The Role of Cl···Cl and C–H···O Interactions in the Crystal Engineering of 4-Å Short-Axis Structures

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Structural chemists and crystallographers have observed that certain intermolecular interactions in organic molecular solids are associated with only certain geometrical motifs. The systematic and predictive use of such motifs in designing and exploiting crystal structures has come to be known as crystal engineering.[1] This concept has been particularly useful in the field of organic solid-state chemistry where reactions are subject to topochemical control, in other words where the course and outcome of a reaction is decisively established by the mutual disposition of reactant molecules in the crystal.[2] The importance of topochemistry has meant a shift in emphasis from crystallographic details to the larger question of what factors and forces direct and determine the structures of organic solids. Such forces are weak; so while organic solid-state chemistry hinges largely on the predictive aspects of crystal engineering, the latter becomes, in turn, an attempt to understand the nature of weak intermolecular interactions.

The term "crystal engineering" was coined by Gerhard Schmidt and led directly from his pioneering work on the solid-state photodimerisation of *trans*-cinnamic acids. Using the crystallographic short axis as the differentiating criterion, Schmidt divided these acids into three structural types α, β, and γ, with the ranges for this axis being >5.1 Å for α, 3.9 ± 0.2 Å for β, and 4.9 ± 0.2 Å for γ. Chemically, these three groups show distinct solid-state reactivity. While the α and β acids form inversion and mirror symmetry dimers on irradiation, the γ-acids are photostable.[2] A particularly good example of crystal engineering is furnished by chlorosubstitution. It was realized that chloro groups pendant on an aromatic nucleus tend to "steer" the crystal structure to the β-mode, characterised by a short axis of ca. 4 Å. The β-structure is an ubiquitous motif (Figure 1). About a hundred such structures for planar chloroaromatics are reported in the 1984 version of the Cambridge Structural Database, and the structure is adopted by about 40 other like compounds whose cell dimensions (unpublished) were recorded by Schmidt and his co-workers Green and Leser.[3] While the reasons for this "chloro effect" were not very clear at that time, considerable progress was

made in devising novel solid-state reactions based on this principle.[4]

Simultaneously, and for the most part independently, there has been much discussion on the existence and nature of short (3.2 to 3.6 Å) Cl···Cl nonbonded contacts in molecular crystals.[5] It is clear that such contacts cannot be modelled satisfactorily using isotropic atom potentials for were such potentials to be used, these intermolecular distances would represent abnormally and unacceptably repulsive interactions. Explanations for such directional effects vary; it has been supposed that the Cl···Cl interaction may be likened to a weak bond (ca. 3% of a covalent bond)[6] while alternatively, the van der Waals radius of Cl has been assumed anisotropic.[7] The approach of adjacent Cl atoms in the crystal has also been likened to an electrophile–nucleophile interaction.[8]

While charting out new reactions is, in general, an obvious application of successful crystal engineering, the study of β-structures in particular is of great relevance in the design of low-dimensional organic metals and superconductors, of which many adopt this mode. Although the synthetic and theoretical efforts in this area have been varied, the structural uncertainties in persuading organic molecules to crystallize in preordained ways seems often to have rendered the search for new organic metals a frustrating task. This gap in our present understanding of these interesting compounds could well be bridged with the methods of crystal engineering as developed by organic solid state chemists.

In the course of our own studies on solid state photochemistry, we observed that several planar oxygenated aromatics such as ethers, coumarins, and quinones also adopt the β-structure and further, that these structures are characterized by the presence of C–H···O hydrogen bonds.[9] Since crystal engineering is very important in any effort in designing new materials either with novel solid state reactivity or with specified

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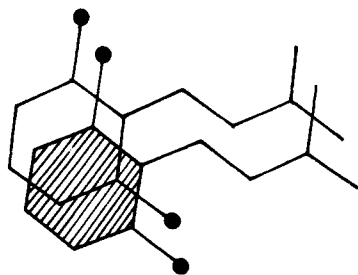(6) Williams, D. E.; Hsu L.-Y. *Acta Crystallogr. Sect. A: Found. Crystallogr.* 1985, A41, 296.

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Figure 1. The β-structure as typified by a schematic view of two stack-related molecules of 2,6-dichlorocinnamic acid.

physical properties (optical, electronic), this Account is concerned with more clearly defining the role of the chloro and oxygenated groups in crystal engineering. We show that the adoption of the β-packing mode by a large number of planar aromatics may be understood if a weakly attractive and directional Cl···Cl or C–H···O interaction is assumed.

