anthracene nucleus is moving with a lateral translation (along L) relative to the oxygen atoms. (1) seems to be ruled out as the main explanation because of the magnitude of the negative $\varepsilon(L)$ value. It is much larger than any bonding-anisotropy effect could be expected to be. This leaves us with the possibility of an L-translation of the whole anthracene nucleus relative to the oxygen atoms, which seem to be partially immobilized along L by 'bonds' to neighbouring molecules. This movement could possibly be phase-related to the oxygen out-of-plane libration; in which case the assumption that we are justified in using u_{ij} values for purposes of calculation would be invalid. There is some evidence that where an outer and otherwise 'mobile' atom takes part in an 'intermolecular bond', that atom *is* to a certain extent immobilized (the hydrogen atoms in urea, for example). The shortest intermolecular bond in anthraquinone (Lonsdale *et al.*, 1966) is that linking C(6) of (000) with an oxygen atom of $(\frac{1}{2}\frac{1}{2}0)$, which is 3·33 Å at +20·5°C and 3.25 Å at −170°C (all other C · · · O and C · · · C intermolecular distances at room temperatures are over 3·5 Å). It is not unreasonable to suppose that a large out-of-plane movement of the oxygen atom would exert some translatory pull on the anthracene nucleus of the neighbouring molecules to which it is attached by such a relatively strong van der Waals force.

Conclusion

The results for anthraquinone indicate two methods of testing for non-rigid-body vibrations in any given molecule for which the axes of libration are known with a good degree of certainty.

(1) First the whole molecule and then limited parts of the molecule should be treated as if they were vibrating as rigid bodies about the molecular axes of inertia. If there are no independent vibrations then the values of translatory and libratory amplitudes should be invariant with respect to the number of atoms taken to determine them. If they are not invariant then the differences can be used to determine the nature of the independent vibrations.

(2) The values of U_{ii}(calc) − U_{ii}(obs) should be examined critically, preferably using data for more than one temperature, to determine whether any individual values are consistently too high to be accounted for by experimental error or as artefacts of the calculation, even when the *average* value is well within the expected e.s.d. If there are such anomalies, these may provide a guide as to which atoms to omit from a 'difference' rigid-body analysis of the thermal data.

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The Electrostatic Interaction Energy of Ionic Lattices with Statistical Distribution of Charges

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The method due to Bertaut (1952) for calculating interaction energies is extended to include statistical distribution of charges on geometric lattices. Explicit expressions are developed for statistically random charge distributions and implicit expressions for statistical charge distributions with correlation between occurrences of charges.

Introduction

Ewald (1921) has developed methods to calculate the electrostatic potential of ionic lattices by the use of theta functions. The rapid convergence of his series makes possible the evaluation of the electrostatic interaction energy and the Madelung constant for ideal ionic crystals. Bertaut (1952) by use of faltung theory has developed general expressions for the electrostatic energy of ideal ionic crystals, which, as a special case,

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contain the Ewald formula. In this paper it is shown that the method of Bertaut (1952) may be extended to include statistically disordered crystals.

Consider a geometric lattice where positive charges are situated on lattice sites α and negative charges on lattice sites β. The positive or negative charges may be distributed on their respective sites:

(I) in an ordered array
(II) in a statistically random way
(III) statistically with correlation between occurrences of charges.

The first and second case are extremes which are seldom fully realized in nature, while statistical distribution with correlation occupies an intermediate position connecting (I) and (II).

Formally the total electrostatic energy, W_T, of an ionic lattice can be expressed as the sum of self energy, W_S, and interaction energy, W_I:

$$W_T = W_S + W_I \,. \tag{1}$$

In this paper general expressions for the interaction energy are derived for cases (II) and (III) described above. The statistically random case is solved explicitly, and practical examples are given. The statistical case with correlation is solved in terms of the statistical random case plus implicit integrals over short range order parameters.

