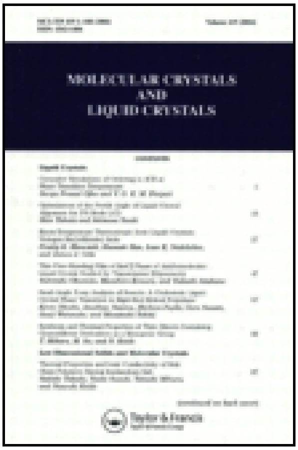

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Theoretical Study of Mesogenic Disc-like Compounds: the Hexa-n-Alkoxy and Hexa-n-Alkanoyloxy Truxenes Series

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Version of record first published: 20 Apr 2011.

To cite this article: J. Lejay & M. Pesquer (1983): A Theoretical Study of Mesogenic Disc-like Compounds: the Hexa-n- Alkoxy and Hexa-n-Alkanoyloxy Truxenes Series, Molecular Crystals and Liquid Crystals, 95:1-2, 31-43

To link to this article: http://dx.doi.org/10.1080/00268948308072405

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 31–43
0026-8941/83/9502-0031/$18.50/0

Printed in the United States of America

A Theoretical Study of Mesogenic Disc-like Compounds: the Hexa-*n*- Alkoxy and Hexa-*n*-Alkanoyloxy Truxenes Series

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(Received August 16, 1982)

This paper presents semi-empirical calculations on the molecular arrangement of a series of truxenes hexaesters and hexaethers, disc-like mesogenic molecules. A preliminary CNDO study shows that the most probable structure of the fluorene is plane. Preferential conformation of the aliphatic chains in an isolated molecule is established. Aliphatic chains in hexaether are perpendicular to the core of the molecules and they stay in the two half-spaces separated by the plane of the core. The interactions between two molecules of ester derivatives show the existence of several conformations and are discussed in this paper.

INTRODUCTION

A new family of liquid crystals has been recently discovered from disc-like molecules.[1,2] It corresponds to a partially regular arrangement of these disc-like molecules, composed of a central part, generally aromatic, substituted by some aliphatic substituents. There is a polymorphism in disc-like liquid crystals.

In the family of hexasubstituted triphenylene derivatives (Figure 1A), one experimentally observes some different sequences (named normal) of transition depending on temperature.[3]

$$K \to D \to N \to I$$

$$K \to D \to I$$

$$K \to N \to I$$

K = crystal, I = isotrop phase.

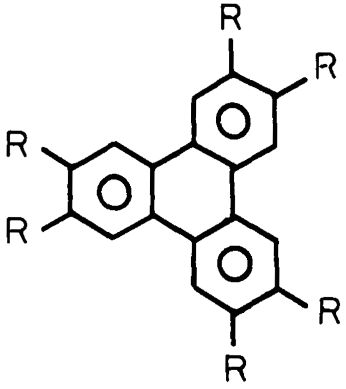


FIGURE 1A Triphenylene molecule.

The D mesophases are viscous, and correspond to a regular or irregular stack of disc-like molecules in column. On the contrary, the nematic phases N of disc-like molecules are fluid.

These series of phase transitions depending on temperature can be modified.

In this way, in the experimental study of some truxene derivatives[4] (Figure 1B) an inverse sequence is observed.

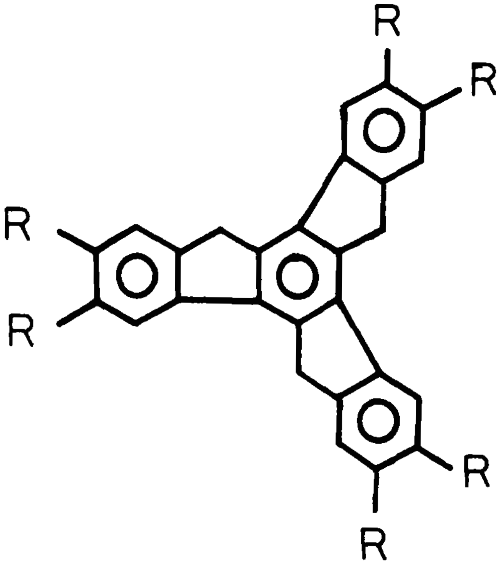


FIGURE 1B Truxene molecule.

