Supplementary Material Available: Further IR spectroscopic data of harmonic ν(C–O) and ν(N–O) frequencies and anharmonicity constants for $Fe(CO)_2(NO)_2$ and $Fe(CO)(NO)_2(H_2)$ (Table IV), lower frequency (>300 cm^{-1}) IR bands of Fe(C-

$O)_2(NO)_2$ (Table VI) and $Fe(CO)(NO)_2(H_2)$ (Table VII), and IR bands of H_2 (Table VIII) and D_2 (Table IX) dissolved in liquid Xe[18] (7 pages). Ordering information is given on any current masthead page.

Microwave Spectra, Electric Dipole Moment, and Molecular Structure of *cis,trans*-1,2,3-Trifluorocyclopropane

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Abstract: The microwave spectra of the normal, monodeuterated, dideuterated, and carbon-13 isotopic species of *cis,trans*-1,2,3-trifluorocyclopropane and *cis,trans*-1,2,3-trifluorocyclopropane-d_3 have been investigated and assigned in the region 26.5–40.0 GHz. The spectral assignments have yielded data sufficient for the complete determination of the molecular geometry in both the normal and trideuterated isotopic species frameworks. The partial r_s parameters in the normal isotopic species framework are $r(C_{1,2}C_3) = 1.478$ (10) Å, $r(C_1C_2) = 1.500$ (3) Å, $r(C_{1,2}H) = 1.076$ (6) Å, $r(C_3H) = 1.085$ (16) Å, $r(C_{1,2}F) = 1.367$ (8) Å, $r(C_3F) = 1.387$ (8) Å, $\theta(HC_{1,2}F) = 109.4$ (8)°, and $\theta(HC_3F) = 114.7$ (15)°, where atom C_3 lies in the *ac* symmetry plane of the molecule. All the ring bonds in the cis,trans isomer have shortened relative to cyclopropane, with the greater reduction occurring in the two equivalent trans ring bonds. The C–F bond distances are found to be inequivalent, with the longer C–F bond occurring in the HCF moiety exclusively trans to neighboring HCF groups. These results are interpreted in the context of several theoretical studies that predict the effect of fluorine substitution on the geometries of substituted cyclopropanes and oxiranes.

A number of experimental[2-7] and theoretical[8-12] studies have been undertaken to elucidate the effect of fluorine substitution on the geometries of fluorinated cyclopropanes and oxiranes. A portion of the theoretical work suggests that the ring bond changes observed in 1,1-difluorocyclopropane[2] and *cis,cis*-1,2,3-trifluorocyclopropane[4] and the contraction of the C_1–C_2 bond in 1,1,2,2-tetrafluorocyclopropane[3] relative to cyclopropane may be rationalized by fluorine-induced charge redistribution in occupied molecular orbitals (MOs) and the resultant forces acting on the ring nuclei.[8] Several of the studies[9,10] further suggest that the greater stability in the trans isomer of the *cis*- and *trans*-1,2-difluorocyclopropanes[13] and the shorter C–C bond distance in the trans isomer of the *cis*- and *trans*-1,2-difluorooxiranes[5,6] may derive from greater conjugative destabilization[14,15] in the corresponding cis forms.

In the present study, the microwave investigation of various isotopic species of *cis,trans*-trifluorocyclopropane[16,17] (Figure 1)

has yielded data sufficient for the complete determination of the molecular geometry of the compound in each of two different frameworks. Coordinates have been calculated in a number of ways and the results intercompared to establish the reliability of the parameters resulting.[18] Trends in the experimentally determined ring geometries of the 1,2-difluorocyclopropanes[19,20] and 1,2-difluorooxiranes[5,6] have been identified and related to the observed ring geometry in *cis,trans*-1,2,3-trifluorocyclopropane in a manner consistent with available theory. Substituent orientation has been examined in several ring systems and the observations correlated with substituent orientation in *cis,trans*-1,2,3-trifluorocyclopropane to provide insight into angular effects observed in that species.

Experimental Section

Synthesis. (1) $C_1HFC_2HFC_3FH$. The normal isotopic species of *cis,trans*-1,2,3-trifluorocyclopropane was synthesized by ozonolysis of 3 mmol of *trans*-1,2-difluoroethylene at –95 °C in 3 mL of CF_3Cl, as described previously.[17,21]

(2) $C_1DFC_2DFC_3FD$. The d_3 isotopic species was synthesized by ozonolysis of 0.75 mmol of *trans*-1,2-difluoroethylene-d_2 at –95 °C in 2 mL of CF_3Cl.

(3) *trans*-$C_1DFC_2HFC_3FH$ and *trans*-$C_1DFC_2HFC_3FD$. These isotopic species were synthesized by ozonizing an equimolar mixture of 1.6 mmol of *trans*-1,2-difluoroethylene-d_0 and -d_2 at –95 °C in 2 mL of CF_3Cl.

(4) *cis*-$C_1HFC_2HFC_3FD$ and *cis*-$C_1DFC_2DFC_3FH$. These isotopic

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Table I. Rotational Transitions (MHz) of the Normal and d_3 Isotopic Species of *cis,trans*-1,2,3-Trifluorocyclopropane

transition	$C_1HFC_2HFC_3FH$ V_{00} ν_{obsd}	$\Delta\nu^a$	$C_1HFC_2HFC_3FH$ V_{01} ν_{obsd}	$\Delta\nu^a$	$C_1HFC_2HFC_3FH$ V_{02} ν_{obsd}	$\Delta\nu^a$	$C_1DFC_2DFC_3FD$ V_{00} ν_{obsd}	$\Delta\nu^a$	$C_1DFC_2DFC_3FD$ V_{01} ν_{obsd}	$\Delta\nu^a$
$2_{21}-3_{31}$	26 601.70	0.25	26 531.56	0.17						
$3_{03}-4_{13}$	28 628.30	0.15	28 684.90	-0.04			27 261.63	0.12		
$3_{12}-4_{22}$	28 214.44	0.30	28 230.57	0.19			26 778.86	0.19		
$3_{13}-4_{23}$	30 417.50	0.30	30 414.59	0.25						
$3_{21}-4_{31}$	31 359.10	0.11	31 291.55	0.26	31 226.65	0.38	29 299.05	0.20	29 227.96	0.32
$3_{22}-4_{32}$	32 396.95	0.09	32 345.02	0.18	32 295.17	0.30	30 260.56	0.13	30 202.12	0.20
$3_{30}-4_{40}$	35 938.24	-0.36	35 831.69	-0.29	35 727.96	-0.30	33 218.40	-0.13	33 104.14	-0.15
$3_{31}-4_{41}$	36 006.42	-0.49	35 903.21	-0.35	35 803.05	-0.14	33 288.91	-0.29	33 178.31	-0.18
$4_{04}-5_{14}$	36 522.58	0.09					34 704.38	0.14		
$4_{13}-5_{14}$	26 598.32	0.11								
$4_{13}-5_{23}$	34 939.30	0.05	34 996.34	-0.17	35 054.28	0.01	33 294.91	-0.04	33 343.73	0.01
$4_{14}-5_{24}$	37 483.84	0.09					35 409.85	0.24		
$4_{22}-5_{23}$	28 831.32	0.04	28 877.22	-0.12						
$4_{22}-5_{32}$	36 509.48	0.05	36 471.82	0.18			34 396.35	-0.03		
$4_{23}-5_{33}$	38 560.43	0.18					36 229.66	-0.05		
$4_{31}-5_{32}$	28 219.73	-0.02								
$4_{32}-5_{33}$	26 913.75	0.05								
$5_{05}-6_{06}$	27 042.60	0.16	26 998.32	0.08	26 954.24	-0.18	26 474.58	0.14	26 431.15	0.13
$5_{14}-6_{15}$	30 702.37	0.06								
$5_{15}-6_{16}$	27 007.76	0.17	26 965.84	0.06	26 924.42	0.25	26 450.58	0.11	26 408.70	-0.26
$5_{23}-6_{24}$	34 084.10	-0.15	34 103.24	-0.19	34 120.00	-0.23	32 871.24	-0.14	32 876.11	-0.18
$5_{24}-6_{25}$	30 058.74	0.04	30 041.37	0.01			29 215.10	0.07		
$5_{32}-6_{33}$	34 539.68	-0.26					33 514.07	-0.17		
$5_{33}-6_{34}$							31 117.23	-0.10		
$5_{41}-6_{42}$	33 129.73	-0.08					32 248.74	-0.17		
$5_{42}-6_{43}$	32 639.25	-0.22								
$6_{06}-7_{07}$	31 256.71	0.06	31 205.05	-0.03	31 153.95	0.05	30 628.38	0.04	30 577.80	0.03
$6_{15}-7_{16}$	34 749.61	-0.01					33 718.40	-0.02		
$6_{16}-7_{17}$	31 245.82	0.07	31 195.19	0.08	31 144.87	0.10	30 621.37	0.08	30 571.54	0.13
$6_{25}-7_{26}$	34 454.45	-0.01					33 508.96	-0.09		
$6_{34}-7_{35}$	36 995.71	-0.32								
$6_{52}-7_{53}$	38 121.03	-0.09								
$7_{07}-8_{08}$	35 479.73	-0.14	35 420.32	-0.15	35 361.28	-0.21	34 788.62	-0.21	34 730.53	-0.19
$7_{17}-8_{18}$	35 476.70	0.07	35 417.60	0.04	35 358.94	0.07	34 786.98	0.13	34 729.15	0.18

