Perfluorocyclopropene: Experimental and Theoretical Studies of Its Structure in Gaseous, Solution, and Crystalline Phases

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Abstract: The structure of 1,2,3,3-tetrafluorocyclopropene, C_3F_4, has been determined at 156 K by X-ray crystallography and in the gas phase by a combined analysis of electron-diffraction data, rotation constants derived from the microwave spectrum, and dipolar coupling constants derived from the liquid crystal ^{19}F NMR spectrum. Structural parameters (distances/pm, angles/deg) for the solid at 156 K and gas phase (distances (r_g), angles ($\angle_\alpha$)), respectively, are the following: $r(C_1{-}C_3) = 145.3(3), 146.1(3)$; $r(C_1{=}C_2) = 129.6(4), 130.7(13)$; $r(C_3{-}F_6) = 137.0(2), 136.1(4)$; $r(C_1{-}F_4) = 131.2(2), 131.5(3)$; $\angle C_1{=}C_2F_5 = 150.4(9), 149.9(6)$; $\angle F_6C_3F_7 = 104.1(2), 105.4(5)$; $\angle C_1{=}C_2C_3 = 63.5(1), 63.4(3)$. These values are in excellent agreement with those obtained in an *ab initio* study of the molecular geometry at the electron-correlated MP2/TZ2P level. The dipole moment of C_3F_4 has been determined from Stark effect measurements to be 1.313(4) D.

Despite the high level of interest which attaches to the structure and bonding in perfluorinated compounds,[2] the smallest molecule of the perfluorocycloalkene class that has been studied hitherto is perfluorocyclobutene, C_4F_6.[3] This situation stems from problems associated with the preparation and manipulation of the simplest member of the class, 1,2,3,3-tetrafluorocyclopropene (perfluorocyclopropene), C_3F_4—a toxic, flammable, explosive gas.[4] However, the need to procure samples of C_3F_4 for research into potential oxygen carriers for blood substitutes, derived from saturation of C═C bonds in a range of cyclic perfluoroolefins with bis(trifluoroamino)oxyl,[5] enabled the present detailed structural investigation to be carried out. Such a study fills an important gap in our knowledge of highly-strained three-membered-ring compounds.

Only three structures of cyclopropenes in the gas phase have been reported, *viz.* cyclopropene, C_3H_4, itself by electron diffraction (GED)[6] and microwave (MW) spectroscopy,[7] perchlorocyclopropene, C_3Cl_4 (GED),[8] and 3,3-difluorocyclopropene, $C_3F_2H_2$ (MW).[9] Although perbromocyclopropene, C_3Br_4, can be prepared on a reasonable scale,[10] its structure has not so far been determined. Perfluorocyclopropene is of particular interest as a subject for structural study, as the extreme ring strain should lead to some unusual structural parameters. The exceptionally large $^{13}C{-}^{19}F$ coupling constant for the bond adjacent to the C═C double bond[11] (larger even than that in perfluoroethyne[12]) is an indication of a high s orbital contribution to this bond, which should be reflected in the geometry. Moreover, the properties of perfluorocyclopropene, including its symmetry, distribution of spin-$^1/_2$ nuclei, and volatility, make it an ideal candidate for a detailed structural study.

Experimental Section

Preparation of Perfluorocyclopropene. C_3F_4 was prepared by the DuPont method, namely dechlorination of 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane,[4] itself synthesized from commercial samples (Fluorochem, U.K.) of 1,2-dichloro-1,2-difluoroethylene and hexafluoropropene oxide (HFPO).[13]

In a typical experiment, a mixture of 1,2-dichloro-1,2-difluoroethylene (1:1 *E*/*Z* mixture, 86.4 g, 0.65 mol) and HFPO (215.0 g, 1.295 mol) was heated *in vacuo* in a stainless-steel autoclave (500 cm^3) at 458 K for 8 h. The vessel was allowed to cool to room temperature and the contents were passed through a trap held at 195 K. Distillation of the material retained in the trap provided a mixture of *cis*- and *trans*-1,2-dichlorotetrafluorocyclopropane (72.0 g), bp 313−315 K (lit.[13] bp 310−313 K), *ca.* 90% pure by GC analysis. A sample of this product (16.0 g) dissolved in absolute ethanol (10 cm^3) was added slowly (1 h) to a heated (328 K) and stirred suspension of zinc dust [25.9 g; pre-

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Table 1. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths for the Combined ED/MW/LCNMR Study of C_3F_4

nozzle-to-plate distance, mm	Δs^c	$s_{\min}{}^c$	$sw_1{}^c$	$sw_2{}^c$	$s_{\max}{}^c$	correl parameter	scale factor, k^a	electron wavelength,^{b} pm
286.04	2	20	40	122	144	0.486	0.785(9)	5.700
128.24	4	60	80	268	320	0.361	0.698(13)	5.700

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapor. [c] In nm^{-1}.

activated with 5% HCl(aq)] and dry zinc bromide (2.9 g) in the same solvent (40 cm^3) contained in a nitrogen-swept flask (250 cm^3) fitted with a water-cooled double-surface condenser connected to a spiral trap held at 195 K. The volatile material that collected in the trap over 6 h was distilled by trap-to-trap fractionation at $\leq$3 mmHg to yield 1,2,3,3-tetrafluorocyclopropene (2.3 g; 26% retained in the 153 K trap). The sample was >99% pure, as judged by GC analysis, and its identity confirmed by reference to its infrared and ^{19}F and ^{13}C NMR spectra.[14] In view of the flammability/explosion hazard for the compound,[4] the sample was stored with strict exclusion of air in a mild-steel cyclinder (500 cm^3) ready for use.

Electron Diffraction. Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[15] The sample was maintained at 195 K and the nozzle at 293 K during the exposure of three plates at each of the long (286 mm) and short (128 mm) camera distances. Scattering factors for benzene were also recorded, to provide calibration of the camera distances and electron wavelength. The plates were traced using a Joyce Loebl MDM6 microdensitometer at the SERC (now EPSRC) Daresbury Laboratory, under the control of a computer program, designed to optimize recovery of data from the plates.[16] Analysis of the data made use of standard data reduction[16] and least-squares refinement[17] programs and scattering factors.[18] The s ranges, weighting points and other experimental details are listed in Table 1.

