C–H ··· O Interactions and the Adoption of 4 Å Short-axis Crystal Structures by Oxygenated Aromatic Compounds

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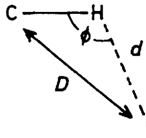
Oxygen atoms, pendant as substituents or occurring within the ring systems of planar aromatic molecules, have a pronounced tendency to direct crystallisation patterns of such compounds to the β-structure, characterised by a 4 Å short axis. They seem to perform this function by stabilising a critical number of hydrogen atoms, covalently bonded to carbon, through short and directionally specific intermolecular C–H ··· O hydrogen bonds. Consequently, the number of 'free' hydrogen atoms which contribute to crystal stabilisation through non-β steering C ··· H interactions is reduced. Both these factors result in the formation of C–H ··· O stabilised two-dimensional entities such as sheets and ribbons. Such entities may be stacked at 4 Å translational separation to generate the entire structure. These concepts are illustrated for some methylenedioxy and alkoxy aromatic systems, quinones, and heterocycles. However, both intra- and inter-sheet C–H ··· O interactions may sometimes be present and the unusual crystal structure of 7-acetoxycoumarin (**5**) shows how a significantly non-planar molecule may still adopt the β-structure if it is particularly well suited for the formation of C–H ··· O bonds. Yet 4-acetoxycinnamic acid (**6**), the crystal structure of which was determined in this work and which has almost the same C:H:O ratio as (**5**), adopts a non-β structure because the number of oxygen atoms available for C–H ··· O bond formation is greatly reduced. The crucial role of the number of such 'available' oxygen atoms and 'H-bonded' and 'free' (C–)H atoms *vis-à-vis* the carbon content is exemplified by the β-steering behaviour of oxygen in some large fused-ring quinones and heterocycles. These trends may also be extended to nitrogen and sulphur heterocycles.

We have seen in the previous paper[1] that a chloroaromatic β-crystal structure (*ca.* 4 Å short axis) may be visualised as a stacking of a two-dimensional entity which is itself stabilised by inter-stack contacts like Cl ··· Cl when these are particularly short. However, a consideration of 6-chloro-3,4-methylenedioxycinnamic acid showed that such significantly short Cl ··· Cl distances do not necessarily occur and that sheet stabilisation seems to arise in large measure from alternative directional and electrostatic interactions such as C–H ··· O and $(C)_2O$ ··· H–O. So, it was felt that intermolecular contacts involving oxygen could in themselves steer crystal structures of planar aromatic compounds to the β-form, and it will be shown here that the 4 Å short-axis structures of several alkoxy and hydroxy aromatic systems, coumarins, quinones, and oxygen heterocycles may all be rationalised in terms of (*a*) sheet-stabilising C–H ··· O and stack-stabilising C ··· C interactions and (*b*) the greater importance of these β-steering forces as compared with the tendency to adopt other non-β packing arrangements.

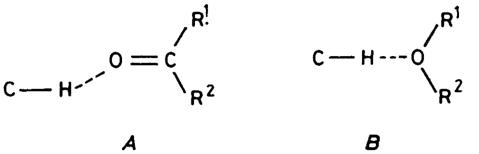
Although short C–H ··· O contacts have been reported regularly in the crystallographic literature, it is only recently, notwithstanding Sutor's early study,[2] that their importance in organic structures has been appreciated and their terminology as 'hydrogen bonds' received without scepticism. In a particularly comprehensive study,[3,4] Taylor and Kennard (TK) have established that 'hydrogen atoms covalently bonded to carbon have a statistically significant tendency to form short intermolecular contacts to oxygen atoms' and that there is considerable directional preference in these C–H ··· O hydrogen bonds. TK also conclude that C–H ··· O contacts are not a steric effect but a distinctly electrostatic phenomenon and that 'the frequency with which they occur suggests that they play a significant role in determining the packing arrangements of some organic crystal structures', Here we have attempted to evaluate this 'significant role' for a few 4 Å β-structures of oxygenated aromatic compounds.

General Considerations.—In this paper we characterise C–H ··· O contacts in the conventional manner as C ··· O (*D*) and H ··· O (*d*) distances. While TK could base their study on structures determined by neutron diffraction, no such structure determinations are available for the crystals of interest to us here, having a 4 Å short axis. Since only *X*-ray data are available in these cases, some of the *d* values are perhaps of limited accuracy. TK have considered in detail C–H ··· O contacts where $d < 2.40$ Å. Such a distance is roughly equivalent to corresponding *D* values between 2.70 and 3.50 Å (Scheme 1).



Scheme 1. $2.70\ \text{Å} < D < 3.50\ \text{Å}$; $d < 2.40\ \text{Å}$; $90° < \varphi < 180°$

Two categories of C–H ··· O bond may be dealt with and are shown in Scheme 2 as *A* and *B*. TK have shown that for carbonyl acceptors, such as *A*, the C–H ··· O contacts tend to lie in the plane containing 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 the H ··· O=C angles to be close to 120°, so that H ··· (sp^2 lobe) ··· O is approximately linear.



Scheme 2.

This trend has also been observed by Murray-Rust and Glusker (MG) for $\mathrm{O \cdots H{-}X}$ (X = N or O) hydrogen bonds involving carbonyl oxygen.[5] For ethereal acceptors such as *B*, however, TK have pointed out that the $\mathrm{C{-}H \cdots O}$ contacts lie nearly in the plane of the oxygen sp^3 orbitals, that is a plane passing through O, bisecting angle R^1OR^2, and perpendicular to the plane defined by R^1, O, and R^2. However, the directional preference within this plane is much less discernible. MG have observed that $\mathrm{H \cdots O}$ directions for $\mathrm{O \cdots H{-}X}$ (X = N or O) bonds involving ethereal oxygen need not lie strictly along the lone pair directions but over a wide angular spread within the aforementioned bisecting plane. Several $\mathrm{O \cdots H{-}X}$ hydrogen bonds have been observed by MG to lie in directions nearly coplanar with R^1, O, and R^2, that is along the line obtained by the intersection of the R^1OR^2 plane and the bisecting perpendicular plane.

