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Mesogenic properties of 1,2,3-tri-[3′-(4″-alkoxyphenyl)-3′-oxo-1′-propenylamino]propane

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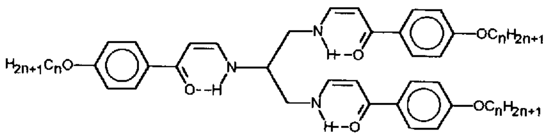
The properties of compounds incorporating three mesogenic cores linked to a central 1,2,3-trisubstituted propane unit are reported. They form S_A and S_C calamitic liquid crystalline phases with a layer spacing in the orthogonal smectic phase significantly smaller than a single molecular length. The mesogenic properties of related molecules with two mesogenic cores depend on the position of the enaminoketone ring with respect to the joint. Intramolecular dipolar interactions of the enaminoketone rings are suggested as being responsible for the hindered frmation of the *trans*-conformational structure of the cores in the dimeric molecules.

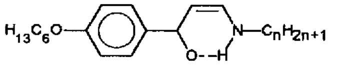
1. Introduction

Dimeric molecules, incorporating two mesogenic cores joined by a flexible of sem-flexible joint, are well known among compounds forming liquid crystals [1, 2]. Trimeric molecules, with three mesogenic cores, are less common, and so far only a few such mesogenic structures have been reported [3–8]. In this communication we briefly describe the properties of the triplets with formula **1** (compounds are denoted for short Tri-*n* where *n* indicates the number of carbon atoms in the terminal alkoxyl chains).



1

The Tri-*n* compounds have been obtained by linking three rigid cores to a central 1,2,3-trisubstituted propane unit. The two ring enaminoketone-phenyl moiety has been used as the rigid core. Such simple core structures formed by an enaminoketone quasi-ring, stabilized by hydrogen bonding, and a phenyl ring (formula **2**) were found to be sufficient to produce mesomorphic materials. For example, the 1-alkylamino-3-(4′-hexyloxyphenyl)-1-propen-3-one (abbreviated as PhE-*n*) exhibits a Cr–S_C–I phase sequence (see the table).



2

The phase transition temperatures (in °C) and in square parentheses the relevant transition enthalpies (in kJ mol^{-1}) from DSC. Monotropic transitions are given in round parentheses.

	Cr		Cr-B		S_C		S_A		I
1 Tri-6	●	110[a]	—		●	(98·4) [1·56]	●	127·6 [5·46]	●
Tri-8	●	120[a]	—		●	(81·0) [1·3]	●	135·7 [4·32]	●
2 PHE-6	●	32·0[b]	—		●	36[b]	—		●
PHE-11	●	35·6[b]	—		●	53·4[b]	—		●
PHE-13	●	52·5[b]	—		●	(51·8[b])	—		●
3 a Dim-O6	●	210·0 [14·06]	—		—		—		●
3 b Dim-7	●	145·3 [12·92]	●	182·4 [5·46]	—		●	197·3 [17·78]	●

[a] Multiple broad peaks.
[b] Temperature given is based on microscopy.

2. Experimental

All enaminoketones, with the exception of 4,4′-di-(3″-oxo-1″-decenyl)aminobibenzyl **3 b**, were obtained by reacting 3-(4′-alkoxyphenyl)-3-oxopropanal *in situ* [9] with 1-alkylamines (C_6–C_{13}), 1,2-diaminoethane and 1,2,3-triaminopropane [10], in proportions determined by the number of NH_2 groups see the scheme. The reaction was conducted using a methanol as solvent. The enaminoketones obtained from 1-alkylamines were in an oily state. They were separated after cooling to −20°C. Crude products were dissolved in hexane at room temperature and cooled quickly to −70°C. The yellowish