Rotational Spectroscopy. Microwave spectra were measured using a conventional Stark modulation spectrometer operating at 100 kHz. Gas samples of 3−10 Pa pressure were introduced into a 3 m stainless steel X-band absorption cell, cooled to dry ice temperature. Under these conditions the sample was stable, no degradation in the spectrum being visible after *ca.* 8 h. For assignment purposes, low-resolution spectra were taken using backward-wave oscillator sources in the 18−40 GHz region with pen-plotter presentation. Assignment was initially made by measurement of the $J = 5 \leftarrow 4$ $K_a = 4$ doublet which modulates at very low fields, and this was confirmed by the use of radio frequency/microwave double resonance (RFMWDR).[19] Several low-energy vibrational states were also assigned by means of this technique, and these will be reported elsewhere.[20] Accurate microwave frequencies were measured using klystron sources and oscilloscope presentation. ^{13}C lines were observed in natural abundance, isotopic lines being distinguished from vibrational satellites of similar intensity by observing the temperature dependence of the relative intensities, and their rotational assignments confirmed *via* RFMWDR. The microwave frequencies of the main and on-axis ^{13}C(3) species (see Figure 1) are given in Table 2, and the spectroscopic constants are given in Table 3.

Liquid Crystal NMR Spectroscopy. Samples of perfluorocyclopropene (*ca.* 0.1 mmol) were dissolved in 0.5 mL of liquid crystals E7 (Merck) and ZLI-4792, which had first been degassed by repeated freeze−thaw cycles, in 5 mm Pyrex glass NMR tubes. A Bruker AS250 spectrometer, operating in the unlocked mode, was used to record the ^{19}F spectra at *ca.* 235 MHz with the sample held at 298 K.

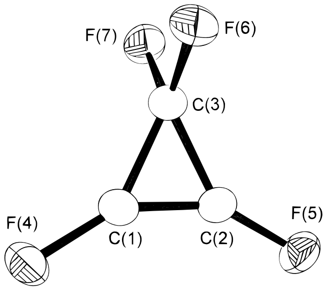

Figure 1. View of a single molecule of C_3F_4 in the crystal structure at 156 K, showing the atom numbering scheme adopted. The molecule possesses crystallographically-imposed 2-fold symmetry, with the axis passing through C(3) and the midpoint of the C(1)−C(2) bond. Thermal ellipsoids represent 50% electron probability.

The spectra, consisting of a doublet of triplets and a triplet of doublets to lower frequency, were very close to first order. They were analyzed using the program SLIQUOR,[21] the J_{FF} and J_{CF} couplings being measured from an ordinary isotropic ^{19}F spectrum in CDCl$_3$, the latter from the ^{13}C satellites. The derived direct dipolar couplings are listed in Table 3.

X-ray Diffraction. Crystal growth: A sample of 1,1,2,3-tetrafluorocyclopropene was sealed inside a Pyrex-glass capillary tube which was glued into a thermally-insulating Tufnol pip. This assembly was fixed in a standard arc-less goniometer head and mounted in the cold stream of an Oxford Cryosystems low-temperature device[22] attached to a Stoë Stadi-4 four-circle diffractometer. The sample (melting point 196−199 K) was solidified by cooling to 155 K. After the use of heating and cooling cycles failed to produce a single crystal, a miniature zone refining method, using an element of electrically-heated resistance wire, was used to achieve control over the interface between solid and liquid phases. The temperature was varied by adjusting the temperature of the cold stream and the heating voltage across the wire until only a seed microcrystal remained at 197.5 K. Slow cooling of the sample yielded an extensive region of homogeneous texture and the volume (0.5 × 0.5 × 0.5 mm^3) exhibiting the sharpest extinction under polarized light was centered. A Polaroid rotation photograph indicated the presence of a single crystal.

Crystal data: C_3F_4, $M = 112.03$, orthorhombic, space group *Pbcn* with $a = 8.282(6)$ Å, $b = 5.140(3)$ Å, $c = 8.268(5)$ Å, $V = 352.0(4)$ Å^3, $T = 156.0(2)$ K, $Z = 4$ (implying that the molecules occupy 2-fold special positions), $D_{\mathrm{calc}} = 2.114$ g cm^{-3}, $\mu = 0.273$ mm^{-1}. Diffraction data were collected on a Stoë Stadi-4 four-circle diffractometer employing graphite-monochromated Mo Kα X-radiation and $\omega-2\theta$ scans. Of the 622 reflections collected ($2\theta_{\max} = 50°$: $0 \leq h \leq 9$, $-3 \leq k \leq 6$, $0 \leq l \leq 9$), 286 unique data ($R_{\mathrm{int}} = 0.047$) were used for structure solution and refinement.

***Ab initio* Calculations.** The geometry of C_3F_4 was optimized at the HF and MP2 levels of theory in conjunction with DZP and TZ2P basis sets, employing standard procedures in the CADPAC5 program package,[23] to assess the importance of both electron correlation and basis set quality (Table 4). The DZP and TZ2P basis sets involve standard Huzinaga-Dunning[24−26] double-ζ (9s5p/4s2p) and triple-ζ

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Table 2. Transition Frequencies (MHz) for the Main and On-Axis Carbon-13 Species of Perfluorocyclopropene

						main species		carbon-13	
$J'K_a'K_c' \leftarrow J''K_a''K_c''$						ν_{obs}	$\Delta\nu_{(obs-calc)}{}^a$	ν_{obs}	$\Delta\nu_{(obs-calc)}$
5	2	3	4	2	2	22128.26	0.05		
5	3	2	4	3	1	22885.70	0.05		
5	4	1	4	4	0	22199.63	−0.01		
6	0	6	5	0	5	21567.75	0.00		
6	1	5	5	1	4	23434.17	0.05		
6	1	6	5	1	5	21566.83	−0.02		
6	2	4	5	2	3	25542.64	−0.04		
6	2	5	5	2	4	23391.14	0.05		
6	3	3	5	3	2	27293.16	0.05		
6	4	2	5	4	1	27267.52	0.03		
7	0	7	6	0	6	25008.64	−0.04		
7	1	7	6	1	6	25008.50	−0.04		
7	4	3	6	4	2	32124.20	0.02	32056.31	0.14
8	3	5	7	3	4	34327.27	0.00		
8	3	6	7	3	5	32121.70	0.07		
8	4	4	7	4	3			36322.23	0.02
8	4	5	7	4	4			33753.48	−0.10
8	5	3	7	5	2	36580.78	−0.04		
8	5	4	7	5	3	34877.22	−0.07	34811.27	0.11
8	6	2	7	6	1			35413.79	0.09
8	6	3	7	6	2	35103.82	0.01	35025.84	−0.02
9	1	8	8	1	7			33682.35	0.05
9	1	9	8	1	8			31845.61	0.02
9	2	7	8	2	6			35536.51	0.03
9	4	5	8	4	4	39926.76	−0.01		
9	4	6	8	4	5			37329.57	−0.10
9	5	5	8	5	4	38862.70	−0.06		
9	6	3	8	6	2	40720.46	0.04		
9	7	2	8	7	1			39577.18	−0.17
9	7	3	8	7	2	39499.15	−0.04	39408.88	−0.03
10	1	10	9	1	9			35282.08	0.00
16	5	12	15	7	9	28020.02	0.01		
17	2	15	17	2	16	28307.60	0.00		
17	3	15	17	1	16	28307.60	0.00		
18	3	15	18	3	16	28222.59	−0.01		
18	4	15	18	2	16	28222.59	−0.01		
23	10	14	23	8	15	25390.52	0.01		
24	9	15	24	9	16	27295.29	−0.05		
24	10	15	24	8	16	27295.87	0.04		
29	13	16	29	13	17	28015.83	0.01		
29	14	15	29	14	16	25441.16	−0.01		
σ_{fit}						0.04 MHz		0.10 MHz	

[a] Errors 1σ.

