SPECTROSCOPY OF 1,4,4-TRIFLUOROCYCLOBUTENE*

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ABSTRACT

A new compound, 1,4,4-trifluorocyclobutene (144FCB), has been obtained as a byproduct in the reduction of perfluorocyclobutene with sodium borohydride. A comprehensive spectroscopic study of 144FCB has been undertaken including microwave, IR, Raman and NMR data. Ground state rotational constants, $A = 3629.34$, $B = 2600.74$, and $C = 2098.93$ MHz, were derived from the microwave data and used to distinguish 144FCB from other possible isomers and to propose a structure. NMR chemical shifts and coupling constants and the vibrational fundamentals are assigned and compared to other members of the cyclobutene family. Frequencies of vibrational fundamentals of 144FCB (cm^{-1}) are: (a') 3126, 2967, 1679, 1457, 1377, 1245, 1179, 1045, 914, 752, 690, 577, 453, 263, 213; (a'') 3000, 1198, 1061, 938, 821, 577, 381, 190, – . A small amount of 3,3,4-trifluorocyclobutene has also been found in the products of the reduction reaction, and its NMR spectra and its IR spectrum are reported.

INTRODUCTION

Several fluorine-substituted cyclobutenes have undergone significant spectroscopic study. In all cases these fluorocyclobutenes have been symmetrically substituted ones. Klaeboe et al. [1] investigated the IR and Raman spectra of perfluorocyclobutene and 1,2-chlorotetrafluorocyclobutene and proposed assignments of all the vibrational fundamentals. Harris and Ditchfield [2] and Robinson and Harris [3] studied the NMR spectra of these two molecules and of 3,3,4,4-tetrafluorocyclobutene (3344FCB) and extracted coupling constants from the complex spectra of the two $(AA'X)_2$ spin systems. No microwave investigations of fluorine-substituted cyclobutenes have been reported.

For cyclobutene itself Bak et al. [4] investigated the microwave spectrum of a number of isotopic modifications and obtained a complete structure. The NMR spectra of cyclobutene have been studied in detail by Hill and Roberts

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*Dedicated to Professor E. Bright Wilson, Jr.

[5]. The vibrational spectra of cyclobutene have been investigated in several laboratories [6–9]. Although questions remain about the assignment of several of the fundamentals of cyclobutene, this assignment assists the interpretation of the vibrational spectra of partly substituted cyclobutenes. A vibrational assignment of *cis*-3,4-dichlorocyclobutene is also in the literature [10].

What has proved to be the unsymmetrically substituted 1,4,4-trifluorocyclobutene (144FCB) became available as a by-product of the synthesis of 3344FCB by reduction of perfluorocyclobutene with sodium borohydride in diglyme [11, 12]. Despite a full NMR investigation of this new substance, it was not possible to distinguish 144FCB from one of its possible isomers, 1,3,3-trifluorocyclobutene (133FCB). Neither arguments based on magnitudes of coupling constants nor on chemical shift values could be relied upon. One cannot assume that a more distant cross-ring coupling constant of either the HH, FF or HF type is larger than a vicinal one. No simple additive pattern of the proton, ^{13}C or ^{19}F chemical shifts seems to exist for these molecules that permits distinguishing between the structures of the two trifluorocyclobutene isomers of interest. In contrast, microwave spectroscopy provides a decisive means of identifying 144FCB.

In this paper a comprehensive spectroscopic study of 144FCB is reported. Our results include the principal moments of inertia of 144FCB and a structure as found from microwave spectroscopy, chemical shifts and coupling constants in comparison with those of perfluorocyclobutene and 3344FCB as obtained from ^{1}H, ^{19}F and ^{13}C NMR spectra, and an assignment of the vibrational fundamentals derived from the IR and Raman spectra. Despite the low symmetry of 144FCB, the structural variety in this molecule makes a virtually complete vibrational assignment possible without recourse to a study of isotopic modifications.

A small amount of an isomer of 144FCB, 3,3,4-trifluorocyclobutene (334FCB), was also obtained as a by-product of the reduction of perfluorocyclobutene. A less extensive spectroscopic investigation of this species has been undertaken than for 144FCB. The full NMR assignment for 334FCB is reported here, which is helpful in interpreting the spectrum of 144FCB, and the principal bands of its IR spectrum.

EXPERIMENTAL

Synthesis [11, 12]

24 mmol of Perfluorocyclobutene (Peninsular Chem Research) were dissolved in 20 ml dry diglyme (Aldrich, dried over sodium metal). This solution was stirred and held at $-15\,^\circ$C while a solution of 2 g of sodium borohydride (50 mmol) in 80 ml of dry diglyme was added dropwise over 2 h. The volatile products were removed by vacuum distillation at room temperature. The over-

all yield was about 30%, measured gasometrically. The products were separated by gas chromatography at 0°C on an 8 m×6 mm column packed with 20% Halocarbon oil (Halocarbon Products, 11-21) on 45/60 mesh Chromosorb P. The principal product was 3344FCB, elution time 1.0. In addition to a few percent of 144FCB, elution time 0.67, small amounts were obtained of *trans-* and *cis*-1-chloro-1,2-difluoroethylene [13], elution times 0.33 and slightly longer; chlorotrifluoroethylene [14], elution time 0.5; and 334FCB, elution time 1.2. Chlorotrifluoroethylene, the presumed starting material in the commercial synthesis of perfluorocyclobutene, was an impurity in the purchased material. The two chlorodifluoroethylenes were considered to be products of the reduction of chlorotrifluoroethylene. Samples of 144FCB and 334FCB were dried by passage through a column containing phosphorus pentoxide.

