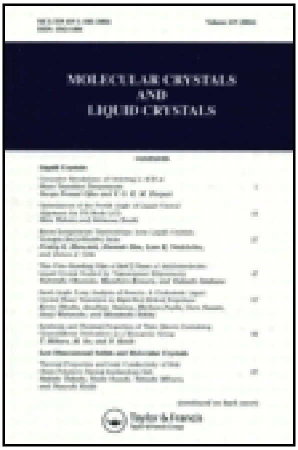

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Polyesters with Mesogenic Elements and Flexible Spacers in the Main Chain: A Further Investigation by Conformational Energy Calculations

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POLYESTERS WITH MESOGENIC ELEMENTS AND FLEXIBLE SPACERS IN THE MAIN CHAIN : A FURTHER INVESTIGATION BY CONFORMATIONAL ENERGY CALCULATIONS

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PCILO conformational calculations have been carried out on several model compounds of thermotropic liquid crystalline polyesters $\vdash OC-R_1-CO-O-R_2 \vdash$ where R_1 = biphenyl, terphenyl and $R_2 = (CH_2)_3$, $-CH_2-C(CH_3)_2-CH_2-$, $-CH_2-C(C_2H_5)_2CH_2-$. The calculated structures can be compared to the X-ray crystallographic data. The conformational characteristics of the carboxyl groups are independent of the number of phenyl rings. The introduction of substituents into the flexible spacer results in a sharpening of the potential energy wells and an increase in the energy barriers.

1. INTRODUCTION

In the past decade, polymeric liquid crystals based on rod-like or rigid chain structures have been studied in some details and have been the subject of a recent book [1]. Such polymers in the crystalline or liquid-crystalline state are of considerable interest and importance since they may be used to prepare films and fibers having good mechanical strength, noticeable thermal stability and excellent resistance to most common solvents.

For low molecular weight liquid crystals, the manner in which the molecules pack together in an ordered arrangement and the thermal stability of the ordered arrangement depend on both the molecular structure and geometry (anisotropy, rigidity, linearity, planarity...) of the mesogenic group and the equilibrium flexibility of the aliphatic spacer [2-4]. These two factors are of interest for both intra and intermolecular interactions. The same factors must be taken into account when attempting to assess the potential liquid crystal behavior of polymers [5-10]. Thus, in this paper, PCILO conformational calculations have been carried out to obtain conformational energy profiles of model compounds related to thermotropic liquid crystalline polyesters of general formula

$$\left[\!-OC-R_1-CO-O-R_2-O-\!\right]$$

where R_1 = biphenyl, p-terphenyl

$R_2 = (CH_2)_3$, $-CH_2-C(CH_3)_2-CH_2-$, $-CH_2-C(C_2H_5)_2-CH_2-$

This method, which accounts for both steric and conjugative effects, has already been used successfully to predict the liquid crystalline nature of solutions of polyamides [11,12].

2. CALCULATION DETAILS

The basic technique employed consists of the PCILO (Perturbative Configuration Interaction using Localized Orbitals) method [13]. The molecules studied are given in Figure 1. The molecules I- V were investigated to examine the rôle of the mesogenic group. The molecules VI-VIII were studied to establish the way in which substituents affect the equilibrium flexibility of the aliphatic spacers.

The internal rotation angles ϕ_i define the orientation of an aromatic ring with respect to the adjacent carboxyl group. The angles ψ_i characterize the relative orienta-

