Conformational and Vibrational Analysis of 2,4-, 2,5- and 2,6-Difluorobenzaldehydes by ab initio Hartree-Fock and Density Functional Theory Calculations

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The optimized molecular structures, vibrational frequencies and corresponding vibrational assignments of the two planar O-*cis* and O-*trans* rotomers of 2,4-, 2,5- and 2,6-difluorobenzaldehyde have been calculated using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) methods with the 6-311++G(d,p) basis set level. The calculations were adapted to the C_S symmetries of all the molecules. The O-*trans* rotomers with lower energy of all the compounds have been found as preferential rotomers in the ground state. The mean vibrational deviations between the vibrational frequency values of the two conformers of all the compounds have been shown to increase while the relative energies increase, and so it has been concluded that the higher the relative energy between the two conformers the bigger is the mean vibrational deviation.

Key words: Difluorobenzaldehydes; Conformers; Vibrations; IR Spectra; Raman Spectra; HF; DFT.

1. Introduction

2,4-, 2,5- and 2,6-difluorobenzaldehydes (DFBs) are benzene derivative molecules, having the chemical formula $C_6H_3(CHO)F_2$. In the last decades coordination chemistry of Schiff bases, derived from aldehydes, has received much attention [1, 2]. Benzaldehydes, lacking electron-donating substituents and possessing electron-withdrawing groups, yield benzoic acids [3, 4]. Ekaeva et al. have reported the Baeyer-Villiger oxidation of fluorobenzaldehydes [3]. Difluorobenzaldehydes can be used as starting substrates in the synthesis of bioactive materials which are for example efficient pesticides and medicines [5]. Itoh et al. have investigated the three structural isomers of fluorobenzaldehydes (*p*-, *m*- and *o*-forms) in detail with matrix isolation infrared (IR) spectroscopy and density functional theory (DFT) calculations, and they have identified two planar rotomers (*syn* and *anti*) for *m*- and *o*-fluorobenzaldehydes [6]. Many studies have been focused on the identification of these two rotomers [7 – 11]. But we have not found similar studies for DFBs.

In this present study we have calculated the optimized molecular geometries and complete vibration spectra of 2,4-, 2,5- and 2,6-DFBs to determine the preferential conformation of the aldehyde (CHO) group in the ground state using ab inito Hartree-Fock (HF) and DFT (B3LYP) methods with the 6-311++G(d,p) basis set and investigated the effect of the change in conformation on the vibrational frequencies.

2. Computational Methods

The vibrational frequencies and optimized structure parameters of DFBs have been calculated by using HF and B3LYP methods with the 6-311++G(d,p) basis set level. All computations have been performed on a personal computer using the Gauss-View molecular visualization program [12] and Gaussian 03 program package [13], and the scale factors of 0.9051 and 0.9614 are used for HF and B3LYP with the 6-311++G(d,p) basis set, respectively [14].

3. Results and Discussion

DFBs are molecules having 14 atoms and belonging to the point group C_S. The three Cartesian displacements of the 14 atoms provide 42 internal modes, namely

