Molecular structure, conformation and electronic spectra of methyl-3-methyl crotonate

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Abstract: A systematic quantum mechanical study of the possible conformations, their relative stabilities and electronic spectra and thermodynamic parameters of methyl-3-methyl crotonate (MMC) has been reported for the electronic ground (S0) and first excited (S1) states using time-dependent and time-independent Density Functional Theory (DFT) with BLYP and B3LYP functionals and RHF methods in extended basis sets 6-31G, 6-31G**, 6-311G** and 6-311+G**. The molecule was considered as a three rotor system having internal rotation about two C-O and a C-C bond, with the possibility of hindered rotation of the methyl groups. Conformations in which the carbonyl and methoxy groups are in cis position are found to be most stable with the methyl group having staggered conformation relative to the carbonyl group. Plot of potential energy curves for rotation about C-C bonds in the S0 and S1 states shows two energy minima corresponding to the Cc and Tc conformations. Plot of potential energy curves in the S0 and S1 states by RHF/6-31G based calculations indicates in each case the presence of two stable rotameric conformations, Cc and Tc separated by 0.645 and 1.653 kcal/mol, respectively. Fully optimized geometries of the two stable conformers in the S0 and S1 states are being reported by RHF and DFT methods using several basis sets. A complete interpretation of the electronic spectra of Cc and Tc conformers of MMC in terms of nature, energy and intensity of electronic transitions have been provided on the basis of time-dependent density functional theory (TDDFT) using BLYP functionals and 6-31G basis set.

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Introduction

α, β-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[1,2], ethyl acrylate[1,2] and methyl methacrylate [3-8] and rotational isomerism about the carbon-carbon single bond leading to s-*cis* and s-*trans* conformers have been reported. However, in the case of methyl-3-methyl crotonate (MMC), Droog *et al* [9] based on infrared

and Raman spectral studies, suggest that the s-trans conformer to be more stable. No systematic attempt seems to have been made to understand conformational, physico-chemical and thermodynamic properties of methyl-3-methyl crotonate in its ground and first excited states. An effort is therefore being made through this communication to fill up the gap in the literature and also to provide a complete interpretation of the electronic spectra of the conformers of MMC from advanced level quantum chemical calculations involving electron correlational effects.

Method of calculation

In order to identify the possible rotational isomers of methyl-3-methyl crotonate (MMC) in the ground (S_0) and first excited (S_1) electronic states, potential energy curves for asymmetric torsion about C_1-C_2 bond (Fig. 1) were obtained by calculating the variation of total energy of the molecule with dihedral angle φ ($C_3C_1C_2O_4$) in interval of 20° in the range 0° to 360° by ab initio SCF-HF calculations using 6-31G basis set. The enthalpy difference between the stable conformers in S_0 and S_1 states are obtained after complete optimization of their geometries. These optimizations for the ground state S_0 were conducted at the RHF level using RHF/6-31G**, RHF/6-311+G** and MP2/6-311+G** and by Density Functional Theory (DFT) using basis set 6-311+G** (Triple zeta with diffuse functions and polarization functions on all atoms). Becke's three parameter (local, non local, Hartree-Fock) hybrid exchange functionals using Lee-Yang-Parr correlational functions (B3LYP) were used in DFT calculations. For the first excited state S_1 the geometries of the stable conformers were optimized by RHF/6-31G** and RHF/6-311+G**. Electronic transitions and oscillator strengths of the two stable conformers of MMC have been calculated using

RHF/6-31G** after accounting for configuration interaction between the singly excited states. Computer softwares Gaussian 98 [10] and GAMESS [11] have been used in all the computations.

Conformational notations

The notations presently used for the conformations of methyl-3-methyl crotonate are analogous to those used previously by Virdi et al. [12] for methyl acrylate. Conformations with respect to dihedral angle $\varphi(C_3C_1C_2O_4)$ are denoted by a capital C (*cis* or *syn*, $\varphi = 0°$) or T (*trans* or *anti*, $\varphi = 180°$) and those with respect to the dihedral angle $\varphi(O_4C_2O_6C_9)$ by lower case letter c(*cis* or *syn*, $\varphi = 0°$) or t (*trans* or *anti*, $\varphi = 180°$) following the capital letter C or T. Rotation of methyl groups about the O_6-C_9 and C_3-C_8 , C_3-C_7 may give rise to either eclipsed or staggered conformations relative to the carbonyl and ethylenic groups, respectively. However, as present calculations show, only the staggered conformations of the methyl group have lower energy and as such, no separate notations are used for isomerism about the C-CH$_3$ bond.

