Conformations of some α β- unsaturated carbonyl compounds and interpretation of electronic spectra

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Abstract

*Quantum chemical studies were conducted on methyl acrylate, methyl trans crotonate and methyl methacrylate in order to study the rotational isomerism and their properties in the ground state (S_0) and first excited state (S_1) electronic states. Density functional theory (DFT) with B3LYP functional and RHF using extended basis sets like 6-31G** and 6-311+G** have been used in present studies. Potential energy curves for the ground state and first excited states of molecules indicate the presence of two stable conformers.*

The optimized geometrical parameters of the stable conformers are being reported. A complete interpretation of the electronic spectra in terms of energy levels, frequency and nature of transition has been made for the stable conformers on the basis of configuration interaction level calculations.

Keywords: *Ab initio* calculation, conformational analysis, optimized geometry, electronic transition.

Introduction

a,b-carboxylic esters have received the attention of spectroscopists and structural chemists due to their importance as model compounds in the understanding of catalytic reactions in enzymes-substrate complex formation. Some conformational studies by spectroscopic and quantum chemical methods on this class of esters such as methyl acrylate[1-4], methyl methacrylate[4-9] and methyl trans crotonate[7-9] rotational isomerism about the carbon-carbon single bond leading to s-*cis* and s-*trans* conformers have been reported.

However, uncertainty continues to exist regarding the relative stability of the two conformers in each case. Vibrational spectra studies of methyl acrylate[1-2] have shown preference for the *trans* conformer, microwave[3], electron diffraction and quantum chemical[5] studies have predicted the s-*cis* conformer to be more stable.

While, in methyl methacrylate dipole, moment measurements by Santhanam et al[5] suggest that it may exist in two conformational forms s-*trans* and s-*cis* with s-*trans* being more stable than the s-*cis*. Based on electron diffraction, vibrational spectra and *ab initio* calculations, Takemasa et al[6] have concluded that the molar fraction of the s-*trans* conformer in the mixture of the s-*trans* and s-*cis* conformers is 0.64. However, based on angle-resolved electron energy loss spectra (EELS) and *ab initio* calculations, Rocco et al[7] suggest that the s-*cis* and s-*trans* conformers are nearly equally populated at room temperature. They have also attempted to assign the electron excitation spectrum of methyl methacrylate.

Based on *ab initio* calculations involving Moller-Plesset correction at the MP2 level, Hollauer et al[8] conclude that s-*cis* conformer is more stable than s-*trans* by 1.61 kcal/mol. Further, the *ab initio* CI and MP2 based calculations[9] lead to different inferences about the relative stability of the two conformers.

Based on the temperature dependence of the infrared and Raman bands in the vapour[10], solution[1] and liquid states[2], it was inferred that the s-*trans* conformer of methyl *trans* crotonate is more stable than its s-*cis* conformer. These results were confirmed by Vsetecka et al[11] from CNDO/2 calculations. However, based on 4-31G level *ab initio* SCF MO calculations, Dulce et al[12] have contradicted these findings and suggested that the s-*cis* conformer is more stable than s-*trans*.

In present communication, results of detailed quantum chemical studies using extended basis sets on the molecular structures of methyl acrylate, methyl methacrylate and methyl *trans* crotonate and their stabilities in the ground and first excited electronic states have been reported. Informations about the geometrical and electronic structure in the ground and first excited electronic states along with electronic spectra have been discussed.

Material and Methods

An asymmetric rotation about the (C=C)-(COOCH3) in a,b-carboxylic esters has been carried out to explore the possible conformers. Based on the potential energy calculation at each point of optimization, potential energy curves were obtained in the both ground state and first excited state by Hartree Fock calculation with 6-31G basis set. Optimized geometries of the stable conformers in the electronic ground state and first excited state were obtained and their comparison for the two states in the same basis sets is obtained. The assignments to electronic transitions for the stable conformers were made by BLYP with 6-31G basis set. GAMESS[13] software was used to perform all theoretical calculation.

