Theoretical Study on the Low-Energy and High-Energy Conformers of the Three Isomers of 1,4-Difluorobutadiene

Hai-Rong Hu and Anmin Tian

Faculty of Chemistry, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China

Ning-Bew Wong*

Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

Wai-Kee Li

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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The low-energy and high-energy conformers of the three isomers of 1,4-diflorobutadiene (DFBD) have been investigated with the Gaussian-3 (G3) and G3//B3LYP (G3B3) methods. The geometrical structures of the conformers have been gradient optimized by the HF and B3LYP methods with the 6-31G(*d*,*p*) basis set. Natural bond orbital (NBO) analysis has also been performed at the same levels of theory. The computational results show that the high-energy and low-energy conformers of a given isomer is essentially the same in geometry, except that their torsional angles about the C−C bonds are different, and among them only the high-energy conformer of the cis−trans isomer is coplanar. Harmonic vibrational frequency analysis indicates that the high-energy conformers are characterized by their smaller separations of the two C═C stretching modes and the reversed order of the $\upsilon(C{=}C)_{sym}$ and $\upsilon(C{=}C)_{asym}$ peaks compared to that of their low-energy conformer partners. NBO analysis indicates that the $\pi-\pi^*$ conjugative interaction in a high-energy conformer is smaller than that in its low-energy conformer partner and that the significant $n-\pi^*$ interactions in the high-energy conformers contribute to their extra stabilities. Through the G3B3 calculations, the conformational energies of the cis−cis, cis−trans, and trans−trans isomers are estimated to be 17.1, 7.9, and 9.8 kJ mol^{-1}, respectively. The stability sequence of the high-energy conformers in different isomers is (cis−trans) > (trans−trans) > (cis−cis), while that of the low-energy conformers is (cis−cis) > (cis−trans) > (trans−trans). The distinctive energy relationships between the conformers of different energy groups are attributed to the intramolecular hydrogen bonds in the high-energy conformers.

Introduction

For many years, chemists have been interested in the conformational analysis of the conjugative systems, such as the effects of conjugation of multiple bonds, the delocalization of the π electrons, and the dynamics of internal rotation about the C−C single bonds. The 1,3-butadiene framework, a simple conjugative system, has drawn extensive attention for conformational studies in the past several decades.[1−4] Theoretical works predict that there exist two stable conformers, namely, the s-trans and s-gauche conformers, in the 1,3-butadiene system, where “s” denotes the configuration about the C−C single bond. Both experimental[1−3] and theoretical[1,4] studies have confirmed that the s-trans conformer is the predominant and lowest-energy structure of 1,3-butadiene. Unlike the 1,3-butadiene molecule, the lowest-energy conformer of the perfluoro- or perchloro-1,3-butadiene is the s-gauche form,[5−7] while in most cases, the s-trans form is commonly the most stable conformer for any 1,3-butadiene analogue.[8] There are a number of factors affecting the conformational preferences of a molecule. They are steric effect, gauche effect, anomeric effect, and intramolecular hydrogen bondings, etc. In either the same or different molecular system, a given factor may favor one conformation, while another factor may favor another conformation. For instance, the steric effect favors the trans conformation in most cases, while the gauche effect and the anomeric effect favor the gauche conformation.[9] As a matter of fact, there always exist concomitant effects which influence the conformational preference in a molecular system competitively or concertedly. Therefore, it is very difficult to pinpoint a precise reason for an observed conformational preference in a molecule with multiple conformations.

From the initial work of Viehe and Franchimont[10] in 1963, the isomers of 1,4-diflorobutadiene (hereafter denoted as DFBD) were known to have an extraordinary temperature-dependent equilibrium[11] that the cis−cis isomer was favored at low temperature, and this was called the cis effect.[10,12] They found that the cis−cis isomer had the lowest energy in the temperature range of 100−150 °C, while the trans−trans isomer was the least stable one despite the greater electronic crowding in the former. Qualitative study on the cis effect in the fluorine containing species has remained a controversy[7,13−16] for decades. The arguments for the cis effect include, for example, the bent-bond interpretation of Wiberg,[14] the four-center interaction proposal of Engkvist et al.,[15] the valence bond reasoning of

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* Corresponding author. E-mail address: bhnbwong@cityu.edu.hk.

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Epiotis,[16] and the involvement of the fluorine lone pair electrons of Foley et al.[7] Craig and co-workers[11] had made an extensive study on the three isomers of the DFBD both experimentally and theoretically. They employed the adiabatic connection methods (ACM) proposed by Becke[17] to predict that the cis−cis isomer was 4.7 kJ mol^{-1} lower in energy than the trans−trans isomer. However, it was underestimated by 1.8 kJ mol^{-1}, a quite significant value, as compared with the experimental data. Similarly, they also underestimated the energy difference between the cis−cis and cis−trans isomers, as well as that between the cis−trans and trans−trans isomers. This suggests that the theoretical method they employed may not be reliable enough to gauge such a small energy difference. To our best knowledge, there was no experimental report on the conformations of the DFBD. Craig et al.[11] had also mentioned the high-energy conformer (or rotamer) of each configurational isomer, but no detailed discussion was reported. On the other hand, it is believed that all these high-energy conformers are involved in the mechanistic pathways of the isomerization reactions among the three isomers, and this is the subject matter of our interest. The aim of this work is to investigate the difference between the low-energy and high-energy conformers in a given isomer and to search for the factors that determine the conformational preference.