That is to say that we notice the apparition of fluid nematic phases N, before the apparition of one or several viscous column phases D

$$K \rightarrow N \rightarrow D \rightarrow I$$

The inverse sequence of phase transitions could be explained by the evolution of the environment structure, that is to say of the molecular conformation and of the position of the molecules one with regard to the other depending on the temperature.

We think that a theoretical study could provide a contribution to this knowledge. We have studied the hexa-*n*-alkanoyloxy and the hexa-*n*-alkoxy truxenes more simply named hexaesters and hexaethers.

The purpose of the present work is first to define precisely the structure of the isolated molecule depending on the length of the aliphatic chains. Then, we shall try to establish the existence of some eventual correlations between molecular conformation and the mesophase.

CALCULATION PROCEDURE

In the series of hexasubstituted triphenylene, some of these compounds have been studied by X-ray diffraction and their structures were established.[5-8] The difficult crystallization of truxene hexaester and hexaether does not permit us to do the same study at the present time, and we had to select the bond lengths and angles resulting from mean values observed in crystal structures of molecules having common chemical groups with the present one (like fluorene).[6]

The selected values are the following (atom labeling corresponds to Figure 2):

$a = C_{VI}\,C_{VII} = 1.47$ Å
$b = C_{VII}\,C_{VIII} = 1.47$ Å
$c = C_{VIII}\,C_{IX} = 1.43$ Å
$d = C_{IX}\,C_{I} = 1.38$ Å
$e = C_{I}\,C_{II} = 1.38$ Å
$f = C_{II}\,C_{III} = 1.40$ Å
$g = C_{III}\,C_{IV} = 1.41$ Å
$h = C_{IV}\,C_{V} = 1.48$ Å
$i = C_{V}\,C_{VI} = 1.41$ Å
$j = C_{IV}\,C_{VIII} = 1.41$ Å

$\widehat{de} = 120°59'$
$\widehat{ef} = 122°14'$
$\widehat{fg} = 116°47'$
$\widehat{gj} = 122°30'$
$\widehat{jc} = 118°5'$
$\widehat{cd} = 119°24'$
$\widehat{jh} = 107°34'$
$\widehat{bj} = 109°35'$
$\widehat{ab} = 105°38'$

$C_I\,0_1 = 1.38$ Å
$0_1\,C_0 = 1.32$ Å
$C_0\,O_2 = 1.24$ Å
$C_0\,C_1 = 1.50$ Å
$C_1\,C_2 = 1.52$ Å
$C_2\,C_3 = 1.53$ Å

By convention, an hexaether or an hexaester C_n represents the molecule in which the aliphatic substituent has *n* carbon atoms.

