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LIQUID CRYSTALS II. THE TAIL DESIGN VIA β-OXYGEN ATOM MODIFICATION FOR THE REMARKABLY ENHANCED STABILITY OF HEXAKIS(ALKANOYLOXY)TRIPHENYLENE MESOPHASE

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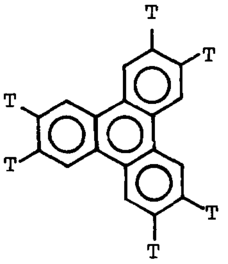
A new family of liquid crystalline compounds, 2,3,6,7,10,11-hexakis(3-oxaalkanoyloxy)triphenylene, was found to exhibit very wide mesomorphic temperature ranges, providing a promising design principle for mesogen construction, β-oxa modification of tail alkyls.

A new type of liquid crystals, the discotic mesophase, attracts strong attentions because of unique mesophase structure, polymorphism/reversed mesophase order, or possible application to low dimensional organic conductors. For the most part, such mesogens have a large size of flat core --- benzene, bipyrane, truxene, phthalocyanine or triphenylene, and these cores are linked to hydrocarbon tails via ester or ether linkages[1-3]. Here, we report a new promising tail design principle for mesogen construction, "β-oxa" modification of tail alkyls. The principle afforded much enhanced mesophase stability for triphenylene hexaester, and is also applicable to other systems such as benzene hexaesters[4] or viologens[5], as preliminarily reported by the authors.

Now we wish to report a new family of liquid crystalline compounds, 2,3,6,7,10,11-hexakis(3-oxaalkanoyloxy)triphenylene, $1\text{-}\mathrm{C}_n\cdot\mathrm{O}^3$ (n=4,6,8,10,12,14, see Chart 1), among which the β-oxygen atom effect was seen particularly effective for $1\text{-}\mathrm{C}_4\cdot\mathrm{O}^3$ and $1\text{-}\mathrm{C}_6\cdot\mathrm{O}^3$ to exhibit the large mesomorphic temperature range (ΔT_M) of 52° and 154°, respectively, in a sharp contrast to $\Delta T_M = 0°$ for the corresponding hydrocarbon compounds, $1\text{-}\mathrm{C}_4$ and $1\text{-}\mathrm{C}_6$ bearing no β-O atom (Chart 1). The largest ΔT_M of 241° was achieved[6] for 3-oxadecanoate ester, $1\text{-}\mathrm{C}_{10}\cdot\mathrm{O}^3$.

Chart 1



$1\text{-}\mathrm{C}_n\cdot\mathrm{O}^3$ ($T=-\mathrm{OCOCH_2O\text{-}C_{n-3}H_{2n-5}}$)

$1\text{-}\mathrm{C}_n$ ($T=-\mathrm{OCOC_{n-1}H_{2n-1}}$)

n	ΔT_M(°C)	ΔT_M(°C) (Ref 1b)
4	52	0
6	154	0
8	207	60
10	241	50.5
12	203	41
14	172	

The present hexaesters of triphenylene, **1**-C$_n$·O^3, was prepared by a treatment of 2,3,6,7,10,11-hexahydroxytriphenylene[7] with the corresponding 3-oxaacyl chloride. In 90 MHz (or 60 MHz) ^{1}H-NMR spectra, absorptions due to the triphenylene protons and CH$_2$ protons α to -OCO- were observed as singlets at δ (from TMS in CDCl$_3$) 7.8-7.9 and 4.3-4.4 ppm, respectively (Table I). The ^{1}H absorptions due to other protons together with IR, FD-MS (see Table I) or ^{13}C-NMR spectra were also satisfactory, supporting the structures of **1**-C$_n$·O^3. The range of mesophase stability was determined by DSC thermal analysis[8] and polarizing microscopy.

Table I. ^{1}H-NMR Absorptions, Selected IR and FD-MS Data of 2,3,6,7,10,11-Hexakis(3-oxaalkanoyloxy)triphenylene, **1**-C$_n$·O3

	^{1}H-NMR (CDCl$_3$,TMS), δ(ppm)^a	ν_{MAX}(cm^{-1})	FD-MS(m/e)
1-C$_4$·O^3	3.6(s,18H), 4.3(s,12H), 7.8(s,6H)	1762, 1110^b	
1-C$_6$·O^3	1.0(t,18H), 1.7(m,12H), 3.7(t,12H) 4.4(s,12H), 7.8(s,6H)	1765, 1110^c	925(M+H$^+$)
1-C$_8$·O^3	0.94(t,18H), 1.1-1.9(m,36H), 3.7(t, 12H), 4.4(s,12H), 7.9(s,6H)	1770, 1102^c	
1-C$_{10}$·O^3	0.89(t,18H), 1.1-1.9(m,60H), 3.7(t, 12H), 4.4(s,12H), 7.9(s,6H)	1760, 1105^c	1261(M+H$^+$)
1-C$_{12}$·O^3	0.89(t,18H), 1.0-1.9(m,84H), 3.7(t, 12H), 4.4(s,12H), 7.9(s,6H)	1770, 1105^c	
1-C$_{14}$·O^3	0.88(t,18H), 1.0-1.9(m,108H), 3.7(t, 12H), 4.4(s,12H), 7.8(s,6H)	1780, 1120^c	

