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Complete Structure of *trans*-3,4-Difluorocyclobutene from Microwave Spectroscopy

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Microwave spectra have been observed with Fourier transform and cold jet expansion techniques in the 6−17 GHz range for *trans*-3,4-difluorocyclobutene, its two $^{13}C_1$ modifications, two d_1 modifications, and the perdeutero species. Watson-type Hamiltonians have been fit with a full set of quartic centrifugal distortion constants for all species except the d_4 species. Complete structures fit with an r_s/r_0 treatment and an r_0 treatment are in satisfactory agreement. Preferred r_s/r_0 results with Costain uncertainties in parentheses are 1.349(4) Å for the C═C bond, 1.503(9) Å for the contiguous C−C bonds, 1.534(4) Å for the distant C−C bond, 1.398(6) Å for the C−F bond, 1.081(3) Å for the ═C−H bond, and 1.102(5) Å for the −C−H bond. Consistent with its C_2 symmetry, the ring is slightly puckered, and the C−F bonds are roughly equatorial. Compared with the structure of cyclobutene, the structure of *trans*-3,4-difluorocyclobutene shows a modest lengthening of the C═C bond and more significant decreases in the C−C bond lengths. These effects are consistent with observations for other fluorine-substituted rings in which contiguous fluorine atom substitution causes CC bond shortening and distant fluorine atom substitution causes CC bond lengthening. The CC bond adjustments in *trans*-3,4-difluorocyclobutene are, however, surprisingly similar to the adjustments observed for 3,3,4,4-tetrafluorocyclobutene.

Introduction

Fluorine substitution causes significant changes in the CC bond lengths in small ring compounds. A number of fluorine-substituted three-membered ring systems were investigated with microwave spectroscopy by Gillies and co-workers.[1] Laurie and co-workers[2] also contributed to these studies. In general, the results showed that fluorine substitution distant from a C−C or C═C bond caused bond lengthening, whereas substitution on the carbons of a C−C or C═C bond caused bond shortening. A number of ab initio investigations have been made of these effects. Among these studies are those of Allen and co-workers,[3] Boggs and Fan,[4] Hertwig et al.,[5] and Han et al.[6]

Four-membered rings substituted with fluorine atoms have also been studied by microwave and electron diffraction methods. Species studied include 3,3,4,4-tetrafluorocyclobutene,[7] 1,3,3-trifluorocyclobutene,[8] hexafluorocyclobutene,[9,10] and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene.[11,12] In cyclobutenes, the effect of fluorine substitution appears to be similar to the effect in three-membered rings but moderated.

The present study of *trans*-3,4-difluorocyclobutene (tDFCB) contributes to knowledge about the effect of fluorine substitution on the bond lengths in cyclobutenes. The key to completing this project was devising syntheses of deuterium isotopomers of tDFCB. tDFCB-d_4 was prepared from cyclooctatetraene-d_8,[13] which was made from acetylene-d_2 by Stevenson's adaptation of the Reppe reaction.[14] Remarkably, it was possible to synthesize tDFCB with some single deuteration in the two different sites. This result was obtained by partial exchange of *cis*-3,4-dichlorocyclobutene (*cis*-DClCB) in sodium deuterioxide at 100 °C followed by replacement of the chlorine atoms with fluorine atoms accompanied by isomerization.

We have investigated the microwave spectra with Fourier transform (FT) and cold supersonic jet techniques. We report the microwave spectra of tDFCB, its two ^{13}C variants, its two d_1 variants, and its d_4 species, from which a complete structure has been derived. The dipole moment of tDFCB was also found by Stark effect measurements.

Experimental Section

Syntheses. tDFCB was prepared from *cis*-DClCB by reaction with silver difluoride and purified by preparative gas chromatography as described before.[13] Most of the preparative work was done on a vacuum system. Progress of the reactions was followed with infrared and NMR spectra. Of course, samples of tDFCB used in this study are equimolar mixtures of its two enantiomers.

Following Stevenson's instructions for the Reppe reaction,[14] cyclooctatetraene-d_8 (COT-d_8) was synthesized in a bomb from acetylene-d_2 with a nickel acetylacetonate catalyst (Aldrich) in dry tetrahydrofuran solvent (refluxed over sodium ribbon with a benzophenone indicator). The acetylene-d_2 was made in a continuous operation on a vacuum system by dripping deuterium oxide (99.9% Aldrich) onto calcium carbide. The C_2D_2 was dried by passing it through a U-tube packed with calcium

