Electron-Diffraction and Theoretical Investigation of the Molecular Structure of Octafluorobicyclo[2.2.0]hex-1(4)-ene in the Gas Phase: Another Example of a Molecule with an Unusually Long C(sp^3)−C(sp^3) Single Bond

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The molecular structure of octafluorobicyclo[2.2.0]hex-1(4)-ene has been measured in the gas phase by electron diffraction at room-temperature aided by results from molecular orbital theory. The results are consistent with D_{2h} symmetry for the molecule. The bond distances (r_g/Å) and bond angles ($\angle_\alpha$/deg) with estimates of 2σ uncertainties are $r(C_1{=}C_4) = 1.376(14)$, $r(C_1{-}C_2) = 1.530(3)$, $r(C_2{-}C_3) = 1.627(5)$, $r(C{-}F) = 1.336(2)$, and $\angle(F{-}C{-}F) = 108.6(3)$. The planes of the $-CF_2$ groups are tipped away from the bisector of the C−C−C angle toward each other by about 2.8°. The measured length of the $C_2{-}C_3$ bond is even greater than the lengths of the structurally similar bonds in hexafluorocyclobutene and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene and agrees with prediction from quantum-mechanical structure optimizations at the B3LYP, B3PW91, and MP2 levels of theory. This and other features of the structure are discussed in terms of the bond-altering effects of electrostatic repulsions and rehybridization arising from electronegativity differences.

Introduction

The structures of certain substituted cyclobutenes have a very interesting feature. When all the hydrogen atoms of the $C_3{-}C_4$ bond (the unique single bond) are replaced by fluorines, this bond appears to be unusually long. For example, an early gas-phase electron-diffraction (GED) investigation of the structure of hexafluorocyclobutene led to $r_a(C_3{-}C_4) = 1.595(16)$ Å,[1] some 0.05 Å greater than the "normal" value for nominal sp^3−sp^3 carbon−carbon single bonds. This unexpected circumstance indicated that a check was in order and led us to reinvestigate the structure of the molecule. The value from our study (r_a = 1.582(11) Å)[2] was a bit smaller than the original one, but nevertheless had to be reckoned as supporting the notion of $C_3{-}C_4$ as very long. A subsequent study of the structurally similar 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene also found this bond to be very long (r_a = 1.598(10) Å).[3]

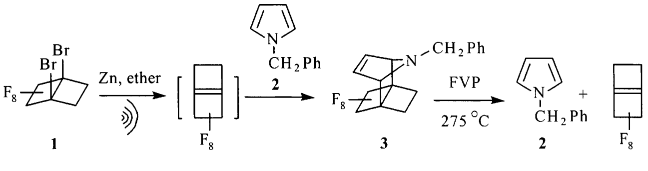
Although the picture from these GED studies seems clear, it is clouded by results from microwave (MW) spectroscopy, which suggest that the bond in question is considerably shorter—1.552(6) Å ($r_s + r_0$) in hexafluorocyclobutene[4] and 1.551(15) Å in 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene,[5] each a bit less than in cyclobutene itself (r_s = 1.566(3) Å).[6] The GED and MW results for these two molecules taken separately are obviously inconsistent and raise the question as to which is the more nearly correct. There are two reasons we favor those from GED. First, it is expected that an $F_2C{-}CF_2$ bond will be longer than an $H_2C{-}CH_2$, as is found in perfluoroethane (r_g = 1.545(8) Å)[7] vs that in ethane (r_g = 1.533(2) Å).[8] Second, we have shown[9] that analysis of the hexafluorocyclobutene structure based on a combination of our GED data with the rotational constants from the MW work leads to a structure, including an r_g value for $C_3{-}C_4$ equal to 1.585(8) Å, which is close to that obtained from the GED data alone. Moreover, this structure fits the measured rotational constants to within 0.3 MHz.