$$\Gamma_{\text{inter.}} = 25\text{A}' + 14\text{A}''.$$

From the character table for the C_S point group, since

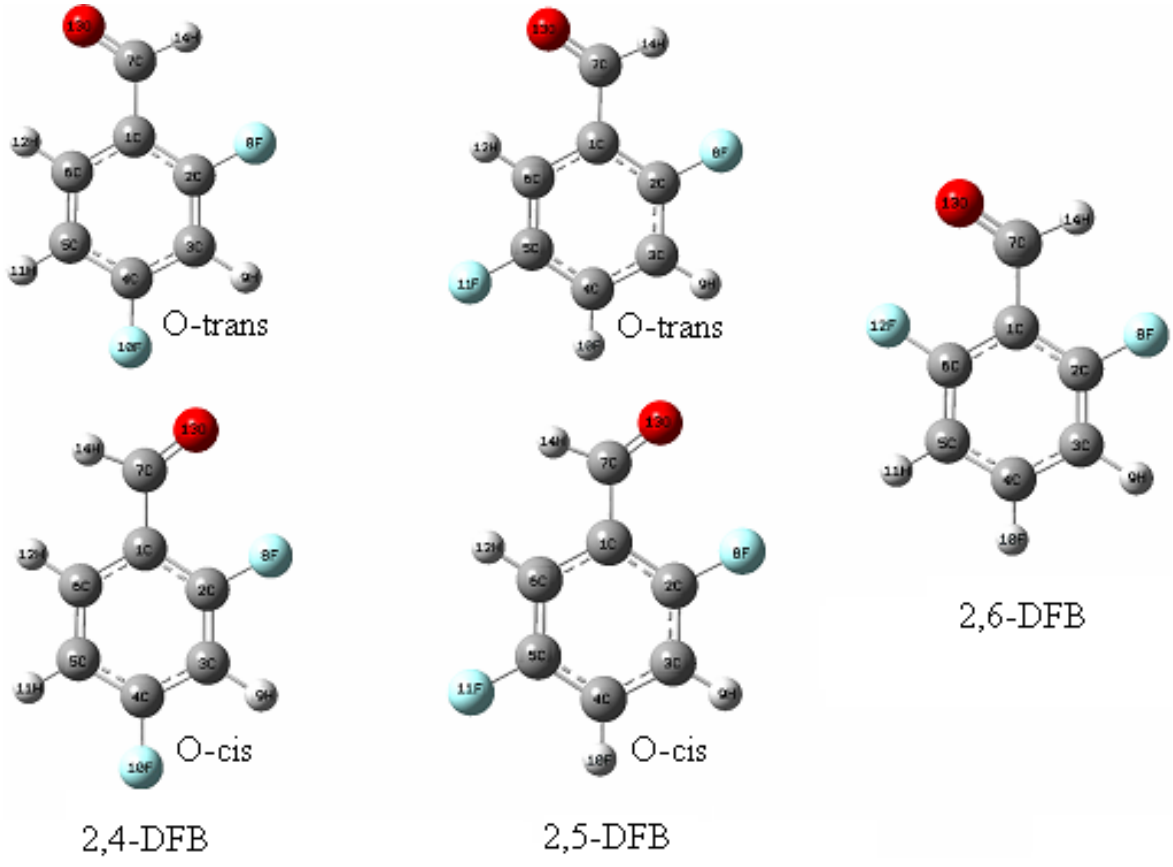

Fig. 1. Calculated optimized structures of the O-*trans* and O-*cis* conformers of 2,4-DFB, 2,5-DFB, and 2,6-DFB.

$\Gamma_{\text{trans.}} = 2\text{A}' + \text{A}''$ and $\Gamma_{\text{rot.}} = \text{A}' + 2\text{A}''$, we get

$$\Gamma_{\text{vib.}} = \Gamma_{39} - \Gamma_{\text{trans.}} - \Gamma_{\text{rot.}} = 25\text{A}' + 11\text{A}''$$

normal modes of vibration. All the vibrations are active both in infrared (IR) and Raman (R). For an N-atomic molecule, $(2N-3)$ of all vibrations are in-plane and $(N-3)$ are out-of-plane [15]. Thus, for the title molecules, 25 of all the 36 vibrations are in-plane and 11 out-of-plane. Since the molecules are in the C_S group, all the vibrations being anti-symmetric through the mirror plane of symmetry σ_h belong to the species A″, and the others being symmetric through σ_h belong to the species A′. Thus, all the vibrations of the A′ species are in-plane, and those of the A″ species are out-of-plane. This is indeed found to be the case by the visual inspection of all the vibrations using the GaussView visualization program.