^{a} $\Delta\nu$ = ν_{obsd} - ν_{calcd} from the rigid-rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz.

species were synthesized by ozonizing an equimolar mixture of 1.25 mmol of *cis*-1,2-difluoroethylene-d_0 and -d_2 at -95 °C in 2 mL of CF_3Cl. Each isotope/isotopic mixture obtained in the foregoing syntheses was isolated by trap-to-trap distillation and purified by preparative gas chromatography. The normal isotopic species was characterized by gas-phase IR, mass spectrometry, and ^1H and ^{19}F NMR spectroscopy.[17,21] The various deuterium isotope/isotopic mixtures were characterized by their gas-phase IR spectra.[17]

Spectroscopy. All isotopic spectra were recorded with a Hewlett-Packard 8400C MRR spectrometer in the range 26.5-40.0 GHz. Transition frequencies were measured to an estimated accuracy of ±0.05 MHz at typical sample pressures of 30-50 mtorr relative to air as measured by a Hastings DV-6 vacuum gauge tube. Signal-to-noise enhancement for ground-state rotational transitions was achieved by packing the absorption cells in dry ice.

The carbon-13 isotopic species were studied in natural abundance.[22] In order to obtain the necessary sensitivity, a 10-ft absorption cell cooled to dry ice temperature was used in a system employing 95-KHz Stark modulation.[7] The accuracy of measured transition frequencies is estimated to be ±0.05 MHz.

Electric dipole measurements of the normal isotopic species were made with the 8400C spectrometer by coupling the dc bias to the 33.3-KHz Stark modulation. One HP-8425B Stark cell and one HP-8421B square wave modulator were used in the measurements. The dc bias was measured with a Keithley 177 Microvolt DMM voltmeter that had been calibrated to an estimated 0.1% accuracy. The average Stark electrode spacing was determined with the M_J = 0 and M_J = 2 lobes of the J = 2 → 3 transition of $^{16}O^{12}C^{32}S$.[23]

Spectra. The known molecular structure of *cis,cis*-1,2,3-trifluorocyclopropane[4] was used to provide a reasonable geometrical model for the normal and deuterium isotopic species of *cis,trans*-1,2,3-trifluorocyclopropane. The structure predicted for the cis,trans isomer corresponded to a slightly prolate asymmetric rotor (K ~ -0.31) characterized by low J R branch μ_a and μ_c type transitions in the region 26.5-40.0 GHz. The predicted absence of Q-branch lines of appreciable intensity in the region investigated led to the expectation of a relatively sparse spectrum.

Microwave assignments confirmed the anticipated spectral character of the normal and deuterated isotopic species. These assignments were made on the basis of Stark effects, line intensity, proximity to predicted transition frequency, and quality of the overall frequency fit. The observed transition frequencies are listed in Tables I and II, and spectral constants obtained from the rigid-rotor fits are given in Table IV.

Assignments were also made for two excited vibrational states of the normal isotopic species and one excited vibrational state of the trideuterated species. Transition frequencies and spectral constants obtained from the rigid-rotor fits are listed in Tables I and IV, respectively. The near-linear variation of corresponding principal moments of inertia among the two excited vibrational states and the ground state of the normal isotopic species suggests that the two excited states correspond to successive excitation of the same vibrational mode. Relative intensity measurements indicate that the lower excited vibrational state of the normal isotopic species lies 178 ± 22 cm^{-1} above the ground state.[24]

Spectral constants for the ground-state isotopic species were utilized to provide improved approximations to the molecular structure of the cis,trans isomer in order to facilitate the carbon-13 assignments.[25] A total of four structural parameters were needed in conjunction with the moment relationships to achieve satisfactory convergence of the predicted geometries. Differences between experimental and calculated rotational constants for the normal isotopic species of each structure were then

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Table II. Rotational Transitions (MHz) of the d_1 and d_2 Isotopic Species of *cis,trans*-1,2,3-Trifluorocyclopropane

transition	$C_1DFC_2HFC_3FH$		$C_1HFC_2HFC_3FD$		$C_1DFC_2HFC_3FD$		$C_1DFC_2DFC_3FH$	
	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$
$3_{03}-4_{13}$			28 130.10	0.33	27 692.04	0.15		
$3_{12}-4_{22}$	27 708.70	0.16			27 255.00	0.19		
$3_{21}-4_{31}$	30 553.95	0.22	30 824.99	0.31	30 038.20	0.28	29 797.86	0.26
$3_{22}-4_{32}$	31 577.94	0.40	31 816.68	0.17	31 016.30	0.19	30 804.53	0.22
$3_{30}-4_{40}$	34 859.80	-0.20	35 256.44	-0.08	34 205.31	-0.15	33 847.26	-0.17
$3_{31}-4_{41}$	34 931.66	-0.29	35 320.50	-0.22	34 272.72	-0.27	33 922.61	-0.25
$4_{04}-5_{14}$	35 920.80	-0.06						
$4_{13}-5_{23}$			34 354.42	-0.36	33 816.65	-0.05	33 865.28	-0.02
$4_{14}-5_{24}$							36 038.01	0.22
$4_{22}-5_{23}$	28 523.25	-0.05						
$4_{22}-5_{32}$	35 711.08	0.03			35 133.41	0.07		
$4_{32}-5_{33}$	26 660.14	0.43						
$5_{05}-6_{06}$	26 801.77	0.05	26 941.60	-0.08			26 570.41	-0.06
$5_{14}-6_{15}$					30 079.07	0.02	29 929.58	0.03
$5_{15}-6_{16}$	26 772.93	0.01	26 906.99	0.15	26 674.39	0.14	26 546.88	0.23
$5_{23}-6_{24}$							33 246.87	-0.13
$5_{24}-6_{25}$					29 520.42	0.04	29 431.41	0.02
$5_{32}-6_{33}$	34 253.76	-0.33						
$5_{42}-6_{43}$					31 997.17	-0.14	32 064.22	-0.21
$6_{06}-7_{07}$	30 988.23	-0.08	31 149.72	-0.06	30 883.71	0.05	30 730.25	0.01
$6_{16}-7_{17}$	30 979.68	0.05	31 138.80	0.02	30 875.03	0.16	30 723.53	0.22
$6_{25}-7_{26}$	34 088.35	-0.05	34 220.20	-0.09	33 859.02	-0.07		
$6_{34}-7_{35}$					36 257.98	-0.33		
$7_{07}-8_{08}$	35 182.39	-0.23	35 366.80	0.01	35 071.65	-0.23	34 896.44	-0.20
$7_{17}-8_{18}$	35 180.29	0.15	35 363.52	0.02	35 069.49	0.16	34 894.67	-0.05

^{a} $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ from the rigid-rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz.

