Molecular Mechanics Study of Ethyl Phenylacetate and Methyl Phenylacetate

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Abstract. Conformational behavior of ethyl phenylacetate and methyl phenylacetate has been studied employing the technique of molecular mechanics. Cis-cis conformers, in which alkyl as well as phenyl groups remains cis to the carbonyl group, are found to be of lower energy as compared to the trans gauche conformer in which alkyl & phenyl groups remains trans & gauche respectively to carbonyl group. Optimised geometries of the cis-cis conformers of both the compounds are reported. The conformational energies for cis-cis and trans-gauche conformers of ethyl phenylacetate and methyl phenylacetate are computed to be 0.5233 kcal/mole and 0.7389 kcal/mole respectively.

1. Introduction

Spectroscopic and quantum mechanical study of the conformational behaviour of formates and their haloderivatives have been made in the past.[1-8] It has been established that the alkyl group remains cis to carbonyl bond in these molecules. Hydrogen bonding, dipole-dipole interaction, lone pair-lone pair repulsion, n-attractive nonbonding interaction and r-conjugative interactions have been employed to justify the higher stability of cis conformers[9]. Existance of conformers has also been demonstrated in higher esters and their derivatives namely acetates and propionates [10-14] and their derivatives. In ethyl phenylacetate (EPA) and methyl phenylacetate (MPA) rotational isomerism is possible due to rotation about RCH_2C (R = phenyl group) and $O-R'(R' = CH_3, C_2H_5)$ bonds. Although, conformational behaviour of haloderivatives of ethyl acetate and methyl acetate seems to be well studied, it seems no effort has been made to understand the geometry and conformations of phenyl derivatives. The present molecular mechanics computations were performed with a view to compute molecular mechanics parameters, conformational energies and optimised geometries of phenyl derivatives of ethyl acetate and methyl acetate.

2. Computational Procedure

Computations were performed using a computer programme of Allinger[15] with

suitable modifications for cyber 180 computer. In the computation of torsional energy V_3 term is ignored for dihydral angle (w) greater than 60^0 if V_1 and V_2 terms are zero, otherwise it is included for all values of w. In the methodology of computations the total energy is calculated as a sum of terms corresponding to compression, bending, Van der Wall and dipole energies. Minimizations of these terms relative to a 'strainless' set by succesive alteration in atomic coordinates lead to a configuration of minimum steric energy. The geometry and atom numbering for EPA and MPA are shown in Figure 1 and 2 respectively. The additional parameters not inbuilt in programme used for moleculer mechanics are listed in Table 1.

Table 1. Additional parameters used for molecular mechanics computation

Bending	ϕ, deg.		K_b
$0 = C - 0$	125.87		2.57
$C_{sp}^3 - C_{sp}^2 - 0$	109.30		1.68
$C_{sp}^3 - 0 - C_{sp}^2$	114.78		2.53
Torsion	V_1	V_2	V_3
$C_{sp}^3 - C_{sp}^3 - 0 - C_{sp}^2$	3.5	-1.65	0.0
$H - C_{sp}^3 - C_{sp}^2 - 0$	0.0	0.0	-0.29
$0 = C_{sp}^2 - 0 - C_{sp}^3$	-0.65	9.2	0.0

$*\phi^0$ = minimum energy bond angle in degrees.

K_b = bending force constant in mdynes A/rad^2

V_1, V_2 and V_3 are first, second and third order torsional constants

3. Result and Discussion

These computations were performed with a view to calculate conformational energies, to know the relative order of stability of different conformers and to get the optimised geometries of most stable conformers. These computations confirm that gauche positions of the phenyl group and trans position of the alkyl group give rise conformers with higher energy. Thus, conformers with cis position of phenyl as well as alkyl groups with respect to carbonyl bond were found to be most stable,. A rotation about C_4-C_5 bond, that is rotation of the plane of phenyl ring revealed that most stable conformers were that in which plane of the phenyl ring coincides with that of the molecular plane containing heavy atoms.

