the NH out-of-plane bending mode. The band occurs also in the range of the reported τ(NH) frequencies in hydrogen-bonded complexes.[45] No other bands due to $(HNCO)_2$ were observed. The perturbed ν_4 HNC in-plane bending mode falls in the region of the ν_2 HCN bending absorption; the absorptions due to perturbed ν_1, HN stretching and ν_5, NCO bending modes may not be observed as their counterparts in the HNCO monomer were also less intense than the bands due to the ν_2 and ν_4 modes. Concentration studies of HNCO isolated in argon or neon matrices seem to be interesting.

Conclusion

The infrared spectra of matrices obtained by codeposition of HCN and O_3 with excess argon gave evidence for a well-defined 1:1 O_3–HCN complex. Two perturbed hydrogen cyanide fundamentals, all three perturbed deuterium cyanide fundamentals, and two perturbed ozone fundamentals were observed for the complex with isotopic substitution at all atomic positions (^{16,18}O; ^{12,13}C; ^{14,15}N). The obtained spectra suggest a unique structure in which C_{2v} symmetry of O_3 molecule is retained and HCN forms nonlinear hydrogen bonds with two terminal O atoms of O_3. This can be contrasted with the O_3–HF complex where HF is hydrogen bonded to a terminal O atom of O_3 molecule.

Photolysis of Ar/O_3/HCN matrices with full arc radiation produced a weak O–HCN complex and the HNCO molecule as primary products of the HCN + O reaction. The perturbed C—H stretching mode was observed for all isotopic protonated complexes, and perturbed C—D and C≡N stretching modes were identified for the corresponding deuterated complexes. The $(HNCO)_2$ dimer is identified as the secondary product of the HCN + O reaction, and the cyclic structure is proposed for the dimer on the basis of the activated N–H out-of-plane bending mode. The primary and secondary products formed in studied HCN + O matrix reactions indicate that HNCO is formed as an intermediate product on the pathway to the final products of the gas-phase HCN + O(^{1}D) reaction.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE 88-20764.

---

[45] Novak, A. *Struct. Bonding* **1974**, *18*, 177.

Hexafluorocyclobutene: Gas-Phase Molecular Structure and Quadratic Force Field from an Electron-Diffraction and ab Initio Study

Attila G. Császár[†] and Kenneth Hedberg[*]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331 *(Received: September 5, 1989; In Final Form: October 25, 1989)*

The molecular structure of hexafluorocyclobutene has been determined by electron diffraction from its vapor at a nozzle tip temperature of 19–20 °C. The data are consistent with molecular symmetry C_{2v}. Values for the distances (r_g/Å), angles ($\angle_\alpha$/deg), and selected rms amplitudes of vibration (l/Å) with estimated 2σ uncertainties are r(C=C) = 1.324 (23), ⟨r(C–F) = 1.336 (3) (weighted average), Δr(C-F) = r(–C–F) – r(=C–F) = 0.032 (12), ⟨r(C–C)⟩ = 1.529 (4) (weighted average), Δr(C–C) = r(–C–C–) – r(=C–C–) = 0.082 (14), ∠(C=C—C) = 95.0 (5), ∠(C=C—F) = 135.2 (12), ∠(–C–C–F) = 114.5 (3), ∠(F–C–F) = 107.6 (5), l(C=C) = l(=C–F) – 0.001 = l(–C–F) – 0.003 = 0.043 (3), l(–C–C) = l(=C–C) + 0.001 = 0.053 (7). The geometry of the molecule was optimized and a quadratic force field determined at the ab initio Hartree–Fock level by using 4-21G and 6-31G* basis sets. Although the calculations are of high quality, they fail to reproduce the large splitting of the C–C single bond distances. The calculated frequencies indicate that reassignment of some of the fundamentals may be necessary.

Introduction

The rationalization of structural effects accompanying the introduction of fluorines into simple hydrocarbons has long challenged chemists. It was early observed that the C–F bonds in fluoromethanes[1] and the C–F and C=C bonds in fluoroethylenes[2] shorten as more fluorine atoms are attached to the carbons. Later, it was noticed that, although the C–F bonds shorten similarly in fluoroethanes, the C–C bonds lengthen in the series 1,2-difluoroethane,[3] 1,1,2,2-tetrafluoroethane[4] and hexafluoroethane.[5] The limited experimental data available for fluoroacetylenes[6] show a shortening of the C≡C and C–F distances upon fluorine substitution. (Theoretical calculations at different ab initio levels predict,[7] however, a slight increase of the C–F distance in F—C≡C—F over that in F—C≡C—H.) Explanations for the observed trends differ in details which are best obtained from the original articles[1–6] and references cited therein. To summarize these explanations briefly, the shortening or lengthening of the bonds is the outcome of competition between orbital hybridization at the carbons and Coulomb repulsion between the atoms. In the language of orbital hybridization the

---

[†] On leave from the Laboratory of Theoretical Chemistry, Eötvös Loránd University, H-1088 Budapest, Múzeum krt. 6-8, Hungary.

[*] Author to whom correspondence should be addressed.

(1) (a) Brockway, L. O. *J. Phys. Chem.* **1937**, *41*, 185. (b) Ghosh, S. N.; Trambarulo, R.; Gordy, W. *J. Chem. Phys.* **1952**, *20*, 605. (c) Bent, H. A. *J. Chem. Phys.* **1960**, *33*, 304, 1258, 1259, 1260 and references cited therein. For some more recent experimental results see e.g.: Clark, N. W.; DeLucia, F. C. *J. Mol. Struct.* **1976**, *32*, 29 (CH_3F); and: Hirota, E.; Tanaka, T.; Sakakibara, A.; Ohashi, Y.; Morino, Y. *J. Mol. Spectrosc.* **1970**, *34*, 222 (CH_2F_2).

(2) (a) Peters, D. *J. Chem. Phys.* **1963**, *38*, 561 and references cited therein. For some more recent experimental results see e.g.: (b) Bhaumik, A.; Brooks, W. V. F.; Dass, S. C. *J. Mol. Struc.* **1973**, *16*, 29 (CHF=CF_2). (c) Carlos, J. L.; Karl, R. R.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177 (CH_2=CHF, CHF=CHF, CH_2=CF_2, CF_2=CF_2). (d) Spelbos, A.; Huisman, P. A. G.; Mijlhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1978**, *44*, 159 (CHF=CHF).

(3) Friesen, d.; Hedberg, K. *J. Am. Chem. Soc.* **1980**, *102*, 3987.

(4) Brown, D. E.; Beagley, B. *J. Mol. Struct.* **1977**, *38*, 167.

(5) Gallaher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389.

(6) For Ch≡CH see: Lafferty, W. J.; Thibault, R. J. *J. Mol. Spectrosc.* **1964**, *14*, 79. Fast, H.; Welsh, H. L. *J. Mol. Spectrosc.* **1972**, *41*, 203. For CH≡CF see: Tyler, J. K.; Sheridan, J. *Trans. Faraday Soc.* **1963**, *59*, 2661. To our best knowledge reliable experimental data for CF≡CH are not available.

