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Crystal and Molecular Structure of Phosphorus Triiodide

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The crystal structure of phosphorus triiodide has been reinvestigated using single-crystal x-ray diffraction techniques. The structure is hexagonal, space group $P6_3$, with $a = 7.133 \pm 0.002$ Å, $c = 7.414 \pm 0.002$ Å, and $Z = 2$. The structure consists of a nearly ideal hexagonal closest packing of iodine atoms with the phosphorus atoms above the plane of iodines, approximately halfway between trigonal and octahedral coordination. A close correspondence is found between the structure of phosphorus triiodide and triiodomethane, and the results suggest that the nonbonded electron pair on phosphorus is stereochemically important.

Introduction

The crystal structure of phosphorus triiodide was originally investigated by Braekken,[1] who determined the iodine atom positions and the space group as $P6_3/m$ or $P6_3$. However, the phosphorus positions were not determined. Wyckoff[2] has suggested that the phosphorus and iodine atoms are coplanar, but this assignment differs from that found in the molecular structure.[3] A redetermination of the structure has been initiated in an effort to redefine fully the structural parameters for the solid.

Experimental Section

Preparation. Crystals of red-orange phosphorus triiodide were prepared by vacuum sublimation. Samples of triiodide were obtained by the reaction of europium diiodide and europium phosphate with silicon dioxide at 900–950 °C.[4] In the crystal growth procedures, the triiodide was sealed in evacuated glass ampules and transported across a temperature gradient bounded by a maximum of 50 °C and a minimum of 20 °C. All manipulations of the triiodide were performed in a nitrogen-filled glovebox, and crystals were immersed in paraffin oil during examination in air. A single crystal (parallelepiped, $a \times a \sin 120° \times c$; corresponding dimensions $0.30 \times 0.20 \times 0.19$ mm) was selected and sealed in a thin-walled (0.01 mm) glass capillary.

Single-Crystal Analysis. Conventional Weissenberg and precession methods were employed for a-axis alignment of the crystal and for the confirmation of the space group assignment as $P6_3/m$ or $P6_3$. Lattice parameters ($a = 7.133$ (2) Å, $c = 7.414$ (2) Å) were refined from powder data obtained with a forward-focusing Guinier camera.[4] Intensity measurements were made using a Weissenberg-geometry single-crystal diffractometer with scintillation detection and pulse height analysis of graphite-monochromatized Mo Kα radiation. Reflections were scanned at 4° min^{-1} in the ω–2θ scan mode using 30-s background counts at both ends of the scan. Selected intensities from the first few levels were remeasured at the end of data collection, and there were no significant changes in their values. The intensities were corrected for Lorentz–polarization and absorption effects ($\mu = 146.6$ cm^{-1}). A total of 500 intensities were collected, and symmetry-equivalent values were averaged to yield a final set of 342 reflections (9 levels, $h = 0$–8); 76 of these were below the minimum observable value.[5]

Structure Determination

A three-dimensional Patterson function, generated from the corrected intensities, permitted location of the iodine atoms. Preliminary refinement of the iodine and phosphorus atom positions was made assuming space group $P6_3/m$ with the iodine atoms in special position 6h and the phosphorus atoms in special position 2c. This calculation gave convergence of the iodine atom positions at a very high R value (46%), but the phosphorus atom z coordinate did not converge in this space group. A difference electron density function was generated and showed the phosphorus atoms to be out of the plane of the iodine atoms. An ordered distribution of phosphorus atoms requires that the space group be $P6_3$, which was employed for subsequent refinement. The origin was fixed by arbitrarily setting the z coordinate of iodine at 0.0.

A full-matrix, least-squares refinement of the atomic parameters and isotropic temperature factors was carried to convergence using the scattering factors of Doyle and Turner[6] and anomalous dispersion corrections of Cromer and Liberman.[7] The weighting scheme of Cruickshank[8] was used throughout. Further refinement proceeded with anisotropic thermal parameters to a residual, R, of 6.5% ($R = 8.8$% including unobserved reflections; $R_w = 9.5$%, $R_w = 14.2$% including unobserved reflections). The final atom coordinates and anisotropic temperature factors are listed in Table I.

Discussion

Bond lengths and angles, of which selected values are presented in Table II, were calculated from the refined atom coordinates and lattice parameters with standard errors calculated using the full variance–covariance matrix of the atom coordinates and standard deviations of the lattice parameters. The values of the phosphorus to iodine nearest neighbor bond distance (2.463 ± 0.005 Å) and iodine–phosphorus–iodine bond angle ($102.0 \pm 0.3°$) agree very well with those reported (2.43 ± 0.04 Å and $102 \pm 2°$) from electron diffraction studies of the gas-phase molecule.[3] A two-dimensional representation of the structure viewed along the c axis is shown in Figure 1 and a three-dimensional drawing of the asymmetric molecular unit showing the thermal ellipsoids is shown in Figure 2.