Results and discussion

Conformational studies

Potential energy curves for rotation about, C_1-C_2 bond for the ground (S_0) and first excited (S_1) electronic states with the ester group in *cis* conformation, are given in Fig.2. It is seen that in both these states, the molecule has two potential minima at $\varphi(C_3C_1C_2O_4)=0°$ and $180°$ corresponding to the *cis*(C) and *trans*(T) conformations relative to the C_1-C_2 bond. Since, in both the cases, the molecule is additionally found to have minimum energy for the *cis* conformation $((\varphi \ (O_4C_2O_6C_9)=0°)$ relative to the C_2O_6 bond,

its conformations at these minima may be identified as Cc and Tc. A plot of the potential energy curve of the methyl group about the O_6-C_9 bond reveals that, as in the case of methyl acrylate[12], it has staggered conformation relative to the carbonyl group in MMC as well.

The relative energies of the two stable Cc and Tc conformers of methyl-3-methyl crotonate and hence the enthalpy difference (neglecting zero point energy) between them as obtained from RHF/6-31G, RHF/6-31G*, RHF/6-31G**, RHF/6-311+G**, MP2/6-311+G** and DFT/6-311+G** for the electronic ground state S_0, are given in Table 1. This table also contains similar information for the first excited state S_1 from RHF/6-31G, RHF/6-31G** and RHF/6-311+G** calculations. While in the S_0 state the enthalpy difference between the Cc and Tc conformers has a value in the range 0.681 ± 0.109 kcal/mol, in the S_1 state it has a higher value in the range 1.437 ± 0.230 kcal/mol. Based on infrared spectral studies, Droog et al. [9], however, predicted trans conformer to be more stable than the cis conformer. No experimental data is, however available in the literature for the comparison purpose.

The rotational barrier between the conformers of MMC in the S_0 and S_1 states in RHF/6-31G are given in Table 1. It may be inferred from Table 1 and Fig. 2 that there is a significant decrease in the rotational barriers Cc/Tc and Tc/Cc from 9.102 kcal/mol and 8.456 kcal/mol, respectively in the S_0 state to 5.260 kcal/mol and 3.607 kcal/mol, respectively, in the S_1 state. This makes conformational isomerism more probable in the excited electronic state than in the ground state. Similar situation is observed in case of methyl methacrylate [13] , where the barriers to inter-conversion reduce in going from S_0 to S_1 states.

The ionization potentials of the Cc and Tc conformers of MMC in RHF and DFT

using different basis sets are given in Table 1. While the RHF calculations predict the

ionization potentials of the Cc and Tc conformers in a narrow range of 10.22 ± 0.08 eV and

10.25 ± 0.08 eV, respectively, DFT calculations provide much lower values of 7.57 eV and

7.62 eV respectively. No experimental values for the ionization potential seem to have been

reported. However, our RHF values are close to the value 9.820 eV reported by Buemi et al.

[14] from HAM/3 calculations reported in case of methyl trans cotonate. It also follows from

Table 1 that the ionization potential in the S_1 state has a lower value than in the S_0 state.

Optimized geometries

Optimized geometries of the Cc and Tc conformers of methyl-3-methyl crotonate

(MMC) in the ground state (S_0) were obtained from RHF (without and with MP2 correction)

and DFT techniques, using the basis functions 6-31G** and 6-311+G**. The optimized

geometries in the excited state (S_1) were obtained from RHF/6-31G** and RHF/6-311+G**

calculations. The results are given in Tables 2 and 3 for the Cc and Tc conformers,

respectively. It may be seen from Table 2 that for the S_0 state RHF and DFT methods give

comparable geometries which differ by a maximum of 0.02 A° in bond length and 2° in bond

angle. The geometries of the Cc and Tc conformers are close to those reported by Droog et al

[9] based on electron diffraction, differing from them by a maximum of 0.03A° in bond length

and 6° in bond angle. A similar observation may be made for the Tc conformer from Table 3.

