Model compounds of poly(methyl methacrylate): conformational analysis

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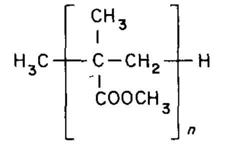
Molecular-orbital calculations have been carried out for monomeric, dimeric and trimeric oligomers of poly(methyl methacrylate). The minimum-energy geometry was achieved in all cases, and the geometrical and electronic parameters obtained were compared with experimental data. A *tttg*$^+$ conformation along the main-chain skeletal sequence was found.

(Keywords: poly(methyl methacrylate); model oligomers; conformational analysis)

INTRODUCTION

Oligomers of poly(methyl methacrylate) (PMMA) are interesting substances because of their stereochemistry in anionic oligomerization. The molecular structure of PMMA has been the object of theoretical investigation in several chain sequences[1–3]. There is interesting research in ^{13}C n.m.r. spectroscopy[4,5], X-ray crystal-structure analysis and ^1H n.m.r. spectroscopy[6]. Furthermore, there is a previous molecular-orbital calculation of their interaction with aluminium atoms[7]. The main aim of this paper is another approach to the molecular structure of PMMA oligomers by mean semiempirical molecular-orbital calculations.

The growth of the PMMA chain by anionic polymerization could be simulated by oligomers of the type:



$$H_3C-\left[\begin{array}{c} CH_3 \\ | \\ C-CH_2 \\ | \\ COOCH_3 \end{array}\right]_n-H$$

We start by studying some of the simplest molecules in order to model the relation among the ester groups in PMMA. These molecules are 2,2-dimethyl propionic ester (MMA monomer), 2,2,4,4-tetramethyl methylglutarate (MMA dimer) and 2,4,6-methylformate 2,4,6-trimethylheptane (MMA trimer). The MMA dimer and MMA trimer can be considered as model compounds of isotactic PMMA in a ... *tt* ... conformation.

The present work is divided in two parts: a conformational study of the model compounds and a calculation of their local electronic densities.

CALCULATION SEQUENCE

We have used two semiempirical molecular-orbital methods. The calculations for the conformational analysis on each individual model have been performed using the PCILO method (perturbative configuration interaction using localized orbitals)[8–10]. The calculations of the electronic densities on each atom and bond indices were approached by means of the CNDO method (complete neglect of differential overlap)[11]. It is known that both methods produce fairly accurate equilibrium geometries and partial charges and have been used by us for other studies of this type[12,13].

The initial geometries were approached beginning from X-ray crystallographic structures of similar compounds reported by Bowen and Sutton[14]. The starting conformations enclose almost all the heavy atoms in the same plane. The initial MMA-trimer conformation was obtained by the substitution of a hydrogen atom by the group $-[C(CH_3)_2COOCH_3]$ in the MMA dimer. The bonds between heavy atoms in these conformations were taken as rotational axes until the minimal-energy conformation is reached.

The geometrical parameters were simultaneously varied taking increments of 10° for rotation angles, 1° for valence angles and 0.1 Å for bond lengths. However, the optimization process was carried out with increments of 5°, 0.25° and 0.02 Å respectively near the minimum of

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the energy. This process is repeated several times (iterative method) until it reaches the optimum conformation. The model compounds used in this work to represent PMMA are shown in *Figure 1*.

RESULTS AND DISCUSSION

The final structure for the MMA monomer is shown in *Figure 2*. It corresponds to a planar conformation with C1 *trans* to O4 and O8 *cis* to C5. The net atomic charges obtained from the CNDO calculations are also shown in *Figure 2*. It should be noted that in the case of MMA monomer the methyl and the C2 group are electron-deficient. Then it is possible to find a weak carbon–carbon bond that can give rise to a tendency for ion formation.

