practically completely explained in terms of modulations of the average structure which are of the Σ_2 symmetry, even though the *average* crystal structure corresponds to a frozen-in Σ_1 modulation.

We argue that the short-range order, which tends locally to preserve the *c*-glide plane, is due to dipole–dipole interactions between molecules. On the other hand, the stability of the lattice over a long range (corresponding to wavevectors close to $\mathbf{q} = 0$) is governed by the short-range repulsive interactions and the ability of the molecules to form a closely packed structure in three different crystallographic planes. In agreement with the general conclusions of Kitaigorodsky (1973) the BEMB2 molecules are more easily able to do this in the space group $P2_1$ than in *Pc*. The 'hole' represents a range of wavevectors for which the strain from the packing forces, as a result of the local breaking of the $P2_1$ symmetry, outweighs the energy gained from the short-range ordering of the molecular dipoles.

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Crystal Packing of Hydrocarbons. Effects of Molecular Size, Shape and Stoichiometry

BY A. GAVEZZOTTI

Dipartimento di Chimica Fisica ed Elettrochimica e Centro CNR, Università di Milano, Milano, Italy

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Abstract

The packing energy (PE) and packing modes of hydrocarbon crystals are analyzed statistically using the Cambridge Structural Database. The correlation of PE with several indices of molecular size is discussed; only 19% of the existing hydrocarbon crystal structures are for molecules with an odd number of carbon atoms. Radial distribution functions of the intermolecular contacts peak at a distance which is 0·3–0·5 Å longer than the corresponding sum of the commonly used van der Waals radii. Short contact populations are correlated with various types of packing forces. An effective molecular free surface and a molecular self-packing coefficient are defined to describe shape effects; using these indices, better correlations with PE are obtained, and evidence of the possible formation of inclusion compounds emerges. The effects of the carbon-to-hydrogen ratio on packing are investigated, using the observed den-

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sities, a partitioning of the calculated PE over contact types, the average PE per atom in the molecule, and the number of contacts per atom within a 7 Å sphere. The molecular coordination number in hydrocarbon crystals is studied by partitioning the PE in successive shells of four to twelve neighbour molecules; the first (four-molecule) shell contributes 33 to 77% of PE, depending on various factors; the contribution of the twelve-molecule shell is invariably close to 100%.

Introduction

In a previous paper (Gavezzotti, 1989) a database comprising 391 fully characterized X-ray crystal structures of hydrocarbon molecules was established. Average values and distributions of many crystal and molecular properties were studied, with particular attention paid to factors that produce an efficient molecular packing. Among the topics at the time left for future investigation were the discrimination between the effects of molecular size and molecular shape on packing energies, and a detailed analysis of the distribution of interatomic contacts for carbon and hydrogen, as well as the partitioning of the total energies according to molecular composition (carbon-to-hydrogen ratio). These topics mainly form the subject of the present paper, which also attempts to define some quantitative molecular-shape parameters.

A brief description of the data retrieval from the literature, of the classification, and of the geometrical assumptions required for the treatment of hydrogen-atom positions is given in the *Appendix*. The reader is referred to previous work (Gavezzotti, 1983, 1985, 1989) for further detail and perspective on the methods applied here for packing analysis; such methods pay tribute to ideas and techniques earlier, or simultaneously, proposed by Kitaigorodski (1961), Williams and coworkers [see *e.g.* Williams & Houpt (1986) and references therein], McBride, Bertman, Cioffi, Segmuller & Weber (1988), the Weizmann Institute groups (Leiserowitz & Schmidt, 1969; Leiserowitz & Hagler, 1983) and Sarma & Desiraju (1986), as well as to the statistical approach in the exploitation of the Cambridge Structural Database (Taylor & Kennard, 1984; Allen, Kennard & Taylor, 1983).

Packing energies

The packing potential energy (PPE) is here calculated as:

$$\mathrm{PPE} = 2\mathrm{PE} = \sum_{i,j} [A\exp(-BR_{ij}) - CR_{ij}^{-6}].$$

R_{ij} is an intermolecular distance in the crystal ($\leq$ 7 Å); A, B and C are empirical parameters for each type of interaction [see Mirsky (1976) for numerical values, also reported and discussed in Gavezzotti & Simonetta (1982) and in Gavezzotti (1989)]. Although PE can be related to the crystal sublimation energy (Pertsin & Kitaigorodski, 1987; Williams & Starr, 1977; Gavezzotti, 1989) we regard it in this context as no more than a weighted sum of intermolecular separations in the crystal, or an overall index of the packing propensity for a given molecule – in other words, the one readily available link between molecular and crystal structures. Parameters have always been fitted to a small number of properties on a restricted sample of test crystals, and transferability to a wider range of molecular types has never really been tested. However, we use PE only for comparisons between different crystals, not for quantitative calculations; parameters are weights, or amplification factors, in the comparisons.

