[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

On the Spatial Configuration of Perfluorocyclobutane

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In recent years some question has arisen concerning the spatial configuration of simple cyclic compounds. Thus electron diffraction data[1] would seem to indicate a planar ring for cyclopentane while third law studies[2] seem to favor a non-planar ring. The Raman and infrared spectra of cyclobutane[3] have been interpreted as indicating a planar model. The extreme stability, even for a fluorocarbon, of perfluorocyclobutane, together with the larger size of the fluorine atom, makes this molecule of special interest in this connection.

It is the purpose of this communication to show that the Raman and infrared spectra of perfluorocyclobutane indicate a planar ring. Additional support of this contention is found in the spectrum of cyclic C_4F_7Cl as well as in a heat capacity measurement for the former compound.

Experimental Details

The investigation of the Raman spectrum was made with a Hilger E-2 spectrograph having a dispersion of 35 Å./mm. at 4400 Å. Illumination was provided by four vertical mercury arcs whose temperature was maintained so low that little continuous background was observed. The light scattered from the vertical Raman tube was passed through a 90° prism and focused on the spectrograph slit with an achromatic lens of 15 cm. focal length.

The samples, which were furnished by the Jackson Laboratory of E. I. du Pont de Nemours and Co., were condensed in Raman tubes of 15-cc. capacity by Dry Ice and acetone; the spectrum was determined in the liquid state at 25–30°. The time of exposure varied between ten and one hundred and twenty-seven hours, about eighty hours being required for a "complete" spectrum. Eastman Kodak Co. spectrographic plates, type 103-0, were used. Qualitative polarization data were obtained for the stronger lines with Polaroid filters. Eleven lines were observed; the values found, together with their estimated intensities and state of polarization where known, are: 192 cm.$^{-1}$, w; 267, S-, dp; 358, S, p; 437, S, dp; 608, w; 651, w; 700, S, p; 1006, m, (dp?); 1215, m; 1278, m-; 1425, m.

The infrared spectrum from 2 to 15 μ was measured by Dr. J. R. Downing of the Experimental Station of E. I. du Pont de Nemours and Company. Four strong bands are found at 964, 1240, 1290 and 1340 cm.$^{-1}$, the last two being very similar in shape and intensity.

Discussion of Results

In attempting to draw conclusions concerning the structure of perfluorocyclobutane the experimental results have been compared with those expected for several models, such expectations being obtained by the usual group theoretical methods. The planar ring model of symmetry D_{4h} alone is in harmony with all the experimental data, the comparison being found in Table I. A possible difficulty is encountered in the number of strong infrared bands. In the region in which the four bands are found one is led to expect three fundamental vibrations—one CF_2 wagging vibration and two C–F stretching vibrations. An explanation lies in the assumption that this is a case of resonance splitting, the fundamental in the neighborhood of 1315 cm.$^{-1}$ interacting with the combination $358 + 964 = 1322$ cm.$^{-1}$. The fact that three infrared active vibrations are then missing is in agreement with the model since the expected magnitude places them beyond 15 μ.

In the similar molecule cyclic C_4F_7Cl all vibrations are infrared active, and one should find seven C–F vibrations and four CF_2 (or CFCl) wagging motions in the same region of the spectrum in which they are found in C_4F_8. Experimentally ten strong bands are observed in this region (6.7–11.5 μ), one of which is extremely broad and must be at least two bands.[4] This is an important point since in several other models the results lead one to expect only the seven C–F vibrations here.

Perhaps the most difficult model to eliminate has a square ring which defines a plane of symmetry and identical diagonal but differing adjacent CF_2 groups, *i. e.*, symmetry D_{2h}. As can be seen in Table I the agreement between expectations and experimental results is not nearly as satisfactory. Most significant is the large discrepancy between the infrared active fundamentals and the number of strong bands observed. It is unlikely that these "missing" bands should all lie beyond 15 μ, for such an assumption results in a heat capacity which is definitely larger than that found. Moreover, it fails to account for the large number of strong bands observed in the infrared spectrum of cyclic C_4F_7Cl between 850 and 1450 cm.$^{-1}$. The alternate possibility that only four of the bands expected between 2 and 15 μ should be strong enough to be classed as fundamentals on the basis of intensity considerations is equally unlikely.

