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Microwave Spectra, Electric Dipole Moment, and Molecular Structure of *cis*-1,2-Difluorocyclopropane

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Abstract: The gas-phase molecular structure of *cis*-1,2-difluorocyclopropane was determined from the microwave spectra of the normal, two dideuterated and five carbon-13 isotopic species. A first-order centrifugal distortion model adequately fit the data to J values of 40. The partial r_s parameters in the normal isotopic frame are $r(C_{1,2}-C_3)$ = 1.503 (4), $r(C_1-C_2)$ = 1.488 (3), $r(C_1-F)$ = 1.368 (6), and $r(C_1-H)$ = 1.093 (4) Å and θ(HCF) = 111.3 (4)°. Carbon-13 data in two different dideuterated isotopic frames confirm the ring bond lengths obtained in the normal isotopic frame. A value of 2.908 (5) D was obtained for the electric dipole moment. All ring bonds in *cis*-1,2-difluorocyclopropane are longer than the corresponding C–C bonds in *trans*-1,2-difluorocyclopropane. However, they are shortened relative to the ring bonds in cyclopropane. The orientation of the HCF group with respect to the ring plane is almost the same for both the cis and trans isomers and does not differ significantly from the CH_2 group orientation in cyclopropane. The structural results are related to theoretical studies which are concerned with fluorine substituent effects in three-membered rings and the "cis effect" in unsaturated systems.

The effect of fluorine substitution upon the geometry of cyclopropane has been studied both theoretically[2-5] and experimentally.[6-8] The preceeding paper has reviewed the literature and also reports on the complete geometry of *trans*-1,2-difluorocyclopropane.[9] A gas-phase structure of *cis*-1,2-difluorocyclopropane is needed to test several aspects of the theoretical work. The structure is also of interest for comparison with the trans isomer and with the known structures of the related cis and trans isomers of 1,2-difluoroethylene oxide.[10,11]

One theoretical approach has utilized charge density difference plots obtained from ab initio wave functions to correctly rationalize the fluorine-induced ring bond changes in several fluorinated cyclopropanes.[2] The theory has predicted an unusual ring bond effect in *cis*-1,2-difluorocyclopropane and 1,1,2,2-tetrafluorocyclopropane which has not been experimentally verified. In these cases, the C–C bonds between the fluoro and methylene groups are predicted to be about the same as in cyclopropane. This theoretical result is not consistent with the general phenomenological observation that fluorination of a hydrocarbon leads to shortening of bonds adjacent to the C–F bonds.

A second theoretical study has used complete geometry optimization at the 4-21 level to obtain cis/trans energy differences as well as molecular structures for the 1,2-difluorocyclopropanes.[4] These calculations have given a lower energy for the trans isomer of 1,2-difluorocyclopropane, an outcome that is consistent with experiment but opposite to the "cis effect" observed in the related 1,2-difluoroethylenes.[12] In the ethylene system, the cis isomer has the lower energy. To help interpret such differences in isomer stabilities, accurate knowledge of the geometric parameters of the isomer pairs such as the difluorocyclopropanes is needed. Such parameters are not only input to ab initio calculations but are also a means of assessing the results of geometry optimizations.

The present paper reports on a microwave study of *cis*-1,2-difluorocyclopropane.[13] A gas-phase structure is obtained from deuterium and carbon-13 isotopomer rotational constant data. The structural results are compared to the gas-phase structure of the trans isomer as well as to other fluorinated cyclopropanes. They are also considered in relation to theoretical studies concerned with the "cis effect" and fluorine substituent effects upon three-membered rings.

Experimental Section

Synthesis. Mixtures of diazomethane and 1,2-difluoroethylene were photolyzed in the liquid phase at −80 °C for the preparation of *cis*-1,2-difluorocyclopropane.[12] The syntheses of the 1,2-d_2 and 3,3-d_2 isotopomers followed the procedure which was described for the same isotopomers of *trans*-1,2-difluorocyclopropane.[9] These samples were used previously in a vibrational study of *cis*- and *trans*-1,2-difluorocyclopropane.[12] Gas chromatography demonstrated that the sample purity was greater than 99%. Isotopic purity was about 99% as shown by NMR and infrared spectra.

Spectroscopy. Stark-modulated spectra were recorded with a Hewlett-Packard 8400C spectrometer at RPI and a Hewlett-Packard 8460A spectrometer at Princeton. Cell pressures of 15 mtorr were used to obtain spectra and to measure transition frequencies to ±0.05 MHz. Absorption cells were cooled to dry ice temperature for the study of carbon-13 isotopomers in natural abundance. The studies at RPI utilized a 10-ft Stark cell which was coupled to a computer-controlled HP 8400C microwave source.[14] This system had sufficient sensitivity in order to identify the low J carbon-13 lines by their Stark effects and to measure the transition frequencies to ±0.05 MHz.

The microwave assignments were confirmed by microwave–microwave double resonance (MMDR) using the "on-off" pump modulation procedure described by Stiefvater.[15] The MMDR experimental apparatus was described previously.[16] Radio frequency–microwave double resonance (RFMDR) was also useful for the microwave assignments of a number of the isotopomers. The method of Wodarczyk and Wilson was used in conjunction with the HP8460A spectrometer and a RFMDR experimental apparatus.[17]

Dipole moment measurements were performed with the HP 8400C spectrometer by adding the 33.3-kHz square wave to the dc bias. One

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Stark modulator was used to drive one HP Stark cell, and the dc bias was measured with a Keithley 177 Microvolt DMM voltmeter which was periodically calibrated to ±0.1% accuracy. Measurements of the $J = 2 \rightarrow 3$ Stark transitions of carbonyl sulfide were used to obtain the average spacing of the Stark septum in the cell.[18]

Spectra

Normal Isotopic Species. Microwave spectral calculations which were based upon a reasonable structural model predicted numerous, strong, low-*J*, *b*-type transitions and somewhat weaker, low-*J*, *c*-type transitions. The experimental spectrum was fairly dense and consisted of many strong transitions with resolvable Stark effects. The low-*J* transitions were assigned with the aid of the spectral calculations and the observed Stark effects and line intensities. Fits of these transitions to a rigid rotor model indicated that centrifugal distortion effects were more significant in the cis isomer than in the trans isomer.[9]

A centrifugal distortion analysis was carried out with the normal isotopic species so that these data could be used in the search for the higher *J* carbon-13 lines in natural abundance.[19] Table I lists the 55 transitions which were fit to obtain the rotational constants and quartic centrifugal distortion parameters given in Table II. MMDR and RFMDR techniques were used to confirm the spectral assignment. Support for the assignment of the higher *J* transitions also comes from the overall quality of the centrifugal distortion fit as well as the observed line intensities.

