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Liquid Crystals

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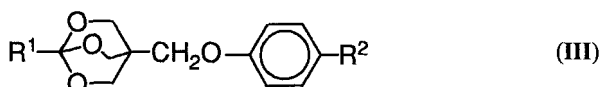
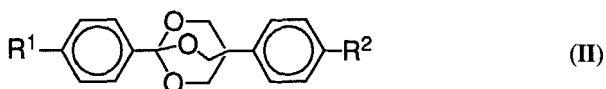
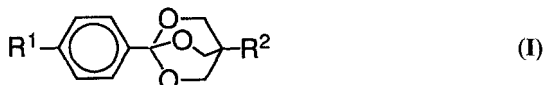
Synthesis and liquid-crystalline properties of compounds incorporating the 2,6,7-trioxa-bicyclo(2.2.2)octane

by R. PASCHKE, H. ZASCHKE, A. HAUSER and D. DEMUS

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(Received 15 March 1989; accepted 18 May 1989)

We have prepared twenty six new derivatives of 2,6,7-trioxa-bicyclo(2.2.2)-octane with the general molecular structures,



R^1 = alkyl, alkyloxy, R^2 = alkyl, alkyloxy, aryl.

All the compounds are mesomorphic the great majority of which exhibit exclusively smectic B phases. In order to characterize this new structural class we measured refractive indices, transition enthalpies and polarizability as well as their viscosity properties for some selected examples.

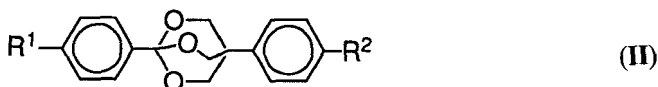
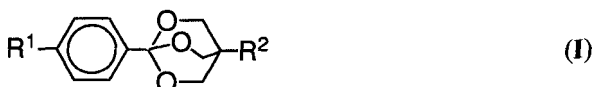
1. Introduction

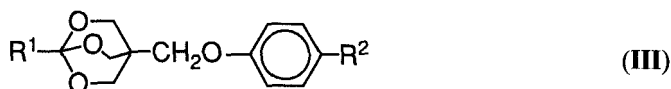
Despite the large number of known liquid crystals many efforts are still made to obtain new materials and to find new structural units useful for forming mesophases. This is necessary in order to fulfil the increasing requirements of present applications but also to enhance our understanding of the theoretical aspects of the liquid-crystalline state.

It was considered to be of interest to prepare and investigate liquid crystals incorporating the 2,6,7-trioxa-bicyclo(2.2.2)octane unit because the linear and rigid bicyclo(2.2.2)octane is well-known for the formation of very stable mesophases [1-3].

2. Synthesis

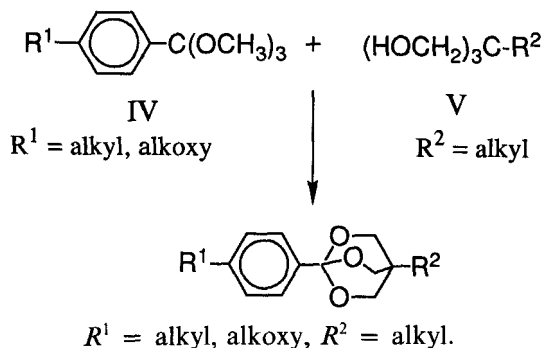
We succeeded in preparing the 2,6,7-trioxa-bicyclo(2.2.2)octane derivatives,



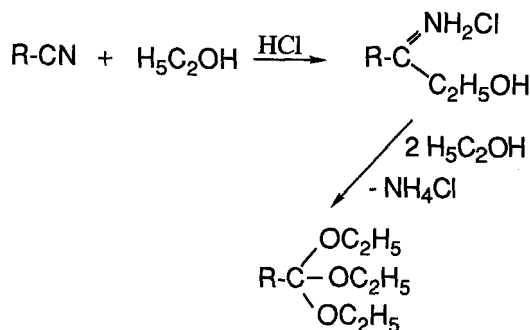


R^1 = alkyl, alkyloxy, R^2 = alkyl, alkyloxy, aryl.

