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Semi-Empirical MNDO SCF-MO Study of the Lower Phosphorus Sulphides, and their Molecular Cation-Radicals

CHRISTOPHER GLIDEWELL

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

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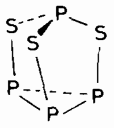
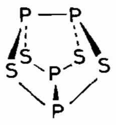
Molecular energies, expressed as ΔH_f° have been calculated for the isomers of P_4S_x ($2 \leqslant x \leqslant 5$), using the MNDO semi-empirical SCF–MO method: structures, energies, and spin-distributions have been similarly calculated for the cation-radicals $P_4S_x^{+}$.

Introduction

In recent years evidence has accumulated for the existence of at least two isomeric forms of each of the phosphorus sulphides P_4S_3, P_4S_4, and P_4S_5 [1–6]. Structural characterization has been achieved for one isomer each of P_4S_3 and P_4S_4, denoted [2] β-P_4S_3 [1] (I) and α-P_4S_4 [2–4] (II) respectively, and for two isomers of P_4S_5, α-P_4S_5 [5] (III) and β-P_4S_5 [6] (IV). Spectroscopic evidence, (infra-red and ^{31}P n.m.r.), has been presented for a second isomer of P_4S_3 [2], of unknown structure, and for β-P_4S_4 [2, 3] (V): no samples of these materials suitable for X-ray examination have been obtained. The structure of (V) follows from its synthesis, by two different routes, and from its ^{31}P n.m.r. spectrum, analysed as AMX_2 [3].


(I)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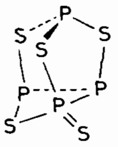
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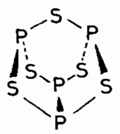
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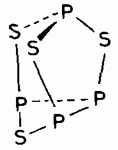
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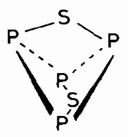
In addition, the existence of a phase P_4S_2 has been reported [7] for which two edge-substituted structures are possible (VI) and (VII).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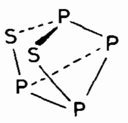
(VII)

The nomenclature [2] particularly of P_4S_4 and P_4S_5 is somewhat confusing as α-P_4S_4 (II) is clearly related to β-P_4S_5 (IV), while β-P_4S_4 (V) is clearly related to α-P_4S_5 (III): the structurally characterized isomer of P_4S_3 (I) has been denoted β-P_4S_3 [2].

In the present paper, we report the results of an MNDO SCF–MO study of the simpler phosphorus sulphides, whose objectives included: the establishment of possible structures for the second isomer of P_4S_3; the determination of the relative energies, as ΔH_f°, of the known isomers of P_4S_4 and P_4S_5; and the determination of the structures and energies of the respective molecular cations, together with their spin distributions.

Calculations

All calculations were undertaken using the MNDO method [7, 8] implemented on a VAX 11/780 computer, using the published parameterization for phosphorus and sulphur [9] with UHF wavefunctions for open-shell species. Molecular geometries were optimised with respect to all independent geometric variables.

Results and Discussion

Isomers of P_4S_3

All known molecular species of general stoichiometry P_4X_n have structures derivable from the P_4 tetrahedral *closo* cage of elemental phosphorus:

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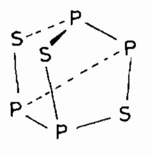
TABLE I. Optimised Molecular Energies and Symmetries of P_4S_x and their Cations.

	Neutral			Cation		
	$\Delta H_f^{\ominus}$/kJ mol^{-1}	Point group	Symmetry of HOMO	$\Delta H_f^{\ominus}$/ kJ mol^{-1}	Point group	Molecular state
(a) Isomers of P_4S_3						
(I)	−227.8	C_{3v}	E	+805.8	C_s	$^2A'$
(VIII)	−180.5	C_1	A	+820.3	C_1	^2A
(IX)	−160.8	C_{3v}	A_1	+805.9	C_{3v}	$^2A_1$
(b) Isomers of P_4S_4						
(II)	−294.5	D_{2d}	B_2	+751.2	D_{2d}	$^2B_2$
α-S_4P_4	−185.0	C_{2v}	B_2	+786.9	C_{2v}	$^2B_2$
(V)	−305.3	C_s	A″	+720.3	C_s	$^2A'$
(c) Isomers of P_4S_5						
(III)	−186.4[a]	C_1	A	+679.2[a]	C_1	^2A
(IV)	−384.9	C_{2v}	A_1	+668.5	C_s	$^2A'$
(d) Isomers of P_4S_2						
(VI)	−33.3	D_{2d}	E	+921.9	C_{2v}	$^2B_1$
(VII)	−51.1	C_s	A′	+984.9	C_s	$^2A'$