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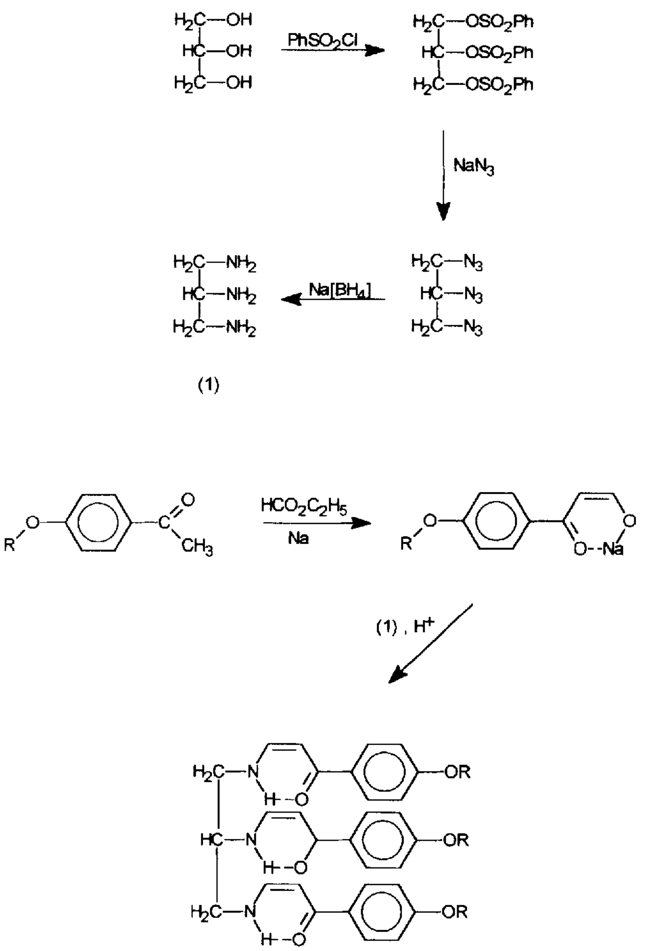
micro-crystals were then collected. Other compounds of this type were obtained as solids from methanol at room temperature and recrystallized from octane. The 4,4′-di-(3″-oxo-1-decenyl)aminobibenzyl was obtained by a similar route by reacting 4,4′-diaminobibenzyl with 3-oxo-decanal. The product was collected at room temperature and recrystallized from toluene. For all compounds, the C, H, N elementary analyses were satisfactory. As our example, we quote the analysis for compound Tri-8: cal 72·6%C, 9·82%H, 5·30%N; found 72·68%C, 9·90%H, 5·25%N.

The NMR spectra of which we quote that for Tri-8:^{1}H-NMR (CDCl$_3$): δ 0·80–1·90 (m, 45H, (CH$_2$)$_6$ CH$_3$); 3·15–3·55 (m, 5H, H^{1,2,3}); 3·98 (t,J=6·5 Hz, 6H, OCH$_2$); 5·69 (d, J=7·8 Hz, 3H, H$^{2'}$); 6·60–6·95 (m, 9H, H$^{1'}$ and H$^{3'',5''}$); 7·82 (d, J=8·9 Hz, 6H, H$^{2'',6''}$); 10·1–10·4 (m, 3H, NH), were consistent with the molecular structures.

The phase transitions were studied by polarizing optical microscopy (Zeiss, Jenapol-U), differential scanning calorimetry (Perkin Elmer DSC7) and X-ray scattering (DRON).

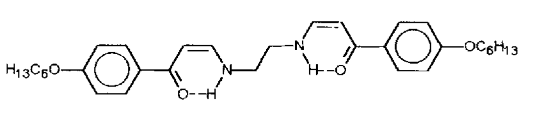


Scheme. The synthesis of the compounds Tri-n.

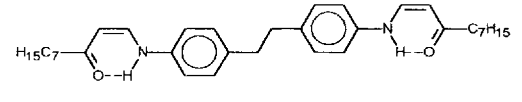
3. Results and discussion

The trimeric derivatives Tri-6 and Tri-8 melt from the crystal to the S$_A$ phase (transition temperatures and relevant enthalpies are collected in the table). When the compounds are supercooled, a tilted smectic, most probably a S$_C$ phase, also appears. The texture of this phase is weakly birefringent, but a schlieren texture, which is characteristic of the S$_C$ phase, was not observed. Conoscopic observations performed on the S$_A$ phase on freely suspended films ($\sim$20 µm) indicated the phase's uniaxial character, confirming free rotation of the molecules around their molecular long axes. The X-ray diffraction studies with powder samples showed that both phases have a liquid-like in-plane order. The layer spacing d in the S$_A$ phase formed the Tri-n, was found to be significantly smaller than the length L of the fully extended molecule ($d/L \sim 0·8$). The d value increases considerably with decreasing temperature (figure 1) in the range corresponding to the S$_A$ phase. The layer spacing determined, which does not coincide either with the molecular length L or with the length of a single calamitic moiety ($\sim L/2$), points to the intercalation of molecules from consecutive smectic layers. The corresponding layer permeation occurs to a length of 3·25 and 3·0 carbon atoms for Tri-8 and Tri-6, respectively. The $d/L \ll 1$ can be explained by taking into account the overall shape of the Tri-n molecule rotating freely around its long axis placed through the centres of molecular mass. The shape of such a molecule can be approximated by two co-axial cylinders with diameters $\sim$5·3 Å and 6·5 Å (figure 2). At a high temperature, the structure of a S$_A$ phase with random head–tail, tail–tail, and head–head mutual molecular orientations can be supposed (figure 2). The loose packing conditions relevant to such a structure would allow for a significant interdigitation of the terminal alkyl chains of the molecules from successive layers. As the temperature of the system decreases, a more efficient packing of molecules which favours head–tail molecular orientation would take place leading to less suitable conditions for terminal chain interdigitation and thus the increase in the smectic layer thickness observed experimentally.

