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Constrained Refinements of the Structure of Tetraphosphorus Trisulphide below the Plastic Transition

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Abstract—The crystal structure of P_4S_3 14 K below its plastic crystal phase transition has been refined to find whether the amplitude of libration is anomalously large. Constrained refinements show there is no detectable molecular distortion owing to crystal forces, and that the molecules move as rigid bodies. The amplitudes of libration of the two symmetry independent molecules are very similar; they show a small variation with direction but are not anomalously large. Measurements nearer the transition are suggested.

1. Introduction

Molecules of P_4S_3 are of globular shape as indicated in Fig. 1, and in common with many globular molecules P_4S_3 crystallizes in a plastic crystal phase.[1] The transition to an ordered crystalline state occurs at 313.90 K with an entropy of transition of 7.85 e.u.[1] Crystallographic studies in this phase[2] show that there are two symmetry independent molecular orientations, and that the molecules pack in a pseudo-h.c.p. (hexagonal close packed) manner. It has been suggested that this form of structural complication involving pseudosymmetry is likely to characterize plastic crystals in their ordered phase.[3] Figure 2 shows the P_4S_3 structure schematically, accentuating the near hexagonal structure.

The room temperature structure measurements are rather close to the transition temperature ($\sim$14 K), and we would therefore expect to see some premonition of the transition. In the plastic phase it is assumed that there is only a weak resistance to molecular reorientation, and thus just below the transition anomalously large librational motions are expected. The present paper contains an anlaysis of the

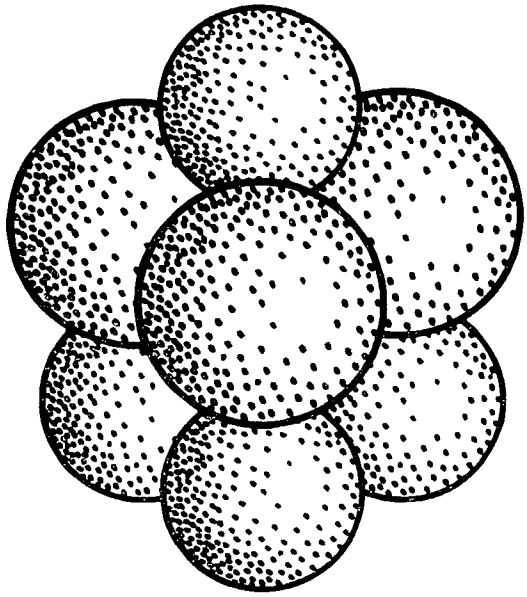

Figure 1. The molecule of P_4S_3, showing its globular nature.

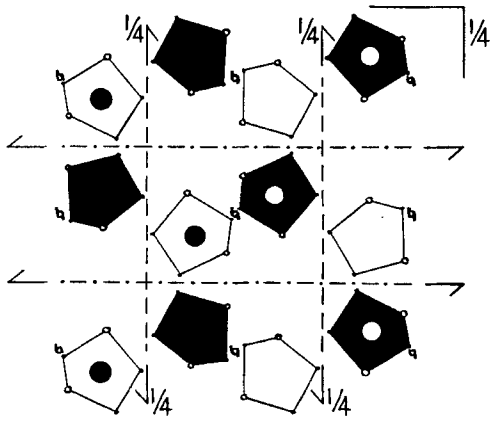

Figure 2. The structure of P_4S_3 projected down the x-axis, showing the symmetry elements of the space group Pmnb. There are two sets of molecules unrelated by symmetry, and one set is marked by centrally placed circles. Molecules lying on one plane of symmetry have been filled in, emphasizing the approximate hexagonal close packing.

available X-ray diffraction data, using the techniques of constrained least squares refinement[4] followed by significance testing.[5] By these techniques the most reliable estimates of librational motion that the data can provide are obtained, and rigorous statistical tests can be used.