Enriched Isotopic Species. The deuterated isotopomers of *cis*-1,2-difluorocyclopropane, $\mathrm{\overline{CDFCDFC}H_2}$ and $\mathrm{\overline{CHFCHFC}D_2}$, were assigned by using the calculated isotopic shifts and employing the same techniques which were described for the normal isotopic species. Seventy-nine lines for the 1,2-d_2 species and 62 lines for the 3,3-d_2 species were least-squares-fit to first order in centrifugal distortion analyses. The rotational constants, the quartic centrifugal distortion constants, and related data are given in Table II. Tables SI and SII in the supplementary material contain spectral assignments and transition frequencies of the 1,2-d_2 and 3,3-d_2 isotopic species, respectively.

Stark effects, line intensities, isotopic frequency shifts, and the quality of the spectral fits support both isotopic assignments. In addition, MMDR and RFMDR experiments confirmed the assignments of a number of transitions used in the centrifugal distortion fits.

Carbon-13 Isotopic Species. Five singly substituted carbon-13 isotopomers of $\mathrm{\overline{CHFCHFC}H_2}$, $\mathrm{\overline{CDFCDFC}H_2}$, and $\mathrm{\overline{CHFCHFC}D_2}$ were assigned in natural abundance. Isotopic shifts, line intensities, and Stark effects were used to obtain these assignments. The computer-controlled spectrometer described previously[14] was particularly useful for this work. The possibility that these transitions are from excited vibrational states of the parent isotopic species was eliminated by relative intensity measurements at room temperature and dry ice temperature.

It was not possible to obtain frequency measurements on enough carbon-13 lines for centrifugal analyses of the five carbon-13 isotopomers. The observed carbon-13 transitions were corrected by substracting the centrifugal distortion correction determined for each parent isotopic transition. These corrected frequencies were fit to a rigid rotor model approximately to within the experimental uncertainty of the frequency measurements. The rotational constants of the five carbon-13 isotopomers obtained from these rigid rotor are given in Table II. The observed line frequencies and rigid rotor fits of the corrected frequencies are listed in Tables SIII–SVII of the supplementary material.

Electric Dipole Moment

The electric dipole moment of the normal isotopic species was determined by measurements of frequency shifts of Stark transitions. The data for each Stark transition were least-squares-fit to the second-order perturbation theory.[20] Table III lists the Stark coefficients obtained from these fits. These Stark coefficients were least-squares-fit to obtain the *b* and *c* dipole components. Table III gives the results of this least-squares fit. $\mu_b = 2.670$ (4) and $\mu_c = 1.152$ (3) D are the magnitudes of the components of the electric dipole moment along the *b* and *c* principal axes. These axes lie in the symmetry plane of the molecule. This plane bisects the C_1–C_2 bond and contains the methylene group. The total dipole moment of 2.908 (5) D falls in this symmetry plane. It is oriented almost parallel to the projection of the C–F bond in the *bc* plane.

Table I. Rotational Transitions (MHz) and Centrifugal Distortion Corrections in *cis*-1,2-Difluorocyclopropane ($\mathrm{\overline{CHFCHFC}H_2}$)

transition	ν_{obsd}	$\nu_{\text{obsd}} - \nu_{\text{calcd}}$[a]	centrifugal distortion correction[b]
1_{01}–2_{12}	18 961.44	0.02	−0.03
1_{10}–2_{21}	27 458.63	0.02	−0.11
1_{11}–2_{20}	29 114.73	−0.01	−0.14
1_{01}–2_{11}	22 884.65	0.00	−0.13
1_{11}–2_{21}	28 766.40	0.02	−0.12
1_{10}–2_{20}	27 807.00	0.03	−0.14
3_{22}–3_{31}	18 168.45	−0.03	−0.33
2_{12}–3_{03}	22 754.13	0.01	−0.37
2_{21}–3_{12}	18 875.46	−0.05	−0.52
2_{11}–3_{22}	34 814.98	−0.01	−0.15
2_{02}–3_{12}	33 602.85	−0.02	−0.53
4_{32}–4_{41}	24 690.78	0.03	−0.91
4_{31}–4_{40}	24 294.31	−0.03	−0.77
3_{13}–4_{04}	30 990.97	−0.02	−0.69
3_{03}–4_{14}	32 569.92	−0.03	−0.34
3_{22}–4_{13}	29 257.29	−0.03	−1.52
3_{21}–4_{13}	27 652.49	−0.05	−1.32
5_{05}–5_{14}	18 339.12	0.00	−1.82
5_{15}–5_{24}	21 335.44	−0.01	−0.64
5_{24}–5_{33}	20 470.69	−0.02	0.03
5_{32}–5_{41}	23 354.30	−0.05	0.67
5_{42}–5_{51}	31 642.37	0.02	−2.11
5_{15}–5_{23}	29 464.01	0.05	−2.76
5_{42}–5_{50}	31 643.45	−0.02	−2.11
4_{32}–5_{23}	31 681.88	0.02	−3.49
6_{25}–6_{34}	22 685.79	0.03	−0.42
6_{43}–6_{52}	31 440.12	0.08	−0.56
6_{42}–6_{51}	31 093.03	0.06	−0.19
6_{33}–6_{43}	21 346.79	−0.01	3.17
6_{43}–6_{51}	31 452.07	0.00	−0.57
6_{42}–6_{52}	31 080.90	−0.04	−0.17
5_{41}–6_{34}	27 870.09	0.04	−2.68
5_{42}–6_{33}	31 735.93	−0.01	−5.27
5_{33}–6_{25}	30 016.57	0.03	−2.37
5_{42}–6_{34}	27 945.76	−0.01	−2.74
5_{41}–6_{33}	31 660.27	0.05	−5.21
7_{07}–7_{16}	28 967.67	0.08	−3.74
7_{17}–7_{26}	29 756.72	−0.09	−2.55
7_{16}–7_{25}	19 987.57	−0.02	−5.67
7_{26}–7_{35}	25 641.82	0.02	−1.58
7_{43}–7_{52}	30 140.17	−0.01	2.65
7_{35}–7_{43}	27 241.62	−0.01	−0.86
7_{43}–7_{53}	30 070.58	−0.07	2.78
9_{27}–9_{36}	21 149.30	−0.04	−11.45
9_{46}–9_{55}	31 711.96	0.09	3.07
9_{45}–9_{54}	26 079.59	−0.01	12.12
10_{28}–10_{37}	26 837.43	−0.06	−18.61
10_{37}–10_{46}	18 836.30	−0.01	−4.48
10_{46}–10_{55}	23 540.06	0.03	15.45
9_{36}–10_{29}	28 225.74	−0.02	14.57
11_{47}–11_{56}	21 782.53	0.05	13.19
12_{48}–12_{57}	21 679.57	−0.04	2.60
$16_{6,10}$–$16_{7,9}$	30 461.28	0.02	58.18
$18_{7,11}$–$18_{8,11}$	32 007.34	0.00	182.71
$21_{7,14}$–$21_{8,13}$	35 150.51	0.01	−82.03

