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A Systematic Analysis of Packing Energies and Other Packing Parameters for Fused-Ring Aromatic Hydrocarbons

By A. Gavezzotti

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

and Gautam R. Desiraju

School of Chemistry, University of Hyderabad, Hyderabad 500134, *India*

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Abstract

A systematic analysis of the energetic and geometric factors that control the packing of condensed aromatics has been carried out using the known crystal structures of several such compounds. Packing energies were calculated and correlated to molecular structure indices. Atom-by-atom and molecule-by-molecule contributions to the packing energies were determined: the first contributions are constant for each type of atom, the second are able to describe in a simple and reproducible way the coordination sphere of a molecule in the crystal and help to define the various aromatic structure types. Some geometrical intermolecular coordinates, also helpful in defining structure types, are described. Molecular rotations in the crystal are discussed in terms of molecular shape *versus* crystal environment. Polymorphism and its relations with basic packing patterns are also examined. It is found that geometrically similar molecules crystallize with the same basic packing motif or cluster, which survives changes in lattice and space-group symmetry.

Introduction

The wealth of information contained in the thousands of crystal structures determined in the last few decades has been exploited to obtain new insights into molecular conformation and energetics (Allen, Kennard & Taylor, 1983; Bürgi & Dunitz, 1983; Chandrasekhar & Bürgi, 1984; Vedani & Dunitz, 1985; Allen, 1986, and references therein). Less common have been attempts to analyze systematically the intermolecular environment of organic molecules in the crystal (Leiserowitz & Hagler, 1983; Sarma & Desiraju, 1986; Ramasubbu, Parthasarathy & Murray-Rust, 1986; Desiraju, 1987*a*), although a better knowledge of the factors that determine organic crystal-packing modes would be highly desirable. The ultimate goal is a simple and realistic theory of crystal structure in terms of molecular structure. Such a theory would be of paramount importance in all fields of organic solid-state chemistry, be it the design of organic materials and conductors, or an understanding of the mechanisms of phase transitions and solid-state reactions. Interest in these matters is rising (Desiraju, 1987*b*; Ramamurthy, Scheffer & Turro, 1987).

We have undertaken an analysis of the geometric and energetic factors which are at the origin of the crystal packing of condensed aromatic hydrocarbons, using a data set which includes nearly all the known (ordered and fully determined) crystal structures of molecules containing only three-coordinated carbon atoms and hydrogens in fused rings; helicenes have been excluded, quaterphenyl has been included as a representative of the polyphenyl family, and [18]annulene as a curiosity that mimics a condensed ring structure with its inner H atoms. This is a homogeneous group of substances, comprising mainly planar molecules, whose shape can be readily visualized by simple models; besides, they

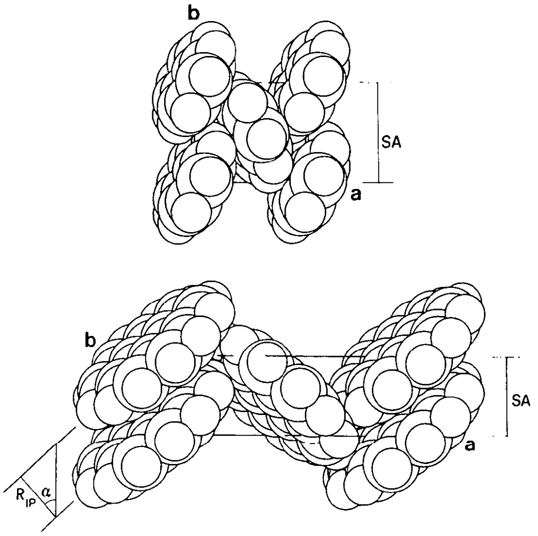

Fig. 1. Examples of HB structure (top, naphthalene) and γ structure (bottom, coronene); projections along *c*. Some important geometrical parameters are shown: SA, shortest cell axis; R_{IP}, interplanar distance; α, shearing angle. R_N (not shown) is the shortest distance between neighbouring centres of mass (for coronene, SA = R_N). van der Waals spheres are to scale.

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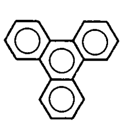

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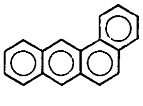

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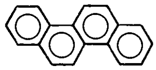

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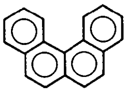

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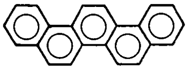

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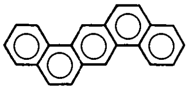

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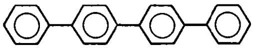

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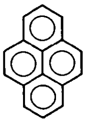

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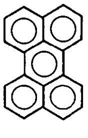

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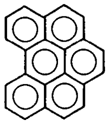

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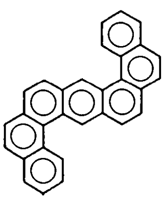

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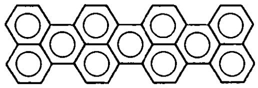

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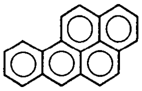

