PCILO and AM1 calculations of vinyl-substituted compounds

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(Received 18 December 1992)

The molecular structure and conformational energies of methyl acrylate, methyl methacrylate, vinyl acetate, methyl propionate, methyl 2-methylpropionate and styrene have been investigated using PCILO (perturbative configuration interaction with localized orbitals) and AM1 (Austin model 1) semiempirical methods with total optimization of geometry. The minimum-energy conformations obtained with both methods have been compared. The heats of formation calculated with the AM1 method are in excellent agreement with experimental values. The rotational barriers were also calculated and there are similarities in shape between the various compounds that do not involve an ester oxygen.

(Keywords: vinyl-substituted polymers; semiempirical calculations; equilibrium geometries)

INTRODUCTION

Theoretical studies of polymers require information about certain parameters such as atomic density, charge distribution, rotational energy function and geometrical features[1]. This information may be obtained by the use of semiempirical quantum-mechanics methods. This type of method has been used only infrequently in the field of synthetic polymers. In this paper we present the results of a systematic study of polymeric systems by the use of the semiempirical methods, PCILO (perturbative configuration interaction using localized orbitals)[2] and AM1 (Austin model 1)[3], software included in the MOPAC package version 4.01[4].

Common polymers derived from mono- and disubstituted ethylene are: poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVA) and polystyrene (PS). Here we present a conformational analysis for their monomers and compounds prepared from methyl acrylate (MA) and methyl methacrylate (MMA) when the C=C bond is saturated with hydrogen atoms. The schematic representation of these compounds is shown in *Figure 1*.

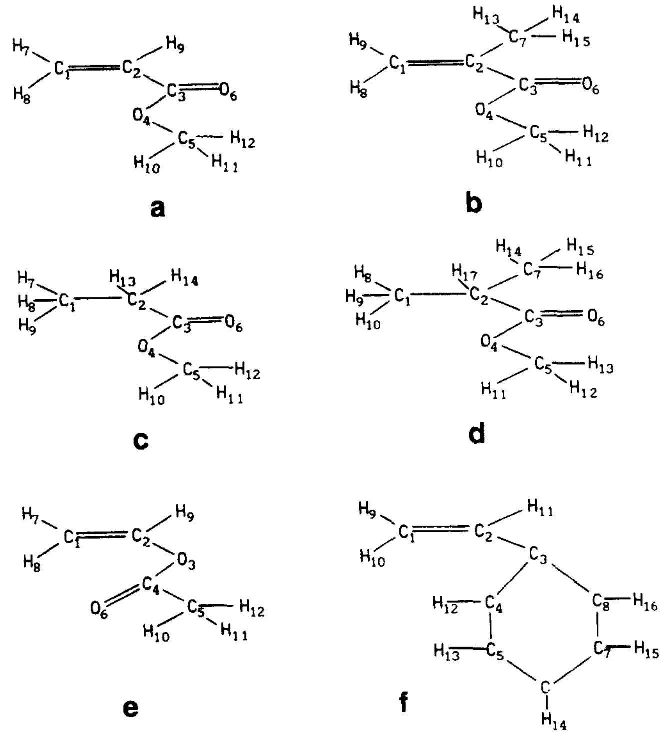

Figure 1 Schematic representation of (a) methyl acrylate, (b) methyl methacrylate, (c) hydrogen-substituted methyl acrylate, (d) hydrogen-substituted methyl methacrylate, (e) vinyl acetate and (f) styrene. The numbers refer to atoms; particular atoms are referred to by these numbers in the text

METHODOLOGY

The equilibrium geometries were obtained with both methods, and the energies were calculated as a function

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0032-3861/93/245143-06

Table 1 Methyl acrylate: bond lengths and bond angles calculated with the PCILO method and in parentheses the AM1 values

Atom	Bond distance (Å)	Reference atom	Bond angle (deg)	Reference atom	Dihedral angle (deg)	
C2	1.342(1.342)	C1				
C3	1.452(1.467)	C2	120.0 (121.58)			
O4	1.373(1.371)	C3	115.75(112.83)	C2	0.0(178.9)	C
C5	1.389(1.428)	O4	111.75(116.57)	C3	180.0(180.0)	C
O6	1.279(1.235)	C3	124.25(129.30)	C2	180.0(−1.1)	C