The main-chain skeletal sequence for MMA dimer is *tt*, as was indicated by Flory and coworkers[20]. The torsion angles are $\phi_1 = -28°$ and $\phi_2 = 5°$ (see *Figure 3a*). The ester group atoms are not in a plane (C9–O8–C7–O15 = 8° and C5–O4–C3–O14 = 15°). The angle χ_1 (C12–C6–C7–O15) that represents the torsion about the C6–C7 bond has a value of 140° with respect to C12, and the angle χ_2 (C10–C2–C3–O14) that corresponds to the torsion about the bond C2–C3 is $-5°$ with respect to C10 (see *Figure 3b*). The inter-dyad angles τ_1 (C13–C6–C1) and τ_2 (C11–C2–C1) are 115.25° and 110°, respectively; on the other hand, the inter-dyad angle θ (C6–C1–C2) is 122.5°.

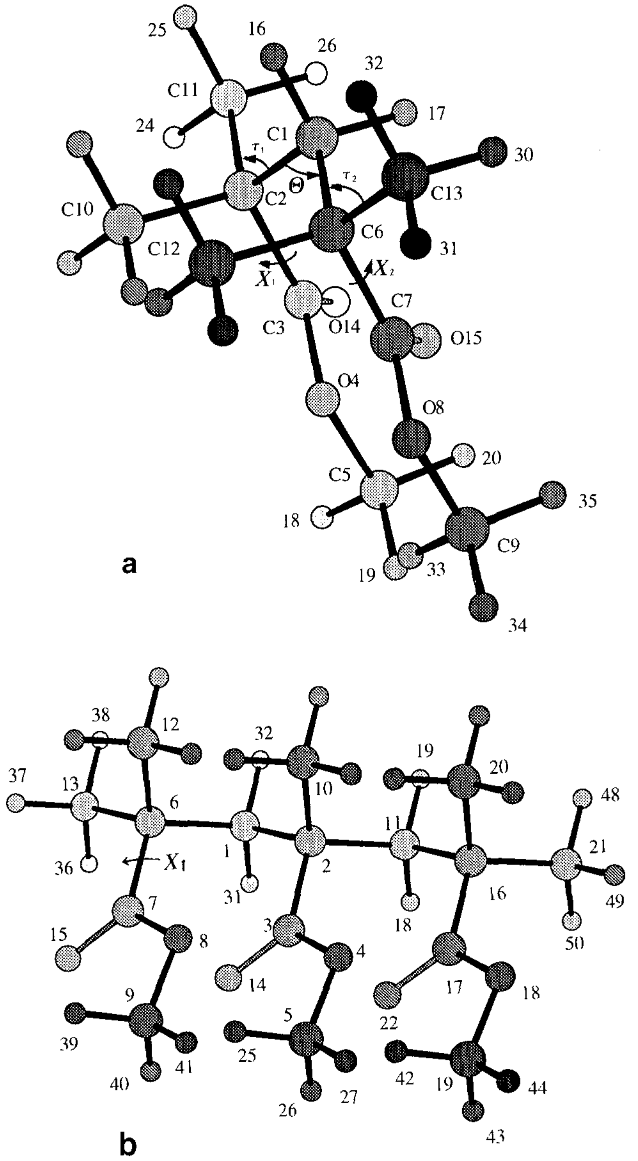

Figure 1 Schematic representation of the model compounds for (a) the dimer and (b) the trimer of PMMA

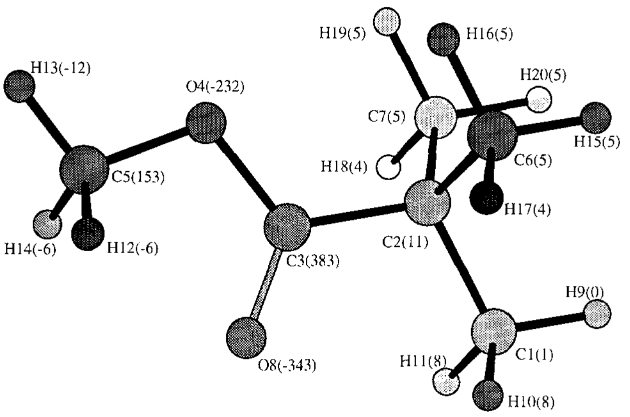

Figure 2 Minimal-energy conformation for the 2,2-dimethyl propionic ester molecule (MMA monomer); in parentheses, the CNDO electron distribution (units of 10^{-3} electrons) are give