Results and Discussion

Conformational studies: Potential energy curves were obtained after geometry optimization at each stage of calculation; it was found that in all the molecules, the heavy atoms of the ester group lie on the same plane and that the methyl and carbonyl groups have a preferred s-*cis* orientation about the C-O bond (Table 1). The methyl group, however, has a staggered conformation relative to the carbonyl group. Further, a b-substituent in unsaturated esters gives rise to a preferred s-*cis* orientation of the carbonyl and vinyl groups about the C-C bond, an a-substituent gives rise to a s-*trans* conformation. Thus, in methyl acrylate and methyl *trans* crotonate, the Cc conformation is more stable than Tc whereas reverse is the case in methyl methacrylate.

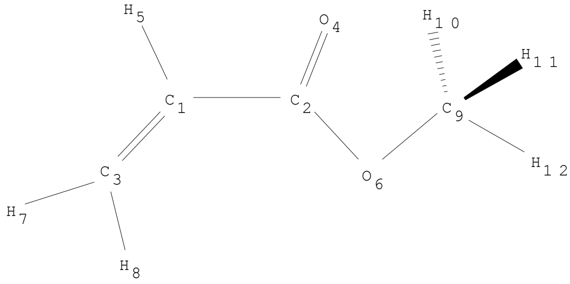


Fig. 1: Schematic representation of methyl acylate. The numbers refer to particular atom referred in the text.

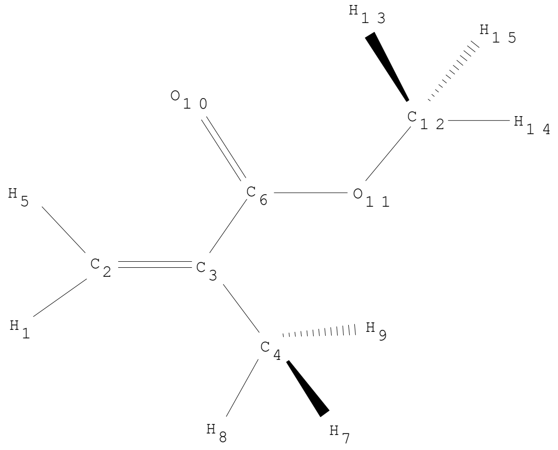


Fig. 2: Schematic representation of methyl methacylate. The numbers refer to particular atom referred in the text

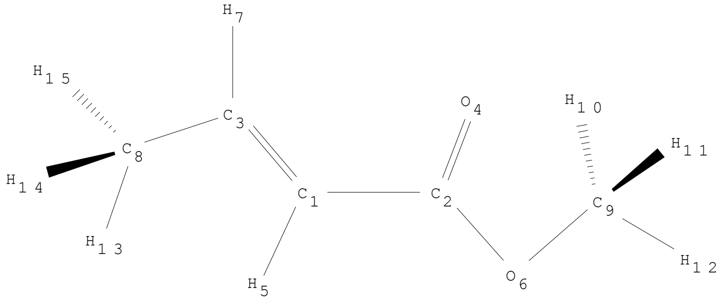


Fig. 3: Schematic representation of methyl *trans* crotonate. The numbers refer to particular atom referred in the text

Table 1
Enthalpy difference between the stable conformers of methyl acrylate(MA), methyl methacrylate(MMA) and methyl *trans* crotonate (MTC) using different methods in ground (S_0) and excited (S_1) states

	Ground state			
	Stable conformers	**RHF/6-31G**	**RHF/ 6-311+G****	**DFT/6-311+G****
MA	Cc	0.499	0.434	0.421
MMA	Tc	0.365	0.449	0.237
MTC	Cc	0.645	0.584	0.723
	Excited state			
	Stable conformers	RHF/6-31G	RHF/6-311+G**	
MA	Tc	1.144	1.445	
MMA	Tc	1.104	2.014	
MTC	Cc	1.653	1.207	

Table 2
Rotational barriers of different conformers of methyl acrylate, methyl methacrylate and methyl *trans* crotonate in ground (S_0) and excited (S_1) states

	Ground state RHF/6-31G (kcal/mol)				Excited state RHF/6-31G (kcal/mol)			
MA	Cc/Tc	8.328	Tc/Cc	7.829	Cc/Tc	8.378	Tc/Cc	9.521
MMA	Tc/Cc	7.665	Cc/Tc	7.360	Tc/Cc	3.921	Cc/Tc	2.817
MTC	Cc/Tc	9.102	Tc/Cc	8.456	Cc/Tc	5.260	Tc/Cc	3.607

In order to get further information about the relative stabilities of the isomeric forms, the total energies for each of the conformer were obtained by complete optimization of their geometries by RHF and DFT methods using different extended basis sets with/without polarization functions as well as by using diffuse functions.

