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SEMI-EMPIRICAL SCF-MO STUDY OF THE MASS SPECTRAL FRAGMENTATION OF TETRAMETHYLDIPHOSPHINE

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Summary

Structures and enthalpies of formation have been calculated, in the MNDO approximation using UHF wave-functions for open shell species, for tetramethyldiphosphine, Me_4P_2, and the major ions in its mass spectrum: $Me_4P_2^+$, $Me_3P_2H^+$, $Me_3P_2^+$, $Me_2P_2H_2^+$ (3 forms), $Me_2P_2H^+$ (3 forms), $Me_2P_2^+$ (3 forms), $MePPCH_2^+$ (3 forms), MeP_2^+ and $MePCH_2^+$, together with all the corresponding neutral fragments. Appearance potentials are calculated for all the ions, and possible fragmentation pathways deduced.

Introduction

In previous papers, we have reported calculations of the structures and energies of all the ionic and neutral fragments relevant to the mass spectral fragmentations of phosphorus hydrides and of the methyl phosphines [1,2]. Here we deal with the mass spectral fragments which arise from tetramethyldiphosphine $(CH_3)_2PP(CH_3)_2$.

The mass spectrum of tetramethyldiphosphine has been studied, together with the spectra of a number of other tetraalkyldiphosphines, by Bogolyubov, Grishin, and Petrov [3], who measured the appearance potentials of a very large number of the fragment ions.

The main features of the spectrum can be described in terms of stoichiometric series of ions, although the existence of these series does not carry any mechanistic implications about the pathways of ion formation. There are five principal ion series: $(CH_3)_nP_2^+$ $(1 \leqslant n \leqslant 4)$; $(CH_3)_3P_2H^+$, $(CH_3)_2P_2H_2^+$, and $(CH_3)_2P_2H^+$; $C_2H_{2n}P^+$ $(1 \leqslant n \leqslant 3)$; CH_nP^+ $(1 \leqslant n \leqslant 5)$; and $P_2H_n^+$ $(1 \leqslant n \leqslant 3)$: in addition the ions $CH_3PPCH_2^+$, $CH_3PCH_2^+$, and $(CH_3)_2PH^+$ are also present. The monophosphorus ions, with the exception of $CH_3PCH_2^+$ have been discussed previously [1,2], as have the ions $P_2H_n^+$.

Calculations

All calculations of structures and energies were made, without any geometrical assumptions, using the MNDO method [4,5] with UHF wavefunctions for open-shell species and using the published parameters for phosphorus [6].

Molecular energies of fragments not previously described [1,2] are listed in Table 1, and the principal geometrical parameters in Table 2. The electronic energy levels of Me_4P_2 are listed in Table 3. Charge and spin distributions for the cations are given in Table 4, and appearance potentials in Table 5.

Results and discussion

Molecular structures

M and M $^+$. There have been a number of experimental studies of the molecular structure of Me_4P_2; the major focus of interest has been the conformation about the PP bond. In an electron diffraction study [7], two conformational models were investigated: in one the conformation was held fixed with a dihedral angle of 180°, i.e. the *anti* conformation, while in the other, the dihedral angle was allowed to refine. Between these two models, there was no significant difference in any geometrical parameter except for the dihedral angle, the freely refining model gave a rather better fit to the experimental data, with the dihedral angle refining to a value of 164 ± 23°, without, however, any correction for shrinkage being obtained. Vibra-

TABLE 1

MOLECULAR ENERGIES, SYMMETRIES AND STATES

		$\Delta H_f^\ominus$ (kJ mol^{-1})	Point group	Molecular state
Me_4P_2 (*anti*)		−305.7	C_{2h}	^1A_g
Me_4P_2 (*syn*)		−275.6	C_{2v}	$^1A_1$
$Me_4P_2^+$ (*anti*)		+524.3	C_{2h}	^2A_g
$Me_3P_2H^+$		+612.7	C_1	^2A
$Me_3P_2^+$		+628.3	C_s	$^1A'$
$Me_2P_2H_2^+$		+713.6	C_2	^2A
		+712.8	C_i	^2A_g
		+706.4	C_s	$^2A'$
$Me_2P_2H^+$ [a]	(isomer *A*)	+731.1	C_s	$^1A'$
	(isomer *B*)	+730.9	C_s	$^1A'$
	(isomer *C*)	+731.7	C_s	$^1A'$
$Me_2P_2^+$ [a]	(isomer *A*)	+879.8	C_2	^2B
	(isomer *B*)	+846.6	C_{2h}	^2A_g
	(isomer *C*)	+825.5	C_{2v}	$^2B_2$
$MePPCH_2^+$ [a]	(isomer *A*)	+928.5	C_s	$^1A'$
	(isomer *B*)	+905.4	C_s	$^1A'$
	(isomer *C*)	+1043.8	C_s	$^1A'$
MeP_2^+		+932.8	C_{3v}	$^1A_1$
$MePCH_2^+$		+930.8	C_s	$^2A''$
$MePCH_2$		−9.4	C_s	$^1A'$

[a] Isomers *A* are based on a *cis*-CPPC skeleton; isomers *B* are based on a *trans*-CPPC skeleton; isomers *C* are based on a C_2PP skeleton.

