

From Molecular to Crystal Structure; Polynuclear Aromatic Hydrocarbons

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Crystal structures of fused-ring aromatic hydrocarbons may be predicted from molecular structures using a model where carbon and hydrogen atoms in a molecule are designated 'stack' and 'glide' promoting solely on the basis of their topological connectivity.

The wealth of crystallographic data now available for organic solids has stimulated the search for better general theories to describe their packing.¹ Towards such an attempt, we have analysed the crystal structures of a group of 32 polynuclear aromatic hydrocarbons. We show that: (i) these hydrocarbons may be classified into four packing types based on their shortest crystallographic axis; (ii) the tendency to adopt one of these types by a particular hydrocarbon depends on the relative contribution of carbon and hydrogen atoms to the molecular surface area; (iii) prediction of packing type for *any* pure polynuclear hydrocarbon is possible from its structural formula alone.

Adapting from earlier work,²⁻⁴ we have defined four basic packing types for aromatic compounds (Figure 1; Table 1). In the simplest herringbone structure [5.4 < short axis (s.a.) < 8.0 Å] the nearest neighbours are nonparallel. In the sandwich-herringbone packing (s.a. > 8.0 Å), the herringbone motif is made up of sandwich-like diads. In the third type, called γ (4.6 < s.a. < 5.4 Å), the main interactions are between parallel translated molecules. The fourth type, called β (s.a. < 4.2 Å) is characterised by 'graphitic' planes. All our 32 structures are monoclinic or orthorhombic and the shortest crystallographic axis is always a screw-axis direction. *This axis is, therefore, a key parameter in separating packing types and defines the crystal structure.* In contrast, the other cell parameters are merely a function of individual molecular geometries.

There is also an energetic basis for our structural classification. In sandwich crystals (which form molecular pairs), the interaction energy to one molecule (the sandwich partner) is unique. However, for herringbone, β -, and γ -structures, there are always pairs of molecules with the same cohesion energy to the reference molecule. Further, for β - and γ -structures, but not herringbone, stabilisation is mainly by the two nearest short-axis translated neighbours.⁵

The crucial link between molecular and crystal structure is the relative ability of a molecule to employ C · · · C and C · · · H interactions. While C · · · C interactions are best optimised between parallel molecules stacked at van der Waals separation, C · · · H interactions are most effective between inclined molecules perhaps because of their supposed Coulombic nature. Therefore C · · · C interactions are

important in β - and γ -structures while C · · · H interactions are important in herringbone packing. By this token, both C · · · C and C · · · H interactions are important for sandwich structures.

Since there is a good correlation between molecular surface area and packing energy, we have computed average values of S_i which are the normal van der Waals surfaces⁶ for carbon and hydrogen atoms of the types A, B₁, B₂, C, D, and E as shown in structure (X). The free surfaces of some of the outer atoms in a molecule (H_D, H_E) may not be completely available for intermolecular contacts. Typical values for S_i (in Å²) are as follows: carbon A (10.8), B₁ (5.8), B₂ (5.8), C (11.2), D (10.4), E (9.2); hydrogen A (6.8), C (6.8), D (5.6), E (5.1).

The number and positioning of C and H atoms in a molecule are the key features in defining structure type. We consider part of the molecular free surface as stack (or layer)-promoting and the rest as glide-promoting. Atoms that help stacking include core atoms (B₂) and part (50%) of the rim carbon atoms (A, B₁, C, D, E). Atoms that help glide packing include the other part (50%) of the rim carbon atoms and all hydrogen atoms. Summing the glide and stack contributions over the molecule gives the overall glide and stack promoting areas S_g and S_{st} . These empirical factors have been obtained after a careful analysis of the crystal structures of compounds (1)–(32).

Figure 2 shows the glide-to-stack ratio S_g/S_{st} as a function of the total molecular surface S_M ($S_M = S_g + S_{st}$) and is a predictive mapping from molecular to crystal structure. It gives a clear-cut division between herringbone structures with the highest S_g/S_{st} values and the rest. The linear fused compounds (1), (2), (3), (33), (34), and (36) and the linear polyphenyls (1), (5), (35), and (12) form two subgroups. Other compounds such as (4), (8), and (10) deviate from these curves inasmuch as their shapes deviate from pseudolinearity. The γ -molecules (18), (21), (22), (24), (25), and (26) with nearly the same shape lie on a smooth curve. Moving down this structural homologous series there is an increase in the 'core' carbon

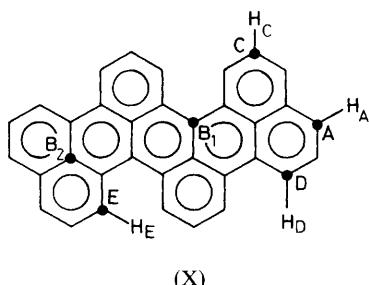
Table 1. Compounds in this study.

