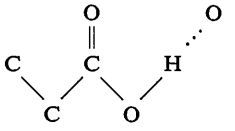
synplanar position observed for the β-carbon atoms of saturated carboxylic acids, as recently pointed out by Dunitz & Strickler (1968). It would appear that the following system of atoms in hydrogen bonded carboxyl groups tends to be planar, with the conformations shown:



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···HO in the range 118·8° to 168·0°. The largest rotation of an O···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 'sp^2 hybridization' of interatomic interactions which are conventionally termed double bonds. If such sp^2 forces exist at all, they are so weak as to be easily overcome in some cases by other structural forces.

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References

Cox, E. M., Dougill, M. W. & Jeffrey, G. A. (1952). *J. Chem. Soc.* p. 4854.

Donohue, J. (1952). *J. Phys. Chem.* **56**, 502.

Duchamp, D. J. & Marsh, R. E. (1968). *Acta Cryst.* In the press.

Dunitz, J. D. & Strickler, P. (1968). *Structural Chemistry and Molecular Biology*, edited by A. Rich & N. Davidson, p. 595. San Francisco: W. H. Freeman.

Fuller, W. (1959). *J. Phys. Chem.* **63**, 1705,

Garrett, B. S. (1954). Oak Ridge Natl. Lab. Rep. 1745, p. 13.

Glusker, J. P., Minkin, J. A. & Patterson, A. L. (1968). *Acta Cryst.* To be published.

Holtzberg, F., Post, B. & Fankuchen, I. (1953). *Acta Cryst.* **6**, 127.

Jeffrey, G. A. & Sax, M. (1963). *Acta Cryst.* **16**, 430.

Jones, R. E. & Templeton, D. (1958). *Acta Cryst.* **11**, 484.

Nordman, C. E., Weldon, A. S. & Patterson, A. L. (1960). *Acta Cryst.* **13**, 418.

Okaya, Y., Stemple, N. R. & Kay, M. I. (1966). *Acta Cryst.* **21**, 239.

Parry, G. S. (1951). *Acta Cryst.* **4**, 131.

Robertson, J. H. (1964). *Acta Cryst.* **17**, 316.

Sharma, B. D. (1968). Private communication.

Trambarulo, R., Clark, A. & Hearns, C. (1958). *J, Chem. Phys.* **28**, 736.

Acta Cryst. (1968). B**24**, 1560

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

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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

observations made for the potassium acetate complex of the cyclohexaamylose (Hybl, Rundle & Williams, 1965).

Cell dimensions and space groups were determined from precession and Weissenberg films taken with Cu $K\alpha$ radiation. No calibration for film shrinkage was made at this stage. In order to prevent loss of water of crystallization during the collection of the X-ray data, the crystals were sealed in thin-walled capillary tubes with a small amount of mother liquor present. Crystal densities were measured twice, by flotation in mixtures of ethanol–carbon tetrachloride–bromoform, and also in mixtures of chloroform–bromoform–ether. Values were checked using another crystal fresh from the mother liquor. These precautions were taken to insure that the water content of the crystals was the same as that of the crystals in equilibrium with the mother liquor, and to prevent loss of the organic guest molecule from the crystal in the presence of organic solvents. (The molar ratio of *p*-nitrophenol to cycloheptaamylose can be varied between 2·5:1 and 0·6:1 by washing the crystalline complex with acetone (Phillips & Baugh, 1966).)

Crystallographic and analytic data for a variety of crystalline complexes of cycloheptaamylose with organic guest molecules are presented in Table 1. The complexes have in each instance 1:1 stoichiometries. The crystal density and elementary analysis are each distinct enough to provide excellent information about the stoichiometry of the complex.

In the case of the X-ray work the number of water molecules was determined from the difference between the observed crystal density and that calculated on the basis of a 1:1 stoichiometry. In almost every instance it may be seen (Table 1) that the X-ray data require the presence of more water molecules than are required for the crystalline samples analysed by chemical methods. While the discrepancy is negligible in the case of, for example, the 2,5-diiodobenzoic acid complex the water contents of crystalline adamantanecarboxylic acid complexes differ substantially according to whether they have been briefly air dried or have been kept in closed capillaries with a portion of the mother liquor.