It has been demonstrated that the thermodynamic properties derived from the G3[18] and G3//B3LYP[19] (hereafter denoted as G3B3) calculations, such as the thermal effect of a reaction and the tiny energy difference between two similar molecules, are in very good agreement (±10 kJ mol^{-1}) with the experimental data. In this work, a more reliable estimation for the conformational energies of the DFBD in the gas phase has been achieved. Furthermore, to discern the origin of the conformational preference in terms of the structural and electronic properties, NBO analysis developed by Reed and Weinhold[20,21] was employed.

Computational Details

To evaluate the equilibrium geometries theoretically converged with respect to the size of the basis sets, Han et al.[22] carried out geometry optimization on the eclipsed forms of 1,2-difluoroethane with various basis sets, such as 6-31G(*d*,*p*), 6-311G(*d*,*p*), and 6-311++G(2*df*,2*p*). As compared with the 6-31G(*d*,*p*) results, they found that using the 6-311G(*d*,*p*) basis set and appending additional diffuse functions could lengthen the C═C bond of 1,2-difluoroethane by 0.005 Å. But further improvement of the basis set to 6-311++G(2*df*,2*p*) shortened it by 0.006 Å, which led to a good agreement between the 6-311++G(2*df*,2*p*) and 6-31G(*d*,*p*) basis sets. Similar trends were observed in the compounds of similar structures.[22] Therefore, they recommended the 6-31G(*d*,*p*) basis set for geometry studies. Our preliminary computational results also confirmed the finding of Han et al. Thus, in this work, we utilized the standard split-valence 6-31G(*d*,*p*) basis set to perform the geometrical gradient optimization for all the conformers at the HF level of ab initio molecular orbital theory. For economic consideration, for post-Hartree−Fock calculations, the hybrid density functional with the Becke's three-parameter functional for exchange, and the Lee, Yang and Parr correlation functional (B3LYP),[17] which includes the electronic correlation correction, were carried out. Furthermore, the NBO analysis and vibrational frequency predictions were performed at the B3LYP/6-31G(*d*,*p*) level of theory. All the calculations were carried out using the Gaussian-98 program package.[23]

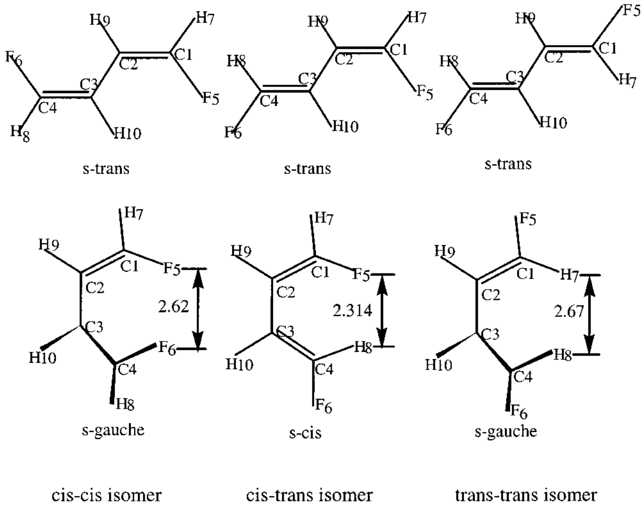

Figure 1. Stable (upper) and high-energy (lower) conformers of the three isomers of 1,4-difluorobutadiene. The interatomic distances shown are in Å.

Results and Discussions

Fully Optimized Geometries. The sketches of all conformers of the DFBD are shown in Figure 1, where the low-energy (s-trans) and high-energy (s-cis or s-gauche) conformers are depicted in the upper and lower rows, respectively. The optimized geometrical parameters for all conformers at two different levels of theory with 6-31G(*d*,*p*) basis set are listed in Table 1.

For the 1,3-butadiene parent molecule, there have been many research works focusing on its conformational analysis (see the review in ref 1). With respect to the geometry, it was found in the most recent report[1] that there were no significant differences between the bond lengths and the bond angles among different conformers both experimentally and theoretically. It has been concluded experimentally that the most stable geometry of the high-energy conformer of 1,3-butadiene in gas phase was the nonplanar s-gauche form rather than the planar s-cis form. This finding has drawn our attention to the same question for the DFBD molecule.

Table 1 is a comparison between the results obtained at HF and B3LYP levels of theory. It is seen that the electronic correlation effects contribute to a slightly increase of the C═C and C−H bond lengths and, on the contrary, a decrease of the C−C single bond length. These effects are also observed in the bond angles. The work of Han et al.[22] seemingly confirms that the B3LYP/6-31G(*d*,*p*) results are in a slightly better agreement with the experimental data, as compared to those of the HF and MP2 methods with the same basis sets. In comparison, the treatments and findings in our DFBD system further confirm those of Han et al. in their 1,2-difluoroethane system.[22] The following discussions are based on our results obtained from the B3LYP calculations.

