Nonplanarity of Tetrafluorocyclobutadiene

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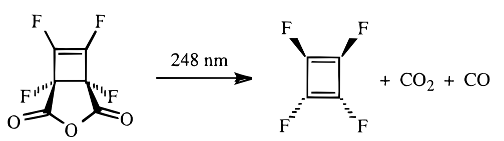
The examination of tetrafluorocyclobutadiene, C_4F_4 (**1**), illuminates striking differences between fluorocarbons and their hydrocarbon analogues.[1,2] While cyclobutadiene, C_4H_4, has been studied extensively,[3−6] due to interest in its antiaromaticity, so far only indirect evidence for the formation of **1** has been provided.[7]

Analysis of the IR spectrum of C_4F_4 leads us to believe that this unstable molecule is nonplanar. This result, though not anticipated by any treatment of C_4F_4 as a mere analog of cyclobutadiene, is reminiscent of the nonplanarity of the calculated structure for the perfluoroallyl radical.[8]

We observe the IR spectrum of **1** (Figure 1, center) when we irradiate tetrafluorocyclobutene-3,4-dicarboxylic anhydride (**2**)[7a] isolated in an Ar matrix at 12 K with a 248 nm light from KrF excimer laser. In addition to C_4F_4, CO_2 and CO are formed. The C_4F_4 was also generated, with lower yield, by irradiation of *cis*- or *trans*-tetrafluoro-3,4-diiodocyclobutene.[9]



(1)

2 **1**

As for an IR spectrum of C_4F_4, we identify a set of peaks which (a) grows in at the same rate on irradiation of **2**, (b) is produced at the same rate that the precursor is destroyed, and (c) disappears at the same rate when **1** is destroyed by prolonged irradiation. The photochemical transformation of **2** to **1** is very clean, with only a trace amount of the perfluorocyclopentadienone[7c] detected. The equimolar concentrations of CO_2, CO, and C_4F_4 in the matrix allow us to estimate the absolute intensities of the C_4F_4 absorptions.[11]

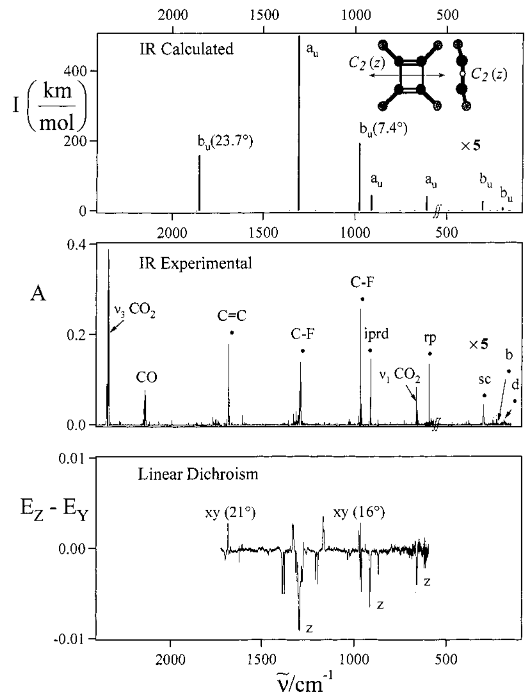


Figure 1. Calculated (B3LYP/cc-pVDZ), unscaled spectrum of C_4F_4 (top). Calculated transition moment directions are referenced to the carbon skeleton plane and are determined in a counterclockwise sense about the C_2 axis. The experimental infrared absorption spectrum of tetrafluorocylobutadiene (C_4F_4) isolated in Ar matrix at 12 K (center). For abbreviations see, Table 1. Linear dichroism spectrum obtained after photoorientation with linearly polarized light at 248 nm (bottom). C_4F_4 bands are marked with appropriate polarizations. Experimental transition moment directions were determined according to ref 13.

Partial bleaching of the C_4F_4 by linearly polarized 248 nm light leads to partial photoorientation of **1**. Polarization measurements indicate that electronic absorption[12] at 248 nm proceeds along the C_2 axis, and the three a_u vibrations show negative dichroism in the IR; for each of them absorption along the photoselection axis Z (E_Z) is smaller than along direction *Y* (E_Y) perpendicular to it ($E_Z < E_Y$). At the same time, the two observed b_u modes show positive dichroism (Figure 1, bottom).

The fundamental vibrations for tetrafluorocyclobutadiene (Table 1) were identified by comparison of observed IR bands

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(12) The UV absorption spectrum was obtained in the instrument where electronic and IR spectral observations are performed simultaneously. This allows for precise correlation between IR and UV absorption growth or decay rates during the course of photolysis at various wavelengths, and thus the extraction of the weak UV absorption bands.

(13) The experimental transition moment directions were determined according to the following formula:[14] $\tan^2 \varphi = (K_x - K_i)/(K_i - K_z)$, where K_x and K_z are the principal orientation factors, and K_i values are the orientation factors of individual observed vibrations ν_i. Since the orientation is uniaxial, as dictated by the photoselected direction *Z*, we can adapt for $K_z = 0.318$ (an average of K_z values for ν_{10}, ν_{11}, and ν_{12}). From the condition that $\Sigma_i = 1$ we determine $K_x = K_y = 0.341$. Although the error bars for our experimental transition moment direction angles are quite large (at least ± 12°), this result supports our claim for a nonplanar structure for **1**. The calculated transition moment directions are notoriously unreliable, and advanced *ab initio* treatment is required to achieve some acceptable precision.[15]

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Table 1. Infrared Absorption Spectrum of Perfluorocyclobutadiene (C_4F_4)[a]

