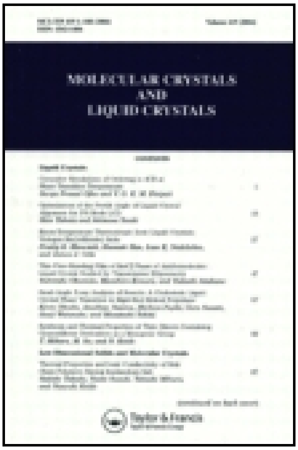

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The Intermolecular Potential and Structure of Crystals of Aromatic Molecules‡

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Abstract—A summary of recent studies of the equilibrium structures of molecular crystals is presented.

Introduction

Three distinct theoretical approaches, of varying sophistication, to our understanding of the equilibrium structure of molecular crystals may be discerned as a result of several publications during the past few years. In the first, which is largely due to Kitajgorodskij, the intermolecular potential is obtained by summing individual, empirically based, atom-atom potential functions which take the form

$$V(r) = -Ar^{-6} + B\exp(-ar)$$

These atom-atom functions have been elaborated by Williams (1965, 1966) and while the approach is open to some criticism, which will be mentioned later, it has been quite successful—even to the extent of providing a reasonably quantitative model for the lattice dynamics of naphthalene and anthracene (Pawley, 1967).

The second view on both the equilibrium structures and molecular motions in crystals of benzene and naphthalene has been developed by Craig, Mason, Pauling and Santry (1965a) and Craig, Dobosh, Mason and Santry (1965b). The intermolecular potential energy is expressed as the sum of the dispersion energy, of the quadrupole-

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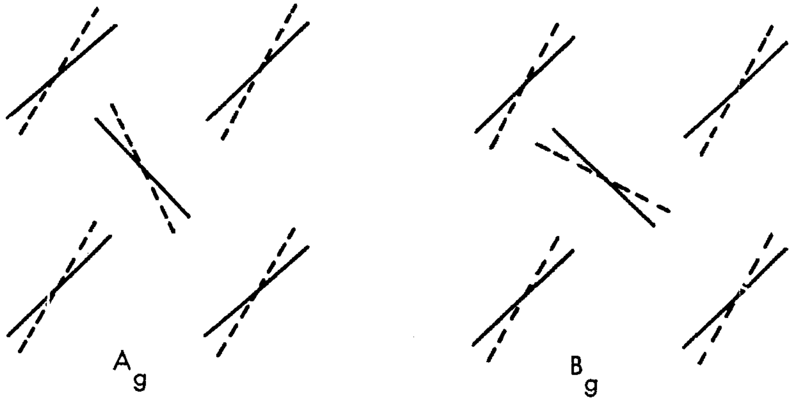
quadrupole coupling terms and of atom-atom repulsions corresponding to orbital penetrations.

$$W = W_{\text{elect}} + W_{\text{disp}} + W_{\text{rep}} \tag{1}$$

The dependence of this intermolecular potential energy on small displacements of the molecules from their equilibrium position is then examined. For example, naphthalene crystallises in the space group $P2_1/_a$, which has the representations A_g, A_u, B_g and B_u of the factor group, C_{2h}. Motions of the molecules from the equilibrium positions according to the representation A_g are space-group preserving while B_g motions



no longer retain the symmetry elements.

A_u and B_u representations would require the coupling of an *ungerade* intramolecular motion to the rigid body movements and have not been considered.

The problem of the equilibrium structure now resolves itself into which of the components of Eq. (1) are sensitive to these motions. In benzene, the electrostatic energy is simply

$$W_{\text{elect}} = \tfrac{1}{2}(Q_0)^2 G^{0,0}$$

where Q_0 is the single non-zero quadrupole component and $G^{0,0}$ is a lattice sum. Q_0 has been measured experimentally and $G^{0,0}$ can be computed by standard methods. The electrostatic energy of benzene is, in fact, minimized close to the equilibrium position but its angular variation only amounts to about 1 cm^{-1} per degree of displacement from the equilibrium structure. (Craig *et al*, 1965b). In napththalene, there are two non-vanishing quadrupole components,

$$Q^{0} = (\tfrac{1}{2})\, e(\psi^{0} \,|\, 3z^{2} - r^{2} \,|\, \psi^{0})$$

and

$$Q^{2c} = 3e(\psi^{0} \,|\, x^{2} - y^{2} \,|\, \psi^{0})$$

and the quadrupole-quadrupole geometrical factors $G^{0,0}$, $G^{0,2c}$ and $G^{2c,2c}$ are not minimized at the equilibrium position (Craig *et al*, 1965a). Undoubtedly, in benzene and naphthalene the electrostatic term is not structurally determining to any significant extent; its contribution to the lattice energy is of the order of 100 cm^{-1} compared with a total of about 5000 cm^{-1}. It is the dispersion energy which forms the major contribution to the attractive part of the intermolecular potential. In benzene, the dispersive energy is given (Craig *et al.*, 1965b) by

$$W_{\mathrm{disp}} = \tfrac{1}{2}\{A^{xx}(1^{xx})^{2} + A^{xy}(1^{xy})^{2} + \ldots\ldots + A^{zz}(1^{zz})^{2}\}$$

where the A's are molecular constants,

$$A^{xx} = -\sum_{r(x)} \sum_{s(x)} \frac{M_{0r}^{2} M_{0s}^{2}}{\Delta E_{0r} + \Delta E_{0s}}$$

