Molecular Structures of Fluorinated Cyclobutenes: A Coupled-Cluster Investigation

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Highly accurate equilibrium molecular structures have been determined for the molecules cyclobutene, 1,2-difluorocyclobutene, 1,2-dicyanocyclobutene, *trans*-3,4-difluorocyclobutene, 1,4,4-trifluorocyclobutene, 3,3,4,4-tetrafluorocyclobutene, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, hexafluorocyclobutene, bicyclo[2.2.0]hex-1(4)-ene, and octafluorobicyclo[2.2.0]hex-1(4)-ene at the CCSD(T) level employing basis sets up to cc-pCVQZ. The resulting definitive structural parameters, those obtained with basis sets of at least cc-pVTZ quality, support several investigations of these species employing microwave (MW) spectroscopy, at the best levels with an average error of only about 3 MHz for the rotational constants. Nevertheless, the computations also point out inadequacies of some of the experimental structural parameters. Vibrationally averaged distances and rotational constants have been obtained at the 6-31G* RHF level. Careful interpretation of the equilibrium and vibrationally averaged theoretical results point out problems with gas electron diffraction (GED) investigations of the molecular structure of hexafluorocyclobutene and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene. Most importantly, the computations prove that the length of the C−C bond opposite to the double bond becomes shorter upon fluorination and not longer, as the GED investigations have indicated.

I. Introduction

To understand structural effects accompanying the introduction of fluorines into simple hydrocarbon rings, fluorinated cyclobutenes have been studied in considerable detail.[1−14] One of the most unusual discoveries of the gas electron diffraction (GED) studies on the systems hexafluorocyclobutene (HFCB)[1−3] and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (DCTC)[5] was the repeated, consistent occurrence of an elongated C_3−C_4 bond, opposite to the C_1=C_2 double bond, about 1.58 Å. This result is somewhat perplexing, as in structural investigations of HFCB,[6] 3,3,4,4-tetrafluorocyclobutene (TFCB),[7] DCTC,[9] 1,4,4-trifluorocyclobutene (cTFCB),[14] and *trans*-3,4-difluorocyclobutene (tDFCB),[10] using microwave (MW) spectroscopy such long C_3−C_4 bonds have never been obtained; in fact, the MW results suggest a C_3−C_4 distance of 1.54−1.55 Å, which is *shorter* than that in cyclobutene (CB), $r_s = 1.566(3)$ Å,[4] a value reasonably well established both experimentally and theoretically (vide infra). Furthermore, a concentrated effort[3] to bring GED and MW results for HFCB in accord resulted one more time in an elongated C_3−C_4 bond not significantly different from the pure GED value.

Though the size of substituted cyclobutenes disallowed large-scale (and thus definitive) ab initio structural investigations in the past, electronic structure results[2,3] obtained from entry-level calculations at the restricted Hartree−Fock (RHF) level all resulted in significantly shorter C_3−C_4 bond lengths for fluorinated cyclobutenes than in the parent cyclobutene. The more recent ab initio calculations on fluorinated cyclobutenes, performed at the RHF and second-order Møller−Plesset (MP2) levels,[8] which should still be considered indecisive about the length of the C_3−C_4 bond, resulted again, independently of the basis set employed, in short C_3−C_4 distances. On the other hand, some density functional theory (DFT) calculations predicted a slightly elongated C_3−C_4 bond.[8] Because theory seemed to remain in contradiction with a careful combined, state-of-the-art GED+MW analysis of the structure of HFCB[3] concerning the length of the C_3−C_4 bond, and because considerably larger calculations are feasible than those reported,[8,13] in this study extensive ab initio geometry optimizations were undertaken to address the structural issues in fluorinated cyclobutenes. The large-scale theoretical calculations, based primarily on the highly accurate[15] coupled cluster (CC) technique CCSD(T), including all single, double, and a perturbative estimate of triple substitutions,[16] with extended basis sets,[17] finally are able to provide definitive structural predictions. Vibrational averaging effects[18] are taken into account to bridge the gap between equilibrium and effective structural parameters.

After a short summary of the computational details results from geometry optimizations at several correlated levels with basis sets of varying quality are reported for the parent molecule cyclobutene (CB), and for related (mostly) fluorinated molecules, almost all of which have been studied by either GED, MW spectroscopy or both: 1,2-difluorocyclobutene (DFCB), 1,2-dicyanocyclobutene (DCCB), *trans*-3,4-difluorocyclobutene, 1,4,4-trifluorocyclobutene, 3,3,4,4-tetrafluorocyclobutene, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, perfluorocyclobutene, bicyclo[2.2.0]hex-1(4)-ene (BH) (basically containing two CB rings fused at the double bond), and octafluorobycyclo[2.2.0]-hex-1(4)-ene (OFBH). After detailed discussion of the most relevant structural results, the paper is ended with concluding remarks.