The initial geometry was constructed from available microwave data on methyl
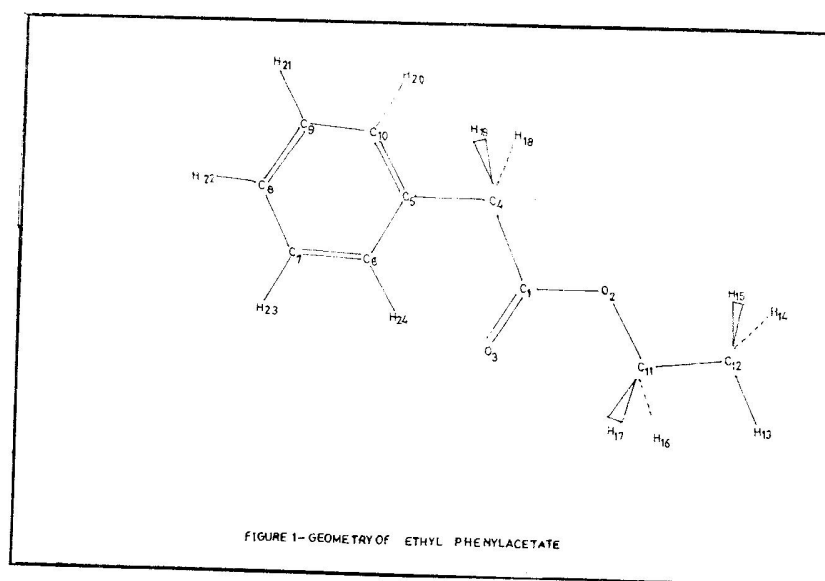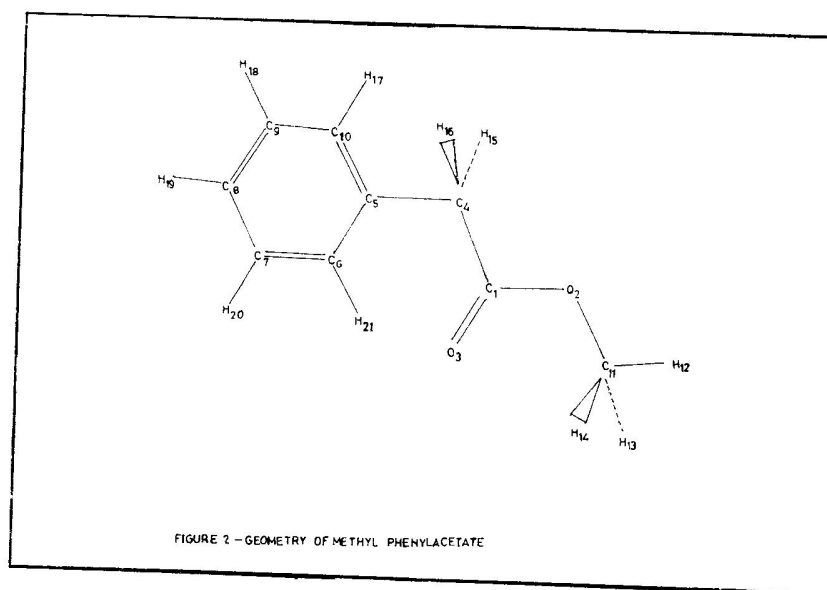
FIGURE 1- GEOMETRY OF ETHYL PHENYLACETATE

Fig. 1. Geometry of ethyl phenylacetate

FIGURE 2 - GEOMETRY OF METHYL PHENYLACETATE

Fig. 2. Geometry of Methyl phenylacetate;

formate[16], ethyl formate[17] and molecular mechanics computations on monohaloacetates[18]. Atoms 1-17 in EPA and atoms 1-14 in MPA were not allowed to move along any of the axes X, Y and Z. It was assumed that they will have same geometrical parameters as in ethyl acetate or in methyl formate. Further, movement of atoms 18, 19 in EPA, atoms 15, 16 in MPA and all the ring atoms were not allowed to move in Y direction so the symmetry and planarity of the molecule were not destroyed. Optimised geometry was computed and is being reported here only for cis-cis isomer of EPA and MPA molecules as these possess highest symmetry and are generally employed for any theoretical computation. Optimised geometrical parameters obtained from present computations for EPA and MPA are shown in table 2. Individual and total energies computated for cis-cis and gauche- trans conformers are listed in table 3. Results of computations for EPA and MPA are condensed in table 2, 3 and 4. These computations shows that cis-cis conformers for EPA and MPA are in lower energy by 0.5223 kcal and 0.7437 kcal respectively than gauche-trans conformers. The geometrical parameters obtained seem to be reasonable as they compare well with related molecules.