Table 1. *Least-squares parameters for the linear fit of PPE to indices of molecular size*

$-\mathrm{PPE}\ (\mathrm{kJ\ mol^{-1}}) = ax + b$; S is the r.m.s. deviation; the standard deviations are given in parentheses. The PPE is calculated at 7 Å cutoff. Small (non-significant) differences from Table V of Gavezzotti (1989) are due to improved efficiency of the programs for the calculation of PPE.

x	a	b	S
N_C	5·87 (15)	76·6 (38)	24·7
W_M	0·469 (13)	72·0 (33)	24·8
Z_V	1·27 (3)	67·8 (42)	25·9
V_M	0·490 (13)	68·2 (42)	27·7
S_M	0·477 (17)	57·7 (50)	29·5
N_T	3·09 (12)	75·7 (54)	33·8
S_{250}	0·498 (13)	27·6 (50)	26·4

Molecular size

Indices of molecular size are the total number of atoms, or of C and H atoms (N_T, N_C, N_H, respectively); the van der Waals envelope volume and surface (V_M, S_M, respectively); the molecular mass (W_M) and the number of valence electrons (Z_V). This last quantity is relevant if it is accepted that intermolecular forces mainly depend on polarization and repulsion among these electrons. Table 1 shows the results of a least-squares analysis of the dependence of PPE on each of these indices. PE = $\frac{1}{2}$PPE, as computed from any of the correlations in Table 1, corresponds approximately to 85% of the sublimation energy (Gavezzotti, 1989).

The best correlation is obtained between PPE and N_C. The PPE–N_T correlation is much worse, and the introduction of two separate coefficients, one for N_C and one for N_H, is not effective either. With the parameters used here, H···H contacts never provide more than a few percent of the total PPE, so that little improvement in the statistics will be obtained

by taking H atoms into account separately. Rather than a true crystal-chemistry effect, this result may reflect a parametrization bias (see below). A better correlation is obtained between PPE and the molecular mass, in which the hydrogen contribution is largely toned down.

Molecular shape: a preliminary analysis

Some initial hints on shape factors in crystal packing can be gathered by inspection of Fig. 1. Out of 391 molecules in the database, only 74, or 19%, have an odd number of carbon atoms. This imbalance should not depend on difficulties in chemical synthesis; more likely, it reflects the relative ease of crystallization of even C-number molecules, presumably through the effects of increased molecular symmetry. Reflection planes, inversion centers, and axes of even order (the most common molecular-symmetry elements) nearly always require an even number of atoms in the molecule. In fact, Fig. 1 and Table 2 clearly reveal that the maximum packing energy attainable by even C-number molecules is always higher than that for odd C-number molecules of comparable size.

A more substantial shape effect appears when one considers the increasing spread of PPE values on increasing N_C (or any other size index). A large number of carbon atoms (size) means a large number of possible isomers and molecular shapes. A change in potential-energy parameters slightly changes some absolute values, but not the essence of this result, as shown in detail in Table 2. One viable approach to a refined definition of molecular-shape factors for crystal packing is therefore to search for molecular indices which reduce the spread in the size/PPE correlations. In other words, one should look for a description of the variations in cohesion energy, where size is the leading coordinate, and shape is the factor responsible for the PPE spread at constant size.

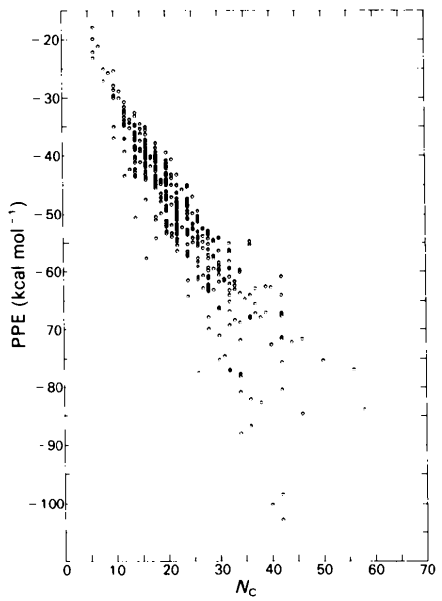

Fig. 1. Plot of PPE *versus* the number of carbon atoms in the molecule (1 kcal = 4·184 kJ).

Table 2. *Maximum PPE and PPE range for a given number of carbon atoms in the molecule*

−PPE (kJ mol^{-1}); refer to Fig. 1 for calculations using Mirsky parameters. 7 Å cutoff in lattice sums.