For use in the microwave study the reaction was run by adding a perfluorocyclobutene solution dropwise to a sodium borohydride solution at 0°C. In this mode of reaction, the reducing agent was in excess throughout the reaction. The products were not separated. NMR spectroscopy showed that the product mixture contained 4.5 times more 144FCB than 3344FCB. No 334FCB was detected in this sample.

Characterization

144FCB and 334FCB, which are new substances, were identified by their mass and NMR spectra. Both had parent mass peaks of 108 with good intensities and had cracking patterns consistent with their structures. The NMR spectra of 144FCB are described below. The proton NMR spectrum of 334FCB consists of complex multiplets at 6.71, 6.43 and 5.37 ppm. The first multiplet, due to one of the vinylic protons (probably C_1H), consists of five doublet splittings ($J_{HF} = 15.0$ Hz, $J_{HF} = 9.5$ Hz, $J_{HH}(HC=CH) = 3.2$ Hz, $J_{HH} = 0.6$ Hz, $J_{HF} = 0.3$ Hz). The second multiplet, due to the other vinylic proton, consists of three doublet splittings ($J_{HF} = 4.2$ Hz, $J_{HH}(HC=CH) = 3.2$ Hz, $J_{HF} = 1.3$ Hz) and one accidental triplet splitting ($J_{HF} = J_{HH} = 2.4$ Hz). The third multiplet due to the CFH protons consists of a large doublet ($J_{HF}(gem) = 58.3$ Hz) split into two patterns with four doublet splittings ($J_{HH} = 2.4$ Hz, $J_{HF}(cis?) = 1.4$ Hz, $J_{HH} = 0.6$ Hz, $J_{HF}(trans?) = 0.5$ Hz). The ^{19}F spectrum has a multiplet at -178.2 ppm due to the CFH part of the molecule and multiplets at -115.5 ppm and at -100.0 ppm due to the two CF_2 fluorine nuclei. These patterns can be explained with $J_{FF}(gem) = 207.0$ Hz, $J_{FF}(trans?) = 19.4$ Hz, and $J_{FF}(cis?) = 12.9$ Hz in addition to the various J_{HF} coupling constants. The proton-decoupled, fluorine-coupled ^{13}C spectrum consists of doublets(d) of triplets(t) at 144.4 and at 139.9 ppm due to the vinylic carbon atoms, a d of t at 118.8 ppm due to the CF_2 carbon atom, and a d of d of d at 93.5 ppm due to the CFH carbon atom. Principal bands in the gas-phase IR spectrum of 334FCB are (cm^{-1}) 3095 A,w; 2975 C,m; 1335 A,vs; 1260 B?,s; 1215 C,s; 1135 A,vs;

1095 C,vs; 1040 B?,m; 980 C,m; 895 C,m; 780 A,m; 710 A,m; 620 B?,m; 525 A,w; 455 ?,m. The absence of significant absorption in the 1550 cm^{-1} region is consistent with no halogen substituents on the carbon atoms of the double bond of a cyclobutene ring. The gas-phase IR spectrum of 144FCB is presented below.

Microwave spectroscopy

Microwave spectra were recorded in the range 26.5–40.0 GHz with a Hewlett-Packard 8460A Stark modulated spectrometer. Radiofrequency microwave double resonance (RFMWDR) spectra were obtained with a tunable amplitude modulated radiofrequency source from 1–20 MHz at 1–3 W output. All microwave data were collected with a PDP-11/23 computer interfaced to the spectrometer. Frequency measurements at pressures of 10–15 mtorr were accurate to ±0.1 MHz. The spectrometer cells were cooled with dry ice.

Nuclear magnetic resonance spectroscopy

Detailed NMR spectra were recorded on a Bruker AF 200-MHz FT instrument. Samples were dissolved in $CFCl_3$, the ^{19}F reference substance, and were supplemented with TMS, the ^1H and ^{13}C reference substance.

Vibrational spectroscopy

Infrared and Raman spectra were obtained mostly as described recently [15]. IR spectra were recorded in 10 cm gas cells with 0.5 cm^{-1} resolution on a Perkin-Elmer 1760 FT spectrometer to 370 cm^{-1} and with 1 cm^{-1} resolution from 500 to 150 cm^{-1} on a Perkin-Elmer 1800 FT spectrometer. The sample cell and the reference cell for the low frequency spectra had 1.6 mm Marlex (Phillips Petroleum) high-density polyethylene windows. Raman spectra were obtained with a Spex Ramalog 5 spectrometer, a Coherent Innova 70 argon-ion laser and a Nicolet 1180 computer. Survey scans were at about 5 cm^{-1} resolution, and more detailed scans were at about 2.5 cm^{-1} resolution.

Mass spectroscopy

The mass spectra were obtained on a Hewlett-Packard instrument consisting of a 5890A gas chromatograph (phenyl methyl silicone OV2 capillary column), a 5970 quadrupole mass spectrometer and an associated computer system.

RESULTS AND DISCUSSION

Microwave spectroscopy

Broad spectral traces revealed Q-branch series with band heads separated by about 2510 MHz. The band heads and their spacing gave initial estimates for $A - (B+C)/2$ and K_p for each series. Trial and error then led to their precise assignment as b-type series of the type $J_{K_p,K_o} - J_{K_p-1,K_o+1}$ with values of $A - C = 1530.4$ MHz and $\kappa = -0.344258$. Model calculations for all possible singly, doubly and triply fluorinated cyclobutene species indicated that these values were only consistent with the 144FCB species. The 133FCB species could be clearly eliminated since a- and c-type selection rules were expected with $A - C = 4300$ MHz and $\kappa = -0.97$. The rotational constants as well as Stark and RFMWDR modulation behavior of many of the lines also eliminated 3344FCB as the carrier of the spectrum. The modulation properties were consistent with two kinds of selection rules (a- and b-type) while the symmetry of the tetrafluoro species permits only one. Although the NMR spectrum indicated that about 20% of the microwave sample was the tetrafluoro species, no transitions for this species have yet been identified.