[a] ν_{calcd} was obtained from a first-order centrifugal distortion analysis. [b] Addition of the centrifugal distortion correction to the rigid rotor frequency equals ν_{calcd}.

Structure

The observation of *b*- and *c*-type transitions as well as the quality of the fits of the Stark coefficients to *b*- and *c*-dipole components

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Table II. Rotational Constants (MHz), Principal Moments of Inertia (amu·Å^2), and Centrifugal Distortion Constants (MHz) for Isotopic Species of *cis*-1,2-Difluorocyclopropane

constants	$CHFCHFCH_2$	$^{13}CHFCHFCH_2$	$CHFCHF^{13}CH_2$	$CDFCDFCH_2$	$^{13}CDFCDFCH_2$	$CDFCDF^{13}CH_2$	$CHFCHFCD_2$	$^{13}CHFCHFCD_2$
A	7926.839 (3)	7890.596 (8)[b]	7708.560 (7)[b]	7433.378 (3)	7405.700 (4)[c]	7242.324 (5)[c]	6986.580 (2)	6958.932 (5)[d]
B	4985.981 (2)	4949.961 (6)	4975.324 (5)	4678.465 (3)	4648.521 (4)	4665.363 (5)	4876.004 (2)	4840.010 (4)
C	3678.207 (2)	3660.692 (6)	3636.062 (5)	3560.844 (3)	3544.414 (4)	3524.403 (5)	3515.776 (2)	3500.724 (4)
I_a	63.755 43	64.048 27	65.560 76	67.987 80	68.241 90	69.781 34	72.335 69	72.623 08
I_b	101.360 0	102.097 6	101.577 1	108.022 4	108.718 3	108.325 8	103.646 2	104.416 9
I_c	137.398 2	138.055 6	138.990 8	141.926 8	142.584 7	143.394 2	143.746 1	144.364 2
τ_1	−0.002 3 (3)			−0.003 0 (5)			−0.004 8 (3)	
τ_2	−0.003 4 (1)			−0.003 1 (2)			−0.003 37 (9)	
τ_3	+0.357 (2)			+0.304 (3)			+0.290 (2)	
τ_{aaaa}	−0.028 7 (3)			−0.022 5 (3)			−0.021 0 (1)	
τ_{bbbb}	−0.031 12 (9)			−0.024 1 (2)			−0.028 18 (8)	
τ_{cccc}	−0.005 72 (8)			−0.005 0 (2)			−0.004 6 (1)	
σ^e	0.798			0.818			0.731	
lines[f]	55	17	13	79	20	12	62	18
J_{max}[g]	21	12	8	26	9	9	25	10

[a] Uncertainties in parentheses are one standard deviation; a conversion factor of 505379.05 MHz·amu·Å^2 was used for the moments of inertia. [b] The centrifugal distortion constants for $CHFCHFCH_2$ were assumed in the least-squares fit. [c] The centrifugal distortion constants for $CDFCDFCH_2$ were assumed in the least-squares fit. [d] The centrifugal distortion constants for $CHFCHFCD_2$ were assumed in the least-squares fit. [e] Standard deviation of the least-squares fit. [f] Number of lines used in the fit. [g] Maximum J value used in the fit.

Table III. Stark Coefficients and Electric Dipole Moment of *cis*-1,2-Difluorocyclopropane

transition		$\Delta\nu/E^2 \times 10^5$[a] obsd	calcd
2_{11}–3_{22}	$M_J = 0$	0.6168	0.6137
	$M_J = 1$	-0.4240	-0.4229
	$M_J = 2$	-3.5353	-3.5327
1_{11}–2_{20}	$M_J = 0$	-2.5213	-2.5006
1_{10}–2_{12}	$M_J = 0$	1.0711	1.0956
3_{03}–4_{14}	$M_J = 1$	4.7046	4.7275
3_{13}–4_{04}	$M_J = 1$	-4.2680	-4.2535
	$\mu_b = 2.670$ (4)[b]		
	$\mu_c = 1.152$ (3)		
	$\mu_T = 2.908$ (5)		

[a] The observed Stark coefficients have units MHz/(V^2/cm^2). [b] The uncertainty is one standard deviation propagated from the least-squares fit and the unit is D.

confirms C_s symmetry for the molecule. Since the methylene group must lie in the symmetry plane, the relationship in eq 1 must hold for isotopic substitution in that plane for a rigid molecule.

