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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · JULY 2002

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Molecular structures of (trifluoromethyl)iodine dihalides CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$): ab initio and DFT calculations

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Received 26 November 2001; accepted 21 February 2002

Abstract

Ab initio and density functional theory calculations have been performed to investigate the equilibrium molecular structures, rotational barriers, vibrational spectra of (trifluoromethyl)iodine dihalides, CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$), with the several basis sets. For each molecule the eclipsed form is found to be more stable than the staggered form. The staggered conformer corresponds to the transition state structure of which energy barrier is less than ~ 0.5 kcal/mol. The natural bond orbital analysis at the restricted Hartree–Fock level shows that the energy preference of an eclipsed form over a staggered form is primarily due to the $\sigma_{\text{IX}} \rightarrow \sigma_{\text{CF}}^*$ interactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: (Trifluoromethyl)iodine dihalides; Ab initio method; Density functional theory method

1. Introduction

The coordination geometry of complexes of the halogens is most usefully correlated with the valence shell electron pair repulsion (VSEPR) theory [1]. According to this bonding model, the interhalogen complex XY_3 , in which central halogen X is in the +3 oxidation state, has the T-shape with two lone pairs of electrons in equatorial positions and the halogen ligands in the remaining equatorial and the axial positions. This T-shaped geometry is established for the trifluorides of chlorine and bromine in the vapor phase [2,3] and for solid ClF_3 [4]. In the solid state BrF_3 , there is an intermolecular $\text{Br} \cdots \text{F}$ contact at 2.49 Å, which is offset from the symmetrical square position although coplanar with the three Br–F bonds of 1.72, 1.84, and 1.85 Å [5]. It can be considered as symmetrically placed above the

center of triangular face, including the two lone pairs of the trigonal bipyramidal arrangement. This interaction can be considered too weak to force a rearrangement to the pseudooctahedral form. In contrast, iodine trichloride achieves a close approach to the square planar arrangement by dimerization, and only the longer bridge distances lead to distortion [6,7].

The (trifluoromethyl)iodine dihalides CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$), are another examples of hypervalent halogen (III) compounds. They can be described as trifluoromethyl-substituted derivatives of iodine trihalide. Since ICl_3 exists only as a dimer in the solid state and no X-ray structure for IF_3 has yet been determined, there has been great interest in the structures of CF_3IX_2 . Structural information for these compounds has been reported by using NMR, X-ray diffraction, and IR and Raman spectroscopy [8–14]. However, a study of ^{13}C and ^{19}F NMR chemical shifts of CF_3IF_2 by Kaupp et al. [15] is the only paper for the theoretical calculation.

In the present study, ab initio and the density

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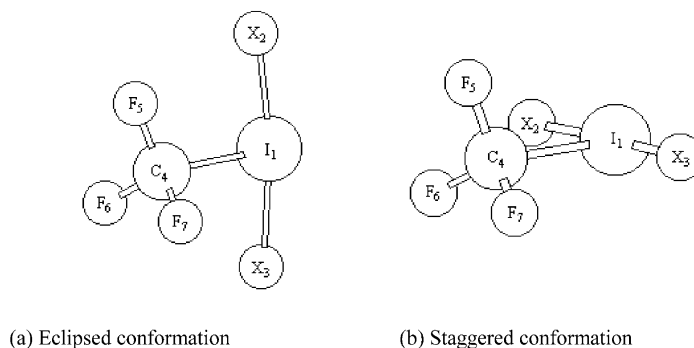


Fig. 1. The molecular structure for CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$). (a) Eclipsed conformation and (b) Staggered conformation.

functional theory (DFT) methods are applied to calculate the geometrical parameters and harmonic vibrational frequencies of trifluoromethyl iodine dihalides CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$). We will compare the computed geometrical parameters with available experimental data and discuss the rotational barriers of these molecules by using population analysis.

