of $C_6X_5^+NH_2Ph$, the adduct from attack on nitrogen. Under conditions favoring the kinetic control of product composition, i.e., in the presence of NMe_3 which ensures fast deprotonation of the primary intermediates, $PhNHC_6X_5$ is the only product observed. Taking into account the detection limit of the radiometric analysis, this corresponds to a k_N/k_{ring} ratio in excess of 10:1. Despite the uncertainty as to the free or CO-solvated nature of the phenylium ion in the present experiments, their result does not conflict with a previously established trend,[25] namely that the N-alkylating ability of carbenium ions in their reaction with gaseous aniline increases with the hardness of the cations.[30]

WARNING: The experiments reported involve the use of tritiated compounds of relatively high volatility, whose safe handling requires adequate confinement, e.g., a standard radiochemical hood.

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Registry No. C_6X_6 (X = H and T), 13967-78-7; PhOH, 108-95-2; PhOMe, 100-66-3; $PhNH_2$, 62-53-3; CO, 630-08-0; $PhOC_6X_5$ (X = H and T), 99747-37-2; HO-*o*-$C_6H_4C_6X_5$ (X = H and T), 99747-38-3; MeO-*o*-$C_6H_4C_6X_5$ (X = H and T), 99747-39-4; MeO-*p*-$C_6H_4C_6X_5$ (X = H and T), 99747-40-7; $PhOCOC_6X_5$ (X = H and T), 99747-41-8; MeO-*p*-$C_6H_4COC_6X_5$ (X = H and T), 99747-42-9; MeO-*o*-$C_6H_4COC_6X_5$ (X = H and T), 99747-43-0; PhCONHPh, 93-98-1; Ph_2NH, 122-39-4; Ph-*o*-$C_6H_4NH_2$, 90-41-5; Ph-*p*-$C_6H_4NH_2$, 92-67-1; Ph-*o*-C_6H_4OMe, 86-26-0.

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

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Abstract: The microwave spectra of *trans*-1,2-difluorocyclopropane were assigned and fitted to a first-order centrifugal distortion model. Microwave transitions of seven deuterium and carbon-13 isotopomers were observed and used to obtain a complete molecular structure. The partial Kraitchman parameters are $r(C_{1,2}–C_3)$ = 1.488 (5), $r(C_1–C_2)$ = 1.466 (4), $r(C–F)$ = 1.383 (3), $r(C_1–H)$ = 1.090 (4), and $r(C_3–H)$ = 1.083 (2) Å and $\theta(HCF)$ = 111.3 (4) and $\theta(HCH)$ = 116.8 (2)°. The electric dipole moment, which is along the 2-fold symmetry axis, was measured to be 1.18 (1) D. All ring bonds in *trans*-1,2-difluorocyclopropane are shorter than the C–C bonds in cyclopropane. However, the orientation of the HCF group with respect to the ring plane does not differ significantly from the CH_2 group orientation in cyclopropane. The observed gas-phase molecular structure is related to several theoretical studies of fluorine-substituent effects in cyclopropane derivatives.

Fluorine substitution on a cyclopropane ring is known to have a marked effect on the ring geometry.[1] In 1,1-difluorocyclopropane, a large shortening of the C–C bond between the CF_2 and CH_2 groups is observed, while the C–C bond opposite the CF_2 group lengthens considerably.[2] All the ring bonds shorten in *cis*,*cis*-1,2,3-trifluorocyclopropane[2] relative to cyclopropane.[4] Hoffmann has discussed the effect of substituents on the cyclopropane ring structure[5] in terms of the Walsh scheme for cyclopropane.[6] However, application of this molecular orbital approach to rings with fluorine substituents does not lead to correct predictions for the ring bond changes.[2,3]

More recently, Deakyne et al. used charge density difference plots obtained from ab initio wave functions to rationalize the experimental ring structure of 1,1-difluorocyclopropane.[7] They identified an additivity rule to correctly predict the ring bond shortening in *cis*,*cis*-1,2,3-trifluorocyclopropane, to predict the unknown ring geometry of *cis*-1,2-difluorocyclopropane, and to predict the ring structure of 1,1,2,2-tetrafluorocyclopropane,[8] which has been partially determined. In both of these 1,2-fluoro-substituted cyclopropanes, the C–C bond between the methylene and fluoro group is predicted to remain nearly the same as in cyclopropane.[7] This prediction is contrary to the general observation that bonds adjacent to C–F bonds are shorter in the fluorocarbon than in the corresponding hydrocarbon.