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carbide cooled in ice and a second U-tube cooled to −50 °C. For a reaction, 0.34 g of Ni(acac)$_2$ and 12.5 mL of dry THF were transferred in a nitrogen-purged dry bag into a 25-mL flask equipped with a thickened neck, a ground joint, and a Teflon-covered stir bar. After this bulb was fitted with a stopcock adapter, the bulb was removed from the dry bag, attached to the vacuum system, and degassed. Then, about 0.35 mol of C_2D_2 was slowly condensed in the stirred THF at dry ice temperature. During production and condensation, the pressure of the C_2D_2 varied from 500 to 650 Torr. After the reaction bulb was cooled to liquid nitrogen temperature, it was flame-sealed at its thickened neck. In the glovebag, ice was carefully scraped off the outside of the cold bulb with a Teflon tool before the bulb was sealed in a 300-mL Parr bomb. The contents of the bomb were heated to 90 °C for 21 h with periodic shaking by hand. During the reaction in the bomb, the glass flask exploded. After the bomb was opened at room temperature, THF and nickel salts were extracted with five 10-mL portions of water. COT-d_8 was extracted with five 10-mL portions of diethyl ether, dried with magnesium sulfate, filtered, and isolated with a Rotovap. A proton-decoupled ^{13}C NMR spectrum showed a deuterium-split triplet ($J_{CD} = 23.9$ Hz) at 131.1 ppm due to COT-d_8 and a singlet due to the residual, undeuterated carbon atom in COT-d_7 at 131.4 ppm. For COT itself, $\delta = 131.5$ ppm. The ^{1}H singlet for COT-d_7 is at 5.70 ppm, whereas $\delta = 5.50$ ppm for COT itself. The "absolute" shifts depend on the variable amounts of THF and diethyl ether in these samples.

COT-d_8 was used to make *cis*-DClCB-d_4 by the same reaction sequence as described for the normal species of tDFCB.[13] The principal infrared absorption bands in the gas-phase spectrum of *cis*-DClCB-d_4 are ~2305, 2231, 1173, 1104, 1001, 887, 790, 700, and 624 cm^{-1}. *cis*-DClCB-d_4 was converted into tDFCB-d_4.[13] Gas-phase infrared absorption bands of tDFCB-d_4 are 2292 m, ?; 2219 ms, C; 1211 vs, C; 1126 m, A; 1101 m, A; 1070 vs, A; 1004 m, B; 969 s, C; 953 m, B; 812 s, B; 766 m, A; 735 ms, A; 572 ms, C; 553 m, B; 379 w, C; 296 m, B; and 159 w, B, in reciprocal centimeters. Intensities are vs, very strong; s, strong; ms, medium strong; m, medium; and w, weak. A, B, C, and ? stand for band shapes.

tDFCB-1-d_1 and tDFCB-3-d_1 were prepared in a mixture by first exchanging *cis*-DClCB, which became commercially available for the exchange studies (Fluka). The exchange of *cis*-DClCB was done as described in detail for *trans,trans*-1,4-difluorobutadiene,[17] except the time was shorter and the temperature lower. Though of low volatility at room temperature, *cis*-DClCB samples were distilled on the vacuum system into the Pyrex-breakseal-equipped quartz reaction vessel before flame-sealing. Exchange was for 24 h at 100 °C in a rocking oven. Higher temperatures led to decomposition of the *cis*-DClCB. Sometimes decomposition to red-brown polymeric material occurred at 100 °C. *cis*-DClCB was removed from the reaction mixture by extraction with several 1-mL portions of diethyl ether. Rotoevaporation left the *cis*-DClCB behind for conversion to tDFCB.[13] Assaying for the small amount of exchange was difficult. The best evidence of exchange was from gas-phase infrared spectra of the tDFCB-d_x material. New, sharp Q branches at 1307, 1272, 894, 868, 816, 794, 771, 672, and 632 cm^{-1}, which grew more intense with a longer time of exchange, reflected deuterium substitution. The number of new peaks suggested that exchange had occurred to give some of both 1-d_1 and 3-d_1 species. The observation of spectra of these two isotopomers in the microwave investigation of tDFCB showed unambiguously that some exchange had occurred at both proton sites in *cis*-DClCB. Very roughly, from intensities in the microwave spectra, we estimate about 5% conversion to the 1-d_1 species and about half this much for the 3-d_1 species.

Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 1760 FT instrument at 0.5 cm^{-1} resolution. Samples were held as gases in a 10-cm Wilmad minicell equipped with potassium bromide or polyethylene windows. NMR spectra were recorded on a Bruker AC-200-MHz instrument. NMR samples were dissolved in deuteriochloroform and held in 5-mm tubes.

Microwave spectra were recorded in the 6−17 GHz region on Balle−Flygare[15] spectrometers at the University of Michigan[7] and at Kent State University.[16,17] The observations on the normal species, including the ^{13}C species in natural abundance, and Stark effect measurements were done at Michigan. Electric fields for the Stark effect measurements were established by charging two 50 cm × 50 cm steel mesh grids placed above and below the cavity and separated by 30 cm. The grids could be charged with up to 10 000 V of opposite polarity, and the electric fields were calibrated by measuring the Stark shift of the $1 \leftarrow 0$ transition of OCS ($\mu = 0.715\,196$ D).[18] The inlet nozzle was coaxial with the microwave beam at Michigan and coaxial or transverse at Kent. The measurements of the three deuterium-substituted species were made at Kent State. Sample mixtures were prepared from about 0.33 mmol of tDFCB and about 1.7 atm of argon driver gas in a 2-L flask. After the pressure of the mixture had dropped to about 1 atm, argon was added to bring the pressure to 1.7 atm again. Useful observations were possible through about four supplements of argon.

