

ization can be obtained even with a mosaic crystal. Analogous considerations are valid for 9 other operating points in Tables 3, 4 and 5.

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## A Method of Calculating Molecular Crystal Structures

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A novel method of calculating the molecular position in a lattice of known dimensions is presented. The repulsive lattice energy is approximated by a sum of quadratic nonbonded interatomic potential functions and the lattice energy sum is minimized by full-matrix least squares. The convergence range from arbitrary trial models is greater than the previously used steepest descent method using ( $\exp-6$ ) nonbonded potentials. Greatly increased speed of convergence is also obtained because of the inclusion of off-diagonal terms and the small number of repulsive interactions which are considered. The calculated packing models are sufficiently accurate to serve as a starting point for structure factor least-squares refinement based on diffraction data.

### Introduction

A situation frequently encountered in the study of molecular crystals by diffraction methods is that the molecular structure is already known approximately, or at least, plausible predictions of the molecular structure can be made from expected bond distances and angles. In order to verify the model and to refine the molecular structure from the diffraction data it is necessary to locate the molecules in the unit cell of the crystal. In addition, the packing structure may be of considerable interest in itself even if the molecular structure is accurately known. For example, several different packing structures may be observed for the same molecular structure. Or, chemical and physical interactions between molecules may be closely related to their mode of packing in the crystal.

The most obvious procedure which can be used to obtain the crystal packing of molecules is to minimize the lattice energy, neglecting thermal effects, using the best available representation of the non-bonded energy\* between the molecules, and assuming pairwise additivity (Williams, 1965a). The most important con-

tribution to the attractive energy in molecular crystals is the London dispersion energy, which has an inverse sixth power dependence on the interatomic separation. This term has the physical meaning of instantaneous dipole-dipole polarization. Terms involving quadrupoles or higher may safely be neglected as an initial approximation.

Several investigators (Kitaigorodskii, 1965; Craig, Mason, Pauling & Santry, 1965) have shown that the contribution to the lattice energy from electrostatic dipoles or quadrupoles is small for typical molecular crystals. Further, the rate of change of electrostatic energy effects with respect to molecular position is small.

The repulsive energy is of primary importance in determining the molecular position, provided the observed lattice constants are retained. The repulsive energy is due to overlap of filled electron shells and is a consequence of the required antisymmetry of the wave function for the system. The increase in repulsion energy with decreasing interatomic separation,  $d$ , may be fitted by a  $d^{-n}$  term, with  $n$  chosen for best fit, or to an exponential  $\exp(-Cd)$  term, with  $C$  chosen for best fit.

The pairwise sum for the lattice energy based on the usual models for the nonbonded energy, such as the

\* For a general discussion of nonbonded energy see, for example, Hirschfelder, Curtiss & Bird (1954).

Lennard-Jones (6-12) formula and the Buckingham (6-exp) formula lead to nonquadratic expressions for the lattice energy. The lattice energy expressed in this form can be minimized by a steepest descents procedure (Williams, 1965*a*) to find the correct packing structure. However, the calculation is lengthy, because a large number of interatomic pairs must be considered. And the convergence properties of the calculation, starting from arbitrary initial packing structures, are rather poor (Williams, 1967). Two problems which may be mentioned for the steepest descent calculation are that quantitative shifts are not directly obtained by this method, and no interaction between different orientational parameters may be included. Thus, shifts are made in rather arbitrary increments along the gradient vector (Williams, 1964). The noninclusion of parameter interactions also makes the steepest descent method analogous to the diagonal-matrix least-squares approximation familiar to crystallographers in least-squares structure factor refinement. In the example of refinement of crystallographic parameters from observed structure factor data it is well established that the full-matrix least-squares method has superior convergence properties compared to the diagonal-matrix approximation. (The least-squares problem, of course, is linearized by expanding the function about a trial model point in a Taylor's series and retaining only the first-order terms.)

