Novel Thermotropic and Lyotropic Double Headed Diol-based Mesogens

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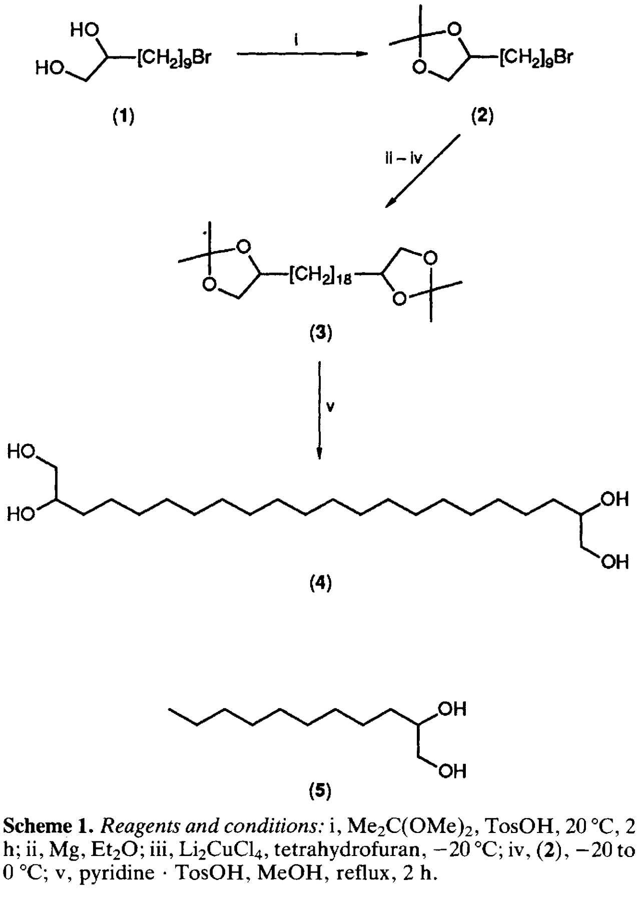
The double headed amphiphilic diol docosane-1,2,21,22-tetraol has been prepared, and it exhibits liquid crystalline behaviour with a much higher clearing temperature than the corresponding half unit undecane-1,2-diol.

Simple n-alkane-1,2-diols with a sufficient length of the alkyl chain can form thermotropic and, after addition of water, also lyotropic liquid crystalline phases which consist of bimolecular layers stabilized by hydrogen bonding.[1] These compounds are looked upon as the most simple model compounds for the large family of liquid crystalline carbohydrate derivatives.[2] In a recent paper we reported that the presence of polar groups at the terminus of the hydrophobic n-alkyl chain linked to the diol unit inhibits liquid crystal formation.[3] Similar behaviour has been observed for mesogenic carbohydrate derivatives.[4] It has, however, been shown that some double headed amphiphiles ('bola-amphiphiles') are capable of forming monolayer lipid membranes[5] and liquid crystalline properties have been observed in the case of double headed amphiphilic carbohydrate derivatives.[6]

In order to ascertain the analogy between amphiphilic diols and amphiphilic carbohydrate derivatives, the bola-amphiphile docosane-1,2-21,22-tetraol (**4**) was prepared as reported below. The synthesis was readily achieved by a Li_2CuCl_4-catalysed cross-coupling reaction[7] followed by deprotection of the 1,2-diol units using pyridinium toluene-*p*-sulphonate (pyridine·TosOH) in wet methanol.[8]

It was established by polarizing microscopy that compound (**4**) is a thermotropic mesogen with an unexpectedly high clearing temperature. The transition from the isotropic liquid at 145 °C can be seen by the rapid formation of batonnets that coalesce to a focal-conic fan-like texture with pseudoisotropic areas indicating a smectic A-type mesophase.[9] At 142 °C a transition to a more ordered liquid crystalline phase occurs, which crystallizes at 83 °C. Reheating gives a melting point of 87 °C. The nature of this mesophase is presently under investigation. Contrary to the bola-amphiphile (**4**) the respective 'half' [undecane-1,2-diol (**5**)][1] only forms a metastable smectic B-type mesophase up to a temperature of 42 °C.



Scheme 1. *Reagents and conditions:* i, $Me_2C(OMe)_2$, TosOH, 20 °C, 2 h; ii, Mg, Et_2O; iii, Li_2CuCl_4, tetrahydrofuran, −20 °C; iv, (**2**), −20 to 0 °C; v, pyridine · TosOH, MeOH, reflux, 2 h.

Table 1. Transition temperatures (°C) and enthalpy changes (in parentheses, kJ/mol) of docosane-1,2,21,22-tetraol (**4**) compared with the transition temperatures of undecane-1,2-diol (**5**).

Compound	Water-free state[a]	Water-saturated state[a]
(**4**)	cr 87 S_I^+ 142 S_A^+ 145 is (20.3) (17.0) (15.2)	cr 65 S_I^+ 108 S_A^+ 166 is
(**5**)	cr 49 (S_B^+ 42) is	cr 26 (S_B^+ 9) S_A^+ 77 is

[a] cr = crystal; S_I^+, S_A^+, S_B^+ = smectic liquid crystals; is = isotropic liquid.

Hence the mesophase stabilization observed in line with the coupling of two amphiphilic n-alkane-1,2-diols *via* their hydrophobic chains is huge and much more significant than observed in the case of amphiphilic carbohydrate derivatives.[6] In order to determine the mesophase stability of the lyotropic mesophase of compound (**4**) in the presence of water, a contact preparation in a sealed capillary was observed on a hot stage by using a polarizing microscope. The mesophase stability of the smectic A phase continuously rises with increasing water content of the sample up to a maximum value of 166 °C, whereas the transition temperature to the more ordered mesophase decreases. The transition temperatures of the water-saturated sample which were obtained by observing compound (**4**) in the presence of an excess of water are given in Table 1. In this way the double headed diol (**4**) may be looked upon as amphotropic material.[10]

As in the case of n-alkane-1,2-diols and other diol compounds[11] the possibility of hydrogen bonding between the diol units is responsible for the occurrence of liquid crystalline phases. Thereby the hydroxy groups are organized in polymeric hydrogen bonding networks,[12] forming parallel sheets which are separated by the alkylene chains. However, in contrast with the simple amphiphilic diols, the polymeric hydrogen bonded networks of the double headed compounds are additionally linked by the alkanediyl chains between the head groups giving rise to a preorientation of the diol groups and thus increasing their ability for self organization. Water molecules are readily built into the hydrogen bonding network of the diol groups and increase the number of perfectly orientated hydrogen bonds, giving enhanced mesophase stability.

Hence the double headed diol based mesogens are new amphotropic materials and offer manifold possibilities as additives to stabilize lipid membranes, liposomes, and other self-organizing assemblies.

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