The ab initio optimized structures of the O-*cis* and O-*trans* conformers of the title molecules are illustrated in Figure 1. The O-*cis* and O-*trans* conformers refer to the configurations of C=O with respect to the 2C-8F bond. The resulting vibrational frequencies for the optimized geometries and proposed vibrational assignments are given in Tables 1 – 3. The tables also show the experimental vibrations of the compounds. The experimental (IR and R) vibration values of the molecules have been found by the spectra obtained from the web page of the Sigma-Aldrich Cooperation [16]. The calculated vibrations are scaled, and the symmetry species of all the vibrations are written in the first column of the tables. Since there are no reported assignments of the IR spectra of the DFBs we have used the assignments of fluorobenzaldehydes as proof [6]. The proposed vibrational assignments in the tables mostly correspond to the assignments given in the reference. However, some vibrational assignments are controversial.

As seen from Tables 1 and 2, the experimental vibration values agree well with the calculated values for

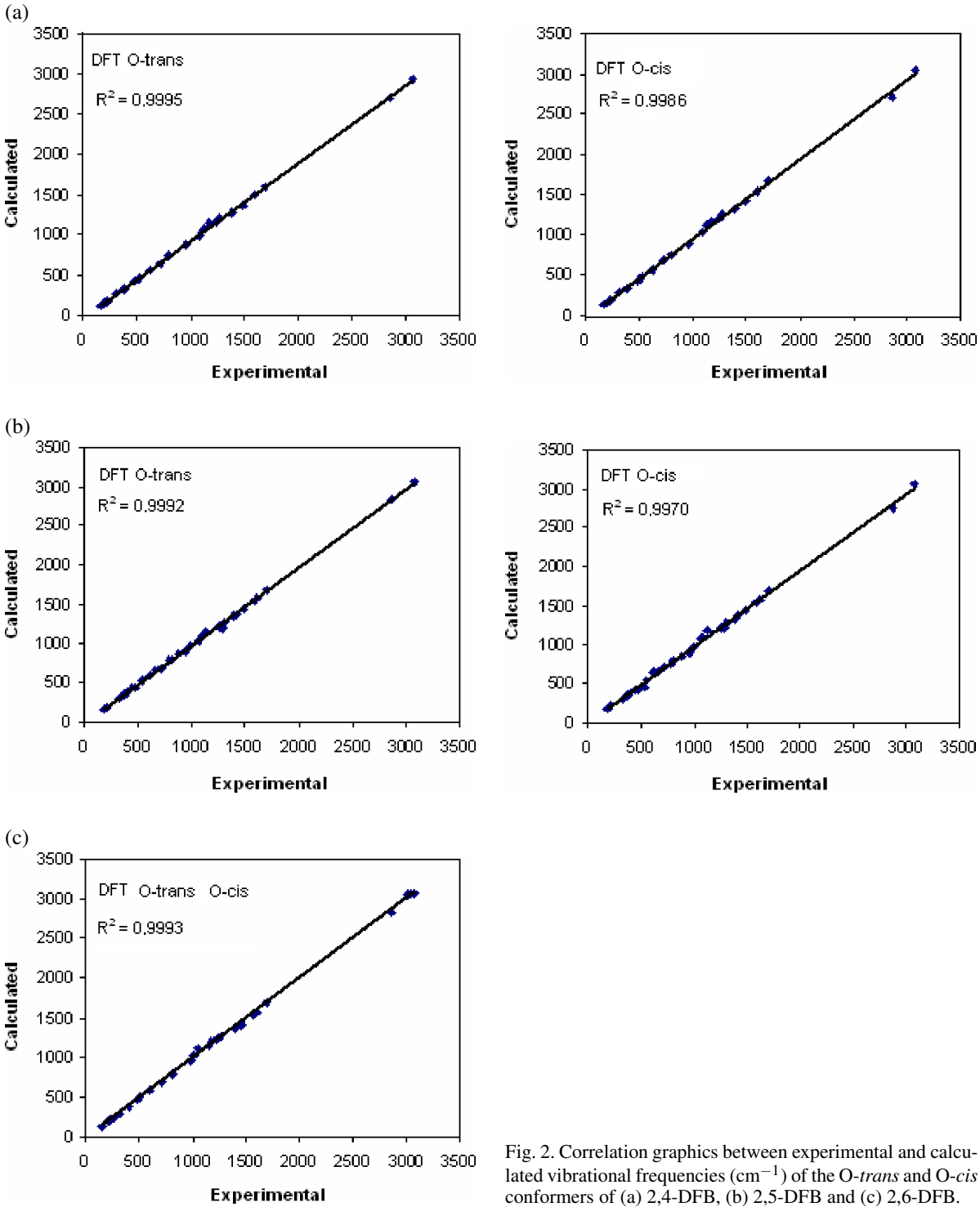

Fig. 2. Correlation graphics between experimental and calculated vibrational frequencies (cm^{-1}) of the O-*trans* and O-*cis* conformers of (a) 2,4-DFB, (b) 2,5-DFB and (c) 2,6-DFB.

Table 1. Experimental and calculated vibrational frequencies of the O-*trans* and O-*cis* conformers of 2,4-DFB. ν shows the stretching, δ the bending, γ the out-of-plane bending, w the wagging, and ρ_r the rocking modes.