An ab initio study by Skancke and Boggs employing complete geometry optimization at the 4-21 level has yielded ring structures for *cis*- and *trans*-1,2-difluorocyclopropane.[9] The calculated differences in the molecular structures of these geometrical isomers are used to explain the absence of the "cis effect" observed for the 1,2-difluorocyclopropanes. In this case, the trans form of 1,2-difluorocyclopropane is 2.8 ± 0.2 kcal/mol lower in energy than the cis form.[10] This result is notable because the cis form

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is generally of lower energy than the trans form in the related unsaturated series of dihaloethylenes.

Durmaz and Kollmar have used ab initio SCF MO methods to investigate the influence of substituents having lone pair electrons on the structure of the cyclopropane ring.[11] In the case of cyclopropyl fluoride, it was found that the adjacent ring bonds shorten and the opposite ring bond lengthens. These results are consistent with the ab initio calculations of Deakyne et al.

Complete gas-phase structures of *cis*- and *trans*-1,2-difluorocyclopropane are needed to test the theoretical work by Deakyne et al.[7] as well as the ab initio optimized geometry study by Skancke and Boggs.[9] In addition, the experimental structures are desired to determine differences in the geometries of the cis and trans isomers. The differences in geometries should help evaluate different theoretical explanations of the "cis effect".[12,13] This paper describes a microwave study of *trans*-1,2-difluorocyclopropane.[14] Sufficient isotopomer data are obtained to determine a complete gas-phase structure. The results are related to fluorine substituent effects observed for other fluorinated cyclopropanes as well as the theoretical studies mentioned above. In the following paper, a gas-phase structure of *cis*-1,2-difluorocyclopropane is reported, and the implications of the structures of both the cis and trans isomers are discussed.

Experimental Section

Synthesis. *trans*-1,2-Difluorocyclopropane was prepared by photolysis of 1,2-difluoroethylene and diazomethane at −80 °C in the liquid phase.[10] 1,2-Difluoroethylene-d_2 was substituted for the normal isotope in the preparation of *trans*-1,2-difluorocyclopropane-*1,2*-d_2. *trans*-1,2-Difluorocyclopropane-*3,3*-d_2 was synthesized by photolysis of a mixture of *trans*-1,2-difluoroethylene and ketene-d_2 in the gas phase. These samples originate from a vibrational spectral analysis of *cis*- and *trans*-1,2-difluorocyclopropane.[10] In that work, the sample purity was estimated to be greater than 99% by gas chromatography. Isotopic purity was also in the 99% range as shown by infrared and NMR spectroscopies.

Spectroscopy. All Stark-modulated spectra were obtained with a Hewlett-Packard 8460A spectrometer at Princeton or a Hewlett-Packard 8400C spectrometer at RPI. Transition frequencies of the normal and enriched isotopes were measured to an accuracy of at least ±0.05 MHz. The spectra were recorded at sample pressures of 25 mtorr.

The carbon-13 isotopomers were studied in natural abundance at dry ice temperature. At RPI, the microwave source of the HP 8400C spectrometer was used in conjunction with a 10-ft Stark cell and a Cromemco Z-2D computer system which permits signal averaging and frequency measurement.[15] This system was sensitive enough to characterize the low J Stark effects of many carbon-13 lines and to measure the transition frequencies to an estimated uncertainty of ±0.05 MHz.

Microwave–microwave double-resonance spectroscopy (MMDR) was carried out by using the "on–off" pump modulation procedure described by Stiefvater.[16] Transitions were pumped in the K band (18.0–26.5 MHz), and double resonances were observed in the R band (26.5–40.0 GHz). The apparatus consisted of a HP 8460A spectrometer which was modified for MMDR.[17]

Dipole moment measurements were performed with the 8460A spectrometer by adding the 33.33-kHz square-wave modulation to the dc bias. Both Stark modulators were used, each driving its respective Stark cell, and adjusted to track together. One modulator was chosen as the reference unit, and the dc bias was measured at the ground-to-base monitor jack of the reference HP 8421C Stark Modulator with a Fluke 895A differential voltmeter. The monitor voltage divider is nonlinear at Stark voltages below 200 V. In the case of *trans*-1,2-difluorocyclopropane, measurements were made only in the linear region of the divider. Measurements of the $J = 2 \rightarrow 3$ Stark transitions of OCS were used to determine the electrode spacing in the Stark cell.[18]

