Theoretical Studies of Geometries of Hexafluoro-1,3-butadiene, Tetrafluoro-1,3-butadiene, and Difluoro-1,3-butadiene Compounds

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The geometrical structures of various isomers of hexafluoro-1,3-butadiene (HFBD), tetrafluoro-1,3-butadiene (TFBD), and difluoro-1,3-butadiene (DFBD) have been studied theoretically. Natural steric and natural resonance theory (NRT) analyses indicate that the lower energy of skew s-*cis* conformer of hexafluoro-1,3-butadiene than that of the s-*trans* conformer is originated from the strong steric repulsions between fluorine atoms particularly in the s-*trans* conformer. The resonance structures generated by NRT also show that the lone electron pairs of fluorine atoms effectively extend the conjugation, and the large differences in energy among the structural isomers of tetrafluoro-1,3-butadiene and difluoro-1,3-butadiene are in part attributed to the differences in the delocalization energies, in addition to the steric repulsion between fluorine atoms. Other interatomic interactions, such as hydrogen bonding, also play important roles in determination of the structures of isomers of tetrafluoro-1,3-butadiene and difluoro-1,3-butadiene.

Key Words : Hexafluorobutadiene, Geometrical structure, Steric interaction, Conjugation, Natural bond orbitals

Introduction

Fluorine compounds often show unique structures and properties. For instance, the helix structures and immiscibility of perfluoro-n-alkanes and their derivatives have drawn intense attention and lead to various applications.[1] Historically predicting the structures of fluorine-containing compounds has been a challenge for electronic structure methods, often requiring high levels of electron correlation and large basis sets. Recent studies, for example, show that accurate description of the C-F bond length of fluorine-containing simple radicals requires calculations, at least, at the MP2/6-311(d) level.[2]

The structure of hexafluoro-1,3-butadiene (HFBD), the simplest perfluorocarbon with a conjugated double bond, has been the subject of many recent studies. The compound is a model system for linear perfluoro conjugated polyenes. It has been shown experimentally as well as theoretically that the skew s-*cis* conformation is the most stable one rather than the s-*trans* conformation. Here, "s" denotes the configuration along the C-C single bond. Comparison of IR and Raman results show that the gas-phase structure of HFBD has no inversion center, indicating that the planar s-*trans* conformation is not the global energy minimum.[3,4] Brundle and Robin interpreted their photoelectron and UV spectra in terms of a nonplanar structure, and predicted a skew s-*cis* conformation with a twisted angle of $42° \pm 15°$.[5] An electron diffraction study was also consistent with a skew s-*cis* conformation and the dihedral angle was estimated to be $47.4° \pm 2.4°$.[6] A combined study of NMR, IR, and Raman spectroscopy also confirms the earlier results.[7] More

recently the vibrational spectrum of perfluoro-1,3-butadiene was assigned and the results were consistent with a C_2 structure (skew s-*cis*).[8] The band due to the torsional motion was assigned and the barrier to planarity was estimated as 986 ± 150 cm^{-1}.

To date, there are only a limited number of theoretical studies of perfluorobutadiene. Choudhury and Scheiner studied the structure of perfluorobutadiene using semi-empirical (MNDO and PRDDO) and *ab initio* (STO-3G) molecular orbital methods.[9] The MNDO potential has a skew s-*trans* minimum, whereas the PRDDO and STO-3G results suggest that the planar s-*trans* conformation is more stable. Dixon studied the structure and vibrational frequencies of HFBD with *ab initio* methods.[10] Although calculations with the 3-21G basis set show that planar s-*trans* conformation is more stable than the skew s-*cis* one, the order reverses when the same calculation is proceeded with the 6-31G* or DZ + polarization basis set. The energy difference between skew s-*cis* and planar s-*trans* conformations is 1.8 kcal/mol with the DZ + polarization basis set. The torsional potential shows that the minimum is at the dihedral angle of 60° in skew s-*cis* conformation. Hudson *et al.* performed *ab initio* studies at the MP2 and B3LYP/6-31(d) levels to explain their resonance Raman spectra of HFBD, and showed that the skew s-*cis* structure is the most stable.[11] Karpfen examined the torsional potential and vibrational properties in detail at the SCF, MP2, and various DFT levels.[12] The study reconfirmed that the skew s-*cis* conformation is the global minimum.

While recent studies indicate that the skew s-*cis* conformation is the global energy minimum, the origin of such behavior has not been fully understood. Dixon[10] and Hudson *et al.*[11] suggested that the steric hindrance between fluorine atoms may play an important role in determining the

stability of conformations of HFBD. In this study, we have carried out *ab initio* calculations and natural bond orbital analysis for HFBD in an effort to elucidate the major factors that govern the molecular structure and energy of the fluorine-containing conjugated polyene. In addition, tetra-fluoro-1,3-butadiene (TFBD) and difluoro-1,3-butadiene (DFBD) have also been studied for comparison with the results of HFBD.

Computational Details

Ab initio calculations are carried out with Gaussian 98 packages[13] at the HF and MP2 levels with the 6-311G(d,p) basis set. The geometries of various structural and confor-mational isomers of HFBD, TFBD, and DFBD are fully optimized, subject to the molecular point group symmetry constraint, i.e. C_{2h}, C_{2v}, and C_2 for the planar s-*trans*, planar s-*cis*, and skew s-*cis* conformations of HFBD, repectively. Each optimized geometry was confirmed to be an energy minimum or a saddle point geometry via vibrational frequency analysis. Natural bond orbital (NBO) analysis, particularly natural steric analysis (NSA)[14] and natural resonance theory (NRT),[15-17] are carried out using NWChem package.[18] The exchange energy between the lone electron pairs of neighboring fluorine atoms, each of which carries three lone pairs of electrons, is estimated by NSA in order to examine the steric effects of the large radius of fluorine atom to the energy of each conformation. The C-C bond order and weights of the major resonance structures in each confor-mation are examined by NRT. All the NBO analyses were performed at the level of HF/6-311G(d,p) for the geometry optimized at the same level. The HF geometries show no

significant differences from the MP2 geometries.

