Molecular packing for planar molecules

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Abstract. The crystal packing of five planar molecules is considered in this paper. Each unit cell contains two non-equivalent molecules whose planes are inclined to each other. It is shown that the angle of inclination between the planes is completely determined by a simple geometrical criterion. A simple sequential arrangement of the four molecules defining the elementary parallelopiped of which the entire crystal is built leads to various configurations from which the one which has the least interaction energy can be picked out. Using a crude Lennard-Jones potential for the non-bonded interaction and a hard sphere model for the atoms, one can compute the crystal structure from the minimum energy criterion and this is found to be in fair agreement with the observed structure. This simple sequential packing with some modifications can provide an useful model for calculating the radial distribution function in amorphous solids involving planar groups.

Keywords. Molecular packing; simulation; minimum energy.

1. Introduction

In studying the spatial structure of melanins, Thathachari (1973, 1975, 1976) has suggested that monomers of different shapes and sizes, but essentially planar, stack in a parallel orientation. Many of the organic planar molecules crystallise in triclinic or monoclinic systems with a bimolecular unit cell. The two non-equivalent molecules in the unit cell are inclined to each other. In the case of long chain planar molecules, the plane of one molecule is rotated about the long axis relative to the plane of the other. There has been no attempt so far to find out a criterion which determines this angle of inclination.

The determination of organic crystal structures from packing considerations was pioneered by the work of Kitaigorodskii (1962). From the experimentally determined structure data Kitaigorodskii classified organic molecules depending on the geometry of their packing. Crystal structures can also be calculated by using a known interaction potential for the non-bonded interaction and finding the structural parameters for which the lattice energy is a minimum. However since the knowledge of the exact form of the non-bonded interaction is not available, Williams (1969, 1972) in a series of papers inverted the problem and used the crystal structure data to obtain reliable potential parameters. These parameters were later used to calculate the lattice vibrational frequencies of the crystal and its anisotropic thermal expansion.

- The purpose of the present paper is to obtain a geometrical criterion which determines the angle of inclination of the planes of neighbouring molecules. This is shown

to be strictly valid in the case of long chain planar molecules for which published crystal structure data are available.

While the use of complex interatomic potentials can be expected to lead to exact crystal structural data, we may need to evolve a simple sequence of packing which, used with a potential with a small number of parameters, will lead to a reasonable agreement with crystal structure data. Such a simple approach will be especially valuable to calculate approximately the radial distribution function in polymers involving planar organic molecules. Such a sequence of packing is proposed and used with a simple Lennard-Jones potential (Subba Reddy 1975). It is seen to lead to a fairly reasonable agreement with crystal structure data for five planar long chain molecules namely tetracene, pentacene, biphenyl, terphenyl and quaterphenyl.

2. X-ray crystal structure data

The crystal structure data of the five long chain planar molecules—tetracene, penta-cene, biphenyl, terphenyl and quaterphenyl—are taken from Wyckoff (1971). The unit cells are either triclinic or monoclinic with two asymmetric units in the cell. The planes of the two asymmetric units are inclined to each other. The inclination about the long axis is denoted by θ. Table 1 gives the unit cell parameters, the positions of the asymmetric units and the angle of inclination θ for the five organic crystal structures.
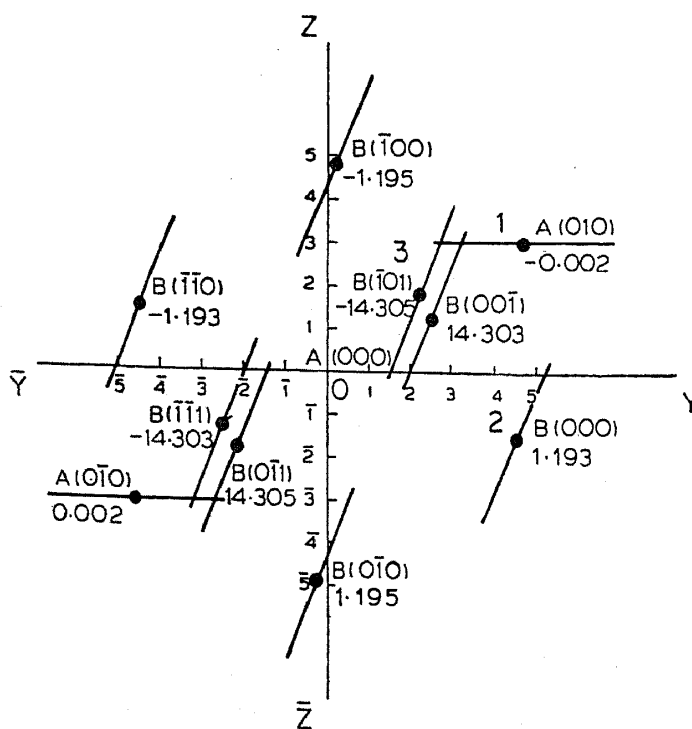