The assignment was completed by finding a number of low J, R-branch transitions predicted to fall in regions based on structural models consistent with the Q-branch parameters. This assignment was aided by RFMWDR experiments involving the nearly degenerate a-dipole connected K_p doublets. For example, the $4_{4,0}-4_{4,1}$ splitting was estimated to be 4.5 MHz. With an r.f. pump frequency of 4.5 MHz, doublets were located in the regions centered around 27 777 and 35 037 MHz which could be assigned to the $3_{3,0}-4_{4,1}$, $3_{3,1}-4_{4,0}$ and $4_{4,0}-5_{5,1}$, $4_{4,1}-5_{5,0}$ pairs. This result gave predictions for other R-branch transitions which were found, thereby confirming the assignment. The assigned transitions are given in Table 1. The rotational and centrifugal distortion constants (Watson's A-reduction, representation $\Gamma[16]$) are given in Table 2. Although the RFMWDR traces clearly indicated the presence of a-dipole selection rules, no a-dipole transitions in the MW region could be unambiguously assigned due to their low intensity. This outcome was consistent with bond dipole estimates which predicted $\mu_a = 0.2$ D and $\mu_b = 2.8$ D ($\mu_{total} = 2.81$ D) for 144FCB. The dipole moment was not determined due to spectral congestion and intensity complications.

A plausible structure which can reproduce the rotational constants within 1 MHz is given in Table 3. The numbering of the atoms is shown in Fig. 1. This model incorporates a planar cyclobutene ring since the observed value of $I_a + I_b - I_c$ is consistent with such a configuration for plausible CH_2 and CF_2 parameters. For a planar ring, $I_a + I_b - I_c = 4m_F c_F^2 + 4m_H c_H^2$ and depends only on the out-of-plane coordinates of the *gem* H and F atoms. The structural parameters in Table 3 are within about 0.02 Å and 2° of similar parameters in

TABLE 1

Microwave transitions (MHz) for 1,4,4-trifluorocyclobutene

J' $(K'_p,\ K'_o)$ - J'' $(K''_p,\ K''_o)$	ν Obs.	Obs. − Calc.[a]	J' $(K'_p,\ K'_o)$ - J'' $(K''_p,\ K''_o)$	ν Obs.	Obs. − Calc.[a]
4 (4, 1) − 3 (3, 0)	27762.18	−0.05	19 (12, 7) − 19 (11, 8)	27738.66	0.16
4 (4, 0) − 3 (3, 1)	27793.61	0.23	19 (12, 8) − 19 (11, 9)	27745.99	0.02
5 (3, 2) − 4 (2, 3)	31236.11	−0.03	20 (12, 8) − 20 (11, 9)	27426.41	0.09
5 (5, 1) − 4 (4, 0)	35035.00	−0.07	20 (12, 9) − 20 (11, 10)	27449.70	−0.13
5 (5, 0) − 4 (4, 1)	35040.00	0.17	13 (13, 1) − 13 (12, 2)	31304.77	−0.02
6 (1, 5) − 5 (2, 4)	27072.20	−0.08	14 (13, 2) − 14 (12, 3)	31233.80	−0.05
6 (3, 4) − 5 (2, 3)	32652.65	0.02	15 (13, 3) − 15 (12, 4)	31146.02	0.00
6 (3, 3) − 5 (2, 4)	37496.07	0.00	16 (13, 4) − 16 (12, 5)	31038.55	0.01
6 (4, 2) − 5 (3, 3)	37620.96	0.06	17 (13, 5) − 17 (12, 6)	30908.22	0.00
6 (4, 3) − 5 (3, 2)	36806.70	−0.07	18 (13, 6) − 18 (12, 7)	30751.37	−0.06
6 (5, 2) − 5 (4, 1)	39756.31	−0.12	19 (13, 7) − 19 (12, 8)	30563.79	−0.14
6 (5, 1) − 5 (4, 2)	39799.09	0.15	21 (13, 8) − 21 (12, 9)	30071.55	0.01
7 (0, 7) − 6 (1, 6)	30249.70	0.03	21 (13, 9) − 21 (12, 10)	30076.92	0.05
7 (1, 7) − 6 (0, 6)	30278.45	0.00	22 (13, 10) − 22 (12, 11)	29766.32	−0.07
7 (1, 6) − 6 (2, 5)	31679.07	−0.02	14 (14, 1) − 14 (13, 2)	33814.11	0.00
7 (2, 5) − 6 (3, 4)	31052.74	0.02	15 (14, 2) − 15 (13, 3)	33745.18	0.05
12 (12, 1) − 12 (11, 2)	28795.18	−0.01	16 (14, 3) − 16 (13, 4)	33660.88	−0.05
13 (12, 2) − 13 (11, 3)	28721.90	0.01	17 (14, 4) − 17 (13, 5)	33559.23	0.04
14 (12, 3) − 14 (11, 4)	28629.67	0.02	18 (14, 5) − 18 (13, 6)	33437.35	0.05
15 (12, 4) − 15 (11, 5)	28515.09	0.00	19 (14, 6) − 19 (13, 7)	33292.33	0.04
16 (12, 5) − 16 (11, 6)	28374.22	−0.07	20 (14, 7) − 20 (13, 8)	33120.78	0.02

[a]Frequencies calculated with constants given in Table 2.