TABLE 2

MOLECULAR GEOMETRIES

		d(CP) (Å)	d(PP) (Å)	d(PH) (Å)	Angle (CPP) (°)	Angle (CPC) (°)	Angle (PPH) (°)	δ(CPPC) (°)	δ(CPPH) (°)	δ(HPPH) (°)	p(CP)	p(PP)
Me_4P_2	(*anti*)	1.758	2.051	–	105.1	105.4	–	69.1,180.0	–	–	0.985	0.956
		1.756	2.047	–	110.9	105.5	–	0.0,116.9	–	–	0.981	0.960
$Me_4P_2^+$		1.762	1.995	–	112.1	110.7	–	54.8,180.0	–	–	–	–
Me_2PPHMe^+		1.762(P(1)–C(1))	2.004	1.346	112.8	113.8	101.2	196.9	53.5	–	–	–
		1.761(P(1)–C(2))			115.4			63.7	186.7			
		1.749(P(2)–C(3))			111.6							
Me_2PPMe^+		1.781(P(1)–C(1))	1.864	–	116.2	116.3	–	180.0	–	–	0.863	1.594
		1.775(P(1)–C(2))			126.4			0.0			0.872	
		1.717(P(2)–C(3))			111.1						1.037	
$Me_2P_2H_2^+$	(C_2)	1.752	1.991	1.348	114.9	–	104.5	71.4	180.0	56.4	–	–
	(C_i)	1.752	1.993	1.348	113.7	–	105.6	180.0	63.6	180.0	–	–
	(C_s)	1.761(P(1))	2.016	1.342(P2)	115.9	116.3	100.4	–	59.4,159.4	–	–	–
$Me_2P_2H^+$	**(A)**	1.715(P(1)–C(1))	1.888	1.350(P2)	110.4	–	113.1	0.0	180.0	–	1.038	1.576
		1.772(P(2)–C(2))			134.1						0.862	
	(B)	1.716(P(1)–C(1))	1.858	1.348(P2)	109.6	–	125.6	180.0	0.0	–	1.038	1.579
		1.776(P(2)–C(2))			121.5						0.860	
	(C)	1.781(P(1)–C(1))	1.855	1.335(P2)	125.6	117.5	101.0	–	0.0	–	0.861	1.672
		1.784(P(1)–C(2))			116.9				180.0		0.860	
$Me_2P_2^+$	**(A)**	1.725	1.891	–	121.2	–	–	51.7	–	–	–	–
	(B)	1.735	1.814	–	121.2	–	–	180.0	–	–	–	–
	(C)	1.785(P(1))	1.843	–	121.4	117.2	–	–	–	–	–	–
$MePPCH_2^+$	**(A)**	1.709(P(1)–C(1))	1.922	–	116.9	–	–	0.0	–	–	1.040	1.343
		1.611(P(2)–C(2))			122.9						1.547	
	(B)	1.709(P(1)–C(1))	1.932	–	105.7	–	–	180.0	–	–	1.068	1.362
		1.618(P(2)–C(2))			107.9						1.521	
	(C)	1.789(P(1)–C(1))	1.953	–	121.1	119.0	–	–	–	–	0.845	0.913
		1.612(P(1)–C(2))			119.9						1.573	
MeP_2^+		1.789(P(1)–C(1))	1.690	–	180.0	–	–	–	–	–	0.801	2.616
$MePCH_2^+$		1.717(C(1))	–	–	–	108.4	–	–	–	–	–	–
		1.670(C(2))										
$MePCH_2$		1.745(C(1))	–	–	–	109.9	–	–	–	–	0.988	–
		1.569(C(2))									1.936	–