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

transition	ν_{obsd}	$\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$[a]	centrifugal distortion correction[b]
$2_{1,2}-2_{2,1}$	25 424.97	0.01	−0.41
$2_{1,1}-2_{2,0}$	23 981.05	0.00	−0.41
$1_{0.1}-2_{1,2}$	20 760.59	0.01	−0.05
$1_{1.0}-2_{2,1}$	37 710.44	0.00	−0.43
$1_{1.1}-2_{2,0}$	38 220.74	0.02	−0.44
$3_{1,3}-3_{2,2}$	26 171.05	−0.02	−0.42
$3_{1,2}-3_{2,1}$	23 348.78	−0.02	−0.39
$2_{0,2}-3_{1,3}$	26 667.44	−0.01	−0.09
$4_{1,4}-4_{2,3}$	27 172.91	−0.03	−0.44
$4_{1,3}-4_{2,2}$	22 614.95	0.02	−0.37
$3_{1,3}-4_{0,4}$	19 449.94	0.00	−0.17
$3_{0,3}-4_{1,4}$	32 366.53	0.01	−0.17
$5_{1,4}-5_{2,3}$	21 869.03	0.00	−0.34
$4_{1,4}-5_{0,5}$	26 677.60	−0.02	−0.35
$4_{0,4}-5_{1,5}$	37 902.19	0.00	−0.28
$4_{4,1}-5_{3,2}$	24 331.45	−0.02	−4.50
$6_{1,6}-6_{2,5}$	29 960.45	0.01	−0.57
$6_{1,5}-6_{2,4}$	21 213.81	0.00	−0.32
$5_{1,5}-6_{0,6}$	33 901.61	0.00	−0.60
$5_{2,4}-6_{1,5}$	19 937.76	0.01	−0.41
$7_{1,7}-7_{2,6}$	31 750.99	0.00	−0.72
$7_{1,6}-7_{2,5}$	20 755.41	0.00	−0.32
$6_{2,5}-7_{1,6}$	28 051.94	0.00	−0.90
$8_{1,8}-8_{2,7}$	33 805.12	0.00	−0.93
$8_{1,7}-8_{2,8}$	20 593.27	−0.01	−0.39
$8_{2,6}-8_{3,5}$	38 480.96	0.00	−1.36
$7_{2,6}-8_{1,7}$	36 293.14	0.00	−1.58
$9_{0,9}-9_{1,8}$	23 423.85	0.00	−1.47
$9_{1,9}-9_{2,8}$	36 117.63	0.00	−1.23
$9_{1,8}-9_{2,7}$	20 813.65	0.00	−0.58
$9_{2,7}-9_{3,6}$	37 331.97	0.01	−1.13
$10_{0,10}-10_{1,9}$	27 340.05	0.00	−2.19
$10_{1,9}-10_{2,8}$	21 488.21	−0.01	−0.94
$10_{2,8}-10_{3,7}$	36 040.18	−0.01	−0.85
$11_{1,10}-11_{2,9}$	22 675.88	0.00	−1.53
$11_{2,9}-11_{3,8}$	34 701.64	−0.01	−0.58
$12_{1,11}-12_{2,10}$	24 423.20	0.00	−2.43
$12_{2,10}-12_{3,9}$	33 433.66	0.00	−0.40
$13_{1,12}-13_{2,11}$	26 760.97	0.00	−3.72
$14_{2,12}-14_{3,11}$	31 610.85	0.00	−0.68
$13_{5,9}-14_{4,10}$	20 584.99	0.00	1.21
$15_{1,14}-15_{2,13}$	33 210.10	−0.01	−7.60
$15_{2,13}-15_{3,12}$	31 288.59	0.00	−1.40
$17_{2,15}-17_{3,14}$	32 278.23	0.00	−4.61
$16_{6,11}-17_{5,12}$	24 034.89	−0.04	2.86
$18_{2,16}-18_{3,15}$	33 714.79	−0.01	−7.35
$19_{2,17}-19_{3,16}$	35 829.47	0.00	−11.00
$18_{6,12}-19_{5,15}$	37 802.81	0.00	−3.18
$20_{2,18}-20_{3,17}$	38 630.83	−0.01	−15.59
$30_{12,19}-31_{11,20}$	18 479.58	−0.01	77.04
$32_{15,18}-33_{14,19}$	18 089.37	0.05	−229.92
$34_{16,19}-35_{15,20}$	21 170.43	0.03	−284.00
$35_{14,22}-36_{13,23}$	19 036.79	0.01	129.50
$36_{17,20}-37_{16,21}$	24 242.77	0.00	−345.88
$38_{15,24}-39_{14,25}$	22 745.42	0.01	155.55
$39_{18,22}-40_{17,23}$	20 544.82	−0.02	−401.41

[a] ν_{calcd} was obtained by using a first-order centrifugal distortion analysis. [b] Subtraction of the centrifugal distortion correction from the ν_{calcd} gives the rigid rotor frequency.

Spectra

Normal Isotopic Species. Geometrical models of *trans*-1,2-difluorocyclopropane suggested that the molecule will have a nearly prolate rotor *b*-type microwave spectrum. An assignment of the experimental spectrum verified the predictions and was obtained after low J transitions were identified by their characteristic Stark effects. Interest in the assignment of the carbon-13 isotopomers in natural abundance led to an investigation of strong higher J transitions in the region of 18–40 GHz.