The previously reported steepest descent method can be used to calculate the lattice constants of the crystal as well as the molecular packing position (Williams, 1967). By carrying out calculations for different space group symmetries it is also possible to predict the packing symmetry, *i.e.* the packing symmetry which leads to the greatest (negative) packing energy. Other properties of the crystal, such as its elastic constants and its heat of sublimation, may be calculated from this model. It is even possible, with suitable simplifying assumptions, to calculate anisotropic coefficients of thermal expansion from this model which are in reasonable agreement with the observed anisotropic expansions (Williams, 1966*a*).

### Least-squares packing analysis

Since in practice the lattice constants and cell symmetry are relatively easy to obtain, we may consider them to be known in considering the problem of finding the molecular positions in the unit cell. The use of the observed unit-cell dimensions effectively incorporates molecular attractions into the packing problem, since the molecular volume is effectively restricted. We then need consider only the nonbonded interatomic repulsions in the packing calculation. As a refinement of this approach it would be possible to include special attractive forces, such as hydrogen bonding or strong coulombic attraction, into the calculation.

The more powerful full-matrix least-squares method may be utilized in packing analysis if the lattice sums

consist of squared terms. A suitable expression for the interatomic nonbonded potential repulsive energy is

$$\varepsilon_r = w(d_0^n - d_c^n)^2, \quad d_c < d_0; \quad \varepsilon_r = 0, \quad d_c > d_0,$$

where  $d_0$  is an empirical constant much like a van der Waals diameter,  $d_c$  is an interatomic distance for the current trial model, and  $w$  is a weighting or scaling factor (Williams, 1968). The repulsive lattice energy is then

$$2E_r(\text{lattice}) = \sum \varepsilon_r, \quad d_c < d_0,$$

where the pairwise sum is taken between atoms in the reference molecule and atoms in the surrounding molecules. An early use of this method was the solution of the crystal structure of dibenzoylmethane, in which case  $n$  was chosen as 2, and  $w=1$ , along with very approximate  $d_0$  values (Williams, 1966*b*). In this example the molecular structure was not known exactly, and several nonplanar molecular models were tried. The possibility of using various molecular models as input to the packing calculation shows the utility of the method in establishing gross features of the molecular architecture.

### Mathematical development

The best fit to the nonbonded potential energy curves near their minima is obtained for the quadratic case ( $n=1$ ), as is discussed in a subsequent section. We therefore simplify the mathematical development by setting  $n=1$ . We derive the equations for the case of general crystal symmetry, although as will be seen later, a simplification occurs if only triclinic, monoclinic, and orthorhombic symmetries are allowed.

We wish to minimize the lattice repulsion energy, a sum of squares.

$$E_r = \frac{1}{2} \sum_{jkm} w(d_0 - d_{jkm})^2, \quad d_{jkm} < d_0.$$

The subscript  $j$  refers to an atom in the asymmetric unit; the subscripts  $k$  and  $m$  refer to atom  $k$  transformed by symmetry operation  $m$ . The normal equations are, using a first order Taylor's series expansion,

$$\mathbf{F}\Delta\mathbf{p} = \mathbf{G},$$

where

$$F_{\alpha\beta} = \sum_{jkm} w \frac{\partial d_{jkm}}{\partial p_\alpha} \frac{\partial d_{jkm}}{\partial p_\beta}$$

and

$$G_\alpha = - \sum_{jkm} w \frac{\partial d_{jkm}}{\partial p_\alpha} [d_0 - d_{jkm}(p^0)],$$

and  $\Delta\mathbf{p}$  is the shift vector leading to a lower value of  $E_r$ , compared to the value  $E_r^0$  calculated at the trial parameters  $\mathbf{p}^0$ . The parameters are three molecular translations and three molecular rotations for each

molecule in the asymmetric unit, except where restricted by symmetry considerations.