II. Computational Details

Several basis sets have been selected for this study. The systematic, correlation-consistent, polarized-valence (aug-)cc-p(C)VnZ [with $n = 2$(D), 3(T), 4(Q)] basis sets of Dunning and co-workers[17] have been used extensively in this study. Split-valence basis sets have also been employed, including the 6-31G*, 6-31G**, and 6-311++G** basis sets.[19,20] All d, f, and g sets of all basis sets, except the 6-31G-type ones where the six Cartesian d functions have been employed, included only the five, seven, and nine pure spherical harmonics, respectively.

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Electronic wave functions and the corresponding analytic forces needed for geometry optimizations, resulting in equilibrium (r_e) structures, were determined by the single-configuration, self-consistent-field, restricted Hartree−Fock (RHF) method,[20] by second-order Møller−Plesset (MP2)[20,21] theory, and by coupled cluster methods including all single and double excitations (CCSD)[22] and CCSD(T).[16] In MP2 and CC geometry optimizations, due to program limitations, all electrons were correlated. Although these optimizations correlated all the electrons, it is known that the (aug-)cc-pV*n*Z basis sets are unable to describe core correlation effects. Therefore, in a few cases all-electron CCSD(T) geometry optimizations were also performed with the aid of the cc-pCV*n*Z ($n = 3$ and 4) basis sets, augmented with tight functions able to describe core-core and core-valence correlation effects. The residual Cartesian gradients in all optimizations were less than 5×10^{-5} hartree bohr^{-1}. All molecules investigated but tDFCB, of C_2 point group symmetry, were constrained to possess at least a symmetry plane during geometry optimizations. Many of the symmetrically substituted molecules were assumed to have C_{2v} symmetry, whereas BH and OFBH were assumed to have D_{2h} symmetry. The stationary points obtained were only checked at the 6-31G* RHF level, where all optimized structures proved to be minima.

Cubic force fields[23] for all compounds have been obtained at the 6-31G* RHF level at the respective optimized geometries. Vibration−rotation interaction constants (α_r^B) to correct the directly measured A_0, B_0, and C_0 rotational constants have been obtained from these force fields. Distance corrections $r_g - r_e$ have also been obtained from these force fields.

All ab initio electronic structure computations were performed with the program package ACES II,[24] whereas DFT(B3LYP) optimizations utilized the program GAUSSIAN94.[25]

III. Results and Discussion

The structural results of the CCSD(T) geometry optimizations, employing various correlation-consistent basis sets up to cc-pCVQZ, obtained for all 10 species considered are collected in Table 1. Note that Table 1 contains not only the directly computed equilibrium geometry results but also $r_g - r_e$ distance corrections and $B_0 - B_e$ rotational constant corrections. All corrections were computed at the 6-31G* RHF level.

A. Comparison of Computed and MW Results. Because, as part of this study, $B_0 - B_e$ rotational constant corrections have been computed, at the reasonably accurate[26,27] 6-31G* RHF level, one can directly compare the theoretical rotational constants with those measured experimentally. It is clear from Table 1 that at the highest levels of theory (cc-pVTZ CCSD(T) and beyond) the computed equilibrium rotational constants agree excellently with the measured ones, the average deviation just slightly exceeds 2 MHz. Especially pleasing is the agreement for those molecules that do not contain hydrogens, suggesting that all heavy atom−heavy atom distances are computed with remarkable precision. Even for CB, where the $B_0 - B_e$ corrections are on the order of 50−100 MHz, the deviations between the cc-pVTZ through cc-pCVQZ CCSD(T) and the experimental rotational constants are only on the order of 1−32 MHz. Due to favorable error compensation, the best agreement between CCSD(T) theory and experiment is observed when the medium-sized cc-pVTZ basis is employed for the ab initio optimization. Although aug-cc-pVTZ and cc-pVQZ CCSD(T) results are farther away from experiment, the changes in this convergent series are so small that they affect none of the conclusions of the present paper. Furthermore, the same results suggest that the cc-pVTZ CCSD(T) equilibrium geometry parameters should be accurate to better than ±0.002 Å and ±0.2°.

