

FULL PAPER

An Investigation of Structural Stability and Internal Rotation in 3-Cyclopropenecarboxaldehyde and 3-Cyclopropenecarboxylic Acid Fluoride by *ab initio* Calculations

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Abstract The structural stability and internal rotation in 3-cyclopropenecarboxaldehyde and 3-cyclopropenecarboxylic acid fluoride were investigated by *ab initio* calculations with a 6-31G* atomic basis in the latter and a 6-311G* atomic basis set in the former case. For the sake of comparison also results obtained with a 3-21G basis are given in the paper. As expected, it turned out that this basis set is not large enough for three-membered rings. The calculations were carried out both at the Restricted Hartree-Fock (HF) and the second order Moller-Plesset (MP2) levels. The *trans*-form is predicted to be the lower energy conformer for both molecules. However, in case of the fluoride the two conformers have nearly the same energy. Full optimization was performed at the transition states and the asymmetric potential function for the CXO internal rotations was predicted for both molecules.

Keywords *Ab initio*, Structural stability, Rotational barrier, 3-Cyclopropenecarboxaldehyde, 3-Cyclopropenecarboxylic acid fluoride

Introduction

The conformational stability and structure of a series of cyclopropane ring compounds containing a CXO group (X = H, F and Cl) have been the subject of several investigations. Rotational and vibrational spectroscopy, *ab initio* cal-

culations and electron diffraction techniques were all employed in these studies [1-5]. Durig et al. have investigated the IR and Raman spectra for cyclopropylcarboxaldehyde [5] and its fluoride [4] and chloride [5] derivatives. They found that these molecules exist predominantly in their *cis*-form in gas phase, while in liquid and solid phases the *trans* form is the more stable one. The *cis* conformer (the carbonyl group eclipses the three-membered ring) was found to be more stable than the corresponding *trans* form (the carbonyl group eclipses the α -hydrogen atom) in the gas phase, because the π -MO-s of the C=O bond can interact with the a_2' extra-ring MO and the e' in-ring MO-s formed by the three-membered ring system. It was suggested, that the significant change in conformational behaviour when going

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from the gas phase to the condensed phases is a result of strong intermolecular interactions which would stabilize the trans form in the condensed phases [2,4,5]. Various derivatives of cyclopropane have been investigated both experimentally and theoretically [6-11].

The stability of cyclopropene [12,13] and many of its derivatives has been demonstrated in the literature [14-17]. In the present study the conformational equilibrium and the internal rotational potential in 3-cyclopropenecarboxaldehyde and 3-cyclopropenecarboxylic acid fluoride were investigated by ab initio calculations. The results of this work are presented in this paper.

Ab Initio Calculations

The Gaussian94 program system [18] running on an IBM RS/6000, model 7015-R24 workstation was used to carry out LCAO-MO-SCF Restricted Hartree-Fock calculations. We want to focus here on the results obtained from the computations using a 6-31G* basis set for the acid fluoride and 6-311G* for the aldehyde. Corresponding results obtained from calculations with the small 3-21G basis are only shown for comparison and emphasize again the well-known fact that a simple valence-split set is insufficient for systems with three-membered ring systems. Further we also performed corrections of the total energy of the conformers with respect to electron correlation using the second order Moller-Plesset (MP2) perturbation theory. The structural parameters of the cis (torsional angle $\theta=0^\circ$) and the trans ($\theta=180^\circ$) conformers of each of the molecules (see Figure 1) were optimized by minimizing the energy with respect to all the geometrical parameters.

The calculated structural parameters, energies, total dipole moments and rotational constants of the two conformers of the molecules are given in tables 1-4. From the results it is obvious, that the inclusion of correlation energy influences some of the geometrical parameters to a considerable extent, while they remain almost constant when going from cis to trans forms. The differences in dipole moment between cis and trans form is larger in the aldehyde, as expected, because there a polar CHO group rotates while in the carboxylic acid the charge distribution in the CFO group is more balanced. Due to the large dipole-moments of the trans isomers it is expected that in condensed phases the trans forms will get an extra stabilization due to the possibility of stronger dipole-dipole interactions than in the corresponding cis-cases.