	Potential functions			
	Mirsky (1976)		Williams (1967) IV*b*	
N_C	Max.	Max.–Min.	Max.	Max.–Min.
12	182	54	170	28
18	227	65	213	62
24	255	62	309	75
30	314	88	352	100
36	363	134	390	141
42	430	175	500	203
15	172	28	—	—
21	226	56	—	—
27	263	44	—	—
33	286	27	—	—

Of course shape patterns can be appreciated on the usual chemical grounds, as for instance in the case of 'cylindrically' extended aliphatic chains, or 'flat' aromatic rings, or 'globular' cages. Steric strain and conformational flexibility also play a role, since crowding increases the intramolecular contacts at the expense of intermolecular ones. The number of internal degrees of freedom, or molecular librations, increases the space 'occupied' by a molecule. Particularly important are low-energy (*e.g.* torsional) librations involving the displacement of large molecular moieties, like phenyl rings joined by formally single bonds to the rest of the molecule.

The main difficulty is reduction of these complex features to a few unequivocally defined and easily calculable quantities, upon which statistical analyses can be performed.

Distribution of intermolecular contacts

An important concept in the definition of favourable molecular shapes for packing is that low PPE's result from a lack of attractive contacts, rather than from the presence of repulsive ones. Indeed, a search for short C···C contacts revealed that there are none in those molecules which have abnormally low PPE's. Short repulsive C···C contacts are thus impossible in hydrocarbon crystals.

Fig. 2 shows histograms for the number of C···C, C···H and H···H contacts found in all our hydrocarbon crystal structures. Only 146 C···C contacts are shorter than 3·4 Å, and none are shorter than 3·2 Å, a distance at which the potential function used here becomes mildly repulsive (+0·67 kJ mol^{-1}). The

highest percentages of these short contacts (44 in number) are found in crystals of planar aromatic compounds, and presumably correspond to moderate attractive interactions between close stacks of aromatic planes. On the other hand, some short C···H, and even more frequently H···H, contacts can be found, especially in methylated compounds. It is impossible to ascertain how much of this effect depends on unavoidable uncertainties in the position of H atoms, which have been artificially located (see *Appendix*). For example, small changes in HCCC torsion angles in methyl groups may improve the packing energy, but full optimization is both impractical and scarcely rewarding, since such fine effects may even be below the threshold of accuracy of the method for the energy calculation. Significantly, there are no H···H contacts below 2·2 Å in aliphatic compounds, for which the H-atom positions in the crystal are, although assumed, quite reliable owing to the simple chemical connectivity of these molecules. On the whole, Fig. 2 confirms the adequacy of the choice of both van der Waals radii and potential functions, since, in terms of these parameters, hydrocarbon crystals appear to be essentially strain free.

A survey of the geometry of H···H contacts has been conducted using neutron diffraction data (Nyburg, Faerman & Prasad, 1987). C—H bond distances of 1·063–1·076 Å were found, close enough to our standardized value (1·08 Å). Hydrogen van der Waals radii between 1 and 1·35 Å were proposed, depending on the mutual orientation of the C—H and H···H vectors; our assumed value of 1·17 Å fits well in this picture, and even H···H contacts around 2 Å (Fig. 2) do not seem so unrealistic.

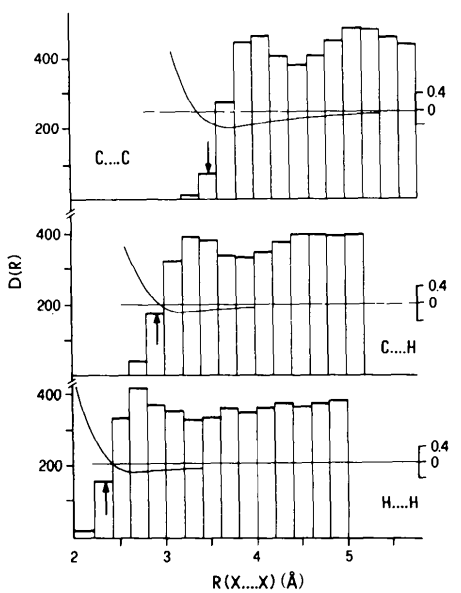

Fig. 2. Radial distribution [$D(R) = N(R)/4\pi R^2 dR$] of intermolecular contacts in 391 hydrocarbon crystals. Non-bonded energy curves are superimposed (ordinate scale on the right, kJ mol^{-1}). Vertical arrows mark the sum of van der Waals radii (1·75 Å for C, 1·17 Å for H).

The radial contact density distributions in Fig. 2 peak at a distance which is slightly larger than the corresponding sum of van der Waals radii (4 *vs* 3·50 for C···C, 3·4 *vs* 2·92 for C···H, and 2·7 *vs* 2·34 Å for H···H contacts). It is not immediately evident whether the peaks correspond to the minima of the Lennard–Jones potentials. A difference of 0·3 Å between the distance of closest approach and the peak of the interaction contact densities had already been observed in crystals containing amino-acid residues (Gould, Gray, Taylor & Walkinshaw, 1985). The interactions within the first peak of the radial distributions constitute a first shell of neighbour interactions, which is mainly responsible for crystal stability; further shells provide a sort of spectator field, as the contact density levels off and the importance of each contact becomes smaller. It is likely that this first shell controls both the dynamic behaviour and the possible reactivity of the molecules in the crystal.