In the β-structures we consider, oxygen occurs as a heterocyclic or quinonoid atom, or as a ketonic, carboxy, ester, or nitro functionality pendant to an aromatic or heteroaromatic skeleton. In most of these cases the molecules have a high degree of planarity, with the substituents also being able to lie nearly coplanar with the ring. If this indeed is the case and if $\mathrm{C{-}H \cdots O}$ bonds tend to be oriented as already described,[3,5] then these bonds will be nearly parallel to the planes of the molecules. A recent study of the crystal structures of some aromatic amino acids indicates that the favoured oxygen position is in the plane of the phenyl ring corresponding to an azimuthal angle of 0°.[6] The apparent free energy difference between an oxygen lying in the plane of the phenyl ring and one lying over the face of the ring is about 4.4 kJ mol^{-1} at 298 K. This preference is due to the electrostatic interaction between electronegative oxygen and the electropositive hydrogen atom on the phenyl ring. All this suggests that $\mathrm{C{-}H \cdots O}$ interactions may stabilise sheet and ribbon entities in a manner similar to $\mathrm{Cl \cdots Cl}$ and $\mathrm{C{-}H \cdots Cl}$ interactions, and that β-structure adoption may hence result. In this context we suggest the following criteria.

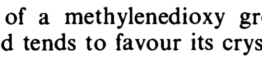
(1) Molecules must, as far as possible, be planar.

(2) $\mathrm{C{-}H \cdots O}$ contacts should occur along directions nearly parallel to the molecular plane so that two-dimensional entities may be optimised.

(3) For a given number of C atoms, the number of both ring and substituent H atoms must be as small as possible and the number of O atoms 'available' for $\mathrm{C{-}H \cdots O}$ bond formation as large as possible.

We now apply these criteria to several categories of planar oxygenated aromatic systems. The examples chosen include compounds the crystal structures of which were determined by us or culled from the crystallographic literature.

Methylenedioxy and Alkoxy Aromatic Systems.—The very similar roles of $\mathrm{C{-}H \cdots O}$, $\mathrm{C{-}H \cdots Cl}$, and $\mathrm{Cl \cdots Cl}$ interactions in stabilising the two sheet structures of the acid **(2)** (short axes 3.88 and 4.10 Å, both $P\bar{1}$) have been discussed in detail in the previous paper. We have already reported that the presence of a methylenedioxy group in a planar aromatic compound tends to favour its crystallisation in the β-form.[7,8] Accordingly, even in the absence of the Cl group, the parent acid **(1)** adopts the β-structure (short axis 3.88 Å, $P\bar{1}$). Its structure is similar to that of **(2)** and is sheet-based with acid molecules forming $\mathrm{O{-}H \cdots O}$ hydrogen-bonded dimers (Figure 1). The sheet is formed because of additional stabilisation of these dimers through $\mathrm{C{-}H \cdots O}$ interactions involving one of the heterocyclic oxygen atoms (*D* = 3.47, *d* = 2.48 Å) and, to some extent, one of the carboxy oxygen atoms (*D* = 3.37, *d* = 2.88 Å). We note that in the acid **(1)** two of the seven (C–)H atoms are tied up in contacts to oxygen and that the tendency to achieve crystal stabilisation through non-β-steering $\mathrm{C \cdots H}$ contacts is, to this extent, mitigated. Figure 1 shows that the sheet is compactly held together by these two types of $\mathrm{O{-}H \cdots O}$ and $\mathrm{C{-}H \cdots O}$ hydrogen-bonding arrangements and that the 'free' in-plane hydrogen atoms are not in repulsive contact. Although the two $\mathrm{C{-}H \cdots O}$ contacts in the acid **(1)** are quite long according to the criteria of TK, it is interesting that their directional preferences are exactly as would be predicted from the analyses of TK and MG; the longer contact involves the carbonyl oxygen rather than the hydroxy oxygen atom and while a very strong $\mathrm{O{-}H \cdots O}$ bond is directed along one of the lobes of this carbonyl oxygen atom, the other lobe is nearly along the $\mathrm{C{-}H \cdots O}$ contact, giving the compelling feeling that angular preferences are maintained in the approach of atoms in a stable crystal structure even though the intermolecular distances are not what could strictly be described as 'short'.[9] The contact involving heterocyclic oxygen is much shorter and probably contributes more significantly to crystal stabilisation. In any event, these two $\mathrm{C{-}H \cdots O}$ contacts, weak as they may be, are sufficient to steer this structure preferentially to a sheet-based β-form.



(1) R = H

(2) R = Cl

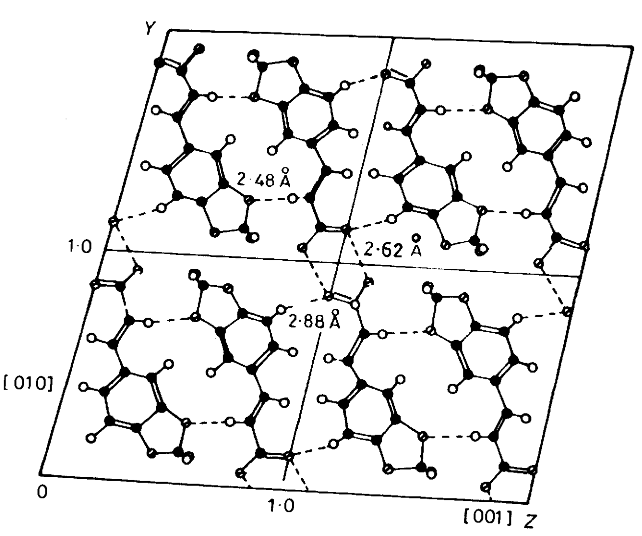


Figure 1. Molecular sheet formation in the crystal structure of the acid (1). Note the in-plane $\mathrm{O{-}H \cdots O}$ and $\mathrm{C{-}H \cdots O}$ bonds

This is an example of a phenomenon, by no means uncommon in molecular crystals, where contacts which could conventionally be termed 'long' or 'not significant' may exercise considerable control over the crystal packing adopted, because other, stronger interactions are absent.* The crystal structure of the acid **(1)** suggests that even 'long' $\mathrm{C{-}H \cdots O}$ contacts are directionally more specific and energetically more important than dispersive forces of the $\mathrm{C \cdots H}$ and $\mathrm{C \cdots C}$ types.