With the aid of a centrifugal distortion analysis, many higher J lines were assigned and fit to obtain the quartic centrifugal distortion parameters.[19] Table I lists the 56 lines which were used

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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 *trans*-1,2-Difluorocyclopropane

constants[a]	$\overline{\mathrm{CHFCHFC}}\mathrm{H_2}$	$^{13}\overline{\mathrm{CHFCHFC}}\mathrm{H_2}$	$\overline{\mathrm{CHFCHF^{13}C}}\mathrm{H_2}$	$\overline{\mathrm{CDFCDFC}}\mathrm{H_2}$	$\overline{\mathrm{CHFCHFC}}\mathrm{D_2}$	$^{13}\overline{\mathrm{CHFCHFC}}\mathrm{D_2}$	$\overline{\mathrm{CHFCHF^{13}C}}\mathrm{D_2}$
A	11 546.499 (1)	11 494.707 (7)[b]	11 152.655 (7)[b]	10 438.526 (4)	9838.180 (2)	9798.460 (5)[c]	9571.277 (4)[c]
B	3 559.9236 (4)	3 546.628 (2)	3 559.882 (3)	3 442.684 (1)	3517.5180 (5)	3504.531 (2)	3517.474 (4)
C	3 071.3756 (4)	3 065.014 (3)	3 042.689 (3)	3 056.944 (1)	2944.8303 (5)	2938.914 (2)	2920.354 (4)
I_a	43.769 03	43.966 24	45.314 69	48.414 79	51.369 16	51.577 40	52.801 63
I_b	141.9635	142.4957	141.9651	146.7980	143.6749	144.2073	143.6767
I_c	164.5449	164.8864	166.0962	165.3217	171.6157	171.9612	173.0540
τ_1	−0.006 93 (7)			−0.0063 (4)	−0.009 69 (9)		
τ_2	−0.002 35 (2)			−0.002 22 (8)	−0.002 76 (2)		
τ_3	+0.1440 (6)			+0.145 (2)	+0.1114 (6)		
τ_{aaaa}	−0.113 07 (5)			−0.0732 (3)	−0.079 60 (8)		
τ_{bbbb}	−0.003 836 (6)			−0.003 44 (3)	−0.003 691 (9)		
τ_{cccc}	−0.001 950 (6)			−0.001 96 (3)	−0.001 675 (5)		
σ[d]	0.281			0.475	0.212		
lines[e]	56	16	15	43	46	12	15
J_{max}[f]	40	13	11	24	28	16	14

[a] Uncertainties in parentheses are one standard deviation. A conversion factor of 505 379.05 MHz· amu·Å^2 was used for the moments of inertia. [b] The centrifugal distortion constants for $\overline{\mathrm{CHFCHFC}}\mathrm{H_2}$ were assumed in the least-squares fit. [c] The centrifugal distortion constants for $\overline{\mathrm{CHFCHFC}}\mathrm{D_2}$ were assumed in the least-squares fit. [d] Standard deviation of the least-squares fit. [e] Number of lines used in the fit. [f] Maximum J value used in the least-squares fit.

in the fit, and Table II contains the parameters obtained from that fit. The overall standard deviation of the fit is similar to the estimated error in the frequency measurements which indicates that first-order theory is sufficient to account for the observed centrifugal distortion effects.[19]

Microwave–microwave double-resonance (MMDR) studies confirmed the assignments of a number of transitions in Table I. Pumping the $12_{1,11}$–$12_{2,10}$ line at 24 425 MHz gave double-resonance signals for the connected $12_{2,10}$–$12_{3,9}$ transition at 33 433.6 MHz and the $12_{0,12}$–$12_{1,11}$ line at 36 139.8 MHz. In addition, the assignment is supported by observation of the correct Stark effects for low J lines, proper line intensities, and the overall quality of the 56-line centrifugal distortion fit.

Isotopically Enriched Species. Highly enriched samples of *trans*-1,2-difluorocyclopropane, which included the 1,2-d$_2$ species, $\overline{\mathrm{CDFCDFC}}\mathrm{H_2}$, and the 3,3-d$_2$ species, $\overline{\mathrm{CHFCHFC}}\mathrm{D_2}$, were assigned by methods similar to those used for the normal isotope. Forty-three lines for the 1,2-d$_2$ species were measured and fit to first-order in the centrifugal distortion analysis.[19] The quartic distortion constants and rotational constants obtained from these fits are found in Table II. A complete list of the assigned transitions for these two isotopes is given in the supplementary material as Tables SI and SII.

The total standard deviation of the least-squares fit for both of these isotopes is comparable to estimates of the uncertainty in the frequency measurements which suggests that the first-order theory is adequate to describe the observed centrifugal distortion effects.