Results and Discussion

Figure 1 shows the geometries of the skew s-*trans* and s-*cis* conformers (C_2) of HFBD optimized at the level of MP2/6-311G(d,p) and numbering of atoms as well. The same numbering of atoms is also used for all other compounds in this study. Listed in Table 1 are the geometrical parameters of several conformations of HFBD, along with those of 1,3-
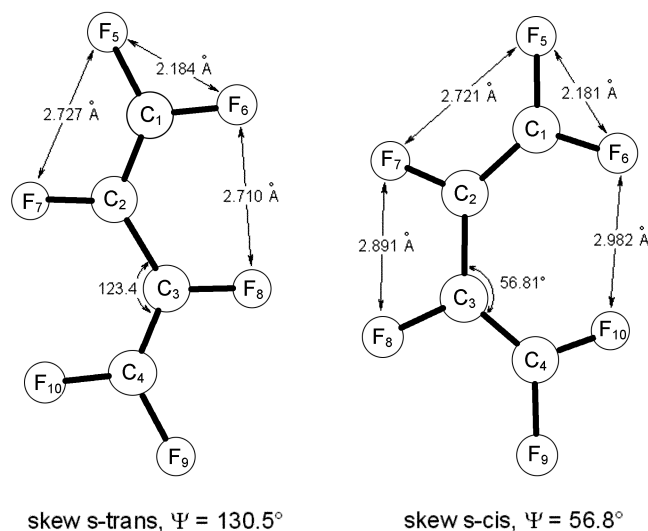

skew s-trans, Ψ = 130.5°   skew s-cis, Ψ = 56.8°

Figure 1. The optimized geometries of the skew s-*trans* and s-*cis* conformers of HFBD. The skew s-*cis* conformation is the global energy minimum of HFBD. Numbering of atoms for HFBD is also shown. The same numbering scheme is used for all other fluoro-1,3-butadiene compounds in this study.

Table 1. Geometrical parameters and NBO analysis of HFBD and 1,3-butadiene

Compound	HFBD					1,3-butadiene	
conformation	planar s-*trans*	skew s-*trans*	planar s-*cis*	skew s-*cis*	expt (Ref. 6)	s-*trans*	s-*cis*
E^a	-749.9248886	-749.9261416	-749.9188676	-749.9277583		-155.5224815	-155.5183756
ΔE^b	0.000	-0.786	3.778	-1.801		0.000	2.576
r(C2,C3)	1.454	1.455	1.465	1.448	1.488	1.460	1.472
r(F5,F6)	2.183	2.184	2.182	2.181	2.181^c	1.856	1.858
r(F5,F7)	2.669	2.727	2.638	2.721	2.767^c		
r(F6,F8)	2.649	2.710	4.355	3.910	4.029^c	2.499	3.686
r(F6,F10)	5.145	4.543	2.593	2.982	2.858^c	4.663	2.535
r(F7,F8)	3.576	3.447	2.515	2.891	2.713^c	3.122	2.537
Ψ^d	180.0	130.5	0.0	56.8	47.4	180.0	39.8
dE(F5:F6)/dE(F9:F10)^e	1.57	1.52	1.54	1.57			
dE(F5:F7)/dE(F8:F9)^e	1.00	0.97	1.16	0.95			
dE(F6:F8)/dE(F7:F10)^e	1.37	0.70					
dE(F6:F10)^e			2.01	0.12			
dE(F7:F8)^e			1.44	0.14			
ΣdE^f	2.74	1.40	3.45	0.26			
B.O./Ionic^g	1.0267/0.0494	1.0178/0.0424	1.0106/0.0345	1.0115/0.0367		1.0331/0.0517	1.0221/0.0424

^{a}Energy in Hartree calculated at the MP2/6-311G(d,p) level. ^{b}Difference in energy in kcal/mol relative to the planar s-*trans* conformation of HFBD. ^{c}Calculated from data in Ref. 6. ^{d}Distortion angle of the carbon skeleton in degree. ^{e}Exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms, three pairs from each. ^{f}Total exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms *except* those between geminal or syn fluorine atoms. ^{g}Total bond order/ionic contribution for C2-C3 obtained from NRT.

butadiene for comparison. As pointed out in previous works, the planar *trans* structure is not an energy minimum, and among the skew structures, the s-*cis* conformation lies 1.015 kcal/mol lower in energy than the s-*trans* one. The energy difference is consistent with the results of previous studies on the torsional potential of HFBD.[12] The torsional angle Ψ of the carbon skeleton in the skew s-*cis* structure, 56.8°, is slightly larger than the values estimated in the previous electron diffraction and photoelectron studies,[6] but agrees well with those of previous theoretical studies.[10-12] We also optimized geometries at the HF/6-311G(d,p) level and compared the energy differences among the conformations. The results are consistent with those obtained at the MP2/6-311G(d,p) level. Only noticeable difference is that the energy difference between the s-*cis* and s-*trans* conformations is smaller at the HF level.