Symmetry	Assignment	Experimental [16] frequency (cm^{-1})	Calculated frequency (cm^{-1}) 6-311++G(d,p)			
			O-*trans*		O-*cis*	
		R	HF	B3LYP	HF	B3LYP
A′	ν(CH)	3087	3039	3096	3037	3094
A′	ν(CH)		3036	3087	3033	3088
A′	ν(CH)		3022	3072	3000	3051
A′	ν(CH) in the CHO	2873	2861	2852	2794	2762
A′	ν(C=O) + δ(C-CHO)	1700	1767	1692	1787	1713
A′	ν(ring) + δ(CH)	1611	1620	1584	1621	1584
A′	ν(ring) + δ(CH)		1598	1563	1592	1562
A′	ν(ring) + ν(CF) + δ(CH)	1502	1495	1461	1500	1465
A′	ν(ring) + δ(CH)		1424	1402	1428	1406
A′	δ(CH) in the CHO	1403	1390	1370	1388	1368
A′	ν(CF) + δ(CH)	1273	1279	1295	1283	1297
A′	ν(ring) + δ(CH)	1251	1234	1234	1230	1248
A′	ν(ring) + δ(CH)	1187	1177	1217	1196	1213
A′	ν(C-CHO) + δ(CH)	1140	1157	1155	1165	1163
A′	ν(ring) + δ(CH)		1109	1109	1118	1122
A′	δ(CH)	1094	1066	1063	1074	1082
A″	γ(CH)		1025	984	1020	980
A″	γ(CH)		985	942	965	953
A′	δ(ring)	970	950	941	959	921
A″	γ(CH)		863	830	867	835
A″	γ(CH)	813	831	801	823	792
A′	δ(ring) + δ(C-CHO)		781	785	778	778
A′	δ(ring)	728	712	707	723	719
A″	γ(ring)		693	668	697	673
A″	γ(ring)	635	636	615	638	612
A′	δ(ring) + δ(C-CHO)	627	619	608	602	601
A′	δ(ring)	527	512	509	517	514
A′	δ(ring) + δ(CF)	495	480	475	468	462
A″	γ(ring) + w(CH) in the CHO		459	450	461	453
A′	δ(ring) + δ(CF)	389	375	372	368	367
A″	w(ring) + w(CH) in the CHO	319	317	308	325	318
A′	ρ_r (CF)		308	304	325	316
A″	ρ_r(ring) + w(CF)	235	227	217	225	216
A′	ρ_r(ring) + ρ_r(CHO)	200	189	186	192	188
A″	w(CH) in the CHO	178	159	160	165	169
A″	w(ring) + ρ_r(CHO)		94	94	69	71