Herringbone: (1) Benzene; (2) Naphthalene; (3) Anthracene; (4) Phenanthrene; (5) Biphenyl; (6) Triphenylene; (7) Benz[a]anthracene; (8) Chrysene; (9) Benzo[c]phenanthrene; (10) Picene; (11) Dibenz[a,h]anthracene; (12) *p,p*-Quaterphenyl; (33) Tetracene; (34) Pentacene; (35) *p*-Terphenyl; (36) Hexacene.

Sandwich herringbone: (13) Pyrene; (14) Perylene; (15) Benzo[ghi]perylene; (16) Dinaphtho[a,h]anthracene; (17) Quaterrylene (benzo[1,2,3-*cd*; 4,5,6-*c'd'*]diperylene).

γ -Structures: (18) Benzo[a]pyrene; (19) 18-Annulene; (20) Dibenz[b,k]perylene; (21) Coronene; (22) Dibenz[bc,ef]coronene; (23) Dibenz[a,j]coronene; (24) Ovalene; (25) Hexabenz[bc,ef,hi,kl,no,qr]coronene; (26) Kekulene.

β -Structures: (27) Tribenzo[*a,i,l*]pyrene; (28) Violanthrene; (29) Tetrabenzo[*a,cd,j,lm*]perylene; (30) Diphenanthro[*abcd,jklm*]perylene; (31) Antra[*cdefg*]benzo[*jk*]naphtho[*opqr*]pentacene; (32) Tetrabenzo[*de,hi,op,st*]pentacene.



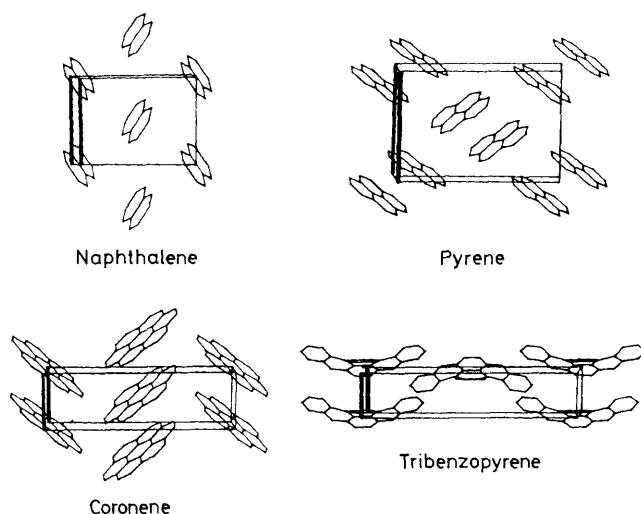


Figure 1. The four basic aromatic crystal packings. The short axes are indicated in each case.

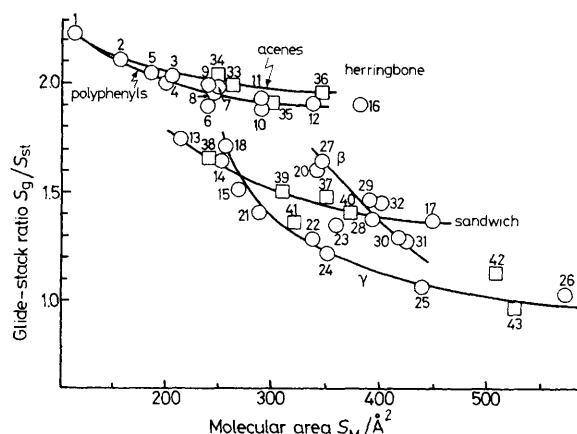
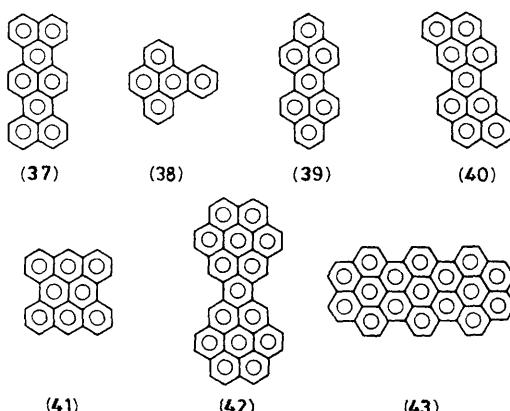


