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THE STRUCTURE OF HEXAFLUOROCYCLOPROPANE

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Abstract—The molecular structure of hexafluorocyclopropane has been determined by electron diffraction in the gas phase. The structural parameters were obtained by applying a least squares program on the experimental molecular intensity: C—C = 1·505 ±0·003A, C—F = 1·314 ±0·001A, and <FCF = 112·2 ± 1·0°. The C—F bond length of hexafluorocyclopropane is in close agreement with the values found in CF_4 and CF_3CF_3. The C—C bond length is about that found in cyclopropane, while the FCF angle of the fluorocarbon is considerably smaller than the HCH angle in the hydrocarbon. The structure of hexafluorocyclopropane shows that the presence of the *gem*-difluoro groups causes a rehydridization of the Walsh or bent bond model sp^2 hybrid carbon AO's to give more nearly sp^3 hybridization. A complete discussion of the above reasoning will be made.

INTRODUCTION

THE molecular structure of hexafluorocyclopropane presents the basis for an interesting study of the effect of electronegativity on the bonding and hybridization in highly strained fluorocarbons. Rehybridization at carbon centers has been proposed by Bent[1] when a substituent is replaced by one with greater electronegativity and that more *p* character tends to be concentrated in carbon orbitals directed toward more highly electronegative groups, such as, e.g. in the replacement of hydrogen by fluorine. It has further been suggested[2] that the replacement of two hydrogens on an sp^2 hybridized carbon by two fluorines causes a rehybridization of the carbon to a state of nearly sp^3 hybridization.

ANALYSIS AND RESULT

The reduced experimental and final theoretical molecular intensity curves are shown in Fig 1. The lower oscillating curve is the difference between them. The refined radial distribution curve and the difference curve between the experimental and theoretical $f(r)$ functions for the best model derived from the least squares analysis are plotted in Fig 2. A D_{3h} symmetry has been assumed to calculate the geometry of hexafluorocyclopropane. The following geometrical parameters were used for the calculations of the molecular geometry: C—C, C—F, and the half value of the non-bonded $F_4{-}{-}{-}F_5$ distance. The structure is shown in Fig 3. The values of all geometrical parameters and the mean amplitudes of vibration were refined by applying a least squares analysis on the reduced molecular intensity. All the geometrical parameters as well as all the mean amplitudes of vibration were allowed to vary. The final values of these parameters were listed in Table 1. The error matrix is reproduced in Table 2. The error limits cited in Table 1 are three times the standard deviations which are the diagonal elements of the error matrix. NO appreciable correlations exist for any pair of parameters.

In Fig 2, the first peak is due to C—F = 1·314A, and C—C = 1.505A. The shoulder of the second peak at 2·181A is contributed by F_4---F_5 which determines the FCF angle. The peak centered at 2·430A is due to C_1---F_6. The rest of the two peaks in the RDR curve are contributed by F_4---F_6 = 2·775A and F_4---F_7 = 3·529A respectively.

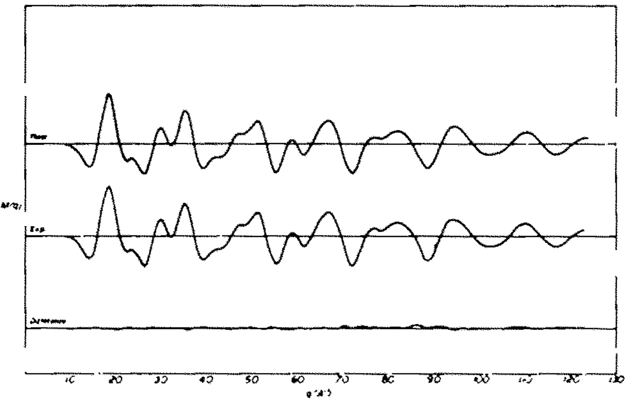

FIG 1. The experimental and theoretical $qM(q)$ curves; the lower oscillating curve is the difference between the theoretical and experimental curves.

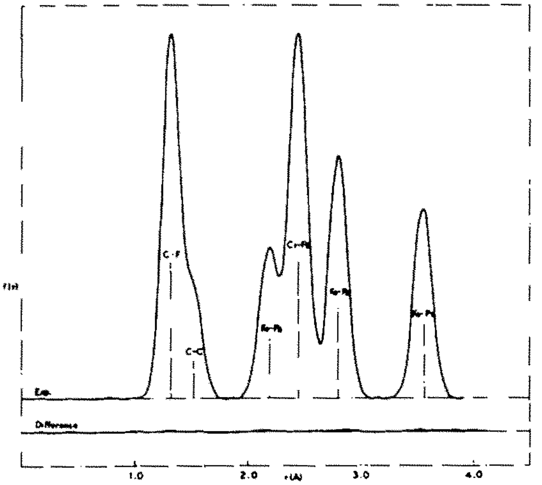

FIG 2. Experimental radial distribution curve and the difference between the experimental and theoretical curves for the best model

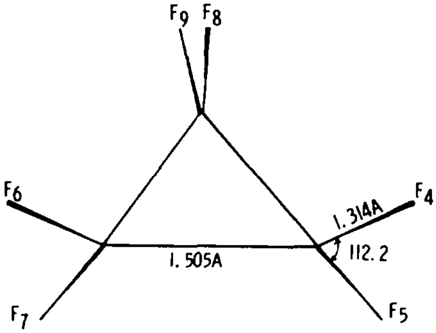

FIG 3. The structure of hexafluorocyclopropane.