TABLE 3

ELECTRONIC ENERGY LEVELS IN Me_4P_2

State	Symmetry	I(eV)	State	Symmetry	I(eV)
$\tilde{X}$	A_g	9.30	$\tilde{J}$	A_g	14.95
$\tilde{A}$	B_u	11.27	$\tilde{K}$	B_u	15.06
$\tilde{B}$	A_g	11.98	$\tilde{L}$	A_g	15.70
$\tilde{C}$	B_u	12.39	$\tilde{M}$	B_u	17.79
$\tilde{D}$	A_g	13.17	$\tilde{N}$	A_g	20.46
$\tilde{E}$	A_u	14.01	$\tilde{O}$	A_u	29.69
$\tilde{F}$	A_g	14.15	$\tilde{P}$	A_g	30.75
$\tilde{G}$	B_u	14.35	$\tilde{Q}$	B_u	32.17
$\tilde{H}$	B_u	14.40	$\tilde{R}$	A_g	32.59
$\tilde{I}$	A_g	14.81			

tional spectroscopy has indicated [8] that in the solid state only the *anti* conformation occurs, while in liquid and gas phases the compound exists as a mixture of *anti* and *gauche* conformers, with the *gauche* more abundant: in the gas phase, a *gauche*/*anti* ratio of 3/2 was estimated [9]. On the other hand, the photoelectron spectrum has been interpreted in terms of a mixture of 16% *gauche* and 84% *anti*

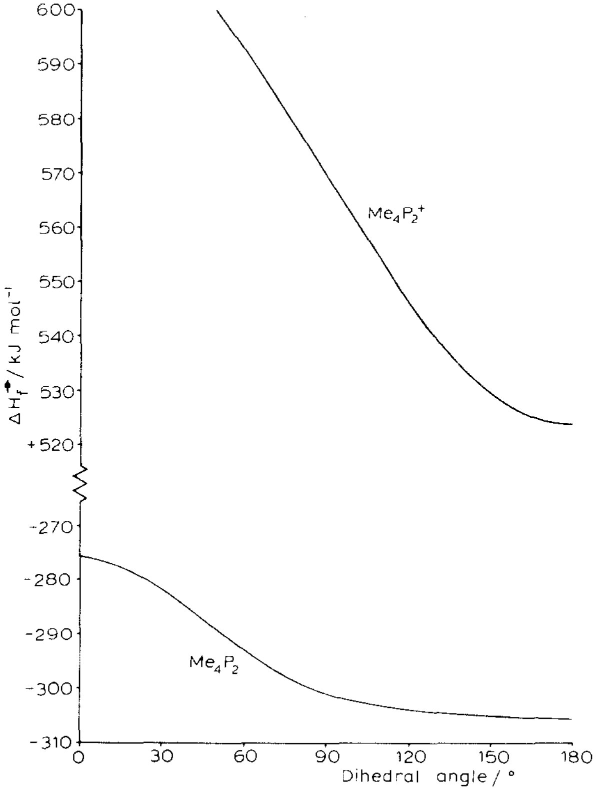


Fig. 1. Variation of $\Delta H_f^\ominus$ with dihedral angle for Me_4P_2 and $Me_4P_2^+$.

[10], the temperature variation of the photoelectron spectrum has been suggested as a means of identifying the individual spectra of the several conformers [11].

The molecular structure of Me_4P_2 calculated by MNDO (Table 2) is in reasonable

TABLE 4

CHARGE AND SPIN DISTRIBUTION IN THE MAJOR FRAGMENTS[a]