In the structures of both **(1)** and **(2)**, sheets are stacked at van der Waals separation to generate the 4 Å short axis. In such a stacking, the methylene hydrogen atoms above and below the planes of the molecular sheets are involved in intermolecular

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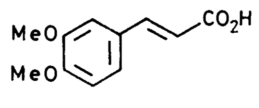
* In this connection, the strong carboxylic hydrogen bonds need not be considered, although they are responsible for the formation of acid dimers, since the packing of these dimers is not controlled by the $\mathrm{O{-}H \cdots O}$ bonds but by weaker forces. In a sense, the basic unit here is not an isolated acid molecule but an $\mathrm{O{-}H \cdots O}$ hydrogen-bonded dimer.

contacts, repulsive in the case of (**1**), with the shortest non-bonded H ··· H distances involving these atoms on stack-translationally related molecules being only 2.14 and 2.16 Å in (**1**) and (**2**), respectively. The β-structure is destabilised by such atoms outside the mean molecular plane but is still probably adopted because of the dominance of the sheet-stabilising C–H ··· O and stack-stabilising C ··· C interactions over the lone H ··· H repulsive contact.

However, if the number of such out-of-plane atoms increases, the β-structure may not be adopted. Although the sheet-structure is stabilised in the acid (**3**) by C–H ··· O contacts (d = 2.33, 2.63, and 2.64 Å), the larger number of out-of-plane atoms (two OMe groups) as compared with those in the acids (**1**) and (**2**) (one O–CH_2–O group) prevents the sheets from being stacked with 4 Å translation. In fact, so prohibitive must these inter-sheet repulsions be that the β-structure is possible neither for the acid (**3**) nor for a large number of simple non-halogenated alkoxy-benzoic and -cinnamic acids. The notable exceptions are 4-methoxy- and 4-ethoxy-benzoic acids where very strong C–H ··· O contacts are observed. These are, respectively, for the methoxy acid, D = 3.03, 3.22, and 3.13 Å, d = 2.60, 2.62, and 2.70 Å, and for the ethoxy acid, D = 3.59 Å, d = 2.50 Å. Still it should be noted that the number of out-of-plane H atoms in these cases is only one.



(3)

Interestingly, the structure adopted by the acid (**3**) is a C–H ··· O stabilised sheet-based non-β variant (termed α by Schmidt)[10] where, in order to minimise inter-sheet alkyl–alkyl repulsion, adjacent sheets are related not by translation but by inversion.[7] Since C ··· C interactions are not as atom-specific as C–H ··· O contacts, the inversion motif is compatible simultaneously with the need to optimise C ··· C contacts between sheets and to avoid 4 Å stacking.

Hydroxy Aromatic Systems.—In general, the hydroxy group does not form good C–H ··· O bonds or lead to β-structure adoption since the dominant structural feature is O–H ··· O–H hydrogen bonding typically around a screw axis of pitch *ca.* 4.8 Å. This familiar pattern is seen in many simple substituted phenols and naphthols. However, if such intermolecular hydrogen bonding between OH groups is absent, C–H ··· O mediated β-structure adoption may result, as for instance in naphthazarin, 1,2-dihydroxyanthraquinone, and methyl 3-nitro-4-hydroxycinnamate (**4**). The common feature in all these compounds is that OH groups are intramolecularly hydrogen-bonded and thus unable to participate in O–H ··· O–H bonding. A projection of the crystal structure of (**4**) down the 4 Å axis is given in Figure 2. This molecule has four distinctive types of (C–)H oxygen acceptors. While the hydroxy group is intramolecularly hydrogen bonded to the nitro group the whole molecule, excluding methyl hydrogen atoms, is accurately planar. Figure 2 shows that ten unambiguous in-plane C–H ··· O bonds are formed around the entire molecular periphery, linking the reference molecule to intra-sheet inversion and glide-related neighbours. The angular preferences for these bonds are in accord with the observations of TK and MG. For instance the two bonds from carbonyl oxygen (d = 2.37 and 2.79 Å) are almost along the sp^2 120° directions, as is the 2.68 Å bond to the nitro oxygen atom. Again, bonds to the ester and hydroxy oxygen atoms nearly bisect the valence angle, as described earlier. Four of the ten (C–)H ··· O distances are quite short (d = 2.37, 2.37, 2.33, and 2.33 Å) and clearly reveal the importance of these electrostatic interactions in sheet stabilisation and through it to a β-structure.

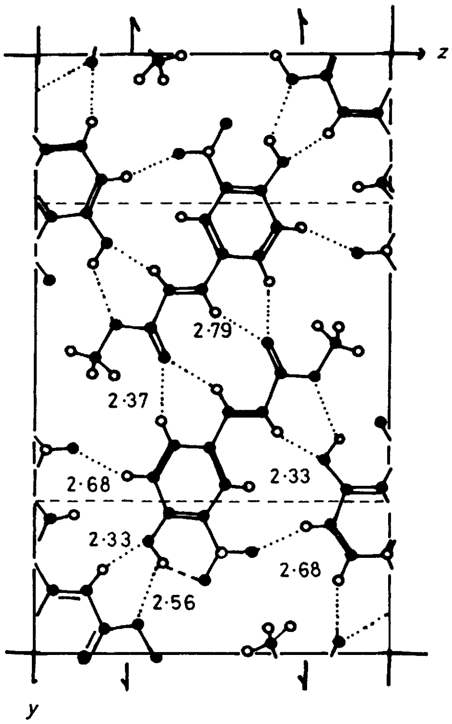
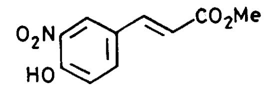