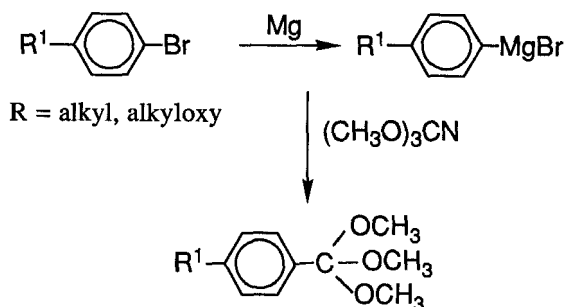
2,6,7-Trioxa-bicyclo(2.2.2)octanes can be obtained by the trans-esterification of acyclic orthoesters (IV) and 2-substituted 2-hydroxymethyl-propane-1,3-diols (V) under reduced pressure.



In order to obtain aliphatic orthoesters we used standard methods via alkylnitriles [4-7].



For our purpose it was also necessary to prepare 4-substituted orthobenzoates. We used the method of Kantlehner [8, 9] and succeeded in preparing 4-alkyl- and 4-alkyloxysubstituted orthobenzoates in good yields;



To synthesize (V) we chose a method to obtain arylsubstituted derivatives (V) [10]; Eight biphenyl analogous compounds (I), seven terphenyl analogous compounds (II) and eleven 4-aryl-2,6,7-trioxa-bicyclo(2.2.2)octanes were prepared; the melting temperatures and transition temperatures are given in tables 1-3. The transition

temperatures were determined using a microscope equipped with a heating stage. The phase classification was performed by texture observations. The smectic A phases show characteristic focal-conic fan textures. The smectic B phases have been identified by the typical lance texture [23]; an example is given in figure 1. The new compounds exhibit extremely low chemical stability and are also very sensitive to heating.

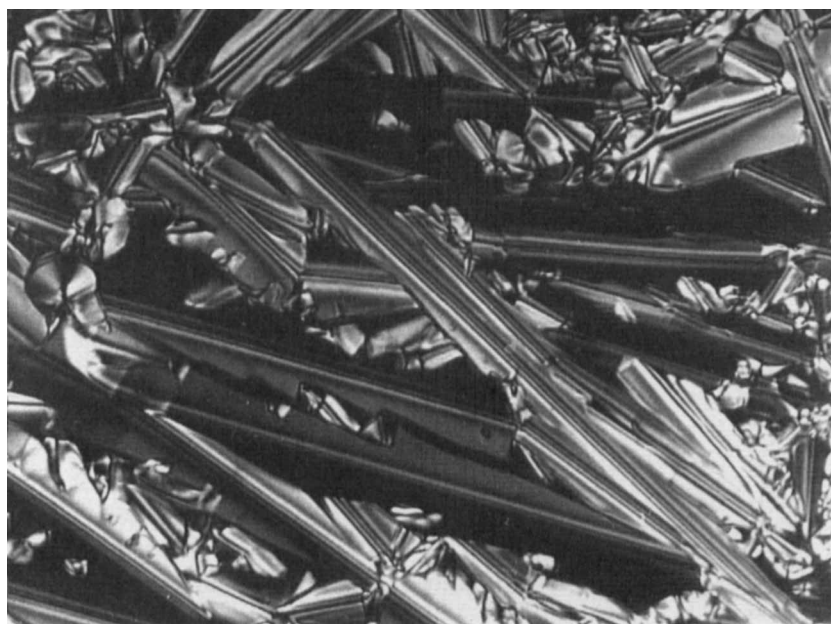
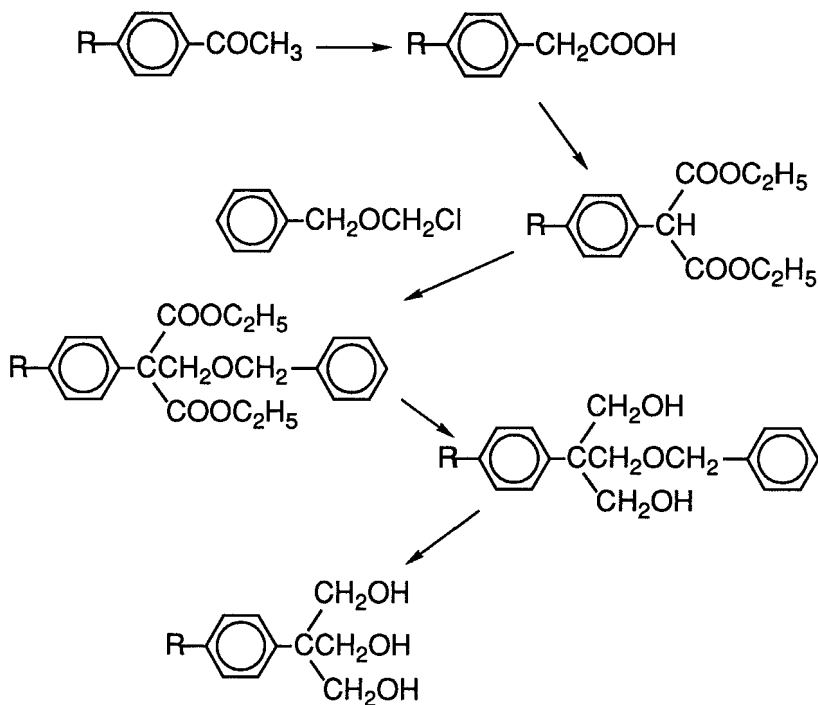
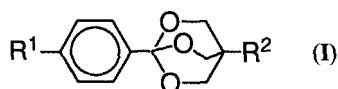