			Charge (*e*)	Spin density				Charge (*e*)	Spin density
$Me_4P_2^+$	(*anti*)	P	+0.138	+0.464	$Me_2P_2^+$	(A)	P	+0.357	+0.436
		C	+0.004	-0.003			C	-0.106	+0.040
Me_2PPHMe^+		P(1)	+0.073	+0.705		(B)	P	+0.285	+0.437
		P(2)	+0.331	+0.218			C	-0.027	+0.046
		C(1)	+0.033	-0.024					
		C(2)	+0.034	-0.023		(C)	P(1)	-0.361	-0.352
		C(3)	-0.069	+0.019			P(2)	+0.701	+1.285
		(P)H	+0.019	+0.013			C	+0.162	+0.049
Me_2PPMe^+		P(1)	-0.369	-	$MePPCH_2^+$	(A)	P(1)	+0.736	-
		P(2)	+0.741	-			P(2)	-0.101	-
		C(1)	+0.168	-			C(1)	-0.278	-
		C(2)	+0.144	-			C(2)	+0.171	-
		C(3)	-0.240	-		(B)	P(1)	+0.677	-
							P(2)	-0.074	-
$Me_2P_2H_2^+$	(C_2)	P	+0.242	+0.470			C(1)	-0.192	-
		C	-0.021	+0.005			C(2)	+0.190	-
		(P)H	+0.074	+0.001					
						(C)	P(1)	-0.264	-
	(C_i)	P	+0.243	+0.469			P(2)	+0.416	-
		C	-0.022	+0.003			C(1)	+0.160	-
		P(H)	+0.072	+0.002			C(2)	+0.303	-
	(C_s)	P(1)	+0.851	+0.027	MeP_2^+		P(1)	-0.335	-
		P(2)	+0.084	+0.480			P(2)	+0.898	-
		C	-0.036	+0.055			C	+0.234	-
		(P)H	+0.022	-0.016					
					Me_2P^+		P	+0.967	-
$Me_2P_2H^+$	(A)	P(1)	+0.800	-			C	-0.308	-
		P(2)	-0.360	-					
		C(1)	-0.253	-	$Me_2P^{\cdot}$		P	+0.076	+1.015
		C(2)	+0.163	-			C	-0.085	-0.064
		(P)H	+0.227	-					
					$MePCH_2^+$		P	+0.751	+0.374
	(B)	P(1)	+0.799	-			C(1)	-0.248	+0.013
		P(2)	-0.357	-			C(2)	-0.028	+0.656
		C(1)	-0.254	-					
		C(2)	+0.176	-	$MePCH_2$		P	+0.071	-
		(P)H	+0.208	-			C(1)	-0.063	-
	(C)	P(1)	-0.358	-			C(2)	-0.136	-
		P(2)	+0.801	-					
		C(1)	+0.153	-					
		C(2)	+0.163	-					
		(P)H	-0.088	-					

[a] The atom numbering follows that of Table 2.

TABLE 5

APPEARANCE POTENTIALS

Ion	Neutral	A.P. calculated (eV)	A.P. observed [a] (eV)	Required ionisation
$Me_4P_2^+$	–	8.60 [b]	8.6	$\tilde{X}$
$Me_3P_2H^+$	CH_2	14.17	10.6	$\tilde{A}$
	$1/2C_2H_4$	9.86		
$Me_3P_2^+$	CH_3	10.75	10.8	$\tilde{A}$
$Me_2P_2H_2^+$ (C_s)	$2CH_2$	19.80	10.8	$\tilde{A}$
	C_2H_4	11.17		
$Me_2P_2H^+$ (B)	C_2H_4+H	13.66	13.2	$\tilde{E}$
	CH_3+CH_2	16.47		
$Me_2P_2^+$ (B)	$2CH_3$	14.08	14.3	$\tilde{A}$
	C_2H_6	11.09		
$MePPCH_2^+$ (B)	$2CH_3+H$	16.93	13.5	$\tilde{D}$
	C_2H_6+H	13.94		
	CH_3+CH_4	13.10		
MeP_2^+	$3CH_3$	16.04	13.5	$\tilde{D}$
	$C_2H_6+CH_3$	13.05		
Me_2P^+	$Me_2P^{\cdot}$	11.29	13.3	$\tilde{B}$
$CH_3PCH_2^+$	Me_2PH	11.43	13.6	$\tilde{I}$
	$Me_2P^{\cdot}+H^{\cdot}$	14.51		

[a] Ref. 3. [b] A.P. of $Me_4P_2^+$ is equivalent to adiabatic I.P.; calculated vertical I.P. is 9.30 eV.

agreement with that found experimentally [7], subject to the usual underestimate of bond distances involving second row elements, here the CP distance is calculated ca. 5% too short, and the PP ca. 6.5% too short. However when the molecular energy is calculated as a function of the dihedral angle, with each of the remaining 47 internal variables independently optimised at each point to give a fully relaxed torsional potential energy curve, only a single energy minimum is found, corresponding to the *anti* conformation. The potential energy curve (Fig. 1) has a very broad mimimum indicating that the torsional dihedral angle can vary by $\pm 40°$ from the *anti* conformation at the cost of only ca. 1 kJ mol^{-1} in energy; however the *gauche* conformation, which is calculated to occur at a dihedral angle of 65.9°, has an energy some 10.8 kJ mol^{-1} above the minimum, and the *syn* conformation, at a dihedral angle of zero, is 30.1 kJ mol^{-1} above the *anti* conformation.