Agreement between the computed CCSD(T) and measured[8] MW structural parameters for cyclobutene is excellent. Especially satisfactory is the agreement between experiment and theory at the cc-pVTZ and cc-pCVQZ CCSD(T) levels. Though this is not surprising for the latter level of theory (this optimization utilized 516 contracted Gaussian functions), a favorable error compensation makes the cc-pVTZ CCSD(T) rotational constants especially accurate.

We are not aware of experimental MW data for 1,2-difluorocyclobutene, for which the computed cc-pVTZ CCSD(T) structural results of Table 1, and the related rotational constants, should be considered definitive.

There is good agreement between the r_0 structural parameters of DCCB and the calculated r_e (r_g) ones. The problems with the r_s substitution structure obtained for this molecule, apparent from the entries of Table 1, have already been discussed in the original publication.[11]

The experimental r_s structure of TFCB[7] is basically correct. Nevertheless, the C═C−C bond angle is too small and, consequently, the C_3−C_4 bond length too short.

The recent r_s structure of DCTC[9] appears to be the least dependable among the substituted cyclobutenes studied. Though rather large uncertainties have been attached to the ring parameters, most structural results are still out of their range.

In summary, our high-quality ab initio structural results obtained at the cc-pVTZ CCSD(T) level and beyond are fully consistent with the available rotational constant data, especially after taking the vibrational averaging into account. Furthermore, the MW geometric structures, obtained by structural analyses based on the rotational constants of several substituted species, are in most cases validated by the present definitive ab initio results. The same ab initio results make possible prediction of yet unobserved rotational constants, for example, those of BH, as follows. Because the cc-pVTZ CCSD(T) rotational constants proved to be excellent for CB, and they can even be improved upon multiplication by a scale factor of 0.9996, adding to the computed rotational constants of BH the $B_0 - B_e$ corrections, obtained at the 6-31G* RHF level, result in the following scaled estimates: $A_0 = 8517.9(30)$, $B_0 = 3409.3(30)$, and $C_0 = 2590.7(30)$ MHz, where the conservative estimated error (2σ) is 3 MHz.

B. Comparison of Theoretical and GED Structural Parameters. GED measures atom−atom distances, and related rms vibrational amplitudes, and thus distances, including nonbonded ones, and not angles should be compared directly to the optimized theoretical results. Furthermore, GED structure analyses result in r_α^0, r_α, r_g, or r_a geometry parameters, thus, similarly to most MW structural studies, direct comparison with equilibrium geometry parameters may not be fully justified. Nevertheless, for the highly rigid structures investigated here the differential vibrational effects are about the same for all molecules, as is clear from the $r_g - r_e$ entries of Table 1.

GED studies have provided various bond lengths for the carbon−carbon double bond of substituted cyclobutenes. The two extremes are the long C═C bond of $r_g = 1.376(14)$ Å for OFBH (ref 12) and the short bond of $r_\alpha^0 = 1.325(24)$ Å for HFCB.[3] Our equilibrium theoretical results show a considerably smaller spread, 1.332 Å (DFCB and OFBH) to 1.349 Å (DCCB), of the C═C bond length around its value in CB, 1.342 Å, all obtained at the cc-pVTZ CCSD(T) level. The calculations

TABLE 1: Selected Structural Results and Rotational Constants, Obtained at the CCSD(T) Level with Various Basis Sets, and Their Experimental Counterparts for Substituted Cyclobutenes[a]