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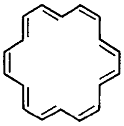

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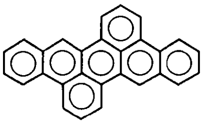

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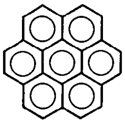

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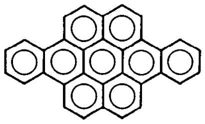

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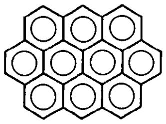

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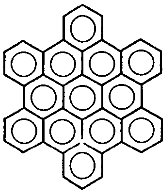

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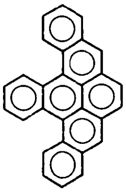

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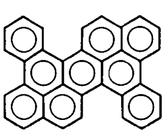

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form a small number of rather sharply defined structural types, whose geometric features have been analyzed and coded in a parallel paper (Gavezzotti & Desiraju, 1988). These types have been called herringbone (HB), sandwich–herringbone (SHB), γ and β, according mainly to the relative orientation of molecular planes in the crystal, which is reflected in the length of the shortest cell axis (SA). HB structures are characterized by SA $> 5{\cdot}4$ Å, γ structures by $4{\cdot}6 <$ SA $< 4{\cdot}0$ Å, while the β structures are identified by SA $< 4{\cdot}0$ Å, corresponding to the shortest possible separation between molecular planes. SHB structures form molecular pairs, which are organized in turn in a herringbone fashion. Fig. 1 helps in the visualization of these structure types, and Table 1 contains essential information about the compounds in the data set.

The crystal potential of aromatic hydrocarbons can be described to a high degree of accuracy by sums of empirical atom–atom non-bonded potentials. Much work has been carried out on the optimization of these potentials, which can be used in the description of equilibrium properties of aromatics, as well as in lattice dynamics or molecular dynamics in crystals [for a comprehensive discussion on the derivation and use of these potentials, see Pertsin & Kitaigorodski (1987)]. We have used a comprehensive set of non-bonded potentials for all atoms commonly occurring in organic molecules [Mirsky, 1978; see, for former applications, Gavezzotti (1982, 1983)] which provides an accurate description of the equilibrium properties of organic molecules in crystals, and is therefore suitable for deriving statistical parameters that describe their structures. To use specific potentials for a certain class of compounds, like Williams' ones for hydrocarbons (Williams, 1967; Williams & Starr, 1977), would have made the results incompatible with previous statistical work on the crystal packing of organic substances. In any case, the good performance of the potentials we use here for hydrocarbons is well documented (Mirsky, 1976); but we maintain that all the trends and generalizations we propose should survive, if perhaps with minor variations in the numerical parameters, any reasonable change of the non-bonded potential-energy functions.

Results

(*a*) *Packing energies*

Table 2 lists the values of some molecular properties, and the packing energy (PE) of the 25 compounds considered here. Although the computational effort required to extend the summations for the lattice energy to 10 Å is virtually nil, a 7 Å limit was adopted, since it is closer to the limit used during the calibration of the functions. It has been pointed out (Brock & Dunitz, 1982) that a larger cutoff may lead to worse results, for the above reason.

Fig. 2 shows a plot of PE *versus* the number of valence electrons, and Fig. 3 PE *versus* the molecular surface. Both correlations are rather good. The slopes are slightly larger than those obtained in the same manner (Gavezzotti, 1985) for organic crystal structures containing heteroatoms. This means that aromatic hydrocarbons form very tightly packed crystals – as is also evident from the fact that the average packing coefficient is 0·748, against 0·712 for general organic compounds (Gavezzotti, 1982). Thus, there is no connection between the strength of lattice forces (which are feeble in aromatic hydrocarbons) and close packing.

Table 1. *Numbering, name and REFCODE in the Cambridge files, and literature citation for the compounds in this study*