Figure 2. A mapping from molecular to crystal structure for polynuclear aromatic hydrocarbons. Glide-stack area ratios are plotted against available molecular surface areas. Compounds (1)–(32) are represented as open circles and compounds (33)–(43) as open squares.

content and therefore stack stabilisation. Compounds (20) and (23) which deviate the most from the disc-like shape are situated the farthest from the γ -curve. The β -structures (27)–(32) are bunched in a well-defined region. All of these molecules are characterised by E-type carbon atoms which lead to molecular nonplanarity, which in turn seems to be essential for β -structure adoption; planar molecules having comparable C:H stoichiometric ratios prefer the γ -structure. We note that β -stacks are held loosely by H \cdots H interactions rather than by C \cdots H interactions. The sandwich structure straddles the gap between herringbone and γ -modes. Molecules (13), (14), (15), and (17) have both internal carbons and external hydrogens and their shapes are cylinder- rather than disc-like. These geometrical features are manifested as S_g/S_{st} values intermediate between herringbone and γ -compounds.

Figure 2 shows that, as S_M increases, all the curves slope downwards. Increasing molecular size, therefore, means increasing the number of core atoms faster than that of the rim



Scheme 1. Some related compounds with unknown crystal structures.

atoms, more so for disc-like molecules (β and γ). Cylinder-like molecules, however, stay way up in S_g/S_{st} on increasing S_M whether they have herringbone or sandwich structures. Discrimination between γ - and sandwich structures therefore becomes easier at higher molecular weights. Separation of the curves is, of course, needed for an unambiguous structure prediction; conversely when several curves intersect, polymorphism or pressure-assisted phase transformations may become possible.^{7,8}

We now use the predictive ability of Figure 2 for compounds (37)–(43) (Scheme 1) whose crystal structures are unknown but are related to the ones discussed already. Comparing the sandwich compounds perylene (14) and quaterrylene (17), we predict that the intermediate (37) will also adopt the sandwich packing in the space group $P2_1/a$ with cell parameters 11.2, 10.5, 14.8 Å, $\beta = 100^\circ$. 1,2-Benzopyrene (38), which is located close to the sandwich curve, almost matches (13) and is therefore predicted to have the same structure. Dibenzopyrene (39) is part of the series (14), (37), and (17) and also lies on the sandwich curve. Dipyrrene (40) is a dibenzo-derivative of (39) and its structure may be either sandwich or γ , more likely the former.

Hydrocarbons (41)–(43) form conducting cation radical salts.⁹ No crystallographic study is available and structural prediction is desirable. Compound (42) is a tetrabenzquaterrylene but its shape is more disc-like than quaterrylene. Its S_g/S_{st} is, therefore, intermediate between sandwich and γ . The introduction of two more rings to give the even more disc-like (43) predictably shifts S_g/S_{st} towards the γ -mode. However, (41) is more elliptically shaped and closely related to ovalene (24); its position lies exactly on the γ -curve.

In this communication we have outlined a new approach towards rationalising and predicting crystal structures based on molecular size, shape, stoichiometry, and topology. The approach is different from previous energy-based methods,^{3,4} in that it dispenses with the accurate calculation of potentials but is equally relevant to the problem of crystal packing. We believe that our approach has a far broader scope since the structural features of each molecule have been consolidated in a sort of overall shape descriptor. Accordingly, it may be expected that whenever similar shapes are found in organic compounds, the effects on crystal structure should be the same, even if the compounds are not pure aromatic hydrocarbons. For example, any elongated molecule with hydrogens on the rim and $S_M < 250$ Å² is expected to adopt the herringbone packing; this is indeed the case for dibenzofuran,

carbazole, and fluorene. Conversely, in many heterocyclic derivatives of compounds (1)–(32), the reduced number of rim-hydrogens causes the β -packing to be adopted.^{10,11}

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