The most plausible model with a puckered ring has the symmetry V_d. Table I also contains a comparison of the experimental results with the

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(1) Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937); Wierl, *Ann. Physik.*, **13**, 453 (1932).

(2) Aston, Fink and Schumann, THIS JOURNAL, **65**, 341 (1943).

(3) Wilson, *J. Chem. Phys.*, **11**, 369 (1943).

(4) To be published later.

group theoretical predications. It is apparent that much less agreement is found here than for the previous case. A number of other models have been considered including those of symmetry C_{2v}, C_{2h}, C_2, C_s and C_1. The differences for the most part are even more than for the V_d model and in no case less than those for the D_{2h} model.

TABLE I

COMPARISON OF EXPERIMENTAL RESULTS WITH EXPECTATIONS FOR VARIOUS MODELS

Item	Model V_d	 D_{2h}	 D_{4h}	Found
Raman lines	21	15	11	11
Strong infrared bands	12	13	6	4[a]
Pol. CF_2 deformation vib.	1	2	1	1
I. R. bands not in R.	0	13	6	$\geqslant 2$
R. C–F stretching vib.	6	4	3	4[b]
R. CF_2 wagging vib.			1	
I. R. C–F stretching vib.	4	4	2	4[b,c]
I. R. CF_2 wagging vib.			1	
C_4H_7Cl I. R. bands in region of above two items	7	7	11	11
C_p	~41	~41	~37.8	37.4

[a] 2–15 μ, see text. [b] These lines (bands) are interpreted as C–F stretching vibrations for the V_d and D_{2h} models and as indicated for the D_{4h} model. [c] The extra band is interpreted as resulting from resonance splitting for the D_{4h} model.

A tentative assignment of the observed frequencies to the fundamental modes of motion of the planar ring model (D_{4h}) has been made in Table II on the basis of expected magnitude and polarization data where available. The inactive frequencies and those beyond 15 μ in the infrared have been estimated through comparison with similar active frequencies in cyclic C_4F_8 and cyclic C_4F_7Cl. Not too much accuracy can be expected for them; they reflect only the region of the spectrum where they may be anticipated according to the above assignment.

The heat capacity of this compound was measured by Jackson Laboratory at 42° and constant pressure and was found to be 37.4 cal./deg./mole.[5] A statistical calculation using the frequencies of Table II gives 37.8 cal./deg./mole for C_p at 42°. The agreement is excellent—much better in fact than one has any right to expect, all things considered. It suggests, however, that the model is fundamentally correct.

TABLE II

THE FUNDAMENTAL FREQUENCIES OF OCTOFLUOROCYCLOBUTANE

Class	Selection rule[a]	Description	Frequency[b] cm.$^{-1}$
A_{1g}	R	C–F stretch	1215
		Ring stretch	700
		CF_2 deformation	358
B_{1g}	R	C–F stretch	1278
		In-place ring bending	437
		CF_2 deformation	266
B_{2g}	R	Ring stretch	608
		CF_2 wagging	1006
E_g	R	C–F stretch	1425
		CF_2 twisting	651
		CF_2 rocking	192
A_{1u}	IR	C–F stretch	1240
		CF_2 rocking	(280)
E_u	IR	C–F stretch	1290
		In-plane ring deformation	(470)
		CF_2 deformation	(360)
		CF_2 wagging	964
A_{2g}	ia	CF_2 wagging	(900)
A_{2u}	ia	CF_2 twisting	(590)
B_{1u}	ia	C–F stretch	(1300)
		CF_2 rocking	
		Out-of-plane ring bending	(100)
B_{2u}	ia	CF_2 twisting	(520)

[a] R = Raman active; IR = infrared active; ia = inactive. [b] ( ) means an estimated frequency; see text.

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Summary

The Raman spectrum of perfluorocyclobutane has been determined. These data together with the infrared spectrum between 2 and 15 μ and a heat capacity measurement, as well as the Raman and infrared spectra of cyclic C_4F_7Cl, are in harmony with the planar ring model of symmetry D_{4h}. Difficulties are found in explaining the data on the basis of a number of models of lesser symmetry.

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(5) Private communication.