(1) Benzene (BENZEN) Bacon, G. E., Curry, N. A. & Wilson, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110. (Neutron, 218 K).
(2) Naphthalene (NAPHTHA10) Brock, C. P. & Dunitz, J. D. (1982). *Acta Cryst.* B**38**, 2218–2228. (239 K).
(3) Anthracene (ANTCED01) Chaplot, S. L., Lehner, N. & Pawley, G. S. (1982). *Acta Cryst.* B**38**, 483–487. (Deuterated, neutron, 16 K).
(4) Phenanthrene (PHENAN12) Kay, M. I., Okaya, Y. & Cox, D. E. (1971). *Acta Cryst.* B**27**, 26–33. (Neutron).
(5) Triphenylene (TRIPHE) Ahmed, F. R. & Trotter, J. (1963). *Acta Cryst.* **16**, 503–508.
(6) 1:2-Benzanthracene (BEANTR) Friedlander, P. H. & Sayre, D. (1956). *Nature (London)*, **178**, 999–1000.
(7) Chrysene (CRYSEN) Burns, D. M. & Iball, J. (1960). *Proc. R. Soc. London Ser. A*, **257**, 491–514.
(8) Benzo[*c*]phenanthrene (BZPHAN) Hirshfeld, F. L., Sandler, S. & Schmidt, G. M. J. (1963). *J. Chem. Soc.* pp. 2108–2125.
(9) Picene (ZZZOYC01) De, A., Ghosh, R., Roychowdury, S. & Roychowdury, P. (1985). *Acta Cryst.* C**41**, 907–909.
(10) Dibenz[*a,h*]anthracene (*a*) orthorhombic form (DBNTHR) Robertson, J. M. & White, J. (1947). *J. Chem. Soc.* pp. 1001–1010; (*b*) monoclinic form (DBNTHR10) Robertson, J. M. & White, J. G. (1956). *J. Chem. Soc.* pp. 925–931.
(11) *p*-Quaterphenyl (QUPHEN) Delugeard, Y., Desuche, J. & Baudour, J. L. (1976). *Acta Cryst.* B**32**, 702–705.
(12) Pyrene (PYRENE02) Hazell, A. C., Larsen, F. K. & Lehmann, M. S. (1972). *Acta Cryst.* B**28**, 2977–2984. (Neutron).
(13) Perylene (PERLEN01) Camerman, A. & Trotter, J. (1964). *Proc. R. Soc. London Ser. A*, **279**, 129–146.
(14) 1:12-Benzperylene (BNPERY) White, J. G. (1948). *J. Chem. Soc.* pp. 1398–1408.
(15) Dinaphtho[1,2-*a*;1′,2′-*h*]anthracene (DNAPAN) Hummelink-Peters, B. G. M. C., van den Hark, T. E. M., Noordik, J. H. & Beurskens, P. T. (1975). *Cryst. Struct. Commun.* **4**, 281–284.
(16) Quaterrylene (QUATER10) Kerr, K. A., Ashmore, J. P. & Speakman, J. C. (1975). *Proc. R. Soc. London Ser. A*, **344**, 199–215.
(17) 3,4-Benzopyrene (BNPYRE10) Iball, J., Scrimgeour, S. N. & Young, D. W. (1976). *Acta Cryst.* B**32**, 328–330.
(18) [18]Annulene (ANULEN) Bregman, J., Hirshfeld, F. L., Rabinovich, D. & Schmidt, G. M. J. (1965). *Acta Cryst.* **19**, 227–233.
(19) 2,3:8,9-Dibenzoperylene (DBPERY) Lipscomb, W. N., Robertson, J. M. & Rossmann, M. G. (1959). *J. Chem. Soc.* pp. 2601–2607.
(20) Coronene (CORONE) Fawcett, J. K. & Trotter, J. (1965). *Proc. R. Soc. London Ser. A*, **289**, 366–376.
(21) 1,2:7,8-Dibenzocoronene (DBZCOR) Robertson, J. M. & Trotter, J. (1961). *J. Chem. Soc.* pp. 1115–1120.
(22) Ovalene (OVALEN01) Hazell, R. G. & Pawley, G. S. (1973). *Z. Kristallogr.* **137**, 159–172.
(23) 1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene (HBZCOR) Robertson, J. M. & Trotter, J. (1961). *J. Chem. Soc.* pp. 1280–1284.
(24) Tribenzopyrene (naphtho[1,2,3,4-*rst*]pentaphene) (TBZPYR) Roberts, P. J. & Ferguson, G. (1977). *Acta Cryst.* B**33**, 1244–1247.
(25) Tetrabenzo[*a,cd,j,lm*]perylene (TBZPER) Kohno, Y., Kohno, M., Saito, Y. & Inokuchi, H. (1975). *Acta Cryst.* B**31**, 2076–2080.

Table 3 shows some comparisons between calculated PE's and measured heats of sublimation, which are affected by uncertainties as large as 15%. The good agreement shown in Table 3 is not unexpected, since heats of sublimation are used in the calibration of potential parameters. Calculations at 7 Å cutoff yield 88 to 93% of the value at 10 Å cutoff, and (on average) 83% of the heat of sublimation. We suggest that an estimate of the heat of sublimation for condensed aromatics, even more reliable than measured values, is, from Fig. 2:

$$0{\cdot}8\Delta H(\text{subl.}) = 1{\cdot}113Z_V + 0{\cdot}573\ \text{kJ mol}^{-1} \tag{1}$$

where Z_V is the number of valence electrons in the molecule. One has however to take into account shape factors. Table 4 is convincing in this respect: the more symmetrical the shape, the higher the packing energy and the packing coefficient. There are no exceptions to this rule; only, it is rather difficult to define in rigorous terms what is meant by a 'symmetrical' shape, beyond a rather subjective visual survey.