The Prevalence of Short Cl• • •Cl Contacts in 4-Å β-Structures of Chloro Compounds

While Schmidt recognized the β-mode as a sharply defined structural type, we have extended his short-axis upper limit for such structures to 4.2 Å since there is a pronounced paucity of planar compounds with axes in the range of 4.2–4.7 Å.[10] This discontinuous distribution of axial values indicates a sharp break in the mode of crystal packing in going from the β to the non-β types and simple geometry and energy calculations convey this essential difference in a semiquantitative fashion. In the β-structure, major stabilization for a molecule is through its interaction with its two 4-Å translational neighbors while other neighbors interact only minimally. In the non-β-structures, however, molecules are stabilized more uniformly by a larger number of near neighbors. In effect, the "molecular coordination" in a β-structure is 2 while that in the non-β-structures between 6 and 10.[11,12]

Short intermolecular Cl···Cl contacts occur very frequently in β-structures of chloroaromatics. Their effects are exemplified by the archetypal compounds hexachlorobenzene, (I) and triclinic 1,4-dichlorobenzene (II).
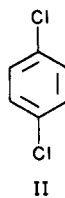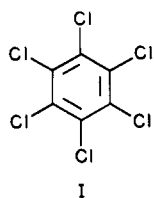

I   II

Figure 2 shows that, for II, in-plane Cl···Cl contacts of 3.38 Å are responsible for the formation of molecular sheets which are then stacked at the van der Waals separation to optimize C···C contacts. In I, Cl···Cl contacts of 3.72 Å result in the molecules being arranged along linear ribbons which are stacked at the short-axis separation (Figure 3). Successive stacks are related by 2-fold screw axes and are held together by additional Cl···Cl contacts of 3.51 Å. The importance of *inter*stack
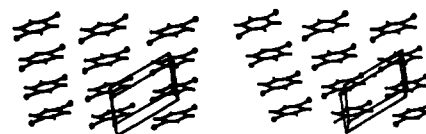
Figure 2. Stereoview of the crystal structure of the triclinic modification of 1,4-dichlorobenzene to show the formation of a molecular sheet. Cl atoms are indicated by heavy circles. The complete structure is generated by a 4-Å stacking of such sheets. Note that while Cl···Cl and C–H···Cl contacts are *intra*sheet (or *inter*stack), the C···C contacts are *inter*sheet (or *intra*stack).
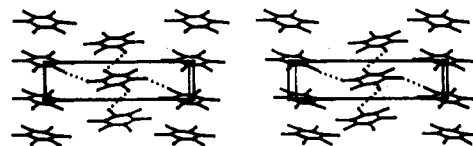
Figure 3. Stereoview of the linear-ribbon-based crystal structure of hexachlorobenzene, I. While Cl···Cl contacts (- - - -) are again *inter*stack, they can be either ribbon-forming or ribbon-linking. The C···C contacts (not shown) are *intra*stack as in all β-structures.

Cl···Cl and *intra*stack C···C interactions in stabilizing these simple β-structures has been discussed by us already.[12] These directional preferences for Cl···Cl and C···C interactions have been further confirmed in the cocrystallization of compounds such as 6-chloro-3,4-(methylenedioxy)cinnamic acid and 2,4-dichlorocinnamic acid as a stoichiometric β-structure molecular complex which is disordered along the 4-Å-stack direction.[13] The fact that the seemingly closely related 3,4-dichlorocinnamic acid gives solid solutions with the methylenedioxy compound only emphasizes that the intermolecular forces in such crystals must be rather specific.[14]

Attractive Nature of Cl• • •Cl Contacts

There is much evidence that Cl atoms in many molecular solids do not function as groups of a certain volume (close packing) but rather through specific anisotropic, electronic effects. In solid Cl_2 itself, the difference between the shortest Cl···Cl nonbonded contact (3.27 Å) and the next shortest contact (3.697 Å) is appreciable. These effects are enhanced in crystalline Br_2 and I_2. In the latter, even the I–I stretch appears in the IR indicating weak intermolecular bonding.[6] That Cl···Cl contacts must be attractive has also been inferred from a study of crystalline II where minimum thermal expansion coefficients were obtained in a direction that corresponds neither to the long molecular axis nor to the shortest intermolecular contacts but rather to a direction in which the Cl···Cl contacts predominate.[15]