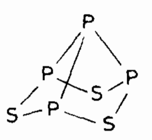
[a] See text.

consequently all isomers considered in this study are of this type. While in principal many other structural types are possible for P_4X_n, none has been observed, with the exception of aryl and alkyl species P_4R_4 which contain a monocyclic P_4 group. However these systems are electron-rich and can be regarded as based upon the P_4^{-4} fragment, expected to be square planar, in contrast to the tetrahedral neutral P_4.

Based upon a tetrahedral P_4 unit, there are three distinct ways in which edge substitution by sulphur can be achieved, (I), (VIII) and (IX).



(VIII)



(IX)

Isomer (I) may be regarded as derived from a tetrahedron P_4 by bridging three edges which have a single phosphorus in common; isomer (IX) by bridging the other three edges of P_4; and isomer (VIII) by bridging a pair of opposite edges, *i.e.* a pair of edges intersected by the S_4 symmetry axis, plus any one of the other four edges. Isomers (I) and (IX) may be expected to exhibit C_{3v} symmetry, but isomer (VIII) can have no symmetry.

Of these three isomers, the experimentally characterized isomer (I) is calculated to have the most negative value of $\Delta H_f^{\ominus}$ (see Table I), with the other two isomers (VIII) and (IX) less stable by some 47 kJ mol^{-1} and 67 kJ mol^{-1} respectively. These differences are significantly larger than the energy difference calculated for the two observed isomers of P_4S_4 (see below).

Isomer (I) optimises to C_{3v} molecular symmetry with a HOMO of E symmetry, and consequently the ion $P_4S_3^+$ is Jahn–Teller sensitive. The optimised geometry of $P_4S_3^+$ has only C_s symmetry, corresponding to a distortion along one of the two *e* bending vibrations ν_9 and ν_{10}. In contrast, isomer (IX), also of C_{3v} symmetry but with a HOMO of A_1 symmetry is calculated to undergo no change of symmetry upon ionisation. It is interesting to note that despite the rather wide range of $\Delta H_f^{\ominus}$ values for the

TABLE II. Calculated Spin Densities ρ[P(3s)].

$P_4S_3^+$:	(I)	P_{apical}, 0.0015; P_{basal}, −0.0023 (x1), 0.0044 (x2)
	(VIII)	P_a, −0.0016; P_b, 0.0264; P_c, −0.0155; P_d, 0.0034
	(IX)	P_{apical}, 0.0509; P_{basal}, 0.0055
$P_4S_4^+$:	(II)	−0.0139 (x4)
	α-S_4P_4	−0.0026 (x4)
	(V)	P_{apical}, −0.0086; P_{basal}, 0.0716 (x1), 0.0039 (x2)
$P_4S_2^+$:	(VI)	0.0040 (x2), −0.0013 (x2)
	(VII)	0.0684 (x1, PS_2); 0.0034 (x1, P_3); 0.0017 (x2, P_2S).

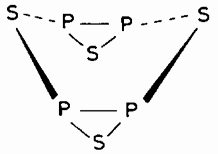
neutral isomers of P_4S_3, the corresponding molecular cations are very similar in energy, particularly the cations of (I) and (IX) (Table I).

Although molecular cations derived from the known phosphorus sulphides have been observed in the gas-phase in mass spectra [2, 10], the molecular constitutions of these ions have not been definitively established, and it is feasible that isomeric forms of the ions different from those of the parent molecules might occur. There does not yet seem to have been any study of these cations using e.s.r. spectroscopy in frozen or fluid solutions: such a study could well yield definite information on the symmetry of such ions, and accordingly we have calculated the spin densities for the phosphorus 3s orbitals in the several isomers (Table II): these spin densities will dominate the hyperfine couplings in the observed e.s.r. spectra. For the three isomeric forms of $P_4S_3^+$ considered here, the spectrum of $(IX)^+$ should consist of a widely-spaced doublet due to coupling to the apical phosphorus, with a much smaller quartet splitting arising from the basal phosphorus nuclei. The spectrum of $(VIII)^+$ will be dominated by two distinct doublet couplings due to P_b and P_c with two much smaller couplings arising from the other two distinct phosphorus nuclei, and the spectrum of $(I)^+$, derived from the common form of P_4S_3 will show rather small couplings throughout, dominated by a triplet arising from two equivalent basal phosphorus nuclei.