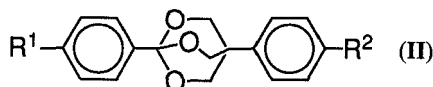
Figure 1. The Lancet texture of the smectic B phase exhibited by compound IIIe (60°C, magnification 100×).

Table 1. The biphenyl analogous 2,6,7-trioxa-bicyclo(2.2.2)octanes.



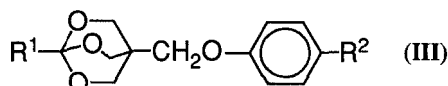
	R^1	R^2	C	S_B	I	
(Ia)	C_6H_{14}	C_5H_{11}	●	74	● (50)	●
(Ib)	C_6H_{13}	C_6H_{13}	●	45	● 64	●
(Ic)	C_6H_{13}	C_8H_{17}	●	35	● 87	●
(Id)	C_5H_{11}	C_7H_{15}	●	46	● 74	●
(Ie)	$C_6H_{13}O$	C_4H_9	●	90	—	●
(If)	$C_6H_{13}O$	C_5H_{11}	●	92	—	●
(Ig)	$C_6H_{13}O$	C_7H_{15}	●	43	● 85	●
(Ih)	$H_{11}C_5$	C_7H_{15}	●	40	● 87	●

Table 2. The Terphenyl analogous 2,6,7-trioxa-bicyclo(2.2.2)octanes.



	R^1	R^2	C	S_B	I	
(IIa)	C_6H_{13}	C_3H_7	●	95	● 193	●
(IIb)	C_6H_{13}	C_5H_{11}	●	96	● 194	●
(IIc)	C_6H_{13}	C_6H_{13}	●	81	● 194	●
(IId)	$C_6H_{13}O$	C_5H_{13}	●	86	● 197	●
(IIe)	$C_6H_{13}O$	C_6H_{13}	●	84	● 182	●
(IIf)	Br	C_5H_{11}	●	222	● (203)	●
(IIg)	Br	C_6H_{13}	●	204	● (198)	●

Table 3. The Aryl substituted 2,6,7-trioxa-bicyclo(2.2.2)octanyl-methylethers.