	$r(C_1{=}C_2)$	$r(C_2{-}C_3)$	$r(C_3{-}C_4)$	$r(C_1{-}X)$	$r(C_4{-}X)$	∠C=C−X	∠C=C−C	$\angle C_3{-}C_4{-}X$	∠X−C−X	A_e	B_e	C_e
Cyclobutene (CB)												
cc-pVDZ	1.3613	1.5315	1.5785	1.0973	1.1058	133.44	94.07	114.71	108.91	12698.87	12024.60	6711.66
aug-cc-pVDZ	1.3637	1.5343	1.5835	1.0959	1.1043	133.45	94.11	114.60	109.17	12655.39	11995.66	6690.81
cc-pVTZ	1.3422	1.5154	1.5654	1.0773	1.0878	133.55	94.22	114.60	109.14	13005.25	12317.15	6870.63
cc-pCVTZ	1.3437	1.5188	1.5684	1.0819	1.0905	133.48	94.24	114.62	109.12	12958.19	12257.61	6841.81
aug-cc-pVTZ	1.3431	1.5163	1.5665	1.0798	1.0902	133.42	94.22	114.36	109.36	12994.27	12284.63	6861.67
cc-pVQZ	1.3407	1.5142	1.5637	1.0796	1.0886	133.47	94.22	114.61	109.10	13025.02	12325.90	6879.48
cc-pCVQZ	1.3409	1.5153	1.5647	1.0808	1.0896	133.44	94.24	114.64	109.07	13010.36	12306.57	6870.23
$r_g - r_e$	0.0058	0.0072	0.0090	0.0187	0.0201							
exp,[4] r_s	1.342(4)	1.517(3)	1.566(3)	(1.083)	1.094(5)	133.5	94.2			13000.14	12309.91	6868.99
										(12892.88)	(12226.11)	(6816.25)
1,2-Difluorocyclobutene (DFCB)												
cc-pVDZ	1.3502	1.5171	1.5823	1.3353	1.1040	135.33	94.39	114.21	110.02	4753.79	3721.71	2145.91
aug-cc-pVDZ	1.3506	1.5184	1.5908	1.3467	1.1023	134.88	94.54	113.96	110.63	4698.05	3713.83	2132.15
cc-pVTZ	1.3316	1.5002	1.5714	1.3232	1.0861	135.25	94.58	113.97	110.42	4853.91	3809.23	2193.72
cc-pCVTZ	1.3340	1.5043	1.5744	1.3242	1.0889	135.12	94.58	114.01	110.38	4826.92	3805.47	2187.23
aug-cc-pVTZ	1.3318	1.5004	1.5734	1.3249	1.0885	134.97	94.62	113.78	110.64	4830.23	3819.08	2192.55
cc-pVQZ	1.3308	1.4998	1.5704	1.3220	1.0869	135.12	94.58	113.96	110.44	4850.49	3821.90	2197.32
$r_g - r_e$	0.0054	0.0066	0.0100	0.0056	0.0200							
1,2-Dicyanocyclobutene (DCCB)												
cc-pVDZ	1.3691	1.5309	1.5764	1.4380	1.1034	133.35	93.98	115.06	109.76	2667.24	1814.29	1095.16
aug-cc-pVDZ	1.3699	1.5326	1.5821	1.4384	1.1021	133.58	93.97	114.97	110.04	2682.06	1798.54	1091.88
cc-pVTZ	1.3485	1.5132	1.5640	1.4166	1.0856	133.63	94.08	114.95	109.94	2753.86	1858.04	1125.21
$r_g - r_e$	0.0054	0.0068	0.0096	0.0058	0.0200							
exp,[11] r_0	1.361	1.515	1.567	1.420	1.088	133.3	93.9			2747.77	1859.74	1124.78
										(2742.89)	(1855.35)	(1121.56)
exp,[11] r_s	1.326(2)	1.522(3)	1.578(2)	1.426(2)			94.7(2)					
trans-3,4-Difluorocyclobutene (tDFCB)												
cc-pVDZ	1.3619	1.5227	1.5640	1.0952	1.3830	134.21	93.55			5543.93	3346.92	2309.41
aug-cc-pVDZ	1.3647	1.5223	1.5641	1.0934	1.4035	134.45	93.52			5543.76	3300.73	2300.60
cc-pVTZ	1.3431	1.5056	1.5495	1.0754	1.3750	134.36	93.68			5681.64	3399.32	2356.43
$r_g - r_e$	0.0059	0.0074	0.0082	0.0186	0.0067							
exp,[10] r_0	1.351	1.495	1.538	1.080	1.400	134.4	93.3			5683.56	3390.27	2358.07
										(5664.02)	(3366.07)	(2345.58)
1,4,4-Trifluorocyclobutene (cTFCB)												
cc-pVDZ	1.3530	1.5152	1.5606	1.3299	1.3593	134.81				3582.58	2567.88	2071.86
aug-cc-pVDZ	1.3543	1.5129	1.5624	1.3399	1.3541	134.76				3545.25	2547.17	2056.69
cc-pVTZ	1.3336	1.4990	1.5467	1.3171	1.3495	134.82				3649.40	2618.39	2115.27
$r_g - r_e$	0.0055	0.0063	0.0082	0.0058	0.0060							
exp[14]										3649.90	2613.41	2110.23
										(3629.31)	(2600.74)	(2098.93)
3,3,4,4-Tetrafluorocyclobutene (TFCB)												
cc-pVDZ	1.3621	1.5206	1.5696	1.0939	1.3541	134.12	93.91	114.81	107.68	2796.75	1950.53	1943.28
aug-cc-pVDZ	1.3646	1.5189	1.5736	1.0920	1.3657	134.48	93.94	115.02	107.34	2775.70	1930.34	1916.24
cc-pVTZ	1.3432	1.5038	1.5601	1.0742	1.3436	134.22	94.14	114.99	107.64	2854.33	1980.33	1967.31
cc-pCVTZ	1.3446	1.5083	1.5654	1.0789	1.3442	134.26	94.20	115.02	107.52	2847.44	1969.92	1961.03
aug-cc-pVTZ	1.3437	1.5039	1.5603	1.0762	1.3459	134.23	94.13	114.91	107.47	2846.20	1977.27	1966.37
$r_g - r_e$	0.0060	0.0072	0.0071	0.0184	0.0059							
exp,[7] r_s	1.350	1.500	1.542	1.080	1.357		93.7		106.2	2852.63	1974.69	1966.19
										(2839.29)	(1961.52)	(1952.95)
1,2-Dichlorotetrafluorocyclobutene (DCTC)												
cc-pVDZ	1.3617	1.5193	1.5693	1.7045	1.3494	134.82	93.92	114.85	108.08	1004.28	986.89	605.98
aug-cc-pVDZ	1.3632	1.5176	1.5740	1.7057	1.3603	134.75	93.98	114.99	107.79	997.66	982.41	603.51
cc-pVTZ	1.3430	1.5029	1.5602	1.6874	1.3390	134.81	94.14	115.01	108.06	1021.90	1007.86	618.20
$r_g - r_e$	0.0052	0.0066	0.0074	0.0051	0.0059							
exp,[5] $r_{g,\alpha}$	1.359(9)	1.500(6)	1.599(10)	1.687(3)	1.340(2)	133.9(3)	94.6(2)		108.2(4)			
exp,[9] r_s	1.311(15)	1.487(15)	1.551(15)				94.6(6)			1026.96	1005.50	618.79
										(1022.44)	(1001.45)	(616.07)
Hexafluorocyclobutene (HFCB)												
cc-pVDZ	1.3550	1.5116	1.5696	1.3194	1.3509	135.21	94.07	114.60	107.95	1447.54	1430.09	969.84
aug-cc-pVDZ	1.3570	1.5115	1.5763	1.3253	1.3607	135.05	94.16	114.81	107.71	1437.55	1414.19	961.87
cc-pVTZ	1.3374	1.4962	1.5618	1.3058	1.3402	135.16	94.30	114.78	107.92	1477.45	1451.24	987.45
$r_g - r_e$	0.0054	0.0065	0.0076	0.0050	0.0059							
exp,[3] r_g	1.319	1.499	1.581	1.307	1.341	135.2	95.0	114.5				
exp,[3] r_α^0	1.325	1.501	1.583			135.1			107.6			
exp,[6] r_s	1.333(6)	1.478(6)	1.552(6)				94.3(2)			1476.06	1450.00	985.34
										(1467.78)	(1443.78)	(980.19)