Isomers of P_4S_4

The data of Table I show that the P_4S_4 isomer whose structure has been definitively characterised by X-ray analysis, α-P_4S_4 (II) is marginally less stable than β-P_4S_4 (V). The calculated structure of α-P_4S_4 found here is in reasonably good agreement with those found experimentally, subject only to the usual [11, 12] proviso, that bond distances involving phosphorus and sulphur are typically calculated by MNDO to be too short by *ca.* 7%; the bond angles, and hence the overall molecular shapes, do not suffer from any such systematic discrepancy. The optimised geometry of α-P_4S_4 has D_{2d} symmetry, as expected: however when the atom identities are reversed (a procedure adopted during the refinement of the structure in order to establish the correct identification of the atoms [2]) the optimisation of the resulting α-S_4S_4 leads to a structure of C_{2v} symmetry, which is also less stable by some 110 kJ mol^{-1} than α-P_4S_4.

Whereas in α-P_4S_4, the calculated bond orders are: P–P, 0.868 (x2); P–S, 0.999; and S–S, 0.046, consistent with the observed structure, in α-S_4P_4 the calculated bond orders are S–S, 0.011 and 0.006; S–P, 0.972 (x4) and 0.966 (x4); and P–P, 0.946 (x2) and 0.028 (x2). The whole shape of the molecule is quite different (X, *cf.* II) from that in α-P_4S_4, as the structure adjusts in order to accommodate trivalent phosphorus and divalent sulphur: these cannot be accommodated by a simple reversal of atom identities within the fixed α-structure.

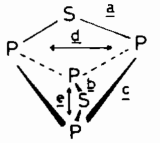


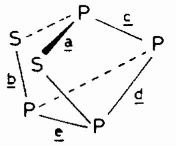
(X)

Of the molecular cations of the P_4S_4 isomers, β-$P_4S_4^+$ has the lowest ΔH_f° and α-$S_4P_4^+$ the highest, just as found for the neutral molecules (Table III). However, the energy differences between the isomeric forms of the cations (range 67 kJ mol^{-1}) are rather smaller than the differences between the neutral isomers (range 120 kJ mol^{-1}).

In each of α-$P_4S_4^+$, of D_{2d} symmetry, and α-$S_4P_4^+$ of C_{2v} symmetry, the four phosphorus atoms are equivalent: in β-$P_4S_4^+$ (*cf.* V), there are three types of phosphorus atom, one apical, and two basal, of multiplicities 1:1:2 respectively. The calculated

TABLE III. Geometries of P_4S_2 Isomers and their Cations.





	(VI), D_{2d}	(VI)$^+$, C_{2v}		(VII)	(VII)$^+$
Distances/Å					
a	1.970 (x4)	1.959 (x2)	a	1.989	1.961
b	(≡a)	1.961 (x2)	b	1.960	1.970
c	2.106 (x4)	2.128 (x4)	c	2.108	2.126
d	2.573 (x2)	2.750 (x1)	d	2.067	2.087
e	(≡d)	2.304 (x1)	e	2.095	2.123
Angles/°					
ac	89.0 (x8)	86.0 (x4)	aa′	101.9 (x1)	113.8 (x1)
bc	(≡ac)	96.7 (x4)	ab	90.8 (x2)	82.1 (x2)
aa′	81.5 (x2)	89.2 (x1)	ac	87.3 (x2)	94.6 (x2)
			bd	89.3 (x2)	95.5 (x2)
bb′	(≡aa′)	72.0 (x1)	be	104.7 (x2)	107.2 (x2)
cc′	75.3 (x4)	65.6 (x2)	cd	84.6 (x2)	75.6 (x2)
		80.5 (x2)	dd′	60.8 (x1)	61.2 (x1)
			de	59.6 (x2)	59.4 (x2)

values of spin-density at phosphorus, ρ[P(3s)] are given in Table II. For β-$P_4S_4^+$, the e.s.r. spectrum should be dominated by a large doublet coupling associated with the unique, basal phosphorus, with very much smaller couplings arising from the other phosphorus atoms: the α-$P_4S_4^+$ isomer, in contrast should have a quintet e.s.r. spectrum with a coupling constant *ca.* 0.2 of the large coupling in the β isomer.