$\Gamma_{vib}(C_{2h}) = 5a_g \oplus 4b_g \oplus 5a_u \oplus 4b_u$

	exptl				calcd[b]			
ν	sym	$\tilde{\nu}$	I	K_u[c] (pol)	$\tilde{\nu}$	I	φ[d]	assignment[e]
1	a_g	—	—		1867	0		C═C sym s
2		—	—		1214	0		C-C sym s
3		—	—		673	0		rb
4		—	—		261	0		F−C−C−F sym b
5		—	—		154	0		F−C═C−F sym b
6	b_g	—	—		1354	0		C−F sym s
7		—	—		755	0		ip ring t
8		—	—		489	0		ip ring d
9		—	—		415	0		ip ring d
10	a_u	1291	535	0.319 (z)	1306	509.7	z	C−F sym s
11		914	32	0.322 (z)	912	43.8	z	ip ring d
12		596	37	0.313 (z)	610	40.3	z	rp
13		221	0.2	—	224	0.1	z	F−C═C−F asym b
14		—	—		159	0.1	z	C−F sym op b
15	b_u	1683	143	0.337 (25°)	1849	158.6	23.7°	C═C asym s[f]
16		968	101	0.340 (16°)	976	193.3	7.4°	C−F asym s
17		300	4	—	303	5.2	20.1°	F−C═C−F asym sc
18		188	1	—	194	1.8	−10.5°	C−F sym op d

[a] Argon matrix, 12 K; $\tilde{\nu}$, in cm^{-1}; I, absolute absorption intensity, in km/mol. [b] Calculated frequencies (B3LYP/cc-pVDZ) are unscaled. [c] K_i is the orientation factor for transition i; $K_i = \langle\cos^2 i\rangle$, $i = x, y$, or z, and i is the angle between the molecular axis i and the photoselection direction Z, averaged aver all possible orientations, as indicated by the pointed brackets. [d] Calculated transition moment directions, the angles φ are determined with respect to the carbon skeleton plane. [e] Approximate mode description: sym = symmetric, asym = asymmetric, ip = in-plane, op = out-of-plane, s = stretch, b = bend, d = deformation, sc = scissors, t = twist, rb = ring breathing, rp = ring puckering. [f] The C═C stretching vibration, at 1683 cm^{-1} proceeds in the direction perpendicular to the C═C bond, and its transition moment is inclined by nearly 24° from the plane created by the carbons.

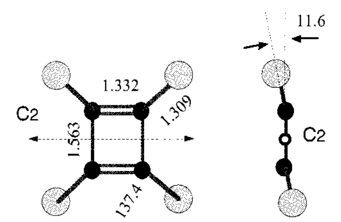


Figure 2. Calculated structure of C_4F_4 (B3LYP/cc-pVDZ). Bond lengths are given in angstroms and angles are in degrees.

Table 2. B3LYP/cc-pVDZ NBO and NAO Population Analysis of Atomic Orbital Character in Bonding Orbitals

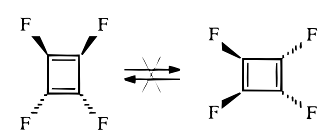
C_4H_4 (D_{2h})			C_4F_4 (C_{2h})		
orbital	% S	% P	orbital	% S	% P
C═C σ bond	38	62	C═C σ bond	28	72
C═C π bond	0	100	C═C π bond	15	85
C−C bond	27	73	C−C bond	30	70
C−H bond	35	65	C−F bond	27	73
ideal: sp^2	33	67	ideal: sp^3	25	75

with the frequencies and intensities obtained from *ab initio* (B3LYP/cc-pVDZ) calculations. The optimized nonplanar structure of **1** is shown in Figure 2.

Our experimental data point to a nonplanar structure for C_4F_4. We observe a peak at 595 cm^{-1} which we assign as the ring-puckering mode on the basis of its frequency and polarization and comparison with C_4H_4.[16] This band shows negative dichroism, as expected for all modes active along the molecular z axis. Were C_4F_4 planar, symmetry would prevent a change in dipole moment for this mode and make it IR inactive. Were C_4F_4 to tautomerize, as does C_4H_4, we would record the same dichroism for all observed in-plane transitions. Instead, we measure distinctly different dichroic ratios for vibrations proceeding in the directions along and perpendicular to the C_2 axis (see Table 1).

The nonplanarity of tetrafluorocyclobutadiene is most likely the result of a conjunction of two effects. Electron withdrawal by the highly electronegative fluorines favors pyramidalization of the carbons, increasing the p-character in the C−F bonds, and this tendency is reinforced by the resulting attenuation of the cyclic conjugation in the π system. A natural atomic orbital (NAO) and natural bond orbital (NBO) population analysis of C_4F_4 (B3LYP/cc-pVDZ) supports this interpretation. The NBO calculation shows that the bonding orbitals of C_4F_4 are all nearly equivalent, having s and p contributions which resemble those of a tetrahedral sp^3 hybrid for carbon atoms, in contrast to cyclobutadiene (C_4H_4) which exhibits the classical bonding characteristics of a carbon atoms with three equivalent sp^2 hybrid orbitals and one π-bonding orbital (Table 2).

The spectra of C_4F_4 show no indications of the valence tautomerization which is observed in C_4H_4.[17] The bond-shift isomerization in C_4H_4 happens *via* heavy atom tunneling,[18] and this is out-of-the-question for **1** in light of the large changes in geometry required.



Unlike the situation in C_4H_4, where interconversion of the two valence tautomers amounts to bond length alternations in the carbon skeleton accompanied by minimal movement of hydrogens, in C_4F_4 substantial additional change of the C−F bond angles (calculated to be over 23°) would be required in order for tautomerization to occur. Perhaps the matrix environment further inhibits tautomerization.[17]

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