a) 90 MHz ^{1}H-NMR except 60 MHz for **1**-C$_4$·O^3 and **1**-C$_6$·O^3. b) KBr pellet
c) Neat liquid film

1-C$_{10}$·O^3, the most mesomorphic member of the present hexaester family, exhibited the crystal-mesophase transition temperature, T_{C-M}, at -14° and the mesophase-isotropic phase transition temperature, T_{M-I}, at 227° (see also DSC

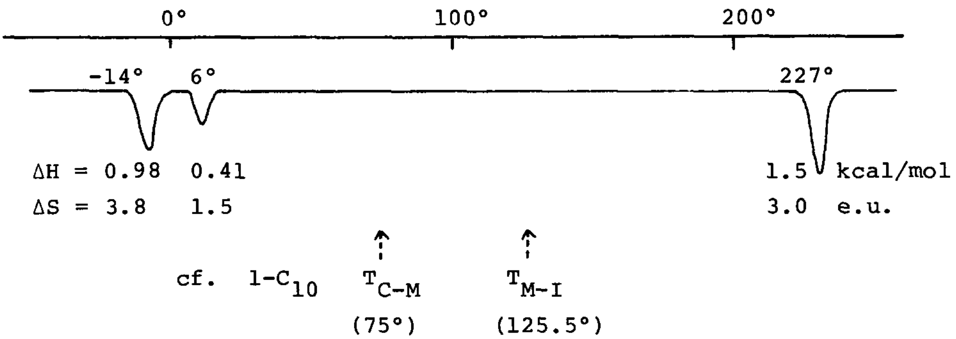


Fig 1. The DSC trace of **1**-C$_{10}$·O^3.

trace, Fig 1)[9]. Apparently β-O atom depresses T_{C-M} and raises T_{M-I} considerably, since the corresponding hydrocarbon ester, $1\text{-}C_{10}$, exhibits the mesophase in the 75–125.5° temperature range[1b]. The C-M transition at the lower temperature (-14°) of $1\text{-}C_{10}\cdot O^3$ occurs with an enthalpy change, ΔH_{C-M}, of 0.98 kcal/mol which is distinctly small, ca. 1/12-fold smaller than the reported ΔH_{C-M} (11.3 kcal/mol overall)[1b] for the hydrocarbon compound, $1\text{-}C_{10}$. More interesting, however, is the fact that ΔH_{C-M} is of a comparable magnitude to the M-I transition enthalpy, ΔH_{M-I}, of 1.5 kcal/mol (Fig 1) for the oxo compound ($1\text{-}C_{10}\cdot O^3$), since this similarity indicates that $1\text{-}C_{10}\cdot O^3$ is, energetically, just between crystalline and isotropic states. This offers a striking contrast with $1\text{-}C_{10}$, the mesophase of which is more like isotropic liquid as judged by the very large ΔH_{C-M}(loc. cit.) and the very small ΔH_{M-I}(0.697 kcal/mol)[1b].

To investigate such the oxygen atom effect in more detail, O atom was introduced at α-, β-, γ- position of $1\text{-}C_8$ by keeping the acyl tail length at eight, or in a side pendant position as in α-CH(OMe). The mesomorphic temperature ranges observed were 59∼60°(α-O), 30∼237°(β-O), -22∼83°(γ-O), and -14∼85°(α-CH(OMe)), respectively, strongly indicating that the introduction of O atom in the main chain or side group depressed T_{C-M} (66°) of $1\text{-}C_8$. This T_{C-M} depression probably comes from the close similarity between crystal and mesophase structures, as judged from ΔH_{C-M} of 1.0 (α-O), 1.9 (β-O), 0.3 (γ-O), or 0.05 kcal/mol (α-CH(OMe)), all of which are considerably smaller than the reported ΔH_{C-M}(4.7 kcal/mol overall)[1b] for the hydrocarbon ester, $1\text{-}C_8$.