Figure 1. Projection of the nearest neighbours for a terphenyl molecule on the YZ plane. A and B refer to the two asymmetric units and the triplet of numbers within brackets gives the cell indices in Wyckoff's notation. The X co-ordinate of the centre of the molecule is also given to 3 decimal places in the figure. The basic parallelo-piped from which the entire structure can be constructed is given by the molecules 0, 1, 2 and 3.

Table 1. Unit cell parameters for some long chain planar molecules

Compound	Chemical structure	Space group and crystal system	Positions of the atoms in the unit cell	Unit cell parameters						
				a	b in Å	c	α	β in degrees	γ	θ
Tetracene	$C_{18}H_{12}$	C_1^i (P1) Triclinic	$(x, y, z); (\frac{1}{2}+x, \frac{1}{2}+y, z)$	7·90	6·03	13·53	100·3	113·2	86·3	50·9
Pentacene	$C_{22}H_{14}$	C_1^i (P1) Triclinic	$(x, y, z); (\frac{1}{2}+x, \frac{1}{2}+y, z)$	7·90	6·06	16·01	101·9	112·6	85·8	52·8
Biphenyl	$C_{12}H_{10}$	C_{2h}^5 (P2₁/a) Monoclinic	$(x, y, z); (\frac{1}{2}+x, \frac{1}{2}-y, z)$	8·12	5·63	9·51	90·0	95·1	90·0	68·0
Terphenyl	$C_{18}H_{14}$	C_{2h}^5 (P2₁/a) Monoclinic	$(x, y, z); (\frac{1}{2}+x, \frac{1}{2}-y, z)$	8·08	5·60	13·59	90·0	91·9	90·0	67·7
Quaterphenyl	$C_{24}H_{18}$	C_{2h}^5 (P2₁/a) Monoclinic	$(x, y, z); (\frac{1}{2}+x, \frac{1}{2}-y, z)$	8·05	5·55	17·81	90·0	95·8	90·0	64·0

For a planar molecule it is advantageous to use an orthogonal system of coordinates (X, Y, Z) such that the Z axis is normal to the plane of the molecule, the X axis is along the length and the Y axis is along the breadth of the molecule. On the other hand, in the crystal structure data, the co-ordinates of the atoms are given in terms of fractions of the primitive translations along the cell edges. Using the standard transformation equations, the co-ordinates of the atoms of the two asymmetric units in the unit cell can be given in the (XYZ) system and the inclination θ of the two asymmetric units relative to each other can be calculated. These values are given in table 1.

Figure 1 gives the projection of the structure down the long axis X, of the molecule for terphenyl. The parallelopiped with the molecules 0, 1, 2 and 3 forms the building block of the crystal, though this is not a unit cell. The molecules 0 and 1 are parallel to each other and the vector distance t_1 between the two is a primitive lattice translation in that direction. The molecules 2 and 3 are parallel to each other but inclined to 0 and 1. The vector distance 0 to 2, t_2 is half the primitive translation in that direction. So also the vector t_3 connecting the centres of 0 and 3. In all the five long chain molecules considered here, the parallelopiped formed by the nearest neighbours consists of two molecules 0 to 1 parallel to each other and two others, 2 and 3, inclined to 0 and 1, but parallel to each other.

