Me_2N)_3$-PNH are oriented in the same way relative to the PN_4 skeleton. The P–N–H angle is much smaller [115(2)°] than the corresponding P–N–Si angle [160.0(2)°]. The compound $(Me_2N)_3$-PNSiMe_3$ is almost C_s symmetric and has a P=N bond [1.542(2) Å], which is much shorter than that of $(Me_2N)_3PNH$. All this points to a marked electronic effect of the silyl group (electron pushing effect of the electropositive silicon) on the nature of the P=N bond.

$(Me_2N)_3PO$

In a number of crystallographic studies $(Me_2N)_3PO$ has been

Table 2 *Ab initio* calculated (MP2/6-31G*) geometrical parameter values for $(Me_2N)_3PF^+$ in its C_3 symmetrical ground state and its transition state of C_s symmetry. Distances are given in Å, angles in °

C_3 symmetry	(ground state)	C_s symmetry	(transition state)
r(P–X)	1.591	r(P–F)	1.582
r(P–N)	1.619	r(P–N_{ip})	1.617
		r(P–N_{oop})	1.636
r(N–C1)	1.475	r(N_{ip}–C)	1.478
r(N–C2)	1.470	r(N_{oop}–C)	1.475
		r(N_{oop}–C′)	1.477
F–P–N	105.6	F–P–N_{ip}	115.2
		F–P–N_{oop}	101.6
N–P–N	113.1	N_{ip}–P–N_{oop}	107.5
		N_{oop}–P–N_{oop}	123.5
P–N–C1	120.7	P–N_{ip}–C	122.6
P–N–C2	124.0	P–N_{oop}–C	122.1
		P–N_{oop}–C′	119.3
C–N–C	115.3	C–N_{ip}–C	113.0
		C–N_{oop}–C′	113.4
$\Sigma \angle$ (N)	360.0	$\Sigma \angle$ (N_{ip})	358.2
		$\Sigma \angle$ (N_{oop})	354.8

found co-crystallised as a solvent molecule with and without significant donor contacts to other constituents of the crystal lattice. Various geometries have been found, but most are close to either C_s[18] or C_3 symmetry.

Here we only want to focus on one example in order to demonstrate that the second minimum on the potential hypersurface is reasonably represented by one structure, where $(Me_2N)_3PO$ is co-crystallised with 1,7-dicarbadodecaborane and forms a hydrogen bridge network through its O atom:[19] the three O–P–N angles are reasonably similar [112.7, 111.5, 111.4°] and do not show the pronounced difference as in our structure of pure $(Me_2N)_3PO$ [118.7(1) and 110.0(1)°]; the N–P–N angles fall over a narrow range [107.3, 106.00, 107.7°], whereas they are different in our structure; and even the three pairs of torsion angles O–P–N–C describing the carbon positions of the NMe_2 groups are similar enough to speak of pseudo C_3 symmetry [−49.5, 133.9/−45.5, 147.6/−48.4, 146.4°]. In principal this indicates a subtle balance between the intramolecular energetics which slightly favours a C_s arrangement and the intermolecular forces and lattice fields like dipole moments, *etc*. According to the calculations the dipole moment of a free C_3 symmetric $(Me_2N)_3PO$ molecule is 19% higher (4.90 D) than that of the C_s symmetric $(Me_2N)_3PO$ (4.13 D), which might lead to a preference of the C_3 geometry in a polar surrounding, an effect which has been observed in many other cases.[20] This might be an important point for HMPA as ligand, where it is placed in a strongly polar surrounding of a metal centre, or as solvent, where the total dipole moment also depends on the solute.

