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Structure of *cis,trans*-1,4-Difluorobutadiene from Microwave Spectroscopy

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Microwave spectra in the 5.5−17.5-GHz region have been observed for *cis,trans*-1,4-difluorobutadiene, for its ^{13}C isotopomers in natural abundance, for the four singly substituted deuterium isotopomers, and for the 1,4-d_2 species. For the parent species fitting 37 lines to a Watson-type Hamiltonian with the five quartic centrifugal distortion constants gave $A = 12\,988.333(1)$, $B = 1467.8791(3)$, and $C = 1318.5845(3)$ MHz. Stark effect measurements on three transitions of the parent species gave a dipole moment of 2.309(5) D with components $\mu_a = 0.660(4)$ D and $\mu_b = 2.213(5)$ D. Surprisingly, the B rotational constant for the 2-d_1 isotopomer, as indexed from the trans end, is larger than that for the normal species, and the rotational constants for the 3-d_1 isotopomer are also anomalous. Nonetheless, a complete, 17-parameter structure is proposed for this planar molecule and compared with density functional theory predictions made with the adiabatic connection method. Structural parameters are also compared with those of butadiene itself.

Introduction

The energy relationships among the three isomers of 1,4-difluorobutadiene (DFBD) are inconsistent with the predictions of conventional qualitative reasoning. Thus, the cis,cis (*Z,Z*) isomer with the fluorine atoms closest has the lowest energy, and the trans,trans (*E,E*) isomer with the fluorine atoms most distant has the highest energy.[1] The cis,trans (*Z,E*) isomer is intermediate in energy. Although these energy relationships are surprising, hybrid Hartree−Fock density functional theory (HF-DFT) calculations made with the adiabatic connection method (ACM)[2] give the correct order of energies and rather good agreement with the observations.[1]

As a contribution to the study of unusual energy relationships between different configurations of small fluorocarbons, we have been applying high-resolution spectroscopic methods to find complete structures. Recent examples include the use of the microwave method to obtain the structure of the gauche rotamer of 1,1,2,2-tetrafluoroethane[3] and the infrared method to obtain the structure of the anti rotamer.[4] Of course, the microwave method depends on the species of interest having a permanent dipole moment, as does *cis,trans*-DFBD, the subject of this report. For the nonpolar trans,trans and cis,cis isomers of DFBD, we have embarked on a parallel study by high-resolution infrared spectroscopy.

Only four experimental papers on the isomers of DFBD have appeared. The first two papers in the early 1960s by Viehe and Franchimont reported the synthesis and characterization of the three isomers and an equilibrium investigation.[5,6] From the reported compositions in the iodine-catalyzed equilibrations at 100 and 150 °C, we computed enthalpies of isomerization by applying the van't Hoff relationship.[1] Thus, the trans,trans isomer lies 6.5 kJ/mol above the cis,cis isomer, and the cis,trans isomer lies 3.8 kJ/mol above the cis,cis isomer. The corresponding values from the ACM calculations are 4.7 and 2.8 kJ/mol, respectively.[1] We have done a thorough investigation of the three isomers by medium-resolution infrared and Raman spectroscopies. For this new work a different method of synthesis was adopted. An early study of the electronic spectra of butadienes, which incorporated the observations of Viehe and Franchimont,[6] was reported by Fueno et al.[7]

A microwave investigation of the structure of *cis,trans*-DFBD, the objective of the present report, is a challenging problem because each bond in this molecule is distinct. Seventeen different structural parameters must be determined for a complete structure of this planar molecule. The ACM/TZ2P calculations not only provided information about the energy differences between the three isomers but also gave useful initial geometries for the microwave work.

For a complete structure determination, isotopically substituted species are needed. With the supersonic jet-cooled beam and Fourier transform microwave method, molecular species singly substituted with ^{13}C are observable in natural abundance. In our recent synthetic studies of the isomers of DFBD, we found that the trans,trans isomer undergoes slow exchange of protons for deuterons in 3 M NaOD/D$_2$O at 120 °C. The rate of exchange of the protons on the fluorine-bearing end carbon atoms is at least 5 times faster than that for the protons on the interior carbon atoms. After exchange, the trans,trans isomer is isomerized into an equilibrium mixture with iodine catalysis. This mixture is separated by gas chromatography. The synthesis method, under limited times of exchange, yields a potpourri of different deuterium isotopomers of *cis,trans*-DFBD, including the 1-d_1, 2-d_1, 3-d_1, 4-d_1, and 1,4-d_2 species. These isotopomers can be distinguished in the microwave spectrum. Although

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trans,trans-DFBD, and presumably the other two isomers, can withstand treatment with 3 M base at 120 °C for weeks with little loss, the DFBDs decompose or polymerize readily in the presence of tiny amounts of acid or oxygen. Thus, the DFBDs must be kept dry, free of oxygen, and stored at low temperature.