We need to evaluate the derivatives of  $d_{jkm}$  with respect to the parameters  $p$ .

$$d_{jkm} = |\mathbf{X}_j - \mathbf{X}_{km}|, \quad (1)$$

where  $X_{ij}$  are the cartesian coordinates ( $i=1,2,3$ ) of atom  $j$ , and  $X_{ikm}$  are the cartesian coordinates of atom  $k$  transformed by symmetry operation  $m$ . We define the  $(3 \times 3)$  symmetry matrix  $s$  and the translation column vector  $\mathbf{t}$  in unit-cell space as

$$\mathbf{x}_{km} = \mathbf{s}_m \mathbf{X}_k + \mathbf{t}_m,$$

where the  $\mathbf{t}_m$  include cell translations as well as those due to screw axes and glide planes.

Crystal unit-cell space may be transformed to reference cartesian space by the matrix  $\mathbf{D}$ . If we choose cartesian axes  $\mathbf{X}_2$  and  $\mathbf{X}_3$  coincident with crystal axes  $\mathbf{b}$  and  $\mathbf{c}^*$ , and  $\mathbf{X}_1$  in the  $\mathbf{ab}$  plane perpendicular to  $\mathbf{bc}^*$ , the elements of  $\mathbf{D}$  are

$$\begin{bmatrix} a \sin \gamma & 0 & c(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma \\ a \cos \gamma & b & c \cos \alpha \\ 0 & 0 & V/ab \sin \gamma \end{bmatrix}$$

where

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma - 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}.$$

Using capital letters for the operators in cartesian space, we have

$$\mathbf{X}_{km} = \mathbf{S}_m \mathbf{X}_k + \mathbf{T}_m, \quad (2)$$

where

$$\mathbf{S}_m = \mathbf{D} \mathbf{s}_m \mathbf{D}^{-1}, \text{ and } \mathbf{T}_m = \mathbf{D} \mathbf{t}_m.$$

In the triclinic, monoclinic, and orthorhombic crystal systems the off-diagonal elements of the  $\mathbf{S}$  matrices are always zero, and the diagonal elements are always  $\pm 1$ . Note that for oblique systems the components of  $\mathbf{T}_m$  are general even though one or more of the components of  $\mathbf{t}_m$  may be zero.

We define the molecular center of rotation at  $X_1^\circ$ ,  $X_2^\circ$ , and  $X_3^\circ$ , the small molecular rotations  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  about the corresponding cartesian axes, and the molecular translations  $\Delta X_1$ ,  $\Delta X_2$ , and  $\Delta X_3$  (Goldstein, 1959, p. 124). For atoms in the reference molecule the new coordinates after rotation and translation are

$$\begin{bmatrix} X'_1 \\ X'_2 \\ X'_3 \end{bmatrix} = \begin{bmatrix} 1 & -\theta_3 & \theta_2 \\ \theta_3 & 1 & -\theta_1 \\ -\theta_2 & \theta_1 & 1 \end{bmatrix} \begin{bmatrix} X_1 - X_1^\circ \\ X_2 - X_2^\circ \\ X_3 - X_3^\circ \end{bmatrix} + \begin{bmatrix} X_1^\circ + \Delta X_1 \\ X_2^\circ + \Delta X_2 \\ X_3^\circ + \Delta X_3 \end{bmatrix} \quad (3)$$

Substitution of equations (3) and (2) into equation (1) yields a closed expression for the nonbonded interatomic distances as a function of the (small) rotations and translations of the reference molecule.

Equation (1) may be expanded into components along the cartesian reference axes in the following form:

$$d_{jkm} = (C_1^2 + C_2^2 + C_3^2)^{1/2},$$

where

$$C_1 = X_{1j} - S_{11}X_{1k} - S_{12}X_{2k} - S_{13}X_{3k} - T_1$$

$$C_2 = X_{2j} - S_{21}X_{1k} - S_{22}X_{2k} - S_{23}X_{3k} - T_2$$

$$C_3 = X_{3j} - S_{31}X_{1k} - S_{32}X_{2k} - S_{33}X_{3k} - T_3.$$

In the latter equations the subscripts on  $S$  and  $T$  refer to cartesian components for a given symmetry transformation,  $m$ . Thus, the derivatives of the distance with respect to a parameter  $p$  are given by

$$\frac{\partial d}{\partial p} = \frac{1}{d} \left( C_1 \frac{\partial C_1}{\partial p} + C_2 \frac{\partial C_2}{\partial p} + C_3 \frac{\partial C_3}{\partial p} \right).$$

Table 1 gives the six derivatives of  $C_1$ ,  $C_2$ , and  $C_3$  with respect to molecular rotation and translation. The derivatives are evaluated, of course, at the trial model coordinates.