The statistical-charge Patterson function

The concept of the statistical Patterson function is now described from which the electrostatic interaction energy is later derived. The faltung of a density distribution function, $\varrho(\mathbf{x})$, with itself is known as the Patterson function:

$$P(\mathbf{u}) = \int_{-\infty}^{\infty} \varrho(\mathbf{x})\varrho(\mathbf{x}+\mathbf{u})dv(\mathbf{x}) = \widehat{\varrho\varrho} \tag{2}$$

Here $\frown$ symbolizes the faltung operation. Statistically the Patterson function is interpreted thus: *To obtain the value of* $P(\mathbf{u})$ *we place ourselves in succession on each charge and observe which charge may be found at a vector distance* $\mathbf{u}$. *The sum of all these surroundings multiplied by the weight of the origin gives* $P(\mathbf{u})$.

For the statistical charge distribution with correlation between occurrences of charges as described under (III), the statistical-charge Patterson function can be written as:

$$\frac{1}{N} P^{*}_{(\mathrm{III})}(\mathbf{u}) = P_{\mathrm{III}}(\mathbf{u}) = \sum_{i,\nu} w_{i|\nu} q^2_{i|\nu} \tilde{\eta}^2_{i|\nu} + \sum_{i,j;\nu\neq\mu} w_{i|\nu} q_{i|\nu} q_{j|\mu} \widehat{W_{ij|\nu\mu}{}^{(\mathbf{u})}\, \widehat{\eta_{i|\nu}\eta_{j|\mu}}} \tag{3}$$

where

N = numbers of cells
$w_{i|\nu}$ = *a priori* probability that site ν be occupied by a charge of kind i.
$W_{ij|\nu\mu}{}^{(\mathbf{u})}$ = *a posteriori* probability that the μth lattice site at a vector distance $\mathbf{u}$ from site ν be occupied by a charge of kind j, if the νth site is occupied by a charge of kind i.
$q_{i|\nu}$ = charge of kind i on lattice site ν.
$\eta_{i|\nu}$ = distribution function of ith charge kind on site ν.
$\tilde{\eta}^2_{i|\nu}$ = faltung of ith charge distribution function with itself at $\mathbf{u}=0$.
$\widehat{\eta_{i|\nu}\eta_{j|\mu}}$ = faltung of ith with jth distribution function at $\mathbf{u}\neq 0$.

The *a posteriori* probabilities represent short range order. They may be written in the form:

$$\left.\begin{aligned} W_{ij|\nu\mu}{}^{(\mathbf{u})} &= w_{j|\mu} + M_{ij|\nu\mu}{}^{(\mathbf{u})} \\ \text{with:}\quad \lim_{u\to\infty} M_{ij|\nu\mu}{}^{(\mathbf{u})} &= 0 \\ M^{(0)}_{ii\,|\nu\nu} &= 1 - w_{i|\nu} \\ M^{(0)}_{ij\,|\nu\nu} &= -w_{j|\nu} \end{aligned}\right\} \tag{4}$$

Using relation (4), equation (3) can be written as:

$$\begin{aligned} P_{(\mathrm{III})}(\mathbf{u}) = {} & \sum_{i,\nu} w_{i|\nu} q^2_{i|\nu} \tilde{\eta}^2_{i|\nu} \\ & + \sum_{i,j;\nu\neq\mu} w_{i|\nu} w_{j|\mu} q_{i|\nu} q_{j|\mu} \widehat{\eta_{i|\nu}\eta_{j|\mu}} \\ & + \sum_{i,j;\nu\neq\mu} w_{i|\nu} q_{i|\nu} q_{j|\mu} \widehat{M_{ij|\nu\mu}{}^{(\mathbf{u})}\, \widehat{\eta_{i|\nu}\eta_{j|\mu}}} \,, \end{aligned} \tag{5}$$