An unusual problem was encountered in handling samples of tDFCB-d_4 prepared for microwave investigations. When the samples were prepared in a 2-L flask that had previously been used for studies of chloromethylsilanes, the tDFCB-d_4 isomerized in a few hours to the corresponding butadiene, as shown by recovering the fluorocarbon from the dilute mixture with argon and checking its infrared spectrum. Principal infrared bands of *trans,trans*-1,4-difluorobutadiene-d_4 are 2271 m, B; 1578 vs, A/B; 1140 w, ?; 1101 vs, A/B; 971 s, A/B; 928 w, ?; 838 w, C; 693 m, C; 680 m, C; and 556 m, ?, in reciprocal centimeters. This isomerization occurs quickly in the gas phase at temperatures above 80 °C but not at room temperature.[17] By testing with samples of less precious undeuterated material, we found that the silanized flask was the culprit. Evidently, the isomerization reaction is catalyzed on a silanized glass surface but not on an ordinary hard glass surface.

Results and Discussion

General Considerations. The trans isomer of 3,4-difluorocyclobutene has a single symmetry element, a C_2 axis, which bisects the CC double bond and the opposite CC single bond. The C_2 axis is the *b* axis of the principal axis system. These relationships are shown schematically in Figure 1. The approximate locations of the *a* and *c* principal axes are also shown in Figure 1. Because the dipole moment points along the *b* axis, the microwave selection rules are exclusively B-type with $\Delta J = +1, 0$; $\Delta K_a = \pm1$; $\Delta K_c = \pm1, +3$. tDFCB is an asymmetric top with $\kappa = -0.385$ for the normal species.

Microwave Spectra and Rotational Constants. For the normal species of tDFCB, 33 lines were observed. Table 1 shows that 16 of these lines are R-branch transitions and 17 are Q-branch transitions. Table 4 gives the rotational constants fit to a Watson-type Hamiltonian (A reduction, I^r representation). In an excellent fit with a standard deviation (SD) of 1.5 kHz, a full set of quartic centrifugal distortion constants has been found.

For the 1-$^{13}C_1$ isotopomer of tDFCB, 18 lines were observed for this species in natural abundance. These lines are in Table

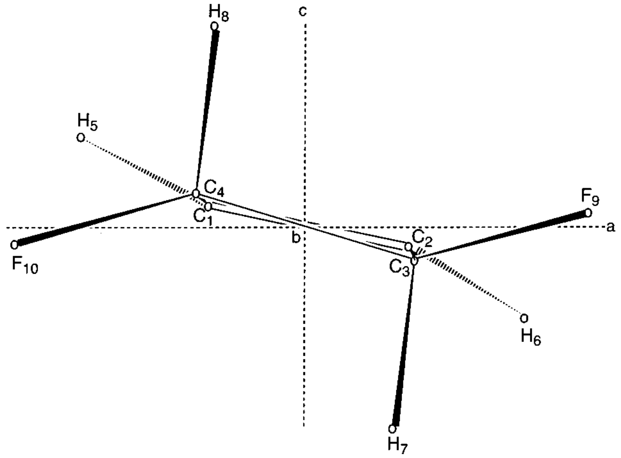

Figure 1. Diagram of one enantiomer of tDFCB looking down the *b* axis, which has its positive direction behind the plane of the paper. The center of mass lies 0.17 Å behind the C_3–C_4 bond.

2. Half are R-branch transitions; half are Q-branch transitions. Table 4 shows that the rotational constants, including a full set of quartic centrifugal distortion constants, were fit with an SD of 0.9 kHz. These centrifugal distortion constants are consistent with those found for the normal species.

As shown in Table 2, 17 lines were observed for the 3-$^{13}C_1$ isotopomer of tDFCB. Nine were R-branch transitions. Table 4 contains the rotational constants, including the full set of quartic centrifugal distortion constants, which were obtained with an SD of 1.8 kHz.

Table 3 contains the observations for the three deuterium isotopomers. The first set consists of 17 transitions for the 1-d_1 species, and the second set consists of 18 transitions for the 3-d_1 species. In both cases, six of the observations are R-branch transitions. The third set of data in Table 3 is for the d_4 isotopomer. Seven of the 17 observations are R-branch transitions. Although Table 5 shows that all five quartic centrifugal distortion constants have been fit for the two d_1 species, the SDs are considerably larger than for the normal species and the ^{13}C species. These larger, though acceptable, uncertainties in the fitting for the deuterium species reflect the broadening of the "lines" due to incompletely resolved deuterium splitting. This effect is greatest for the d_4 isotopomer. For fitting the rotational constants for this species, it was necessary to transfer Δ_J, δ_J, and δ_K from the normal species. In addition, the K_a values for the deuterium isotopomers do not go as high as for the normal and ^{13}C species. Despite the greater uncertainties in fitting the centrifugal distortion constants for the deuterium isotopomers, the constants fit are in reasonable accord with those for the normal species.