The case of more than one rigid molecule in the crystallographic asymmetric unit may easily be handled by dividing the derivatives into grouped sums applicable to each rigid molecule. The packing problem becomes more difficult of solution because of the additional variables which are introduced specifying the rotation and translations of each rigid molecule in the asymmetric unit. Nonbonded contacts between different molecules in the asymmetric unit having the same symmetry transformation must be included.

Since a large portion of the time required for the calculation is in making up a table of contacts less than  $d_0$ , it is expedient to preserve this table in the computer memory and to use it for several least-squares cycles. In the case of grossly incorrect starting positions, it is also found expedient to limit the magnitude of the

Table 1. Derivatives of  $C_1$ ,  $C_2$ , and  $C_3$  with respect to molecular rotation and translation

The center of rotation is taken at the origin; for non-origin rotation the  $i$ th component of the rotation center,  $X_i^\circ$ , is subtracted from  $X_{ij}$  and  $X_{ik}$ .

Parameter	$C_1$	$C_2$	$C_3$
$\theta_1$	$S_{12}X_{3k} - S_{13}X_{2k}$	$-X_{3j} + S_{22}X_{3k} - S_{23}X_{2k}$	$X_{2j} + S_{32}X_{3k} - S_{33}X_{2k}$
$\theta_2$	$X_{3j} - S_{11}X_{3k} + S_{13}X_{1k}$	$-S_{21}X_{3k} + S_{23}X_{1k}$	$-X_{1j} - S_{31}X_{3k} + S_{33}X_{1k}$
$\theta_3$	$-X_{2j} + S_{11}X_{2k} - S_{12}X_{1k}$	$X_{1j} + S_{21}X_{2k} - S_{22}X_{1k}$	$S_{31}X_{2k} - S_{32}X_{1k}$
$\Delta X_1$	$1 - S_{11}$	$-S_{21}$	$-S_{31}$
$\Delta X_2$	$-S_{12}$	$1 - S_{22}$	$-S_{32}$
$\Delta X_3$	$-S_{13}$	$-S_{23}$	$1 - S_{33}$

parameter shifts. For example, we have limited shifts to 0.1 radian or 0.2 Å per cycle. The incremental rotation matrix shown in equation (3) is not exactly orthonormal. The related orthonormalized matrix must be used to shift the atomic coordinates in order to preserve the molecular shape (Whittaker, 1944, p. 7). The elements of this related orthonormalized matrix are:

$$\begin{bmatrix} \xi^2 - \eta^2 - \zeta^2 + \theta^2 & 2(\xi\eta - \zeta\theta) & 2(\xi\zeta + \eta\theta) \\ 2(\xi\eta + \zeta\theta) & -\xi^2 + \eta^2 - \zeta^2 + \theta^2 & 2(\eta\zeta - \xi\theta) \\ 2(\xi\zeta - \eta\theta) & 2(\eta\zeta + \xi\theta) & -\xi^2 - \eta^2 + \zeta^2 + \theta^2 \end{bmatrix}$$

where

$$\theta = [1.0 - 0.25(\theta_1^2 + \theta_2^2 + \theta_3^2)]^{1/2}$$

$$\xi = \theta_1/2 \quad \eta = \theta_2/2 \quad \zeta = \theta_3/2.$$

The physical significance of this matrix is a counter-clockwise rotation  $|\theta|$  about an axis having direction cosines  $\xi, \eta, \zeta$ .

The orthonormalized incremental rotation matrix is then applied to the atomic coordinates and to the input orientation matrix. Because of the possibility of an error in the input matrix, and to avoid the cumulative effects of rounding errors on orthonormality, a further check is desirable. This check may be made on input and periodically during least-squares cycles.