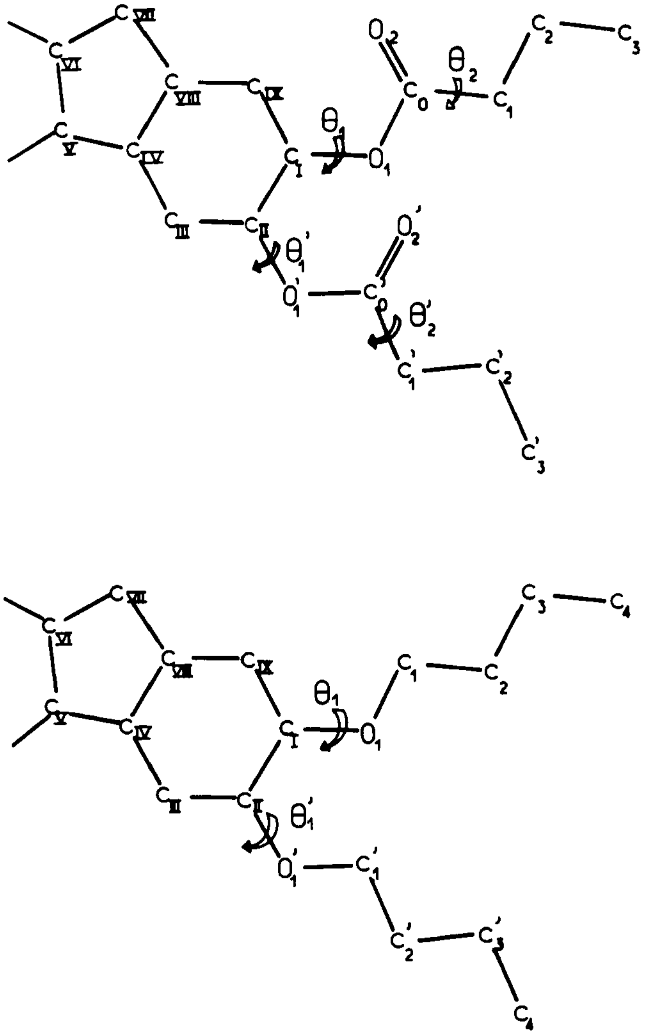


FIGURE 2 Schematic representation of one third of ester (a) and ether (b) truxene derivatives, with torsional angles.

The number of atoms involved in this calculation (for example, we have to consider 171 atoms in hexaester C_7 of truxene, and a multiple of this number for the intermolecular interactions) is too high to permit a quantical calculation. So the calculation of conformational energy has been performed by using semiempirical methods, based on interaction potential.

This methodology has been used and discussed throughout the study of hexaether and hexaester of tryphenylene organization.[7] The results lead to a very good agreement with crystallography and X-ray diffraction measurements in the mesophase.[8]

This causes us to use this methodology to study the truxene derivatives, about which we have a very few experimental informations.

First, we recall the basic principles of the method. The potential energy of molecular interaction is equal to a sum of interactions between pairs of atoms i and j. These two atoms are nonbonded in the case of intramolecular interaction and they belong to two different molecules in the case of intermolecular calculation.

We can write the energy as a sum of an electrostatic potential U_{el} and a van der Waals potential U_{rw}.

The electrostatic contribution is given by Coulomb's law

$$U_{el} = 332 \sum_{i,j} \frac{q_i q_j}{\varepsilon R_{ij}}$$

332 is a conversion factor to get U_{el} in kcal · mole^{-1} when interatomic distances are given in Å, q_i and q_j are the partial charges centered on nonbonded i and j atoms calculated by the CNDO/2 method.[9] ε, the dielectric constant, is taken to equal 1. Among all van der Waals potential possible calculation methods, Lennard Jones' function (6–12)[13] constitutes a good representation of these interactions because it takes into account, in a satisfying way, the interatomic repulsions for the short distances

$$U_{rw} = \sum_{i,j} -\frac{A_{ij}}{R_{ij}^6} + \frac{B_{ij}}{R_{ij}^{12}}$$

The A_{ij} and B_{ij} coefficients are calculated from simple expressions involving experimental results,[10] and depend on the nature and the hybridation states of i and j atoms.

THE ISOLATED MOLECULE CONFORMATION

An energetic study of the fluorene molecule (Figure 3) using the method of the molecular orbital CNDO[9] depending on the dihedral angle α formed by the $C_1C_2C_3$ plane and the benzenic cycle plane, shows that the most probable structure for this molecule is the plane structure (Table I). Because the truxene molecule contains the fluorene skeleton, it is a convenient approximation to assume that the truxene is also planar.

