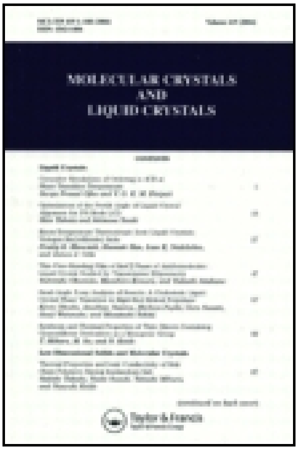

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A. Ghanem [a] , P. Meurisse [a] , F. Laupreatre [a] & C. Noëulz [a]

[a] Laboratoire de Physicochimie Structural et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231, Paris Cedex, 05, France

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Conformational Analysis of Thermotropic Liquid Crystalline Polyesters †

A. GHANEM, P. MEURISSE, F. LAUPRÊTRE, and C. NOËL

Laboratoire de Physicochimie Structurale et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231 Paris Cedex 05, France.

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PCILO conformational calculations have been carried out on several model compounds of thermotropic liquid crystalline polyesters [—OC—φ—φ—φ—CO—O—R—O—] where $R = (\text{—CH}_2\text{—})_2$; $(\text{—CHCH}_3\text{—})_2$; $(\text{—CHCH}_3\text{—CH}_2\text{—})$. Several conformations corresponding to the *trans* and *gauche* states of the C–C single bonds are preferred, the *TGT* form being of lower energy than the *TTT* form. The replacement of $\text{—CH}_2\text{—}$ group by $\text{—CH(CH}_3\text{)}$ group results in a decrease of the number of the energy minima, an increase in the energy of the molecule in all the preferred conformations, compared to that of the *TGT* form, a sharpening of the potential energy wells and an increase in the energy barriers. The presence of a methyl group also shifts the aliphatic chain away from the ideal *trans* and *gauche* positions.

1. INTRODUCTION

Recently some of the present authors undertook to synthesize and characterize a polymer system with thermotropic liquid crystal properties associated with the presence of mesogenic moieties in the main chain.[1-6] The general formula is:

$$[\text{—OC—R}_1\text{—CO—O—R}_2\text{—O—}]$$

where R_1 = biphenyl or terphenyl and R_2 = linear or branched alkyl segments. These polyesters possess some conformational flexibility in

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that rotations about the bonds between the phenylene rings are possible and flexible spacers can give rise to different conformations. Since from FTIR, ESR and NMR investigations the thermal behavior of these polyesters appears to be a sequence of changes from the solid crystalline state to an isotropic liquid phase gradually liberating one degree of freedom after another, this flexibility may be important in this regard.

In a previous paper[7] PCILO conformational calculations were carried out to obtain conformational energy profiles of model compounds related to polyesters mentioned above. The molecules A–E (see Figure 1) were investigated to examine the rôle of the mesogenic group. For both biphenyl and *p*-terphenyl derivatives these calculations gave a torsional angle of 40° between the planes of adjacent rings. Moreover, the conformational characteristics of the carboxyl

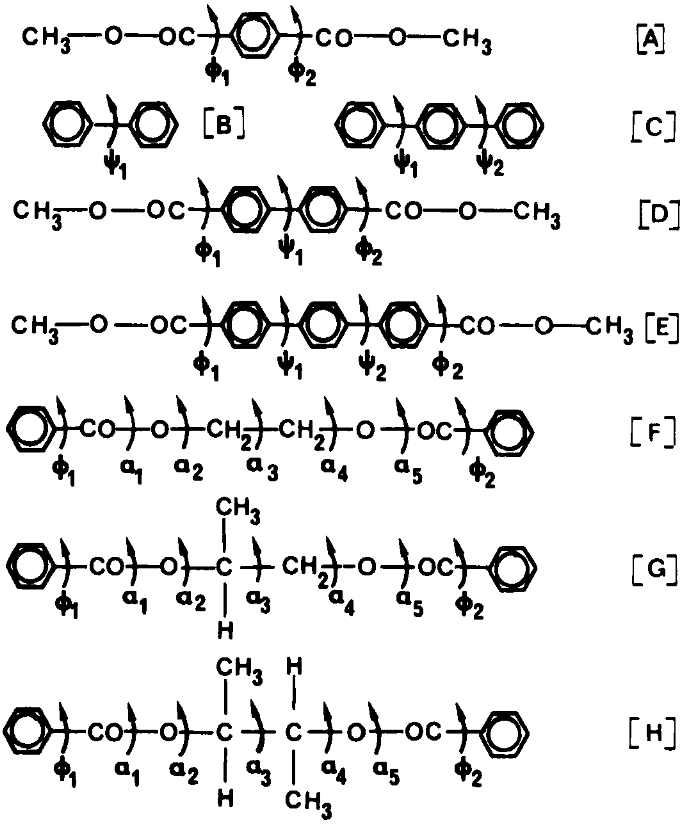


FIGURE 1 Schematic diagrams of molecules A–H.

