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Semiexperimental Equilibrium Structures for *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene by the Mixed Estimation Method and Definitive Relative Energies of the Isomers

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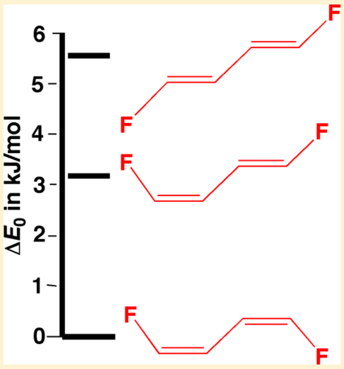
Supporting Information

ABSTRACT: Equilibrium molecular structures accurate to 0.001 Å and 0.2° have been determined for *cis,cis*- and *trans,trans*-1,4-difluorobutadiene by the semiexperimental mixed estimation method. In this method, structures are fitted concurrently to equilibrium rotational constants and bond parameters obtained from an intermediate level of electronic structure theory. The effect of fluorine substitution on the carbon backbone of butadiene is surprisingly small. Definitive energy differences for the ground states were computed, employing the focal-point analysis (FPA) technique, between the trans,trans and cis,cis isomers ($\Delta H°_0$ = 5.6(3) kJ mol^{-1}) and the cis,trans and cis,cis isomers ($\Delta H°_0$ = 3.2(2) kJ mol^{-1}) of 1,4-difluorobutadiene. These differences confirm the exceptional relationship that the trans,trans isomer has the highest energy and the cis,cis isomer the lowest energy, endorsing what was reported earlier on the basis of experimental observations in benzene solution.



1. INTRODUCTION

Development of the semiexperimental (SE) method for finding equilibrium structures, r_e^{SE}, of molecules,[1] supplemented with the mixed estimation approach,[2] has made possible determination of structures with bond lengths accurate to about 0.001 Å, and a similar four-digit accuracy for bond angles, for small and medium-sized systems. This accuracy represents a significant improvement over that of standard purely experimental techniques, such as X-ray crystallography, gas electron diffraction, and high-resolution molecular spectroscopy making direct use of ground-state (GS) rotational constants. Structural parameters involving hydrogen atoms are usually also well determined within the SE approach. In the GS, positions of atoms in a molecule are blurred by zero-point vibrations, but at equilibrium, the atoms are at rest.

The SE method alone depends on the ability to determine equilibrium rotational constants for a full suite of isotopologues and/or isotopomers. The equilibrium rotational constants, occupying a central place in the SE method, are derived from observed GS rotational constants and the lowest-order vibration−rotation interaction constants (spectroscopic "alphas"). For molecules beyond about 5 atoms, it is extremely time-consuming to determine these alphas experimentally to acceptable accuracy. It is much easier and still perfectly satisfactory[3] to compute them from quadratic and cubic force fields[4] determined via electronic structure techniques. The mixed estimation method depends on predicting r_e^{BO}, equilibrium Born−Oppenheimer, bond lengths and bond angles at a reasonably high level of electronic structure theory and then concurrently fitting a structure to equilibrium moments of inertia and computed structural parameters, *with both types of data accompanied by appropriate uncertainties.* Advantages of the mixed estimation method are that it can compensate for an incomplete set of experimental rotational constants and for small and thereby poorly determined Cartesian coordinates in the principal axis system.

Structures accurate to at least 0.002 Å are needed to assess the subtle geometric electronic changes in molecules caused by substitution of heteroatoms or the effects of conjugation in nonaromatic systems. Recent examples where this accuracy was achieved for conjugation include butadiene and hexatriene, where the effects of π-electron delocalization have been established with respect to localized C═C and sp^2−sp^2 single bonds.[5,6] As to substitution effects, the significant structural

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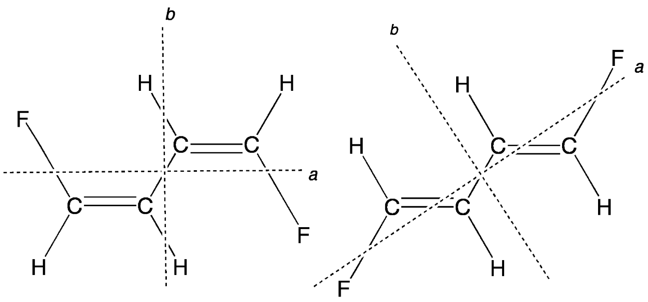
changes on CC bonds in three- and four-membered rings,[7] as well as the effect of fluorination on the highly symmetric structure of benzene,[8] are now firmly established. A related question is the effect of fluorine substitution on the CC bond lengths of 1,4-difluorobutadiene (DFBD). Previously, a semiexperimental structure of *cis,trans*-DFBD (ctDFBD) was determined from rotational constants obtained from a microwave investigation[9] in conjunction with the mixed estimation method.[10] Here we extend this study to the other two, cis,cis (cc) and trans,trans (tt), isomers of DFBD.

Our interest in the isomers of 1,4-difluorobutadiene is also based on the unusual energy relationship between these species. Although the proximity of electron-rich regions is closest for the cis,cis (cc) isomer, it has the lowest energy, as found by experiment in benzene solutions and by electronic structure computations at modest levels.[11,12] The trans,trans isomer has the highest energy, and the cis,trans (ct) isomer has an intermediate energy. This "cis effect" can be observed for several molecules, where the cis isomer has a lower energy than the corresponding trans isomer in molecules with double bonds, in particular in 1,2-dihaloethenes.[13] A related effect also occurs in saturated halocarbons, including 1,2-difluoroethane, in which the gauche rotamer is of lower energy than the anti rotamer (called the "gauche effect").[14,15] As part of the present work, definitive energy differences between the three DFBD isomers are computed within the framework of the focal-point analysis (FPA) technique.[16,17]

Obtaining a sufficient number of rotational constants for different isotopologues of ccDFBD and ttDFBD needed for determining an accurate r_e^{SE} structure is difficult. Figure 1 gives the schematic structures of these two species and the approximate locations of the principal axes of rotation. Of course, the fluorine atoms cannot be substituted with stable isotopes. Synthesizing the ^{13}C species would be a major challenge. Fortunately, it appears that GS rotational constants for the singly substituted ^{13}C species can be predicted with useful accuracy, as shown with examples from the ct isomer in section 3. Presumably, GS rotational constants for the singly substituted ^{18}F species can also be predicted with good accuracy. GS rotational constants have been determined experimentally for the parent species,[18] the *2-d*$_1$ species,[19] and the *1-d*$_1$ species[20] of the cc and tt isomers of DFBD. For ttDFBD GS rotational constants were also determined experimentally for the *1,4-d*$_2$ species.[20] Results for these nonpolar isomers of DFBD came from the analysis of high-resolution infrared (IR) spectra.



cis,cis trans,trans

Figure 1. Schematic structures of *cis,cis*- and *trans,trans*-DFBD with approximate orientations of principal rotational axes.

2. COMPUTATIONAL DETAILS

Three levels of electronic structure theory have been used in this study: second-order Møller–Plesset perturbation theory (MP2),[21] coupled cluster theory including single and double excitations (CCSD)[22] augmented with a perturbational estimate of the effects of connected triple excitations, CCSD(T),[23] and the Kohn–Sham density functional theory (DFT)[24] using Becke's three-parameter hybrid exchange functional[25] and the Lee–Yang–Parr correlation functional,[26] together denoted as B3LYP.

