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# Liquid-crystalline compounds containing tricyclo(4.4.0.$0^{3,8}$)-decane (twistane) and spiro(3.3)heptane ring systems[†]

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A new series of liquid-crystalline materials containing the tricyclo(4.4.0.$0^{3,8}$)-decane (twistane) and further examples of materials containing the spiro(3,3)heptane system have been prepared and their thermal properties examined. The mesomorphic properties are compared with those of the benzene, trans-cyclohexane and bicyclo(2.2.2)octane derivatives. The replacement of the benzene ring in related compounds by the twistane ring results in a lowering of the melting and the clearing points as well as a narrowing of the mesophase interval. The esters of spiro(3,3)heptane prepared exhibit smectic mesophases with a narrow temperature interval.

Liquid crystals containing the bicyclo(2.2.2)octane (BCO) system were examined for the first time by Dewar *et al.* [1–4] and later [5–7] it was shown that replacement of the benzene (Bz) ring in a typical liquid crystal material by BCO can lead to an increase in the thermal stability of the mesophase and to a widening of the mesomorphic temperature range. These results were proved by further work on the synthesis and the investigation of the properties of liquid-crystalline materials containing the BCO unit, essentially through the work of Gray *et al.* [8–12].

In the present study we report further investigations of the influence on mesomorphic properties of replacement of central and terminal benzene rings in well-known liquid crystal structures by other saturated systems. Here we report for the first time properties of esters containing the twistane (TW) ring system, together with esters containing the spiro(3,3)heptane system, first used by Gray and co-workers as a component of liquid crystal structures [13, 14]. The transition temperatures of these compounds are now compared with those of the benzene, trans-cyclohexane (CH) and bicyclooctane derivatives.

Tricyclo(4.4.0.$0^{3,8}$)decane (twistane) (cf. figure 1) is a rigid, bridged, tricyclic structure composed solely of six-membered rings, twisted in the same sense. This system has a cylindrical shape, which is related geometrically to that of BCO [15].

The bridgehead–bridgehead distances in TW and BCO are quite similar. Using 8-alkyltwistanol, some liquid-crystalline esters have been obtained; their melting

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[†] This paper was presented at the Sixth Liquid Crystal Conference of Socialist Countries, 26–30 August 1985.

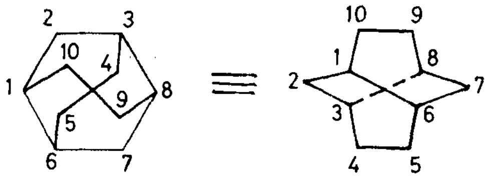
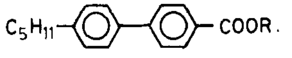


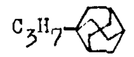
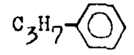
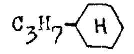
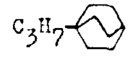
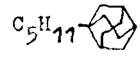
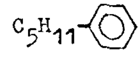
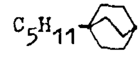
Figure 1. The structure of tricyclo(4.4.0.0$^{3,8}$)decane (twistane).

points and other transition temperatures are shown in table 1 together with those of the Bz, CH and BCO derivatives for comparison. The TW derivatives I and V exhibit nematic phases and have lower melting and clearing points, but narrower mesomorphic ranges, compared with the BCO compounds IV and VII.

The twist conformation of TW does not appear to allow the *p*-phenylene rings of neighbouring molecules to pack as efficiently as compared to BCO compounds, and this may explain the decrease in the mesophase thermostability of TW derivatives in comparison with BCO compounds.

Table 1. Transition temperatures, in °C, of twistane, benzene, cyclohexane and bicyclooctane derivatives



| Compound | *R* | K | | S | | N | | I | Reference |
|---|---|---|---|---|---|---|---|---|---|
| I |  | ● | 94·5 | – | | ● | 120·5 | ● | – |
| II |  | ● | 108·0 | ● | 142·0 | ● | 178·0 | ● | [16] |
| III |  | ● | 78·0 | – | | ● | 153·0 | ● | – |
| IV |  | ● | 128·0 | – | | ● | 188·0 | ● | – |
| V |  | ● | 70·0 | – | | ● | 127·0 | ● | – |
| VI |  | ● | 93·0 | ● | 145·0 | ● | 175·0 | ● | [16] |
| VII |  | | 117·0 | – | | ● | 195·0 | ● | [6,7]<br>[18] |

In accord with their influence upon the thermostability and the temperature range of mesophase existence the fragments examined can be arranged respectively in the following orders:

BCO > Bz > CH > TW; CH > Bz > BCO > TW.