$$\Delta I_b + \Delta I_c - \Delta I_a = 0 \qquad (1)$$

ΔI_b and ΔI_c are the differences in the b and c principal moments of inertia of the normal and substituted isotopic species. The b and c principal axes lie in the symmetry plane; hence, ΔI_a is the corresponding difference in the a principal moment of inertia in which the a principal axis is perpendicular to the symmetry plane. Experimental values of eq 1 should be close to zero for isotopic substitution in the symmetry plane. Application of eq 1 to $CHFCHF^{13}CH_2$ and $CHFCHFCD_2$ where $CHFCHFCH_2$ is the normal isotopomer and to $CDFCDF^{13}CH_2$ where $CDFCDFCH_2$ is the normal isotopomer gives values of 0.004 37, 0.053 84, and −0.022 74, respectively, which confirms the location of the methylene group in the symmetry plane.

The molecular structure was determined from the principal moments of inertia in a number of different ways. As can be seen in Table IV, there are 15 unique atomic coordinates required to calculate the molecular structure. A partial substitution structure, p–r_s, was obtained by using the Kraitchman method to calculate the singly substituted atomic coordinates in the normal isotopic frame, $CHFCHFCH_2$. These substitution coordinates include the $C_{1,2}$ and C_3 carbons.[21] Chutjian's equations for C_s symmetry were used to calculate the $H_{1,2}$ substitution coordinates from the 1,2-d_2 principal moments of inertia in the same mass frame.[22,23] There are no sign ambiguities for these substitution coordinates because none of the atoms lie close to an axis or the center of mass. The three fluorine and four C_3 hydrogen coordinates were obtained from a least-squares fit[24] of the first-moment relations, $\sum_i m_i b_i = 0$ and $\sum_i m_i c_i = 0$, the cross-product equation, $\sum_i m_i b_i c_i = 0$, the three second-moment relations, $P_{aa} = \sum_i m_i a_i^2$, and all the second-moment relations for isotopic species which had not been utilized in the substitution coordinate calculations.

Table IV gives the atomic coordinates which were calculated as described above in the column designated p–r_s. The molecular structure derived from these coordinates is listed in Table V under p–r_s. The propagated errors in the p–r_s structural parameters given in Table V were obtained from Costain uncertainties in the p–r_s atomic coordinates. The propagated errors in bond distances and angles which involve the fluorine and C_3 hydrogen coordinates include the coordinate uncertainties obtained from the least-squares fit of the moment relations. With the exception of structural parameters involving the C_3 hydrogens, H_3 and H_3', the uncertainty in the geometry is small. These H_3 and H_3' parameters

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Table IV. Atomic Coordinates (Å) of *cis*-1,2-Difluorocyclopropane

		Δ_0^{1a}	r_0^{2b}	r_0^{3c}	r_0^{4d}	$p\text{-}r_s^{5e}$
$C_{1,2}$	*a*	±0.7465 (41)	±0.7464 (42)	±0.7465 (41)	±0.7465 (42)	±0.7438
	b	−0.3369 (25)	−0.3392 (47)	−0.3368 (25)	−0.3338 (71)	−0.3292
	c	−0.4335 (7)	−0.4349 (26)	−0.4351 (17)	−0.4339 (40)	−0.4362
C_3	*a*	0.0	0.0	0.0	0.0	0.0
	b	−1.2643 (25)	−1.2644 (28)	−1.2641 (25)	−1.2634 (30)	−1.2633
	c	0.4828 (7)	0.4803 (48)	0.4767 (62)	0.4761 (69)	0.4760
F	*a*	∓1.3638 (15)	∓1.3638 (15)	∓1.3638 (15)	∓1.3638 (15)	∓1.3645 (1)
	b	0.7369 (8)	0.7364 (17)	0.7373 (9)	0.7384 (28)	0.7385 (7)
	c	0.1438 (6)	0.1432 (15)	0.1457 (20)	0.1486 (87)	0.1522 (23)
$H_{1,2}$	*a*	±1.3120 (12)	±1.3120 (12)	±1.3120 (12)	±1.3120 (12)	±1.3148
	b	−0.6980 (23)	−0.6981 (24)	−0.6979 (23)	−0.6979 (24)	−0.7012
	c	−1.2921 (14)	−1.2922 (14)	−1.2923 (14)	−1.2923 (14)	−1.2913
H_3	*a*	0.0	0.0	0.0	0.0	0.0
	b	−2.3070 (29)	−2.354 (90)	−2.283 (25)	−2.15 (42)	−2.05 (12)
	c	0.2075 (118)	0.31 (20)	0.249 (44)	0.10 (41)	0.016 (83)
$H_{3'}$	*a*	0.0	0.0	0.0	0.0	0.0
	b	−1.0015 (59)	−0.88 (26)	−1.048 (48)	−1.303 (698)	−1.47 (15)
	c	1.5287 (27)	1.514 (38)	1.5276 (33)	1.545 (30)	1.531 (7)

[a] The r_0 coordinates were obtained from least-squares fits of the moment of inertia data to the atomic coordinates. The errors were determined from deviations of the least-squares fits. In the case of r_0^1 τ, the methylene C–H bonds were constrained to be equal and the CCC plane bisects the HCH angle. [b] Only the methylene C–H bonds were constrained to be equal in the r_0^2 fit. [c] In the r_0^3 fit, the CCC plane bisects the HCH angle. [d] No geometrical constraints were placed on the r_0^4 fit. [e] The r_s coordinates include atoms $C_{1,2}$, C_3, and $H_{1,2}$; the F, H_3, and $H_{3'}$ coordinates were obtained from a least-squares fit of the moment relations.