The reason for the difference between the GED and MW results for these molecules remains unclear. Nor do molecular orbital calculations resolve the question: for hexafluorocyclobutene optimizations yield $r(C_3{-}C_4)$ values ranging from 1.544 Å (HF/6-31G(d)) to 1.584 Å (LDA+BP/TZP),[10] and for 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene from 1.543 Å (HF/6-31G(d)) to 1.571 Å (B3LYP/cc-pVDZ). It does appear that higher level theoretical calculations predict larger values for the bond in question, and given that the r_g (thermal average) type of distance from GED is expected to be greater than the r_e type from theory, these calculations lend support to the GED values. Nevertheless, the question is still not settled, so to add further data on the experimental side we have undertaken a GED investigation of octafluorobicyclo[2.2.0]hex-1(4)-ene, hereafter OFBH. As is seen in Figure 1, this molecule consists of two fused four-member rings sharing a carbon−carbon double bond and resembles the halocyclobutenes mentioned above in that the environment of bonds $C_2{-}C_3$ and $C_5{-}C_6$ is similar to that of bond $C_3{-}C_4$ in the cyclobutenes.

Experimental Section

The synthesis of OFBH is outlined in Scheme 1 and was carried out at Dartmouth College;[11] full details are to be published later.

SCHEME 1



Samples of OFBH (estimated >98% pure) were sent to Oregon State University in sealed glass ampules. To prepare for the diffraction experiments, an ampule was placed in a nitrogen glovebag and frozen to 77 K. The top of the ampule was re-

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10.1021/jp022518q CCC: $25.00

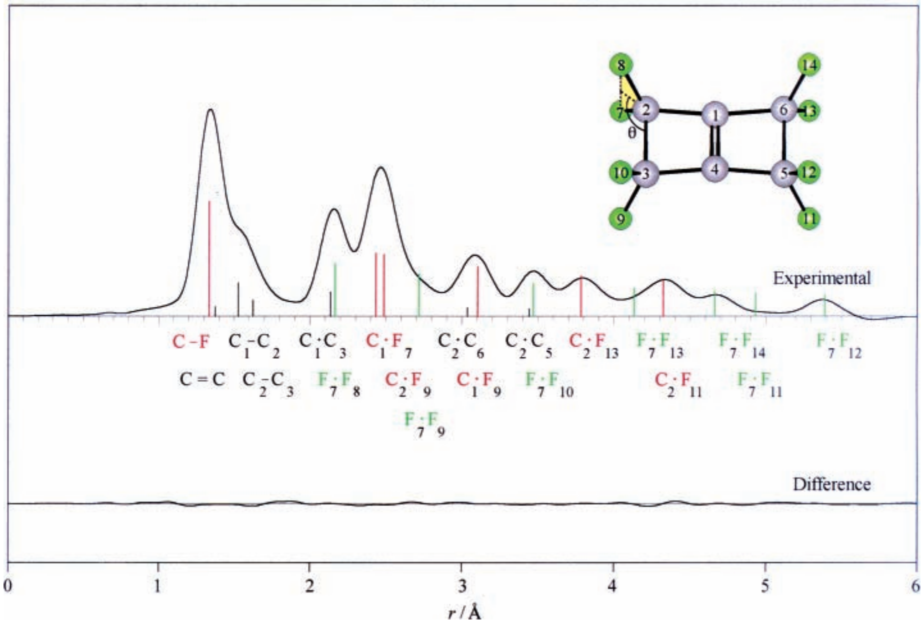

Figure 1. Radial distribution curves and model diagram for octafluorobicyclo[2.2.0]hex-(1,4)-ene. The vertical bars on the experimental curve have lengths proportional to the weights of the terms. The identification of distances is indicated by the labels. The distances tend to be distributed in groups of two or three; the labels from top to bottom for each group identify the bars from left to right in each group. The damping factor for the experimental curve was $\exp(-0.002s^2)$. The difference curve is experimental minus theoretical.

