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Structure of 9,9,10,10-Tetrachloroanthracene

Abstract. *The crystal structure of 9,9,10,10-tetrachloroanthracene has been determined by x-ray analysis. The structure is characterized by dovetailed packing of crystallographically independent molecules. The anthracene skeletons are planar, and the molecules have approximately* D_{2h} *symmetry. Bond distances and angles are summarized and the stereochemical implications of the results are discussed.*

We have completed the x-ray structure analysis of a tetrasubstituted derivative of anthracene, 9,9,10,10-tetrachloroanthracene. This study is part of a program devoted to analysis of the role played by molecular packing in the electronic properties of solids. Furthermore, this analysis, as well as that of the structure of 10,10-dibromoanthrone (*1*) illustrates the extent to which dihalo-substitution at the carbon No. 9 or No. 10 position of anthracenes may affect the expected conformation.

This compound was prepared by the method of Meyer and Zahn (*2*). Cream-colored crystals (mp 153° to 157°C) were obtained from the reaction mixture. The specimen selected for x-ray study was rod-shaped, 1.27 mm in length, and 0.1 mm in diameter (average).

The crystallographic data are: $a = 10.93$ Å, $b = 13.90$ Å, $c = 9.89$ Å, $\beta = 116.25°$; monoclinic; space group $C2/m$; $Z = 4$; molecular weight = 317.80; density (obs.), 1.55 g/cm^3; density (calc.), 1.56 g/cm^3; linear absorption coefficient, μ (CuKα) = 76.53 cm^{-1}, μ (MoKα) = 8.67 cm^{-1}.

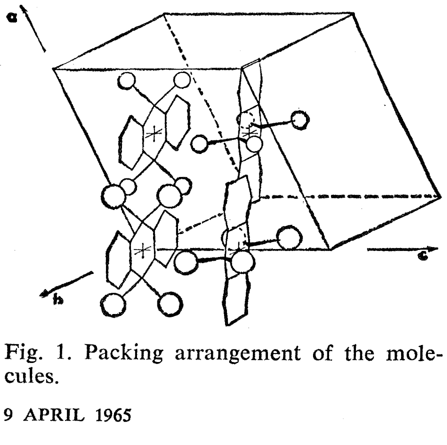

Fig. 1. Packing arrangement of the molecules.

The structure was solved by inspection of a sharpened three-dimensional Patterson function. Despite the presence of well-resolved heavy-atom interactions in this function, the solution was somewhat complicated by the usual space-group ambiguity among $C2/m$, $C2$, and Cm, and by unusual occupancy of special positions. The centers of the four molecules in the unit cell occupy two sets of twofold special positions of point-group symmetry $2/m$; namely positions $2a$ and $2c$ of space group $C2/m$ (No. 12).

A refinement of the structure based on 791 reflections has led to an R factor of 13.6 percent. The parameters involved in the refinement were position and anisotropic thermal parameters for all atoms and one scale factor. Figure 1 illustrates the arrangement of the four molecules whose centers lie at 0,0,0; ½,½,0; 0,0,½; and ½,½,½. These molecules are positioned so that the carbon skeletons are all nearly perpendicular to the c-axis direction. Neighboring molecules are turned, with respect to each other, by 90 deg about the c-axis direction. As a result, chlorine atoms from each molecule "nest" in the terminal rings of adjacent molecules and form infinite rows along the c-axis.

Figure 2 shows the bond distances and bond angles of the two crystallographically independent molecules. Representative standard deviations are 0.03 Å for the distances and 1.5 deg for the angles. The dimensions of the outer rings of both molecules approximate closely those found for benzene.

Within the experimental error the dimensions of both molecules are identical, the carbon skeletons are planar, and the carbon-atom skeleton is perpendicular to the plane formed by the four chlorine atoms in each molecule. Thus the molecule approximates very closely the symmetry of three mirror planes intersecting at right angles (D_{2h}), even though this condition is not demanded by the symmetry constraints of the space group.

The planarity of the carbon framework represents a strained form of the cyclohexa-1,4-diene ring in the center of the molecule. This conformation tends to relieve tight intramolecular contacts between the chlorine atoms and the hydrogen atoms at the 1 : 8 and 4 : 5 anthracene positions (*3*). For the present compound, these contacts are about 2.9 Å, only slightly shorter than the sum of the van der Waals radii, 3.0 Å. On the other hand, tentative results on 10,10-dibromoanthrone (*1*) indicate a slight buckling of the carbon framework, presumably a result of the greater halogen-halogen repulsions in this molecule as compared to tetrachloroanthracene.