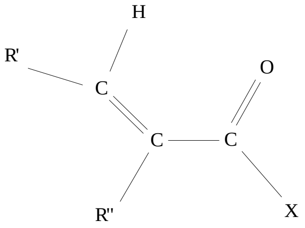
It is observed that the RHF calculation gives similar values for the enthalpy difference between the two conformers, which is not more than 0.64 kcal/mol for all molecules. The rotational barrier between the more stable and less stable conformers in unsaturated esters is found to lie in 7.665 and 9.102 kcal/mol range and the barrier between the less stable and the more stable conformers is in the 7.360 and 8.456 kcal/mol range in the ground state.

The small enthalpy difference combined with the large rotational barrier in the unsaturated esters suggests that the two conformers in all the molecules may lie in comparable concentrations under normal conditions.

Electronic excitation to the first excited state S_1 in the unsaturated esters is found to marginally increase the enthalpy difference between the two conformers, while substantially reducing the rotational barrier between them by as much as 2.817 kcal/mol (MMA). This is a unique observation in the case of esters as the corresponding aldehydes and acid halides[14] show an increase in the rotational barrier on electronic excitation. A marginal increase in the enthalpy difference and a substantial decrease in the rotational barrier may promote conformational transformations in the S_1 state. In methyl acrylate, a reversal in the relative stability of the conformers is observed; the Tc conformer in methyl acrylate became more stable than Cc respectively in the S_1 state whereas reverse was the case in the S_0 state.

Although similar reversal in the relative stabilities of conformers on electronic excitation has been reported for acrolein[15] and methyl vinyl ketone[16], no experimental data is available in the literature on these molecules to confirm our findings.

Our conclusions regarding the preferred conformations in the presently studied a, b-unsaturated ester molecules in the electronic ground state as well as a change in conformation on electronic excitation to the S_1 state, as in methyl acrylate, can be rationalized by considering the following three types of forces and the balance between them.



1. Coulombic force between the oxygen atom of the carbonyl group and the substituent at the vinyl group (R¢); in our case hydrogen or methyl. This would depend upon the steric orientation of these groups and may be called as steric interaction.
2. The force of repulsion between the p-electrons of the carbon-carbon double bond with those of the carbonyl group.
3. Force of repulsion between the p-electrons of the carbon-carbon double bond with the bond between the carbonyl carbon atom and its substituent (X) which has a partial p-bond character. This force acts in a direction opposite to the one mentioned at point 2 above.

Thus, in the case of methyl acrylate (MA) and methyl *trans* crotonate (MTC), the attraction between the hydrogen of the vinyl group and the oxygen atom of the carbonyl group tends to stabilize the s-*cis* conformation. Similarly in the case of methyl methacrylate (MMA), the force of attraction between the methyl substituent at the a-position and the oxygen atom of the carbonyl group gave it a preferred *trans* conformation. Electronic excitation gives an ionic character to the carbonyl group with a large negative charge on the oxygen atom. This tends to increase the force of repulsion of the oxygen atom with the p-electron of the vinyl group of methyl acrylate and results in a preferred s-*trans* conformation for them in the S_1 state.

Optimized geometries: A comparison of the optimized geometries of the stable conformers of each molecule shows that with the change of conformation, the bond lengths remain practically unaffected but the angles C-C=O, C-C-O, C-C=C and C-C-X (X = H or CH_3) change by up to 4.0°. While angles C-C=C and C-C-O in *cis* conformations are smaller than those in the *trans* conformation, the reverse is the situation with angles C-C=O and C-C-X (X = H or CH_3). These changes in angles can be explained in terms of increased repulsive force between the p-electrons of C=C and C-O bonds and a corresponding reduced repulsion between similar electrons of the C=C and C=O in the *trans* conformation as compared to the *cis* conformation.