the O-*cis* and O-*trans* conformers of 2,4- and 2,5-DFB. The correlation graphics at the DFT 6-311++G(d,p) level are drawn in Figure 2. The correlation factors in Table 4 also show agreement for both conformers. But the correlation values for the O-*trans* conformers are far better than for the O-*cis* conformers. This is an expected result, since the calculated energy values of the O-*trans* conformers are lower than those of the O-*cis* conformers, so the preferential conformations of the two molecules in the ground state are the O-*trans* conformers. However, Strand et al. have obtained that the O-*trans* conformer of *o*-fluorobenzaldehyde is more stable than the O-*cis* conformer by 3.2 kcal/mol, while the O-*cis* conformer of *m*-fluorobenzaldehyde is more stable than the O-*trans* conformer by 0.1 kcal/mol [17].

Table 5 shows the sum of electronic and zero-point energies of the O-*cis* and O-*trans* conformers of the molecules, calculated at the HF and DFT(B3LYP) 6-311++G(d,p) level. These results are given without introducing any correction. The table also shows the mean vibrational deviations ($|\Delta\nu|_{ave}$) between the calculated vibrational frequency values of the two conformers, and the relative energies. As seen, the mean vibrational deviation increases, while the relative energy increases. Therefore we state that the more different the molecular structure of the two conformers is, the higher is the relative energy between them, and this causes a bigger mean vibrational deviation. This comment has also been given for 2-, 3- and 4-pyridine carboxaldehydes in our previous study [18]. As we said before, for 2,5-DFB, the experimental vibration values correspond mainly to the O-*trans* conformer of the molecule. Furthermore, since the energy differences between the two conformers are larger than the one

Table 2. Experimental and calculated vibrational frequencies of the O-*trans* and O-*cis* conformers of 2,5-DFB. ν shows the stretching, δ the bending, γ the out-of-plane bending, w the wagging, and ρ_r the rocking modes.

Symmetry	Assignment	Experimental [16] frequency (cm^{-1})		Calculated frequency (cm^{-1}) 6-311++G(d,p)			
				O-*trans*		O-*cis*	
		IR	R	HF	B3LYP	HF	B3LYP
A′	ν(CH)	3080	3084	3037	3087	3031	3086
A′	ν(CH)			3032	3083	3018	3075
A′	ν(CH)			3019	3076	3012	3064
A′	ν(CH) in the CHO	2868	2876	2868	2856	2798	2769
A′	ν(C=O) + δ (C-CHO)	1705	1702	1773	1696	1794	1717
A′	ν(ring)	1623	1623	1629	1590	1631	1591
A′	ν(ring) + δ(CH)	1594	1597	1609	1567	1603	1563
A′	ν(ring) + ν(CF) + δ(CH)	1490		1492	1456	1498	1461
A′	ν(ring) + δ(CH)	1430	1430	1412	1392	1414	1395
A′	δ(CH) in the CHO	1404	1402	1387	1370	1378	1359
A′	ν(CF) + δ(CH)	1309	1308	1264	1288	1263	1293
A′	ν(ring) + δ(CH)	1265	1263	1238	1227	1245	1226
A′	ν(ring) + δ(CH)	1196	1195	1182	1211	1212	1222
A′	ν(ring) + δ(CH)	1138	1138	1153	1158	1164	1188
A′	ν(C-CHO)+δ(CH)	1099	1092	1086	1108	1090	1109
A′	δ(CH)	1068		1067	1063	1069	1083
A″	γ(CH)	1002	1003	1022	984	1019	981
A″	γ(CH)	965	967	968	939	966	926
A′	δ(ring) + δ(C-CHO)	949	951	942	921	930	918
A″	γ(CH)	888		919	880	902	864
A″	γ(CH)	826	814	844	808	848	810
A′	δ(ring) + δ(C-CHO)	790		791	790	771	765
A′	δ(ring)	723	722	703	699	736	734
A″	γ(ring)	672		700	676	695	678
A′	δ(ring) + δ(C-CHO)	623	627	609	607	658	656
A″	γ(ring)	558	549	565	546	568	551
A′	δ(ring) + δ(CF)	548		535	533	465	462
A″	γ(ring) + w(CH) in the CHO		486	451	443	447	436
A′	δ(ring)	453		446	443	438	436
A′	δ(ring) + δ(CF)		405	391	388	398	397
A″	w(ring) + w(CH) in the CHO		382	379	365	377	363
A′	ρ_r (CF)		325	310	307	321	318
A″	w(ring) + ρ_r(CHO)		216	197	192	217	219
A′	ρ_r(ring) + ρ_r(CHO)		190	180	177	188	187
A″	w(CH) in the CHO		167	156	150	148	142
A″	w(ring) + ρ_r(CHO)			103	107	70	80