groups were found to be independent of the number of phenyl rings. In other words, the main consequence of the replacement of a phenyl ring by a biphenyl or a *p*-terphenyl group is to increase the axial (length to diameter) ratio, that is to say the anisotropy, of the system. A prominent feature of these results is that polyesters with $R_1 = p$-terphenyl provide a rich source of liquid crystals which are more thermally stable than those of the biphenyl analogues.[1,2,8,9] On the other hand polyalkylene terephthalates do not form liquid crystals.

The present study is an extension of this previous work. The molecules F–H (Figure 1) were studied to establish the way in which substituents affect the equilibrium flexibility of the aliphatic spacer.

2. DESCRIPTION OF CALCULATIONS

The calculation of the conformational energies of model compounds of polyesters is accomplished by the PCILO (Perturbative Configuration Interaction using Localized Orbitals) method[10] which has already been used successfully to predict the liquid crystalline nature of

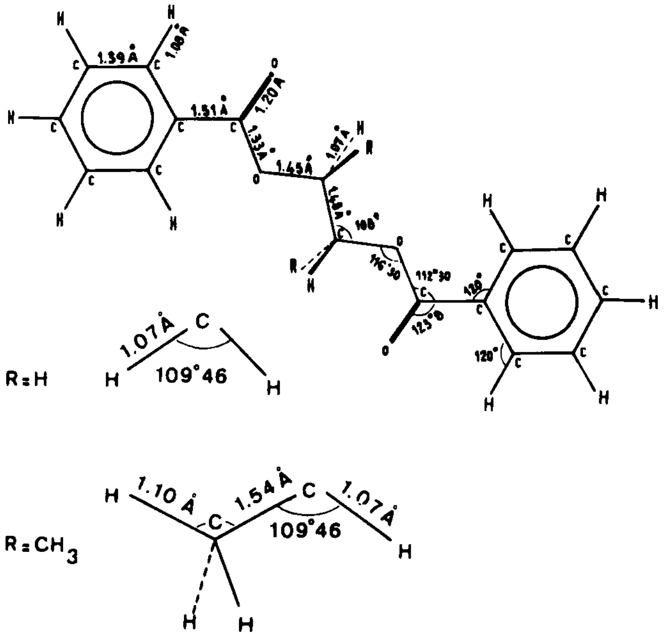


FIGURE 2 Bond angles and bond lengths of molecules F–H.

solutions of polyamides[11,12]. The molecules studied are given in Figure 1. The internal rotation angles ϕ_i define the orientation of an aromatic ring with respect to the adjacent carboxyl group. The internal rotation angles α_i are taken as 180° in the all-trans conformation of the flexible spacer. X-ray crystallographic data reported for benzoate and terephthalate esters[13-17] and aromatic and aliphatic polyesters[18-26] indicate that ϕ_1, ϕ_2, α_1 and α_5 approach 180°. The observed deviations are usually less than 10°. On the basis of this experimental evidence and from the conclusions drawn from the previous calculations, the φ—CO—O— group was assumed to be planar in molecules F–H. Hence, the only parameters taken into account for calculations were the angles α_2, α_3 and α_4 which define the geometry of the flexible spacer. The geometrical input data are given in Figure 2. Calculations were carried out with angles varied by intervals of 30° followed by closer scans at 10° intervals in the neighbourhood of potential minima.

