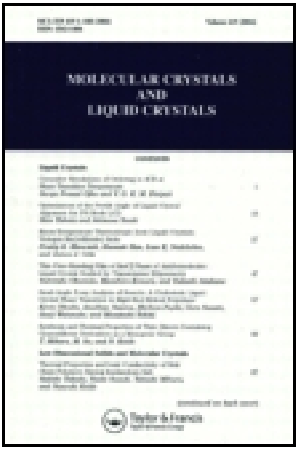

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Novel Cubane Mesogens

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NOVEL CUBANE MESOGENS

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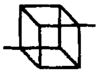
Abstract: As part of a research programme in which we are examining the effects of introducing certain novel ring types into the core structures of suitable mesogenic systems, we now report results obtained using the 1,4-disubstituted cubane structure. From data on two types of ester, large decreases in the N-I transition temperatures have been observed compared with those for analogous esters incorporating more commonly used ring types.

A characteristic of nematogens is the lath-like nature of their molecular structures, and a suitable geometry that allows formation of rod-like disubstituted derivatives, in which the bonds to the substituents are co-linear, is provided in 1,4-disubstituted benzenes (I), the related 4,4'-disubstituted biphenyls (II),[1] and 1,4-disubstituted bicyclo(2.2.2)octanes (III).[2a,b] Recently we have been investigating the potential liquid crystalline behaviour of 1,4-disubstituted cubanes (IV) which represent another system which is axially symmetrical. At the Eighth International Liquid Crystal Conference in Kyoto, Japan, it


(I)

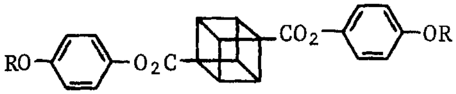

(II)


(III)


(IV)

was reported[3] that nematic behaviour had been observed in certain cubane systems, and this induces us to report now work done during the last fifteen months, the results of which provide a comparison of the nematic character of 1,4-disubstituted cubanes, bicyclo(2.2.2)octanes, benzenes, and cyclohexanes. In the first instance, molecular models of these compounds showed that cubane, bicyclo(2.2.2)octane, and benzene have similar molecular dimensions and it was of interest to determine whether the similar molecular sizes would be reflected in similar properties of the nematogens.

We have prepared two systems containing the cubane unit, *ie*, the 1,4-diesters (V), which are analogous to the Dewar diesters,[2b] and the 4-alkyl-substituted monoesters (VI).

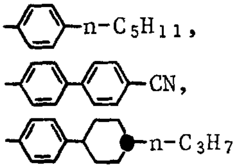


(V)

$R = CH_3$, n-C_4H_9

(VI)

$R = C_3H_7$; $R' =$

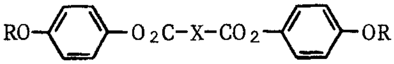


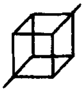
The transition temperatures for the diesters and monoesters are given in Tables I and II. It is clear from these results that the presence of the cubane nucleus greatly decreases T_{N-I} in comparison with the values for the corresponding benzene, cyclohexane, and bicyclo(2.2.2)octane derivatives. The values in Table I for the methoxy compounds show that for the structural change benzene → cubane, T_{N-I} decreases by 101.3°C, whereas for cyclohexane → cubane, T_{N-I} decreases by 63.6°C, and for bicyclo(2.2.2)octane → cubane, T_{N-I}

decreases by 89.1°C. A similar comparison for the monoesters in Table II shows that for benzene → cubane, T_{N-I} decreases by 80°C, for cyclohexane → cubane, T_{N-I} decreases by 89°C, and 78.1°C, and for bicyclo(2.2.2)octane → cubane, T_{N-I} decreases by 115.5°C, 118.6°C, and 104.6°C. Clearly the presence of the cubane system reduces the thermal stability of the nematic phase very considerably.

TABLE I

Transition temperatures (°C) for diesters



X	R	C-N/I	N-I
	CH_3	175.1	179.7
	C_4H_9	150.0	(132.9)[a]
	CH_3	211.0	281.0
	C_4H_9	189.0	235.0
	CH_3	140.2	243.3[b]
	CH_3	152.0	268.8[b]
	C_4H_9	114.2	230.1

[a] monotropic transition

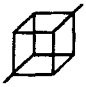
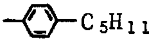
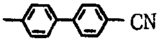
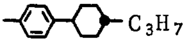
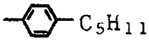
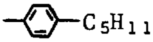
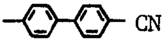
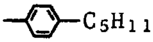
[b] MJS Dewar and AC Griffin, *J Amer Chem Soc*, *97*, 6662 (1975).