TABLE 1 (Continued)

	$r(C_1{=}C_2)$	$r(C_2{-}C_3)$	$r(C_3{-}C_4)$	$r(C_1{-}X)$	$r(C_4{-}X)$	$\angle C{=}C{-}X$	$\angle C{=}C{-}C$	$\angle C_3{-}C_4{-}X$	$\angle X{-}C{-}X$	A_e	B_e	C_e
					Bicyclo[2.2.0]hex-1(4)-ene (BH)							
cc-pVDZ	1.3385	1.5451	1.6108		1.1057		95.06	114.29	109.03	8254.76	3319.80	2522.06
aug-cc-pVDZ	1.3406	1.5495	1.6158		1.1045		95.09	114.17	109.37	8222.23	3304.34	2510.44
cc-pVTZ	1.3186	1.5286	1.5985		1.0879		95.25	114.14	109.28	8434.29	3396.92	2578.44
aug-cc-pVTZ	1.3188	1.5295	1.5994		1.0902		95.26	114.00	109.42	8426.21	3391.18	2575.37
cc-pVQZ	1.3180	1.5286	1.5958		1.0887		95.22	114.21	109.22	8448.73	3396.67	2579.77
$r_g - r_e$	0.0057	0.0064	0.0101		0.0201							
					Octafluorobicyclo[2.2.0]hex-1(4)-ene (OFBH)							
cc-pVDZ	1.3513	1.5366	1.6059		1.3427		94.75	114.18	108.79	1008.29	528.84	461.71
aug-cc-pVDZ	1.3536	1.5358	1.6117		1.3530		94.82	114.23	108.56	996.46	525.85	458.83
cc-pVTZ	1.3316	1.5193	1.5988		1.3325		95.05	114.33	108.77	1018.96	540.87	470.71
$r_g - r_e$	0.0056	0.0065	0.0077									
exp,[12] $r_{g,\alpha}$	1.376(14)	1.530(3)	1.627(5)		1.336(2)							