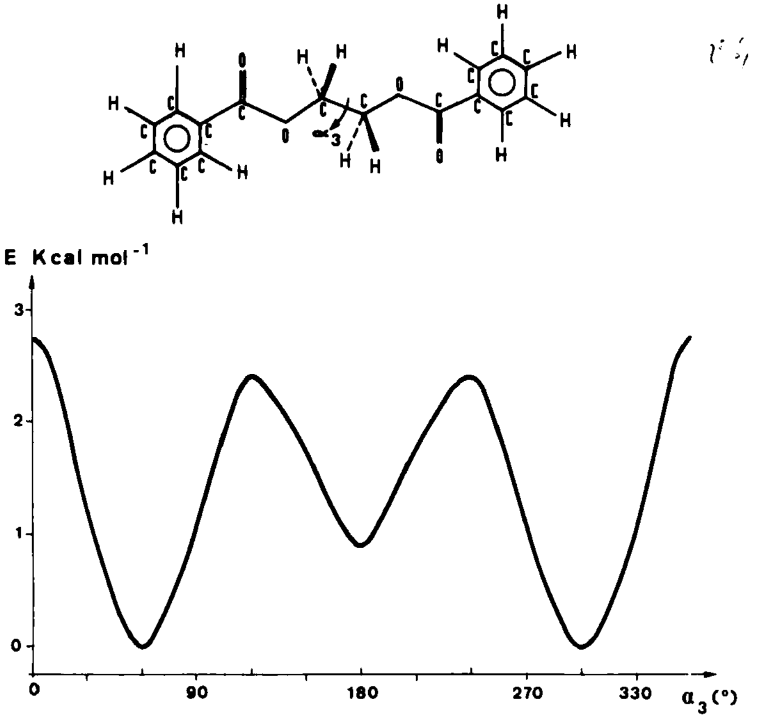


FIGURE 3 Conformational energy plotted versus α_3 ($\alpha_2 = \alpha_4 = 180°$) for ethylene glycol dibenzoate.

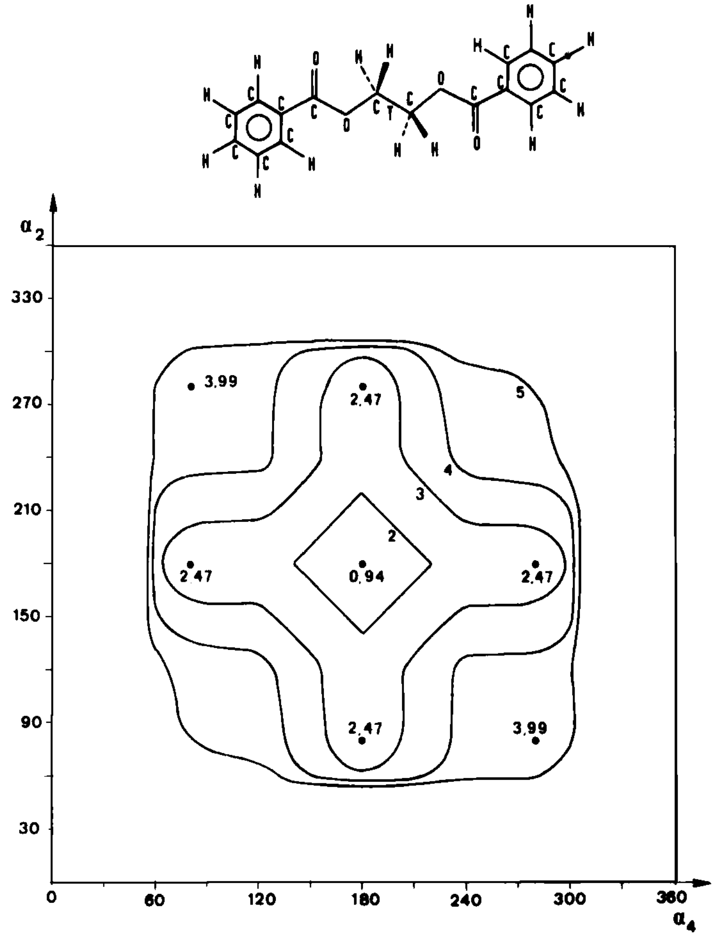


FIGURE 4 Conformational energy map $[\alpha_2, \alpha_4]$ of ethylene glycol dibenzoate. $[\alpha_3 = 180°]$.