Table V. Interatomic Distances (Å) and Angles (deg) in *cis*-1,2-Difluorocyclopropane

	r_0^{1a}	r_0^2	r_0^3	r_0^4	$p\text{-}r_s^5$	Theoretical[b]
$C_{1,2}$–C_3	1.502 (3)	1.500 (5)	1.500 (5)	1.500 (7)	1.503 (4)	1.506
C_1–C_2	1.493 (6)	1.493 (6)	1.493 (6)	1.493 (6)	1.488 (3)	1.498
C_1–F	1.367 (3)	1.368 (5)	1.368 (3)	1.368 (8)	1.368 (6)	1.385
C_1–H	1.090 (3)	1.088 (4)	1.088 (3)	1.090 (5)	1.093 (4)	1.067
C_3–H	1.078 (3)	1.10 (9)	1.073 (12)	1.07 (4)	1.075 (30)	1.069
C_3–H′	1.078 (5)	1.10 (10)	1.044 (27)	0.96 (42)	0.91 (12)	1.072
$\theta(HC_{1,2}F)$	111.0 (3)	111.0 (4)	111.1 (3)	111.3 (5)	111.3 (4)	112.6
$\theta(HC_3H)$	118.9 (7)	119.0 (16)	114.0 (3)	111.4 (4)	109.0 (10)	116.6
$\theta(FC_1C_2)$	116.9 (2)	116.8 (3)	116.8 (2)	116.8 (5)	117.0 (3)	117.5
$\theta(FC_{1,2}C_3)$	116.9 (1)	116.8 (2)	116.9 (2)	116.9 (5)	116.7 (5)	117.3
$\theta(HC_1C_2)$	121.3 (2)	121.3 (3)	121.3 (2)	121.3 (3)	121.5 (3)	
$\theta(HC_2C_3)$	122.3 (2)	122.4 (4)	122.2 (3)	121.9 (6)	121.6 (4)	

[a] r_0 structures 1–4 were calculated from the r_0 atomic coordinates listed in Table IV. The p–r_s structure was calculated from the p–r_s atomic coordinates given in Table IV. [b] The theoretical structure is from Skancke and Boggs' calculations (ref 4).

Table VI. Ring Bond Lengths (Å) in *cis*- and *trans*-1,2-Difluorocyclopropanes and 1,2-Difluoroethylene Oxides

	$r(C_1\text{–}C_2)$	$r(C_2\text{–}C_3)$	ref
$CH_2CH_2CH_2$	1.514 (2)	1.514 (2)	25
trans-$CHFCHFCH_2$	1.466 (4)	1.488 (5)	9
cis-$CHFCHFCH_2$	1.488 (3)	1.503 (4)	this work
	r(C–C)	r(C–O)	
CH_2CH_2O	1.466 (2)	1.431 (1)	*a*
trans-CHFCHFO	1.436 (4)	1.395 (8)	11
cis-CHFCHFO	1.451 (3)	1.409 (4)	10

[a] Structure from: Hirose, C. *Bull Chem. Soc. Jpn.* **1974**, *47*, 1311.

are not sensitive to the existing moment of inertia data. Deuterium isotopomers singly substituted at the H_3 and H_3' positions are required to locate these atoms more precisely.

The $C_{1,2}$ and C_3 carbon coordinates can be determined via the Kraitchman method[21] in the 1,2-d_2 isotopic frame. The r_s ring bonds in this frame are $r(C_{1,2}\text{–}c_3)$ = 1.503 (4) Å and $r(C_1\text{–}C_2)$ = 1.486 (3) Å. The r_s C_1–C_2 bond length was also calculated in the 3,3-d_2 isotopic frame and gave $r(C_1\text{–}C_2)$ = 1.487 (3) Å. These r_s ring bonds are in excellent agreement with the values determined in the normal isotopic frame (see the column titled p–r_s in Table V for a comparison).

The three second-moment equations for all the isotopic species listed in Table II as well as the first-moment and cross-product equations were used in a least-squares fit[24] to obtain a complete r_0 structure, designated r_0^4 in Tables IV and V. The r_0 structures designated r_0^1, r_0^2, and r_0^3 were obtained from least-squares fits of the same moment of inertia data used for r_0^4. However, two structural constraints involving the HCH group were imposed upon the fits. In the case of r_0^1, the CCC ring plane bisects the HCH angle, and the C_3–H and C_3–H′ bond distances are equal. In the r_0^2 fit, the constraint of angle bisection was removed, while the equal C_3–H and C_3–H′ bond distance constraint was removed in the r_0^3 fit. The results of these calculations are listed in Tables IV and V. The coordinate errors are standard deviations from the least-squares fits. These errors were used to obtain the propagated errors in the structural parameters.

With the exception of parameters which involve the methylene hydrogens, there is good agreement between the various r_0 bond distances and angles. Comparison of any one of these r_0 structures with the p–r_s structure reveals small differences which provide an estimate of the maximum uncertainties derived from vibrational effects. In the following section, the preferred p–r_s parameters are used in discussions of structural effects.

Discussion

C–C Ring Bonds. In the preceeding paper on the molecular structure of *trans*-1,2-difluorocyclopropane, the effect of fluorine substitution upon ring bond lengths was discussed for a series of fluorinated cyclopropanes. The experimental results derived from microwave studies of 1,1-difluorocyclopropane,[6] *cis*,*cis*-1,2,3-trifluorocyclopropane,[7] and *trans*-1,2-difluorocyclopropane[9] show that the C–C ring bonds adjacent to fluorine-substituted carbons shorten relative to cyclopropane.[25] As illustrated in Table VI,

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Table VII. Comparison of Internal Angles (deg), ω_X (deg), and τ_X (deg) in Cyclopropanes

angle	$CH_2CH_2CH_2$[a]	*cis*-$CHFCHFCH_2$[b]	*trans*-$CHFCHFCH_2$[c]
$\theta(FC_2C_1)$		117.0 (3)	117.3 (3)
$\theta(FC_2C_3)$		116.7 (5)	118.4 (3)
$\theta(HC_2C_1)$	117.7 (4)	121.5 (3)	119.7 (3)
$\theta(HC_2C_3)$	117.7 (4)	121.6 (4)	121.1 (4)
ω_H	57.5 (4)	52.8 (3)	54.1 (3)
τ_H	0.0	-0.2 (7)	-2.0 (7)
ω_F		58.5 (3)	57.3 (3)
τ_F		0.5 (9)	-1.7 (7)

[a] Reference 25. [b] This work. [c] Reference 9.

cis-1,2-difluorocyclopropane follows this trend since the C_1–C_2 and C_2–C_3 ring bonds are shorter than those in cyclopropane.