Except β-O, these O atoms were found also depressing of T_{M-I}, viz., from 126° for $1\text{-}C_8$ to 60°(α-O), 83°(γ-O), 85°(α-CH(OMe)), respectively. Only β-O atom further stabilized $1\text{-}C_8\cdot O^3$ mesophase relative to the isotropic phase, raising T_{M-I} (237° for $1\text{-}C_8\cdot O^3$). A possible interpretation for this stabilization is the enhanced mesophase orderness (probably due to the enhanced intermolecular interaction in the mesophase), based on the observa-

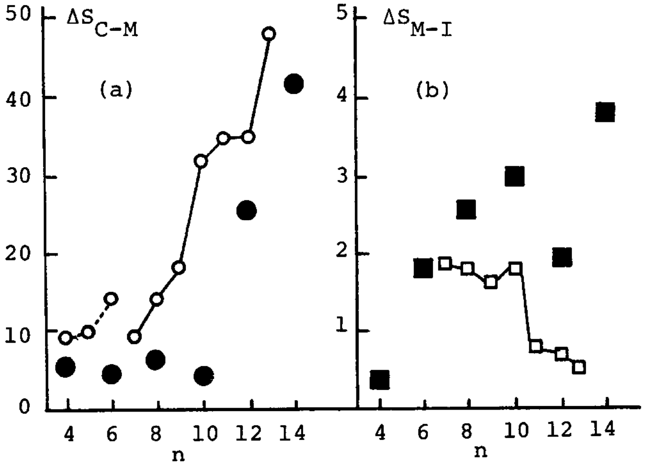


Fig 2. The C-M transition entropy(●) and M-I transition entropy(■) of $1\text{-}C_n\cdot O^3$. Open circles and squares refer to ΔS for $1\text{-}C_n$ (Ref 1b).

tion that ΔS_{M-I} for $\mathbf{1}$-$C_n \cdot O^3$ is appreciably larger than ΔS_{M-I} for $\mathbf{1}$-C_n, and the trend holds throughout the $\mathbf{1}$-$C_n . O^3$ series (n=8-14) (see Fig 2b).

A conclusion then may be drawn that the present β-O atom effect operates in two ways, viz., depressing T_{C-M} and raising T_{M-I}, on triphenylene hexaester. These two effects show the tendency depicted in Fig 3, demonstrating the first successful tail design via β-oxygen atom modification for the remarkably enhanced stability of hexakis(alkanoyloxy)triphenylene mesophase.

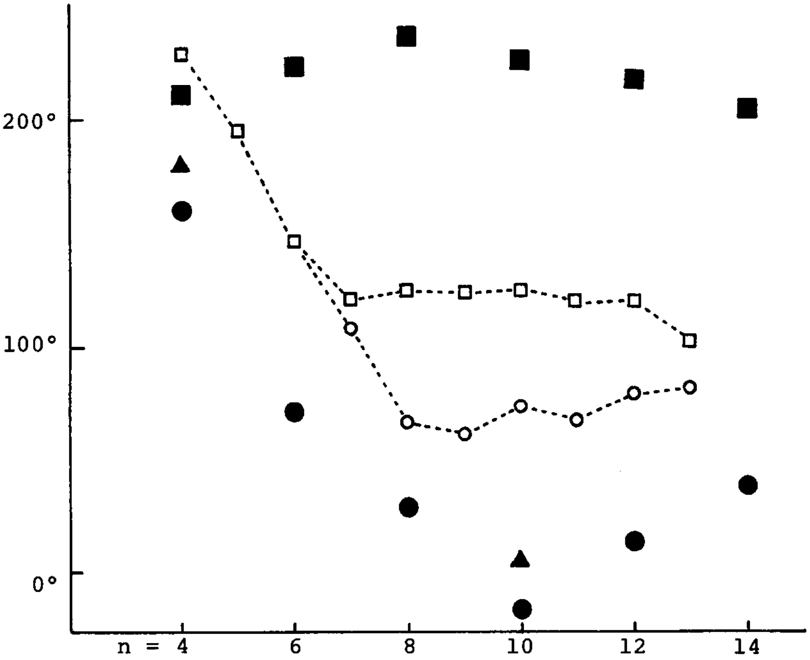


Fig 3. Dependence of T_{C-M}(●) and T_{M-I}(■) of $\mathbf{1}$-$C_n \cdot O^3$ on the tail length n. Inserted points which are connected by broken lines are T_{C-M} and T_{M-I} for $\mathbf{1}$-C_n (Ref 1b). T_{M-M} is indicated by ▲.

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6) The magnitude of the largest ΔT_M observed is comparable to ΔT_M of 247° for octakis(dodecyloxymethyl)phthalocyanine-Cu, the most mesomorphic discotic ever reported(Ref 3a).
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8) The DSC data(Fig 1,2) were well reproducible in repeated DSC scanning.
9) The peak at 6° remained after further, careful recrystallizations of spectroscopically pure sample. It is tentatively assigned to a M_1-M_2 transition.

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