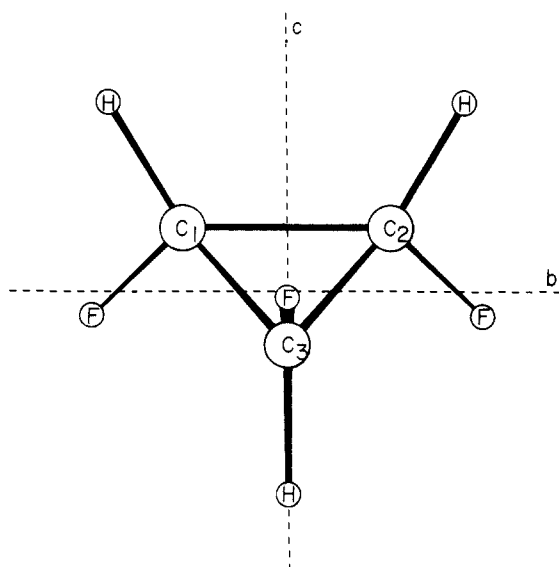**Figure 1.** *cis,trans*-1,2,3-Trifluorocyclopropane ($C_1HFC_2HFC_3FH$). The relative orientation of the principal axes in the normal isotopic species framework is depicted above with the *bc* plane parallel to the plane of the page. The *a* axis, not shown, is directed into the page. In each of the isotopically substituted species of the molecule, C_3 denotes the carbon bearing the fluorine that is exclusively trans to neighboring fluorines.

applied to the corresponding calculated carbon-13 rotational constants. Rotational constants derived in this manner typically predicted transition frequencies within ±2 MHz of the experimental value. Transition assignments were based on Stark effects, line intensity, expected isotopic shift, and quality of the overall frequency fit. Line intensities of the assigned transitions increased as the absorption cell temperature was lowered, indicating that the transitions occurred in the ground vibrational state. Observed transition frequencies of the monosubstituted carbon-13 analogues of the normal and trideuterated isotopic species are listed in Table III and spectral constants obtained from the rigid-rotor fits are given in Table IV.

If vibration–rotation effects are neglected, differences in second moments perpendicular to a symmetry plane should vanish for isotopic substitution in that plane.[18] Among the species $C_1HFC_2HFC_3FH$, $C_1HFC_2HFC_3FD$, $C_1HFC_2HF^{13}C_3FH$ and $C_1DFC_2DFC_3FD$, C_1DF-

C_2DFC_3FH, $C_1DFC_2DF^{13}C_3FD$, the relevant second moment difference did not exceed 0.027 μÅ^2. The foregoing result is consistent with C_s symmetry in those species.

Dipole Moment. The $3_{21} \rightarrow 4_{31}$ and $4_{13} \rightarrow 5_{23}$ transitions were used to determine the electric dipole moment of the normal isotopic species in the ground vibrational state. Stark shifts of the $M_J = 1$ and $M_J = 2$ lobes of these transitions were least-squares fit to second-order perturbation theory, yielding the Stark coefficients and dipole moment components listed in Table V. The quality of the fit to two dipole moment components is consistent with C_s symmetry in the ground-state normal isotopic species.

Structure. The isotopic data permitted calculation of ground-state partial r_s and r_0 coordinates in both the normal and trideuterated isotopic species framework. Substitution coordinates were obtained for each of the carbons and hydrogens (deuteriums) with Kraitchman's equations.[26] The fluorine coordinates were then least-squares fit to the three second-moment relations of each of the four isotopic species not used in the Kraitchman calculations as well as the three second-moment relations and principal axis conditions of the parent isotopic species to yield the partial r_s coordinates listed in Tables VI and VII.[25] As a check, substitution coordinates were also calculated for the two equivalent hydrogens (deuteriums) using Chutjian's equations for symmetric disubstitution.[27] The results of the Chutjian calculations, listed at the end of Tables VI and VII, agree favorably with the single-substitution results.

In order to obtain an estimate of vibrational effects, coordinates were least-squares fit to the second-moment relations of all 10 isotopic species as well as the principal axis conditions of the parent isotopic species to yield the r_0 coordinates listed in Tables VI and VII.[25] The r_0 calculations further support the substitution results for the small *a* coordinate of the two equivalent hydrogens (deuteriums). Structural parameters resulting from the partial r_s and r_0 coordinates are listed in Table VIII. The uncertainties shown derive from Costain uncertainties in the partial r_s coordinates and fitting uncertainties in the complete r_0 coordinates, propagated into the distances and angles through the standard relation for propagation of random error.[18] The Costain uncertainties for the unique carbon and hydrogen (deuterium) were determined from experimentally determined pseudoinertial defect differences, as described later in this section. Application of the Costain relation resulted in an overly conservative estimate of the uncertainty in the small *c* coordinate of the unique fluorine atom. The estimated error in that coordinate was obtained from the center-of-mass relation and the Costain uncertainties in the *c* coordinates of all the other atoms.[18]

Two additional calculations were undertaken to reevaluate the small *a* coordinate of the two equivalent hydrogens (deuteriums) and redeter-

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Table III. Rotational Transitions (MHz) of Carbon-13 Isotopic Species of *cis,trans*-1,2,3-Trifluorocyclopropane

transition	$^{13}C_1HFC_2HFC_3FH$ ν_{obsd}	$\Delta\nu^a$	$C_1HFC_2HF^{13}C_3FH$ ν_{obsd}	$\Delta\nu^a$	$^{13}C_1DFC_2DFC_3FD$ ν_{obsd}	$\Delta\nu^a$	$C_1DFC_2DF^{13}C_3FD$ ν_{obsd}	$\Delta\nu^a$
$2_{21}-3_{31}$	26 428.02	0.03						
$3_{03}-4_{13}$	28 556.26	0.11	28 508.92	0.05				
$3_{12}-4_{22}$	28 116.96	0.05						
$3_{13}-4_{23}$					28 553.26	0.12	28 575.68	0.05
$3_{21}-4_{31}$	31 178.13	−0.04			29 148.19	0.07	29 239.54	−0.05
$3_{22}-4_{32}$	32 218.79	−0.04	32 320.21	−0.03	30 111.51	0.05		
$4_{04}-5_{14}$	36 422.27	0.03	36 374.08	0.03	34 614.97	−0.12	34 571.41	−0.04
$4_{13}-5_{14}$	26 515.41	0.04						
$4_{13}-5_{23}$	34 846.06	−0.12	34 799.88	−0.03	33 216.41	−0.23		
$4_{14}-5_{24}$							35 295.27	0.09
$4_{31}-5_{32}$	28 198.01	−0.06						
$4_{40}-5_{41}$	27 179.87	−0.01						
$4_{41}-5_{42}$	27 051.75	0.04						
$5_{05}-6_{06}$			26 973.28	0.20				
$5_{14}-6_{15}$					29 615.47	0.03	29 632.88	0.02
$5_{15}-6_{16}$	26 937.02	0.16						
$5_{24}-6_{25}$	29 980.95	−0.02	29 967.18	−0.09	29 141.56	−0.10	29 130.74	−0.05
$5_{42}-6_{43}$					31 665.01	0.18		
$5_{50}-6_{51}$					31 590.52	0.18		
$6_{06}-7_{07}$	31 174.20	0.04	31 176.60	0.03	30 549.51	−0.02	30 552.92	0.03
$6_{15}-7_{16}$			34 658.36	0.16	33 619.23	−0.13	33 633.11	−0.10
$6_{16}-7_{17}$	31 164.12	0.12	31 165.24	0.01	30 542.98	0.01	30 545.68	0.17
$6_{25}-7_{26}$			34 354.90	−0.14			33 417.12	−0.12
$7_{07}-8_{08}$	35 386.96	−0.22	35 389.18	−0.09				
$7_{17}-8_{18}$	35 384.18	−0.03	35 385.82	−0.05				

^{a} $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ from the rigid-rotor fits. The estimated accuracy of ν_{obsd} is ±0.05 MHz.