Further indication of the attractive nature of Cl···Cl interactions is provided by the failure of the chloromethyl exchange rule in many polychloroaromatics. Since these two substituent groups have nearly the same volume (Cl, 20 Å³; Me, 24 Å³) a replacement of one by the other is not expected to change the crystal structure if the packing is strictly governed by the rules enunciated by Kitaigorodskii.[16] Although valid for a

(10) For instance, out of the approximately 600 chloro compounds we considered, the tally of structures having short axes less than 4.2 Å, between 4.2 and 4.7 Å, and greater than 4.7 Å are around 100, 10, and 490 respectively.

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large number of nonpolar, irregularly shaped aliphatic molecules, the Cl–Me rule breaks down for chloroaromatics.[17] Hexachloro and hexamethylbenzene, for instance, have completely different crystal structures. Further, one notes that for a large number of such compounds, substitution of a Cl group by the electronically similar though geometrically dissimilar Br group (volumes: Cl 20 Å^3; Br 26 Å^3) does not alter the crystal structure. Typical examples are 1,4-dibromobenzene, hexabromobenzene, terephthaloyl bromide, 2-bromo-1,4-naphthoquinone, and 2-bromobenzoic acid.
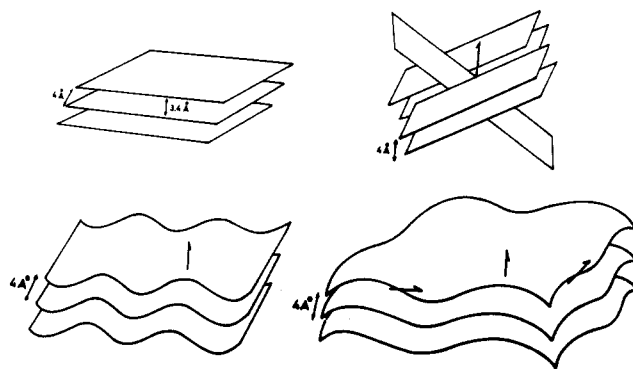
A very suggestive manifestation of such effects is shown by the pair of compounds, 2,2′-dichloro- and 2,2′-dimethylbenzidine. The molecular conformations of these two in the solid state are quite different as are the crystal structures. While the angle between the two rings in the dimethyl compound is 86°, the corresponding angle for the dichloro derivative is only 36° with the two intramolecular Cl atoms being only 3.36 Å apart. Such anomalies and the unusually short intermolecular Cl···Cl distances in many chloroaromatic β-structures show up the limitations inherent in a purely geometrical approach and must be regarded as indicators for specific Cl···Cl intermolecular interactions that cannot be incorporated into the geometrical model.

Packing Motifs for Planar Chloroaromatic Crystal Structures

Although close to 150 chloro compounds are known to have the β-structure, published data exist for only about 100 of these. Structural data for these compounds are obtained from the Cambridge Database or by manual inspection. Almost all of them are aromatic and most, barring a few biphenyls, are planar. Inspection of these β-compounds reveals a wide range of benzenoid, heterocyclic, and fused-ring compounds, side chains of different lengths, several types of functional groups (–OH, –CN, –OMe, –CO$_2$H, –NO$_2$, quinones), and varying abilities for other structure-stabilizing interactions (dipole–dipole, hydrogen bonding).

In spite of this chemical variety, all these hundred-odd compounds share a common crystallographic feature, a 4-Å short axis. Remarkably, most of these structures have in-plane Cl···Cl and/or C–H···Cl contacts which may be considered, to some extent, as "short". The range of values for the shortest Cl···Cl contacts in this group of structures is from 3.27 to around 4.10 Å. Significantly, in those structures where the shortest Cl···Cl contacts are at the higher end of the range, additional stabilization seems to be achieved through C–H···Cl "hydrogen bonds" in the range of 2.8 to 3.3 Å.