Isomers of P_4S_5

For the β-isomer, the geometry of the neutral molecule optimised to C_{2v} symmetry (IV) as expected [6]: the HOMO, of A_1 symmetry, although containing contributions from all the atoms, is most concentrated in the direct P–P bond, and within 0.25 eV is the next highest molecular orbital of B_1 symmetry; this again contains contributions from all the atoms, but is most concentrated on the other two phosphorus atoms whose coefficients indicate that this orbital is P···P antibonding. Despite the small energy range (<1 eV) spanned by the first five occupied orbitals, there is no simple correlation between these and the corresponding orbitals in the D_{2d} structure of α-P_4S_4, to which the C_{2v} structure of β-P_4S_5 is closely related [*cf.* (II) and (IV)]. The only correspondence is between the second occupied orbital, E at −12.09 eV in α-P_4S_4, and the second and third occupied orbitals, B_1 and B_2 at −11.74 eV and −11.89 eV respectively in β-P_4S_5. Upon vertical ionisation of β-P_4S_5, there is considerable electronic reorganisation (*cf.* Koopmans' theorem) so that the SOMO is now B_1 (rather than A_1) with a B_1 level within 0.08 eV of it. It is possible that this accidental pseudo symmetry, with B_1 and B_2 levels of the vertically ionised cation masquerading as an E-type in D_{2d} pseudo-symmetry, might rationalise the calculated equilibrium geometry of β-$P_4S_5^+$ which relaxes from the C_{2v} symmetry of the vertically ionised species to only Cs symmetry corresponding to the adiabatic ionisation. If C_{2v} symmetry is imposed on the geometry optimisation of β-$P_4S_5^+$, the $\Delta H_f^\ominus$ value resulting is some 23 kJ mol^{-1} higher than for the free optimisation, but the electronic structure nonetheless still has only C_s symmetry, regardless of the symmetry imposed on the nuclear framework.

The $\Delta H_f^\ominus$ values calculated for α-P_4S_5 and its cation, both of which contain a phosphorus (V) atom are almost certainly too high: it is a well-known feature of the MNDO method that calculated $\Delta H_f^\ominus$ values are too high in compounds of S(IV) and P(V).

Isomers of P_4S_2

The existence of a phase of composition P_4S_2 has been reported [7]: although no definitive evidence of structure was obtained, it was suggested on the basis of other physical data that this phase represented a genuine, discrete compound, and furthermore that this compound had a structure derived by edge-substitution in a P_4 cage. Of the two isomeric possibilities (VI) and (VII), the form (VII) in which substitution occurs at adjacent edges was favoured over isomer (VI), where non-adjacent edges are substituted.

Free optimisation of the molecular geometry of (VII) leads to a structure of overall C_s symmetry (Table III): this symmetry is retained upon ionisation. The isomer(VI) optimises to D_{2d} symmetry with $\Delta H_f^{\ominus}$ some 18 kJ mol^{-1} less negative than for (VII). Vertical ionisation of (VI), whose HOMO has E symmetry, gives a Jahn–Teller sensitive ion, which distorts along one of the two B_2 vibrational modes, the out-of-phase PSP angle deformation mode where in one angle PSP becomes significantly larger and one smaller than in the neutral parent. Whereas for the neutral molecules (VII) was less stable than (VI), this is reversed for the cations and $(VII)^+$ is more stable than $(VI)^+$ by some 63 kJ mol^{-1}.

The e.s.r. spectrum of the cation $(VII)^+$ is expected to be dominated by a large coupling to a single phosphorus (Table II), with very much smaller couplings to the remaining phosphorus nuclei. In contrast, the cation $(VI)^+$ will exhibit no large phosphorus couplings in its e.s.r. spectrum.

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