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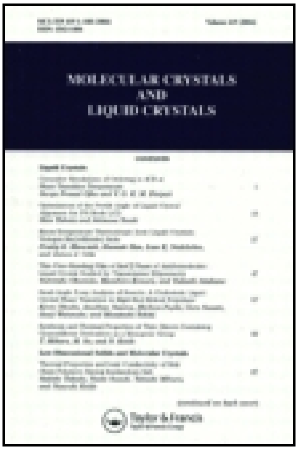

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Theoretical Conformations of Mesogenic Disc-Like Stacked Molecules. Truxenes Hexaethers and Hexaesters Series

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Theoretical Conformations of Mesogenic Disc-Like Stacked Molecules. Truxenes Hexaethers and Hexaesters Series.

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This paper presents the study of molecular arrangement by semi-empirical calculations of truxenes hexaethers and hexaesters series. In a first time, conformations of several molecules stacked are established. There are three structures corresponding to the hexaethers derivatives. The first one is very sensitive to the length chains, the two others depend only on the interaction between the cores and the atoms near the core. For the hexaesters two structures exist, corresponding to the two different isolated molecules structures. The first one does not vary with the length chains increase, the other one is very sensitive to the number of carbons in the aliphatic part. The study of two interacting columns shows that they interpenetrate each other a little, so they can slip from each others.

I. INTRODUCTION

The hexa-*n*-alkanoyloxy and hexa-*n*-alkoxy truxene, usually called hexaesters and hexaethers can give columnar mesophases, different from the nematic and smectic mesophases. In the experimental study of the hexaesters of truxene a polymorphism according to an inverse sequence is observed. There is also a reentrant phenomenon. According to nomenclature due to C. Destrade and co-workers (1), this sequence can be written:

$$\begin{tikzcd}
K \arrow[r] & N_D \arrow[r] \arrow[d] & D_{rd} \arrow[r] & D_h \arrow[r] & I \\
 & D_h & & &
\end{tikzcd}$$

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Quite differently, the hexaethers exhibit the same polymorphism as observed in the triphenylenes:

$$K \rightarrow D_{ho} \rightarrow I$$

The reentrant phenomenon is no longer observed. In a previous paper (2), (referred to hereafter as I), we have studied the isolated molecules conformation of these compounds and the dimer structures. The next step in the calculation consists in evaluating the interaction of a stack of molecules, in order to explain the origin of the molecular conformation. So we have to examine the interaction between:

—molecules inside one column
—molecules belonging to two different columns.

In this work, we shall use the model, developed in I. We recall the general equations of this method. Following potential 6-12 method of Sheraga (3), we write the total energy as a sum of an electrostatic potential U_{el} and a Van der Waals potential U_{vw}.

$$U_T = U_{vw} + U_{el}$$

U_{vw} is calculated from Lennard Jone's function:

$$U_{vw} = \sum_{i,j}\left(-\frac{A_{ij}}{r_{ij}^{6}} + \frac{B_{ij}}{r_{ij}^{12}} \right)$$

Where the A_{ij} and B_{ij} coefficients depend on the nature of the i and j atoms and r_{ij} is the interatomic distances.

The electrostatic contribution is given by Coulomb's law:

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

332 is a conversion factor to get U_{el} in kcal mole^{-1} when interatomic distances are given in Å. ε, the dielectric constant is taken equal to 1. q_i and q_j are the partial charges centered on nonbonded i and j atoms calculated by the CNDO/2 method (4).

The CNDO/2 method is used to evaluate the partial charge because this method is parametrized to reproduce the observed dipole moments. As the total charge of the molecule is zero, the monopole–monopole approximation seems convenient to calculate the

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electrostatic contribution. Indeed, the minimization of the total intermolecular energy of liquid crystals shows that the variations of the electrostatic contribution are weak as the leading term of interaction arises from the Van der Waals potential.

Stack energies is the sum of the intermolecular energies and of intramolecular energies of each molecule in the stack. To obtain the energy minima we first calculate the intermolecular energies depending on the distance a between parallel cores and on the rotation angle α of one core according to the other. The behaviour of these two parameters are different: a small variation of the distance between cores induce a small variation of the energy. But a small variation of the rotation angle α does induce a large variation of the energy, and as large this variation as the aliphatic chain is larger. Indeed the small rotation on angle α modified largely the position of the H atoms on the end of aliphatic chains, which is emphasized by the number of molecules in the stack. So, in this kind of calculation, it is easy to obtain quickly intermolecular equilibrium distances; but numerous calculations are needed to refine the rotation angles of one molecule according to the other in order to obtain the minimum energy (versus distances and rotation angles).

The stack pictures depending on the number of molecules and corresponding results are describe in chapter III. In chapter IV we include the variation of intramolecular energies (when molecules are inserted in a stack) depending on the length of aliphatic chains and we discuss the total energy of stacks. (In all this paper, the energies are given in kcal mole^{-1}).

II. THE ISOLATED MOLECULE CONFORMATION

A tabulation of results obtained in I, appears in Table I. Only one conformation of the isolated molecule is possible for the hexaether truxene derivatives. The chains stay perpendicularly to the plane of the central core.

