The Bis(methylene) Metaphosphite, $[P(CH_2)_2]^-$, and Tris(methylene) Metaphosphate, $[P(CH_2)_3]^-$, Families of Anions. An Experimental and *Ab initio* Study *

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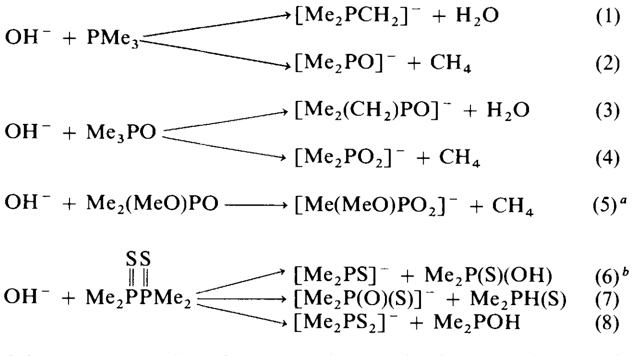
Collisional activation of a number of phosphorus-containing anions yields families of negative ions based on bis(methylene) metaphosphite, $[P(CH_2)_2]^-$, and tris(methylene) metaphosphate, $[P(CH_2)_3]^-$, structures. Individual product ions produced include $[P(CH_2)_2]^-$, $[CH_2PO]^-$, $[CH_2PS]^-$, $[PO_2]^-$, $[POS]^-$, and $[PS_2]^-$, together with $[P(CH_2)_3]^-$, $[(CH_2)_2PO]^-$, $[CH_2PO_2]^-$, $[(CH_2)_2PS]^-$, $[CH_2P(O)(S)]^-$, and $[CH_2PS_2]^-$. *Ab initio* calculations indicate that all bonds to phosphorus (in these ions) show appreciable double bond character, and that all methylene-containing phosphorus anions have coplanar atoms except $[P(CH_2)_3]^-$, which shows out-of-plane twisting of the methylene groups to give an ion of D_3 symmetry.

There has recently been theoretical and experimental interest in multiply bonded phosphorus systems, both neutral species[1–6] and ions. Ions which have been studied include $[PO]^-$,[7–9] $[PCH_2]^-$,[10] $[PO_2]^-$,[8,11,12] $[POS]^-$,[13] $[PO_3]^-$,[14] $[PS_3]^-$,[15] and $[P(CH_2)_3]^-$.[16] Two ions of particular interest in the context of this paper are the metaphosphite ion $[PO_2]^-$, the ground state of which has C_{2v} symmetry, and has a calculated (6-31 G*) PO bond length of 1.48 Å and OPO angle of 118°,[12] and the tris(methylene) metaphosphate ion $[P(CH_2)_3]^-$ which is calculated (MP2/3-21 + G*) to have a minimum-energy D_3 structure with the CH_2 groups twisted 19° from the molecular plane.[16] This ion has not been observed experimentally but complex salts containing the $[P(=C\langle)_3]^-$ moiety have been isolated.[1]

We have undertaken a study directed towards the formation of the ions bis(methylene) metaphosphite, $[P(CH_2)_2]^-$, tris(methylene) metaphosphate, $[P(CH_2)_3]^-$, and related species. This paper describes the formation and possible structures of six $[PXY]^-$ ions (X and Y = CH_2, O, or S), and six $[PXYZ]^-$ ions (X, Y, and Z = CH_2, O, or S). The experimental method adopted for the formation of appropriate ions involves the formation of suitable precursor ions by reaction of OH^- with the neutral species PMe_3, Me_3PO, $Me_2(MeO)PO$, and $Me_2P(S)P(S)Me_2$ in the chemical ionization source of a VG ZAB 2HF mass spectrometer, and collisional activation of the precursor ions with helium in a collision cell to form a variety of product ions including species $[PXY]^-$ and $[PXYZ]^-$ (Scheme 1).



$$OH^- + PMe_3 \longrightarrow [Me_2PCH_2]^- + H_2O \qquad (1)$$
$$OH^- + PMe_3 \longrightarrow [Me_2PO]^- + CH_4 \qquad (2)$$
$$OH^- + Me_3PO \longrightarrow [Me_2(CH_2)PO]^- + H_2O \qquad (3)$$
$$OH^- + Me_3PO \longrightarrow [Me_2PO_2]^- + CH_4 \qquad (4)$$
$$OH^- + Me_2(MeO)PO \longrightarrow [Me(MeO)PO_2]^- + CH_4 \qquad (5)^a$$
$$OH^- + Me_2\overset{S}{\overset{\|}{P}}\overset{S}{\overset{\|}{P}}Me_2 \longrightarrow [Me_2PS]^- + Me_2P(S)(OH) \qquad (6)^b$$
$$\longrightarrow [Me_2P(O)(S)]^- + Me_2PH(S) \qquad (7)$$
$$\longrightarrow [Me_2PS_2]^- + Me_2POH \qquad (8)$$