2. Computational details

For CF_3IF_2 and CF_3ICl_2 , there are two possible conformations with C_s symmetry as shown in Fig. 1. The molecular geometries of the two conformers for each compound are fully optimized at the various levels of theory using GAUSSIAN 98 program [16]. For the iodine atom, the relativistic effect plays an important role since there are many core electrons. Thus, by using the all-electron 3-21G(d) basis set and the effective core potential (ECP) for the central iodine atom, we investigated the relativistic effect extensively. We used two kinds of the ECPs of LaJohn et al.; one is the small-core ECP in which the 4d electrons as well as the 5s and 5p electrons are included in the valence space, and the other is the large-core ECP in which the only 5s and 5p electrons are included in the valence space [17]. In order to investigate the effect of the size of the basis set employed, we used the 3-21G(d) and 6-311 + G(2d) basis sets for the heavy atoms other than the iodine atom.

At the beginning of our work, the two-layer ONIOM method [18] was applied to these compounds. For both compounds, IH_3 was used as a model system in the high layer. At the ONIOM(B3LYP/3-21G(d):HF/3-21G(d))

level, calculated bond lengths lie between the values computed at B3LYP/3-21G(d) level and those at the HF/3-21G(d) level, but closer to those at the MP2/3-21G(d) level. However, if the basis sets larger than 3-21G(d) were employed on the whole system, the calculation could not be performed both for the real (CF_3IX_2) and model systems (IH_3) because the basis sets larger than 3-21G(d) are not available for the iodine atom. Thus, we cannot get better description for ligand groups of CF_3IX_2 with this ONIOM method.

We have carried out the geometry optimization at the restricted Hartree–Fock (RHF) levels. The electron correlation on the geometry optimization is taken into account intensively by the Becke's three-parameter hybrid method (B3LYP) [19,20] in the DFT and the second-order Moeller–Plesset perturbation (MP2) method. Vibrational frequency analyses were performed at the RHF and B3LYP levels with all the basis sets mentioned above. At the MP2 level, they were carried out only with the ECPs for the iodine atom. Our calculations indicate that optimized structures of the eclipsed conformers are at stationary points corresponding to local minima without imaginary frequencies, whereas the staggered conformers are in transition states. These conformational preference of CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$) and the rotational barriers were investigated by the natural bond orbital (NBO) analyses [21–23].

3. Results and discussion

3.1. Molecular structure of CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$)

The molecular structures of CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$) are

Table 1

Geometrical parameters for CF₃IF₂ (distances, Å; angles, °) at the various levels of calculation

	RHF			B3LYP			MP2			Experiment ^a
	I ^b	II	III	I	II	III	I	II	III	
I–F ₂	1.956	1.979	1.951	2.011	2.048	2.027	1.997	2.023	1.998	1.982(2)
I–F ₃	1.964	1.987	1.960	2.018	2.051	2.032	2.003	2.029	2.005	1.982(2)
I–C ₄	2.176	2.211	2.191	2.221	2.268	2.254	2.182	2.182	2.168	2.174(6)
C ₄ –F ₅	1.287	1.276	1.279	1.316	1.308	1.306	1.316	1.309	1.311	1.291(4) ^c
C ₄ –F ₆	1.294	1.282	1.285	1.323	1.315	1.313	1.324	1.317	1.319	1.291(4) ^c
F ₂ ...F ₅	2.614	2.591	2.576	2.693	2.677	2.649	2.637	2.608	2.590	
F ₂ –I ₁ –C ₄	86.9	85.7	85.7	87.9	86.2	86.0	87.1	86.3	86.2	82.71(9)
F ₃ –I ₁ –C ₄	81.4	79.2	79.7	82.9	80.6	80.6	81.4	79.9	80.1	82.71(9)
F ₂ –I ₁ –F ₃	168.3	164.9	165.4	170.8	166.8	166.6	168.5	166.2	166.3	165.4(2)
I ₁ –C ₄ –F ₅	109.9	109.0	109.3	109.2	108.8	108.6	109.8	109.5	109.6	109.9(3) ^c
I ₁ –C ₄ –F ₆	108.8	107.1	107.6	108.8	107.5	107.4	108.9	107.9	108.2	109.9(3) ^c
F ₅ –C ₄ –F ₆	109.9	111.2	110.9	110.2	111.1	111.3	110.0	110.6	110.4	108.8(4) ^c
F ₆ –C ₄ –F ₇	109.4	111.0	110.5	109.5	110.6	110.7	109.2	110.3	110.0	108.8(4) ^c
F ₂ –I ₁ –C ₄ –F ₅	120.4	120.4	120.4	120.4	120.5	120.4	120.5	120.5	120.5	

