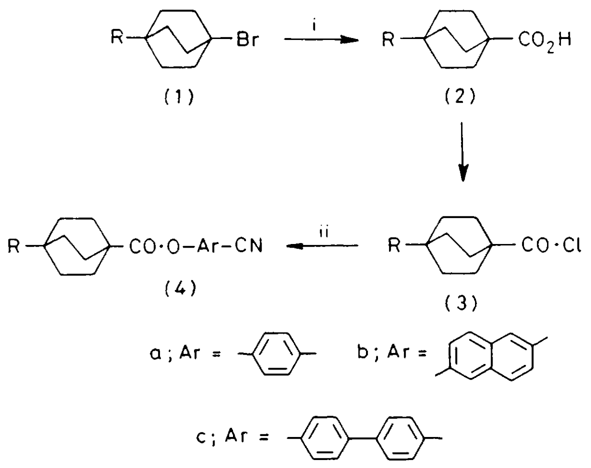
Bicyclo[2.2.2]octane Esters exhibiting Wide-range Nematic Phases

By George W. Gray* and Stephen M. Kelly

(*Department of Chemistry, The University of Hull, Hull* HU6 7RX)

Summary Three types of ester incorporating the 1,4-disubstituted bicyclo[2.2.2]octane ring have been prepared and found to exhibit wide-range nematic phases at higher temperatures than those of analogous mesogens containing the 1,4-disubstituted phenylene or *trans*-1,4-disubstituted cyclohexane ring.

BASED on earlier work on diesters,[1] the 1,4-disubstituted bicyclo[2.2.2]octane ring has been regarded as detrimental to the manifestation of liquid crystal properties. However, recently it has been reported[2] that some of a range of mono- and di-esters containing the 1,4-disubstituted bicyclo-[2.2.2]octane ring do exhibit higher nematic to isotropic liquid transition temperatures than analogous materials in which the 1,4-disubstituted phenylene ring replaces the bicyclo-octane ring. In this more recent work,[2] all the esters were formed from the bicyclo-octanols and aromatic carboxylic acids. In contrast, the esters (**4**) prepared by us were derived from bicyclo-octane carboxylic acids and phenols, and we find that they consistently exhibit liquid crystal transitions at higher temperatures than analogous mesogens in which the bicyclo-octane ring has been replaced by a 1,4-disubstituted phenylene[3] or a *trans*-1,4-disubstituted cyclohexane ring.[4] These observations are consistent with recent findings for other 1,4-disubstituted bicyclo[2.2.2]-octane mesogens not of the ester type reported by Gray and Kelly.[5]



Reagents: i, Ag_2SO_4–H_2SO_4, HCO_2H-hexane; ii, HOArCN, xylene–pyridine.

These results are of importance in relation to current commercial requirements for a range of stable nematogens displaying a spectrum of physical behaviour, *e.g.* birefringence, viscosity, nematic–isotropic liquid transition temperatures, for use in electro-optical displays.

The esters (**4**) of the 1-carboxy-4-substituted bicyclo-[2.2.2]octane (**2**) were prepared in three steps. Firstly, the 1-bromo-4-substituted bicyclo[2.2.2]octane (**1**) prepared from a method of Holtz and Stock,[6] was converted into the 1-carboxy-4-substituted bicyclo[2.2.2]octane (**2**) by a modified Koch–Haaf reaction.[6] The ester (**4**) was generated by an adapted literature method[1] from the acyl chloride (**3**) prepared in the normal way. After routine purification the ester (**4**) was obtained with a high degree of purity and in good yield.

The structures of the esters (**4**) were established by analysis of ^1H n.m.r., i.r., and mass spectra. G.l.c. and resistivity measurements indicated a high degree of purity ($\geqslant 99.5\%$). Transition temperatures for a selection of the esters are given in the Table.

TABLE. Transition temperatures (in °C) for compounds (**4**).

	Crystal–nematic/isotropic			Nematic–isotropic		
R	(**4a**)	(**4b**)	(**4c**)	(**4a**)	(**4b**)	(**4c**)
n-Butyl	98	108	143	(96)[a]	202	285·5
n-Pentyl	89	106	143·5	109	203·5	282·5
n-Hexyl	77	98	134	102	204	270

[a] Monotropic transition.

This communication is published by permission of the Director H.M.S.O. and the authors thank the U.K. Ministry of Defence for a research grant. The authors also thank Dr. A. Mosley and Mr. D. G. McDonnell for helpful discussions.

(*Received, 29th August* 1979; *Com.* 907.)

[1] M. J. S. Dewar and R. S. J. Goldberg, *J. Amer. Chem. Soc.*, 1970, **92**, 1582.
[2] R. C. Gayvandov and E. J. Kovshev, presented at the Seventh International Liquid Crystal Conference, Bordeaux, France, 1978.
[3] R. T. Klingbiel, D. J. Genova, T. R. Criswell, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1974, **96**, 7625; D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 249.
[4] D. Demus, H-J. Deutscher, F. Kuschel, and H. Schubert, DDR Patent, 1974, 105,701: D. Demus, 'Non Emissive Electro-optic Displays,' eds. A. R. Kmetz and F. K. Von Willison, Plenum Press, New York and London, 1976, p. 83; G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, 1979, **53**, 147.
[5] S. M. Kelly and G. W. Gray, *Angew. Chem. Internat. Edn.*, to be published.
[6] H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5183.