Table 3
Optimized geometries and bond population of the Cc and Tc conformer of methyl acrylate in the ground (S_0) and excited (S_1) states in RHF/6-31G basis set

Internal Coordinates	Cc				Tc					
	Bond order		Bond length/ Bond angle		Bond order		Bond length/ Bond angle		Change in bond angle Cc to Tc	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	0.991	1.015	1.487	1.431	1.003	1.034	1.486	1.432		
$C_1=C_3$	1.870	1089	1.318	1.337	1.868	1.833	1.319	1.338		
$C_2=O_4$	1.763	1.712	1.186	1.263	1.751	1.680	1.186	1.270		
$C_2C_1C_3$			128.80	128.50			124.30	124.10	3.5	4.4
$C_1C_2O_6$			111.20	118.30			113.80	119.60	2.6	1.3
$C_1C_2O_4$			125.20	122.20			122.80	121.30	2.4	0.9
$C_2C_1H_5$			116.70	110.60			113.70	115.10	3.0	4.5

Table 4
Optimized geometries and bond population of the Tc and Cc conformer of methyl methacrylate in ground (S_0) and excited (S_1) states in RHF/6-31G basis set

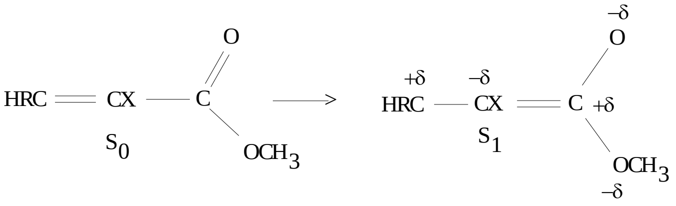
Internal Coordinates	Tc				Cc				Change in bond angle Tc to Cc	
	Bond order		Bond length/ Bond angle		Bond order		Bond length/ Bond angle			
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_3-C_6	0.978	1.008	1.495	1.446	0.971	0.999	1.498	1.441		
$C_2=C_3$	1.869	1.836	1.321	1.336	1.869	1.858	1.321	1.339		
$C_6=O_{10}$	1.769	1.705	1.211	1.280	1.771	1.712	1.210	1.273		
$C_2C_3C_6$			120.93	120.63			117.05	123.30	3.88	2.67
$C_3C_6C_{10}$			122.92	122.17			124.97	121.71	2.05	0.46
$C_3C_6O_{11}$			114.10	119.44			112.10	119.65	2.00	0.21

Table 5
Optimized geometries and bond population of the Cc and Tc conformer of methyl *trans* crotonate in ground (S_0) and excited (S_1) states in RHF/6-31G basis set

Internal Coordinates	Cc				Tc					
	Bond order		Bond length/ Bond angle		Bond order		Bond length/ Bond angle		Change in bond angle Cc to Tc	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	1.002	1.028	1.482	1.456	1.017	1.049	1.481	1.456		
$C_1=C_3$	1.845	1.831	1.322	1.507	1.844	1.806	1.322	1.512		
$C_2=O_4$	1.752	1.702	1.187	1.190	1.741	1.667	1.191	1.193		
$C_2C_1C_3$			120.79	121.83			124.37	125.48	3.58	3.65
$C_1C_2O_6$			111.21	112.33			113.98	113.28	2.77	0.95
$C_1C_2O_4$			125.59	123.92			122.95	123.11	2.64	0.81
$C_2C_1H_5$			116.78	117.69			113.68	114.56	3.10	3.13

Electronic excitation to the S_1 state, however, brings about considerable changes both in the bond lengths and bond angles of the two stable conformers of all the molecules, particularly in C=O, C=C and C-C bonds and C-C=O, C-C-O, C-C=C and C-C-X (X = H or CH_3) angles. Thus, it is found that in all molecules except MTC, where the S_1 state arises out of n-p* transition, the C=O and C=C bond lengths increase by about 0.09 Å and 0.02 Å respectively and the C-C bond length decreases by 0.05 Å. In MTC, where the S_1 state arises out of p-p* transition, the corresponding changes are 0.003, 0.18 and 0.03 Å respectively. Similarly, the bond angle C-C=O decreases by as much as 1.67°.

The change in bond lengths and bond angles on electronic excitation can be explained in terms of redistribution of electronic charge and resonance effects as per the following scheme.



This explanation is supported by the present calculations which show in the S_1 state, a net negative charge on the two oxygen atoms of the carbonyl and methoxy groups as well as the carbon atom of the vinyl group and a net positive charge on the carbon atom attached to the carbonyl group and the carbon atom at the b-position.