for 2,4-DFB, the relative energy is higher, and so a bigger vibrational deviation occurs (Table 5). On the other hand, for 2,6-DFB, due to the symmetry of this molecule, the two conformers are equally populated, and the observed vibrations should correspond to the average of those of each conformer. Therefore, the relative energy and mean vibrational deviation are zero. For this molecule, the correlation factors and graphics are given in Table 4 and in Fig. 2, respectively.

Table 6 shows the calculated optimized structure parameters (bond lengths and bond angles) for all the molecules. The experimental parameters obtained from the gas electron diffraction (GED) data of *o*-fluorobenzaldehyde [C_6H_4(CHO)F] are also given [17]. The calculated parameters in the table seem to be close to their corresponding experimental values. For all the title molecules the largest differences of the calculated geometries from the experimental ones are 0.038 Å (HF) and 0.023 Å (B3LYP) for the bond lengths and 4.3° (HF) and 3.7° (B3LYP) for the bond angles.

4. Conclusion

The vibrational frequencies, optimized molecular structures and corresponding vibrational assignments of the *cis* and *trans* conformations of 2,4-, 2,5- and 2,6-DFBs have been calculated using HF and B3LYP methods with the 6-311++G(d,p) basis set level. It has been shown that the preferential conformers of all the molecules in the ground state are the O-*trans* conformers. The mean vibrational deviation between the vibrational frequency values of the two conformers of all the compounds increases, while the relative energy in-

Table 3. Experimental and calculated vibrational frequencies of 2,6-DFB. ν shows the stretching, δ the bending, γ the out-of-plane bending, w the wagging, and ρ_r the rocking modes.

Symmetry	Assignment	Experimental [16] frequency (cm^{-1})	Calculated frequency (cm^{-1}) 6-311++G(d,p)	
		R	HF	B3LYP
A′	ν(CH)	3100	3034	3089
A′	ν(CH)	3062	3029	3084
A′	ν(CH)	3032	3008	3065
A′	ν(CH) in the CHO	2887	2865	2847
A′	ν(C=O) + δ (C-CHO)	1706	1782	1704
A′	ν(ring) + δ(CH)	1622	1625	1591
A′	ν(ring) + δ(CH)	1581	1591	1552
A′	ν(ring) + ν(CF) + δ(CH)	1475	1467	1438
A′	ν(ring) + δ(CH)	1460	1451	1420
A′	δ(CH) in the CHO	1414	1405	1385
A′	ν(CF) + δ(CH)	1278	1282	1285
A′	ν(ring) + δ(CH)	1241	1241	1241
A′	ν(ring) + δ(CH)	1190	1182	1207
A′	ν(C-CHO)+δ(CH)	1158	1155	1157
A′	ν(ring) + δ(CH)	1063	1084	1132
A′	δ(CH)	1023	1038	1039
A″	γ(CH)		1016	989
A′	δ(ring)	995	1012	978
A″	γ(CH)		989	936
A″	γ(CH)		889	859
A″	δ(ring) + δ(C-CHO)	827	800	799
A′	γ(CH)		798	766
A′	γ(ring)	717	705	693
A″	δ(ring)		695	678
A″	γ(ring)	604	621	593
A′	δ(ring) + δ(C-CHO)		586	582
A′	δ(ring)	522	506	505
A′	γ(ring) + w(CH) in the CHO	492	490	477
A″	δ(ring) + δ(CF)		477	472
A′	δ(ring) + δ(CF)	412	392	389
A″	ρ_r (CF)	324	316	311
A′	w(ring) + w(CH) in the CHO	273	270	260
A″	ρ_r(ring) +w(CF)	246	236	226
A′	ρ_r(ring) + ρ_r(CHO)	215	202	199
A″	w(CH) in the CHO	165	139	135
A″	w(ring) + ρ_r(CHO)		58	65

