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Van der Waals interaction and the packing of molecular crystals.

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The position and the orientation of a molecule of known geometry in a molecular crystal can be found by locating the deepest minima of the intramolecular van der Waals potential energy, calculated as a function of the six rotational and translational degrees of freedom. The simple case of hexamethylbenzene is reported.

We have previously (Liquori, 1959; De Santis, Giglio, Liquori & Ripamonti, 1963; De Santis, Giglio, Liquori & Ripamonti, 1965) shown that the most stable helical conformations of linear macromolecules may be predicted by locating the minima of the intramolecular van der Waals potential energy. The satisfactory results obtained in those cases have induced us to apply this method to the analysis of the structure of molecular crystals. A few recent approaches to this problem have been reported (Williams, 1965; Craig, Mason, Pauling & Santry, 1965; Kitaigorodskii, 1965).

The first case we have studied is that of hexamethylbenzene, the crystal structure of which has been solved by X-ray diffraction (Lonsdale, 1929*a*, *b*; Brockway & Robertson, 1939). By fixing bond lengths and bond angles *a priori* the potential energy has been calculated as a function of the rotational degrees of freedom only, since the center of symmetry of the molecule is at the origin of the unit cell (the space group is $P\bar{1}$ and there is one molecule per unit cell). The potential energy of a set of the nearest-neighbour 20 molecules was obtained by adding the separate terms corresponding to pairwise 'non-bonded' interactions $C \cdots C$, $CH_3 \cdots CH_3$ and $C \cdots CH_3$. These were represented by the same functions as those used in previous calculations (De Santis, Giglio, Liquori & Ripamonti, 1963; Bartell, 1960; Mason & Kreevoy, 1955). The hexamethylbenzene molecule was rotated in a right-handed orthogonal coordinate system $OXYZ$ oriented with respect to the triclinic crystallographic system $Oabc$ in such a way that the Oc and OZ axes coincided and the Ob axis lay in the YZ plane (Fig. 1). The total potential energy was expressed as a function of the Eulerian angles ψ_1, ψ_2, ψ_3 defined according to Goldstein (1951). The calculations were performed on an IBM 1620 computer using angular increments of 20° except in the regions of the minima where the angular increments were 2°. The computing time was about 90 hours. The deepest minimum was located at $\psi_1 = 0{\cdot}9°$, $\psi_2 = 0{\cdot}3°$, $\psi_3 = 0{\cdot}9°$, the interpolation method of Shoemaker, Donohue, Schomaker & Corey (1950) being used. This corresponds very closely to the arrangement of the molecules in the crystal structure.

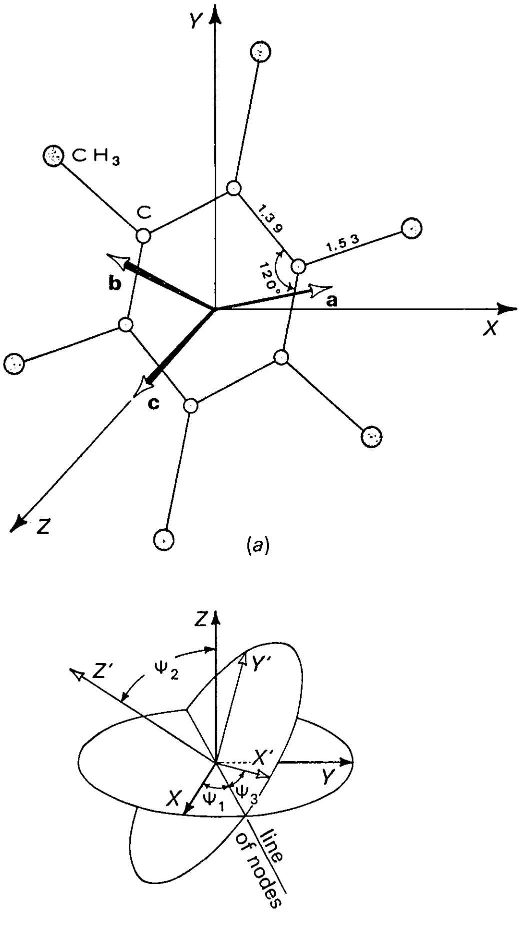

Fig. 1. (*a*) Relationship between the orthogonal axes X, Y, Z and the crystallographic axes a, b, c. The hexamethylbenzene molecule is shown with bond lengths and angles used in the calculations. (*b*) The Eulerian angles ψ_1, ψ_2, ψ_3 relating the rotated axes X', Y', Z' to the original unrotated orthogonal axes X, Y, Z.