Figure 2. Sheet formation for methyl 4-hydroxy-3-nitro-*trans*-cinnamate (4)



(4)

Acetoxy Aromatic Systems.—Even though coumarin contains two oxygen atoms it has a stable non-β structure (short axis 5.68 Å) and an unstable β-modification. Yet it forms β-structures when complexed with mercury(II) chloride (short axis 4.03 Å) or when a chloro group is substituted as in the 6-chloro (4.03 Å) or the 4-methyl-7-chloro derivative (4.08 Å). The adoption of the β-structure in the latter two cases may be due to the presence of the chloro group. Seemingly more intriguing is the behaviour of 7-acetoxycoumarin (**5**), which has the β-structure. Its 3.88 Å short axis implies an almost certainly repulsive stacking of the methyl groups (van der Waals radius 2.0 Å). Although a β-steering role was ascribed to the acetoxy substituent on the basis of this structure determination,[11] a computer retrieval of 59 other phenyl, naphthyl, and heterocyclic acetoxy compounds by us from the Cambridge Structural Database (CSD) showed that not one adopted the β-structure. Hence it was felt that the crystal structure of the coumarin (**5**) is most unusual and it was decided to examine this and related structures in greater detail.

The coumarin (**5**) is monoclinic, and with the short axis being non-unique and the molecular plane parallel to the unique axis in the space group $P2_1/c$, it may be expected to crystallise in a planar sheet-based structure.[8] Indeed, the projection of the structure looking down the short axis [Figure 3(*a*)] is in the form of a molecular sheet. The sheets are aligned parallel to (102) and the entire structure is generated by stacking such

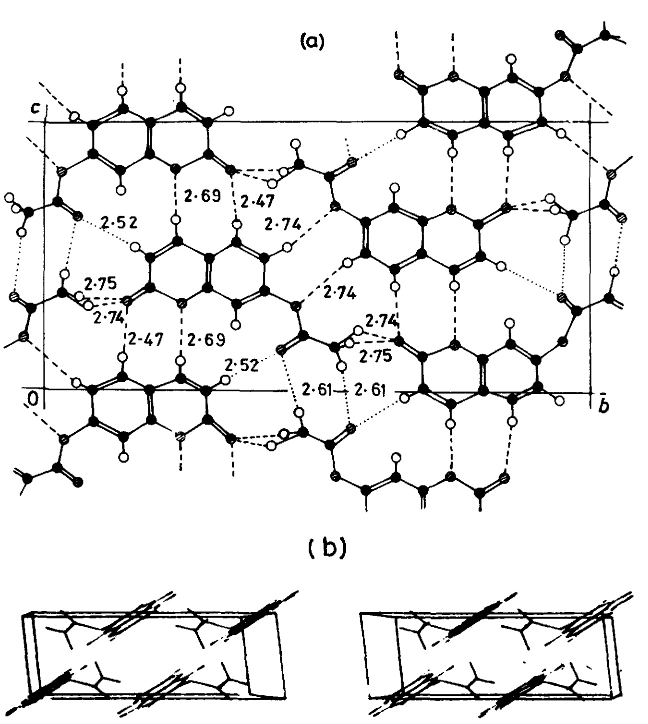
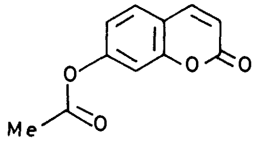
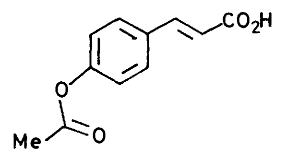


Figure 3. (*a*) Sheet formation in 7-acetoxycoumarin (**5**); intra- and inter-sheet C–H ··· O bonds are shown as dashed and dotted lines, respectively. (*b*) Stereoview of the crystal structure of the coumarin (**5**) to show the inter-sheet C–H ··· O bonds



(5)



(6)

sheets at short axis separation. Thus, in conceptual terms, the β-structures of the coumarin (**5**) and the acid (**1**) are similar, with the arrangement of molecules in a sheet optimising as large a number of C–H ··· O contacts as possible. In the structure of the coumarin (**5**), the reference molecule is linked therefore to inversion- and glide-related neighbours by several strong and directionally specific C–H ··· O interactions, lengths of which are given in Figure 3(*a*). The approaches of the C–H ··· O bonds to the coumarin carbonyl oxygen and the heterocyclic oxygen atom are almost exactly what might have been expected from the analyses of TK and MG. Further, all the eight (C–)H atoms are involved in C–H ··· O contacts and it is the absence of 'free' (C–)H atoms which minimises the need to have C ··· H contacts and with it the tendency to adopt a non-β-structure.

An interesting feature in the molecular structure of the coumarin (**5**) is that the mean planes of the aromatic ring and the acetoxy substituent make a relatively large angle of 60° to one another. By criterion (1) and from the example of the alkoxy compounds such as (**3**), this molecular non-planarity should constitute an almost insurmountable barrier to 4 Å stacking. However, in the structure of the coumarin (**5**), the acetoxy group of the reference molecule is involved in C–H ··· O contacts not only with an intra-sheet inversion-related neighbour (D = 3.62 Å, d = 2.74 Å) but also with inter-sheet glide-related (D = 3.48 Å, d = 2.52 Å) and inversion-related (d = 2.61 Å) molecules. Figure 3(*b*), a stereo-view of the crystal structure of the coumarin (**5**), shows how the acetoxy group links sheets through C–H ··· O contacts involving carbonyl oxygen. This means that such interactions, in effect, link molecules both within and between sheets. Therefore, the repulsive contacts inherent in stacking a non-planar molecule at 4 Å translation are offset by the stabilisation gained from a large number of intra- and inter-sheet C–H ··· O contacts. The acetoxy carbonyl group probably plays an important role in stabilising the interlayer structure and with it the β-packing since 7-methoxycoumarin (short axis 6.83 Å), which lacks such a carbonyl group, does not crystallise in a β-structure.

