

explanation of our observations and those of other workers.^{6,16}

Acknowledgment.—We are grateful to Professor A. Burlingame and to Sherri Firth for the oxygen-18 determinations, and to Dr. M. J. Jorgenson for many helpful and stimulating discussions.

(16) The transfer of a proton from the hydroxyl to the carbonyl group of benzoic acid in methanol is dependent on the square of methanol concentration. This has been interpreted in terms of a cyclic transition state where the proton transfer occurs through two hydrogen-bonded methanol molecules: E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

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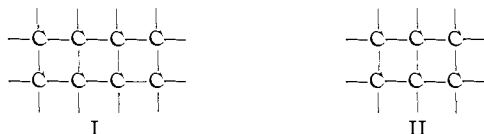
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The Configuration of C_8F_{12} , a Saturated Dimer of Hexafluorobutadiene

Sir:

The synthesis of a fully saturated dimer of hexafluorobutadiene was reported some years ago.¹ A two-step thermal reaction beginning with hexafluorobutadiene resulted in a volatile solid which melted at 40° and boiled at 80°. The related fluorocarbons $C_8Cl_4F_8$ and C_8H_{10} were also synthesized by Miller.² It was suggested on the basis of the conditions of the syntheses that the carbon skeletons for these compounds may be



X-Ray diffraction photographs of $C_8Cl_4F_8$ and C_8F_{10} were very suggestive of considerable disorder in these crystals.³ The intensities of Bragg reflections fell off extremely rapidly with increasing angle of scattering. On the other hand, a full sphere of X-ray data using Cu K α radiation was obtained for C_8F_{12} . The material crystallizes in the triclinic system with unit cell dimensions $a = 6.02$, $b = 6.29$, $c = 7.27$ Å., $\alpha = 103.6^\circ$, $\beta = 107.9^\circ$, $\gamma = 106.4^\circ$ and contains one molecule per unit cell. The density is computed to be 2.29 g./cm.³. Statistical tests on the X-ray data strongly indicated a centrosymmetric cell. Phases determined by the symbolic addition procedure⁴ led to an electron density map which could be satisfied only by a disordered structure. A satisfactory least-squares refinement was obtained with an acentric molecule which may reverse direction at random from cell to cell, giving rise to an approximate centrosymmetric average cell. The R -factor is 17.7% and the bond lengths and angles are reasonable. A complete description of the structure determination of C_8F_{12} will be published elsewhere.

The carbon skeleton of the C_8F_{12} molecule is not in the form of the three-ring system shown in I, but rather has two bridge bonds to form four-membered and five-membered rings (tricyclo[3.3.0.0^{2,6}]octane). The sym-

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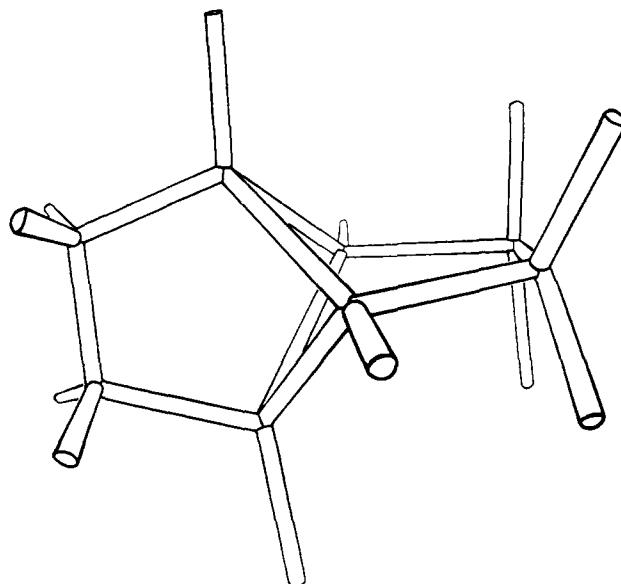
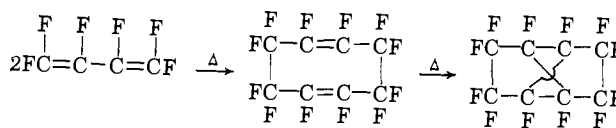


Fig. 1.—Model for the bonding pattern in C_8F_{12} shown in perspective. The principal axis of the molecule, a fourfold axis of rotary reflection (or rotary inversion), runs from left to right in the diagram.

metry of the molecule is D_{2d} . The stereochemical nature of the bonding pattern is displayed in the perspective drawing of Fig. 1.

The C_8F_{12} molecule is very compact and ellipsoidal in shape which accounts for its very high density. Its high volatility can be associated with its low surface area. Both the configuration and physical properties can be compared with those of adamantane⁵ and twistane.⁶ In C_8F_{12} it is interesting to note that the average C–F bond length for one fluorine atom attached to a carbon atom is 1.367 Å. as compared to 1.326 Å. for the average C–F when two fluorine atoms are attached to a carbon atom. This is in agreement with results obtained from electron diffraction studies of the vapors of fluorocarbons, where monofluorides have an average value of 1.38 Å. for the C–F whereas the average value for C–F in polyfluorides is 1.33 Å.⁷

In view of the configuration (Fig. 1), the chemical reactions which led to the synthesis of C_8F_{12} may perhaps be



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