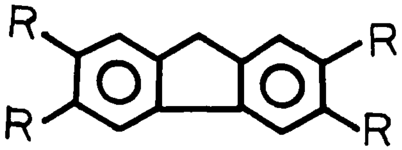


FIGURE 3 Fluorene molecule.

TABLE I

Fluorene energy (eV) vs the dihedral angle α (°)

α (degree)	Energy (eV)
0	−2722.20
10	−2721.06
20	−2717.23

In the conformational chains study, the threefold symmetry of these molecules permits us to reduce the calculations considering just a third of the molecule.

A preliminary study about the hexaesters and hexaethers C_7 indicates that the *trans*position corresponds to a minimum of the energy in the aliphatic chains.

In the following part, we suppose the chain to be in the *trans* conformation and the independent displacement of the chains I (from C_0 to C_3) and II (from C'_0 to C'_3) can then be modified by the only variations of the torsion angles Θ (Figure 2). A positive value of Θ keeps the chain under the plane of the core.

We do not consider the rotation around 0_1—C_1 bond because the corresponding rotational barrier is too high. A positive value of Θ_1 places the chain under the molecular plane. The results of this study are reported in Table II.

TABLE II

Geometrical parameters of ester and ether truxene derivatives chains

	Θ_1 (°)	Θ_2 (°)	Θ'_1 (°)	Θ'_2 (°)
ester C_3	−92	−94	+87	+91
ester C_4	−93	−99	+87	+94
ester C_7	−93	−100	+86	+95
ester C_{11}	−93	−101	+86	+96
ether C_3	−91	—	+89	—
ether C_7	−90	—	+88	—
ether C_{11}	−91	—	+89	—

The values of the angles Θ_1, Θ_2, Θ_1', Θ_2' correspond to the energetic minimum for the ester (C_3, C_4, C_7, C_{11}) and ether derivatives (C_3, C_7, C_{11}).

The first rotation (Θ_1, Θ_1') puts the chains perpendicular to the plane of the central core, one chain being over this plane, the other one under.

The second rotation ($\Theta_2 = \Theta_2' = 0$) does not modify the chain position in the case of the ethers (thus, in the following, we shall consider only the Θ_1 and Θ_1' rotation for the ethers).

Yet, this rotation turns down the chains in a plane roughly parallel to the truxene core for the ester derivatives. (They stay, however in the two half-spaces, separated by the plane of the core.) The most stable conformations of the isolated molecules are then different for ether and ester derivatives.

Variation of energy vs one angle gives a good picture of the conformational freedom of the molecule. In the propyl ester case, we suppose chain II to be in its most stable conformation and the other one, chain I, is allowed to rotate around the $C_1$0 (angle Θ_1). The plot of E vs Θ_1 is shown in Figure 4 and the following conclusions can be drawn:

—Around the minimum ($\Theta_1 = -92°$) the chain can turn considering that a variation of 35° around this minimum makes an energy variation equal to 1 kcal.