^a Ref. [10].^b Notation for the basis sets employed on the iodine atom: I is for 3-21G(d); II for small-core LaJohn's ECP; III for large-core LaJohn's ECP. The 6-311 + G(2d) basis sets are employed on the heavy atoms other than the iodine atom.^c Averaged over crystallographically distinct values (the CF₃ group of crystalline CF₃IF₂ is disordered).

calculated at the RHF level as well as the B3LYP and MP2 levels. Since the bond lengths and angles for both compounds calculated with the 6-311 + G(2d) basis set for all the atoms except the central iodine atom are closer to experimental values than those with the 3-21G(d) basis set, we will discuss the results of the calculation with 6-311 + G(2d) basis set. For simplicity in the subsequent discussions and table headings, we use the following notation indicating the basis set employed on the central iodine atom: the basis set I is for the all-electron 3-21G(d) basis set, the basis set II for the small-core ECP of LaJohn et al., and the basis set III for the large-core ECP of LaJohn et al.

The computed geometrical parameters are shown in Tables 1 and 2 along with the available experimental data [10,14]. According to the result of frequency calculations, we know that the staggered conformers are in a transition state, so our discussion is restricted within the structures of eclipsed conformers. The calculated bond lengths for both compounds at the MP2 level are somewhat longer than those at the RHF level and somewhat shorter than those at the B3LYP level. However, they are largely in good agreement with the experimental values. The iodine-containing bond

lengths I–X (X = F, Cl) with the ECP for the iodine atom are somewhat longer than those with the all-electron 3-21G(d) basis set. The I–Cl bond length in particular with the ECP is quite longer than the corresponding experimental values. This large difference of the bond lengths calculated with the all-electron basis set and ECPs implies that the relativistic effect plays a very important role in CF₃ICl₂. It should also be kept in mind that all calculations were performed for free molecules in the gas phase. Some deviations from experimentally observed values can thus be attributed to the strong intermolecular contacts in the crystalline solid state.

The calculated bond angles at each level are also very close to the experimental values. At the MP2/II level, the calculated bond angles ∠X₂–I₁–X₃ in both compounds are 166.2 and 172.7°, respectively, which are in good agreement with the corresponding experimental values. This deviation from the ideal value of 180° reflects the VSEPR theory. The same aspect is observed for ClF₃ and BrF₃ with angles of 174 and 170.4°, respectively [4,5]. The calculated bond angles ∠X₂–I₁–C₄ is wider by ~5° than the bond angle ∠X₃–I₁–C₄. This is probably due to the repulsion between X₂ and F₅ atoms. At the MP2/II level, the

Table 2

Geometrical parameters for CF₃ICl₂ (distances, Å; angles, °) at the various levels of calculation