	R^1	R^2	$T/^\circ C$				I
			C	S_B	S_A	N	
(IIIa)	CH ₃	OC ₈ H ₁₇	● 86	●	—	—	●
(IIIb)	CH ₃	Ph-C ₆ H ₁₃	● 144	●	—	—	●
(IIIc)	CH ₃	COO-Ph-OC ₄ H ₉	● 45	● 135	● 155	—	●
(IIId)	C_7H_{15}	OC ₅ H ₁₁	● 68	● 86.5	—	—	●
(IIIe)	C_7H_{15}	OC ₆ H ₁₃	● 42	● 90	—	—	●
(IIIf)	C_7H_{15}	OC ₇ H ₁₅	● 48	● 93	—	—	●
(IIIg)	C_7H_{15}	OC ₈ H ₁₇	● 45	● 94	—	—	●
(IIIh)	C_7H_{15}	C_6H_{13}	● 44	● 72	—	—	●
(IIIi)	C_7H_{15}	CN	● 92	—	—	—	●
(IIIj)	C_7H_{15}	CH ₂ -CH ₂ -CN	● 82	—	—	—	●
(IIIk)	$C_6H_{13}O$ -Ph	CN	● 169	—	—	● (166)	●

3. Physical properties

Several members of the three homologous series were chosen for the investigation of their viscosity as, transition enthalpies, refractive indices, order parameters and molecular polarizabilities. Shear viscosity measurements (minimum viscosity η_2 using the notation of Helfrich [11]) were performed using the Rheotest 2 (Medingen, G.D.R.). The error of the viscosity measurements is approximately ± 5 mPs. The transition enthalpies, ΔH , were obtained by calorimetry (Perkin-Elmer DSC 2). The ordinary and extraordinary refractive indices were measured at 589 nm using an Abbé refractometer. The necessary homeotropic alignment of the mesomorphic samples was achieved by coating the prisms with a surfactant (lecithin). The accuracy of the refractive indices measurements is in the region $\pm 5 \times 10^{-4}$.

4. Results

The refractive indices (n_e , n_o) of certain compounds of the homologous series II are given in table 4. They have been calculated using the interpolation formula,

$$n_i = a + b\vartheta + c \exp(0.18\vartheta) + d \exp(0.20\vartheta), \quad (i = e, o), \quad (1)$$

where ϑ is the celsius temperature and a , b , c , d are adjustable parameters.

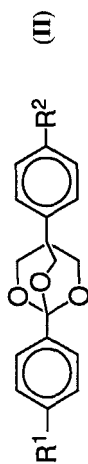
The relative polarizability anisotropy $\Delta\alpha/\bar{\alpha}$ has been determined without the use of density values by application of the formula given by Vuks [12, 13]. If the order parameter S is unknown an extrapolation method must be used to determine the relative polarizability anisotropy $\Delta\alpha/\bar{\alpha}$ and the temperature dependence of the order parameter. The best method for this purpose is the mean field extrapolation procedure of Tough and Bradshaw [14] (see also [15, 16]). It has been shown that the mean field extrapolation method [14, 18] gives better results than the Haller extrapolation [17]. The polarizability anisotropy $\Delta\alpha$ can be calculated with good accuracy from the relative polarizability anisotropy $\Delta\alpha/\bar{\alpha}$ using bond polarizabilities [19, 20] for the evaluation of $\bar{\alpha}$ if the density values are not available [18].