The maximum of the potential curve for the internal rotation of the CXO group about the CC single bond was obtained by variation of the CXO torsional angle θ by 10° increments from 0° (cis) to 180° (trans). All the remaining parameters were kept fixed at their values for the stable conformers. After determination of θ for the maximum, full geometry optimization was carried out at this transition state, keeping only θ fixed. Additionally, in order to obtain the potential curve, full geometry optimizations (besides θ) for all

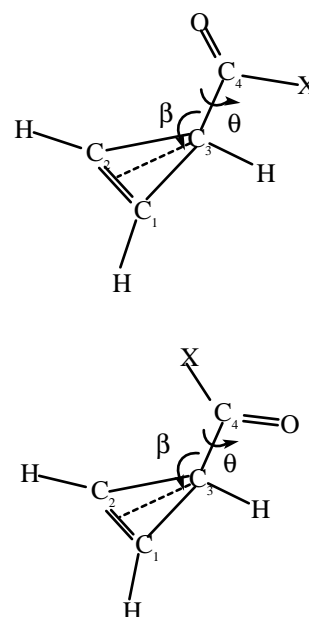


Figure 1 Molecular structure of 3-cyclopropenecarboxaldehyde ($X=H$) and 3-cyclopropenecarboxylic acid fluoride ($X=F$) in cis (upper panel) and in trans (lower panel) conformation

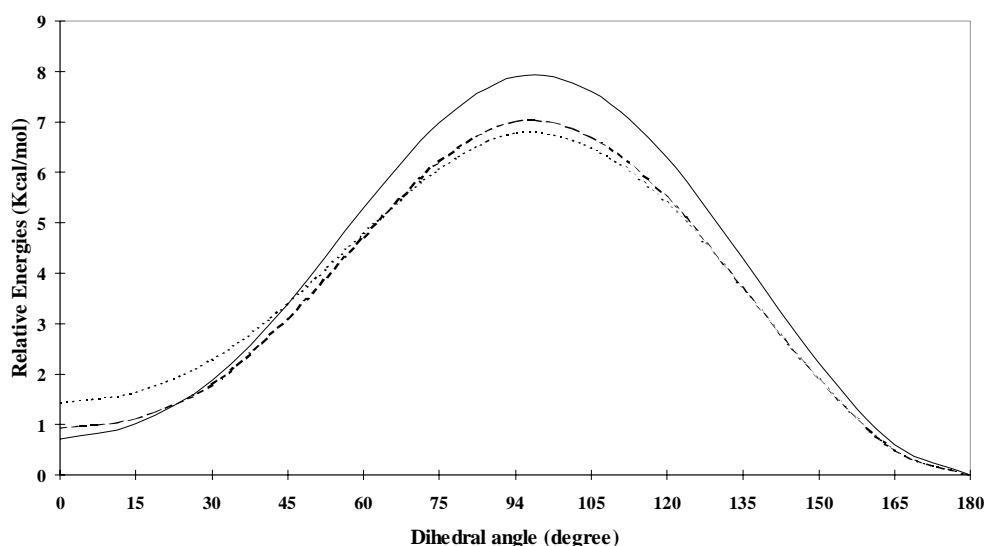
parameters were carried out at points where θ was varied by 15° increments again between the cis and the trans form.

The torsional potential obtained in this way was fitted by a least squares procedure with the help of a Fourier cosine series in the dihedral angle θ :

$$V(\theta) = \sum_n \frac{V_n}{2} [1 - \cos(n\theta)] \quad (1)$$

We found that the series can be truncated after $n=6$. The potential function was used to calculate the barrier to internal rotation and they are given in tables 2 and 4. These potentials are useful to calculate the transitions between the rotational states in this potential for the CXO torsion. The potential functions are shown in Figures 2 and 3. Figure 2 indicates that in the case of the aldehyde there is a considerable energy difference between the cis and trans conformers. The correlation energy change as function of θ seems to be negligibly small in the regions close to the absolute minimum, but becomes more pronounced when approaching the maximum and when moving closer to the relative minimum. In case of the acid fluoride the correlation correction turns out to be negligible in the entire range of the torsional angle. In the latter case the two minima are nearly degenerate. The 3-21G curves are, as expected, considerably in error.