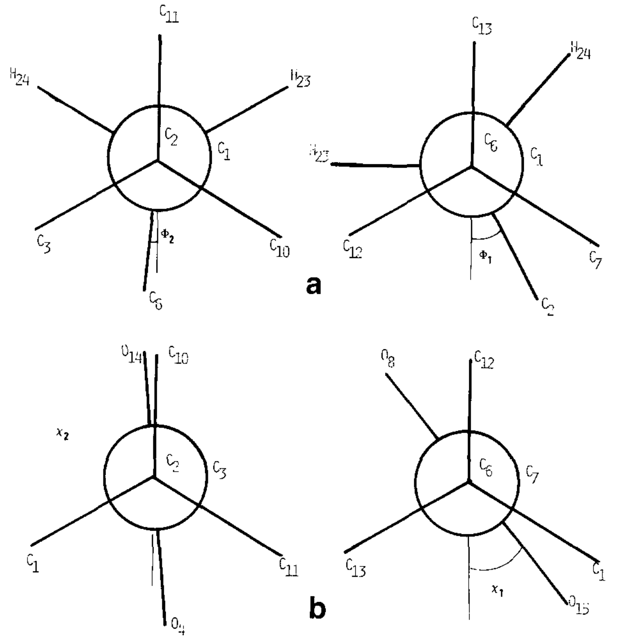

Figure 3 Newman diagrams for PMMA lowest-energy conformation: (a) torsion angles for the main chain ϕ_1 and ϕ_2; (b) torsion angles for the ester groups χ_1 and χ_2

Partial charges and electron densities on selected atoms of the MMA dimer are reported in *Table 2*. It has been noted that equivalent atoms of the ester groups have differential partial charge values and the carbon of the methoxy group is less positive than the carbon of the carbonyl group. This behaviour is in agreement with reported data[7,18]. In the same way, the oxygen of the methoxy group is found to be less negative than the oxygen atom of the carbonyl group as was observed earlier[17].

There is a very short interatomic distance between C3 and O15 (1.79 Å). The cause of this phenomenon could be intramolecular interaction[15,16]. This is even more evident from the value of the bond density of 0.256 for this pair of atoms as is shown in *Table 3*.

The total electronic populations for C10, C11 C12, C13 and C6 indicate that these atoms are electron-deficient, and the corresponding C–C bonds are weak.

The MMA trimer was formed by substituting the group –[C(CH_3)$_2$COOCH_3] instead of H24 in the MMA dimer. The Newman diagram corresponding to the final geometry is shown in *Figure 4*. The respective geometry optimization parameters are reported in *Table 1* and the corresponding total electronic population is shown in *Table 2*.

The conformation of the main chain is *tttg*$^+$ along the skeletal sequence C13–C6–C1–C2–C11–C16–C20. The ester group O15–C7–O8–C9 is nearly perpendicular to the plane formed by the skeletal bonds C13–C6–C1 and the carbonyl group oriented on the opposite side of the α-methyl carbon atom (C12). The plane formed by the ester group (O14–C3–O4–C5) bisects the plane defined by the skeletal bonds C1–C2–C11 and the carbonyl group (C3=O14) *cis* to the bond C2–C10. It would be expected that ester group O22–C17–O18–C19 would have been perpendicular to the plane defined by the skeletal bonds (C11–C16–C20) because of the

Table 1 Optimized distances and angles (PCILO)

(a) MMA monomer

Distance	(Å)	Valence angle	(deg)
C2–C3	1.47	C2–C3–O4	116.8
C3–O4	1.37	C2–C3–O8	124.8
O4–C5	1.39	C3–O4–C5	110.9
O3–O8	1.27	O4–C3–O8	118.4

(b) MMA dimer

Distance	(Å)	Dihedral angle	(deg)	Valence angle	(deg)
C1–C2	1.53	C1–C6–C7–O8	195.0	C1–C2–C3	109.5
C2–C3	1.49	C3–C2–C1–C6	305.0	C2–C3–O4	117.0
C3–O4	1.37	C2–C1–C6–C7	32.0	C2–C3–O14	125.0
O4–C5	1.38	C1–C6–C7–O15	15.0	C3–O4–C5	109.5
C3–O14	1.27	C1–C2–C3–O4	−60.0	C1–C2–C10	115.25
		C9–O8–C7–O15	8.0	C6–C1–C2	122.5
		C1–C2–C3–O14	120.0	C2–C1–H16	108.0
		C5–O4–C3–O14	15.0	C6–C7–O8	117.0
				C6–C7–O15	109.5