3. Geometric criterion for determining the angle of inclination θ between the planes of the asymmetric groups in the unit cell

Figure 2 shows the projection on the YZ plane of the three molecules 0, 1 and 2. The molecules 0 and 1 are parallel and the vector distance between their centres is the lattice translation t_1. The nearest distance in projection between the hydrogen atoms in molecules 0 and 1 is d (line AB in figure 2) and this vector makes an angle δ with the normal to the plane of the molecule 0. $d_n/2$ is the half width of the molecule (line OA in figure 2). From figure 2 considering the molecules 0 and 1 it is clear that
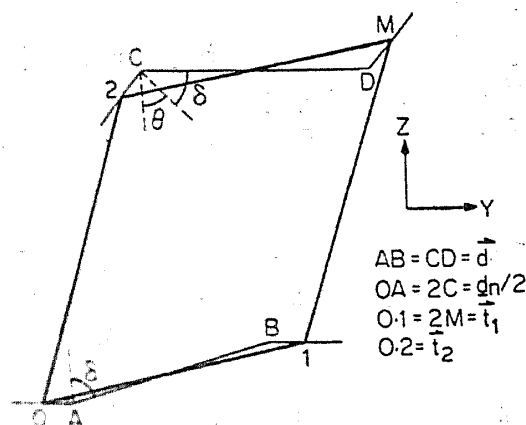

$$AB = CD = \bar{d}$$
$$OA = 2C = \underline{d}_n/2$$
$$O{\cdot}1 = 2M = \bar{t}_1$$
$$O{\cdot}2 = \bar{t}_2$$

Figure 2. Illustrating the geometric criterion for determining θ. Please see text for the explanation of the symbols.

$$t_{1y} = d_n + d \sin \delta,$$

$$t_{1z} = d \cos \delta. \tag{1}$$

Molecule 2 is obtained from molecule 0 by a translation t_2 and a rotation of its plane through an angle θ about the X axis. Molecule M is similarly obtained from molecule 2 by the lattice translation t_1 and so its plane is also inclined by the same angle θ relative to the plane of 1. We now impose the condition that the shortest distance between the hydrogen atoms in the parallel molecules 2 and M is also d, the same as for molecules 0 and 1 and it makes the same angle δ with the normal to the plane though on the other side of the plane. Considering the vector t_1 between the molecules 2 and M in figure 2 we see that

$$t_{1y} = d_n \cos \theta + d \sin (\theta + \delta),$$

$$= (d_n + d \sin \delta) \cos \theta + d \cos \delta \sin \theta. \tag{2}$$

simplifying we get

$$(1 - \cos \theta)/\sin \theta = \tan (\theta/2) = t_{1y}/t_{1z}. \tag{3}$$

The imposition of the condition that molecules 2 and M are arranged in a geometrically similar fashion to 0 and 1, gives the angle of inclination between the asymmetric units in terms of the Y and Z components of the lattice translation vector of the nearest neighbours of parallel orientation. In table 2 we have collected the X, Y and Z components of the vector t_1, and the angle of inclination θ between the planar units obtained from Wyckoff's crystal structure data. The last column gives the angle θ calculated from equation (3). The agreement between the calculated and measured values is exceptionally good indicating that the condition of geometrical similarity in arrangement of the pairs of molecules of parallel orientation is strictly valid at least for long chain planar molecules. Thus at least one parameter of the crystal structure is precisely determined by this condition. This is an important result.

4. Sequential packing of molecules and computer simulation of the crystal structure

The above geometric relation suggests that one can adopt a simple sequential packing of the molecules to arrive at a computer simulation of the crystal structure. This is

Table 2. Testing the validity of equation (3) from structural data

Molecule	Vector t_1 from Wyckoff's data in Å			θ from expt. in degrees	θ from equation (3) in degrees
	t_{1x}	t_{1y}	t_{1z}		
Tetracene	1·61	5·21	2·58	50·9	52·7
Pentacene	−1·70	5·18	2·65	52·8	54·4
Biphenyl	−0·03	4·66	3·16	68·0	68·2
Terphenyl	0·00	4·65	3·12	67·7	67·2
Quaterphenyl	0·00	4·70	2·95	64·0	63·2

described below. The origin is taken as the centre of the reference molecule 0. The location of the centre of molecule $i(i=1, 2$ or $3)$ is then specified by the three coordinates R_i, α_i and β_i. R_i is the length of the vector t_i. α_i is the complement of the angle between the vector t_i and the Z axis of the reference molecule. β_i is the angle which the projection of t_i on the XY plane makes with the X axis. The cartesian co-ordinates of the centre of molecule i are calculated from R_i, α_i and β_i. The separation S_{kl} between two atoms k and l is defined by