(10s6p/5s3p) sets of contracted Gaussian functions augmented with one and two sets of Cartesian d-type polarization functions, respectively, with orbital exponents $_{\alpha d}$(C) = 0.8 and $_{\alpha d}$(F) = 1.2 (one set) and $_{\alpha d}$(C) = 1.5, 0.375 and $_{\alpha d}$(F) = 2.0, 0.6667 (two sets). It has been shown elsewhere that precise geometrical parameters are determined for cyclic species at the MP2 level of theory with a flexible basis set that includes polarization functions.[27] In addition, an harmonic force field was calculated at the MP2/DZP level for the MP2/DZP optimized geometry. The fundamental vibrational frequencies are reported in Table 5. The calculations were performed on the Convex C3840 at the University of London Computer Centre.

Force-Field Calculations. The program ASYM40[28] was used to convert the theoretical (MP2/DZP level) Cartesian force field to one described by symmetry coordinates using the internal coordinates described in Table 6. An optimum fit of the theoretical to the experimental[29] frequencies was achieved by a refinement of the *ab initio* force constants using five scaling factors (Table 7). Root-mean-square amplitudes of vibration (u), perpendicular amplitudes of vibration (K), and harmonic vibrational corrections to the observed rotation and dipolar coupling constants (B_0 and D_0, respectively) were then calculated from the scaled force constants using ASYM40.

Structural Analysis

Microwave. Perfluorocyclopropene shows a rich a-type asymmetric-rotor spectrum ($\kappa = +0.24$) with many vibrational satellites, as expected from vibrational studies.[29] Both the ground state and excited state spectral intensities show the 10:6 nuclear spin statistical weightings associated with the exchange of two equivalent pairs of fluorine atoms ($I = {}^1/_2$), thus establishing the C_{2v} symmetry of the molecule. The value of $2P_{cc}{}^0 = 88.2694(5)$ u Å^2 for the main species implies a structure with two equivalent out-of-plane fluorine atoms, giving the apical (r_0) F···F distance directly as 2.15549(1) Å. This is 0.02 Å shorter than the value of 2.17297(2) Å derived in the same way for 3,3-difluorocyclopropene.[9] From the harmonic force field, the value of the inertial defect (the only other contribution to $P_{cc}{}^0$) is calculated to be $\Delta = +0.166(12)$ u Å^2, giving the zero-point average (r_z) F···F distance as 2.1575(1) Å. The change in $P_{cc}{}^0$ with substitution of ^{13}C at C(3) on the symmetry axis indicates a shrinkage of 9.7×10^{-5} Å in the C−F bonds, assuming no change in FCF angle. This agrees well with the value of 1.2×10^{-4} Å calculated from the mean-square amplitudes using the expression given by Kuchitsu *et al.*[30] Measurement of the microwave spectrum for the off-axis ^{13}C species would permit an independent microwave structure to be determined. However, the assignment of this species has so far been prevented by interfering vibrational satellite lines.

The permanent dipole moment lies along the C_2 symmetry axis such that $\mu_{total} = \mu_a$ and $\mu_b = \mu_c = 0$. The dipole moment has been determined from high-resolution Stark measurements on the $|M| = 1$ lobes of the $J = 6 \leftarrow 5$ $K_a = 4$ doublet for the vibrational ground state using the ac/dc method.[19] The results are summarized in Table 8. In deriving the experimental second-order Stark coefficients, it was necessary to make corrections for fourth-order effects which were significant at higher fields. The waveguide electrode spacing was calibrated by measurement of the $|KM| = 1$ lobes of the $J = 2 \leftarrow 1$ transition in methylacetylene.[31] The dipole moment of 1.313(4) D obtained for perfluorocyclopropene agrees well with the vector sum of 3,3-difluorocyclopropene (2.98 D),[9] cyclopropene (0.46 D),[32] and the C−F bond moment obtained from *cis*-1,2-difluoroethene ($\mu_{total} = 2.43$ D).[33] This agreement confirms that the positive end of the dipole moment in cyclopropene itself is at the double bond end of the molecule, in accord with theoretical predictions.[34] Earlier Zeeman measurements of the microwave spectrum of cyclopropene had suggested the opposite conclusion.[35]

Electron Diffraction. Assuming that perfluorocyclopropene has C_{2v} symmetry, six independent parameters are required to define the structure. As the radial-distribution curve (Figure 2) contains only four distinct peaks, it was expected that strong correlation between parameters would make it difficult to refine all the the geometrical parameters; in particular, the C=C and two different C−F bond lengths would be very similar to one another. The independent parameters (Table 9) needed to represent the four different bonded distances were chosen to be their weighted mean (p_1), the difference between r(C−C) and the weighted mean of the C=C and C-F bond lengths (p_2), the difference between r(C=C) and the average of the C−F bond lengths (p_3), and the difference between the two different

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Table 3. Microwave Rotation Constants $(B)^a$ and LCNMR Dipolar Couplings (D) for C_3F_4

constant	obsd (B_0/MHz or D_0/Hz)^b	Harmonic correction/ MHz or Hz	corrected (B_z/MHz of D_α/Hz)^b	calcd (B_{calc}/MHz or D_α/Hz)	weight^c
microwave (normal species)					
A	2886.2269(47)	−1.68	2884.547(168)	2884.554	3.1
B	2443.0385(10)	−2.08	2440.959(208)	2440.953	2.0
C	1720.7566(23)	−0.66	1720.097(66)	1720.089	20.2
microwave (^{13}C on-axis)					
A	2886.2810(189)	−1.68	2884.601(172)	2884.575	3.0
B	2438.0689(40)	−2.07	2435.999(207)	2435.948	2.1
C	1718.2353(36)	−0.65	1717.586(65)	1717.594	20.8
LCNMR					
$D_{4,5}{}^d$	5.433(39)	−0.015	5.418(78)	5.417	14.5
$D_{6,7}{}^d$	400.517(39)	2.911	403.428(301)	403.423	1.0
$D_{4,6}{}^d$	−59.956(21)	0.153	−59.803(75)	−59.804	15.5
$D_{4,5}{}^e$	−0.254(472)	0.001	−0.253(472)	1.527	0.0
$D_{6,7}{}^e$	312.215(255)	2.292	314.507(343)	314.512	0.7
$D_{4,6}{}^e$	−45.225(236)	−0.135	−45.360(238)	−45.381	1.6
$D_{3,4}{}^e$	−27.590(470)	0.073	−27.517(471)	−27.236	0.4
$D_{1,5}{}^e$	−2.797(549)	−0.034	−2.831(549)	−2.889	0.3
$D_{1,6}{}^e$	−25.501(325)	−0.113	−25.614(327)	−34.393	0.0
$D_{3,6}{}^e$	80.067(328)	2.139	82.206(392)	82.220	0.6
$D_{1,4}{}^e$	−94.335(573)	8.550	−85.785(1030)	−85.691	0.1