(c) MMA trimer

Distance	(Å)	Dihedral angle	(deg)	Valence angle	(deg)
C1–C2	1.53	C1–C2–C3–O4	−60	C1–C2–C3	109.5
C2–C3	1.49	C2–C3–O4–C5	−177	C2–C3–O4	117
C3–O4	1.37	C1–C2–C3–C14	120	C3–O4–C5	109.5
O4–C5	1.39	C3–C2–C1–C6	−50	C2–C1–C6	122.5
C1–C6	1.53	C2–C1–C6–C7	30	C1–C6–C7	109.5
C6–C7	1.49	C1–C6–C7–O8	135	C6–C7–O8	117
C7–O8	1.37	C1–C6–C7–O15	−45	C7–O8–C9	109.5
O8–C9	1.39	C6–C7–O8–C9	171	C1–C2–C10	109.5
C2–C10	1.53	C2–C1–C6–C12	−90	C1–C2–C11	110
C2–C11	1.53	C2–C1–C6–C13	150	C1–C6–C12	115.25
C6–C12	1.53	C1–C2–C3–C10	120	C1–C6–C13	115.25
C6–O13	1.53	C1–C2–C3–C11	−120	C2–C3–O14	125
C3–O14	1.27	C1–C2–C11–C16	175	C6–C7–O15	125
C7–C15	1.27	C2–C11–C16–C17	−30		
C11–O16	1.53	C2–C11–C16–C20	90		
C16–C17	1.49	C2–C11–C16–C21	−150		
C17–C18	1.37	C11–C16–C17–O22	−19		
C18–C19	1.39	C16–C17–O18–C19	−172		
C16–C20	1.53	O14–C3–O4–C5	3		
C16–C21	1.53	O22–C17–O18–C19	7		
C17–O22	1.27	O15–C7–O8–C9	−9		
		C3–C2–C1–H23	−170		

shape of the molecule; however, it is deviated. The dihedral angles C17–O18–C19–O22, C5–O4–C3–O14 and C9–C8–C7–O15 are 7°, 3° and 9°, respectively.

The bond angles CH_2–C–CH_2 are 115.25° (*tt* state), 110° (*tt* state) and 115.28° (tg^+ state) for C13–C6–C1, C1–C2–C11 and C11–C16–C20 respectively, in good agreement with the values calculated by conformational statistics for four bond segments embedded in PMMA chains[2,3], and also with the X-ray crystal analysis considerations of stereoregular oligomers of methyl methacrylate with respect to the non-equivalence of the methylene protons on in-chain and final end units of the trimers[6]. The large angles for C–CH_2–C described in the literature[3] are also observed. Bond lengths and bond angles for side chains show little differences among the three monomeric units.