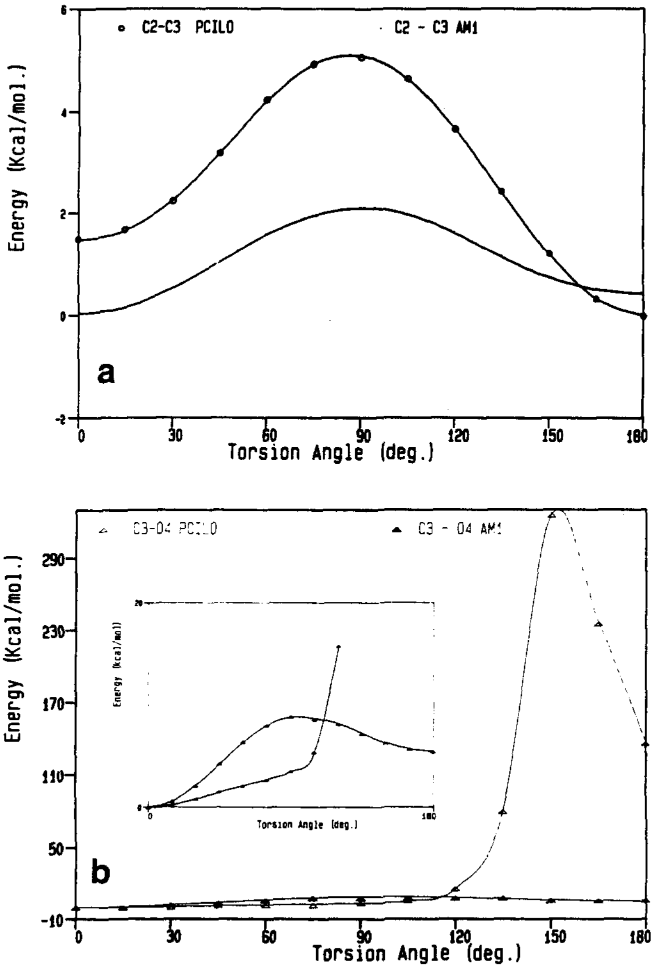

Figure 2 Energy for rotation about (a) the C2–C3 bond and (b) the C3–O4 bond calculated for methyl acrylate by the AM1 and PCILO methods

Table 2 Methyl acrylate: electron densities calculated with the PCILO and AM1 methods

Atom	AM1	PCILO
C1	−0.131	0.015
C2	−0.191	−0.015
C3	0.328	0.260
O4	−0.276	−0.176
C5	−0.063	0.129
O6	−0.355	−0.259

of the geometrical parameters. The PCILO calculations were performed with optimization of polarizabilities for the localized molecular orbitals in each conformation. The optimization sequence was:

(i) Bond lengths — these parameters were changed with increments of 1.0 Å; near the minimum the changes were reduced to 0.02 Å.

(ii) Bond angles — the variation was 1.0°; near the minimum the changes were reduced to 0.25°.

(iii) Torsion angles — these parameters were changed with increments of 10°, and 5° near the minimum.

This process must be repeated several times in order to reach an energy minimum (iterative process).

The AM1 calculations were performed using the Pulay converger in SCF (self-consistent field), the geometries were optimized by the BFGS (Broyden–Fletcher–Goldfarb–Shanno) method, and there were no symmetry constraints imposed on the molecules in each particular case (i.e. all the geometrical parameters were varied simultaneously in all cases).

Geometrical parameters cited in the literature[5] were used as initial geometries in order to find the structure of minimum energy.

The y axis in the energy vs. torsion angle curves corresponds to the difference in heat of formation relative to the minimum value for the AM1 line, and to the energy difference up to third order with respect to the perturbation relative to the minimum PCILO line.

RESULTS AND DISCUSSION

Methyl acrylate

The relevant geometric features for the optimized structure of MA monomer unit are shown in *Table 1*; in this case internal coordinates have been used to represent the geometry of the monomer structural unit. The most relevant feature is the different orientation of the ester group. In the final PCILO geometry, the ester group is planar with the bond C3–O4 *cis* to the C1–C2 bond, while the AM1 calculations show the ester group planar with the same bond in a *trans* configuration. However, it is reported that there is no distinction experimentally between the *cis* and the *trans* isomers[5].

The other geometrical values are in good agreement with those cited in the literature[5,6]. The calculated AM1 heat of formation is $-70.04\,\mathrm{kcal\,mol^{-1}}$, in excellent agreement with the experimental values[7,8] of -69.99 and $-70.1\,\mathrm{kcal\,mol^{-1}}$.