DISCUSSION

The structure of hexafluorocyclopropane derived from this study shows various interesting features. The C—C bond length (1·505 ±0·003A) agrees with that in cyclopropane[5] (1·510 ±0·002A) within experimental error. The C—F bond length (1·314 ±0·001A) of this molecule is about the same as those in CF_4 (1·323 ±0·005A)[6] and CF_3CF_3 (1·32 ±0·01A).[7] This value is smaller than the value reported for $CF_2{=}CF_2$ (1·33 ±0·02A)[8] although still within the rather large experimental error for the latter compound. Several other *gem*-difluoro containing compounds have similar C—F values: $CF_2{=}CH_2$ (1·321 ± 0·005A)[9] and F_2CN_2 (1·315 ± 0·004A).[4]

The FCF angle of 112·2° in hexafluorocyclopropane is smaller than the HCH angle (115·1°)[5] in cyclopropane. This value of the FCF angle corresponds to the carbon hybrid AO's[2, 10] forming the C—F bonds having a state of $sp^{2\cdot65}$ hybridization instead of the $sp^{2\cdot36}$ state for cyclopropane. This angle also implies that the two carbon hybrid orbitals used in forming the C—C bonds would have an angle of 107·0°, giving C—C bonds which are bent by 23·5°. The hybridization state for these carbon HAO's would be $sp^{3\cdot42}$ instead of the $sp^{3\cdot95}$ state for cyclopropane. The existence of bent bond orbitals in three-member carbon rings has been experimentally established by x-ray diffraction.[11]

The large strain energy of hexafluorocyclopropane (68·6 kcal/mole)[2] compared to that of cyclopropane (27·5 kcal/mole) seems in large part explainable now that the structure of hexafluorocyclopropane is known. In the case of cyclopropane the C—H bonds are strengthened, relative to an unstrained saturated hydrocarbon, by the rehybridization change and bond shortening while the bent C—C bonds are weakened, the net effect being an increase in strain. For hexafluorocyclopropane the C—F bonds, relative to an unstrained saturated fluorocarbon, would be expected to have similar bond energies to the extent that the C—F bonds of the former are sp^3 hybridized and have similar bond lengths, and weaker with the departure from sp^3 hybridization to sp^2, while the C—C bonds are weakened because of their bent nature. Both of these effects are in the direction of a larger strain energy for hexafluorocyclopropane than for cyclopropane.

The Walsh model of cyclopropane[12] assumes the carbon atoms to be sp^2 hybridized. The Walsh model for hexafluorocyclopropane can be described in terms of each carbon having two $sp^{2\cdot65}$ HAO's used in forming the C—F bonds, an unhybridized p AO and a $sp^{1\cdot21}$ HAO for overlapping in the center of the ring.

A SCF-MO calculation and population analysis for hexafluorocyclopropane will be submitted for publication later.

CONCLUSIONS

The effect on structure of replacing hydrogen with fluorine in a strained 3-membered ring system is seen to be quite striking. Although sp^2--sp^5 hybridization serves as a simple model of the bonding in the bent description of cyclopropane this work bears out earlier predictions that hexafluorocyclopropane should be more nearly sp^3 hybridized.

EXPERIMENTAL

Sectored electron diffraction patterns were taken with a 70 kv electron beam at two sample-to-plate distances of 251·8 and 124·6 mm. The sample was kept at 0° during scattering. MgO diffraction patterns were recorded concurrently to establish the scale factor. The patterns were microphotometered with a double beam Jarrell-Ash microdensitometer interfaced with a digital recorder.[3] Diffraction patterns covered the range of q(q = $[40/\lambda]\sin\theta/2$) from 9-58 and 28-125A^{-1} for long and short sample-to-plate distances respectively. The procedure for data reduction and structure analysis has been described in several previous publications.[4]

TABLE 1. GEOMETRICAL PARAMETERS OF HEXAFLUOROCYCLOPROPANE

	r_{ij}	l_{ij}
C−C	1·505 ±0·003A	0·0469 ±0·0030A
C−F	1·314 ±0·001A	0·0526 ±0·0021A
$(F_4$---$F_5)/2$	1·091 ±0·002A	0·0585 ±0·0027A
F_4CF_5	112·2 ±1·0°*	