Scheme 1. Formation of precursor ions. [a] The deprotonation reaction $OH^- + Me_2(MeO)PO \longrightarrow [Me(MeO)(CH_2)PO]^- + H_2O$ is also observed. [b] The competitive deprotonation reaction yielding the ion $[Me_2\overset{S}{\overset{\|}{P}}\overset{S}{\overset{\|}{P}}(Me)(CH_2)]^- + H_2O$ is a minor process

Results and Discussion

Collisional activation (c.a.) mass spectra were determined with a VG ZAB 2HF mass spectrometer; details are given in the Experimental section.

A. Formation of Precursor Ions.—The eight precursor ions used in this study were formed by reactions (1)—(8) in Scheme 1. Most reactions are straightforward, *e.g.* deprotonation[17] [equations (1)—(3)] and nucleophilic displacement [equation (6)]. The reactions shown in equations (2), (4), (5), and (7) are of a standard type which have been studied extensively in cognate systems, particularly for alkylsilanes[18] and boranes.[19] For example, in the case of reaction (2) the initial adduct $[Me_3POH]^-$ should transform through the ionic complex $[Me^-(Me_2POH)]$ to the products, $[Me_2PO]^-$ plus methane. The formation of $[Me_2PS_2]^-$ [equation (8)] seems unusual; a plausible mechanism could involve rearrangement of neutral $Me_2P(S)P(S)Me_2$ to $Me_2P(S)SPMe_2$ followed by nucleophilic displacement to yield directly $[Me_2PS_2]^-$.

$$[Me_2PCH_2]^- \longrightarrow [CH_2PCH_2]^- + CH_4 \qquad (9)$$
$$[Me_2PO]^- \longrightarrow [CH_2PO]^- + CH_4 \qquad (10)$$
$$[Me_2(CH_2)PO]^- \longrightarrow [CH_2PO]^- + C_2H_6 \qquad (11)$$
$$[Me_2PS]^- \longrightarrow [CH_2PS]^- + CH_4 \qquad (12)$$
$$[Me_2PO_2]^- \longrightarrow [PO_2]^- + C_2H_6 \qquad (13)$$
$$[Me(MeO)PO_2]^- \longrightarrow [PO_2]^- + OMe_2 \qquad (14)$$
$$[Me_2P(O)(S)]^- \longrightarrow [POS]^- + C_2H_6 \qquad (15)$$
$$[Me_2PS_2]^- \longrightarrow [PS_2]^- + C_2H_6 \qquad (16)$$

Scheme 2. Formation of two-co-ordinate phosphorus negative ions by collisional activation

B. Formation of the Bis(methylene) Metaphosphite Ion and Related Species.—The c.a. mass spectra of the product ions of equations (1)—(8) are shown in the Table. The c.a. mass spectra

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* *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, Torr ≈ 133 Pa. a.u. = hartree = $4.359\,8 \times 10^{-8}$ J.

Table. Collisional activation mass spectra of product ions from equations (1)—(8) and of some deuterium-labelled derivatives[*]