Experimental Section

Syntheses. *trans,trans*-DFBD was synthesized as before.[1] For exchange reactions 3 M NaOD was prepared by putting small portions of a weighed amount of sodium metal in deuterium oxide (Aldrich, 99.9% deuterium purity). In a typical reaction, 2.5 mL of 3 M NaOD was syringed into a 50-mL standard-wall-thickness, fused quartz flask equipped with a graded seal and a Pyrex breakseal, and connected to a vacuum system. (Pyrex flasks did not hold up well under the prolonged, strongly basic and hot conditions of the exchange reaction.) After three freeze−pump−thaw cycles to remove air, 1−2 mmol of *trans,-trans*-DFBD was condensed on the liquid nitrogen cooled ice, and the flask was flame sealed. The sealed flask was kept in a rocking oven at 120 °C for about 10 days to effect exchange on about 1/3 of the protons on the end carbon atoms. Some exchange of protons also took place on the interior carbon atoms, and a useful amount of exchange on both end carbon atoms occurred. More exchange would have replaced molecules with single deuteration on the interior carbon atoms with molecules having multiple deuteration. With the reaction mixture at room temperature, the breakseal was opened, and the *trans,trans*-DFBD was removed by repeated vaporizations into a small volume on the vacuum system until the pressure was that of water vapor alone. Water was removed from the sample by distilling it through a phosphorus pentoxide containing column.

Progress of the stereospecific exchange reaction was monitored with gas-phase infrared spectroscopy. Diagnostic bands were the Q branches of C-type bands due to out-of-plane modes. They are 934 cm^{-1} for the normal *trans,trans*-DFBD species,[1] 920 and 685 cm^{-1} for the 1-d_1 species, 916 and 725 cm^{-1} for the 2-d_1 species, 893 and 681 cm^{-1} for the 1,4-d_2 species, 880, 727, and 665 cm^{-1} for the 1,2,4-d_3 species, and 693 and 680 cm^{-1} for the d_4 species. The frequencies for the *trans,trans*-DFBD-d_4 species were confirmed with an authentic sample of this material, which was obtained from the isomerization of *trans*-3,4-difluorocyclobutene-d_4. The assignments for the infrared bands of the isotopomers of intermediate degrees of deuteration were based on the evolution of peaks as the length of time for the exchange increased and on frequencies calculated with Titan software (Jaguar 3.5, a combined product of Wavefunction/Schroedinger). These calculations were done with the B3LYP hybrid HF-DFT formalism, which is essentially equivalent to ACM, and a 6-31G** basis set.

Iodine-catalyzed isomerization of *trans,trans*-DFBD and isolation of *cis,trans*-DFBD by gas chromatography were done as described before.[1]

Infrared Spectra. Infrared spectra were recorded on an Perkin-Elmer 1760 FT instrument with a resolution of 0.5 cm^{-1}. Gas samples were held in a 10-cm Wilmad minicell equipped with potassium bromide windows.

Microwave Spectra. Microwave spectra in the range 5.5−17.5 GHz were recorded using a Fourier transform microwave spectrometer described in detail elsewhere.[8,9] Two 36-cm-diameter aluminum mirrors, spherical radius of curvature of 84 cm, are used to establish a resonant cavity; one mirror can be moved to tune the resonant frequency. The mirrors are separated by up to 80 cm. A Hewlett-Packard 83711B synthesized frequency generator provides the microwave radiation, which is coupled into the chamber by an L-shaped antenna. Molecular emission is detected using the same antenna, and the frequency is reduced by a heterodyne circuit and digitized by a Keithley-MetraByte DAS-4101 data acquisition board in a personal computer. Automatic scanning of the spectrometer is achieved using a National Instruments PC-LPM-16 counter-timer board to generate pulses which position the mirrors as the frequency is stepped.

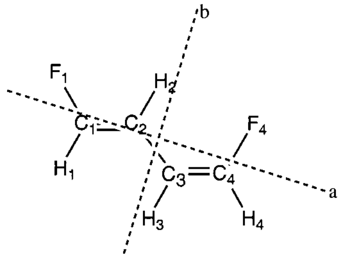

Figure 1. Schematic diagram with atom numbering and approximate locations of the principal axes for *cis,trans*-1,4-difluorobutadiene.