	RHF			B3LYP			MP2			Experiment ^a
	I ^b	II	III	I	II	III	I	II	III	
I ₁ –Cl ₂	2.444	2.530	2.508	2.486	2.596	2.581	2.461	2.562	2.542	2.478(2)
I ₁ –Cl ₃	2.455	2.542	2.520	2.495	2.602	2.588	2.468	2.566	2.547	2.457(2)
I ₁ –C ₄	2.212	2.266	2.240	2.258	2.311	2.298	2.217	2.215	2.199	2.229(10)
C ₄ –F ₅	1.284	1.270	1.273	1.313	1.305	1.303	1.313	1.307	1.308	1.303(10)
C ₄ –F ₆	1.290	1.275	1.279	1.320	1.311	1.309	1.320	1.314	1.315	1.299(7)
Cl ₂ ···F ₅	2.928	2.959	2.941	2.977	3.027	3.004	2.921	2.956	2.938	
Cl ₂ –I ₁ –C ₄	90.0	89.4	89.5	90.1	89.5	89.5	89.6	89.7	89.7	88.7(3)
Cl ₃ –I ₁ –C ₄	84.1	83.1	83.3	85.1	84.3	84.2	83.3	82.9	83.0	82.9(3)
Cl ₂ –I ₁ –Cl ₃	174.0	172.5	172.8	175.2	173.8	173.7	172.9	172.7	172.7	171.62(9)
I ₁ –C ₄ –F ₅	110.1	108.6	109.1	109.6	108.7	108.4	110.1	109.5	109.8	109.9(6)
I ₁ –C ₄ –F ₆	108.3	106.3	106.8	108.3	107.1	106.9	108.4	107.5	107.7	107.9(6)
F ₅ –C ₄ –F ₆	110.0	111.6	111.2	110.2	111.3	111.4	110.0	110.7	110.5	110.0(6)
F ₆ –C ₄ –F ₇	110.1	112.1	111.6	110.1	111.3	111.5	109.9	110.9	110.6	111.1(8)
Cl ₂ –I ₁ –C ₄ –F ₅	120.3	120.2	120.3	120.3	120.3	120.3	120.4	120.3	120.3	

^a Ref. [14].^b Notation for the basis sets employed on the iodine atom: I is for 3-21G(d); II for small-core LaJohn's ECP; III for large-core LaJohn's ECP. The 6-311 + G(2d) basis sets are employed on the heavy atoms other than the iodine atom.

interatomic distances X₂···F₅ are 2.608 and 2.956 Å for CF₃IF₂ and CF₃ICl₂, respectively, and somewhat shorter than their corresponding sum of van der Waals radii, 2.7 and 3.15 Å [24]. These results are consistent with the fact that the computed bond angles ∠I₁–C₄–F₅ for both compounds are slightly larger than the ∠I₁–C₄–F₆.

To study the geometrical characteristics mentioned above, we performed population analysis. The atomic charges and bond populations have been computed using the natural population analysis (NPA) [21–23] at the B3LYP levels. Table 3 summarizes interesting properties for (trifluoromethyl)iodine dihalides. A large difference between the atomic charges of the central iodine atoms for both compounds is due to the difference of electronegativity of the fluorine and chlorine atoms. The bond order of I₁–C₄ in CF₃IF₂ is slightly higher than that of CF₃ICl₂, which can be justified by a decrease of the bond length I₁–C₄ as shown in Tables 1 and 2. The I₁–F₂ and I₁–F₃ bonds for CF₃IF₂ have lower bond orders than the corresponding bonds for CF₃ICl₂. This may be because the highly oxidized iodine atom can bind more strongly to the chlorine atom, which is more polarizable than the fluorine atom. In addition, the electron delocalization over the X₂–I–X₃ through the σ_{IX} →

σ_{IX}^{*} consolidates the I–X bond better in CF₃ICl₂ than in CF₃IF₂.

3.2. Vibrational spectra

The vibrational spectra of CF₃IX₂ are calculated at the RHF level as well as the B3LYP and the MP2 levels. The calculation at the MP2 level was performed with only the basis sets II and III. The results are presented and compared with the experimental data in Table 4. In CF₃IX₂, the stretching and deformation modes ν(CF₃) and δ(CF₃) of the CF₃ group calculated at the RHF level have quite higher frequencies than those at the B3LYP and MP2 level. The asymmetric stretching and deformation frequencies, ν_{as}(CF₃) and δ_{as}(CF₃) usually increase when the core electrons of the iodine atom are replaced by the ECP, while the symmetric stretching and deformation frequencies, ν_s(CF₃) and δ_s(CF₃) decrease. The differences between the calculated frequencies of the deformations δ_{as}(CF₃, A') and δ_{as}(CF₃, A'') for both compound are less than 8 cm^{–1}, and these modes are nearly degenerated. The stretching frequencies ν(IF₂) of CF₃IF₂ are higher by around 300 cm^{–1} than the corresponding ν(ICl₂) of CF₃ICl₂. The asymmetric ν_{as}(IX₂) is higher than the symmetric ν_s(IX₂). The