Both spectral assignments are confirmed by observation of the correct Stark effects for the low J lines as well as similar Stark patterns to the normal isotope for higher J lines. In addition, the proper intensities and expected isotopic shifts support the assignments. MMDR experiments also provided definitive evidence for the assignment of the 3,3-d$_2$ species. A pump frequency of 25 140 MHz which connects the $13_{2,11}$ and $13_{3,10}$ levels gave a double resonance at 39 739.98 MHz for the $13_{3,10}$–$13_{4,9}$ transition. Similarly, pumping the $12_{1,11}$–$12_{2,10}$ levels and $14_{2,12}$–$14_{3,11}$ levels produced double-resonance signals at 38 965.0 MHz ($12_{0,12}$–$12_{1,11}$) and 33 492.1 MHz ($14_{1,13}$–$14_{2,12}$), respectively.

Carbon-13 Isotopic Species. The two singly substituted carbon-13 isotopomers of *trans*-$\overline{\mathrm{CHFCHFC}}\mathrm{H_2}$ and *trans*-$\overline{\mathrm{CHFCHFC}}\mathrm{D_2}$ were investigated in natural abundance. Distinct Stark transitions could not be observed for the higher J lines. However, the carbon-13 intensities as well as the similar unresolved Stark envelopes for the isotopomer and parent aided considerably in the assignment process for these higher J transitions. The weaker lower J lines were examined with the computer-controlled spectrometer described previously[15] to determine the Stark patterns.

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

transition	$(\Delta\nu/E^2)$[a]	dipole moment[b]
2_{11}–$2_{20}$$M_J = 2$	−8.659 (20)	1.173 (5)
3_{13}–3_{22} $M_J = 2$	0.9301 (40)	1.179 (5)
3_{13}–3_{22} $M_J = 3$	3.149 (60)	1.187 (10)
av		1.18 (1)

[a] The observed Stark coefficients are MHz/(V^2/cm^2) × 10^6. [b] The total dipole moment (D) lies along the b principal axis, which is the symmetry axis.

MMDR experiments which included a number of transitions for each of the four carbon-13 isotopic species listed in Table II confirmed the assignments. In addition, relative intensity measurements at room temperature and dry ice temperature demonstrated that the assigned spectra were not arising from excited vibrational states of the corresponding parent isotope.

Sufficient carbon-13 transitions were not observed to permit a centrifugal analysis of the four carbon-13 isotopic species. Spectral fits were obtained by subtracting the centrifugal distortion correction determined for each parent transition from the observed transition frequency of the same carbon-13 line. The resulting corrected frequency was fit to a rigid rotor model. This procedure fit the carbon-13 transitions to yield differences between corrected and calculated frequencies to within the estimated experimental uncertainty of the frequency measurements (~0.05 MHz). Table II lists the carbon-13 rotational constants obtained from these fits. The observed and corrected transition frequencies as well as the differences between the corrected and calculated line frequencies are found in Tables SIII-SVI of the supplementary material.

Electric Dipole Moment. Shifts in the frequency of three Stark transitions from their zero-field lines were measured at a number of values of the applied field to determine the dipole moment of the normal isotopic species, $\overline{\mathrm{CHFCHFC}}\mathrm{H_2}$, in the ground vibrational state. The data were adequately described by second-order Stark theory.[20] A least-squares fit of the data gave the Stark coefficients listed in Table III and a μ_b dipole component of 1.18 ± 0.01 D. The analysis confirms the C_2 symmetry expected for the molecule.

Structure. There are 13 nonzero atomic coordinates required to determine the complete molecular structure of *trans*-1,2-difluorocyclopropane. Since the moments of inertia for seven isotopic species were obtained in the spectral analysis, the structure may be calculated in a number of different ways. The Kraitchman

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

		p–r_s[a]	r_0[b]
$C_{1,2}$	*a*	±0.5839	±0.5822 (13)
	b	+0.0455 (2)	+0.0437 (14)
	c	±0.4431	±0.4430 (2)
C_3	*b*	−1.2499	−1.2491 (6)
$F_{1,2}$	*a*	±1.7929 (3)	±1.7932 (3)
	b	+0.4419 (1)	+0.4428 (7)
	c	∓0.1002 (1)	∓0.0998 (2)
$H_{1,2}$	*a*	±0.4809	±0.4799 (10)
	b	+0.3871	+0.3864 (13)
	c	±1.4734	±1.4735 (3)
$H_{3,3}$	*a*	∓0.5394	∓0.5394 (6)
	b	−1.8173	−1.8173 (2)
	c	±0.7479	±0.7479 (5)

[a] The r_s coordinates include the *a* and *c* carbon 1,2 coordinates, the C_3 *b* coordinate, and all the hydrogen coordinates; the fluorine coordinates and the small *b* carbon coordinate were obtained from a least-squares fit to the moment relations. [b] The r_0 coordinates were obtained from a least-squares fit of all the moment of inertia data to all the atomic coordinates; the errors were determined from deviations of the least-squares fit.