moved and the sample containing portion was attached to a stainless steel micrometer-equipped Whitey valve using swagelock fittings and Teflon ferrules. The valve and sample were removed from the glovebag and attached to the diffraction apparatus. Excess nitrogen was removed from the frozen sample. Suitable vapor pressure was obtained with the bulk sample held at 0 °C. Long (LC) and middle (MC) camera diffraction photographs, nominally 75 and 30 cm were taken with a room-temperature nozzle tip. Other experimental conditions: exposure times, 2.0−2.5 min (both distances); beam currents, 0.60−0.7 μA; sector, r^3; plates, 8″ × 10″ Kodak electron-image film; development, D-19 diluted 1:1; electron wavelength, 0.04894 Å; wavelength calibration standard, CO_2 (r_a(C=O) = 1.1646 Å, r_a(O−O) = 2.3244 Å). Three plates from each distance were selected for analysis. Improved procedures similar to those described earlier[12] were used for obtaining the total scattered intensities (s^4I_T) and removing the backgrounds. To enhance ring intensities and reduce background noise, the experimental intensity curves presented in Figure 2 are the average of three microphotometer traces of each plate. Ranges of these data were $2.0 \leq s/\text{Å}^{-1} \leq 16.25$ and $8.0 \leq s/\text{Å}^{-1} \leq 38.5$ at intervals $\Delta s = 0.25$. The molecular intensities are available as Supporting Information.

The experimental radial distribution curve is shown in Figure 1 and was obtained by leveling each composite intensity curve by multiplication with $(Z_CZ_F/A_CA_F)\exp(-0.002s^2)$, where $A = s^2F$ (F is an electron scattering amplitude), before Fourier transformation. Intensity data in the inaccessible region $s \leq 2.0$ Å^{-1} were taken from the final theoretical fit.

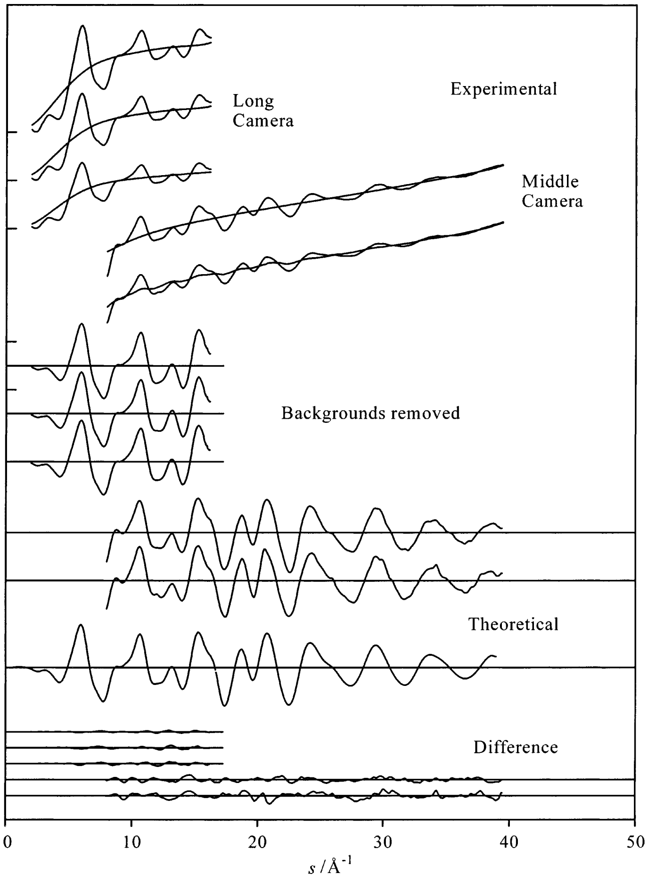

Figure 2. Intensity curves for octafluorobicyclo[2.2.0]hex-(1,4)-ene. Data from individual plates on the ascending curves are shown magnified 3 times with respect to the backgrounds on which they are superimposed. The theoretical curve is for model A. The difference curve is experimental minus theoretical.