For small displacements of the molecules this dispersion energy is again approximately constant varying at most by 2 cm^{-1} for a 5° change in orientation.

It is when we examine the repulsive forces that we find a strong dependence on molecular orientation. These short-range forces have always been represented by empirical functions

$$W_{\mathrm{rep}} = \sum B \exp(-CR)$$

although Craig *et al.* (1965a, b) and Bannerjee and Salem (1966) provide an estimate of the potentials in terms of the quantum mechanical exchange integral, approximating the repulsive potential function as being proportional to S^{2}/R where S is the overlap integral and R is the internuclear distance. For aromatic hydrocarbons, the repulsive component of the intermolecular potential can be written in the following way:

$$W_{\text{rep}} = \sum U_1(C_A C_B) + \sum U_2(C_A H_B) + \sum U_2(H_A C_B) \quad \sum U_3(H_A H_B)$$

Of these functions, Craig *et al.* (1965a), summarized the evidence that the hydrogen–hydrogen repulsion functions are of special importance in determining molecular orientation although it was also realized that the *total* repulsive energy depends primarily upon C...H contacts. In accord with this, the calculated variations of the hydrogen–hydrogen repulsive interactions show a deep minimum within 2–3° of the observed equilibrium structure. The position of the calculated minimum is fortunately insensitive to the precise form of the potential function for the hydrogen–hydrogen repulsions.

The third approach is due to Rae and Mason (1968) and Mason and Rae (1968), developing earlier work by Salem (1960, 1962) and Bannerjee and Salem (1966). Craig, Mason, Pauling and Santry (1965a), Craig, Dobosh, Mason and Santry (1965b) and Bannerjee and Salem (1966) treat the London dispersive forces as anisotropic molecule–molecule interactions using *molecular* polarizabilities to estimate these interactions. It is not difficult, however, to see that this approach may have some limitations which need investigation. The London expression for the dispersion potential is

$$V = -\frac{3}{2R^6}\,\frac{\overline{\Delta E}\,\overline{\Delta E'}}{\overline{\Delta E}+\overline{\Delta E'}}\,\alpha\alpha'$$

and may be conveniently rewritten to exclude the mean excitation energies,

$$V = -\frac{1}{R^6}\alpha\alpha'\left[\frac{\alpha}{\langle(\sum r_i)^2\rangle} + \frac{\alpha'}{\langle(\sum r_i')^2\rangle}\right]$$

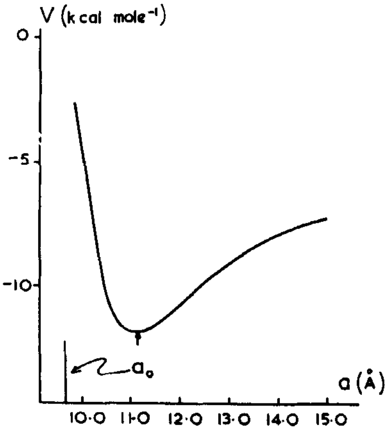
to provide an expression including the polarizabilities of the electronic systems, α and α', and calculable quantum mechanical averages. The application of these results to isolated atoms gives the well-known function of the form $\sum A_{ij} R_{ij}^{-6}$ where A_{ij} is a constant provided by the above equations. But, for molecules, it is clearly the case that the assumptions of a spherically symmetric potential or of the attractive centres being at the atomic nuclei, which are implicit in the above expressions for V, are not likely to be valid. The dispersion interaction is better calculated through a summation of individual bond–bond interactions and this has recently been effected for benzene and triazine by Rae and Mason (1968) and Mason and Rae (1968). Apart from the fact that these new calculations predict lattice energies and unit cell constants to within a few per cent, they are also of interest in providing a theoretical basis for the empirical atom–atom parameters of Kitajgorodskij and Williams. The fact that the only electrons " located " at the position of the atomic nucleii in a complex molecule are the core electrons with negligible polarizability is a substantial objection to the atom–atom approach and yet that it works is clear and may be due to