TABLE 2

Rotational and centrifugal distortion constants for 1,4,4-trifluorocyclobutene

A (MHz)	3629.31(1)[a]	Δ_J[b]	(kHz)	0.32(12)
B (MHz)	2600.74(1)	Δ_K	(kHz)	0.38(17)
C (MHz)	2098.93(1)	δ_J	(kHz)	0.11(2)
		δ_K	(kHz)	−0.61(36)

[a]The number in parentheses is one standard deviation in the fit.
[b]Watson A reduction (I^r). Δ_{JK} was not well determined; the fit gave −0.13(22) kHz.

species such as cyclobutene [4] and fluorine-substituted cyclopropanes [17] except for the C–C single bond opposite the double bond. This parameter is 0.05 Å shorter than in cyclobutene. The C=C bond and the bond between the fluorine-substituted carbon atoms are also approximately 0.02 Å shorter than in cyclobutene while the C–C bond opposite the fluorine substituents is about 0.02 Å longer. These distances are consistent with C–C bond shortening adjacent to fluorine-substituted carbon atoms in cyclopropanes and cyclopropenes [17, 18]. This finding may not be significant, since the spectrum of only one isotopic species was assigned. Lengthening of some bonds and commensurate

TABLE 3

Structural parameters[a] for 1,4,4-trifluorocyclobutene consistent with the rotational constants

Bond	Value (Å)	Angle	Value (deg.)	Angle	Value (deg.)
C_1H_5	1.080	$C_1C_2C_3$	93.7	$C_1C_4H_9$	114.0
C_4H_9	1.080	$C_2C_3C_4$	87.6	$C_3C_4H_9$	116.7
C_1C_2	1.320	$C_3C_4C_1$	85.0	$C_2C_3F_7$	114.6
C_2C_3	1.500	$C_4C_1C_2$	93.7	$C_4C_3F_7$	115.9
C_1C_4	1.535	$C_1C_2F_6$	134.6	$F_7C_3F_8$	107.5
C_3C_4	1.516	$C_3C_2F_6$	131.7	$H_9C_4H_{10}$	109.0
C_2F_6	1.370	$C_2C_1H_5$	135.0		
C_3F_7	1.348	$C_4C_1H_5$	131.3		

[a]See Fig. 1 for atom numbering. The molecule is assumed to have C_s symmetry. The structure is not unique (see text).
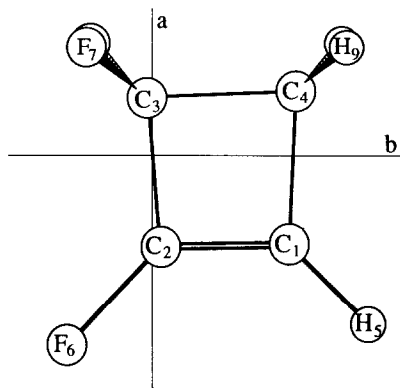

Fig. 1. Numbering of atoms and location of the principal moment of inertia axes in 1,4,4-trifluorocyclobutene.

shortening of others or changes in the FCC angles, etc., will also fit the rotational constants. It does not seem worthwhile to speculate further on the best structure at this time.

NMR spectroscopy

The 144FCB molecule is an AA′DMM′X spin system. As such, a first-order analysis of the ^{1}H and ^{19}F NMR spectra should not suffice. The ^{1}H and ^{19}F spectra appear, however, to be those expected for an A_2DM_2X system. Thus, J_{AM} and $J_{AM'}$ coupling constants are not distinguishable, and the J_{AA} and J_{MM} constants do not make an observable contribution to the spectrum. In the proton spectrum, the vinylic proton signal consists of a doublet ($J = 7.7$ Hz) of triplets ($J = 11.8$ Hz), each "line" of which is a triplet ($J = 1.0$ Hz). The meth-

ylenic proton signals are a doublet ($J = 12.3$ Hz) of triplets ($J = 3.1$ Hz), each "line" of which is a doublet ($J = 1.0$ Hz). The vinylic ^{19}F signal is an eleven-line spectrum, which, with overlaps, fits the 18-line pattern of a triplet ($J = 12.3$ Hz) split into doublets ($J = 7.7$ Hz) and in turn into triplets ($J = 4.0$ Hz). The methylenic ^{19}F signal is a doublet ($J = 11.8$ Hz) split into triplets ($J = 3.1$ Hz) and into doublets again ($J = 4.0$ Hz).

These pseudo-first-order spectra are a consequence of tight coupling through the dominant size of the $J_{FF}(gem)$ coupling constant in comparison with the $J_{HH}(gem)$ and the two J_{HF} coupling constants. From the spectra of 334FCB, reported above, we obtained good approximations for three of these constants: $J_{FF}(gem) = J_{MM} = 207$ Hz, $J_{HF}(cis) = J_{AM} = 1.4$ Hz, and $J_{HF}(trans) = J_{AM'} = 0.5$ Hz. For $J_{HH} = J_{AA}$ a value of about 13 Hz was obtained from the spectrum of 3-fluorocyclobutene [19]. Using these coupling constants and the standard analysis for an AA$'$MM$'$ system [20], we find that the AA$'$MM$'$ spectrum reduces to two triplets with internal spacings of $(J_{AM} + J_{AM'})/2$, an average value for the J_{HF} coupling constants between methylene groups.

Table 4 contains a summary of the ^{1}H and ^{19}F NMR parameters for 144FCB in comparison with published values for the related molecules, 3344FCB and perfluorocyclobutene. The three pertinent parameters for cyclobutene are given in a footnote to Table 4. As indicated above, the value for $^3J_{H4F3}$ is an average of the *cis* and *trans* values. The average value of 3.1 Hz is not far from the average value of 0.9 Hz for 334FCB. The good agreement between the value of 11.8 Hz for the cross-ring $^4J_{H1F3}$ in 144FCB and one of the two coupling constants, 11.16 Hz, reported for 3344FCB decides the assignment for 3344FCB. For 3344FCB we conclude that this cross-ring J_{HF} coupling constant of 11.16 Hz is markedly larger than the *vic* J_{HF} constant of -1.65 Hz. In 144FCB the other cross-ring HF coupling constant, vinylic F to methylenic H, is similarly large at 12.3 Hz. For perfluorocyclobutene an equivalent ambiguity in assigning the two values of J_{FF} as cross-ring or *vic* seems also to be resolved by the results for 144FCB. Since the *vic* value is $^3J_{F2F3} = 4.0$ Hz in 144FCB, the value of 6.77 Hz is a better choice than 16.36 Hz for the *vic* coupling constant in perfluorocyclobutene.