The lower energy of the skew s-*cis* conformation, relative to that of the s-*trans* one, appears to be quite unusual on the basis of the usual assumption that the s-*trans* structure is more stable than the s-*cis* one. Evidently the skew s-*cis* structure of HFBD has a thread of connection with the helix structure of the perfluoro-n-alkane,[1] which is more stable than the planar zig-zag structure. As Dixon found in the *ab initio* study,[10] the lower energy of the skew s-*cis* conformation is accompanied with the larger interatomic distances between adjacent fluorine atoms. Other than the distances between the geminal (F5:F6 and F9:F10) or syn (F5:F7 and F8:F9) fluorine atoms, the shortest interatomic distances between adjacent fluorine atoms in the skew s-*cis* conformation are r(F6,F10) = 2.982 Å and r(F7,F8) = 2.891 Å, respectively. They are to be compared with r(F6,F8) and r(F7,F10), both of which are 2.649 Å for the planar (C_{2h}) *trans* structure, or 2.710 Å for the skew (C_2) s-*trans* structure.

It is interesting that the interatomic distance between the syn fluorine atoms, r(F5,F7), also serves as a rough indicator for the strong steric hindrances between F6:F8 and F7:F10 in the s-*trans* conformation and between F6:F10 and F7:F8 in the s-*cis* conformation. r(F5,F7) of planar s-*trans* and s-*cis* conformations are 2.669 and 2.638 Å, respectively, whereas those of skew s-*trans* and s-*cis* conformations are 2.727 and 2.721 Å, respectively. Note that the van der Waal radius of fluorine atom is about 1.47 Å. The steric hindrance is expected most severe in the planar s-*cis* conformation; the steric hindrances between F6:F10 and between F7:F8 cause the syn fluorine atoms (F5:F7) to be closer, resulting in a short distance of 2.638 Å. However, the steric hindrances are much less significant in the skew s-*cis* structure, leading to a larger distance of 2.721 Å. Another evidence of the severe steric hindrance in the planar s-*cis* structure is the longer C-C bond, which is stretched out to alleviate the strong steric hindrances between the adjacent fluorine atoms.

However, those interatomic distances are all indirect evidences for the steric hindrances. When two fluorine atoms approach each other, the large electron clouds of lone electron pairs of the two fluorine atoms start interacting, causing steric repulsion. Recently Badenhoop and Weinhold

have introduced an effective way of estimating the degree of the steric hindrance, called natural bond analysis of steric interactions.[14] The NBO decomposition of the wave function into localized bond and lone pair orbitals allows the steric repulsion to be expressed in terms of relative energy changes of individual NBOs upon orthogonalization, consistent with earlier treatment of "Pauli repulsions."[19] The approach separates the purely steric or exchange contributions from delocalization or charge transfer, induction, electrostatic, or other effects. Quantitative estimation of steric repulsion between fluorine atoms in HFBD would provide more direct verification for the lower energy of the s-*cis* conformation. Therefore, NSA has been conducted in order to examine closely the exchange repulsions between the lone electron pairs of contacting fluorine atoms.

The exchange repulsion energies dE between the adjacent fluorine atoms of HFBD obtained by NSA are listed in Table 1. The present analysis show that the exchange repulsions between syn or geminal fluorine atoms change only slightly regardless of the molecular conformation. However, the exchange repulsions between other adjacent fluorine atoms vary dramatically with the conformations. Table 1 shows that the large exchange repulsion energies, dE(F6:F8) and dE(F7:F10) for the s-*trans* conformation and dE(F6:F10) and dE(F7:F8) for the s-*cis* conformation, in the planar structures are greatly reduced in the skew structures, consistent with the variation of interatomic distances between the fluorine atoms. The total exchange repulsion ΣdE between fluorine atoms is, as shown in Table 1, the lowest in the skew s-*cis* conformation. Distortion of the s-*cis* conformer greatly increases the interatomic distances, r(F6,F10) and r(F7,F8), which in turn reduce the steric repulsions between the fluorine atoms. On the other hand, distortion of the s-*trans* conformer does not changes r(F6,F8) and r(F7,F10) as much. The present results on the variation of interatomic distances between the fluorine atoms and the exchange repulsion energies indicate that the stability of the skew conformations of HFBD are largely attributed to the steric hindrance between adjacent fluorine atoms, due to the large van der Waals radius. And among the two skew conformations, the skew s-*cis* conformer is more stable because of the lower steric hindrance between fluorine atoms in the structure, relative to that of the skew s-*trans* conformer.

As another factor that may affect the structures of the conformations, we consider the change in conjugation along the carbon skeleton. As shown in Table 1, the difference in total exchange repulsion energy is slightly larger than the difference in energy between the conformations. The conjugation energy will be certainly reduced in the skew structures, particularly in the skew s-*cis* conformation with the large torsional angle of almost 60°. It is thus expected that the difference in energy between the conformations is roughly equal to the differences in the total exchange repulsion and the conjugation energy. In order to estimate the magnitude of the conjugation energy, NRT[15-17] analysis is proceeded, which estimates the bond order and valency
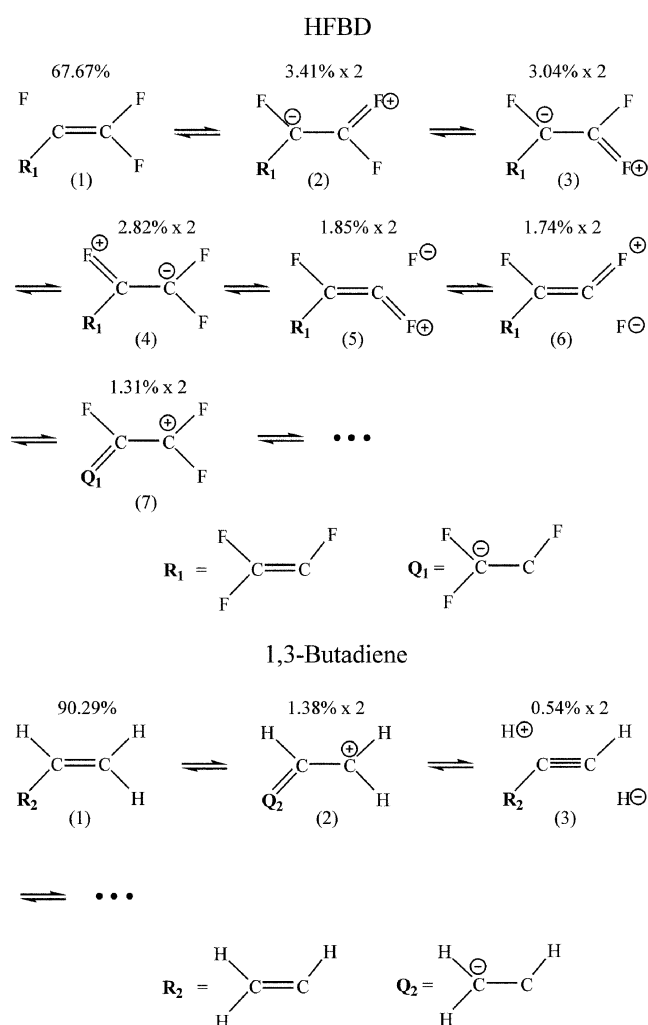
Figure 2. The major resonance structures of the skew s-*cis* conformer of HFBD and 1,3-butadine. The weights of the resonance structures are also shown. Essentially the same resonance structures with similar weights are found for the s-*trans* conformer.

