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The Heats of Formation and Structures of some Phosphorus Sulphides

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The heats of formation of several phosphorus sulphides are calculated directly by the molecular orbital-bond index method. The results agree well with known data and establish valid and useful bond energy terms for the P–P and P–S bonds. It is suggested that these can be used in a predictive manner for other structures containing these bonds which are, as yet, thermochemically unexplored. Four possible geometrical isomers of P_4S_5 are studied and an order of stability established for them. The 'normal' form is shown to be the most stable by a small margin. The molecule P_4S_6, analogous to P_4O_6 is also shown to be thermodynamically stable.

Introduction

The phosphorus sulphides exhibit a fascinating and often puzzling variety of structures which are based essentially on the P_4 tetrahedron [1]. The molecules of P_4S_3, P_4S_5, P_4S_7 are shown in Fig. 1. P_4S_{10} has the same basic geometry as P_4O_{10}.

Some thermochemical data are available for these compounds [2–4] and we here present the results of calculations of the heats of formation by the MOBI method [5–7]. We have further investigated isomers of P_4S_5 (Fig. 1) in order to try to rationalise the differences between these isomers. Finally, we have studied the unknown molecule P_4S_6 in order to discover whether or not it is thermodynamically stable.

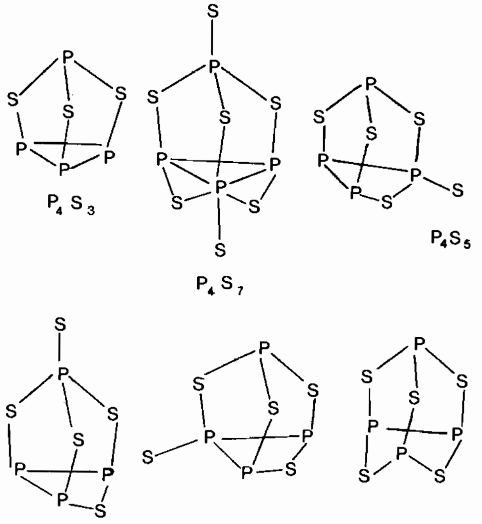

Fig. 1. Structures of P_4S_3, P_4S_7, and three possible isomers of P_4S_5. The structure of P_4S_{10} is geometrically similar to that of P_4O_{10}.

Method and Results

The molecular orbital-bond index method (MOBI) has been fully documented in the literature [5–7], and its use in determining heats of formation has been exploited. Although no phosphorus compounds

TABLE I. Input Atomic Orbital Data.[a]

	Orbital Exponent			VSIP			One-centre Repulsion Integral
	3s	3p	3d	3s	3p	3d	
P	1.750	1.300	0.667	19.37	10.84	1.45	12.291
S	1.967	1.517	0.833	20.52	10.78	1.80	13.812

[a] Ref. 9.

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TABLE II. Calculated and Experimental Heats of Atomisation of Phosphorus Sulphides (kcal $mole^{-1}$).

	Calculated	Experimental
P_4S_3	537.5	538.0
P_4S_5 normal	683.5	682.2
Isomer A	682.5	
Isomer B	681.5	
Isomer C	607.9	
P_4S_7	826.0	828.2
P_4S_{10}	1037.9	1036.6
P_4S_6	742.9	

have been studied previously, the method works well for silicon compounds [7] where the 3d orbitals are included. For both phosphorus and sulphur, the empty 3d orbitals need to be included, hence the problem of the phosphorus sulphides imposes a stringent test of the method.

The basic calculations required for generating the matrix of bond indices were carried out at the CNDO/INDO level [8, 9] and the input data are in Table I. The geometrical data for the compounds were abstracted from ref. 1. For such compounds we need bond energy parameters for the P–P, S–S, and P–S bonds. The P–P and S–S bond energy parameters are readily obtainable from the heats of sublimation [10] of yellow phosphorus (P_4) and orthorhombic sulphur. These yield values of 50.33 and 65.65 kcal $mole^{-1}$ for a unit P–P and S–S bond, respectively.

The calculations for the five phosphorus sulphides yield the results presented in Table II. Here the P–S bonding parameter has been evaluated so as to yield the best overall least squares agreement with the empirical data used in the calibration. The final P–S energy parameter is 47.7 kcal $mole^{-1}$ and the RMS error is 1.45 kcal $mole^{-1}$. Clearly, the bond energy parametrisation gives a good account of the energetics of these molecules and, hence, we may use them predictively to examine the case of P_4S_5. This case is interesting in that the 'normal' (or experimental) form is shown to be the most stable although nor markedly so: isomers A and B, in which the terminal sulphur occupies a different site, are almost as stable. Indeed, the energy difference is small enough that, if entropies are similar, one would expect a proportion of these isomers present in the 'normal' form. It is interesting that the all-S-bridged isomer is far less stable than other isomers.

The bond index matrix for P_4S_5 is revealing in that it shows that the stability sequence is a rather fine balance of the S–S and P–P bonding in the cages. As we noted in previous work on phosphorus oxides [12] the P–P bonding is not strong in such systems. It is found that the component of P–P bonding which renders the P_4 tetrahedron stable is degraded substantially in the sulphides and oxides. The average bond index relevant to each P–P bond amounts to only about 0.2.

A further feature of interest illustrated by the figures is that the binding energy per sulphur atom decreases as the number of sulphur atoms increases.

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