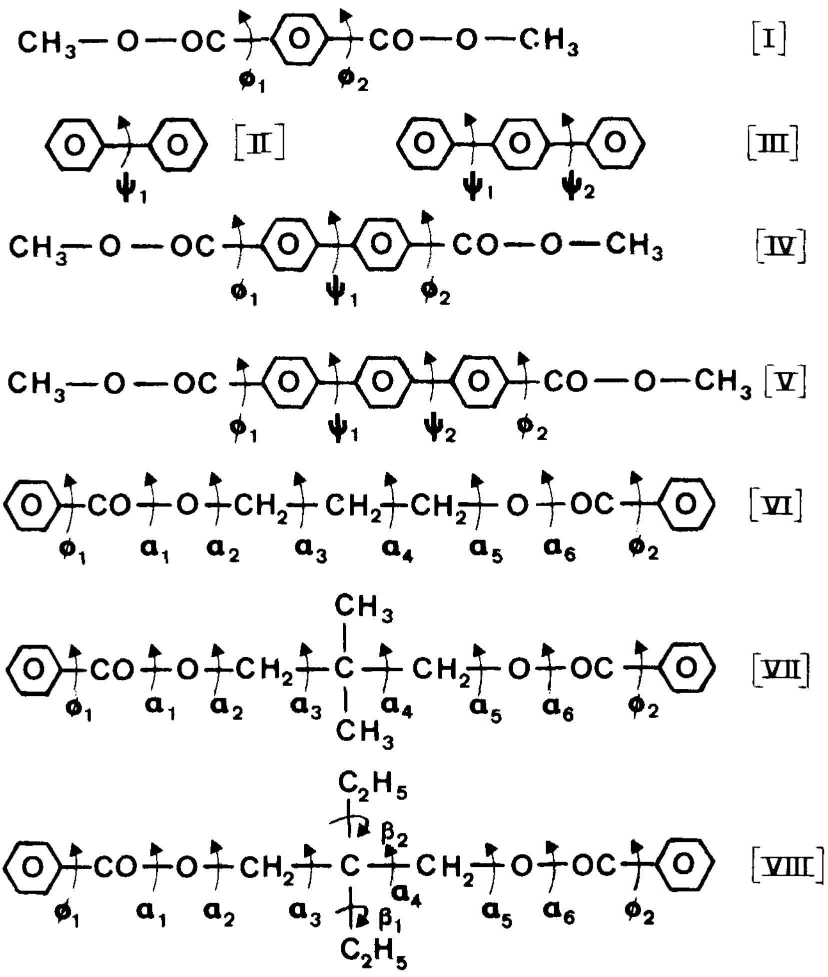


FIGURE 1 - Schematic diagrams of molecules I-VIII

tion of two adjacent rings. The angles α_i and β_i are taken as 180° in the all-trans conformations of the flexible spacer and substituents, respectively. For molecules I, IV and V, ϕ_i = 0 corresponds to the "cis" configuration of the carboxyl groups relative to the aromatic core of the molecules. The geometrical parameters used are given in

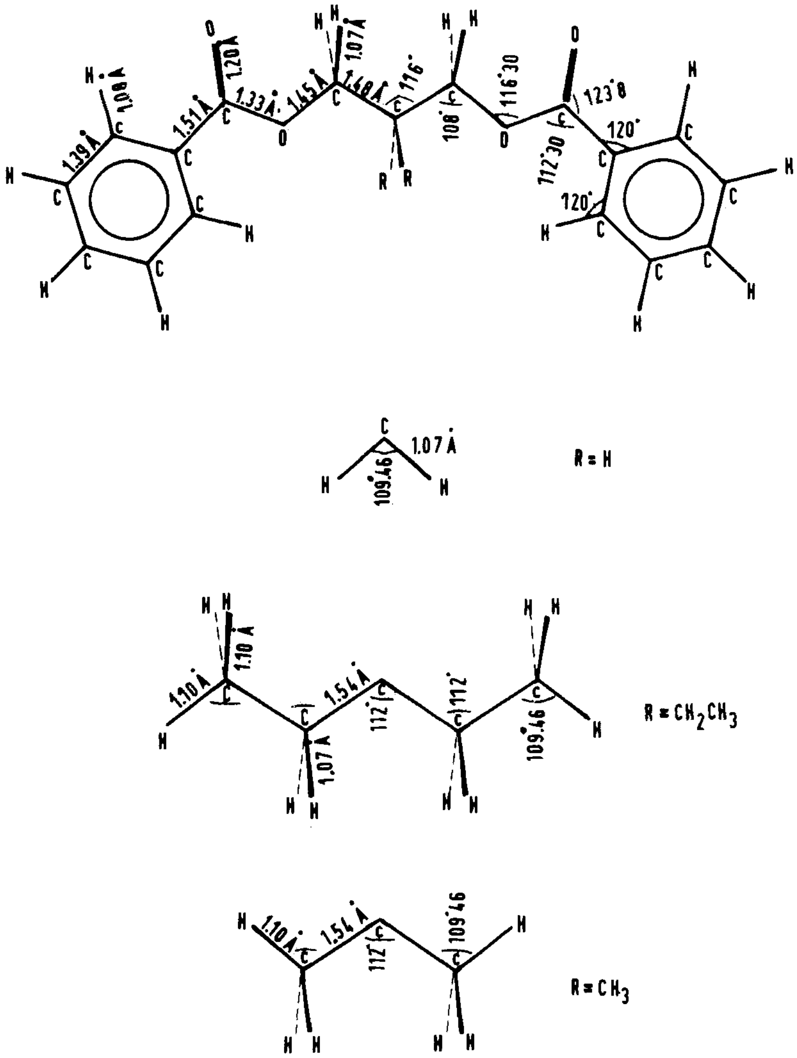


FIGURE 2 - Bond angles and bond lengths of molecules VI-VIII

Figures 2 and 3. Calculations were carried out with angles varied in intervals of 30°.