Table 2 Total electronic population

	MMA trimer		MMA dimer		MMA monomer	
Atom	PCILO	CNDO	PCILO	CNDO	PCILO	CNDO
1	3.973	3.963	3.981	3.965	3.997	3.999
2	3.997	4.014	3.993	4.014	3.973	3.989
3	3.487	3.514	3.540	3.544	3.707	3.617
4	6.200	6.257	6.192	6.255	6.185	6.232
5	3.851	3.851	3.841	3.837	3.856	3.847
6	3.988	3.998	3.987	3.995	3.990	3.995
7	3.802	3.633	3.784	3.638	3.990	3.995
8	6.174	6.225	6.176	6.223	6.288	6.343
9	3.852	3.855	3.845	3.847	1.001	1.000
10	4.003	4.001	3.994	3.994	0.995	0.992
11	3.976	3.964	3.987	3.992	0.996	0.992
12	3.989	3.992	3.991	3.997	1.010	1.006
13	4.989	3.997	3.986	3.991	1.010	1.012
14	6.492	6.374	6.487	6.423	1.010	1.006
15	6.204	6.311	6.158	6.268	0.999	0.995
16	3.988	3.982	1.005	1.009	0.995	0.995
17	3.799	3.764	0.995	1.003	0.999	0.996
18	6.176	6.228	1.020	1.025	0.999	0.996
19	3.848	3.848	1.023	1.021	0.995	0.995
20	3.992	3.999	1.006	0.999	0.999	0.995
21	3.986	3.994	0.994	0.987		
22	6.159	6.196	1.003	1.006		
23	1.007	1.008	0.996	0.998		
24	0.999	1.006	0.996	0.992		
25	1.024	1.021	0.995	0.999		
26	0.999	0.996	0.999	0.998		
27	1.014	0.999	0.989	0.988		
28	0.991	0.986	0.999	0.998		
29	1.005	1.003	1.002	0.996		
30	0.986	1.010	0.992	0.989		
31	0.998	1.012	0.999	0.993		
32	1.008	1.010	0.998	0.997		
33	0.995	0.993	1.017	1.012		
34	0.998	0.995	1.013	1.004		
35	1.000	0.994	1.012	0.999		
36	0.992	0.990				
37	1.004	0.999				
38	0.996	0.997				
39	1.016	1.011				
40	1.006	0.994				
41	1.016	1.007				
42	1.016	1.020				
43	1.010	1.004				
44	1.012	1.014				
45	0.989	0.989				
46	1.002	1.006				
47	0.999	1.004				
48	0.993	0.991				
49	0.998	1.004				
50	0.999	1.002				

The distances between C3 and O15 or O22 atoms are short enough to give rise to an intramolecular stabilizing interaction. Again, these interactions are evident from the electronic population bond indices and densities shown in *Table 3*. Intramolecular hydrogen bonds can exist also between O22 with H26 and O15 with H27 because oxygen–hydrogen distances are smaller (1.87 and 1.85 Å respectively) than expected.

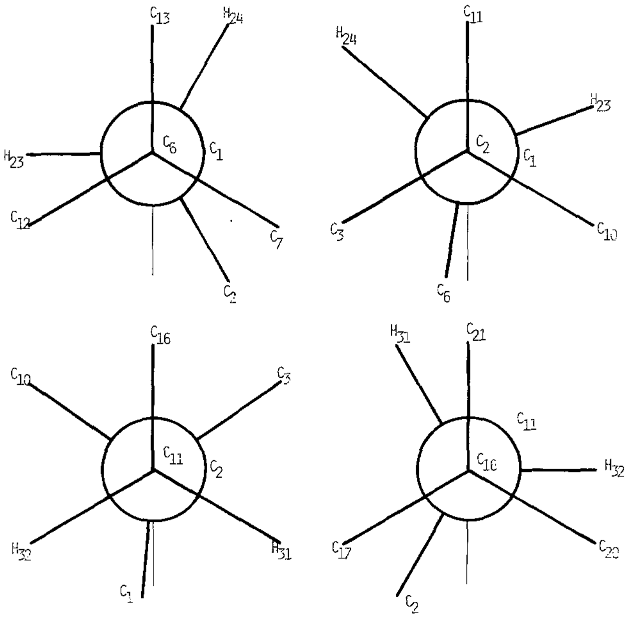

Figure 4 Newman diagrams showing the torsion angles for the main chain for the PMMA trimer minimum-energy conformation

Table 3 Relevant bond indices and bond densities for the PMMA model compounds

		Bond	
	Bond	Index	Density
Monomer	C2–C3	1.002	1.5306
	C3–O4	1.021	1.232
	O4–C5	1.002	1.177
	C3–O8	1.787	1.676
Dimer	C2–C3	0.978	1.391
	C3–O4	0.984	1.211
	O4–C5	1.005	1.194
	C3–O14	1.608	1.643
	C3–O15	0.171	0.256
	C6–C7	0.997	1.488
	C7–O8	1.027	1.233
	O8–C9	0.997	1.190
	C7–O15	1.735	1.664
Trimer	C2–C3	0.984	1.484
	C3–O4	1.000	1.220
	C3–O14	1.507	1.611
	O4–C5	0.998	1.175
	C3–O15	0.069	0.111
	C3–O22	0.151	0.215
	C6–C7	0.994	1.486
	C7–O8	1.027	1.233
	O8–C9	0.997	1.173
	C7–O15	1.739	1.672
	C16–O17	0.985	1.481
	C17–O18	0.986	1.214
	C17–O22	1.725	1.640
	O18–C19	1.004	1.177