Some rotational barriers were calculated for various bonds. In all cases results were obtained by both methods. The result for the bond C2–C3 was $3.4\,\mathrm{kcal\,mol^{-1}}$ with PCILO and $2.1\,\mathrm{kcal\,mol^{-1}}$ for AM1; the corresponding graph is shown in *Figure 2a*, and for the bond C3–O4 in *Figure 2b*. Both barriers are symmetrical about 180°.

The calculated partial charges (or electron densities) at various atomic centres are shown in *Table 2*. It should

Table 3 Relevant geometrical parameters for vinyl acetate, calculated with the PCILO (AM1) methods

Atom	Bond distance (Å)	Reference atom	Bond angle (deg)	Reference atom	Dihedral angle (deg)	
C2	1.336(1.335)	C1				
O3	1.384(1.396)	C2	120.0(117.28)			
C4	1.379(1.377)	O3	102.0(118.38)	C2	255(180)	C1
C5	1.468(1.488)	C4	117.4(111.94)	O3	105(179)	C2
O6	1.278(1.230)	C4	118.5(119.13)	O3	285(−0.6)	C2

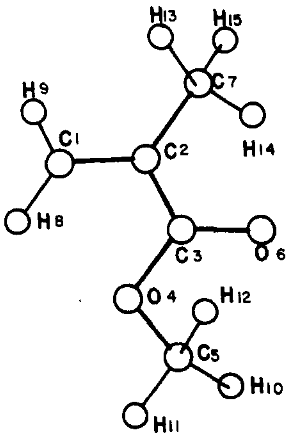

Figure 3 Final conformation calculated for methyl methacrylate

be noted that the partial charge on O4, the oxygen atom of the methoxy functional group, is found to be less negative than that of the carbonyl oxygen (O6), which is in disagreement with the corresponding partial charges reported in ref. 9.

Methyl methacrylate

The final conformation geometry is shown in *Figure 3*. The results obtained with both methods are in good agreement as well as with those found in the literature[9]. The minimum-energy conformation shows that the non-hydrogen atoms lie almost in the same plane as the carbonyl bond, C3–O6, which is found *trans* to the C1–C2 bond. The shape of the plots for the rotational barriers (*Figure 4*) is somewhat different for the AM1 and PCILO methods. The explanation for this difference arises from the intrinsic philosophy of each method: for AM1 there is simultaneous optimization, but not for PCILO.

Vinyl acetate

Some relevant geometric features for the monomer of vinyl acetate are shown in *Table 3*. In the final PCILO conformation the bond C3–C4 is 75° out of the plane formed by C1–C2–O3, whereas in the case of the geometry obtained with the AM1 method all the non-hydrogen atoms are in the same plane (see *Figure 5b*). This last form is in agreement with literature data[10,11]. A comparison of the dipole moment, ionization potential and heat of formation (experimental values vs. calculated values) is shown in *Table 4*.

The AM1 rotational barrier for the bond C2–O3 is 2.44 kcal mol^{-1}. Partial charges over several atoms are shown in *Table 5*. It should be noted that the partial charge on C2 is very different, even in sign, when it is calculated by the different methods. There is a very significant difference in electronic distribution between vinyl acetate and methyl acrylate; in both compounds the PCILO electronic densities alternate in sign but with different order. Some relevant bond orders are shown in *Table 6*.