For the cis−cis isomer, the low-energy conformer has an s-trans planar conjugative structure, which is 18.0 kJ mol^{-1} more stable than the s-gauche form at the B3LYP/6-31G(*d*,*p*) level of theory. This value is comparable to that in the 1,3-butadiene system.[1] A more precise estimation of the conformational energies had been performed with the G3 method, and the results for the cis−cis isomer are presented below. The s-gauche conformer is found to be not rigorously planar, and its torsional angle about the C−C bond is 30.9°. This value is close to that (37.8°) of the high-energy conformer of the 1,3-butadiene[1] but deviates significantly from that (58.4°) of the perfluoro-1,3-

TABLE 1: Optimized Geometries[a] and Total Energies[b] of the Three Isomers Using Different Methods with the 6-31G(*d*,*p*) Basis Sets. Bond Lengths Are in Å, Bond Angles in Degrees and Energies in Hartree

structural parameters	HF		B3LYP	
cis−cis DFBD	s-trans	s-gauche	s-trans	s-gauche
r(C1═C2)	1.314	1.314	1.335	1.336
r(C2−C3)	1.463	1.472	1.451	1.459
r(C3═C4)	1.314	1.314	1.335	1.336
r(C1−H7)	1.072	1.073	1.084	1.085
r(C1−F5)	1.332	1.324	1.350	1.342
r(C2−H9)	1.074	1.076	1.085	1.087
θ(C1═C2−C3)	124.0	126.9	124.1	128.3
θ(C2−C3═C4)	124.0	126.9	124.1	128.3
θ(C2═C1−H7)	125.3	124.2	125.6	124.0
θ(C2═C1−F5)	122.2	123.4	121.9	123.6
θ(F5−C1−H7)	112.5	112.4	112.5	112.3
θ(H9−C2═C1)	117.4	116.0	117.3	115.0
θ(F6−C4═C3)	122.2	123.4	121.9	123.6
θ(F6−C4−H8)	112.5	112.4	112.5	112.4
θ(H10−C3−C2)	118.6	117.1	118.6	116.7
τ(C1C2C3C4)	180.0	41.9	180.0	30.9
E(total)	−352.55005	−352.54318	−354.39147	−354.38458
cis−trans DFBD	s-trans	s-cis	s-trans	s-cis
r(C1═C2)	1.314	1.314	1.335	1.335
r(C2−C3)	1.463	1.470	1.451	1.459
r(C3═C4)	1.314	1.316	1.335	1.337
r(C1−H7)	1.072	1.071	1.084	1.084
r(C1−F5)	1.331	1.333	1.350	1.353
r(C4−F6)	1.328	1.329	1.346	1.347
r(C4−H8)	1.073	1.070	1.086	1.082
r(C2−H9)	1.076	1.075	1.087	1.086
r(C3−H10)	1.074	1.076	1.086	1.086
θ(C1═C2−C3)	124.4	128.5	124.3	128.3
θ(C2−C3═C4)	122.2	126.4	122.6	126.3
θ(C2═C1−H7)	125.3	125.1	125.6	125.5
θ(C2═C1−F5)	121.1	122.6	121.8	122.2
θ(F5−C1−H7)	112.6	112.3	112.6	112.3
θ(H9−C2═C1)	116.8	115.3	116.7	115.1
θ(F6−C4═C3)	121.7	120.5	121.7	120.5
θ(F6−C4−H8)	112.4	112.6	112.5	112.9
θ(H10−C3−C2)	118.6	116.5	118.6	116.9
τ(C1C2C3C4)	180.0	0.0	180.0	0.0
E(total)	−352.54842	−352.54518	−354.38999	−354.38722
trans−trans DFBD	s-trans	s-gauche	s-trans	s-gauche
r(C1═C2)	1.314	1.313	1.335	1.334
r(C2−C3)	1.463	1.474	1.451	1.464
r(C3═C4)	1.314	1.313	1.335	1.334
r(C1−H7)	1.073	1.073	1.086	1.086
r(C1−F5)	1.328	1.328	1.346	1.346
r(C2−H9)	1.077	1.077	1.088	1.088
θ(C1═C2−C3)	122.6	123.0	123.0	123.4
θ(C2−C3═C4)	122.6	123.0	123.0	123.4
θ(C2═C1−H7)	125.7	125.7	125.7	125.6
θ(C2═C1−F5)	121.6	121.7	121.6	121.8
θ(H9−C2═C1)	118.5	118.6	118.1	118.1
θ(F6−C4═C3)	121.6	121.7	121.6	121.8
θ(F6−C4−H8)	112.5	112.6	112.7	112.7
θ(H10−C3−C2)	118.9	118.5	118.9	118.5
τ(C1C2C3C4)	180.0	49.62	180.0	40.6
E(total)	−352.54734	−352.54430	−354.38883	−354.38431

[a] The symmetries are taken into account in the geometric parameters. The point groups for the molecule are the following: (i) cis−cis isomer, C_{2h} for the s-trans and C_2 for the s-gauche conformers; (ii) cis−trans isomer, C_s for both s-trans and s-cis conformers; (iii) trans−trans isomer, C_{2h} for the s-trans and C_2 for the s-gauche conformers. [b] The zero-point vibrational energy corrections are included in the total energies shown in italic font.

butadiene.[6] In comparing the s-gauche conformer with the s-trans conformer, the C═C and C−C bonds in the former are 0.001 and 0.008 Å longer, respectively. In general, the C═C bonds in any conformer of the DFBD are relatively shorter than that of the 1,3-butadiene in our previous work.[24] This agrees with the trends observed in the systems of fluoroethylene[13] and perfluoro-1,3-butadiene[6] that the C═C bond length decreases as the hydrogen atom is substituted by fluorine. However, this trend does not apply to the C−C single bond of the DFBD. Table 1 shows that the C−C single bond in the s-gauche conformer is 0.008 Å longer than that in the s-trans conformer, while the C−F bond is 0.008 Å shorter in the former. On the other hand, all the C−H bonds seem to remain the same in all of the high-energy conformers. These differences in bond lengths indicate that the conjugative interaction is somewhat weaker in the high-energy conformers. It is also shown that the θ(C═C−C) bond angle of a high-energy conformer is slightly larger (∼4°) than that of its low-energy conformer partner for all isomers. The calculated F−F distance between the two fluorine atoms bonded to C1 and C4 is about 2.62 Å, which is less than the van der Waals diameter of a fluorine atom.[6] Thus, the geometric differences mentioned above may result from the strong steric repulsion between the two fluorine atoms in the s-gauche conformer, which may also explain the different stabilities of these two conformers.