that are closely related to classical resonance theory concepts. The estimated bond orders of the C-C bond in HFBD conformers, along with the ionic contributions, are listed in Table 1. The planar s-*trans* conformation, which is more favorable in terms of conjugation energy, carries a slightly higher bond order with a higher ionic contribution. The higher ionic contribution to the total bond order is certainly correlated with the resonance structures having electric charges along the C-C bond. Despite the changes in the bond order, the C-C bond is essentially a single bond, as shown in Table 1, and the bond order varies only slightly about 0.015 depending on the conformations.

The major resonance structures of skew s-*cis* HFBD, generated from NRT analysis, are compared with those of 1,3-butadiene in Figure 2, where the structures are shown in the decreasing order of resonance weights. The weights of the resonance structures of the s-*cis* conformer are almost the same as those of the s-*cis* conformer. The resonance structures clearly show that the lone electron pairs of

fluorine atoms effectively extend the conjugation, and most variations in the resonance structures occur around the C=C bonds. It is also notable that the weight of resonance structure (7), which gives the double bond character to the C-C bond, is in fact relatively small and similar to that of resonance structure (2) of 1,3-butadiene. Therefore, it is expected that rotation along the C-C bond of HFBD increases the molecular energy only slightly, which can be easily compensated by reduction in the exchange repulsion between fluorine atoms. Simple multiplication of the bond energy (normally about 88 kcal/mol) of a single C-C bond and the increase in bond order (0.0267) of the C-C bond of planar s-*trans* HFBD gives less than 2.4 kcal/mol. By rotation along the C-C bond, this conjugation energy reduces to 1.6 and 1.0 kcal/mol for the s-*trans* and s-*cis* conformations, respectively.

Next we have conducted *ab initio* and NBO calculations for several structural as well as conformational isomers of tetrafluoro-1,3-butadiene and difluoro-1,3-butadiene. The steric hindrance between fluorine atoms is expected much lower in these partly fluorinated conjugated polyenes. However, there may be other important interatomic interactions affecting the geometry of the conformers, such as hydrogen bonding with fluorine atoms or π-electrons. It has been reported that the s-*cis* conformer is the most stable one for some of partly chlorinated or brominated 1,3-butadiene compounds.[7] Both chlorine and bromine atoms carry much larger van der Waals radii than the fluorine atom does, causing stronger steric hindrance, but they are expected to form much weaker hydrogen bonds. Therefore, partly fluorinated 1,3-butadiene compounds are again good model compounds to examine the importance of the steric hindrance between fluorine atoms, along with effects of other interatomic interactions in partly halogenated polyenes.