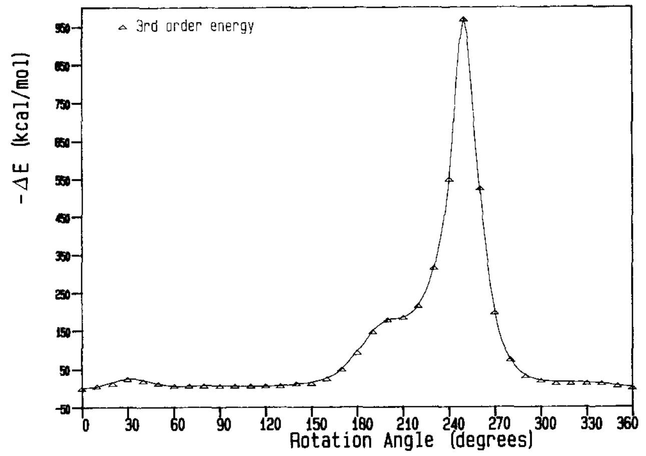

Figure 5 C6–C7 energy barrier for MMA trimer. Zero degrees corresponds to the minimal-energy conformation, and rotation is clockwise looking from C6 to C7

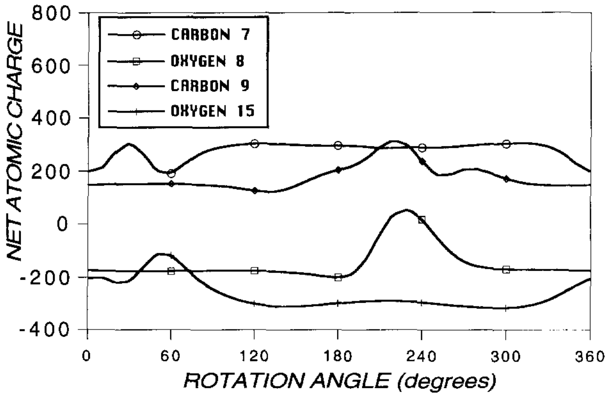

Figure 6 Net atomic charges of MMA-trimer ester atoms (C7, O8, C9, O15) (units of 10^{-3} electrons) as a function of the torsional angle of O8. Zero degrees corresponds to the minimal-energy conformation, and rotation is clockwise looking from C6 to C7

The intramolecular attractions mentioned above can explain the short distances between O14–O22 and O14–O15 in spite of the repulsions among the three oxygen atoms. In *Table 2* are shown the atomic charge values. It can be seen that the bonds between the carbon atoms C12, C13 with C6 and C20, C21 with C16 will be weak because they are electron-deficient. Therefore, one of these methyl groups can leave the molecule. Then the interaction of the carbonyl oxygen atom O14 with O15 and O22 seems to preclude that this conformation would be that of the minimum energy. It was necessary to study this conformation in more detail.

It is possible to find the angle–energy curve (see *Figure 5*) by allowing the variation of χ_1, the dihedral angle for rotation around the C6–C7 bond. The net charge variations with χ_1 (see *Figures 6* and *7*) can also be found.

The rotational barrier is shown in *Figure 5*. The initial conformation corresponds to the minimal energy with O15 15° out of the plane formed by C1–C6–C7. Both ester groups are almost parallel at 310°. The distances for C3–C7, O4–O8, C5–C9 and O14–O15 are 2.57, 2.6, 2.87 and 2.57 Å, respectively. The minimum-energy conformation is that in which the ester groups form an angle of 50°. In this conformation the C7–O15 bond is oriented to the bond C3–O14.