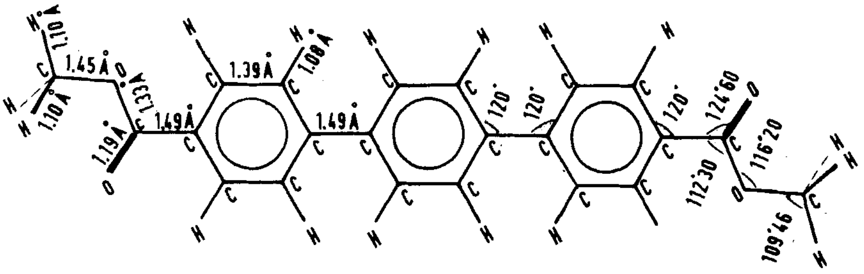


FIGURE 3 - Bond angles and bond lengths of molecules I-V

3. RESULTS AND DISCUSSION

3.1. Models For The Mesogenic Group

Methyl Terephthalate

Conformational energy contour for the benzene ring rotation about the $C_{aromatic}$ - CO adjacent bonds is shown in Figure 4. Two energy minima are found at $\phi_1 = \phi_2 = 0°$ and $\phi_1 = 0°$, $\phi_2 = 180°$. The former corresponds to the "cis" configuration of the carboxyl groups relative to the central

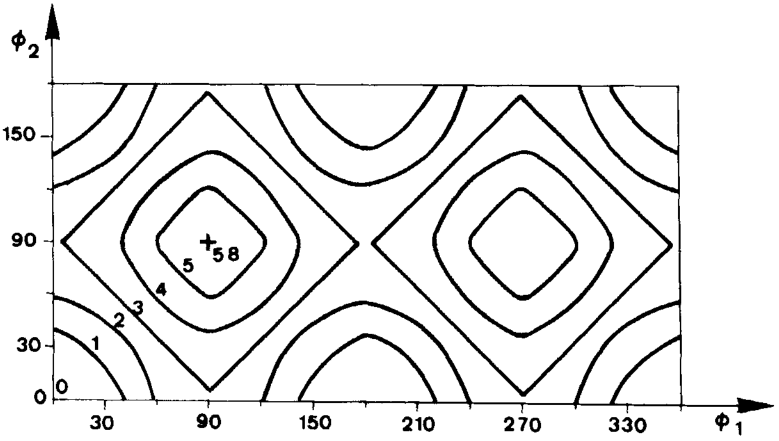


FIGURE 4 - Conformational energy map[ϕ_1, ϕ_2] of methyl terephthalate

ring and the latter coïncides with the "trans" configuration. The height of the energy barrier is 2,9 $\mathrm{Kcal.mol^{-1}}$. The energy maximum is obtained when $\phi_1 = \phi_2 = 90°$. Besides, ϕ_1 and ϕ_2 rotations are independent.

For comparison, it is useful to cite earlier empirical calculations carried out by Hummel and Flory [14] and Tonelli [15] in an attempt to determine the preferred (minimum energy) angles and evaluate the energy barriers for methylbenzoate and terephthalate moiety, respectively. Very similar potential energy maps were obtained. The equilibrium conformations also correspond to the planar "cis" and "trans" configurations. Only the height of the energy barrier differs : 5 $\mathrm{Kcal.mol^{-1}}$ and 3 $\mathrm{Kcal.mol^{-1}}$ according to Hummel and Flory [14] and Tonelli [15], respectively. Such discrepancies may be due to the difficulty in evaluating conjugation energy in empirical calculations.

These results are in reasonable agreement with experimental observations on dimethyl terephthalate. Indeed, the energy difference between the "cis" and "trans" isomers was found to be 0.05 $\mathrm{Kcal.mol^{-1}}$ from dipole moment measurements in solution [16]. Besides, Infrared and Raman studies [17] indicated that the populations of the "cis" and "trans" conformers are nearly the same in the melt. Finally, the molecular conformation in the crystalline state was found to be the "trans" one, the phenyl ring standing at an angle of 4.7° to the plane of the carboxyl group [18].