Figure 3 shows the structures of five TFBD compounds, and Table II lists their geometrical parameters optimized at the MP2/6-311G(d,p) level. 1,1,4,4-TFBD is the lowest in molecular energy among the TFBD compounds studied, and 1,2,3,4-TFBD (I) the highest. The difference in energy more than 20 kcal/mol is not usual for compounds with the same chemical formula and no particular strain or variation in the structure. The major resonance structures for the skew s-*cis* conformers of 1,1,4,4-TFBD and 1,2,3,4-TFBD (I) generated by NRT analysis are shown in Figure 4. The s-*trans* conformers also have essentially the same resonance structures with similar weights. Clearly, the weights of the resonance structures other than structure (1) are greater for 1,1,4,4-TFBD, and structures (4) and (5) are not even found from 1,2,3,4-TFBD (I) in Figure 4. The lone electron pairs of fluorine atoms extend the conjugation, and the positive charge on a fluorine atom in resonance structures (2)-(5) of 1,1,4,4-TFBD is stabilized by the neighboring electron-rich fluorine atom. On the other hand, the negative charge of resonance structures (2) and (3) of 1,2,3,4-TFBD is located next to another fluorine atom, causing coulombic repulsion with the electron-rich fluorine atom. The present NRT result clearly indicates that the low energy of 1,1,4,4-TFBD is
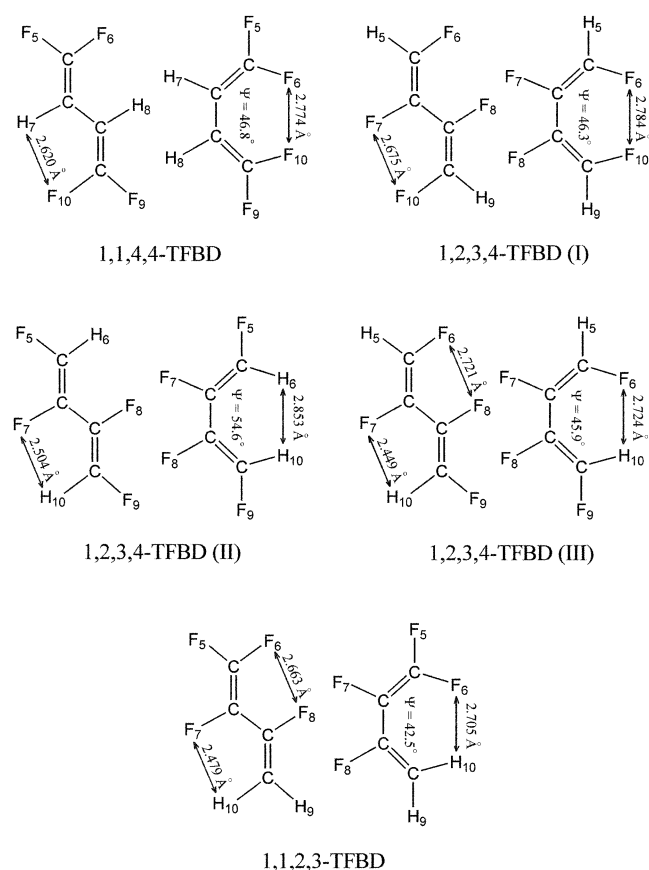
Figure 3. Conformations of the TFBD compounds studied in this work. The interatomic distances between atoms 6 and 10 and distortion angles of the skew s-*cis* conformers are indicated. All the s-*trans* conformers have planar structures, and the interatomic distances between atoms 6 and 8 and between atoms 7 and 10 are also indicated.

mainly attributed to the delocalization stabilization.

Unlike HFBD, the planar s-*trans* conformation is the energy minimum rather than the skew s-*trans* structure for all TFBD compounds studied. Among the TFBD's studied here, only 1,1,4,4-TFBD has been the subject of experimental structural studies. Mutual exclusion of infrared and Raman frequencies are observed in a previous study[20] of 1,1,4,4-TFBD, and NMR[21] and X-ray[22] results are also consistent with a planar s-*trans* conformation. The hydrogen atoms in the TFBD's greatly reduce the chances of steric repulsion between fluorine atoms particularly in the s-*trans* conformation. Only 1,2,3,4-TFBD (I) has both F6:F8 and F7:F10 contacting fluorine atom pairs. However, even in this compound, the steric repulsion is expected to be much weaker than in HFBD since the fluorine atoms have more room to sway due to lack of steric repulsions between the geminal and the syn fluorine atoms. As a result, the planar s-*trans* conformation becomes the energy minimum for all five TFBD's, and they are also the global minimum except for 1,2,3,4-TFBD (I).

For 1,2,3,4-TFBD (I), the skew s-*cis* conformer is the global energy minimum. 1,2,3,4-TFBD (I) is also the highest in molecular energy among the three isomers of 1,2,3,4-
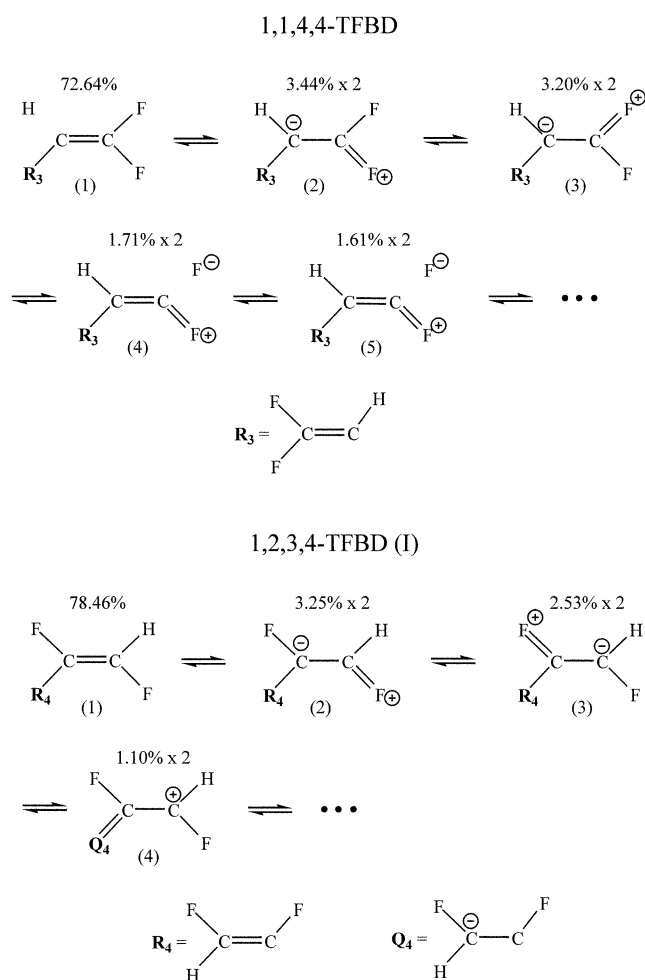

Figure 4. The major resonance structures of the skew s-*cis* conformers of 1,1,4,4-TFBD and 1,2,3,4-TFBD (I). The weights of the resonance structures are also shown. Essentially the same resonance structures with similar weights are found for the s-*trans* conformers.