Conversely, the geometric difference within each of the other two conformer pairs are not exactly the same as that in the cis−cis isomer. In the cis−trans isomer, one of the C═C bond remains the same, while the other C═C bond and the C−C single bond are both slightly (∼0.008 Å) longer in the s-cis conformer. Also, the two C−H$_c$ (c = central) bonds are almost the same, while the C4−H8 bond is 0.004 Å shorter in the s-cis conformer. Different conformations exhibit a small effect from the bending bond angles, except that the θ(C1═C2−C3) and θ(C2−C3═C4) are slightly larger in the s-cis conformer. Its torsion angle about the C−C single bond is almost negligible, which suggests that the s-cis conformer is essentially coplanar. Its F5−H8 bond (2.314 Å) is shorter than the sum of the van der Waals radii of fluorine and hydrogen, which are 1.47 and 1.20 Å, respectively.[6] This may explain that the planar structure of this conformer is attributed to the intramolecular hydrogen bonding. At both levels of HF and B3LYP/6-31g(*d*,*p*), the trans−trans isomer resembles the cis−cis isomer in that the θ(C1═C2−C3) and θ(C2−C3═C4) within a conformer are the same and that the C−C bond within the same isomer is slightly longer in the s-gauge form. However, in comparison between their s-gauche conformers, the torsional angle about the C−C bond is significantly larger in the trans−trans isomer. If the steric repulsion were the determining factor for the nonplanar property of the s-gauche conformer, the torsional angle in this conformer of the trans−trans isomer could be smaller than that of the cis−cis isomer due to the relatively smaller repulsion between the two inner hydrogen atoms than that between the two inner fluorine atoms. Therefore, there should be another intramolecular interaction resulting from the lone pair electrons of the fluorine. Comparing the three high-energy conformers show that the s-cis conformer of the cis−trans isomer is more stable than the s-gauche forms of the cis−cis and trans−trans isomers by 5.8 and 4.5 kJ mol^{-1}, respectively, at the B3LYP/6-31G(*d*,*p*) level. Thus, the energy difference of the high-energy and the low-energy conformers of a given isomer can be used as an index for assigning the relative stabilities of the three high-energy conformers. Among them, the s-cis conformer of the cis−trans isomer exhibits highest stability due to the intramolecular hydrogen bonding in this conformer.

Harmonic Vibrational Frequency Analysis. The harmonic vibrational frequencies and infrared intensities in each conformer pair of the three isomers, together with the experimental data,

TABLE 2: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) for the Two Conformers of the cis−cis Isomer[a]

	s-gauche form				s-gauche form	
approx. υ assignment	sym	exp (ref 17)	ref 17	this work	sym	this work
s ν(C−Ht) str[b]	A_g	−	3232	3234(0)[c]	A	3219(4)
s ν(C−Hc) str		−	3205	3207(0)		3185(2)
s ν(C=C) str		−	1740	1758(0)		1733(98)
s δ(C−Hc) def, ν(C−C) str		−	1445	1468(0)		1464(22)
s δ(C−H) def		−	1284	1288(0)		1296(47)
ν(C−C) str, δ(C−Hc) def		−	1166	1176(0)		932(6)
s ν(C−F) str, δ(C−Hc) def		−	972	982(0)		1128(102)
s δ(C=C−C) def		−	767	768(0)		174(0.4)
s δ(C−F) def		−	230	227(0)		652(4)
s χ(C−H) wag	A_u	914 w[d]	953 vw	950(2)		922(0.3)
s χ(C−H) wag		762 s[d]	788 s	784(44)		765(40)
s χ(C−F) wag, χ(C−Ht) wag		330	338 m	336(19)		355(16)
τ(C−C) torsion		78 w	89 w	91(2)		83(0.4)
a χ(C−H) wag	B_g	−	934	922(0)	B	919(4)
a χ(C−H) wag		−	808	817(0)		805(8)
a χ(C−F) wag, χ(C−Hc) wag		−	585	576(0)		551(0)
a ν(C−Ht) str	B_u	3109 m	3233 m	3236(20)		3217(26)
a ν(C−Hc) str		3092 m	3213 m	3214(2)		3177(6)
a ν(C=C) str		1624 vs	1681 vs	1698(153)		1737(34)
a δ(C−H) def		1340 m	1364 m	1379(7)		1407(5)
a δ(C−H) def		1215 s	1244 s	1245(98)		1290(12)
a ν(C−F) str, δ(C−Hc) def		1044 vs	1061 vs	1072(219)		1069(16)
a δ(C=C−C) def		644 w	643 m	640(6)		882(10)
a δ(C−F) def		165 m	162 m	157(7)		231(9)

[a] All notations in this table apply to Tables 3 and 4. All the calculated frequencies are not scaled. [b] In each fundamental mode, “s” denotes symmetric, and “a” denotes asymmetric. [c] The values in the parentheses are the calculated intensities. [d] vs = very strong, m = medium, w = weak. The experimental data and calculated results are reported in ref 17.