Several atom-centered, fixed-exponent Gaussian basis sets of the correlation-consistent (cc) family[27] have been used for the electronic structure computations. The geometry optimizations utilized polarized triple- (cc-pVTZ) and quadruple-ζ (cc-pVQZ)[27] basis sets, which are abbreviated as VTZ and VQZ, respectively, throughout this paper [with these basis sets the frozen core (FC) approximation was used at correlated levels], and the correlation-consistent polarized weighted core–valence quadruple-ζ basis set (cc-pwCVQZ),[28] abbreviated here as CVQZ. The latter basis is used to improve the computed structure by the inclusion of core correlation effects.[29] The geometry optimizations were executed with Gaussian03 (G03) on the supercomputer at Oberlin College or with Gaussian09 (G09) on the Ohio Supercomputer (OSC).[30]

Relative energies determined within the FPA approach[16,17] utilized the aug-cc-pV*n*Z Gaussian basis sets (n = 2–6) and the CFOUR electronic structure package.[31] The relativistic energy corrections were computed within the mass-velocity and one-electron Darwin (MVD1) scheme.[32,33] Anharmonic zero-point energies were computed for the FPA analysis employing CFOUR and G09 at the frozen-core MP2/VTZ and B3LYP/aug-cc-pVTZ levels, respectively. The reference structures of the cis,cis and trans,trans forms utilized for determining the FPA relative energies correspond to the best r_e^{SE} structures obtained as part of this work. The reference structure of the cis,trans form was taken from ref 10.

To estimate the electronic contribution to rotational constants, the g-tensor was computed using G03 at the B3LYP/6-311+G(3df,2pd) level. To determine the equilibrium rotational constants, alpha/2 sums are needed for the expression $B_e^\beta = B_0^\beta + {}^1/_2\sum_k \alpha_k^\beta$, where β represents the a, b, and c principal axes and k scans over the fundamental vibrations. These alpha/2 sums for the various isotopologues were computed with the program VIBROT from cubic force fields determined with G03 using the MP2/VTZ method.[34]

3. PREDICTION OF ROTATIONAL CONSTANTS

GS rotational constants for the four ^{13}C ctDFBD isotopologues are known from microwave spectroscopy.[10] Table 1 lists these observed rotational constants and two sets of predicted GS rotational constants. First, equilibrium rotational constants were calculated for each isotopologue at the MP2(FC)/VTZ level. Theoretical GS rotational constants were then found by subtracting the alpha/2 sums from the computed equilibrium rotational constants. As to the second set (data column 3 of Table 1), scale factors based on the ratios of observed and calculated A_0, B_0, and C_0 rotational constants of the parent species were defined. These scale factors were then applied to the initial, computed values of the GS rotational constants of the four ^{13}C species of ctDFBD (data column two in Table 1) to obtain improved predictions. As shown in the last column of Table 1, the agreement between the improved (scaled)

Table 1. Comparison of Predicted and Observed Ground-State Rotational Constants (in MHz) for the ^{13}C Isotopologues of *cis,trans*-DFBD

	observed[a]	calc[b]	predicted[c]	% obs − pred
		Normal		
A_0	12988.33256	13073.20531		
B_0	1467.87921	1457.26056		
C_0	1318.58436	1310.80715		
		-1-^{13}C$_1$ Trans End		
A_0	12936.89597	13022.62732	12938.08294	−0.0092
B_0	1455.98104	1445.48111	1456.01393	−0.0023
C_0	1308.45528	1300.76950	1308.48716	−0.0024
		-2-$^{13}C_1$		
A_0	12987.23622	13071.93149	12987.06702	0.0013
B_0	1467.15791	1456.55035	1467.16382	−0.0004
C_0	1317.99827	1310.22795	1318.00173	−0.0003
		-3-$^{13}C_1$		
A_0	12742.05516	12825.07159	12741.80976	0.0019
B_0	1465.88139	1455.31640	1465.92089	−0.0027
C_0	1314.38217	1306.68770	1314.44047	−0.0044
		-4-^{13}C$_1$ Cis End		
A_0	12912.11123	12995.90802	12911.5371	0.0045
B_0	1451.54352	1441.14312	1451.64432	−0.0069
C_0	1304.61374	1296.98612	1304.68133	−0.0052

[a] Reference 10. [b] Calculated at the MP2(FC)/cc-pVTZ level of electronic structure theory. [c] Scale factors for obs/calc are 0.9935079 for A_0, 1.0072867 for B_0, and 1.0059332 for C_0.

predictions and observation is always better than 0.01%. So far, the description how to predict reliable GS rotational constants of ctCFBD, a case where they are experimentally accessible and tests are possible, exemplifies the method used for the cc- and ttDFBD isotopologues.

We presume that using this method to predict the GS rotational constants of singly substituted ^{18}F species is equally good. This test was repeated for several similar molecules, the favorable results are given in Table S1 of the Supporting Information. In addition, the utility of this method was confirmed with the $^{13}C_1$ isotopologues of *cis-* and *trans*-hexatriene.[35]

Theoretical GS rotational constants were found for the ^{13}C and ^{18}F isotopologues of the cc and tt isomers of DFBD from equilibrium rotational constants and alpha/2 sums predicted with the MP2(FC)/VTZ model and the scaling method described in the first paragraph of this section. These GS rotational constants are listed in Table 2.

4. AB INITIO STRUCTURE

Preliminary estimates of the Born−Oppenheimer equilibrium structures, r_e^{BO}, of the DFBD isomers were determined at the frozen core (FC) CCSD(T)/VTZ level. During these geometry optimizations, whose results are reported in Table 3, the molecular structures of the cc and tt isomers were determined employing C_{2h} point-group symmetry. Initially, the effects of further basis set improvement (VTZ → VQZ) were investigated at the MP2 level. For the bond lengths, the largest change was found for the C−C and C=C bond lengths, which were decreased by a little more than 0.002 Å in both isomers. The largest bond angle change was found for the angle ∠C2C1H1, which was increased by a little more than 0.2°. Correlating all electrons (AE) at the MP2/CVQZ level led to the expected shortening of the bond lengths (CC, 0.003 Å; CF, 0.002 Å; CH, 0.0015 Å). The bond angles remained almost unaffected, the largest change being a small decrease of the ∠C2C1H1 angle (0.04° for the cc isomer and 0.05° for the tt isomer). When these two sets of small corrections were added to the CCSD(T)/VTZ structures, we obtained the r_e^{BO}(I) estimate to r_e^{BO}:

$$\begin{aligned} r_e^{BO}(\mathrm{I}) = {} & r[\mathrm{CCSD(T)\_FC/VTZ}] \\ & + r\{\mathrm{MP2(FC)[VQZ{-}VTZ]}\} \\ & + r[\mathrm{MP2(AE)/pwCVQZ}] \\ & - r[\mathrm{MP2(FC)/pwCVQZ}] \end{aligned} \tag{1}$$

As a check on the quality of r_e^{BO}(I), the structures were also optimized in lengthy computations at the CCSD(T)_FC/VQZ level. These optimizations yielded an r_e^{BO}(II) estimate to r_e^{BO}:

$$\begin{aligned} r_e^{BO}(\mathrm{II}) = {} & r[\mathrm{CCSD(T)\_FC/VQZ}] \\ & + r[\mathrm{MP2(AE)/pwCVQZ}] \\ & - r[\mathrm{MP2(FC)/pwCVQZ}] \end{aligned} \tag{2}$$

All the results are reported in Table 3. The results collected support the usual assumption that for regions of the potential energy surface of molecules for which single-reference methods are adequate the approximation of determining the effects of basis set improvement at the MP2 level is very good.

5. SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURES

5.1. Cis,Cis Isomer.

The GS and the SE equilibrium rotational constants for the cc isomer are given in Table 2. The GS inertial defect of the parent species, Δ_0 = −0.086 u Å^2, is rather small, confirming that the molecule is planar. The corresponding semiexperimental equilibrium inertial defect, Δ_e = −0.029 u Å^2, is significantly different from zero. Inclusion of the electronic correction reduces this value to Δ_e = −0.024 u Å^2. Thus, Δ_e is only slightly smaller than the ground-state value, whereas it is expected to be at least 1 order of magnitude smaller. This discrepancy indicates that the equilibrium semiexperimental rotational constants are not fully compatible with a planar molecule. The main source of error is certainly the rovibrational corrections applied (the alpha/2 sums). However, it is difficult to estimate the accuracy of the computed rovibrational corrections because the errors are mainly systematic. A statistical analysis of published results shows that, in the best cases, the error in alpha/2 sums is about 2%, though it can be as large as 10%.[36] It is generally larger (in percentage) for the *A* constants than for the *B* and *C* constants. If we assume that the error in Δ_e comes mainly from the *A* constant (the errors on *B* and *C* partly cancel each other), we can make the following estimate:

$$\begin{aligned} \Delta_e &= I_c^e - I_b^e - I_a^e \\ &= I_c^0 - I_b^0 - I_a^0 - [\varepsilon_c - \varepsilon_b - (\varepsilon_a + \delta\varepsilon_a)] \end{aligned} \tag{3}$$

where superscript e designates equilibrium, the ε_i ($i = a, b, c$) are defined as $\varepsilon_i = I_i^0 - I_i^e$ and can be calculated from the alpha/2 sums, and Δ_e = 0. Then,

$$\begin{aligned} \delta\varepsilon_a &= -\Delta_0 + \varepsilon_c - \varepsilon_b - \varepsilon_a \\ &= 0.086 + 1.297 - 0.964 - 0.390 \\ &= 0.029 \end{aligned} \tag{4}$$

Table 2. Conversion of Ground-State Rotational Constants to Equilibrium Rotational Constants for *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene (in MHz, unless Otherwise Stated)

		B_0	α_e^{BO} [b]	B_e^{SE} [c]	obs − calc			B_0	α_e^{BO} [b]	B_e^{SE} [c]	obs − calc
		Cis,Cis						Trans,Trans			
parent observed	A	13386.363	139.768	13526.957	−9.132	parent observed	A	31500.696	102.575	31865.607	−36.138
	B	1608.536	4.949	1613.502	−0.007		B	1168.276	−0.042	1173.335	−0.025
	C	1436.336	5.312	1441.652	−0.010		C	1126.683	−0.010	1131.733	−0.001
	Δ^a	−0.086		−0.024			Δ^a	−0.074		−0.027	
1-$^{13}C_1$ predicted	A	13226.930	137.016	13364.752	−8.751	1-$^{13}C_1$ predicted	A	31155.230	99.928	31514.230	−31.065
	B	1593.906	4.890	1598.813	0.029		B	1159.942	−0.042	1164.929	−0.021
	C	1422.836	5.248	1428.088	0.027		C	1118.490	−0.010	1123.471	0.010
	Δ^a	−0.086		−0.026			Δ^a	−0.074		−0.028	
2-$^{13}C_1$ predicted	A	13251.556	137.798	13390.164	−8.774	2-$^{13}C_1$ predicted	A	31317.130	101.657	31678.606	−39.714
	B	1607.876	4.893	1612.786	−0.004		B	1167.161	−0.039	1172.177	−0.015
	C	1434.263	5.264	1439.531	0.012		C	1125.412	−0.009	1130.420	0.004
	Δ^a	−0.091		−0.028			Δ^a	−0.075		−0.027	
1-d_1 observed	A	12571.905	122.674	12695.306	−7.046	1-d_1 observed	A	27630.837	85.583	27923.566	−26.092
	B	1581.318	5.264	1586.598	−0.197		B	1159.372	−0.050	1164.398	−0.037
	C	1405.118	5.451	1410.573	−0.010		C	1112.851	−0.003	1117.843	−0.019
	Δ^a	−0.122		−0.059			Δ^a	−0.068		−0.023	
2-d_1 observed	A	12578.662	125.991	12705.381	−7.611	2-d_1 observed	A	28150.863	87.830	28456.251	−26.898
	B	1608.411	4.925	1613.352	−0.025		B	1166.867	−0.046	1171.880	0.016
	C	1426.419	5.243	1431.666	−0.019		C	1120.558	−0.004	1125.547	−0.009
	Δ^a	−0.088		−0.024			Δ^a	−0.054		−0.007	
1-$^{18}F_1$ predicted	A	13455.222	140.333	13596.390	−9.465	1,4-d_2 observed	A	24591.945	74.320	24833.195	−19.230
	B	1640.472	5.101	1645.591	0.033		B	1150.364	−0.053	1155.372	0.019
	C	1462.585	5.464	1468.053	0.044		C	1099.066	0.004	1104.008	−0.021
	Δ^a	−0.091		−0.030			Δ^a	−0.046		0.000	
						1-$^{18}F_1$ predicted	A	31544.678	102.903	31910.153	−37.133
							B	1193.129	−0.042	1198.311	0.035
							C	1149.845	−0.009	1155.018	0.062
							Δ^a	−0.076		−0.029	

[a] Inertial defect, $\Delta = I_c - I_a - I_b$ in u Å^2. [b] Rovibrational correction obtained from the cubic force field calculated at the MP2(FC)/VTZ level of theory. [c] Includes the *g*-factor correction. SE = semiexperimental.

Table 3. Ab Initio Structure in Internal Coordinates for *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene (in Å and deg)

method:	MP2(FC)	MP2(FC)	MP2(FC)	MP2(AE)	CCSD(T)_FC	CCSD(T)_FC		
basis set:	VTZ	VQZ	pwCVQZ	pwCVQZ	VTZ	VQZ	r_e^{BO}(I)	r_e^{BO}(II)
				Cis,Cis				
r(C—C)	1.4475	1.4454	1.4450	1.4418	1.4559	1.4537	1.4506	1.4505
r(C═C)	1.3337	1.3313	1.3309	1.3277	1.3367	1.3339	1.3311	1.3307
r(CH inner)	1.0793	1.0789	1.0788	1.0773	1.0812	1.0809	1.0793	1.0794
r(CF)	1.3425	1.3419	1.3416	1.3394	1.3450	1.3442	1.3422	1.3420
r(CH outer)	1.0789	1.0780	1.0779	1.0765	1.0806	1.0798	1.0783	1.0784
∠(CCC)	123.80	123.81	123.81	123.82	123.76	123.77	123.78	123.78
∠(C3C2H inner)	119.46	119.54	119.55	119.53	119.10	119.18	119.16	119.16
∠(C1C2H inner)	116.74	116.64	116.65	116.65				
∠(CCF)	121.98	121.82	121.83	121.85	121.82	121.68	121.68	121.70
∠(CCH outer)	125.20	125.41	125.41	125.37	125.38	125.59	125.55	125.55
				Trans,Trans				
r(C—C)	1.4479	1.4458	1.4455	1.4422	1.4562	1.4539	1.4506	1.4508
r(C═C)	1.3331	1.3305	1.3301	1.3269	1.3362	1.3331	1.3299	1.3304
r(CH inner)	1.0821	1.0815	1.0815	1.0800	1.0841	1.0836	1.0821	1.0820
r(CF)	1.3399	1.3397	1.3395	1.3372	1.3421	1.3416	1.3393	1.3396
r(CH outer)	1.0806	1.0796	1.0796	1.0781	1.0824	1.0816	1.0801	1.0799
∠(CCC)	121.85	121.81	121.79	121.84	121.92	121.90	121.95	121.93
∠(C3C2H inner)	119.62	119.63	119.64	119.62	119.30	119.31	119.29	119.29
∠(C1C2H inner)	118.53	118.56	118.57	118.54				
∠(CCF)	121.78	121.60	121.60	121.63	121.61	121.43	121.46	121.46
∠(CCH outer)	125.24	125.50	125.50	125.45	125.42	125.69	125.64	125.63