Calculations on $(Me_2N)_3PF^+$

The cation $(Me_2N)_3PF^+$ is isoelectronic to the series of compounds $(Me_2N)_3P–X$ (X = BH_3, CH_2, NH or O) and just this year a structure determination of the ethyl analogue $(Et_2N)_3$-PF^+ in the form of the salt $[(Et_2N)_3PF^+][VMes_3F^−]$ (Mes = 2,4,6-trimethylphenyl) was published.[21] Although no crystallographic symmetry is imposed on the geometry of the cation, it is very close to C_3 symmetry. On the evidence of our results described above this was unexpected and so we carried out *ab initio* calculations for the cation geometry to exclude the distorting influence of the anion on the structure. Surprisingly the calculations also favoured C_3 over C_s symmetry by a small energy difference of 4.6 kJ mol⁻¹ (MP2/6-31G*). Relevant geometrical parameter values of the C_3 geometry are listed in Table 2, the two conformers are displayed in Fig. 2. We could not find close intramolecular H···H distances which would explain this finding and an analysis of the electronic contributions of the constituents of $(Me_2N)_3PF^+$ seems to be too com-

Table 3 *Ab initio* calculated (MP2/6-311G**) geometrical parameter values for $(H_2N)_3PF^+$ in its C_s symmetrical ground state and its transition state of C_3 symmetry. Distances are given in Å, angles in °, energies in Hartrees

| C_s symmetry	(ground state)	C_3 symmetry	(transition state)
r(P–F)	1.556	r(P–X)	1.561
r(P–N_{ip})	1.604	r(P–N_{ip})	1.609
r(P–N_{oop})	1.617		
r(N_{ip}–H)	1.012	r(N–H1)	1.011
r(N_{oop}–H)	1.011	r(N–H2)	1.010
r(N_{oop}–H′)	1.012		
F–P–N_{ip}	118.4	F–P–N_{ip}	107.6
F–P–N_{oop}	101.1		
N_{ip}–P–N_{oop}	105.8	N–P–N	111.3
N_{oop}–P–N_{oop}	125.6		
P–N_{ip}–H	120.5	P–N–H1	120.4
P–N_{oop}–H	120.8	P–N–H2	122.4
P–N_{oop}–H′	120.1		
H–N_{ip}–H	115.4	H–N–H	116.0
H–N_{oop}–H′	114.8		
$\Sigma \angle$ (N_{ip})	356.4	$\Sigma \angle$ (N)	358.8
$\Sigma \angle$ (N_{oop})	355.7		
E	−607.8271989	E	−607.8251296
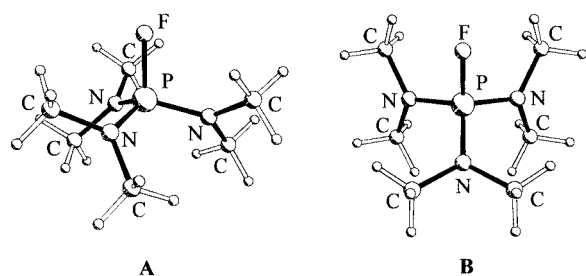
Fig. 2 *Ab initio* calculated molecular geometries of the C_3 and C_s structures of $(Me_2N)_3PF^+$.

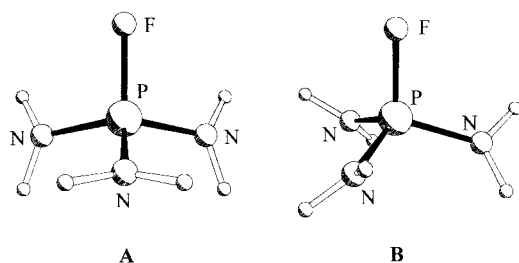**Fig. 3** *Ab initio* calculated molecular geometries of the C_s and C_3 structures of $(H_2N)_3PF^+$.

plex to provide us with a reliable explanation for these findings. The closest H · · · H distances between methyl groups of different NMe_2 units are 2.639 and 2.684 Å in the C_s conformer, but this cannot be used as an argument in favour of the C_3 geometry, as the closest H · · · H distances in $(Me_2N)_3PCH_2$, the compound with the narrowest N–P–N angle, are only 2.356 and 2.534 Å in the C_s conformer, which represents the global minimum.

We therefore reduced the complexity by examining the parent system $(H_2N)_3PF^+$ (shown in Fig. 3, geometry parameter values in Table 3), which is contradictorily predicted to adopt C_s symmetry, with this ground state being 5.4 kJ mol⁻¹ (MP2/6-311G**) lower than a C_3 geometry, which is not a local minimum on the potential hypersurface. This value has to be compared with that of $(H_2N)_3P$ in which the C_3 geometry is 10.3 kJ mol⁻¹ higher in energy than the C_s arrangement (MP2/6-311G**).