Table 4. Correlation factors for all title molecules.

Molecule	6-311++G(d,p)			
	O-*trans*		O-*cis*	
	HF	B3LYP	HF	B3LYP
2,4-DFB	0.9992	0.9995	0.9985	0.9986
2,5-DFB	0.9990	0.9992	0.9973	0.9970
2,6-DFB	0.9993	0.9993	0.9993	0.9993

creases, and so it has been concluded that the higher the relative energy between the two conformers of the molecules the bigger is the mean vibrational deviation.

Table 5. Sum of electronic and zero-point energies, relative energies and mean vibrational deviations of the O-*cis* and O-*trans* conformers of all title molecules.

Molecule	HF [6-311++G(d,p)] (Hartree/particle)		Relative energy	$\|\Delta\nu\|_{ave}$	B3LYP [6-311++G(d,p)] (Hartree/particle)		Relative energy	$\|\Delta\nu\|_{ave}$
	O-*trans*	O-*cis*	(kcal/mol)		O-*trans*	O-*cis*	(kcal/mol)	
2,4-DFB	−541.174705	−541.169912	3.0057	9.8333	−544.109504	−544.105683	2.2391	10.3333
2,5-DFB	−541.171603	−541.166613	3.1292	14.3611	−544.107497	−544.103467	2.5272	15.3611
2,6-DFB	−541.166654	−541.166654	0	0	−544.102052	−544.102052	0	0

Table 6. Calculated optimized structure parameters for all title molecules.