To compare the molecular dimensions of benzene, bicyclo(2.2.2)-octane, and cubane more accurately than is possible by constructing molecular models, we have carried out force-field calculations[4] and have then calculated the relevant dimensions shown in Table III. The calculations for the

TABLE II

Transition temperatures (°C) for monoesters

$n\text{-}C_3H_7\text{-}X\text{-}CO_2R$

X	R	C-N/I	N-I
		51.0	[-60.0][a]
		107.5	170.9
		100.9	116.4
		14.0	20.0[c]
		32.5	(29.0)[b,d]
		94.5	249.0[e]
		29.5	55.5[f]
		142.0	289.5[f,g]
		156.0	221.0[h]

[a] virtual transition

[b] monotropic transition

[c] R Steinstrasser, *Z Naturforsch*, *B27*, 774 (1972).

[d] D Demus, H-J Deutscher, J Kushel, and H Schubert, *DDR Patent*, 105,701 (1974).

[e] GW Gray and DG McDonnell, *Mol Cryst Liq Cryst*, 53, 147 (1979).

[f] GW Gray and SM Kelly, *J Chem Soc, Chem Commun*, 465 (1980).

[g] GW Gray and SM Kelly, Proc Eighth Int Liquid Crystal Conference, Kyoto, Japan, June-July, 1980, to be published.

[h] SM Kelly, unpublished results.

TABLE III

Molecular dimensions (Å) for benzene, bicyclo(2.2.2)octane, and cubane[a]

	$C_1\cdots\cdot C_4$[b]	$H(C_1)\cdots\cdot(C_4)H$[c]	$H\cdots\cdot H$ width[d]	$C\cdots\cdot C$ width[e]
Benzene	2.78	4.97	4.31	2.41
Bicyclo(2.2.2)octane	2.55	4.77	5.61	2.88
Cubane	2.68	4.87	4.59	2.53

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

[b] Distance from C_1 to C_4.

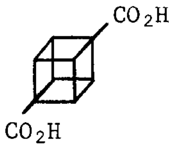
[c] Distance between the hydrogen atoms on C_1 and C_4.

[d] Diameter of the cylinder swept out by the hydrogen atoms on rotation about the C_1C_4 axis.

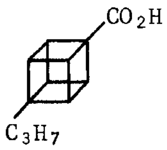
[e] Diameter of the cylinder swept out by the carbon atoms on rotation about the C_1C_4 axis.

length along the molecular axis show that the order is benzene > cubane > bicyclo(2.2.2)octane and for the width across the molecular axis, bicyclo(2.2.2)octane > cubane > benzene. For both dimensions, cubane has an intermediate value, and it is therefore even more surprising that it has such a dramatic effect on the N-I value. One marked difference between cubane and bicyclo(2.2.2)octane is that the former polycyclic compound is much more resistant to molecular deformation by compression along or twisting about the C_1C_4 axis. Such differences may be reflected in results relating to the elastic constants or other physical parameters for the nematic phases of the cubanes. Physical studies aimed at producing such data are now being carried out and will form the basis of a future publication.

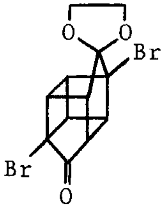
Experimental: The cubane diesters and monoesters were prepared by esterification of cubane-1,4-dicarboxylic acid (VII) and 4-propylcubane-1-carboxylic acid (VIII) respectively, *via* the acid chlorides. Compound (VII) was



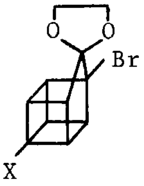
(VII)



(VIII)



(IX)



(X), X = CO_2CH_3
(XI), X = CH_2OH

prepared from (IX)[5,6] by hydrolysis to the diketone dihydrate which gave (VII) by a double Favorskii ring contraction.[7] Compound (VIII) was prepared, *via* (X),[6] from the toluene-*p*-

sulphonyl derivative of (XI) by reaction with $EtMgBr/Li_2CuCl_4$/THF[8] followed by hydrolysis of the acetal and a Favorskii ring contraction.

References

[1] GW Gray in *Advances in Liquid Crystals*, ed GH Brown (Academic Press, New York, 1976), Chap 1, p1 and references cited therein.

[2] (a) GW Gray and SM Kelly, *J Chem Soc, Chem Commun*, 974 (1979) and 466 (1980); GW Gray and SM Kelly, *J Chem Soc, Perkin II*, in press; N Carr, GW Gray, and SM Kelly, *Mol Cryst Liq Cryst*, in press.

(b) MJS Dewar and RM Riddle, *J Amer Chem Soc*, *97*, 6658, (1975); MJS Dewar and AC Griffin, *J Amer Chem Soc*, *97*, 6662 (1975).

[3] B Grant, Proc Eighth Int Liquid Crystal Conference, Kyoto, Japan, June-July, 1980, invited lecture E-2, to be published.

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

[5] PE Eaton and TW Cole, *J Amer Chem Soc*, *86*, 3157 (1964).

[6] NB Chapman, JM Key, and KJ Toyne, *J Org Chem*, *35*, 3860 (1970).

[7] T Luh and LM Stock, *J Org Chem* *37*, 338 (1972).

[8] G Fouquet and M Schlosser, *Angew Chem Internat Ed Engl*, *13*, 82 (1974).

Acknowledgements

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