Table IV. Rotational Constants^a (MHz) and Principal Moments of Inertia^b (μÅ^2) of *cis,trans*-1,2,3-Trifluorocyclopropane

		A	B	C	I_A	I_B	I_C
$C_1HFC_2HFC_3FH$	V_{00}	4754.97 (1)	3145.73 (1)	2114.07 (1)	106.2843 (3)	160.6556 (3)	239.0551 (6)
$C_1HFC_2HFC_3FH$	V_{01}	4739.40 (2)	3153.98 (1)	2109.98 (1)	106.6336 (3)	160.2352 (6)	239.5180 (7)
$C_1HFC_2HFC_3FH$	V_{02}	4724.25 (2)	3162.15 (2)	2105.93 (1)	106.9756 (5)	159.8213 (12)	239.9794 (9)
$C_1DFC_2DFC_3FD$	V_{00}	4377.25 (1)	3029.69 (1)	2081.94 (1)	115.4559 (3)	166.8089 (3)	242.7449 (5)
$C_1DFC_2DFC_3FD$	V_{01}	4360.65 (2)	3036.99 (2)	2078.03 (1)	115.8954 (5)	166.4077 (10)	243.2013 (8)
$C_1DFC_2HFC_3FH$		4604.49 (2)	3110.98 (1)	2099.19 (1)	109.7578 (5)	162.4500 (7)	240.7498 (8)
$C_1HFC_2HFC_3FD$		4661.26 (2)	3098.69 (2)	2110.97 (1)	108.4211 (4)	163.0946 (9)	239.4060 (7)
$C_1DFC_2HFC_3FD$		4514.70 (2)	3064.16 (1)	2096.14 (1)	111.9409 (4)	164.9321 (6)	241.0994 (7)
$C_1DFC_2DFC_3FH$		4463.41 (2)	3076.30 (1)	2084.88 (1)	113.2272 (4)	164.2816 (7)	242.4021 (7)
$^{13}C_1HFC_2HFC_3FH$		4720.80 (1)	3140.95 (1)	2108.83 (1)	107.0538 (2)	160.8999 (3)	239.6486 (3)
$C_1HFC_2HF^{13}C_3FH$		4747.78 (3)	3131.54 (1)	2108.89 (1)	106.4454 (6)	161.3836 (4)	239.6422 (3)
$^{13}C_1DFC_2DFC_3FD$		4348.75 (2)	3025.41 (1)	2076.82 (1)	116.2126 (5)	167.0448 (4)	243.3425 (7)
$C_1DFC_2DF^{13}C_3FD$		4371.22 (2)	3016.57 (1)	2077.01 (1)	115.6152 (6)	167.5345 (6)	243.3202 (5)

^{a} The uncertainty in parentheses represents one standard deviation in the rigid-rotor fit. ^{b} The conversion factor is equal to 505379.1 μÅ^2 MHz.

Table V. Stark Coefficients and Electric Dipole Moment of *cis,trans*-1,2,3-Trifluorocyclopropane

	$\Delta\nu/E^2 \times 10^4$,^{a} MHz/(V/cm)^2 obsd	calcd
$3_{21}-4_{31}$ $M_J = 1$	0.0306	0.0279
$3_{21}-4_{31}$ $M_J = 2$	0.1207	0.1213
$4_{13}-5_{23}$ $M_J = 1$	0.0210	0.0204
$4_{13}-5_{23}$ $M_J = 2$	0.0807	0.0808
μ_a = 0.69 (1)^b	μ_T = 1.28 (2)	
μ_c = 1.07 (1)		

^{a} The Stark coefficients were calculated with the conversion factor 0.503404 MHz/(DV/cm). ^{b} The unit is debyes. Quantities in parentheses are estimated uncertainties in the last digit(s) of the parameter cited, obtained from one standard deviation of the least-squares fit.

Table VI. Atomic Coordinates (Å) of the Normal Isotopic Species of *cis,trans*-1,2,3-Trifluorocyclopropane^a

atom	a coord	b coord	c coord
$C_{1,2}$	0.1842 (0.1828)	∓0.7498 (∓0.7482)	0.4617 (0.4590)
$H_{1,2}$	−0.0862 (−0.0869)^b	∓1.2867 (∓1.2884)	1.3538 (1.3542)
$F_{1,2}$	1.1965 (1.1972)	∓1.4099 (∓1.4103)	−0.1761 (−0.1768)
C_3	−0.7618 (−0.7621)	0.0 (0.0)	−0.3908 (−0.3886)
H_3	−0.5680 (−0.5678)	0.0 (0.0)	−1.4583 (−1.4597)
F_3	−2.1051 (−2.1045)	0.0 (0.0)	−0.0456 (−0.0470)

^{a} Entries enclosed in parentheses are r_0 coordinates; entries not enclosed in parentheses are single-substitution partial r_s coordinates. ^{b} The corresponding double-substitution coordinates are −0.0860, ∓1.2867, and 1.3535 Å respectively for the a, b, and c coordinates.

mine the corresponding carbon–hydrogen (deuterium) bond lengths. In the first calculation, substitution coordinates were used wherever possible with the exception of the small hydrogen a coordinate and the fluorine coordinates, which were fit to the second-moment relations and principal axis conditions employed in the previous partial r_s calculations. In this

manner, the small a coordinate of the equivalent hydrogens (deuteriums) was determined to be −0.2109 and −0.1661 Å in the normal and trideuterated isotopic species frames, respectively, with corresponding carbon–hydrogen bond lengths of 1.114 and 1.105 Å. Variation observed between these and previous results, within a given isotopic species framework, presumably arises from less-than-perfect compatibility of substitution coordinates with effective moment and principal axis rela-

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Table VII. Atomic Coordinates (Å) of the d_3 Isotopic Species of *cis,trans*-1,2,3-Trifluorocyclopropane[a]

atom	a coord	b coord	c coord
$C_{1,2}$	0.1953 (0.1924)	∓0.7497 (∓0.7482)	0.4475 (0.4454)
$D_{1,2}$	−0.0613 (−0.0729)[b]	∓1.2864 (∓1.2884)	1.3426 (1.3419)
$F_{1,2}$	1.2019 (1.2038)	∓1.4099 (∓1.4103)	−0.1959 (−0.1953)
C_3	−0.7576 (−0.7565)	0.0 (0.0)	−0.3956 (−0.3976)
D_3	−0.5665 (−0.5673)	0.0 (0.0)	−1.4714 (−1.4697)
F_3	−2.0989 (−2.0972)	0.0 (0.0)	−0.0484 (−0.0497)

[a] Entries enclosed in parentheses are r_0 coordinates; entries not enclosed in parentheses are single-substitution partial r_s coordinates. [b] The corresponding double-substitution coordinates are −0.0680, ∓1.2863, and 1.3429 Å respectively for the a, b, and c coordinates.

Table VIII. Structural Parameters[a] of *cis,trans*-1,2,3-Trifluorocyclopropane

	partial r_s(I)[b]	partial r_s(II)[b]	r_0
$r(C_{1,2}C_3)$	1.478 (10)	1.477 (7)	1.473 (12)
$r(C_1C_2)$	1.500 (3)	1.499 (3)	1.496 (6)
$r(C_{1,2}H)$	1.076 (6)[c]	1.075 (7)[c]	1.080 (7)
$r(C_{1,2}F)$	1.367 (8)	1.365 (7)	1.368 (14)
$r(C_3H)$	1.085 (16)	1.093 (10)	1.089 (8)
$r(C_3F)$	1.387 (8)	1.385 (4)	1.385 (8)
$\theta(HC_{1,2}F)$	109.4 (8)	109.1 (10)	109.2 (10)
$\theta(HC_3F)$	114.7 (15)	114.6 (11)	114.6 (6)
$\theta(HC_1C_2)$	119.9 (3)	120.0 (4)	120.0 (5)
$\theta(HC_{1,2}C_3)$	124.8 (12)	125.1 (14)	124.8 (17)
$\theta(FC_1C_2)$	118.9 (5)	118.9 (5)	118.9 (10)
$\theta(FC_{1,2}C_3)$	116.7 (6)	116.9 (4)	117.0 (3)
$\theta(HC_3C_{1,2})$	117.0 (11)	116.7 (9)	116.8 (5)
$\theta(FC_3C_{1,2})$	118.5 (9)	118.8 (6)	118.7 (7)

[a] All distances are in angstroms; all angles are in degrees. Quantities in parentheses are estimated uncertainties in the last digit(s) of the parameter cited. [b] Structure I is the partial r_s structure obtained from single substitution at each of the carbons and hydrogens in the normal isotopic species frame. Structure II is the partial r_s structure obtained from single substitution at each of the carbons and deuteriums in the d_3 isotopic species frame. [c] Corresponding bond lengths utilizing double-substitution coordinates for the hydrogens (deuteriums) are 1.075 and 1.077 Å for structures I and II, respectively.

tions. The error introduced by the discrepancy is both mass and coordinate dependent and is expected to be particularly significant for the equivalent hydrogens (deuteriums).[28] Analysis suggested most of the error derives from differences between substitution and effective c coordinates, which affect the hydrogen a coordinate determination through the ac cross product. Deletion of the ac cross product from the previous calculations yielded $r(C_{1,2}H) = 1.079 \pm 0.011$ Å and $r(C_{1,2}D) = 1.079 \pm 0.007$ Å in the normal and trideuterated isotopic species frames, respectively. The uncertainties derive from fitting uncertainty in the small hydrogen a coordinate and Costain uncertainty in other coordinates. The bond lengths obtained in this manner agree favorably with partial r_s results (Table VIII).