$[\mathrm{Me_2PCD_2}]^-$	76 ($\mathrm{H}^{\bullet}$) 68, 75 ($\mathrm{H_2} + \mathrm{D}^{\bullet}$) 58, 61 ($\mathrm{CH_4}$) 100, 60 (MeD) 78
$[\mathrm{Me(CD_3)PCH_2}]^-$	77 ($\mathrm{H}^{\bullet}$) 100, 76 ($\mathrm{H_2} + \mathrm{D}^{\bullet}$) 38, 75 (HD) 33, 62 ($\mathrm{CH_4}$) 37, 61 (MeD) 34, 59 ($\mathrm{CD_3H}$) 42
$[\mathrm{Me_2PO}]^-$	76 ($\mathrm{H}^{\bullet}$) 100, 75 ($\mathrm{H_2}$) 56, 62 ($\mathrm{Me}^{\bullet}$) 51, 61 ($\mathrm{CH_4}$) 42, 47 ($\mathrm{C_2H_6}$) 4
$[\mathrm{Me(CD_3)PO}]^-$	78 ($\mathrm{H}^{\bullet}$) 100, 77 ($\mathrm{H_2} + \mathrm{D}^{\bullet}$) 33, 76 (HD) 25, 64 ($\mathrm{Me}^{\bullet}$) 62, 62 (MeD) 68, 61 ($\mathrm{CD_3}^{\bullet}$) 65, 60 ($\mathrm{CD_3H}$) 23, 47 ($\mathrm{C_2H_3D_3}$) 9
$[\mathrm{Me_2(CH_2)PO}]^-$	90 ($\mathrm{H}^{\bullet}$) 94, 75 ($\mathrm{CH_4}$) 100, 61 ($\mathrm{C_2H_6}$) 13, 47 ($\mathrm{C_3H_8}$) 10
$[\mathrm{Me_2PO_2}]^-$	92 ($\mathrm{H}^{\bullet}$) 100, 78 ($\mathrm{Me}^{\bullet}$) 53, 77 ($\mathrm{CH_4}$) 58, 63 ($\mathrm{C_2H_6}$) 18
$[\mathrm{Me(MeO)PO_2}]^-$	106 ($\mathrm{H}^{\bullet}$) S, 92 ($\mathrm{Me}^{\bullet}$) 28, 77 ($\mathrm{CH_2O}$) 100, 75 (MeOH) 26
$[\mathrm{Me_2PS}]^-$	92 ($\mathrm{H}^{\bullet}$) 19, 91 ($\mathrm{H_2}$) 100, 78 ($\mathrm{Me}^{\bullet}$) 49, 77 ($\mathrm{CH_4}$) 13, 63 ($\mathrm{C_2H_6}$) 2, 33 ($\mathrm{C_2H_5P}$) 6
$[\mathrm{Me_2P(O)(S)}]^-$	108 ($\mathrm{H}^{\bullet}$) 100, 107 ($\mathrm{H_2}$) 18, 94 ($\mathrm{Me}^{\bullet}$) 4, 93 ($\mathrm{CH_4}$) 15, 79 ($\mathrm{C_2H_6}$) 5, 33 ($\mathrm{C_2H_5PO}$) 1
$[\mathrm{Me_2PS_2}]^-$	124 ($\mathrm{H}^{\bullet}$) 100, 110 ($\mathrm{Me}^{\bullet}$) 85, 109 ($\mathrm{CH_4}$) 65, 95 ($\mathrm{C_2H_6}$) 25, 91 ($\mathrm{H_2S}$) 12, 78 (MeS) 9, 63 ($\mathrm{C_2H_6S}$) 2, 33 ($\mathrm{C_2H_5PS}$)

[*] Given as: m/z (species lost) abundance (%).

of product ions from the reactions of OH^- with $\mathrm{PMe_2(CD_3)}$ are also shown in the Table. The data in the Table provide information concerning a large number of interesting product ions including a family of ions related to $[\mathrm{P(CH_2)_2}]^-$. The formation of such ions from each of the eight precursor ions is summarised in equations (9)—(16) (Scheme 2).

A typical c.a. mass spectrum is shown in Figure 1. The $[\mathrm{Me_2PCH_2}]^-$ ion fragments by competitive losses of $\mathrm{H}^{\bullet}$, $\mathrm{H_2}$, $\mathrm{CH_4}$, $\mathrm{C_2H_6}$, and $\mathrm{MePCH_2}$. Elimination of methane yields the base peak in the spectrum; the origin of this loss has been explored by deuterium labelling. The data listed in the Table for $[\mathrm{Me_2PCD_2}]^-$ and $[\mathrm{Me(CD_3)PCH_2}]^-$ show (*i*) that the ions fragment without scrambling of the label,[*] (*ii*) that $[\mathrm{Me_2PCD_2}]^-$ loses $\mathrm{CH_4}$ [equation (17)] and MeD [equation (18)] in the ratio 1.3:1, and (*iii*) that $[\mathrm{Me(CD_3)PCH_2}]^-$ loses $\mathrm{CH_4}$:$\mathrm{CH_3D}$:$\mathrm{CD_3H}$ in the ratio 1.7:1:1.7. Thus there are two losses of $\mathrm{CH_4}$: the major loss indicates formation of the bis(methylene) metaphosphite ion, $[\mathrm{P(CH_2)_2}]^-$ [equation (9); see also equation (17)].

$$[\mathrm{Me_2PCD_2}]^- \begin{array}{l} \nearrow [\mathrm{CH_2PCD_2}]^- + \mathrm{CH_4} \quad (17) \\ \searrow [\mathrm{MePCD}]^- + \mathrm{MeD} \quad (18) \end{array}$$

We have not studied the intimate mechanisms of the reactions in Scheme 2 by *ab initio* calculations since they appear analogous to standard reactions of other systems.[18,19] The majority are likely to proceed through methyl anion complexes, *e.g.* $[\mathrm{Me}^-(\mathrm{MePCH_2})]$ for equation (9). Such a bound methyl anion can effect deprotonation [reactions (9), (10),[†] and (12)] or an internal S_N2 reaction [equations (11), (13), (15), and (16)]. Reaction (14) is entirely analogous, involving nucleophilic displacement in a bound methoxide anion complex.