The preliminary films of crystalline cycloheptaamylose and of the 1:1 complexes indicated a strong dominating

Table 1. *Initial data on complexes of cycloheptaamylose with organic guest molecules*

Organic guest	Space group	Dimensions of cell*	Molecules per cell	Density ($g.cm^{-3}$)	Molecular weight from X-ray data	Molecular weight from chemical analysis
None	$P2_1$	$a=10{\cdot}31$ Å $b=20{\cdot}86$ $c=15{\cdot}09$ $\beta=109°29'$	2	obs. 1·43	1:1 Complex with $10H_2O$ mol. wt. 1318	1:1 Complex with $12H_2O$ mol. wt. 1351 Calc: C, 37·33; H, 7·01 Found: C, 37·15; H, 6·70
1-Adamantane-carboxylic acid†	$C1$	$a=9{\cdot}13$ Å $b=24{\cdot}53$ $c=17{\cdot}48$ $\alpha=91°59'$ $\beta=100°39'$ $\gamma=101°42$	2	obs. 1·42	1:1 Complex with $16H_2O$ mol. wt. 1608	1:1 Complex with $10H_2O$ mol. wt. 1495 Calc: C, 42·57; H, 7·15 Found: C, 42·38; H, 7·03
1-Adamantane carboxylic acid	$P1$	$a=9{\cdot}56$ Å $b=12{\cdot}13$ $c=16{\cdot}14$ $\alpha=99°18'$ $\beta=96°26$ $\gamma=87°37$	1	obs. 1·44	1:1 Complex with $15H_2O$ mol. wt. 1624	1:1 Complex with $10H_2O$ mol. wt. 1495 Calc: C, 42·57; H, 7·15 Found: C, 42·45; H, 7·26
m-Bromobenzoic acid	$C2$	$a=19{\cdot}23$ Å $b=24{\cdot}58$ $c=15{\cdot}80$ $\beta=108°30'$	4	obs. 1·47	1:1 Complex with $13H_2O$ mol. wt. 1566	1:1 Complex with $10H_2O$ mol. wt. 1516 Calc: C, 38·82; H, 6·32 Br, 5·27 Found: C, 38·98; H, 6·08 Br, 4·96
m-Toluic acid	$C2$	$a=18{\cdot}86$ Å $b=24{\cdot}67$ $c=15{\cdot}76$ $\beta=109°32$	4	obs. 1·42	1:1 Complex with $11H_2O$ mol. wt. 1478	
m-Iodobenzoic acid	$C2$	$a=18{\cdot}88$ Å $b=24{\cdot}77$ $c=15{\cdot}69$ $\beta=110°$	4	obs. 1·53	1:1 Complex with $11H_2O$ mol. wt. 1589	1:1 Complex with $9H_2O$ mol. wt. 1545 Calc: C, 38·09 H, 6·07 I, 8·21 Found: C, 38·41; H, 5·93 I, 8·08
2,5-Diiodobenzoic acid	$C2$	$a=19{\cdot}09$ Å $b=24{\cdot}65$ $c=15{\cdot}70$ $\beta=109°43'$	4	obs. 1·60	1:1 Complex with $9H_2O$ mol. wt. 1676	1:1 Complex with $8H_2O$ mol. wt. 1653 Calc: C, 35·61; H, 5·49 I, 15·35 Found: C, 35·68; H, 5·46 I, 15·15

Table 1 (*cont.*)

