On the Flexibility of the Mesogenic Unit in Some New Liquid-Crystalline Main-Chain Polyethers: The Case of the *α,α′*-Diphenoxy-*p*-xylene Group

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Received March 13, 1991

ABSTRACT: The degree of flexibility of a mesogenic unit constituted by nonsubstituted aromatic rings bridged by $-CH_2O-$ groups was examined by a geometrical and energetical analysis. The energetical analysis was effected by the calculation of maps of the conformational energy, using three different sets of energy parameters for the nonbonded interactions, according to Flory, Allinger, and Scheraga. The maps present three well-separated regions of lower energy, one corresponding to extended conformations and the other two corresponding to bent conformations. The flexibility was evaluated through the calculation of the absolute probabilities to have extended or bent conformations for this unit, on the basis of the calculated energy maps. The results indicate that, at the temperature at which LC behavior is observed for the polymers in which these units are inserted (460 K), a large fraction of nonextended conformations (at least ≈50%) is foreseen for the isolated mesogenic unit. It is concluded that a relevant effect of the stabilization of the extended conformations may arise by the fact that the considered units are inserted in a polymer chain. An evaluation of the contribution to the stabilization of the extended conformations with respect to the bent conformations due to the different shapes of the three energy minima regions is also given.

Introduction

It is well-known that liquid-crystalline (LC) phases in segmented chain polymers are connected with the presence in the macromolecules of segments with a pronounced shape anisometry (mesogenic units). Moreover, the shape of these segments should not be affected by changes in conformation; therefore, the mesogenic units should possess a relatively rigid molecular structure.

Recently, Jonsson et al.[1] synthesized some new LC thermotropic main-chain polyethers of the general formula $[-OC_6H_4OCH_2C_6H_4CH_2OC_6H_4O(CH_2)_n-]_x$ with $n = 7-12$. All the studied polyethers present a thermal transition from the crystalline phase to the LC phase in the range 460 ± 15 K. These polymers are the first examples of main-chain LC polymers with $-CH_2O-$ bridging groups between aromatic rings in the mesogenic unit.

The quoted authors have investigated the conformational characteristics of the mesogenic unit present in their polymers via the synthesis and characterization of a model compound, *α,α′*-diphenoxy-*p*-xylene $[C_6H_5OCH_2C_6H_4CH_2OC_6H_5]$.

They stated that this molecule meets the usual requirements for a molecule to constitute a mesogenic segment in LC polymers. In particular, to establish that this molecule possess a rigid linear conformation, they used a non detailed computer-based conformational analysis, from which they concluded that the most stable conformation is extended with the two outer phenylene rings lying in the same plane and that the energy required to move one of the outer rings from the described position to a position that would make the molecule nonlinear (to the secondary energy minimum) is 16.2 kJ/mol. On the other hand, they found that the model compound does not possess liquid crystallinity, but they remarked that this result does not mean that diphenoxy-*p*-xylene units are unsuitable as mesogens.

Almost contemporarily to the quoted paper, Percec and Yourd published a series of works in which they present new main-chain thermotropic polyethers and copolyethers constituted by alternating aromatic and aliphatic rings bridged by methyleneoxy units (without the presence in the chain of flexible spacers)[2] or by groups containing two aromatic rings bridged by dimethylene units alternated along the chain by flexible spacers containing odd and/or even numbers of methylene units.[3-6] Schematic formulas of the two classes of polymers by Percec and Yourd, as well as that of the class of polymers by Jonsson et al., are indicated in Figure 1. Percec and Yourd, at variance with Jonsson et al., underline the flexible character of the $-OCH_2-$ and $-CH_2CH_2-$ bridging groups in their polymers, so that the mesogenic units in which these groups are bridging units are expected to give rise to a number of different conformational isomers which are in dynamic equilibrium and of which only the most stable conformer adopts an extended linear conformation suitable for a mesogenic behavior. Therefore, they suggested to classify these mesogenic units as rodlike mesogens based on conformational isomerism or, alternatively, flexible rodlike mesogens, although no quantitative evaluation of the flexibility of mesogenic units containing these bridging groups is present in their papers.