A study of the packing arrangements of these β-compounds shows that the manner in which Cl···Cl, C–H···Cl, and C···C interactions are manifested in structures like I and II is fairly common and that these steering interactions are applicable in almost all the cases. Conceptually, the simplest manner of optimizing Cl···Cl interactions is by forming a planar molecular sheet with such sheets being stacked along the 4-Å axis to generate

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Figure 4. Two-dimensional motifs formed by the optimisation of Cl···Cl interactions in β-structures of planar chloro aromatics compounds: planar sheet, linear ribbon, singly corrugated sheet, doubly corrugated sheet.

the crystal structure (Figure 4). Both triclinic and monoclinic β-structures show this planar motif, although a monoclinic β-structure may display other motifs too. Twelve such triclinic structures were found (2-chlorothioxanthone, 6,6′-dichloroindigo, 6-chloro-3,4-(methylenedioxy)cinnamic acid, etc.). A planar sheet is obtained in a monoclinic space group such as $P2_1/c$ if the short axis is nonunique and the molecular plane is parallel to or almost parallel to the unique axis. This situation is a common one (15 compounds) with typical examples being 3-chlorobenzoic acid, 2,6-dichloro-4-nitroaniline, and 4-chlorobenzonitrile.

If the 4-Å axis coincides with the monoclinic direction, the linear ribbon and singly corrugated-sheet motifs are the result. Figure 4 shows that the position of the screw axis relative to the molecular plane, determines largely which of these two motifs is adopted. In either case, the motif is stacked in the 4-Å direction to complete the structure. These two types account for almost 45 β-structures (hexachlorobenzene, 4-chlorocinnamic acid, 2,5-dichloroaniline, etc.). A doubly corrugated sheet (Figure 4) may be obtained if mutually perpendicular screw axes are present and if the plane of the molecule is inclined to all the crystal axes. This is illustrated by 15 orthorhombic structures. Stacking of doubly corrugated sheets in these structures is similar to the planar-sheet stacking described earlier (1,3,5-trichlorobenzene, N-(2,4-dichlorobenzylidene)aniline).

Crystal Engineering of Chloroaromatic Compounds

Since it is possible to correlate a large number of 4 Å chloroaromatic structures on the basis of directional in-plane Cl···Cl and C–H···Cl interactions, one may reverse the argument and identify features which favor the adoption of the β-structure for such compounds. The following criteria, have been formulated after careful consideration of a large amount of structural data for several β and non-β crystals.

(a) Molecules Must Be Planar. Although lack of molecular planarity need not necessarily prevent stabilization of sheets or ribbons, nonplanar molecules cannot be stacked very effectively at 4-Å separation and hardly any chloro β compound contains groups which would prevent molecular planarity. Even for the nonplanar biphenyls, the dihedral angles between the rings (30–40°) are generally smaller than those in the crystal structures of related non-chloro biphenyls (around 90°). These smaller angles are observed in spite of ortho

substituents and perhaps indicate a driving force towards a more planar conformation and through it to a Cl···Cl stabilized planar-sheet β-structure.

(b) The Number of Cl Atoms Must Be as Large as Possible. Other factors being the same, more Cl substituents will result in more Cl···Cl interactions and a greater likelihood of the β-structure. Thus, while chlorobenzene has a non-β-structure and 1,4-dichlorobenzene is trimorphic with one non-β- and two β-forms, only the β-structure is obtained for 1,3,5-trichloro- and other higher polychlorobenzenes. Again, while 4-chloroaniline does not have the β-structure, it is found for 2,5-dichloro-, 2,4,6-trichloro-, and 2,3,4,5,6-pentachloroaniline.

(c) Stronger Intermolecular Interactions Must Not Be Present. Since Cl···Cl interactions are relatively weak, they can steer crystal structures effectively only in the absence of more dominating forces. However, chloro-substituted acids and phenols are important exceptions. In, for instance, 4-chlorocinnamic acid and the three monochlorobenzoic acids, hydrogen-bonded dimer formation is the most notable feature in crystal stabilization, but since these dimers are themselves nearly planar, they may crystallize in sheets or ribbons. Alternatively, 2,3-, 2,4-, and 3,4-dichlorophenols crystallize as hydrogen-bonded helices with a 4-Å pitch and having a hydrophilic "core" and a hydrophobic "exterior". These helices are themselves linked by Cl···Cl contacts so that, in effect, these very weak interactions are possible within the framework of a distinctive and strong hydrogen-bonding pattern. Incidentally these three are among the four chloro β-structures with crystal symmetries higher than orthorhombic and the reasons for the adoption of these unusual space groups has been discussed previously.[11]