Structure Analysis

Theoretical Calculations. Quantum mechanical calculations for OFBH were carried out with the Gaussian 98W program set[13] at four levels of theory, each with five different basis sets. The results are given in Table 1. Besides affording structural comparisons with experiment, these calculations provided quadratic force fields that could be used in normal coordinate calculations to generate the various correction terms necessary for the interconversion of distance types (r_α, the distance be-

TABLE 1: Theoretical Values of Bond Distances (r_e/Å) and Bond Angles ($\angle_e$/deg) in Octafluorobicyclo[2.2.0]hex-1(4)-ene

level/basis	r(C−F)	r(C=C)	Δr	r(C$_1$−C$_2$)	r(C$_2$−C$_3$)	$\angle$(F−C−F)	$\angle$(C$_2$−C$_3$−F)
HF/							
6-31G(d)	1.320	1.308	0.012	1.517	1.578	108.5	114.3
6-311G(d)	1.315	1.307	0.008	1.516	1.584	108.4	114.4
6-311++G(d,p)	1.315	1.307	0.008	1.516	1.589	108.4	114.5
cc-pVTZ	1.312	1.305	0.007	1.517	1.588	108.2	114.6
aug-cc-pVTZ	1.313	1.304	0.009	1.517	1.591	108.2	114.6
B3LYP/							
6-31G(d)	1.344	1.334	0.010	1.529	1.604	108.9	114.2
6-311G(d)	1.343	1.330	0.013	1.528	1.610	108.6	114.4
6-311++G(d,p)	1.344	1.330	0.014	1.526	1.616	108.4	114.6
cc-pVTZ	1.341	1.326	0.015	1.525	1.613	108.4	114.6
aug-cc-pVTZ	1.341	1.326	0.015	1.526	1.616	108.3	114.6
B3PW91/							
6-31G(d)	1.340	1.332	0.008	1.524	1.600	108.9	114.2
6-311G(d)	1.338	1.329	0.009	1.523	1.605	108.7	114.4
6-311++G(d,p)	1.338	1.330	0.008	1.522	1.610	108.5	114.6
cc-pVTZ	1.336	1.327	0.009	1.522	1.609	108.5	114.6
aug-cc-pVTZ	1.336	1.326	0.010	1.523	1.612	108.4	114.6
MP2/							
6-31G(d)	1.348	1.344	0.004	1.522	1.591	108.9	114.0
6-311G(d)	1.338	1.346	−0.008	1.525	1.599	108.9	114.2
6-311++G(d,p)	1.340	1.347	−0.007	1.522	1.606	108.8	114.4
cc-pVTZ	1.335	1.341	−0.006	1.522	1.602	108.7	114.4
aug-cc-pVTZ	1.337	1.342	−0.005	1.522	1.604	108.6	114.4

TABLE 2: Refined (r_α) and Calculated (r_e) Parameter Values for Octafluorobicyclo[2.2.0]hex-1(4)-ene[a]