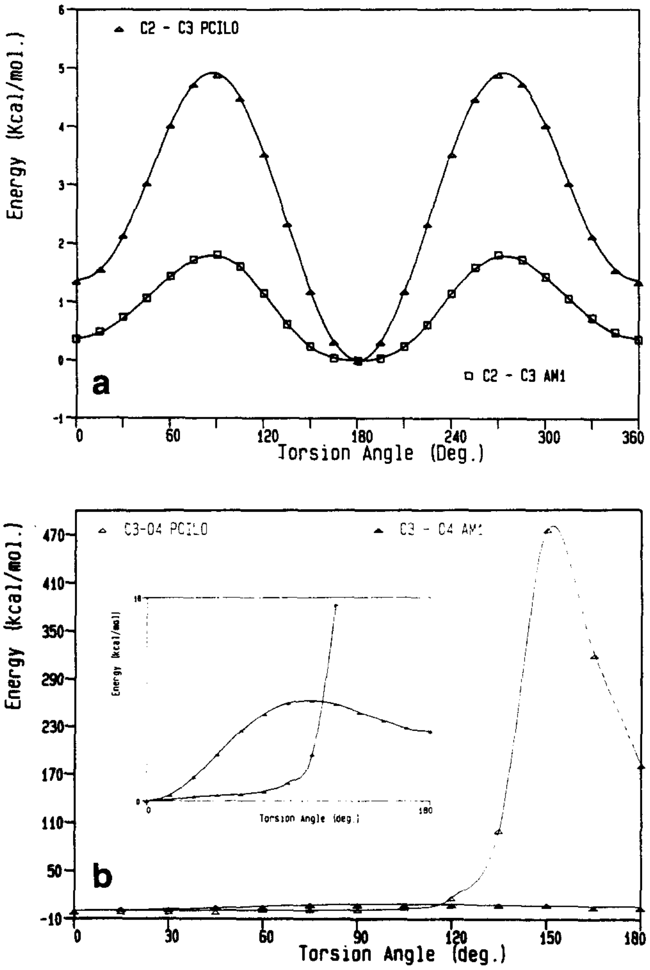

Figure 4 Energy for rotation about (a) the C2–C3 bond and (b) the C3–O4 bond calculated for methyl methacrylate by the AM1 and PCILO methods

Table 4 Comparison of experimental and calculated values of dipole moment, ionization potential and heat of formation of vinyl acetate

	Experimental[12–14]	Calculated
μ (D)	1.75	1.73
IP (eV)	9.85	9.9
ΔH_f (kcal mol^{-1})	−75.5	−67.78

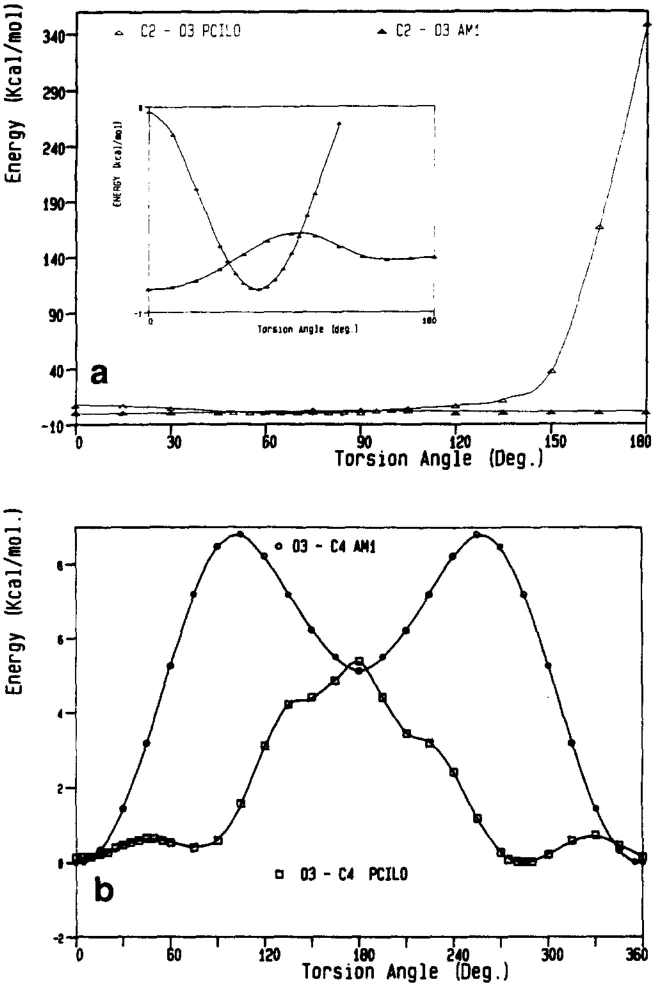

Figure 5 Energy for rotation about (a) the C2–C3 bond and (b) the C3–O4 bond calculated for vinyl acetate by the AM1 and PCILO methods

Table 5 Vinyl acetate: net atomic charges calculated with the PCILO and AM1 methods

Atom	AM1	PCILO
C1	−0.258	−0.120
C2	−0.032	0.189
O3	−0.243	−0.195
C4	0.311	0.305
C5	−0.219	−0.062
O6	−0.340	−0.257

Table 6 Some relevant bond order values for vinyl acetate calculated with the AM1 method