The hexaester derivatives show two conformations. The first one, noted conformation A, corresponds to $\theta_2 = -\theta_2'$ (the rotation angles θ are defined in I). The chains stay in the two half-spaces separated by the plane of the core, in planes roughly parallel to the truxene core. They have the same general orientation. The second conformation, B, corresponds to $\theta_2 = \theta_2'$, i.e. the chains get away along opposite directions.

The obtained structures are drawn schematically on Figure 1.

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TABLE I

Geometrical parameters of ester and ether C_n truxene derivatives chains. n is the number of carbons in the chains.

	Chains	θ_1(°)	θ_2(°)	θ'_1(°)	θ'_2(°)
Ethers	C_7	−90	—	+88	—
	C_8	−90	—	+88	—
	C_{11}	−91	—	+88	—
Esters *A* type	C_7	−93	−100	+86	+95
	C_{11}	−93	−100	+86	+96
	C_{13}	−93	−101	+86	+96
Esters *B* type	C_7	−93	+94	+86	+94
	C_{11}	−93	+94	+86	+94
	C_{13}	−93	+94	+86	+94

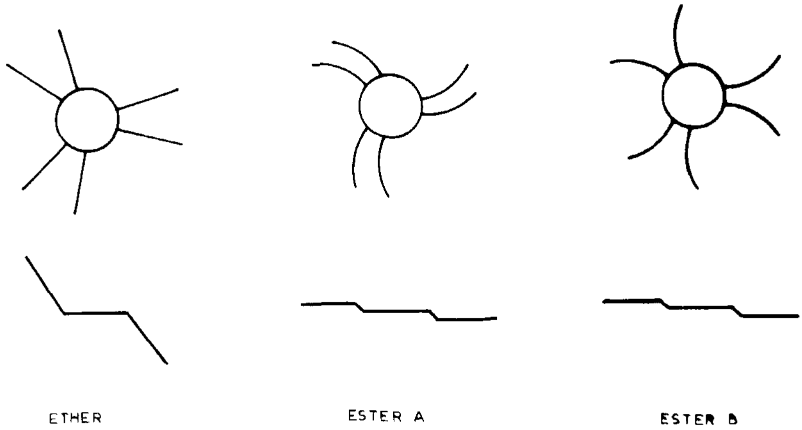

FIGURE 1 Scheme of different structures obtained for the truxene hexaethers and hexaesters derivatives.

III. RESULTS AND ANALYZE FOR SEVERAL MOLECULAR PACKINGS

The results corresponding to the ethers and esters derivatives structures are reported in Tables II and III. Each number corresponds to an intermolecular energy minimum (values in brackets), for the selected parameters. These are indicated in Figure 2. A threefold axis crosses the center of each molecule. The calculated energy depends on the distance between parallel cores, a, and on the rotation angle, α, of one core according to the other. ($\alpha = 0$ and $a = 0$ correspond to superimposed molecules). For the study of three interacting molecules, the

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TABLE II

Results on ethers molecules stacks

Number molecules in the column	Nomenclature	Type I			Type II			Type III		
		C_7	C_8	C_{11}	C_7	C_8	C_{11}	C_7	C_8	C_{11}
2 molecules	α(°) a(Å)	23° 3.60	23° 3.59	23° 3.58				61° 3.75	61° 3.75	62° 3.75
		(−35.89)	(−36.46)	(−37.94)				(−31.66)	(−32.72)	−32.35
3 molecules	α(°) a(Å)	23° 3.58	24° 3.54	23° 3.54	31° 3.46	31° 3.45	32° 3.46	60° 3.67	61° 3.70	62° 3.68
		(−74.94)	(−76.54)	(−79.09)	(−74.09)	(−76.51)	(−79.33)	(−69.22)	(−71.54)	(−72.25)
4 molecules	β(°) b(Å)	22° 3.68	22° 3.63	21° 3.69	31° 3.51	31° 3.49	32° 3.49	60° 3.64	61° 3.64	61° 3.64
a b a	α(°) a(Å)	23° 3.60	22° 3.64	22° 3.59	31° 3.51	31° 3.53	32° 3.49	60° 3.65	61° 3.68	62° 3.67
		(−115.62)	(−117.59)	(−126.8)	(−118.83)	(−123.27)	(−134.65)	(−108.67)	(−113.54)	(−121.71)
5 molecules	β(°) b(Å)	22° 3.65	22° 3.65	21° 3.69	31° 3.51	31° 3.52	32° 3.50	60° 3.65	61° 3.65	61° 3.65
ab ba	α(°) a(Å)	23° 3.58	22° 3.58	23° 3.58	31° 3.52	31° 3.53	32° 3.51	60° 3.65	61° 3.65	62° 3.65
		(−157.20)	(−160.45)	(−178.80)	(−164.15)	(−170.74)	(−190.45)	(−148.22)	(−155.56)	(−170.18)
5 molecules	β(°) b(Å)	22° 3.63	22° 3.63	21° 3.69	31° 3.51	31° 3.52	32° 3.50	60° 3.65	61° 3.65	61° 3.59
ab ab	α(°) a(Å)	23° 3.63	22° 3.63	22° 3.59	31° 3.52	31° 3.53	32° 3.51	60° 3.65	61° 3.65	62° 3.63
		(−156.86)	(−161.05)	(−175.26)	(−164.15)	(−170.74)	(−190.45)	(−148.22)	(−155.56)	(−170.58)

The nature of the parameters for a stack of molecules is mentionned in the column named "nomenclature". The distances a and b are given in Angstrom and are visualize on Figure 2 with the molecule rotation angles α and β.