(*b*) *Packing-energy contributions*

The regularity of the packing mode of aromatic hydrocarbons is evident if one considers the value of the packing energy per interatomic contact within the 7 Å cutoff sphere. The values (Table 2) are all within the range 48–62 J mol^{-1} per contact. Another aspect of this uniformity is the packing-energy contribution of each atom, which is constant for each atomic species (within a narrow range, see Table 5). The homomeric principle (Gavezzotti, 1982), which states exactly that, is thus strictly obeyed in this very homogeneous class of compounds. The relatively large r.m.s. deviations for the average surfaces, $\bar{S}$, of H atoms (and, consequently, of the average energy, $\bar{E}$, for the same atoms) is due to molecular conformation effects: H atoms in the so-called 'bay regions' of condensed aromatics point towards each other instead of pointing outwards, overlap in part with intramolecular neighbours, and are partly screened from intermolecular interactions.

The estimate of ΔH(subl.) from Z_V [equation (1)] is not consistent with the data in Table 5: there are two different C atoms, and neither provides four times as much packing energy as one H atom. We are dealing with two different, incompatible models. An even more accurate estimate of the sublimation energies for condensed aromatics is therefore

$$0{\cdot}8\Delta H(\text{subl.}) = \tfrac{1}{2}(12{\cdot}1n_{\text{CH}} + 7{\cdot}49n_{\text{C}})\ \text{kJ mol}^{-1} \tag{2}$$

where n_{CH} and n_{C} are the number of CH groups and C atoms bound only to other C atoms, respectively. The excellent agreement of this formula with data in Table

Table 2. *Packing indices*

S_M, V_M, molecular surface and volume (Å^2, Å^3); C_K, Kitaigorodski packing coefficient; PE, packing energy (kJ mol^{-1}); PE/contact, packing energy per intermolecular contact within a 7 Å cutoff sphere (J mol^{-1} contact^{-1}).

	Space group	Z	S_M	V_M	C_K	PE	PE/contact
HB structures							
(1) Benzene	*Pbca*	4	108	84·4	0·687	37·4	48
(2) Naphthalene	$P2_1/a$	2	154	128·8	0·728	58·5	50
(3) Anthracene	$P2_1/a$	2	202	175·2	0·770	79·8	51
(4) Phenanthrene	$P2_1$	2	198	173·3	0·708	72·3	51
(5) Triphenylene	$P2_12_12_1$	4	238	218·4	0·754	96·4	54
(6) Benzanthracene	$P2_1$	2	245	219·6	0·713	90·2	54
(7) Chrysene	$I2/c$	4	241	217·9	0·742	95·3	53
(8) Benzophenanthrene	$P2_12_12_1$	4	241	218·6	0·728	91·0	52
(9) Picene	$P2_1$	2	284	262·3	0·744	114·6	54
(10) Dibenzanthracene							
(*a*) orthorhombic	*Pcab*	4	289	265·7	0·750	108·2	51
(*b*) monoclinic	$P2_1$	2	286	261·9	0·736	106·8	51
(11) Quaterphenyl	$P2_1/a$	2	336	305·1	0·753	134·3	51
SHB structures							
(12) Pyrene	$P2_1/a$	4	212	189·5	0·720	79·5	53
(13) Perylene	$P2_1/a$	4	253	234·7	0·762	106·6	56
(14) Benzperylene	$P2_1/a$	4	267	251·3	0·738	107·3	55
(15) Dinaphthoanthracene	$P2_1/c$	4	373	352·0	0·735	138·4	52
(16) Quaterrylene	$P2_1/a$	4	450	445·4	0·795	209·5	58
γ structures							
(17) Benzopyrene	$P2_1/c$	4	255	233·8	0·755	108·9	58
(18) [18]Annulene	$P2_1/a$	2	296	254·1	0·747	100·1	46
(19) Dibenzoperylene	$A2/a$	4	341	325·2	0·771	146·4	55
(20) Coronene	$P2_1/a$	2	281	265·7	0·743	119·3	59
(21) Dibenzocoronene	$C2/c$	4	358	354·2	0·777	161·4	58
(22) Ovalene	$P2_1/a$	2	352	344·9	0·771	161·1	62
(23) Hexabenzocoronene	$P2_1/a$	2	431	447·1	0·800	215·1	62
β structures							
(24) Tribenzopyrene	$Pn2_1m$	2	339	323·0	0·761	142·1	56
(25) Tetrabenzoperylene	*Pcab*	8	390	384·1	0·754	163·5	58

3, and with other schemes for the calculation of sublimation energies (Bondi, 1963) can be easily checked.

We will now try to find an energetic basis for the classification of packing patterns sketched in the introduction. Clearly, the mutual orientation of molecular planes in the crystal depends on the relative importance of C···C *versus* C···H contacts, H···H contacts never providing more than 6% of the total PE [except for the very special cases of benzene (8%) and [18]annulene (6·4%)]. The number of first neighbour molecules is another important index. The packing energies have been split into the various contributions as needed, and the results are shown in Table 6.