Ionisation to form the molecular cation $Me_4P_2^+$ causes only minor changes in the CP and PP bond lengths, of $+0.004$ and -0.056 Å respectively, however, larger changes are found in the bond angles at phosphorus, the calculated sum of angles increasing from 315.6° in the neutral parent to 334.9° in the cation. Since the top two molecular orbitals in the neutral diphosphine are associated primarily with phosphorus lone pairs (see below, Electronic structures) these structural changes are entirely straightforward, and are similar to those found in the single and double ionisations of PH_3 [2]. As with the neutral diphosphine, the potential energy of the cation was calculated as a function of the torsional angle about the PP bond. In this case the optimisations converged satisfactorily only for a range of dihedral angle δ, $180° > \delta > 59.8°$: these limits represent exactly the *anti* and *gauche* conformations, respectively. When attempts were made to approach the *syn* conformation, i.e. with δ in the range $59.8° > \delta > 0°$, the resulting geometries were entirely unsatisfactory with almost planar phosphorus atoms, associated with rather low $\Delta H_f^\ominus$ values. However within the range of δ for which satisfactory convergence was achieved, there is again only a single energy minimum (Fig. 1), corresponding to the *anti* conformation, but now the potential energy curve is much steeper than that for the neutral parent, and a change in dihedral angle of ±40° now requires the input of some 22 kJ mol^{-1}, compared with only 1 kJ mol^{-1} in the neutral. In the cation the *gauche* conformation is 68.6 kJ mol^{-1} above the *anti* compared with 10.18 kJ mol^{-1} in the neutral parent.

Fragment ions. The ion Me_2PPHMe^+ exists in an *anti* type conformation with two methyl groups almost *trans* to one another, and the P*H* also almost *trans* to a methyl (see Table 2 for dihedral angles). In contrast the heavy atom skeleton of Me_2PPMe^+ is planar, and if this ion is to be regarded as arising from *P*-methylation of either *cis*- or *trans*-MePPMe, the skeletal planarity is immediately intelligible: consistent with this interpretation is the observation (Table 2) that although the CP bond orders in this ion are very similar to that in Me_4P_2, the PP bond order is 1.59 compared with only 0.96 in the parent diphosphine.

Three structures, all with *anti* type conformations, are possible for the fragment ion $Me_2P_2H_2{}^+$. The C_2 and C_i forms are both based on CPPC frameworks with CPPC dihedral angles of 71.4 and 180.0°, respectively; the C_s isomer is based on a C_2PP framework. Distinct minima were found for all of these possibilities but their energies are very close (Table 1). In particular there is negligible difference between the energies of the two CPPC conformers: similarly these two conformers are almost identical in their bond lengths and angles, whereas minor differences are apparent for the C_s (C_2PP) isomer (Table 2).

For each of the ions Me_2PPH^+, $Me_2P_2{}^+$, and $MePPCH_2{}^+$ three heavy atom frameworks were investigated (Table 1): isomers denoted **A** are based on a *cis*-CPPC skeleton, isomers **B** are based on a *trans*-CPPC skeleton, and isomers **C** are based on a C_2PP skeleton. All isomers of Me_2PPH^+ have planar P_2C_2H frameworks, and they can, like $Me_3P_2{}^+$, be regarded as protonated or methylated derivatives of the planar diphosphine-2, P_2H_2 [2]. The PP bond orders for the two CPPC isomers are 1.58 while that for isomer **C** is 1.67, all similar to that in $Me_3P_2{}^+$. As in the fragment ion $Me_2P_2H_2{}^+$, the three isomers are of almost identical energies. Two of the three isomers of $Me_2P_2{}^+$ have planar frameworks, but optimisations starting from a *cis* configuration converge to a dihedral angle of 51.7°; their energies are markedly different with the isomer Me_2PP^+ having the lowest $\Delta H_f^\ominus$ and the 51.7° isomer the highest: this is the order found previously [2] for the isomers of $P_2H_2{}^+$. The isomers of $MePPCH_2{}^+$ again have planar heavy-atom frameworks, and in all of them the CH_2 group is coplanar with the CPPC skeleton, thereby maximising the π-overlap. The CP bond orders involving the CH_3 group are all close to unity, but those involving the CH_2 group are greater than 1.50 (Table 2): however the PP bond orders are all lower than those found in the isomers of $Me_2P_2H^+$, although the bond order sums are greater.

In the neutral fragment $MePCH_2$ the CH_2 group is coplanar with the CPC framework, and the PC bond orders are indicative of single and double bonds between the phosphorus atom and the CH_3 and CH_2 groups respectively. Rotation of the CH_2 to be perpendicular to the CPC framework requires the input of some

162 kJ mol^{-1} and is accompanied by major structural changes: the CP distances change from 1.745 and 1.569 to 1.719 and 1.551 Å, and the CPC angle increases from 109.9 to 157.9°: this increase to near linearity at phosphorus enables p_π–p_π overlap between CH_3P and CH_2 to be maintained, consistent with both the short P=C distance, 1.551 Å and the high bond order, 1.819 Å. The bond order sum at phosphorus decreases from 2.974 only to 2.779 Å. A similar rotation in the cation radical $CH_3PCH_2^+$ requires only some 22 kJ mol^{-1}, and the geometrical changes are more modest; for example the CPC angle increases from 108.4 only as far as 126.6°. Consistent with the HOMO in $MePCH_2$ being associated with the π(P–C) bond, this CP distance is increased from 1.569 to 1.670 Å upon ionisation.

