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# Novel Liquid Crystalline Derivatives of Cubanes and Hydrogenolyzed Cubanes

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# Novel Liquid Crystalline Derivatives of Cubanes and Hydrogenolyzed Cubanes†

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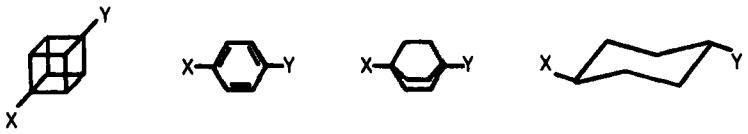
The N-I transition temperatures for a range of 4-propyl 1-monoesters and several 1,4-diesters of cubane, bicyclo(2.2.2)octane, cyclohexane and benzene have been determined. The differences between the values for the monoesters and diesters of each system and between those for the various ring systems for the mono- and di-ester series are discussed. Cubane has a very poor ability to generate nematic phases of high thermal stability, and the relative nematic stability of the benzene derivatives are significantly different in the two series, the diesters with a central benzene ring having the highest N-I transition temperatures. The values for diesters and monoesters of dihydrocubane are compared with those for cubanes and the effect of deviations from colinearity of the substituent bonds and of changes in flexibility are discussed.

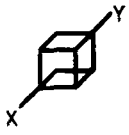
## INTRODUCTION

In a previous paper[1] we reported our initial work on the synthesis of novel mesogens with the 1,4-disubstituted cubane unit (I) as the core structure. The compounds we had prepared were esters of 4-propylcubane-1-carboxylic acid and diesters of cubane-1,4-dicarboxylic acid. These compounds are axially symmetrical, as are 1,4-disubstituted benzenes (II) and 1,4-disubstituted bicyclo(2.2.2)octanes (III), and should have the ideal lath-like molecular structure which is characteristic of nematogens.

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982.




(I) (II) (III) (IV)




(V)

## RESULTS AND DISCUSSION

In this paper we give further examples of nematogens of 1,4-disubstituted cubanes and we compare their $T_{N-I}$ values with those of the corresponding 1,4-disubstituted bicyclo(2.2.2)octanes, *trans*-1,4-disubstituted cyclohexanes (IV) and 1,4-disubstituted benzenes. In addition, we compare the nematic character of cubane and dihydrocubane (V) mono- and diesters. The transition temperatures for the monoesters and diesters are shown in Tables I and II respectively. In these Tables, references to literature values have already been quoted;[1] additional compounds now cited have been prepared in the course of this work.

It is immediately clear for both sets of values that cubane is not capable of generating nematic phases with a high thermal stability and the order of decreasing nematic thermal stability is for *monoesters*,

$$\text{Bicyclo-octane} \overset{31^\circ}{>} \text{cyclohexane} \overset{5.5^\circ}{>} \text{benzene} \overset{76^\circ}{>} \text{cubane}$$

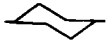
and for *diesters*,

$$\text{Benzene} \overset{9.5^\circ}{>} \text{bicyclo-octane} \overset{24^\circ}{>} \text{cyclohexane} \overset{63^\circ}{>} \text{cubane}$$

The values above the inequality signs show the average value by which the N-I transition temperatures of compounds on the left are greater than those on the right. Although cubane is the worst system in each set, the order for the other systems changes and some explanation has to be provided either for benzene derivatives moving to the top, or, conversely, for bicyclo-octane and cyclohexane systems moving down the order of diesters as compared with the order for monoesters.

TABLE I

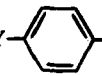
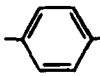
Transition temperatures (°C) for $C_3H_7$-X-$CO_2$-  -Y