Samples were prepared by diluting about 0.33 mmol of *cis,-trans*-DFBD with argon to approximately 1.7 atm in a 2-L flask. Samples prepared in this way could be used through at least four subsequent dilutions by recharging with argon after the pressure had dropped to about 1 atm. The sample was expanded into the vacuum chamber perpendicularly to the axis of the resonant cavity. In this arrangement the Doppler splittings were usually unresolved, and the rotational line widths were typically 25 kHz fwhm.

An electric field for Stark effect measurements was established by charging two solid aluminum plates, 30 × 30 × 0.5 cm, mounted on the mirror guide rails with Lucite spacers. The plates are separated by 27 cm and can be charged up to 10 000 V with opposite polarity. The electric field was calibrated after each measurement by observing the Stark shift of the 1 ← 0 transition of OCS (μ = 0.715 196 D).[10]

Quantum Mechanical Calculations. The adiabatic connection method used in this study is based on the hybrid exchange-correlation functional proposed by Becke, in which a term representing the exact Hartree−Fock exchange energy is included along with a linear combination of several widely used functionals, both local and gradient corrected.[11] We used the original coefficients proposed by Becke in the ACM formalism implemented with the TURBOMOLE program.[12] All geometry optimizations were performed using basis sets of triple-ζ quality plus two sets of polarization functions (TZ2P) per atom.[13]

Other Calculations. A version of Dr. A. Maki's ASYM program was used to fit the rotational constants. Professor R. Schwendeman's program in the University of Michigan modification, STRFIT87, was used for structure fitting.

Results and Discussion

Selection Rules and Initial Predictions. Figure 1 is a schematic structure for *cis,trans*-DFBD with the atoms numbered. The locations of the *a* and *b* principal axes which lie in the plane of the molecule are shown approximately. It is evident that this molecule has dipole moment components along both the *a* and *b* axes with the μ_b component being the larger one. Thus, *a*-type and *b*-type selection rules apply for pure rotational transitions of this rather prolate asymmetric top, which has $\kappa = -0.9744$ for the normal species. Initial predictions of microwave transitions were made from the rotational constants computed from the Cartesian coordinates found with the ACM/TZ2P calculations.

TABLE 1: Microwave Transitions for *cis,trans*-1,4-Difluorobutadiene

J'	K_a'	K_c'	J''	K_a''	K_c''	ν/MHz	$\Delta\nu^a$/kHz
2	0	2	1	0	1	5 571.477	−1.8
3	0	3	2	0	2	8 353.601	−1.5
3	1	2	2	1	1	8 582.416	−2.2
3	1	3	2	1	2	8 134.570	0.4
4	0	4	3	0	3	11 131.391	−2.0
4	1	3	3	1	2	11 441.493	−0.9
4	1	4	3	1	3	10 844.410	−1.7
4	2	3	3	2	2	11 144.823	−1.1
5	0	5	4	0	4	13 903.422	−1.2
5	1	4	4	1	3	14 299.062	1.7
5	1	5	4	1	4	13 552.838	−0.9
5	2	3	4	2	2	13 957.976	0.0
5	2	4	4	2	3	13 929.190	−0.3
5	3	3	4	3	2	13 937.486	2.5
6	2	4	5	2	3	16 762.626	0.7
6	2	5	5	2	4	16 712.330	−0.5
6	3	4	5	3	3	16 726.774	1.5
1	1	1	0	0	0	14 306.848	6.3
1	1	0	1	0	1	11 669.676	8.8
2	1	2	1	0	1	16 944.026	−4.2
2	1	1	2	0	2	11 820.418	3.8
3	1	2	3	0	3	12 049.233	3.1
4	1	3	4	0	4	12 359.331	0.2
5	1	4	5	0	5	12 754.967	−0.9
6	1	5	6	0	6	13 241.376	−2.1
5	2	4	6	1	5	16 515.960	−1.3
7	1	6	7	0	7	13 824.698	−5.4
6	2	5	7	1	6	13 220.288	−1.2
6	2	4	7	1	7	17 498.991	−2.0
7	2	6	8	1	7	9 855.799	−3.0
7	2	5	8	1	8	15 406.734	2.6
8	2	6	9	1	9	13 434.304	−0.7
10	1	9	10	0	10	16 228.189	−0.4
9	2	7	10	1	10	11 593.310	1.8
10	2	8	11	1	11	9 896.153	−0.8
13	3	11	14	2	12	17 012.299	2.6
14	3	12	15	2	13	13 787.080	−1.7

[a] Observed − calculated.