The molecular structures of all the monophosphorus fragments have been described previously [1,2].

Electronic structures

The electronic structure of Me_4P_2 has been investigated by photoelectron spectroscopy [10,11]. In the *anti* conformer, the two highest occupied molecular orbitals, consisting primarily of positive and negative combinations of the phosphorus lone pairs of symmetry classes A_g and B_u in point group C_{2h} are found to have vertical ionisation energies [10] of 7.88 and 9.54 eV, a difference of 1.66 eV, whereas in the *gauche* conformer of C_2 symmetry these two orbitals are effectively orthogonal, and

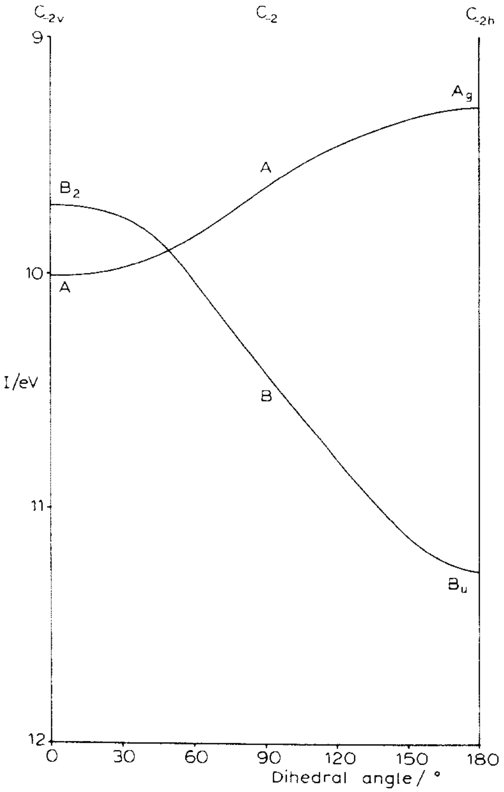


Fig. 2. Variation of binding energies, equivalent to Koopmans' theorem vertical ionisation energies, with dihedral angle for Me_4P_2.

so have negligible interaction, and hence there is a single vertical ionisation energy at 8.79 eV, very close to the mean of 7.88 and 9.54 eV. Further ionisation energies were reported [10] at 10.33, 11.22, 11.83, 12.8, 13.2, 13.6, and 16.5 eV, and it was suggested that the first three of these could be associated primarily with the electrons of the PP and CP bonds.

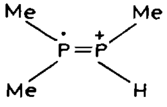
We have plotted the calculated Koopmans' theorem vertical ionisation energies for the first two levels in Me_4P_2 as a function of the dihedral angle (Fig. 2). For the *anti* conformation, the calculated ionisation energies are 9.30 (A_g) and 11.27 eV (B_u), a separation of 1.97 eV, somewhat larger than the experimental value, but subject of course to the uncertainties inherent in the use of Koopmans' theorem. The two energy levels become identical at a value of the dihedral angle of ca. 51°, which is rather less than the dihedral angle of 65.9° corresponding to the *gauche* conformation of the methyl groups, suggesting that the effective orientations of the lone pair orbitals cannot be straightforwardly deduced from those of the PP and CP bond directions, and indeed within the low symmetry C_2 of the *gauche* conformation, there is no constraint of the bond directions on the lone pair orientations. At values of the dihedral angle less than 51°, the HOMO is of B symmetry in C_2 becoming B_2 at the C_{2v} *sym* conformation, where the A_1–B_2 gap is 0.3 eV, much less than for the *anti* conformation: at the *gauche* conformation of the methyl groups, the A–B gap is 0.33 eV with the A orbital the less tightly bound.

Table 3 summarises the electronic energy levels of Me_4P_2 in terms of their vertical, Koopmans' theorem, ionisation energies, and symmetry classes in point group C_{2h}. The four deepest levels, around 30 eV consist primarily of C(2*s*)–P(3*s*) interactions localised in C–P bonds, and the next two at 20.46 and 17.79 eV are respectively the in-phase and out-of-phase combinations of P(3*s*) contributing to the P–P bond.