0022-3654/90/2094-3525$02.50/0

increased number of fluorines attached to a carbon atom increases the s character of the carbon bonds and tends to shorten *all* the bonds around that carbon. Coulomb repulsion occurs mainly between the induced positive charges on the carbon atoms; these charges lead to withdrawal of electrons from the bond between carbons and to its consequent lengthening.

If fluorine atoms are present in unstrained ring compounds, e.g., in benzene,[8] the structural effects are qualitatively similar to those described above. In strained ring systems the effects of fluorine substitution are less clear, but a lengthening of the C–C bonds in perfluorocyclopropane[9] and perfluorocyclobutane[10,11] relative to the parent hydrocarbons[12] has been observed. Other strained ring systems of interest are cyclobutene and hexafluorocyclobutene (hereafter HFCB). The gas-phase molecular structure of HFCB has been investigated in an electron-diffraction study[10] and that of cyclobutene (r_s type) by microwave spectroscopy.[13] The skeletal bond lengths $C_1{=}C_2$, C_2–C_3, and C_3–C_4 were found to be 1.342 (4) Å, 1.517 (3) Å, and 1.566 (3) Å in the hydrocarbon (thus both the sp^2–sp^3 and sp^3–sp^3 C–C single bonds are longer than normal) and 1.342 (6) Å, 1.508 (3) Å, and 1.595 (16) Å in a HFCB (uncertainty in the last value estimated by us from that given for $\angle C_1C_2C_3$). The value for $r(C_3–C_4)$ in HFCB is surprisingly large under any circumstances, particularly so in view of the fluorine effect mentioned above that could be expected to decrease it relative to the value in cyclobutene, and it seemed to us that a check was merited. We decided to reinvestigate the structure with data that extended to higher scattering angles than in the earlier study,[10] and to take account of the effects of vibrational averaging ("shrinkage") in the analysis. It was hoped that these steps would both improve the precision of the distance results and provide better values for some of the amplitudes of vibration that appear to be unreasonably small. We also planned to carry out some relatively high level ab initio calculations designed to explore various aspects of the structural and vibrational problems.

It should be mentioned at the outset that our experimental results for the structure of HFCB, including the C_3–C_4 distance, are in very good agreement with those from the earlier work. Our values for the vibrational amplitudes of the bonds are larger, however. Some puzzling problems concerned with the optimized theoretical structure and with the spectroscopic side of the vibrational problem remain.

Experimental Section

Sample. The sample of HFCB was purchased from Specialty Chemicals, Inc. The claimed purity was 100%; no impurity was detected by mass spectrometry. The purchased material was used as received.

Experimental Conditions. The electron-diffraction data were obtained with the Oregon State apparatus. Conditions of the experiments were as follows: sector shape, r^3; plates, 8 in. × 10 in. medium-contrast Kodak projector slide; development, 10 min in D-19 diluted 1:1; nominal nozzle-to-plate distances, 750 mm (long camera), 300 mm (middle camera), and 120 mm (short camera); nominal electron wavelength, 0.058 Å (calibrated in separate experiments with CO_2: $r_a(C{=}O) = 1.1646$ Å and $r_a(O{\cdot}O) = 2.3244$ Å); exposure times, 90–360 s; beam currents, 0.3–0.9 μA; ambient apparatus pressure during experiments, (1.0–2.0) × 10^{-5} Torr; nozzle temperature, 19–20 °C; bath temperature, −30 °C. Three plates from the long, four from the middle, and two from the short camera distance were selected for analysis. The corresponding ranges of intensity data were $2.00 \le s/Å^{-1} \le 13.50$, $6.75 \le s/Å^{-1} \le 32.75$, and $22.00 \le s/Å^{-1} = 53.00$; the data interval was $\Delta s = 0.25$ Å^{-1}. The procedures used

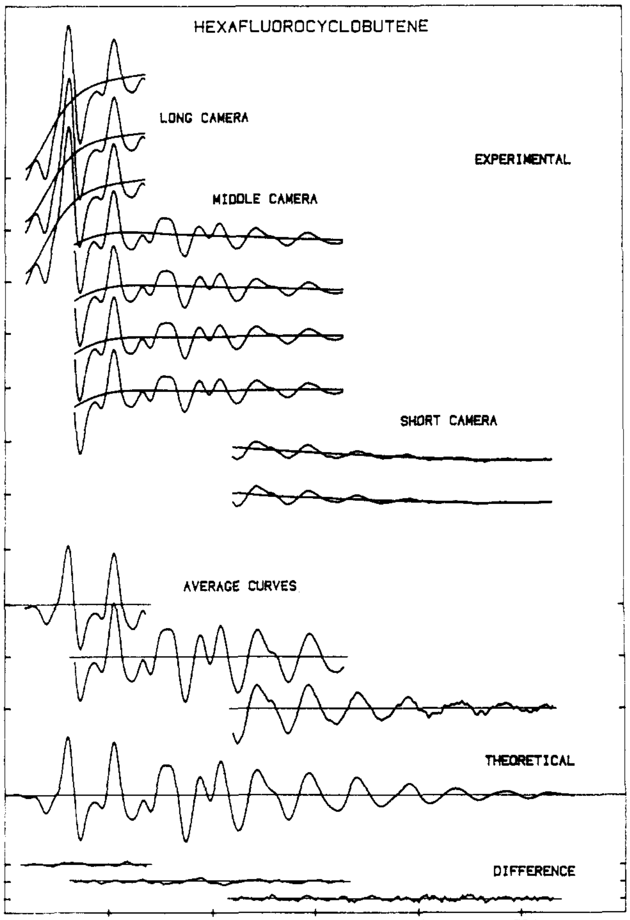

Figure 1. Intensity curves for hexafluorocyclobutene. The s^4I_t experimental curves are shown magnified 5 times with respect to the backgrounds on which they are superimposed. The average curves are $s[s^4I_t - \text{background}]$. The theoretical curve is for model A of Table IV.

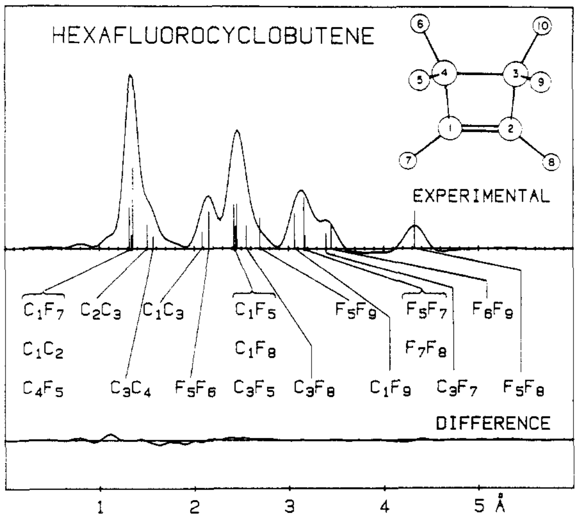

Figure 2. Radial distribution curves for hexafluorocyclobutene. The experimental curve was calculated from a composite of the average intensities with use of theoretical data for the region $0 \le s/Å \le 2.00$ and $B/Å^2 = 0.0010$. The vertical lines have lengths proportional to weights of the indicated distances.