The second calculation to reevaluate the small a coordinate of the equivalent hydrogens (deuteriums) made use of the Pierce second-difference method.[29] Since the method employs second differences in moments, vibrational effects should have been reduced to a greater degree than was obtained by the use of Kraitchman's equations. Four isotopic species were required for each calculation, with substitution in each of two different frameworks. The necessary coordinate transformation between the two frameworks was obtained from Kraitchman coordinates of the unique hydrogen (deuterium) by a method developed by Rudolph.[30]

An error analysis indicated that the major source of error in the second-difference determinations was the magnitude of the second difference in the planar moments ΔP_{aa}. The latter quantity was largest, and the attendant uncertainty was least in calculations involving species that are symmetrically disubstituted at the equivalent hydrogens (deuteriums). Under this condition, application of the second-difference method yielded $r(C_{1,2}H) = 1.081 \pm 0.006$ Å and $r(C_{1,2}D) = 1.083 \pm 0.005$ Å in the normal and trideuterated isotopic species frames, respectively. The uncertainties derive from experimental uncertainty in rotational constants

for the small hydrogen a coordinate and Costain uncertainty in other coordinates. The bond lengths obtained in this manner agree favorably with the partial r_s results in Table VIII. Details of the results of the second-difference determinations are summarized in Table SI of Supplementary Material.

As shown in Table VIII, the carbon–carbon and carbon–hydrogen bond lengths obtained from Kraitchman coordinates differ by 0.002 Å or less between the normal and trideuterated isotopic species framework result, with the single exception of the bond between the unique carbon and unique hydrogen. The latter bond length differs by 0.008 Å between the two frameworks, which is roughly an order of magnitude greater than the difference expected from uncertainty in the pertinent rotational constants. Inspection of parameters derived from substitution coordinates reveals that the discrepancy is primarily associated with location of the unique hydrogen. This finding is not unexpected, since the experimental pseudoinertial defect difference[18] is larger for the unique hydrogen than for the unique carbon.

The presence of a finite second-moment difference, ΔP_{bb}, on isotopic substitution in the ac symmetry plane introduces some ambiguity into the determination of the in-plane atom coordinates.[28] This difference had been previously neglected in the Kraitchman calculations by setting ΔP_{bb} equal to zero. Under this condition the quantity $\Delta I_a + \Delta I_c - \Delta I_b$ also equates to zero, permitting the elimination of one of the ΔI's from Kraitchman's equations and the formulation of "specialized" forms of Kraitchman's equations.[18,31] Parameters resulting from coordinates obtained with specialized forms of Kraitchman's equations are listed in Table SII of Supplementary Material. To a first approximation, the coordinates obtained from the specialized forms of Kraitchman's equations differ from the substitution coordinates in Tables VI and VII by an amount equal to $(2\mu x)^{-1}|\Delta P_{bb}|$, where μ is the reduced mass for the substitution and x is the magnitude of the coordinate.[31] The latter quantity is assigned as the Costain uncertainty in the substitution coordinates of the unique carbon and unique hydrogen (deuterium) listed in Tables VI and VII. Ambiguities due to finite experimental pseudoinertial defect differences are absent in the coordinate determinations of the other atoms in the cis,trans isomer. The Costain uncertainties in these are estimated as $0.0015x^{-1}$, where x is the magnitude of the coordinate and a "typical" pseudoinertial defect difference of 0.006 μÅ^2 is assumed.[18] The uncertainties that have been assigned are intended to reflect investigator confidence in the reported parameters as estimates of equilibrium parameters.

Discussion

Ring Structure. Table IX compares bond lengths experimentally determined for a series of fluorinated cyclopropanes. The carbon–carbon bond length in cyclopropane has been determined to be 1.514 ± 0.003 Å by rotational Raman spectroscopy[32] as compared with the gaseous electron-diffraction r_a value of 1.510 ± 0.002 Å.[33] As Table IX demonstrates, introduction of fluorine induces a shortening of the carbon–carbon bonds adjacent to the substitution site, relative to cyclopropane. In 1,1-difluorocyclopropane,[2] the C_1–$C_{2,3}$ bonds shorten to 1.464 ± 0.002 Å, while the C_2–C_3 bond, opposite the substitution site, lengthens to 1.553 ± 0.001 Å. In 1,1,2,2-tetrafluorocyclopropane,[3] the C_1–C_2 bond length has shortened to 1.48 Å. The C_3–$C_{1,2}$ bond length is as yet undetermined for 1,1,2,2-tetrafluorocyclopropane. Table X compiles bond lengths experimentally determined for a series of fluorinated oxiranes, where a similar ring bond effect is demonstrated relative to ethylene oxide.[34]

Numerous theoretical studies have been undertaken in order to elucidate the substituent-induced ring bond changes observed in the substituted cyclopropanes. Hoffmann has used the Walsh model of bonding in cyclopropane to successfully explain ring effects associated with π-acceptor substituents.[35,36] By this scheme, the dominant interaction consists of the mixing of a low-lying unoccupied acceptor orbital with the highest occupied Walsh orbital of appropriate symmetry. Following the labeling

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Table IX. Comparison of Cyclopropyl Bond Lengths[a]

compd	C_1–C_2	C_2–C_3[b]	C_1–H	C_1–F	C_3–H	C_3–F	ref
CH₂CH₂CH₂	1.514 (3)	1.514 (3)	1.081 (3)		1.081 (3)		32
cis-CHFCHFCH₂	1.488 (3)	1.503 (4)	1.093 (4)	1.368 (6)	c		19
trans-CHFCFHCH₂	1.466 (4)	1.488 (5)	1.090 (4)	1.383 (3)	1.083 (2)		20
cis,cis-CHFCHFCHF	1.507 (1)	1.507 (1)	1.095 (2)	1.354 (2)	1.095 (2)	1.354 (2)	4
cis,trans-CHFCHFCFH	1.500 (3)	1.478 (10)	1.076 (6)	1.367 (8)	1.085 (16)	1.387 (8)	this work

[a] All distances are in angstroms. Uncertainties are in parentheses. [b] C_3 denotes the unique carbon. [c] This parameter is not well determined.

Table X. Comparison of Oxiranyl Bond Lengths[a]

compd	C–C	C–O	C–H	C–F	ref
CH₂CH₂O	1.465 (2)	1.431 (3)	1.086 (2)		34
cis-CHFCHFO	1.451 (3)	1.409 (4)	1.093 (4)	1.345 (7)	5
trans-CHFCFHO	1.436 (4)	1.395 (8)	1.098 (4)	1.363 (4)	6
CF₂CF₂O	1.426 (4)	1.391 (2)		1.329 (2)	7

[a] All distances are in angstroms. Uncertainties are in parentheses.

convention employed by Jorgensen and Salem,[37] the relevant Walsh orbital corresponds to the antisymmetric member of the degenerate 3E′ pair. As a consequence of the mixing, electron density is transferred from a nominally Walsh orbital to an extended π-system that encompasses the substituent. Since the Walsh orbital is bonding at the C_1–C_2 and C_1–C_3 bonds but antibonding at the C_2–C_3 bond, the interaction leads to lengthening of the vicinal C_1–$C_{2,3}$ bonds and shortening of the distal C_2–C_3 bond.

