X-Ray Studies of Three Crystalline Fluorocarbons Showing Rotational Disorder

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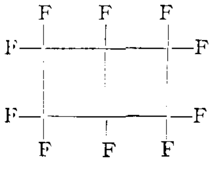
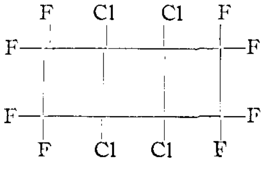
We have carried out X-ray investigations of three fluorocarbons believed to contain cyclobutane ring systems and find in each case that "molecular rotation" exists in the crystalline phase stable just below the melting point. Professor W. T. Miller kindly supplied samples of four related fluorocarbons, $C_4Cl_4F_4$, C_6F_{10}, $C_8Cl_4F_8$ and C_8F_{12}. Conditions of synthesis suggest that C_6F_{10}[1] is a bicyclohexane and that $C_8Cl_4F_8$[2] and C_8F_{12}[3] are tricyclooctanes as indicated by the formulas





The $C_4Cl_4F_4$ is known to be 1,2,3,4-tetrachlorotetrafluorocyclobutane, but may contain one or more of the four possible isomers. The high temperatures used during synthesis[4] may have induced molecular rearrangement (if required) to give predominantly the most stable isomer, presumably the isomer in which two halogen atoms of the same kind attached to any two adjacent carbon atoms are *trans* to one another. Of the four compounds listed only C_8F_{12} does not show rotational disorder in the crystal. A one-molecule triclinic unit of space group $P\bar{1}$ or P1 has been established by other workers in this Laboratory, but attempts to determine the atomic arrangement are thus far unsuccessful.

At room temperature $C_4Cl_4F_4$, C_6F_{10} and $C_8Cl_4F_8$ are clear, colorless, volatile solids, the first two being especially soft materials commonly formed into adhesive masses. At one atmosphere the liquid ranges given for $C_4Cl_4F_4$ and C_6F_{10} are, respectively, 42.3 ± 0.3 to 130.1 ± 0.2°, and 40–41°. The triple point of $C_8Cl_4F_8$ seems to be above one atmosphere; a sublimation vapor pressure of 740 mm. at 164° is given. All three materials behave chemically as saturated compounds of relatively high thermal stability.

Experimental

Samples of all three materials were introduced into thin-walled Pyrex capillary tubes by sublimation under vacuum, the tubes then being sealed off. By choosing for each substance an appropriate working temperature range within which a temperature gradient along the tube was maintained, a single crystal completely filling one end of the tube could be grown by sublimation. Cylindrical specimens of the desired radii and of more than adequate length could be grown in this way. It was possible also to prepare a satisfactory powder specimen of the least volatile compound, $C_8Cl_4F_8$.

Our data were derived mostly from single crystal photographs, the Weissenberg equi-inclination technique playing the major role. For each substance photographs were taken with two or more orientations of the crystal, and Laue and precession techniques also were employed in careful checks of the X-ray symmetry class. Except for the Laue photographs, characteristic CuKα radiation filtered through nickel foil was used. As the cylindrical specimens proved to be either optically isotropic or uniaxial, grew in the tubes without obviously preferred orientations, and displayed no developed faces, the problem of accurately orienting specimens had to be solved by X-ray methods alone. A rather efficient procedure which appears to have some new features was developed to this end and will be reported elsewhere.

Qualitative flotation experiments to set upper and lower limits to the density were carried out for each compound, thereby facilitating the determination of the number of molecules within the unit cell. We did not attempt to determine highly accurate values for the lattice constants of the cells given by the X-ray patterns. However, we did make some very long exposures in a search for reflections which might require larger cells or which might be significant in selecting the most probable space group.