---

(7) The HF/3-21G (MP2/6-311G**) values of the bond lengths/Å for the different compounds are as follows: in C_2H_2 $r(CC) = 1.1875$ (1.2141), $r(CH) = 1.0509$ (1.0638); in C_2HF $r(CC) = 1.1776$ (1.2071), $r(CF) = 1.2973$ (1.2791), $r(CH) = 1.0483$ (1.0615); in C_2F_2 $r(CC) = 1.1652$ (1.1962), $r(CF) = 1.3018$ (1.2862).

(8) There are numerous studies on the structures of the different fluorobenzenes, for papers prior to 1982 as well as for ab initio geometry optimization results at the HF/4-21 level of some of these compounds see: Boggs, J. E.; Pang, F.; Pulay, P. *J. Comput. Chem.* **1982**, *3*, 344.

(9) Chiang, J. F.; Bernett, W. A. *Tetrahedron* **1971**, *27*, 975.

(10) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Mol. Struct.* **1971**, *7*, 89.

(11) Alekseev, N. V.; Barsdain, P. P. *Zh. Strukt. Khim.* (Eng. *Transl.*) **1974**, *15*, 181.

(12) Cyclopropane: (a) Jamamoto, S.; Nakata, N.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1985**, *89*, 3298. (b) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538. Cyclobutane: Almenningen, A.; Bastiansen, O.; Skancke, P. N. *Acta Chem. Scand.* **1961**, *15*, 711.

(13) Bak, B.; Led, J. J.; Nygaard, L.; Rastrup-Andersen, J.; Sørensen, G. O. *J. Mol. Struct.* **1969**, *3*, 369.

TABLE I: Structural Results for Hexafluorocyclobutene and for Cyclobutene[a]

	hexafluorocyclobutene				cyclobutene		
	exptl		theor		exptl	theor	
parameter	this work[b] (r_α, $\angle_\alpha$)	ref 10[c] (r_a, $\angle_a$)	4-21[d,e] (r_e, $\angle_e$)	6-31G*[d] (r_e, $\angle_e$)	ref 13 (r_s[f])	4-21[e] (r_e, $\angle_e$)	6-31G** (r_e, $\angle_e$)
$r(C_1-X)$	1.307 (10)	1.319 (12)	1.328	1.297	1.083	1.069	1.076
$r(C_3-X)$	1.341 (4)	1.336 (6)	1.360	1.326	1.094	1.081	1.086
$r(C{=}C)$	1.319 (23)	1.342 (6)	1.319	1.315	1.342	1.325	1.322
$r(C_2-C_3)$	1.499 (5)	1.508 (3)	1.516	1.494	1.517	1.538	1.515
$r(C_3-C_4)$	1.581 (11)	1.595 (16)	1.563	1.544	1.566	1.591	1.562
$\angle C{=}C{-}C$	95.0 (5)	94.8 (3)	94.6	94.4	94.2	95.0	94.5
$\angle C{=}C{-}X$	135.2 (12)	133.6 (29)	134.4	135.2	133.5	133.4	133.4
$\angle C_3-C_4-X$	114.5 (3)	114.5	114.4	114.7	114.5	114.5	114.9
$\angle X-C-X$	107.6 (5)	109.2	108.8	107.9	109.2	109.9	108.7

[a] Distances (r) in angstroms; angles ($\angle$) in degrees. In parameter list X = F or H. For numbering of atoms see Figure 2. Theoretical calculations made at the Hartree–Fock SCF level. [b] Model A of Table IV. Uncertainties (in parentheses) are estimated 2σ. [c] Model A of ref 10. Uncertainties are estimated 3σ. [d] Reference geometry in the force field calculation. [e] Without offset values. Well-established values (see refs 18 and 33) for the bond distances at this level of theory are −0.026 Å for C–F, +0.005 Å for C–H, and +0.021 Å for C=C; for the C–C distances the following formula for the correction applies:[18] $\Delta r(\text{corr}) = 0.16(1.45 - r_{\text{th}})$, where r_{th} is the theoretical 4-21 C–C bond length. [f] Uncertainties estimated to be 0.005 Å in distances and 0.5° in angles.

for obtaining the total scattered intensities ($s^4I_t(s)$) and molecular intensities ($sI_m(s)$) have been described elsewhere.[14,15] Curves of the intensity data superimposed on their computer-generated backgrounds are shown in Figure 1. The data are available as supplementary material.

Figure 2 shows the final experimental radial distribution ($rD(r)$) of distances calculated in the usual way[14b] from the modified molecular intensity $I'(s) = sI_m(s)Z_CZ_FA_C^{-1}A_F^{-1}\exp(-0.001s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron-scattering amplitude.[16] The scattering amplitudes and phases were taken from tables.[16] The assignment of the interatomic distances is indicated by the vertical bars; they have lengths proportional to the weights of the terms.

Theoretical Calculations

Molecular Structures. Complete geometry optimizations of the molecules cyclobutene and HFCB were carried out at the ab initio Hartree–Fock level with use of the program GAUSSIAN-86.[17] Two split-valence basis sets were used: Pulay et al.'s 4-21G[18] and Hariharan and Pople's 6-31G**.[19] Results of these calculations are summarized in Table I. The calculations for cyclobutene were done to test their reliability for this type of strained ring. As is seen from Table I, the agreement between experiment and theory for cyclobutene is excellent at the 6-31G** level, and even at the 4-21 level if the conventional small offset values[18] are supplied to correct for the systematic deficiencies of the theory. They also give results in very good agreement with the experimental ones[13] for the small differences between the two types of C–C and C–H distances. The C=C distance from each basis set turns out to be too short—a well-known problem at the Hartree–Fock level. The agreement of the calculated structures with that measured for cyclobutene, particularly that from the larger basis, suggests that the similar HF/6-31G* optimized geometry of HFCB will be of high accuracy.