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

parameter	p–r_s[a]	r_0[b]	theoretical[c]
$C_{1,2}$–C_3	1.488 (5)	1.485 (1)	1.508
C_1–C_2	1.466 (4)	1.463 (1)	1.484
C_1–F	1.383 (3)	1.386 (1)	1.384
C_1–H	1.090 (4)	1.091 (1)	1.068
C_3–H	1.083 (2)	1.083 (1)	1.069
$\theta(HC_{1,2}F)$	111.3 (4)	111.2 (1)	
$\theta(HC_3H)$	116.8 (2)	116.7 (1)	
$\theta(FC_1C_2)$	117.3 (3)	117.3 (1)	
$\theta(FC_{1,2}C_3)$	118.4 (3)	118.4 (1)	
$\theta(HC_1C_2)$	119.7 (3)	119.8 (3)	
$\theta(HC_1C_3)$	121.1 (4)	121.2 (4)	

[a] The p–r_s structural parameters were determined by using the p–r_s atomic coordinates listed in Table IV. [b] The r_0 structural parameters were calculated from the r_0 atomic coordinates given in Table IV. [c] The theoretical parameters are taken from Skancke and Bogg's calculations (ref 8).

substitution method[21] can be used to obtain the coordinates of the hydrogen ($H_{1,2}$ and H_3) and carbon ($C_{1,2}$ and C_3) atoms. Then, one first-moment equation ($\sum_i m_i b_i = 0$) and the cross-product relation ($\sum_i m_i a_i c_i = 0$) may be combined with the three normal isotope second-moment equations ($P_{aa} = \sum_i m_i a_i^2$, $P_{bb} = \sum_i m_i b_i^2$, and $P_{cc} = \sum_i m_i c_i^2$) to calculate the remaining fluorine coordinates.

The structural fitting program STRFIT[22] was used to calculate the structure as described above. Since doubly substituted deuterium isotopomers were assigned for both the $H_{1,2}$ and H_3 hydrogen atoms, Chutjian's equations for double substitution[23] are required to determine these coordinates. In this case, $CDFCDFCH_2$ and $CHFCHFCD_2$ retain the C_2 axis of symmetry; hence, Chutjian's equation for C_2 symmetry was used in the calculation.[24,25] Kraitchman's single substitution method gave a small *b* $C_{1,2}$ carbon coordinate so that this coordinate and the three fluorine coordinates were obtained in a least-squares fit to the five-moment equations. The remaining *a* and *c* $C_{1,2}$ carbon coordinates and the *b* C_3 carbon coordinate were calculated from Kraitchman's single-substitution equations.[21] Since the C_3 carbon lies along the C_2 axis, the option to set ΔP_{aa} and ΔP_{cc} to zero was used in STRFIT for the Kraitchman calculation of the *b* C_3 carbon coordinate. Table IV lists the atomic coordinates obtained from STRFIT. The molecular structure derived from these coordinates is a partial Kraitchman structure because four coordinates have to be calculated from the moment relations. This structure, denoted p–r_s, is given in Tables IV and V.

A complete r_0 structure was obtained by least-squares fitting the 13 unique atomic coordinates to the 3 second-moment equations for all 7 isotopes as well as the first-moment and cross-product equations. Table IV and V list the atomic coordinates and structural parameters, denoted r_0, which were derived from this calculation.

Costain uncertainties in the p–r_s atomic coordinates were used to determine the propagated error in the distances and angles. These structural uncertainties are listed in parentheses adjacent to the p–r_s parameters in Table V. Since the *b* C1,2 carbon coordinate and *c* fluorine coordinate are quite small (<0.15 Å), the Costain uncertainty does not provide a realistic estimate of the uncertainty in these two coordinates. A least-squares fit of the five-moment equations (utilized to get the p–r_s structure) was used to obtain these coordinates, and the standard deviations determined in the fit provide a better estimate of the small coordinate uncertainties.[26] These least-squares estimates of the small coordinate uncertainties were used for the propagated error in the p–r_s parameters listed in Table V which depend upon these coordinates.

The uncertainties in the complete r_0 structural parameters are given in parentheses adjacent to the r_0 in Table V. These uncertainties are propagated from the standard deviations of the complete r_0 atomic coordinates.

The rotational constants of *trans*-$CHFCHFCD_2$ and *trans*-$^{13}CHFCHFCD_2$ may be used in a Kraitchman calculation to obtain the $C_{1,2}$ carbon coordinates in the 3,3-d_2 frame. These coordinates give a C_1–C_2 bond distance of 1.466 (4) Å which is identical with the substitution distance for this bond in the d_0 frame (see Table V).