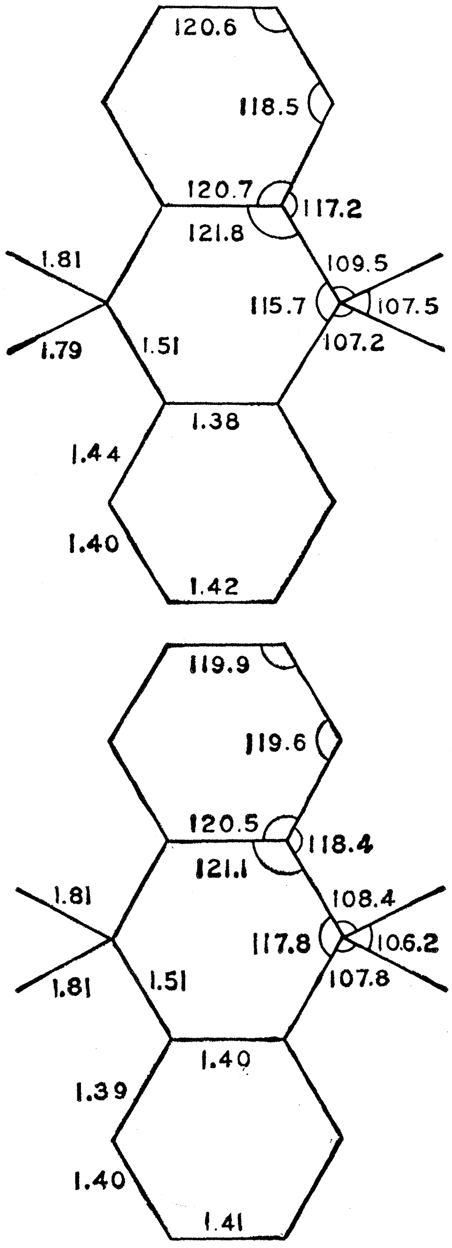

Fig. 2. Bond distances (Å) and bond angles (deg) for 9,9,10,10-tetrachloroanthracene.

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References and Notes

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4. We are indebted to Dr. T. K. Mukherjee of this laboratory for synthesizing the compound and to P. Connolly for estimating the intensity data.

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A Clathrate Crystalline Form of Silica

Abstract. *The low-density cubic form of silica (impure), melanophlogite, has a clathrate-type structure that incorporates organic molecules, including long straight-chain hydrocarbons. The structure is analogous to that of the clathrate crystalline hydrates of composition $6X \cdot 46H_2O$ or $8X \cdot 46H_2O$. This is the first known example of a silicate framework structure with the pentagonal dodecahedron as a framework element.*

The structures of forms of ice (*1*) are of interest in relation to the polymorphs of silica because of the strong tendency for both SiO_2 and H_2O to form tetrahedrally linked framework structures. The structural analogy between ordinary ice (ice I) and tridymite is well known. Some of the better-characterized crystalline phases of H_2O and SiO_2, together with their densities relative to the corresponding forms ice I and tridymite, are compared in Table 1. The arrow symbol shows which pairs of polymorphs actually are structural analogs. The significance of the relationships in Table 1 will be discussed more fully elsewhere, but I wish to call attention here to an interesting comparison between the bottom pairs of entries in the table.

The low-density form of silica, melanophlogite, has been studied by Skinner and Appleman (*2*), who report the x-ray crystallographic data listed in Table 2. The least-dense ice-like phases available for structural comparison are the fully hydrogen-bonded crystalline hydrates (*3*, *4*), of which one type, the 12-Å gas hydrate of composition $6X \cdot 46H_2O$ (with X = CH_4, H_2S, CO_2, SO_2, . . .), is listed in Table 1. I wish to show that published x-ray data support the idea that melanophlogite is the structural analog of the 12-Å crystalline hydrate.