In Fig. 2 a section of the potential energy map at $\psi_1 = 0°$ is shown. The average differences between the coordinate values determined by X-ray analysis of the crystal structure and those derived from the position of the minimum in the potential energy map are:

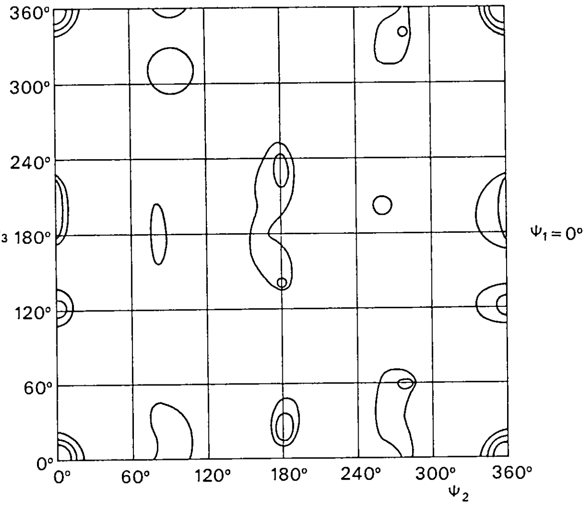

Fig. 2. Section at $\psi_1 = 0°$ of the potential energy map. The contour lines are drawn at −10, 0 and 20 kcal.mole^{-1}.

$$x=0{\cdot}037\ \text{Å}\quad y=0{\cdot}058\ \text{Å}\quad z=0{\cdot}045\ \text{Å}$$

with a possible uncertainty of about ±0·002 Å. It therefore appears that, in spite of the approximation involved in the choice of potential functions, this type of calculation can be used to predict the molecular packing of crystals of unknown structure with satisfactory accuracy, when the molecular shape and size are known. This method will be extended to more general cases where the molecules lie at general positions in the unit cell. In addition, the information about the potential energy minima might be used in order to analyse thermal movements in molecular crystals in terms of rigid-body molecular oscillations.

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X-ray determination of the lattice parameters of potassium dihydrogen phosphate at elevated temperatures.

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A precision determination of the lattice parameters of tetragonal potassium dihydrogen phosphate has been made over the temperature range 25–150°C. The lattice parameters at room temperature are $a=7{\cdot}4528\pm 0{\cdot}0004$, $c=6{\cdot}9683\pm 0{\cdot}0004$ Å. The principal coefficients of thermal expansion have been evaluated and are found to follow the equations

$$\alpha_a=10{\cdot}10\times 10^{-6}+21{\cdot}68\times 10^{-8}t-2{\cdot}62\times 10^{-10}t^2$$
$$\alpha_c=28{\cdot}73\times 10^{-6}+17{\cdot}65\times 10^{-8}t+1{\cdot}83\times 10^{-10}t$$

The results of a systematic study of the temperature variation of the lattice parameters of some phosphates and arsenates isomorphous with potassium dihydrogen phosphate (KDP) at elevated temperatures have been reported from this laboratory (Deshpande & Khan, 1963, 1965*a*, *b*, 1966). Similar results on KDP itself are presented in this communication.

A symmetric focusing camera designed by Sirdeshmukh (1963) was used for obtaining powder photographs with filtered copper radiation. Six Cu $K\alpha_1\alpha_2$ doublets at high angles were used for calculating the lattice parameters by Cohen's analytical procedure. The values of the lattice parameters at five temperatures are given in Table 1.

Table 1. *Lattice parameters of potassium dihydrogen phosphate at various temperatures*

Temperature	*a*	*c*
26°C	7·4528 Å	6·9683 Å
64	7·4583	6·9771
86	7·4628	6·9833
121	7·4698	6·9962
151	7·4785	7·0068

The coefficients of thermal expansion, $\alpha_a=(1/a_{25})(da/dt)$ and $\alpha_c=(1/c_{25})(dc/dt)$, were evaluated from the data in Table 1 by the graphical procedure discussed by Deshpande & Mudholker (1961). The values of the coefficients of expansion are given in Table 2. Both the coefficients increase with temperature in an almost linear fashion. However, taking into account the slight non-linearity, the temperature variation of the coefficients of expansion can be represented by the following equations:

$$\alpha_a=10{\cdot}10\times 10^{-6}+21{\cdot}68\times 10^{-8}t-2{\cdot}62\times 10^{-10}t^2$$
$$\alpha_c=28{\cdot}73\times 10^{-6}+17{\cdot}65\times 10^{-8}t+1{\cdot}83\times 10^{-10}t^2$$

where t is the temperature in °C. The mean coefficients of expansion for the range 25–150°C were also calculated and have values $\alpha_a=26{\cdot}9\times 10^{-6}\,{}^\circ\text{C}^{-1}$ and $\alpha_c=46{\cdot}4\times 10^{-6}\,{}^\circ\text{C}^{-1}$.

Table 2. *Coefficients of thermal expansion of potassium dihydrogen phosphate at various temperatures*

Temperature	$\alpha_a\times 10^6$	$\alpha_c\times 10^6$
40°C	18·8	35·9
60	21·5	40·3
80	25·5	43·8
100	29·5	48·8
120	32·9	51·7
140	34·9	57·4

Values for the lattice parameters of KDP at room temperature have been given by Ubbelohde & Woodward (1947), Klug & Alexander (1954) and recently by Haussühl (1964). The values obtained in this work at 26°C are $a=7{\cdot}4528\pm 0{\cdot}0004$, $c=6{\cdot}9683\pm 0{\cdot}0004$ Å. These values are in reasonable agreement with those given by the workers mentioned above. The density calculated from our values is 2·337 g.cm⁻³ which compares well with the experimental