$$S_{kl} = R_{kl} - (r_k + r_l). \tag{4}$$

R_{kl} is the distance between the centres of the two atoms and r_k and r_l are the van der Waal radii of the two atoms. The van der Waal's radius for C is taken as 1·7 Å and for hydrogen 1·19 Å. The shorter radius of 1·7 Å for carbon is used in order not to miss the strains in various packings. If the modulus of separation S_{kl} is less than 0·01 Å, the atoms are taken to be in contact. In packing the four molecules, we impose a constraint that no two atoms intersect i.e. S_{kl} is not less than $-0·01$ Å for any pair of atoms. This implies a simple hard sphere model.

Having placed the reference molecule 0 at the origin, we next arrange the molecule 1 so that several atoms in this molecule are in contact with several atoms in molecule 0. For this the centre of molecule 1 is located at a sufficiently large distance R_1 from the centre of molecule 0 along a given direction (α_1, β_1). The minimum separation, S_{min}, between the atoms in molecule 1 and those in molecule 0 is calculated. Also the angle ω made by the line joining the centres of the two atoms at minimum separation with the line of centres of the two molecules is found. Now the distance between the centres of the two molecules is reduced from R_1 to $R_1-S_{min} \cos \omega$ keeping α_1, β_1 fixed. Again the minimum separation between the atoms are calculated. Repeating this procedure once or twice brings the molecules 0 and 1 in contact. The angles (α_1, β_1) can be still freely varied.

Having arranged molecule 1 relative to molecule 0, the angle of inclination θ of the plane of molecule 2 relative to the plane of molecule 0 is calculated from equation (3). The angle θ can be expressed in terms of α_1 and β_1 and is given by

$$\tan (\theta/2) = \tan \alpha_1/\tan \beta_1. \tag{5}$$

The molecule 2 with this orientation is then placed along a direction α_2, β_2 from 0 and at a large distance. Following the procedure adopted for molecule 1, the centre of molecule 2 is shifted along this direction till it touches molecule 0. However the molecule 2 will not touch molecule 1. Now the angle α_2 is varied together with R_2 keeping β_2 constant till molecule 2 touches both molecule 0 and 1. It is obvious that only β_2 is a freely variable parameter for molecule 2. Having arranged molecules 0, 1 and 2, we have to arrange molecule 3 which is parallel to 2, to achieve the maximum number of contacts with molecules 0, 1 and 2. To make the molecule 3 touch all the three molecules will be a time consuming process. We notice that the X co-ordinate of molecule 3 will be approximately equal to the length of the molecule. The molecule 3 will only touch molecules 0, 1 or 2 at the extremities. The number of contacts between molecule 3 and other molecules will be minimal. So it was thought sufficient to adjust molecule 3 so that it touches one of the three molecules and does not intersect the other two.

Thus for a given value of α_1, β_1, β_2 and β_3 we arrive at a possible configuration of the building block. The energy of this building block may be calculated using a form of the nonbonded interatomic potential. If the energy is calculated for several such configurations, the configuration having the minimum energy can then be picked out. This gives the vectors t_1, t_2 and t_3 from which unit cell parameters and the unit cell volume may be calculated.

One may question such a sequential arrangement on the ground that once molecule 1 is adjusted and the molecule 2 is brought into contact with 0, then molecule 1 may change its position. It is not suggested here that the crystal structure develops physically according to the sequential packing. In any crystal packing calculation, the energy is calculated for various spatial arrangements of the molecules 0, 1, 2 and 3. All that is suggested here is that different spatial arrangements can be obtained using this sequential packing. The final arrangement with minimum energy gives the actual structure.

The advantage of the above method is that the final energy depends only on a few parameters (α_1, β_1, β_2 and β_3) and the search for a minimum energy can be carried out using the technique of Box (1965) for obtaining the minimum of a function of several variables under nonlinear inequality constraints. The schematic of the search procedure is given in figure 3. Such a simple sequential packing will also lend itself to slight modifications for the calculation of packing in amorphous structures.