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TABLE III

Results of some esters molecules stacks

Number of molecules in a column	Nomenclature	*A*	*A*	*A*	*B*	*B*	*B*
		Ester C_7	Ester C_{11}	Ester C_{13}	Ester C_7	Ester C_{11}	Ester C_{13}
2	$\alpha(°)$ $a(Å)$	46 3.49	47 3.48	45 3.40	17 4.42	17 4.40	13 4.53
		(−38.65)	(−43.67)	(−45.3)	(−31.96)	(−40.43)	(−44.34)
3	$\alpha(°)$ $a(Å)$	40 3.46	41 3.42	42 3.40	17 4.42	17 4.38	13 4.52
		(−88.59)	(−99.35)	(−103.03)	(−65.47)	(−84.95)	(−91.64)
4	$\beta(°)$ $b(Å)$	39 3.44	39 3.41	39 3.40	17 4.41	17 4.34	13 4.50
	$\alpha(°)$ $a(Å)$	46 3.49	42 3.42	45 3.40	17 4.41	17 4.36	13 4.52
		(−138.50)	(−158.53)	(−165.49)	(−98.99)	(−129.65)	(−139.14)
5	$\beta(°)$ $b(Å)$	41 3.44	40 3.41	41 3.40	17 4.41	17 4.36	13 4.51
ab ba ou ab ab	$\alpha(°)$ $a(Å)$	41 3.44	41 3.41	41 3.40	17 4.41	17 4.36	13 4.51
		(−190.59)	(−217.17)	(−225.60)	(−132.40)	(−174.25)	(−186.48)

a, b, α and β are visualize on Figure 2 for each stack type.

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molecule which lies at the mid position of the system is referred as zero level, the two other molecules being symmetrically arranged with respect to this central system. In the case of four interacting molecules, we have assumed the existence of dimers. The pair of identical dimers defined by the set of parameters (α, a) evaluated in I, are brought together along the three fold axis related to each molecule. β is the rotation angle between the two dimers and b, the distance between them. When the minimum of the interaction energy is obtained for the couple (β, b), we allow a change of the dimer parameters (α, a) in order to evaluate iteratively the best couple (β, b). The study of five interactive molecules constitutes a necessary step to verify the assumption of the existence of dimers in columns. Two sequences can be taken into account:

—The molecules are symmetrically arranged with respect to the central one. We call this sequence *abba* (Figure 2).

—An alternation of dimers is observed. This sequence corresponds to the two isoenergetical situations *abab* and *baba* (Figure 2). Unsymmetric configurations as *abcd* are much less probable because the high disorder leads to unstabilizing energies.

The analyze of Tables II and III shows a different behavior of the ethers and esters derivatives. For the ethers derivatives, three energy minima are obtained (structures I, II, III). For a stack of esters molecules we note only one configuration corresponding to an energy minimum. As for isolated molecule, two structures A and B exist, we shall observe two kinds of stacks for these compounds, corresponding to each of them.

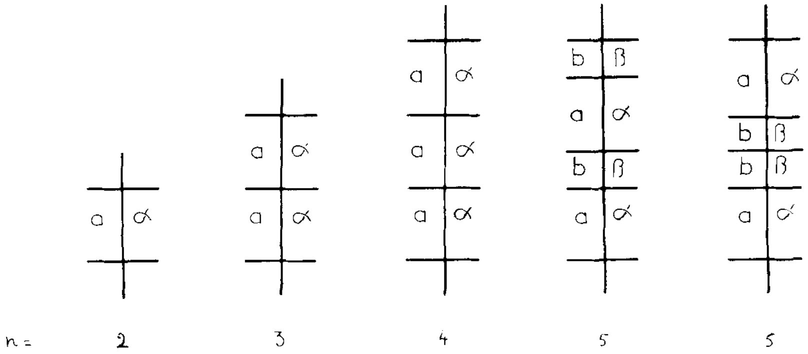

FIGURE 2 Stacks scheme with the different geometrical parameters used in this calculation. n corresponds to the number of molecules in the stack. a and b represent intermolecular distances and α and β are rotation angles of two successives molecules.

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A. Hexaethers of truxene

1. Minimum I investigation

a) General trends. In the case of two molecules, it is worth mentionning that the rotation angle between two neighbouring molecules is equal to 23°, whatever is the length of the chain. This value corresponds exactly to the angle between two adjacent chains in the isolated molecule (angle of C_{I}, threefold axis, C_{II} of Paper I). The chain lengthening has a tendency to approach the molecules for a stack of two or three systems. For larger columns (4 or 5 molecules), this tendency is no longer observed. Indeed, as the chains are perpendicular to the core, their increasing number provokes some steric hindrances between chain ends belonging to no-neighbouring molecules as the length of the chain increases. This phenomenon has a larger effect than the shortening of "*a*" with the length increase observed in the two or three molecules stack.