From this discussion of the coupling constant patterns in 144FCB, 3344FCB and perfluorocyclobutene, it is obvious that these NMR parameters could not have distinguished 144FCB from its isomer 133FCB, nor can a useful pattern be discerned in the chemical shifts that would have made a distinction certain between these two isomers.

Table 4 includes NMR parameters from the proton-decoupled, ^{19}F-coupled ^{13}C spectra of 144FCB, 3344FCB and perfluorocyclobutene. All of these data are from our laboratories. In general, the CF coupling constants are in good agreement throughout the series of molecules. The chemical shift for the vinylic carbon (CH) in 144FCB is surprisingly low in comparison with 3344FCB.

TABLE 4

NMR parameters for 1,4,4-trifluorocyclobutene and two other fluorocyclobutenes[a]

Molecule[e]	δ_{H1}	δ_{H4}	δ_{F2}	δ_{F3}	$^3J_{H1H4}$	$^3J_{H1F2}$	$^4J_{H1F3}$	$^3J_{H4F3}$	$^4J_{H4F2}$	$^3J_{F2F3}$
[structure]	5.47[b]	2.58[b]	−105.5	−113.9	1.0[b]	7.7	11.8	3.1	12.3	4.0
[structure]	6.76[c]			−111.9[c]			11.16[c]			
[structure]			−130.4[d]	−120.3[d]						6.77[d]

	δ_{C1}	δ_{C2}	δ_{C3}	δ_{C4}	$^1J_{C2F2}$	$^1J_{C3F3}$	$^2J_{C2F3}$	$^2J_{C1F2}$	$^2J_{C3F2}$	$^2J_{C4F3}$	$^3J_{C1F3}$	$^3J_{C4F2}$
[structure]	111.4	147.0	120.0	36.2	347	277	26.4	5.1	26.9	23.0	16.1	18.5
[structure]	143.5	143.5	120.7	120.7		286	19.3			25.6	19.3	
[structure]	135.4	135.4	114.4	114.4	338	284	24.6	~0	27.9	23.4	24.6	26.8

[a]Chemical shifts in ppm relative to internal TMS or CFCl$_3$; coupling constants in Hz.
[b]For cyclobutene, 6.03 ppm, 2.57 ppm, and 1.00 Hz (or possibly −0.35 Hz), respectively [5].
[c]Coupling constant could not be distinguished from −1.65 Hz [3].
[d]Coupling constant could not be distinguished from ±16.36 Hz [2].
[e]Numbering schemes for molecules:
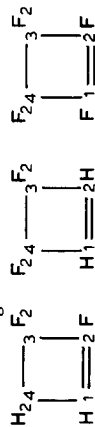
Note: the numbering scheme for trifluorocyclobutene is inconsistent with the 144FCB name. After the MW and NMR spectroscopic work was complete, the 144FCB name was adapted for consistency with IUPAC rules.

Evidently, the vinylic fluorine atom in 144FCB exerts a potent electronic influence on its neighboring vinylic carbon (CH) atom.

Vibrational spectroscopy

Vibrational spectra of 144FCB are shown in Figs. 2–4. Figure 2 is the gas-phase IR spectrum. Figure 3 is the extension of the gas-phase IR spectrum into the lower frequency region. The Raman spectrum in Fig. 4 is of the liquid at −55°C under survey conditions.

Our microwave study, like previous work on cyclobutenes including cyclobutene itself [4, 21, 22], has indicated that the ring in 144FCB is essentially planar. The vibrational spectra are fully consistent with this molecule having a symmetry plane as its single symmetry element. The molecule belongs to the C_s point group and has for its 24 normal modes: 15 a' (IR, type-A/B gas-phase band shapes; Raman, polarized bands) +9 a'' (IR, type-C gas-phase band shapes; Raman, depolarized bands). Were the ring not planar in its lowest energy state, 144FCB would have no symmetry element. All the Raman bands would be polarized. Yet, inspection of Fig. 4 shows a number of bands that appear to be depolarized (perpendicular polarization intensity/parallel polarization intensity = 0.75) as required for C_s symmetry.

The orientation of the principal axes of the moments of inertia in 144FCB, based on the microwave results, is shown in Fig. 1. The I_b axis is essentially parallel to the C=C bond, the I_a axis is nearly coincident with the C_2–C_3 bond, and the I_c axis is perpendicular to the plane of the ring. The spacing between
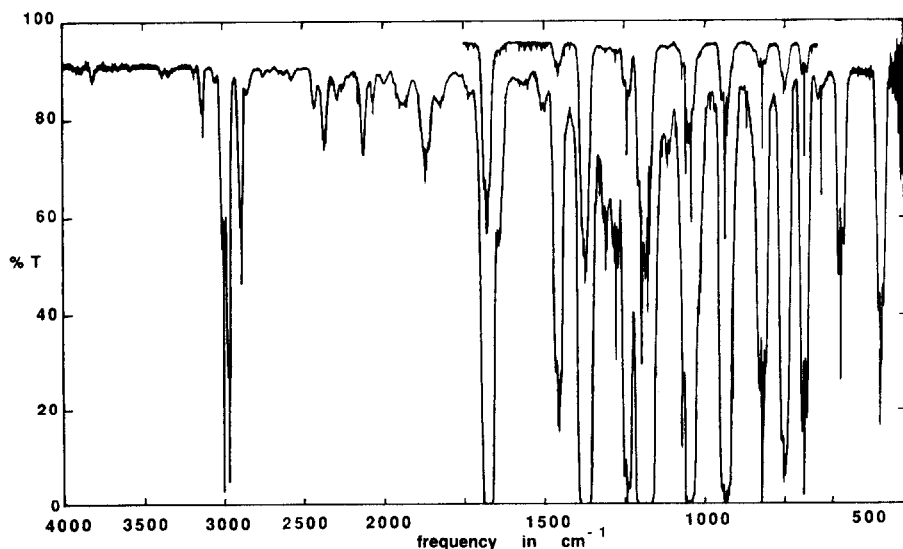