Dipole Moment. Three transitions were investigated fully with the Stark effect. Six Stark shifts of up to -2.206 MHz were measured for the $|M| = 0$ lobe of the $2_{02}-1_{11}$ transition. The $|M| = 1$ lobe of this transition shifted too slowly for calibrated measurements. For the $2_{21}-2_{12}$ transition, nine Stark shifts were measured for the $|M| = 1$ lobe (up to 1.422 MHz), and seven shifts were measured for the $|M| = 2$ lobe (up to 2.582 MHz). For the $3_{13}-2_{02}$ transition, seven Stark shift measurements (up to 3.191 MHz) were made for the $|M| = 1$ lobe, and five measurements (up to 3.920 MHz) were made for the $|M| = 2$ lobe. The $|M| = 0$ lobes of both the $2_{21}-2_{12}$ and $3_{13}-2_{02}$ transitions shifted too slowly for calibrated measurements. The Stark effect on the $1_{11}-0_{00}$ line was also investigated but seemed to split further at ±3000 V. The experimental slopes of Stark effect for the five $|M|$ lobes were fit to the *b* component of the dipole moment by use of second-order Stark coefficients calculated from the rotational constants of the parent species given in Table 4. Table 6 compares the observed and calculated Stark shifts for the five $|M|$-lobes investigated fully. The dipole moment was found to be 2.0296(6) D directed along the *b* axis.

Structure Fitting. Fitting of the structure of tDFCB was done in two ways. In the first way r_s substitution coordinates were found for the two types of carbon and hydrogen atoms. These Cartesian coordinates in the principal axis framework of the parent species are given in Table 7. With the Cartesian coordinates of the carbon and hydrogen atoms held fixed at the substitution values, the Cartesian coordinates for the fluorine atoms were found by fitting to all of the rotational constants. These r_0-like coordinates for the fluorine atoms are given in Table 7. This overall set of Cartesian coordinates is designated as r_s/r_0. Geometric parameters derived from the r_s/r_0 set are given in the second column of Table 8, and Costain uncertainties are given for these parameters.[19]

A second set of coordinates was found for all of the atoms in a global fitting of the rotational constants for the six isotopic species. Thirteen independent parameters are being fit to 18 rotational constants. For this fitting process the C_2 symmetry condition was imposed on symmetrically equivalent atoms, and three first moments were constrained to zero as were the second planar moments, P_{ab}, P_{ac}, and P_{bc}. The Cartesian coordinates found in this way are not reported, but the resulting geometric parameters are given in the third column in Table 8. Costain uncertainties are essentially the same for these r_0 geometric parameters as for the r_s/r_0 set and are not separately supplied in Table 8. With one exception the bond lengths obtained by the two procedures differ by less than 0.004 Å. The exception is the C−C bond length for the single bonds adjacent to the C=C bond. In this case the difference is 0.008 Å. Differences in bond angles determined by the two methods are 0.5° or less. Thus, we have confidence in the structure fitting for tDFCB and prefer the r_s/r_0 coordinates.

Column 4 in Table 8 gives geometric parameters found by a hybrid B3LYP DFT calculation with a 6-311+G** basis set. This calculation was done with the Titan software supplied jointly by Wavefunction, Inc., and Schrödinger, Inc. For the most part the comparison between the r_e parameters of the DFT calculation and the r_s/r_0 parameters, which are somewhat different measures of the structure, is satisfactory. However, the calculated C_3–C_4 bond length is 0.024 Å longer than the experimental one, and the calculated C_3–H_7 bond length is 0.008 Å shorter than the r_s/r_0 value. A question exists about the C−F bond length as well. Although the experimental C−F bond length is close to the DFT prediction, it is likely that the two measures of this bond length are too long. DFT calculations tend to overestimate C−F bond lengths.[20] For the experimental results, an underestimate of the C_3–C_4 bond length would be compensated by overestimates of the C−H and C−F bonds, as seems to be the case. Thus, we conclude that the C_3–C_4 bond length is likely to be closer to 1.540 Å than the r_s value of 1.534 Å. The C_3–H_7 and C_3–F_9 bonds are likely to be shorter by about 0.010 Å than the r_s/r_0 values.

A possible cause of error in the r_s value for the C_3–C_4 bond length is the small *b* coordinate for these atoms (Table 7). However, because the C_3–C_4 bond is largely perpendicular to the *b* axis, uncertainty in the *b* coordinate has a small effect on the derived C−C bond length. A deficiency in r_s parameters for a cyclobutene ring was reported recently for 1,2-dicyanocyclobutene.[21] Some ab initio bond parameters were used to initiate the r_0 refinement.