[a] Bond lengths (r) in ångstroms, bond angles ($\angle$) in degrees, rotational constants (A, B, C) in MHz. X = H or F, but for DCCB, BH, and OFBH, depending on the given molecule. The experimental rotational constants have been corrected to correspond to equilibrium values (the corrections have been computed at the 6-31G* RHF level), the directly measured A_0, B_0, and C_0 rotational constants are given in parentheses. The distance corrections $r_g - r_e$ have been computed at the 6-31G* RHF level.

support neither the very short C═C bond length of the joint GED and MW study[3] for HFCB nor the very long bond length in OFBH.[12]

The difference between the C═C and C─F bond lengths may not be obtained as accurately from GED experiments as the average value, because the relative weight of the C═C/C─F scattering is small and decreases with increasing fluorination. Let Δr be defined as $\Delta r = r_e(C{-}F) - r_e(C{=}C)$, where $r_e(C{-}F)$ is the weighted average of the C─F bond lengths. In DFCB, with a short C─F bond length, Δr is negative, −0.0084 Å at the cc-pVTZ CCSD(T) level, changing to −0.0069 Å at the aug-cc-pVTZ CCSD(T) level. In TFCB, with a long C─F bond length, Δr is positive, +0.0004 Å at the cc-pVTZ CCSD(T) level. (Note, at the same time, the incorrect result obtained with the small and inflexible cc-pVDZ basis set.) This comparison again reveals discrepancies between theory and GED experiments.

As mentioned in the Introduction, most of the controversy between GED and MW structural determinations of fluorinated cyclobutenes focused on the length of the $C_3{-}C_4$ bond, opposite to the $C_1{=}C_2$ double bond. In HFCB[2,3] and DCTC[5] substantial lengthening of the $C_3{-}C_4$ bond was obtained by GED, which was accompanied by the artificial simultaneous shortening of the C═C bond (consequently, the computed and measured $C_1{-}C_4$ bond lengths, of which there are two in these molecules, agree nicely). According to all of our high-level ab initio structural estimates, the length of the $C_3{-}C_4$ bond in HFCB should be *shorter* than that in CB. Even when possible effects due to the different definitions of the distances are taken into account, the GED+MW $C_3{-}C_4$ bond length[3] proves to be much too long. (In fact, for r_g-type distances the relative decrease of the $C_3{-}C_4$ bond length upon fluorination becomes even more pronounced.) Consequently, the discrepancy between structural results of HFCB obtained by MW spectroscopy and GED results dating back to 1971[1] is resolved in favor of the MW structure exhibiting a shortened $C_3{-}C_4$ distance upon fluorination.

C. Geometric Results from Lower Levels of Theory. After discussion of the definitive CCSD(T) results and the geometric variations in fluorinated cyclobutenes, it is worth taking a look at results obtained from lower levels of theory, presented in Table 2 for the difference between the $C_3{-}C_4$ bond length in HFCB, TFCB, and DCTC and that of CB.

It is a well recognized general tendency in ab initio geometry optimizations that enlargement of the one-particle basis set tends to shorten bonds, whereas extension of the n-particle treatment, as it includes more electron correlation effects, tends to elongate bonds. Thus, if a bond is believed to be calculated too short both at the RHF and MP2 levels, just as $C_3{-}C_4$ in the case of fluorinated cyclobutenes (cf. Table 1), then not necessarily enlargement of the basis but use of an electron correlation treatment more sophisticated than MP2 is mandatory. If, for HFCB, the highly correlated CCSD(T) treatment, using modest basis sets, fails to yield $C_3{-}C_4$ bond lengths in the range of the GED measurements, then it cannot be expected that by enlarging the basis set calculations will converge to the GED results instead of the MW ones. Manifestations of these arguments are clearly visible in Table 2.