Figure 2 The potential function for the CHO rotation for 3-cyclopropenecarboxaldehyde, as obtained at HF/3-21G (solid line), HF/6-311G* (dotted line) and MP2/6-311G* (dashed line) levels of calculation



Discussion

The conformational stability of gaseous cyclopropylcarboxaldehyde and its halides in the cis conformations was explained on the basis of the Walsh-Hoffman bonding model for the cyclopropane ring [19,20]. Since the results reported in the present study for cyclopropene derivatives are exactly the opposite of those found for cyclopropanes, we want to discuss qualitatively the reasons for the stability of the cis conformers in the latter case also. In fig. 4 we show a sketch of the shape of the in-ring (formed from carbon sp^2 orbitals) and out-of-ring (formed from carbon 2p orbitals) orbitals of cyclopropane together with the MO-s of the p-bond in the CO group. It is clear that the filled π -MO of the CO group has a symmetry which allows it to interact with the lowest virtual out-of-ring a_2' orbital of the ring formed by p-orbit-

als. In this way the π -MO of the CO group gets a slight stabilization as it is shown in the schematic MO diagram in Figure 4 (only very qualitatively). In the same way it is possible for the virtual π^* MO of the CO group to act as acceptor orbital for the occupied out-of-ring e' MO-s of the ring. Since the a_2' orbital appears to be lower in energy than π^* it is to be expected that the situation where the ring MO acts as acceptor and the CO-MO as donor has a larger contribution in the final state of the system than the reverse one. Therefore, the cis conformer with the CO group being able to act as donor orbital for the ring has a lower energy than the trans form. A lone pair orbital at oxygen points to the ring and can interact only with occupied ring orbitals leading to a repulsion between the corresponding charge densities. However, since the ring MO-s are mainly localized within the plane of the ring we assume this repulsion to be not important.

Figure 3 The potential function for the CFO rotation for 3-cyclopropenecarboxylic acid fluoride, as obtained at HF/3-21G (solid line), HF/6-31G* (dotted line) and MP2/6-31G* (dashed line) levels of calculation