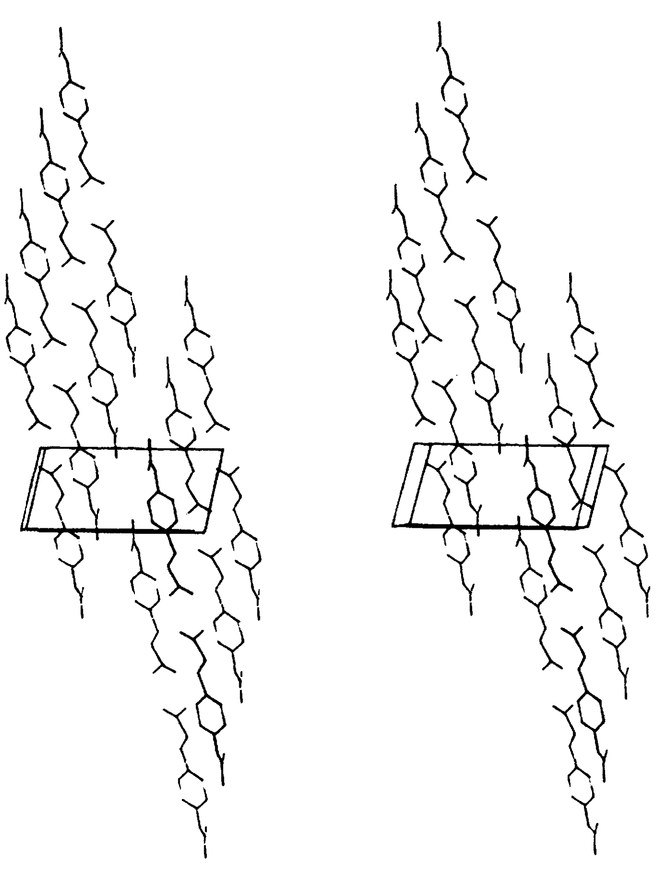


Figure 4. Stereoview of the herring-bone crystal structure of 4-acetoxycinnamic acid (**6**)

Both inter- and intra-sheet C–H ··· O contacts are structure-determining in the case of the coumarin (**5**), not only because the number of oxygen atoms available for such bonding is relatively large, but also because the number of hydrogen atoms is comparatively small for this molecular size. As stated in criterion (3), the relative number of C, H, and O atoms in an aromatic molecule appears to be a crucial factor in determining whether a β-structure is adopted or not, but a survey of a large number of such structures indicates that this concept is still difficult to quantify, since small changes in molecular shape, structure, and C:H:O ratio may alter the crystal packing type drastically.[8] In this connection, it is interesting that 4-acetoxycinnamic acid (**6**) crystallises with a short axis of 5.92 Å. The *X*-ray analysis of (**6**) was undertaken since the C:H:O ratios in (**5**) ($C_{11}H_8O_4$) and (**6**) ($C_{11}H_{10}O_4$) are similar. Further, there is a considerable body of structural data on the simple cinnamic acids and steering-group effects (Cl, NO_2, alkoxy) are well documented in this family.[7,10].

Figure 4 is a stereoview of the crystal structure of the acid (**6**). Like other cinnamic acids, molecules form O–H ··· O hydrogen-bonded dimers. However, these do not link up

Table 1. Some comparisons between the crystal structures of 7-acetoxycoumarin (**5**) and 4-acetoxycinnamic acid (**6**)

	(**5**)	(**6**)
M, space group, *Z*	$C_{11}H_8O_4$, $P2_1/c$, $Z = 4$	$C_{11}H_{10}O_4$, $P\bar{1}$, $Z = 2$
Short axis (Å)	$a = 3.833$	$a = 5.924$
Structural type	β (planar sheet)	Herring-bone
Packing coefficient	0.74	0.63
Number of (C–)H, (–C–)H, and (O–)H atoms per molecule	5, 3, 0	6, 3, 1
Number of O atoms per molecule available for C–H ··· O bonding	4	2
Number of C–H ··· O bonds with $d < 2.75$ Å	14	4
d Values for these bonds (Å)	2.47, 2.47, 2.52, 2.52, 2.61, 2.61, 2.69, 2.69, 2.74, 2.74, 2.74, 2.74, 2.75, 2.75	2.50, 2.50, 2.60, 2.60
D Values for these bonds (Å)	3.40, 3.40, 3.47, 3.47, 3.56, 3.56, 3.60, 3.60, 3.50, 3.50, 3.62, 3.62, 3.30, 3.30	3.52, 3.52, 3.67, 3.67
Number of C ··· C, C ··· H, and H ··· H contacts per molecule[a]	50, 8, 20	36, 38, 19
Energy contributions (negative; in kJ mol^{-1}) from eight nearest neighbour molecular co-ordinating units[b,c]	41(T), 41(T), 13, 13, 6, 6, 3, 3	35(T), 35(T), 20, 18, 7, 7, 5, 5

[a] A short contact is defined as one where the atoms are closer than a distance where −0.05 kJ mol^{-1} stabilisation energy is gained. [b] The potentials used are the ones developed by D. E. Williams for the EXP-6-1 model with coulombic terms included explicitly. [c] T refers to molecules related to the reference molecule by short-axis translation.