Thus, for a four molecules stack, "*b*", increases from 3.58 Å to 3.69 Å. The five molecules *abba* or *abab* compounds of ethers C_7 or C_8 have quite similar energies, that permit to suppose the existence of regular or irregular structure in the mesophase. On the contrary, as soon as the chain length increases, the steric hindrances between the chain ends of no-neighbouring molecules favour the irregular structure (*abba*). This point will be discussed further in the following for the hexaethers C_{11} derivatives.

b) Hexaethers C_{11} compounds analyze. The dimer angle equal to 23° corresponds to the central angle between the 0_1 atom, threefold axis, $0_1'$ atom of ref. 2, that is to say the chain at the positive level for the higher molecule, lies above the chain at the negative level for the lower molecule. In the trimer, the third molecule lies in a similar position, while the intermolecular distance is a little shorter. From the three molecules to the four molecules stack, one observes a decrease of angles (β and α), correlated to an increase of intermolecular distances (both *a* and *b*). Furthermore, the differences of β compared to α and *a* compared to *b* corroborate the assumption of dimers in the columns: we have pairs of molecules (parameters *a* and α) in interaction (*b* and β). The change in distances and angles can be explained by an increase of the steric hindrances between chains ends. The slight difference of β (21° compared to 23°) provokes some large modifications in the columns. Indeed, if we consider the whole regular structure, as the trimer one ($\alpha = \beta = 23°$), the extremity of negative level chains of the first molecule, touches the extremity of positive level chains of the fourth one. This is comforted by the calculation. The

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regular conformation, $\alpha = \beta = 23°$ and $a = b = 3.54$ Å, is very unfavourable, $E_T = +1053$ kcal mole^{-1}. On another hand, the irregular conformation $\alpha = 23°$, $\beta = 20°$ and $a = b = 3.54$ Å gives an energy of -109.39 kcal mole^{-1}. We can notice that a very small variation of the dimers rotation angle in the tetramere, induces a large energetic variation, favouring or not one of the conformations. Those angular variations are very important and their effects are already observed in the dimers. The energies for $\alpha = 23°$ and $a = 3.54$ Å or 3.58 Å are quite similar, but if $\alpha = 20°$ the energetic minimum is reached for $a = 3.89$ Å.

The big "b" value with regard to the "a" one, can be explained by the contribution of each molecule in a column on the total energy.

The results obtained from different values of a, b, α and β are listed in Table IV. In this table, E_{nm} is the interaction energy between the n^{ieth} and the m^{ieth} molecule and E_n, the energy of a stack of n molecules. When $\beta = 20°$, we can notice that the E_{23} variations induce the variations of the total energy E_4. The absolute value of the E_{23} energy decreases with the b distance, considering that the Van der Waals repulsive terms become important. When $\beta = 21°$, $\alpha = 23°$ the E_{23} variations are smaller and the E_4 variation is depending on the great E_{14} one, that is to say on some unstabilizing interactions between distant molecules ($d = 3.69$ Å + 3.58 Å = 7.27 Å). There are some interactions between the chains extremities, which decrease when b increases.

We can conclude that the adjunction of one molecule to a trimer stabilizes the whole system increasing the distance between the two central molecules. For $\beta = 21°$ and $\alpha = 23°$ the E_{nm} do not vary a lot and the structure corresponding to $b = 3.69$ Å is the more stable conformation.

The pentamer *abab* investigation shows that the structure of the tetramer is kept, and that for the same reasons. But we are going to explain why the pentamer *abba* is more stable. The total energy of the pentamer *abab* (Figure 2) can be written as:

$$E_5 = 2E_{12} + 2E_{23} + 3E_{13} + E_{14} + E_{25} + E_{15}$$

and equals -175.26 kcal mole^{-1} for the parameters (21°, 22°, 3.69 Å, 3.59 Å).

The E_{nm} energies are given in Table IV. The contributions E_{15} and E_{25} are respectively -0.706 and -8.18. For the symmetric stack *ab ba*, we have obtained $E_5 = 2E_{12} + 2E_{23} + 2E_{14} + 2E_{13} + E_{15} + E_{24}$

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for the parameters (21°, 23°, 3.69 Å, 3.58 Å), the total energy is equal to -178.80, $E_{14} = -9.04$, $E_{15} = -2.84$ and $E_{24} = -2.80$ kcal mole^{-1}.

We have seen in Table IV that for $\beta = 21°$ and $\alpha = 23°$, the interaction energy E_{14} is positive, but the distance between the first and the fourth molecules is greater in the *abba* pentamer than in the *abab* one. We have no more the *aba* sequence ($a = 3.58$ Å, $b = 3.69$ Å) with the E_{14} unstabilizing (Table IV).