Vibrational Force Field. To take account of shrinkage effects in the experimental distance measurements appropriate distance conversions are needed. These are given by $r_a = r_\alpha + \delta r + K - l^2/r = r_g - l^2/r$, where the centrifugal distortions δr, the perpendicular amplitude corrections K and the root-mean-square amplitudes of vibration l can be calculated from a quadratic vibrational force field. Results of adjustments of an empirical force field to the measured fundamentals of HFCB[20] led to unreasonable values for several of the constants, and accordingly we decided to calculate the quadratic force field of HFCB at the HF/4-21G and HF/6-31G* level with use of the analytic second derivatives package of GAUSSIAN-86. These calculations were done at the optimized geometries to allow a simple transformation of the calculated Cartesian force constants to symmetry constants.[21] Frequencies were then calculated from the theoretical force fields by well-known methods. It is well established that most calculated frequencies at these levels of theory are larger than the experimental ones by about 10%.[22-24] It has also been established that scale factors, valid from molecule to molecule, for the different types of internal force constants may be introduced to correct for the systematic deficiencies of theory and for the anharmonicity of the measured fundamentals.[25] Standard scale factors obtained for HF/4-21G calculations apply to constants derived from corrected theoretical reference geometries,[18,26] i.e., the optimized structures to which have been added the offset parameter values mentioned above. Since we wished to employ the results without use of offset values, slight modifications of certain of these scale factors were deemed appropriate. There appears to have been little attention paid to scalings for force constants obtained from calculations at the HF/6-31G* level. A set of scale factors was derived as follows. The assigned wavenumbers for both HFCB[20] and the very similar 1,2-dichlorotetrafluorocyclobutene[20] (whose structural investigation is in progress in this Laboratory[27]) were first compared with the calculated values multiplied by 0.89,[24] and a difference greater than 50 cm^{-1} was adopted as the criterion for elimination of the corresponding mode. The excluded modes were ν_n, n = 3, 10, 14, 15, 19, and 21 for HFCB, and n = 3, 8, 9, 10, and 14 for 1,2-dichlorotetrafluorocyclobutene. Scale factors for the symmetrized force constants were then adjusted by least

---

(14) (a) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500. (b) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 1003.

(15) Hedberg, L. *Abstracts of Papers*, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1974; p 37.

(16) The elastic amplitudes and phases were from: Schafer, L.; Yates, A.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055. Inelastic amplitudes used in the background removal were from: Cromer, D. T.; Mann, J. B. *J. Chem. Phys.* **1967**, *47*, 1892. Cromer, D. T. *Ibid.* **1969**, *50*, 4857.

(17) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowitz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, Em. M.; Pople, J. A. GAUSSIAN-86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(18) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.

(19) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta (Berlin)* **1973**, *28*, 213.

(20) Klaeboe, P.; Nielsen, C. J.; Powell, D. L. *Spectrochim. Acta* **1987**, *43A*, 983.

(21) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer III, H. F., Ed.; Plenum Press, New York, 1977; Vol. 4, pp 153–185.

(22) Fogarasi, G.; Pulay, P. In *Annual Review* of *Physical Chemistry*; Rabinovitch, B. S., Ed.; Annual Reviews; Palo Alto, CA, 1984; Vol. 35, pp 191–213.

(23) Hout, R. F. Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(24) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

(25) (a) Fogarasi, G.; Pulay, P. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier; Amsterdam, 1985; Vol. 14, pp 125–219. (b) Blom, C. E.; Otto, L. P.; Altona, C. *Mol. Phys.* **1976**, *32*, 1137.

(26) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

(27) Thomassen, H.; Hedberg, K., work in progress.

TABLE II: Definition of Symmetry Coordinates and Values of Scale Factors for Hexafluorocyclobutene

	coordinates[a]	descripn	scale factors	
			4-21	6-31G*
a_1				
S_1	Δr_{12}	C=C str	0.76	0.76
S_2	Δr_{34}	–C–C– str	0.92	0.80
S_3	$\Delta(r_{23} + r_{14})$	=C—C– str	0.92	0.80
S_4	$\Delta(r_{17} + r_{28})$	=C—F str	0.90	0.75
S_5	$\Delta(r_{39} + r_{3,10} + r_{45} + r_{46})$	–C–F str	0.90	0.75
S_6	$\Delta(\alpha_{712} - \alpha_{714} + \alpha_{821} - \alpha_{823})$	C=C—F bend	0.80	0.81
S_7	$\Delta(\alpha_{93,10} + \alpha_{546})$	CF_2 sciss	1.00	0.85
S_8	$\Delta(\alpha_{543} + \alpha_{643} - \alpha_{541} - \alpha_{641} + \alpha_{934} + \alpha_{10,34} - \alpha_{932} - \alpha_{10,32})$	CF_2 wag	1.00	0.85
a_2				
S_9	$\Delta(r_{45} - r_{46} - r_{39} + r_{3,10})$	–C–F str	0.90	0.75
S_{10}[b]	$\Delta(\gamma_{1742} - \gamma_{2813})$	=C—F oop	0.74	0.83
S_{11}	$\Delta(\alpha_{543} - \alpha_{643} + \alpha_{541} - \alpha_{641} - \alpha_{934} + \alpha_{10,34} - \alpha_{932} + \alpha_{10,32})$	CF_2 rock	1.00	0.85
S_{12}	$\Delta(\alpha_{543} - \alpha_{643} - \alpha_{541} + \alpha_{641} - \alpha_{934} + \alpha_{10,34} + \alpha_{932} - \alpha_{10,32})$	CF_2 twist	1.00	0.85
S_{13}[b]	$\Delta(\tau_{4123} - \tau_{1234} + \tau_{2341} - \tau_{3412})$	ring tors	1.00	1.12
b_1				
S_{14}	$\Delta(r_{45} - r_{46} + r_{39} - r_{3,10})$	–C–F str	0.90	0.75
S_{15}[b]	$\Delta(\gamma_{1742} + \gamma_{2813})$	=C—F oop	0.74	0.83
S_{16}	$\Delta(\alpha_{543} - \alpha_{643} + \alpha_{541} - \alpha_{641} + \alpha_{934} - \alpha_{10,34} + \alpha_{932} - \alpha_{10,32})$	CF_2 rock	1.00	0.85
S_{17}	$\Delta(\alpha_{543} - \alpha_{643} - \alpha_{541} + \alpha_{641} + \alpha_{934} - \alpha_{10,34} - \alpha_{932} + \alpha_{10,32})$	CF_2 twist	1.00	0.85
b_2				
S_{18}	$\Delta(r_{23} - r_{14})$	=C—C– str	0.92	0.80
S_{19}	$\Delta(r_{17} - r_{28})$	=C—F str	0.90	0.75
S_{20}	$\Delta(r_{39} + r_{3,10} - r_{45} - r_{46})$	–C–F str	0.90	0.75
S_{21}	$\Delta(\alpha_{712} - \alpha_{714} - \alpha_{821} + \alpha_{823})$	C=C—F bend	0.80	0.81
S_{22}	$\Delta(\alpha_{93,10} - \alpha_{546})$	CF_2 sciss	1.00	0.85
S_{23}	$\Delta(\alpha_{543} + \alpha_{643} - \alpha_{541} - \alpha_{641} - \alpha_{934} - \alpha_{10,34} + \alpha_{932} + \alpha_{10,32})$	CF_2 wag	1.00	0.85
S_{24}	$\Delta(\alpha_{412} - \alpha_{123} + \alpha_{234} - \alpha_{341})$	ring bend	1.00	0.85