Biphenyl and p-Terphenyl

Values of the conformational energy, taken relative to that for the coplanar form are plotted versus ψ_1 in Figure 5. The present calculations give an absolute conformational energy minimum at $\psi_1 = 40°$ which is in good agreement with the torsional angle of approximately 42° between the pla-

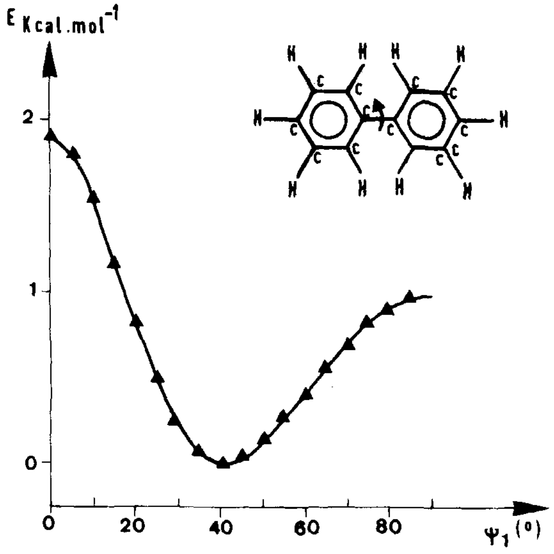


FIGURE 5 - Conformational energy shown as a function of torsional angle ψ_1 for biphenyl.

nes of the rings in the vapor state [19]. The height of the energy barrier is 1.9 Kcal.mol^{-1}. It is worthnoting that the dihedral angle ψ_1 lies in the range 20-25° in solution [20, 21] and in the melt [22] while biphenyl is planar or nearly so in the crystalline state [23-27]. The coplanar conformation is hindered by steric interferences involving ortho hydrogen. However, in the crystalline state intermolecular interactions favor the coplanar form by its more efficient packing and, in so doing, counteract the intramolecular steric hindrance, especially since the barriers to coplanarity are relatively low [28]. It is to be noted that the present PCILO results are consistent with earlier calculations using semi-empirical methods [29-32].

For p-terphenyl, PCILO calculations give an absolute conformational energy minimum at $\psi_1 = \psi_2 = 40°$ in agreement with previous empirical calculations performed by Rietveld et al [33]. The height of the energy barrier for the rotation of the central ring relative to the adjacent rings is twice that determined for the rotation of the rings about the 1,1' bond in biphenyl, which has been found experimentally [34].

Molecules IV and V

Values of the conformational energy, taken relative to that for the coplanar form are plotted versus ψ_1 in Fig. 6 for the planar conformation of the φ-CO-O- groups in the molecule IV. As observed for biphenyl, the energy minimum is obtained when $\psi_1 = 40°$. Experimental evidence indicates values of approximately 40° in the crystalline state [35] and 30° in the liquid crystalline state [36] for 4,4'-disubstituted biphenyls. Indeed, in these compounds intermolecular interactions are reduced compared with biphenyl and the crystalline form is closely related to the vapor form. On the other hand, conformational energy contour for the phenyl ring rotation about the $C_{aromatic}$ - CO adjacent bond is shown in Figure 7 for $\psi_1 = 40°$. As observed for methylterephthalate, two energy minima are found at $\phi_1 = \phi_2 = 0°$ and $\phi_1 = 0°$, $\phi_2 = 180°$. It appears from these results that the most stable conformations of molecule IV can be deduced from the preceding studies of methyl terephthalate and biphenyl. Besides, the heights of the energy barriers for each of the rotations ϕ_1, ϕ_2 and ψ_1 are the same as those determined for these two simpler model compounds.

