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## Liquid Crystals

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# Some studies on liquid crystals incorporating three membered linking units combined with 1,3 linked rings†

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From studies of molecular models, by the combination of more than one 'wrong' building unit (three membered linking units, 1,3-linked rings, 1,3-*cis*-saturated rings), molecules exhibiting close to linear conformations are feasible. Accordingly, a number of suitable substances have been synthesized. All of them exhibit a moderate to strong depression of clearing temperature. Surprisingly, the extent of the depression decreases with conformational mobility of the linking unit and is, in contrast to normally constructed liquid crystal molecules, not affected by the presence of lateral substituents in the terminal ring.

## 1. Introduction

Liquid crystalline phases are almost exclusively formed by compounds whose molecular structures possess at least the following specific building principles: six membered rings in the rigid core, 1,4-linkage of the rings, *trans*-configuration of saturated rings, and linking units with 0, 2 or 4 atoms in the bridge. In the literature, many examples are found which demonstrate that deviation from one of these principles leads to a strong deterioration or often disappearance of liquid crystalline properties. This behaviour is generally attributed to the loss of molecular linearity.

From studies of molecular models we found that by combining more than one 'wrong' building unit, molecules are feasible which exhibit conformations close to linear (see example in the figure). Consequently a number of suitable substances incorporating combinations of 1,3-linked rings, 1,3-*cis*-configured saturated rings and three membered linking units have been synthesized and their mesomorphic properties studied.

## 2. Synthesis

The synthesis of the unusual cores required alternative synthetic routes to some extent, depending on the location of the three membered linking units and the 1,3-substituted ring, as well as on the *cis*-configuration of this ring. Two examples are outlined in the scheme.

## 3. Results and discussion

In table 1, the thermodynamic properties of compounds with different three membered linking units are

collated. The series on the right and left differ in the location of the bridging group. In the left series all the clearing temperatures (virtual, measured for solutions in PCH5 or in the non-polar mixture CM-6093) are disappointingly low. If the bridging unit is located between the first two rings (right side), the clearing points are generally higher. Therefore all the subsequent investigations were made exclusively on this sub-structural type.

A comparison of different three membered linking units is made in table 2. The figures show that the clearing points decrease in the order  $4 > 7 \geq 5 > 8 > 9 = 6$ . This leads to the somewhat surprising conclusion that the clearing temperatures increase with additional conformational mobility of the bridge.

From the model (see the figure), it follows that one ring attached to the three membered bridge must possess a 1,3-substitution pattern in order to reach optimal linearity of the molecule. Consequently, substituents in the *para*-position have to be considered as lateral substituents. This seems indeed to be correct, as shown in table 3. The *meta*-substituted phenyl ring leads to a somewhat higher clearing temperature than the *para*-substituted ring. This effect disappears if the substituent is much smaller than chlorine, e.g. as small as fluorine.

In table 4, the mesomorphic properties of compounds with one to three substituents are compared. Surprisingly, the introduction of additional substituents in the phenyl ring does not change the clearing point at all. This is in sharp contrast to the usual observation that lateral substituents including fluorine cause strong depressions of clearing points.

## 4. Conclusions

The results clearly show that none of the compounds with three membered linking units in combination with

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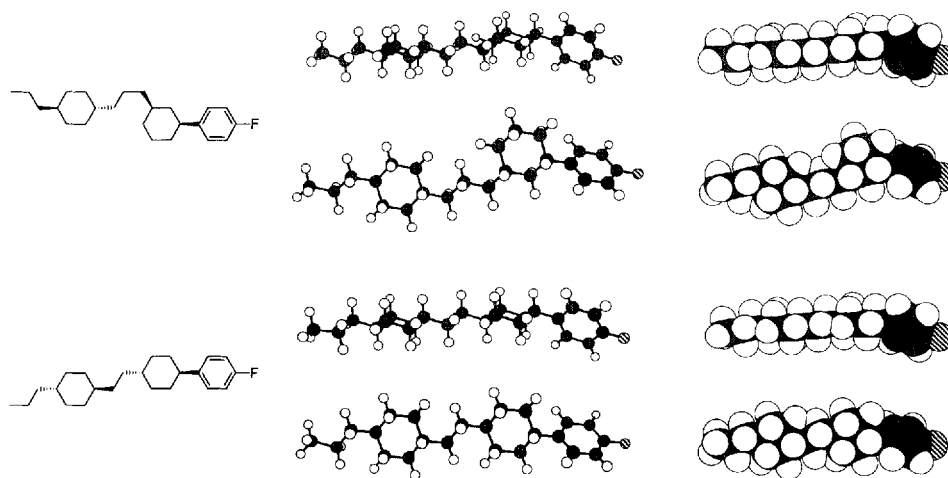
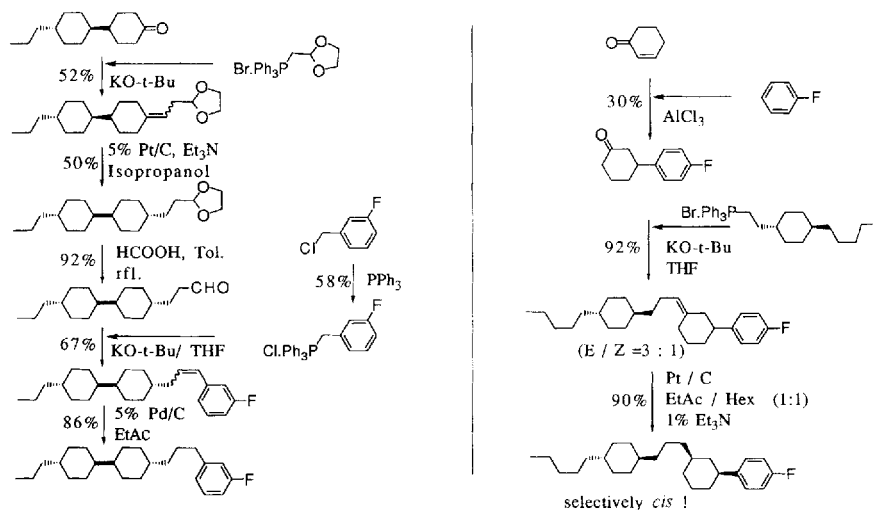


