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Molecular Structures of Dodecafluoro-*n*-Pentane, Hexadecafluoro-*n*-Heptane and Dodecafluoro-Isopentane

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During the last years many chemists have focused their attention on the fluorocarbons, partly because of their industrial importance, but also because of their interesting similarities to the hydrocarbons.

The low scattering power of the hydrogen atom makes electron diffraction studies of the hydrocarbons difficult, and in many cases important details of the structures are lost. This difficulty does not occur with fluorocarbons, and we have therefore found it worth while to study some of these compounds. Results of earlier investigations of some ring fluorocarbons have already been published[1]. This paper deals with three open-chain aliphatic perfluorocarbons.

Dodecafluoro-*n*-pentane

The $\frac{\sigma(r)}{r}$ curve obtained for this molecule using the electron diffraction method with a rotating sector is shown in Fig. 1. The peaks which are important for determining the structure are numbered with Roman numerals. Peak I, occuring at 1.38 Å, is mainly caused by the C-F bond distance; this peak is very little influenced by the C-C bond distance.

Peak II is composed of contributions from distances of the type $F_1—F_1'$ and $C_1—F_2$. The position of the maximum is in agreement with the assumption of tetrahedral symmetry around the carbon atoms. Peak III and IV are caused by distances of the type $F_1—F_2$ and $C_1—F_3$. The heights of the peaks and their positions indicate that no free rotation occurs about the C—C bond. Fluoro atoms linked to neighbouring carbon atoms must be either in the trans-position or in the so-called "gauche" position. However, it is clear that we are by no means dealing with a rigid molecule for which peak III would be about twice as high as peak IV. Sterically hindred rotation about the equili-

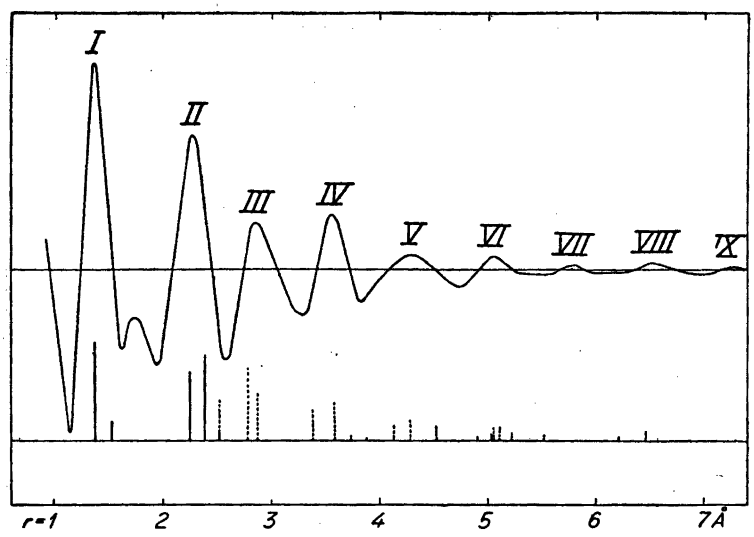

Fig. 1. $\frac{\sigma(r)}{r}$ *-curve of dodecafluoro-n-pentane.*

brium position would be expected to diminish the heights of both peaks, but would have more influence on the peak due to "gauche" F—F distances. A detailed study of the relative heights and shapes of these two peaks might have yielded quantitative information about the amplitude of the restricted rotation about the C—C bonds. The reason, why we did not undertake such a study is because we were afraid of overestimating the method in its present state. We do feel, however, that discussions of the type indicated might be satisfactorily carried out in less complex cases.

Peaks V—IX are of significance for the shape of the carbon skeleton as a whole. The line diagram under the $\frac{\sigma(r)}{r}$ curve corresponds to a rigid molecule with a planar carbon skeleton. This model seems to explain the experimental curve satisfactorily, particularly when allowance is made for vibrations. The following additional models giving a satisfactory fit with the four inner peaks of the $\frac{\sigma(r)}{r}$ curve, have been studied:

1) Carbon atoms C_1, C_2, C_3 and C_4 lie in one plane, and the plane containing C_3, C_4 and C_5 is rotated 60° out of this plane.
2) The carbon atoms C_2, C_3 and C_4 lie in one plane, and the C_1 and C_5 atoms are rotated out of the plane in *opposite* directions.

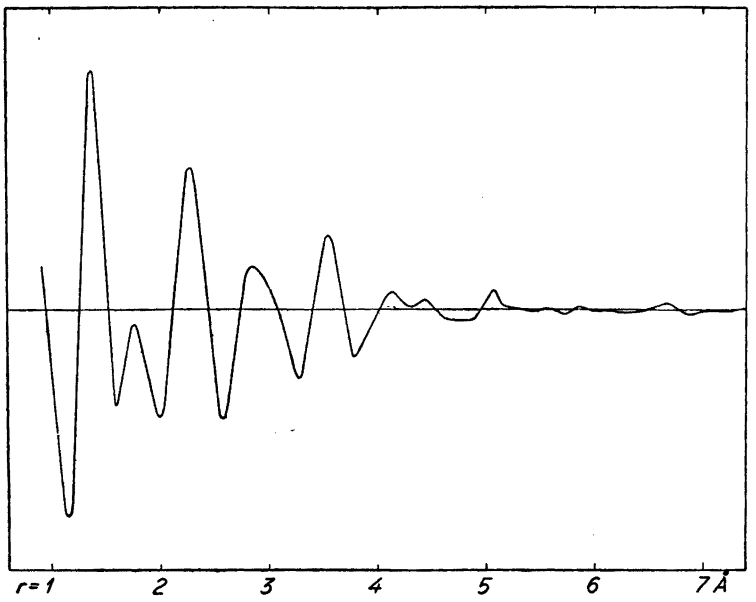

Fig. 2. $\frac{\sigma(r)}{r}$ *-curve of hexadecafluoro-n-heptane.*

3) Like 2), but the atoms C_1 and C_5 are rotated out of the plane in the *same* direction.