[a] From the MW spectra, centrifugal distortion constants (kHz) for the normal species were as follows (III^r representation): $D_J = 0.2831(57)$, $D_{JK} = -0.3927(39)$, $D_K = 0.0265(92)$, $d_1 = (0.0)$, and $d_2 = 0.0052(16)$. Identical values were assumed for the ^{13}C species. [b] Figures in parentheses are the estimated standard deviations. [c] Relative to the GED data. [d] E7 solvent. [e] ZLI-4962 solvent.

Table 4. Theoretical Geometrical Parameters for C_3F_4 (distances/pm, angles/deg)^a

	level of theory basis set			
parameter	HF/DZP	HF/TZ2P	MP2/DZP	MP2/TZ2P
$r(C_2-C_3)$	144.8	144.6	146.9	146.5
$r(C_1-C_2)$	128.4	128.0	132.2	131.2
$r(C_1-F_4)$	128.5	128.3	131.0	130.8
$r(C_3-F_6)$	133.1	133.0	135.7	135.6
$\angle C_1C_2F_5$	150.1	149.8	150.0	149.8
$\angle F_6C_3F_7$	105.8	105.7	105.7	105.8

[a] For atom numbering scheme, see Figure 1.

Table 5. Observed (Anharmonic) and Calculated (Harmonic) Fundamental Vibrational Frequencies (cm^{-1}) for C_3F_4

		theoretical		
symmetry	mode	unscaled^a	scaled^b	expt^c
a_1	ν_1	1991	1945	1940
	ν_2	1422	1362	1367
	ν_3	945	929	929
	ν_4	720	700	709
	ν_5	517	506	509
	ν_6	250	245	243
a_2	ν_7	620	609	616
	ν_8	209	205	205^d
b_1	ν_9	1387	1349	1331
	ν_{10}	917	887	892
	ν_{11}	797	783	781
	ν_{12}	263	253	251^e
b_2	ν_{13}	1126	1108	1109
	ν_{14}	564	554	551
	ν_{15}	179	176	(250)^e
rms % error (excluding ν_{15})		2.7	0.7	

[a] Calculated at the MP2/DZP level. [b] Calculated at the MP2/DZP level and scaled using the constants given in Table 6. [c] See ref 29. [d] Corrected value from liquid-phase Raman spectra. [e] The ordering of ν_{12} and ν_{15} are reversed relative to the tentative assignment of ref 29.

Table 6. Internal Coordinates, Symmetry Coordinates, and Scaling Factors for C_3F_4

(a) Internal Coordinates

bond stretches		angle bends		out-of-plane bends	
R_1	C_1-C_2	α_1	$F_5-C_2-C_1$	η_1	$C_2-F_5-C_1-C_3$
R_2	C_1-C_3	α_2	$F_4-C_1-C_2$	η_2	$C_1-F_4-C_2-C_3$
R_3	C_2-C_3	β_1	$F_6-C_3-C_1$		
R_4	C_2-F_5	β_2	$F_6-C_3-C_2$		
R_5	C_1-F_4	β_3	$F_7-C_3-C_1$		
R_6	C_3-F_7	β_4	$F_7-C_3-C_2$		
R_7	C_3-F_6				

(b) Symmetry Coordinates and Scale Factors

species	symmetry coordinate^a	description
a_1	$S_1 = \Delta R_1$	C═C stretch
	$S_2 = \Delta R_2 + \Delta R_3$	C−C symmetric stretch
	$S_3 = \Delta R_4 + \Delta R_5$	═C−F symmetric stretch
	$S_4 = \Delta R_6 + \Delta R_7$	−C−F symmetric stretch
	$S_5 = \Delta\alpha_1 + \Delta\alpha_2$	F−C═C−F in-plane bend
	$S_6 = \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4$	CF_2 scissor
a_2	$S_7 = \Delta\eta_1 - \Delta\eta_2$	F−C═C−F out-of-plane bend
	$S_8 = \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4$	CF_2 twist
b_1	$S_9 = \Delta R_2 - \Delta R_3$	C−C antisymmetric stretch
	$S_{10} = \Delta R_4 - \Delta R_5$	═C−F antisymmetric stretch
	$S_{11} = \Delta\alpha_1 - \Delta\alpha_2$	F−C═C−F in-plane bend
	$S_{12} = \Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4$	CF_2 wag
b_2	$S_{13} = \Delta R_6 - \Delta R_7$	−C−F antisymmetric stretch
	$S_{14} = \Delta\eta_1 + \Delta\eta_2$	F−C═C−F out-of-plane blend
	$S_{15} = \Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4$	CF_2 rock

[a] Not normalized.

C−F bond lengths (CF minus CF_2 distance) (p_4). The other two parameters were defined to be the angles C═CF (p_5) and FCF (p_6).

The radial-distribution curve (Figure 2) shows all the interatomic bonded distances lying under the feature centered at *ca.* 131 pm. The $F\cdots F$ nonbonded distance of the CF_2 group accounts for the feature at *ca.* 216 pm, with the three nonbonded $C\cdots F$ distances and the two other $F\cdots F$ nonbonded distances associated with the features at *ca.* 252 and 348 pm, respectively.

Three refinements were undertaken in which ED data alone (ED), ED data combined with rotation constants (ED/MW), and ED data combined with rotation and dipolar coupling constants (ED/MW/LCNMR) were analyzed. The results are compared in Table 9.

For the ED data alone, it was possible to refine simultaneously five of the six independent geometrical parameters and four amplitudes of vibration. As a result of the high correlation

Table 7. Scaled Quadratic Force Constants[a,b] for C_3F_4 from the MP2/DZP Level Force Field

a_1	S_1	9.723					
	S_2	−0.824	4.396				
	S_3	0.417	−0.133	7.475			
	S_4	−0.465	1.006	0.462	6.381		
	S_5	−0.362	0.375	0.083	−0.060	1.100	
	S_6	0.273	0.073	0.128	−0.618	0.094	2.710
a_2	S_7	0.591					
	S_8	0.289	1.224				
b_1	S_9	4.469					
	S_{10}	−0.516	6.839				
	S_{11}	0.313	0.132	0.888			
	S_{12}	0.234	0.116	0.098	2.230		
b_2	S_{13}	5.010					
	S_{14}	−0.059	0.294				
	S_{15}	−0.596	0.090	0.618			

[a] Stretching constants in aJ Å^{-2}, bending constants in aJ rad^{-2}. [b] The refined scale constants for the diagonal elements were 0.957 ($F_{1,1}$), 0.879 ($F_{2,2}$, $F_{9,9}$), 0.970 ($F_{3,3}$, $F_{4,4}$, $F_{10,10}$, $F_{13,13}$), 0.968 ($F_{5,5}$, $F_{7,7}$, $F_{11,11}$, $F_{14,14}$), and 0.963 ($F_{6,6}$, $F_{8.8}$, $F_{12,12}$, $F_{15,15}$). Off-diagonal elements were scaled by the square root of the product of the pertinent diagonal scale factors.