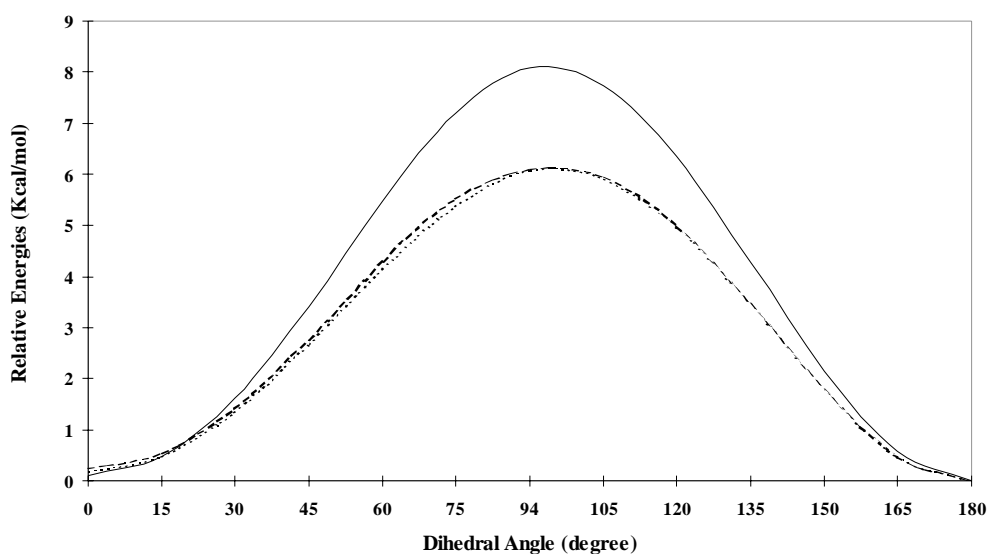


Table 1 Optimized structural parameters of 3-cyclopropenecarboxaldehyde

Parameter [a]	HF/3-21G		HF/6-311G*		MP2/6-311G*		Microwave [b]	
	Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans
Bond lengths [Å]								
r(C ₃ -C ₄)	1.480	1.477	1.497	1.490	1.494	1.488	1.490	1.497
r(C ₁ -C ₃ =C ₂ -C ₃)	1.527	1.529	1.503	1.509	1.521	1.524	1.522	1.520
r(C ₁ =C ₂)	1.274	1.277	1.268	1.270	1.297	1.299		
r(C ₄ =O)	1.210	1.209	1.183	1.183	1.216	1.215	1.211	1.209
r(C ₄ -H)	1.087	1.090	1.098	1.100	1.111	1.115	1.104	1.107
r(C ₃ -H)	1.073	1.072	1.083	1.081	1.092	1.091	1.086	1.085
r(C ₁ -H=C ₂ -H)	1.057	1.058	1.066	1.067	1.077	1.078		
Bond angles [°]								
(C ₃ C ₂ C ₁ =C ₃ C ₁ C ₂)	65.3	65.3	65.1	65.0	64.7	64.7		
(C ₂ C ₃ C ₁)	49.3	49.3	49.9	50.0	50.6	50.6	58.6	58.9
(C ₃ C ₄ O)	124.5	124.9	124.7	124.4	123.9	124.4	123.1	123.4
(C ₃ C ₄ H)	114.5	113.0	115.0	114.7	115.5	114.1	115.7	115.0
(C ₄ C ₃ H)	116.0	115.6	113.8	113.2	115.7	114.4	115.4	114.0
(C ₂ C ₁ H=C ₁ C ₂ H)	151.8	151.1	151.9	151.2	151.9	151.4		
β	120.5	120.6	122.9	122.8	121.3	121.9		
θ	0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0

[a] β and θ are the angle of the carbonyl group with the ring and CHO torsional angle respectively.

[b] Structural parameters of cyclopropanecarboxaldehyde obtained from reference [4]

Table 2 Relative energies (kcal/mol), barrier to interconversion (kcal/mol), potential coefficients (kcal/mol), total dipole moments (Debye), and rotational constants (MHz) of 3-Cyclopropenecarboxaldehyde

Parameter	HF/3-21G		HF/6-311G*		MP2/6-311G*	
	Cis	Trans	Cis	Trans	Cis	Trans
Relative energies [a]	0.70	0.00	1.44	0.00	0.94	0.00
Barrier to interconversion						
cis to trans barrier	7.20		5.35		6.08	
trans to cis barrier	7.90		6.79		7.02	
θ [b]	94.50		94.30		94.20	
V ₁	0.54		-0.03		0.31	
V ₂	7.72		6.46		6.80	
V ₃	-0.71		-0.45		-0.57	
V ₄	-0.01		0.25		-0.06	
V ₅	0.13		0.40		0.21	
V ₆	0.20		0.42		0.26	
Dipole moment [μ ₁]	2.95	3.97	2.96	3.92	3.07	4.09
Rotational constants						
A	13085	21070	13598	21330	12922	20589
B	4273	3264	4172	3285	4212	3239
C	3964	3153	3917	3170	3930	3120

[a] Total energies of the trans conformation are, -227.25390, -228.60316 and -229.32220 Hartrees, calculated by HF/3-21G, HF/6-311G*, and MP2/6-311G* levels respectively

[b] Optimized CHO dihedral angle (degree) at the transition state

Table 3 Optimized structural parameters of 3-cyclopropanecarboxylic acid fluoride

Parameter [a]	HF/3-21G		HF/6-31G*		MP2/6-31G*		Microwave [b]	
	Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans
Bond lengths [Å]								
r(C ₃ -C ₄)	1.469	1.467	1.491	1.488	1.485	1.483	1.490	1.492
r(C ₁ -C ₃ =C ₂ -C ₃)	1.524	1.522	1.498	1.499	1.511	1.512	1.522	1.520
r(C ₁ =C ₂)	1.274	1.274	1.268	1.290	1.295	1.296		
r(C ₄ =O)	1.186	1.187	1.171	1.171	1.201	1.201	1.188	1.185
r(C ₄ -F)	1.359	1.357	1.326	1.326	1.369	1.371	1.353	1.360
r(C ₃ -H)	1.069	1.070	1.079	1.079	1.089	1.090	1.085	1.085
r(C ₂ -H=C ₁ -H)	1.057	1.057	1.067	1.067	1.078	1.078		
Bond angles [°]								
(C ₁ C ₂ C ₃ =C ₂ C ₁ C ₃)	65.2	65.3	65.0	64.9	64.6	64.6		
(C ₂ C ₃ C ₁)	49.6	49.4	50.0	50.2	50.8	50.8	58.6	58.8
(C ₃ C ₄ O)	129.5	128.0	128.3	126.8	128.4	127.7	127.7	127.6
(C ₃ C ₄ F)	110.5	112.1	119.1	112.8	110.6	111.6	111.2	111.9
(C ₄ C ₃ H)	115.1	113.3	113.4	110.8	114.9	112.1	115.1	112.3
(C ₂ C ₁ H=C ₁ C ₂ H)	152.1	152.9	152.4	152.1	152.2	152.1		
β	119.7	121.8	121.9	124.7	120.7	123.7		
θ	0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0

[a] β and θ are the angle of the carbonyl group with the ring and CFO torsional angle respectively.