In the present paper we use the constraint procedure in two ways, one involving the molecular shape, the other involving the thermal motion. As can be seen from Fig. 1 the molecules have 3m symmetry when in the free state, whereas in the crystalline state only one of the symmetry planes is used. It is expected for small globular molecules that there will be only a minimal distortion of the molecules from the free state symmetry on crystallization. If this distortion is small compared with the standard deviations in atomic positions resulting from the structure analysis, then it is clearly unnecessary to allow any distortion in the analysis. This greatly reduces the number of parameters to be determined from the data, with the result that those parameters which are used are determined with more accuracy. In the P_4S_3 structure it is also reasonable to insist that the symmetry unrelated molecules have the same shape, giving a further reduction in the parameter set. The statistical tests used to check the validity of applying these constraints are discussed later in the paper. Details of the constraint method are out of place here as they are fully explained elsewhere.[4]

The constraint involving the thermal motion is discussed in context in the next section.

2. Model Refinements

The data used in the refinements were the 959 observable reflections of Leung *et al.*[2] The weight w_i for the i-th observation was obtained from the empirical scheme[6]

$$w_i = [2F_{\min} + F_i^{\text{obs}} + 2(F_i^{\text{obs}})^2/F_{\max}]^{-1}$$

with $F_{\min} = 10$ and $F_{\max} = 500$. The scattering factors used for sulphur and phosphorus were the neutral atom scattering factors of Doyle and Turner.[7]

Calculations were performed on three different models (see Table 1). In Model I the shape of the molecules was constrained so that both

TABLE 1 Reliability Factors for the Various Models

Model	Constraints used	Number of parameters	R_w	R
I	Rigid body + shape	35	857	0.093
II	Rigid body	49	847	0.093
III	Unconstrained	73	824	0.092

symmetry independent molecules were of identical shape, conforming to the free state 3m symmetry. Four parameters are required to specify the molecule completely, and these are described by Fig. 3. The molecular axes X, Y, Z used here have an origin near to the molecular centre of gravity. To obtain the atomic positions in the crystal structure this basic molecule is first rotated through an angle θ about the X-axis, and then placed on the plane of symmetry with

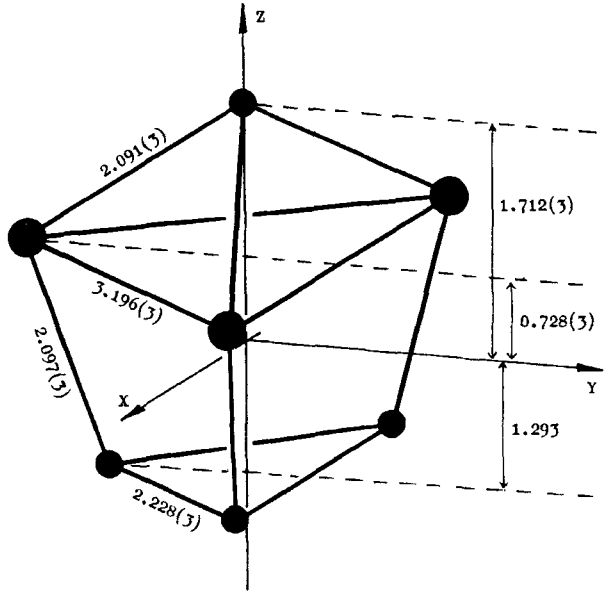

Figure 3. The molecule of P_4S_3 with the final bond lengths and their errors. Parameters used in the model are those with values 3.196, 2.228, 1.712, 0.728 and 1.293, but as there are only four independent parameters the last parameter was fixed and therefore appears with no error. Correction for the effect of libration[10] requires all the bond lengths to be increased by 0.3%.

coordinates y_0, z_0 for its origin. θ, y_0 and z_0 were all variable parameters, and a set of these parameters was necessary for each independent molecule. The best values found were

	y_0 in Å	z_0 in Å	θ in degrees
Molecule 1	1.198 (2)	−1.512 (2)	−34.14 (6)
Molecule 2	4.792 (2)	−1.927 (2)	28.87 (6)

Thus Model I used 10 variable parameters to position all the atoms, whereas Models II and III, where all shape constraints were removed, required 24.