Table 8. Stark Measurements and Dipole Moment[a] of Perfluorocyclopropene

field, kV m^{-1}	$\Delta\nu_{obs}$, MHz	$\Delta\nu_{(obs-calc)}$, MHz
2.6907	−0.54	0.02
9.5878	−2.07	−0.01
20.887	−4.51	−0.01
44.384	−9.44	0.05
56.494	−12.08	−0.06
68.566	−14.56	−0.05
80.848	−16.99	0.02
92.544	−19.32	0.05
142.01	−29.00	0.02
156.21	−31.73	−0.03
$6_{42} \leftarrow 5_{41}$, $\lvert M \rvert = 1$; $\mu_{calc} = 1.3155(59)$ D		
2.6907	0.68	−0.01
9.5604	2.28	−0.02
20.887	4.94	0.01
36.405	8.56	0.06
56.383	13.02	−0.01
80.821	18.44	−0.03
92.374	21.00	0.00
109.12	24.65	0.02
122.78	27.52	−0.03
142.12	31.62	−0.01
157.65	34.87	0.02
$6_{43} \leftarrow 5_{42}$, $\lvert M \rvert = 1$; $\mu_{calc} = 1.3112(36)$D; $\mu_{av} = 1.313(4)$D		

[a] Errors 2σ; calibration μ(methylaceytlene) = 0.7839(10) D; 1D ≈3.33564 × 10^{-30} C m.

between parameters, attempts to refine p_3 caused the refinement to become unstable; the R_G factor oscillated unpredictably between 0.09 and 0.11 and p_3 had a typical esd of 5−7 pm. Since fixing the value of p_3 in the final refinement undoubtedly leads to an underestimate of the errors for other refining parameters with which it is correlated, it was included instead as an extra observation with a value of −2.0 pm, having an uncertainty of ±1.0 pm. This uncertainty was based upon an *R*-factor study of the parameter. Subsequent refinement of p_3 yielded a value of −1.8(9) pm and more realistic esd's for other parameters. In particular, the esd for the C═C double bond increased by a factor of eight, *i.e.* $r(C_1{-}C_3) = 131.4(8)$ pm, compared to 131.2(1) pm for p_3 fixed. Attempts to refine other amplitudes of vibration lead to them adopting unrealistically large or small values. These parameters were fixed therefore at the values from the theoretical computations. For the final cycle, $R_G = 0.083$ ($R_D = 0.048$).

The combined analysis of the ED data and rotation constants allowed all of the amplitudes of vibration to be refined simultaneously, but it remained necessary to keep p_3 as an extra observation rather than refining freely. All six rotation constants were fitted well within the estimated uncertainties of the corrected experimental values indicating a high degree of compatibility between the ED and MW data. Relative to the ED-only refinement, there was a slight increase (0.005) in R_G.

For each liquid-crystal solvent, two additional independent parameters, the orientation parameters S_{xx} and S_{zz}, were required to fit the three dipolar F···F couplings in the ED/MW/LCNMR refinement. For the E7 solvent, it proved impossible to fit all three D_α values simultaneously within their experimental uncertainties, such attempts leading to ΔD_α(calc − corr) of *ca.* 1.4, 9.6, and 3.2 Hz for $D_{4,5}$, $D_{6,7}$, and $D_{4,6}$, respectively. Fitting two of the three couplings at a time revealed that the value of $D_{6,7}$ was always calculated to be greater than the corrected experimental value. This misfit must be associated with an anisotropic component of the indirect $J_{6,7}$ coupling[36] which has not been included in the calculation. This anisotropy could be refined for $D_{6,7}$ in each solvent as the ratio $J_{aniso}(F_6\cdots F_7)/2S_{zz}$, p_{11} (Table 9).

Of the five dipolar ^{13}C−F couplings, only two could be fitted within their uncertainties when combined with the F···F couplings. However, it was noted that the misfit of the couplings for the two bonded C−F pairs, $D_{1,4}$ and $D_{3,6}$, was proportionate to their respective D_α. This, again, must be a consequence of anisotropy in *J*. A parameter J_{aniso}(C−F)/2D_α(C−F), p_{12}, was then included in the model to allow for this. The anisotropy in $J_{1,6}$ also appeared to be very marked, as witnessed by the *ca*. 9 Hz misfit for $D_{1,6}$. Since no further structural information would be forthcoming by inclusion of an extra refineable parameter for $J_{aniso(1,6)}$, the value of $D_{1,6}$ was given zero weight in the final refinement. Similarly for $D(F_4\cdots F_5)$, which was calculated consistently in excess of its very small observed value (Table 3).

Inclusion of the dipolar ^{13}C−F couplings permitted p_3 to be refined freely. Thus, in the final refinement, all six of the independent geometrical parameters were refined simultaneously, and the resultant molecular parameters have the greatest physical significance. Clearly, without all of the extra data, the quality of the fit seems better (the *R* factors are lower), but is perhaps unreasonably good, suggesting that in one way or another the data have been over-interpreted. The resulting parameter sets are, therefore, distorted in unpredictable ways, confirming that it is important to use as much data as possible in the determination of molecular structures.

The success of the final ED/MW/LCNMR refinement, for which $R_G = 0.088$ ($R_D = 0.048$), may be assessed on the basis of the difference between the experimental and calculated radial-distribution curves (Figure 2). Figure 3 offers a similar comparison between the experimental and calculated molecular-scattering curves, while the interatomic distances and vibrational amplitudes of the optimum refinement are listed in Table 9 and the least-squares correlation matrix is shown in Table 10.

X-ray Diffraction. Structure solution and refinement: Automatic direct methods[37] identified the positions of all atoms, which were then refined with anisotropic thermal parameters.[38] The experimental data were markedly affected by extinction, but a correction factor [1.36(9)] was successfully refined. The weighting scheme [$w^{-1} = \sigma^2(F_o2) + (0.036P)^2 + 0.17P$], $P =$

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(36) (a) Lounila, J.; Jokisaari, J. *Prog. NMR Spectrosc.* **1982**, *15*, 249. (b) Gerritsen, J.; MacLean, C. *J. Magn. Reson.* **1971**, *5*, 44. (c) den Otter, G. J.; Maclean, C. J. *Chem.* Phys. **1974**, *3*, 119. (d) Barfield, M. *Chem. Phys. Lett.* **1970**, *4*, 518.