Both the C_1–C_2 and C_2–C_3 bonds are longer in the cis isomer than the trans isomer of 1,2-difluorocyclopropane. As can be seen in Table VI, this result continues the trend observed earlier in *cis*- and *trans*-1,2-difluoroethylene oxide where the C–C and C–O bond lengths are longer in the cis isomer.[10,11] Consideration of the C–C and C–O bond lengths for the fluorinated ethylene oxides demonstrates that ring bonds adjacent to fluorine-substituted carbons also shorten relative to ethylene oxide. Hence, the experimental structures provide strong evidence that fluorination of cyclopropane and ethylene oxide produces qualitatively similar ring bond length changes.

These experimental data are not entirely consistent with theoretical work. Ab initio results by Deakyne et al. have predicted that the C_1–C_2 bond for *cis*-1,2-difluorocyclopropane is approximately 0.01–0.02 Å shorter than in cyclopropane.[2] This prediction is qualitatively consistent with the experimental C_1–C_2 bond length which is 0.026 Å shorter than the C–C bond length in cyclopropane (see Table VI). However, the agreement is not so good between the ab initio study and the experimental work for the C_2–C_3 bond length in *cis*-1,2-difluorocyclopropane. For this bond length, the ab initio work finds no bond shortening relative to cyclopropane, contrary to the observed shortening of 0.011 Å.

It is possible that the source of the discrepancy between the experimental and ab initio studies results from the interpretation of the charge density difference maps calculated for 1,1,2,2-tetrafluorocyclopropane.[2] The overall charge redistribution in the cyclopropane ring which is induced by tetrafluoro substitution leads to a net charge gain between C_1 and C_2 carbons. This charge gain has the effect of displacing C_1 and C_2 inward, toward the center of the ring. It leads to a shortening of the C_1–C_2 bond length in 1,1,2,2-tetrafluorocyclopropane.[2] By considering changes in charge distributions, orbital diagrams, and overlap populations for 1,1,2,2-tetrafluorocyclopropane and *cis*-1,2-difluorocyclopropane, the C_1–C_2 bond length in the cis isomer is predicted to be shortened by roughly half the magnitude of the same bond in the tetrafluoro derivative. This prediction qualitatively agrees with the experimental result.

However, the charge density difference map shows a charge buildup both behind and in front of the C_3 carbon which makes it difficult to determine the force acting upon C_3. Deakyne, et al. reasoned by analogy to Be_2 that the back charge buildup dominates which displaces C_3 away from the C_1–C_2 bond. The net effect of the C_1, C_2, and C_3 displacements is to leave the C_2–C_3 bond length unchanged in 1,1,2,2-tetrafluorocyclopropane. Similarly, the C_2–C_3 bond length should remain unchanged in *cis*-1,2-difluorocyclopropane.[2] If the charge gain both in front of and behind C_3 effectively cancel out, then C_3 will not be displaced. Since the C_1 and C_2 atoms move inward above the C_1–C_2 axis, the C_2–C_3 bond must shorten relative to cyclopropane. Clearly, it is more difficult to predict ring bond changes for the C_2–C_3 bond in the 1,2-difluorocyclopropanes using the charge density difference maps because unlike the C_1–C_2 bond, it depends upon both $C_{1,2}$ and C_3 carbon displacements.

A complete geometry optimization at the 4-21 level was reported for *cis*- and *trans*-1,2-difluorocyclopropane.[4] In qualitative agreement with experiment, this work finds that both isomers have shortened C_1–C_2 and C_2–C_3 ring bonds relative to cyclopropane. In the case of the trans isomer, the degree of ring shortening is underestmated by about 0.02 Å for both the C_1–C_2 and C_2–C_3 bonds. However, the calculations for the cis isomer show better agreement with the experimental bond lengths. As shown in Table V, the theoretical and experimental C_2–C_3 bond lengths are in close agreement, while the C_1–C_2 bond distance is underestimated by 0.01 Å.

HCF and HCH Groups. The HCF angle is identical for *cis*- and *trans*-1,2-difluorocyclopropane and equal to 111.2°. As discussed in the preceeding paper, a value of 111.3° is consistent with HCF angles which have been experimentally determined for other fluorinated cyclopropanes. It also is in good agreement with the value of 112.6° determined by Skancke and Boggs by complete geometry optimization.[4]

While the C_1–H bond lengths are almost identical for *cis*- and *trans*-1,2-difluorocyclopropane, there are distinct differences in the C–F bond length for these isomers. The cis isomer has a C–F bond length of 1.368 (8) Å compared to the trans isomer C–F bond distance of 1.383 (3) Å. The same trend was observed, previously, for 1,2-difluoroethylene oxide where C–F bond lengths were determined to be 1.345 (7) and 1.363 (4) Å, respectively, for the cis and trans isomers.[10,11] It is interesting to note that the ab initio study by Skancke and Boggs found the C–F bond lengths to be 1.385 and 1.384 Å, respectively, for the cis and trans isomers of 1,2-difluorocyclopropane.[4] It is difficult to determine whether the agreement for the trans isomer is fortuitous or not since the 4-21 basis set does not generally describe polar bonds very well.[4] Skancke and Boggs found that the C–F bonds in *cis*- and *trans*-1,2-difluoroethylene are overestimated by 0.03 Å using both the 4-21 and the 4-31 G basis sets. Since C–F bond distances in other fluorinated cyclopropanes are about 1.355 Å, the trans C–F bond distance seems to be abnormally long. Clearly, the experimental results demonstrate that these limited basis sets do not always overestimate C–F bond lengths. Hence, it is not possible always to assume that C–F bonds will be overestimated by these limited basis sets when making comparisons between molecules.

