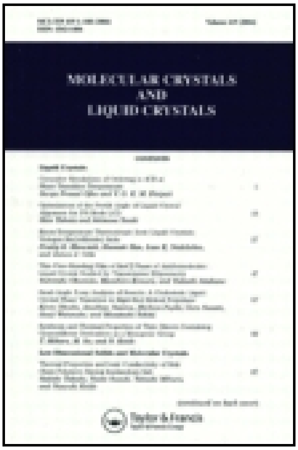

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Liquid Crystalline Bicyclo[1.1.1]pentane Derivatives

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Liquid Crystalline Bicyclo[1.1.1]pentane Derivatives

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New liquid crystalline bicyclo[1.1.1]pentane derivatives have been prepared. Nematic and smectic A, B and C phases have been observed. When the bicyclo[1.1.1]pentyl unit is incorporated in a terminal alkyl chain, it acts as a chain stiffener without changing the transition temperature significantly. A bicyclo[1.1.1]pentyl unit placed at the end of the mesogenic moiety acts almost like a ring; the liquid crystal transition temperatures are increased significantly compared to analogous compounds without the bicyclo[1.1.1]pentyl unit. A bicyclo[1.1.1]pentyl unit in the centre of the mesogenic moiety only gives rise to low clearing points.

Keywords: Bicyclo[1.1.1]*pentane derivatives, calamitic liquid crystals, alicyclic rings*

Bicyclo[1.1.1]pentane units should be ideal building blocks for the construction of liquid crystals. They are rigid, linearly connecting and rotationally symmetric systems like the frequently used bicyclo[2.2.2]octanes. The first investigations on monomeric[1,2,3] and polymeric[3,4,5] compounds could not confirm these positive expectations. Low ordered phases (N, S_A, S_C) either have not been found or have been observed only with low liquid crystal transition temperatures. Seemingly more highly ordered phases could be observed. However, the compounds examined thus far cannot give a full picture of the role of the bicyclo[1.1.1]pentyl unit in liquid crystal systems. In order to increase our understanding of that role, we have synthesized and investigated a series of bicyclo[1.1.1]pentane derivatives with the bicyclo[1.1.1]pentyl unit incorporated in different positions of the mesogenic moiety or the terminal alkyl chain. It was expected that bicyclo[1.1.1]pentyl units would primarily stabilize N and S_B phases and destabilize S_C and S_A phases as the cyclohexane and bicyclo[2.2.2]octane units do.

Compounds **1–4** with a bicyclo[1.1.1]pentyl unit in the centre of the mesogenic moiety (see Table I) exhibit high melting points and extremely low clearing points. Only in the case of compound **3** could a monotropic nematic phase be noticed. Compound **1** could be cooled to below room temperature without showing a mesogenic phase. By dissolving these compounds in liquid crystalline host mixtures, primarily S_C-phases are destroyed.

TABLE I

Mesogenic compounds with a bicyclo[1.1.1]pentyl unit in the centre of the mesogenic groups. (The compounds were tested in FELIX mixtures of the Hoechst AG.)

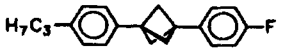
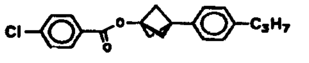
No		Phase Transitions	Comments
1		(0) Cr 67.1 I	destroys S_C in mixtures
2		(90) Cr 95.6 I	
3		Cr 118.1 N 62.4 I	destroys S_C in mixtures
4		(112) Cr 150.6 I	

TABLE II

Mesogenic compounds with a bicyclo[1.1.1]pentyl unit at the end of the mesogenic groups.

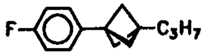
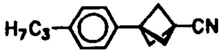
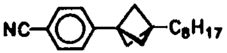
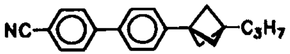
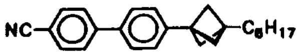
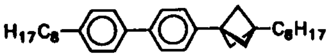
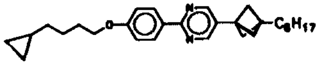
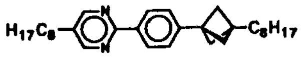
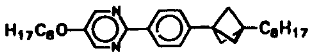
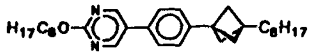
No		Phase Transitions	Comments
5		Cr 8 I	
6		Cr <0 N <10 I	
7		Cr 40 I	
8		Cr 123.0 N 146.2 I	mp_2 100.2
9		Cr 97.2 S_A 108.5 N 120.5 I	two solid modifications
10		Cr <20 S_B 103 I	LC at room temperature
11		Cr 53 S_B 83 I	
12		Cr 49.8 S_A 69.8 N 84.4 I	
13		Cr 51 S_C 63 S_A 113 N 121 I	Cr_2 to Cr_1 at 45
14		Cr 85 S_B 113 S_A 115 I	

TABLE II (*Continued*)

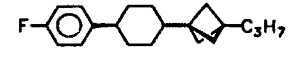
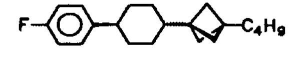
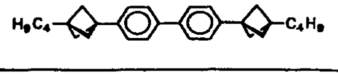
15		Cr 57.0 N 63.7 I	
16		Cr 54.3 N 63.2 I	
17		Cr 128 S_B 142.6 N 170.2 I	

TABLE III

Comparison of the bicyclo[1.1.1]pentyl with a propyl,[8] cyclohexyl[6] and bicyclo[2.2.2]octyl unit.[7]