The optical anisotropy of the terphenyl analogue (II) in the smectic B phase (table 4 is a factor of two smaller than in typical smectic B phases [21] but lies in the same range as that found for dioxane derivatives [22]). In table 4, the values of the order parameter S and of the mean field interaction parameter A are shown to lie in a typical region for smectic B phases; the polarizability anisotropy values are smaller than in other smectic B phases [21]. Some compounds show very poor alignment in the refractometer. Thus, it is possible only to obtain refractive indices by extrapolation from measurements in nematic mixtures at the same reduced temperature according to the equation,

$$\Delta n = x_N \Delta n_N + x_M \Delta n_M, \quad (4)$$

where x_N and x_M are the mole fraction of the compound N and the nematic mixture M in which N is dissolved respectively. Δn is the optical anisotropy of the mixture of the compounds N and M ; Δn_N and Δn_M are the optical anisotropies of the compound N and of the nematic mixture M respectively. The results obtained for 2,6,7-trioxa-bicyclo(2.2.2)octanyl-methylether (III) are given in table 5. The order parameters calculated from extrapolated refractive indices show lower values for the compounds (IIIe) and (III f) than for the mixture Mi 5. The elongation of the alkyl chain (IIIe) to (III f) increases the order parameter and the relative polarizability anisotropy (table 5). The compounds investigated by calorimetry (table 4) exhibit small melting enthalpies; the clearing enthalpies ΔH_{S_B} have relatively high values which are typical

Table 4. Transition enthalpies, ΔH , relative polarizability anisotropies $\Delta\alpha/\bar{\alpha}$, polarizability anisotropies $\Delta\alpha$ and mean field interaction parameters A/T , refractive indices and order parameters of the smectic B phases of the terphenyl analogous 2,6,7-trioxa-bicyclo(2.2.2)octanes,



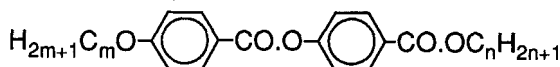
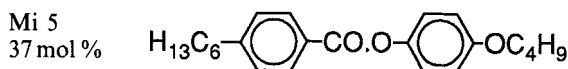
R^1	R^2	$\Delta H_{CSB}/$ kJ mol^{-1}	$\Delta H_{SB}/$ kJ mol^{-1}	$\Delta\alpha/\bar{\alpha}$	$\Delta\alpha/$ 10^{-24} cm^3	A/T_{SB}			
$-\text{C}_6\text{H}_{11}$	$-\text{C}_6\text{H}_{13}$	12.5	10.2	0.359	19.65	8.98			
$-\text{C}_6\text{H}_{13}$	$-\text{C}_6\text{H}_{13}$	18.3	10.4	0.356	20.15	8.30			
$-\text{C}_6\text{H}_{13}$	$-\text{OC}_6\text{H}_{13}$	18.7	9.2	0.365	20.83	8.24			
			9	140	120	110	100	80	75
$-\text{C}_3\text{H}_{11}$	$-\text{C}_6\text{H}_{13}$	1.576	1.577	1.580	1.583	1.591	1.587	1.595	1.597
		1.462	1.464	1.467	1.470	1.476	1.473	1.479	1.480
		0.749	0.754	0.757	0.759	0.763	0.761	0.753	0.764
$-\text{C}_6\text{H}_{13}$	$-\text{C}_6\text{H}_{13}$	1.568	1.573	1.576	1.579	1.588	1.584	1.593	1.595
		1.462	1.462	1.466	1.470	1.475	1.473	1.478	1.479
		0.733	0.739	0.744	0.749	0.757	0.753	0.760	0.761
$-\text{C}_6\text{H}_{13}$	$-\text{OC}_6\text{H}_{13}$	1.576	1.576	1.578	1.582	1.591	1.586	1.595	1.598
		1.465	1.465	1.467	1.469	1.475	1.472	1.478	1.479
		0.730	0.730	0.737	0.743	0.752	0.748	0.757	0.758

Table 5. Refractive indices, order parameters and relative polarizability anisotropies $\Delta\alpha/\bar{\alpha}$ of the nematic mixture Mi5 and for 2,6,7-trioxa-bicyclo(2.2.2)octanylethers (extrapolated refractive indices from mixture $X_N = 0.1$ with mixture Mi 5),

(III)