Table 4. Internal Coordinate Values for *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene (in Å and deg)

		r_e^{SE} [b]			
m predicates:	r_e^{BO} [a]	5[c]	9[d]	0	9[d]
n isotopologues:		3/4[e]	3[e]	6/7[f]	6/7[f]
		Cis,Cis			
r(C—C)	1.4505	1.450(2)	1.451(1)	1.440(12)	1.4504(6)
r(C═C)	1.3307	1.330(1)	1.330(1)	1.337(11)	1.3300(5)
r(C—H inner)	1.0794	1.089(9)	1.080(1)	1.076(13)	1.0796(6)
r(C—F)	1.3420	1.344(1)	1.341(1)	1.348(7)	1.3423(4)
r(CH outer)	1.0784	1.076(3)	1.079(1)	1.0731(46)	1.0787(6)
∠(CCC)	123.78	123.6(1)	123.71(8)	122.9(15)	123.68(5)
∠(C3C2H inner)	119.16	118.7(10)	119.18(10)	120.2(16)	119.18(6)
∠(C1C2H inner)					117.14(8)
∠(CCF)	121.70	121.7(1)	121.61(6)	121.88(7)	121.64(4)
∠(CCH outer)	125.55	126.4(2)	125.66(9)	126.7(8)	125.58(6)
		Trans,Trans			
r(C—C)	1.4506	1.443(4)		1.430(15)	1.4502(10)
r(C═C)	1.3299	1.327(2)		1.339(8)	1.3301(7)
r(C—H inner)	1.0821	1.102(7)		1.079(10)	1.0824(10)
r(C—F)	1.3393	1.337(2)		1.345(6)	1.3391(8)
r(CH outer)	1.0801	1.077(6)		1.084(6)	1.0812(10)
∠(CCC)	121.95	123.6(3)		121.3(9)	121.91(9)
∠(C3C2H inner)	119.29	117.1(10)		120.1(12)	119.26(10)
∠(C1C2H inner)					118.83(13)
∠(CCF)	121.46	121.2(2)		121.7(3)	121.31(5)
∠(CCH outer)	125.64	125.0(3)		125.8(3)	125.77(7)

[a] See last column of Table 3. [b] The numbers given in parentheses are the standard deviations of the parameters in the unit of the last digit. For the fitted parameters they are obtained from the least-squares fit and for the derived parameter [∠(C1C2H) inner] from the law of propagation of errors. Note that no parameters are fixed. [c] *r*(C—C), *r*(C═C), *r*(C—F), ∠(CCC), and ∠(CCF) are taken from the data in column 1 with uncertainties of 0.002 Å for bond lengths and 0.2° for bond angles. [d] Predicates taken from the data column 1 with uncertainties of 0.002 Å for bond lengths and 0.2° for bond angles. [e] Normal species and deuterated species, 3 for cis,cis and 4 for trans,trans. [f] All isotopologues, 6 for the cis,cis form and 7 for the trans,trans isomer (Table 2).

This value is to be compared with the residual equilibrium inertial defect, before the electronic correction, of −0.029 u Å^2. These values show excellent agreement. The relative error $\delta\varepsilon_a/\varepsilon_a$ is then 7.4%. We will see below that this error is in good agreement with the residuals of the *A* constants in the structural fits, i.e., about 10 MHz. For this reason, the *A* rotational constants were given lower weight in the subsequent fits with an uncertainty of 100 MHz.

There is also a particular problem with the rotational constants of the *1-d*$_1$ species of the cc isomer. The residual inertial defect, Δ_e = −0.064 u Å^2 (before the electronic correction), is much too large. This problem can be traced to the accuracy of the experimental data. Although the sum $B + C$ should be fairly accurate, the individual values are perhaps not. If we increase *B* by 0.05 MHz and decrease *C* by the same amount, Δ_e is reduced to −0.035 u Å^2. This small change is compatible with the standard deviations of the GS rotational constants, $\sigma(B_0)$ = 0.045 MHz and $\sigma(C_0)$ = 0.030 MHz. A reevaluation of the analysis of the rotational structure in the high-resolution IR spectrum of ccDFBD-*1-d*$_1$ suggests that the uncertainties in B_0 and C_0 are about twice as large as reported.[20] Furthermore, if we calculate the GS inertial defect from the MP2(FC)/VTZ force field, we can conclude that it should be almost identical for the parent and for the *1-d*$_1$ species, thereby confirming the inaccuracy of at least one GS rotational constant for the d$_1$ species.

Table 4 contains internal coordinate values resulting from the different fits. The second data column of Table 4 gives a first fit using the equilibrium rotational constants of the parent cc isomer and its two deuterated species, as well as five predicate values [*r*(C—C), *r*(C═C), *r*(C—F), ∠(CCC), and ∠(CCF)] taken from the first data column of Table 4, with an uncertainty of 0.002 Å for bond lengths and 0.2° for bond angles. This determination of the positions of the carbon, fluorine, and hydrogen atoms is not satisfactory. The inner (C2H2) bond length is particularly inaccurate. This failure is due to the *a* coordinate of the H2 atom being quite small, *a*(H2) = −0.159 Å (vide infra). Furthermore, the standard error of the outer (C1H1) bond length is as large as 0.0028 Å, pointing out a possible problem with the rotational constants of the *1-d*$_1$ species. Actually, this problem was expected from the abnormal value of the inertial defect, as seen above. To minimize this problem, a new fit was made with a complete set of predicate values (nine), as shown in data column three in Table 4. This fit was satisfactory, and the parameters, although not very precise, were found to be in good agreement with the r_e^{BO} values, as seen in Table 4. Furthermore, the rotational constants of the ^{13}C species and of the hypothetical ^{18}F species were calculated from this fitted structure and were compared to their predicted values, as described in section 3. The pleasing agreement with the predicted rotational constants, as seen in Table 5, confirms that GS rotational constants for single ^{13}C and single ^{18}F substitution can be predicted accurately.

Subsequently, a new fit for the cc isomer was made with the full set of rotational constants (semiexperimental and predicted) but without predicate values, as shown in data column four of Table 4. Unfortunately, the result was not satisfactory, the standard deviations of the parameters turned

Table 5. Predicted Equilibrium Rotational Constants for *cis,cis*-1,4-Difluorobutadiene (in MHz)

species		*A*	*B*	*C*
1-^{13}*C*	calc[a]	13364.91	1598.71	1428.05
	pred[b]	13364.75	1598.81	1428.09
	calc − pred	0.15	−0.11	−0.04
2-^{13}*C*	calc[a]	13390.20	1612.73	1439.51
	pred[b]	13390.16	1612.79	1439.53
	calc − pred	0.04	−0.06	−0.02
1-^{18}*F*	calc[a]	13596.78	1645.42	1467.95
	pred[b]	13596.21	1645.59	1468.05
	calc − pred	0.57	−0.17	−0.11

[a] Calculated from the r_e^{SE} structure of Table 4, data column 5. [b] Ab initio predicted; see section 3.