It is further noted from Tables 2 and 3 that the change of conformation from the more stable

Cc isomer to less stable Tc isomer does not change the molecular geometry appreciably,

except in a few bond angles. Thus, the DFT results show that while the bond angles $C_2C_1C_3$

and $C_1C_2O_6$ increase by 3.91° and 2.87°, respectively, the angle $C_1C_2O_4$ and $C_2C_1H_5$

decrease by 2.72° and 3.36°, respectively. However, a comparison of the optimized geometries of the molecule in the S_0 and S_1 states in the same basis set 6-311+G** (Table 2) shows that the electronic excitation in Cc conformer results in a decrease in C_1C_2 bond length by about 0.026 A° and an increase in the C_1C_3 bond length by 0.185 A°. More significantly, in the S_1 state, the angle $C_1C_3C_8$ decrease by about 3.84° and the angles $C_2C_1C_3$ and $C_1C_2O_6$, increase by about 1.04° and 1.12°, respectively. A similar situation is observed in the case of the Tc conformer in S_1 state (Table 3). These changes may be explained in terms of electron redistribution in the excited state. As shall be seen later, the first excited state of MMC arises out of π_e-π_e* excitation involving the π electrons of the vinyl group. This leads to a decrease in the C_1C_3 bond order and a corresponding increase in the C_1C_2 bond order and explains the change in these bond lengths.

Electronic transitions

In an attempt to understand the nature of electronic transitions in terms of their energies and oscillator strengths (O.S.), ab initio calculations by RHF/6-31G** method were performed for both the stable Cc and Tc conformers of methyl-3-methyl crotonate. Configuration interaction between the singly excited electronic states was considered. Main configurations and the mixing coefficients of the singlet ground and excited states have been determined and are given in Table 4. In the case of the Cc conformer of methyl-3-methyl crotonate, the calculations predict the first electronic transition at 5.96eV (O.S.=0.6216) which, on the basis of the mixing coefficients and the molecular orbital coefficients of the involved states, may principally be assigned to the π_e- π_e* transition in the ethylenic group, slightly perturbed by π_e- π*$_{co}$ of the carbonyl group. Another allowed transition $^1A' \rightarrow {}^1A'$ with mixing

coefficient 0.641 is predicted at 9.19 eV (O.S. = 0.1667) which may be assigned to $n\pi_{O6}$ -

π^*_e, involving the lone pair of the oxygen atom of the $COCH_3$ chromophoric group. In

addition to the above, three forbidden bands in the 0-10 eV range corresponding to the

transition $^1A' \rightarrow {}^1A''$ have been predicted at 6.42 eV (O.S. = 0.0002), 7.91 eV (O.S. = 0.0012)

and 8.99 eV (O.S. = 0.0009). These correspond to $n\sigma_{O4}$- π_e^*, $n\sigma_{O6}$- π_e^* and σ_{mix}- π_e^*

transitions as given in Table 4. No experimental data is available for the MMC for

comparison purpose

The electronic transition in the Tc conformer of methyl-3-methyl crotonate are close

to those in the Cc conformer and may be given the same assignments.

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Table1.Total energy, ionization potential and rotational barrier of different conformers
of methyl-3-methyl crotonate in ground (S_0) and excited (S_1) states

Ground state (S_0)

Basis sets	Relative energy (kcal/mol)		Ionization potential (eV)		Rotational barrier (kcal/mol)	
	Conformation		Conformation			
	Cc	Tc	Cc	Tc	Cc/Tc	Tc/Cc
RHF/6-31G	0.0[a]	0.645	10.240	10.249	9.102	8.456
RHF/6-31G*	0.0[b]	0.772	10.169	10.213		
RHF/6-31G**	0.0[c]	0.789	10.159	10.203		
RHF/6-311+G**	0.0[d]	0.584	10.298	10.346		
MP2/6-311+G**	0.0[e]	0.572	10.232	10.267		
DFT/6-311+G**	0.0[f]	0.723	7.574	7.620		

Excited state (S_1)

	Cc	Tc	Cc	Tc	Cc/Tc	Tc/Cc
RHF/6-31G	0.0[g]	1.653	10.156	10.178	5.260	3.607
RHF/6-31G**	0.0[h]	1.452	9.181	9.206		
RHF/6-311+G**	0.0[i]	1.207	9.348	9.379		

[a] Absolute value –215656.35 kcal/mol
[b] Absolute value –215754.55 kcal/mol
[c] Absolute value –215762.81 kcal/mol
[d] Absolute value –215813.17 kcal/mol
[e] Absolute value –216507.02 kcal/mol
[f] Absolute value –217118.61 kcal/mol
[g] Absolute value –215603.30 kcal/mol
[h] Absolute value –215742.15 kcal/mol
[i] Absolute value –215793.29 kcal/mol

Table 2. Optimized geometries of the Cc conformer of methyl-3-methyl crotonate in the ground (S_0) and excited (S_1) states in different basis sets