Table VI. Ring-Bonding Effects in Fluorinated Cyclopropanes

	$r(C_1–C_2)$[a]	$r(C_2–C_3)$[a]
$CH_2CH_2CH_2$[b]	1.514 (2)	1.514 (2)
$CF_2CH_2CH_2$[c]	1.464 (2)	1.553 (1)
$CF_2CF_2CH_2$[d]	1.48	
trans-$CHFCHFCH_2$[e]	1.466 (4)	1.488 (5)
cis,cis-$CHFCHFCHF$[f]	1.507 (1)	1.507 (1)

[a] Bond lengths in Å. [b] Structure from ref 3. [c] Structure from ref 1. [d] Structure from ref 7. [e] This work. [f] Structure from ref 2.

Discussion

Ring Bond Shortening. Table VI compares the C_1–C_2 and $C_{1,2}$–C_3 ring bonds determined experimentally for a series of fluorinated cyclopropanes. In 1,1-difluorocyclopropane, the C_1–C_2 and C_1–C_3 bonds (equal by symmetry) have been shortened by 0.05 Å compared to cyclopropane.[2] Interestingly, the C–C bond opposite the CF_2 group in 1,1-difluorocyclopropane is extraordinarily long for a carbon–carbon single bond at 1.553 Å.[2] 1,1,2,2-Tetrafluorocyclopropane has a shortened C_1–C_2 bond length, while the C_2–C_3 and C_1–C_3 bond lengths are not known.[8] All the C–C ring bonds in *cis,cis*-1,2,3-trifluorocyclopropane are a little shorter than in cyclopropane.[3]

Deakyne et al. provided a qualitative explanation of the ring-bonding effects observed for 1,1-difluorocyclopropane and 1,1,2,2-tetrafluorocyclopropane from ab initio results employing charge density difference maps.[7] They demonstrated that knowledge of ring bond changes in 1,1-difluorocyclopropane can be used to correctly predict ring bond changes in *cis,cis*-1,2,3-trifluorocyclopropane. This technique predicts a C_1–C_2 bond length of 1.49 Å in *cis*-1,2-difluorocyclopropane which is 0.01 Å

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longer than the C_1–C_2 bond length in 1,1,2,2-tetracyclopropane.[7] In the following paper, it will be shown that this prediction is qualitatively correct.

Deakyne et al. did not consider possible ring bonding effects due to fluorine substituents oriented trans to one another. However, the experimental results in Table VI clearly show large changes in the ring bonds for *trans*-1,2-difluorocyclopropane. The 0.05-Å shortening of the C_1–C_2 bond in *trans*-1,2-difluorocyclopropane is almost the same as for the observed C_1–C_2 and C_1–C_3 bonds of 1,1-difluorocyclopropane. In fact, this C_1–C_2 bond is 0.014 Å shorter than the corresponding C_1–C_2 bond in 1,1,2,2-tetrafluorocyclopropane which is peculiar because increasing fluorination at the 1,2-carbon positions shortens the C_1–C_2 bond in other fluorocarbons. For example, the C–C bond is shorter in perfluoroethylene oxide than in *cis*- and *trans*-1,2-difluoroethylene oxide.[27]

Skancke and Boggs have reported the results of a complete geometry optimization at the 4-21 level for *cis*- and *trans*-1,2-difluorocyclopropane.[9] They computed a shortening of both the C_1–C_2 and C_2–C_3 (C_1–C_3 bond equivalent to C_2–C_3 by symmetry) ring bonds for both isomers relative to cyclopropane. The C_1–C_2 bond is predicted to be shorter than the C_2–C_3 bond, and the effect is more pronounced for the trans isomer. As shown in Table V, these predictions for *trans*-1,2-difluorocyclopropane are in qualitative agreement with the experimental results. However, Skancke and Boggs' calculations underestimate the amount of ring bond shortening by about 0.02 Å for both the C_1–C_2 and C_2–C_3 bonds.

HCF and HCH Groups. There are two aspects of the HCF and HCH group geometries which are relevant to the discussion. One is the internal geometry of the groups, and the other is orientations of the groups with respect to the ring. The HCF angle of 111.3° compares well with HCF angles determined for *cis,cis*-1,2,3-trifluorocyclopropane (112.3°)[3] and *cis*- and *trans*-1,2-difluoroethylene oxide (111.0[28] and 110.5,[27] respectively). However, the C–F bond length of 1.383 Å is unusually long for a fluorocarbon.[29] It is about 0.03 Å longer than the corresponding C–F distances in 1,1-difluorocyclopropane (1.355 Å)[1] and *cis,cis*-1,2,3-trifluorocyclopropane (1.354 Å).[3]

It is noteworthy that Skancke and Boggs computed C–F distances of 1.385 and 1.384 Å, respectively, for the *cis*- and *trans*-1,2-difluorocyclopropanes.[9] Since the 4-21 basis set overestimated the C–F bond lengths in the 1,2-difluoroethylenes by 0.03 Å, they concluded that the calculated values compared well with the value of 1.354 Å found for *cis,cis*-1,2,3-trifluorocyclopropane. The results listed in Table V show that the C–F bond length in *trans*-1,2-difluorocyclopropane compares well to the ab initio 4-21 basis set result.