Table 6. Comparison of the Cartesian Coordinates for *cis,cis*-1,4-Difluorobutadiene As Derived from Kraitchman's Equations with Those from the Fitted r_e^{BO} Structure (in Å)

	r_e^{BO}[a]		Kraitchman			
	a	*b*	*a*	*b*	Δ*a*	Δ*b*
			Using I_a and I_b			
C1	1.7044	0.6796	1.7016	0.6795	0.0029	0.0001
C2	0.3754	0.6208	0.3741	0.6203	0.0012	0.0004
F1	2.4574	−0.4307	2.4594	−0.4291	−0.0020	−0.0015
H1	2.2941	1.5829	2.2999	1.5833	−0.0059	−0.0003
H2	−0.1588	1.5589	−0.1702	1.5582	0.0114	0.0007
			Using I_b and I_c			
C1	1.7044	0.6796	1.7016	0.6783	0.0029	0.0013
C2	0.3754	0.6208	0.3741	0.6169	0.0012	0.0039
F1	2.4574	−0.4307	2.4594	−0.4361	−0.0020	0.0054
H1	2.2941	1.5829	2.3001	1.5719	−0.0060	0.0110
H2	−0.1588	1.5589	−0.1702	1.5583	0.0114	0.0006

[a] See last column of Table 3.

out to be large and the condition number[2] to be extremely high, $\kappa = 10981$. This ill-conditioning is mainly due to the presence of several small coordinates, in particular $a(\mathrm{H2}) = 0.159$ Å and $a(\mathrm{C2}) = 0.375$ Å. Normally, when one small coordinate is present, it can still be determined by the first-moment equation, which is automatically fulfilled in a least-squares fit. However, as ccDFBD has a centrosymmetric equilibrium structure, the first-moment equation is always verified whatever the value of the Cartesian coordinates. To get around this difficulty, the full set of predicate values was reintroduced. The resulting fit, as seen in the last column of Table 4, was satisfactory, the condition number reduced to $\kappa = 288$. The standard deviations of the parameters were small, and the parameters were in good agreement with the r_e^{BO} values of Table 3. Parameters in the last column of Table 4 are accepted as the best estimate of the equilibrium structure of ccDFBD.

It is interesting to look at the residuals of the fit in Table 2. The median of the residuals for the *A* constants is 8.8 MHz, in good agreement with the discussion of the inertial defect, which see above. The median of the residuals for the *B* and *C* constants is 27 and 15 kHz, respectively, indicating that most of these constants are accurate. However, there is one exception: the *B* constant of the *1-d*$_1$ species, for which the residual is as large as −197 kHz. This large residual and the abnormal value of the inertial defect confirm that the *B* rotational constant of the *1-d*$_1$ species is inaccurate. However, a larger value for this *B* constant would be accompanied by a smaller value of the *C* constant, thereby degrading its agreement with the fit.

To get more insight into the difficulties in obtaining an accurate structure using only rotational constants, it is useful to apply Kraitchman's equations for planar molecules[37] and to compare the derived Cartesian coordinates with those obtained from the best fit with predicates. This analysis can be done using either the *A* and *B* or the *B* and *C* rotational constants (assuming that the inertial defect is zero). Results for the cc isomer are given in Table 6. In both cases two coordinates are inaccurate, $a(\mathrm{H1})$ and, in particular, $a(\mathrm{H2})$. For $a(\mathrm{H2})$, the inaccuracy is a consequence of this coordinate being quite small, 0.159 Å, making it sensitive to small errors. $a(\mathrm{H1})$ is determined mainly by $B(1\text{-}d_1)$. The discrepancy indicates that this experimental rotational constant is inaccurate, as anticipated from the discussion on the inertial defect. When the *B* and *C* rotational constants are used, $b(\mathrm{H1})$ also becomes inaccurate. As this coordinate is sensitive to the rotational constants *B* and *C* of the *1-d*$_1$ species, the problem with $b(\mathrm{H1})$ confirms that at least one of these rotational constants is inaccurate. With these two exceptions, the other coordinates are accurate, thereby confirming that the predicted rotational constants are accurate enough.

5.2. Trans,Trans Isomer. The GS and semiexperimental equilibrium rotational constants for the tt isomer are given in Table 2. Predicate values for the bond parameters were found as for the cc isomer and given in Table 3. The same general procedure for structure fitting was followed for the tt isomer as for the cc isomer. The results are given in Table 4.

The overall situation for the tt isomer is quite similar to that found for the cc isomer. The GS inertial defect of the parent species, $\Delta_0 = -0.074$ u Å^2, is reasonably small, but the semiexperimental equilibrium inertial defect, $\Delta_e = -0.032$ u Å^2, is significantly different from zero. Inclusion of the electronic correction reduces Δ_e to −0.027 u Å^2. This value is still non-negligible, indicating that the equilibrium semiexperimental rotational constants are not fully compatible with a planar molecule. As for the cc isomer, the main source of error is certainly the rovibrational correction (inaccuracy of the alpha/2 sums). The *A* constant is about 27 times larger than the *B* and *C* constants. Furthermore, the errors on *B* and *C* partly cancel each other. Thus, it seems justified to assume that the error mainly comes from the *A* constants. Using eq 4, we find $\delta\varepsilon_a = 0.032$ u Å^2, which is again almost identical to the residual equilibrium inertial defect. This indicates that the semiexperimental *A* constants are about 60 MHz too small. This discrepancy is in qualitative agreement with the residuals of the *A* constants in the structural fits (vide infra). Again, the *A* constants were given lower weights in the fits with an uncertainty of 100 MHz. Inspection of the GS and equilibrium inertial defects (see Table 2), indicates a possible accuracy problem in the experimental values for the rotational constants of the *2-d*$_1$ and *1,4-d*$_2$ species as the inertial defects are smaller than expected compared to those of the other isotopologues.

A fit using only the observed semiexperimental rotational constants and five predicate values to specify the positions of the heavy atoms was not satisfactory, the internal coordinate values of the hydrogen atoms had large standard errors. A fit with seven sets of rotational constants (four observed and three predicted) but without predicate values was also not satisfactory, the system of normal equations was ill-conditioned, similar to what was observed for the cc isomer. Again, this complication is due to the presence of several small coordinates: $b(\mathrm{C1}) = -0.426$ Å, $b(\mathrm{C2}) = 0.304$ Å, and $b(\mathrm{F})$

= 0.148 Å. As for the cc form, this difficulty can be resolved by the introduction of a full set of predicate values, as seen in the last column of Table 4. In this last fit, the standard deviations of the parameters were small, and the parameters were in good agreement with the r_e^{BO} values of Table 3. The residuals for the rotational constants of the last fit are given in Table 2. As expected, the residuals are large for the *A* constants; however, the residuals for the *B* and *C* constants do not show any outlying behavior. The bond parameters for ttDFBD in the last column in Table 4 are the accepted ones.

6. STRUCTURAL COMPARISONS

Table 7 provides a comparison of the equilibrium geometric parameters of the three isomers of DFBD and *trans*-*s*-butadiene (BD). The differences are small and would be largely unnoticeable if the method were less accurate than 0.001 Å. The C—C and C=C bond lengths and the CCF bond angles are essentially constant across the three isomers of DFBD. Other bond parameters in the cis half of the ct isomer correlate with the cc isomer, and other bond parameters in the trans half of the ct isomer correlate with the tt isomer. The most significant difference between the cc and tt isomers is the larger CCC bond angle in the cc isomer, reflecting relief of greater crowding of electron-rich regions in this species. The outer CH bonds are a few 0.001 Å longer in the tt isomer, whereas the C−F bond length is shorter by a similar amount in the tt isomer. The length of the inner CH bond is essentially the same except in the tt isomer. The large C=CH bond angles involving the fluorine-substituted carbon atoms reflect the expected enhancement of a carbon p orbital contribution to the strong CF bond and the consequent depletion of p character in the carbon orbital contribution to the CH bond orbital. This reduced p character of the CH bond leads to a larger C=CH angle.