TABLE 3: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) for the Two Conformers of the cis−trans Isomer

	s-trans form				s-cis form	
approx. υ assignment	sym	exp (ref 17)	ref 17	this work	sym	this work
ν(C−Ht)$_{\mathrm{cis}}$ str	A'	3114 m	3232 w	3275(103)	A'	3236(8)
ν(C−Hc)$_{\mathrm{trans}}$ str		3082 m	3208 m	3255(5)		3201(2)
ν(C−Ht)$_{\mathrm{trans}}$ str		3070 w	3205 w	3247(12)		3257(3)
ν(C−Hc)$_{\mathrm{cis}}$ str		−	3190 vw	3229(1.4)		3189(12)
s ν(C=C) str		1690 m	1743 m	1745(24)		1716(79)
a ν(C=C) str		1629 vs	1687 vs	1692(128)		1733(64)
s δ(C−Ht)$_{\mathrm{cis}}$ def		1391 m	1421 m	1428(14)		1431(11.5)
s δ(C−Ht)$_{\mathrm{trans}}$ def		1313 w	1339 w	1342(2.3)		1352(1)
s δ(C−Hc) def		1253 m	1282 m	1272(16)		1302(5.3)
a δ(C−Hc) def		1224 m	1250 m	1239(26)		1276(29)
ν(C−C) str, a ν(C−F) str		1155 m	1168 m	1167(25)		995(6)
ν(C−F)$_{\mathrm{trans}}$ str, ν(C−C) str		1129 vs	1153 vs	1149(156)		1189(150)
ν(C−F)$_{\mathrm{cis}}$		1017 s	1023 s	1024(99)		1080(81)
s δ(C=C−C)$_{\mathrm{cis}}$ def		706 w	719 w	715(5)		164(1)
δ(C−F)$_{\mathrm{trans}}$ def		504 m	510 m	508(18)		497(10)
δ(C−F)$_{\mathrm{cis}}$ def		308 w	308 vw	312(1.4)		302(8)
τ(C−C) torsion		138 w	142 w	148(2.4)		102(4)
s χ(C−H)$_{\mathrm{trans}}$ wag	A''	929 s	964 s	956(41)	A''	962(35)
a χ(C−H)$_{\mathrm{cis}}$ wag		887 m	921 m	898(5)		912(4)
a χ(C−H)$_{\mathrm{trans}}$ wag		824 m	860 w	833(2.3)		849(0.3)
s χ(C−H)$_{\mathrm{cis}}$ wag		758 s	779 m	764(24)		763(30)
s χ(C−F) wag		−	526 w	518(5)		533(4)
a χ(C−F) wag		230 vw	236 vw	238(1)		230(1)
a δ(C=C−C) def		−	140 w	136(1)		808(12)

are listed in Tables 2−4. In the past several decades, experimental attempts to determine the vibrational frequencies of the high-energy conformers have been unsuccessful (see ref 1). However, both experimental and theoretical investigations on the unsubstituted 1,3-butadiene are still ongoing (see ref 1 and the literatures cited therein). It is very difficult for us to thoroughly separate a high-energy conformer of low population but high reactivity from its low-energy conformer partner due their tiny energy difference. Thus, it is very difficult to accurately assign the spectra data relying on current experimental technique. In light of the previous works on unsubstituted and substituted 1,3-butadienes,[1,5,7,11] it remains a hot and controversial topic to perform spectroscopic study on unsubstituted and fluorine substituted 1,3-butadienes. It is particularly important to obtain new experimental data, especially in the gas phase, to confirm our computational results. So far, there is no reference to verify our vibrational frequency assignments for the high-energy conformers. In this work, theoretical harmonic frequency analysis has been performed, and the relative stabilities of all three high-energy conformers of the DFBD system had been determined.

In Tables 2−4, the assignments for the fundamental modes were derived from normal-coordinate analysis according to their potential energy distribution (PED), in which the local internal

TABLE 4: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) for the Two Conformers of the trans−trans Isomer

	s-trans form				s-gauche form	
approx. υ assignment	sym	exp. (ref 17)	ref 17	this work	sym	this work
s ν(C−Ht) str	A_g	−	3210	3212	A	3215(7.5)
s ν(C−Hc) str		−	3182	3179		3185(2.5)
s ν(C═C) str		−	1745	1759		1729(20)
s δ(C−Ht) def		−	1351	1368		1347(0.4)
s δ(C−Hc) def		−	1315	1312		1309(1.4)
s ν(C−F) str		−	1183	1195		1193(8)
s ν(C−C) str, δ(C−H) def		−	1176	1160		1042(0.4)
s δ(C═C−C) def		−	410	408		124(3)
s δ(C−F) def, δ(C−H) def		−	385	383		389(5)
s χ(C−H) wag	A_u	934 s	970 s	979(87)		960(76)
s χ(C−H) wag		798 w	831 vw	820(0)		826(10)
s χ(C−F) wag, χ(C−Hc) wag		227 w	238 w	226(3)		181(2)
τ(C−C) torsion		154 w	127 vvw	122(0.2)		195(0.03)
a χ(C−Hc) wag	B_g	−	910	923	B	940(14)
a χ(C−H) wag		−	865	853		855(2)
a χ(C−F) wag		−	402	406		431(1)
a ν(C−Ht) str	B_u	3086 m	3210 m	3212(26)		3212(13)
a ν(C−Hc) str		3056 wm	3189 wm	3186(12)		3177(16)
a ν(C═C) str		1638 vs	1692 s	1714(170)		1739(131)
a δ(C−Ht) def		1306 wm	1334	1345(7)		1348(1.2)
a δ(C−Hc) def		1221 ms	1243	1245(31)		1275(12)
a ν(C−F) str, δ(C−Hc) def		1088 vs	1107 vs	1125(317)		1177(301)
a δ(C−F) def, δ(C−Hc) def		621 ms	624 m	619(36)		382(2)
a δ(C═C−C) def		133 w	146 w	142(3)		696(34)