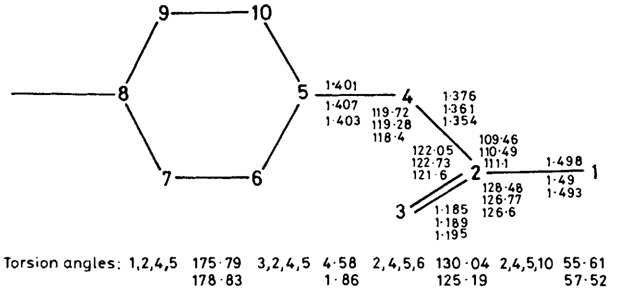
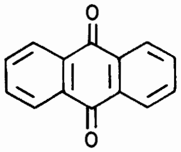


Figure 5. Acetoxy group bond lengths (Å) and angles (°) for the acid (**6**) (top), the coumarin (**5**) (middle), and the mean value for 59 CSD-retrieved acetoxy compounds (bottom). Torsion angles are shown only for compounds (**6**) (top) and (**5**) (bottom)

through C–H ··· O bonds to yield sheets as in the acids (**1**) and (**2**) and the packing is of the conventional herring-bone type with a large molecular co-ordination and a sizable energy contribution from C ··· H interactions. Table 1, which lists energy contributions from co-ordinating molecular units for a reference molecule in the structures of (**5**) and (**6**), reveals the important differences between the two structures. The packing densities in the two cases are distinctly different and the low value for the acid (**6**) is revealed by the crystallographic disorder of the olefinic linkage. Now, it may be noted that in the structurally distinct molecules (**5**) and (**6**), the intramolecular geometries of the acetoxy group are exceedingly similar; not only are bond and torsion angles identical but also the torsion angles between the mean planes of the aromatic and acetoxy moieties are nearly the same (*ca.* 60°). These geometrical details are a common feature in almost all the 59 (non-β) acetoxy aromatic structures retrieved from the CSD (Figure 5) and in a series of polyacetoxy-benzenes and -anthracenes studied recently.[12] From the foregoing it should be clear that the β-structure for (**5**) is largely due to a synergistic effect involving both the coumarin skeleton and the acetoxy substituent rather than to inherent 'steering' properties of the acetoxy fragment itself.

To understand why compounds (**5**) and (**6**) adopt different crystal structures, one must turn to the number of H and O atoms in the two structures given that the number of C atoms is the same. In the coumarin (**5**) there are five (C–)H atoms and three aliphatic H atoms. While the latter number is unchanged in the acid (**6**), there is one more (C–)H atom and an extra (O–)H atom. The telling difference between these structures may, however, not be the number of H atoms but the fact that whereas all four O atoms in (**5**) may form strong C–H ··· O bonds, only two of the four O atoms in the acid (**6**) are 'available' for such bonding. The two other O atoms are involved in carboxy hydrogen bonding and perhaps at best only one of them, the carbonyl oxygen, may participate in weak C–H ··· O bonds, as in the acids (**1**) and (**2**). One concludes therefore that the coumarin (**5**) adopts the β-structure only because of an unusually large number of C–H ··· O bond acceptors, coupled with a small number of hydrogen atoms and also because C–H ··· O bonding is inter-sheet as well as intra-sheet. In considering crystal structures of highly non-planar aromatic acetoxy compounds, (**5**) appears to be the exception whereas (**6**) typifies the group.

C:H:O *Ratios and the Likelihood of* β*-Structure Adoption in Quinones.*—A survey of several aromatic crystal structures shows that, other factors being the same, the relative numbers of carbon and hydrogen atoms per molecule are of crucial importance in determining whether a β-structure is adopted or not.[8,13] Fused-ring compounds like anthracene, coronene, and ovalene adopt non-β structures, but when oxygen atoms are introduced as substituents or within the ring framework in similar hydrocarbons, the tendency for β-structure adoption increases markedly. Thus a large number of fused-ring quinones crystallise in this structure even though the parent hydrocarbons do not. Typical examples are compounds (**7**)—(**12**).[14] In most of these structures there is good evidence for the existence of specific C–H ··· O bonds. These may be of some significance energetically since the relevant distances are rather short. For instance, the following intra-sheet C ··· O and (C–)H ··· O distances have been reported: pyranthrone (**10**), $D = 3.23$ Å; violanthrone (**11**), $D = 3.31$, 3.49, and 3.66 Å, $d = 2.40$, 2.68, and 2.70 Å; isoviolanthrone (**12**), $D = 3.46$ and 3.57 Å. Such short contacts 'tie up' some of the peripheral H atoms effectively and thereby stabilise the formation of corrugated sheets which are 4 Å stacked to generate the entire structure. Although the importance of C–H ··· O interactions in stabilising quinone crystal structures has been discussed in depth by Bernstein, Cohen, and Leiserowitz, in their comprehensive review,[14] and while experimental evidence based on solid-state ^{13}C n.m.r. spectroscopy for such effects has appeared recently,[15] 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.



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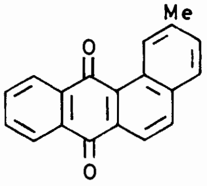

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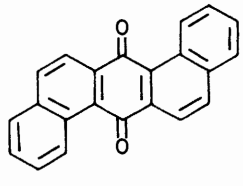

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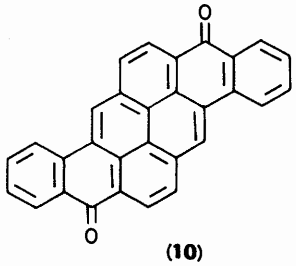

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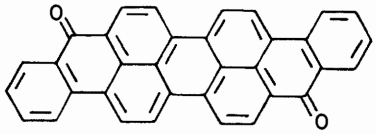

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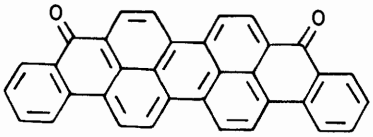
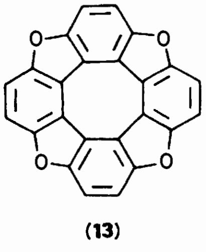


(12)

Examples (7)—(12) show that the presence of the quinonoid oxygen atom actively 'steers' the crystal structure towards a 4 Å stacking mode since it is directly responsible for C–H $\cdots$ O based-sheet formation.