3. RESULTS AND DISCUSSION

Molecule F: ethylene glycol dibenzoate

Conformations TYT

Values of the conformational energy are plotted versus α_3 ($\alpha_2 = \alpha_4 = 180°$) in Figure 3. The energy minima are found at $\alpha_3 = \pm 60°$ (0 Kcal.mol^{-1}) and $\alpha_3 = 180°$ (0.9 Kcal.mol^{-1}) which coincide with the *TG*$^+$*T* (or *TG*$^-$*T*) and *TTT* conformations. The heights of the energy barriers for conformational changes *TTT* → *TGT*, *TGT*

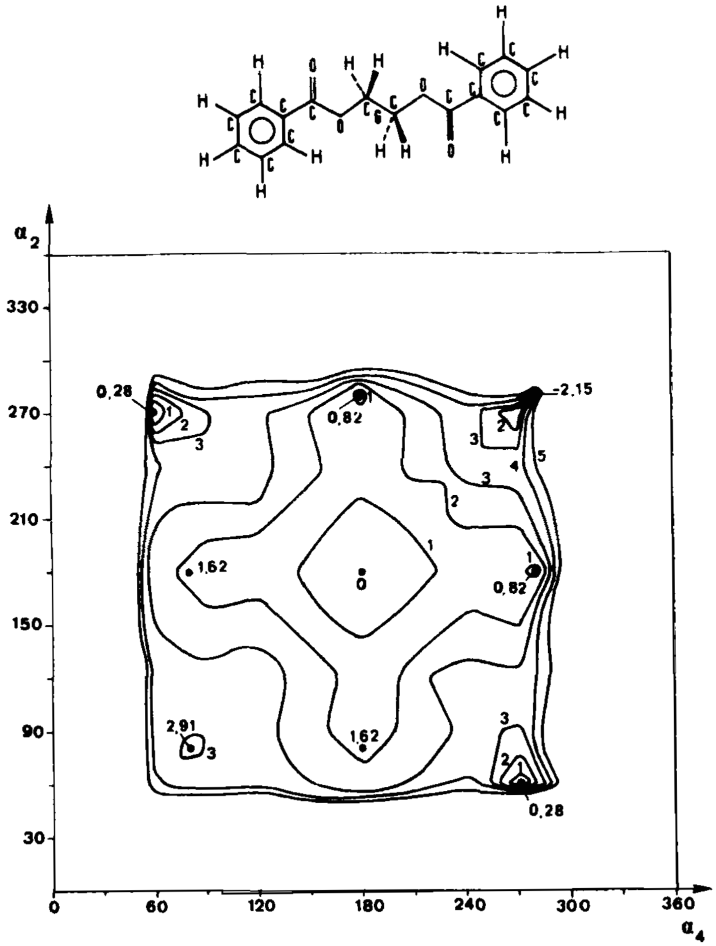


FIGURE 5 Conformational energy map $[\alpha_2, \alpha_4]$ of ethylene glycol dibenzoate. $[\alpha_3 = 60°]$.

$\rightarrow$ TTT and $TG^+T \rightarrow TG^-T$ are 1.5 Kcal.mol^{-1}, 2.4 Kcal.mol^{-1} and 2.8 Kcal.mol^{-1}, respectively.

The present study is in agreement with experimental data reported for poly(ethylene terephthalate) in solution, in the melt or in the amorphous glassy state.[27—32] The most characteristic feature for this polymer is a decisive preference for the *gauche* conformation over the *trans* around the —CH_2—CH_2— bonds. Different authors reported that poly(ethylene terephthalate) exists from 93–70% in the *gauche* conformation. In unoriented poly(ethylene terephthalate), the ratio of the ethylenic linkage in the *gauche* conformation to that in the *trans* conformation is 88 : 12.[27,30-32] Using,[33]

$$n_g/n_t = g\exp\{-(E_g - E_t)/RT\}$$

where n_i is the fraction in the i-th conformation, $n_g + n_t = 1$ and the statistical factor $g = 2$ because there are two equivalent *gauche* states, Loew and Sacher[34] found that E_g is lower than E_t by 0.806 Kcal.mol^{-1}, which is in close agreement with the 0.9 Kcal.mol^{-1} derived from present calculations.

The good agreement between the PCILO calculations and data reported for disordered phases of poly(ethylene terephthalate) is not surprising. Indeed, the PCILO calculations were made on isolated molecules and did not treat intermolecular interactions. However, they are no longer satisfactory when very strong intermolecular interactions must be taken into account. For example, X-ray crystallographic data[14a,22] reported for ethylene glycol dibenzoate and poly (ethylene terephthalate) in the crystalline state indicate that the ethylenic linkage adopts a *trans* conformation: intermolecular interactions favor the *trans* conformation by its more efficient packing and, in so doing, counteract the intramolecular interaction.