	experiment				theory				
parameter	model A	model X	model Y	model Z	HF/ 6-31G(d)	B3LYP/ 6-311G(d)	B3LYP/ aug-cc-pVTZ	MP2/ cc-pVTZ	MP2/ aug-cc-pVTZ
r(C−F)	1.323(2)	1.327(2)	1.328(2)	1.322(2)	1.320	1.343	1.341	1.335	1.337
Δr(C−F,C=C)[b]	−0.047(14)	[0.013]	[0.030]	[−0.070]	0.012	0.013	0.016	−0.006	−0.005
r(C$_1$−C$_2$)	1.523(3)	1.531(4)	1.536(5)	1.523(3)	1.517	1.527	1.526	1.522	1.522
r(C$_2$−C$_3$)	1.622(5)	1.601(7)	1.592(8)	1.624(5)	1.578	1.610	1.618	1.602	1.604
$\angle$(F−C−F)	108.6(3)	108.6(3)	108.6(3)	108.4(2)	108.5	108.6	108.3	108.7	108.6
$\angle\theta$[c]	134.7(5)	135.6(6)	136.0(6)	134.6(4)	134.8	135.1	135.4	135.1	135.0
R[d]	0.111	0.119	0.122	0.114					
$\angle$(C$_1$−C$_2$−C$_3$)	85.2(2)	84.6(2)	84.5(2)	85.6(1)	84.9	84.7	84.5	85.1	85.1
$\angle$(C$_2$−C$_1$−C$_4$)	94.8(2)	95.4(2)	95.5(2)	94.4(1)	95.1	95.3	95.5	94.9	94.9
$\angle$(F$_7$−C$_2$−C$_3$)	114.2(2)	114.6(3)	114.8(3)	114.3(2)	114.3	114.4	114.6	114.4	114.4

[a] Uncertainties are 2σ and contain estimates for correlation and systematic errors. Distances (r) are in ångstroms and angles ($\angle$) are in degrees. [b] Δr(C−F,C=C) = r(C−F) − r(C=C). In model A refinement of this parameter is equivalent to simultaneous refinement of the two bond distances. [c] The angle between C$_2$−C$_3$ and the bisector of $\angle$(F−C−F). [d] Goodness of fit factor: $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_{m,i}(\mathrm{obsd}))^2]^{1/2}$, where $i = s_iI_{m,i}(\mathrm{obsd}) - s_iI_{m,i}(\mathrm{calc.})$.

tween average atomic positions, r_g, the thermal average distance, and r_a, the parameter appearing in the GED scattering formulas) as well as theoretical values for vibrational amplitudes. We chose the force field of the B3LYP/6-311G(d) calculation[14] and used the program ASYM40[15] to obtain the quantities desired. We also carried out a number of similar calculations for OFBH molecules assumed to have D_2 or C_2 symmetry. With complete optimizations these structures always reverted to ones of D_{2h} symmetry with no imaginary frequencies predicted, and if they were constrained to C_2 or D_2 the energies were always greater than those for D_{2h} at the same theoretical level and basis set. We thus adopted the assumption of D_{2h} symmetry for the molecule in our structure refinements.

Structural Model. With the assumption of D_{2h} symmetry, the r_α structure of OFBH can be described with four distance- and two angle parameters. Convenient parameters are the bond lengths r(C$_1$−C$_2$), r(C$_2$−C$_3$), and C−F, and the difference Δr(C−F,C=C) = r(C−F) − r(C=C), the bond angle $\angle$(F−C−F), and an angle θ, which is the angle between C$_2$−C$_3$ and the bisector of the angle F$_7$−C$_2$−F$_8$ (Figure 1). There are 19 different interatomic distances in the model, each with its associated amplitude of vibration. These 19 vibrational amplitude parameters were formed into 10 groups for group refinement. Amplitude differences between group members were held at theoretical values. These may be seen in Table 3.

Refinement Results. Refinement of the structure was carried out by least squares in the usual way[16] by fitting a theoretical scattering curve simultaneously to the five observed curves (Figure 2). A simultaneous adjustment of all parameters converged to the values listed in Tables 2 and 3 as model A. It is seen that the value of the parameter Δr(C−F,C=C) from this refinement has a relatively large uncertainty, a consequence of the small weight of the scattering from the C=C term, which is only about $^1/_{12}$th as much as from the C−F term.[17] Even with this uncertainty taken into account, however, the value of Δr(C−F,C=C) differs appreciably from theory. Accordingly, we investigated the effect of variation in Δr(C−F,C=C) on the other parameters by a series of refinements in which Δr(C−F,C=C) was not adjusted but instead kept fixed at values throughout the range −0.09 Å to +0.05 Å. Parameter values from three of these refinements carried out at intervals of Δr(C−F,C=C) that define a reasonable range of the variable are also given in Table 2. These are discussed in the next section. The correlation matrix for the parameters of the preferred model A is found in Table 4.