Ignoring benzene and (18), the average percentage C···C PE is 61·0 for HB, 65·2 for SHB, 66·9 for β, and 68·7 for γ structures. The trend reflects the increasing importance of C···C interactions in these classes, but this quantity alone does not allow discrimination between structure types: in fact, it is more

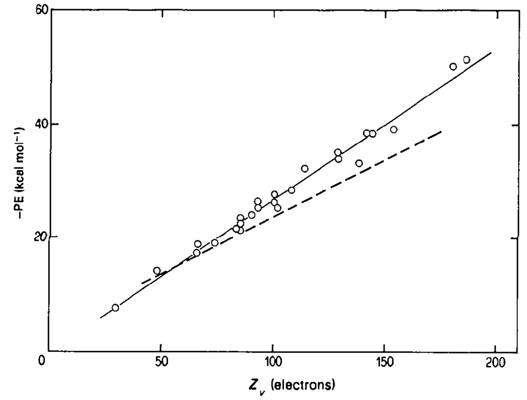

Fig. 2. Plot of the packing energy (7 Å cutoff) *versus* the number of valence electrons, Z_V. The broken line is the same plot for general organic compounds (Gavezzotti, 1985). Slopes are 0·266 and 0·202 kcal mol^{-1} electron^{-1} for the two lines, respectively (1 cal = 4·184 J).

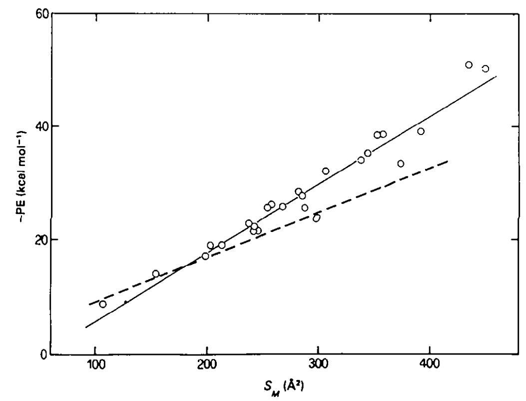

Fig. 3. Plot of packing energy *versus* molecular surface, S_M (see also caption to Fig. 2). Slopes are 0·120 and 0·077 kcal mol^{-1} Å^{-2} for the two lines, respectively (1 cal = 4·184 J).

Table 3. *Calculated packing energies and experimental heats of sublimation* (kJ mol^{-1})

	Packing energy		
	10 Å cutoff	7 Å cutoff	Heat of sublimation
(1) Benzene	40·6	37·4	44·8[a]
(2) Naphthalene	64·4	58·5	64·0–70·3[a]; 72·0[c]
(3) Anthracene	88·7	79·8	90·8–100[b]; 98·7[d]
(4) Phenanthrene	80·3	72·3	86·6[a]; 90·8[e]
(12) Pyrene	89·5	79·5	103·8[e]
(5) Triphenylene	107·9	96·4	107·1[a]
(20) Coronene	134·3	119·3	128·4[a]; 144·3–148·5[f]
(22) Ovalene	181·2	161·1	206·7[f]

References: (*a*) Kitaigorodski (1973); (*b*) Bondi (1963); (*c*) Morawetz (1972*a*); (*d*) Dygdala & Stefanski (1980); (*e*) Smith, Stewart, Osborn & Wiscott (1980); (*f*) Morawetz (1972*b*).

Table 4. *Packing energies* (kJ mol^{-1}) *and packing coefficients of isomers*

	Packing potential energy	Packing coefficient
(3) Anthracene	159·6	0·770
(4) Phenanthrene	144·6	0·708
(5) Triphenylene	192·8	0·754
(6) Benzanthracene	180·4	0·713
(7) Chrysene	190·6	0·742
(8) Benzophenanthrene	182·0	0·728
(9) Picene	229·2	0·744
(10) Dibenzanthracene		
(*a*) orthorhombic	216·4	0·750
(*b*) monoclinic	213·6	0·736
(13) Perylene	213·2	0·762
(17) Benzopyrene	217·8	0·755
(19) Dibenzoperylene	292·8	0·771
(24) Tribenzopyrene	284·2	0·761

Table 5. *Average packing potential energies* ($\bar{E}$, kJ mol^{-1}) *and surfaces* ($\bar{S}$, Å^2) *for each atomic species in condensed aromatics*

R.m.s. deviations are given in parentheses.

	Number of samples	$\bar{E}$	$\bar{S}$
–H	354	3·35 (46)	6·35 (69)
⩾C–	238	7·49 (67)	5·80 (13)
⩾C–(H)	354	8·79 (67)	10·70 (53)

strictly connected with the stoichiometric C/H ratio in the molecule. Thus, molecules which form parallel sandwich pairs in the crystal obtain as much stabilization from C···H contacts as molecules that pack with large angles between molecular planes. This is another aspect of the homomeric principle.