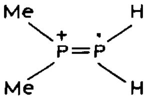
Table 4 presents the charge and spin density distributions on carbon, phosphorus and phosphorus-bound hydrogen for the major fragments: the residual charge and spin density is resident on the hydrogen atoms of the methyl groups. These data reveal some of the detail of the electronic structure of the fragments and give some clues to the likely fragmentation pathways.

Several general features of these data may be noted: in general the net charges on carbon atoms are rather small, and in many of the cations studied in this work, a large proportion of the overall charge is localised on the hydrogen atoms of the methyl groups. Secondly we note that carbon atoms in cation radicals generally carry very low spin densities, which may be either positive or negative, but in contrast to charge, the spin density carried by the hydrogen atoms is now very low. From comparisons we have made [12] for a rather small selection of radicals, spin densities at hydrogen calculated by MNDO or by INDO compare fairly satisfactorily with those calculated by ab initio techniques using fairly large basis sets (e.g. 4–31G* or 6–311G**).

In those cation radicals in which the two phosphorus atoms are both three-coordinate but chemically distinct, such as Me_2PPHMe^+ and the C_s isomer of $Me_2P_2H_2{}^+$, the phosphorus atom which is approximately neutral carries most of the spin

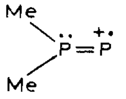


(I)

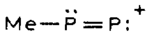


(II)

density, so that these two ions should be represented thus (I and II). They are therefore expected to fragment to yield, respectively ($Me_2P^{\bullet}$ and $MePH^+$) and

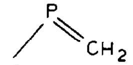


III

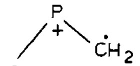


(IV)

(Me_2P^+ and $PH_2^{\bullet}$). By contrast in Me_2PP^+ the one-coordinate phosphorus atom carries both a large charge (0.701 *e*) and a large spin density (+1.285), and must be represented as III, while MeP_2^+ must be represented as IV and hence will fragment by loss of P^+ rather than of a neutral P atom. In Me_2P^+ and $Me_2P^{\bullet}$ the charge and spin respectively are localised almost completely on the phosphorus atom: in $MePCH_2$ no atom carries a charge greater than 0.14 *e* so that this species should be



(V)



(VI)

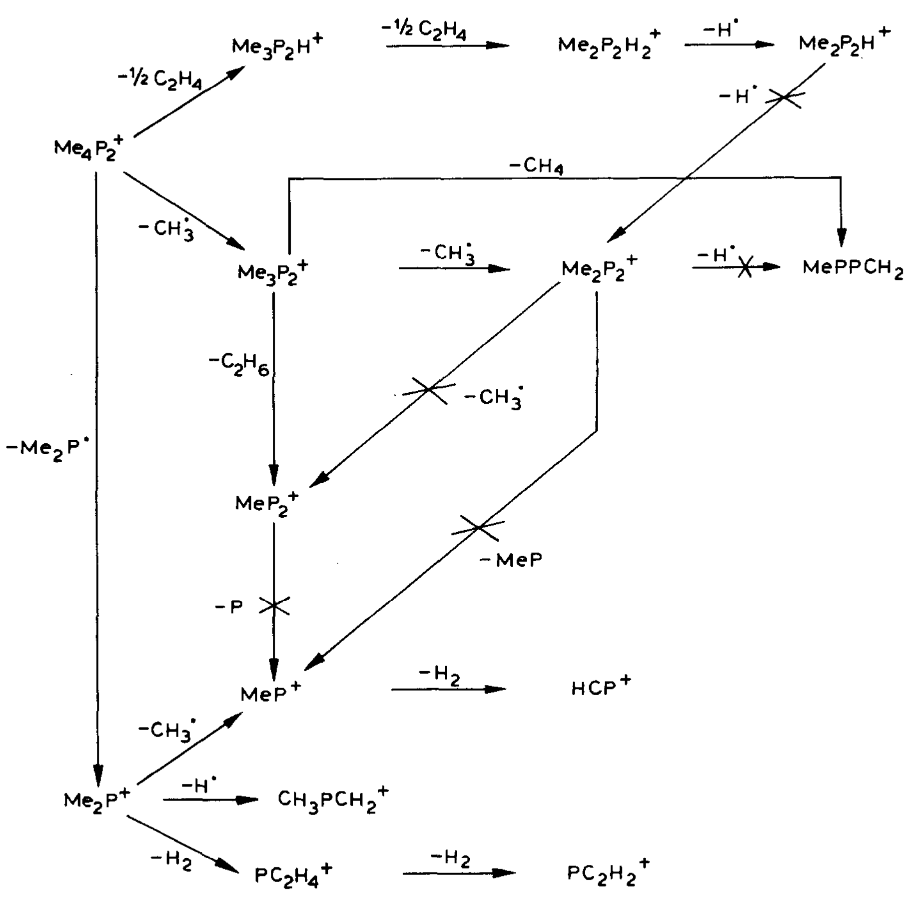
represented as V, while in the corresponding cation $MePCH_2^+$ the charge is mainly carried by phosphorus, and the spin by the carbon of the methylene group (VI).