TABLE 3: Interatomic Distances (r/Å) and Root-Mean-Square Amplitudes of Vibration (l/Å) for Model A of Octafluorobicyclo[2.2.0]hex-1(4)-ene[a]

	experimental					theoretical[b]	
distance	r_α	r_g	r_a	l		r_e	l
$C_1{=}C_4$	1.370	1.376(14)	1.374	0.041	(2)	1.330	0.041
$C_2{-}F_7$	1.323	1.336(2)	1.334	0.045		1.343	0.045
$C_1{-}C_2$	1.523	1.530(3)	1.528	0.049	(5)	1.527	0.052
$C_2{-}C_3$	1.622	1.627(5)	1.625	0.052		1.610	0.055
$C_1{\cdot}C_3$	2.131	2.137(6)	2.135	0.057	(3)	2.115	0.053
$F_7{\cdot}F_8$	2.148	2.168(4)	2.166	0.061		2.181	0.057
$C_1{\cdot}F_7$	2.423	2.437(4)	2.435	0.071	(4)	2.444	0.068
$C_2{\cdot}F_9$	2.479	2.489(5)	2.487	0.075		2.486	0.072
$F_7{\cdot}F_9$	2.709	2.722(9)	2.717	0.124		2.720	0.121
$C_2{\cdot}C_6$	3.036	3.038(6)	3.037	0.070	(5)	3.042	0.066
$C_1{\cdot}F_9$	3.096	3.105(6)	3.103	0.087		3.097	0.087
$C_2{\cdot}C_5$	3.442	3.444(5)	3.443	0.057	(6)	3.441	0.058
$F_7{\cdot}F_{10}$	3.457	3.472(7)	3.470	0.085		3.486	0.085
$C_2{\cdot}F_{13}$	3.781	3.788(6)	3.784	0.109(9)		3.797	0.114
$F_7{\cdot}F_{13}$	4.133	4.143(9)	4.131	0.217	(13)	4.148	0.220
$C_2{\cdot}F_{11}$	4.324	4.327(6)	4.324	0.113		4.336	0.115
$F_7{\cdot}F_{14}$	4.658	4.665(8)	4.662	0.117	(16)	4.686	0.105
$F_7{\cdot}F_{11}$	4.942	4.945(7)	4.934	0.238		4.960	0.225
$F_7{\cdot}F_{12}$	5.389	5.391(7)	5.389	0.106(14)		5.418	0.097

[a] Uncertainties are 2σ and contain estimates for correlation and systematic errors. Amplitudes in curly brackets were refined as a group. [b] Distances are Gaussian 98W B3LYP/6-311G(d) and amplitudes were calculated with Asym40 using Gaussian force fields.

Discussion

The most interesting result of our investigation of OFBH is the length of the $C_2{-}C_3$ bond, which, as in the structurally similar perhalocyclobutenes, is much greater than the 1.53–1.54 Å usually found for sp^3 bonds between carbon atoms. Although there is no doubt about this point, there is uncertainty about the exact value of $r(C_2{-}C_3)$. As is seen from the data for models X, Y, and Z in Table 1, the value of $r(C_2{-}C_3)$ is correlated with that of $\Delta r(\mathrm{C{-}F,C{=}C})$, which is not quite so precisely determined (model A) as the other parameters. Moreover, the refined value of $\Delta r(\mathrm{C{-}F,C{=}C})$ differs from the theoretical values by more than its measured uncertainty, raising a question about which—experimental or theoretical—is the more reliable. It is at present not possible to answer this question, but the question has no relevance to the larger matter of whether the $C_2{-}C_3$ bond is long. As Table 2 shows, the experimental value for this bond is much greater than the normal range of values for a $C_{sp^3}{-}C_{sp^3}$ bond regardless of the value of $\Delta r(\mathrm{C{-}F,C{=}C})$. All our theoretical results (Table 1) also indicate the bond to be long, particularly those from larger basis sets and higher levels of theory. Two things are worth noting here: first, theoretical values (r_e) are expected to be *less* than experimental ones (r_a or r_g) lending support for the longer experimental value of $r(C_2{-}C_3)$, and second, in contrast to the DFT results, the highest level ab initio calculations, MP2 with bases 6-311G(d) and larger, have $\Delta r(\mathrm{C{-}F,C{=}C})$ negative in agreement with experiment.