Stabilization of dipole–dipole interactions leads to a very interesting variant of the β-structure and is illustrated by compounds such as 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin, III, and 1,2,3-trichlorobenzene which
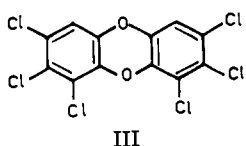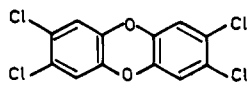
III   IV

is probably the only simple polychlorobenzene not to adopt the β-structure. Both the 1,3,5- and 1,2,3-isomers adopt structures based on a doubly corrugated sheet. However, while the former has a 4-Å axis, the unusual feature in the crystal structure of the latter is that adjacent molecules which are stacked at van der Waals separation are related not by translation but by inversion. Both translation- and inversion-related sheets probably afford the same extent of C···C stabilization but the inversion motif is distinctly preferred here since the not-inconsiderable molecular dipoles would then be antiparallel. We note that the dioxin, III, which has a dipole moment, adopts a very similar structure where Cl···Cl stabilized sheets are inversion related. In contrast, 2,3,7,8-tetrachlorodibenzo-p-dioxin, IV, with no dipole moment adopts the β-structure.[18]

Another chloroaromatic-sheet-based structure where 4-Å stack translation is not possible because of the

dipole–dipole repulsion which would then result is 1,2-dicyano-3,4,5,6-tetrachlorobenzene. In fact, hardly any cyanochlorobenzene adopts the β-structure unless the number of Cl atoms is large and/or that of the CN groups small (2,4,6-trichlorobenzonitrile, 4-chlorobenzonitrile). In most other cyanochlorobenzenes the dominant interactions are –C≡N···Cl rather than the weaker Cl···Cl ones.

C–H • • •O Interactions and β-Structures

Although short C–H···O contacts have been reported regularly in the crystallographic literature,[19] it is only recently that their importance has been appreciated and their terminology as "hydrogen bonds" received without scepticism. In an comprehensive study, Taylor and Kennard have concluded that the frequency with which they occur suggests that they play a significant role in determining crystal packings.[20] Here we attempt to evaluate this role for a few 4-Å structures of oxygenated aromatics drawing upon the analogy of the chloro compounds already described.

C–H···O contacts are characterized by either C···O (D) or H···O (d) distances and for significant bonds 2.70 Å < D < 3.50 Å. Two categories of C–H···O bonds, shown below as A and B, may be considered. For carbonyl

A   B
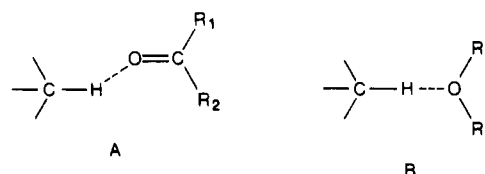
acceptors such as A, C–H···O contacts tend to lie in the planes defined by the oxygen sp^2 lone pairs, that is, the mean plane of O, C, R_1, and R_2. Within this plane, there is a marked preference for H···O=C angles to be close to 120°, so that the approximately linear C–H···O bonds are directed towards the sp^2 lobes.[20] This trend has also been observed by Murray–Rust and Glusker for O···H–X (X = N, O) hydrogen bonds involving carbonyl oxygen.[21] For ethereal acceptors such as B, however, C–H···O contacts tend to lie in the plane of the oxygen lone pairs. This plane bisects angle R_1OR_2. Further, several bonds have been observed to lie along the line obtained by the intersection of the R_1OR_2 plane and the bisecting perpendicular plane.[21]

Since C–H···O bonds appear to be quite directional in character, the β-steering properties of the type described for the chloro substituent may be extended to them also. For many oxygenated substituents on aromatic rings, C–H···O bonds tend to be nearly parallel to the molecular planes.[22] It is therefore expected that these interactions may stabilize sheet and ribbon motifs and through them, a β-structure.