This check may be made by first normalizing the third column of the input rotation matrix. Then the second column is formed by the vector product of the first and third columns, normalizing and preserving chirality. The first column is then formed by the normalized vector product of the second and third columns, again preserving chirality. In this manner the input orientation matrix may be periodically reorthonormalized.

### Nonbonded potential parameters

The best interatomic nonbonded potential parameters in the specified quadratic functional form are those which yield the best fit and fastest convergence to a variety of observed crystal structures. The criterion of best fit to a series of hydrocarbon structures has already been used to derive (exp -6) potential parameters. This same procedure could be applied to derive  $w$  and  $d_0$  for the quadratic functions.

A less time-consuming approach is to fit the best available (exp -6) functions with quadratic functions. We have used this approach for C...C, C...H, and H...H potentials. The (exp -6) potentials which were fitted (Williams, 1967) are (in kcal.mole<sup>-1</sup> and Å):

$$E_{CC} = -568d^{-6} + 83630 \exp(-3.60d)$$

$$E_{CH} = -125d^{-6} + 8766 \exp(-3.67d)$$

$$E_{HH} = -27.3d^{-6} + 2654 \exp(-3.74d).$$

The quadratic potential function is zero at its minimum. A possible way to derive values for  $w$  and  $d_0$  would be fit the repulsive part only of the (exp -6) potential. A second alternative would be to add the

depth of the potential well to the (exp -6) functions and then do a least-squares fit. A third alternative would be to fit the first derivatives (force) of the quadratic potential to the first derivatives of the (exp -6) potential. In each case the fit would encompass the range of repulsive contacts normally found in the crystal.

We have chosen the third alternative and have made a weighted least-squares fit as summarized in Table 2. The weighting scheme used corresponds to the assumption of uniform relative error in the first derivatives. The fit of the functions at the grid points is given in Table 3. The energy range covered is about 400 cal.mole<sup>-1</sup>. The mean error of fit is 12 cal.mole<sup>-1</sup>, being somewhat better for C...C and somewhat worse for H...H interactions. In the latter case more grid points were included to reflect the wide range and importance of the H...H interactions. The goodness of fit obtained was believed sufficient in view of the probable errors in the (exp -6) functions being fitted. This fitting procedure is of course not limited to (exp -6) potentials but can be used with (6-12) or any other potential type which is available for the atomic interactions of interest.

Table 2. *Least-squares fits of quadratic potentials to (exp -6) potentials, based on the first derivative and constant relative error*

Potential type	C...C	C...H	H...H
Grid increment (Å)	0.1	0.1	0.1
Lower limit (Å)	3.2	2.5	2.2
Upper limit (Å)	3.6	3.0	2.9
$d_0$ (Å)	3.65	3.03	2.88
$w$ (kcal.mole <sup>-1</sup> Å <sup>2</sup> )	1.87	1.56	1.00
$\Delta E$ (max) (cal.mole <sup>-1</sup> )*	12	17	24
$\Delta E$ (mean) (cal.mole <sup>-1</sup> )*	7	12	18

\* The difference in energy between the quadratic and (exp-6) functions when a subtractive constant,  $\Delta$ , for best fit is applied to the quadratic potential.

Table 3. *Comparison of quadratic and (exp -6) potentials (cal.mole<sup>-1</sup>)*

	$d$ (Å)	(exp-6)	Quadratic- $\Delta$
C...C $\Delta=80$	3.2	301	301
	3.3	139	151
	3.4	36	38
	3.5	-27	-37
	3.6	-64	-75
C...H $\Delta=42$	2.5	396	389
	2.6	224	241
	2.7	113	123
	2.8	43	37
	2.9	-1	-17
H...H $\Delta=12$	3.0	-26	-41
	2.2	468	446
	2.3	304	321
	2.4	192	216
	2.5	119	130
2.6	71	65	
2.7	39	19	
2.8	18	-6	
2.9	6	-11	