Table 7. Comparison of Geometric Parameters for Various Butadienes (Distances in Å and Angles in Degrees)

		ctDFBD[a]			
	ccDFBD	cis half	trans half	ttDFBD	butadiene[b]
r(C—C)	1.4504	1.4469		1.4502	1.4539
r(C=C)	1.3300	1.3302	1.3297	1.3301	1.3376
r(C—H inner)	1.0796	1.0804	1.0800	1.0824	1.0847
r(C—F)	1.3423	1.3425	1.3385	1.3391	
r(C—H outer)	1.0787	1.0786	1.0807	1.0812	1.0819(c), 1.0793(t)
∠(CCC)	123.68	124.19	121.56	121.91	123.6
∠(C1C2H inner)	117.14	116.4	119.0	118.83	119.9
∠(CCF)	121.64	121.51	121.52	121.31	
∠(C2C1H outer)	125.58	125.7	125.6	125.77	121.5(c), 121.0(t)

[a]Reference 10. [b]Reference 5.

The only structural clue to the lower energy of cc isomer relative to the tt isomer is the longer CF bond in the cc isomer. However, this outcome is opposite to the difference in bond lengths in the cis and trans isomers of 1,2-difluoroethylene, where the lower energy cis isomer has the shorter CF bond length.[13]

Comparison of bond parameters of the DFBD isomers with BD[5] shows the effects of fluorine substitution (Table 7). The CCC bond angle in the tt isomer is 1.7° smaller than in BD. Thus, the electronic influence of fluorine substitution decreases this angle in the tt isomer only for the CCC angle to be increased to 123.68° in the cc isomer to relieve congestion of electron-rich regions. Although the outer CH bond lengths of the DFBD isomers agree rather well with the corresponding cis or trans CH bond lengths in BD, the inner CH bond lengths are shorter than in BD. The shortening of the CF bonds in the tt isomer could be related to some double bond character in the CF bonds in this isomer. Throughout the three isomers of DFBD, the effects of fluorine substitution on bond lengths in the carbon atom backbone are smaller than the large effects found in 1,1-difluorocyclopropane.[7] In the latter molecule the CC bonds involving the F-substituted carbon atom are shortened by 0.033 Å, and the distant CC bond is lengthened by 0.043 Å, as compared to case of cyclopropane itself.[7] In the DFBD isomers the C=C bonds are shortened by only about 0.008 Å compared to those of BD.[5] The central C—C bond is also *shortened* a bit, by 0.004 Å in the cc and tt isomers and 0.007 Å in the ct isomer.

7. RELATIVE ENERGIES OF THE ISOMERS

An excellent way to determine relative energies of classes of molecules, especially of isomers, is provided by the focal-point analysis (FPA) method.[16,17] It has been used successfully to determine relative conformer or isomer energies a number of times even for large and complex biomolecules, including amino acids, such as glycine,[38] alanine,[39] and proline.[40]

Table 8. Focal-Point Analysis of the Relative Energy of the ttDFBD and ccDFBD Isomers (in cm^{-1})[a]

	ΔE_e(RHF)	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	ΔE_e[CCSD(T)]
aug-cc-pVDZ	588.7	+100.0	−61.4	+9.2	636.5
aug-cc-pVTZ	526.8	+140.4	−56.6	+13.4	624.0
aug-cc-pVQZ	523.4	+138.4	−55.1	+13.5	620.2
aug-cc-pV5Z	523.1	+138.6			
aug-cc-pV6Z	523.0	+137.8			
CBS	[523.0]	[+136.8]	[−54.0]	[+13.6]	**[619.4]**
extrapolation	$a + b(n+1)\exp(-9\sqrt{n})$ $(n = 5, 6)$	$a + bn^{-3}$ $(n = 5, 6)$	$a + bn^{-3}$ $(n = 3, 4)$	$a + bn^{-3}$ $(n = 3, 4)$	

ΔE_0(final) = ΔE_e[CCSD(T)/CBS] + Δ_{core}[CCSD(T)/cc-pwCVQZ] + Δ_{rel}[CCSD(T)/cc-pwCVQZ] + Δ_{ZPVE}[MP2(FC)/cc-pVTZ] = 619.4 − 3.5 + 0.5 − 146 = **470(21)** cm^{-1}

[a]The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy RHF → MP2 → CCSD → CCSD(T). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced. See text for the uncertainty estimate of the final value.

Table 9. Focal-Point Analysis of the Relative Energy of the ctDFBD and ccDFBD Isomers (in cm^{-1})[a]

	ΔE_e(RHF)	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	ΔE_e[CCSD(T)]
aug-cc-pVDZ	334.8	+27.9	−22.6	+0.9	341.0
aug-cc-pVTZ	303.0	+53.7	−19.8	+2.9	339.8
aug-cc-pVQZ	300.8	+55.1	−19.1	+2.9	339.6
aug-cc-pV5Z	300.7	+54.3			
aug-cc-pV6Z	300.6	+54.1			
CBS	[300.6]	[+53.8]	[−18.6]	[+2.9]	**[338.6]**
extrapolation	$a + b(n+1)\exp(-9\sqrt{n})$ $(n = 5, 6)$	$a + bn^{-3}$ $(n = 5, 6)$	$a + bn^{-3}$ $(n = 3, 4)$	$a + bn^{-3}$ $(n = 3, 4)$	

ΔE_0(final) = ΔE_e[CCSD(T)/CBS] + Δ_{core}[CCSD(T)/cc-pwCVQZ] + Δ_{rel}[CCSD(T)/cc-pwCVQZ] + Δ_{ZPVE}[B3LYP/aug-cc-pVTZ] = 338.6 − 0.1 + 0.2 − 79 = **260(16)** cm^{-1}

[a] The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy RHF → MP2 → CCSD → CCSD(T). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced. See text for the uncertainty estimate of the final value.

Through convergent FPA computations, the energy differences between the isomers of DFBD have been determined accurately for the first time. Other recent energy calculations for the cis and trans isomers were at lower levels of theory.[14,15]

Part of the FPA approach is the determination of the complete basis set (CBS) and full configuration interaction (FCI) limits for each isomer. These limits of electronic structure theory can be approached efficiently by using the correlation-consistent (aug-)cc-pVnZ basis sets and the coupled cluster (CC) hierarchy. In this study explicit electronic energy, E_e, computations have been performed by employing the aug-cc-pVnZ [n = 2(D), 3(T), 4(Q), 5, 6] Gaussian basis sets and the RHF (restricted Hartree−Fock), MP2, CCSD, and CCSD(T) levels of theory. Extrapolations to the CBS limit followed well-established two-parameter formulas.[41,42] As seen in Tables 8 and 9, for the energy differences for pairs of isomers of DFBD convergence toward both the CBS and FCI limits is extremely fast; thus, the associated uncertainties of the relative energies are small, on the order of a couple of cm^{-1} for the CBS FCI values. Correlation-consistent basis sets with diffuse functions are employed specifically to treat the possible hydrogen bonding and long-range interactions.

Showing rapid convergence to the CBS limit, the RHF relative energies for both the tt−cc and ct−cc pairs are converged to better than 0.5 cm^{-1} using the aug-cc-pVQZ basis set. The electron correlation energy increments in the MP2 → CCSD → CCSD(T) sequence show less rapid but still fast convergence. HF theory proves somewhat unreliable for the conformational energetics, showing some 10% error even with large basis sets. The MP2 correlation energy correction, as usual, is too large, in the CBS limit MP2 overestimates the correlation energy difference between the isomers by up to 40%. With a more sophisticated treatment of electron correlation, CCSD results in an excellent estimate, which is corrected by the inclusion of triples by just a small amount. The final frozen-core result for the tt−cc relative energy is ΔE_e[CCSD(T)/CBS] = 619.4 cm^{-1}. Several benchmark studies[16,17,43−46] have shown that δ[CCSDT(Q)] relative-energy increments are typically about an order of magnitude smaller than δ[CCSD(T)] increments. On the basis of the CCSD and CCSD(T) relative energy increments, incorporation of connected quadruple excitations in the coupled-cluster wave function series is deemed to be unnecessary in the present case. Appending the effect of core electron correlation (Δ_{core}), computed at the CCSD(T)/CVQZ level, we obtain ΔE_e = 615.9 cm^{-1} for the tt−cc energy difference. The relativistic correction is minuscule, only 0.5 cm^{-1}. Considering all sources of error, our final equilibrium energy difference is ΔE_e = 619.4(50) cm^{-1}, in which the uncertainty estimate represents a 95% confidence interval. A completely similar analysis yields an estimate of ΔE_e = 338.6(50) cm^{-1} for the energy difference between the ct and cc isomers, firmly establishing the energy order of these isomers.