More significant is the partitioning of PE into contributions from each molecule in the coordination sphere. We call $E_{MM}(n)$ the percentage contribution to the total PE from the first n molecules in this sphere (Table 6). In crystals with a centre of symmetry not coincident with a molecular centre of symmetry, the E_{MM} to one molecule (the centrosymmetrical one) is always unique; in SHB structures, this interaction is also predominant, and the building block of the crystal structure is the sandwich pair. This one interaction provides about 30% of the packing energy, about as much as $E_{MM}(2)$ in HB structures. In γ and β structures, $E_{MM}(2)$ provides 50–60% of PE, just like $E_{MM}(3)$ in SHB. $E_{MM}(4)$ provides 40–70% of the total PE, and there is a rough dependence of this quantity on the overall molecular bulk, as described by the molecular surface (Fig. 4). Note how orthorhombic packing [compound (8)] and irregular shapes [compound (15)] deviate conspicuously from the curve: all these structures are close-packed in the Kitaigorodski sense ($C_K > 0{\cdot}7$), but we may define those along or above the curve in Fig. 4 as 'compact coordination sphere' (c.c.s.) structures, and those below as 'scattered coordination sphere' (s.c.s.) structures. A pure face-centered cubic lattice is an extreme example of s.c.s. structure, since 12 nearest neighbours contribute equally to PE, and $E_{MM}(4)$ is 33%. Benzene is not far from this situation, and, in fact, it has four neighbours contributing 10·4% each, four contributing 7·1% each, and four 6·2% each. If benzene were to collapse into a perfect sphere, the cell edges might well become equal, and the *Pbca* herringbone motif would turn into the quincunx arrangement which is contradistinctive of f.c.c. packing. As is well known (Kitaigorodski, 1973), for all compounds $E_{MM}(12)$ is greater than 90% of the total packing energy.

(*c*) *Geometrical indices*

The PE partitioning over surrounding molecules in the coordination sphere does not reveal the geometrical character of the interaction. As sketched in Fig. 1, three geometrical quantities are important in this respect: (1) the shortest cell axis, SA; (2) the shortest distance between centres of mass, R_N; and (3) the shortest distance between parallel molecular planes, R_{IP}. It is also convenient to define a 'shearing angle', α (Fig. 1; $\cos\alpha = R_{IP}/R_N$).

Table 7 reports numerical values for the above quantities. For all the monoclinic HB structures, R_N is remarkably constant (5–5·2 Å) and much shorter than SA; the first neighbours are thus related by a symmetry element, rather than pure translation. For SHB and γ, R_{IP} is about 3·5 Å, or twice the van der Waals radius of carbon, indicating the formation of tight pairs. For γ structures, R_N = SA, indicating that pairs are formed by pure translation. But while for SHB the values of R_N and R_{IP} are almost equal and α is small, the γ structures have larger R_N values, and hence larger α values. Finally, the β structures are characterized by SA $= R_N = R_{IP}$, indicating the formation of columns of molecules along the direction of the shortest cell edge.

(*d*) *Molecular rotations in the crystal*

Table 8 shows the calculated barriers to rotation in the molecular plane, obtained by computing the packing potential energy of the crystal as a function of the rotation angle of one molecule in the crystal. Compounds not appearing in this table showed impossibly high barriers to this rotation. It is worth pointing out that the barriers were calculated using

Table 6. *Contributions to the packing energy*

%C···C, %C···H, percentage packing-energy contributions of C···C and C···H contacts; $E_{MM}(n)$ percentage contributions of the first n neighbours in the coordination shell; C/H stoichiom., C/H surface, C/H ratios in the molecule, stoichiometric or total surface of C per total surface of H atoms.

	%C···C	%C···H	$E_{MM}(n)$ $n = 1$	2	3	4	C/H stoichiom.	C/H surface
HB structures								
(1)	50·8	41·2	—	21	—	41	1·00	1·65
(2)	57·5	36·9	—	26	—	51	1·25	1·83
(3)	62·3	32·7	—	28	—	56	1·40	1·97
(4)	59·7	35·6	—	31	—	56	1·40	2·00
(5)	60·3	35·0	—	42	—	61	1·50	2·23
(6)	60·8	34·4	—	33	—	63	1·50	2·08
(7)	61·8	33·8	—	30	—	61	1·50	2·14
(8)	60·9	34·7	—	37	—	53	1·50	2·07
(9)	62·6	33·5	—	33	—	63	1·57	2·24
(10*a*)	63·5	31·8	—	19	—	38	1·57	2·17
(10*b*)	63·8	33·6	—	33	—	65	1·57	2·17
(11)	58·3	36·3	—	33	—	65	1·33	2·14
SHB structures								
(12)	65·0	31·3	31	—	52	58	1·60	2·12
(13)	64·1	32·6	31	—	52	62	1·67	2·30
(14)	65·6	31·2	33	—	53	62	1·83	2·40
(15)	63·0	33·4	24	—	46	53	1·67	2·24
(16)	68·1	29·0	35	—	60	71	2·00	2·72
γ structures								
(17)	64·5	31·6	—	54	—	67	1·67	2·21
(18)	52·3	41·3	—	50	—	60	1·00	1·75
(19)	63·7	32·6	—	46	—	60	1·75	2·44
(20)	69·2	27·9	—	58	—	67	2·00	2·44
(21)	69·5	27·5	—	51	—	66	2·00	2·69
(22)	72·8	24·8	—	63	—	72	2·29	2·70
(23)	72·6	24·7	—	62	—	71	2·33	3·19
β structures								
(24)	66·2	30·4	—	61	—	69	1·75	2·31
(25)	67·6	29·2	—	64	—	74	1·89	2·49