Organic guest	Space group	Dimensions of cell*	Molecules per cell	Density ($g.cm^{-3}$)	Molecular weight from X-ray data	Molecular weight from chemical analysis
2-Bromo-5-t-butylphenol	$C2$	$a=19{\cdot}19$ Å $b=24{\cdot}58$ $c=15{\cdot}97$ $\beta=109°10'$	4	obs. 1·41	1:1 Complex with $9H_2O$ mol. wt. 1511	1:1 Complex with $10H_2O$ mol. wt. 1540 Calc: C, 40·44; H, 6·72 Br, 5·18 Found: C, 40·30; H, 6·73 Br, 4·45
m-t-Butylphenol	$C222_1$	$a=19{\cdot}15$ Å $b=24{\cdot}33$ $c=62{\cdot}78$	16	obs. 1·38	1:1 Complex with $13H_2O$ mol. wt. 1520	1:1 Complex with $10H_2O$ mol. wt. 1461 Calc: C, 42·73; H, 6·90 Found: C, 42·74; H, 7·22
Phenylmercuric acetate	$P22_12_1$	$a=17{\cdot}66$ Å $b=11{\cdot}45$ $c=32{\cdot}74$	4	obs. 1·69	1:1 Complex with $12H_2O$ mol. wt. 1685	

* The estimated experimental errors are ±0·02 Å in *a* and *c*, ±0·01 Å in *b*, and ±15′ in measurements of the angles.
† This is obviously not the smallest possible unit cell but was chosen in this form to show the correlation with the other adamantane complex.

Table 2. *Similarities between structures of cycloheptaamylose complexes crystallizing in the different space groups*

	a	*b*	*c*	Number of molecules in unit cell
Fundamental repeat units	9 Å	12 Å	16 Å	
Multiplicities for:				
$P2_1$	1	2	1	2
$P1$	1	1	1	1
$C1$	1	2	1	2
$C2$	2	2	1	4
$P22_12_1$	2	1	2	4
$C222_1$	2	2	4	16

effect of the macro structure on the intensities of the *hk*0 zone. The heaviest reflections formed concentric hexagons in the type of pattern one would expect from a benzene ring. At 2 Å resolution on the Patterson map, looking down the *c* axis, concentric circles of peaks appear around the origin, the diameter of the innermost circle corresponding closely to that expected for the amylose torus. A similar effect of the macro structure was observed in the case of the hexaamylose and used to place the sugar residues in the unit cell (Hybl, Rundle & Williams, 1965). Not only is this hexagonal pattern on the films observed for all complexes in space group $C2$, it is also present in the triclinic cases, one of these in fact ($C1$) showing pseudo C centering and pseudo *mm* symmetry. The second triclinic space group $P1$ has no pseudo C centering but still maintains a relationship on this *hk*0 zone. These observations led us to investigate the correspondence of cell dimensions and to postulate a basic repeat unit due to the amylose itself. Table 2 shows the relationship of all cell dimensions to the basic unit.

At present we are attempting to elucidate the complete three-dimensional structure of one of these amylose complexes in order to investigate the stereochemistry of fit of the guest to host molecule.

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References

CRAMER, F. (1954). *Einschlussverbindungen.* Heidelberg: Springer-Verlag.

FRENCH, D. (1957). *Advanc. Carbohydrate Chem.* **12**, 189.

HYBL, A., RUNDLE, R. E. & WILLIAMS, D. E. (1965). *J. Amer. Chem. Soc.* **87**, 2779.

PHILLIPS, G. O. & BAUGH, P. J. (1966). *J. Chem. Soc.* A, p. 387.

SENTI, F. R. & ERLANDER, S. (1964). *Non-Stoichiometric Compounds,* p. 588. New York: Academic Press.

THOMA, J. A. & STEWART, L. (1965). *Starch: Chemistry and Technology,* Vol. I, p. 209. New York: Academic Press.

VANETTEN, R. L., SEBASTIAN, J. F., CLOWES, G. A. & BENDER, M. L. (1967). *J. Amer. Chem. Soc.* **89**, 3242.

VANETTEN, R. L., CLOWES, G. A., SEBASTIAN, J. F. & BENDER, M. L. (1967). *J. Amer. Chem. Soc.* **89**, 3253.