Appearance potentials

The appearance potentials of a number of the fragment ions in the mass spectrum of Me_4P_2 have been measured [3] and some conjectures have been offered concerning the neutral fragments associated with the ions observed. In Table 5 we list the observed and calculated appearance potentials for the major fragment ions. For many of the fragment ions, particularly the smaller ones, a wide range of neutral fragments is possible: we have been guided initially in our suggested neutrals by those indicated by Bogolyubov and his colleagues [3], but have in many cases suggested other possibilities also.

The calculated appearance potential of the molecular ion $Me_4P_2^+$, which is equivalent to the adiabatic ionisation energy, is identical with that observed, 8.6 eV: similarly the calculated A.P. of $Me_3P_2^+$, with loss of a methyl radical, is identical to the experimental value. Further methyl loss to yield $Me_2P_2^+$ and MeP_2^+ appears from the data of Table 4 to be stepwise in the case of $Me_2P_2^+$, but concerted for MeP_2^+, where the neutral fragments are C_2H_6 and $CH_3^{\bullet}$.

The ions Me_2PPHMe^+ and $Me_2P_2H_2^+$ were suggested by Bogolyubov to arise by loss of one or two CH_2 groups from the parent ion $Me_4P_2^+$; our calculations, by contrast suggest that the neutral fragments lost here are 1/2 C_2H_4 and C_2H_4, respectively. It is not possible to distinguish between the possible isomeric forms of $Me_2P_2H_2^+$ (see Tables 1 and 2) on the basis of A.P. data: the same is true also for $Me_2P_2H^+$, $Me_2P_2^+$, and $MePPCH_2^+$. The A.P. of the ion $Me_2P_2H^+$ is best accommodated by the neutral fragments ($C_2H_4 + H^{\bullet}$) suggesting that it arises from $Me_2P_2H_2^+$ by loss of a hydrogen atom. On the other hand loss of hydrogen from $Me_2P_2H_2^+$ to yield $Me_2P_2^+$ requires appearance potentials of 17.10 eV if the neutrals are $C_2H_4 + 2H$, i.e. stepwise hydrogen loss or of 12.62 eV if the neutrals are $C_2H_4 + H_2$, i.e. concerted hydrogen loss; the observed A.P. is however reproduced almost exactly if the neutrals are $2CH_3^{\bullet}$, suggesting that formation of $Me_2P_2^+$ from



SCHEME 1. Fragmentation pathways for $Me_4P_2{}^+$.

$Me_2P_2H_2{}^+$ is unimportant, even though $Me_2P_2H^+$ appears to be formed from $Me_2P_2H_2{}^+$. It is not possible to distinguish between the neutral pairs (C_2H_6 + H$^•$) and (CH_4 + $CH_3{}^•$) in the formation of $MePPCH_2{}^+$, the route involving ($2CH_3{}^•$+ H$^•$), i.e. hydrogen loss from $Me_2P_2{}^+$, is ruled out however on energetic grounds. $CH_3PCH_2{}^+$ must be formed by loss of a hydrogen atom from Me_2P^+, rather than by loss of Me_2PH from the parent molecular ion.

Molecular fragmentation

When the energies of the fragment ions and their corresponding neutral fragments are compared with the energy levels of Table 3, the minimum ionisation processes required for the appearance of individual fragments can be deduced, these are listed in Table 5 for the more important ions. Only the molecular cation $Me_4P_2{}^+$ itself can be formed upon ionisation to the $\tilde{X}$ state, but ionisation to the $\tilde{A}$ state can yield $Me_3P_2H^+$, $Me_3P_2{}^+$, $Me_2P_2H_2{}^+$ and $Me_2P_2{}^+$, ionisation to the $\tilde{B}$ state can yield Me_2P^+ while ionisation to the $\tilde{D}$ state is required for the formation of $MePPCH_2{}^+$ and $MeP_2{}^+$.

By use of the deductions made from appearance potential data and from earlier work [2], a Scheme containing some of the allowed and forbidden ionisations can be drawn up.

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