Calculated nonbonded distances

C_1---F_6	2·4297A	0·0867 ±0·0024A
F_4---F_6	2·7748A	0·1306 ±0·0063A
F_4---F_7	3·5295A	0·0873 ±0·0039A

* Calculated value

TABLE 2. ERROR MATRIX

	C−C	C−F	$(F_4$--$F_5)/2$	^{l}C−C	^{l}C−F	$^{l}F_1$--F_6	$^{l}F_4$--F_5	$^{l}F_4$--F_6	$^{l}F_4$--F_7
C−C	0·0008								
C−F	−0·0003	0·0003							
$(F_4$--$F_5)/2$	0·0004	0·0002	0·0005						
^{l}C−C	0·0000	−0·0003	−0·0002	0·0010					
^{l}C−F	0·0003	0·0001	0·0002	−0·0003	0·0007				
$^{l}F_1$--F_6	0·0003	0·0001	−0·0003	−0·0001	0·0005	0·0008			
$^{l}F_4$--F_5	0·0005	0·0002	0·0002	−0·0002	0·0005	0·0004	0·0009		
$^{l}F_4$--F_6	−0·0005	−0·0001	0·0004	0·0003	0·0005	−0·0002	0·0004	0·0021	
$^{l}F_4$--F_7	0·0001	0·0001	0·0002	−0·0002	0·0006	0·0005	0·0005	0·0006	0·0013

APPENDIX A. COORDINATES OF HEXAFLUOROCYCLOPROPANE

	X	Y	Z
C_1	0·7526	0·0	0·0
C_2	0·0	1·3036	0·0
C_3	−0·7526	0·0	0·0
F_4	1·3873	−0·3664	1·0906
F_5	1·3873	−0·3664	−1·0906
F_6	0·0	2·0365	1·0906
F_7	0·0	2·0365	−1·0906
F_8	−1·3873	−0·3664	1·0906
F_9	−1·3873	−0·3664	−1·0906

APPENDIX B

Set 1		Set 2			
q	Intensity	*q*	Intensity	*q*	Intensity
9	0·1335	28	0·5807	77	0·5485
10	0·1425	29	0·6305	78	0·5427
11	0·1448	30	0·6395	79	0·5426
12	0·1436	31	0·6101	80	0·5441
13	0·1452	32	0·5823	81	0·5466
14	0·1530	33	0·5895	82	0·5460
15	0·1826	34	0·6218	83	0·5458
16	0·2376	35	0·6359	84	0·5438
17	0·2976	36	0·6195	85	0·5423
18	0·3428	37	0·5795	86	0·5358
19	0·3473	38	0·5348	87	0·5288
20	0·3242	39	0·5153	88	0·5220
21	0·2962	40	0·5130	89	0·5207
22	0·2922	41	0·5214	90	0·5254
23	0·2991	42	0·5235	91	0·5322
24	0·3041	43	0·5229	92	0·5402
25	0·3042	44	0·5242	93	0·5433
26	0·3001	45	0·5337	94	0·5426
27	0·3090	46	0·5460	95	0·5404
28	0·3314	47	0·5529	96	0·5388
29	0·3517	48	0·5523	97	0·5364
30	0·3620	49	0·5537	98	0·5328
31	0·3588	50	0·5611	99	0·5303
32	0·3556	51	0·5668	100	0·5272
33	0·3615	52	0·5613	101	0·5210
34	0·3757	53	0·5416	102	0·5206
35	0·3865	54	0·5232	103	0·5205
36	0·3828	55	0·5083	104	0·5205
37	0·3705	56	0·5118	105	0·5219
38	0·3571	57	0·5260	106	0·5241
39	0·3498	58	0·5391	107	0·5260
40	0·3532	59	0·5412	108	0·5280
41	0·3583	60	0·5377	109	0·5305
42	0·3579	61	0·5334	110	0·5298

APPENDIX B *Cont.*

Set 1 q	Intensity	Set 2 q	Intensity	q	Intensity
43	0·3568	62	0·5339	111	0·5276
44	0·3584	63	0·5388	112	0·5257
45	0·3625	64	0·5484	113	0·5233
46	0·3656	65	0·5549	114	0·5203
47	0·3669	66	0·5587	115	0·5181
48	0·3654	67	0·5618	116	0·5164
49	0·3658	68	0·5582	117	0·5186
50	0·3681	69	0·5492	118	0·5210
51	0·3690	70	0·5383	119	0·5231
52	0·3657	71	0·5245	120	0·5234
53	0·3562	72	0·5161	121	0·5234
54	0·3426	73	0·5212	122	0·5233
55	0·3376	74	0·5327	123	0·5225
56	0·3400	75	0·5429	124	0·5224
57	0·3473	76	0·5466		
58	0·3521				

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