Microwave Spectra. For the normal species 37 microwave transitions were observed. These lines are given in Table 1. Seventeen of the transitions are *a*-type; 20 are *b*-type. We took pains to find lines with K_a'' up to 3, although they were hard to observe at the very low temperatures of the expanded beam (2 K or less). Such transitions help define the *K*-dependent centrifugal distortion constants. All of the *a*-type transitions are R-branch lines. For the *b*-type transitions about half are Q-branch lines.

Due to the limited amounts of samples available, finding lines for the isotopomers was challenging. First, lines were found for the four ^{13}C species in natural abundance. The rotational constants for the ^{13}C species were used to improve the predictions for the deuterium isotopomers. For the initial search for lines of specific deuterium isotopomers in the grand mixture, the scanning mode of the spectrometer was used. Locating lines for the 2-d_1 and 3-d_1 isotopomers was particularly difficult because of the low concentration of these species and because the frequencies of observed lines were surprisingly different from predictions. Splittings due to deuterium nuclear quadrupole coupling broadened the lines of the deuterated species to give slightly uncertain line positions. This effect was most pronounced in the spectrum of the 1,4-d_2 species.

Tables of lines for four ^{13}C isotopomers and five deuterium isotopomers studied are provided in Supporting Information as Tables 1S−4S and Tables 5S−9S, respectively. The number of rotational transitions in each of these supplementary tables can be found in Tables 2 and 3.

Rotational Hamiltonians. Watson-type rotational Hamiltonians in the asymmetric rotor reduction and the I^r representation were fitted for all 10 isotopomers. The data set for the normal species was rich enough in higher K_a'' lines to permit good fits for the five quartic centrifugal distortion constants. Table 2 gives the rotational constants fitted for the normal species and the standard deviation of the fit. The deviations of the individual calculated frequencies from the observed frequencies for this fit are in Table 1. Table 2 includes the fitted Hamiltonians for the four carbon isotopomers. Due to limitations in the data sets for all four of the ^{13}C-substituted species, the δ_J, δ_K, and Δ_K centrifugal distortion constants were held at the values found for the normal species.

Table 3 gives the rotational constants fitted for the five deuterium isotopomers. With the exception of the 1,4-d_2 species, δ_J, δ_K, and Δ_K were transferred from the normal species. For the 1,4-d_2 species, only δ_J and δ_K were transferred.

The anomalies in the rotational constants for the 2-d_1 and 3-d_1 species (see below) led us to examine closely the assignments and fittings of lines for these species. As shown in Table 3, the overall uncertainties in fitting the lines for each species are acceptably small despite the broadening in “lines” due to deuterium quadrupole splitting. When lines were rejected one-by-one in fitting Hamiltonians of each isotopomer, there was no evidence of a spurious line. Using all five quartic centrifugal distortion constants of the normal species gave *A*, *B*, and *C* values that differed only in the third or fourth decimal place from those reported in Table 3. Because predictions for the lines of the 2-d_1 and 3-d_1 species were relatively poor, we searched extensively in the vicinity of the reported lines. Thus, it is likely that we would have found lines for alternative assignments.

A number of unassigned lines remain from the investigation of the complex mixture of isotopomers. This mixture contains d_2 species in addition to the 1,4-d_2 species assigned, and it contains ^{13}C variants of deuterated species. Argon complexes with the various butadiene species are also likely. Consideration of some of these possible isotopomers gave no new assignments. Of course, none of the unassigned lines was accounted for by good predictions of remaining, unobserved weak lines for the reported species.

Additional evidence in support of the correct assignments for the 2-d_1 and 3-d_1 species is that the rotational constants for both species give anomalous Cartesian coordinates. Furthermore, the hydrogen atoms that are substituted in these two species are well positioned for significant interactions with the low-frequency torsion around the C−C bond and thus are good candidates for rotation-interaction constants that vary with deuterium−hydrogen substitution. Imaginary Kraitchman coordinates have been reported before, most recently in a ^{13}C variant of alanamide[14] and in the Ar−D$_2$S complex.[15]

Dipole Moment. Table 4 gives the results of the dipole moment investigation of the normal species of *cis,trans*-DFBD with the Stark effect. Two |*M*| lobes from each of two *a*-type lines and one *b*-type line were investigated. Stark shifts of the *a*-type lines were tracked 1.1−1.9 MHz; shifts for the *b*-type line were tracked 2.2−3.5 MHz. The experimental shifts were then fitted to the *a*- and *b*-components of the dipole moment using second-order Stark coefficients calculated from the rotational constants given in Table 2 for the normal species. The *a*-component of the dipole moment is 0.660 (4) D, and the *b*-component of the dipole moment is 2.213 (5) D. The overall dipole moment is 2.309 (5) D. From these dipole moment measurements, we anticipated *b*-type transitions being about 10