The characteristic feature of the spiro(3,3)heptane (SH) ring system is the following: the substituents in the second and the fifth positions are located in two perpendicular planes that exclude the possibility of forming the rigid linear structure which is typical for the majority of liquid crystal structures. This effect depresses the liquid

Table 2. Transition temperatures, in °C, of spiroheptane, cyclohexane and bicyclooctane derivatives *R*–*X*–OOC–*Y*–COO–*X*–*R*.

| Compound | *R* | *X* | *Y* | *K* | | S | | N | | I | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VIII | $OCH_3$ |  |  | ● | 117·0 | ● | | – | 119·3 | ● | – |
| IX | $OCH_3$ |  |  | ● | 143·0 | ● | | ● | 243·0 | ● | [17] |
| X | $OCH_3$ |  |  | ● | 152·0 | – | | ● | 269·0 | ● | [3] |
| XI | $OC_6H_{13}$ |  |  | ● | 97·0 | ● | 108·0 | ● | 188·0 | ● | [17] |
| XII | $OC_6H_{13}$ |  |  | ● | 101·6 | ● | | – | 102·0 | ● | – |
| XIII | $C_5H_{11}$ |  |  | ● | 66·6 | ● | | – | 67·2 | ● | – |
| XIV | $C_5H_{11}$ |  |  | ● | 123·0 | ● | | – | 156·0 | ● | – |
| XV | $C_5H_{11}$ |  |  | ● | 152·0 | – | | ● | 178·0 | ● | [18] |
| XVI | $CH_3$ |  |  | ● | 154·0 | ● | | – | 182·0 | ● | – |
| XVII | $CH_3$ |  |  | ● | 208·0 | – | | ● | 253·0 | ● | – |

crystal properties of spiro(3,3)heptane-2,5-dicarboxylic acid derivatives (cf. table 2, and figure 2).

The liquid-crystalline compounds VII, XII, XIII and XIV have considerably lower clearing points than the compounds containing Bz, CH and BCO ring systems. This can be connected with a loose molecular packing, induced by the distortion of the linear structure, and increased distances between the molecules. The mesophase temperature ranges are rather narrow for all the compounds obtained with the spiroheptane unit as a central fragment of the molecular skeleton.

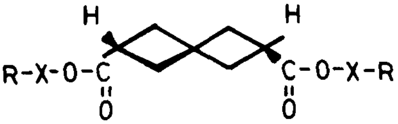


Figure 2. The structure of spiro(3,3)heptane-2,5-dicarboxylic acid derivatives.

All the compounds VIII, XII–XIV, XVI synthesized, except for compound XVII (nematic), exhibit smectic properties. Lengthening of the alkyl chain in the SH unit results only in a decrease of the melting temperature. Replacing the benzene ring in XIII by the BCO (XIV) unit considerably affects both the melting and clearing temperatures, as well as the mesophase range. The results obtained confirm once more the decisive role of rigidity and steric factors in determining the existence of the liquid-crystalline state.

Transition temperatures were determined using a Mettler-FP-5 apparatus with a polarizing microscope, MIN-8. N.M.R. spectra were determined using solutions in carbon tetrachloride, deuterochloroform and deuteroacetone using a BS-467 Tesla spectrometer (60 MHz) with tetramethylsilane as internal standard. I.R. spectra were recorded for chloroform solutions using a UR-20 spectrometer. All new compounds gave satisfactory elemental analyses. All twistane derivatives have been obtained by a novel cyclization process, which will be published later. 2,5-Spiro(3,3)heptanedicarboxylic acid was prepared by a method reported previously [19]. The esters were prepared by acylation of the corresponding alcohols with the acid chlorides in pyridine solution by the usual method.

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