2. Minimum II investigation

It is in each case the most stable conformation. This minimum of energy does not exist in the dimer. It corresponds to the angles α or β roughly equal to 31°. This angle value clarifies the structure, because if the chains are remote a little from each others, the steric hindrances are reduced. It results that:

—At each number of molecules per column and each length of the chains, the obtained points give the most stable energetic conformation.

—For a number of interacting molecules, the distances between the cores do not depend on the length of the chains.

—Inside a column, molecules are regularly stacked and the distances between the cores are of course shorter than those obtained with the minimum I (Table II).

3. Minimum III investigation

This new conformation is observed for the angles α and β roughly equal to 60°. In that case, a group of two aliphatic chains of a

TABLE IV

Interaction energy of each pair of molecules in hexaether C_{11} stack (minimum I), in function of column parameters

Parameters								
β(°)	α(°)	b(Å)	a(Å)	E_{12}	E_{23}	E_{13}	E_{14}	E_4
20	23	3.89	3.58	−37.94	−35.31	−2.71	−6.23	−122.82
20	23	3.69	3.58	−37.94	−32.92	−3.01	−4.90	−119.58
20	23	3.54	3.54	−37.81	−24.70	−3.24	−2.58	−109.39
21	22	3.89	3.59	−37.52	−35.70	−2.71	−8.88	−125.09
21	22	3.69	3.59	−37.52	−36.61	−2.96	−9.21	−126.78
21	23	3.89	3.59	−37.91	−37.70	−2.75	+12.60	−104.50
21	23	3.69	3.59	−37.91	−36.61	−3.02	+21.21	−97.32

molecule lies between the two groups of neighbouring molecule. In a column, the first and the third molecules are exactly superimposed.

While increasing the interatomic interactions, this corresponds to a decrease of the distances and an energetic stabilization. But the leading interactions for the structure as a function of the chain length are those of type E_{nn+3}. Indeed, the chains are perpendicular to the core plane so that their ends are far from the core. This explains the difference of structure between C_7, C_8 compounds and C_{11} compounds.

Note: It is hard to make good three-dimensional representations of molecules in stacks, because of numerous atoms which interact in these systems. For example we represent in Figure 3 the structure of two molecules of ether in interactions for $\alpha = 23°$ and $\alpha = 61°$, showing the spacial occupation in these systems. If we add one

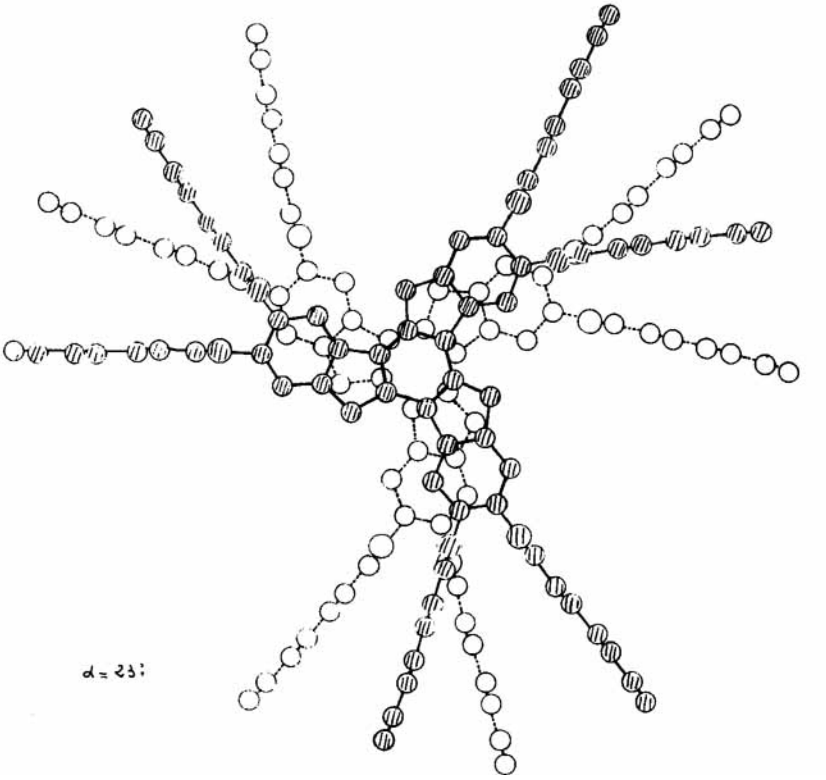

FIGURE 3 Representation of two hexaether truxene molecules in a column (in the plane of the molecular core) corresponding to two values of minimal energies. One may note the importance (and the difference) of space occupation by aliphatic chains although H atoms has not been reported.