Internal Coordinates	Ground state (S_0)					Excited state (S_1)	
	RHF/ 6-31G**	RHF/ 6-311+G **	MP2/ 6-311+G**	DFT/ 6-311+G**	Experimental[†]	RHF/ 6-31G**	RHF/ 6-311+G**
C_1C_2	1.480	1.482	1.482	1.478	1.470	1.456	1.456
C_1C_3	1.322	1.322	1.345	1.336	1.345	1.508	1.507
C_2O_4	1.192	1.201	1.214	1.210	1.219	1.195	1.190
C_1H_5	1.075	1.075	1.086	1.084	1.086	1.074	1.074
C_2O_6	1.346	1.344	1.355	1.356	1.360	1.329	1.327
C_3C_7	1.501	1.505	1.504	1.505	1.505	1.501	1.502
C_3H_8	1.497	1.497	1.497	1.494	1.505	1.497	1.498
O_6C_9	1.435	1.435	1.435	1.437	1.460	1.416	1.415
C_9H_{10}	1.081	1.081	1.092	1.091		1.081	1.082
C_9H_{11}	1.081	1.081	1.092	1.091		1.081	1.082
C_9H_{12}	1.079	1.079	1.088	1.088		1.081	1.080
C_8H_{13}	1.083	1.084	1.093	1.092		1.086	1.086
C_8H_{14}	1.086	1.087	1.095	1.096		1.089	1.089
C_8H_{15}	1.086	1.087	1.095	1.096		1.089	1.089
C_7H_{16}	1.083	1.081	1.088	1.085		1.078	1.077
C_7H_{17}	1.086	1.087	1.095	1.096		1.091	1.089
C_7H_{18}	1.085	1.086	1.095	1.096		1.091	1.089
$C_2C_1C_3$	120.58	120.79	120.68	121.12	119.8	121.62	121.83
$C_1C_2O_4$	125.51	125.59	126.34	126.37	120.0	123.90	123.92
$C_2C_1H_5$	117.92	117.78	117.34	116.85	118.8	117.85	117.69
$C_1C_2O_6$	111.33	111.21	110.24	110.56	116.0	112.32	112.33
$C_1C_3C_7$	126.77	126.20	125.71	125.45	123.4	124.53	124.60
$C_1C_3C_8$	125.13	125.12	124.43	125.26	123.8	121.46	121.28
$C_2O_6C_9$	116.88	116.43	114.16	115.90	113.0	116.66	117.19
$O_6C_9H_{10}$	110.62	110.56	110.43	110.52		110.64	110.59
$O_6C_9H_{11}$	110.62	110.56	110.43	110.52		110.64	110.59
$O_6C_9H_{12}$	105.93	105.83	105.43	105.53		105.85	105.76
$C_3C_8H_{13}$	111.88	111.85	111.48	112.09		111.72	111.66
$C_3C_8H_{14}$	110.34	110.18	110.41	110.54		111.90	111.82
$C_3C_8H_{15}$	110.34	110.18	110.41	110.54		111.90	111.82
$C_3C_7H_{16}$	112.81	112.88	112.77	112.64		112.69	112.88
$C_3C_7H_{17}$	109.20	109.14	109.17	109.60		110.87	110.86
$C_3C_7H_{18}$	109.21	109.14	109.17	109.60		110.87	110.86
$C_3C_1C_2O_4$	0.0	0.0	0.0	0.0		0.0	0.0
$C_2C_1C_3C_8$	180.0	180.0	180.0	180.0		180.0	180.0
$O_4C_2O_6C_9$	0.0	0.0	0.0	0.0		0.0	0.0

[†] Ref. 9

Table 3. Optimized geometries of the Tc conformer of methyl-3-methyl crotonate in the ground (S_0) and excited (S_1) states in different basis sets