		ϑ	45.0	48.0	50.0	53.0	56.0	60.0
<i>R</i> : -OC ₆ H ₁₃ (IIIe)	n_e		1.631	1.626	1.623	1.618	1.610	1.583
	n_o		1.477	1.474	1.473	1.474	1.476	1.480
	S		0.504	0.484	0.472	0.444	0.414	0.334
<i>R</i> : -OC ₇ H ₁₅ (III f)	n_e		1.691	1.685	1.681	1.675	1.667	1.628
	n_o		1.491	1.489	1.487	1.484	1.481	1.491
	S		0.513	0.494	0.479	0.456	0.427	0.366
Mi 5	ϑ		20.0	30.0	40.0	50.0	60.0	65.0
	n_e		1.640	1.632	1.623	1.614	1.600	1.590
	n_o		1.496	1.494	1.492	1.491	1.492	1.495
	S		0.644	0.618	0.581	0.540	0.482	0.443

Composition of Mi 5
 MI5 R : -OC₆H₁₃ R : -OC₇H₁₅
 0.512 0.738 0.907

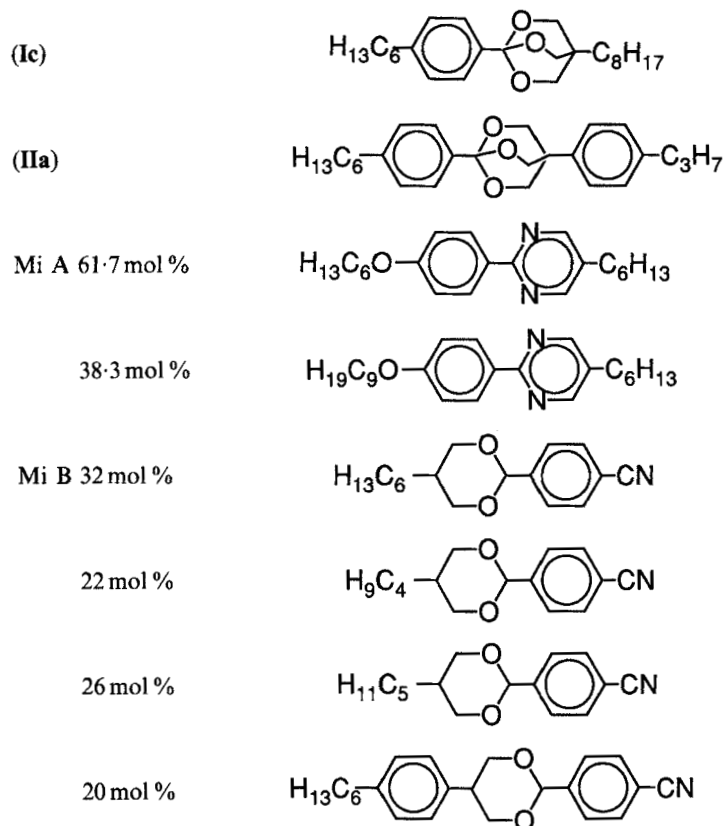


24 mol % $n = 1, m = 6$
 27 mol % $n = 5, m = 8$
 12 mol % $n = 6, m = 7$

for the S_B -I transition. In table 6 results of viscosity measurements are presented. Since measurements in the smectic B phases of the pure compounds are not possible, we studied the influence of the addition of trioxa-bi-cyclo-octane derivatives to unpolar (Mi A) and polar (Mi B) nematic mixtures. The addition of the two-ring compound Ic does not significantly change the viscosity or the activation energy (obtained by an Arrhenius plot). The addition of the three-ring compound IIa, however, causes a strong increase in the viscosity.