Figure. Views of molecular models incorporating a three membered linking unit and one *cis*-cyclohexane ring (upper half) and a conventional two membered linking unit and *trans*-configured rings (lower half).

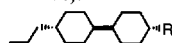


Scheme. Synthesis of two different representative compounds incorporating three membered linking units and a 1,3-substituted phenyl ring (left side) or a *cis*-1,3-substituted cyclohexane ring (right side).

Table 1. Transition temperatures in °C and enthalpies of fusion of compounds incorporating different three membered linking units located between rings two and three (left side) or between rings one and two (right side). Values in parentheses represent extrapolated clearing points in PCH5 as solvent or in the non-polar mixture CM-6092 as solvent (numbers in italics). <sup>a</sup> Smectic B phase.

	R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>	R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>
1		• 48.3	• (-92) (-83)	•	36.5	4	• 35.2	• 29.5 <sup>a</sup>	•	40.3
2		• 56.5	• (-82)	•	35.6	5	• 80.4	(13.0) (13.0)	•	43.5
3		• 25.3	• (-102)	•	24.8	6	• 83.0	• (-42.0)	•	41.0

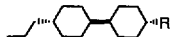
Table 2. Transition temperatures in °C and enthalpies of fusion of 3-fluorophenyl derivatives differing in the nature of their three membered linking units. Values in parentheses represent extrapolated transition temperatures in PCH5 as solvent or in the non-polar mixture CM-9062 as solvent (numbers in italics).



R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>	R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>
	• 35.2	• 29.5 <sup>a</sup>	•	40.3		• 67.7	• (-2.5)	•	33.5
	• 80.4	• (13.0)	•	38.1		• 42.9	• (-41.0)	•	32.9
	• 60.0	• (19.5)	•	33.8		• 83.0	• (-42.0)	•	41.0

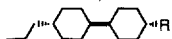
<sup>a</sup> Smectic B phase.

Table 3. Transition temperatures in °C and enthalpies of fusion of compounds incorporating a *meta*- or a *para*-substituted phenyl ring. Values in parentheses represent extrapolated transition temperatures in PCH5 as solvent.



R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>	R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>
	• 48.5	• (5.0)	•	30.8		• 103.0	• (-22)	•	35.1
	• 67.7	• -(2.5)	•	33.5		• 81.8	• (-1)	•	36.0

Table 4. Transition temperatures in °C and enthalpies of fusion of compounds incorporating phenyl rings with increasing numbers of fluorine substituents. Values in parentheses represent extrapolated transition temperatures in PCH5 as solvent or in the non-polar mixture CM-9062 as solvent (numbers in italics).



R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>	R	Cr	N	I	$\Delta H/$ kJ mol <sup>-1</sup>
	• 67.7	• (-2.5)	•	33.5		• 76.8	• (-3.5)	•	35.0
	• 80.4	• (13.0)	•	38.1		• 82.9	• (7.5)	•	40.3
	• 60.0	• (19.5)	•	33.8		• 63.8	• (13.0)	•	36.6

Table 5. Transition temperatures in °C of fluorophenyl derivatives with directly linked ring or a two membered linking unit for comparison.

Compound	Cr	N	I	Ref.
	• 88.6	• 158.5	•	[1]
	• ?	• 137	•	[2]

a 1,3-(*cis*)-substituted ring achieves the mesophase range of ethylene- or directly-linked conventional analogues (cf. table 5).

The following observations are however of basic interest:

- Location of the three membered bridge between the central ring and the ring bearing the side chain (terminal position) is less favourable to the mesophase than location between the central ring and the head ring.
- Restricted conformational mobility of the three membered linking unit leads to lower clearing points than do more flexible linking units.
- In accordance with the model, higher clearing points result if the three membered bridge is linked to the ring at the 3-position rather than at the usual 4-position.

— Lateral substitution of the head group, usually known to depress the mesophase, has virtually no effect on the mesophases of the compounds investigated here.

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