With regard to π-donors, Hoffman surmised that the dominant interaction would consist of the mixing of the highest occupied donor orbital with the low-lying unoccupied Walsh orbital of appropriate symmetry, labeled 1A₂′ in the convention of Jorgensen and Salem. Since this Walsh orbital is antibonding at all bonds, the interaction would lead to lengthening of all the cyclopropyl bonds,[36] in contradistinction to the shortening of the vicinal cyclopropyl bonds observed for cyclopropanone,[38] methylenecyclopropane,[39] and 1,1-difluorocyclopropane.[2] Neither can the observed vicinal shortening be rationalized by invoking donor interaction with either of the two remaining unoccupied Walsh orbitals, since of these, the symmetric 4E′ orbital has antibonding character at the vicinal C_1–$C_{2,3}$ bonds, while the antisymmetric 4E′ orbital has a small orbital coefficient at C_1,[37] effectively negating any significant interaction with donor orbitals.

Using orbital composition and energy splitting diagrams obtained by ab initio calculation, Deakyne et al. concluded that the shortening of the vicinal C_1–$C_{2,3}$ bonds observed in cyclopropanone, methylenecyclopropane, and 1,1-difluorocyclopropane arose primarily from charge redistribution in occupied SS symmetry orbitals (cyclopropyl MOs 2A₁′ and/or 2E′) that shifted charge density from C_1 to the region of the C_1–$C_{2,3}$ bonds.[8,40] Lengthening of the distal C_2–C_3 bond in these compounds was attributed mainly to charge redistribution in occupied SA symmetry orbitals (cyclopropyl MO 3E′), which resulted in increased C_2–C_3 antibonding overlap. Conclusions identical with those outlined above were reached for 1,1-difluorocyclopropane by using charge density difference plots in conjunction with the orbital composition diagrams.

Owing to limitations of population analysis in these strained systems and complexity of the energy splitting diagram, charge density difference plots were used in conjunction with orbital composition diagrams to analyze the effect of symmetric 1,2-fluoro substitution in 1,1,2,2-tetrafluorocyclopropane.[8] By this method,

Deakyne et al. concluded that charge redistribution associated with occupied SS and SA symmetry orbitals (cyclopropyl MOs 2E′ and 3E′, respectively) would lead to shortening of the C_1–C_2 bond. Opposing effects of these same orbitals with respect to the C_3–$C_{1,2}$ bond led to the expectation that the C_3–$C_{1,2}$ bond length in 1,1,2,2-tetrafluorocyclopropane would remain essentially unchanged relative to cyclopropane.

On the basis of trends in the atomic charge distributions calculated for a series of fluorinated cyclopropanes, Deakyne et al. hypothesized that successive fluorination would modify the cyclopropyl structure in an additive manner. Using the additivity postulate in conjunction with their result for 1,1-difluorocyclopropane, Deakyne et al. were able to rationalize the slight shortening of the C–C bond distance observed in cis,cis-1,2,3-trifluorocyclopropane.[4] Extension of the additivity postulate to cis-1,2-difluorocyclopropane using the theoretical result for 1,1,2,2-tetrafluorocyclopropane leads to the expectation that the C_1–C_2 distance in cis-1,2-difluorocyclopropane would be intermediate to the C_1–C_2 distances in cyclopropane and 1,1,2,2-tetrafluorocyclopropane, while the C_3–$C_{1,2}$ distance should be invariant.[8] As Table IX demonstrates, the former expectation is borne out qualitatively by the experimental result; however, the latter expectation is not, since the C_3–$C_{1,2}$ distance in cis-1,2-difluorocyclopropane is reduced by about 0.01 Å relative to cyclopropane.

In contrast, the density difference plot calculations for perfluorooxirane predict shortening of all ring bonds relative to ethylene oxide.[9] In this case, shortening of the C–C and C–O bonds proceeds from charge redistribution in occupied SS and SA symmetry orbitals (oxiranyl MOs 4A₁ and 2B₂ for C–C shortening; oxiranyl MOs 4A₁ and 3B₂ for C–O shortening), which decreases antibonding overlap and increases bonding overlap in these bonds. The observed shortening of the C_3–$C_{1,2}$ bonds in the 1,2-difluorocyclopropanes and of the C–O bonds in the 1,2-difluorooxiranes and perfluorooxirane (Tables IX and X), as well as the many parallel structural trends in the cyclopropyl and oxiranyl series, suggests that the C_3–$C_{1,2}$ bond in 1,1,2,2-tetrafluorocyclopropane is very likely shortened relative to cyclopropane. Further experimental work is needed to test this conjecture.

In their study of the fluorocyclopropanes, Deakyne, Allen, and Craig did not consider possible differential effects associated with trans vs. cis orientation of the substituents. Skancke and Boggs have reported theoretical structures of cis- and trans-1,2-difluorocyclopropane obtained with complete geometry optimization at the 4-21 level.[10] In both isomers, the C_1–C_2 and C_3–$C_{1,2}$ bonds were found to shorten relative to cyclopropane, with the greater reduction occurring in the C_1–C_2 bonds. The main geometrical feature differentiating the two isomers was the appreciably shorter C_1–C_2 bond in the trans form. Using population analysis in conjunction with the optimized geometries, Skancke and Boggs were able to rationalize the shorter C_1–C_2 bond in the trans isomer and the greater stability of that form in terms of a destabilizing electron delocalization in the cis isomer, in accordance with Bingham's explanation of the "cis effect" in the substituted ethylenes.[14,15] Similarly, in the oxiranyl series, Deakyne, Cravero, and Hobson found that orbital composition diagrams suggested a shorter C–C bond in the trans form of the 1,2-difluorooxiranes. In this case, greater stability was predicted for the trans form due to the greater fluorine interaction with MO 5A₁ in the cis isomer, which depletes bonding charge density in the ring, raising the energy of the bonding orbital produced by the interaction.[9] In

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Table XI. Comparison of Cyclopropyl Methylene Angles[a]

compd	θ(HC₁X)	θ(HC₃Y)[b]	ω(H₁)[c]	ω(F₁)	ω(H₃)	ω(F₃)	τ(H₁)[c]	τ(F₁)	τ(H₃)	τ(F₃)	ref
CH₂CH₂CH₂	114.9 (7)[d]	114.9 (7)[f]	57.5 (4)		57.5 (4)		0.0		0.0		32
cis-CHFCHFCH₂	111.3 (4)[e]	h	52.8 (3)	58.5 (3)	h		-0.2 (7)	0.5 (9)	0.0		19
trans-CHFCFHCH₂	111.3 (4)[e]	116.8 (2)[f]	54.1 (3)	57.3 (3)	58.3 (2)		-2.0 (7)	-1.7 (7)	2.4 (4)[i]		20
cis,cis-CHFCHFCHF	112.3 (2)[e]	112.3 (2)[g]	53.3 (2)	59.0 (2)	53.3 (2)	59.0 (2)	0.0	0.0	0.0	0.0	4
cis,trans-CHFCHFCFH	109.4 (8)[e]	114.7 (15)[g]	51.7 (9)	57.4 (5)	58.3 (13)	56.4 (11)	-6.7 (15)	3.5 (13)	0.0	0.0	this work

[a] All angles are in degrees. Uncertainties are in parentheses. [b] C₃ denotes the unique carbon. [c] These angles are defined in Figure 2. [d] X = H. [e] X = F. [f] Y = H. [g] Y = F. [h] This parameter is not well determined. [i] Each of these hydrogens is rotated toward the HCF group to which it is cis.