Oxygen Heterocyclic β-*Structures*.—A heterocyclic oxygen 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 $\cdots$ O bond acceptor. Consider the heterocycles (13) and (14). The molecular shape and size of (13) and coronene bear some similarity, and (13) and (14), $C_{18}H_{10}O_2$, are functionally similar. However, while (13) has a β-structure, (14) and coronene do not. These observations may be explained on the basis of sheet-stabilising C–H $\cdots$ O interactions in (13). The number of H atoms is eight, which is less than coronene and, of these, four are involved in fairly specific C–H $\cdots$ O contacts to heterocyclic oxygen (D = 3.47, d = 2.53 Å) and hence need not be stabilised through C $\cdots$ H interactions. The delicate role of molecular size is exemplified in a comparison of (13) and (14). The latter probably has too few oxygen atoms and too many hydrogen atoms to adopt a C–H $\cdots$ O sheet-based structure, especially since heterocyclic oxygen is a much weaker C–H $\cdots$ O bond acceptor than, say, carbonyl oxygen.



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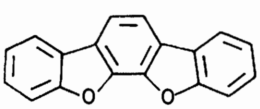
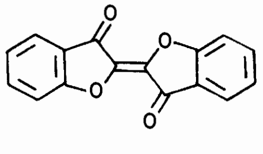


(14)

The involvement of heterocyclic oxygen in promoting β-structure adoption is further evidenced in a number of other compounds. Benzoic, phthalic, and cinnamic acids (stable form) do not have the β-structure but 2-furoic acid (short axis 4 Å), furan-3,4-dicarboxylic acid (3.79 Å), and 2-furylacrylic acid (3.88 Å) do. In all these cases the heterocyclic oxygen is involved in inter-stack C–H $\cdots$ O interactions. Similarly, tetrachlorodibenzofuran does not adopt the β-structure owing to molecular non-planarity, yet the addition of a single oxygen atom to give 2,3,7,8-tetrachlorodibenzo-*p*-dioxin not only ensures planarity but also results in a β-structure. The differences between compounds (15) and (16) may also be understood along similar lines. 2,2′-Bi-benzofuranylidene-3,3′-dione (15), $C_{16}H_8O_4$, is non-planar and a minor change in its structure gives the planar biphthalidyl (16), $C_{16}H_8O_4$. While (16) has the β-structure, (15) does not.



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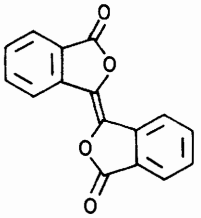
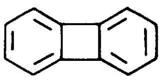


(16)

Non-oxygen Heterocycles.—Since a variety of other hetero atoms may also change C:H ratios in aromatic compounds and/or act as (C–)H bond acceptors, it is anticipated that the β-steering behaviour of heterocyclic oxygen will be paralleled by that of other atoms, notably N and S. Thus 3-pyridyl- (short axis 3.84 Å) and 2-thienyl-acrylic acids (short axis 3.91 Å) adopt the β-structure even though cinnamic acid itself is dimorphic with the β-form metastable.

In general while the lower aromatic hydrocarbons do not adopt the β-structure, this packing is possible for the corresponding aza analogues. Biphenylene (17), $C_{12}H_8$, does not have a β-structure, but such a structure is adopted by bipyridylene (18), $C_{10}H_6N_2$ (short axis 3.8 Å). Again the same structure is observed in *s*-triazolo[1,5-*b*]pyridazine (19), $C_5H_4N_4$ (short axis 3.74 Å) and flavanthrene (20), $C_{28}H_{14}N_2$ (short axis 3.85 Å). Similarly, whereas 1- and 2-naphthol and their methyl ethers do not adopt the β-structure, this structure is favoured in compounds like 8-hydroxyquinoline (short axis 3.91 Å), 2-hydroxyquinoxaline, (4.3 Å), and 1,5-dimethoxy-1,5-naphthyridine (4.01 Å). Further, 2,3,7,8-tetrachloroanthracene (21) does not adopt the β-structure, but replacement of one or two of the C–H groups with nitrogen or oxygen results in the β-structure, as evidenced by 2,3,7,8-tetrachlorophenazine (22) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (23). In conclusion, it is emphasized that a large number of heterocyclic compounds seem to adopt the β-packing as a consequence of a reduced number of (C–)H atoms and a notable tendency to form sheet- or ribbon-stabilising contacts of the C–H $\cdots$ N, C–H $\cdots$ S, N $\cdots$ S, O $\cdots$ S, O $\cdots$ Cl, and S $\cdots$ Cl types.

An area where a study of such intra-sheet (intra-ribbon) interactions may yield valuable insights is the structural chemistry of segregated stack crystal structures of conducting donor–acceptor complexes. The prototype, TTF–TCNQ, has a β-structure ($P2_1/c$, b = 3.81 Å) characterised by the short-axis stacking of corrugated ribbons with a profusion of lateral inter-stack contacts of the C–H $\cdots$ N (2.54, 2.62, 2.81 Å), C–H $\cdots$ S



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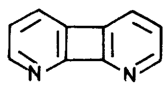

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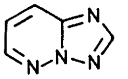

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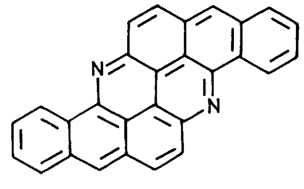

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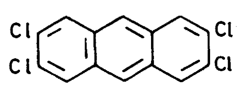

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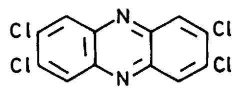

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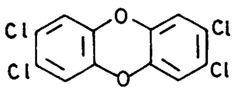

(23)

(2.89, 3.02 Å), and N ··· S (3.20, 3.30 Å) types. It is suggested that crystal engineering of segregated stack structures for such materials could be attempted through a consideration of inter- rather than intra-stack contacts.[16]