We have already reported that the presence of a methylenedioxy group in an aromatic tends to favour its crystallization in the β-form.[9] Accordingly, acid V adopts the β-structure which is sheet-based with acid molecules forming O–H···O hydrogen-bonded dimers (Figure 5). The sheet motif is formed because of additional stabilization of these dimers through C–H···O

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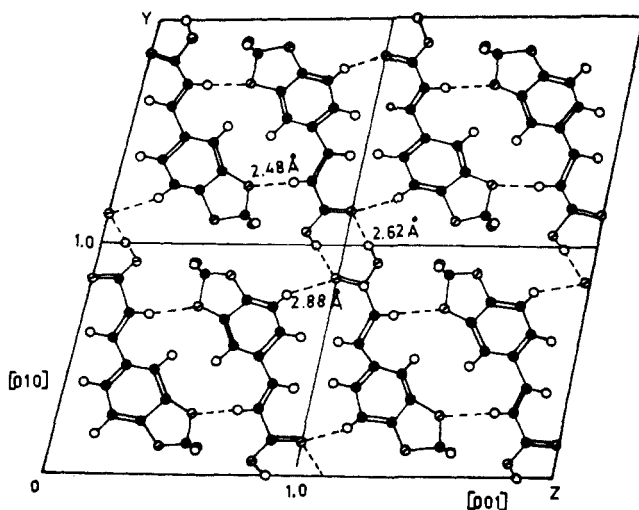
Figure 5. Molecular sheet formation in the crystal structure of 3,4-methylenedioxycinnamic acid, V. O–H⋯O and C–H⋯O bonds are indicated as dashed lines.

interactions involving one of the heterocyclic oxygens ($D = 3.47$, $d = 2.48$ Å) and, to some extent, one of the carboxyl oxygens ($D = 3.37$, $d = 2.88$ Å). Figure 5 shows that the sheet is compactly held by O–H⋯O and C–H⋯O hydrogen bonding. Although the two C–H⋯O contacts in acid V are quite long, one should note that their directional preferences are exactly as would be predicted.[20,21] The longer contact involves carbonyl oxygen and while a strong O–H⋯O bond is directed along one of the lobes of this atom, the other lobe is nearly along the C–H⋯O contact, giving the compelling feeling that angular preferences are maintained in the approach of atoms in a stable crystal structure even across appreciable intermolecular distances. In any event, these two C–H⋯O contacts, weak as they may be may be, are sufficient to steer this structure to a sheet-based β-form.

In V, sheets are stacked at van der Waals separation to generate the 4-Å short axis. In such stacking, the methylene hydrogens atoms which are located above and below the planes of the molecular sheets are involved in repulsive intermolecular contacts with the shortest nonbonded H⋯H distance being only 2.14 Å. The β-structure is destabilized by these out-of plane atoms, and consequently, if the number of such atoms increases, it need not even be adopted. Although the sheet structure is stabilized in acid VI by C–H⋯O contacts ($d = 2.33$, 2.63, 2.64 Å), the larger number of out-of-plane atoms (two –OMe groups) as compared to acid V (–O–CH$_2$–O–) prevents the sheets from being stacked with 4-Å translation.[9] In fact, so prohibitive must these intersheet repulsions be that the β-structure is possible neither for acid VI nor for a large number of simple nonhalogenated alkoxybenzoic and alkoxycinnamic acids. The notable exceptions are 4-methoxy and 4-ethoxybenzoic acids where very strong C–H⋯O contacts are observed. The space group and short axis considerations, which were used to categorize the chloro β-structures may also be applied to the oxygenated compounds. Thus, while acid V being triclinic ($P\bar{1}$, Z
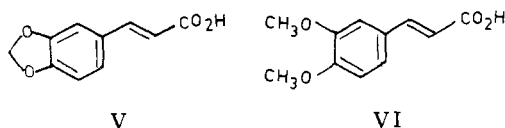
= 2) crystallizes as planar sheets, 4-methoxybenzoic acid ($P2_1/a$, c short, molecular plane not parallel to b) crystallizes in nearly corrugated sheets and 4-ethoxybenzoic acid ($C2/c$, b short) forms singly corrugated sheets.

Interestingly, the structure adopted by acid VI is a C–H⋯O stabilized sheet-based α-structure where, in order to minimize intersheet alkyl–alkyl repulsion, successive molecules in the stack are related not by translation but by inversion. This type of structure was identified by Schmidt and has been described earlier in this Account for compounds like 1,2,3-trichlorobenzene. Since C⋯C interactions are not as atom specific as C–H⋯O contacts, the inversion motif is compatible simultaneously with the need to optimize C⋯C contacts between sheets and to avoid a 4-Å axis.