TFBD's studied. For the s-*trans* conformer of 1,2,3,4-TFBD (I), strong steric repulsions are expected between the fluorine atoms (F6:F8 and F7:F10) on the basis of the small interatomic distances, while for the s-*cis* conformer, the steric repulsions between F6:F10 and F7:F8 are reduced greatly by distortion of the carbon skeleton. The NSA results summarized in Table 2 also show that the steric repulsions between fluorine atoms are indeed much lower in the skew s-*cis* conformer than in the planar s-*trans* conformer only in 1,2,3,4-TFBD (I). Therefore, the lower energy of the skew s-*cis* conformer of 1,2,3,4-TFBD (I), relative to that of the skew s-*trans* one, is primarily attributed to the lower steric repulsions between fluorine atoms, similar to that found in HFBD.

1,2,3,4-TFBD (II) is the lowest in energy among the isomers of 1,2,3,4-TFBD. For the s-*cis* conformer of 1,2,3,4-TFBD (II), the hydrogen atoms at atomic positions H6 and H10 eliminate the steric repulsion between F6 and F10 that exists in the s-*cis* conformer of 1,2,3,4-TFBD (I) (see Figure 3). Elimination of steric repulsion between fluorine atoms also occurs greatly in the s-*trans* conformer, leading to a

Table 2. Geometrical parameters and NBO analysis of TFBD's

compound	1,1,4,4-TFBD		1,2,3,4-TFBD (I)		1,2,3,4-TFBD (II)		1,2,3,4-TFBD (III)		1,1,2,3-TFBD	
conformation	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*
E^a	-551.8207713	-551.8165088	-551.7825349	-551.7835201	-551.7883679	-551.7855815	-551.7855860	-551.7842974	-551.7976057	-551.7947397
ΔE^b	0.000	2.675	23.994	23.375	20.333	22.082	22.079	22.888	14.537	16.335
r(C2,C3)	1.453	1.464	1.456	1.457	1.455	1.456	1.455	1.458	1.458	1.461
r(5,6)	2.171	2.165	2.044	2.784	2.049	2.044	2.047	2.046	2.179	2.181
r(5,7)	2.574	2.548	2.528	2.588	2.729	2.741	2.540	2.581	2.670	2.706
r(6,8)	2.620	3.836	2.675	4.021	2.504	3.756	2.721	4.032	2.663	4.052
r(6,10)	5.039	2.774	5.171	2.784	4.704	2.853	4.929	2.724	4.901	2.705
r(7,8)	3.164	2.632	3.561	2.755	3.553	2.865	3.558	2.763	3.553	2.707
r(7,10)	2.620	3.836	2.675	4.021	2.504	3.756	2.449	3.860	2.479	3.915
r(8,9)	2.574	2.548	2.528	2.588	2.729	2.741	2.722	2.741	2.580	2.582
r(9,10)	2.171	2.165	2.044	2.047	2.049	2.044	2.047	2.046	1.876	1.872
Ψ^c	180.0	46.8	180.0	46.3	180.0	54.6	180.0	45.9	180.0	42.5
dE(F5,F6)^d	1.68	1.76							1.66	1.49
dE(F5,F7)^d					0.77	0.82			1.01	0.97
dE(F6,F8)^d			1.19				0.98		1.40	
dE(F6,F10)^d		0.35		0.37						
dE(F7,F8)^d				0.32		0.17		0.36		0.44
dE(F7,F10)^d			1.19							
dE(F8,F9)^d					0.77	0.82	0.84	0.81		
dE(F9,F10)^d	1.68	1.76								
ΣdE^e	0.00	0.35	2.38	0.69	0.00	0.17	0.98	0.36	1.40	0.44
B.O./Ionic^f	1.0264/ 0.0442	1.0174/ 0.0361	1.0226/ 0.0477	1.0114/ 0.0384	1.0238/ 0.0474	1.0176/ 0.0441	1.0217/ 0.0498	1.0137/ 0.0435	1.0170/ 0.0658	1.0107/ 0.0587

^{a}Energy in Hartree calculated at the MP2/6-311G(d,p) level. ^{b}Difference in energy in kcal/mol relative to the planar s-*trans* conformation of 1,1,4,4-TFBD. ^{c}Distortion angle of the carbon skeleton in degree. ^{d}Exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms, three pairs from each. ^{e}Total exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms *except* those between geminal or syn fluorine atoms. ^{f}Total bond order/ionic contribution for C2-C3 obtained from NRT.

lower energy of 1.75 kcal/mol relative to that of the skew s-*cis* conformer. However, it is interesting that despite the less degree of repulsion, the interatomic distance between H6 and H10 in the skew s-*cis* conformer of 1,2,3,4-TFBD (II) is larger than that between F6 and F10 in the skew s-*cis* conformer of 1,2,3,4-TFBD (I) as shown in Figure 3. The larger interatomic distance stems from the larger distortion of the carbon skeleton in 1,2,3,4-TFBD (II), which, in turn, leads to a larger distance between F7 and F8.

Table 2 shows that the exchange repulsion between F7 and F8 of 1,2,3,4-TFBD (II) is the smallest among the 1,2,3,4-TFBD's. This suggests that the hydrogen atoms may interact strongly with the π-electrons and/or the fluorine atoms on the opposite side of the molecule. Large distortion of the carbon skeleton causes the hydrogen atom to locate closer to and above the double bond, possibly forming a hydrogen bond with π-electrons, similar to those hydrogen bonds observed in many crystal structures, where π-electrons in multiple bonds and aromatic rings function as weak hydrogen bond acceptors.[23] The distortion also shortens the distance to the fluorine atoms on the opposite side, increasing the possibility of interaction through hydrogen bonds or dipole interactions. However, the interaction between the hydrogen and fluorine atoms is probably not so strong due to the large interatomic distances (~4 Å) in 1,2,3,4-TFBD (II). A strong evidence of hydrogen bonding

with a fluorine atom is found in the skew s-*cis* conformer of 1,2,3,4-TFBD (III). In the skew s-*cis* conformer, the hydrogen (H10) and the fluorine atoms (F6) at the ends are located closer to each other in comparison with the corresponding atoms of other 1,2,3,4-TFBD's, while the steric repulsions between F7 and F8 are expected similar in all three compounds. Another evidence of hydrogen bonding with fluorine is found from 1,1,2,3-TFBD. The interatomic distance between H6 and F10 is the shortest among the corresponding distances of the five TFBD's, and the distortion angle is smallest. We, therefore, conclude that not only the steric repulsion between fluorine atoms but other interactions such as hydrogen bonding may play significant roles in determination of the structure of a conjugated fluorocarbon.