The replacement of biphenyl by terphenyl, as occurs in the molecule V, is of interest in this study particularly with regard to the extent to which lengthening of the mesogenic moiety affects the conformational characteristics. Again, the energy minima are found at $\phi_1 = \phi_2 = 0°$ or $\phi_1 = 0°$, $\phi_2 = 180°$ and $\psi_1 = 40°$, $\psi_2 = \pm 40°$. Besides, as

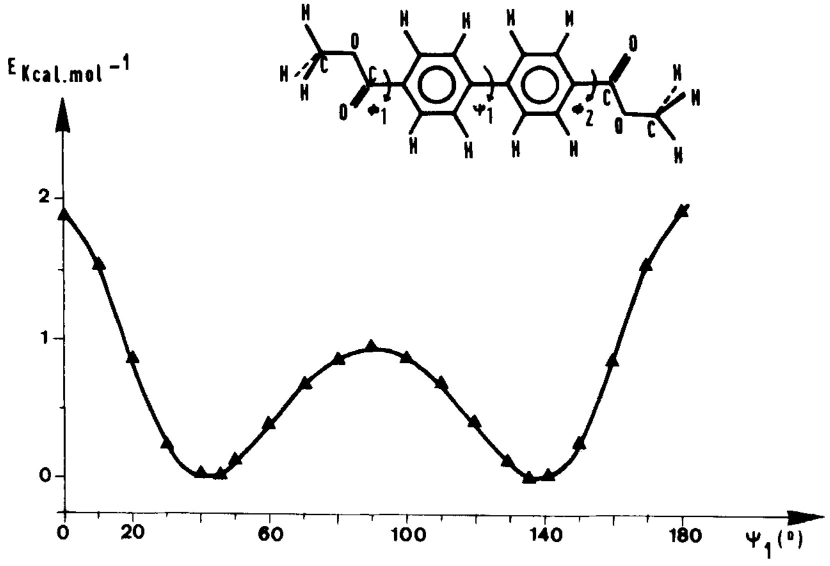


FIGURE 6 - Conformational energy shown as a function of torsional angle ψ_1 for molecule IV[$\phi_1=\phi_2=0$]

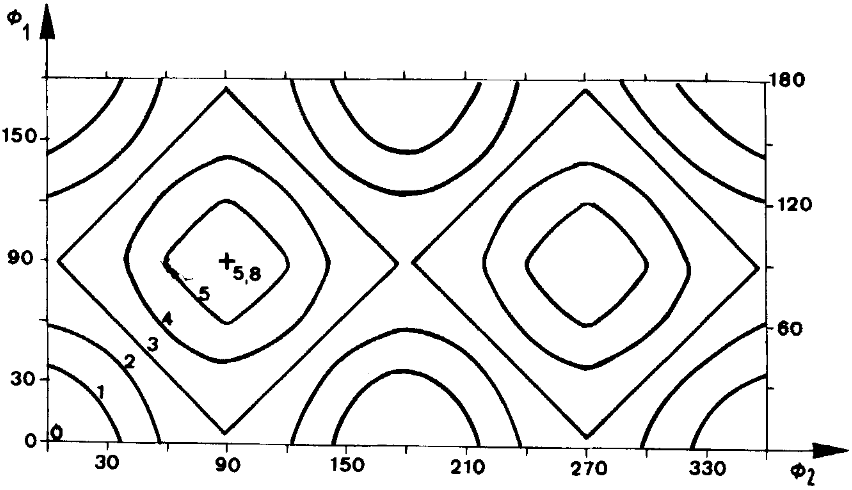


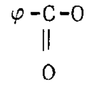
FIGURE 7 - Conformational energy map [ϕ_1,ϕ_2] of molecule IV. [ψ_1 = 40°]

observed for molecule IV, the heights of the energy barriers for each of the elementary rotations are the same as those determined for methyl terephthalate and p-terphenyl. The 4.8 $Kcal.mol^{-1}$ energy barrier derived from present calculations for the internal rotation of the outer rings, assuming independent rotation of each of the three rings of the terphenyl unit, is in close agreement with the 5 $Kcal.mol^{-1}$ deduced from ^{1}H and ^{13}C NMR relaxation data for polyester with R_1 = p-terphenyl and $R_2 = (CH_2-CH_2-O)_3\ CH_2-CH_2-$[37]. In the same way, the 3.8 $Kcal.mol^{-1}$ barrier height calculated under the same assumption is consistent with the 3-3.5 $Kcal.mol^{-1}$ experimental activation energy for the internal inner ring rotation about the long axis of the p-terphenyl moiety[37].

A prominent feature of the preceding results is that the conformational characteristics of the carboxyl groups are independent of the number of phenyl rings. In other words, the main consequence of the replacement of phenyl ring by biphenyl or p-terphenyl is to extend the linearity, the rigidity and the anisotropy of the system. The theory of polymer liquid crystals attaches great importance to these geometrical factors[38]. For instance, according to Flory and Ronca[39], for an undiluted system, it exists a critical value of the axial (length to diameter) ratio for liquid crystal formation. Thus, polyesters $[OC-R_1-COO-R_2]$ with R_1 = p-terphenyl provide a rich source of liquid crystals which are more thermally stable than those of the biphenyl analogues[40-43]. On the other hand, polyalkylene terephthalates do not form liquid crystals.