Bond	Bond order
C1–C2	1.919
C2–O3	0.980
O3–C4	0.994
C4–C5	0.945
C4–O6	1.819

Styrene

Two initial configurations were taken for the calculation of rotational barriers around the C2–C3 bond using the AM1 method. In the first configuration all the atoms are in the same plane. In the second one the plane formed by H9–C1–H10 is perpendicular to the plane formed by H11–C2–C3. For both cases the initial conformation (0°) has the C1–C2 double bond *cis* to the C3–C4 bond. Then the C2–C3 bond is defined as the axis for rotation; the rotation was made with increments of 15° from 0° to 180° (as a consequence of the molecular symmetry). The minimum-energy conformation yielded was that in which the aromatic ring is ±15° with respect to the double-bond plane.

The heat of formation obtained is 38.69 kcal mol^{-1}, again in excellent agreement with the reported values[15,7,3,14] of 35.4, 35.22, 38.8 and 35.3 kcal mol^{-1}. The rotational barrier is shown in *Figure 6* and the net atomic charges are given in *Table 7*. It should be noted that all the carbon atoms are negatively charged while the hydrogen atoms are positive. The bond angle C1–C2–C3 has a value of 125°, which is comparable with the value of 124° from ref. 16.

The results are somewhat different when the calculation is performed with the PCILO method. Here the valence bond on C3 was changed from 120° to 128° with increments of 1.0° and near the minimum with smaller increments of 0.3°, and a rotational barrier around the C2–C3 bond was calculated for each C3 valence bond value. In this case the increments were of 10° from 0° (C1–C2 *trans* to C3–C4) up to 180°. The aromatic ring orientation goes from 0° to +25° when the C3 valence bond value goes from the equilibrium value to 120°. The minimum-energy conformation is planar, with a C–C–C angle of 127.2°.

Methyl propionate

The methyl propionate is formed by hydrogen saturation of the double bond of methyl acrylate. The

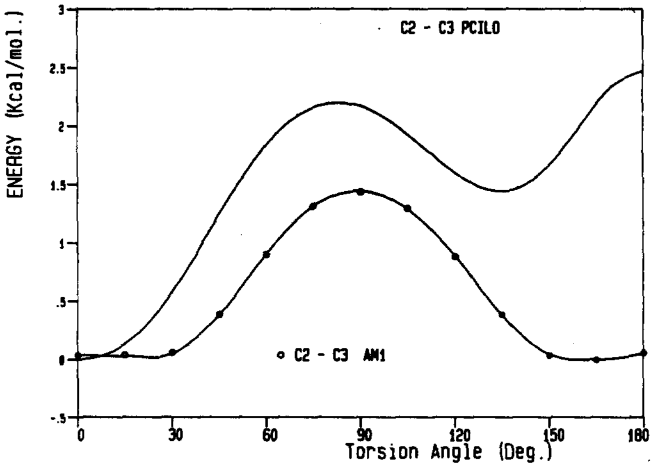

Figure 6 Energy *versus* C3 torsion angle for styrene, calculated with AM1 and PCILO methods

Table 7 Styrene: net atomic charges calculated with the PCILO and AM1 methods

Atom	PCILO	AM1	Atom	PCILO	AM1
C1	−0.052	−0.209	H9	0.011	0.113
C2	0.035	−0.125	H10	0.007	0.114
C3	0.055	−0.046	H11	−0.014	0.122
C4	−0.020	−0.119	H12	−0.013	0.132
C5	0.011	−0.131	H13	−0.013	0.131
C6	0.012	−0.127	H14	−0.013	0.130
C7	0.009	−0.131	H15	−0.013	0.132
C8	0.008	−0.118	H16	−0.012	0.132