Structural data for a typical 12-Å hydrate (*5*), $6Cl_2 \cdot 46H_2O$, are shown in Table 2 for comparison with melanophlogite. Both are cubic, and the ratio of cell sizes 13.40/11.92 (= 1.13) is very close to the ratio 3.09/2.76 (= 1.12) between the Si—Si distances in β-tridymite and the $H_2O—H_2O$ distances in ice I (Table 2). The space group reported (*2*) for melanophlogite, $P4_232$, is simply a subgroup of the space group of chlorine hydrate, $Pm3n$ (complete symbol $P4_2/m32/n$), obtained from the latter by dropping the mirror planes. Thus a tetrahedrally linked SiO_2 framework of the size and symmetry required for melanophlogite, with Si—Si distances close to the value 3.1 Å that occurs in the common polymorphs of silica, may be constructed. A degradation in symmetry, as from $Pm3n$ to $P4_232$, would not be unexpected; it is a familiar feature in silica polymorphs, represented by the nonquenchable high-low (β to α) transitions, in which slight structural distortions apparently improve the bond angles in the structure at the expense of some of the symmetry elements of the high-temperature forms (*6*).

The proposed hydrate-analog structure for melanophlogite indicates 46 units of SiO_2 per unit cell, instead of the 48 reported by Skinner and Appleman (*2*). The difference between these figures arises because Skinner and Appleman did not take into account the content of sulfur and organic compounds present in the melanophlogite crystals; they argued instead that "the organic pigment is mechanically included in the crystals and does not affect the crystal structure of melanophlogite." In view of the hydrate analog, the foreign constituents, which invariably make up 7.7 to 12 percent by weight of the crystals (*2*), are essential structural elements, playing the same stabilizing role in filling the large open cavities in the melanophlogite structure that the molecules CH_4, SO_2, H_2S, and others play in the 12-Å crystalline hydrates. Both structures are in this sense clathrates, and the somewhat variable content of the guest constituents in melanophlogite is accordingly understandable. If the unit cell contains 46 units of SiO_2 plus a guest contribution in proportion to the weight fraction of foreign constituents to SiO_2 reported in the analysis by Skinner and Appleman (*2*), the calculated density of melanophlogite is 2.06 g cm^{-3}; this value is in better agreement with the measured density 2.05 ± 0.013 g cm^{-3} than the value 1.99 calculated (*2*) on the basis of 48 units of SiO_2 per unit cell, with no foreign constituents.

Table 1. Partial list of H_2O and SiO_2 polymorphs.

H_2O				SiO_2		
Form	Cryst.	ρ/ρ_{ice}		Form	Cryst.	$\rho/\rho_{tridymite}$
Ice VII	cubic	1.82		stishovite	tetrag.	1.95
Ice V	monocl.	1.34		coesite	monocl.	1.33
Ice II	hex.	1.27		α-quartz	hex.	1.20
Ice III	tetrag.	1.24*	←→	silica K	tetrag.	1.14
Ice Ic	cubic	1.00	←→	β-cristobalite	cubic	1.00
Ice I	hex.	1.00	←→	β-tridymite	hex.	1.00
$6X \cdot 46H_2O$	cubic	0.90†	←?→	melanophlogite	cubic	0.86†

* The symbol ←→ designates pairs of structurally analogous polymorphs. † Framework density only. Hex, hexagonal; tetrag, tetragonal; mono, monoclinic.

The guest material in the analyzed sample (*2*) consists, per unit cell, of about 2 atoms of sulfur, 3 of carbon, 6 of oxygen, and 24 of hydrogen. The actual chemical form in which this material is incorporated into the crystals is not known, but spectroscopic measurements (*2*) indicate that abundant hydrocarbons are present, as well as H_2O and CO_2. There are conflicting indications whether the sulfur is present as H_2S, SO_2, SO_3, or perhaps bonded to the organic constituents. If the species present were SO_2, H_2O, and CH_4, there should be only 16 H atoms per unit cell, which is somewhat too few. The number of guest molecules per unit cell would be 7, one less than the number of polyhedral cavities available in the hydrate-analog clathrate structure (*5*, *7*). All of these molecules are small enough to fit easily into the six larger polyhedral cavities in the structure (tetrakaidecahedra, free diameter 5.8 to 6.8 Å, depending on degree of bending of the Si—O—Si linkage); and H_2O, CH_4, or H_2S could also fit easily into the two smaller cavities (pentagonal dodecahedra, free diameter 4.4 to 5.8 Å).

The spectroscopic evidence (*2*) suggests that hydrocarbons of various sizes are present, and the yellow to brown color of many of the crystals suggests incorporation of long-chain conjugated