The question about the relative lengths of the C=C and C–F bonds is also interesting. Theoretical values for the these distances are seen in Table 1, and each is consistent with the ranges found experimentally in other molecules. Typical values for C–F/C=C from GED, in ångströms with 2σ uncertainties, are 1.344(4)/1.325(24) (r_g, hexafluorocyclobutene), 1.340(2)/1.359(9) (r_g, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene), 1.326(3)/1.400(30) (r_a, 1,2-bis(trifluoromethyl)dithiete[18]), and 1.327(2)/1.373(13) (r_g, 1,1-bis(trifluoromethyl)ethylene[19]). There are many others, but the essential points are that relative lengths of C–F and C=C bonds in different compounds vary and that the length of the C=C bond is often greater than the C–F by even more than we find in OFBH. Our experimental result $\Delta r(\mathrm{C{-}F,C{=}C}) = -0.047$ Å ($2\sigma = 0.010$ Å) leaves little doubt that the C=C bond is the longer in OFBH. Although small differences in the quality-of-fit R factors are not always reliable predictors of the best model, it is worth noting that the quality of the fit to the experimental data is poorer by about 5% when the bonds are of equal length and worsens further as $\Delta r(\mathrm{C{-}F,C{=}C})$ becomes more positive.

Although the C–F bond length in OFBH is calculated to be slightly longer than is observed, the main reason that the theoretical and experimental values of $\Delta r(\mathrm{C{-}F,C{=}C})$ differ seems to lie in the length of the C=C bond. This bond is experimentally about 0.035 Å longer than is found in aliphatic hydrocarbons, but its value is consistent with those found when perfluoromethyl or methylene groups are attached. Examples are those cited above. The experimental and theoretical values for the $C_1{-}C_2$ bond length are in good agreement, and typical of $C_{sp^3}{-}C_{sp^2}$ type bonds. The plane of the $-CF_2$ groups does not quite bisect $\angle C_1C_2C_3$: each of the two groups is tipped toward the other by about 2.8°, about the same amount found in hexafluorocyclobutene (2.4°) and in 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (3.0°).

We have explained the elongation of the $C_3{-}C_4$ bond in hexafluorocyclobutene as due to the competing effects of

TABLE 4: Correlation Matrix (×100) for Parameters of Model A of Octafluorobicyclo[2.2.0]hex-1(4)-ene