Going back to the paper of Jonsson et al. it was surprising for us, in agreement with the qualitative considerations of Percec and Yourd, that nonsubstituted benzenic rings, linked by flexible methylol groups, may give rise to a so conformationally rigid segment to justify by itself a liquid-crystalline behavior of their polymers at a temperature of about 200 °C. Particularly we were surprised by the high value that the authors found for the secondary conformational energy minimum corresponding to the nonlinear conformation that is most easily realized. Considering also that the model compound of their mesogenic unit does not possess liquid crystallinity, it seemed worthwhile to us to examine with a detailed conformational analysis, geometrical and energetic, what the real degree of flexibility of this mesogenic unit is.

In this paper we present the results of our analysis on the quoted diphenoxyxylene unit, while a more complete conformational analysis of other mesogenic segments presenting methyleneoxy or dimethylene bridging units as, for example, those present in the polymers of Percec and Yourd is in progress.

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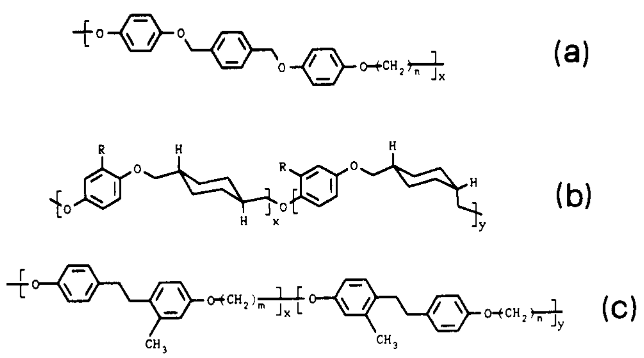

Figure 1. Schematic formulas of some new classes of LC thermotropic main-chain polyethers or copolyethers with $-CH_2O-$ or $-CH_2CH_2-$ bridging groups between two similar or nonsimilar rings. (a) Polymers by Jonsson et al.,[1] discussed in this paper. (b and c) Polymers by Percec and Yourd.[2-6]

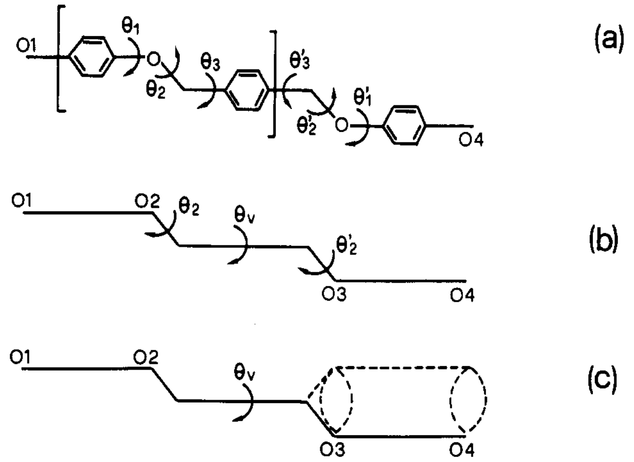

Figure 2. Schematic representation of the mesogenic segment studied in this paper. (a) All the torsion angles determining the conformations are indicated. The portion in brackets is that for which the energy maps are calculated. (b) Only the torsion angles which determine the length (and roughly the shape) of the segment are indicated. (c) The envelope of the shapes of the segment of Figure 2b for $\theta_2 = \theta_2' = 180°$ for any value of θ_v is represented.

Geometrical Analysis

The studied mesogenic unit is represented in Figure 2a, where the torsion angles which determine all the possible conformations are also indicated. However, the torsion angles which determine the shape of the segment in view of a potential mesogenic behavior are only the three indicated in Figure 2b, where virtual bonds that cross the benzenic rings are introduced.

It is fairly evident from the scheme of Figure 2b that extended conformations which present pronounced shape anisometry may be obtained only with values of the torsion angles θ_2 and θ_2' near 180°, while in Figure 2c it is shown that for these values of θ_2 and θ_2' the extended shape is almost independent of the value assumed by θ_v.

An evaluation of the variations ($\Delta\theta$) from the values of 180° allowed for θ_2 and θ_2' to maintain a near-extended conformation for the schematic segment of Figure 2b, independently on θ_v, may be obtained from the curve of Figure 3 in which the minimum value of the distance O1–O4 (D) is reported as a function of $\Delta\theta$ if θ_2 and θ_2' assume all the possible values in the range $180° \pm \Delta\theta$, for any value of θ_v. It is evident from Figure 3 that for any value of θ_2 and θ_2' in the range $180 \pm 30°$ the conformation keeps highly extended; in fact for the values of θ_2 and θ_2' extremes of the considered intervals the minimum distance O1–O4 is less than 10% (1.4 Å) of its all-trans length (18.4 Å).

