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Molecular conformation and arrangement of a disc like compound by semi-empirical calculations

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Résumé. — L’hexapropylester du 2, 3, 6, 7, 10, 11 hexahydroxytriphenylène, molécule discoide appartenant à une série de composés, dont certains présentent une phase thermotrope nouvelle a fait l’objet d’une étude conformationnelle par des méthodes semi-empiriques. La conformation préférentielle correspond à des chaînes alternativement situées au-dessus et au-dessous du noyau triphénylène, le groupement ester faisant un angle de 56° avec ce dernier. Les molécules s’associent par paires très stables correspondant à une configuration bien définie. Un arrangement des molécules en colonnes est proposé.

Abstract. — The 2, 3, 6, 7, 10, 11 hexahydroxy triphenylene hexapropylester, a disc like molecule belonging to a series of compounds, some of which show a new mesomorphic and thermotropic phase has been studied by semi-empirical conformational analysis. In the preferential conformation, propyl ester chains are alternatively situated about and under the triphenylene core, the ester group making an angle of 56° with this latter. Molecules are associated in very stable pairs, with a rather specific configuration. A molecular arrangement in columns is proposed.

Introduction. — It is a well-known fact that a great number of rod like molecules are able to give a nematic, smectic or cholesteric phase (liquid crystal). Recently it has been shown that disc like molecules are able to give a thermotropic mesomorphic phase (called discotic mesophase) which is in fact, a new state of matter, very different from nematic or smectic phases [1, 3]. A few families of mesogenic disc like molecules having somewhat different symmetry are known at the present time ; a review on their discotic mesophases has been published very recently by J. Billard [1].

The first molecules which have been synthesized and showing a discotic mesomorphic behaviour are :

— the hexasubstituted benzene derivatives : benzene-\(n\)-alkanoates, with a \(6/m\) symmetry [2],

— the hexasubstituted triphenylene derivatives, with a \(3\ m\) symmetry [3].

Other molecules with a non hexagonal or trigonal symmetry and showing nevertheless a discotic mesophase have been studied ; this is the case for rufigallol (1, 2, 3, 5, 6, 7 hexahydroxy 9, 10-anthraquinone) hexa-\(n\)-alkanoates with a \(2/m\) symmetry [4].

We first take an interest to the hexasubstituted triphenylene derivatives whose general formulae is :
Three homologous series have been synthesized up to now with:

\[ R=O-C\text{H}_{2n+1} \] (hexaethers) [5]
\[ R=O-C\text{C}_n\text{H}_{2n+1} \] (hexaesters) [5]
\[ R=O-C\text{C}_n\text{H}_{2n+1} \] hexabenzoates [6].

Very recently an optical texture very similar to a nematic one has been observed for the latter series and a molecular arrangement proposed [7]. The crystal structure of the hexapropylester (the molecule of the second series with \( n = 3 \)) has been solved [8]; molecules in the crystal are associated in pairs with their triphenylene cores parallel and 3.43 Å apart. These dimers give columns arranged in an hexagonal lattice. It must be kept in mind that pairs in a column are separated by a distance as large as 17.1 Å, aliphatic chains of one column being inserted in the free space of the neighbouring ones.

The purpose of the present work is to look at the conformational freedom of the isolated molecule and the possibility of forming pairs; eventually to refine the geometry and stability of such pairs. In a following paper we shall propose a mechanism for the crystalline to the mesomorphic phasis transition.

1. Methodology. — 1.1 Molecular Geometry. —
Bond lengths and angles used in the present paper result from mean values observed in crystal structures of molecules having common chemical groups with the present one [9]. As far as C-C, C-O distances and C-C-C, C-C-O, O-C-O angles are concerned, data come from X-ray diffraction; for C-H distances and C-C-H angles they result from neutron diffraction. The selected values are the following:

- C-C (ring) : 1.40 Å
- C-O : 1.40 Å
- C-O : 1.34 Å
- C-C-C : 1.20 Å
- C-C-C : 1.50 Å
- C-C-C : 1.53 Å
- C-H (ring) : 1.07 Å
- C-H (chain) : 1.09 Å

See figure 1 for atom labelling.

1.2 Calculation Procedure. — The calculation of conformational energy has been performed by using semi-empirical methods described by Schraga [10]. For each conformation the total energy \( E_T \) is calculated as:

\[ E_T = E_{\text{VW}} + E_{\text{el}} + E_{\text{rot}} \]

where \( E_{\text{VW}} \), \( E_{\text{el}} \) and \( E_{\text{rot}} \) are respectively the Van der Waals, electrostatic and torsional contributions.