Table XII. Comparison of Oxiranyl Methylene Angles[a]

compd	θ(XCY)	ω(H)[b]	ω(F)	τ(H)[b]	τ(F)	ref
CH₂CH₂O	116.5 (4)[c]	58.3 (2)		7.6 (3)		34
cis-CHFCHFO	111.0 (4)[d]	51.9 (3)	58.9 (4)	13.2 (7)	4.8 (12)	5
trans-CHFCFHO	110.5 (4)[d]	52.4 (4)	58.1 (4)	10.8 (12)	6.9 (11)	6
CF₂CF₂O	109.0 (2)[e]		54.5 (1)		10.6 (4)	7

[a] All angles are in degrees. Uncertainties are in parentheses. [b] These angles are defined in Figure 2. [c] X = Y = H. [d] X = H. Y = F. [e] X = Y = F.

either of the latter two studies, the ring bond to C₃ (or O) was found to be essentially identical between the cis and trans forms of the 1,2-difluorinated species.

As demonstrated in Table IX, both the C₁-C₂ and the C₃-C₁,₂ bonds of the cis- and trans-1,2-difluorocyclopropanes[19,20] shorten relative to cyclopropane,[32] with the greater reduction occurring in the C₁-C₂ bonds. Furthermore, inspection shows that the reduction is more pronounced in both the C₁-C₂ and the C₃-C₁,₂ bonds of the trans isomers. As demonstrated in Table X, similar trends obtain for the analogous bonds in the cis- and trans-1,2-difluorooxiranes.[5,6] As Table IX shows, all ring bonds contract relative to cyclopropane in the 1,2,3-trifluorocyclopropanes.[4,16] In the case of cis,trans-1,2,3-trifluorocyclopropane, the C₃-C₁,₂ bonds (the "trans" bonds) are numerically 0.022 Å shorter than the C₁-C₂ bond (the "cis" bond), mirroring an equivalent difference between the C₁-C₂ bonds in the cis- and trans-1,2-difluorocyclopropanes. Moreover, each ring bond of the cis,trans isomer is shorter than its corresponding member in the cis,cis isomer, paralleling an analogous trend observed between cis and trans isomers in the 1,2-difluorocyclopropanes and 1,2-difluorooxiranes.

HCF Groups. Inspection of Tables IX and X reveals that the C-F bonds are approximately 0.02 Å shorter in cis-1,2-difluorooxirane and cis-1,2-difluorocyclopropane than in the corresponding trans isomers. A similar contraction is observed in the C₁,₂-F bonds of cis,trans-1,2,3-trifluorocyclopropane relative to the C₃-F bond. Skancke and Boggs calculated identical C-F bond lengths in the cis- and trans-1,2-difluorocyclopropanes but noted that their result was puzzling in light of the greater C-F bond overlap population in the cis isomer.[10]

With the exception of perfluoroethylene oxide, Tables XI and XII indicate that the orientation of the fluorines in the compounds listed closely approximates the orientation of the hydrogens in the unsubstituted parent compound. The more salient angular changes in the HCF groups of these compounds relative to the parent compound appear to derive from displacements of the hydrogens, as has been noted previously.[5] Contraction of the XCX angle in perfluoroethylene oxide relative to ethylene oxide may be rationalized by analogy to MO arguments presented by Kollman to explain angular trends in the fluorinated ethylene series.[41] The latter study ascribes the closing of the XCX angle in 1,1-difluoroethylene relative to ethylene to preferential charge withdrawal from the b₂ (2p_y) symmetry AO of carbon by the more
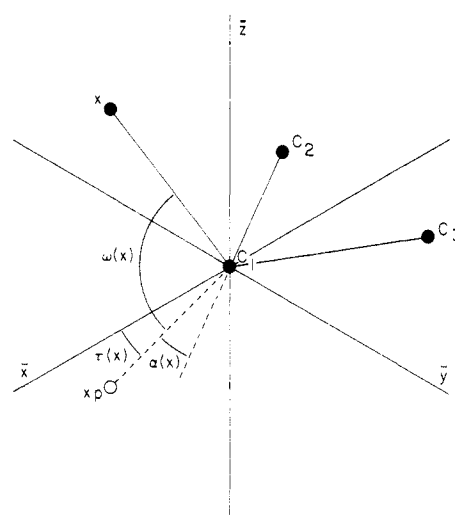

Figure 2. Definition of the angles ω, τ, and α. As shown above, the cyclopropyl ring atoms C₁, C₂, and C₃ are situated in the x̄ȳ plane such that x̄ axis bisects θ(C₃C₁C₂). x_p is the projection of atom x in the x̄ȳ plane. Under these conditions, ω(x) = θ(xC₁x_p) and τ(x) = θ(x̄C₁x_p). The sign of τ(x) is chosen to be the same as the sign of the quantity θ(xC₁C₂) - θ(xC₁C₃). α(x) denotes the angle made by x_p with respect to the C₁C₂ bond axis (cf. ref 45). The same relations are employed in the oxiranyl systems, with atom O replacing atom C₃.

electronegative fluorines. Consequent to charge depletion in the y direction, the fluorines move in toward one another to take advantage of the higher electron density in the a₁ symmetry AO of carbon that is directed along the x (C=C) axis. The XCX angular trend is continued in the cyclopropanes for 1,1-difluorocyclopropane (θ(FCF) = 108.4°).[2] A similar result would presumably obtain for the yet undertermined FCF angles in 1,1,2,2-tetrafluorocyclopropane.

In the course of this study it became apparent that neither internal angles (θ(HCC), θ(FCC)) or fluoromethylene angles (θ(HCF), θ(HCH), θ(FCF)) would readily lend themselves to describing the orientation of individual substituents. In order to facilitate a discussion of angular trends, additional angles were required specifying the orientation of individual substituents relative to the cyclopropyl or oxiranyl ring plane. These angles, labeled ω and τ, are provided in Tables XI and XII. As depicted in Figure 2, ω(x) denotes the angle between the C-X bond and the ring plane. τ(x) denotes the angle between the projection of C-X in the ring plane and the bisector of angle C₃C₁C₂ (or OC₁C₂), taken in a positive sense if the displacement is toward C₃ (or O). The uncertainties shown are the propagated error from

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cis,trans-1,2,3-Trifluorocyclopropane

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Table XIII. Comparison of Methylene Hydrogen Orientation in Several Ring Compounds[a]

Δω(H),[b] deg	0.0	0.9	1.3	0.8	H_c	1.8	H_c	0.7
					H_r	−0.6°	H_b	−0.7
							H_a	1.0
Δτ(H),[b] deg	0.0	−0.5	3.6	7.6	H_c	2.5	H_c	−1.9
					H_r	1.5	H_b	−1.2
							H_a	9.6
ref	32	2	42	34	43		44	

[a] The comparison is made relative to cyclopropane. [b] Δω(H) = ω(H) − 57.5°. Δτ(H) = τ(H) − 0.0°. ω and τ are defined in the text and Figure 2.

uncertainties in the angles from which ω and τ are derived.[18]

General trends in ω and τ in the compounds cited in Tables XI and XII suggest that several of the angular effects observed in *cis,trans*-1,2,3-trifluorocyclopropane may be explained by some form of attractive interaction between hydrogen and the highly electronegative fluorines. The positive value of τ(F_1) and the large value of ω(H_3) (and θ(HC$_3$F)) tend to diminish the distance between atoms F_1 and H_3 in the cis,trans isomer. In a similar fashion, the fluoromethylene groups in *trans*-1,2-difluorocyclopropane and the fluoromethylene hydrogens in *trans*-1,2-difluorooxirane are rotated toward one another by about 2° relative to the corresponding cis isomer. Examples of other compounds where a similar effect may be operative are cited in Table XIII, with cyclopropane as the reference. A positive value of Δω and/or Δτ tends to decrease the distance between hydrogen and the electronegative substituent. For each compound cited, Δω is positive for hydrogen cis to the electronegative substituent. For the last two entries, Δω is negative for hydrogen exclusively trans to the electronegative substituent. Δτ is generally positive with the exception of 1,1-difluorocyclopropane and oxaspiropentane. Δτ is particularly large for methylene substituents in the oxiranyl systems; in oxaspiropentane, for example, the cyclopropyl group is tilted toward the oxiranyl oxygen by 9.7°.[44]

Fujimoto et al. have examined several simple three-membered ring compounds and find that the CH bending angle, α, may be related to the extent of mixing of a π* MO of ethylenic fragment into the occupied MOs of the ring.[45] α, defined in Figure 2, decreases as τ becomes increasingly positive. In oxirane the high electronegatively of oxygen leads to poor π* mixing, resulting in a slightly distorted ethylenic fragment and a small value of α (i.e., a large positive value of τ). In cyclopropanone the antibonding character of the C=O fragment and resultant high energy of that fragment orbital lead to greater π* mixing, resulting in a long C–C bond and a large value of α (i.e., a less positive value of τ). Curiously enough, both of the entries in Table XIII that have negative τ values also possess an extraordinarily long C–C bond (1.55 Å) between the methylene groups.