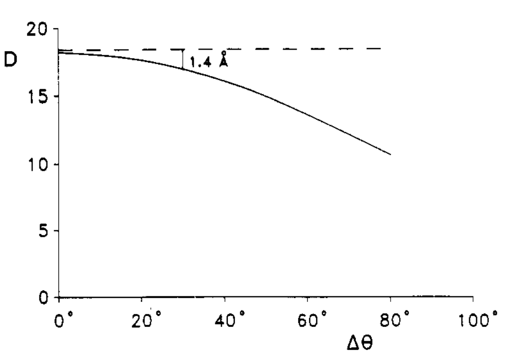

Figure 3. Minimum value (in Å) of the distance O1–O4 (D) of Figure 2b as a function of $\Delta\theta$ if θ_2 and θ_2' assume all the possible values in the range $180° \pm \Delta\theta$, for any value of θ_v. The broken line indicates the maximum value obtainable for the distance O1–O4; the maximum shortening (1.4 Å) of this distance for $\Delta\theta = 30°$ is also indicated.

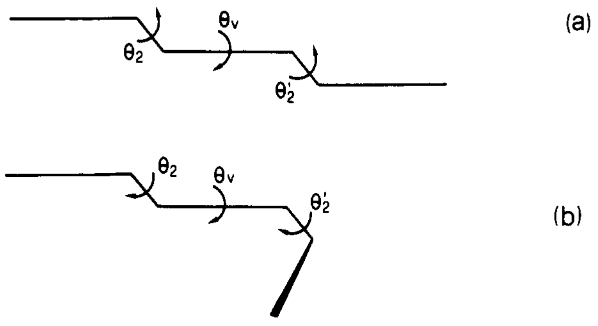

Figure 4. Comparison between two representative shapes of the segment of Figure 2b corresponding to different energy minimum conformations: (a) $\theta_2 = \theta_v = \theta_2' = 180°$, (b) $\theta_2 = \theta_v = 180°$, $\theta_2' = -60°$.

Due to the 3-fold character of the torsional energy function of the CH_2–O bonds, the only other possible shapes of the molecule corresponding to minimum energy conformations (as we will see better later in detail) are those corresponding to values of θ_2 and/or θ_2' around ±60°. These conformations are surely unsuitable for a mesogenic behavior, independently of the value assumed by θ_v. As an example, a conformation of the schematic molecule of Figure 2b, corresponding to $\theta_2 = 180°$, $\theta_v = 180°$, and $\theta_2' = -60°$, is reported in Figure 4 in comparison with a conformation corresponding to $\theta_2 = \theta_2' = \theta_v = 180°$.

Energetical Analysis

(a) Method of Energy Calculation. The internal energy has been calculated as a function of the relevant conformational parameters as the sum of two energy terms:

$$E = E_{\mathrm{tor}} + E_{\mathrm{nb}}$$

E_{tor} is the sum of the torsional potential energy contributions around the single bonds, calculated according to the general formula

$$(k_t/2)(1 + \cos n\theta)$$

E_{nb} is the sum of the energy contributions due to the interactions between nonbonded atoms (separated by more than two bonds) at a distance r, calculated according to one of the formulas

$$(Ar^{-12} - Cr^{-6}) \quad \text{or} \quad (A'e^{-Br} - Cr^{-6})$$

depending on the potential function used.

The calculation of the nonbonded energy applied to isolated molecules tends to give energies which are lower for more compact conformations as if atoms separated by many bonds but neighboring in space were attracted among

Table I
Geometric Parameters Used in the Calculations of the Conformational Energy

bond lengths, Å		bond angles, deg	
$C-C_{ar}$	1.51	$C_{ar}-C-O$	115.0
$C_{ar}-C_{ar}$	1.39	$C-O-C_{ar}$	115.0
$C-O$	1.45	$C-C_{ar}-C_{ar}$	120.0
$C_{ar}-O$	1.41	$C_{ar}-C_{ar}-C_{ar}$	120.0
$C-H$	1.10	$C_{ar}-C-H$	109.2
$C_{ar}-H$	1.08	$O-C-H$	109.2
		$C_{ar}-C_{ar}-H$	120.0
		$H-C-H$	108.0

themselves. Whereas this occurrence may be appropriate in the evaluation of the conformational energy of a gaseous molecule, the effect may be considered as spurious in the case of molecules in consensed matter. For this reason the nonbonded energy has been calculated by a special procedure already used by us in previous papers:[7,8] for distances which are greater than that corresponding to the minimum value of energy, the potential energy function has been taken as zero, whereas, for distances which are lower, the energy has been calculated as the difference between the calculated value with the appropriate potential functions and the value of the same functions at the point of minimum. A near-equivalent procedure was suggested by Flory et al.[9,10] for the study of the conformations of polymers in solution.