The Van der Waals term has been calculated using the well-known Lennard-Jones function:

\[ E_{\text{VW}} = \sum_{ij} \left[ -\frac{A_{ij}}{(r_{ij})^6} + \frac{B_{ij}}{(r_{ij})^12} \right] \]

where \( r_{ij} \) is the distance between \( i \) and \( j \) atoms, \( A_{ij} \) and \( B_{ij} \) are coefficients which depend on the nature and the hybridation states of \( i \) and \( j \) atoms; the values used here are those of Hopfinger [11].

The electrostatic contribution is given by the relationship:

\[ E_{\text{el}} = \sum_{ij} \frac{q_i q_j}{\varepsilon r_{ij}} \]

where \( q_i \) and \( q_j \) are the partial charges centred on non-bonded \( i \) and \( j \) atoms calculated by the CNDO/2 method, with the formalism and parameters of Pople and Beveridge [12]; 332 is a conversion factor to get \( E_{\text{el}} \) in kcal.mole\(^{-1}\), \( \varepsilon \) the dielectric constant taken equal to 1.

The rotational energy is calculated through the following formulae:

\[ E_{\text{rot}}(\theta) = \frac{1}{2} E_{\text{max}}(\theta) (1 + \cos n\theta) \]

where \( E_{\text{max}}(\theta) \) is the barrier height and \( n \) the periodicity of the function. For the rotation around \( O_1-C_0 \), \( E_{\text{max}}(\theta) = 8.75 \text{ kcal.mole}^{-1} \) as for ethyl acetate [13], so this rotation is not allowed. For the rotations

\(^{(1)} \text{ All energy terms are expressed in kcal.mole}^{-1}.\)

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Fig. 1. — Schematic representation of the studied molecule, with torsional angles. Hydrogen atoms are not represented.
around C\textsubscript{2}H\textsubscript{2}O bond (\(\theta_1\)) and C\textsubscript{6}-C\textsubscript{1} bond (\(\theta_2\)), \(E_{\text{max}}(\theta)\) is close to 0.5 kcal. mole\(^{-1}\), as for acetoxymethyl in carbohydrates [14] and acetic acid [15] respectively. These rotations barriers are very low. On the other hand, the rotation barrier in ethane, about 2.7 kcal. mole\(^{-1}\), is much higher; that is why we suppose the propyl chain to be in the trans conformation.

2. Conformation of the isolated molecule. — The molecule here studied is the hexapropylester of triphenylene. In a first step we suppose that it has a threefold axis of symmetry as it is the case in the crystal. So there are two independent chains called I and II, whose movements can be described by four torsional angles : \(\theta_1, \theta_2, \theta_1', \theta_2'\) (see Fig. 1); they are defined as follows : \(\theta_1, \theta_1'\) correspond to the \([\text{C}_1\text{v}-\text{C}_1-\text{O}_1-\text{C}_\text{O}]\) and \([\text{C}_i,\text{v}-\text{C}_i\text{v}-\text{O}_i-\text{C}_\text{O}]\) dihedral angles and \(\theta_2, \theta_2'\) correspond to the \([\text{C}_1\text{v}-\text{C}_1-\text{O}_1-\text{C}_\text{O}]\) and \([\text{O}_i-\text{C}_i\text{v}-\text{C}_i\text{v}-\text{C}_\text{O}]\) angles for chains I and II respectively; a positive value is relative to a clockwise rotation around a given bond when looking from the aromatic core to the end of the chain.

The starting conformation \((\theta_1 = \theta_1' = -90^\circ; \theta_2 = \theta_2' = 180^\circ)\) is relative to chains I and II respectively situated above and under the triphenylene ring. The total energy \(E_T\) is minimized in the following way:

- \(\theta_1\) is varied while the other angles are maintained invariant; the energy \(E_T\) varies with \(\theta_1\) and reaches a minimum for some \(\theta_1\) value, let us say \(\theta_1\)\text{min}\.

\(\theta_1\) is then fixed to its minimum value and \(\theta_2\) varied, while \(\theta_1'\) and \(\theta_2'\) are invariant. This procedure is successively used for all torsional angles considered. Angular steps are taken equal to \(1^\circ\).

The conformation of lowest energy is obtained for:

- \(\theta_1 = \theta_1' = -56^\circ; \theta_2 = \theta_2' = -77^\circ\). The \(\theta_1\) value is similar to that found in the crystal structure of diphenylsuccinate, the angle between the phenyl cycle and the carboxylate group being equal to \(64^\circ\) [16].