The structure consists of a nearly ideal hexagonal closest packing of iodine atoms, with the phosphorus atoms ($z = 0.146$) located between the octahedral ($z = 0.25$) and trigonal

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Table I. Atomic and Thermal Parameters of Phosphorus Triiodide and Triiodomethane[a]

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PI_3	I(6c)	0.0337 (3)	0.3475 (2)	0.0	0.0193 (3)	0.0188 (3)	0.0249 (4)	0.0048 (2)	0.003 (1)	0.0034 (6)
	P(2b)	$^1/_3$	$^2/_3$	0.146 (2)	0.045 (5)	0.045 (5)	0.006 (2)	0.023 (4)	0	0
HCI_3[b]	I(6c)	0.04	0.35	0.0						
	C(2b)	$^1/_3$	$^2/_3$	0.099						

[a] Uncertainties in last digit appear in parentheses. [b] HCI_3 data are from ref 8.

Table II. Selected Bond Distances and Bond Angles of Phosphorus Triiodide[a,b]

(i) Interatomic distances, Å					
P(1)-I(1)	3×	2.463 (5)	I(1)-I(5)	4×	4.399 (1)
P(1)-I(5)	3×	3.670 (8)	I(1)-I(8)	2×	4.444 (2)
I(1)-I(2)	2×	3.829 (3)	I(4)-I(7)	2×	4.449 (3)
(ii) Angles, Deg					
I(1)-P(1)-I(2)	3×	102.0 (3)	I(1)-P(1)-I(7)	3×	160.6 (4)
I(1)-P(1)-I(8)	3×	90.7 (1)	I(5)-I(1)-I(8)	3×	60.41 (5)
I(1)-P(1)-I(5)	3×	89.4 (1)			

[a] Numbers in parentheses after the atomic symbol refer to atoms labeled in Figure 1. [b] Uncertainties in the last digit of distances and angles appear in parentheses.

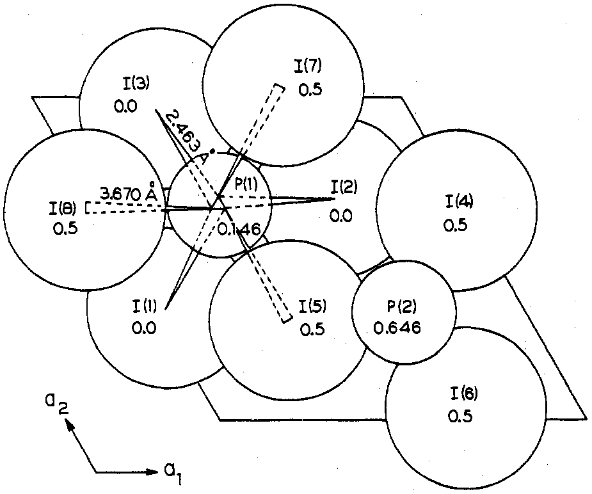

Figure 1. Two-dimensional representation of the phosphorus triiodide structure viewed along the *c* axis. The *z* coordinates of each atom are indicated and atomic symbols with numbers in parentheses are to be used in conjunction with Table II. The coordination geometry around one phosphorus atom is shown.

(z = 0.0) coordination sites. A pyramidal molecular geometry is obviously maintained in solid PI_3. In Figure 1, the molecule is viewed along its threefold axis and is defined by iodines I(1)–I(3) and by phosphorus P(1), which is 1.088 Å above the plane of the iodines. In comparison, the triiodides of As, Sb, and Bi are rhombohedral ($R\bar{3}$, BiI_3 (or $FeCl_3$) type with the halide atoms in nearly perfect hexagonal closest packed positions.[2] Since the metallic elements are centered in the octahedral sites, identification of molecular units is not possible, and the crystals appear to be substantially ionic in nature. The presence of an electron pair directed toward the three iodine atoms (I(5), I(7), and I(8)) above phosphorus (P1) in Figure 1 is indicated by their displacement from closest packed positions. The upper three iodines, which are associated with three different triiodide molecules, are noticeably farther apart than those of the lower set. This result is consistent with the findings of Andersson and Åstom,[9] who have observed the stereochemical effects of nonbonded electron pairs on the solid-state structures of several lead and antimony compounds.

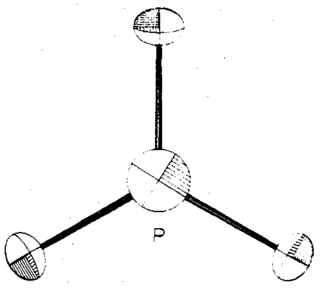

Figure 2. ORTEP diagram of PI_3 viewed along the *c* axis. The thermal ellipsoids are at the 50% probability level.

Comparison of the lattice parameters (a = 6.818 Å, c = 7.524 Å) and atomic coordinates (Table I) of triiodomethane[10] (also $P6_3$) with the results for the triiodide confirms that the two compounds are isostructural as suggested originally by Braekken.[1] For triiodomethane, the hydrogen atom occupies the same position as the electron pair in phosphorus triiodide. This is to be expected because of the isoelectronic relationship between the carbon–hydrogen moiety and nitrogen. The trihalides of boron (BCl_3, BBr_3, and BI_3) have space group $P6_3/m$ and are not isostructural with phosphorus triiodide as has been suggested,[2] but the two structures do have similar closest packed halide positions.

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Registry No. PI_3, 13455-01-1.

Supplementary Material Available: Listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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