Quantitative indices of molecular shape

If it is accepted that low cohesion energies in crystals result from the lack of attractive contacts, then some indices to describe the screening of intermolecular contacts, due to molecular conformation, must be constructed. One way of describing this effect – the filling of atomic coordination spheres by intramolecular contacts – is to define an effective molecular surface, as follows. Hydrogen atoms are neglected, and the atomic radii of carbon atoms are artificially set at 2·50 Å. The free surface (S_{250}) calculated for such 'inflated' molecular objects does not include parts from clefts or niches. Similar definitions of contact or accessible surfaces have been proposed earlier (Herrmann, 1972; Valvani, Yalkowski & Amidon, 1976), while various molecular steric indices, without the context of crystal packing, have been proposed in papers by Meyer [see Meyer (1988) and references therein].

Another intuitive requirement for the formation of attractive interactions is that the molecular envelope be as smooth and even as possible, since indentations are usually detrimental. A descriptor for this property can be constructed by taking the volume, V_P, of the parallelepiped whose dimensions are the differences in x, y and z between extreme points (including atomic radii) of the molecule in the inertial reference frame. A self-packing coefficient, C_{self}, can then be calculated as

$$C_{self} = V_M/V_P.$$

The meaning of C_{self} can be better appreciated by considering its value for simple solids. It is equal to 0·524 for a sphere or an ellipsoid, while it rises to 0·6 for a diatomic molecule at a favourable internuclear separation. The average value of C_{self} for 391 hydrocarbon molecules is 0·382 (94); Fig. 3 shows typical fluctuations owing to molecular connectivity and conformation.

A high C_{self} usually produces a high PPE; the converse does not follow. The highest value was found for quaterrylene, which does have a packing energy much higher than average, but, in favourable cases, even highly bent or twisted molecules with low C_{self} can achieve efficient molecular interlocking in the solid state. When this is the case, the C_{self} of close-packed dimers must exceed that of the isolated molecule, and the value must increase as larger and larger clusters are formed, until it finally merges into the crystal-packing coefficient, C_K (usually around 0·7). In fact, the lowest C_{self} was found for a compound (Fig. 3) whose packing energy is, on the other hand, quite normal. No molecule with C_{self} lower than 0·2 was found, so that this must be an inherent lower limit for hydrocarbon molecules.

Very low values of C_{self} may be obtained for cross-shaped coordination patterns, as in molecular complexes with transition metals. Thus, $Ni(NCS)_2$-$(4\text{-Phpy})_4$ has $C_{self} = 0{\cdot}145$ [see Nassimbeni, Niven & Taylor (1987) for the molecular structure; the Ni atom is octahedrally coodinated with the two NCS groups in *trans* positions]. Remarkably, this compound attains a quite relevant cohesion energy in its own crystal (444 kJ mol^{-1}; the standard PPE = 423 kJ mol^{-1} for its molecular surface of 786 Å^2, computed as if it were a pure hydrocarbon according to the data in Table 1), but readily forms inclusion compounds (Werner clathrates) with a variety of organic solvent molecules (Nassimbeni *et al.*, 1987; Lavelle, Nassimbeni, Niven & Taylor, 1989). Thus, a low C_{self} may be a necessary, but not sufficient condition for formation of solvates or clathrates.

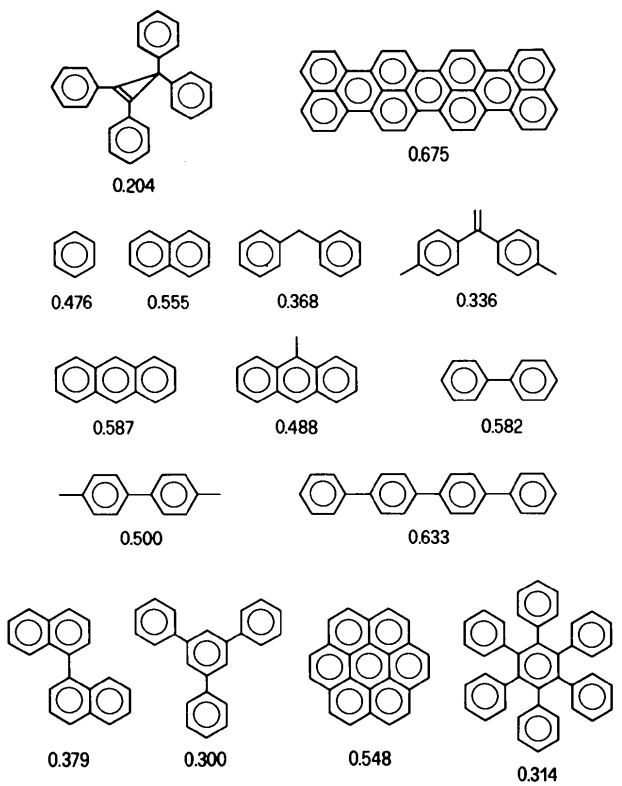

Fig. 3. Self-packing coefficients for various molecules. Top row: minimum and maximum values.