potentials that have been derived mainly from equilibrium or near-equilibrium crystal properties, so that it is remarkable that significant trends pertaining to large-amplitude motions can be derived. Besides, the values quoted for the barriers are simply the difference between zero rotation and the highest point in the PPE curve in a completely rigid environment. For these reasons, with such a model one must be satisfied with an indication of the number and location of the minima in the curve, and with a rough estimate of a low (< 50 kJ mol^{-1}), medium ($50 < E_{\rm att} < 500$ kJ mol^{-1}) or high (>500 kJ mol^{-1}) barrier. The explicit introduction of terms representing polar forces could only alter details of the potential-energy profile, which, in the small interatomic separation regime where the barriers arise, is overwhelmingly dominated by repulsive terms. The main obstacle to quantitative calculations is perhaps the crudeness of the rigid-lattice assumption; in fact, the qualitative to semiquantitative agreement obtained with this model (Gavezzotti & Simonetta, 1982) became almost quantitative in a calculation for naphthalene, allowing cooperation of surrounding molecules by small motions of the first nearest-neighbours (Gavezzotti & Bellezza, 1987).

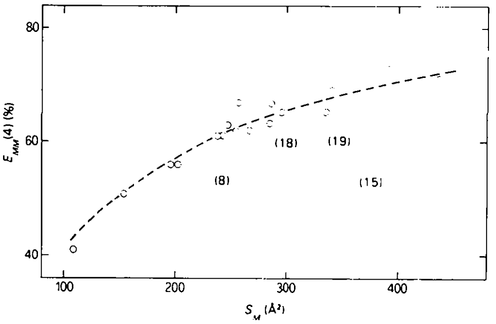

Fig. 4. Percentage packing-energy contribution of the first four neighbours, $E_{MM}(4)$, *versus* molecular surface. Outliers are denoted by their compound numbers.

There is a close relationship between the molecular elongation ratio, or length-to-width ratio [as computed assuming R(C—C) = 1·40, R(C—H) = 1·08 Å, all angles 120°, and a van der Waals radius for hydrogen of 1·17 Å; see Table 8] and the barrier height. An upper threshold of 1·30 for this ratio can be set for rotation to be possible.

A more interesting observation concerns the survival of the barrier down to a cutoff of 4 Å in the lattice sums for the potential energy. This implies that the disturbance of the lattice by the molecular rotation is highly localized. Only a few short intermolecular contacts do in fact contribute in a significant way to the barrier, while the rest of the intermolecular environment is but a spectator.

All the above arguments confirm the view, already expressed (Bianchi, Gavezzotti & Simonetta, 1986) that

Table 7. *Geometrical indices that describe the packing of planar molecules (see text)*

	SA	R_N	R_{IP}^*	α
HB structures				
(1)	6·92	5·08	—	—
(2)	5·973	5·08	—	—
(3)	6·00	5·15	—	—
(4)	6·166	5·14	—	—
(5)	5·260	5·26	—	—
(6)	6·50	5·08	—	—
(7)	6·196	5·21	—	—
(8)	5·785	5·79	—	—
(9)	6·154	5·17	—	—
(10*a*)	—	7·02	—	—
(10*b*)	6·590	5·17	—	—
(11)	5·610	4·93	—	—
SHB structures				
(12)	8·47	3·96	3·53	27
(13)	10·263	3·87	3·46	27
(14)	9·890	4·14	3·37	36
(15)	8·167	4·97	—	—
(16)	10·630	3·73	3·41	24
γ structures				
(17)	4·534	4·54	3·49	40
(18)	4·800	4·80	3·16	49
(19)	5·230	5·23	3·42	49
(20)	4·702	4·70	3·46	43
(21)	5·220	5·22	3·45	49
(22)	4·700	4·70	3·45	49
(23)	5·110	5·11	3·48	47
β structures				
(24)	4·026	4·03	4·03	0
(25)	7·656	3·90	3·83†	0

* No close parallel molecular planes in HB structures.
† The unit cell contains two layers of molecules.

Table 8. *Elongation index and calculated and experimental barriers to in-plane molecular rotation* (kJ mol^{-1})

The elongation index is defined as molecular width/molecular length, using R(C—C) = 1·40, R(C—H) = 1·08 Å, all angles 120°, and a van der Waals radius for H of 1·17 Å. Results by Boyd, Fyfe & Wright (1974) are for William's IV set of non-bonded potentials (Williams, 1967). True barriers are twice the values quoted in Boyd *et al.*

