The Synthesis of 1,4-Disubstituted Bicyclo[2.2.2]octanes exhibiting Wide-range, Enantiotropic Nematic Phases

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The 1,4-disubstituted bicyclo[2.2.2]octane ring has been incorporated in certain cyano-substituted systems to produce series of mesogens exhibiting wide-range nematic phases. 1-(4-Cyanophenyl)- and 1-(4′-cyanobiphenyl-4-yl)-4-n-alkylbicyclo[2.2.2]octanes are colourless stable materials, whose nematic phases are of low birefringence and of positive dielectric anisotropy. This combination of properties renders eutectic mixtures of these materials attractive for electro-optical display devices, especially those involving the cholesteric–nematic phase change mode. The liquid crystal transition temperatures of these mesogens are higher than those of analogous mesogens embodying a 1,4-disubstituted benzene ring or a *trans*-1,4-disubstituted cyclohexane ring in place of the 1,4-disubstituted bicyclo[2.2.2]octane ring. The compounds therefore demonstrate the capacity of the bicyclo-[2.2.2]octane ring to give rise to interesting nematic materials.

THE operating requirements of electro-optical display devices involving the twisted nematic mode [1] were met very satisfactorily by eutectic mixtures [2] of the 4-n-alkyl- and 4-n-alkoxy-4′-cyanobiphenyls and the 4-n-alkyl-4″-cyano-*p*-terphenyls discovered by Gray and Harrison.[3] The nematic materials previously utilised in such display devices had several disadvantageous properties, *e.g.* colouration, chemical–photochemical instability, *etc.*, attributable to the central linking unit between the two benzene rings in compounds such as cyano-substituted stilbenes and Schiff's bases, azo-compounds, and azoxy-compounds. The absence of such a central linkage in the cyano-biphenyls and -*p*-terphenyls represented an important development in the search for better nematogens for reliable commercial use, and stimulated interest across a wide range of disciplines.

It is of relevance to note that all the above mentioned mesogens incorporate 1,4-disubstituted benzene rings in their structures, and this seemed consistent with the view that liquid crystal properties should be dependent upon the anisotropy of molecular polarisability as stipulated in the Maier–Saupe theory of the nematic phase.[4] Indeed, the vast majority of compounds that are known to form liquid crystals are aromatic in nature, although exceptions such as the cholesteryl alkanoates are familiar materials. It was however surprising, when Demus *et al.*[5] and then Gray and McDonnell [6] replaced the benzene ring of the acid moiety of certain cyano-substituted aryl benzoate esters, by a *trans*-1,4-disubstituted cyclohexane ring and thereby produced mesogens which not only had *lower* melting points, but also, in many cases, had *higher* clearing points than their totally aromatic analogues. This seemed to conflict with the accepted view of the molecular factors most favourable to nematic behaviour, and led to the synthesis by Eidenschink *et al.*[7] of the cyclohexane analogues of the cyano-biphenyls and -*p*-terphenyls, *i.e.* the *trans*-1-n-alkyl-4-(4-cyanophenyl)cyclohexanes (PCHs) and *trans*-1-n-alkyl-4-(4′-cyanobiphenyl-4-yl)cyclohexanes (BiCHs). These materials again exhibit wider range nematic phases, sometimes persisting until higher temperatures than those of the related, fully aromatic systems. Clearly therefore, accurate correlations between molecular structure and liquid crystal properties require more than casual judgements of the anisotropy of molecular polarisability in terms of the aromatic character of the molecule and the likely conjugative interactions that may arise within it.

As a result of these studies, a range of stable nematogens of high positive dielectric anisotropy has become available in the last few years for use in electro-optical displays. However, progress demands that such displays shall fulfil an increasing range of functions, and as the displays grow in sophistication, this places new demands upon the liquid crystal materials and the requirements laid down for their physical characteristics.