coordinate systems recommended by Pulay[25] were employed for DFBD. From these Tables, it is clear that our theoretical evaluation on the frequencies and the corresponding intensities for the two conformers of each isomer are in good agreement with the most recent high-resolution IR spectroscopic data obtained by Craig et al.[11] The all real frequencies of the conformers suggest that the optimized conformers of each isomer are minima on the PES.

Possibility of Impurity in the Samples. It is quite surprising to note that the calculated spectra of the two conformers in a given isomer are essentially the same in a few bands. Furthermore, the low-energy conformers of both cis−cis and trans−trans isomers belong to the C_{2h} point group, and their fundamental modes consist of nine in-plane vibrations of A_g symmetry, four out-of-plane A_u vibrations, three out-of-plane B_g vibrations, and eight in-plane B_u vibrations. Among these vibrations, only the A_u and B_u modes are IR active. But when we reexamined the experimental spectra reported by Craig et al.,[11] two peaks were observed in the 1600−1650 cm^{-1} region of their gas-phase IR spectra. Also, more than two bands attributed to C−H stretching modes appeared in the 3000−3200 cm^{-1} region. According to the symmetry analysis, it seems impossible to observe so many IR peaks in these regions experimentally. This might only be explained in that the samples obtained by Craig et al.[11] were population mixtures of mainly low-energy conformers and some high-energy conformers for these two isomers. As for the cis−trans isomer, both of its two conformers are of C_s symmetry, which ensures all the fundamental modes IR active. Among these modes, seventeen in-plane vibrations have A' symmetry, and the remaining seven out-of-plane modes have A'' symmetry. The similarity between the vibrational spectra of the two conformers suggests the possibility of the population impurity.

Difference between Each Pair of Conformers. Vibrational normal-mode analysis reveals that the frequencies assigned to the C═C stretching modes of these species are different despite of the lack of significant variation of the C═C bond length among them. Foley et al.[7] proposed that the hybrid B3LYP method was the most reliable one in predicting the vibrational frequencies for hexafluoro-1,3-butadiene in comparison with the HF, MP2, and BLYP methods. Since the difference among the low-energy conformers had been discussed in our previous work,[24] more efforts will be spent on the high-energy conformers in this work. From our calculation at the B3LYP/6-31G(*d*,*p*) level of theory and by comparing the two C═C stretching bands between the two conformers of a given isomer, it is found that the C═C stretching frequency, both symmetric and asymmetric, is smaller in the high-energy conformer. This suggests that the conjugative interaction in the high-energy conformers is weaker, which is in agreement with the geometric data that the C═C bond is shorter in this conformer. It is worth mentioning that the C═C symmetrical stretching modes for the low-energy conformers of the cis−cis and trans−trans isomers (both with C_{2h} symmetry) are infrared inactive but Raman active, while this mode for the cis−trans isomer with lower symmetry (C_s) is both IR and Raman active. In all the high-energy conformers, these two stretching vibrational modes are both IR and Raman active because of their lower symmetry.

Investigation on the cis−cis isomer has been performed. For the planar s-trans conformer, the frequencies of its (C═C)$_{\mathrm{asym}}$ and (C═C)$_{\mathrm{sym}}$ vibrational bands are 1698 and 1758 cm^{-1}, respectively. For the nonplanar s-gauche conformer, however, the corresponding frequencies are 1737 and 1733 cm^{-1}, respectively. This shows that the difference of the C═C stretching modes in the s-gauche conformer is only about 10% of that in the s-trans form. Such a small difference is a characteristic of the nonplanar conjugative structure, which is in good agreement with the argument of De Maré[1] for 1,3-butadiene. In addition, the frequency sequences of the υ(C═C)$_{\mathrm{sym}}$ and υ(C═C)$_{\mathrm{asym}}$ in these two conformers are reversed. Similar results were observed in the two conformers of 1,3-butadiene studied by De Maré.[1]

Investigation on the cis−trans isomer indicates that the frequency difference of the υ(C═C)$_{\mathrm{sym}}$ and υ(C═C)$_{\mathrm{asym}}$ is about 17 cm^{-1} (1733 vs 1716 cm^{-1}) for the planar s-cis conformer of the cis−trans isomer at the B3LYP/6-31G(*d*,*p*) level. This difference is significantly larger than that (4 cm^{-1}) in the s-gauche conformer of the cis−cis isomer. This, in turn, accounts