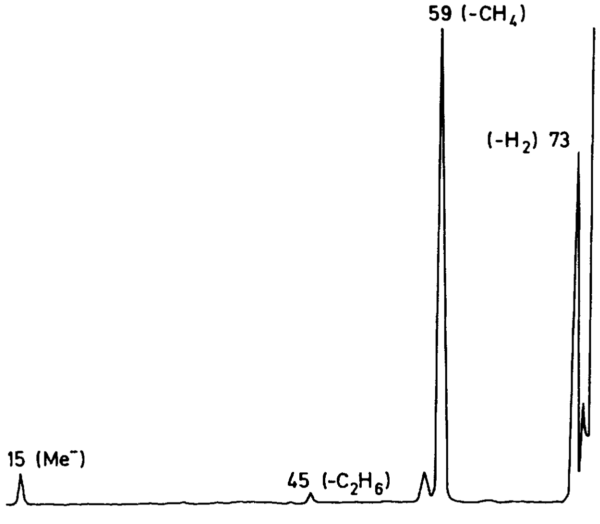

Figure 1. Collision activation mass spectrum of $[\mathrm{Me_2PCH_2}]^-$ (values given are m/z)

$$[\mathrm{Me_2PCH_2}]^- \longrightarrow [\mathrm{P(CH_2)_3}]^- + \mathrm{H_2} \tag{19}$$

$$[\mathrm{Me_2PO}]^- \longrightarrow [\mathrm{(CH_2)_2PO}]^- + \mathrm{H_2} \tag{20}$$

$$[\mathrm{Me_2(CH_2)PO}]^- \longrightarrow [\mathrm{(CH_2)_2PO}]^- + \mathrm{CH_4} \tag{21}$$

$$[\mathrm{Me_2PO_2}]^- \longrightarrow [\mathrm{CH_2PO_2}]^- + \mathrm{CH_4} \tag{22}$$

$$[\mathrm{Me(MeO)PO_2}]^- \longrightarrow [\mathrm{CH_2PO_2}]^- + \mathrm{MeOH} \tag{23}$$

$$[\mathrm{Me_2PS}]^- \longrightarrow [\mathrm{(CH_2)_2PS}]^- + \mathrm{H_2} \tag{24}$$

$$[\mathrm{Me_2P(O)(S)}]^- \longrightarrow [\mathrm{CH_2P(O)(S)}]^- + \mathrm{CH_4} \tag{25}$$

$$[\mathrm{Me_2PS_2}]^- \longrightarrow [\mathrm{CH_2PS_2}]^- + \mathrm{CH_4} \tag{26}$$

Scheme 3. Formation of $[\mathrm{P(CH_2)_3}]^-$ together with oxygen and sulphur analogues

C. Formation of the Tris(methylene) Metaphosphate Anion and Related Species.—Precursor ions used for the formation of $[\mathrm{P(CH_2)_3}]^-$ and related ions are shown in Scheme 1. Full c.a. mass spectra of those ions are listed in the Table. In Scheme 3 are summarised those collision induced processes [equations (19)—(26)] which produce three-co-ordinate phosphorus anions. The reactions shown in equations (19) and (20) are of particular importance: we have studied these processes by deuterium labelling (see Table).

The collision induced dissociations of $[\mathrm{Me_2PCD_2}]^-$ and $[\mathrm{Me(CD_3)PCH_2}]^-$ indicate no H/D scrambling prior to fragmentation (Table). The $[\mathrm{Me_2PCH_2}]^-$ ion loses $\mathrm{H}^{\bullet}$ and $\mathrm{H_2}$ in the ratio 1:5 (see Figure 1), $[\mathrm{Me_2PCD_2}]^-$ loses $\mathrm{H}^{\bullet}$ and ($\mathrm{H_2} + \mathrm{D}^{\bullet}$) in the ratio 1.2:1, and $[\mathrm{Me(CD_3)PCH_2}]^-$ loses $\mathrm{H}^{\bullet}$, ($\mathrm{H_2} + \mathrm{D}^{\bullet}$), and HD in the ratio 3:1.1:1. Thus a major loss of $\mathrm{H_2}$ from $[\mathrm{Me_2PCH_2}]^-$ involves both methyl groups. A plausible rationale for the process is shown in equation (27). Similarly,