[b] Structural parameters of cyclopropanecarboxylic acid fluoride obtained from reference [2].

Table 4 Relative energies (kcal/mol), barrier to interconversion (kcal/mol), potential coefficients (kcal/mol), dipole moments (Debye), and rotational constants (MHz) of 3-Cyclopropanecarboxylic acid fluoride

Parameter	HF/3-21G		HF/6-31G*		MP2/6-31G*	
	Cis	Trans	Cis	Trans	Cis	Trans
Relative energies [a]	0.10	0.00	0.19	0.00	0.24	0.00
Barrier to interconversion						
cis to trans barrier	7.99		5.90		5.86	
trans to cis barrier	8.09		6.09		6.10	
θ [b]	93.50		95.00		94.00	
V ₁	0.60		0.53		0.45	
V ₂	8.05		6.02		6.09	
V ₃	-0.58		-0.56		-0.48	
V ₄	-0.17		0.04		0.07	
V ₅	-0.10		0.02		0.01	
V ₆	0.02		0.04		0.03	
Dipole moment μ _t	4.01	4.23	3.72	4.10	3.91	4.24
Rotational constants						
A	8493	8311	8662	8450	8268	8101
B	2800	2999	2796	2956	2774	2942
C	2399	2528	2409	2509	2375	2481

[a] Total energies of the trans conformation are , -227.30468 , -228.63504 and -229.34848 Hartrees, calculated by HF/3-21G, HF/6-31G*, and MP2/6-31G* levels respectively.