None of these three models gave very good agreement with the outer part of the experimental $\frac{\sigma(r)}{r}$ curve. We therefore concluded that a planar model is most probable. The possibility of an equilibrium between the planar model and a certain proportion of model 1) and/or 2) cannot, however, be excluded, and is indeed probable from other evidences [2]. (Model 3 is excluded of steric reasons.)

Hexadecafluoro-*n*-heptane

Fig. 2 shows the $\frac{\sigma(r)}{r}$ curve obtained for hexadecafluoro-*n*-heptane. The form of the curve is very similar to that obtained for perfluoro-*n*-pentane, and C—F bond distance is found to be the same as in that compound, *viz.* 1.38 Å. No deviation from the tetrahedral angle is found. The striking similarity between the two $\frac{\sigma(r)}{r}$ curves of Fig. 1 and Fig. 2 suggested that there must be similarities in the two structures. A detailed study shows that here,

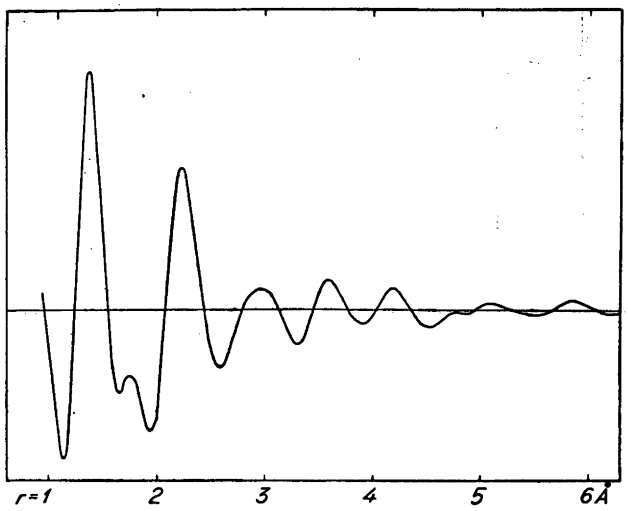

Fig. 3. $\frac{\sigma(r)}{r}$*-curve of dodecafluoro-isopentane.*

as before, the model containing a planar zigzag carbon skeleton is in very good agreement with the $\frac{\sigma(r)}{r}$ curve. Other models, analogous to those mentioned for the dodecafluoro-*n*-pentane, have been studied, but none of them agree satisfactorily with the $\frac{\sigma(r)}{r}$ curve. Once again the possibility of a mixture, consisting mainly of the structure with the planar zigzag carbon skeleton together with contributions from non planar structures, cannot be excluded.

Dodecafluoro-isopentane

As might be expected the $\frac{\sigma(r)}{r}$ curve of dodecafluoro-isopentane (Fig. 3) differs in several details from those of the two compounds already discussed. However, the similarities are still very striking. The C—F bond distance of 1.38 Å, the presence of tetrahedral angles, and the trans configuration of the fluorines are easily verified. Two models were considered:
1) The carbon atoms C_1, C_3, C_4 and C_5 lie in one plane. (Fig. 4), 2) The carbon atoms C_1, C_3 and C_4 lie in one plane, C_2 and C_5 lie in a parallel plane.

It was found that the first model gave the better agreement with the experimental $\frac{\sigma(r)}{r}$ curve.

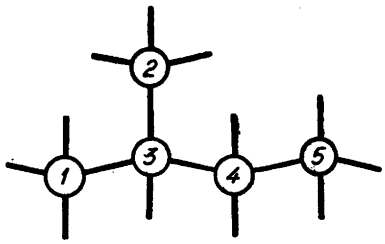

Fig. 4. Dodecafluoro-isopentane.

We have tried to estimate, in each case, the stability of the various alternative models by consideration of the van der Waals forces between non-bonded atoms. Our conclusions support the results of the electron diffraction investigation.

SUMMARY

The structures of dodecafluoro-*n*-pentane, hexadecafluoro-*n*-heptane and dodecafluoro-isopentane have been studied by the electron diffraction sector method. In all the three cases the C—F bond distance is found to be 1.38 Å. No attempt of precision assignment of the bond lengths have been made. The most stable forms of the molecules are found to be those with zigsag carbon skeletons. There is restricted rotation about the C—C bonds.

Samples of the three compounds in a high state of purity were placed at the disposal of our laboratory by Professor G. H. Cady, of the University of Washington, Seattle, and we wish to express our gratitude to him. We also want to thank the Head of the Department Professor O. Hassel for his encouraging interest in our work.

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