Parameter	Exp. [17]	Calculated [6-311++G(d,p)]									
		2,4-DFB				2,5-DFB				2,6-DFB	
		O-*trans*		O-*cis*		O-*trans*		O-*cis*			
		HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP
Bond lengths (Å)											
C(1)-C(2)	1.397	1.383	1.397	1.392	1.403	1.381	1.396	1.388	1.401	1.390	1.403
C(2)-C(3)	1.393	1.378	1.385	1.376	1.385	1.379	1.387	1.378	1.387	1.374	1.382
C(3)-C(4)	1.397	1.376	1.386	1.378	1.387	1.381	1.391	1.384	1.393	1.383	1.393
C(4)-C(5)	1.404	1.383	1.391	1.378	1.388	1.382	1.391	1.376	1.388	1.384	1.393
C(5)-C(6)	1.393	1.377	1.386	1.381	1.388	1.369	1.379	1.373	1.381	1.377	1.386
C(6)-C(1)	1.408	1.394	1.404	1.391	1.403	1.393	1.401	1.391	1.403	1.383	1.405
C(1)-C(7)		1.385	1.482	1.485	1.482	1.490	1.486	1.490	1.486	1.491	1.487
C(2)-F(8)	1.344	1.322	1.351	1.309	1.338	1.326	1.353	1.314	1.341	1.323	1.353
C(3)-H(9)	1.103	1.073	1.082	1.073	1.082	1.074	1.084	1.073	1.083	1.073	1.082
C(4)-F(10)		1.318	1.347	1.318	1.347						
C(4)-H(10)						1.074	1.082	1.074	1.083	1.075	1.083
C(5)-H(11)	1.103	1.073	1.083	1.073	1.082					1.073	1.082
C(5)-F(11)						1.326	1.352	1.326	1.353		
C(6)-H(12)	1.103	1.074	1.083	1.076	1.085	1.073	1.083	1.075	1.084		
C(6)-F(12)										1.310	1.340
C(7)-O(13)	1.221	1.186	1.212	1.182	1.207	1.185	1.211	1.181	1.206	1.183	1.209
C(7)-H(14)	1.120	1.091	1.104	1.097	1.112	1.090	1.104	1.096	1.111	1.090	1.104
Bond angles (°)											
C(1)-C(2)-C(3)	122.2	122.9	122.9	122.2	122.3	122.2	122.5	121.5	121.8	123.7	123.8
C(2)-C(3)-C(4)	118.2	117.1	117.0	117.8	117.7	118.8	118.8	119.7	119.6	118.0	118.1
C(3)-C(4)-C(5)	120.5	122.9	123.0	122.8	122.9	119.2	119.0	119.0	118.9	121.0	120.8
C(4)-C(5)-C(6)	120.8	118.1	118.2	117.6	117.7	122.0	122.3	121.5	121.8	118.8	119.0
C(5)-C(6)-C(1)	119.2	121.4	121.4	122.3	122.2	119.3	119.2	120.1	119.9	122.6	122.8
C(6)-C(1)-C(2)	119.1	117.6	117.5	117.4	117.3	118.5	118.2	118.1	117.9	115.8	115.4
C(6)-C(1)-C(7)		120.6	120.6	118.4	118.4	120.0	120.0	117.7	117.6	124.1	124.3
C(2)-C(1)-C(7)	123.9	121.8	121.9	124.2	124.5	121.5	121.8	124.2	124.5	120.1	120.2
C(1)-C(2)-F(8)		119.3	119.3	120.4	120.2	119.4	119.3	120.6	120.3	118.3	118.2
C(3)-C(2)-F(8)		117.8	117.8	117.4	117.5	118.4	118.2	117.9	117.9	118.0	117.9
C(2)-C(3)-H(9)		121.6	121.6	120.9	120.9	119.7	119.7	119.1	119.2	119.8	119.7
C(4)-C(3)-H(9)		121.3	121.4	121.3	121.3	121.5	121.5	121.2	121.2	122.3	122.2
C(3)-C(4)-F(10)		118.3	118.2	118.2	118.2						
C(5)-C(4)-F(10)		118.8	118.8	119.0	118.9						
C(3)-C(4)-H(10)						121.2	121.3	121.1	121.3	119.5	119.6
C(5)-C(4)-H(10)						119.6	119.7	119.9	119.9	119.5	119.6
C(4)-C(5)-H(11)		122.0	122.1	122.2	122.2					119.2	119.1
C(6)-C(5)-H(11)		119.9	119.7	120.6	120.1					121.9	121.9
C(4)-C(5)-F(11)						118.6	118.4	119.2	119.0		
C(6)-C(5)-F(11)						119.4	119.3	119.3	119.2		
C(5)-C(6)-H(12)		120.5	120.9	119.1	119.5	120.9	121.3	119.4	119.9		
C(1)-C(6)-H(12)		118.1	117.7	118.7	118.3	119.8	119.4	120.5	120.1		
C(5)-C(6)-F(12)										117.8	117.8
C(1)-C(6)-F(12)										119.6	119.4
C(1)-C(7)-O(13)		123.2	123.4	126.5	126.7	123.0	123.2	126.2	126.5	125.0	125.2
C(1)-C(7)-H(14)		115.9	115.7	113.1	112.6	115.9	115.7	113.2	112.8	114.2	113.9
O(13)-C(7)-H(14)		120.9	120.9	120.4	120.6	121.1	121.1	120.1	120.1	120.8	120.9

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