

Short Communications

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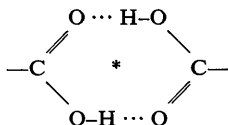
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Concerning the planarity of the carboxylic acid dimer configuration. By JERRY DONOHUE, *Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104, U.S.A.*

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A literature survey of the geometry of the hydrogen bonding in carboxylic acids which do not form centric dimers shows that for a given carboxyl group the position of an oxygen atom accepting a hydrogen bond from the hydroxyl group is close to synplanar to the carbonyl group; there is no corresponding restriction with regard to the position of a hydroxyl group which is donating a hydrogen bond to the carbonyl group. It follows that invocation of sp^2 hybridization and localized electron pairs to explain the planarity of centric carboxylic acid dimers is unnecessary, and that in the case of some acids which do not form dimers this theory leads to the wrong prediction.

Jeffrey & Sax (1963) pointed out that when two carboxyl groups are hydrogen bonded across a center of symmetry



the planes defined by the carbon and oxygen atoms of each group must be parallel, but that, contrary to expectation, coplanarity of the whole system was the exception, rather than the rule. They tabulated the observed separations, which ranged from 0.011 Å to 0.549 Å, in crystals of 12 different carboxylic acids.

Robertson (1964) then pointed out that these 8-membered rings are approximately planar, and that a displacement of 0.5 Å corresponds to a rotation of the $O \cdots O$ vector by only 10° out of the plane. He presented an explanation of the planarity phenomenon in terms of sp^2 hybridization of the carbonyl oxygen atom and the attraction by a lone pair of electrons, 120° from the $C=O$ bond, to the hydrogen atom, together with a statement that the acid proton is not merely attracted to the electronegative oxygen atom as such, but is specifically drawn towards its lone pairs of electrons (the positions of which are presumably fixed by the sp^2 hybridization).

I wish to point out that it is unnecessary to invoke sp^2 hybridization, specific positions of lone pairs, or other such 'quantum mechanical' arguments in order to explain the observed planarity of centric carboxylic acid dimer groups, but that this is a natural consequence of two other simple observed geometrical properties, one of the carboxyl group, the other of the $O-H \cdots O$ hydrogen bond system. The first of these is the coplanarity of all four atoms of the carboxyl group, a condition which has been observed both in isolated molecules of gaseous formic acid (Trambarulo, Clark & Hearn, 1958) and in crystals of oxalic acid dihydrate† (which do not contain the familiar dimer groups,

the carboxyl group hydrogen bonded instead to a water molecule) (Garrett, 1954); the second is the close proximity to linearity of the three atoms in an $O-H \cdots O$ hydrogen bond (Donohue, 1952; Fuller, 1959). From the combination of these two conditions it follows that centric dimer groups must be coplanar, with small deviations from either or both of them leading to small deviations from coplanarity, as observed by Jeffrey and Sax.

These two conditions, however, do not require that the dimer groups be centric. Experimentally it has been found that most of them are, but the reason for this is not entirely clear. More interesting, therefore, are the geometries of the hydrogen bonding to and from carboxyl groups which do not form centric dimers, as well as those which do not even form dimers. Search of the literature was terminated when a dozen of such carboxyl groups were discovered. Selected features of these groups are presented in Fig. 1. The compounds include: acetic acid (Jones & Templeton, 1958; Sharma, 1968), citric acid (Nordman, Weldon & Patterson, 1960; Glusker, Minkin & Patterson, 1968), formic acid (Holtzberg, Post & Fankuchen, 1953), α -oxalic acid (Cox, Dougill & Jeffrey, 1952), DL-tartaric acid monohydrate (Parry, 1951), D-tartaric acid (Okaya, Stemple & Kay, 1966), and trimesic acid (Duchamp & Marsh, 1968). The views shown in Fig. 1 are all perpendicular to the best planes through the heavy atoms of the carboxyl groups.

The following points are to be noted:

1. The identification of the carboxyl oxygen atoms as to which is carbonyl and which is hydroxyl is unambiguous (except in the case of formic acid) on the basis of $r_{C=O} < r_{C-OH}$ and $\angle C-C-OH < \angle C-C=O$. (In the case of D-tartaric acid, which was studied by neutron diffraction, these two criteria are confirmatory rather than necessary.)