Variation of energy versus one or several angles around the minimum energy point give good pictures of the conformational freedom of the molecule.

a) One of the two chains, chain II for example, is supposed to be in its most stable conformation \((\theta_1 = -56^\circ; \theta_1' = -77^\circ)\) when the other one, chain I presently is allowed to rotate around the C\textsubscript{2}H\textsubscript{2}O bond, the propyl ester chain being fixed in its most stable conformation. The plot of \(E\) versus \(\theta_1\) is shown in figure 2. It can be seen that \(\theta_1\) is restricted to move between:

- \(-48^\circ\) and \(-73^\circ\) : one chain is above, the other one under, the triphenylene core (configuration i);

- \(76^\circ\) and \(125^\circ\) : both chains are on the same side of the triphenylene core (configuration ii);

for \(\Delta E \leq 0.6\) kcal (RT at room temperature).

The energy difference between the two configurations is only 0.4 kcal. mole\(^{-1}\).

b) This time, only the \(\theta_2\) angle of chain I is allowed to change, \(\theta_1\) being fixed to its minimum value. The plot of \(\Delta E\) versus \(\theta_2\) is shown in figure 3. It can be seen that \(\theta_2\) can move in a rather large interval between:

- \(-120^\circ\) and \(-40^\circ\) for \(\Delta E \leq 0.6\) kcal,

- \(-180^\circ\) and \(-20^\circ\) for \(\Delta E \leq 1.35\) kcal.

c) Both \(\theta_1\) and \(\theta_2\) were allowed to vary; the \((\theta_1, \theta_2)\) plot is shown in figure 4. It appears that if \(\theta_1\) variations are limited, \(\theta_2\) ones are very large.

d) If we take now the whole molecule, a minimization over all angles gives for the torsional angles the same values as previously obtained, showing that there are no interference between chains fixed to contiguous benzene rings.

With \(\Delta E \leq 1.35\) kcal (corresponding to the probability of finding \(\theta_1\) around its minimum value equal to 0.9), the domains are somewhat larger especially for configuration i;

- from \(-45^\circ\) to \(-90^\circ\) for configuration i;
- from 73 to 140^\circ for configuration ii.

The conformation (i) with the plane of the ester chains perpendicular to the aromatic core considered further is about 1 kcal. mole\(^{-1}\) above the minimum configuration.
3. Conformational study of dimer. — The molecules are supposed to lie on a threefold axis (Oz) as it is the case in the crystal. They are allowed to move along this axis and around it. The distance between parallel cores is called $d$ and the rotation angle $\alpha$ (the $\alpha = 0^\circ$ position is relative to molecules coinciding in projection along Oz).

In a first attempt, both molecules are supposed to be in the configuration I with the plane of their chains perpendicular to their aromatic core. The energy of interaction has been calculated for $d$ varying between 3 and 7 Å and $\alpha$ between 0 and 120°. Steps have been taken equal to 0.1 Å for $d$ and 20° for $\alpha$.

A rather sharp minimum appears for $d \simeq 3.3$ Å and $\alpha \simeq -45^\circ$; it is relative to a dimer in which $O_2$ oxygen atoms of one molecule lie opposite to two adjacent hydrogen atoms of the other molecule (see Fig. 5).

The corresponding association energy between the two molecules is quite high ($^{(2)}$): $\Delta E \simeq -58$ kcal, owing to numerous Van der Waals interactions between the aromatic cores and probably also to dipole-dipole interactions involving carboxylate groups.

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$^{(2)}$ It must be kept in mind that energy calculated through semi-empirical functions cannot be directly compared to experimental value if any.
Let us recall that for rod like mesomorphic compounds in which head to tail pairs are observed the association energy calculated in the same way is about $-30 \text{ kcal}$ [17, 18].

4. Conclusion. — Semi-empirical calculations show that molecules of triphenylene hexaesters form pairs, whose stability is very high. It is likely that such pairs remain in the mesophase and probably to some extent in the liquid phase. With the hypothesis of ester chains perpendicular to the triphenylene core, the examination of molecular models shows that two such pairs cannot approach each other nearer than 7.5 Å along the $z$ axis. An arrangement like the one shown in figure 6 may be obtained, if we suppose that molecules form independent columns parallel to the $z$ axis. Interactions are of Van der Waals type between pairs in a given column and between neighbouring columns.

References