In the preceding paper, both the HCF group orientation with respect to the CCC ring and CF and CH bond orientations in *trans*-1,2-difluorocyclopropane were compared with cyclopropane.[9] This comparison was made by looking at the internal angles and two additional angles, designated ω_X and τ_X. ω_X is the angle between the H or F substituent and the cyclopropyl ring plane. τ_X is the angle between the projection of the substituent X in the ring plane and the bisector of the $C_3C_1C_2$ angle where C_3 is the unique carbon and C_1 is the carbon to which X is bonded. These angles for *cis*- and *trans*-1,2-difluorocyclopropane are compared to cyclopropane in Table VI.

The FCC angles and ω_f are almost the same in the two 1,2-difluorocyclopropanes, and they do not differ significantly from the HCC and ω_H angles in cyclopropane. This means that the 1,2-difluoro substitution for both the cis and trans isomers leads to CF bond orientations with respect to the ring which are virtually identical with the CH bond orientations in cyclopropane. A similar effect was noted for *cis,cis*-1,2,3-trifluorocyclopropane[7] and the cis and trans isomers of 1,2-difluoroethylene oxide.[10,11]

In contrast to the CF bonds, comparison of the HCC angles and ω_H for *cis*- and *trans*-1,2-difluorocyclopropane with HCC and ω_H in cyclopropane shows that the $C_{1,2}H$ bonds have moved toward the ring plane in the cis and trans difluoro isomers relative to cyclopropane. The result of this orientational change is the observed contraction of the HCF angles in the cis and trans difluoro derivatives relative to the HCH angle in cyclopropane. *cis,cis*-1,2,3-Trifluorocyclopropane[7] and *cis*- and *trans*-1,2-difluoroethylene oxide[10,11] also exhibit the same CH bond movements which lead to HCF angle contractions.

Symmetry in cyclopropane requires τ_H to be zero since the HCH plane must be perpendicular to the ring plane. The small negative values of τ_F and τ_H for *trans*-1,2-difluorocyclopropane indicate that the HCF group has tilted very slightly toward the adjacent HCF group. In the case of *cis*-1,2-difluorocyclopropane, τ_H and τ_F are almost zero which means that there is no movement of the HCF groups toward each other.

Isomeric Differences. In general, disubstituted ethylenes are more stable when the substituents are trans to one another. However, a number of 1,2-dihaloethylenes do not follow this rule, despite unfavorable bond dipole repulsions and steric crowding. In these unusual systems, the cis isomer is of lower energy than the trans. A well-known example is 1,2-difluoroethylene where the cis form is 1080 cal/mol lower in energy than the trans form.[26] From the experimental point of view, this anomalous relationship has been called the "cis effect". A similar effect is found in a preference for the gauche rotamer over the trans rotamer in 1,2-difluoroethane. In this system, the energy of the gauche isomer (uncorrected for zero-point vibrational energies) is lower by 580 (90) cal/mol.[27]

The puzzle of the cis effect has attracted the interest of a number of theoreticians. Binkley and Pople employed an extended basis set and standard geometry within the restricted Hartree–Fock model to calculate a cis/trans energy difference of 260 cal/mol with the correct sign for the 1,2-difluoroethylenes.[28,29] Introduction of some electron correlation with a more limited basis set yielded results that implied that electron correlation effects gave a further energy advantage to the cis isomer.[28]

Dykstra and co-workers made a thorough ab initio study of the role of polarization functions, which were absent from the Binkley and Pople work, as well as electron correlation on the two isomers of 1,2-difluoroethylene. They found that polarization functions played a larger role than electron correlation in accounting for the lower energy of the cis isomer.[30] A very flexible basis set without electron correlation yielded a cis/trans energy difference of 800 cal/mol for optimized geometries. In a separate study, Cremer had shown that both polarization functions and electron correlation contributed to the energy difference.[31] In calculating the equilibrium geometry of the two isomers, Dykstra et al. found that electron correlation rather than polarization functions played the larger role.[30] Unfortunately, these geometry-optimization calculations cannot be critically evaluated by comparison with experimental values. The experimental structure of the trans isomer derived from electron diffraction studies[32,33] is not comparable in quality to the microwave strucure of the cis isomer.[34] Nonetheless, it appears that the energy difference between the two isomers of difluoroethylene can be calculated with the right sign and to a close numerical approximation by means of current levels of theory.

Several qualitative electronic arguments have been advanced to explain the cis effect. For the 1,2-dichloroethylenes, Pitzer and Hollenberg suggested that resonance structures of the type $Cl^{-}{:}CH{-}CH{=}Cl^{+}$, which implies a role for electron correlation,[28] favor the cis isomer.[35] Epiotis argued for a net attraction of nonbonded fluorine atoms in cis isomers due to an interaction between nonbonded electrons and unfilled antibonding molecular orbitals of the FCCF backbone.[36-39] Bingham explained the anomalous energy difference in terms of a larger *de*stabilization of the trans isomer than the cis isomer due to greater electron delocalization in the FCCF π^* orbital of the trans isomer.[40] The various ab initio calculations do not distinguish clearly between these qualitative arguments. However, Bingham's proposal finds support in force constant data, NMR chemical shifts, and photoelectron spectra.[4]

Bingham's proposal correctly predicts the opposite of a cis-effect outcome for the relative energies of the cis and trans isomers of 1,2-difluorocyclopropane. Experimental measurements have shown that the trans isomer is 2800 ± 200 cal/mol lower in energy than the cis isomer.[12] In this case, the nonplanar pathway in the trans isomer is said to impede electron delocalization more than the planar FCCF pathway in the cis isomer. Thus, *de*stabilization due to electron delocalization in the antibonding FCCF orbital of the cis isomer is greater.