Experimental

X-Ray Structure Determination of 4-*Acetoxycinnamic Acid* (**6**).—The acid (**6**) was prepared from 4-hydroxybenzaldehyde by literature procedures; well formed crystals suitable for *X*-ray data collection were obtained from acetone. Crystal data: $C_{11}H_{10}O_4$, $M = 206$, $P\bar{1}$, $a = 5.924\,4(4)$, $b = 7.809\,4(7)$, $c = 11.911\,9(7)$ Å, $\alpha = 86.178(6)$, $\beta = 77.503(5)$, $\gamma = 70.682(7)^\circ$, $V = 5.08 \times 10^{-26}$ cm^3, $F(000) = 216$, $\mu = 7.77$ cm^{-1} (Cu-K_α), $D_c = 1.35$ g cm^{-3}. Intensity data were collected for a small irregularly shaped crystal with an Enraf–Nonius CAD-4 diffractometer by the general procedures described in the previous paper. A total of 754 reflections were considered non-zero at the 2.5σ significance level out of 1 676 possible reflections with $3 < \theta < 55^\circ$. The weights were taken at $1.00/\{[\sigma(F_o)]^2 + (0.0045F_o)^2\}$. The structure was solved with the MULTAN 80 program. Isotropic least-squares refinement revealed peaks which corresponded to a disorder involving the olefinic carbon atoms C(7) and C(8). Refinement of the occupancy factors for the two possible positions of these atoms converged successfully at values of nearly 0.65 and 0.35, respectively. Least-squares refinement incorporating positional and anisotropic temperature parameters for all non-hydrogen atoms [including C(7), C(7′), C(8), and C(8′)] gave a final R value of 0.041 and an R_w value of 0.041. The final atomic co-ordinates for the acid (**6**) are given in Table 2 and the atom-numbering scheme is in Figure 6.*

Table 2. Fractional atomic co-ordinates for the acid (**6**)[a–c]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
C(1)	−0.004 4(10)	0.648 6(8)	0.792 4(5)
C(2)	0.135 4(11)	0.488 1(8)	0.834 7(5)
C(3)	0.379 6(10)	0.409 9(7)	0.788 0(5)
C(4)	0.486 1(8)	0.491 5(7)	0.696 2(4)
C(5)	0.353 9(10)	0.649 2(7)	0.649 9(5)
C(6)	0.108 0(10)	0.725 2(7)	0.699 0(6)
C(7)	−0.271 1(32)	0.705 4(16)	0.865 5(13)
C(7′)	−0.247 4(46)	0.771 7(33)	0.818 3(17)
C(8)	−0.416 9(24)	0.848 1(15)	0.842 2(14)
C(8′)	−0.423 9(26)	0.728 8(27)	0.916 2(12)
C(9)	−0.671 2(13)	0.880 7(15)	0.931 2(10)
C(10)	0.851 2(19)	0.252 7(7)	0.616 7(4)
C(11)	1.120 1(10)	0.214 5(8)	0.579 5(6)
O(1)	−0.786 3(14)	1.028 7(9)	0.885 9(5)
O(2)	−0.765 8(11)	0.814 6(7)	1.014 7(5)
O(3)	0.737 8(6)	0.429 2(4)	0.651 9(3)
O(4)	0.740 6(6)	0.150(3)	0.616 4(3)
H(2)	0.058(9)	0.433(6)	0.898(4)
H(3)	0.481(8)	0.297(6)	0.813(4)
H(5)	0.437(9)	0.701(6)	0.577(4)
H(6)	0.028(8)	0.846(7)	0.661(4)
H(7)	−0.327(3)	0.622(2)	0.935(1)
H(7′)	−0.317(5)	0.892(3)	0.770(2)
H(8)	−0.381(2)	0.939(2)	0.935(1)
H(8′)	−0.371(3)	0.606(3)	0.965(1)
H(11A)	1.153(11)	0.320(9)	0.542(6)
H(11B)	1.201(12)	0.104(9)	0.533(5)
H(11C)	1.180(12)	0.203(9)	0.633(6)
HO	−0.929(12)	1.057(8)	0.926(5)

[a] For labelling of atoms see Figure 6. [b] Estimated standard deviations are given in parentheses. [c] Primed atoms belong to the disordered olefinic linkage of the acid (**6**).

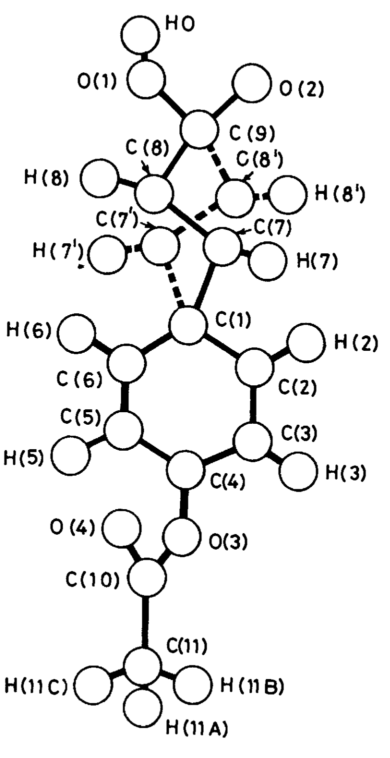

Figure 6. Atom-numbering scheme for 4-acetoxycinnamic acid (**6**)

Conclusions

Directionally specific C–H ··· O contacts to carbonyl, ether, and heterocyclic oxygen atoms may stabilise sheet- (ribbon)-based 4 Å short axis β-structures for oxygenated aromatic systems. The role of the oxygen atom is two-fold: to establish

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Lists of bond lengths and angles and of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

sheet-stabilising C–H $\cdots$ O contacts and to reduce effectively the number of in-plane hydrogen atoms which must be stabilised by non-β-steering C $\cdots$ H interactions. This role may be extended to other heteroatoms such as N or S.

Acknowledgements

References to crystal-structure determinations have not been cited, for reasons of brevity. A part of this work was presented at the XIIIth Congress of the International Union of Crystallography, Hamburg, August 1984. We thank Dr. W. Jones, Department of Physical Chemistry, University of Cambridge, for arranging for the diffractometer data collection. Financial assistance from the D.S.T. (S.E.R.C.) is gratefully acknowledged.

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