In all our energy calculations the values of the bond lengths and of the bond angles have been left fixed to the values reported in Table I. The bond angles around the oxygen atom and the CH_2 group have been set equal to 115° as found for the crystalline structure of dibenzyl,[11] in which the value of the torsion angle equivalent to our θ_1 and θ_3 of Figure 2a is about 90°.

The torsional potential barriers around the $C_{ar}-O$ and $C_{ar}-C$ bonds were assumed as 6-fold and have been considered to be equal to each other. They are reported by Hopfinger[12] for the $C_{ar}-C$ bond. The torsional potential barrier around the C–O bond is 3-fold and is also reported by Hopfinger.[12]

For the nonbonded interactions three different sets of parameters were used according to three different authors, Flory,[10] Allinger,[13] and Scheraga.[14] All the values of the energy parameters used are reported in Table II.

(b) Results and Discussion of Energy Calculations. The energetical analysis of the possible conformations of the mesogenic segment indicated in Figure 2a has been effected by the calculation of maps of the conformational energy.

The maps really calculated are those relative to the only portion in brackets in Figure 2a, as a function of the three torsion angles there indicated ($\theta_1, \theta_2, \theta_3$), in the reasonable hypothesis that, for the entire mesogenic segment, the energies of the possible conformations (with exclusion of a little fraction of nonextended high-energy conformations which are not relevant for the scope of this paper) could be obtained as the sum of those of two conformations of the indicated portion. The maps have been calculated at intervals of 10° for the variables θ_1, θ_2, and θ_3. θ_1 and θ_3 were varied only in the range 0–170° due to the planarity of the phenyl group. θ_2 has been varied only in the range 0–180° because the complete map with the θ_2 variable in the range 0–360° presents a symmetry center having coordinates $\theta_1 = 90°$, $\theta_2 = 180°$, and $\theta_3 = 90°$. In fact the conformations having sets of values ($\theta_1, \theta_2, \theta_3$) correspondingly equal in absolute values, but opposite in sign, are enantiomorphous and therefore isoenergetic.

As expected, the complete maps present essentially three well-separated regions of lower energy around the sections (θ_1, θ_3) defined by $\theta_2 = 180°$ and $\theta_2 \approx \pm 60°$. In particular, the sections containing the minima are for $\theta_2 = 180°$ and $\theta_2 = \pm 60°$ both for the functions of Allinger and Scheraga, while they are for $\theta_2 = 180°$ and $\theta_2 = \pm 70°$ for the functions of Flory.

Figure 5 shows only the nonequivalent sections of the calculated maps containing the energy minima for the three different sets of functions used.

In Figure 6 are reported the values of the absolute energy minima, for the various sections (θ_1, θ_3), as a function of θ_2 for the three different sets of functions used.

Our first observation on the maps is that, independently of the functions used, the two nonequivalent low-energy regions present correspondingly quite similar shapes. In particular, the minima in the region corresponding to $\theta_2 = 180°$ are very large and the values of the minima in the region corresponding to θ_2 near ±60° are confined in a limited range with respect to both θ_1 and θ_3. As for the energy barriers between the minima regions, they are situated in the sections of the maps with $\theta_2 = \pm 120°$ for all sets of functions and are in all cases comprised between 10 and 15 kJ/mol. This may be seen from Figure 6 which also indicates the trends of the minimum energy varying the shape of the molecule, which is principally connected with the value of θ_2.

For the difference of energy between the absolute minima in the two regions with the functions of Scheraga it is practically zero (0.5 kJ/mol), while with the functions of Allinger it is 2.5 kJ/mol and with the functions of Flory it is 5 kJ/mol. The energy differences obtained with the set of Flory and Scheraga, which use functions of the kind Lennard-Jones, may be attributed to the much lower van der Waals radii of Scheraga's functions (see Table III) and in particular of the C_{ar} (1.70 Å for Scheraga, 1.95 Å for Flory). This fact makes the functions of Scheraga much softer than Flory's. More difficult is the comparison with Allinger's functions that are of different kinds and that, while given an intermediate value for the difference between the two energy minima, with respect to Flory's and Scheraga's functions, appear to behave in a way more similar to the Flory ones for what concerns the shape of the minima regions.