### Trial packing models

An obvious way to generate starting models for packing analysis is to use a grid for the angles and translations sufficiently fine to ensure convergence. This procedure is practical for packing analysis, in contrast to structure factor least squares, because of the wider convergence range of the former. A false minimum in the packing problem may quickly be rejected by comparing the observed and calculated values of the structure factors for a few low angle reflections. The correct minimum in the packing problem may also be recognized by the magnitude of the repulsion energy,  $2E_r$ . (Alternatively, the repulsion-only model could be used for a more complete lattice energy calculation using the (exp -6) potential functions. This value could then be compared with an estimate of the heat of sublimation.) While many false minima are usually encountered in the packing problem, in every case so far studied the false minima have always a larger calculated repulsion energy than the correct minimum. The nonbonded contacts at the false minimum will also show unreasonably short distances.

The number and range of grid points to be considered may be reduced by consideration of several factors. Hirshfeld (1968) has shown how the space group symmetry may be used to reduce the number of trial packing models. These considerations lead immediately to the conclusion that only a portion of the unit cell, the 'Cheshire cell', need be considered in the packing problem. The grid points may also be reduced by the fact that the molecule cannot be too close to symmetry elements without translation, *i.e.* inversion centers, mirror planes, and rotation axes, unless the molecule itself has that symmetry. Strong X-ray reflections may also limit the volume of trial parameter space to be scanned. For example, the orientation of a planar molecule might be revealed by an especially strong reflection, and only the translation position requires scanning over a wide range.

The convergence range of least-squares packing analysis is wider than the steepest descent packing analysis which has been used with (exp -6) potential functions. We report the results of convergence studies for several hydrocarbon crystal structures. In each case the location of the hydrogen repulsion center was assumed shifted inward by 0.07 Å (Williams, 1965*b*). For aromatic hydrogen the effective C-H bond length was thus taken as 1.027 Å.

#### Benzene

Since the molecule has a crystallographic center of symmetry, only three rotation parameters are needed (Bacon, Curry & Wilson, 1964). Preliminary investigations indicated that special orientations, such as the molecular plane parallel to a cell edge, should be avoided. We wished to consider only a small number of angular grid points, and the following (3 × 3) rotation matrices were devised. Starting molecular coordinates

(in the *XY* plane) were first shifted a small amount (+2 deg) by rotating successively about the *X*, *Y*, and *Z* cartesian axes. This was followed by rotation of ±20 or ±60 deg about each axis. For example, the following initial rotation matrix was used in the case of a -20 deg rotation about the *Y* axis:

$$\begin{bmatrix} \cos(-20) & 0 & -\sin(-20) \\ 0 & 1 & 0 \\ \sin(-20) & 0 & \cos(-20) \end{bmatrix} \\ \times \begin{bmatrix} \alpha & -\beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha & 0 & -\beta \\ 0 & 1 & 0 \\ \beta & 0 & \alpha \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \alpha & -\beta \\ 0 & \beta & \alpha \end{bmatrix}$$

where  $\alpha = \cos(2)$  and  $\beta = \sin(2)$ . Thus twelve trial models on a coarse angular grid were generated with avoidance of special symmetry situations. (An alternate approach would be to make use of molecular symmetry as discussed by Hirschfeld (1968) and generate trial models using Eulerian angles.)

No information about the observed packing structure was contained in any of the trial models. In the benzene case we found rapid and smooth convergence to the correct observed structure in every case. With specification of four least-squares cycles per contact table, an average of five tables was required to obtain convergence. On an IBM 360 model 30 computer the average time required for convergence was 2.5 minutes.

For comparison, the same trial models were subjected to steepest descent refinement using (exp -6) potentials. The calculation took about 12 times longer and four of the 12 trial models failed to converge to the observed structure.