An inverse relationship has been observed between the bond lengths and bond orders of the corresponding bonds, both in the case of change of conformation as well as in the case of electronic excitation. Thus, in all unsaturated molecules the bond orders of the C=O and C=C bonds decrease with an increase in their lengths on electronic excitation. Likewise a decrease in the length of C-C single bond in between the carbonyl and vinyl double bonds leads to a corresponding increase in its bond order on electronic excitation.

Electronic transitions: The electronic transitions in all the ester molecules were obtained by time-dependent DFT method using extended basis sets and by incorporating configuration interactions between singly excited states. Based on the calculated frequencies, oscillator strengths and nature of the involved molecular orbitals, a complete assignment of some of the prominent electronic transitions in the 5-9 eV range in each molecule could be made. In the molecules under study, the electronic transitions can be broadly divided into four categories.

(a) n-p* transitions involving the electron lone pair of the carbonyl oxygen atom and the p* orbitals of the vinyl group.
(b) n-p* transitions involving the electron lone pair of the methoxy oxygen atom and p* orbital of the vinyl group.
(c) p-p* transitions involving the p and p* molecular orbitals of the vinyl and carbonyl groups.
(d) Others which include s_{mix}-p* transitions and n-p* transitions involving higher energy p* orbitals. A large amount of mixing is observed in p* orbitals of the vinyl and carbonyl groups.

The first type of n-p* transitions is symmetry forbidden and consequently has low intensity. They are found to experience a lower frequency shift with increasing conjugation in the molecules and therefore appear at 296.99, 211.43 and 193.20 nm in methyl acrylate, methyl methacrylate and methyl *trans* crotonate respectively. The second type of n-p* transition involving the lone pair of electrons of the oxygen atom of the methoxy group is found to appear in a some what lower frequency range 145 to 229 nm.

The third type of transitions namely the p-p* transitions is allowed by symmetry considerations and experiences a bathchromic shift with increased conjugation in the system due to b-substitution by an electron donating group such as methyl or methoxy. This band is predicted at 197.78 nm (experimental 194 nm) in methyl acrylate and 207.87 nm (experimental 212 nm) in methyl *trans* crotonate. The miscellaneous transitions such as s_{mix}-p_e* or n-p* appear at very high energies.

Thus, the s_{mix}-p_e* transitions in methyl methacrylate and methyl *trans* crotonate are expected near 144.20 and 137.88 nm. The change of conformation does not appreciably affect either the energy or the nature of electronic transitions.

Conclusion

It may be concluded on the basis of present quantum chemical calculations that esters molecule exists as a mixture of two rotational isomers namely *trans* and *cis*, both in the electronic ground (S_0) and excited (S_1) states. In the S_0 and S_1 states, the average enthalpy difference between the two conformers by RHF/6-311+G(d,p) is 0.489 kcal/mol and 1.555kcal/mol respectively.

In the S_0 and S_1 states, both in the *trans* and *cis* conformers, the methyl group (CH_3) exists in a preferred staggered conformation relative to the carbonyl group. Not much difference is found in the optimized geometries of the *trans* and *cis* conformers in the S_0 state which differs only in some bond lengths. However, major changes occur in few bond angles like CCO, COC and OCO. Electronic excitation produces appreciable changes in molecular geometry, both in bond lengths and bond angles.

Table 6
Calculated transition and assignments Cc and Tc conformers of methyl acrylate, methyl methacrylate and methyl trans crotonate

	MA		MMA		MTC	
	Cc	Tc	Tc	Cc	Cc	Tc
$n \rightarrow \pi^*$	296.99	300.28	211.43	218.54	193.20	196.13
$\pi \rightarrow \pi^*$	197.78	193.21	162.53	193.51	207.87	205.00
Others ($\sigma_{mix} \rightarrow \pi^*_e$ or n-π^*)			144.20	149.04	137.88	135.98
			139.41	146.92	134.93	135.65

These changes may be explained in terms of charge redistribution on moving from the S_0 to S_1 state. An inverse relation is found to exist between the lengths and bond orders of the CC, CO and OC bonds. Time-dependent Density Functional theory (TD-DFT) using BLYP functionals and 6-31G** basis set predicts three major absorption bands. Based on the oscillator strengths of these bands, the conformer may be assigned to the n-π*, π-π* and Others ($\sigma_{mix} \rightarrow \pi^*_e$ or n-π*) transitions.

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