TABLE 5: Stabilization Energies of Donor−Acceptor Interaction with Respect to Those of Fluorine in Different Isomers

donor (*i*)	acceptor (*j*)	interaction	*E*(2) (kJ mol^{-1})	
	cis−cis DFBD		s-trans	s-gauche
[a]BD(2) C1−C2	[a]BD*(2) C3−C4	$\pi-\pi^*$	14.0	10.9
[a]LP(3) F5	[a]BD*(2) C1−C2	$n-\pi^*$	22.3	23.4
	cis−trans DFBD		s-trans	s-cis
BD(2) C1−C2	BD*(2) C3−C4	$\pi-\pi^*$	13.5	11.7
LP(2) F5	BD*(1) C4−H8	$n-\pi^*$	0.0	**0.8**[b]
LP(3) F5	BD*(2) C1−C2	$n-\pi^*$	22.3	21.7
LP(3) F6	BD*(2) C3−C4	$n-\sigma^*$	22.4	22.8
	trans−trans DFBD		s-trans	s-gauche
BD(2) C1−C2	BD*(1) C1−C2	$\pi-\pi^*$	14.3	9.4
LP(3) F5	BD*(2) C1−C2	$n-\pi^*$	22.2	21.8

[a] BD denotes the occupied bond orbital, and BD* denotes the formally empty antibonding orbital. LP and RY* denote the occupied lone pair and anti-Rydberg orbitals of fluorine, respectively. [b] The value in bold font is of great interest.

for the planar structure of the high-energy conformer of the cis−trans isomer. As shown in Table 4, the high-energy conformers of the trans−trans and the cis−cis isomers are quite similar. Their C=C stretching mode splittings are both small and smaller than that of the planar high-energy conformer of the cis−trans isomer. Their frequency sequences of the $\upsilon(\mathrm{C{=}C})_{\mathrm{sym}}$ and $\upsilon(\mathrm{C{=}C})_{\mathrm{asym}}$ are also reversed. The smaller difference of C=C stretching modes in the high-energy conformer as compared to that of the s-trans low-energy form is a common character for all three isomers of DFBD.

Natural Bond Orbital Analysis. For a better understanding of the high-energy forms of these isomers, natural bond orbital (NBO) analysis has been carried out at the B3LYP/6-31G(*d*,*p*) level of theory. The selected donor−acceptor interaction stabilization energy terms may partly account for the differences among the conformers of the three isomers.

It is well-known that fluorine atom exhibits two competitive effects. They are electron-withdrawing induction (−I) due to its high electronegativity and electron-donating conjugation (+C) due its lone-pair electrons. These factors can be quantitatively rationalized in terms of the NBO donor−acceptor charge transfer (CT) interaction model.[18,25] The stabilization energy, called *E*(2) in Table 5, obtained from this CT interaction is derived subsequently from the second-order Møller−Plesset perturbation (MP2) theory with the Fock matrix in the NBO basis. To determine the relative stabilities of these conformers, attention is paid to the π orbitals and the lone pair electrons of fluorine as electron-donor and electron-acceptor, respectively. The calculated results suggest that the stabilization energy terms contributed from its acceptor property are negligible.

Specifically, let us first examine the cis−cis isomer, whose high-energy conformer is the nonplanar s-gauche form with C_2 point group symmetry. In comparing the stabilization energy terms, $\pi-\pi^*$ and $n-\pi^*$, from Table 5, it can be seen that the most outstanding CT stabilization energies between the occupied orbital $n(\mathrm{F}_5)$ of the lone pair electrons and the adjacent empty $\pi^*(\mathrm{C{=}C})$ orbital are 22.3 and 23.4 kJ mol^{-1} for the s-trans and s-gauche conformers, respectively. This $n-\pi^*$ term appears slightly larger in the s-gauche conformer, but the $\pi-\pi^*$ term is much larger (14.0 vs 11.0 kJ mol^{-1}) in the s-trans form. This indicates that the $\pi-\pi^*$ conjugative interaction in the high-energy conformer is weakened while the $n-\pi^*$ interaction is enhanced. For the cis−trans isomer, the $\pi-\pi^*$ interactions are slightly more complicated because the two substituted fluorine atoms lie in different orientations of the essentially planar molecule, where the additional stabilization terms, $n(\mathrm{F}_6)-\pi^*$ and $n(\mathrm{F}_5)-\sigma^*(\mathrm{C4{-}H8})$, are observed. Their contributions to the stability of the high-energy conformer overcompensate the slight decease of the $n(\mathrm{F}_5)-\pi^*$ term. Although the contribution from the $n(\mathrm{F}_5)-\sigma^*(\mathrm{C4{-}H8})$ CT term is just 0.8 kJ mol^{-1}, it is still significant, while it is not found in the other two isomers. This implies the existence of the weak intramolecular hydrogen bond interaction and, hence, that it accounts for the highest stability and essentially planar structure of this high-energy conformer. For the trans−trans isomer, the $\pi-\pi^*$ term declines from the s-trans form to s-gauche form, and the $n(\mathrm{F}_5)-\pi^*$ term also decreases slightly. This may provide an explanation on the differences in geometry and stability between the two high-energy conformers of two different isomers.

Conformational Energies of the Isomers Using G3 Theory. To our best knowledge, there is no experimental report on quantitative evaluations about the conformational energetic relationship between the conformer pair in each of the three isomers, even though this unusual equilibrium relationship has been sensed both experimentally and theoretically.[11] Some precise works[17,18] on the evaluation of thermodynamic properties using G3 and G3B3 theories had been reported recently. The accuracy in calculation was significantly improved by enlarging the basis sets, adding a spin−orbital correction to the energies of the atomic species and the core correlation correction to the total energy. In this work, the G3 and G3B3 calculations have also been performed for the high-energy conformers of the three isomers, and the results are shown in Table 6.