For comparison it is useful to cite semi-empirical calculations carried out by Sundararajan *et al.*[35] to explore the conformations in ethylene glycol diacetate. Several conformations corresponding to the *trans* and *gauche* states of the C—O and C—C bonds are preferred which differ very little in energy from the *TTT* form. Of special interest is the fact that the *TGT* energy is higher than the *TTT* energy by only 0.24 Kcal.mol^{-1}. From these results and the present PCILO calculations it appears that the energy difference between the *TTT* and the *TGT* conformations is expected to be rather small for compounds X—CO—O—CH_2—CH_2—O—OC—X. Hence, slight modifications in the chemical structure and/or in the crystallization conditions, which influence the structure and the alignment of the chains, may play a significant role in the determination of the preferred conformation. For example, the ethylenic linkage adopts a *trans* conformation in ethylene glycol di(meta chlorobenzoate)[36] but a *gauche* conformation in ethylene glycol di(para chlorobenzoate)[14c].

Conformations XYZ ($Y = T, G^+, G^-$)

Conformational energy contours of molecule F for the internal rotations α_2 and α_4 are shown in Figures 4 ($\alpha_3 = 180°$) and 5 ($\alpha_3 = 60°$). The energy is quoted in Kcal.mol^{-1} relative to the minimum for the *TGT* form. Energies were also computed at intervals of 10° in α_2, α_3 and α_4 in the region of minima. The lowest minima thus obtained correspond to the conformations given in Table I. These results are qualitatively in agreement with the semi-empirical calculations carried out by Sundararajan et al.[35] for ethylene glycol diacetate, assuming $\alpha_2 = \alpha_4$ owing to the chemical symmetry of the molecule. These authors have also found several minima which coincide with the *TTT* (1.10 Kcal.mol^{-1}), TG^+T (or TG^-T) (1.34 Kcal.mol^{-1}), $G^+G^+G^+$ (or $G^-G^-G^-$) (1.12 Kcal.mol^{-1}), G^+TG^+ (or G^-TG^-) (1.56 Kcal.mol^{-1}) and $G^+G^-G^+$ (or $G^-G^+G^-$) (1.93 Kcal.mol^{-1}) conformations.

The present PCILO calculations indicate that most of the conformations *XYZ* are less stable than the *TTT* and $TG^{\pm}T$ forms. Antiparallel arrangement of the $C=0$ dipoles must be invoked to explain the low energy derived for the $G^+G^-G^+$ (or $G^-G^+G^-$) form. On the other hand, the lowest energy minimum, which corresponds to the $G^+G^+G^-$ (or $G^-G^+G^+$, $G^-G^-G^+$ and $G^+G^-G^-$) conformation is not due to any single factor but rather to a combination of factors. The reason why these conformations have not yet been found is not obvious but the possibility of poor packing in the lattice may be a case.

Molecule H: 2,3-butanediyl dibenzoate

Conformations TYT

Values of the conformational energy are plotted versus $\alpha_3(\alpha_2 = 190°$, $\alpha_4 = 170°)$ in Figure 6. Again, the most stable conformations are *TTT*, TG^+T and TG^-T. It is to be noted, however, that the steric hindrance of the methyl groups results i) in appreciable shifts from the ideal *trans* and *gauche* positions for perfect staggering (Table II) ii) in a higher energy barrier $TG^+T \leftrightarrow TG^-T$.

Conformations XYZ $(Y = T, G^+, G^-)$

Conformational energy contours of molecule H for the internal rotations α_2 and α_4 are shown in Figures 7 ($\alpha_3 = 180°$) and 8 ($\alpha_3 = 60°$). Energies were also calculated at intervals of 10° in α_2, α_3 and α_4 in the neighborhood of the minima. The energy values for all the minima are given in Table III.