Models I and II were treated in the same way as regards the thermal motion. It is clear that if a molecule moves as a rigid body there must be relationships between the various atomic mean square displacements, these latter being parameters determinable from the diffraction measurements. It is customary to ignore the correlations, introduce parameters for all these displacements (as we have done in Model III) and then analyse the results for rigid body motion. Models I and II, however, incorporate all the rigid body correlations. The thermal motion for any one molecule can be described by three tensors, usually denoted **T**, **L** and **S**.[8] These are respectively the mean square translational displacement, the mean square librational displacement and translation-libration cross terms. These tensors must conform to the molecular site symmetry, requiring in our particular case only 12 non-zero components, whereas considering the atomic motions as independent requires 24 parameters. This applies to both of the symmetry independent molecules. Each molecule requires its own set of tensors **T**, **L** and **S** as there is no physical reason for expecting these tensor sets to be equivalent.

All three models were refined by a least squares procedure. The empirical weighting scheme was tested and found satisfactory in each case.[6] The goodness of fit for any model is characterized by the residual,

$$R_w = \sum_i w_i \Delta_i^2$$

$$\Delta_i = |F_i^{\text{obs}}| - |F_i^{\text{calc}}|,$$

and these are presented in Table 1. The customary R-factor,

$$R = \sum_i |\Delta_i| / \sum_i |F_i^{\text{obs}}|$$

is also given, and in all cases this was less than $R = 0.16$ of Leung *et al.*[2] Our improvement was attributable to the use of a more realistic model for thermal motion and the exclusion of the " accidentally absent " reflections.

We now have to decide which models are physically plausible. Either Model III contains too many redundant parameters or Models I or II involve too strict a constraint. To compare Models I and III for example we must calculate[5,8]

$$\mathscr{R}_{\text{obs}} = [R_w(\text{I})/R_w(\text{III})]^{1/2}$$

and compare this with the appropriate statistical distribution for the ratio, namely

$$\mathscr{R}_\alpha = \left\{ \frac{N-n}{M-N} \cdot F_\alpha + 1 \right\}^{1/2}.$$

Here M = number of observations (959),
N = number of parameters in III (73),
n = number of parameters in I (35),
α = the probability level,
F_α = the α point on the F-distribution with $N-n$ and $M-N$ degrees of freedom.

Values for $\mathscr{R}_{\text{obs}}$, $\mathscr{R}_{0.25}$ and $\mathscr{R}_{0.01}$ are presented in Table 2. As $\mathscr{R}_{\text{obs}}$ was less than the appropriate $\mathscr{R}_{0.25}$ for all the three comparisons that can be made, we conclude with confidence that the fully constrained Model I cannot be improved on by the introduction of the extra parameters of Model III, and therefore only the results from the

TABLE 2 Reliability Factor Ratios and Points of the $\mathscr{R}$-distribution

Models compared	$\mathscr{R}_{\text{obs}}$	Probability levels 0.25	0.01
I/II	1.006	1.009	1.016
II/III	1.014	1.016	1.024
I/III	1.020	1.024	1.034

Model I need be presented here. The atomic positions are given in Table 3; the basic parameters from which these have been generated have already been given. The individual atom temperature parameters can be derived from the tensor components given in Table 4.

TABLE 3 Coordinates of the atoms in Ångströms. The orthorhombic cell has $a = 9.660$, $b = 10.597$, $c = 13.671$ Å. The numbering and labelling of atoms follows Leung *et al.*[2] The z-coordinates have been altered by a lattice translation.