In their 4-21 level, ab initio investigation of the isomers of 1,2-difluorocyclopropane, Skancke and Boggs computed a cis/trans energy difference of −3900 cal/mol,[4] which is in fair agreement with the experimental value. This result was computed for geometry-optimized structures. They interpret their calculations as support for the electron-delocalization interpretation of Bingham. There is greater delocalization of charge and a longer C_1–C_2 bond length in the cis isomer.[4] While the equal C–F bond lengths in the two isomers seemed inconsistent with greater delocalization of electrons in the cis form, the larger overlap population for this bond in the cis form might indicate greater partial double-bond character.[4]

The results of the present microwave study for the two cyclopropane isomers seem to reinforce Skancke and Boggs' findings. The C–F bond is shorter in the cis isomer than in the trans isomer, and the C_1–C_2 bond length is longer.

Further support for the importance of electron delocalization comes from the theoretical work of Deakyne et al. on the cis and trans isomers of 1,2-difluoroethylene oxide, which are isoelectronic with the 1,2-difluorocyclopropane isomers.[41] These workers used minimal STO-3G basis sets to find that the trans isomer is more stable than the cis. The explanation for this result is an enhanced electron-delocalization argument. However, it differs from Bingham's reasoning in the *stabilization* of an "FCCF"-bonding orbital is smaller in the cis isomer than in the trans isomer. These authors go on to suggest that the energy difference in the 1,2-difluorocyclopropane isomers found by Skancke and Boggs may depend on the same stabilization argument.

The structural data for the difluorocyclopropanes seems to be inconsistent with the proposal that nonbonded attractions between cis fluorine atoms are significant. In *cis*-1,2-difluorocyclopropane, the F···F distance is 2.73 Å, which is virtually the same as the 2.74-Å distance in *cis*-1,2-difluoroethylene.[34] Yet, the relative stabilities of the two isomer pairs is reversed. Also, there is very little difference in the CCF angles or the τ_F angles for the two isomers of 1,2-difluorocyclopropane. In contrast, for the 1,2-difluoroethylene molecules, the CCF angle of the trans isomer appears to be larger than for the cis isomer,[33,33,42] which is opposite

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to what would be expected for a significant nonbonded F···F attraction in the cis isomer.

Further, higher level theoretical investigations of the properties of the *cis*- and *trans*-1,2-difluorocyclopropane molecules are needed. To date, neither polarization functions nor configuration interaction has been applied to calculations of the difluorocyclopropanes. The accurate geometric parameters and the dipole moments of both isomers reported in the present papers as well as the observed energy difference should be a stimulus to such work.

Conclusions

The complete gas-phase structure of *cis*-1,2-difluorocyclopropane was determined from microwave spectral data. The C–C bonds have shortened relative to the ring bonds in cyclopropane. All the C–C bonds are longer in *cis*-1,2-difluorocyclopropane than the corresponding bonds in *trans*-1,2-difluorocyclopropane. The C–F bond distance in the cis isomer is within the range of C–F bond distances which have been observed for other fluorinated cyclopropanes. However, the trans C–F bond is unusually long.

An ab initio investigation by Skancke and Boggs of *cis*- and *trans*-1,2-difluorocyclopropane at the 4-21 level determined geometry optimized structures which are in qualitative agreement with the experimental structures.[4] For the trans isomer, the amount of bond shortening is underestimated by 0.02 Å for both types of ring bonds. In the case of the cis isomer, the agreement is better for these ring bonds. A second ab initio study by Deakyne et al. employing charge density difference maps predicts the observed shortening of the C_1–C_2 bond in the cis isomer. However, it does not find bond shortening for the adjacent C_2–C_3 bond in the cis isomer. This result is contrary to the observed shortening of 0.011 Å and may be due to difficulty in interpreting the charge density difference map for a situation where both $C_{1,2}$ and C_3 carbon displacements are significant.

The microwave structural results also provide support for theoretical interpretations of the observed −2800 ± 200 cal/mol cis-to-trans energy difference of 1,2-difluorocyclopropane.[12] According to Bingham's qualitative argument, greater destabilization is found in the cis form due to larger electron delocalization in the antibonding "FCCF" orbital.[40] Skancke and Boggs indicate that their ab initio calculations offer support for Bingham's proposal.[4] The microwave studies find a shorter C–F bond and a longer C_1–C_2 bond in the cis isomer. These results tend to support Skancke and Boggs' work and are consistent with the electron-delocalization explanation.

Several structural results suggest that nonbonded attractions between vicinal fluorines[36-39] are not significant for the 1,2-difluorocyclopropanes. The F···F distances are almost identical for *cis*-1,2-difluoroethylene and *cis*-1,2-difluorocyclopropane in spite of the reversal in energy differences of the two isomeric pairs. Also, the CCF angles and the τ_F angles are virtually the same for *cis*- and *trans*-1,2-difluorocyclopropane.

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Supplementary Material Available: Rotational transitions and centrifugal distortion corrections for cyclopropane compounds (12 pages). Ordering information is given on any current masthead page.

Temperature Dependence of the Substrate and Positional Selectivity of the Aromatic Substitution by Gaseous *tert*-Butyl Cation

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Abstract: The temperature dependence of the substrate and positional selectivity of the alkylation of benzene and toluene by radiolytically formed t-Bu^+ ions has been investigated in isobutane gas at 720 torr in the range 0–140 °C. The Arrhenius plot of the empirical k_T/k_B ratio is linear over an extended (0–100 °C) interval, and its slope corresponds to a difference of 3.6 ± 0.4 kcal mol^{-1} between the activation energy for the *tert*-butylation of benzene and of toluene. The positional selectivity of the alkylation is affected by the temperature as well, the p:$^1/_2$m ratio decreasing from ca. 27 at 0 °C to 7.5 at 140 °C. The results are interpreted as evidence that under conditions typical of radiolytic experiments the activation mechanism of the addition of t-Bu^+ to arenes, a typical ion–molecule reaction, is essentially thermal, as expected at the high-pressure limit of gas-phase ionic processes.

Aromatic substitution by gaseous cations has been the focus of considerable interest, and the subject of extensive investigations, carried out by mass spectrometric,[1] radiolytic,[2] and nuclear decay[3] techniques over a pressure range of several orders of magnitude. However, very little is known on the temperature dependence of the reaction rate, since most of the studies have been carried out

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