2. The deviations of the acceptor oxygen atoms from the mean planes of the carboxyl groups lie between 0.051 and 0.379 Å; none is as large as the 0.549 Å reported by Jeffrey & Sax for a centric dimer. The largest rotation of an $O \cdots O$ vector out of carboxyl plane is only 8° .

3. The acceptor oxygen atoms are positioned so that the system $O=C-OH \cdots O$ is synplanar, with the angles $C-OH \cdots O$ in the range 108.5° to 131.9° . The inferred position of the hydrogen atom is strongly reminiscent of the

† The positional parameters given by Garrett lead to a best plane for the carboxyl group having the following atomic displacements: C, -0.002 Å; O(1), $+0.002$ Å; O(2) $+0.001$ Å; H(3), -0.001 Å.

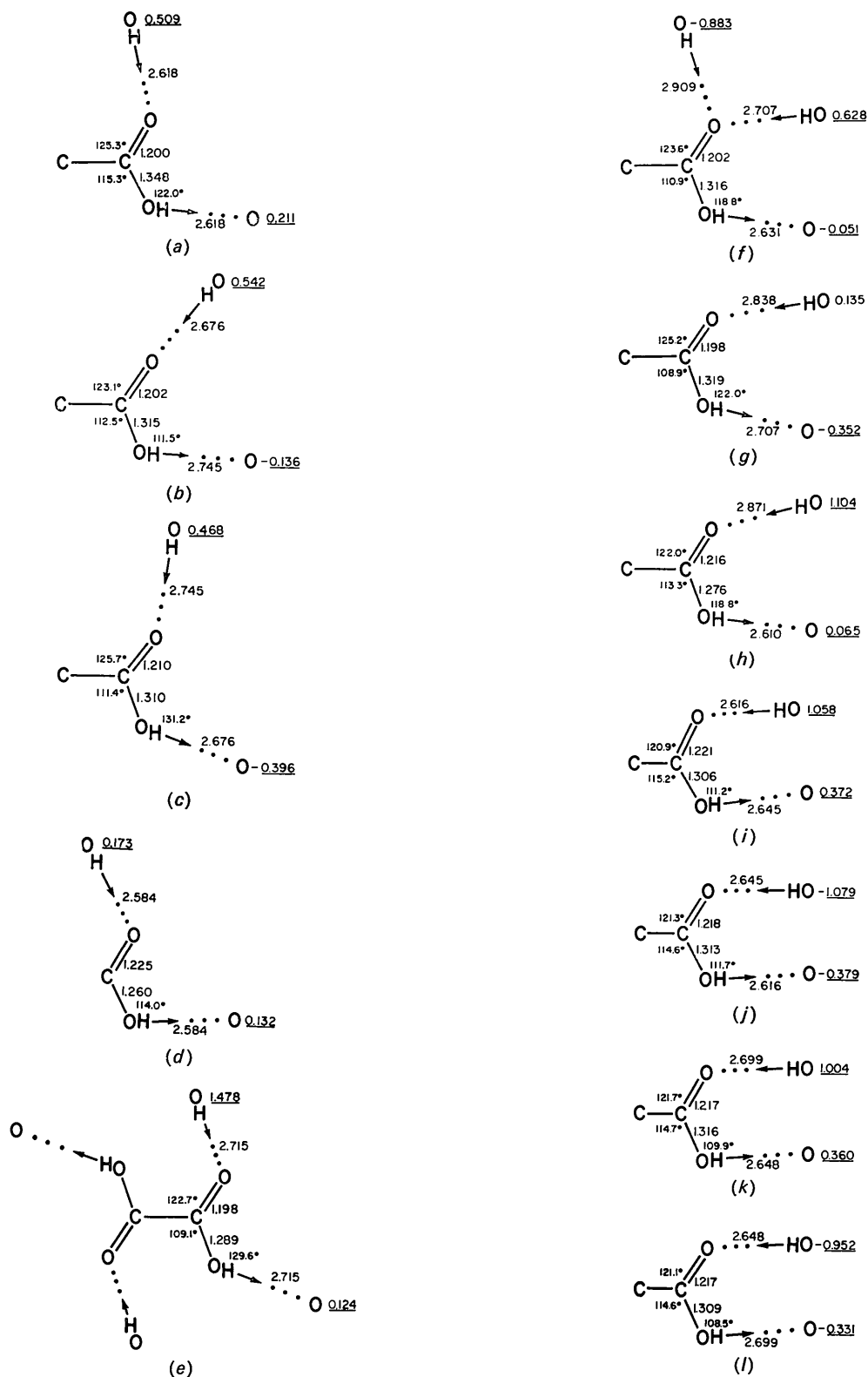
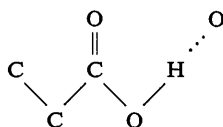