Table 3

Calculated atomic charges and bond orders of CF₃IX₂ (X = F, Cl) at the B3LYP levels

		I ₁	X ₂	X ₃	C ₄	F ₅	F ₆
<i>Atomic charge</i>							
X=F	B3LYP/I	1.362	−0.644	−0.652	0.876	−0.307	−0.318
	B3LYP/II	1.340	−0.659	−0.667	0.902	−0.297	−0.309
	B3LYP/III	1.292	−0.649	−0.658	0.923	−0.295	−0.307
X=Cl	B3LYP/I	0.897	−0.435	−0.448	0.920	−0.304	−0.315
	B3LYP/II	0.883	−0.456	−0.468	0.939	−0.292	−0.303
	B3LYP/III	0.812	−0.434	−0.448	0.959	−0.290	−0.300
		I ₁ –X ₂	I ₁ –X ₃	I ₁ –C ₄	C ₄ –F ₅	C ₄ –F ₆	
<i>Bond order</i>							
X=F	B3LYP/I	0.496	0.486	0.817	0.931	0.918	
	B3LYP/II	0.461	0.451	0.782	0.946	0.932	
	B3LYP/III	0.470	0.460	0.773	0.950	0.936	
X=Cl	B3LYP/I	0.607	0.594	0.780	0.937	0.925	
	B3LYP/II	0.542	0.533	0.755	0.953	0.941	
	B3LYP/III	0.543	0.533	0.743	0.957	0.946	

stretching mode $\nu(\text{CI})$ of CF₃IF₂ is slightly higher than that of CF₃ICl₂, and it is consistent with the experiment. The $\nu(\text{CI})$ modes highly depend on the theory of calculation, and are quite lower at the B3LYP level than at the MP2 level. Rocking modes $\rho(\text{CF}_3, \text{A}'')$ for the both compounds have almost the same frequency, while $\rho(\text{CF}_3, \text{A}')$ is higher by 15 cm^{−1} in CF₃IF₂ than in CF₃ICl₂. The deformation modes $\delta(\text{IX}_2)$ and out-of-plane distortion $\gamma(\text{IX}_2)$ have the higher frequency in CF₃IF₂ than in CF₃ICl₂. The torsional modes τ for both compounds have almost the same frequency. Generally, the calculated vibrational frequencies with the basis set I quite differ from those with the basis sets II and III. The use of the ECP may give the more reliable results for frequencies. Although in some cases, the core-valence partitioning have a significant effect on calculated bond lengths, vibrational frequencies, and other molecular properties [17,25], the calculated frequencies for CF₃IX₂ with the large-core ECP are essentially the same as those with small-core ECP. It seems likely that the effect of electron correlation has to be included in the study of vibrational spectra for CF₃IX₂. However, the B3LYP method underestimates the calculated frequencies in the region of 200–300 cm^{−1}, and shows some deviation from the experimental values.

3.3. Natural bond orbital analyses for rotational barriers

Our calculations show that for each compound, an eclipsed conformer is more stable than the corresponding staggered conformer. It is found that an eclipsed conformation corresponds to the potential energy minimum, while a staggered conformation is at a local energy maximum which is in the transition state. Therefore the rotational barrier for the trifluoromethyl group is estimated from the relative energies of two conformers for each molecule. The magnitudes of barriers to rotation of the CF₃ group for both molecules are summarized in Table 5. Generally, the calculated values with ECPs for iodine are lower than those with the all-electron 3-21G(d) basis set. The small rotational barrier less than ~0.5 kcal/mol suggests that the CF₃ group can rotate almost freely about the C–I bond. Especially, the rotational barriers of CF₃IF₂ are lower than those of CF₃ICl₂ at all the calculation levels. This fact is consistent with the experimental results in the crystal; the CF₃ group in CF₃IF₂ is considerably disordered, while the CF₃ group in CF₃ICl₂ is in the eclipsed position.