TABLE 1: Observed Microwave Transitions for *trans*-3,4-Difluorocyclobutene

$J'(K_a',K_c')-J''(K_a'', K_c'')$	freq[a]	O−C[b]	$J'(K_a',K_c')-J''(K_a'',K_c'')$	freq[a]	O−C[b]
1(1,1)−0(0,0)	8009.606	4.0	2(2,1)−2(1,2)	9955.268	0.7
2(1,2)−1(0,1)	12 700.757	−2.7	3(2,2)−3(1,3)	11 638.072	−0.6
2(0,2)−1(1,1)	8853.762	1.3	3(3,0)−3(2,1)	12 988.716	−3.6
3(1,3)−2(0,2)	17 001.148	0.9	3(3,1)−3(2,2)	14 192.821	0.6
3(0,3)−2(1,2)	14 606.151	−0.5	4(1,3)−4(0,4)	10 278.507	−0.3
3(1,2)−2(2,1)	11 572.551	0.9	4(2,3)−4(1,4)	13 894.630	−0.6
4(1,4)−3(2,1)	7485.657	0.1	4(3,1)−4(2,2)	11 894.547	0.5
4(2,3)−3(3,0)	8391.568	0.0	4(3,2)−4(2,3)	14 838.370	1.4
4(2,2)−3(3,1)	11 698.032	−0.2	5(1,4)−5(0,5)	14 314.410	−0.8
5(1,5)−4(2,2)	8040.850	−0.5	5(2,3)−5(1,4)	8844.440	−0.5
5(2,4)−4(3,1)	12 804.374	−0.4	5(2,4)−5(1,5)	16 658.070	0.3
5(3,3)−4(4,0)	9811.660	−0.2	5(3,2)−5(2,3)	10 798.262	−0.4
5(3,2)−4(4,1)	10 969.944	−1.7	5(3,3)−5(2,4)	15 987.531	0.2
6(2,5)−5(3,2)	15 964.529	1.1	6(2,4)−6(1,5)	11 690.637	−0.7
6(4,3)−5(5,0)	10 405.686	−0.3	6(3,3)−6(2,4)	10 327.149	0.0
6(4,2)−5(5,1)	10 686.131	0.7	6(3,4)−6(2,5)	12 715.183	2.4
			6(4,2)−6(3,3)	16 960.051	−1.1

[a] Frequencies are given in megahertz. [b] Observed − calculated values are given in kilohertz.

TABLE 2: Observed Microwave Transitions for the 1-^{13}C and 3-^{13}C Isotopomers of *trans*-3,4-Difluorocyclobutene

	DFCB-1-$^{13}C_1$		DFCB-3-$^{13}C_1$	
$J'(K_a',K_c')-J''(K_a'',K_c'')$	freq[a]	O−C[b]	freq[a]	O−C[b]
1(1,1)−0(0,0)	7874.534	0.4	7992.630	1.5
2(1,2)−1(0,1)	12 520.050	−0.5	12 673.940	−2.5
2(0,2)−1(1,1)	8873.623	0.8	8820.763	−0.3
3(1,3)−2(0,2)	16 776.159	−0.1	16 966.737	2.6
3(0,3)−2(1,2)	14 556.847	−0.3	14 560.086	−1.2
3(1,2)−2(2,1)	11 784.398	−0.3	11 506.604	0.8
4(1,4)−3(2,1)	7484.146	−0.2	7488.336	−0.5
4(2,3)−3(3,0)	8711.153	−0.4	8341.328	1.5
4(2,2)−3(3,1)	12 161.997	0.8	11 606.522	−1.6
2(2,1)−2(1,2)	9686.984	0.4	9933.873	0.4
3(2,2)−3(1,3)	11 396.834	−0.3	11 602.372	−0.7
3(3,0)−3(2,1)	12 459.291	0.1	12 987.205	−0.2
3(3,1)−3(2,2)	13 722.615	0.2	14 175.360	−0.1
4(1,3)−4(0,4)	10 323.249	0.5	10 208.699	0.8
4(2,3)−4(1,4)	13 686.298	−0.5	13 840.195	−1.0
4(3,1)−4(2,2)	11 352.364	1.6	11 901.951	−1.2
4(3,2)−4(2,3)	14 401.888	−1.5	14 812.104	1.7
5(2,3)−5(1,4)	8808.469	−0.1		

[a,b] See Table 1.

Table 8 includes structural comparisons between tDFCB, cyclobutene, 3,3,4,4-tetrafluorocyclobutene and perfluorocyclobutene based on microwave investigations. Electron diffraction results give shorter $C=C$ bonds and markedly longer $C-C$ bonds in halocyclobutenes.[10,11] This discrepancy is not understood. One recent theoretical study based on DFT methods supports the electron diffraction findings;[5] another supports the spectroscopic results.[6]

In the following discussion, we focus on the spectroscopic results. Compared to cyclobutene, tDFCB shows the familiar pattern of the $C=C$ bond being somewhat elongated, by 0.007 Å, in the presence of fluorine substitutents on the carbon atoms opposite the double bond. Despite some doubt about the r_s $C_{3-}C_4$ bond length between the two fluorine-substituted carbon atoms, it seems certain that this bond has shortened significantly compared to that of cyclobutene. The $C-C$ bond with one of its carbon atoms substituted with fluorine is shortened by about 0.014 Å. Turning to a comparison of tDFCB and tetrafluorocyclobutene, we find the $C=C$ bond is lengthened about the same amount with two or four fluorine atom substitutents. The shortening of the two types of $C-C$ bonds is also almost the same in tDFCB as in tetrafluorocyclobutene. Thus, surprisingly little difference exists in the bond lengths in the cyclobutene rings for these two fluorocyclobutenes.