$$[\mathrm{Me_2PCH_2}]^- \longrightarrow \{\mathrm{H}^-[\mathrm{MeP(CH_2)_2}]\} \longrightarrow [\mathrm{P(CH_2)_3}]^- + \mathrm{H_2} \tag{27}$$

$$[\mathrm{Me_2PO}]^- \longrightarrow \{\mathrm{H}^-[\mathrm{Me(CH_2)PO}]\} \longrightarrow [\mathrm{(CH_2)_2PO}]^- + \mathrm{H_2} \tag{28}$$

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[*] There is no evidence of H/D scrambling in these systems, *e.g.* there is no loss of $\mathrm{CD_2H_2}$ from $[\mathrm{Me(CD_3)PCH_2}]^-$. There is a report[20] that proton exchange occurs for $[\mathrm{Me_3P^+CH_2}^-]$ in the condensed phase; perhaps this is an inter-molecular transfer.

[†] The ion $[\mathrm{Me(CD_3)PO}]^-$ loses MeD and $\mathrm{CD_3H}$ in the ratio 1:2.9 (Table). Reaction (10) is likely to proceed through $[\mathrm{Me}^-(\mathrm{MePO})]$, thus initial C–P bond cleavage must have a large secondary deuterium isotope effect. An analogous situation is observed for the loss of methane from the t-butoxide negative ion.[21]

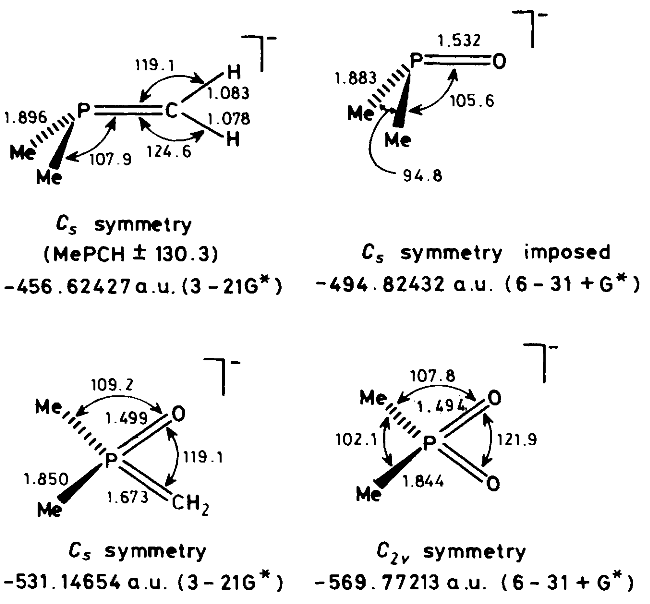

Figure 2. *Ab initio* calculations on precursor ions (distances in Å, angles in °)

$$[Me_2(CH_2)PO]^- \longrightarrow \{Me^-[Me(CH_2)PO]\}^- \longrightarrow [(CH_2)_2PO]^- + CH_4 \quad (29)$$

$$[Me(MeO)PO_2]^- \longrightarrow [MeO^-(MePO_2)] \longrightarrow [CH_2PO_2]^- + MeOH \quad (30)$$

$[Me_2PO]^-$ loses H• and H_2 in the ratio 1.8:1, while $[Me(CD_3)PO]^-$ loses H•, (D• + H_2), and HD in the ratio 4:1.3:1. Again a major loss of H_2 comes from both methyl groups and we suggest the mechanism shown in equation (28). We have not carried out labelling studies on other precursor ions shown in Scheme 3, but we believe reactions (24) and (25) are analogous to (19) and (20) respectively. Reactions (21)—(23) and (26) are of standard type [*cf.*, for example, equations (29) and (30)].

D. Ab initio Structural Studies.—The results of *ab initio* calculations on the more important of the precursor ions (see Scheme 1) are shown in Figure 2. Those of two-co-ordinate phosphorus anions (Scheme 2) and three-co-ordinate phosphorus anions (Scheme 3) are shown in Figures 3 and 4 respectively.