For comparison, the dimeric molecules **3a**, **3b** incorporating two core units, with a simple cylindrical shape, were also studied.



3a



3b

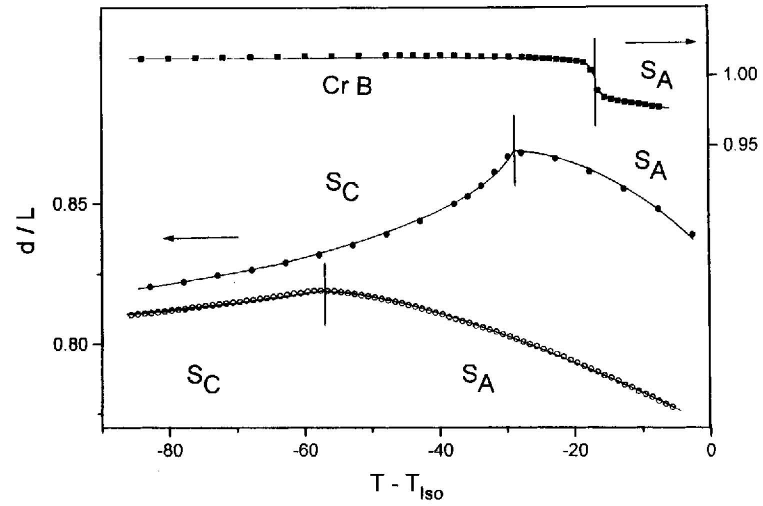


Figure 1. Variation of d/L with temperature for the compounds **1** (Tri-6 ●; Tri-8 ○) and compound **3b** ■.

The derivative **3a** melts to the isotropic phase, and does not form liquid crystalline phases even if supercooled, while the compound **3b** possesses S_A and CrB phases over a broad temperature range (see table). The layer spacing determined coincides well with the molecular lengths (figure 1), and is nearly temperature independent as expected for molecules with a uniaxial cylindrical shape. The small jump in the d/L value at the S_A–CrB transition is due to changes in the orientational and transitional order of the molecules.

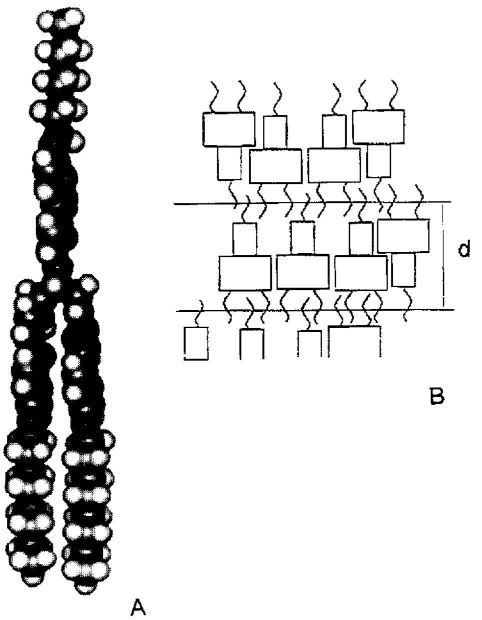


Figure 2. (A) the model of the Tri-8 molecule; (B) schematic drawing of molecular packing for the Tri-*n* compounds in the S_A phase.

The different liquid crystalline properties of compounds **3a** and **3b** are rather surprising, since in the first approximation we would expect that in both cases, steric hindrance would favour mesogenic conformers with *trans*-arrangements of the bulky core units. The different behaviour of compounds **3a** and **3b** is probably related to the different strengths of the dipolar intramolecular interactions. This assumption is supported by molecular energy calculations performed with Hyperchem 4.1 molecular modelling software using the molecular-mechanics procedure. Although the calculations relate only to the single molecule, and so should be treated with caution, they show that the molecules with a *cis*-conformation of the bulky groups adopts a pyramidal shape in which the distance between the enaminoketone dipoles is 3·74 Å and 6·31 Å for **3a** and **3b**, respectively. For compound **3b** in which the dipoles are at a larger distance, the mesogenic conformer with a co-linear disposition of the core groups has the lowest energy and would dominate. The competition between dipolar and van der Waals interactions leads in molecule **3a** to an energy minimum for the non-mesogenic conformer. The conformer in which the core groups are bent at an angle 43° has nearly 20% lower energy than the co-linear one.

4. Conclusions

We have reported novel trimeric compounds incorporating an enaminoketone ring, capable of forming S_A and S_C calamitic liquid crystals phases. The geometry of these molecules can be approximated by two co-axial cylinders. Such a geometry influences molecular close packing conditions inside the smectic layers resulting in a low value of $d/L \sim 0{\cdot}8$. For related dimeric molecules with a uniaxial shape, $d/L \sim 1$ was found.

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