As shown in Table 8, the lower energy for the cc isomer is captured at the RHF level. Electron correlation reinforces this difference by almost 100 cm^{-1}.

Anharmonic zero-point vibrational energy (ZPVE) estimates are computed to be 185.2, 184.5, and 183.5 kJ mol^{-1} at the MP2/cc-pVTZ level for the cc, ct, and tt isomers, respectively. The corresponding anharmonic ZPVE values at the B3LYP/aug-cc-pVTZ level are 183.2, 182.3, and 181.4 kJ mol^{-1} amounts, respectively. The harmonic values are higher by about 2.1(1) kJ mol^{-1}. Thus, ZPVE decreases the tt−cc and ct−cc energy separations by substantial 146(20) and 79(15) cm^{-1}, respectively, taking the average of the computed values. This yields, ΔE_0 = 470(21) and 260(16) cm^{-1} for the relative energies, respectively. Thus, ZPVE effects constitute about one-quarter of the energy differences at 0 K. The increased uncertainty estimates refer basically to our inability to determine highly accurate anharmonic ZPVE corrections for the isomers studied.

Direct comparison of the present theoretical values with experiment needs correction of the computed values for temperature and pressure effects. This adjustment is straightforward to do via techniques of statistical mechanics. Nevertheless, because the presently available experimental results[11,12] were obtained in benzene solution at 378 K, hindering direct comparison, these corrections are not reported here. We note that qualitative observations of the gas-phase equilibrium composition at 373 K, made during synthetic work,[19] showed an outcome similar to that found in benzene solution.

8. CONCLUSIONS

Ground-state rotational constants for the parent and deuterated species of *cis*,*cis*- and *trans*,*trans*-1,4-difluorobutadiene are known from high-resolution IR spectroscopy. Thanks to ab initio calculations and subsequent scaling corrections, it was possible to predict the ground-state rotational constants of the ^{13}C and ^{18}F species with useful accuracy. Corrections for vibration−rotation interaction and electronic effects have given semiexperimental equilibrium rotational constants. Despite the full data sets, the semiexperimental equilibrium structures based on rotational constants are somewhat inaccurate. This failure is mainly due to the presence of several small coordinates whose harmful effect cannot be counterbalanced by the first-moment equations because of the centrosymmetric structure of these molecules. However, ab initio calculations and a mixed estimation procedure have led to acceptable planar semi-experimental equilibrium structures (r_e^{SE}) for both isomers studied. As the final r_e^{SE} structure is very close to the ab initio r_e^{BO} structure used for the mixed estimation, one may wonder whether it is useful to determine an r_e^{SE} structure. Doing so has two advantages: (i) the theoretical r_e^{BO} structure proves to be compatible with the semiexperimental equilibrium rotational constants (in other words, the r_e^{SE} structure confirms the accuracy of the r_e^{BO} structure found at an intermediate level of theory); (ii) the standard deviations of the fitted parameters of the r_e^{SE} structure are smaller than the assumed uncertainties of the predicate data (i.e., the final r_e^{SE}structure should be more accurate than the r_e^{BO}structure).

Systematic differences are found between the structures of the three isomers of 1,4-difluorobutadiene. When fluorine substitution is cis, as in the cc or ct isomers, the CCC angle is larger than when fluorine substitution is trans. The CH bonds are a few 0.001 Å longer in the tt isomer, whereas the C−F bond length is shorter by a similar amount in the tt isomer.

Effects of fluorine substitution in butadiene are also considered. In particular, the effects of fluorine substitution on the carbon atom backbone in butadiene are muted in comparison with the corresponding effects on the C_3 ring in 1,1-difluorocyclopropane.

Highly accurate energy differences between the isomers DFBD are computed. The experimental energy differences found from equilibrium measurements in benzene solution are consistent with the new, definitive results from theory: under all circumstances studied cis,cis is the most stable and trans,trans the least stable isomer of 1,4-difluorobutadiene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 contains tests of predictions of GS rotational constants for isotopologues of 1,1-difluoroethylene, *cis*-1,2-difluoroethylene, and *trans*-1,2-difluoroethylene.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Stanton, J.; Vasquez, J. Semiexperimental Equilibrium Structures; Computational Aspects. In *Equilibrium Molecular Structures*; Demaison, J., Boggs, J. E., Császár, A. G., Eds.; CRC Press: Boca Raton, FL, 2011; pp 53−87.

(2) Demaison, J. The Method of Least Squares. In *Equilibrium Molecular Structures*; Demaison, J., Boggs, J. E., Császár, A. G., Eds.; CRC Press: Boca Raton FL, 2011; pp 29−52.

(3) Dunn, K. M.; Boggs, J. E.; Pulay, P. Vibrational Energy Levels of Hydrogen Cyanide. *J. Chem. Phys.* **1986**, *85*, 5838−5846.

(4) Császár, A. G. Anharmonic Force Fields. *WIREs Comput. Mol. Sci.* **2012**, *2*, 273−289.

(5) Craig, N. C.; Groner, P.; McKean, D. C. Equilibrium Molecular Structures for Butadiene and Ethylene: Compelling Evidence for Π-Electron Delocalization in Butadiene. *J. Phys. Chem. A* **2006**, *110*, 7461−7469.

(6) Craig N. C.; Chen, Y.; Fuson, H. A.; Tian, H.; van Besien, H.; Conrad, A. R.; Tubergen, M. J.; Rudolph, H. D.; Demaison J. Microwave Spectra of the Deuterium Isotopologues of *cis*-Hexatriene and a Semiexperimental Equilibrium Structure. *J. Phys. Chem. A* **2013**, *117*, DOI: 10.1021/jp311035c

(7) Craig, N. C.; Feller, D.; Groner, P.; Hsin, H. Y.; McKean, D. C.; Nemchick, D. J. Vibrational Spectroscopy of 1,1-Difluorocyclopropane-d_0, -d_2, -d_4: The Equilibrium Molecular Structure. *J. Phys. Chem. A* **2007**, *111*, 2498−2506.

(8) Demaison, J.; Rudolph, H.-D.; Császár, A. G. Deformation of the Benzene Ring upon Fluorination: Equilibrium Structures of All Fluorobenzenes. *Mol. Phys.* **2013**, *111*, 1539−1562.

(9) Craig, N. C.; Oertel, C. M.; Oertel, D. C.; Tubergen, M. J.; Lavrich, R. J.; Chaka, A. M. Structure of *cis,trans*-1,4-Difluorobutadiene from Microwave Spectroscopy. *J. Phys. Chem. A* **2002**, *106*, 4230−4235. See slightly revised rotational constants in the Supporting Information for ref 10.

(10) Demaison, J. F.; Craig, N. C. Semiexperimental Equilibrium Structure for *cis,trans*-1,4-Difluorobutadiene by the Mixed Estimation Method. *J. Phys. Chem. A* **2011**, *115*, 8049−8054.