Using S_{250} as a leading size parameter and C_{self} as a shape corrector greatly improves the fit of PPE for large molecules. A dramatic reduction of the r.m.s. deviation is found over a sample of 69 crystals of molecules with $S_M > 400$ Å^2 (r.m.s. in square brackets; all values for PPE in kJ mol^{-1}):

$$\text{PPE} = 0{\cdot}351\ (126)S_M + 121\ (60) \qquad [47{\cdot}2]$$

$$\text{PPE} = 0{\cdot}527\ (100)S_{250} + 118\ (52) \qquad [41{\cdot}8]$$

$$\text{PPE} = 0{\cdot}577\ (75)S_{250} + 307\ (45)C_{self} - 113\ (44) \qquad [32{\cdot}2]$$

The signs or the coefficients in the above correlation confirm that C_{self} cooperates with size in producing a large packing energy. Over the complete sample of 391 crystals with molecules of any size the effect is less conspicuous, but still significant:

$$\text{PPE} = 0{\cdot}477\ (17)S_M + 57{\cdot}7\ (50) \qquad [29{\cdot}5]$$

$$\text{PPE} = 0{\cdot}498\ (13)S_{250} + 27{\cdot}6\ (50) \qquad [26{\cdot}4]$$

$$\text{PPE} = 0{\cdot}548\ (13)S_{250} + 119\ (15)C_{self} + 36{\cdot}8\ (96) \qquad [24{\cdot}6]$$

$$\text{PPE} = 6{\cdot}24\ (15)N_C + 83{\cdot}3\ (142)C_{self} + 36{\cdot}0\ (75) \qquad [23{\cdot}7]$$

Saturation and intermolecular forces

Saturation, in the ordinary chemical sense, is an important factor in crystal packing. For hydrocarbons, it can conveniently be represented by a C/H ratio for the number of atoms (stoichiometric ratio, R_{st}):

$$R_{st} = N_C/N_H$$

or for the surface or volume, when total molecular surfaces and volumes are subdivided into contributions from carbon and from hydrogen atoms (Gavezzotti & Desiraju, 1988; Desiraju & Gavezzotti, 1989).

There is a weak correlation between R_{st} and the crystal density, D_x (Fig. 4):

$$D_x = 0{\cdot}22\,(1)R_{st} + 0{\cdot}94\,(1)\ \text{g cm}^{-3} \quad [0{\cdot}06]$$

There is, however, a considerable spread, especially around $R_{st} = 1$. Acetylenic and allenic compounds are at the lower boundary of the scatterplot, while saturated globular compounds are at the upper boundary. This demonstrates that the high carbon content of acetylenic molecules does not produce a correspondingly dense crystal, and reveals the existence of some longer-range interactions in such crystals, presumably between the polarizable π electrons of the triple bonds or of the cumulene systems. These interactions may not require close molecular contact to reach their optimum. The acetylene crystal itself has in fact been a stumbling block in the theories of empirical potentials [see *e.g.* Marchi & Righini (1985) and references therein]. Our result is a purely geometrical inference, and therefore does not depend on potential-energy calculations or parameters. Whenever a breakdown of close packing is observed, the presence of interactions other than van der Waals ones is deduced.

As might have been expected, there is no correlation between the stoichiometric ratio R_{st} and the packing coefficient C_K (see Fig. 5). In D_x (molecular mass divided by cell volume) a carbon atom counts 12 times as much as a hydrogen atom, while for C_K (molecular volume divided by cell volume) this ratio is reduced to 4·6, on average (Gavezzotti, 1989). Thus, D_x is more sensitive to the C/H ratio than C_K. The efficient occupation of space, reflected in a high C_K, is likely to depend rather on shape than on stoichiometry. Therefore, one would be tempted to build a molecular index that correlates with C_K to describe molecular shape. In practice, however, C_K has a rather narrow range of variation and is too sensitive to a number of other factors, among which is the accuracy in the estimation of molecular volumes.

Carbon and hydrogen coordination spheres

The total PPE can be subdivided into contributions from contact types (E_{CC}, E_{CH} and E_{HH}, respectively). Dividing the total number of intermolecular atom–atom contacts within a 7 Å sphere by the number of atoms in the molecule gives the average number of contacts per atom, N_A; it is a measure of the filling of the molecular coordination sphere in the crystal. Dividing PPE by the number of contacts or of atoms gives the average energy per contact, E_R, or per atom, E_A, respectively. Values of these quantities are collected in Table 3.