N	parameter	$100\sigma_{LS}$[a]	r_1	r_2	r_3	r_4	$\angle_5$	θ_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}
1	$r(C{-}F)$	0.04	100															
2	$\Delta r(\mathrm{C{-}F,C{=}C})$[b]	0.51	−66	100														
3	$r(C_1{-}C_2)$	0.09	−5	19	100													
4	$r(C_2{-}C_3)$	0.18	−30	−29	−46	100												
5	$\angle(C_7{-}C_2{-}C_8)$	8.5	2	36	14	15	100											
6	θ[c]	15.4	5	12	44	−37	−11	100										
7	$l(C_1{=}C_4)$	0.05	37	50	11	−5	28	5	100									
8	$l(C_1{-}C_2)$	0.17	−8	16	34	−39	−1	21	−24	100								
9	$l(C_1{-}C_3)$	0.08	−33	−45	−3	25	−23	−2	−3	−13	100							
10	$l(C_1{-}C_7)$	0.08	8	11	18	−32	−4	−21	27	4	3	100						
11	$l(C_2{\cdot}C_6)$	0.16	8	11	14	−1	17	5	25	−4	3	14	100					
12	$l(C_2{-}C_5)$	0.18	7	12	9	−7	10	−12	16	1	−3	19	−3	100				
13	$l(C_2{\cdot}F_{13})$	0.28	−2	−5	−11	<1	3	−27	4	−4	1	15	8	10	100			
14	$l(F_7{\cdot}F_{13})$	0.34	2	−2	1	−1	<1	−14	7	−4	5	13	<1	<1	−2	100		
15	$l(F_7{\cdot}F_{14})$	0.53	5	5	−11	−1	7	−6	4	−2	−5	3	<1	−2	<1	10	100	
16	$l(F_7{\cdot}F_{12})$	0.48	3	1	−4	12	4	−1	7	−4	1	6	3	2	<1	9	12	100

[a] Standard deviations from least squares. Distances in ångströms, angles in degrees. [b] $\Delta r(\mathrm{C{-}F,C{=}C}) = r(\mathrm{C{-}F}) - r(\mathrm{C{=}C})$. θ is the angle between $C_2{-}C_3$ and the bisector of $\angle(F{-}C{-}F)$.

rehybridization and charge repulsion in which repulsion is the more important. The argument is the following. Because of the electronegativity difference of carbon and fluorine, the Mulliken charges (HF/6-31G(d)) on the carbons of the bond are +0.70, whereas they are −0.24 in cyclobutene itself, and although rehybridization at these carbons tends to shorten the bond (the electrons attracted to the fluorines are mainly drawn from p orbitals leaving the carbon bonds with more s character), charge repulsion dominates to make the C_3-C_4 bond longer in hexafluorocyclobutene. The same argument may be applied to OFBH. In this case the Mulliken charges from the same level of theory[20] are found to be +0.82 on the carbons of the C_2-C_3 bond, which corresponds to the C_3-C_4 bond in hexafluorocyclobutene, and −0.35 on the attached fluorines which is nearly the same as on the fluorines of hexafluorocyclobutene (−0.36). Although the reliability of individual Mullikan charges may be debated, the differences between them for atoms in similar environments might reasonably be expected to be more accurate because errors in the approximations tend to cancel out. With this assumption, the repulsion between atoms of the $C_{sp^3}-C_{sp^3}$ bond is deemed to be greater in OFBH than in hexafluorocyclobutene, and because the expected rehybridization is about the same, a greater elongation of the $C_{sp^3}-C_{sp^3}$ bond is expected in the former. These simple arguments may also be invoked to account for the C═C bond length in OFBH. This bond is longer by about 0.045 Å in this molecule than in hexafluorocyclobutene and the atoms bear a Mulliken charge of −0.21 vs +0.33 in hexafluorocyclobutene; thus, charge repulsion should result in a slightly longer bond in hexafluorocyclobutene. However, the nearly linear arrangement of the two single bonds from C_1 ($\angle C_2-C_1-C_6 = 189.8°$) implies more s character for them and hence more p character for the σ bond of the $C_1{=}C_4$ link. This would weaken and lengthen the double bond. Another factor that could play a role in the C═C bond-length differences just cited is cross-ring repulsion. Cross-ring repulsion has been offered as a partial explanation for the long bond in cyclobutane[21] and is estimated to have an effect on the bonds in cyclobutene. It should also play a role in both hexafluorocyclobutene and in OFBH, but the effect on the C═C bond should be twice as great in OFBH because the force on each atom arises from two rings instead of one.

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Supporting Information Available: Tables of symmetry coordinates, force constants, and wavenumbers and of scattered molecular intensities. This material is available free of charge via the Internet at http://pubs/acs/org.

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