Broadly speaking, the replacement of the —CH_2— groups by —$CH(CH_3)$— groups results in i) an increase in the energy of the molecule in all the preferred conformations compared to that of the TG^+T (or TG^-T) form. ii) a sharpening of the potential energy wells

TABLE I

Preferred *XYZ* conformations for ethylene glycol dibenzoate

α_2,	α_3,	α_4	Conformation	ΔE (Kcal.mol^{-1})
180,	180,	180	TTT	0.94
180,	60,	180	TG^+T, TG^-T	0
180,	180,	80	$TTG^+, TTG^-, G^+TT, G^-TT$	2.47
80,	180,	280	G^+TG^-, G^-TG^+	3.99
80,	40,	290	$G^+G^+G^-, G^-G^+G^+, G^-G^-G^+, G^+G^-G^-$	−5.7
180,	60,	80	$TG^+G^+, G^+G^+T, G^-G^-T, TG^-G^-$	1.62
180,	60,	280	$TG^+G^-, G^-G^+T, G^+G^-T, TG^-G^+$	0.82
80,	60,	80	$G^+G^+G^+, G^-G^-G^-$	2.91
280,	60,	280	$G^-G^+G^-, G^+G^-G^+$	−2.13

together with an increase in the energy barriers. Thus, molecule H appears more rigid than molecule F from a dynamic point of view. iii) a decrease of the number of energy minima. For example some conformations are hindered by repulsive effects involving either the two methyl groups ($G^+G^+G^-$ or $G^+G^-G^-$) or one CH_3 group

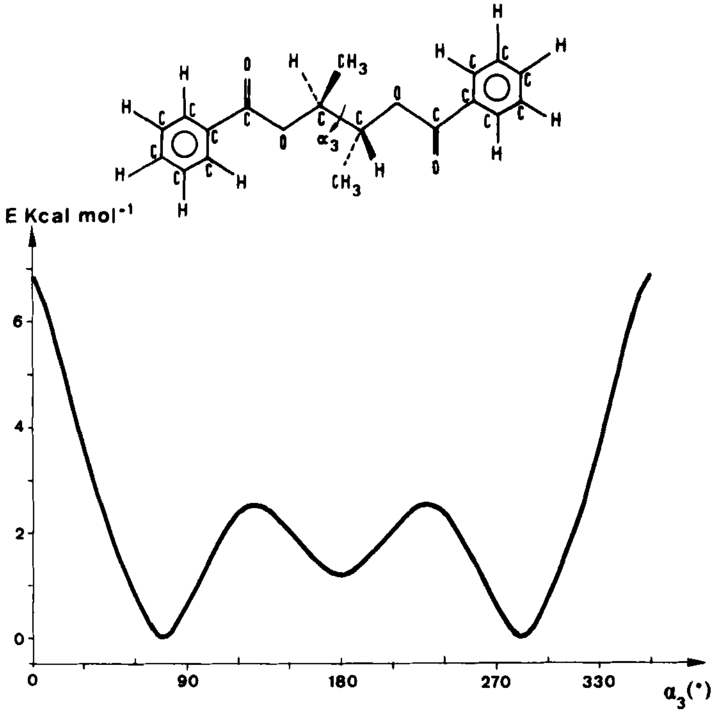
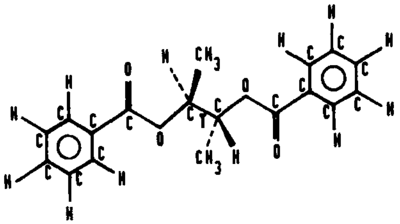


FIGURE 6 Conformational energy plotted versus α_3 ($\alpha_2 = 190°, \alpha_4 = 170°$) for 2,3-Butanediyl dibenzoate.

TABLE II

Preferred *TYT* conformations for 2, 3-butanediyl dibenzoate

					ΔE Kcal.mol^{-1}		
Conformation	α_2	α_3	α_4	E Kcal.mol^{-1}	II↔I	I, II→III	III→II, I
(I) TG^+T	190	75	170	0	6.8		
(II) TG^-T	190	−75	170	0		2.6	
(III) TTT	190	180	170	1.2			1.2