(37) Sheldrick, G. M. *SHELXS-86*, *Acta Crystallogr.* **1990**, *A46*, 467.

(38) Sheldrick, G. M. *SHELXL-93*, program for crystal-structure refinement, University of Göttingen, Germany, 1993.

Table 9. Geometrical Parameters for the Electron-Diffraction Study of C_3F_4 (r, u/pm, angle/deg, J/Hz)[a,b]

	independent parameter	ED r_α°	ED/MW r_α°	ED/MW/LCNMR r_{av}
p_1	$^1/_7[2r(C_1{-}C_3) + r(C_1{-}C_2) + 2r(C_1{-}F_4) + 2r(C_3{-}F_6)]$	136.7(1)	136.4$_1$(3)	136.4(1)
p_2	$r(C_1{-}C_3) - {}^1/_5[r(C_1{-}C_2) + 2r(C_1{-}F_4) + 2r(C_3{-}F_6)]$	14.1(3)	13.3(4)	13.3(3)
p_3	$r(C_1{-}C_2) - {}^1/_2[r(C_1{-}F_4) + r(C_3{-}F_6)]$	−1.8(9)[c]	−2.3(9)[c]	−2.8(16)
p_4	$r(C_1{-}F_4) - r(C_3{-}F_6)$	−4.6(7)	−4.8(5)	−4.9(4)
p_5	$\angle C_1C_2F_5$	149.1(7)	149.7(3)	149.9(6)
p_6	$\angle F_6C_3F_7$	107.0(4)	105.6(3)	105.4(5)
p_7	S_{xx}(E7) (×100)			−0.231(3)
p_8	S_{zz}(E7) (×100)			4.407(6)
p_9	S_{xx}(ZLI-4792) (×100)			−0.065(18)
p_{10}	S_{zz}(ZLI-4792) (×100)			3.310(19)
p_{11}	$J_{aniso}(F_6 \cdots F_7)/2S_{zz}$			−886(16)
p_{12}	$J_{aniso}(C{-}F)/2D_\alpha(C{-}F)$			0.164(45)

dependent distance		ED			ED/MW			ED/MW/LCNMR		
		r_a	u		r_a	u		r_a	u	
r_1	$C_1{-}C_3$	146.8(3)	5.0(f)		146.0(3)	5.7(7)		145.9(3)	5.8(7)	
r_2	$C_1{-}C_2$	131.4(8)	4.0(f)		131.0(8)	3.6	(3)	130.6(13)	3.6	(4)
r_3	$C_3{-}F_6$	135.6(3)	4.6(f)		135.8(3)	4.1		136.0(4)	4.1	
r_4	$C_1{-}F_4$	131.3(4)	4.2(f)		131.3(3)	3.7		131.4(3)	3.7	
r_5	$C_3 \cdots F_4$	266.4(3)	7.8(7)		265.1(4)	8.5(7)		265.0(5)	8.5(8)	
r_6	$F_6 \cdots F_7$	218.0(4)	4.6(5)		216.1$_9$(2)	4.6(5)		216.1$_9$(2)	4.6(5)	
r_7	$C_1 \cdots F_5$	252.7(7)	6.2	(4)	252.6(4)	6.4	(3)	252.4(8)	6.5	(4)
r_8	$C_1 \cdots F_6$	247.0(4)	7.6		247.1(4)	7.8		247.2(6)	7.9	
r_9	$F_4 \cdots F_5$	355.5(19)	8.1	(5)	356.5(2)	7.7	(2)	356.6(3)	7.6	(3)
r_{10}	$F_4 \cdots F_6$	347.9(6)	10.4		347.4(1)	9.8		347.4(1)	9.7	

[a] For atom numbering scheme, see Figure 1. [b] Figures in parentheses are the estimated standard deviations. [c] Refined as an extra observation. See the text.

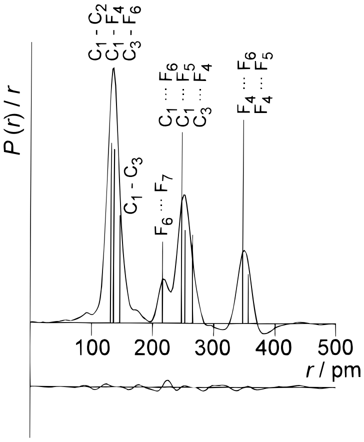

Figure 2. Observed and final weighted difference radial-distribution curves for C_3F_4. Before Fourier inversion the data were multiplied by s $\exp[(-0.00002s^2)/(Z_C - f_C)(Z_F - f_F)]$.

$^1/_3[\mathrm{MAX}(F_o^2,0) + 2F_c^2]$ gave final convergence with $R[256F_o \geq 4\sigma(F_o)]$, wR[all data] = 0.0283, 0.0771, respectively, $S[F^2]$ = 1.126 for 34 refined parameters, and the final F synthesis showed no peaks out with +0.18 → −0.21 e Å^{-3}. The principal geometrical parameters are given in Table 11, all other crystallographic information being available as supporting information. A thermal ellipsoid plot of a single molecule is shown in Figure 1, and Figure 4 illustrates the molecular packing in the crystal; these figures were prepared using SHELXTL/PC.[39]

Discussion

The measurements described here provide the first structural information for 1,2,3,3-tetrafluorocyclopropene. The analyses of both the electron-diffraction and the single-crystal X-ray data are consistent with the spectroscopic evidence that the molecule consists of a three -membered ring incorporating a C=C double bond with C_{2v} symmetry in the gas phase and crystallographic C_2 symmetry in the solid phase. Values of the principal bond distances and angles derived from the three methods employed in this work are compared in Table 11.

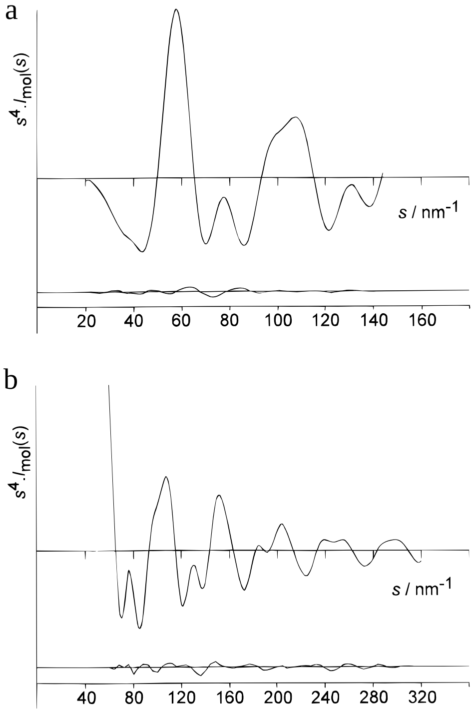

Figure 3. Observed and final weighted difference molecular-scattering intensity curves for C_3F_4. Nozzle-to-plate distances were (a) 286.0 and (b) 128.2 mm.