All calculations employed the standard routines of GAUSSIAN 86.[22] The approximate ground singlet-state geometries of the smaller molecules (Figures 3 and 4) were obtained by the Berny optimization procedure at the RHF/3-21G* level (*d*-type functions added to phosphorus and sulphur centres only). The modest mass storage demands of this basis set allowed us to confirm that we had found in each case an energy minimum by way of a test of wavefunction stability and a harmonic frequency analysis, independent of any imposed symmetry. The geometries were then refined within the established symmetries at extended basis sets: for example, 6-31G* (*d*-type functions on all non-hydrogen centres) and 6-31 + G* (additional low exponent functions at all centres). These final geometries and absolute energies are listed in Figures 3 and 4. The inclusion of low exponent (or diffuse) functions made no significant change to geometries, as would be expected since these functions improve the representation of the outer parts of the molecule (important in van der Waals and hydrogen bonding) and have little effect for normal bonds. On the other hand, consistent inclusion of *d*-type 'polarisation' functions on phosphorus was essential to reproduce normal bond lengths since the orbitals extending from phosphorus clearly incorporate significant *d*-orbital character.†

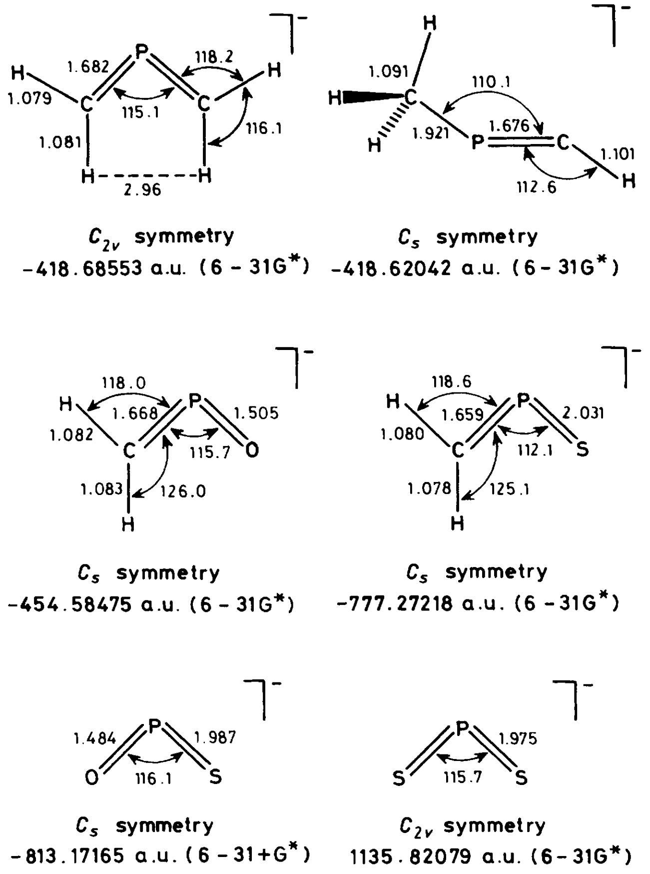

Figure 3. *Ab initio* calculations on two-co-ordinate phosphorus anions (distances in Å, angles in °)

The strategy of structure determination described above was also attempted for the larger ions presented in Figure 2, but the harmonic frequency analysis failed through insufficient file space for all ions except $[Me_2PO_2]^-$. Accordingly, the geometries of $[Me_2(CH_2)PO]^-$ and $[Me_2PCH_2]^-$ were optimised without symmetry constraints at 3-21G* and each was found to adopt a plane of symmetry, mirroring the methyl groups, and embracing the OPC and the PCH_2 centres respectively. $[Me_2PO]^-$ was assumed to have C_s symmetry and was optimised at the 6-31 + G* level.

The Me–P distances displayed in Figures 2 and 3 (1.84—1.92 Å) conform with the range of values found experimentally.[23] In Figures 2 and 3 we identify these in conventional valence bond formalism as single bonds. In contrast, the phosphorus–methylene distances listed in Figures 2—4 are significantly shorter (1.63—1.70 Å). Our calculated phosphorus–methylene distance for $[P(CH_2)_3]^-$ is 1.68 Å, which compares favourably with the previously calculated value of 1.67 Å,[16] and with the crystallographically determined range of 1.67—1.69 Å found for a fluorenyl trimethylsilyl derivative of the tris(methylene) metaphosphate ion.[1] We agree with these earlier reports that such distances signify that phosphorus–methylene bonds