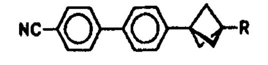
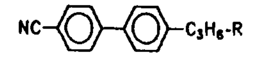
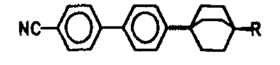
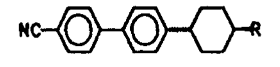
R				
C_3H_7	Cr 123.0 N 146.2 I	Cr 13.5 N 28 I	Cr 180.5 N 276 I	Cr 133 N 230 I
C_8H_{17}	Cr 97.2 S_A 108.5 N 120.5 I	Cr 52.6 S_A 57 N 57 I	Cr 126 S_A 155 N 140.5 I	Cr 61 S_A 147 N 188 I

TABLE IV

Mesogenic compounds with a bicyclo[1.1.1]pentyl unit as part of the alkyl chains. Data for compounds **28**,[11] **29**,[12] **30**,[13] and **31**[12] were taken from the literature.

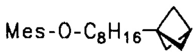
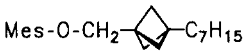
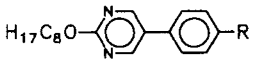
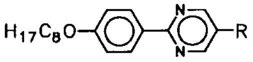
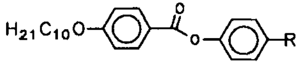
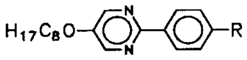
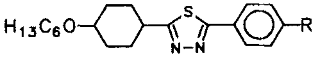
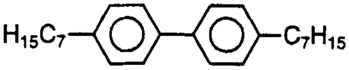
Mes	 Mes-O-C_8H_{16}–	 Mes-O-CH_2–…–C_7H_{15}	Mes-O-$C_{11}H_{23}$
	**18** Cr 89 S_C 79 S_A 83 I	**23** Cr 110 S 108 I	**28** Cr 76 S_C 9 S_A 99 I
	**19** Cr 62 S_C 83 I	**24** Cr 79 S 104 I	**29** Cr 60 S_C 102 I
	**20** Cr 62 S_C 77 S_A 79 I	**25** Cr 84 S_2 66 S_C 89 N 95 I	**30** Cr 71 S_C 88 S_A 89 N 90 I
	**21** Cr 32 S_C 74 S_A 90 I	**26** Cr 69 S_C 95 S_A 100 N 103 I	**31** Cr 56 S_C 85 S_A 97 I
	**22** Cr 119 S_C 128 S_A 146 I		

Table II presents compounds with a bicyclo[1.1.1]pentyl unit directly attached to the end of a mesogenic group. Two-ring systems like compound **6** exhibit clearing-points near 0°C, three-ring systems show clearing points near 100°C. Both low ordered (N, S_A, S_C) and highly ordered (S_B) phases were observed.

A direct comparison of compounds **8** and **9** with analogous compounds having a bicyclo[2.2.2]octane unit,[7] a *trans*-1,4-disubstituted cyclohexane ring[8] or a ($CH_2CH_2CH_2$)-alkyl chain[6] in place of the bicyclo[1.1.1]pentyl unit is possible (see Table III). All systems show the same types of phases, but very different clearing points. Those of the bicyclo[1.1.1]pentanes are between the clearing points of materials with the open alkyl chain and those of the cyclohexanes. Comparison of **17** with the analogous open chain compound **27** discloses an interesting feature: The nematic phase is more stabilized than the smectic B phase.



27 Cr 35 S_B 61.7 I[9]

Table IV lists compounds, in which the bicyclo[1.1.1]pentyl unit is part of the alkyl chain. Compounds **23–26** contain this unit near the mesogenic moiety, **18–22** have this unit linked terminally. These compounds are compared with the analogous compounds having an open alkyl chain.

In principle, all three groups of compounds possess the same properties (same phases, nearly the same transition temperatures). The bicyclo[1.1.1]pentyl unit has almost no effect on these properties when it is part of the alkyl chain. When it is close to the mesogenic moiety, it elevates the transition temperatures slightly and strengthens the nematic character (**23–26**). On the other hand the terminally linked unit depresses the transition temperatures slightly, and the nematic phase is diminished at the expense of the S_A phase. The melting points do not show any uniform trend. Interestingly **21** shows a remarkably low melting point.

CONCLUSION

A bicyclo[1.1.1]pentyl unit placed in the alkyl chain does not change the transition temperatures significantly. The positive effects of a more rigid group are partially compensated by an increased flexibility around the bonds attached to the bridgehead positions (lower rotational barriers). A bicyclo[1.1.1]pentyl unit attached directly to the mesogenic moiety has partly the effect of a ring: the transition temperatures are clearly higher than those of compounds without the additional unit. With a bicyclo[1.1.1]pentyl unit in the centre of the mesogenic moiety, only very low clearing points are observed.

The melting points of several of the investigated compounds are rather high. In contrast to the cyclohexane and bicyclo[2.2.2]octane derivatives, no undesired preference for the highly ordered smectic phases is noticed.

EXPERIMENTAL

The synthesis of the compounds will be reported elsewhere.[10] The compounds listed in Table IV were prepared in cooperation with Hoechst AG. All new compounds were purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether mixtures and/or recrystallised from methanol; their structures were confirmed by spectroscopic techniques (IR, ^{1}H and ^{13}C NMR) and their molecular formulas established by elemental analyses or high resolution mass spectrometry.

The liquid crystal transition temperatures were determined by optical microscopy utilising a polarising microscope in conjunction with a Mettler FB82 heating stage. Assignment of the phases was done on the basis of characteristic textures as well as contact preparations with reference compounds.

Acknowledgement

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