	Elongation index	Exptl barrier	Cutoff distance (Å) 10	7	5	4	Boyd *et al.*
(1)	1·10	16·7*	14·2	14·2	12·1	14·6	21·8
(2)	1·24	90·8†	161	162	161	158	156
(3)	1·57	—	Very high				
(12)	1·27	61·1*	246	246	246	246	228
(18)	1·00	—	25·5	24·7	28·5	26·4	—
(13)	1·27	—	500	500	499	500	—
(14)	1·12	—	125	125	124	120	—
(20)	1·00	25·1*	14·2	14·2	14·6	20·9	19·2
(23)	1·13	—	267	268	271	270	—

* Fyfe & Veregin (1984).
† McGuigan, Strange & Chezeau (1983).

the ease of rotation in the crystal depends merely on molecular shape, and not on crystalline properties. Thus, a flat molecule with an elongation ratio near to unity will rotate easily in any crystal structure (at least, within the context of the forces that are at stake in the present discussion). For example, it has been shown (Gavezzotti, 1987) that benzene solvate molecules rotate in a host crystal with a barrier which is quite similar to that for rotation in the pure benzene crystal.

Table 9. *Some packing indices for different crystal phases*

Distances in Å, energies in kJ mol^{-1}.

(*a*) Benzene

	Orthorhombic 138 K	Orthorhombic 218 K	Monoclinic* 2·5 GPa, 294 K
Space group	*Pbca*	*Pbca*	$P2_1/c$
Z	4	4	2
D_x (g cm^{-3})	1·092	1·053	1·287
SA	6·81	6·92	5·38
R_N	5·02	5·08	4·55
Packing energy	38·6	37·4	35·0†
E_{MM}(4) (%)	41·3	42·6	40·7
Rotation barrier	20·9	14·2	30·5

(*b*) Dibenzanthracene

	Orthorhombic	Monoclinic
Space group	*Pcab*	$P2_1$
Z	4	2
D_x (g cm^{-3})	1·237	1·297
SA	8·22	6·59
R_N	7·02	5·28
E_{MM}(2) (%)	18·8	33·1
E_{MM}(4) (%)	37·6	65·1
%C···C	63·5	63·8
%C···H	31·8	33·6

* Fourme, André & Renaud (1971).
† Short H···H repulsive contacts.

Finally, a comparison (Table 8) of activation-energy barriers computed with the present potential-energy parameters and with Williams' parameters shows a very close agreement between the two sets of values.

Polymorphism

Aromatic hydrocarbons show a great propensity to polymorphism. This is apparently an obstacle to any attempt at structural classification, and, indeed, the possibility of different crystal structures for the same

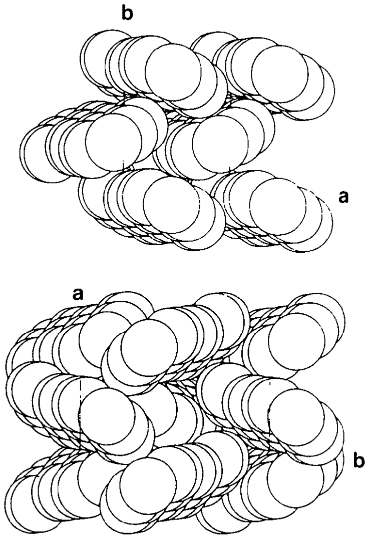

Fig. 5. Monoclinic (top) and orthorhombic (bottom) dibenzanthracene; packing diagrams with van der Waals spheres (projection along c; H atoms omitted for clarity).

compound raises the general question of whether crystal structure control and engineering are realistic concepts at all. In practice the problem is much less severe.

Anthracene has a triclinic polymorph (Ramdas *et al.*, 1980) which is obtained from the monoclinic structure by a shearing motion that does not alter the HB packing. Tetracene undergoes pressure- and temperature-induced phase transitions (Jankowiak, Bässler & Kutoglu, 1985, and references therein) which involve molecular rotations of 6, 9 or 15°, again quite insufficient to change the basic packing pattern. This type of polymorphism is caused by rather flat free-energy surfaces, owing to weak packing forces (which also cause poor crystal quality and twinning problems).

A more drastic ambiguity concerns the orthorhombic–monoclinic dilemma which affects benzene and dibenzanthracene. Table 9 shows the relevant packing indices. For benzene, the two structures are quite similar, both being of the s.c.s. type; R_N and $E_{MM}(4)$ are nearly the same (but note that, for the high-pressure form, the non-bonded energy potentials may be inadequate, as revealed for instance by the fact that the H···H interaction energy is repulsive). The barriers to molecular rotation increase, as expected, as the temperature decreases and the pressure increases. Dibenzanthracene displays a transition from a c.c.s. monoclinic structure to an s.c.s. orthorhombic one, the latter being quite similar to the crystal structures of benzene and 2,6-dimethylnaphthalene (Kitaigorodski, 1961). Even in this case, Fig. 5 shows convincing evidence that the HB motif is present in both forms; it is a pleasure to recognize that we are only restating what was so neatly expressed by J. D. Bernal and D. Crowfoot a long time ago (1935). It appears therefore that the overall packing patterns, on which the conceptual basis of crystal structure classification and of crystal engineering is built, do not change in the polymorphs of these hydrocarbon molecules.

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