To compare the results of our energy calculations with that of ref 1, it is observed that, for the entire mesogenic segment of Figure 2a (corresponding to the model compound of Jonsson et al.), the minimum energy difference between the bent conformation that is most easily realized, that is, one of the two corresponding to (θ_2, θ_2') = (180°, ≈±60°), and the most favorable extended conformation, that is, that corresponding to (θ_2, θ_2') = (180°, 180°), obviously remains 0.5, 2.5, or 5 kJ/mol according to the different sets of functions. These numbers are to be compared with the much higher value of 16.2 kJ/mol reported for the secondary energy minimum for the mesogenic unit in the quoted paper. Our results indicate that the quoted molecule does not possess a rigid linear conformation at least on the simple analysis based only on the difference of energy between the minima.

Evaluation of the Flexibility

Keeping in mind that, beyond the minimum difference of energy between the bent and the extended conformation, a further stabilization of the extended conformation may arise from the higher degree of freedom that this conformation possesses with respect to the bent conformation,

Table II
Parameters Used in the Energy Calculations for the Three Different Authors[a] According to the Formulas Reported in the Text

interacting pair	Flory $A \times 10^{-3}$	Flory C	Scheraga $A \times 10^{-3}$	Scheraga C	Allinger $A' \times 10^{-3}$	Allinger B	Allinger C
$C\cdots C_{ar}$	2595.9	1867	1196	1548	128.2	3.77	758.2
$C_{ar}\cdot C_{ar}$	4065.6	2311	1196	1548	114.3	3.67	797.1
$C_{ar}\cdot O$	1607	1606	858	1536	27.7	3.88	138.5
$C\cdots H$	238.7	536	159	536	173.2	4.18	554.7
$C_{ar}\cdot H$	393.6	666	159	536	155.9	4.06	598.8
$O\cdots H$	132.5	446	105	519	38.1	4.31	101.2
$H\cdots H$	30.6	197	18.7	195	211.3	4.53	418.7
$C_{ar}\cdot LP$[b]					100.5	4.45	219.8
$H\cdots LP$					135.1	5.03	142.3

torsion angle	k_t	n
C_{ar}–C–O–C_{ar}	9.0	3
C_{ar}–C_{ar}–C–O	2.4	6
C_{ar}–C_{ar}–O–C	2.4	6

[a] A is expressed in kJ·mol^{-1}·Å^{12}, A' is expressed in kJ·mol^{-1}, B is expressed in Å^{-1}, C is expressed in kJ·mol^{-1}·Å,^{6} and k_t is expressed in kJ·mol^{-1}. [b] Lone pair.

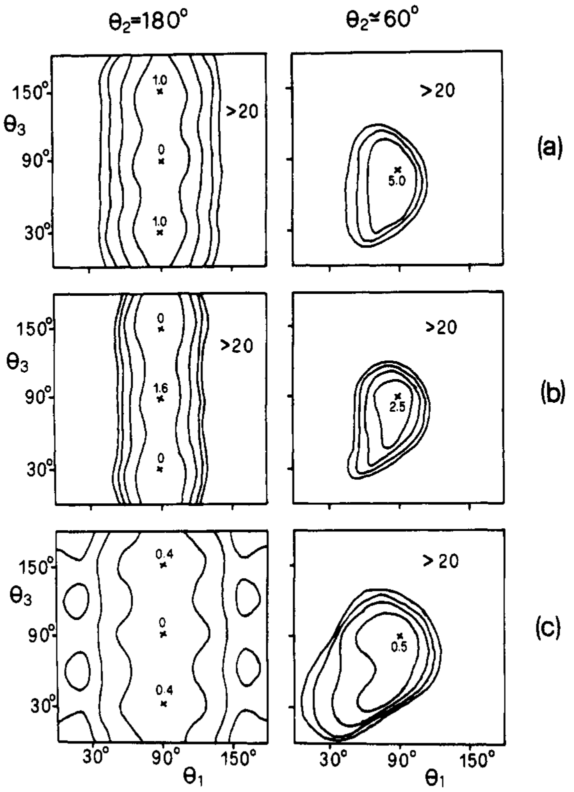

Figure 5. Sections, for the indicated values of θ_2, of the energy maps containing the two nonequivalent minima, for the portion in brackets in Figure 2a, according to the different sets of functions used: (a) Flory, (b) Allinger, (c) Scheraga. The level curves are reported at intervals of 5 kJ/mol with respect to the absolute minimum obtained for each kind of function, assumed as zero. Only the minima are indicated.