[a] Atom numbering from Figure 2. Normalization factors have been omitted. [b] The out-of-plane (γ_{ijkl}) and torsion (τ_{ijkl}) coordinates are defined according to: Califano, S. *Vibrational States*; Wiley: New York, 1976; pp 85–87. γ is positive if the sign of the product $\mathbf{r}_{ij}\cdot(\mathbf{r}_{ik} \times \mathbf{r}_{il})$ is positive. τ_{ijkl} is positive when, viewed in the direction $k \rightarrow j$, $\mathbf{r}_{kl}$ rotates counterclockwise with respect to $\mathbf{r}_{ji}$.

squares[26] to give the best possible fit to the remaining observed wavenumbers. The HFCB symmetry coordinates and the scale factors for the force constants are given in Table II and our scaled quantum mechanical (SQM[26]) force fields for the molecule are listed in Table III. We have selected the higher level results as the best model of the force field. Although, as discussed below, there are some questions about this force field, the correction terms needed for the ED work ($\delta r + K$ as well as the amplitudes l) are not very sensitive to small changes in it. We are confident that the force field is adequate for calculation of these corrections to the accuracy needed. The correction terms calculated from the force field with use of the program ASYM20[28] can be deduced from Table IV.

Experimental Structure Determination

Refinements of the r_α-type structure were carried out by least squares,[29] adjusting a theoretical $sI_m(s)$ curve simultaneously to three sets of experimental data that comprised equally weighted averages of the data obtained at each camera distance. Tests for planarity of the carbon skeleton were first carried out. Torsion around the C=C double bond and changes in the rock angles of the CF_2 groups were introduced. Refinements of such models tended to restore the carbon skeleton to planarity. We concluded that our data hold no evidence for a structure having symmetry less than C_{2v} and our final refinements were based on models of this symmetry.

With a C_{2v} symmetry assumption eight geometrical parameters are required to define the structure. These were chosen to be the distances $\langle r(C{-}F)\rangle = [r(C_1{-}F) + 2r(C_3{-}F)]/3$, $\Delta r(C{-}F) = r(C_3{-}F) - r(C_1{-}F)$, $\langle r(C{-}C)\rangle = [r(C_3{-}C_4) + 2r(C_2{-}C_3)]/3$, $\Delta r(C{-}C) = r(C_3{-}C_4) - r(C_2{-}C_3)$, $r(C{=}C)$, and the angles $\angle(C{=}C{-}F)$, $\angle(F{-}C{-}F)$, and $\angle(C_1{-}C_2{-}M)$, where M is the midpoint of a line joining the two fluorines of the CF_2 group. The effect of vibrational anharmonicity was included in the intensity function. Anharmonicity coefficients $\kappa = al^4/6$ were calculated with the Morse anharmonicity constants equal to 2.4 Å^{-1} for C–F bonds, 2.1 Å^{-1} for C–C and C=C bonds, and zero for all nonbond distances.[30,31] The structure was defined in terms of r_α distances and the corrections to give r_g and r_a gotten as described earlier. There are also 18 vibrational amplitude parameters. The amplitudes (l) for each of the distance pairs $C_2{-}C_3$ and $C_3{-}C_4$, $C_1{\cdot}C_3$ and $F_5{\cdot}F_6$, $F_5{\cdot\cdot}F_7$ and $F_7{\cdot\cdot}F_8$, and $C_3{\cdot\cdot}F_7$ and $F_6{\cdot\cdot}F_9$ were handled as single parameters by restricting their differences to calculated values. Two other amplitude groups were also formed and handled similarly, one corresponding to the bond distances $C_1{-}F$, C=C, and $C_3{-}F$; and one to the nonbond distances $C_1{\cdot}F_5$, $C_1{\cdot}F_8$, $C_3{\cdot}F_5$, and $C_3{\cdot}F_8$. Table IV contains results for two models. In model A all structural parameters were refined simultaneously. In model B differences between the lengths of the two types of C–C single bonds and C–F bonds were held at 0.049 and 0.029 Å, respectively, the values in the optimized structure from the HF/6-31G* calculation: the former difference is appreciably less than the experimental one and it was of interest to explore the consequences of an experimental error in the two distances involved. Lacking good reason to the contrary, we take model A as the preferred model. The structure-defining parameters for this model are shown in Table I. Table V is the correlation matrix for the model and curves for it are shown in Figures 1 and 2.

Discussion

Molecular Structure. When account is taken of uncertainties in the measurements, ours and the earlier results for the structure of HFCB are in very good agreement. There is thus little doubt that the $C_3{-}C_4$ distance is longer than that in cyclobutene itself (Table I) and that the other ring distances are shorter. The lengthening of $C_3{-}C_4$ may be qualitatively understood from concepts of the competing effects of rehybridization and electronegativity. In HFCB electrons attracted by the electronegative fluorine atoms are preferentially drawn from p orbitals which increases the average s character of the bonds formed by the carbons. The charges (Mulliken charges obtained from HF/6-31G** calculations) on carbons C_3 and C_4, slightly negative (−0.24) in cyclobutene, are quite positive (+0.70) in HFCB; the $C_3{-}C_4$ bond in HFCB is lengthened because Coulomb repulsion dominates the rehybridization shortening. On the other hand, the $C_2{-}C_3$ bond is shorter in HFCB than in cyclobutene because of the nominal positive charge on C_2 (+0.33), smaller than on C_3, has been reduced by back p_π bonding from the fluorine atom and rehybridization dominates. The picture in these terms is less clear for the double bond, especially because of the large uncertainty in the measured value, but in any event the relative lengths in HFCB vs cyclobutene appear to be the same as in *cis*-1,2-difluoroethylene (r_{av} = 1.327 (11) Å)[2d] vs ethylene (r_z = 1.335 (3) Å).[32] Further, the C–F bond lengths in HFCB are slightly shorter than those of similar type in *cis*-1,2-difluoroethylene and in 1,1,2,2-tetrafluoroethane. The r_g values are $C_1{-}F$ = 1.315 (10) Å and $C_3{-}F$ = 1.347 (4) Å in HFCB, 1.335 (4) Å in the difluoroethylene,[2d] and 1.364 (4) Å in the tetrafluoroethane.[4]

The F–C–F bond angle, at 107.6 (5)° is clearly smaller than the tetrahedral value. The explanation is that, although for HFCB the *average* p character of the four hybrid bonds formed by carbon

---

(28) Hedberg, L. *Abstract of Papers*, Eighth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1978, p 49.

(29) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.

(30) Andrews, E. B.; Barrow, R. F. *Proc. Phys. Soc.* **1951**, *64A*, 481.

(31) Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 805.