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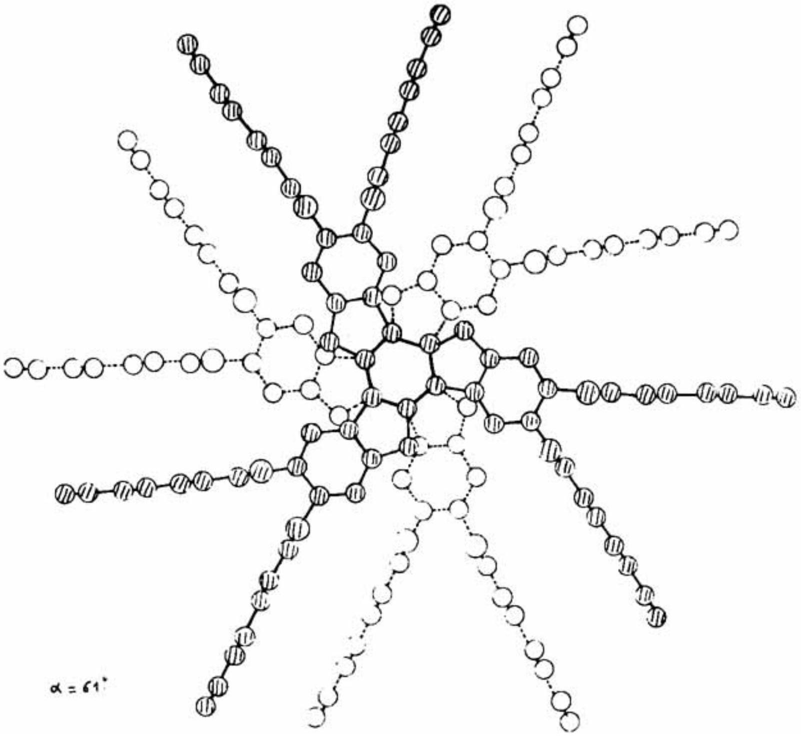

FIGURE 3 (*Continued*)

molecule or more, the drawing will be very difficult to interpret and the discussion of the interactions issued from the visualisation could be incorrect. Only results of the computational procedure can give unambiguous interpretation of the origin of the stabilization (or destabilization) i.e. interatomic distances between atoms belonging to different molecules and the corresponding interatomic energies between these two atoms.

B. Esters derivatives study

Whatever is the isolated molecule, we note that the results are roughly regular. The aliphatic chains are lying near the molecular cycle. We can always say that the esters molecules can be assimilated to a crown

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enclosing the chains, while for the ethers, the chains are perpendicular to the central core and are very extended in space. So, for the esters, the interactions between the chains extremities, belonging to outlying molecules, will be very low. That is the reason why almost the same intermolecular distances are observed, whatever the number of molecules in a column is.

1. A derivatives. In the case of the A derivatives, we note a large regularity.

The total energy mainly depends on the interactions E_{nn+1} and E_{nn+2} similar to the ones observed in the dimer and the trimer. Thus, these interactions correspond to the two structures observed in these compounds:

—If the number of molecules in a column is even, this column is built up by a stacking of dimers having the isolated dimer parameters. So that the distances between two monomers exhibit an alternation.

—If the number of molecules is odd, all the interactions are intermediate.

The structure is regular and all the molecules are disposed as in the trimer. An helicoidal structure must appear for this structure.

2. B derivatives. Whatever the chains length is, a large regularity is also observed for the B esters compounds. It must be a helicoidal structure according to this stack.

For the C_7 and C_{11} compounds, two molecules are separated by an angle equal to 17°. While for the C_{13} derivatives, we note a decrease of this value (equal to 13°) and a great distance between the central core (d is roughly equal to 4.51 Å). We can simply explain this phenomenon considering only one dimer. Indeed, we recall that in the isolated molecule, two neighbouring chains belonging to the same benzyl lie in the two half spaces separated by the central group. The addition of another molecule creates some strong interactions between the chains extremities of these two molecules. That is what we have shown in the figure. In this scheme, we see that the chain at the positive level (+) of the low molecule, touches the chain at the negative level of the high molecule and that, all the more as the chains are long. So, to decrease the repulsion, the molecules tend to turn less (α decreases from C_7 to C_{13}) and to get away from each other (d increases). To conclude, we can say that for the molecules of B structure, the increase of chains makes the columns longer and longer for the same number of molecules and sets these ones very regularly (Figure 4).