E_{CC} and E_{HH} follow the expected trend as a function of carbon content. The absolute values of these partitions depend strongly on parametrization, as demonstrated by the last rows of Table 3, and it is clearly impossible to attach a physical meaning to the subdivision, irrespective of the parameter set which happens to be used. Trends, however, survive and can be interpreted. Since different parameter sets produce more or less the same total PPE's, E_R and E_A are much less parameter-dependent. N_A depends in principle on the imposed C—H bond distance, but fluctuations are very small.

E_R is small for aliphatic compounds, which have a large number of H···H contacts; it increases for aromatics, and is highest for the tightly packed, carbon-rich planar condensed aromatics. N_A follows the opposite sequence, but is unexpectedly high for the planar aromatics, no doubt as a consequence of tight packing. The e.s.d. of this quantity is especially small in this class of structurally homogeneous molecules.

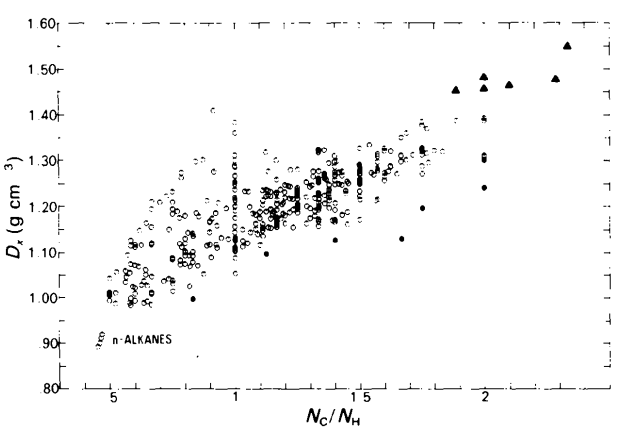

Fig. 4. Scatterplot of calculated crystal density *versus* C:H stoichiometric ratio. Black dots: acetylenic or allenic compounds. Triangles: condensed (planar) aromatics.

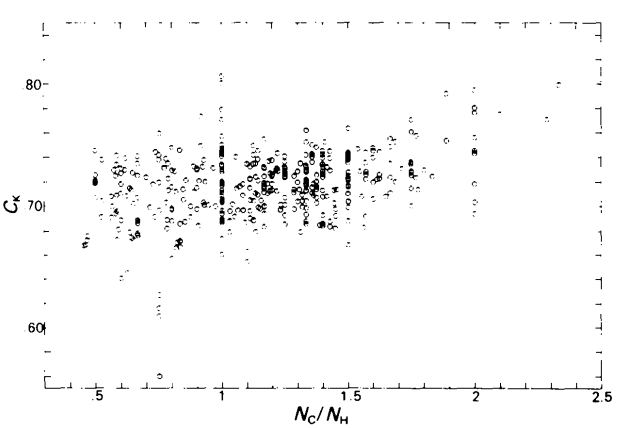

Fig. 5. Scatterplot of the Kitaigorodski packing coefficient *versus* the stoichiometric ratio. The one outlier at low C_K has no obvious explanation.

Table 3. *Average (over a class of molecules) of the average number (over each molecule) of intermolecular contacts per atom, N_A, energy per contact, E_R, and energy per atom, E_A; averages of the percent contribution to the PPE*

7 Å cutoff throughout; units are J mol^{-1} contact $^{-1}$ for E_R, kJ mol^{-1} atom $^{-1}$ for E_A. Estimated standard deviations are given in parentheses.

Class	No. of molecules	N_A	$-E_R$	$-E_A$	%C···C	%H···H
Aliphatics	19	145 (12)	29 (3)	4·23 (67)	31 (2)	18 (2)
Aliphatics/aromatics	85	119 (11)	42 (7)	4·98 (79)	49 (9)	9 (4)
Cyclophanes	38	117 (12)	39 (4)	4·52 (42)	50 (5)	8 (2)
gem-Phenyl	25	104 (11)	42 (4)	4·44 (71)	53 (5)	7 (2)
Helicenes	24	104 (6)	49 (5)	5·06 (59)	60 (4)	5 (1)
Aromatics	53	113 (11)	48 (4)	5·44 (67)	57 (4)	5 (1)
Planar aromatics	23	117 (5)	55 (4)	6·44 (38)	65 (5)	4 (1)
All	391	118 (15)	43 (8)	4·98 (88)	51 (10)	8 (4)
n-Decane*		148	33	4·85	29	20
		(148)	(31)	(4·52)	(41)	(4)
Naphthalene*		129	50	6·49	58	6
		(127)	(56)	(7·03)	(65)	(0·3)

* Values in parentheses were calculated using Williams' (1967) parameters.