where $w_{i|\nu} w_{j|\mu}$ represent functions periodic with $\mathbf{u}$ or

$$P_{(\mathrm{III})}(\mathbf{u}) = P_S(\mathbf{u}) + P_I(\mathbf{u}) + P_{I,M}(\mathbf{u}) \,, \tag{6}$$

where $P_S(\mathbf{u})$ represents the first sum, $P_I(\mathbf{u})$ the second sum, and $P_{I,M}(\mathbf{u})$ the last sum of (5). If no short range order exists then $M_{ij|\nu\mu}{}^{(\mathbf{u})} = 0$ consequently $P_{I,M}(\mathbf{u}) = 0$ and (6) reduces to:

$$P_{(\mathrm{II})}(\mathbf{u}) = P_S(\mathbf{u}) + P_I(\mathbf{u}) \,, \tag{7}$$

thus representing statistical random distribution of charges as described under (II).

The electrostatic interaction energy

The electrostatic interaction energy of a statistical distribution with correlation between occurrences of charges, $W_{I(\mathrm{III})}$, is the sum of two terms:

$$W_{I(\mathrm{III})} = W_{I(\mathrm{II})} + W_{I,M} \,, \tag{8}$$

where

$$W_{I(\mathrm{II})} = \tfrac{1}{2} \int \frac{P_I(\mathbf{u})}{u} dv(\mathbf{u}) \tag{9}$$

is the interaction energy due to a statistical random charge distribution and

$$W_{I,M} = \tfrac{1}{2} \int \frac{P_{I,M}(\mathbf{u})}{u} dv(\mathbf{u}) \tag{10}$$

is an additional term which contains short range order parameters of the form $M_{ij|\nu\mu}{}^{(\mathbf{u})}$.

The interaction energy due to a statistical random point charge distribution, $W'_{I(\mathrm{II})}$, may conveniently be expressed by defining an average density distribution function:

$$a(\mathbf{x}) = \sum_{i,\nu} w_{i|\nu} q_{i|\nu} \delta(\mathbf{x} - \mathbf{r}_\nu) . \qquad (11)$$

Here the Dirac δ function replaces the charge distribution function η, and $\mathbf{r}_\nu$ is the vector to the νth lattice site. $a(\mathbf{x})$ is a periodic function and may be developed in a Fourier series:

$$a(\mathbf{x}) = V^{-1} \Sigma \overline{F(\mathbf{h})} \exp(-2\pi i \mathbf{h} . \mathbf{x})$$

with the Fourier transform

$$\overline{F(\mathbf{h})} = \sum_{\nu} q_\nu \exp(2\pi i \mathbf{h} . \mathbf{x}_\nu) \qquad (12)$$

where

$q_\nu = \sum_{i} w_{i|\nu} q_{i|\nu}$

$\mathbf{x}_\nu$ = fractional coordinates of the charges in the unit cell

$\mathbf{h}$ = reciprocal vector.

Making use of the fact that the Fourier transform of a product, $\mathscr{F}\{\overline{F(\mathbf{h})} . \overline{F(\mathbf{h})}^*\}$, is equal to the faltung of the Fourier transformed functions, there results:

$$\begin{aligned} A(\mathbf{u}) = \widehat{aa} &= V^{-1} \sum_{h} |\overline{F(\mathbf{h})}|^2 \exp(2\pi i \mathbf{h} . \mathbf{u}) \\ &= \sum_{i,\nu} w^2_{i|\nu} q^2_{i|\nu} \delta(\mathbf{u}) \\ &+ \sum_{i,j;\nu\neq\mu} w_{i|\nu} w_{j|\mu} q_{i|\nu} q_{j|\mu} \delta(\mathbf{r}_{\nu\mu} - \mathbf{u}) \\ &= A_S + A_I \end{aligned} \qquad (13)$$

where

A_S represents the first and A_I the second term in equation (13), and

$\mathbf{r}_{\mu\nu} = \mathbf{r}_\nu - \mathbf{r}_\mu$.