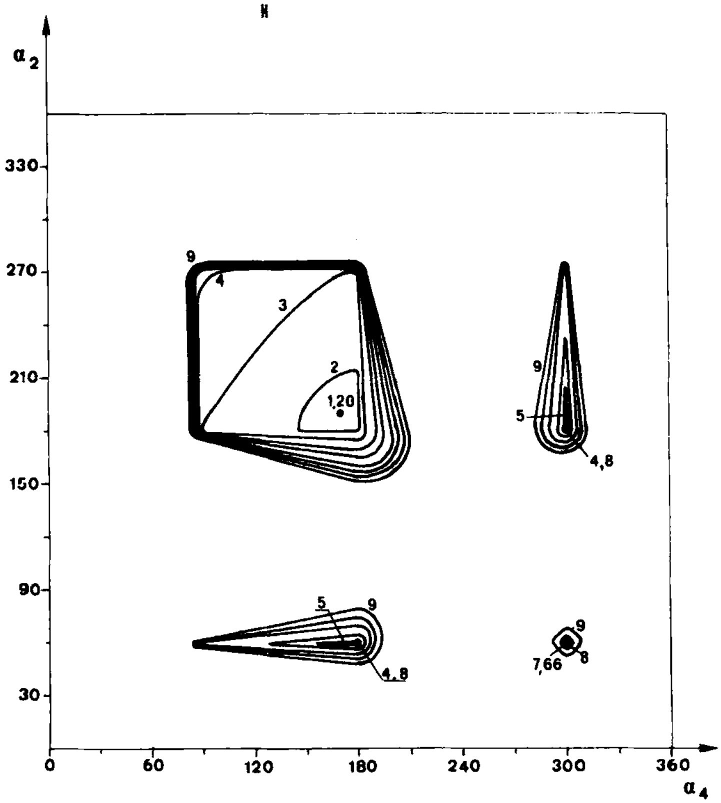


FIGURE 7 Conformational energy map $[\alpha_2, \alpha_4]$ of 2, 3-Butanediyl dibenzoate. $[\alpha_3 = 180°]$.

TABLE III

Preferred *XYZ* conformations for 2, 3-butanediyl dibenzoate

$\alpha_2, \alpha_3, \alpha_4$			Conformation	ΔE (Kcal.mol^{-1})
190,	180,	170	TTT	1.2
195,	75,	170	TG^+T, TG^-T	0
60,	170,	170	G^+TT, TTG^-	4.53
60,	180,	300	G^+TG^-	7.66
290,	40,	80	$G^-G^+G^+, G^-G^-G^+$	−5.23
190,	70,	80	TG^+G^+, G^-G^-T	1.04
280,	70,	170	G^-G^+T, TG^-G^+	0.89
190,	70,	290	TG^+G^-, G^+G^-T	4.87
280,	50,	290	$G^-G^+G^-, G^+G^-G^+$	1.98

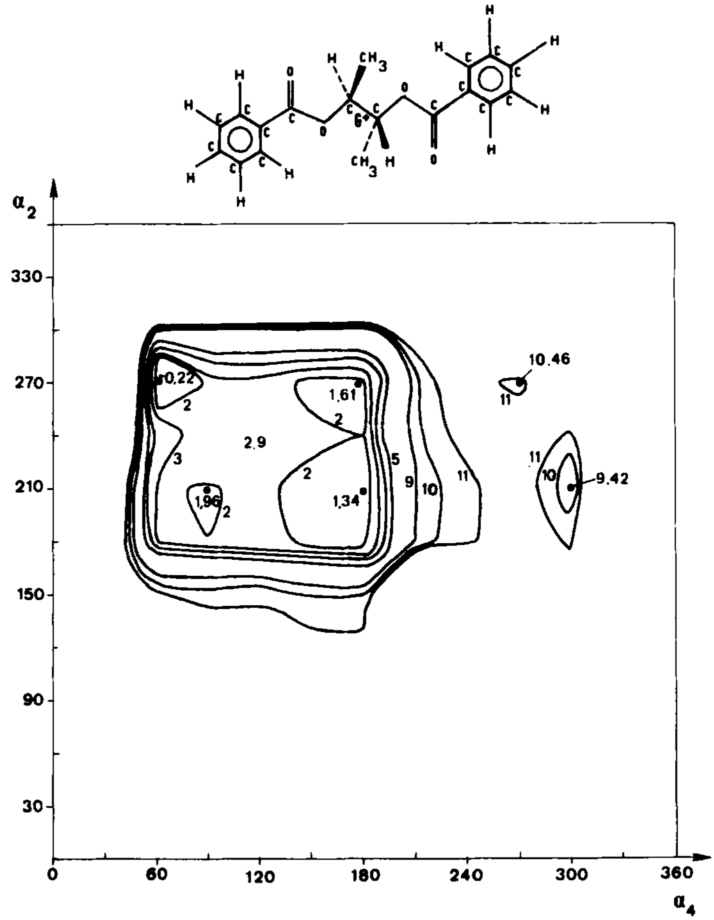
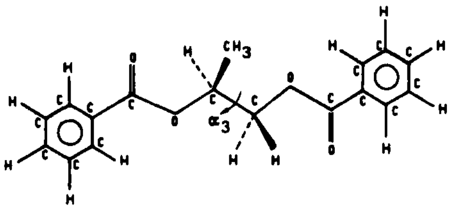


FIGURE 8 Conformational energy map $[\alpha_2, \alpha_4]$ of 2, 3-butanediyl dibenzoate. $[\alpha_3 = 60°]$.