(11) Viehe, H.-G.; Franchimont, E. Geometrische Isomerenpaare mit Bevorzugter *cis*-Struktur, VI 1.4-Difluor- und 1.4-Dichlor-butadien-(1,3). *Chem. Ber.* **1964**, *97*, 602−609.

(12) Craig, N. C.; Neese, C. F.; Nguyen, T. N.; Oertel, C. M.; Pedraza, L. Vibrational Spectroscopy of the Three Isomers of 1,4-Difluorobutadiene. *J. Phys. Chem. A* **1999**, *103*, 6726−6739. The experimental values for the energy differences for cc-to-ct and ct-to-tt were exchanged in Figure 1.

(13) Feller, D.; Craig, N. C. Ab Initio Coupled Cluster Determination of the Equilibrium Structures of *cis*- and *trans*-1,2-Difluoroethylene and 1,1-Difluoroethylene. *J. Phys. Chem. A* **2011**, *115*, 94−98.

(14) Yamamoto, T.; Kaneno, D.; Tomoda, S. The Origin of Cis Effect in 1,2-Dihaloethenes: The Quantitative Comparison of Electron Delocalizations and Steric Exchange Repulsions. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1415−1422.

(15) Chaudhuri, R. K.; Hammond, J. R.; Freed, K. F.; Chattopadhyay, S.; Mahapatra, U. S. Reappraisal of *cis* Effect in 1,2-Dihaloethenes: An Improved Virtual Orbital Multireference Approach. *J. Chem. Phys.* **2008**, *129*, 064101/1−9.

(16) Allen, W. D.; East, A. L. L.; Császár, A. G. Ab Initio Anharmonic Vibrational Analyses of Non-Rigid Molecules. In *Structures and Conformations of Non-Rigid Molecules*; Laane, J., Dakkouri, M., van der Veken, B., Oberhammer, H., Eds.; Kluwer: Dordrecht, The Netherlands, 1993; pp 343−373.

(17) Császár, A. G.; Allen, W. D.; Schaefer, H. F., III. In Pursuit of the Ab Initio Limit for Conformational Energy Prototypes. *J. Chem. Phys.* **1998**, *108*, 9751−9765.

(18) Craig, N. C.; Moore, M. C.; Neese, C. F.; Oertel, D. C.; Pedraza, L.; Masiello, T. High-Resolution Infrared Spectra of the Two Nonpolar Isomers of 1,4-Difluorobutadiene. *J. Mol. Spectrosc.* **2009**, *254*, 39−46.

(19) Craig, N. C.; Easterday, C. C.; Nemchick, D. J.; Williamson, D. F. K.; Sams, R. L. Rotational Analysis of Bands in the High-resolution Infrared Spectra of *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene-2-d_1. *J. Mol. Spectrosc.* **2012**, *272*, 2−10.

(20) Craig, N. C.; Chen, Y.; Lu, Y.; Neese, C. F.; Nemchick, D. J.; Blake, T. A. Analysis of the Rotational Structure in the High-resolution Infrared Spectra of *cis,cis*- and *trans,trans*-1,4-Difluorobutadiene-1-d_1 and *trans,trans*-1,4-Difluorobutadiene-1,4-d_2. *J. Mol. Spectrosc.* **2013**, *288*, 18−27.

(21) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.

(22) Purvis, G. D., III; Bartlett, R. J. A Full Coupled-cluster Singles and Doubles Model: the Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(23) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A. Fifth-order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

(24) Kohn, W.; Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. *J. Phys. Rev. A* **1965**, *140*, 1133−1138.

(25) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(26) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

(27) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(28) Peterson, K. A.; T. H. Dunning, T. H., Jr. Accurate Correlation Consistent Basis Sets for Molecular Core−valence Correlation Effects: the Second Row Atoms Al−Ar, and the First Row Atoms B−Ne Revisited. *J. Chem. Phys.* **2002**, *117*, 10548−10560.

(29) Császár, A. G.; Allen, W. D. The Effect of 1s Correlation on D_e, r_e, and ω_e of First-Row Diatomics. *J. Chem. Phys.* **1996**, *104*, 2746−2748.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.: Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revisions C.02, 2004 and E.01, 2007 and *Gaussian 09*, revision C.01, 2011; Gaussian, Inc.: Wallingford, CT.

(31) *CFOUR*, a quantum chemical program package written by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G., with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; et al. For the current version, see http://www.cfour.de.

(32) Tarczay, G.; Császár, A. G.; Klopper, W.; Quiney, H. M. Anatomy of Relativistic Energy Corrections in Light Molecular Systems. *Mol. Phys.* **2001**, *99*, 1769−1794.

(33) Cowan, R. D.; Griffin, D. C. Approximate Relativistic Corrections to Atomic Radial Wave Functions. *J. Opt. Soc. Am.* **1976**, *66*, 1010−1014.

(34) Groner, P.; Warren, R. D. Approximate r_e Structures from Experimental Rotational Constants and ab initio Force Fields. *J. Mol. Struct.* **2001**, *599*, 323−335.

(35) Craig, N. C.; Tian, H.; Blake, T. A. Analysis of the Rotational Structure in the High-Resolution Infrared Spectrum of *trans*-Hexatriene-1-$^{13}C_1$; A Semiexperimental Equilibrium Structure for the C_6 Backbone of *trans*-Hexatriene. *J. Phys. Chem. A* **2012**, *116*, 3148−3155.

(36) Vogt, N.; Vogt, J.; Demaison, J. Accuracy of Rotational Constants. *J. Mol. Struct.* **2011**, *988*, 119−127.

(37) Kraitchman, J. Determination of Molecular Structure from Microwave Spectroscopic Data. *Am. J. Phys.* **1953**, *21*, 17−24.

(38) Kasalová, V.; Allen, W. D.; Schaefer, H. F., III; Czinki, E.; Császár, A. G. Molecular Structures of the Two Most Stable Conformers of Glycine. *J. Comput. Chem.* **2007**, *28*, 1373−1383.

(39) Jaeger, H. M.; Schaefer, H. F., III; Demaison, J.; Császár, A. G.; Allen, W. D. Lowest-Lying Conformers of Alanine: Pushing Theory to Ascertain Precise Energetics and Semi-Experimental R_e Structures. *J. Chem. Theory Comput.* **2010**, *6*, 3066−3078.

(40) Allen, W. D.; Czinki, E.; Császár, A. G. Molecular Structure of Proline. *Chem.—Eur. J.* **2004**, *10*, 4512−4517.

(41) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. Basis-Set Convergence of Correlated Calculations on Water. *J. Chem. Phys.* **1997**, *106*, 9639−9646.

(42) Tasi, G.; Császár, A. G. Hartee-Fock Limit Energies and Structures with a Few Dozen Gaussians. *Chem. Phys. Lett.* **2007**, *438*, 139−143.

(43) Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquéz, J.; Stanton, J. F. HEAT: High Accuracy Extrapolated *Ab Initio* Thermochemistry. *J. Chem. Phys.* **2004**, *121*, 11599−11613.

(44) Császár, A. G.; Szalay, V.; Senent, M. L. *Ab Initio* Torsional Potential and Transition Frequencies of Acetaldehyde. *J. Chem. Phys.* **2004**, *120*, 1203−1207.

(45) Császár, A. G.; Leininger, M. L.; Szalay, V. The Enthalpy of Formation of CH_2. *J. Chem. Phys.* **2003**, *118*, 10631−10642.

(46) Császár, A. G.; Allen, W. D.; Yamaguchi, Y.; Schaefer, H. F., III. *Ab Initio* Determination of Accurate Potential Energy Hypersurfaces for the Ground Electronic States of Molecules. In *Computational Molecular Spectroscopy*; Jensen, P., Bunker, P. R., Eds.; Wiley: New York, 2000; pp 15−68.