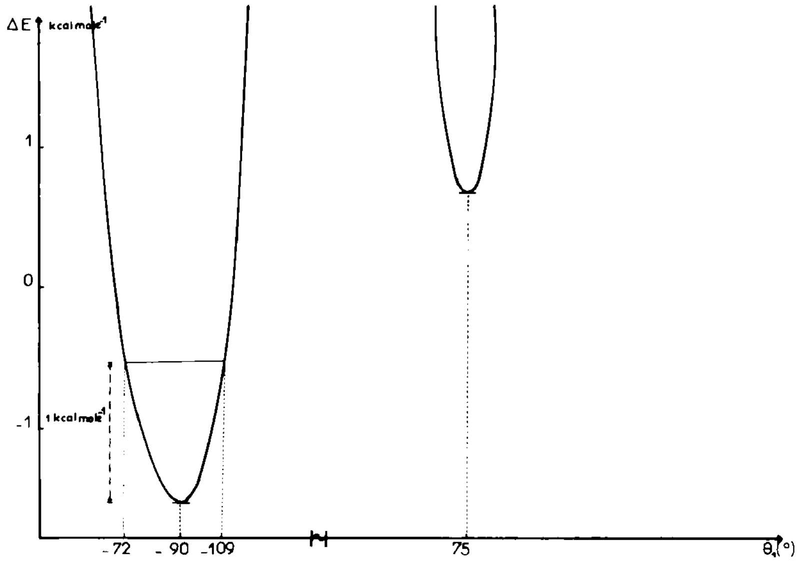


FIGURE 4 Energy (kcal mole^{-1}) vs Θ_1 (°) plot for hexaester C_3.

—There is a second minimum for $\Theta_1 = 75°$ corresponding to the conformation in which the two chains stand in the same half space. It occurs at 2,2 kcal, largely over the first minimum.

In this position, the chains are more fixed, considering that an energetic variation of 1 kcal permits only a variation of 15° around this minimum. Outside these two regions, carboxylate oxygens are either too close to each other or too close to the hydrogen of the aromatic core.

Now, only the Θ_2 angle of chain I can change, Θ_1 being fixed to its minimum value. The plot of E vs Θ_2 is shown in Figure 5. The lowest minimum, obtained for $\Theta_2 = 266°$ (or $\Theta_2 = -94°$) is energetically near a second minimum, slightly higher ($\Delta E = 0.4$ kcal), at $\Theta_2 = 91°$. This small difference indicates that we shall have to take into account in the following study these two values of Θ_2'. We note that a variation of 70° around the minimum value, involves an energetic variation equal to 1 kcal.

The same behavior is observed in some compounds with longer chains. The energy difference between the two minima is about 0.2 kcal for some C_{11} derivatives.

CONFORMATIONAL STUDY OF TWO MOLECULES IN INTERACTION

The interaction between two molecules constitutes a necessary step before studying a stack of molecules in column and the interactions between columns.

Moreover, some hexaester of triphenylene dimers seem to exist at least in the crystal.[5]

The conformational study of dimers is carried out using the following approximations:

—the molecules are supposed to be in their most stable conformation (as discussed in the part above)
—they can move along and around the same threefold axis.

The calculated energy is dependent on the distance between parallel cores d and on the angle α of rotation of one according to the other. Results of calculations are summarized in Table III. For each compound (chains geometry corresponds to the lowest energy conformation specified in Table II) we reported α and d corresponding to the lowest intermolecular energy E.

The distance $d = 3.41$ Å calculated for the truxene is close to the values found experimentally for the benzo-pérylène ($d = 3.38$ Å)[11] or the coronene ($d = 3.40$ Å).[12]