The foregoing explanation seems to satisfactorily account for large positive τ values in oxiranyl systems and the negative τ values in 1,1-difluorocyclopropane and oxaspiropentane. It is not readily apparent that it can rationalize subtler angular effects such as the difference between τ(H) and τ(F) values in the *cis*- and *trans*-1,2-difluorooxiranes or the angular effects observed in *cis,trans*-1,2,3-trifluorocyclopropane. Extension of the explanation to oxaspiropentane and spiropentane would predict more negative τ(H_b) and τ(H_c) values for the methylenes in oxaspiropentane than in spiropentane (τ(H) = −2.3°)[46] since the intermediate C–C

bond in the former molecule is longer by 0.03 Å. This expectation is not borne out, as inspection of Table XIII shows. The more positive τ(H_b) and τ(H_c) values in oxaspiropentane compared to spiropentane are, however, consistent with an attractive interaction between hydrogens H_b and H_c and the oxygen in oxaspiropentane.

As previously indicated, the last two entries of Table XIII show an increase in ω(H) for hydrogen cis to the electronegative substituent but a decrease in ω(H) for hydrogen trans to the electronegative substituent relative to cyclopropane. An analogous trend is evidenced between the cis,trans isomeric pairs in Tables XI and XII. Between the two members of each such pair the ω value for a particular substituent is seen to be greater when that substituent is cis to fluorine. As a result, ω(F) is greater in the fluoromethylene groups of the cis member, while ω(H_1) is greater in the fluoromethylene groups of the trans member, of each cis,trans isomeric pair.

In *cis,trans*-1,2,3-trifluorocyclopropane, atom H_3 is cis to two fluorines; consequently one would expect that ω(H_3) in this isomer would be greater than ω(H_1) in *trans*-1,2-difluorocyclopropane, as is the case. A finite value of τ, which might be evident in a less symmetrically substituted atom, must be incorporated into ω(H_3) in an additive manner, consistent with the premise of an attractive interaction between atoms H_3 and F_1, F_2. As a result, ω(H_3) in the cis,trans isomer is 4.2° greater than ω(H_1) in *trans*-1,2-difluorocyclopropane. Atom F_3, on the other hand, is trans to two fluorines; consequently one would expect that ω(F_3) in the cis,trans isomer would be less than ω(F) in *trans*-1,2-difluorocyclopropane, as is the case. The decrement would be moderated by interaction between atom F_3 and H_1, H_2. As a result, ω(F_3) is only 0.9° less than ω(F) in *trans*-1,2-difluorocyclopropane. The net effect of the displacements is a 3.4° increase in θ(HC$_3$F) in the cis,trans isomer relative to θ(HCF) in *trans*-1,2-difluorocyclopropane.

The equivalent fluorines in the cis,trans isomer are both cis and trans to vicinal fluorines. Consistent with the foregoing, one would expect ω(F_1) in the cis,trans isomer to be intermediate to ω(F) values in the *cis*- and *trans*-1,2-difluorocyclopropanes, as is the case. ω(H_1) should similarly be intermediate to ω(H_1) values in the *cis*- and *trans*-1,2-difluorocyclopropanes. The difference in ω(H_1) values between the cis,trans isomer and *cis*-1,2-difluorocyclopropane is not outside the aggregate error in these angles. Accordingly, θ(HC$_1$F) in the cis,trans isomer may not differ significantly from θ(HCF) in the *cis*- and *trans*-1,2-difluorocyclopropanes.

A large negative value of τ(H_1) in the cis,trans isomer (−6.7°) indicates that the equivalent hydrogens are rotated toward the fluoromethylene group to which the hydrogens are cis. As a result, the cis-vicinal H–H distance is less in the cis,trans isomer (2.57 Å) than in *cis*-1,2-difluorocyclopropane (2.63 Å), even though the intermediate carbon–carbon bond length is longer in the cis,trans isomer. A similar but less pronounced rotation in the same sense (2.4°) is observed for the methylene hydrogens in *trans*-1,2-difluorocyclopropane. These displacements are quite puzzling. Further theoretical work may be necessary to provide

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a conceptual framework that accounts for the intriguing substituent orientation trends observed in the fluorinated oxiranes and cyclopropanes.

eter, which was used to carry out the work.

Supplementary Material Available: Tables of the Pierce double substitution result for equivalent hydrogens and parameters obtained from specialized forms of Kraitchman's equations (2 pages). Ordering information is given on any current masthead page.

Electronic Structure Factors of Carbon–Hydrogen Bond Activation. The Photoelectron Spectroscopy of (Cyclohexenyl)manganese Tricarbonyl[1]

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Abstract: The He I and He II ionizations for (cyclohexenyl)manganese tricarbonyl, a molecule which exhibits an activated C–H bond, are reported. Comparisons are made to the electronic structures of (methylcyclopentadienyl)manganese tricarbonyl, (cyclohexadienyl)manganese tricarbonyl, and (cyclohexadiene)iron tricarbonyl. Electronic structure factors contributing to the initial activation of the C–H bond are discussed in terms of two limiting descriptions that have been presented in the literature. These descriptions are labeled σ activation, involving the donation of C–H σ bonding orbital electron density into the empty metal orbitals, and σ^* activation, involving electron density flow in the opposite direction, i.e., from filled metal levels into the empty C–H σ^* antibonding level. Both processes are shown to be possible based only on geomertry, symmetry, and overlap considerations. The experimental data demonstrate that the principal electronic structure mechanism for the early stages of C–H bond lengthening and interaction with the metal exhibited in (cyclohexenyl)manganese tricarbonyl is σ activation. The data are also related to variable-temperature NMR studies of this complex which show that fluxionality proceeding through a 16 e^- intermediate is more favorable than that through an 18 e^- intermediate with a full metal-hydrogen bond. Both bond strength and ionization energy data show that the C–H activation of (cyclohexenyl)manganese tricarbonyl stops at the agostic stage because there is no net gain in carbon-carbon or metal-carbon bonding to compensate the loss of the C–H bond.

The study of small molecules activated by transition metals is an important aspect of the continuing investigations of metal-assisted chemistry and catalysis. One of the most important classes of small molecule–metal interactions involves the specific activation of the C–H bond.[2,3] Aliphatic hydrocarbons are abundant industrial materials but are generally unreactive in the absence of a catalyst because the C–H bond is relatively strong and difficult to attack both sterically and electronically. Both surface[4-6] and homogeneous systems capable of activating hydrocarbons have been reported. In fact the discrete molecules which activate C–H bonds include metals representing both ends of the transition series and the lanthanides and actinides.[7-18] The relationship between

Scheme I. (A) σ and (B) σ^* Activation Modes
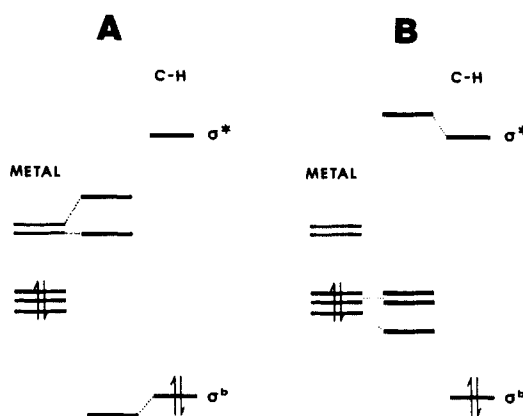
the electron count or availability at the metal (i.e., electron rich or poor) and the metal's ability to insert into the C–H bond has not been fully developed.

There are two limiting case electronic descriptions for initiation of carbon–hydrogen bond activation.[19] We will refer to these by the names σ activation and σ^* activation. The first occurs when the C–H σ (bonding) orbital donates electron density into an empty metal level. This model is depicted in Scheme IA.

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