#### Naphthalene

Out of the twelve starting orientations, two led to the observed structure, with  $2E_r = 0.77$  kcal.mole<sup>-1</sup>. The other ten orientations led to one or another of five false minima with  $2E_r$  values of 4.25, 5.36, 8.85, 18.14, or 23.87 kcal.mole<sup>-1</sup>. Thus the correct structure (Cruickshank, 1957) had the lowest  $E_r$  and was easily recognizable. On the average, seven contact tables were generated, requiring 4.6 minutes for convergence to a minimum.

An examination of the nature of the false minima structures was made. In each case an incorrect mode of molecular interlocking was obtained. This problem is illustrated in Figs. 1 and 2. Fig. 1 shows the observed structure, while Fig. 2 shows the false minimum at  $2E_r = 4.25$  kcal.mole<sup>-1</sup>. Packing analysis was unable to surmount the energy barrier separating the two structures. In an attempt to overcome this problem, we have used initially expanded lattice constants, gradually contracting to the observed cell dimensions. This procedure simulates to some extent the process of crystallization. The results so far have been disappointing. We conclude that convergence to the correct minimum

can normally be attained only when the observed molecular interlocking scheme is accessible from the trial model.

#### Phenanthrene

The crystal is acentric and two molecular translation coordinates are required as well as three rotations (Trotter, 1963). For trial models we used the same twelve angular orientations and a 1 Å grid in the 'Cheshire' cell. Convergence to the observed structure was obtained in as many as four angular orientations for a given translational starting point. A large number of false minima were found with  $2E_r$  ranging from 2.53 to 19.38 kcal.mole<sup>-1</sup>, compared to 1.25 kcal.mole<sup>-1</sup> for the observed structure.

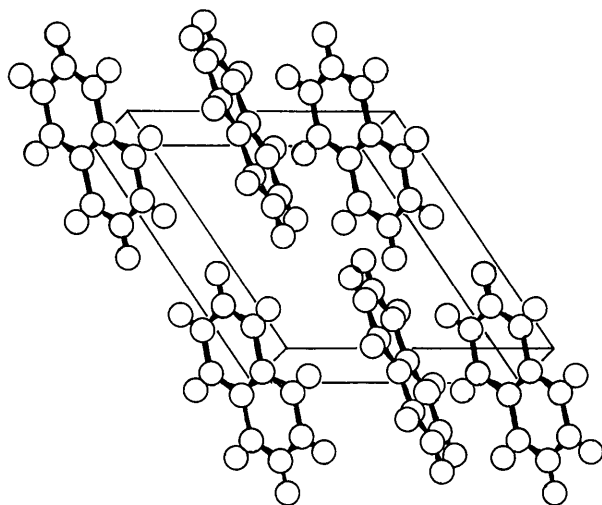


Fig. 1. The observed naphthalene packing structure,  $2E_r = 0.77$  kcal.mole<sup>-1</sup>.

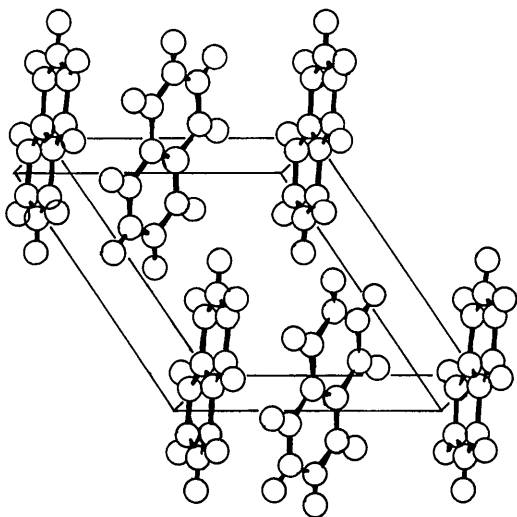


Fig. 2. A false minimum for the naphthalene packing structure,  $2E_r = 4.25$  kcal.mole<sup>-1</sup>.

#### Triptycene

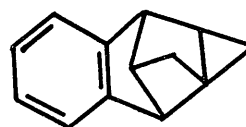
The crystal is acentric, space group  $P2_12_12_1$ , and all six rotation and translation parameters are required (Neuman, 1967). The  $a$  and  $c$  lattice constants are nearly identical, leading to duplicate false minima with  $a$  and  $c$  interchanged, with nearly identical values of  $2E_r$ . Diffraction data quickly eliminated the incorrect choice of axes.