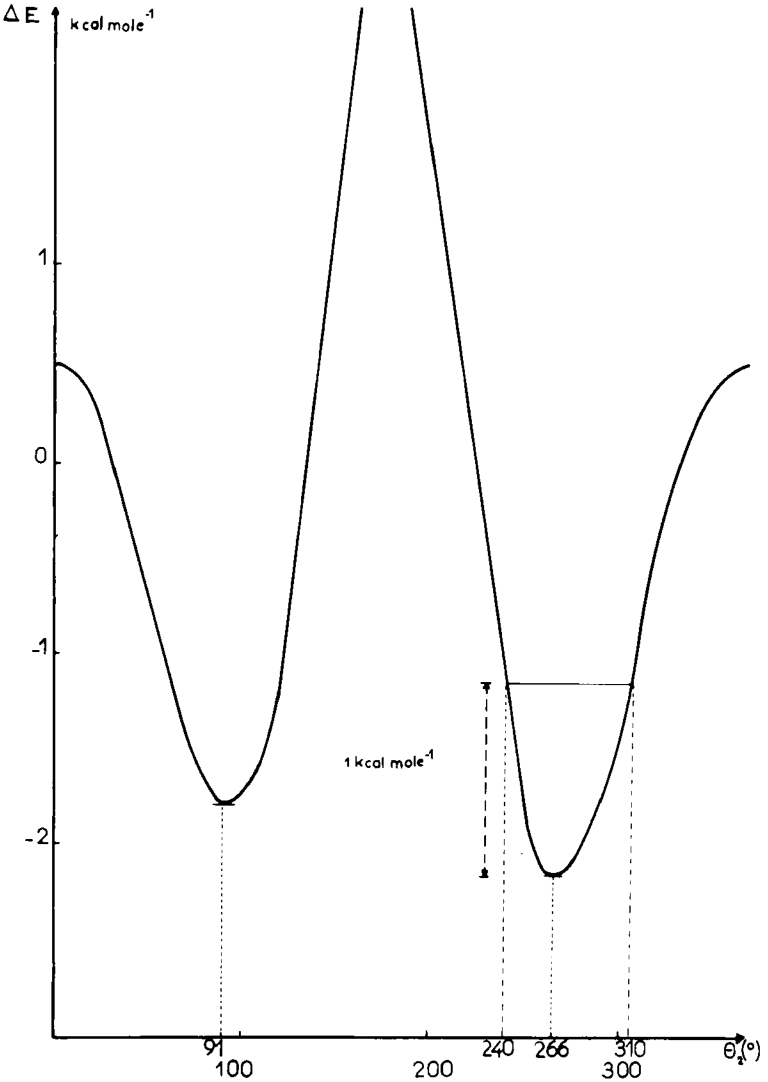


FIGURE 5 Energy (kcal mole^{-1}) vs Θ_2 (°) plot for hexaester C_3.

The angle $\alpha = 30°$ results from the repulsion of the hydrogen atoms bound with C_{VII} of one molecule, with the hydrogen atoms bound with C_{VII} of the other molecule.

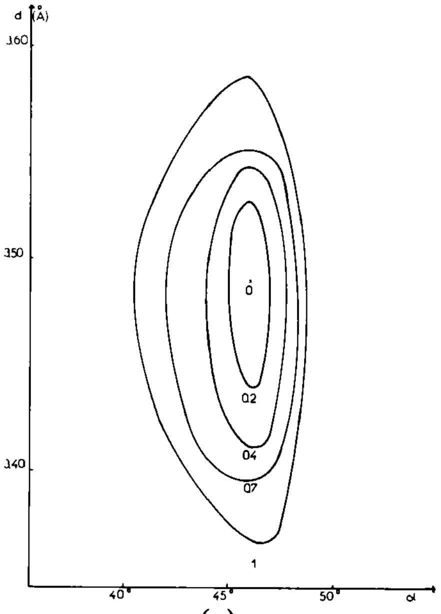
TABLE III

Geometrical parameters and intermolecular energy of hexaester and hexaether dimers

	α (degree)	d (Å)	E (kcal)
truxene	30	3.41	−63.08
ester C_3	55	3.56	−31.63
	41	3.50	−31.74
ester C_4	54	3.54	−33.853
	41	3.50	−33.154
ester C_7	46	3.49	−38.683
ester C_{11}	47	3.48	−43.67
ether C_3	−26	3.52	−30.6
ether C_7	−23	3.60	−35.89
ether C_{11}	−24	3.58	−37.94

There is a range of minimum for the hexaester C_3 and C_4 derivatives, because the chains are short and do not interfere. The chains keep the molecules away more than the truxene. Only one minimum can be considered for the C_7 and C_{11} derivatives.

In this position, we show that the carbonyl oxygen bound to C_1 of one molecule is at a distance, $d = 3.0$ Å, to the hydrogen of aromatic core of the other molecule. This value is close to the equilibrium distance of a



(*a*)

FIGURE 6 Energy contours (kcal mole^{-1}) vs α and d for hexaester C_3(a), C_7(b), and C_{11}(c).