C:H:O Ratios and the Likelihood of β-Structure Adoption

A survey of several aromatic compounds shows that, other factors being the same, the ratio of carbon to hydrogen atoms is of crucial importance in determining whether a β-structure is adopted or not. This is because of the differing relative importance of C⋯C and C⋯H interactions in these two situations. Generally, a higher C/H ratio favors the β-mode. So while benzene, naphthalene, anthracene, pyrene, coronene, VII, and ovalene, VII (C/H atomic ratios 1.00, 1.25, 1.40, 1.60, 2.00, 2.29) adopt non-β packings, the higher hydrocarbons IX–XI (C/H ratios 2.11, 2.11, 1.75) adopt the β-structure. Seemingly, the higher fused ring compounds such as IX–XI become increasingly graphitic
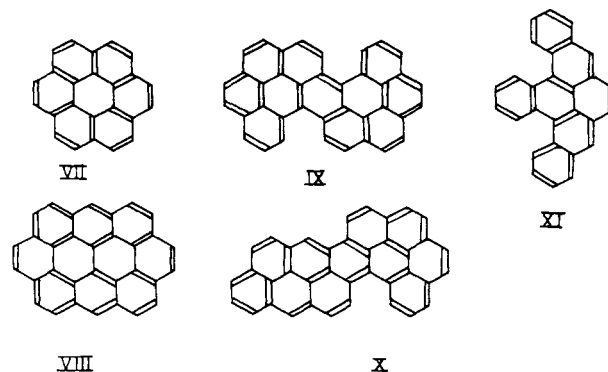

and tend toward this ultimate β-structure where crystal stabilization is exclusively through C⋯C interactions. Even so, the C/H ratios above need not discriminate between β and non-β-modes in a straightforward manner since, by this token, VII and VIII should be expected to adopt the β-structure. However, in these two compounds, all the H atoms are situated on the molecular rim and therefore more likely to be involved in non-β steering C⋯H contacts. In contrast, the degree of "exposure" of some of the H atoms in compounds IX, X, XI is somewhat reduced.[23] This "shielding" of H atoms raises the "effective" C/H ratio and promotes β-structure adoption.

When oxygen atoms are introduced as substituents or within the framework of polycyclic hydrocarbons, the tendency for β-structure adoption increases markedly. Thus many fused quinones crystallize in this structure even though the parent hydrocarbons do not. Typical examples are XII–XVII. In most of these cases there

(23) Gavezzotti, A. *J. Am. Chem. Soc.* **1985**, *107*, 962.

V   VI
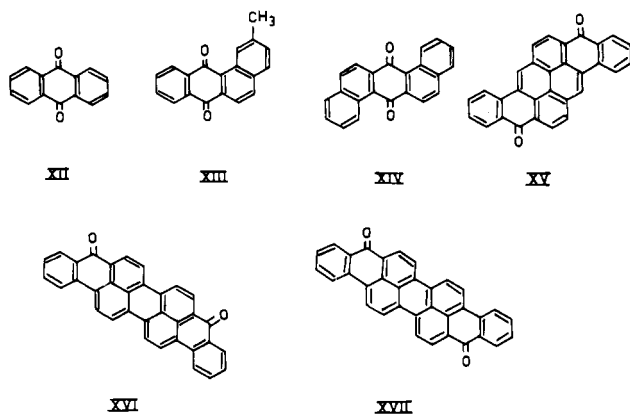
is good evidence for the existence of specific C–H···O bonds which may be of some significance energetically. For instance, the following intrasheet D and d distances have been reported: pyranthrone, XV, D = 3.23 Å; violanthrone, XVI, D = 3.31, 3.49, 3.66 Å, d = 2.40, 2.68, 2.70 Å; isoviolanthrone, XVII, D = 3.46, 3.57 Å. Such short contacts "tie-up" some of the peripheral H atoms effectively and thereby stabilize the formation of corrugated sheets which are 4-Å stacked to generate the entire structure. Corrugation occurs because there are always some "free" (C–H) atoms on the molecular rim. The space group details for compounds XII–XVII follows accordingly: XII, $P2_1/a$, b short; XIII, $Pca2_1$, b short; XIV, $P2_1$, b short; XV, $P2_1/n$, b short; XVI, $P2_1$, c short, molecular plane not parallel to b; XVII, $P2_1/c$, b short. Although the importance of C–H···O interactions in stabilizing quinone crystal structure has been discussed in depth[24] and while experimental evidence for such effects has appeared recently,[25] we believe that this work is the first attempt at establishing a link between these C–H···O interactions and a β-structure for quinones. The structures of XII–XVII show that the presence of the quinoid oxygen actively "steers" the crystal structure towards a 4-Å stacking mode since it is directly responsible for C–H···O based sheet formation.