3.2. Models For The Flexible Spacer

Molecule VI

X-ray crystallographic data reported for benzoate and terephthalate esters [18, 44-47] and aromatic and aliphatic polyesters [48-56] indicate that ϕ_1, ϕ_2, α_1 and α_6 approach 180°. The observed deviations are usually less than 10°. On the basis of these experimental evidences and from the conclusions drawn from the calculations reported in the preceding section, the  $\varphi\text{-}\overset{\displaystyle O}{\underset{}{C}}\text{-}O$ (φ-C(=O)-O) group was assumed to be planar in molecules VI, VII and VIII. Hence, in the case of molecule VI, the only parameters taken into account for calculations were the angles α_2, α_3, α_4 and α_5 which define the geometry of the flexible spacer $(CH_2)_3$.

Conformational energy contour of molecule VI for the two methylene group rotations α_3 and α_4 ($\alpha_2 = \alpha_5 = 180°$) is shown in Figure 8. Three energy minima are found at $\alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = 180°$ (0 Kcal.mol^{-1}), $\alpha_2 = \alpha_3 = \alpha_5 = 180°$, $\alpha_4 = \pm 60°$ (- 0.43 Kcal.mol^{-1}) and $\alpha_3 = \alpha_4 = \pm 60°$, $\alpha_2 = \alpha_5 = 180°$ (- 0.96 Kcal.mol^{-1}) which coincide with the TTTT, TGTT (or $T\bar{G}TT$) and TGGT (or $T\overline{GG}T$) conformations. The heights of the energy barriers for conformational changes TTTT → TGTT and TGTT → TGGT are 2.5 Kcal.mol^{-1} and 2.6 Kcal.mol^{-1}, respectively, assuming that the farthest bonds remain in the trans position during the conformational changes. It is to be noted that these three conformations also correspond to energy minima with respect to the angles α_2 and α_5. The present study is in agreement with previous empirical calculations carried out by Poulin-Dandurand et al [57] after assuming $\alpha_2 = \alpha_5$ and $\alpha_3 = \alpha_4$. These authors found two energy minima at $\alpha_2=\alpha_3=\alpha_4=\alpha_5=180°$

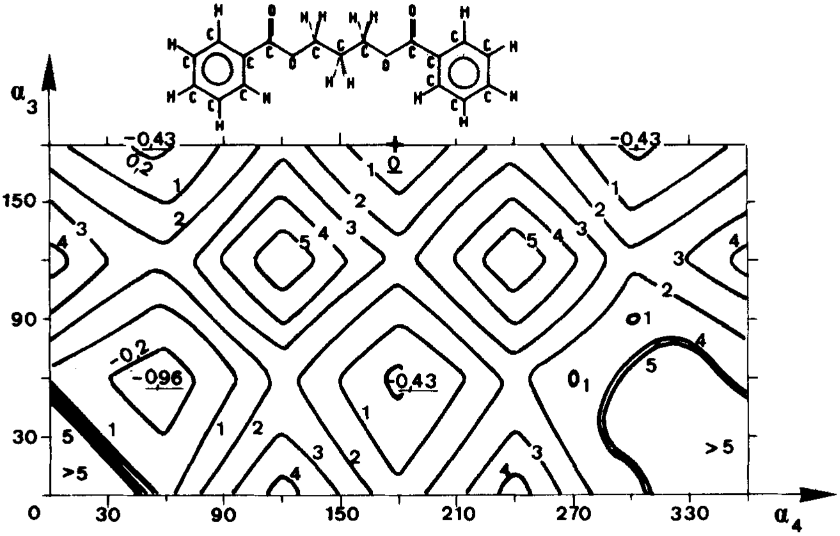


FIGURE 8 - Conformational energy map [α_3, α_4] of molecule VI. [α_2 = α_5 = 180°]

(1.73 Kcal.mol^{-1}) and $\alpha_2 = \alpha_5 = \pm 175°$, $\alpha_3 = \alpha_4 \pm 60°$ (1.10 Kcal.mol^{-1}).