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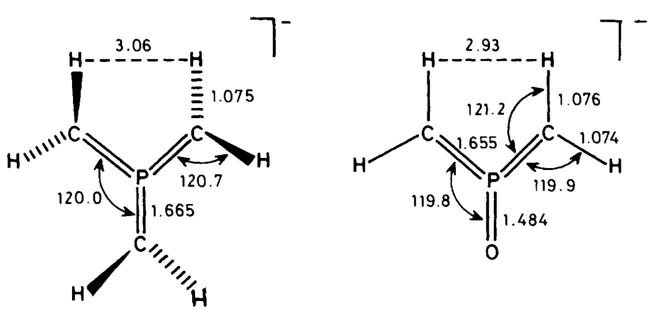
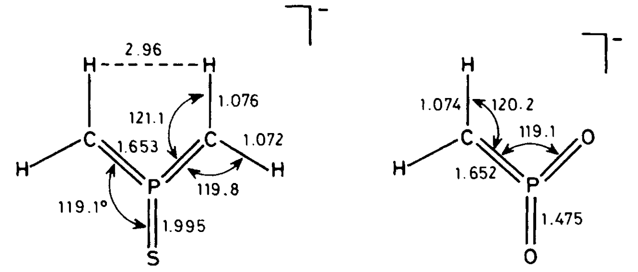
† A referee has suggested that the ground states of the reported anions could have radical character. This possibility can be excluded since the wavefunction for each species is stable when the RHF condition is lifted.



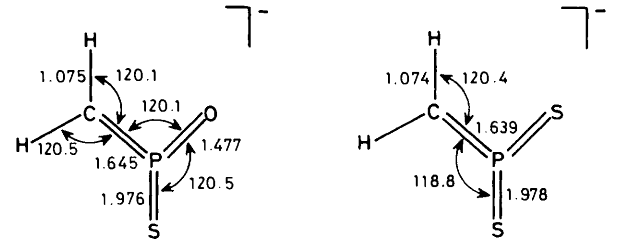
D_3 symmetry (22.2° twist optimum) -457.66784 a.u. (6-31G*)

C_{2v} symmetry -493.58329 a.u. (6-31G*)



C_{2v} symmetry -816.25363 a.u. (6-31G*)

C_{2v} symmetry -529.52694 a.u. (6-31+G*)



C_s symmetry -848.07888 a.u. (6-31+G*)

C_{2v} symmetry -1174.82711 a.u. (6-31G*)

Figure 4. *Ab initio* calculations on three-co-ordinate phosphorus anions (distances in Å, angles in °)

possess significant double bond character, since all the methylene groups shown in Figures 3 and 4 are planar, implying little carbanion character.

A similar situation applies for the phosphorus–oxygen distances listed in Figures 2—4. A phosphorus–oxygen single bond is normally in the range 1.55—1.67 Å;[23] our calculated phosphorus–oxygen distances are in the range 1.48—1.53 Å, indicative of appreciable double bond character. These values should be compared with the calculated value of 1.475 Å for $[PO_3]^-$,[16] and of 1.47 Å for phosphine oxide.[16,24] We have accordingly drawn the valence-bonded structures in Figures 2—4 to reflect this prevailing double bonding between oxygen and phosphorus.

We undertook the calculation of geometries and absolute energies to provide support for the structures of precursor and product ions suggested by our experimental observations (Schemes 1—3). Sometimes there are cases of possible isomerism where the thermodynamic stability of each isomer needs to be established. An illustration concerns the losses of methane from $[Me_2PCH_2]^-$; here, two product ions, $[P(CH_2)_2]^-$ and $[MePCH]^-$, are formed [*cf.* equations (17) and (18)]. Both ions are shown in Figure 3; the bis(methylene) metaphosphite ion is the more stable by 40 kJ mol^{-1}.

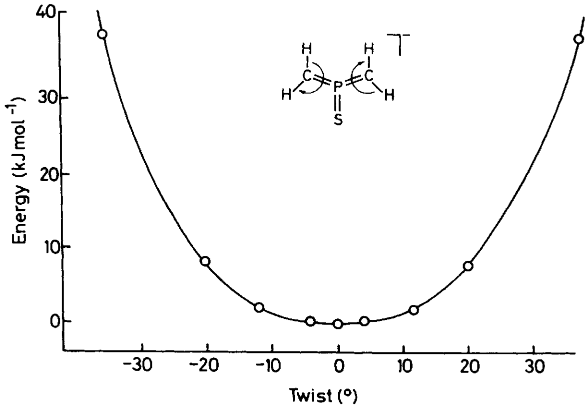


Figure 5. Potential energy *versus* degree of twist (within C_2 symmetry) in $[(CH_2)_2PS]^-$ at 6-31G* level.