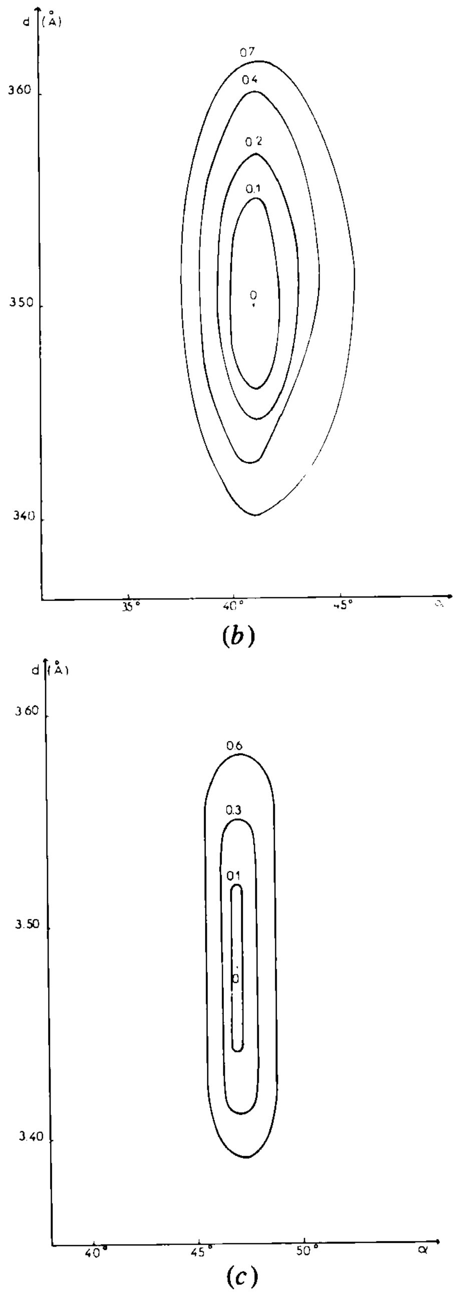


FIGURE 6 (continued)

TABLE IV

Hexaester dimer conformation: $\Theta_1 = -\Theta_1'$ and $\Theta_2 = \Theta_2'$

Composés	α (degree)	d (Å)	E (kcal)
C_7	17	4.42	−31.96
C_{11}	17	4.39	−40.44

O—H pair in the potential atomic methods[10] which stabilizes the dimer. The isoenergy graphs vs d and α (Figures 6(a–c)) show that the chain length extension, reduces the degree of rotation possibility of one molecule according to the other. We have shown above the existence of a second minimum for the ester derivatives corresponding to $\Theta_1 = -\Theta_1'$ and $\Theta_2 = O_2'$. This chain conformation leads to a formation of less stable pairs, in which the hexaester molecules are more distant (Table IV), $d = 4.4$ Å, instead of $d = 3.4$ Å for $\Theta_2 = -\Theta_2'$.

The most stable conformation of hexaether pair is obtained for some intermolecular distance d larger than these found for their ester homologous. This is due to the fact that the lateral chains are completely perpendicular to the plane core, the O—H attraction has disappeared and the α angle is close to the one of the nonsubstituted molecules. The stabilization energy E is lower.

CONCLUSION

The molecular arrangement of the studied hexaester and hexaether has been carried out using semiempirical calculations of atomic potential. The results give some insight to the structural characteristics of these compounds. In particular, the ester derivatives study shows the existence of several possible conformations that we shall try to relate to the polymorphism of these compounds. The molecular cohesion of the studied dimers appears to be less strong than the one observed in their homologous of the triphenylene series. Hexaether derivatives seem to have a simple behavior: the lateral chain extension does not alter the dimer structure. These encouraging results allow us to undertake the plurimolecular system study by using a limited number of geometric parameters.

Acknowledgments

We are grateful to Dr. C. Destrade and H. T. Nguyen of the "Centre de Recherches Paul Pascal" for helpful conversation which initiated this project.

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