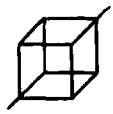
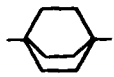
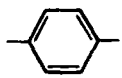
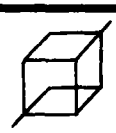
| X | Y | C-$S_E$/$S_B$/N/I | $S_E$-$S_B$ | $S_B$-$S_A$ | $S_B$/$S_A$-N | N-I |
|---|---|---|---|---|---|---|
|  | -$C_5H_{11}$ | 51 | - | - | - | [-60][b] |
| | -  -CN | 107.5 | - | - | - | 171 |
| | -  -$C_3H_7$ | 110 | - | - | - | 118 |
| | -  -$C_5H_{11}$ | 99.5 | - | - | - | 108 |
| | -  -$C_7H_{15}$ | 71 | - | - | - | 97 |
| | -  -$C_3H_7$ | 101 | - | - | - | 116 |
|  | -$C_5H_{11}$ | 29.5 | - | - | - | 55.5 |
| | -  -CN | 142 | - | - | - | 289.5 |
| | -  -$C_3H_7$ | 131 | - | - | - | 232 |
| | -  -$C_5H_{11}$ | 93 | - | - | 97 | 217 |
| | -  -$C_7H_{15}$ | 83 | - | 108 | 148.5 | 202 |
| | -  -$C_3H_7$ | 156 | - | - | - | 221 |
|  | -$C_5H_{11}$ | 32.5 | - | - | - | (29)[a] |
| | -  -CN | 94.5 | - | - | - | 249 |
| | -  -$C_3H_7$ | 108.5 | - | - | - | 199 |
| | -  -$C_5H_{11}$ | 71 | 108 | - | 113 | 188 |
| | -  -$C_7H_{15}$ | 80 | 108 | 124 | 132.5 | 176.5 |
|  | -$C_5H_{11}$ | 14 | - | - | - | 20 |
| | -  -CN | 126 | - | - | - | 245 |
| | -  -$C_3H_7$ | 109 | - | - | - | 195 |
| | -  -$C_5H_{11}$ | 101 | - | - | - | 184 |
| | -  -$C_7H_{15}$ | 89.5 | - | - | 92 | 170 |
|  | -  -$C_3H_7$ | 84 | - | - | - | 142 |
| | -  -$C_5H_{11}$ | 73 | - | - | - | 130 |
| | -  -$C_7H_{15}$ | 62 | - | - | 74.5 | 120.5 |

[a]monotropic transition
[b]virtual transition

Although it may be argued that cyclohexane would become worse than benzene in the diesters because a central, flexible cyclohexane ring may produce a significant disalignment of its substituent groups by a hinging effect, it is difficult to understand why bicyclo-octane should behave in this way, since any twisting or compression that occurs in this ring system does not seriously affect the colinearity of the 1,4-bonds. It is also worth noting

TABLE II

Transition temperatures (°C) for Y–  –$O_2C$-X-$CO_2$–  –Y

| X | Y | C-N/I | N-I |
|---|---|---|---|
|  | $-OCH_3$ | 175 | 180 |
| | $-OC_4H_9$ | 150 | (133)[a] |
|  | $-OCH_3$ | 152 | 267 |
| | $-OC_4H_9$ | 114 | 230 |
|  | $-OCH_3$ | 140 | 243 |
|  | $-OCH_3$ | 211 | 281 |
| | $-OC_4H_9$ | 189 | 235 |
|  | $-OCH_3$ | 157 | (144)[a] |
| | $-OC_4H_9$ | 99 | 129 |

[a]monotropic transition

that the average difference in $T_{N-I}$ for bicyclo-octane and cyclohexane in the two series is not markedly different (31° and 24°), and a more probable explanation for the change in order may be that benzene is a more effective unit in the diesters. A central position for benzene in the diesters would allow conjugation throughout the molecule and so enhance the anisotropy of molecular polarizability, $\Delta\alpha$. This explanation is also attractive because it can be applied to other exceptional cases where benzene appears superior to bicyclo-octane or cyclohexane.[2] In each of these exceptional systems, benzene is particularly effective when it is a central unit or when it carries an atom with at least one lone pair of electrons (oxygen or nitrogen), and an enhanced molecular polarizability should operate in these cases also.

If the change in the order for the diesters can be explained in this way, then the fundamental series which requires further explanation is that for the monoesters and their order may be justified in the following way.

(a) Bicyclo-octane is the best system because of a favorable combination of properties such as its molecular polarizability, the colinearity of its 1,4-bonds and its ability to flex, which allows good packing and filling of space between the molecules.

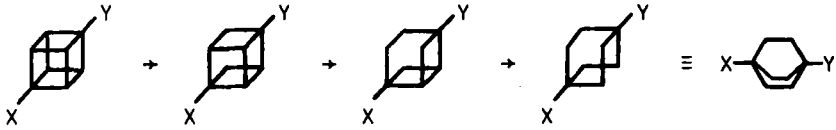
(b) Cyclohexane also has considerable flexibility which helps its packing and space-filling characteristics, but if in flexing, the 1,4-bonds deviate from colinearity, this would be disadvantageous.

(c) Benzene is highly polarizable and its 1,4-bonds are colinear, but it is rigid, not readily deformable, and its packing/space filling ability is not as good as bicyclo-octane or cyclohexane. In addition, its conjugative interactions are less significant in a non-central position.

(d) Cubane is a poor system for reasons which are examined more closely below.