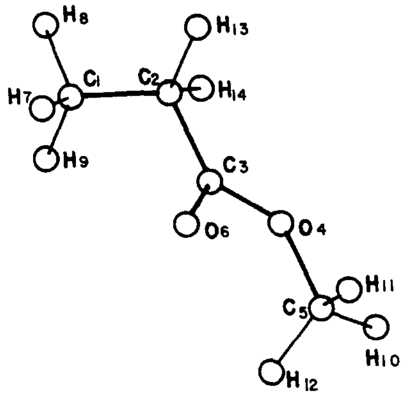

Figure 7 Final conformation calculated for methyl propionate

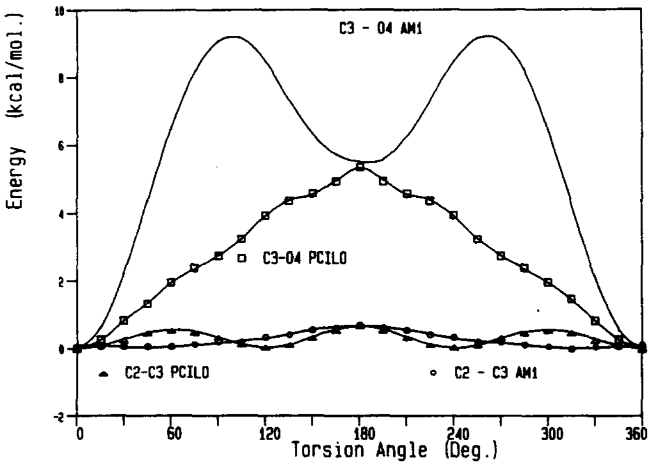

Figure 8 Energy *versus* the C3 and O4 torsion angles calculated for methyl propionate by the AM1 and PCILO methods

Table 8 Methyl propionate: net atomic charges calculated with the PCILO and AM1 methods

Atom	PCILO	AM1	Atom	PCILO	AM1
C1	0.007	−0.212	H8	0.002	0.083
C2	−0.022	−0.155	H9	0.011	0.083
C3	0.268	0.299	H10	−0.012	0.119
O4	−0.170	−0.231	H11	−0.014	0.084
C5	0.152	−0.640	H12	−0.014	0.084
O6	−0.260	−0.351	H13	0.021	0.116
H7	0.011	0.097	H14	0.021	0.116

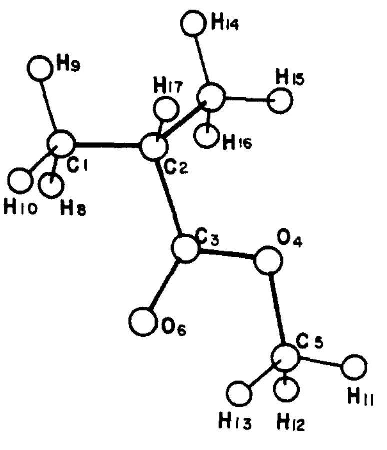

Figure 9 Final conformation calculated for methyl 2-methylpropionate

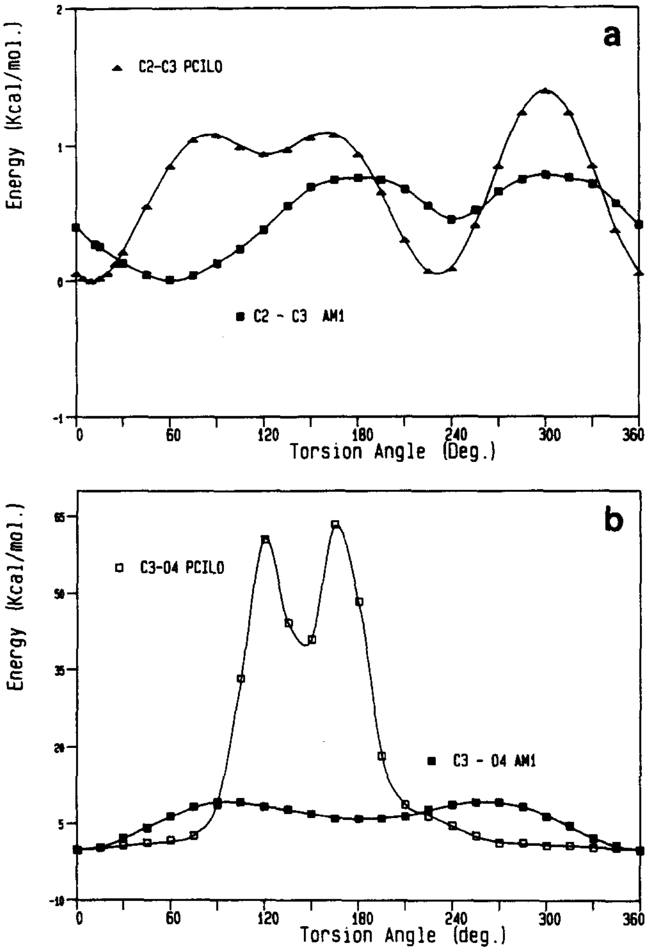

Figure 10 Energy for rotation about (a) the C2–C3 bond and (b) the C3–O4 ester bond calculated for methyl 2-methylpropionate by the AM1 and PCILO methods