TABLE 2: Rotational Constants for *cis,trans*-1,4-Difluorobutadiene and Its ^{13}C Isotopomers

	normal species[a]	1-$^{13}C_1$ species[a,b]	2-$^{13}C_1$ species[a,b]	3-$^{13}C_1$ species[a,b]	4-$^{13}C_1$ species[a,b]
A/MHz	12 988.3327 (11)	12 936.8965 (29)	12 987.2362 (32)	12 742.0553 (37)	12 912.1155 (47)
B/MHz	1467.8791 (3)	1455.9823 (13)	1467.1578 (11)	1465.8823 (13)	1451.5446 (17)
C/MHz	1318.5845 (3)	1308.4561 (9)	1317.9982 (8)	1314.3842 (12)	1304.6133 (15)
Δ^c/amu Å^2	0.0716	0.0706	0.0696	0.0754	0.0721
Δ_K/kHz	86.88 (28)	86.88	86.88	86.88	86.88
Δ_{JK}/kHz	−4.560 (19)	−4.49 (22)	−4.60 (19)	−4.80 (46)	−3.97 (58)
Δ_J/kHz	0.2177 (13)	0.243 (27)	0.215 (19)	0.257 (26)	0.215 (34)
δ_J/kHz	0.038 71 (38)	0.038 71	0.038 71	0.038 71	0.038 71
δ_K/kHz	1.49 (16)	1.49	1.49	1.49	1.49
$\Delta\nu_{rms}$/kHz	3.0	6.1	6.0	6.8	8.7
no. lines	37	13	15	13	13
max K_a''	3	2	1	1	1
max J''	15	6	6	6	6

[a] Uncertainties in last two numbers are given in parentheses. [b] Centrifugal distortion constants δ_J, δ_K, and Δ_K transferred from the normal species. [c] Inertial defect, $\Delta = I_c - (I_a + I_b)$.

TABLE 3: Rotational Constants for the Deuterium Isotopomers of *cis,trans*-1,4-Difluorobutadiene

	1-d_1 species[a,b]	2-d_1 species[a,b]	3-d_1 species[a,b]	4-d_1 species[a,b]	1,4-d_2 species[a,c]
A/MHz	12 352.4725 (10)	12 573.6276 (29)	11 858.8738 (19)	12 581.5453 (23)	11 976.9679 (70)
B/MHz	1450.7903 (3)	1468.3643 (13)	1466.2918 (12)	1434.0869 (6)	1417.5117 (18)
C/MHz	1298.1265 (2)	1314.6405 (8)	1304.6768 (6)	1287.1450 (4)	1267.3562 (10)
Δ^d/amu Å^2	0.0536	0.0520	0.0788	0.0626	0.0450
Δ_K/kHz	86.88	86.88	86.88	86.88	55.7 (38)
Δ_{JK}/kHz	−4.248 (50)	−4.46 (31)	−3.91 (27)	−3.531 (95)	−3.55 (36)
Δ_J/kHz	0.1981 (40)	0.248 (21)	0.177 (20)	0.1848 (76)	0.175 (24)
δ_J/kHz	0.038 71	0.038 71	0.038 71	0.038 71	0.038 71
δ_K/kHz	1.49	1.49	1.49	1.49	1.49
$\Delta\nu_{rms}$/kHz	2.4	5.3	3.2	5.1	11.3
no. lines	24	13	12	22	19
max K_a''	2	1	1	2	1
max J''	8	5	5	7	7

[a] Uncertainties in last two numbers are given in parentheses. [b] Centrifugal distortion constants δ_J, δ_K, and Δ_K transferred from the normal species. [c] Centrifugal distortion constants δ_J and δ_K transferred from the normal species. [d] Inertial defect, $\Delta = I_c - (I_a + I_b)$.

TABLE 4: Comparison of the Observed and Calculated Stark Effects for *cis,trans*-1,4-Difluorobutadiene

		$\Delta\nu/\epsilon^2$/(MHz cm^2/kV^2)	
transition	$\|M\|$	observed	calculated[a]
$3_{03}-2_{02}$	0	−21.0	−21.3
	1	−16.0	−16.3
$3_{12}-2_{11}$	1	−9.88	−9.92
	2	−39.3	−39.4
$2_{11}-2_{02}$	1	39.5	39.2
	2	97.0	96.9

[a] Calculated using $\mu_a = 0.660$ D and $\mu_b = 2.213$ D and the rotational constants in Table 3.