Similarly, a heterocyclic atom also has a distinctly β-steering propensity since not only does it affect the C/H ratio but it also serves as an in-plane C–H···O bond acceptor. Consider the heterocycles XVIII and XIX. The molecular shape and size of XVIII, $C_{24}H_8O_4$, bears
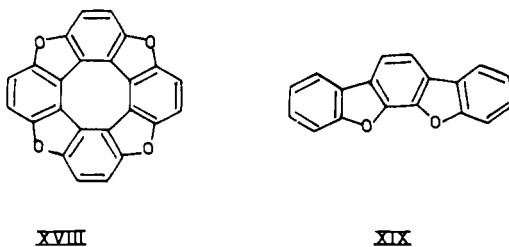
some similarity to VII, $C_{24}H_{12}$; again XVIII and XIX, $C_{18}H_{10}O_2$, are functionally similar. However, while XVIII has a β-structure, both XIX and VII do not. Sheet-stabilizing C–H···O interactions in XVIII account for this difference in behavior. The number of H atoms in XVIII is smaller than in VII and, of these, four are

involved in C–H···O contacts to heterocyclic oxygen (D = 3.47, d = 2.53 Å) and hence need not be stabilized through C···H interactions. The delicate role of molecular size is exemplified in a comparison of XVIII and XIX. XIX probably has too few oxygen atoms and too many hydrogen atoms to adopt a C–H···O sheet-based structure, especially since heterocyclic oxygen is a weak C–H···O bond acceptor.

Non-Oxygen Heterocycles

It is hardly surprising that the behavior of oxygen is paralleled by other hetero atoms such as nitrogen and sulphur. Thus 2-furyl-, 3-pyridyl-, and 2-thienylacrylic acid all adopt the β-structure even though β-*trans*-cinnamic acid is only metastable.[26] In particular, heterocyclic sulphur seems to have a notable tendency to form sheet- or ribbon-stabilizing S···S and S···Cl contacts. That such contacts are highly directional is well-known[27] but their importance in designing organic materials has not been fully appreciated or exploited by chemists in general. For instance, thione XX has a linear-ribbon 4-Å β-structure and is converted into the unusual topochemical dimer XXI on solid-state irradiation.[28]
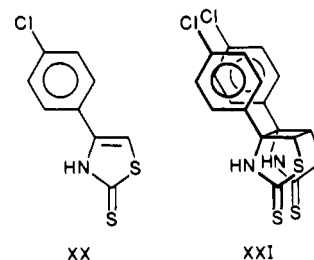
Mention has been made of the β-structures of organic metals. While the structure of TTF-TCNQ may be understood in terms of a 4-Å stacking of ribbons, the interplay between *intra-* and *inter*stack contacts is even more crucial in the superconductor (BEDT–TTF)$_2$I$_3$.[29] While much attention has been paid to the stacking behaviour of such molecules, we suggest as an alternative that the crystal engineering of segregated stack conductors may be profitably attempted through a consideration of *inter-* rather than *intra*stack contacts.[30]

Conclusions

The work summarized in this Account shows that there are important differences between β and non-β packings for planar aromatics and that *any* inplane interaction such as Cl···Cl and C–H···O may, in principle, be used to steer a crystal structure into the 4-Å modification. As we see it, the nub of the issue is that while the β-steering Cl···Cl and C–H···O contacts are *inter*stack, the C···C contacts are *intra*stack.

"Why 4-Å structures? Why not choose α-structures?" was the comment of the referee for this paper. Why not indeed? The β-mode is but one of four distinct structure types for planar aromatics,[31] and the reader

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will note that we have concentrated here on flat rigid molecules with only moderately polar substituents, artfully avoiding aliphatic groups with all their variations in conformation and stereochemistry. Clearly the canvas is vast and β-structures are, if anything, a convenient starting point. Crystal engineering is *not* an esoteric type of crystallography but rather addresses the problem of intermolecular interactions. Its most positive aspect is that it has successfully drawn the field of chemical physics into the ambit of organic solid-state chemistry. This conjunction is significant and has all the prospects for synergistic growth.