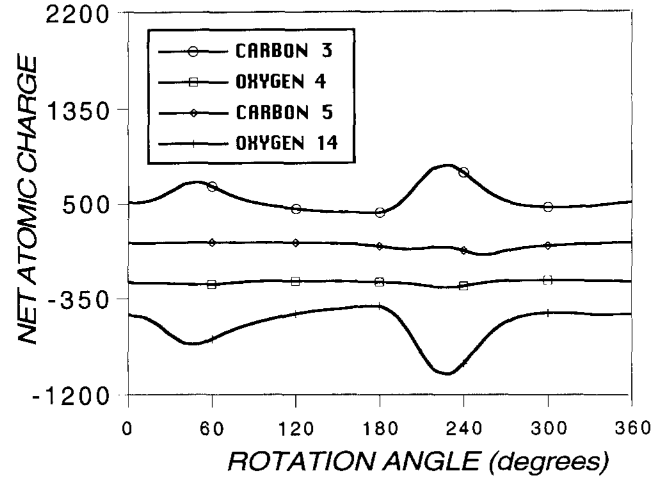

Figure 7 Net atomic charges of MMA-trimer ester atoms (C3, O4, C5, O14) (units of 10^{-3} electrons) as a function of the torsional angle of O8. The minimal-energy conformation corresponds to zero degrees, and rotation is clockwise looking from C6 to C7

There is a maximum of 23 kcal mol^{-1} obtained with the PCILO method when both ester groups are perpendicular (40° in *Figure 5*). Furthermore, the maximum is present at 240°. It is found when the ester groups are perpendicular with the C7–O8 bond oriented to the C3–O14 bond. It represents a conformation in which C5 and C9 methyl groups are so close that the distance between their hydrogen atoms (H27 on C5 and H39 on C9) is too short. An interesting feature is that the net charges on the carbonyl atoms in both bonds (C3–O14 and C7–O15) change in an opposite manner and there is no crossing of the curves in the region of interest between 300° and 90° (see *Figures 6* and *7*).

The variation of the net charges is not important. The strongest change happens in sterically forbidden conformations. Therefore, it is interesting to note that the charge on the C3 curve has a shape similar to that of the total-energy curve (see *Figure 5*). The order of the partial charges is inverted on O8 and O15 in the interval between 35° and 75°, i.e. O15 is less negative than O8. This is the only case where our results are in agreement with reported data[7]. The partial charges follow the same trend found in the dimer for this interval, i.e. the methoxy carbon atoms are less positive than the corresponding carbonyl carbon atoms and the methoxy oxygen atoms are less negative than their corresponding carbonyl oxygen atoms.

Bond density results for the ester groups obtained by the CNDO method show an electronic delocalization on the central ester group. Net atomic charges for the C6 and C16 methyl groups show the lability of the C–C (methyl) bonds at the equilibrium conformation.

CONCLUSIONS

The final geometry of the MMA monomer shows the ester group to be planar. This is in agreement with the experimental evidence reported before[18,19] for several esters, where the bond O–CH_3 is *trans* to the C–C bond.

The ester groups of the MMA dimer do not maintain their planarity. They have a conformation like that found for methyl acetate by electron diffraction[21]. The C3–O15 distance of 1.79 Å and the bond density indicate a possible intramolecular interaction. The net atomic charges on the hydrogens H21, H24, H27 and H30 and their corresponding carbon atoms C10, C11, C12 and C13 are positive, giving the possibility of ion formation.

The geometrical parameters change in the case of MMA trimer taking MMA-dimer minima as a reference. The ester groups remain in the same conformation they had in the dimer (out of plane), but with a smaller torsional angle. The preference of the MMA trimer for the conformation shown in *Figure 4* can give a significant role to an intramolecular π-type interaction between the central ester group and the carbonyl oxygen atoms from the other ester group. This last argument is supported for the following observations:

(a) An electronic delocalization on the ester groups and small but significant values for the interaction between the carbonyl atoms are observed from the bond density values.

(b) The distances from O15 and O22 to the central ester group are short enough to allow interactions.

(c) The rotational barrier of the C6–C7 bond is small and the energy increases only when the angle of twist is found between 150° and 300° from the equilibrium conformation. The barrier may actually be increased owing to the proximity of the methyl groups on O8 and O4.

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