TABLE 2: Lower-Level ab Initio Results for the Relative Bond Length, Δr/Å, of the C3─C_4 Bond in Fluorinated Cyclobutenes As Compared to That in Cyclobutene Itself[a]

		Δr		
method	basis	HFCB	TFCB	DCTC
RHF	6-31G**	−0.018	−0.020	−0.019
	6-311++G**	−0.011	−0.014	−0.013
	cc-pVTZ	−0.009	−0.012	−0.011
	cc-pVQZ	−0.006	−0.009	−0.008
MP2	6-311++G**	−0.003	−0.005	−0.006
	cc-pVTZ	−0.002	−0.004	−0.004
	aug-cc-pVTZ	−0.002	−0.004	
CCSD	cc-pVDZ	−0.010	−0.010	−0.010
	cc-pVTZ	−0.005	−0.006	−0.006
CCSD(T)	cc-pVTZ	−0.004	−0.005	−0.005
DFT(LDA+BP)[b]	TZP	+0.007		
DFT(B3LYP)	6-311++G**	+0.004	+0.000	+0.001
	cc-pVTZ	+0.005	+0.002	+0.003

[a] HFCB = hexafluorocyclobutene; TFCB = 3,3,4,4-tetrafluorocyclobutene; DCTC = 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene. [b] Ref 13.

All RHF and MP2 calculations predict short $C_3{-}C_4$ bond lengths for HFCB, TFCB, and DCTC. For example, the longest calculated $C_3{-}C_4$ bond length for HFCB at the levels of theory probed is 1.564 Å obtained at the 6-31G* MP2 level, which, nevertheless, should be compared to 1.567 Å calculated at the same level of theory for CB. One tendency, namely the significant elongation of the $C_3{-}C_4$ bond at the MP2 level of theory as compared to RHF is clear. This is expected, however, from all past experiences with ab initio methods, and its extent, about 0.015 Å, is clearly not enough to make the calculated $C_3{-}C_4$ bond length of HFCB longer than that in the parent cyclobutene even at this level of theory. Note, at the same time, that all density functionals investigated, including the highly popular B3LYP, predict wrong changes in the $C_3{-}C_4$ bond length upon fluorination.

Therefore, one can conclude that all levels of ab initio electronic structure theory are in agreement in that fluorination in cyclobutenes does not result in a substantially elongated C_3-C_4 bond; in fact, all levels correctly predict a contraction of this bond, in agreement with the definitive CCSD(T) results.

D. Structural Features of Fluorinated Cyclobutenes. We noted in our earlier study[2] that in fluorinated cyclobutenes "shortening or lengthening of the bonds is the outcome of competition between orbital rehybridization at the carbons and Coulomb repulsion between the atoms. In the language of orbital rehybridization the increased number of fluorines attached to a carbon atom increases the s character of the carbon bonds and tends to shorten *all* the bonds around that carbon. Coulomb repulsion occurs between the induced positive charges on the carbon atom; these changes lead to withdrawal of electrons from the bond between carbons and to its consequent lengthening." As became clear in sections III.A and III.B, none of the experimental studies yielded fully dependable and consistent structures for fluorinated cyclobutenes. Therefore, in this subsection a somewhat qualitative discussion of the structural features of fluorinated cyclobutenes is based principally on high-quality equilibrium CCSD(T) geometric parameters of the present study.

First explore the changes in the C=C bond length upon fluorination. If the hydrogens attached to C=C are substituted with fluorines, the bond, as expected by rehybridization arguments, contracts, e.g., by 0.010 Å for DFCB. Fluorine substitution on C_3-C_4 has an order of magnitude smaller effect on $r(C=C)$; for TFCB and tDFCB, the change is a consistent lengthening by only about 0.001 Å. The effect of fluorination on $C_1=C_2$ and C_3-C_4 does not prove to be additive, in HFCB the change is a reduction in r_e by -0.005 Å. Note that the GED $r_\alpha^0(C=C)$ distance of 1.325(24) Å[2,3] appears to be too short for HFCB though the correct value lies well within the claimed error limit. The C=C bond length in BH is significantly and consistently shorter by about 0.024 Å than in C_4H_6. Unlike all other CC bonds investigated in this study, this bond becomes somewhat longer upon perfluorination, though still shorter in OFBH than in HFCB, most likely as a direct consequence of ring strain. Therefore, unlike for HFCB, the experimentally determined GED value,[17] $r_g(C=C) = 1.376(14)$ Å, now appears to be too long.