Internal Coordinates	Ground state (S_0)					Excited state (S_1)	
	RHF/ 6-31G**	RHF/ 6- 311+G **	MP2/ 6-311+G**	DFT/ 6-311+G**	Experim ental[†]	RHF/ 6-31G**	RHF/ 6-311+G**
C_1C_2	1.480	1.481	1.480	1.477	1.470	1.456	1.456
C_1C_3	1.322	1.322	1.344	1.336	1.345	1.513	1.512
C_2O_4	1.213	1.212	1.216	1.211	1.219	1.196	1.193
C_1H_5	1.078	1.079	1.087	1.085	1.086	1.073	1.074
C_2O_6	1.347	1.344	1.354	1.355	1.360	1.327	1.324
C_3C_7	1.502	1.506	1.504	1.503	1.505	1.501	1.500
C_3H_8	1.498	1.498	1.498	1.495	1.505	1.497	1.498
O_6C_9	1.448	1.442	1.443	1.447	1.460	1.416	1.416
C_9H_{10}	1.081	1.081	1.091	1.091		1.081	1.081
C_9H_{11}	1.081	1.081	1.091	1.091		1.081	1.081
C_9H_{12}	1.079	1.080	1.088	1.088		1.079	1.079
C_8H_{13}	1.083	1.083	1.093	1.091		1.086	1.086
C_8H_{14}	1.086	1.086	1.095	1.095		1.089	1.089
C_8H_{15}	1.086	1.086	1.095	1.095		1.089	1.089
C_7H_{16}	1.071	1.074	1.086	1.084		1.0767	1.078
C_7H_{17}	1.081	1.087	1.097	1.096		1.0900	1.091
C_7H_{18}	1.081	1.086	1.096	1.096		1.0900	1.091
$C_2C_1C_3$	124.33	124.37	124.48	125.03	119.8	125.39	125.48
$C_1C_2O_4$	123.08	122.95	123.73	123.65	120.0	123.02	123.11
$C_2C_1H_5$	113.70	113.68	114.12	113.49	118.8	114.60	114.56
$C_1C_2O_6$	113.89	113.98	112.98	113.43	116.0	113.36	113.28
$C_1C_3H_7$	118.75	118.66	118.42	118.36	123.4	118.19	118.24
$C_1C_3C_8$	124.63	124.67	123.94	124.78	123.8	121.09	120.93
$C_2O_6C_9$	116.71	116.28	115.07	115.83	113.0	116.76	116.31
$O_6C_9H_{10}$	110.62	110.58	110.51	110.57		110.57	110.52
$O_6C_9H_{11}$	110.62	110.58	110.51	110.57		110.57	110.52
$O_6C_9H_{12}$	105.89	105.79	105.31	105.47		105.89	105.79
$C_3C_8H_{13}$	111.82	111.79	111.43	112.04		111.69	111.65
$C_3C_8H_{14}$	110.39	110.22	110.45	110.57		111.88	111.79
$C_3C_8H_{15}$	110.39	110.22	110.45	110.57		111.88	111.79
$C_3C_7H_{16}$	113.40	113.41	113.39	113.24		112.75	113.11
$C_3C_7H_{17}$	109.09	109.10	109.05	109.52		110.83	110.81
$C_3C_7H_{18}$	109.12	109.10	109.24	109.52		110.83	110.81
$C_3C_1C_2O_4$	180.0	180.0	180.0	180.0		180.0	180.0
$C_2C_1C_3C_8$	180.0	180.0	180.0	180.0		180.0	180.0
$O_4C_2O_6C_9$	0.0	0.0	0.0	0.0		0.0	0.0

[†] Ref. 9

Table 4. Calculated transition energies, oscillator strengths and assignments along with the main configurations and mixing coefficients for the singlet ground and excited states.

Cc	Symmetry	Assignments	Transition energy eV	Transition energy nm	Oscillator strength	Mixing coefficients and main configurations [§]
Ground state [†] $E= -343.735558h$	$^1A'$					1.000 [2222222/000000]
a	X $^1A'$	$\pi_e \rightarrow \pi^*_e$ π^*_{CO}	5.96	207.87	0.6216	0.685 [2222221/100000]
b	X $^1A'$	$n\pi_{O6} \rightarrow \pi^*_e$	9.19	134.93	0.1667	0.641 [2222122/100000] -0.196 [2222122/000010]
a	X $^1A''$	$n\sigma_{O4} \rightarrow \pi^*_e$	6.42	193.20	0.0002	0.616 [2222212/100000] -0.302 [2222212/000010]
b	X $^1A''$	$n\sigma_{O6} \rightarrow \pi^*_e$	7.91	156.81	0.0012	0.465 [2212222/100000] 0.374 [2221222/100000]
c	X $^1A''$	$\sigma_{mix} \rightarrow \pi^*_e$	8.99	137.88	0.0009	0.561 [1222222/100000] 0.292 [2212222/100000] -0.166 [2221000/100000]
Tc Ground state [†] $E= -343.734301h$	$^1A'$					1.000 [2222222/000000]
a	X $^1A'$	$\pi_e \rightarrow \pi^*_e$ π^*_{CO}	6.05	205.00	0.6956	0.683 [2222221/100000]
b	X $^1A'$	$n\pi_{O6} \rightarrow \pi^*_e$	9.14	135.65	0.0890	0.649 [2222122/100000] -0.193 [2222122/000010]
a	X $^1A''$	$n\sigma_{O4} \rightarrow \pi^*_e$	6.32	196.13	0.0002	0.618 [2222212/100000] -0.274 [2222212/000010]
b	X $^1A''$	$n\sigma_{O6} \rightarrow \pi^*_e$	8.08	153.39	0.0021	0.414 [2212222/100000] 0.373 [2221222/100000]
c	X $^1A''$	$\sigma_{mix} \rightarrow \pi^*_e$	9.11	135.98	0.0018	0.445 [1222222/100000] -0.358 [2212222/100000] -0.166 [2221000/100000]