Of special interest is the fact that the three crystalline forms of polyoxacyclobutane $\vdash O \leftarrow CH_2 \rightarrow_3]_n$ evidenced by X-ray diffraction and Infrared spectroscopy can be generated from the preceding conformations [58, 59]. Crystal modifications I, II and III are the planar-zigzag TTTT, glide-type TTTGTTT$\bar{G}$ and helix TGGT, respectively. The crystal structure of poly(trimethylene terephthalate) was determined by X-ray diffraction [48, 57]. The molecular chain takes the conformation TGGT which corresponds to the lowest minimum observed in the present study.

Molecule VII

Conformational energy contour of molecule VII for the internal rotations α_3 and α_4 (α_2 = α_5 = 180°) is shown in

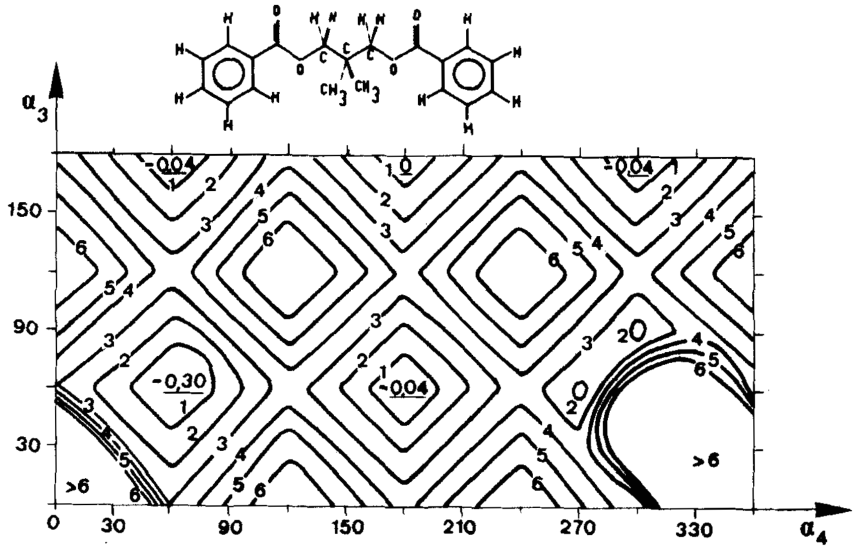


FIGURE 9 - Conformational energy map [α_3, α_4] of molecule VII. [$\alpha_2 = \alpha_5 = 180°$]

Figure 9. Again, the most stable conformations are TTTT, TGTT and TGGT. However, the steric hindrance of the methyl groups results in narrower potential energy wells and higher energy barriersTTTT → TGTT (3.6 Kcal.mol^{-1}) and TGTT → TGGT (3.5 Kcal.mol^{-1}). Such an effect was also observed by Poulin-Dandurand et al.[57]. It is to be noted that the crystal modifications[60] of polyether $[-O-CH_2-C(CH_3)_2CH_2]_n$ can be generated from the calculated conformations.

Molecule VIII

Results obtained for molecules VI and VII emphasize the importance of conformations TTTT, TGTT and TGGT of the flexible spacer. Besides, they show that the replacement of the central methylene group by - $C(CH_3)_2$ - increases the energy of the other minima. Thus, for molecule VIII