TABLE 5: Cartesian Coordinates (Å) for *cis,trans*-1,4-Difluorobutadiene in the Principal Axis System

	ACM/DFT			MW[a]		
atom[b]	a	b	c	a	b	c
C_1	−1.6890	−0.3942	0.0	−1.6833	−0.3967	0.0
C_2	−0.4364	0.0445	0.0	−0.4130	0.0576	0.0
C_3	0.6917	−0.8570	0.0	0.6866	−0.8712	0.0
C_4	1.9668	−0.4867	0.0	1.9752	−0.4841	0.0
H_1	−1.9968	−1.4321	0.0	−2.0121	−1.4281	0.0
F_1	−2.7307	0.4466	0.0	−2.7302	0.4508	0.0
H_2	−0.2550	1.1115	0.0	−0.2377	1.1253	0.0
H_3	0.5074	−1.9239	0.0	0.5121[c]	−1.9402[c]	0.0
H_4	2.8125	−1.1591	0.0	2.8493	1.1392	0.0
F_4	2.3373	0.8036	0.0	2.3126	0.8194	0.0

[a] Coordinates for the carbon atoms and hydrogen atoms, H_1 and H_4, are $r_s$values with signs corresponding to ACM/DFT values. Coordinates for the other atoms are from the r_s/r_0 fitting, in which the C−H_2 and C−H_3 bond lengths and C_1=C_2−H_2 and C_4=C_3−H_3 bond angles were held at the ACM/DFT values. [b] See Figure 1 for atom numbering. [c] For the r_s fitting of H_3, $a = 0.6082$ Å and $b = -1.9309$ Å; also, $a(F_1) = 2.732$ Å, $b(F_1) = 0.448$ Å, $a(F_4) = 2.309$ Å, $b(F_4) = 0.822$ Å.

times as intense as the *a*-type transitions. Though weaker than the *b*-type transitions, *a*-type transitions were stronger than expected. Both types of transitions are needed for a good definition of all the rotational constants.

Structure Fitting. The small inertial defects, Δ, of less than 0.08 MHz for the various isotopomers, as reported in Tables 2 and 3, are consistent with an expected planar structure for *cis,trans*-DFBD. A planar structure for the molecule was assumed in the structure fitting.

Cartesian coordinates for the CCCC chain and for the hydrogen atoms on the terminal carbon atoms were found by the Kraitchman single substitution method.[16] These coordinates, which are in Table 5, are in reasonable agreement with the r_e coordinates computed by the ACM/TZ2P method, which are also given in Table 5. The only questionable sign to be attached to the Kraitchman results is for the small *b* coordinate of C_2. The Cartesian coordinates from the ACM/TZ2P calculations give a strong indication that the sign of the *b* coordinate of C_2 is positive. Furthermore, if a negative sign for $b(C_2)$ is used, the results for the bond lengths and bond angles in the carbon atom chain are unreasonable. For the assumption of a negative sign, the C_1=C_2 bond length is 1.315 Å, the C_2−C_3 bond length is 1.368 Å, the C_1=C_2−C_3 bond angle is 128.6°, and the C_2−C_3=C_4 bond angle is 126.8°.

Attempts to compute Cartesian coordinates for H_2 (Figure 1) from the rotational constants for the 2-d_1 species by the Kraitchman method failed because *B* for this isotopomer is larger than *B* for the normal species. Although r_s Cartesian coordinates for H_3 can be computed from the rotational constants for the 3-d_1 species, the resulting C_3−H_3 bond length of 1.063 Å and

TABLE 6: Geometric Parameters for *cis,trans*-1,4-Difluorobutadiene

Bond Length/Å

	$C_1{=}C_2$	C_2-C_3	$C_3{=}C_4$	C_1-H_1	C_2-H_2	C_3-H_3	C_4-H_4	C_1-F_1	C_4-F_4
r_s/r_0[a]	1.349 (11)	1.439 (18)	1.345 (2)	1.083 (4)	1.082[b]	1.083[b]	1.092 (2)	1.347 (3)	1.347 (3)
r_0	1.334	1.411	1.345	1.081	1.082[b]	1.083[b]	1.091	1.351	1.348
DFT	1.327	1.444	1.328	1.083	1.082	1.083	1.080	1.339	1.342

Bond Angle/deg

	$C_1{=}C_2-C_3$	$C_2-C_3{=}C_4$	$C_2{=}C_1-H_1$	$C_1{=}C_2-H_2$	$C_4{=}C_3-H_3$	$C_3{=}C_4-H_4$
r_s/r_0[a]	120.1 (18)	123.1 (8)	127.4 (11)	119.0[b]	116.0[b]	126.4 (3)
r_0	123.5	124.5	125.3	119.0[b]	116.0[b]	126.4
DFT	122.1	125.2	125.8	119.0	116.0	125.3