Fig. 2. IR spectrum of gaseous 1,4,4-trifluorocyclobutene. Pressures 50 and 3 torr.
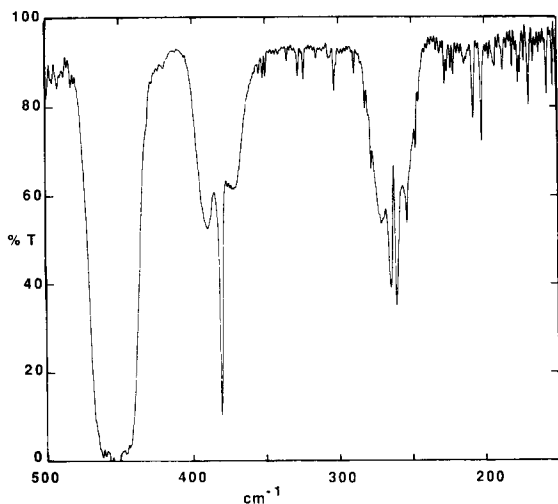
Fig. 3. IR spectrum of gaseous 1,4,4-trifluorocyclobutene in the low frequency region. Pressure 270 torr. Fine structure is due to some uncompensated atmospheric water.
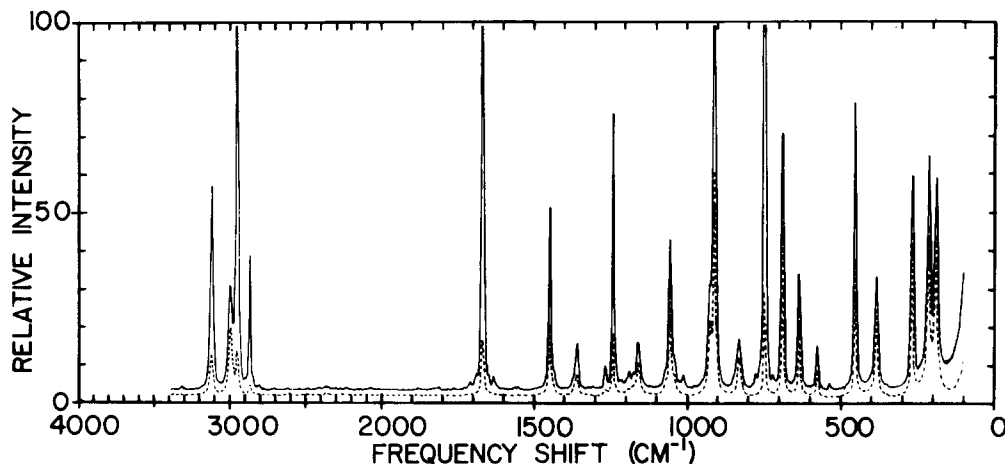

Fig. 4. Raman spectrum of liquid 1,4,4-trifluorocyclobutene at $-55\,^{\circ}$C.

R and P branches of type-C bands should be greater than the corresponding spacing in type-A to type-B bands.

Table 5 gives the assignments of fundamental vibration frequencies of 144FCB to bands in the IR and Raman spectra. Included in this table are the PR spacings of bands. Table 5 includes some weaker spectral features, which are assigned as binary combination tones. Yet weaker features which have also been assigned satisfactorily as binary combinations have been omitted from the table for brevity.

As seen in Figs. 2 and 3 eleven of the fifteen a' fundamentals of 144FCB

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TABLE 5

Observed vibrational frequencies (cm^{-1}) and assignments for 1,4,4-trifluorocyclobutene