The next point of interest is the relative length of the two possible C−F bonds. As expected, the $-C_3-F$ and $=C_1-F$ bond lengths are substantially different. At the cc-pVTZ CCSD(T) level the difference in DFCB vs TFCB is 0.020 Å with the $-C_3-F$ bond being longer. Basically, the same result is obtained for HFCB, though the calculated difference grows to a more substantial $+0.034$ Å. In HFCB these differences can be easily rationalized by s−p hybridization arguments; furthermore, the difference is fully consistent with the GED value,[2,3] $+0.034$ Å.

Due to ring strain both the sp^2-sp^3 and sp^3-sp^3 C−C single bonds are longer than normal in CB. MW structural analysis, in accordance with simple rehybridization arguments, suggested that upon fluorination these bonds become shorter. GED experiments, on the other hand, resulted in elongated C−C bonds. Computations support the simple picture that all C−C bonds become shorter upon fluorination.

Rigidity of the cyclobutene ring can be seen from the minuscule variations in the C=C−C angles among the substituted cyclobutenes. At the cc-pVTZ CCSD(T) level the spread in this angle among the substituted cyclobutenes considered is only 0.5°, where the computed values spread around that in CB, 94.22°. Therefore, in the case of the r_s structure of DCCB not only the C=C bond length can be questioned but also this bond angle, being too large at 94.7(2)°. The r_0 value of 93.9° seems to be much more dependable. The 95.0° bond angle determined using results from GED experiments[2,3] for HFCB also appears to be too large; according to the CCSD(T) geometry optimizations this bond angle hardly changes upon perfluorination. This problem is a direct consequence of the much elongated GED+MW[3] C_3-C_4 bond. (Because the C=C−C bond angle is very close to 90°, the length of the C_3-C_4 bond depends to a great degree on the actual value of this angle: though a difference of 0.7° between the theoretical and experimental values appears to be relatively small, in the particular case of HFCB, this difference translates into a C_3-C_4 elongation of almost 0.04 Å.)

Overall, it seems that orbital rehybridization arguments are sufficient to rationalize structural changes in halogenated cyclobutenes and it is not necessary to invoke Coulomb repulsion to explain gross structural features for this class of compounds.

IV. Summary

In their recent study on the structure of *trans*-3,4-difluorocyclobutene Craig and co-workers[10] noted the following: "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 the structures from experimental data."

In this study both routes have been pursued, resulting in the following important findings about the structure of substituted cyclobutenes, including 1,2-difluorocyclobutene, 1,2-dicyanocyclobutene, *trans*-3,4-difluorocyclobutene, 1,4,4-trifluorocyclobutene, 3,3,4,4-tetrafluorocyclobutene, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, hexafluorocyclobutene, bicyclo[2.2.0]hex-1(4)-ene, and octafluorobicyclo[2.2.0]hex-1(4)-ene and their ab initio determination:

(1) When the effective rotational constants measured by microwave spectroscopy are corrected for vibrational effects, they become very close to the equilibrium constants computed at the definitive CCSD(T) level employing basis sets of cc-pVTZ quality and beyond. Due to favorable error compensation, the best agreement is observed when the medium-sized cc-pVTZ basis is employed for the ab initio optimizations, resulting in an overall average deviation of less than 3 MHz. Consequently, the related equilibrium (and vibrationally averaged) geometry parameters should be considered as the best representations available today for this class of compounds.

(2) Discrepancies between structural results of hexafluorocyclobutene and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene obtained by MW spectroscopy and GED, including apparent contradictions dating back to 1971, are resolved in favor of the MW structures exhibiting shortened CC distances upon fluorination. Most importantly, length of the C−C bond opposite to the double bond becomes shorter upon fluorination and not longer, as the GED investigations have indicated.

(3) It is important to point out that all ab initio computational levels lower than CCSD(T) result in qualitatively the same structures, lending further support to the conclusions of this study regarding the effects of fluorination on the cyclobutene ring. The DFT exchange-correlation functionals investigated,

in particular B3LYP, are not able to provide definitive structural predictions for this class of compounds.

(4) All tendencies observed in the structures of fluorinated cyclobutenes (and bicyclo[2.2.0]hex-1(4)-ene) can be simply rationalized by orbital rehybridization arguments, namely that the increased number of fluorines attached to a carbon atom increases the s character of the carbon bonds and tends to shorten *all* the bonds around that carbon. Ring strain and Coulomb repulsion effects are only needed to explain finer characteristics in the structures of fluorinated cyclobutenes.

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