Results and Discussion

Some general results applying to all three compounds are given first. Intensities of Bragg reflections fall off extremely rapidly with increasing angle of scattering. Despite very long exposures the maximum values of the Bragg angle θ corresponding to recorded reflections are: $C_8Cl_4F_8$, 40°; C_6F_{10}, 30°; and $C_4Cl_4F_4$, 25°. The Bragg reflections appear against unusually strong backgrounds of diffuse scattering which tend to develop into definite patterns. For $C_4Cl_4F_4$ and C_6F_{10} especially, diffuse spots accompany most or all of the Bragg reflections of fair intensity. For the latter compound certain reciprocal lattice points appear to be joined as surfaces of diffuse scattering, although the intensity remains larger in the neighborhood of a Laue maximum. Three such surfaces, reflecting the hexagonal symmetry of the crystal, were recognized. A further description of the thermally diffuse scattering will not be attempted as details of these patterns are significant only when recorded with an experimental refinement beyond that we have used.

Data characteristic of the individual compounds follow.

$C_4Cl_4F_4$.—The unit cell of $C_4Cl_4F_4$ is body-centered cubic with a = 7.95 ±0.10 Å., and contains two molecules to give a calculated density of 1.75 g./cc. The Laue symmetry class is the highest possible, O_h-m3m, and the probable space group[5] is restricted to the set without special criteria, Im3m, I432 and $I\bar{4}3m$, with, in our case, the respective minimum molecular symmetries of m3m, 43 and $\bar{4}3m$.

$C_8Cl_4F_8$.—The unit cell of $C_8Cl_4F_8$ is face-centered cubic with a = 11.07 ± 0.10 Å., and contains four molecules to give a calculated density of 1.92 g./cc. The Laue symmetry class is m3m, and the probable space group[5] is limited to one of the set Fm3m, F432 and $F\bar{4}3m$ with required molecular symmetries (one molecule per lattice point) of m3m, 43, $\bar{4}3m$. The group $F\bar{4}3m$ might be considered less probable as freely grown crystals are octahedra of quite uniform face development.

C_6F_{10}.—The unit cell of C_6F_{10} is hexagonal with a = 6.95 ± 0.10, c = 11.2 ± 0.10 Å., (c/a = 1.61 as compared with 1.63 for hexagonal closest packing of spheres), and contains two molecules to give a calculated density of 1.86 g./cc. The Laue symmetry is 6/mmm, and the probable space group[5] is

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[1] A. H. Fainberg and W. T. Miller, private communication.

[2] F. W. McLafferty, Doctoral Thesis, Cornell University, 1950.

[3] M. Prober and W. T. Miller, This Journal, 71, 598 (1949).

[4] R. T. Carroll, Doctoral Thesis, Cornell University, 1952.

[5] "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1952, Vol. I.

one of the set P62c, P6_3mc and P6_3/mmc requiring the glide plane vanishings {*hh.l*} for *l* odd. No such reflections were observed, but a total of only 21 forms of all types could be recorded. However, a threefold axis (and additional symmetry) will be required of the molecule in any case.

Rigorous application of space group theory requires every atom to have a single equilibrium position; assuming further only that discrete molecules of the assigned composition exist in the crystals we arrive at the following conclusions. No discrete molecule having just four atoms of one kind, *e.g.*, 4Cl in $C_4Cl_4F_4$ or $C_8Cl_4F_8$, can have the symmetry of m3m or 43. Further, no molecule $C_4Cl_4F_4$ or $C_8Cl_4F_8$ of chemically reasonable nature can meet the requirements of $\bar{4}3m$; in particular, neither a cyclobutane nor a tricyclooctane framework, however distorted, can do so. Nor does it seem possible to devise a configuration with threefold symmetry which is also chemically plausible for a molecule C_6F_{10}. Certainly the bicyclohexane framework cannot have a threefold axis.