Since the molecule is globular, we first found the best calculated packing position for spheres in the observed lattice, using a quadratic potential with a large  $d_0$ . A broad minimum was found at  $(\frac{1}{4}, \frac{1}{8}, 0)$ . The same minimum position was found with better definition by finding the best translation position of a hypothetical icosahedral 'molecule' in the observed unit cell.

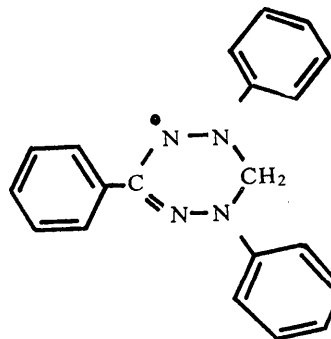
Using this initial position for the molecular center, we obtained convergence to the observed structure in three of the twelve trial angular orientations. An average of nine contact tables were generated, requiring approximately 12 minutes for each trial model to converge. Atomic movements of over 4 Å were noted in going from a trial model to the correct structure.

#### Solution of the diffraction phase problem for unknown structures

In addition to the triptycene structure discussed above, the packing structures of two other compounds have recently been solved by this method. The crystal structure of the hydrocarbon  $C_{13}H_{12}$  (I) has been determined by Katz, Knox & Neuman (1968). The crystal structure of the stable free radical 1,3,5-triphenylverdazyl ( $C_{20}N_4H_{17}$ , II) has also been determined (Williams, 1969). In the latter case molecular flexibility due to rotations of the phenyl groups was considered. By varying the phenyl rotations on a grid the correct molecular packing was obtained at the lowest lattice repulsion energy.



(I)



(II)

### Calculated packing structures

Except for benzene, false minima were sometimes obtained for each structure. It is significant that in no case among the many false minima examined was the packing function less than that for the observed structure minimum. Thus packing analysis provides an independent check of structures determined by diffraction methods. In cases where ambiguity in the diffraction-determined structure exists, perhaps because of inaccurate data, packing analysis might clarify the packing structure.

The presence or absence of an inversion center can be investigated by performing packing calculations in both centric and acentric space groups. Similarly, gross molecular geometry may be investigated by packing analysis. An example would be distinguishing between *cis-trans* isomers on the basis of how well the molecules pack in the observed unit cell.

At the correct minimum, the goodness of fit of the calculated packing structures of hydrocarbons is entirely adequate to solve the diffraction phase problem. The absence of a symmetry center does not make packing analysis more difficult, unless additional rotational or translational degrees of freedom are introduced into the packing problem. Typically, the fit to hydrocarbon structures is such that all carbon atoms are located to within about 0.1 Å, and refinement from this point by structure factor least squares is straightforward.

In dealing with unknown structures it is desirable to predict the minimum value of  $2E_r$ . We have calculated minimum  $2E_r$  values for a series of hydrocarbon structures as follows: benzene, 0.88; naphthalene, 0.76; anthracene, 2.44; phenanthrene, 1.25; pyrene, 1.55; chrysene, 1.41; triphenylene, 3.16; perylene, 2.26; n-pentane, 2.51; n-hexane, 2.16; n-octane, 2.69; and triptycene, 3.12 kcal.mole<sup>-1</sup>.

Examination of the repulsions at the calculated minimum indicates that H...H interactions predominate.

With the simple assumption of a constant repulsive contribution for each hydrogen in each structure we arrive at figures of 0.10 to 0.25 kcal.mole<sup>-1</sup> per hydrogen atom for both aromatic and aliphatic hydrocarbons. The procedure of counting hydrogen atoms appears better than trying to find a constant ratio of repulsive energy to the total lattice energy (heat of sublimation). Further work is needed to estimate the repulsion for materials other than hydrocarbons.

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