The NBO analysis [21–23] at the RHF/I level shows that this energy preference of an eclipsed form over a staggered form is primarily due to the

Table 4

Calculated vibrational frequencies (not scaled) (cm^{-1}) for CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$)

	RHF			B3LYP			MP2		Experiment ^a	
	I	II	III	I	II	III	II	III	Raman	IR
$\text{X}=\text{F}$										
$\tau(\text{A}'')$	40	43	43	55	35	29	38	36	51	
$\delta(\text{IF}_2, \text{A}')$	177	178	185	135	142	150	164	170		
$\gamma(\text{IF}_2, \text{A}'')$	235	225	233	224	195	194	199	205	213	
$\delta(\text{IF}_2, \text{A}')$	236	234	243	196	183	192	205	215	248	
$\rho(\text{CF}_3, \text{A}'')$	291	283	287	253	242	246	265	269	263	
$\nu(\text{Cl}, \text{A}')$	321	300	306	276	251	251	289	291	285	281
$\rho(\text{CF}_3, \text{A}')$	326	313	319	284	272	277	293	298		
$\nu_s(\text{IF}_2, \text{A}')$	593	560	559	532	482	482	508	512		477
$\nu_{\text{as}}(\text{IF}_2, \text{A}')$	618	569	574	570	520	511	540	535	499	506
$\delta_{\text{as}}(\text{CF}_3, \text{A}'')$	595	601	600	531	535	537	542	542		
$\delta_{\text{as}}(\text{CF}_3, \text{A}')$	604	607	607	539	540	542	550	548	546	548
$\delta_s(\text{CF}_3, \text{A}')$	835	823	826	746	739	738	758	757	756	
$\nu_s(\text{CF}_3, \text{A}')$	1187	1121	1137	1052	1025	1018	1084	1089		1050
$\nu_{\text{as}}(\text{CF}_3, \text{A}'')$	1388	1443	1427	1200	1234	1242	1248	1240	1108	
$\nu_{\text{as}}(\text{CF}_3, \text{A}')$	1418	1467	1453	1229	1260	1269	1273	1266		1199
$\text{X}=\text{Cl}$										
$\tau(\text{A}'')$	42	39	40	35	30	32	36	36		
$\gamma(\text{ICl}_2, \text{A}'')$	135	120	124	121	104	104	107	110		
$\delta(\text{ICl}_2, \text{A}')$	145	135	139	117	103	107	119	123		
$\delta(\text{ICl}_2, \text{A}')$	162	147	153	137	121	124	134	139	160	
$\nu_s(\text{ICl}_2, \text{A}')$	324	286	289	286	244	241	253	255	247	
$\rho(\text{CF}_3, \text{A}'')$	293	281	286	254	241	244	267	272		
$\nu_s(\text{ICl}_2, \text{A}')$	303	264	272	256	232	230	274	276	265	262
$\rho(\text{CF}_3, \text{A}')$	311	302	307	273	255	258	278	281	279	278
$\nu_{\text{as}}(\text{ICl}_2, \text{A}')$	338	282	283	328	295	293	319	317	292	291
$\delta_{\text{as}}(\text{CF}_3, \text{A}')$	600	603	603	537	537	540	542	543		
$\delta_{\text{as}}(\text{CF}_3, \text{A}'')$	600	608	607	535	539	541	547	547		546
$\delta_s(\text{CF}_3, \text{A}')$	827	794	804	738	729	726	753	754	750	739
$\nu_s(\text{CF}_3, \text{A}')$	1142	1072	1085	1023	1000	992	1056	1060	1059	1024
$\nu_{\text{as}}(\text{CF}_3, \text{A}'')$	1407	1474	1457	1213	1253	1262	1262	1256	1226	1220
$\nu_{\text{as}}(\text{CF}_3, \text{A}')$	1429	1488	1473	1236	1271	1279	1279	1274	1245	1277

^a Refs. [10,14].