Table 2. Final geometries of the cis-cis conformer of ethyl phenylacetate and methyl phenylacetate

Geometrical Parameters*	EPA	MPA
C_1-O_2	1.26	1.26
C_1-O_3	1.20	1.20
C_1-C_4	1.54	1.54
O_2-C_{11}	1.38	1.38
C_4-C_5	1.49	1.49
$C_4-H_{18} = C_4-H_{19} / C_4-H_{15} = C_4-H_{16}$	1.09	1.09
$C_5-C_6 = C_6-C_7 = C_7-C_8 = C_8-C_9 = C_9-C_{10}$	1.39	1.39
$C_6-H_{24} = C_7-H_{23} = C_8-H_{22} = C_9-H_{21} = C_{10}-H_{20}$		
$/C_6-H_{17} = C_7-H_{18} = C_8-H_{19} = C_9-H_{20} = C_{10}-H_{21}$	1.09	1.09
$C_{11}-C_{12}$	1.54	----
$C_{11}-H_{16} = C_{11}-H_{17} / C_{11}-H_{12}-C_{11}-H_{13}$	1.09	1.09
$C_{12}-H_{14} = C_{12}-H_{15}$	1.09	....
$O_2-C_1-O_3$	125.87	125.87
$O_2-C_1-C_4$	109.3	109.3

Geometrical Parameters*	EPA	MPA
$O_3-C_1-C_4$	124.83	124.83
$C_1-O_2-C_{11}$	114.78	114.78
$C_1-C_4-C_5$	110.27	110.27
$C_1-C_4-H_{18} / C_1-C_4-H_{15}$	109.47	109.47
$C_1-C_4-H_{19} / C_1-C_4-H_{16}$	109.47	109.47
$C_5-C_4-H_{18} / C_5-C_4-H_{15}$	109.11	109.11
$C_5-C_4-H_{19} / C_5-C_4-H_{16}$	109.11	109.11
$H_{18}-C_4-H_{19} / H_{15}-C_4-H_{16}$	109.47	109.47
$C_4-C_5-C_6 = C_4-C_5-C_{10}=C_6-C_5-C_{10} = C_5-C_6-C_7 =C_6-C_7-C_8 = C_7-C_8-C_9$	120.00	120.00
$C_5-C_6-H_{24} = C_7-C_6-H_{24} =C_6-C_7-H_{23} = C_8-C_7-H_{23} =C_7-C_8-H_{22} = C_9-C_8-H_{22} / C_5-C_6-H_{17} = C_7-C_6-H_{17} =C_6-H_7-H_{18} = C_6-C_7-H_{18} =C_7-C_8-H_{19} = C_9-C_8-H_{19}$	120.00	120.00
$O_2-C_{11}-H_{12} = C_2-C_{11}-H_{13} =O_2-C_{11}-H_{14}$	....	109.47
$H_{12}-C_{11}-H_{13} = H_{12}-C_{11}-H_{14} = H_{13}-C_{11}-H_{14}$	...	109.47
$C_2-C_{11}-C_{12}$	113.00	...
$O_2-C_{11}-H_{16} = O_2-C_{11}-H_{17}$	107.68	...
$C_{12}-C_{11}-H_{16} = H_{16}-C_{11}-H_{17} = H_{16}-C_{11}-H_{17}$	109.47	...
$C_{11}-C_{12}-H_{13} = C_{11}-C_{12}-H_{14} = C_{11}-C_{12}-H_{15}$	109.47	...
$H_{13}-C_{12}-H_{14} = H_{13}-C_{12}-H_{15} = H_{14}-C_{12}-H_{15}$	109.47	...

* Geometrical parameters with two atoms represent bonds, while with three atoms represent angles

	Ethyl phenylacetate		Methyl phenylacetate	
	cis-cis	gauche-trans	cis-cis	gauche-trans
Compression	0.4105	0.3951	0.2663	0.2739
Bending	1.2736	1.4099	1.3547	1.4033
Stretch bend	0.0711	0.0562	0.0310	0.0241
van der Wall's 1,4 energy	7.2793	7.1380	6.0361	6.0031
Others	-0.4991	-0.8234	-0.4594	-0.6184
Torsional	2.4213	3.4869	2.4114	3.4713
Torsional bend	0.000	0.000	0.00000	0.0011
Dipole	-2.6940	-2.8787	-2.7280	-2.9090
Total	8.2626	8.7849	6.9124	7.6513

Table 3. Final steric energy (kcal/mole) of ethyl phenylacetate and methyl phenylacetate

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