Fig. 1. Twelve carboxyl groups, together with their donor and acceptor oxygen atoms, viewed perpendicular to their mean planes. The underlined numbers give the distance in Å of the outlying atoms from these planes. (a) Acetic acid; (b) and (c), citric acid; (d) formic acid; (e) α -oxalic acid; (f) and (g) D-tartaric acid; (h) DL-tartaric (racemic) acid monohydrate; (i), (j), (k) and (l) trimesic acid.

synplanar position observed for the β -carbon atoms of saturated carboxylic acids, as recently pointed out by Dunitz & Strickler (1968). It would appear that the following system of atoms in hydrogen bonded carboxyl groups tends to be planar, with the conformations shown:



4. There is no apparent regularity with regard to the positions of the donor OH groups. Nearly all of them are not even approximately synplanar, and they lie from 0.135 to 1.478 Å from the planes of the carboxyl groups, with the angles $C=O \cdots HO$ in the range 118.8° to 168.0° . The largest rotation of an $O \cdots O$ vector out of a carboxyl plane is 33° .

It thus would seem that the observed planarity of carboxylic dimer groups does *not* lend support to the widely used and currently fashionable characterization as 'sp² hybridization' of interatomic interactions which are conventionally termed double bonds. If such sp² forces exist at all, they are so weak as to be easily overcome in some cases by other structural forces.

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Interrelated space groups observed for complexes of cycloheptaamylose with small organic molecules. By J. A.

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The cell dimensions and space groups of a variety of 1:1 complexes of organic guest molecules with cycloheptaamylose have been determined by X-ray crystallography. The molecular weights calculated from the X-ray data agree with those calculated from the stoichiometries obtained by chemical analysis. Different organic guest molecules cause marked changes in the crystallographic space groups of the complexes. An isomorphous series has been obtained which includes guest molecules having one or two heavy atoms. Determination of the complete molecular structure of some of these complexes is in progress.

Cycloheptaamylose is a cyclic polymer of D-glucose containing seven units with α -1:4 glycosidic linkages. The molecular conformation is probably a torus as was found for cyclohexaamylose by X-ray analysis of the crystalline complex with potassium acetate (Hybl, Rundle & Williams, 1965). Cyclohexaamylose, cycloheptaamylose and cyclooctaamylose all form inclusion complexes with a wide variety of substances (Cramer, 1954; French, 1957; Senti & Erlander, 1964; Thoma & Stewart, 1965).

The cycloamyloses have recently been shown to cause a remarkable stereoselective acceleration of the cleavage of phenyl esters in homogeneous aqueous solution (VanEtten, Sebastian, Clowes & Bender, 1967). The mechanism of this rate acceleration has been established as involving the reaction of the complexed ester molecule with an alkoxide ion

derived from the secondary hydroxyl groups of the cycloamylose (VanEtten, Clowes, Sebastian & Bender, 1967). Most importantly for the present study, the magnitudes of the rate accelerations do not parallel the stabilities of the cycloamylose-ester complexes but can be explained on the basis of the stereochemistry of the amylose-guest complex (VanEtten, Sebastian, Clowes & Bender, 1967). We have been examining the crystallographic characteristics of a variety of 1:1 complexes.

Crystalline complexes were obtained by mixing equimolar amounts of host and guest material in neutral aqueous solution and allowing the mixture to cool. Analytical samples were dried briefly by spreading and blotting them on filter paper and were then transferred to closed vials. Efflorescence of some of these samples was noted, consistent with