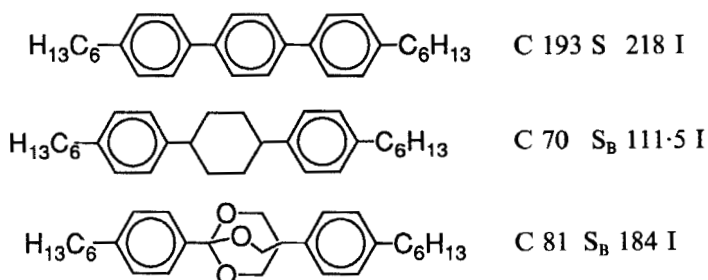
5. Conclusion

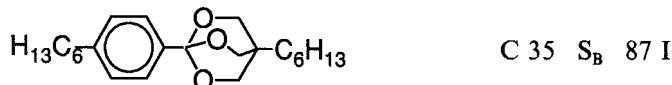
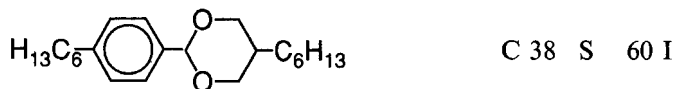
The 2,6,7-trioxa-bicyclo(2.2.2)octane ring represents a further structural unit for the formation of the liquid-crystalline state. From the structural viewpoint the trioxa-bicyclo-octane derivatives may be compared with the analogous bicyclooctane derivatives. Gray *et al.* [25] have synthesized certain 1-*n*-alkyl-4-(4-subst phenyl)-bicyclo-(2.2.2)octanes which are nematic but with considerably lower clearing temperatures than our similar compounds I. A direct comparison is not possible since the terminal substituents are not equal. A comparison to the analogous derivatives of benzene, cyclohexane and dioxane reveals the strong potential mesogeneity of the

Table 6. Viscosity coefficients η_2 of the compounds (Ic) and (IIa) in two mixtures and Arrhenius activation energies E_a .

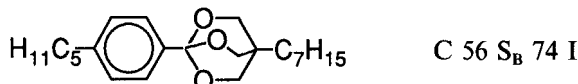
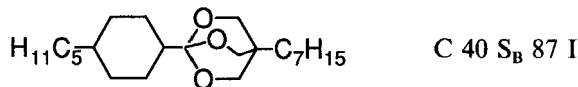
	Mi A	Mi A + 15% IIa	Mi A + 20% IIa	Mi A + 5% Ic
$E_a/\text{kJ mol}^{-1}$	38.2	34.2	35.2	36.4
η_2/mPs (293 K)	69	114	136	69
(298 K)	53	90	107	53
	Mi B	Mi B + 15% IIa	Mi B + 5% Ic	
$E_a/\text{kJ mol}^{-1}$	34.2	39.5	32.5	
η_2/mPs (293 K)	59	106	65	
(298 K)	46	81	52	

trioxa-bicyclo-octane ring;

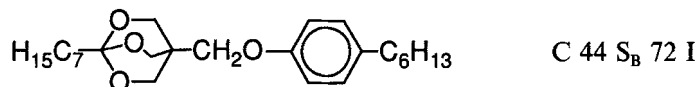
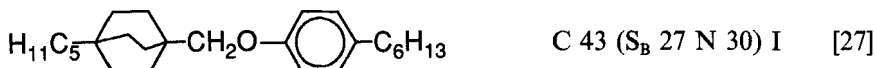
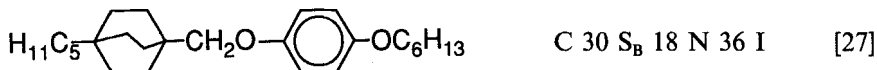
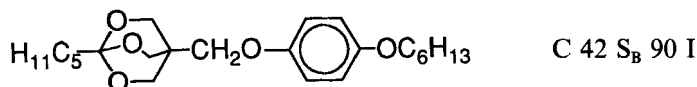
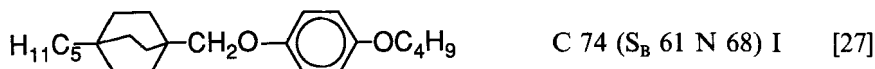
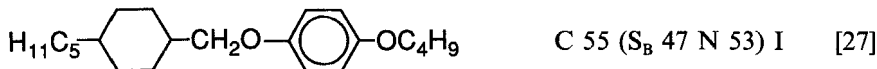




A change of the position of the oxygen atoms within the 2,6,7-trioxa-bicyclo-(2.2.2)octane ring does not result in significant changes in the clearing temperatures or a modification of the mesophases behaviour.