Figure 5 shows the structures of the five DFBD compounds studied, and the optimized geometrical parameters are summarized in Table 3. 1,2-DFBD is the highest in energy among the DFBD's and 1,4-DFBD the lowest. The molecular energy varies more than 8 kcal/mol among the DFBD's. Figure 6 shows the major resonance structures of the skew s-*cis* conformers of 1,2-DFBD and 1,1-DFBD. Clearly 1,1-DFBD has more effective resonance structures, and particularly resonance structures (5) and (6) are not even present for 1,2-DFBD. The lone electron pairs of fluorine atoms again extend the conjugation, and the resulting positive
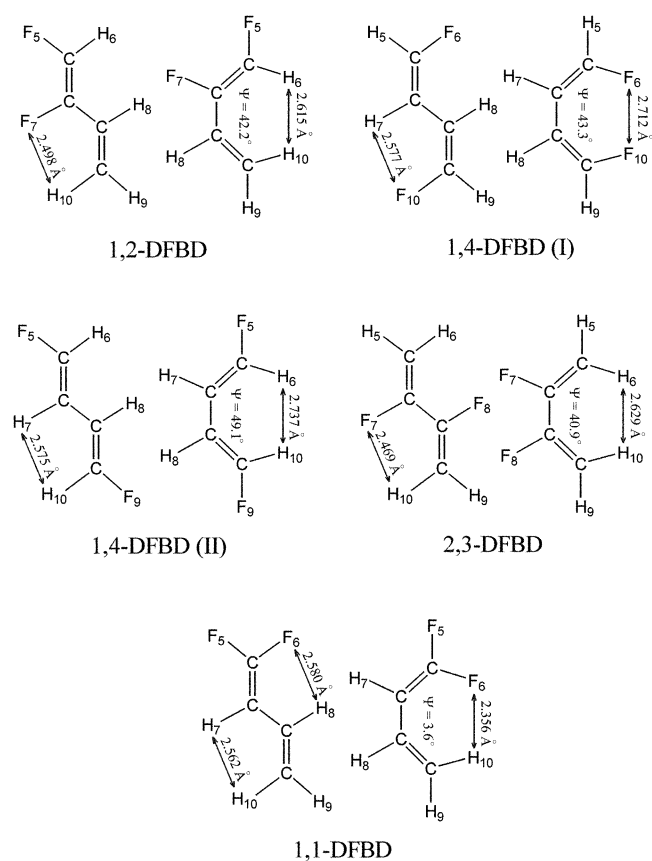
Figure 5. Conformations of the DFBD compounds studied in this work. The interatomic distances between atoms 6 and 10 and distortion angles in the skew s-*cis* conformers are indicated. All the s-*trans* conformers have planar structures and are the global energy minima. The interatomic distances between atoms 6 and 8 and between atoms 7 and 10 in the s-*trans* conformers are also indicated.

charge on a fluorine atom is stabilized by the neighboring electron-rich fluorine atom in 1,1-DFBD. On the other hand, the negative charge in a resonance structure of 1,2-DFBD is often located next to the other fluorine atom, causing Coulombic repulsion with the electron-rich fluorine atom. The order in molecular energies of DFBD's in Table 3 can be explained in terms of the stability of the major resonance structures.

For all five compounds of DFBD, the planar s-*trans* conformation is the global energy minimum, which is consistent with previous experimental results.[7,24,25] The geometrical parameters of the conformers of 1,4-DFBD are in good agreement with the results of a recent *ab initio* study for 1,4-DFBD isomers.[26] Similar to the case of TFBD, an evidence of intramolecular interaction other than steric repulsion of fluorine atoms is found from 1,4-DFBD. Despite the absence of steric repulsion between fluorine atoms, the interatomic distance of 2.737 Å between H6 and H10 of s-*cis* 1,4-DFBD (II) is larger than that of 2.712 Å between F6 and F10 in s-*cis* 1,4-DFBD (I), and the distortion angle is also larger in 1,4-DFBD (II). This large distortion moves the hydrogen atoms to a location favorable to form a hydrogen bond with π-electrons. Another strong evidence of intra-
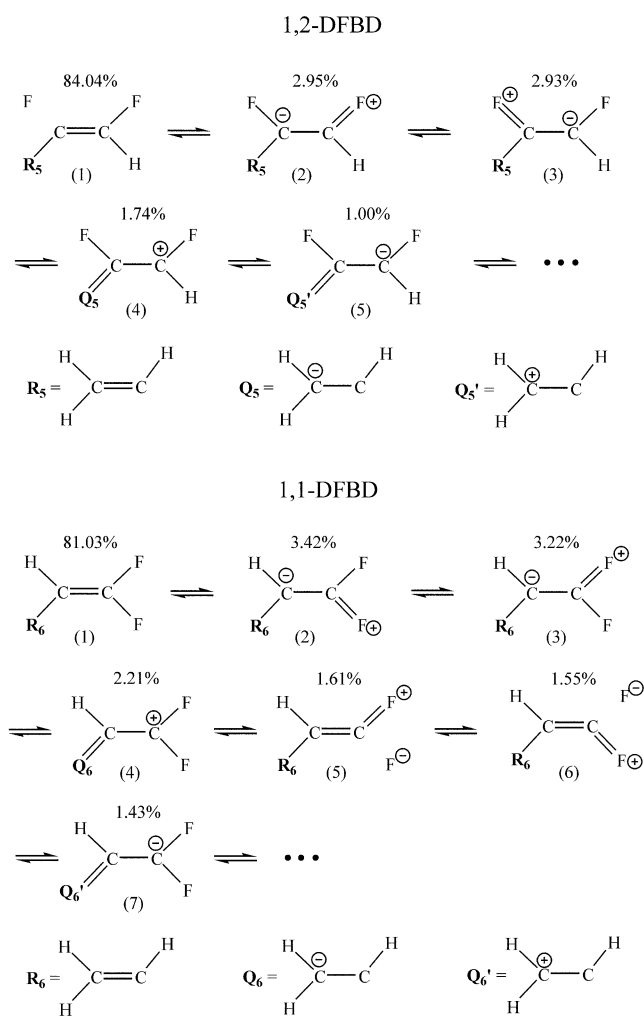