Bond Angle/deg

	$C_2{=}C_1-F_1$	$C_3{=}C_4-F_4$	$H_1-C_1-F_1$	$C_3-C_2-H_2$	$C_2-C_3-H_3$	$H_4-C_4-F_4$
r_s/r_0[a]	121.3 (11)	121.2 (2)	111.3 (2)	120.9 (7)	120.9 (8)	112.3 (1)
r_0	123.1	121.2	111.6	117.5	119.5	112.4
DFT	121.8	122.2	112.4	118.9	118.8	111.9

[a] Costain uncertainties in parentheses. [b] Values from ACM/TZ2P calculation used in fitting. If r_s values for H_3 are used, the C_3-H_3 bond length is 1.063 Å, the $C_4{=}C_3-H_3$ bond angle is 111.0°, and the $C_2-C_3-H_3$ bond angle is 125.9°.

the resulting $C_4{=}C_3-H_3$ bond angle of 111.0° seem too small. Thus, the rotational constants for the 3-d_1 isotopic species are also questionable for use in structure fitting but in a less obvious way than are the rotational constants for the 2-d_1 species. The distances of the H_2 and H_3 hydrogen atoms from the *b* axis are not so small, about 0.25 and 0.5 Å, respectively, as to suggest significant complications due to differences in vibration−rotation coupling between the normal species and the 2-d_1 and 3-d_1 isotopomers. Nonetheless, such an effect must be causing the difficulty in applying the substitution method for these two hydrogen atoms.

Given the problems in determining Cartesian coordinates for H_2 and H_3 by the substitution method, we resorted to fixing the two CH bond lengths and corresponding C═C−H angles for these hydrogen atoms at the values found in the ACM/TZ2P calculations and then doing a constrained r_s/r_0 fitting to find the fluorine coordinates. Thus, the chain of carbon atoms and the end hydrogen atoms were held at the r_s Cartesian coordinates, and the interior CH bond lengths and bond angles were held at the ACM/TZ2P bond parameters. The observed rotational constants for the 2-d_1 and 3-d_1 species were omitted, and the coordinates for the two fluorine atoms were fitted. Adding the puzzling rotational constants for the 2-d_1 or the 3-d_1 species to the fitting gave results for the Cartesian coordinates of the fluorine atoms in agreement within 0.001 Å of the results when these two sets of rotational constants were omitted. Of course, the standard deviation in the fit of parameters was somewhat larger when all of the rotational constants were used. An attempted fitting with r_s coordinates for the carbon atoms and the end hydrogen atoms and the two interior C−H bond lengths, but not the interior C═C−H angles, held at the ACM/TZ2P values did not converge with all 10 sets of rotational constants in use. The accepted result for the Cartesian coordinates for the interior hydrogen atoms and the fluorine atoms, arising from the fitting with the rotational constants for the 2-d_1 and 3-d_1 species omitted, is given in Table 5. These coordinates are in reasonable agreement with the coordinates from the ACM/TZ2P calculations, which, of course, gives r_e coordinates, which differ somewhat from r_s/r_0 coordinates. The full set of Cartesian coordinates was then used to compute the geometric parameters presented in Table 6.

Some other fitting experiments were carried out. An r_s/r_0 fitting was done in which the r_s Cartesian coordinates were used for H_3, ACM/TZ2P parameters were used for the C_2-H_2 bond length and the $C_1{=}C_2-H_2$ bond angle, and the rotational constants for the 3-d_1 isotopomer were included. The Cartesian coordinates were, of course, changed for H_3 but were little changed for the fluorine atoms. The results of this calculation are given in footnotes in Tables 5 and 6. As noted above, the C_3-H_3 bond length is 1.063 Å and the $C_4{=}C_3-H_3$ bond angle is 111.0°. Possibly these are meaningful results for the C_3-H_3 bond, but they are surprisingly far from the results of the quantum mechanical calculations.

A less-constrained, global r_0 fitting was also done but was less satisfactory than the r_s/r_0 fitting. The C−H bond lengths and C═C−H bond angles for the two interior hydrogen atoms were constrained to the ACM/TZ2P parameters. The eight sets of rotational constants, excepting those for the 2-d_1 and 3-d_1 species, were used, and the full set of atomic coordinates was fitted. Uncertainties in the fitting of the coordinates for H_2 and H_3 were as large as 0.14 Å. Although we do not report the set of Cartesian coordinates from this fit, we do give the corresponding geometric parameters, labeled r_0, in Table 6. Significant differences from the parameters from the r_s/r_0 fitting are apparent. At best, this comparison suggests that the accepted r_s/r_0 parameters are reasonable. A more favorable and convincing comparison is between the r_s/r_0 parameters and those found in the ACM/TZ2P calculation of an r_e structure, which are also reported in Table 6.