An explanation for the poor ability of the cubane ring system to generate nematic phases of high thermal stability is not provided by a comparison of the molecular dimensions of cubane, bicyclo-octane and benzene. Both for length along the molecular axis and width across the molecular axis, cubane has values intermediate between those of bicyclo-octane and benzene.[1] The most reasonable explanation for cubane being the worst of these systems may be that cubane is a rigid and angular structure, and as a result it will probably show poor packing and space-filling properties. It is also interesting to note that none of the cubane mesogens we have prepared show smectic properties which would be indicative of good packing and space filling.

Although the suggestion that cubane is rigid, angular and inflexible may be qualitatively acceptable, the extent of such effects is difficult to quantify. However, some indication of the effect of an increasing flexibility on $T_{N\text{-}I}$ values may emerge by considering the series of substituted cubanes, dihydrocubanes, tetrahydrocubanes and bicyclo-octanes shown below.




(I) (V) (VI) (III)

1,4-Disubstituted cubanes can be converted into 1,4-disubstituted bicyclo(2.2.2)octanes by successive hydrogenolyses,[3] and so a rigid system with colinear 1,4-bonds becomes a more flexible system with colinear 1,4-bonds. The dihydro- and tetrahydro-cubane rings are progressively less strained than cubane and the flexibility of the systems should increase as the strain energy of the systems decreases in approximately equal steps (see Table III). The colinearity of the 1,4-bonds has, however, been lost for the

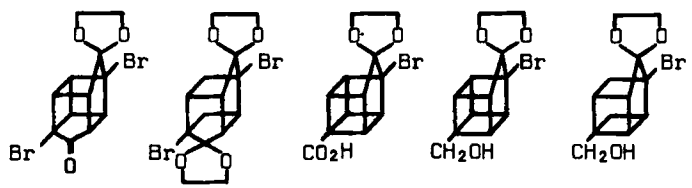
dihydro- and tetrahydro-compounds and the deviations from colinearity of the 1,4-bonds for the four ring systems are shown in Table III. We are attempting to prepare mono- and di-esters of (V) and (VI) and some results for the dihydro systems are given in Tables I and II.

The dihydrocubane diesters (Table II) show a *decrease* in $T_{N-I}$ values compared with the cubane diesters, and the *increase* in flexibility of the dihydro-system, which we believe should lead to an *increase* in $T_{N-I}$, must be offset by the deviation from colinearity (22°) which will have a strong effect on the overall molecular linearity in the case of a centrally placed dihydrocubane system. For the monoesters, the lack of colinearity appears to be less serious when it arises at the end of a molecule and is more than offset by the increased flexibility of the dihydro-system leading to higher $T_{N-I}$ values.

Eventually we hope to prepare the mono- and di-esters of the tetrahydrocubanes (VI) and it may be of interest to speculate that both the monoesters and diesters would be expected to have higher $T_{N-I}$ values than the corresponding dihydrocubanes because of the further increase of flexibility and the reduced deviation from colinearity.

## EXPERIMENTAL

An outline of the preparation of the cubane mono- and di-esters is given in Ref. 1. The following is a brief outline of the preparation of the dihydrocubane mono- and di-esters; full experimental details will be published elsewhere. Dihydrocubane diesters were prepared from (VII)[5] which was converted into the bisethylene acetal, hydrogenolyzed to (VIII), hydrolyzed




(VII) (VIII) (IX) (X) (XI)

to the diketone and ring contracted to the diacid [(V); X = Y = $CO_2H$]. The route to the dihydrocubane monoesters also starts with (VII) which is converted into (IX) and then into (X) by reduction of the methyl ester. Hydrogenolysis of (X) gives (XI) and the subsequent steps are analogous to those mentioned in Ref. 1 for the cubane monoesters.

The esters of the di-acids and mono-acids were prepared by conventional procedures, as were those for the cyclohexane and benzene systems.

TABLE III

| | Deviation of substituent bonds from colinearity[a] | Strain Energy[b] (kcal/mole) |
|---|---|---|
| Cubane ((I), X = Y = H) | 0° | 155.7 |
| Dihydrocubane ((V), X = Y = H) | 22° | 108.0 |
| Tetrahydrocubane ((VI), X = Y = H) | 12° | 59.9 |
| Bicyclo(2.2.2)octane ((III), X = Y = H) | 0° | 11.3 |

[a]Calculated from the atomic co-ordinates produced by using the program STRAIN.[4]
[b]Calculated by using the program STRAIN.[4]

## Acknowledgments

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4. The program STRAIN (University of Stirling, Scotland) uses the method of E. M. Engler, J. D. Andose and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).
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