To illustrate the method we assume the simple 6–12 Lennard-Jones potential for the nonbonded interactions. The interaction energy between a pair of nonbonded atoms at a distance r is given by
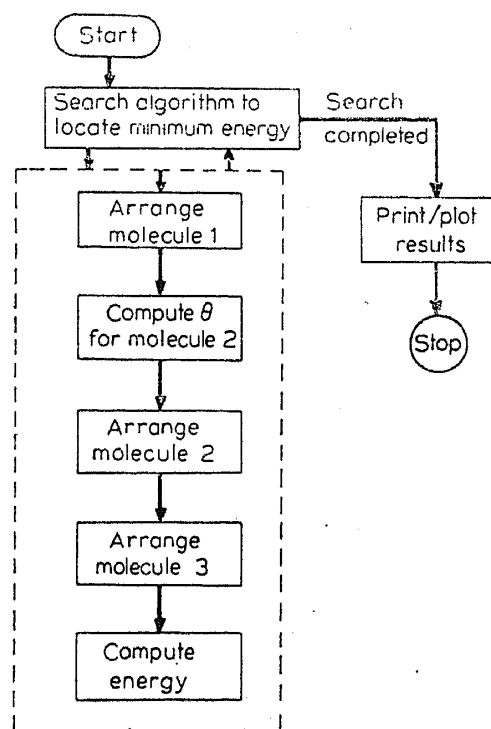
$$\epsilon(r) = -A/r^6 + B/r^{12}. \tag{6}$$

Figure 3. Overview of the search algorithm.

Since our aim was only to show that this sequential packing led to reasonably fair agreement with actual structure data we did not use more refined potentials such as the ones used by Williams (1969, 1972). The parameters A and B are taken from the work of Subba Reddy (1975). The values for C-C, C-H and H-H nonbonded interactions are given in table 3.

In carrying out the computer simulation with this sequential packing we may restrict the range of values for the angles α_1, β_1, β_2 and β_3 using some geometrical considerations which will be illustrated taking the example of pentacene. In figure 4 we plot the molecule 1 relative to molecule 0 in the XY plane. The molecule is made up of a number of benzene rings strung together. We see that the maximum number of contacts (and hence a very low energy) will be obtained if the centre of molecule 1 is shifted along X by half the distance between the opposite edges of the benzene ring. For this arrangement the angle between the line of centres and the Y axis, ζ, will be given by $\tan \zeta = 1 \cdot 2/5 = 0 \cdot 24$ where $1 \cdot 2$ Å is the half width of the benzene ring and 5 Å is the width of the pentacene molecule. So $\zeta = 12 \cdot 5°$. Thus the value of β_1 is allowed to range between 75 to 120°, which is a wider range than what is indicated by above geometric consideration. In order to fix the range of α_1, we note that $R_1 \sin \alpha_1$ measures the height of the centre of molecule 1 over the centre of molecule 0.

Table 3. The interaction parameters in the 6-12 Lennard-Jones potential for non-bonded interactions

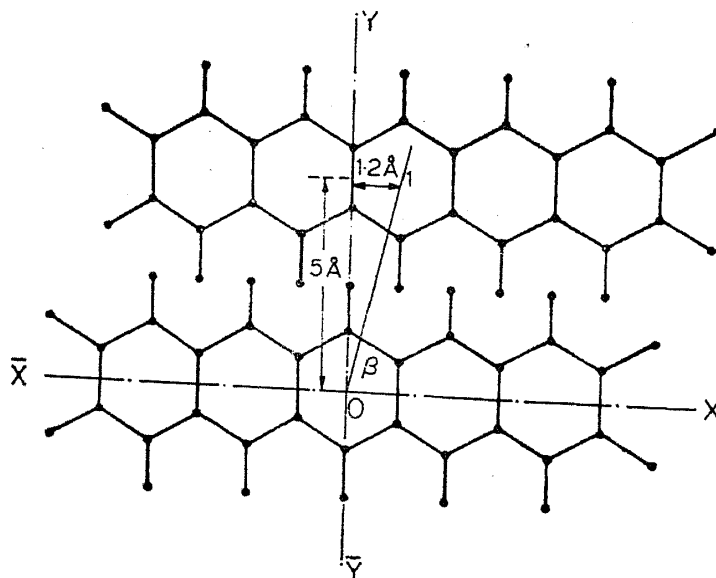| Type of interaction	Energy constants	
	A in eV $\times$ Å^6	B in eV $\times$ Å^{12}
C–C	370	$28 \cdot 6 \times 10^4$
C–H	128	$3 \cdot 8 \times 10^4$
H–H	$46 \cdot 7$	$0 \cdot 45 \times 10^4$

Figure 4. To illustrate how the approximate value of the angle β_1 is fixed in the case of pentacene.