In Table 6, the Costain estimates of uncertainties in the bond parameters, except for those for the interior hydrogen atoms, are given for the r_s/r_0 fittting. These uncertainties are appreciable for the parameters that involve C_2, which has a small *b* coordinate. Given the problems in finding coordinates for H_2 and H_3, we must attach significant uncertainties to the assumed parameters for these two atoms. Uncertainties of ±0.015 Å in the bond lengths and ±1.5° in the bond angles for the interior hydrogen atoms appear appropriate in view of the Costain uncertainties for the other parameters and the comparison between the observed values and the ACM/TZ2P values for the other CH bonds.

Because of the uncertainties in the structure fitting for *cis,-trans*-DFBD, we must be cautious in interpreting the bond parameters. A further reason for caution is the absence of a full spectroscopic investigation of butadiene itself. The published structural parameters for butadiene are derived from an electron diffraction study. Consequently, the structural parameters for the carbon atom backbone should be well-determined, but the parameters for the C−H bonds are questionable. For the carbon atom backbone, electron diffraction gives 1.348(1) Å for $C_1=C_2$, 1.468(2) Å for C_2-C_3, and 124.3(1)° for $C_1=C_2-C_3$.[17] We have computed the structure of butadiene by the ACM/TZ2P method. The results are 1.333 Å for $C_1=C_2$, 1.450 Å for $C_{2-}C_3$, 124.2° for $C_1=C_2-C_3$, 1.081/1.084 Å for C_1-H, 1.086 Å for C_2-H, 121.6/121.34° for $H-C_1=C_2$, and 119.4° for $C_1=C_2-H$. The longer C−H bond length is for the C−H bond cis to the C−C bond; the larger H−C═C bond angle is for the trans configuration.

Comparing ACM/TZ2P results for the cis,trans isomer and butadiene itself avoids the complication of the theory giving equilibrium parameters and spectroscopic data giving ground-state parameters. The theoretical results show a small but systematic effect of the fluorine substituents on the C═C and C−C bond lengths. All three bond lengths are 0.005−0.006 Å shorter in *cis*,*trans*-DFBD. This contraction in CC bond lengths implies a strengthening of the bonding throughout the carbon backbone due to delocalization of electron density from the fluorine atoms. Differences are also found in the C═C−C bond angles. In the cis,trans isomer the $C_1=C_2-C_3$ bond angle is smaller by 2.1° and the $C_2-C_3=C_4$ bond angle is larger by 1.0°. These bond angle adjustments are consistent with repulsive effects of the fluorine substituents.

Comparison of experimental parameters with the theoretical parameters for the two butadienes provides other insights. In the following discussion, we refer to the r_s/r_0 values in Table 6. The focus is on the carbon atom backbone because of the limited experimental data for butadiene and uncertainties in experimental CH bond lengths due to the differential effects of anharmonicity in CH and CD bonds. For butadiene, the experimental CC bond lengths are longer than the theoretical ones by 0.015−0.018 Å, and the experimental C═C−C bond angle is larger by only 0.1°. For *cis*,*trans*-DFBD a different pattern of comparison between experiment and theory exists for the bond lengths and the bond angles. Here the experimental values for the $C_1=C_2$ bond and the $C_3=C_4$ bond are longer than the theoretical ones by 0.022 and 0.017 Å, respectively, but the C_2-C_3 bond is shorter by 0.005 Å. The experimental values for the $C_1=C_2-C_3$ bond angles are smaller than the theoretical ones by about 2.0°.

The larger differences between the experimental and theoretical values for the *cis*,*trans*-DFBD than for butadiene could suggest doubt about the experimental values, which, of course, were not obtained in an unambiguous manner. Another possibility is that the contribution of the additional electrons and the high electronegativity of fluorine make the calculations for the cis,trans isomer more approximate. A third possibility is that the comparison between experiment and theory for butadiene is accidentally favorable because of deficiencies in the experimental data for this molecule. Because of this latter question and the lack of information about the CH bonds in butadiene, we have launched a full investigation of the structure of butadiene with high-resolution infrared methods. It seems best to wait until these results are available to pursue the comparisons more vigorously.

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Supporting Information Available: Supplementary Tables S1−S9 contain the observed microwave lines, their assignments, and the deviations of each line in the fitting of the Hamiltonians for the carbon and deuterium isotopomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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