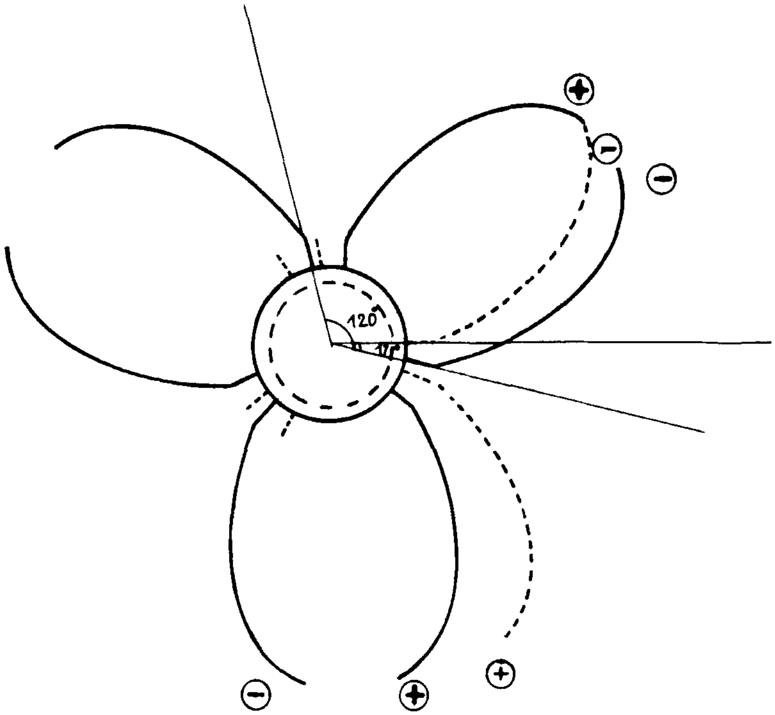

FIGURE 4 Two molecules of truxene hexaester C_{11} (B structure) stacked. The low molecule is drawn with continuous line, the high molecule with dotted line. The chains on top of the central core are quoted + and the chains under it are quoted −.

IV. STUDY OF THE CHAINS POSITION IN A STACK

We can think that, in a stack of several molecules, the chains have not the same position than in the isolated molecule. The rotation possibilities are:

a—The variation of the angles θ_1, θ_1', θ_2, θ_2'. In that case, the total energy is the sum of the intermolecular energy and the intramolecular energy of each molecule in the system. The calculations shows that, although the intermolecular energy is a little reduced, the intramolecular energy increases a lot. That is to say that the new chains position which stabilizes the system a little, does not compensate the unstabilization of the isolated molecule. We give as an example the results obtained in the trimer study. We change the positions of the chains belonging to the central molecule. Results are listed in Table V.

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TABLE V

Analysis of energy variations in function of the rotation of the aliphatic chains of the central molecule in a trimer

	Angles variation	Intermolecular energy variation	Intramolecular energy variation	Total variation
ester C_{11}	$\Delta\theta_1 = 11°$ $\Delta\theta_1' = 11°$	-3.5	$+5.1$	$+1.6$
ether C_7	$\Delta\theta_1 = 10$ $\Delta\theta_1' = 11°$	-0.76	$+0.8$	0

b—The variation of the aliphatic chains extremities. A variation of the chains ends does not induce any stability, whatever is the number of the studied atoms.

So, we can conclude that in a column, the most favourable situation corresponds to molecules conformation roughly the same one as the isolated molecules.

V. INTERACTION BETWEEN TWO COLUMNS

The columns are compound of five molecules and have the structure previously obtained. The used parameters are, the distance between the two threefold axis, d, and the rotation angle, γ, of one column around its axis, the other being fixed (Figure 5). There are a lot of minima, each corresponding to some very small area. On account of the calculation time length, we have only studied the C_7 derivatives (5

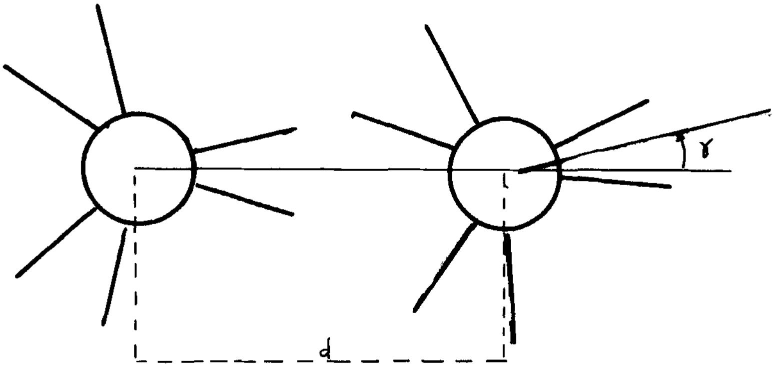

FIGURE 5 Intercolumnar parameters: d distance and γ rotation of a molecule in regard of the other.

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TABLE VI

Interaction between two columns of five molecules (hexaethers and hexaesters C_7)

	Ester C_7 *A*	Ester C_7 *B*	Ether C_7		
column diameter	30.4 Å	27.4 Å	30.8 Å		
			type I	type II	type III
parameters of the column	41° 3.44 Å	17° 4.41 Å	22° 3.63 Å	31° 3.51 Å	60° 3.65 Å
	41° 3.44 Å	17° 4.41 Å	23° 3.63 Å	31° 3.52 Å	60° 3.65 Å
γ, d	64° 28 Å	54° 29 Å	0° 30 Å	5° 30 Å	55° 27 Å
	(−2.89)	(−2.66)	(−2.63)	(−2.77)	(−14.62)
	100° 28 Å	0° 28 Å	59° 30 Å	26° 29 Å	21° 30 Å
	(−4.48)	(−3.43)	(−2.79)	(−2.76)	(−4.22)

structures) and the C_{11} derivatives (2 structures). The results reported in Table VI and Table VII correspond to the lowermost energies.