When the two molecules are arranged such that they have maximum contacts, as shown in figure 4, the maximum height between the two molecules will roughly be twice the radius of the carbon atom i.e. 3·4 Å. The distance between the centres for the orientation shown in figure 4 is given by

$$R_1 = (1·2^2 + 5^2 + 3·4^2)^{1/2} = 6·16 \text{ Å}.$$

So $\quad \sin \alpha_1 = 3·4/6·16 \text{ or } \alpha_1 = 33·5°.$

The value of α_1 was therefore varied in the range 15 to 40°. To fix the favourable orientation of molecule 2 relative to 0 and 1, β_2 was varied over the range 0 to 120°. As mentioned already α_2 was fixed by the requirement that molecule 2 should touch molecules 1 and 0.

The value of α_3 was chosen so that molecule 3 did not slide over molecule 0, 1 or 2 but made contact with one of these molecules at the end. This limited α_3 to the range 0 to 15 degrees. The value of β_3 was varied within $\pm 20°$ about the X axis.

For all the molecules studied the same constraints on the ranges of $\alpha_1, \beta_1, \beta_2, \alpha_3$ and β_3 were used. The volume of the parallelopiped formed by the 4 molecules was calculated using the relation

$$V = t_1 (t_2 \times t_3). \tag{7}$$

To calculate the energy of the 4 interacting molecules, all distances between an atom in molecule i and another in molecule j less than 4 Å were listed out. If $R(\mu_i, \nu_j)$ is the distance between atom in molecule i and atom in molecule j, satisfying the above conditions, then the interaction energy between this pair of atoms is given by

$$\epsilon(\mu_i \nu_j) = -(A_{\mu\nu}/[R(\mu_i \nu_j)]^6) + (B_{\mu\nu}/[R(\mu_i \nu_j)]^{12}), \tag{8}$$

and this was included in the computation of the energy of the 4 molecules.

Once the vector t_1, t_2 and t_3 are obtained the calculation of the crystallographic unit cell dimensions is straightforward. In the case of triclinic and monoclinic crystals, the choice of primitive translations is not unique. So to obtain the primitive translations conforming to Wyckoff's choice, we look at the projection of the crystal structure in the YZ plane as in figure 1 and identify the molecules 0, 1, 2 and 3 with the label A or B and the corresponding cell indices given in Wyckoff. In Wyckoff's notation the vector distance between molecule B and that of A in the same cell is $\frac{1}{2}(a+b)$ for all the structures listed, where a, b, c are the primitive translations of Wyckoff's choice. In figure 1 for example the molecules 0, 1, 2 and 3 are given in Wyckoff's notation as $A(000)$, $A(010)$, $B(000)$ and $B(\bar{1}01)$. So we may now express t_1, t_2 and t_3 in terms of the primitive translations a, b and c in Wyckoff's notation. Thus the lattice parameters a, b, c, α, β and γ can be calculated once the three translations t_1, t_2 and t_3 are obtained by minimising the energy.

5. Results

Table 4 gives the results of this computer simulation for the five long chain aromatic molecules. In the table the symbols for the molecules 0, 1, 2 and 3 in terms of Wyckoff's notation are given. Since we choose the molecule 0 arbitrarily it can either be molecule A or molecule B in Wyckoff's notation. But once we identify the molecule 0, the types of the other molecules are automatically fixed. The table gives the components of the vectors t_1, t_2 and t_3 in the orthogonal system. The volume of the parallelopiped formed by the molecules 0, 1, 2 and 3 is given in the table. For comparison the volume calculated from Wyckoff's data is also given. The lattice parameters a, b, c, α, β and γ deduced from t_1, t_2 and t_3 are also given. These lattice parameters may be compared with those from crystallographic data given in table 1. We see that

(i) The lattice constants b and c are in good agreement with the measured value, the maximum deviation in c amounting to about 0·5 Å in 9·5 Å in biphenyl. The agreement in c improves as the length of the molecule increases.