$\sigma_{\text{IX}} \rightarrow \sigma_{\text{CF}}^*$ interactions. The second-order perturbative energies $E^{(2)}$ of these interactions are presented in Table 6. The stabilization energy $E^{(2)}$ associated with the delocalization from $\text{I}_1\text{--X}_3$ to $\text{C}_4\text{--F}_5$ is signi-

Table 5

Calculated rotational barriers (kcal/mol) for CF_3IX_2 ($\text{X} = \text{F}, \text{Cl}$)

	RHF			B3LYP			MP2		
	I	II	III	I	II	III	I	II	III
$\text{X}=\text{F}$	0.36	0.42	0.40	0.20	0.17	0.17	0.34	0.33	0.30
$\text{X}=\text{Cl}$	0.56	0.49	0.50	0.30	0.25	0.26	0.53	0.40	0.41

ficantly larger in the eclipsed form than in the staggered form. We can estimate the total delocalization energy, $E^{(2)}(\sigma_{\text{IX}} \rightarrow \sigma_{\text{CF}}^*)$, which is the sum of the individual delocalization energy from two σ_{IX} to three σ_{CF}^* orbitals. The eclipsed conformation is more stabilized than corresponding staggered conformation by 0.15 and 0.27 kcal/mol for CF_3IF_2 and CF_3ICl_2 , respectively. These values are confirmed by the deletion energy, $E_{\text{del}}(\sigma_{\text{IX}} \rightarrow \sigma_{\text{CF}}^*)$, and comparable to the rotational barriers as shown in Table 5. In other words, it is quite probable that the stronger hyperconjugation between both σ orbitals of the I--X bonds and σ^* orbitals of the C--F bonds in the eclipsed conformer

Table 6

Second-order perturbative energies (kcal/mol), $E^{(2)}$, of the $\sigma_{IX} \rightarrow \sigma_{CF}^*$ interactions for CF_3IX_2 ($X = F, Cl$) calculated at the RHF/I level

σ	σ^*	X=F			X=Cl		
		Eclipsed	Staggered	Δ^a	Eclipsed	Staggered	Δ
I ₁ –X ₂	C ₄ –F ₅	0.07	0.02		0.10	0.00	
	C ₄ –F ₆	0.14	0.43		0.12	0.48	
	C ₄ –F ₇	0.14	0.08		0.12	0.13	
I ₁ –X ₃	C ₄ –F ₅	0.78	0.02		0.97	0.00	
	C ₄ –F ₆	0.04	0.08		0.09	0.13	
	C ₄ –F ₇	0.04	0.43		0.09	0.48	
$E^{(2)}(\sigma_{IX} \rightarrow \sigma_{CF}^*)$		1.21	1.06	0.15	1.49	1.22	0.27
$E_{del}(\sigma_{IX} \rightarrow \sigma_{CF}^*)$		1.02	0.90	0.12	1.14	0.95	0.19

^a The delocalization energy difference between two conformers.

causes the molecular energy of this conformation to decrease mainly by the electron delocalization.

4. Conclusions

The equilibrium structures, rotational barriers, vibrational spectra of CF_3IX_2 ($X = F, Cl$) have been investigated at RHF, B3LYP and MP2 levels. For each molecule the eclipsed form is found to be more stable than the staggered form. The staggered conformer corresponds to the transition state structure of which energy barrier is less than ~ 0.5 kcal/mol. The NBO analysis at the RHF/I level shows that the energy preference of an eclipsed form over a staggered form is primarily due to the $\sigma_{IX} \rightarrow \sigma_{CF}^*$ interactions. MP2 method can reproduce those experimental molecular geometries and vibrational frequencies better than RHF and B3LYP method at the various levels of calculation. In general, the use of the ECPs gives the results closer to the experiment.

Acknowledgement

This work was supported by Korea Research Foundation Grant 2001-015-DP0248.

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