Figs. 6 and 7 show the values of N_A and E_A for each crystal structure. Some effects of saturation and molecular shape can be appreciated by an examination of these figures and of Table 3. Aliphatic compounds have relatively small hydrogen atoms at the outer edge of the molecule, and these are responsible for the very large number of intermolecular contacts. Since a larger number of smaller atoms can fit in a given coordination sphere, small, globular, saturated molecules have high N_A values (Fig. 8). Since, however, the H···H contributions to PPE are smaller than those involving carbon atoms, this large number of contacts does not always produce a large cohesion energy. Whatever the choice of parameters, the above argument holds, inasmuch as it is reasonable to assume that attractive intermolecular potentials are ultimately proportional to the number of valence electrons and to their polarizabilities. In the language of atom–atom potential models, a stable crystal is one in which the available space is filled with energetically rich C···C contacts, and a favourable packing, depending on shape and saturation, is one in which hydrogens are either few, or stand as little as possible in the way when C···C contacts are to be established.

Table 3 also shows a detailed comparison of variations of N_A and E_A for aromatic compounds. N_A is low due to unsaturation; E_A goes from very low values in cyclophanes, to low values for *gem*-phenyl compounds, and to average values for helicenes; values are higher for plain aromatics, and highest for the condensed aromatics. The trend of increasing E_A thus parallels the decrease of molecular folding and strain. Steric crowding and molecular strain also produce a 'crystal strain', or a decrease in cohesion energy.

N_A is thus a purely geometrical, parameter-independent index of the quality of molecular packing, incorporating both the effects of saturation and of intramolecular screening.

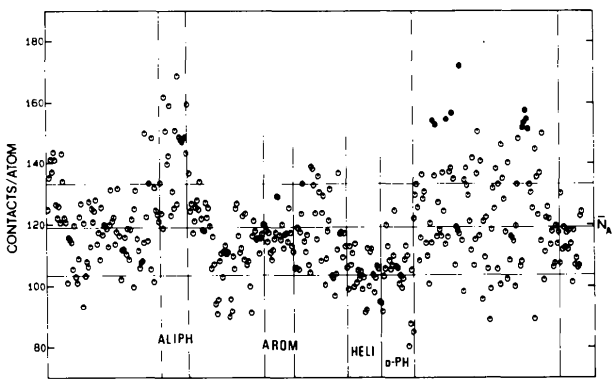

Fig. 6. Average number of contacts per atom (7 Å cutoff) for each of the crystal structures. Black dots: compounds in Fig. 8. The horizontal lines mark the average and the $\pm\sigma$ range. ALIPH: aliphatics; AROM: condensed aromatics; HELI: helicenes; *o*-PH: *gem*-phenyl compounds (see *Appendix*).

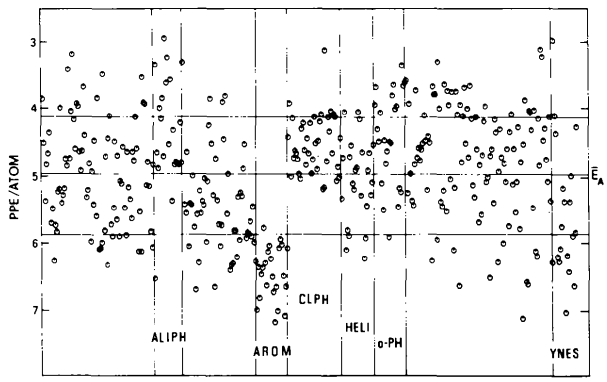

Fig. 7. Average contribution per atom to PPE for each of the crystal structures. Horizontal lines and labels as in Fig. 6; CLPH: cyclophanes, YNES: acetylenic or allenic compounds.

Molecular coordination sphere

We rank the molecules surrounding a reference molecule in the crystal in order of decreasing importance for packing, by computing the molecule–molecule interaction energy for each neighbour; then, the percent of PPE of the first N neighbours, called $E_{MM}(N)$, is a quantitative measure of the molecular coordination sphere in the crystal. Average values are reported in Table 4. It has been known for a long time (Kitaigorodski, 1973) that the molecular coordination number in organic crystals is usually 12; this remarkable insight, proposed in times when only a limited number of structures were available, is confirmed by the data in Table 4, where one sees that $E_{MM}(12)$, or the contribution from the first 12 neighbours, is 96% of the total packing energy on the average. As N increases, $E_{MM}(N)$ increases smoothly, and the e.s.d.'s decrease. $E_{MM}(4)$, or the contribution from the very first coordination shell, is sensitive to molecular shape, but is not correlated with any of our packing indices. It is high for linear molecules (like the *n*-alkanes) or for flat molecules (like the planar aromatics), and small for small, globular molecules (see Fig. 8); the geometrical reasons for this are evident. The range of variation of $E_{MM}(4)$ is from 32·9 (remarkably, a close packing of spheres gives 33·3%) to 76·6%. Correspondingly, structures can be classified as having a 'scattered coordination sphere' (s.c.s.) or a 'compact coordination sphere' (c.c.s.); but one is puzzled by the fact that the same compound (dibenzanthracene) can adopt both, in two different polymorphs (Gavezzotti & Desiraju, 1988).