(ii) The lattice parameter a computed with the simple Lennard-Jones potential comes out significantly smaller than the measured values in all crystals, the error being roughly between 0·4 Å to 0·74 Å in a lattice constant of about 8 Å.

(iii) The angles α, β and γ are found to be reproduced within about 2·5° in most of the cases. Only in biphenyl the angle β is off by 5°. Biphenyl is the shortest of the molecules considered. The value of γ is reproduced much better than the values of α and β.

(iv) The computed volume is smaller than the measured volume, the deviation is not more than 8% of the actual volume. The error in volume mainly arises due to the disagreement in the lattice constant a.

(v) The angle of inclination θ determined from the simulation is always lower than the measured angle. Since this angle is determined by t_{1y} and t_{1z}, the errors in these components are responsible for the error in θ.

Considering the fact that we have used a very crude potential we may conclude from the above results that:

(i) The simple sequential packing procedure with minimum energy criterion that has been discussed in this paper is indeed able to reproduce the crystal structures reasonably well. The use of more elaborate potentials like those of Williams (1969, 1972) with the sequential packing can be expected to lead to better agreement with experiment.

(ii) The lattice constants b, c and the angles α, β and γ do not seem to be highly sensitive to the nature of the potential used. They are more or less determined by the dimensions of the molecule. On the other hand we may expect the lattice parameter a to improve significantly with the use of more accurate potentials.

(iii) The angle θ, as well mentioned in § 3 is completely determined by the Y and Z co-ordinates of molecule 1 relative to the centre of molecule, 0. As far as these co-ordinates are also determined by the interatomic potential, θ depends on the interatomic potential. So a better choice of the interatomic potential will yield a better value of θ.

The sequential packing procedure described here involves only five variables in it and it is gratifying that such a simple procedure appears to work well even with

Table 4. Computed crystal structure data for five long chain planar molecules

Compound	Number of the molecule	Wyckoff's symbol	Translations t_1, t_2 and t_3			Angle of inclination θ in degrees	Volume of the parallelopiped 0123 in Å³	Volume from crystal structure data in Å³	Lattice parameters from computer simulation					
			X	Y	Z				a Å	b Å	c Å	α	β	γ (in degrees)
Tetracene	0	A(0, 0, 0)	0	0	0	40·2	266·7	291·4	7·50	6·15	13·48	99·4	113·7	85·2
	1	A(0, $\bar{1}$, 0)	1·43	5·60	2·11									
	2	B(0, $\bar{1}$, 0)	−0·33	1·46	4·40									
	3	B($\bar{1}$, $\bar{1}$, $\bar{1}$)	−11·57	4·38	−0·28									
Pentacene	0	B(0, 0, 0)	0	0	0	41·3	339·5	345·6	7·36	6·23	16·02	99·5	110·5	84·8
	1	B(0, $\bar{1}$, 0)	−1·52	5·65	2·13									
	2	A(1, 0, 0)	0·08	1·44	4·37									
	3	A(1, 0, 1)	−15·75	1·02	1·95									
Biphenyl	0	B(0, 0, 0)	0	0	0	50·0	201·8	216·8	7·38	5·52	10·05	89·4	100·2	90·9
	1	B(0, 1, 0)	0·12	5·00	2·33									
	2	A(0, 1, 0)	−0·57	4·10	−2·10									
	3	A(1, 1, 1)	10·10	2·30	1·20									
Terphenyl	0	A(0, 0, 0)	0	0	0	50·7	283·8	307·3	7·43	5·49	13·92	90·5	89·4	89·9
	1	A(0, 1, 0)	−0·04	4·96	2·35									
	2	B(0, 0, 0)	0·83	4·04	−2·09									
	3	B($\bar{1}$, 0, 1)	−14·38	2·13	1·33									
Quaterphenyl	0	B(0, 0, 0)	0	0	0	50·2	368·6	393·3	7·40	5·50	18·15	91·8	94·0	89·9
	1	B(0, 1, 0)	0	4·98	2·33									
	2	A(1, 1, 0)	−0·80	4·01	−2·11									
	3	A(0, 1, 1)	18·72	1·64	1·64									

a crude interatomic potential. One may think of using this procedure with slight variations when planar molecules are packed to give amorphous structures.

Acknowledgement

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