(32) (a) Ballik, E. A.; Ramsay, D. A. *Astrophys. J.* **1963**, *137*, 84. (b) Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

TABLE III: Values off Quadratic SQM HF/6-31G* (HF/4-21) Force Constants for Hexafluorocyclobutene[a]

				a_2				
a_1				S_9	S_{10}	S_{11}	S_{12}	S_{13}
S_1	8.803			5.269	0.054	0.732	0.106	−0.099
	(8.318)			(6.120)	(0.027)	(0.789)	(0.132)	(−0.074)
S_2	−0.100	3.891			0.639	0.089	−0.032	−0.288
	(0.016)	(3.556)			(0.565)	(0.072)	(−0.029)	(−0.247)
S_3	0.086	0.143	4.165			0.796	0.034	−0.139
	(0.144)	(0.168)	(4.081)			(0.719)	(0.013)	(−0.154)
S_4	0.571	−0.155	0.084	6.851			0.996	0.006
	(0.446)	(−0.198)	(−0.005)	(7.594)			(1.118)	(−0.014)
S_5	−0.141	0.492	0.529	0.306	6.626			0.346
	(−0.159)	(0.424)	(0.437)	(0.238)	(7.100)			(0.302)
S_6	0.034	0.037	0.006	0.055	−0.021	0.564		
	(0.065)	(0.027)	(−0.022)	(0.063)	(−0.022)	(0.546)		
S_7	0.135	−0.217	−0.167	−0.105	0.337	−0.017	1.767	
	(0.104)	(−0.157)	(−0.177)	(−0.092)	(0.323)	(−0.010)	(1.771)	
S_8	0.078	0.096	−0.104	0.003	−0.042	−0.121	−0.033	1.444
	(0.094)	(0.052)	(−0.110)	(−0.004)	(−0.029)	(−0.098)	(0.002)	(1.528)
					b_1			
b_2					S_{14}	S_{15}	S_{16}	S_{17}
S_{18}	4.403				5.250	−0.097	0.490	−0.141
	(4.061)				(6.115)	(−0.054)	(0.552)	(−0.149)
S_{19}	−0.402	6.330				0.470	−0.158	0.049
	(−0.424)	(7.145)				(0.457)	(−0.125)	(0.047)
S_{20}	0.694	−0.020	6.224				0.791	−0.011
	(0.666)	(−0.045)	(6.799)				(0.696)	(−0.094)
S_{21}	−0.148	0.112	0.016	0.615				0.872
	(−0.122)	(0.113)	(0.022)	(0.583)				(0.867)
S_{22}	−0.232	−0.037	0.389	0.017	1.729			
	(−0.234)	(−0.025)	(0.330)	(0.012)	(1.783)			
S_{23}	0.075	0.115	−0.002	0.032	0.048	1.369		
	(0.113)	(0.109)	(−0.026)	(0.031)	(0.043)	(1.476)		
S_{24}	−0.114	−0.423	−0.351	−0.006	0.166	−0.024	1.698	
	(−0.131)	(−0.460)	(−0.339)	(−0.018)	(0.146)	(−0.051)	(2.132)	

[a] Ab initio values scaled with factors from Table II. Units are consistent with energy in attojoules and coordinates in angstroms or radians.

TABLE IV: Results of Structure Refinements for Hexafluorocyclobutene[a]

	preferred model (A)					model B		
parameter	$(r_\alpha, \angle_\alpha)$	$(r_g{}^b)$	$(r_a{}^b)$	(l)	(l_{calcd})	$(r_\alpha, \angle_\alpha)$	$(r_a{}^b)$	(l)
C_1–F_7	1.307 (10)	1.315	1.313	0.044 (3)	0.043	1.310 (4)	1.317	0.044 (2)
C_1=C_2	1.319 (23)	1.324	1.323	0.043 (3)	0.042	1.317 (25)	1.320	0.043 (2)
C_3–F_9	1.341 (4)	1.347	1.345	0.046 (3)	0.045	1.339 (4)	1.344	0.046 (2)
C_2–C_3	1.499 (5)	1.502	1.500	0.052 (7)	0.050	1.510 (4)	1.511	0.061 (5)
C_3–C_4	1.581 (11)	1.584	1.582	0.053 (7)	0.051	1.559 (4)	1.559	0.062 (5)
$C_1 \cdot C_3$	2.082 (8)	2.084	2.083	0.050 (6)	0.051	2.082 (9)	2.083	0.050 (6)
$F_5 \cdot F_6$	2.164 (5)	2.171	2.170	0.056 (6)	0.057	2.163 (5)	2.169	0.056 (6)
$C_1 \cdot F_5$	2.423 (10)	2.428	2.426	0.068 (4)	0.066	2.426 (10)	2.428	0.069 (4)
$C_1 \cdot F_8$	2.428 (19)	2.435	2.434	0.058 (4)	0.056	2.444 (20)	2.450	0.059 (4)
$C_3 \cdot F_5$	2.461 (9)	2.465	2.463	0.070 (4)	0.068	2.445 (7)	2.447	0.071 (4)
$C_3 \cdot F_8$	2.543 (11)	2.548	2.546	0.068 (4)	0.066	2.541 (11)	2.544	0.069 (4)
$F_5 \cdot F_9$	2.694 (15)	2.700	2.695	0.121 (18)	0.113	2.684 (14)	2.685	0.120 (19)
$C_1 \cdot F_9$	3.070 (8)	3.073	3.071	0.074 (7)	0.078	3.069 (5)	3.070	0.075 (8)
$F_5 \cdot F_7$	3.177 (15)	3.183	3.180	0.096 (7)	0.103	3.158 (12)	3.161	0.089 (9)
$F_7 \cdot F_8$	3.174 (40)	3.181	3.179	0.086 (7)	0.093	3.234 (27)	3.240	0.079 (9)
$C_3 \cdot F_7$	3.389 (10)	3.392	3.391	0.061 (7)	0.055	3.391 (7)	3.393	0.062 (7)
$F_6 \cdot F_9$	3.456 (12)	3.460	3.457	0.087 (7)	0.081	3.447 (11)	3.449	0.088 (7)
$F_5 \cdot F_8$	4.318 (6)	4.320	4.318	0.099 (9)	0.096	4.319 (6)	4.319	0.099 (9)
R^c	0.075					0.077		

[a] Distances (r) and amplitudes (l) in angstroms; angles ($\angle$) in degrees. Quantities in parentheses are estimated 2σ. For definitions of the distance types see text. [b] Uncertainties estimated to be the same as for r_α. [c] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

C_3 is less than in pure sp^3 bonds, the two bonds to the fluorines claim relatively more p character than do those to the adjacent carbons. In cyclobutene[13] the methylene groups are tipped toward each other so that the planes containing them do not bisect the C–C–C angles. In HFCB the two CF_2 groups are also tipped toward each other, by about 2°. Both results are consistent with a bond order for C_3–C_4 that is less than for C_1–C_4.