Comparing (13) with (5) and (7) it is immediately seen that the interaction terms, A_I, are identical with $P'_I(\mathbf{u})$ where the prime indicates $\delta \to \eta$, *i.e.* point charge distribution. Therefore, the interaction energy of a statistical random point charge distribution, $W'_{I(\mathrm{II})}$, is given by:

$$\begin{aligned} W'_{I(\mathrm{II})} &= \tfrac{1}{2} \int \frac{A(\mathbf{u})}{u} dv(\mathbf{u}) - \tfrac{1}{2} \int \frac{A_S(\mathbf{u})}{u} dv(\mathbf{u}) \\ &= \frac{1}{2V} \sum_{h} |\overline{F(\mathbf{h})}|^2 \int \frac{\exp(2\pi i \mathbf{h} . \mathbf{u})}{u} dv(\mathbf{u}) \\ &\quad - \tfrac{1}{2} \int \frac{A_S(\mathbf{u})}{u} dv(\mathbf{u}) \\ &= \frac{1}{2\pi V} \sum_{h} \frac{|\overline{F(\mathbf{h})}|^2}{h^2} - \tfrac{1}{2} \int \frac{A_S(\mathbf{u})}{u} dv(\mathbf{u}) . \end{aligned} \qquad (14)$$

In this form equation (14) is divergent. In order to achieve convergence it is necessary to replace the Dirac δ functions with spherosymmetric charge distribution functions (Gauss function). The formalism for this substitution developed by Bertaut (1952) need not be repeated. It suffices to rewrite Bertaut's formulae (34) and (35), and refer the reader to Bertaut's paper for charge overlap corrections and further details.

Thus the interaction energy for statistically random charge distribution (II) is

$$W_{I(\mathrm{II})} = \frac{1}{2\pi V} \sum_{h} \frac{|\overline{F(\mathbf{h})}|^2}{h^2} |\varphi(h)|^2 - 2\pi \int_0^\infty u p'(u) du (\Sigma q^2_\nu) \qquad (15)$$

or

$$W_{I(\mathrm{II})} = \frac{1}{2\pi V} \sum_{h} \frac{|\overline{F(\mathbf{h})}|^2}{h^2} |\varphi(h)|^2 - \int_{-\infty}^\infty |\varphi(h)|^2 dh (\Sigma q^2_\nu) \qquad (16)$$

where $\varphi(h) = \int \sigma(x) \exp(2\pi i \mathbf{h} . \mathbf{x}) dv(\mathbf{x})$ is the Fourier transform of the spherosymmetric, normalized charge distribution function, $\sigma(x)$, and $p'(u) = \widehat{\sigma\sigma}$.

The electrostatic interaction energy of a statistical distribution with correlation between the occurrences of charges, (8), can be expressed by (15) or (16) plus $W_{I,M}$ (equation 10). $W_{I,M}$ may be evaluated in direct space as indicated by (10), or the summation may be carried out in Fourier space. In either case the convergence is assured by the damping character of

$$\lim_{u\to\infty} M_{ij|\nu\mu}{}^{(\mathbf{u})} = 0 .$$

Explicit functional forms for $W_{I,M}$ will be the subject of a future paper.

Examples

The statistically random distribution is illustrated by AlMg spinel. In the unit cell of normal spinel eight Mg^{2+} are situated on tetrahedrally oxygen-coordinated sites, and sixteen Al^{3+} on octahedrally oxygen-coordinated sites. In inverse spinel with statistical distribution eight Al^{3+} occupy the tetrahedrally coordinated sites, and eight Al^{3+} plus eight Mg^{2+} are assumed to be statistically random distributed on octahedrally coordinated sites. In statistical spinel the cations are assumed to be distributed in a statistically random way on tetrahedrally and octahedrally coordinated sites. For the calculation of the interaction energy a lattice constant of 8·080 and a parameter of 0·235 were assumed.