The structural parameters for perfluorocyclopropene derived by the *ab initio* calculations at the MP2 level of theory are in excellent quantitative agreement with those refined from the electron-diffraction pattern (Table 11). From Table 4, it is clear that an account of the correlated motion of electrons is essential if such good quantitative agreement between theory and experiment is to be obtained. The inclusion of electron correlation at the MP2 level leads to a marked increase in all

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(39) Sheldrick, G. M. University of Göttingen, Germany, 1992. Siemens Analytical Xray Instrumentation Inc., Madison, Wisconsin.

Table 10. Least-Squares Correlation Matrix (×100) for the Combined ED/MW/LCNMR Study of C_3F_4[a]

p_1	p_2	p_3	p_4	p_5	p_6	p_7	p_8	p_9	p_{10}	p_{11}	p_{12}	u_1	u_4	u_5	u_6	u_8	u_{10}	k_1	k_2	
100	**54**	**95**	24	**−81**	**86**	16	**−56**	44	−14	3	**83**	−21	49	−11	26	**−60**	**54**	43	31	p_1
	100	28	−41	1	18	5	−27	22	9	−15	19	**−63**	−26	47	12	15	13	5	13	p_2
		100	45	**−94**	**94**	17	**−55**	42	−18	7	**90**	−2	**66**	−30	26	**−75**	**58**	49	32	p_3
			100	**−70**	**70**	9	−10	5	0	0	**69**	**50**	**80**	**−70**	16	**−71**	37	44	19	p_4
				100	**−96**	−16	46	−34	18	−9	**−93**	−20	**−82**	**51**	−25	**86**	**−57**	**−53**	−31	p_5
					100	17	−47	35	−11	2	**97**	10	**77**	−45	27	**−81**	**59**	**55**	33	p_6
						100	−25	−25	5	1	19	0	12	−5	4	−13	10	9	5	p_7
							100	**−76**	23	−3	−40	11	−27	5	−14	34	−30	−23	−17	p_8
								100	−27	2	26	−10	19	−2	10	−25	22	17	12	p_9
									100	**−95**	9	−4	−12	6	−1	14	−8	−4	−2	p_{10}
										100	−16	7	7	−6	0	−8	2	0	0	p_{11}
											100	10	**75**	−43	26	**−78**	**57**	**54**	32	p_{12}
												100	**50**	**−70**	26	−41	−4	9	0	u_1
													100	**−73**	7	**−79**	46	**64**	28	u_4
														100	−34	**62**	−31	−39	−10	u_5
															100	−32	4	4	−10	u_6
																100	−48	−41	−18	u_8
																	100	49	36	u_{10}
																		100	28	k_1
																			100	k_2

[a] Significant values are shown in **bold**. *k* is a scale factor.

Table 11. Comparison of the Principal Geometrical Parameters (*r*/pm, angle/deg) for C_3F_4 As Determined by Electron Diffraction, X-ray Diffraction, and *ab Initio* Computations[a,b]

parameter	E/MW/LCNMR (r_g, $\angle_\alpha$)	X-ray	*ab initio*[c] (r_e)
$r(C_1-C_3)$	146.1(3)	145.3(3)	146.5
$r(C_1-C_2)$	130.7(13)	129.6(4)	131.2
$r(C_3-F_6)$	136.1(4)	137.0(2)	135.6
$r(C_1-F_4)$	131.5(3)	131.2(2)	130.8
$\angle C_1C_2F_5$	149.9(6)	150.4(9)	149.8
$\angle F_6C_3F_7$	105.4(5)	104.1(2)	105.8
$\angle C_1C_2C_3$	63.4(3)	63.5(1)	63.4

[a] For atom numbering scheme, see Figure 1. [b] Figures in parentheses are the estimated standard deviations. [c] MP2/TZ2P level.

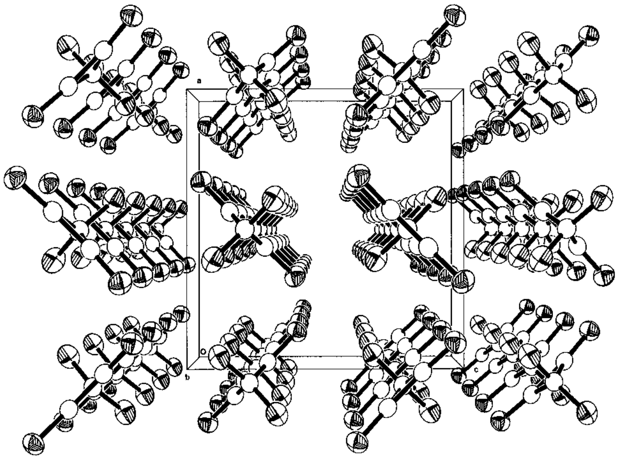

Figure 4. View of the packing of C_3F_4 molecules in stacks along the crystallographic *b* axis.

bond lengths relative to the uncorrelated, lower-level HF computations; this is the standard variation in predicted bond lengths for electron precise molecules.[40] In terms of basis set quality, it is well known that the use of polarization functions is essential when employing a wave function which accounts for electron correlation,[40] and for perfluorocyclopropene, on extending the one-particle basis set from DZP to TZ2P, there is only a small change in the calculated structural parameters (a small contraction of the charge cloud leading to a slight decrease in bond distances). Thus, at the MP2 level with the DZP or TZ2P basis set, theoretical structural parameters offer good support for those derived experimentally.[41]

The calculated harmonic vibrational frequencies for C_3F_4 are listed in Table 5. In comparison with the experimental fundamental vibrational frequencies, the predicted values are in the correct order and at the MP2/DZP level (the highest level for harmonic vibrational frequencies available to us in this work) are generally about 2−3% higher than the experimental values. The exception is the lowest frequency b_2 mode, assigned to the CF_2 rocking motion, ν_{15}, for which the predicted harmonic frequency is much lower than the experimental fundamental frequency reported by Craig *et al.*[29] Although this is a common feature in determining low-magnitude bending vibrational frequencies of multiply-bonded species,[42] it seems likely that the experimental vibrational investigation failed to observe this low-frequency mode since the region of the infrared spectrum at <200 cm^{-1} was not investigated. However, microwave vibrational satellite intensities show that the a_2 CF_2 twisting mode is the lowest frequency fundamental mode in the molecule indicating that ν_{15} (b_2) is underestimated by the theoretical computation.