Table 4. *Percent of the packing energy owing to the first N neighbour molecules in the crystal*

Average values for hydrocarbon crystal structures with no more than one molecule in the asymmetric unit. Estimated standard deviations are given in parentheses.

N	$E_{MM}(N)$ (%)
4	54 (8)
6	70 (7)
8	81 (5)
10	90 (3)
12	96 (2)

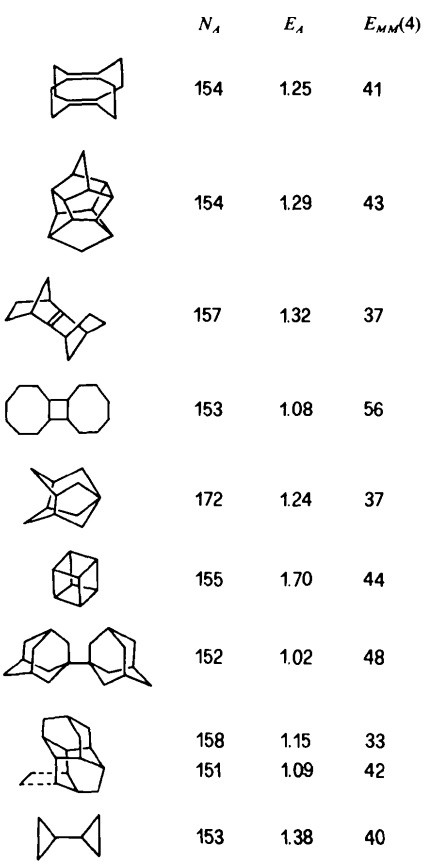

Fig. 8. Structural formulae for compounds with very high numbers of contacts per atom (black dots in Fig. 6).

APPENDIX

The hydrocarbon database, retrieved from the Cambridge Structural Database (CSD) (Allen *et al.*, 1983) contains 391 crystal structures, divided in subgroups according to the chemical nature of the compounds; among these are the aliphatic group, with sp^3 C atoms only; the aliphatic/aromatic group, with alkyl-substituted aromatics; the cyclophane group, with aromatic rings held face to face; the *gem*-phenyl group, with *gem*-polyphenyl substitution; the helicene group; the aromatic group, with sp^2 C atoms only in aromatic ring structures; and the planar aromatic group, with condensed ring systems and planar shape. H atoms were located by geometrical considerations, using C—H = 1·08 Å. Other details of the CSD search and of the procedures for H-atom location are to be found in Gavezzotti (1989). The deposited material for this last paper contains the CSD REFCODEs.

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Molecular-Packing Analysis of Molecular Complexes Containing Hexafluorobenzene or Fluoranil

BY TOR DAHL

Institute of Mathematical and Physical Sciences, University of Tromsø, N-9000 Tromsø, Norway

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Abstract

Molecular-packing analyses of nine molecular complexes between hexafluorobenzene or fluoranil and methylated benzenes or aromatic amines have been performed using lattice-energy calculations in the atom-to-atom approach. Energy minimization with molecular orientations and positions and cell parameters as variables gave, for most of the complexes, structures somewhat different from the experimental structures. Minimization of energy was also performed with only the crystallographic axes as variables. For the experimental structures and the structures obtained after the energy minimizations the contributions to the lattice energy from dispersion, repulsion and Coulombic interactions within one single stack and between different stacks were calculated. The results indicate that for some complexes there are stacking interactions in addition to those predicted by the analytical potentials, which have a substantial effect on the molecular packing. For other complexes, where the interactions in the stacks are weak, the molecular packing seems to be influenced by additional interactions between different stacks, probably directional F···H interactions.

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Introduction

Lattice-energy calculations based on analytical atom-to-atom potentials show that for many compounds the molecular packing giving the lowest calculated energy agrees fairly well with that of the experimental structure (Williams & Cox, 1984). In molecular complexes, however, there are usually special kinds of interactions, not included in the analytical potentials, in addition to the traditional van der Waals interactions. These additional interactions may cause differences between the experimental and lowest-energy structures. The purpose of the present work was to analyse such differences in complexes containing hexafluorobenzene (HFB) or tetrafluoro-*p*-benzoquinone (fluoranil) and from the observed trends try to draw conclusions concerning special kinds of interactions in these complexes.

The nature of the molecular complexes containing HFB has been a matter of dispute (Swinton, 1974). In the crystalline state the partner molecules are stacked alternately in infinite columns as in ordinary charge-transfer complexes, but the importance of charge-transfer interactions is doubtful because of the low electron affinity of HFB (Wentworth,

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