[b] Optimized CHO dihedral angle (degree) at the transition state

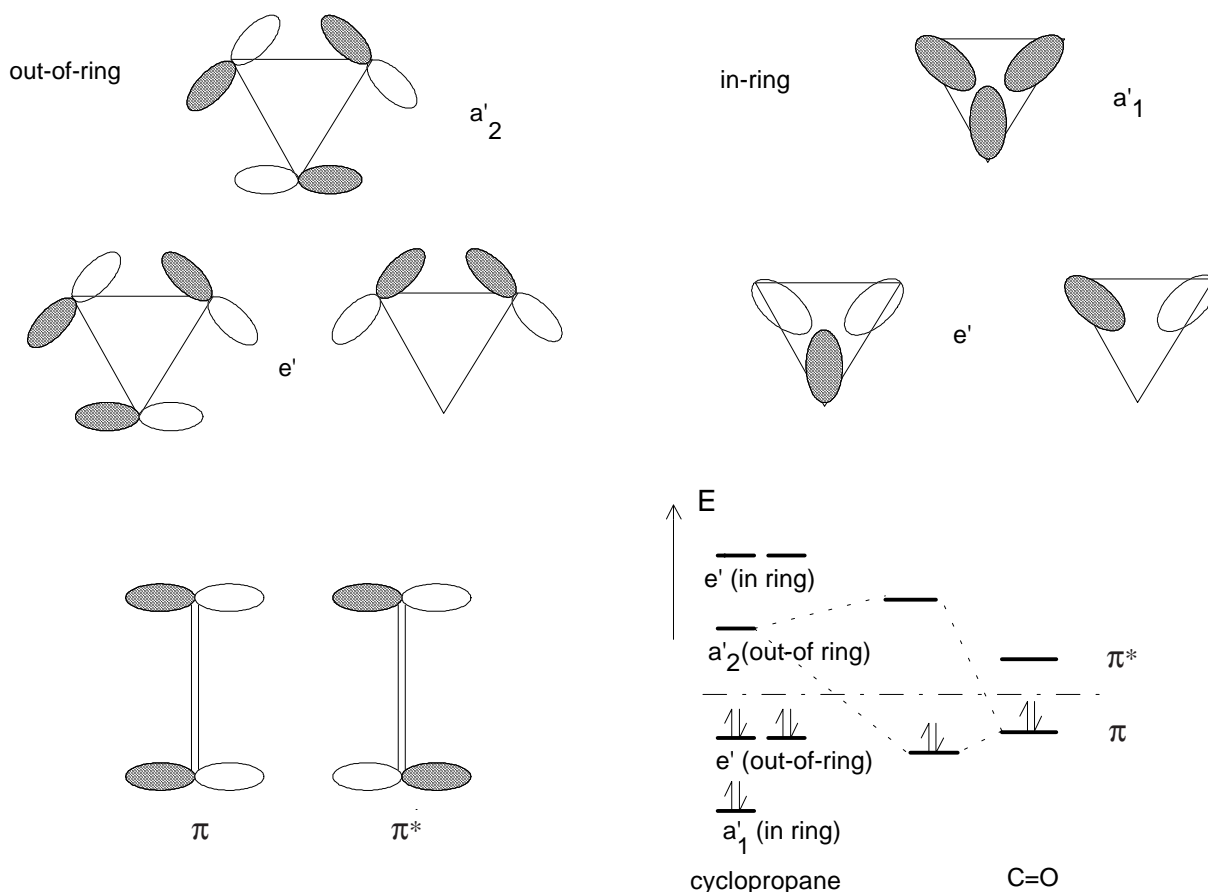


Figure 4 Sketch of the Walsh orbitals of cyclopropane, together with a sketch of the π orbitals of the CO group, and a very qualitative MO diagram for the occupied π MO of a cis CO group acting as donor orbital for the virtual a'_2 orbital of the ring

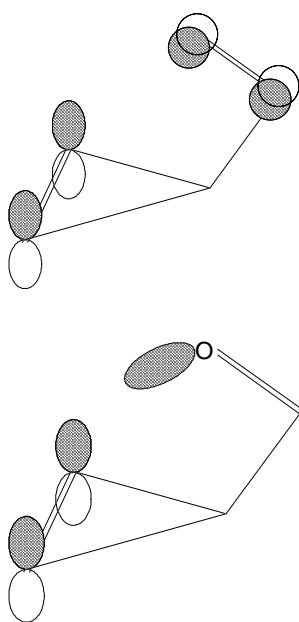
When the hydrogen atom is replaced by a fluorine atom the energy difference between the two conformers is lowered. The main reason for that should be the large electronegativity of fluorine as compared to hydrogen. Due to this the π MO of the CO group is a less effective donor orbital and therefore the stabilization of the cis form as compared to the trans configuration is reduced.

In our cyclopropene derivatives the situation is completely different due to the CC double bond in the ring. Walsh type orbitals can be constructed again, but now from sp lobes at C_1 and C_2 , and an sp^2 lobe at C_3 . But here the double bond plays the dominant role. The bonding orbital of this bond is shown in fig. 5. It is obvious that π^*_{CC} can act again as an acceptor orbital for π_{CO} as donor, while the possibility of π^*_{CO} being acceptor orbital for π_{CC} does not exist due to symmetry. Further, the effectivity of π_{CO} being a donor orbital for π^*_{CC} is much reduced as compared to the cyclopropane case because of a smaller overlap and the more unfavorable energetic positions of the MO-s. However, as sketched also in Figure 5, here the charge density of one of the lone pairs at oxygen points directly to that part of the charge density of the CC double bond which is above the molecular plane. Therefore, the main interaction between the ring and the CO

group in the cyclopropene derivatives is the repulsion between the charge distributions of the double bond in the ring and a lone pair orbital at oxygen. Thus in case of the aldehyde clearly the trans form has to be lower in energy than the cis form.

In case of the fluoride, both conformers show repulsion between lone pairs and the CC double bond in the ring. Since the attractive interactions between CO and CC double bond orbitals play a minor role here, we expect that the two conformers of the fluoride should differ less in energy than in the case of the aldehyde. However, also in the fluoride the trans form should be slightly more stable than the cis form, because the oxygen lone pair in the cis form points directly to the charge cloud of the CC bond in the cis case, while the electron density of the lone pairs on fluorine in the trans form is less directed to the bond. However, this balance is too subtle that the conclusion can be drawn without actual calculation. Thus the energy difference between the conformers should be smaller in the fluoride (0.24 kcal/mol) than it is in the aldehyde (0.94 kcal/mol), what is actually the case. Since in both systems the dipole moments are larger in the trans conformers than they are in the cis forms, we do not expect that the relative stability of the trans form as compared to the

Figure 5 Sketch of the occupied π MO of the CC bond together with one of the oxygen lone pairs (upper panel) and with the π MO of the CO group (lower panel) in the cis form of cyclopropenecarboxaldehyde



cis conformer will change in condensed phases, where the trans forms are even more favored due to dipole-dipole interactions.

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