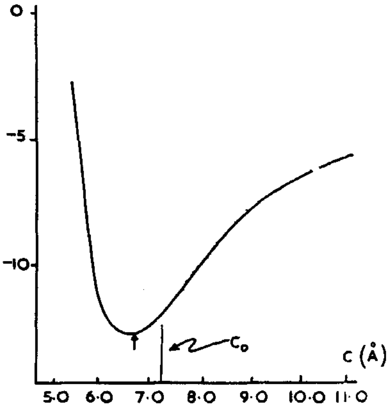
(i) averaging, over the different orientations in the crystal structure, of deviations from spherical symmetry in the bond–bond interactions,

(ii) the fact that the C–H attractive centre is located only 0.3 Å from the hydrogen atom and empirical non-bonded H---H coefficients may therefore be compared with calculated (C–H)---(H–C) coefficients; empirical C---C interactions can be compared with a combination of the $(\text{C–C})\sigma\ldots(\text{C–C})\sigma$, $\pi\ldots\pi$ and $(\text{C–C})\sigma\text{---}\pi$ interactions. In benzene, we obtain

$$36A_{\text{C---C}} = 36\bar{A}[(\text{C–C})\sigma\text{---}(\text{C–C})\sigma] + \bar{A}(\pi\text{---}\pi) + 12\bar{A}[(\text{C–C})\sigma\text{---}\pi]$$

which can be evaluated to give $A_{\text{C---C}} = -522\text{Å}^6$ kcal mole^{-1} compared with Williams' empirical value of -535Å^6 kcal mole^{-1}. But the agreement between the calculated and empirical values for $A_{\text{H---H}}$ is very poor, a fact which can be traced to a recognition that in the case of (C–H)---(H–C) interactions, the distances of approach are smaller and the location of the attractive centre quite critical. Thus, the theoretical values for the dispersive coefficients refer to an attractive centre on the C–H bond 0.3 Å from the hydrogen atom, while the empirical estimate of Williams' is based on the centre being only 0.07 Å from the hydrogen atom. After correction for this difference and also taking into account σ-orbital contraction of the hydrogen atom, $A_{\text{H---H}}$ (calc) becomes -68 Å^6 kcal mole^{-1} compared with the earlier theoretical estimate of $-$ 150Å kcal mole^{-1} and the empirical value of $-$ 36Å^{6} kcal mole^{-1}.





When we turn to a crystal of a molecule such as S-triazine, the immediately obvious question relates to the importance, or otherwise, of the electrostatic forces between molecules in which there is a charge asymmetry in the ground state. The first impression is that these forces are important—in contrast to the "herringbone" structure of benzene, triazine packs into a structure in which there are infinite stacks of parallel molecules. Moreover, each molecule in a stack is rotated by 60° with respect to its neighbour so that a nitrogen atom is placed immediately above a carbon atom and *vice-versa*—surely an ideal arrangement for maximizing electrostatic contributions to the lattice energy. This impression is not, however, supported by a closer investigation (Mason and Rae, 1968) which shows that like benzene, the electrostatic forces are of only marginal importance. The analysis of the triazine structure is also of interest in relation to the question of the effective repulsive potential of the nitrogen lone pair electrons; a very satisfactory account of the equilibrium structure and of the lattice energy is provided by simulating the lone pair repulsion through the placing of a hydrogen atom at the centroid of the electron distribution of the lone pair.

The question then arises as to why benzene does not crystalize in a triazine-like arrangement since this is one in which dispersion interactions are maximized. The Figure shows the total lattice energy of benzene in the triazine lattice plotted against the cell dimensions. Replacement of the nitrogen atoms by C–H groups gives rise to additional H–H repulsions which imply that the potential energy is not minimized until the " a " axis of the triazine cell is 1.6 Å longer than the experimental value, while the " c " axis is predicted as being 0.6 Å shorter (so as to maximize the dispersive interactions). In this new cell, it seems clear that the barrier to free rotation of the benzene molecules about their six-fold axes would be very small. In other words, the probability of an ordered structure is low and, in fact, such a structure might be representative of the liquid rather than the solid state. There is some evidence from diffraction data that liquid benzene does contain parallel-stacked molecules separated by 3.6Å (De Boer, 1936). It would be very worthwhile to analyze more precise X-ray data of liquid benzene and related systems such as naphthalene since apart from the question discussed briefly here, such information would be invaluable for discussions of energy transfer in such systems.

By way of summary, the present status of semi-empirical calculations of lattice-energy and equilibrium structures of molecular crystals is reasonable—they seem sufficiently well developed to encourage their being extended to more complex systems. Their theoretical basis is much more secure than that of the atom–atom approach but is far from complete. At present, it is the repulsive component of the intermolecular potential function that is the most difficult to deal with in a truly rigorous way. Our present analyses of the structures of crystalline hydrogen and deuterium may be helpful in this respect. One also suspects that quantitative interpretation of the crystal thermal expansion data will be valuable in refining expressions for the intermolecular potential as will observations of low temperature phase transitions such as have been observed recently by Coppens and Sabine (1968) for S-triazine.

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