Generally speaking, the effects of fluorine substitution in perfluorocyclobutene are as expected. The $C=C$ bond shrinks 0.009 Å in going from cyclobutene to perfluorocyclobutene, and the contiguous $C-C$ bonds shrink a large 0.039 Å. The opposite $C-C$ bond shrinks only 0.014 Å, which is substantially less than for four fluorine substituents in tetrafluorocyclobutene. Is there a competing F···F repulsion effect?

Overall, the parameters for fluorine-substituted cyclobutene rings found from microwave spectroscopy seem consistent. The persistence of this finding deepens the mystery about the substantially longer CC bonds found by electron diffraction. Two routes appear to be open for resolving this discrepancy. One is more extensive quantum chemical calculations carried out at the highest levels of theory. The other is the use of computed vibration−rotation constants to secure r_e structures from experimental data.

Two other features of the structure of tDFCB deserve consideration. One is the shortening of the $C-F$ bond in going from tDFCB to 3,3,4,4-tetrafluorocyclobutene. With allowance for an overestimate of the $C-F$ bond length in tDFCB, the shortening remains appreciable. (The $C-F$ bond length for perfluorocylobutene is assumed and thus cannot be compared.) The dramatic shortening of a $C-F$ bond when another fluorine atom is added geminally is a well-known effect.[20]

When the dipole moment of tDFCB is compared with the dipole moment of the tetrafluoroethane, the incremental increase seems too small. In going from the oppositely directed dipole moment of cyclobutene of 0.13 D[22] to the dipole moment of tDFCB, the increment is 2.16. In going from the dipole of tDFCB to the 3.43 D dipole moment of tetrafluorocyclobutene,[7] the increment is 1.40 D. This smaller increment is understandable because of the shorter $C-F$ bonds and consequently smaller bond moments in tetrafluorocyclobutene.

The second feature is the slight puckering of the cyclobutene ring in tDFCB. In contrast, the symmetrically substituted 3,3,4,4-tetrafluoro- and perfluorocyclobutenes have planar rings, as does cyclobutene itself.[7,9,22] The puckering in the cyclobutene ring of tDFCB, which is folded along the C_1C_3 diagonal, can be seen in Figure 1 and by comparing the *c* coordinates for equivalent carbon atoms in Table 7. The C_3 atom with the attached fluorine atom up is below the average cyclobutene plane, whereas the C_4 atom with the fluorine atom down is above the average plane. The carbon atoms connected by the double bond are oppositely positioned with respect to the average plane and closer to it than the C_3C_4 carbon atoms. The $C-F$ bonds

TABLE 3: Observed Microwave Transitions for the 1-d_1, 3-d_1, and d_4 Isotopomers of *trans*-3,4-Difluorocyclobutene

	DFCB-1-d_1		DFCB- 3-d_1		DFCB- d_4	
$J'(K_a',K_c')-J''(K_a'',K_c'')$	freq[a]	O−C[b]	freq[a]	O−C[b]	freq[a]	O−C[b]
1(1,1)−0(0,0)	7670.553	1.5	7857.923	−1.1	7100.962	−9.1
2(1,2)−1(0,1)	12 232.055	−5.3	12 534.700	0.5	11 513.046	8.8
2(0,2)−1(1,1)	8824.377	4.1	8846.517	0.3	8749.842	−9.2
2(2,1)−1(1,0)					16 890.796	−12.3
3(1,3)−2(0,2)	16 409.391	−0.6	16 836.911	5.4	15 578.050	20.7
3(0,3)−2(1,2)	14 387.998	−0.8	14 540.591	−3.8	14 027.040	16.2
3(1,2)−2(2,1)	11 914.418	1.8	11 631.859	−1.8	12 250.190	25.4
2(2,0)−2(1,1)	6516.676	−2.4	6869.276	2.5		
2(2,1)−2(1,2)	9327.064	−0.3	9543.368	−14.2	8066.659	−10.0
3(1,2)−3(0,3)	6853.472	−9.7	6634.656	7.8	6289.876	15.4
3(2,1)−3(1,2)			6531.921	7.7		
3(2,2)−3(1,3)	11 052.038	8.9	11 156.314	2.0	9703.208	−14.8
3(3,0)−3(2,1)	11 800.516	2.0	12 451.988	5.7	9843.395	−8.3
3(3,1)−3(2,2)	13 118.736	1.5	13 605.934	1.0	11 176.810	−6.0
4(1,3)−4(0,4)	10 285.864	−3.1	9852.093	4.1	9520.784	0.3
4(2,2)−4(1,3)	6887.433	3.2	6964.114	4.1		
4(2,3)−4(1,4)	13 357.578	2.6	13 319.165	−6.5	11 881.134	4.1
4(3,1)−4(2,2)	10 693.624	−4.3	11 403.243	3.1	8826.398	−5.2
4(3,2)−4(2,3)	13 830.121	−1.4	14 224.578	−8.1	11 902.980	30.6
5(3,2)−5(2,3)					8074.979	−10.5

[a,b] See Table 1.