Results of our previous work[24] using the G3B3 theory are in better agreement with the experimental data than most of the recent reports. This suggests that the G3B3 method is superior in predicting the thermodynamic properties, especially in the accurate estimation of the tiny energy differences in a molecular system. Table 6 shows that the G3 and G3B3 results are in good agreement with each other and that the energy sequence of the three high-energy conformers of the DFBD is *E*(s-gauche of cis−cis) > *E*(s-gauche of trans−trans) > *E*(s-cis of cis−trans). This indicates that the high-energy conformer of trans−trans conformer is slightly more stable than that of the cis−cis isomer. However, results of the B3LYP/6-31G(*d*,*p*) and MP2 methods predict that the s-gauche conformer of the trans−trans isomer is slightly less stable than that of the cis−cis isomer, and this is contradictory to the G3B3 results. This reminds us to reconsider the levels of B3LYP and MP2 with the 6-31G-(*d*,*p*) basis sets and the intramolecular interaction. Furthermore, it may be rational to add the spin−orbital correction, which is recently found to be important in the halide-containing system

TABLE 6: Calculated Enthalpies (ΔHs) of the Three Isomers with G3B3 Theory

isomer	conformer	H_{G3} (hartree)	ΔH_{G3} (kJ mol^{-1})	H_{G3B3} (hartree)	ΔH_{G3B3} (kJ mol^{-1})	$\Delta H_{\mathrm{ref\ 17}}$ (kJ mol^{-1})
cis−cis	s-trans	−354.24774	0.0	−354.25447	0.0	0.0
	s-gauche	−354.24170	**15.8**	−354.24797	**17.1**	**19.4**
cis−trans	s-trans	−354.24649	0.0	−354.25315	0.0	0.0
	s-cis	−354.24351	**7.9**	−354.25021	**7.9**	**10.0**
trans−trans	s-trans	−354.24557	0.0	−354.25215	0.0	0.0
	s-gauche	−354.24197	**9.5**	−354.24850	**9.8**	**12.5**

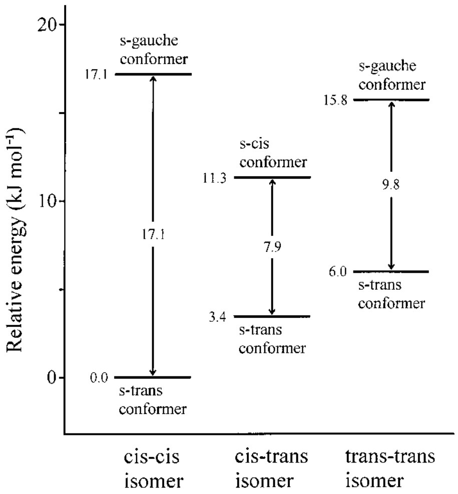

Figure 2. Relative energies for all conformers of DFBD.

but is less weighted in the G3B3 calculation. Thus, we can only obtain reliable energetic properties, especially the small energy difference in a conformational system, at high computational level. The conformational energies of the cis−cis, cis−trans, and trans−trans isomers, estimated by the G3B3 method, are 17.1, 7.9 and 9.8 kJ mol^{-1}, respectively. In summary, the energies of all conformers of the DFBD system obtained in this work are shown in Figure 2.

Conclusions

Optimized geometries and vibrational frequency analysis of the conformers of the 1,4-diflorobutadiene system have been performed at the B3LYP/6-31G(*d*,*p*) level of theory. The NBO analysis has been employed to interpret the difference among the conformers in terms of the electronic structure and the effect of substituted fluorine on their relative stabilities.

For a given isomer, the geometry of the high-energy conformer is essentially the same as that of its low-energy conformer partner, except that the C=C conjugative interaction is weaker in the former, while the θ(C−C=C) bond angle there is generally larger. The torsional angles about the C−C bonds in the high-energy conformers of the cis−cis and trans−trans isomers are 30.9° and 41.6°, respectively, while the high-energy conformer of the cis−trans isomer is essentially planar. Harmonic vibrational frequency analysis indicates that the difference of the two C=C stretching frequencies is smaller than that in its low-energy conformer partner. This relatively smaller separation of the C=C stretching modes is the characteristic of the high-energy conformer in a conjugative system, which is also consistent with their geometric difference. In addition, the positions of the $\upsilon(C=C)_{sym}$ and $\upsilon(C=C)_{asym}$ in the high-energy and low-energy conformers are reversed in order. The NBO analysis reveals that the $\pi-\pi^*$ conjugative interaction is commonly weaker in the high-energy conformer and that the $n-\pi^*$ interaction may account for the different stabilities in a given conformer pair. Also, NBO analysis suggests the existence of the intramolecular hydrogen bonding in the high-energy conformer of the cis−trans isomer. The conformational energies of the cis−cis, cis−trans, and trans−trans isomers estimated from the G3B3 calculations are 17.1, 7.9, and 9.8 kJ mol^{-1}, respectively. The high-energy conformer of the cis−trans isomer is more stable than that of the cis−cis and trans−trans isomers by 5.8 and 4.5 kJ mol^{-1}, respectively. Obviously, this relationship is quite different from that of the three low-energy conformers, which may be attributed to the existence of the intramolecular hydrogen bonding in the s-cis conformer of the cis−trans isomer.

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