The interaction energies were found to be:

1. Normal spinel	5568 kcal.mole^{-1}
2. Inverse spinel with statistical distribution	5416 kcal.mole^{-1}
3. Statistical spinel	5442 kcal.mole^{-1}

(random distribution of cations on both cation-sites) The small differences in the electrostatic energies indicate that the spinel type is not primarily governed by electrostatic forces. The repulsions terms amount to about 10–15% of the lattice energy and cannot be neglected. It should be pointed out the variation of the oxygen parameter has not been taken into account as has already been done by Verwey, de Boer & van Santen (1948), who already give the energy values for 1 and 2.

This paper is part of an investigation of the cation distribution in mixed crystals. We thank the Deutsche Forschungsgemeinschaft for financial assistance. One of us (K.H.) wishes to express his appreciation to the National Science Foundation for a postdoctoral fellowship.

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The Structure of Mercuri-iodide Ions. I. Trimethylsulphonium Mercuritriiodide $(CH_3)_3SHgI_3$

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Trimethylsulphonium mercuritriiodide, $(CH_3)_3SHgI_3$, crystallizes in spacegroup $P2_1/c$ with cell dimensions $a = 8{\cdot}51 \pm 0{\cdot}03$, $b = 15{\cdot}57 \pm 0{\cdot}05$, $c = 11{\cdot}69 \pm 0{\cdot}12$ Å, $\beta = 128{\cdot}0^\circ \pm 0{\cdot}4^\circ$ and four molecules per cell. Intensity data were collected with an Arndt & Phillips automatic linear diffractometer and Mo $K\alpha$ radiation and the structure was solved by Patterson and Fourier syntheses with least-squares refinement. The HgI_3^- ion is planar trigonal and the $(CH_3)_3S^+$ ion is pyramidal.

Introduction

In the analysis of the structures of proteins by the isomorphous replacement method, it is required to introduce a heavy atom into the crystal structure without displacing the protein molecules in any way. One of the most successful heavy atom groups to be used with a number of proteins is an ion derived from K_2HgI_4. At low resolution the precise nature of the complex is not important but the use of these derivatives at a resolution higher than 6 Å has been hampered by lack of knowledge of the nature of the heavy atom group. Sillen (1949) has investigated the nature of the mercuri-iodide ions present in solution as a function of the concentration of iodine and has shown that at any one concentration of iodine a number of different ions can be present.

Bluhm, Bodo, Dintzis & Kendrew (1958) have investigated the probable nature of the ion included in the derivative of sperm-whale myoglobin by a titration experiment carried out in the same conditions as those used in crystallization and obtained results suggesting that the complex included is HgI_3. Furthermore, they discovered that a mercuri-iodide group is incorporated in the myoglobin molecule at two sites and, following the work of Smiles (1900) on complexes of mercuric iodide and methyl sulphide, they speculated that the two methionine residues in sperm-whale myoglobin might be involved in the complex formation. Kendrew, Watson, Strandberg, Dickerson, Phillips & Shore (1961) have since shown, however, by locating the methionine residues, that they are not involved in the complex formation and very recently Scouloudi (1965) has shown that most of the mercuri-iodide in the complex with seal myoglobin is present in the form of a roughly planar HgI_3 group.

Rây & Adhikary (1930) had already shown that one of the compounds of Smiles was composed of two singly charged ions, $(CH_3)_3S^+$ and HgI_3^-, and that another consisted of two singly charged positive ions and one doubly charged negative ion, namely $2(CH_3)_3S^+$ and HgI_4^{2-}. These general conclusions have been confirmed and the configurations of the mercuri-iodide ions have been determined in the studies of these two compounds that are reported in this and the following paper. A preliminary account of the work has already been published (Fenn, Oldham & Phillips, 1963).

Experimental

The compound was prepared by the method of Rây & Adhikary (1930). Needle-shaped crystals were grown from a solution of $(CH_3)_3SHgI_3$ in acetone, and from oscillation, Weissenberg and precession photographs it was established that the crystal system is mono-

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