We conclude that for all three substances the molecules in the crystal must have sufficient rotational mobility to give the observed diffraction symmetries as statistical averages over groups of cells containing molecules in various orientations. Previously cited data on the Bragg intensities, the diffuse background scattering, and the physical properties of the crystals support this conclusion. However, the "molecular rotation" cannot be unhindered as is shown by direct experimental evidence of the following sort. Were the rotation entirely "free" the effective electron density in the molecule would be independent of angular variables, *i.e.*, be spherically symmetric, and the reflection intensity would be determined by the value of the quadratic form. But, for example, in $C_8Cl_4F_8$ (333) has several times the intensity of (511), and (551) is far more intense than (711). A slightly different analysis applies to the several possibilities for placing two molecules of C_6F_{10} within the hexagonal unit. Unrestricted rotation of the molecule about the threefold axis (cylindrically symmetric electron density) would in every case require a characteristic extinction of certain reflections which are experimentally recorded. The existence of a restricting potential of appropriate symmetry can scarcely be doubted; the strong coupling of rotation with lattice vibrations is indicated.

We have not attempted to calculate Bragg intensities from an assumed model. Except possibly for $C_4Cl_4F_4$, our lack of definite knowledge of the equilibrium molecular configurations makes the problem a poor choice for study of molecular rotation; and, in contrast with the diffuse background, the Bragg intensities are not sufficiently sensitive to details of the model to promise a strong case for a particular assumed configuration. The simplest case of $C_4Cl_4F_4$ is probably quite complex. Assuming that we have the stable isomer and that the cyclobutane ring is markedly puckered as in C_4Cl_8[6] and C_4F_8[7] to give a molecule of symmetry D_{2d}, there are two alternative configurations to be considered. The four chlorine and the four fluorine atoms give two bisphenoids having a common center, the one elongated the other flattened along the unique axis. Probably there are two not very different minima in the molecular energy corresponding to the assignment of chlorine atoms to one or the other bisphenoid. The packing shapes of the two configurations, as formulated by analogy with C_4Cl_8 and C_4F_8, are quite different. Either gives easy packing relations within the unit cube for many but not for random orientations of adjacent molecules. Perhaps inversion of molecular configuration between the two extremes plays an important role in the mechanism of "rotation" in the crystal; a further study utilizing data from the purified isomer might be quite profitable.

Based upon the formulas with condensed rings for C_6F_{10} and $C_8Cl_4F_8$, packing models having an assumed angle of folding of 120° between rings sharing an edge (with or without puckering of the individual rings) appear to give packing relations within the respective cells much like the case of $C_4Cl_4F_4$; certain molecular orientations give easy packing relations, but reorientation must involve a coöperative mechanism. We may conclude that the bond diagrams suggested by the methods of synthesis are not inherently improbable in terms of our structural data.

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[6] T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

[7] H. F. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 1952).

Studies in Low Concentration Chemistry. VIII. Some Properties of Tracer Yttrium, Antimony and Silver in Solution

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The purpose of these experiments was to investigate the radiocolloidal properties of several ions in very low concentration solutions. Yttrium-90, antimony-125 and silver-111 were used as tracers.

Experimental

Solutions.—Solutions of yttrium-90 0.01 *N* in hydrochloric acid and silver-111 0.01 *N* in nitric acid were prepared by previously reported methods.[1] A solution of antimony-125 0.01 *N* in hydrochloric acid was prepared by dilution of a stock solution obtained from the Oak Ridge National Laboratory. The concentrations of the yttrium and silver solutions were established as below 10^{-8} *M* and about 10^{-8} *M* by spectrographic analysis,[2] and the concentration of the antimony was established at about 10^{-7} *M* by a microchemical test by Feigl.[3]

Techniques.—Adjustments of *p*H, sample preparations, radioactivity measurements, as well as filtration, centrifugation and adsorption techniques have been described in a previous paper.[4] The main difference in procedure is that

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[1] G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953); G. K. Schweitzer and J. W. Nehls, *ibid.*, **74**, 6186 (1952).

[2] Private communications from J. H. Gillette, Oak Ridge National Laboratory, and T. DeVries, Purdue University.

[3] F. Feigl, "Laboratory Manual of Spot Tests," Academic Press, Inc., New York, N. Y., 1943.

[4] G. K. Schweitzer and W. N. Bishop, THIS JOURNAL, **75**, 6330 (1953).