final geometry yielded by the AM1 method is shown in *Figure 7*. There is a difference of 43° in the torsional angle of the ester group. However, the rotational barrier for the axis C2–C3 shows a minimum at −45° for O6. Nevertheless this barrier is approximated between the range of 60° and −60°, where the minimum calculated with the PCILO method is placed. The heat of formation is $-102.5\,\mathrm{kcal\,mol^{-1}}$ obtained by the AM1 method. This result is in excellent agreement with the experimental value[17] of $-108\,\mathrm{kcal\,mol^{-1}}$. The ester group is planar in both calculations. The C3–O4 rotational barriers (see *Figure 8*) are too high to allow any other conformation. The net atomic charges are shown in *Table 8*.

Methyl 2-methylpropionate

The initial conformation for this compound was the same as that obtained for methyl methacrylate but without the double bond. The minimum-energy conformation is shown in *Figure 9*. The agreement between both calculations is good. The corresponding rotational barriers are shown in *Figure 10*; again they were calculated by both methods. The differences found are not significant because the heights of the two minima of the barriers are very small. The C2–C3 rotational barriers for this compound are smaller than those obtained for methyl methacrylate (see *Figure 4*) by 1.0 and $3.8\,\mathrm{kcal\,mol^{-1}}$ in AM1 and PCILO calculations, respectively. These differences could be related to the molecular rigidity caused by the double bond in methyl methacrylate.

REFERENCES

1 See for example: Poland, D. and Scheraga, H. A. *Biochemistry* 1967, **6**, 3792; Scheraga, H. A. *Chem. Rev.* 1971, **71**, 196; Vacatelli, M. and Flory, P. J. *Macromolecules* 1986, **19**, 405

2 Diner, S., Malrieu, J. P. and Claverie, P. *Theor. Chim. Acta* 1969, **13**, 1; Malrieu, J. P., Claverie, P. and Diner, S. *Theor. Chim. Acta* 1969, **13**, 18

3 Dewar, M. J. S., Zoeblisch, E. G., Ealy, E. F. and Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, **107**, 3902; Dewar, M. J. S. 'The Molecular Orbital Theory of Organic Chemistry', McGraw-Hill, New York, 1969; Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 1977, **99**, 4899, 4907

4 Stewart, J. J. P. and Dewar, M. J. S., MOPAC 4.0, Quantum Chemistry Program Exchange, No. 455, Bloomington, IN, 1987

5 Bowen, H. J. M. and Sutton, L. E. 'Tables of Interatomic Distances and Configurations in Molecules and Ions', Chemical Society, London, 1958

6 Yoon, D. Y., Suter, U. W., Sundararajan, P. R. and Flory, P. J. *Macromolecules* 1975, **8**, 784

7 Lange, N. A. 'Handbook of Chemistry' (Ed. J. A. Dean), 12th Edn., McGraw-Hill, New York, 1979

8 Perry, R. H. and Chilton, C. H. 'Chemical Engineer's Handbook' (Ed. H. B. Crawford), 5th Edn., McGraw-Hill, New York, 1973

9 Chakraborty, A. K., Davis, H. T. and Tyrrel, M. *J. Polym. Sci. (A) Polym. Chem.* 1990, **28**, 3185

10 Sundararajan, P. R. *Macromolecules* 1978, **11**, 256

11 Ghesquire, D. and Arnaud, R. *J. Polym. Chem.* 1979, **83**, 2029

12 'Encyclopedia of Polymer Science and Technology' (Ed. N. M. Bikales), Wiley, New York, 1971, Vol. 15, pp. 534

13 Honk, K. N. and Munchansen, L. L. *J. Am. Chem. Soc.* 1976, **98**, 937

14 Streitwieser, A., Jr and Heathcock, C. H. 'Introduction to Organic Chemistry', Macmillan, London, 1976

15 Pedley, J. B. and Rylance, G. 'Sussex–NPL Computer-analysed Thermochemic Data: Organic and Organometallic Compounds', Sussex University, Brighton, 1977

16 Almlof, J. E., Isacsson, P. V. and Mjoberg, P. J. *Chem. Phys. Lett.* 1974, **26**, 215

17 'American Institute of Physics Handbook' (Ed. D. E. Gray), 3rd Edn., McGraw-Hill, New York, 1972