TABLE 4: Rotational Constants for *trans*-3,4-Difluorocyclobutene and Its ^{13}C Isotopomers

	normal species[a]	DFCB-1-$^{13}C_1$ [a]	DFCB-3-$^{13}C_1$ [a]
A/MHz	5664.02410 (29)	5551.77544 (30)	5651.97158 (62)
B/MHz	3366.070 00(19)	3355.779 63(20)	3353.025 02(51)
C/MHz	2345.580 58(16)	2322.760 59(19)	2340.658 63(47)
κ[b]	−0.384 959	−0.360 165	−0.388 541
Δ_K/kHz	5.344(11)	5.140(22)	5.345(46)
Δ_{JK}/kHz	−1.689(10)	−1.659(19)	−1.694(40)
Δ_J/kHz	0.7762(39)	0.7669(68)	0.8204(14)
δ_J/kHz	0.2412(18)	0.2390(39)	0.2768(99)
δ_K/kHz	0.832(12)	0.7935(21)	1.080(61)
$\Delta\nu_{rms}$/kHz	1.5	0.89	1.8

[a] Uncertainties in the last two digits are given in parentheses. [b] $\kappa = (2B - A - C)/(A - C)$.

TABLE 5: Rotational Constants for Three Deuterium Isotopomers of *trans*-3,4-Difluorocyclobutene

	DFCB-1-d_1[a]	DFCB-3-d_1[a]	DFCB-d_4[a]
A/MHz	5389.7970 (21)	5519.5361 (27)	4894.9361 (44)
B/MHz	3318.5603 (22)	3316.5159 (29)	3182.0695 (16)
C/MHz	2280.7565 (17)	2338.3887 (23)	2206.0355 (15)
κ[b]	−0.332 396	−0.385 048	−0.274 027
Δ_K/kHz	4.81 (17)	5.21 (22)	3.02 (44)
Δ_{JK}/kHz	−1.56 (14)	−1.98 (19)	−1.45 (21)
Δ_J/kHz	0.75 (11)	0.85 (14)	0.7762[c]
δ_J/kHz	0.221 (27)	0.248 (36)	0.2412[c]
δ_K/kHz	0.89 (17)	1.47 (24)	0.8316[c]
$\Delta\nu_{rms}$/kHz	5.6	7.5	17.0

[a,b] See Table 4. [c] Transferred from the fitting for the normal species.

TABLE 6: Comparison of the Observed and Calculated Stark Effects for *trans*-3,4-Difluorocyclobutene

		$\Delta\nu/\epsilon^2$/(MHz cm^2/kV^2)[a]	
transition	$\|M\|$	observed	calculated[b]
$2_{02}-1_{11}$	0	−22.1	−22.1
$2_{21}-2_{12}$	1	5.71	5.69
	2	25.9	25.9
$3_{13}-2_{02}$	1	16.6	16.6
	2	61.4	61.4

[a] $\Delta\nu$ is the frequency shift from the line position in zero field. ϵ is the electric field in kilovolts per centimeter. [b] Calculated with μ = 2.0296(6) D and the rotational constants in Table 4.

TABLE 7: Cartesian Coordinates for *trans*-3,4-Difluorocyclobutene[a,b]

atom	a/Å	b/Å	c/Å
C(1)	−0.615 06	1.323 90	0.276 75
C(2)	0.615 06	1.323 90	−0.276 75
C(3)	0.652 69	−0.173 14	−0.403 14
C(4)	−0.652 69	−0.173 14	0.403 14
H(5)	−1.319 42	2.095 19	0.554 10
H(6)	1.319 42	2.095 19	−0.554 10
H(7)	0.529 46	−0.608 05	−1.408 39
H(8)	−0.529 46	−0.608 05	1.408 39
F(9)	1.738 29	−0.809 40	0.204 83
F(10)	−1.738 29	−0.809 40	−0.204 83

[a] See Figure 1 for atom numbering and coordinate definitions. [b] r_s coordinates are given for carbon and hydrogen atoms; r_0 coordinates are given for fluorine atoms.

are largely equatorial, and the associated C−H bonds are largely axial. The puckering is also seen in the $C_1C_2C_3C_4$ dihedral angle of 7.5° in Table 8, which is found in the DFT calculation as well as in the experimental results. The Costain uncertainty in this dihedral angle is greater than the angle itself, whereas the statistical uncertainty in the fitting is much less (footnote *h* in Table 8). Thus, the extent of puckering is somewhat uncertain. A surprising consequence of the ring puckering is that the $C_4-C_1=C_2-C_3$ dihedral angle of 7.6° hinged around the double bond is larger than the $C_1-C_4-C_3-C_2$ dihedral angle of 6.7° hinged around the unique C_3-C_4 bond. This difference is not obvious in Figure 1 nor by thinking about the isolated properties of single and double bonds. This difference is a geometric consequence of the shorter C=C bond and the longer C−C bond.

Despite the noticeable dihedral angle hinged around the double bond and a twist angle for the $H_5-C_1=C_2-H_6$ array of 5.4° in the r_s/r_0 structure, the C=C−H array and the contiguous C−C=C grouping lie in a plane. The sum of the $C_4-C_1=C_2$, $C_4-C_1-H_5$, and $H_5-C_1=C_2$ angles is 360°.