we proceeded to evaluate the flexibility of the mesogenic unit of the polymers of Jonsson et al. through the calculation of the absolute probability (P_{TT}) to have an extended conformation for this unit, according to our energy maps. This probability was obtained by squaring the absolute probability (P_T) to have an extended conformation for the portion in brackets in Figure 2a.

The values of P_T (and consequently P_{TT}) were calculated in two different ways: (a) by reducing the three minimum energy regions to the points of lowest energy of Figure 6, that is, without taking into account the different shapes of the energy minima regions; (b) by considering the different shapes of the energy minima regions as are evident from Figure 5, that is, taking into account the different degrees of freedom that the extended and the bent conformations may present with respect to the rotation of the benzenic rings around the virtual bonds (see Figure 2).

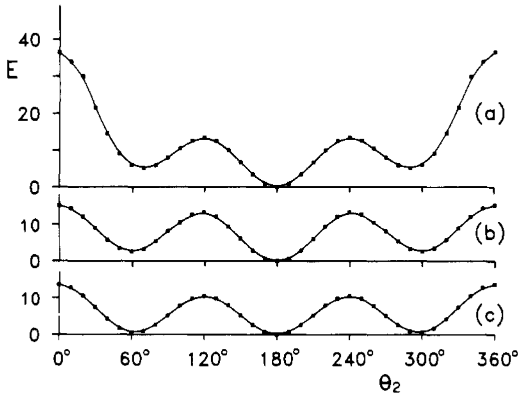

Figure 6. Values of the energy corresponding to the conformations of absolute minimum energy for the various sections (θ_1, θ_3) of the three calculated energy maps, as a function of θ_2, according to the different sets of functions used: (a) Flory, (b) Allinger, (c) Scheraga. The energies (expressed in kJ/mol), as for the maps, are referred to the lowest absolute minimum obtained for each kind of function, assumed as zero.

Table III
van der Waals Radii of the Various Chemical Species for the Three Different Authors

atomic species	van der Waals radii/Å Flory	Scheraga	Allinger
C	1.80	1.70	1.75
C_{ar}	1.95	1.70	1.85
O	1.60	1.52	1.65
H	1.30	1.20	1.50
LP[a]			1.20

[a] Lone pair.

Correspondingly the values of P_T and P_{TT} will be indicated as $[(P_T)_a, (P_{TT})_a]$ and $[(P_T)_b, (P_{TT})_b]$.

In case a we have assumed that the portion in brackets in Figure 2 may assume only the three conformations corresponding to the lowest points of minima for θ_2 = 180° and $\theta_2 \approx \pm 60°$. The differences of energy, ΔE, between the two nonequivalent minima are, as seen before, 5.0, 2.5, and 0.5 kJ/mol, according to the functions of Flory, Allinger, and Scheraga, respectively. Consequently the

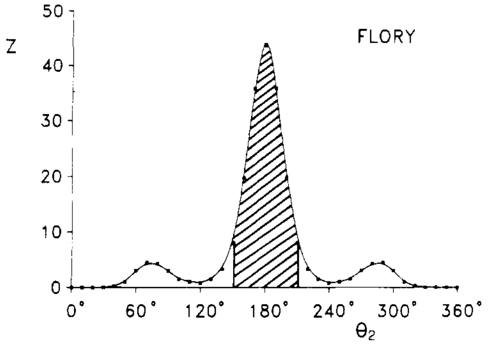

Figure 7. Partial conformational partition function Z, at 460 K, as a function of θ_2 calculated from the sections of the energy map relative to the portion in brackets in Figure 2a, assuming the set of functions of Flory.

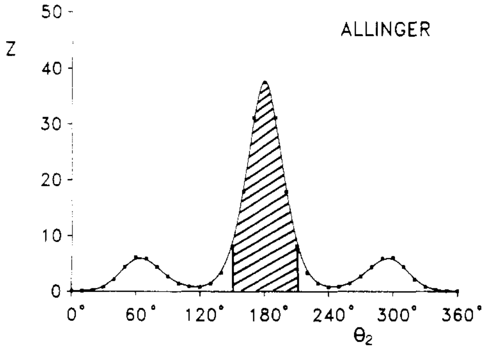

Figure 8. Partial conformational partition function Z, at 460 K, as a function of θ_2 calculated from the sections of the energy map relative to the portion in brackets in Figure 2a, assuming the set of functions of Allinger.