		Molecule 1, labelled S_i, P_i	Molecule 2, labelled $S_{i'}$, $P_{i'}$
S_1	x	5.647	0.817
	y	1.554	5.951
	z	−0.392	−1.736
S_3	y	−0.737	3.528
	z	−1.945	−0.398
P_1	x	6.131	1.301
	y	2.456	4.730
	z	−2.222	−3.370
P_3	y	0.859	3.041
	z	−3.304	−2.437
P_4	y	0.238	5.619
	z	−0.095	−0.429

TABLE 4 Components of the tensors **T** (in Å²), **L** (in deg.²) and **S** (in Å.deg.). The components not given are zero by symmetry. Errors for $\mathbf{T}_{ij}$, $\mathbf{L}_{ij}$ and $\mathbf{S}_{ij}$ are 0.001, 1.2 and 0.02 units respectively

Molecule 1						Molecule 2					
$\mathbf{T}_{11}$	0.030	$\mathbf{L}_{11}$	20.6	$\mathbf{S}_{31}$	0.08	$\mathbf{T}_{11}$	0.033	$\mathbf{L}_{11}$	22.4	$\mathbf{S}_{31}$	−0.03
$\mathbf{T}_{22}$	0.034	$\mathbf{L}_{22}$	26.8	$\mathbf{S}_{12}$	0.24	$\mathbf{T}_{22}$	0.037	$\mathbf{L}_{22}$	17.1	$\mathbf{S}_{12}$	0.22
$\mathbf{T}_{33}$	0.033	$\mathbf{L}_{33}$	15.8	$\mathbf{S}_{13}$	0.12	$\mathbf{T}_{33}$	0.030	$\mathbf{L}_{33}$	25.1	$\mathbf{S}_{13}$	−0.03
$\mathbf{T}_{23}$	0.002	$\mathbf{L}_{23}$	−1.3	$\mathbf{S}_{21}$	0.03	$\mathbf{T}_{23}$	0.001	$\mathbf{L}_{23}$	−2.3	$\mathbf{S}_{21}$	0.12

3. Discussion

Our overall conclusion is clear and is not surprising. There is no detectable distortion of the molecules from their free state symmetry,

and the motion of the molecules is of a rigid body type. Both of these are characteristics of many molecular crystals which undergo the plastic crystal phase transition, but until now they had not been found occurring together in any of the molecular crystals so far analysed by constraint procedures. Of greatest interest to us is the extent of the librational molecular motion, as it might be expected to be anomalously large owing to the proximity of the transition. However, we see from Table 4 that the diagonal components of **L** indicate no greatly preferred axis of libration. The averages of these elements are 21.1 and 21.5 degrees^2 for the two independent molecules, showing that the librational amplitudes do not differ significantly. These values are only marginally larger than 21 and 19 degrees^2 found for naphthalene and pyrene respectively,[4] suggesting that the librational motion in P_4S_3 is not excessive.

This conclusion does not alter even when we take account of the fact that both naphthalene and pyrene are of smaller mass than P_4S_3 and have lower moments of inertia on average. A rough calculation involving the moment of inertia can be made using[9]

$$\overline{\phi_I^2} = 4050 \frac{h}{\pi^4 I \nu} \coth\left(\frac{h\nu}{2kT}\right).$$

This gives the mean square librational displacement in degrees^2 about an axis with moment of inertia I, assuming that all the librational modes have a frequency ν (Einstein model). Assuming a temperature $T = 300$ K, and average values for $\overline{\phi}^2$ ($= \bar{L}_{ii}$) and I, the equation is satisfied for $\nu \sim 47$ cm^{-1}. This is by no means an exceptionally low librational frequency. We are therefore led to conclude that there is no premonitory behaviour observable by X-ray diffraction at 14 K below the transition. Measurements made much closer to the transition temperature and analysed in this way would therefore be of great interest. We hope to be able to do this, either with X-rays or with neutrons, using temperature intervals much smaller than is at present customary in crystallographic studies.

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