DFT calculations were done for several configurations of the ring to assess the potential well in the vicinity of the minimum. With the dihedral angle of the ring constrained to 0° for a planar ring, the electronic energy is 3.3 kJ/mol above the minimum energy with the puckered ring. With the dihedral angle

TABLE 8: Geometric Parameters for *trans*-3,4-Difluorocyclobutene and Related Cyclobutenes[a]

parameter	r_s/r_0[b]	r_0	DFT	cyclobutene[c]	3,3,4,4-tetrafluoro-cyclobutene[d]	hexafluoro-cyclobutene[e]
$C_1{=}C_2$	1.349(4)	1.351	1.339	1.342(4)	1.348(3)	1.333(6)
$C_1{-}C_4$	1.503(9)	1.495	1.508	1.517(3)	1.502(3)	1.478(6)
$C_3{-}C_4$	1.534(4)	1.538	1.558	1.566(3)	1.536(3)	1.552(6)
$C_1{-}H_5$	1.081(3)	1.080	1.081	1.083(3)	1.079(1)	
$C_3{-}H_7$	1.102(5)	1.104	1.092	1.094(5)		
$C_3{-}F_9$	1.398(6)	1.400	1.395		1.358(2)	1.358[f]
$C_1{=}C_2{-}C_3$	93.3(2)	93.3	93.9	94.2(5)	93.6(1)	94.3(2)
$C_2{-}C_3{-}C_4$	86.2(5)	86.2	85.7	85.8(5)	86.4(2)	85.7(2)
$C_2{=}C_1{-}H_5$	134.4(2)	134.4	134.3	133.5(5)	134.3	
$C_4{-}C_1{-}H_5$	132.3(3)	132.3	131.8	132.3	132.1(2)	
$C_2{-}C_3{-}H_7$	117.8(5)	118.3	116.5			
$C_4{-}C_3{-}H_7$	112.6(4)	112.6	113.4	114.5(5)		
$C_2{-}C_3{-}F_9$	115.9(4)	116.2	116.5		116.3	
$C_4{-}C_3{-}F_9$	115.6(5)	115.5	115.8		115.6	
$H_7{-}C_3{-}F_9$	107.7(6)	107.2	107.8			
$C_1{=}C_2{-}C_3{-}C_4$[g]	−7.5 (10.7)	−7.5[h]	−7.0	0	0	0
$C_4{-}C_1{=}C_2{-}C_3$[g]	7.6 (9.5)	7.7[h]	7.3	0	0	0
$C_2{-}C_3{-}C_4{-}C_1$[g]	6.7 (9.6)	6.8[h]	6.3	0	0	0
$H_5{-}C_1{=}C_2{-}H_6$[g]	5.4 (8.4)	5.5[h]	6.3	0	0	0

[a] Bond lengths are given in angstroms; bond angles are given in degrees. [b] Costain uncertainty is shown in parentheses. [c] Reference 22. Uncertainty is shown in parentheses. [d] Reference 7. Uncertainty is shown in parentheses. [e] Reference 11. Uncertainty is shown in parentheses. [f] Assumed. [g] Torsional angle. [h] The $\mathbf{r_0}$ uncertainties in the fitting are 1.6° for $C_1C_2C_3C_4$, 1.5° for $C_4C_1C_2C_3$, 1.6° for $C_2C_3C_4C_1$, and 2.4° for $H_5C_1C_2H_6$.

constrained to 7.05°, the opposite sign of the dihedral angle in the DFT calculation for the electronic energy minimum, the energy is 12.5 kJ/mol. With the dihedral angle constrained to −14.1°, the energy is 5.1 kJ/mol. The gas-phase frequency for the lowest vibrational mode of the *a* symmetry species of tDFCB is 171 cm^{-1},[13] a mode that must be largely the change in extent of ring puckering in the potential well around the dihedral angle of −7.5°. The frequency for this mode is 184 cm^{-1} in the liquid phase,[13] a large frequency shift with phase change for a low-frequency mode. This change in frequency with phase change must reflect the sensitivity of the potential function for ring puckering to interactions with neighboring molecules, which is likely mediated through the polar C−F bonds.

Summary

Rotational constants for six isotopomers of tDFCB have been obtained from microwave spectroscopy. The dipole moment of 2.0295(6) D points along the C_2 symmetry axis and gives B-type selection rules. Structure fitting yields complete r_s/r_0 and r_0 structures in good agreement with each other. The experimental parameters are in satisfactory agreement with the r_e parameters from a DFT/6-311+G** calculation, except for the unique C−C bond, which is 0.021 Å longer in the calculation. The experimental bond lengths in the tDFCB ring correlate with the influence of fluorine substitution on cyclobutene rings found in other microwave investigations. Fluorine substituents cause shortening of contiguous CC bonds and lengthening of distant CC bonds. However, in comparison with the spectroscopic results, the longer C−C bonds in halogen-substituted cyclobutenes found by electron diffraction remain an unsolved puzzle. The ring is somewhat puckered with the C−F bonds oriented in roughly equatorial directions.

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