Finally it is appropriate to compare the measured structures of cyclobutene and HFCB with the theoretical ones computed at the Hartree–Fock level as part of the present study. The agreement (see Table I) is excellent for cyclobutene even at the 4-21 level, especially if the small offset values[18,33] are applied to correct for the systematic deficiencies of the calculation. The calculations correctly predict a long C_3–C_4 distance for this compound. The agreement of the calculated 6-31G* structure for HFCB with the experimental r_α one (r_α-type distances are more nearly equal to calculated r_e values than are r_a or r_g) is also very good except for the C_3–C_4 bond where the calculated value is nearly 0.04 Å smaller. The magnitude of this difference is somewhat disturbing in view of the otherwise good agreement between calculated and observed values of the bond lengths. (A similar difference has been found in the case of 1,2-dichloro-

---

(33) Fogarasi, G.; Császár, A. G. *Spectrochim. Acta* **1988**, *44A*, 1067.

TABLE V: Correlation Matrix (×100) for Parameters of Model A[a]

	parameter	σ^b	r_1	r_2	r_3	r_4	r_5	$\angle_6$	$\angle_7$	$\angle_8$	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}
1	$r(\mathrm{C_1{-}F})$	0.30	100	-47	19	22	-60	44	41	40	69	-8	-27	13	2	-41	-54	17	1
2	$r(\mathrm{C_3{-}F})$	0.15		100	8	-13	-36	-20	21	-82	-78	<1	-25	1	-4	25	21	-36	-1
3	$r(\mathrm{C_2{-}C_3})$	0.18			100	-40	-30	31	-20	-3	13	43	<1	19	11	-7	2	<1	<1
4	$r(\mathrm{C_3{-}C_4})$	0.35				100	-13	-56	52	26	19	-60	12	-44	10	-7	<1	1	1
5	$r(\mathrm{C{=}C})$	0.81					100	-32	-67	30	<1	<1	51	-17	3	19	40	14	<1
6	$\angle(\mathrm{C{=}C{-}F})$	41.17						100	4	13	21	43	-43	65	-24	-14	-37	7	-3
7	$\angle(\mathrm{C{-}C{-}M})$	34.71							100	-9	-6	-25	-42	11	10	-32	-40	-7	-2
8	$\angle(\mathrm{F{-}C{-}F})$	18.69								100	69	-12	9	3	4	-20	-18	30	1
9	$l(\mathrm{C{=}C,C{-}F})$	0.07									100	-15	14	6	-1	-21	-19	32	7
10	$l(\mathrm{C_2{-}C_3,C_3{-}C_4})$	0.24										100	-5	30	<1	-2	-7	-2	-5
11	$l(\mathrm{C_1{\cdot}C_3,F_5{\cdot}F_6})$	0.19											100	-36	2	15	34	11	4
12	$l(\mathrm{C{\cdot}F_5,C{\cdot}F_8})$	0.09												100	-1	-5	-17	4	<1
13	$l(\mathrm{F_5{\cdot}F_9})$	0.61													100	-24	-18	5	-2
14	$l(\mathrm{C_1{\cdot}F_9})$	0.24														100	57	3	9
15	$l(\mathrm{F_5{\cdot}F_7,F_7{\cdot}F_8})$	0.23															100	2	6
16	$l(\mathrm{C_3{\cdot}F_7,F_6{\cdot}F_9})$	0.22																100	6
17	$l(\mathrm{F_5{\cdot}F_8})$	0.28																	100

[a] Distances (r) and amplitudes (l) in angstroms; angles ($\angle$) in degrees. For numbering of atoms see Figure 2. For explanations about grouping of the amplitudes see text. [b] Standard deviations (×100) from least squares.

TABLE VI: Wavenumbers ($\mathrm{cm^{-1}}$) for Fundamentals of Hexafluorocyclobutene

	calculated[a]					
	HF/4-21	HF/6-31G*		measured		
$\tilde{\nu}_i$	SQM	scaled	SQM	ref 20	ref 34	characterization of mode[b]
a_1						
1	1788	1818	1781	1795	1799	C=C, =C—F str
2	1413	1410	1404	1418	1418	-C-F, =C—C-, -C-C- str
3	1170	1178	1178	1375	1387	-C-C-, =C—C- str
4	975	967	959	959	1136	=C-F, -C-F str; wag
5	665	669	664	683	966	-C-F str; sciss
6	453	451	461	465	684	sciss
7	271	278	283	279	469	wag; =C—C- str
8	229	229	232	228	286	=C—C—F bend
a_2						
9	1281	1221	1223	1180	1182	-C-F str
10	687	673	696	576	493	oop; rock
11	469	481	489	496	337	oop; rock; twist
12	228	223	230	235	174	twist; oop
13	84	82	96	98	98	tors; rock
b_1						
14	1268	1206	1178	1126	1282	-C-F str
15	566	565	580	507	638	oop; rock; twist
16	197	208	215	212	187	twist; oop
17	182	183	188	181	146	rock; oop
b_2						
18	1446	1399	1392	1281	1259	=C—F str; ring bend
19	1336	1280	1279	1174	1171	-C-F, =C—C- str
20	978	969	962	970	983	-C-F, =C—F, =C—C str; wag
21	831	820	840	913	579	wag; =C—C—F bend
22	648	614	622	636	429	-C-F str; ring bend; sciss
23	435	413	426	428	238	sciss; ring bend
24	252	254	258	263	217	=C—F bend; =C—C str

[a] SQM wavenumbers were calculated from the SQM force fields of Table III. Scaled HF/6-31G* wavenumbers are ν(calcd) × 0.89; see text. [b] Symmetry coordinates indicated are those dominant in each normal mode. For definitions of symmetry coordinates see Table II.

tetrafluorocyclobutene.[27]) It is unfortunate that the rotational constants for HFCB have not been measured. Those calculated from the r_α of our model A are A = 1470.4 MHz, B = 1452.2 MHz, and C = 983.6 MHz. These should be very slightly smaller than the corresponding B_0's.

Vibrational Spectrum. An early assignment[34] of the gas-phase vibrational spectrum of HFCB has been recently revised by Klaeboe, Nielsen, and Powell (KNP).[20] The two sets of wavenumber assignments together with those obtained from our force fields are given in Table VI. In general the experimental and theoretical results are seen to be in good agreement; in some cases, however, there are rather large discrepancies. SQM force fields are usually of good quality[22-26] and the wavenumbers calculated from them generally agree with experimental observation to within considerably less than 100 $\mathrm{cm^{-1}}$. Thus, we regard the larger discrepancies as disagreement between theory and experiment that merits reexamination from the experimental side. Some remarks follow.

An interesting experimental observation is that the C=C stretching wave number of HFCB[20] at 1795 $\mathrm{cm^{-1}}$ is considerably higher than the similar wavenumbers of ethylene (1630 $\mathrm{cm^{-1}}$)[35] and cyclobutene (1564 $\mathrm{cm^{-1}}$).[36] This increase may seem somewhat surprising in view of the calculated C=C stretching force constants: ~8.8 (HFCB) vs ~9.0 (ethylene[26]) and ~8.5 $\mathrm{aJ{\cdot}Å^{-2}}$ (cyclobutene[37]). It turns out that the increased wavenumber for C=C in HFCB is dominantly a mass effect: if one substitutes

---

(34) Nielsen, J. R.; El-Sabban, M. Z.; Alpert, M. *J. Chem. Phys.* **1955**, *23*, 324.