The size of this system $(H_2N)_3PF^+$ allows for a more rigorous theoretical treatment than can be employed for the $(Me_2N)_3P$

compounds. However, up to the MP2/6-311+G** level of theory the results did not depend very much on the degree of sophistication and consistently favoured the C_s geometry. An improvement of the treatment of electron correlation at the QCISD/6-31G* level did not change the situation.

Dipole moments and atomic charges

In order to obtain a set of data suitable for comparison of the molecular properties of the compounds $(Me_2N)_3P–X$ we calculated the molecular dipole moments and atomic charges (Mulliken charges) for the C_s arrangements and where possible for the C_3 geometries as well. These values are listed in Table 4.

It is interesting to see that there is no monotonous increase in the dipole moments in the series X = BH_3, CH_2, NH, O, F⁺, as could be expected and is calculated for the charge of the phosphorus atom. Clearly the borane adduct and the cationic fluorine compound have exceptional values for the dipole moments and the reason has thus to be found in the particular nature of the X group. The borane compound is the only one with negatively polarised hydrogen atoms attached to the X atom, which leads to a larger charge separation between the phosphonium unit and the centre of the negative charge in the middle of the triangle spanned by the H atoms.

The fluorine compound is the only cation in the isoelectronic series. It has the most positively charged phosphorus centre, but the fluorine atom is much less negatively charged (−0.41 e) than the oxygen atom in $(Me_2N)_3PO$ (−0.76 e). This leads in total to a dipole moment less than half the value for $(Me_2N)_3PF^+$ as compared to $(Me_2N)_3PO$. The positive charge is found distributed over the whole molecule, including the periphery of hydrogen atoms.

The charges of the nitrogen atoms of the dimethylamino groups are surprisingly invariant as well for the different X groups, but also for the different molecular symmetries resulting in markedly different geometries and P–N bond lengths for these units. The small changes do not allow for a sensible interpretation of these results.

Conclusion

With the structure determination of $(Me_2N)_3PBH_3$, $(Me_2N)_3$-PNH and $(Me_2N)_3PO$ and the calculations on $(Me_2N)_3P–X$ (X = BH_3, CH_2, NH, O or F⁺) we have established data which allow for a systematic comparison of the effects of the X group in $N_3P–X$ units of an isoelectronic series of compounds. However, the nature of the bonding in these compounds seems to be a subtle balance between various contributions, which are neither easy to separate nor to quantify. Such contributions include lone pair–lone pair repulsion, planarisation of nitrogen, deformation of the co-ordination sphere of phosphorus, van der Waals repulsion between the methyl groups in the periphery, interaction between the electron distribution in the P–X bond and the PN_3 fragment, *etc.*

All molecules, except $(Me_2N)_3PF^+$, prefer C_s geometries, although the C_3 geometries (where possible) are also local minima on the potential hypersurface and can be found if the surrounding dictates the structure by polarity or steric requirements as observed in the case of $(Me_2N)_3PO$. The ion $(Me_2N)_3PF^+$ prefers the C_3 over the C_s conformation, although the non-methylated $(H_2N)_3PF^+$ does the opposite and there are no close H · · · H distances in $(Me_2N)_3PF^+$, which could serve to rationalise this. However, not only is there a preference for the C_3 conformation in $(Me_2N)_3PF^+$, the other conformer does not even correspond to a local minimum in this case. The energy differences between the C_3 and the C_s conformations (where possible) does not show any obvious dependence on electronic requirements of the X groups.

An analysis of the dipole moments of the compounds reveals that the hydrogen atoms in the X groups may play a significant

Table 4 *Ab initio* calculated molecular dipole moments μ^a/D and atomic charges q/e (Mulliken charges) (MP2/6-31G*) for the molecules $(Me_2N)_3P–X$ with X = BH_3, CH_2, NH, O or F^+ in C_s and where appropriate in C_3 symmetry