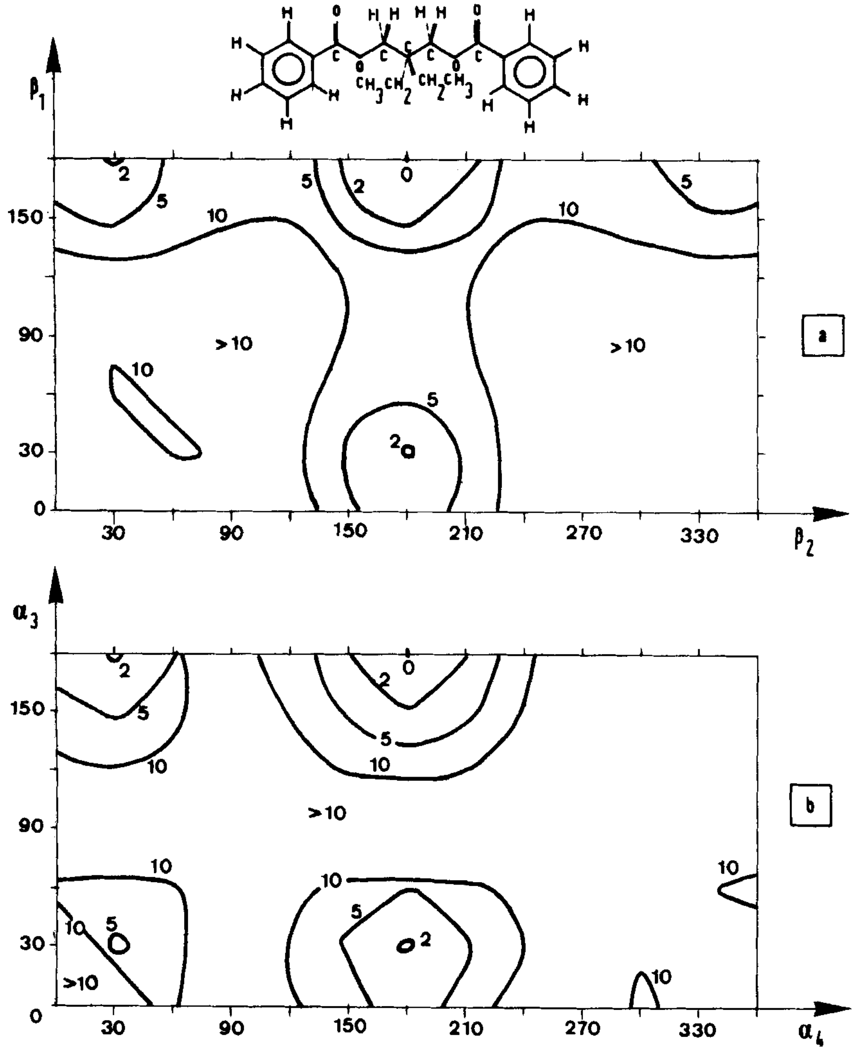


FIGURE 10 - Conformational energy map (a) [β_1, β_2)] (b) [α_3, α_4] of molecule VIII. [TTTT conformation of the main aliphatic chain] .

only the geometries TXYT were studied as a function of the angles α_3, α_4, β_1 and β_2, assuming $\alpha_1 = \alpha_2 = \alpha_5 = \alpha_6 = 180°$.

First calculations were performed after assuming a trans conformation for the main aliphatic chain. The resultant conformational energy map for the β_1 and β_2 rotations, which characterize the geometry of the ethyl substituents, is shown in Figure 10 (a). The energy minimum is found for $\beta_1 = \beta_2 = 180°$, i.e. the conformations trans-trans of the lateral ethyl groups. Then, calculations were carried out as a function of α_3 and α_4 ($\beta_1 = \beta_2 = 180°$). Figures 10(a) and (b) show that the most extended geometry of molecule VIII in which both the main aliphatic chain and the lateral groups adopt an all trans conformation is a stable form. It is noteworthy that the potential energy wells narrow as the size of the substituents increases.

Secondly, conformational energies were calculated for the TGGT conformation of the main aliphatic chain. Results indicate that the $-CH_2-C(CH_2CH_3)_2-CH_2-$ sequence is stable when the conformations of the lateral ethyl groups are either GG or $\overline{GG}$. The heights of energy barriers are higher than 10 Kcal.mol^{-1}.

In the third calculations, the TGTT conformation of the sequence $-CH_2-\overset{|}{\underset{|}{C}}-CH_2-$ was considered. An energy minimum is found at $\beta_1 = 0$ and $\beta_2 = 60°$. Again, one observes sharp potential energy wells and high energy barriers.

From these results one can conclude that the stable conformations of molecule VIII correspond to : $\alpha_3 = \alpha_4 = \beta_1 = \beta_2 = 180°$ (0 Kcal.mol^{-1}), $\alpha_3 = \alpha_4 = \beta_1 = \beta_2 = 60°$ (- 0.46 Kcal.mol^{-1}), $\alpha_3 = \alpha_4 = 60°$, $\beta_1 = \beta_2 = -60°$ (0.09 Kcal.mol^{-1}) and $\alpha_3 = \beta_2 = 60°$, $\alpha_4 = \beta_1 = 180°$ (0.30 Kcal.mol^{-1}). The replacement of $-CH_2-$ by $-C(CH_3)_2-$ and $-C(C_2H_5)_2$ results in a sharpening of the potential energy wells together with an increase in the energy barriers. Thus, molecule VIII appears more rigid than molecules VII and VI from a dynamic point of view.

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