Figure 6. The major resonance structures of the skew s-*cis* conformers of 1,2-DFBD and 1,1-DFBD. The weights of the resonance structures are also shown. Essentially the same resonance structures with similar weights are found for the s-*trans* conformers.

molecular hydrogen bonding is found from the skew s-*cis* conformation of 1,1-DFBD, where r(6,10) is surprisingly small (2.356 Å) and the conformer is nearly planar (Ψ = 3.6°). The strong hydrogen bond between the hydrogen and fluorine atoms ties them together and suppresses the carbon skeleton from distortion.

Conclusions

Ab initio studies along with natural resonance theory and natural steric analyses have been carried out for fluoro-1,3-butadiene compounds, HFBD, TFBD, and DFBD. Strong steric repulsions are present between fluorine atoms in conjugated fluoropolyenes, often causing unusual structures. Particularly the large steric repulsions in the planar structures of HFBD lead to the stable skew s-*trans* and s-*cis* conformations. The NSA results indicate that the low energy of the skew s-*cis* conformation of HFBD is attributed to the relatively weaker steric repulsions between the fluorine

Table 3. Geometrical parameters and NBO analysis of DFBD's

compound	1,2-DFBD		1,4-DFBD (I)		1,4-DFBD (II)		2,3-DFBD		1,1-DFBD	
conformation	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*	s-*trans*	skew s-*cis*
E^a	-353.6586949	-353.6543067	-353.6662289	-353.6599525	-353.6626308	-353.6598682	-353.6684219	-353.6627250	-353.6722172	-353.6679749
ΔE^b	0.000	2.754	-4.728	-0.789	-2.470	-0.736	-6.104	-2.529	-8.485	-5.823
r(C2,C3)	1.453	1.461	1.454	1.465	1.454	1.467	1.466	1.471	1.456	1.464
r(5,6)	2.045	2.047	2.028	2.022	2.029	2.031	1.876	1.873	2.167	2.164
r(5,7)	2.723	2.726	2.459	2.417	2.566	2.573	2.584	2.585	2.572	2.525
r(6,8)	2.499	3.683	2.577	3.866	2.575	3.638	2.469	3.882	2.580	4.043
r(6,10)	4.672	2.615	5.020	2.712	4.732	2.737	4.648	2.629	4.861	2.356
r(7,8)	3.340	2.632	3.146	2.576	3.157	2.661	3.533	2.668	3.142	2.432
r(7,10)	2.498	3.893	2.577	3.866	2.575	3.638	2.469	3.882	2.562	3.904
r(8,9)	2.451	2.454	2.459	2.417	2.566	2.573	2.584	2.585	2.440	2.390
r(9,10)	1.860	1.858	2.028	2.022	2.029	2.031	1.876	1.873	1.857	1.854
Ψ^c	180.0	42.2	180.0	43.3	180.0	49.1	180.0	40.9	180.0	3.6
dE(F5,F6)^d									1.75	1.90
dE(F5,F7)^d	0.78	0.81								
dE(F6,F10)^d				0.51						
dE(F7,F8)^d								0.62		
ΣdE^e	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.62	0.00	0.00
B.O./Ionic^g	1.0315/ 0.0563	1.0200/ 0.0443	1.0257/ 0.0433	1.0240/ 0.0430	1.0384/ 0.0551	1.0236/ 0.0420	1.0173/ 0.0470	1.0044/ 0.0355	1.0290/ 0.0726	1.0209/ 0.0654

^{a}Energy in Hartree calculated at the MP2/6-311G(d,p) level. ^{b}Difference in energy in kcal/mol relative to the planar s-*trans* conformation of 1,2-DFBD. ^{c}Distortion angle of the carbon skeleton in degree. ^{d}Exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms, three pairs from each. ^{e}Total exchange repulsion energy between the lone electron pairs of adjacent fluorine atoms *except* those between geminal or syn fluorine atoms. ^{f}Total bond order/ionic contribution for C2-C3 obtained from NRT.

atoms in the molecular structure. According to the results of NRT analysis, the C-C bond of 1,3-butadiene is essentially a single bond, and remains almost the same even after substitution with fluorine atoms. Substitution of fluorine atoms effectively extends the conjugation, and in the resonance structures, the electron-rich fluorine atom can stabilize a positive charge nearby. The unusually large differences in molecular energy among the compounds of TFBD and DFBD are attributed to the differences in delocalization energies. While the steric repulsion between fluorine atoms is an important factor in determination of the molecular structure of the conjugated fluoropolyene, evidences also suggest that other interatomic interactions, such as hydrogen bonding, play important roles.

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