	X										
	BH_3		CH_2	NH	O		F^+		$(H_2N)_3PF^+$	
	C_s	C_3	C_s	C_s	C_s	C_3	C_s	C_3	C_s	C_3
μ	5.21	5.96	2.592	3.27	4.13	4.90	2.02	2.05	3.17	2.63
$q(P)$	1.45	1.41	1.48	1.58	1.70	1.68	1.72	1.70	1.60	1.62
$q(X)$	−0.20	−0.20	−0.83	−0.97	−0.76	−0.76	−0.41	−0.42	−0.38	−0.38
$q(N)^b$	−0.79	−0.78	−0.77	−0.78	−0.78	−0.78	−0.76	−0.76	−0.97	−1.00
$q(N_{oop})$	−0.77		−0.76	−0.77	−0.77		−0.75		−0.97	

^{a} Reference point for the dipole moments is the centre of mass of the molecules. ^{b} Denotes the "in plane" nitrogen atom in the case of C_s symmetry.

Table 5 Crystallographic data for $(Me_2N)_3PBH_3$, $(Me_2N)_3PNH$ and $(Me_2N)_3PO$

	$(Me_2N)_3PBH_3$	$(Me_2N)_3PNH$	$(Me_2N)_3PO$
Formula	$C_6H_{21}BN_3P$	$C_6H_{19}N_4P$	$C_6H_{18}N_3OP$
Formula weight	177.04	178.22	179.20
T/K	158(2)	163(2)	163(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	$P2_1/n$	$P2_1/m$
a/Å	12.996(2)	8.2190(9)	6.398(1)
b/Å	11.174(1)	10.0901(3)	12.570(3)
c/Å	7.679(1)	12.1644(14)	6.428(1)
β/°	96.29(1)	97.512(6)	104.19(3)
U/Å^3	1108.4(2)	1000.1(2)	501.2(2)
Z	4	4	2
μ/mm^{-1}	0.201	0.228	0.232
Reflections collected/ independent	4672	2863/2177	3326/1671
R_{int}	0.026	0.013	0.024
Final R $(F > 4\sigma(F^2))$	0.0207	0.0360	0.0427
$wR2$ (all data)	0.0556	0.1054	0.1162

role, *e.g.* for the exceptionally high dipole moment in $(Me_2N)_3$-PBH_3. The charge of the phosphorus centre in $(Me_2N)_3P–X$ is the only value which is readily explained by the increasing electronegativity of the group X or its binding atom along the first period of the Periodic Table.

The electronic nature of the N_3PX unit is so complicated that it seems impossible to generalise findings to identify trends with varying X groups. The largely different chemical reactivity confirms these conclusion drawn from structural and electronic properties. More detailed investigations, theoretical in particular, are necessary to provide us with a more detailed picture of these differences.

Experimental

Materials

A sample of $P(NMe_2)_3$ was prepared by the ammonolysis of PCl_3 with $HNMe_2$ according to a literature procedure.[22] The compound $(Me_2N)_3PBH_3$ was synthesized by treating $P(NMe_2)_3$ with $BH_3\cdot THF$ and was purified by distillation,[22] $(Me_2N)_3PNH$ and $(Me_2N)_3PO$ were commercial samples.

Single crystal X-ray diffraction experiments

Cylindrical crystals of $(Me_2N)_3PNH$ and $(Me_2N)_3PO$ (>0.8 mm long, *ca.* 0.4 mm diameter) were grown from the melt in a capillary by cooling the sample at *ca.* 60 K h^{-1} after growing a seed crystal in a solid–liquid equilibrium established close to the melting point. A crystal of $(Me_2N)_3PBH_3$ grown from a hexane solution was selected and mounted under argon in a glass capillary. No absorption correction was applied for all three structures. The structure solutions were carried out by direct methods,[20] the refinements on F^2.[21] All H atom positions were located in Fourier-difference maps and isotropically

refined. The crystal data and refinement parameters for the three compounds are listed in Table 5.

CCDC reference number 186/1590.

See http://www.rsc.org/suppdata/dt/1999/3177/ for crystallographic files in .cif format.

Ab initio calculations

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 program.[23] Geometry optimisations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 (only geometry optimisations) levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G*,[24] 6-31G*[25] basis sets, while the larger basis set was used for calculations at the MP2 level of theory. The geometries of $(H_2N)_3PF^+$ were calculated in a series of theory levels up to QCISD/6-31G* for C_3 and C_s symmetry.

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