In the first line, we give the column diameter c which represents the largest calculated distance in the core plane when we project all the atoms. When the diameter c is larger than d, the columns interpenetrate each others. This is actually observed for all the points indicated in the tables. However, these interpenetrations and the corresponding interaction energies being slight, we can suppose that the columns can slip from each other. We repeated this study while shifting one column with regard of the other of the value $a/2$. Molecules in different columns are no more facing and are intercalated. We have roughly obtained the same results than previously. That corroborates our hypothese of sliping columns. It is interesting to note the great interaction energy between two columns of type III hexaethers C_7, for $\gamma = 55°$. We have seen that the rotation angle between two molecules in a column is equal to 60°, every two chains groups of one molecule lies between two groups of the neighbouring

TABLE VII

Interaction between two columns of five molecules (hexaethers and hexaesters C_{11})

	ester C_{11}	ether C_{11}
column diameter c	38,7 Å	39.7 Å
parameters of the column	37° 3.41 Å	32° 3.50 Å
	37° 3.41 Å	32° 3.51 Å
γ, d	21° 37 Å	20° 38 Å
	(−2.606)	(−1.86)
	54° 35 Å	63° 39 Å
	(−5.54)	(−1.89)

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molecule. Space around the cores is not very encumbered and the chains belonging to the neighbouring column can penetrate more deeply. The columns slip will be, if it is possible, more difficult to observe. However, the intercolumnar energy (-14.62 kcal mole^{-1}) of this conformation with regard of the energies of type II or III does not make up the energies difference of the isolated columns. The structure of two type II columns seems to be the most stable one for the hexaether C_7 derivatives.

On the Figure 6 we represent a stack of the structure corresponding to the interaction between stacks of ethers (type III) when the rotation angle between two consecutive molecules in a column is 60°, which corresponds to $\gamma = 55°$. For other derived structures, a representation is dangerous in reason of the complexity of the position of the chains.

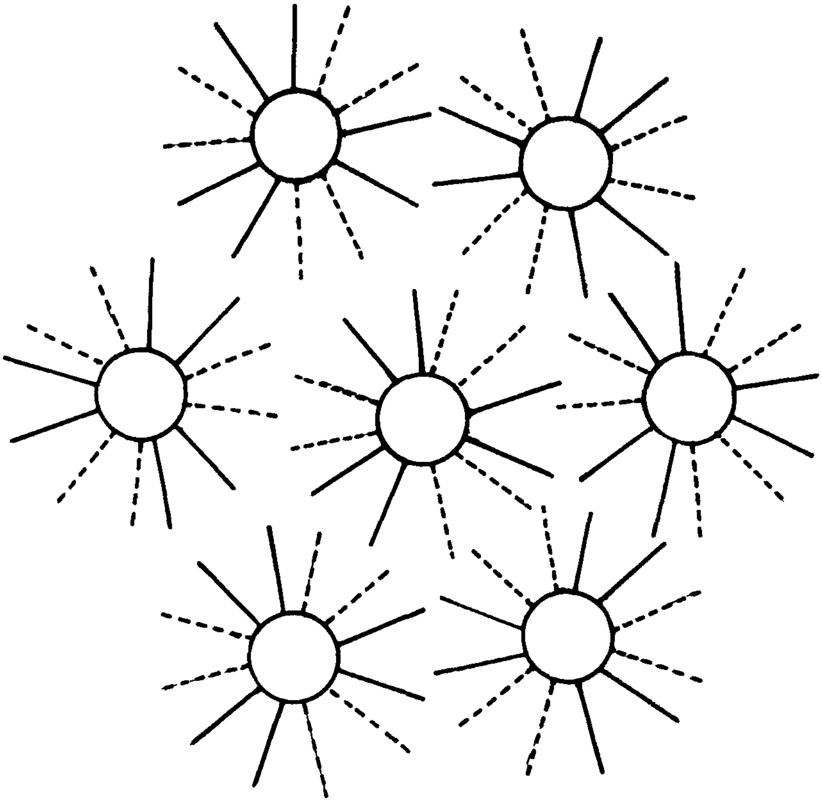

FIGURE 6 Shematic aspect of bimolecular stacks in interactions (structure of type III).

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CONCLUSION

The analysis of molecular interactions for a stack of ester or ether derivatives has shown the importance of the isolated molecule configuration. The chains position is determining for the molecules behaviour in a column. Thus, the hexaethers have different conformations than the hexaesters. For the esters compounds, we have shown the existence of two different structures, directly related to the two isolated molecule configurations. Into the first case $A(\theta_2 = -\theta_2')$, the stack structure does not depend on the chains length. The conformation is due to the interactions between the cores and between the atoms near the cores. The second conformation, $B(\theta_2 = \theta_2')$, is very sensitive to the number of carbons in the aliphatic part. A chain length increase results in an increase of the distance between molecules and the energy of the system varies quite largely with a slight variation of any geometrical parameter. The ethers derivatives exhibit three different structures for the same isolated molecule conformation. Configurations II and III do not depend on the chains length.

Study of interactions between two columns shows that they can slip from each others according to the slight interaction energy obtained. We can find some columns constituted by alot of molecules but also some piece of column like trimer or tetramer.

Comparison with experimental results is difficult in particular, because the crystal phase cannot be study by X-ray diffraction. However recent X-ray measurements in the mesomorpic phase (1,5) corroborates some observations resulting of our calculations (in particular, the relations between structures and chain lengths). But, assignment of close calculated structures with mesomorphic phases seems premature.

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