Liquid-crystalline 2,6,7-trioxa-bicyclo(2.2.2)octanes show a strong tendency to form the smectic B phase. This fact is underlined by the results obtained from the synthesis of 2,6,7-trioxa-bicyclo(2.2.2)octanylethers. Only two of these exhibit a liquid-crystalline phase different from S_B. This is emphasised in the comparisons,



Despite the relative wide mesophase regions and the low double refraction which is advantageous for some purposes, the new compounds are not useful for practical applications since their chemical and thermal stability is poor. The compounds also tend to have high viscosities like the bicyclo-octanes. Only a few of the new compounds are nematic the majority instead exhibit smectic B phases.

6. Experimental

6.1. 1-(4-Alkyl-phenyl)-4-alkyl-2,6,7-trioxa-bicyclo(2.2.2)octanes
 (0.01 mol) 4-Substituted orthobenzoate 2-alkyl-2-hydroxy-methyl-propoane-1,3-dioles (0.02 mol) and a trace of p-toluensulphonic acid were stirred under reduced

pressure (1.6 kPa); the temperature was gradually raised to 100°C during 1 hour. The heating was continued until the mixture reached a temperature of 150°C. The residue crystallized upon cooling and was recrystallized from hexane (yields 45–60 per cent).

6.2. 1-(4-Alkyl-phenyl)-4-(4-alkyl-phenyl)-2,6,7-trioxa-bicyclo(2.2.2)octanes

4-Substituted orthobenzoate (0.005 mol) was added to 2-(4-alkyl-phenyl-2-hydroxymethyl-propane-1,3-dioles (0.005 mol) and a trace of p-toluenesulphonic acid. The mixture was heated to 100°C within one hour under reduced pressure (0.0144 kPa) while stirring. This temperature was maintained for an additional hour, then the ethanol was distilled off. The product was recrystallized from hexane (yields 50–60 per cent).

6.3. 4-Bromomethyl-1-methyl-2,6,7-trioxa-bicyclo(2.2.2)octanes

Dried potassium carbonate (0.053 mol) cyclohexanone (40 ml) and 4-alkyl-phenol (0.053 mol) are refluxed for 3 hours. The mixture was evaporated and the residue was recrystallized from hexane (yields: 40–60 per cent). The compounds were identified by ¹H.N.M.R. spectra and elemental analysis. The N.M.R. data and values for the elemental analysis are:

	Elemental analysis		¹ H.N.M.R. (CDCl ₃ /ppm)
	C/%	H/%	
(Ia)	76.30	9.83	0.8–1.6 (m, 22H), 2.52 (t, 2H), 4.06 (2, 6H), 7.02–7.50 (q, 4H)
	76.23	9.72	
(Ib)	76.67	10.00	0.8–1.6 (m, 2H), 2.54 (t, 2H), 4.6 (s, 6H), 7.04–7.50 (q, 4H)
	77.14	10.41	
(IIa)	79.19	9.17	0.8–1.6 (m, 16H), 2.53 (t, 2H), 2.52 (t, 2H), 4.44 (s, 6H), 7.08 (m, 4H), 7.1–7.58 (q, 4H)
	79.67	9.15	
(IIb)	79.52	9.00	0.8–1.6 (m, 20H), 2.56 (t, 4H), 4.44 (s, 6H), 7.09 (m, 4H), 7.1–7.58 (q, 4H)
	79.64	9.17	
(III d)	70.94	9.36	0.76–1.8 (m, 24H), 3.60 (s, 2H), 4.06 (s, 6H), 6.72 (s, 4H)
	70.95	9.35	
(III e)	71.43	9.52	0.74–1.80 (m, 26H), 3.60 (s, 2H), 4.06 (s, 6H), 7.72 (s, 4H)
	71.78	9.77	

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