TABLE IV

Preferred *TYT* conformations for 1,2-Propanediyl dibenzoate

Conformation	α_2	α_3	α_4	E Kcal.mol^{-1}	ΔE Kcal.mol^{-1}		
(I) TG^+T	195	60	180	0.4		I→II 3.2	I→III 2.9
(II) TG^-T	190	− 65	180	0	II→I 3.6		II→III 2.16
(III) TTT	195	185	180	1.09	III→I 2.2	III→II 1	



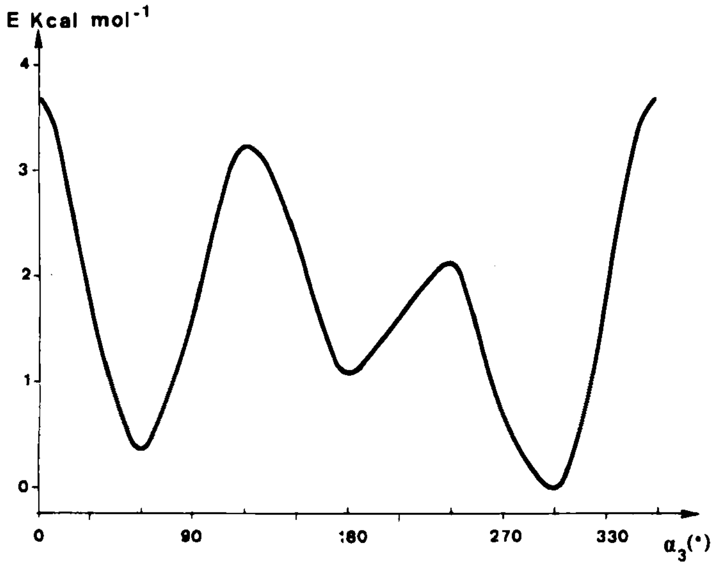


FIGURE 9 Conformational energy plotted versus α_3 ($\alpha_2 = \alpha_4 = 180°$) for 1,2-Propanediyl dibenzoate.

and lone pairs of the oxygen atom of the CO group (e.g.: TTG^+ or G^-TT).

The crystal structure of 2,3-butanediyl dibenzoate was determined by X-ray analysis[37]. The values of α_2, α_3 and α_4 were found to be 203°, 179° and 146° which does not differ noticeably from the actual *TTT* conformation.

Molecule G: 1,2-propanediyl dibenzoate

As calculation times are much longer for unsymmetrical molecules, the only conformations studied were *TTT*, *TGT*, G^+TG^-, G^-TG^+, $G^-G^+G^-$ and $G^+G^-G^+$ which can give rise to ordered phases.

Again results obtained for molecule G emphasize the importance of conformations *TTT*, TG^+T and TG^-T, the TG^-T form being of lower energy than the TG^+T one. The G^+TG^-, G^-TG^+, $G^-G^+G^-$ and $G^+G^-G^+$ are no longer stable. The present results are consistent with the experimental findings that the isotactic poly (oxypropylene) chain [—O—CH(CH$_3$)—CH$_2$—]$_n$ adopts a *TGT* conformation in the crystalline state. As observed for molecule H, the steric hindrance of the methyl group results in appreciable shifts from the ideal *trans* and *gauche* positions for perfect staggering (Table IV, Figure 9). It is to be noted that the presence of a methyl group in 1,2 propanediyl bis(p-chlorobenzoate) also shifts the aliphatic chain away from a *trans* arrangement [$\alpha_2 = 152°$, $\alpha_3 = 190°$, $\alpha_4 = 185°$][39]. The replacement of CH$_2$ group by —CH(CH$_3$) also leads to an increase in both the energy of the molecule in the *TTT* conformation and the energy barrier $TG^+T \rightarrow TG^-T$. However, these effects are less marked than for molecule H.

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