IR, gas			Raman. liq.			Assignment	
Freq.[a]	Shape[b]	Int.[c]	Freq.	Pol.[d]	Int.		
3126.0(16)	A?	w	3131	p	m	ν_1 fund.	a'
3000.3(20)	C	m	3007	dp?	m	ν_{16} fund.	a''
2966.6(16)	A	m	2964	p	vs	ν_2 fund.	a'
2886.6(15)	A/B	m	2880	p	m	$2924 = \nu_3 + \nu_6$	A' F.R. with ν_2
2425	?	w				$2431 = \nu_3 + \nu_{10}$	A'
2368	B?	w				$2371 = \nu_4 + \nu_9$	A'
2123	?	w				$2129 = \nu_5 + \nu_{10}$	A'
1867	B?	w				$1870 = \nu_7 + \nu_{11}$	A'
						$1867 = \nu_8 + \nu_{20}$	A''
			1691	p	w	$1698 = \nu_6 + \nu_{13}$	A'
1678.6(16)	B	vs	1670	p	vs	ν_3 fund.	a'
			1653	p	w	$1666 = \nu_9 + \nu_{10}$	A'
1640		m	1635	p	w	$1642 = \nu_5 + \nu_{14}$	A'
			1564	p	vw	$1577 = \nu_{19} + \nu_{21}$	A'
1456.8(16)	B	m	1452	p	m	ν_4 fund.	a'
			1440	p?	w	$1442 = \nu_{10} + \nu_{11}$	A'
1377.1(12)	B	vs	1367	p?	w	ν_5 fund.	a'
			1359	p?	w		
1328.8	Q	w				$1329 = \nu_{10} + \nu_{12}$	A'
1309.8	B/A	m				$1319 = \nu_{19} + \nu_{22}$	A'
1278.9(15)	A	m	1269	p	w	$1278 = 2 \times \nu_{21}$	A'
1244.6(15)	A?	s	1243	p	s	ν_6 fund.	a'
1197.9(20)	C	vs	1160	dp	w	ν_{17} fund.	a''
1178.9(14)	A?	s	1191	p	vw	ν_7 fund.	a'
			1177	p	vw		
1117.7		w				$1128 = \nu_{19} + \nu_{23}$	A'
1110.4						$1127 = \nu_9 + \nu_{15}$	A'
1072.3	C?	m	1072	dp	w	$1071 = \nu_{11} + \nu_{22}$	A''
1060.7	C?	m	1057	dp	m	ν_{18} fund.	a''
1044.7(14)	A?	s	1044	p?	w	ν_8 fund.	a'
937.7(21)	C	s	927	dp?	w-sh	ν_{19} fund.	a'
914.1	Q	m	913	p	vs	ν_9 fund.	a'
821.4(19)	C	m	831	dp	w	ν_{20} fund.	a''
			777	p	vw	$789 = \nu_{12} + \nu_{15}$	A'
752.4(16)	B	m	748	p	vs	ν_{10} fund.	a'
690.4(15)	A	m	688	p	s	ν_{11} fund.	a'
639.0(20)	C	w	634	dp	m	ν_{21} fund.	a''
577.0(16)	A	m	575	p?	w	ν_{12} fund.	a'
			536	p	vw	$530 = 2 \times \nu_{14}$	A'
453.2(16)	A/B	m	453	p	s	ν_{13} fund.	a'
380.6(19)	C	m	384	dp	m	ν_{22} fund.	a'
262.9(16)	A/B	w	265	p?	m	ν_{14} fund.	a'
			213	dp?	m	ν_{15} fund.	a'
			190	dp	m	ν_{23} fund.	a''

[a]PR spacing in parentheses. [b]Band shape: A, B, C and A/B blend. [c]vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [d]p = polarization ratio less than 0.75; dp = polarization ratio equal to or greater than 0.75.

appear in the gas-phase IR spectrum as bands of type-A-to-type-B shape. These frequencies are 3126, 2967, 1679, 1457, 1377, 1245, 752, 690, 577, 453, and 263 cm^{-1}. All are confirmed by polarized bands in the Raman spectrum (Fig. 4). Although the IR band for ν_9 at 914 cm^{-1} is a questionable feature on the shoulder of a much stronger band, the very strong, polarized counterpart in the Raman spectrum leaves no doubt about this assignment.

The spectral evidence for two more a' fundamentals of 144FCB, ν_7 and ν_8, being in the 1190 and 1050 cm^{-1} regions, respectively, is unmistakable. Overlaps with bands due to a'' modes in each of these regions causes doubt about the choices between the two symmetry species. The a' fundamental near 1190 cm^{-1} is largely CF stretching and thus, as expected, weak in the Raman spectrum and subjected to a large frequency shift in going from the gas phase to the liquid phase. Thus, the Raman spectrum is of no help in settling this assignment. From the band shapes in the IR spectrum it is felt that the higher frequency component is the better candidate for a type-C shape of the a'' mode, whereas the lower frequency component, 1179 cm^{-1}, is a better choice for a type-A shape and for ν_7. Although the overlapped bands in the IR spectrum in the 1050 cm^{-1} region have even less distinctive shapes than those in the 1190 cm^{-1} region, the Raman spectrum suggests that the higher frequency component is the a'' mode. Although the higher frequency component has the greater intensity, this band has a depolarization ratio of 0.75. Furthermore, the lower frequency shoulder, which was better separated when observed with 2.5 cm^{-1} resolution than is shown in Fig. 4, appears to be polarized. Thus, 1045 cm^{-1} seems to be ν_8. This choice of the lower frequency band for ν_8 is consistent with the higher frequency feature being the better choice for the type-C band of an a'' mode. As part of the discussion of the assignment of the a'' fundamentals, the remaining a' fundamental will be considered.

144FCB has nine a'' fundamentals. The evidence for the selection of 1198 cm^{-1} for ν_{17} and of 1061 cm^{-1} for ν_{18} has been discussed in the previous paragraph. Five other fundamentals are represented by well-defined type-C band shapes in the IR spectra, Figs. 2 and 3. In addition, large values of PR branch spacings in the 19–21 cm^{-1} range correlate with type-C band shapes. These bands are at 3000, 938, 821, 577 and 381 cm^{-1}. All but the 938-cm^{-1} band have obvious, depolarized counterparts in the Raman spectrum, Fig. 4. The reasonably distinct shoulder at 927 cm^{-1} (seen better at 2.5 cm^{-1} resolution than in Fig. 4) appears to be depolarized and thus supports the 938 cm^{-1} assignment.