The orientation of the HCF group with respect to the CCC ring plane can be compared to the CH_2 group orientation in cyclopropane. Table V lists the magnitudes of the internal angles $\theta(FC_2C_1)$, $\theta(FC_2C_3)$, $\theta(HC_2C_1)$, and $\theta(HC_2C_3)$ which should be compared with the value of 117.7 (4)° reported for θ(HCC) in cyclopropane.[30] The FCC angles are almost the same as the HCC angles in cyclopropane. This shows that the orientation of the C–F bond with respect to the CCC ring in *trans*-1,2-difluorocyclopropane is very similar to the orientation of the C–H bond with respect to the CCC ring in cyclopropane. In order for the HCF angle to be approximately 4° less than the HCH angle in cyclopropane,[30] the HCC angles associated with the HCF group must increase relative to cyclopropane. Hence, it is principally the C–H bond orientation with respect to the CCC ring in the HCF group which has changed in comparison to cyclopropane.

These C–F and C–H bond orientations can be described more quantitatively by defining two new angles, ω_X and τ_X, where X designates the substituent bonded to the carbon atom. ω_X is the angle between the X 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 bonded to the X substituent. τ_X is taken to be positive if the projection of X on the ring plane falls toward the C_3 carbon. ω_H = 57.5 (4)° for cyclopropane which is simply one-half the HCH angle due to symmetry.[30] τ_H must be zero in cyclopropane, which is also due to symmetry since the HCH plane is perpendicular to the cyclopropyl ring plane.

The corresponding values of ω_X and τ_X for the HCF group in *trans*-1,2-difluorocyclopropane are ω_H = 54.1 (3)°, ω_F = 57.3 (3)°, τ_H = −2.0 (7)° and τ_F = −1.7 (7)°. Comparison of these angles to those in cyclopropane demonstrates that the HCF group has tilted very slightly (~2.0 (7)°) toward the adjacent HCF group since τ_H and τ_F are of negative sign and are almost equal. In contrast, ω_H is more than 3° less than ω_H in cyclopropane, while ω_F is almost identical with ω_H in cyclopropane. It follows that a 1,2-fluorine substitution in the trans configuration of the cyclopropyl ring leads to the contraction of 4° of the HCF angle relative to the HCH angle in cyclopropane. Furthermore, this contraction results from a reorientation of the substituents in which the fluorine maintains approximately the same orientation as the hydrogens in cyclopropane, while the hydrogen substituent of the HCF group has moved closer to the ring plane.

Large differences in the internal structure of the HCH group or its orientation to the ring are not found between *trans*-1,2-difluorocyclopropane and cyclopropane. The C–H bond distance of 1.089 (3) Å and HCH bond angle of 115.1 (1.0)°s in cyclopropane[30] are similar to the structural parameters listed in Table V for the CH_2 group. ω_H and τ_H for the methylene group in *trans*-1,2-difluorocyclopropane are 58.3 (2)° and 2.4 (4)°, respectively. Since τ_H is not equal to zero, the CH_2 must be twisted slightly in a sense which moves the hydrogens toward the hydrogen atoms bonded to the HCF carbons.

Conclusions

Microwave spectral data have permitted the determination of a complete gas-phase structure for *trans*-1,2-difluorocyclopropane. Both the C_1–C_2 and $C_{1,2}$–C_3 ring bonds have shortened markedly in comparison to cyclopropane. The shortening is qualitatively consistent with an ab initio complete geometry optimized structure obtained by Skancke and Boggs.[9] It differs from ab initio results for *cis*-1,2-difluorocyclopropane and tetrafluorocyclopropane where the $C_{1,2}$–C_3 bonds are predicted to remain about the same as the C–C bond lengths in cyclopropane.[7]

The C–F bond length is unusually long for a fluorinated cyclopropane. However, the orientation of the HCF group with respect to the ring is similar to *cis,cis*-1,2,3-trifluorocyclopropane and to the CH_2 groups in cyclopropane. In the following paper, the gas-phase structure of *cis*-1,2-difluorocyclopropane will be compared to the trans structure. The ring bond effects as well as the HCF group structures and orientations with respect to the ring are important to understanding the absence of the "cis" effect in *cis*- and *trans*-1,2-difluorocyclopropane.[10]

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Supplementary Material Available: Rotational transitions and centrifugal distortion corrections for cyclopropane compounds (8 pages). Ordering information is given on any current masthead page.

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