(35) Duncan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221.

(36) Aleksanyan, V. T.; Garkusha, O. G. Izv. *Akad. Nauk. SSSR, Ser. Khim.* **1976**, 2227.

(37) Császár, A. G., unpublished results.

J. Phys. Chem. **1990,** *94,* 3531-3539 **3531**

the =C–F fluorines with chlorines, for example, the wavenumber drops[20] even when the C=C force constant is essentially unchanged.[27]

In both experimental studies[20,34] two a_1 bands near 1400 cm^{-1} were assigned based partly on the polarized nature of these bands in the Raman spectrum. Important indications of our theoretical calculations are (a) there should be only one a_1 fundamental at around 1400 cm^{-1} (ν_2), (b) the highest b_2 fundamental (ν_{18}) should also be placed in this region, (c) ν_3 (the third a_1 fundamental) is about 1150 cm^{-1} and has a very high depolarization ratio suggesting that it could be observed as depolarized in the Raman, and (d) still another b_2 fundamental should be found at a wavenumber as high as 1320 cm^{-1} (ν_{19}). It is disturbing that the experimental studies show all the bands around 1400 cm^{-1} (1420, 1383, and 1375 cm^{-1}; KNP) to be definitely polarized in the Raman; one possible candidate, however, as a combination band around 1380 cm^{-1} is ~980 cm^{-1} (b_2) + ~420 cm^{-1} (b_2).

The present theoretical results further suggest that the highest a_2 and b_1 fundamentals at HFCB are fairly near each other with wavenumbers about 1200 cm^{-1}. Thus, a band should be found in both the IR and Raman spectra of HFCB in this region. Furthermore, according to the calculated intensities, the highest b_1 fundamental (ν_{14}) should have the greatest intensity in the IR spectrum. The strongest and in the 1140–1340-cm^{-1} region is at 1174 cm^{-1} in the gas. Thus it seems reasonable to assign the band at 1174 cm^{-1} to ν_{14} and a somewhat higher wavenumber to ν_9.

The calculations are perfectly in line with all but three of KNP's assignments below 1000 cm^{-1}. The exceptions are ν_{10} (~120 cm^{-1}), ν_{15} (~70 cm^{-1}), and ν_{21} (~–70 cm^{-1}), where the differences in parentheses are theoretical minus experimental. It is very likely that the assignment of ν_{10} should be revised; however, experimental verification could be complicated by the fact that calculation predicts this band to almost coincide with ν_5. The experimental assignment of ν_{15} was quite uncertain[20] and the calculation predicts that it should be at a somewhat higher wavenumber. Lastly, from past experience it is quite unlikely that a force field calculation at the Hartree–Fock SCF level for a molecule like HFCB would place a fundamental at too low a wavenumber, which suggests a new assignment for ν_{21} may be in order.

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE84-11165 and CHE88-10070 to Oregon State University. We are grateful to the College of Science of OSU for a generous grant of computing time.

Supplementary Material Available: From each plate: tables of total intensities, final backgrounds, and molecular intensities (15 pages). Ordering information is given on any current masthead page.

7-Azaindole and Its Clusters with Ar, CH_4, H_2O, NH_3, and Alcohols: Molecular Geometry, Cluster Geometry, and Nature of the First Excited Singlet Electronic State

Seong K. Kim and Elliot R. Bernstein*

Chemistry Department, Colorado State University, Fort Collins, Colorado 80523

(Received: September 11, 1989)

Mass-resolved excitation vibronic spectra of jet-cooled 7-azaindole and its clusters with Ar, CH_4, NH_3, H_2O, D_2O, CH_3OH, and C_2H_5OH are reported and analyzed with regard to molecular and cluster geometry and the nature of the first excited singlet state. Large changes in the various spectra are observed upon clustering and upon deuteration of 7-azaindole. The observed vibronic spectra of both 7-azaindole and its clusters can be rationalized with two general assumptions: (1) the hydrogen attached to the pyrrole nitrogen of 7-azaindole is out of the molecular plane in the first excited singlet state; and (2) the observed spectra are characterized by strong $n\pi^*$–$\pi\pi^*$ mixing not completely removed by the clustering. MOPAC5 calculations of molecular geometry suggest that the S_1 state is nonplanar. Additional cluster potential energy calculations suggest that the formation of cyclic hydrogen-bonded clusters is not likely for these gas-phase 1:1 or 1:2 7-azaindole/solvent clusters: the major gas-phase solvent clustering probably takes place at the π-system of the 7-azaindole molecule.

I. Introduction

7-Azaindole (see Figure 1a, 7AZI) is suggested to have two very interesting and important properties in solution: (1) when solvated by hydrogen-bonding solvents (such as water, alcohols, ammonia, or even itself), it is thought to form a cyclic structure through a double hydrogen bond (Figure 1b);[1-3] and (2) it will tautomerize (Figure 1c) in protic solvent solutions via a cyclic hydrogen-bonded intermediate.[1,2,4-8] Such behavior is suggestive of the behavior of DNA bases,[9] and thus, 7AZI has been a particularly attractive and compelling system for study.

Spectra of isolated 7AZI and/or 7AZI clustered with various hydrogen-bonding and non-hydrogen-bonding solvents should aid in the elucidation of the energetics and dynamics involved in both the cyclic hydrogen-bonded solvation structures and in the tautomerization process. Supersonic jet expansion techniques coupled with laser spectroscopy and mass resolution (mass-resolved excitation spectroscopy) are, of course, an excellent experimental approach to the study of molecular and cluster structure and energetics. Through these techniques coupled with state of the art molecular orbital semiemperical calculations and potential energy cluster structure calculations, a good deal can be learned

---

(1) Taylor, C. A.; El-Bayoumi, M. A.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1969,** *63,* 253.

(2) Ingham, K. C.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1974,** *96,* 1674.

(3) Stäglich, P.; Zander, M. *Z. Naturforsch.* **1976,** *31a,* 1391.

(4) Tokumura, K.; Watanabe, Y.; Itoh, M. *J. Phys. Chem.* **1986,** *90,* 2362. Tokumura, K.; Watanabe, Y.; Udagawa, M.; Itoh, M. *J. Am. Chem. Soc.* **1987,** *109,* 1346.

(5) bulska, H.; Chodkowsks, A. *J. Am. Chem. Soc.* **1980,** *80,* 3259.

(6) Hetherington, W. M.; Micheels, R. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979,** *66,* 230.

(7) McMorrow, D.; Aartsma, T. J. *Chem. Phys. Lett.* **1986,** *125,* 581.

(8) Moog, R. S.; Bovino, S. C.; Simon, J. C. *J. Phys. Chem.* **1988,** *92,* 6545.

(9) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry I*; Freeman: San Francisco, CA, 1980.

0022-3654/90/2094-3531$02.50/0