Two bands of comparable intensity at 213 and 190 cm^{-1} in the Raman spectrum remain for possible assignment to ν_{23} and ν_{24} and the lowest frequency a' mode. As seen in Fig. 3, neither of these Raman bands has an observable counterpart in the gas-phase IR spectrum at a pressure as high as 270 torr. Of the three modes under consideration the one that is likely to be weak and overshadowed in the Raman spectrum is ν_{24}, the ring puckering mode. Weak Raman bands for ring puckering are found for cyclobutene [8], perfluorocy-

clobutene ($\nu_{\text{pucker}} = 98 \text{ cm}^{-1}$) [1], 3344FCB ($\nu_{\text{pucker}} = 132 \text{ cm}^{-1}$) [23], 1-fluorocyclobutene (261 cm^{-1}, [24]), 1-chlorocyclobutene, (211 cm^{-1} [24]), 3-fluorocyclobutene (221 cm^{-1}, [24]) and 3-chlorocyclobutene (196 cm^{-1} [24]). From a consideration of these puckering frequencies, we estimate the puckering frequency of 144FCB at 150–200 cm^{-1}. Both observed bands have depolarization ratios near the depolarized limit. However, the one at 213 cm^{-1} seems to have a somewhat smaller ratio and thus to be the best candidate for the a' mode. Thus, ν_{15} is assigned to 213 cm^{-1}, and ν_{23} is assigned to 190 cm^{-1}. The ring puckering frequency remains unassigned.

Table 6 summarizes the assignments of the vibrational fundamentals of 144FCB and gives qualitative descriptions of these modes in terms of symmetry coordinates. Also included in the table are correlations with pertinent fun-

TABLE 6

Summary of the vibrational fundamentals of 1,4,4-trifluorocyclobutene and correlation with comparable modes of cyclobutene; frequencies in cm^{-1}

Sym. species		Approx. description[a]	144FCB	Cyclobutene[b]
a'	ν_1	=CH str	3126	3066/3058
	ν_2	sym CH_2 str	2967	2943/2936
	ν_3	C=C str	1679	1570
	ν_4	sym CH_2 bend	1457	1449/1432
	ν_5	CC str/sym CF_2 str	1377	
	ν_6	=CH bend	1245	1185/1296
	ν_7	=CF str	1179	
	ν_8	CC str	1045	1116/1214
	ν_9	CH_2 rock	914	875/888
	ν_{10}	sym CF_2 str/CC str	752	
	ν_{11}	CC stretch	690	980
	ν_{12}	CCCC bend	577	906
	ν_{13}	=CF bend	453	
	ν_{14}	sym CF_2 bend	263	
	ν_{15}	CF_2 rock	213	
a''	ν_{16}	asym CH_2 str	3000	2953
	ν_{17}	asym CF_2 str	1198	
	ν_{18}	CH_2 torsion	1061	1142/1074
	ν_{19}	asym CH_2 bend	938	1015/847
	ν_{20}	=CH flap	821	815/635
	ν_{21}	=CF flap	577	
	ν_{22}	asym CF_2 bend	381	
	ν_{23}	CF_2 torsion	190	
	ν_{24}	ring pucker		

[a]sym = symmetric w.r.t. ring plane; asym = antisymmetric w.r.t. ring plane; str = stretch.
[b]When two frequencies are given, they are paired as a_1/b_1 and a_2/b_2.

damentals of cyclobutene [7]. A few of these assignments and descriptions of modes have been modified by work that is in progress in our laboratories on related halo-substituted cyclobutenes [24]. In many cases two frequencies of cyclobutene are cited. The averages of two =CH frequencies and of two CH_2 frequencies in cyclobutene correlate with single frequencies for =CH and CH_2 modes in 144FCB. With some allowance for bond strengthening of CH bonds due to fluorine substitution, the correlations between CH modes in cyclobutene and 144FCB are good. The C=C stretching frequency is raised about 100 cm^{-1} by mixing with CF stretching, a well recognized effect in systems with fluorine-substituted double bonds [25]. Mixing of the C–C stretching coordinates with CF stretching coordinates causes substantial differences between "C–C" modes in 144FCB and cyclobutene. The likely frequency for CCCC ring bending in 144FCB appears to be much lower than in cyclobutene. This difference could be due to the anchoring of one side of the 144FCB ring by the heavy fluorine atoms.

CONCLUSIONS

Two new fluorocyclobutenes, 1,4,4-trifluorocyclobutene (144FCB) and 3,3,4-trifluorocyclobutene (334FCB), have been identified. The 144FCB molecule has been submitted to an extensive spectroscopic investigation. The ambiguity in the structural assignment of 144FCB in comparison with isomeric 1,3,3-trifluorocyclobutene has been removed by microwave spectroscopy. Double resonance experiments and b-type selection rules have led to assignments of 42 rotational lines and to the rotational constants for the normal isotopic species. A provisional structure for 144FCB, fitted to the three moments of inertia, is consistent with a planar cyclobutene ring. Relative to cyclobutene, this structure is consistent with shortening of CC bonds for fluorine-substituted carbon atoms and to lengthening of the remaining CC bond. This fluorine-substitution effect correlates with similar changes in three-membered rings.

With the structure of 144FCB settled, the NMR spectra (^{1}H, ^{19}F, and ^{13}C) have been assigned in detail. Interpretation of this tightly coupled AA′DMM′X system was aided by the simpler interpretation of the NMR spectra of the 334FCB isomer. Cross-ring and vicinal J_{HH}, J_{FF} and J_{HF} coupling constants have been distinguished and shown not to correlate with the distance between the nuclei. These findings resolve ambiguities left in the previous assignments of some of the coupling constants for 3,3,4,4-tetrafluorocyclobutene and perfluorocyclobutene.

With the exception of the ring puckering mode, ν_{24}, all the vibrational fundamentals of 144FCB have been assigned in the gas-phase IR and liquid-phase Raman spectra. The structural variety of this molecule makes such an interpretation possible without a study of isotopic modifications. The frequencies for the hydrogen-atom modes in 144FCB correlate rather well with the corre-

sponding fundamentals of cyclobutene. C–C stretching modes in 144FCB are strongly mixed with CF stretching modes. Consequently, "C–C" stretching frequencies in 144FCB do not correlate well with those in cyclobutene.

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