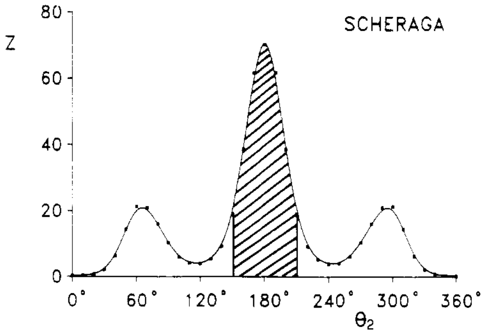

Figure 9. Partial conformational partition function Z, at 460 K, as a function of θ_2 calculated from the sections of the energy map relative to the portion in brackets in Figure 2a, assuming the set of functions of Scheraga.

values of $(P_T)_a$, calculated according to the formula

$$(P_T)_a = 1/(1 + 2e^{-\Delta E/RT})$$

are, at 460 K, 0.66, 0.49, and 0.36 and the values of $(P_{TT})_a$ are 0.44, 0.24, and 0.13, respectively.

In case b we have calculated for each θ_2 section of our maps the quantity

$$Z = \sum_{\theta_1,\theta_3} e^{-\Delta E(\theta_1,\theta_3)/RT}$$

including all the points θ_1 and θ_3 for which $\Delta E(\theta_1,\theta_3) \leq 20$ kJ/mol, where $\Delta E(\theta_1,\theta_3)$ refers to the absolute minimum for each set of functions used. The results of our calculations for $T = 460$ K are reported as a function of θ_2 in Figures 7–9. Then, assuming as extended conformations all those corresponding to values of θ_2 comprised in the interval 180 ± 30°, we have calculated the absolute probability to have an extended conformation, $(P_T)_b$, by the ratio of the area dashed on Figures 7–9, with respect to the total area under each curve. The so calculated values are 0.75 for Flory, 0.66 for Allinger, and 0.46 for Scheraga. Considering now the complete mesogenic unit of the polymers of Jonsson et al., the absolute probabilities of an extended conformation $(P_{TT})_b$, calculated by squaring the $(P_T)_b$ values, are 0.56, 0.44, and 0.21, respectively. These results are summarized in Table IV.

Table IV
Values of the Absolute Probabilities To Have an Extended Conformation for the Portion in Brackets of Figure 2a, P_T, and for the Complete Mesogenic Unit, P_{TT}, According to the Three Sets of Functions Used[a]

	$(P_T)_a$	$(P_T)_b$	$(P_{TT})_a$	$(P_{TT})_b$
Flory	0.66	0.75	0.44	0.56
Allinger	0.49	0.66	0.24	0.44
Scheraga	0.36	0.46	0.13	0.21

[a] $(P_T)_b$ and $(P_{TT})_b$ differ from $(P_T)_a$ and $(P_{TT})_a$ for taking into account or not the different shapes of the energy minima (see text).

Conclusions

Comparison of the values of $(P_{TT})_a$ with the values of $(P_{TT})_b$ shows an evident effect of the increasing of the stabilization for the extended conformation if you take into account the different shapes of the minima. We note also that the differences between the three authors, especially between Flory and Allinger, are reduced if we refer to the most significant values of $(P_{TT})_b$. However, even if we do not consider the low value of $(P_{TT})_b$ foreseen using the very soft Scheraga functions and consider the higher values of $(P_{TT})_b$ obtained using the Flory and Allinger functions, we have to recognize that the considered mesogenic unit, not inserted in a polymer chain, should assume at the temperature of 460 K a large fraction of nonextended conformations (at least ≈50%). This result, together with the observation[1] that the model compound α,α′-diphenoxy-*p*-xylene, corresponding to this mesogenic unit, does not present LC behavior, brings us to conclude that a further and relevant effect of the stabilization of the extended conformation may arise by the fact that the considered segments are inserted in a polymeric chain.

Acknowledgment. We are grateful to Prof. A. Sirigu for very useful discussions. We thank the "Ministero dell'Università e della Ricerca Scientifica" and CNR (Italy) for financial support.

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