The geometrical parameters defining the low-temperature solid-phase structure of C_3F_4 are very similar to those found in the gas phase, as anticipated for a rigid-ring structure. This further vindicates the combined analysis of GED, MW, and LCNMR data which assumes an identical molecular structure in both the gas phase and the liquid-crystal solvents. The packing in the crystal is shown in Figure 4. The molecules are ordered in linear chains of coplanar C_3 rings aligned, in each chain, along the dipole-moment vector. The difference electron-density map through the C_3 molecular plane (Figure 5) shows

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(40) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(41) It should be borne in mind, however, that this procedure involves comparison of two different structure types, namely r_α (from GED) and r_e (from calculation) geometries. For example, see: Hargittai, I.; Hargittai, M. *Molecular Structures and Energetics, Vol. II, Physical Measurements*; VCH: New York, 1988; Chapter 20, p 417.

(42) This procedure involves comparison of two different types of vibrational frequencies, namely fundamental (from IR and Raman spectroscopy) and harmonic (from calculation). For example, see (a) Simandiras, E. D.; Handy, N. C.; Amos, R. D. *J. Phys. Chem.* **1988**, *92*, 1739. (b) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3187.

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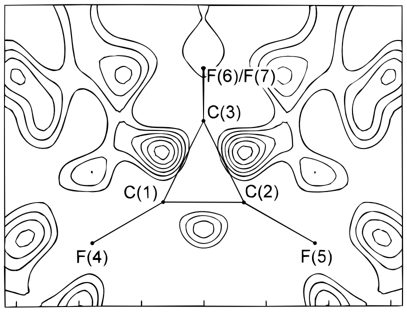

Figure 5. Difference electron-density map of the C_3 plane in C_3F_4. The density contours span the range 0.03−0.18 e Å^{-3}.

Table 12. Ring Bond Lengths (r/pm) for Cyclopropenes with C_{2v} or Pseudo-C_{2v} Symmetry[a]

substituent							
1	2	3	3	method[b]	r(C═C)	r(C−C)	ref
H	H	H	H	ED	130.4(3)	151.9(12)	6
H	H	H	H	MW	129.59(4)	150.9(1)	7
Cl	Cl	Cl	Cl	ED	132.0(10)	147.9(11)	8
H	H	F	F	MW	132.1(1)	143.8(7)	9
F	F	F	F	ED/MW/LC	130.7(13)	146.1(3)	this work
F	F	F	F	XRD	129.6(4)	145.3(3)	this work
Ph	Ph	NO_2	H	XRD	130.0(6)	148.3(8)[c]	43
Ph	Ph	Ph	H	XRD	129.3(4)	151.6(4)[c]	44
H	H	C_3H_3	H	XRD	129.0(1)	151.2(1)[c]	45

[a] Figures in parentheses are the estimated standard deviations. [b] XRD = X-ray diffraction of a single crystal; ED = gas-phase electron diffraction; MW = microwave spectroscopy; LC = liquid-crystal NMR spectroscopy. [c] Mean value.

the location of the highest positive residual electron density. Although neither the quality nor the resolution of the X-ray diffraction data allows the significance of this phenomenon to be established unequivocally, the position of the maximum outside of the C_3 ring, but close to the C_1−C_3 vector, is intriguing. It may represent tentative evidence for nonlinearity of the C−C single bonds.

Table 12 shows C−C ring bond lengths for cyclopropenes having C_{2v}, or very nearly C_{2v}, symmetry. Although care must be exercised in comparing geometrical parameters derived from different techniques, relative to C_3H_4 itself,[6,7] the variation in the C═C double bond length is small in contrast to that for the C−C single bonds. There is a contraction of C_1−C_3 and C_2−C_3 on substitution of a π donor at C(3), this being most pronounced for 3,3-difluorocyclopropene for which $\Delta(C_3H_4-C_3H_2F_2) = 7.1(7)$ pm from the MW data. This effect, which is also observed for cyclopropanes, has been rationalized for halogen substitution by Allen *et al*. on the basis of charge-density differences, obtained from *ab initio* wave functions, relative to cyclopropene.[46] Such computations predict that upon substitution of halogen for hydrogen, the adjacent C−C bonds are shortened and the distal C−C bond is lengthened. Successive halogenation, at least for fluorine, is predicted to modify the ring distances in an additive manner following a simple scalar superposition rule.

Table 13. Theoretical Geometry Optimizations[a] for Cyclopropene and Its Halogeno (X = F, Cl) Derivatives (r_e/pm)

compd	r(C═C)	r(C−C)	r(═C−X)	r(>C−X)
C_3H_4	131.3	151.8		
3,3-$C_3H_2F_2$	133.9	145.2		136.4
3,3-$C_3H_2Cl_2$	132.7	147.1		177.6
1,2-$C_3H_2F_2$	129.6	151.9	131.9	
1,2-$C_3H_2Cl_2$	130.8	151.9	168.8	
C_3F_4	132.2	146.9	131.0	135.7
C_3Cl_4	132.4	147.8	167.8	177.2

[a] MP2/DZP level.

Since only the structures of 3,3-difluoro-,[9] perfluoro- and perchlorocyclopropene[8] have been determined experimentally, we have optimized (MP2/DZP level) the structures of all dihalageno- and perhalogenocyclopropenes (X = F or Cl[47]) possessing C_{2v} symmetry (Table 13) in order to better appraise the reliability of the aforesaid superposition rule.[46] The agreement between the parameters for which experimental data are available is good, and allows the relative magnitudes of the theoretical values to be compared with confidence.

For the 3,3-disubstituted cyclopropenes, the C−C single bonds are predicted to be shorter, and the C═C double bonds longer, than for C_3H_4.[46] The opposite trend is predicted for the 1,2-disubstituted compounds. Such parameter variations are observed for the theoretical geometries (Table 13) and confirmed experimentally for 3,3-difluorocyclopropene (Table 12). Based on a 4-fold scalar addition, the perhalogenocyclopropenes are expected to exhibit a shortening of the C−C single bonds and no change in the C═C double bond, relative to C_3H_4.[46] However, although C_3F_4 and C_3Cl_4 have shorter C−C single bonds than C_3H_4, both demonstrate longer C═C double bond lengths at the MP2/DZP level. Notably, these theoretical changes in r(C═C) are borne out for the experimental structure of C_3Cl_4, $\Delta(C_3Cl_4-C_3H_4) = 1.6(10)$ pm (GED), but not for C_3F_4, $\Delta(C_3F_4-C_3H_4) = 0.3(13)$ pm (GED), *i.e.* no significant change. Clearly, further experimental structural determinations of such cyclopropenes are desirable.

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Supporting Information Available: A full listing of data pertinent to the crystal structure determination, including atomic coordinates and isotropic and anisotropic displacement parameters (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(47) DZP basis set for Cl involves the standard Huzinaga−Dunning double-ζ basis set (see: (a) Huzinaga, S. *Approximate Atomic Wavefunctions*; University of Alberta: Edmonton, 1971. (b) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, p 1) with one set of d-type polarization functions having α_d(Cl) = 0.75.