We confirm the previously reported result[16] that the stable form of $[P(CH_2)_3]^-$ is that where the methylene groups are twisted out of plane [19° (ref. 16), 22° (this study)] to give an ion of D_3 symmetry [the D_3 structure is more stable than the coplanar D_{3h} structure by only 6.3 kJ mol^{-1} (ref. 16), 6.7 kJ mol^{-1} (this study)]. This D_3 symmetry is achieved by relaxation from any random and staggered setting of the methylene groups that we have tried. In contrast, all other methylene-containing phosphorus anions listed in Figures 3 and 4 have all atoms coplanar and show no out-of-plane twisting of methylene groups. If these ions are allowed to relax from an initial twisted conformation *they always become coplanar.* A particular illustration of this feature is shown for $[(CH_2)_2PS]^-$ in Figure 5.

The methylene group twist in $[P(CH_2)_3]^-$ involves small energy changes and probably results from a small force acting on a very small phosphorus–methylene torsional force constant. This seems reasonable since there is only partial π bonding due to poor overlap of the diffuse phosphorus p and d orbitals with the carbon p orbitals. It is not clear however what this displacing force is. We agree with Schaefer and co-workers[16] that the cause does not lie in steric overcrowding. If it did, we would observe similar twisting in the bis(methylene) derivatives (illustrated in Figures 3 and 4) since they have similar inter-hydrogen distances to those of $[P(CH_2)_3]^-$. However, we think it unlikely that the twist results from long-range coulombic repulsion between the methylene groups,[16] since such an effect should occur for any pair of methylene groups and thus be evident for bis(methylene) derivatives. We do not observe such effects.

In summary, collisional activation studies of phosphorus-containing negative ions suggest the formation of a number of stable product negative ions related to $[P(CH_2)_2]^-$ and $[P(CH_2)_3]^-$. *Ab initio* calculations support these observations, and indicate that bonds to phosphorus in the species $[PXY]^-$ and $[PXYZ]^-$ (X, Y, and Z = CH_2, O, or S) have substantial double bond character. However the double bonds are inherently diffuse and torsionally weak, since when either X = Y = CH_2 or X = Y = Z = CH_2 it requires little energy to rotate the planar methylene groups out of the molecular plane. For example, Figure 5 illustrates for $[(CH_2)_2PS]^-$, that for as little as 16 kJ mol^{-1}, a displacement of 30° can be effected.

In the specific case of $[P(CH_2)_3]^-$ the ground-state conformer has D_3 symmetry [twist angle 19° (ref. 16), 22° (this study)]. This behaviour manifests itself only when there are three methylene groups arranged around phosphorus. In all ions containing two methylene groups, *ab initio* calculations indicate ground-state structures in which all the atoms are coplanar.

Experimental

Negative ion chemical ionization mass spectra and collisional activation (c.a.) mass spectra were measured with an MM VG ZAB 2HF mass spectrometer. The chemical ionization slit was used in the ion source: ionizing energy 70 eV (tungsten filament), ion source temperature 180 °C, and accelerating voltage -8 kV. All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[25,26] The reagent ion OH^- was formed from water (introduced through the septum inlet system maintained at 100 °C).[27] The indicated source pressure of water was typically 5×10^{-4} Torr. Trimethylphosphine was introduced into the ion source through a specially constructed gas inlet system. $Me_2(MeO)PO$ was introduced through the septum inlet at 150 °C. Solids were introduced through the direct probe: $Me_3P{=}O$ and $[Me_2P(S)]_2$ with an indicated probe temperature of 20 °C. The substrate pressure was typically 5×10^{-7} Torr. The estimated total pressure in the ion source was 10^{-1} Torr. The pressure of helium in the second collision cell (for c.a. mass spectra) was 2×10^{-7} Torr, measured by an ion gauge situated between the collision cell and the electric sector. This produced a decrease in the main beam signal of *ca.* 10% and thus corresponds to essentially single collision conditions.

Trimethylphosphine was prepared by heating $[\{AgI(PMe_3)\}_4]$;[28] trimethylphosphine oxide,[29] dimethyl(methoxy)phosphine oxide,[30] and tetramethyldiphosphine disulphide[31] were prepared by reported procedures. Helium used was of purity 99.997%.

Preparation of $PMe_2(CD_3)$.—Dimethylphosphine was prepared from tetramethyldiphosphine disulphide in 60% yield by a reported procedure.[32] Dimethylphosphine was converted into $Me_2(CD_3)P(HI)$ by reaction with $[^2H_3]$methyl iodide at 0 °C by a reported procedure[33] (yield 47%). The product was liberated (in a vacuum system directly attached to the ZAB 2HF mass spectrometer) by heating a mixture of the above salt (30 mg) and finely powdered potassium hydroxide (20 mg) at 200 °C.

Acknowledgements

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