[†] Energy in Hartree

[§] Seven higher energy occupied molecular orbitals and three lower energy unoccupied orbitals have been listed

Figure captions:
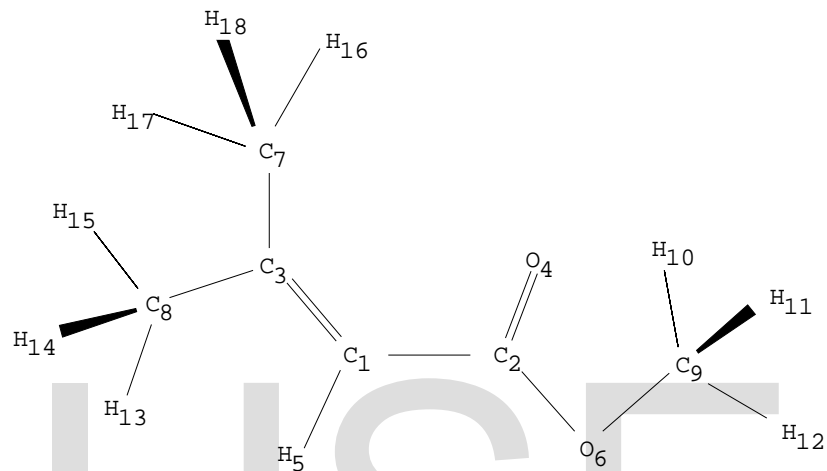
1. Numbering of atoms of methyl-3-methyl crotonate.

Fig. 1

2. Potential energy curves of methyl-3-methyl crotonate for rotation about C_1-C_2 bond in S_0 (Series 1) and S_1 (Series 2) states. $\varphi(O_4C_2O_6C_9)=0^0$ and
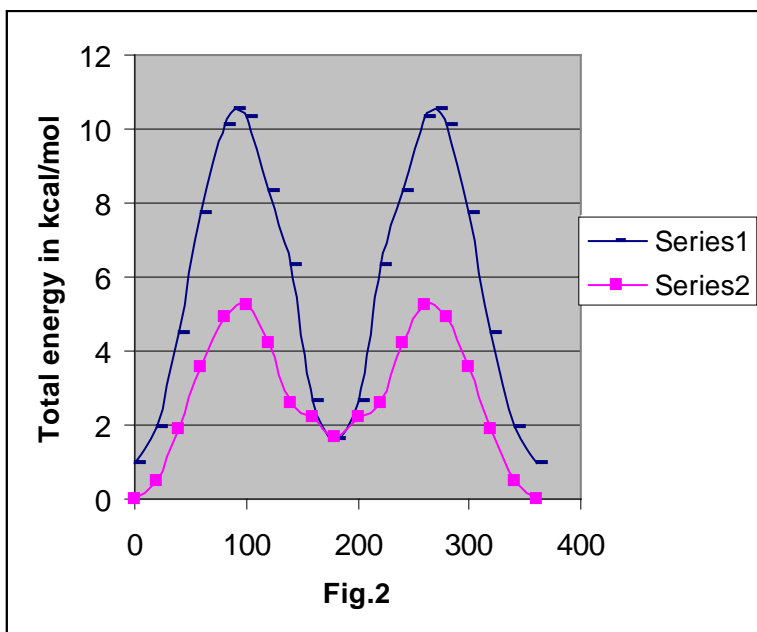
Fig.2

$\varphi(C_2O_6C_9H_{12})=180^0$. The abscissa is the angle of rotation θ about C_1-C_2 bond relative to Cc conformation for which the dihedral angle $\varphi(C_3C_1C_2O_4)=0^0$. The ordinates for Series 1 are shifted by 1 kcal/mol above Series 2.