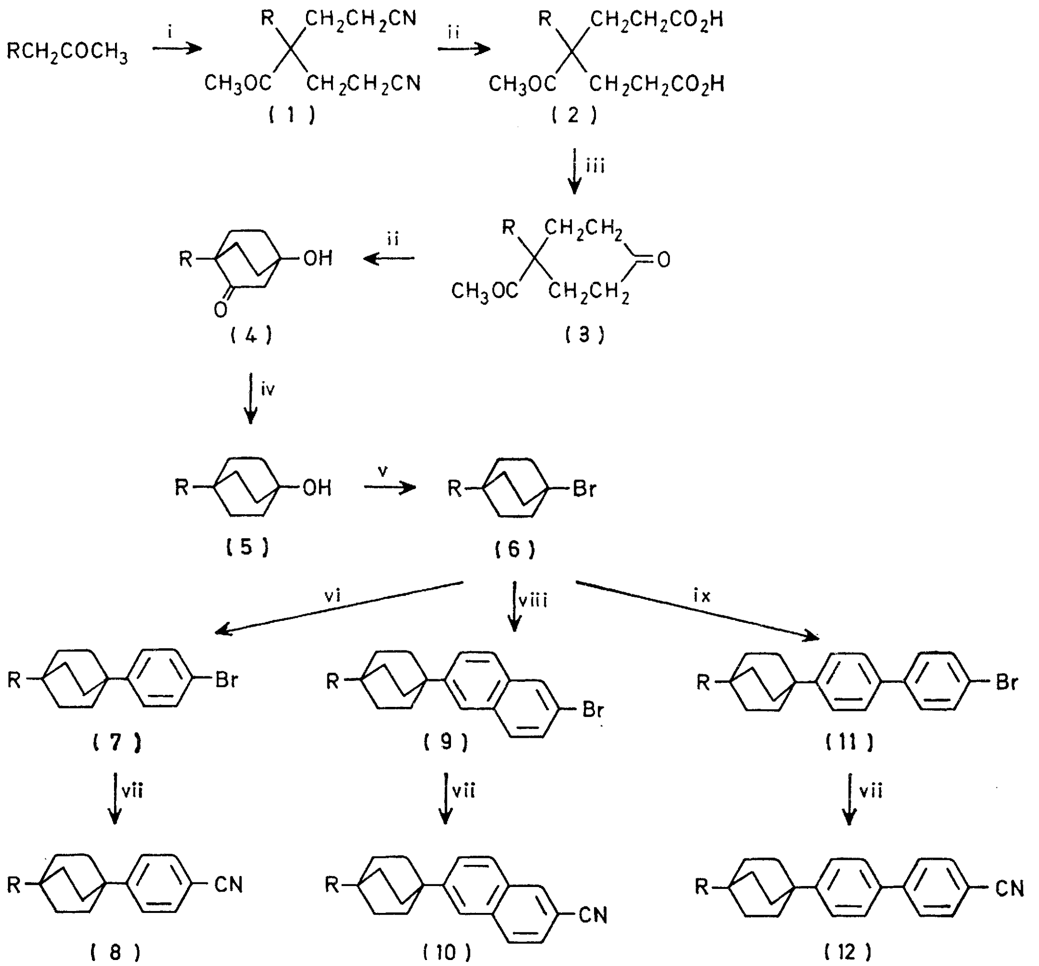
RESULTS AND DISCUSSION

As a logical development of the work outlined above, it was considered that incorporation of the 1,4-disubstituted bicyclo[2.2.2]octane ring in similar molecular structures to those of the cyano-biphenyl and cyano-*p*-terphenyls, and the PCH and BiCH materials would create new mesogens which would not only manifest wide-range nematic phases of similar birefringence to the nematic phases of the *trans*-1,4-disubstituted cyclohexanes, but also might have other interesting properties arising from the resulting changes in elastic constants. Thus it was decided to prepare the 1-n-alkyl-4-(4-cyanophenyl)bicyclo[2.2.2]octanes (8), the 1-n-alkyl-4-(4′-cyanobiphenyl-4-yl)bicyclo[2.2.2]octanes (12), and the 1-n-alkyl-4-(6-cyano-2-naphthyl)bicyclo[2.2.2]octanes (10) (see Scheme).

The aim was to prepare 1-n-alkyl-4-bromobicyclo[2.2.2]octanes (6) by the method of Holtz and Stock,[8] using terminal alkyl substituents from methyl to n-heptyl. The aliphatic bromides (6) would then be utilised in novel Friedel–Crafts alkylation reactions with bromobenzene, 2-bromonaphthalene, and 4-bromobiphenyl to yield 1-n-alkyl-4-(4-bromophenyl)bicyclo[2.2.2]octanes (7), 1-n-alkyl-4-(6-bromo-2-naphthyl)bicyclo[2.2.2]octanes (9), and 1-n-alkyl-4-(4′-bromobiphenyl-4-yl)bicyclo[2.2.2]octanes (11), respectively.

These aryl bromides would then be cyanated to yield the desired nitriles (8), (10), and (12). Tables 1 and 2 and Figures 1 and 2 present thermodynamic data for the fourteen mesogens of types (8) and (12).

The liquid crystal transition temperatures recorded in Tables 1 and 2 and plotted against the number of carbon atoms in the alkyl chains in Figures 1 and 2 show that the melting points (C–N, C–I) do not change regularly as the series are ascended. The clearing points (N–I) on the other hand do change in a systematic manner as the alkyl chains lengthen. The clearing points are lowest for short alkyl chains, then rise dramatically for chains containing three to five carbon atoms, and finally fall away gradually for the longest alkyl chains that have been used. As a result of the alternation in the N–I values, the clearing points lie on two distinct curves for each series. The mesogens possessing alkyl chains with an odd number of carbon atoms relate to the upper curve, while that with an even number of carbon atoms relate to the lower curve. Many of the bicyclo[2.2.2]octanes (8) and (12) therefore exhibit enantiotropic nematic phases of wide range at higher temperatures than the corresponding mesogens containing a 1,4-disubstituted benzene ring or a *trans*-1,4-disubstituted cyclohexane ring in place of the bicyclo-octane ring.* For example, the N–I value of compound (8) with R = n-pentyl is 100°, whereas the corresponding PCH derivative has N–I 55° and the corresponding biphenyl has N–I 35°. These observations conflict with some results obtained by Dewar and Goldberg on diesters,[9] but are consistent with the recent findings of Gray and Kelly on monoesters,[10] and with some of the results of Gayvandov and Kovshev,[11] and demonstrate the ability of 1,4-disubstituted bicyclo[2.2.2]octane to give rise to pronounced nematic properties when it is incorporated in a suitable molecular structure.



SCHEME Reagents: i, CH_2=CHCN–OH^-; ii, OH^-; iii, $(CH_3CO)_2O$; iv, H_2NNH_2–H_2O–OH^-–diethylene glycol; v, $ZnBr_2$–HBr; vi, $AlCl_3$–PhBr; vii, CuCN; viii, $AlCl_3$–$C_{10}H_7Br$-2; ix, $AlCl_3$–PhC_6H_4Br-4

Because of the wide-range nematic phases that were given by many of the compounds (8) and (12), it was concluded that the 1-n-alkyl-4-(6-cyano-2-naphthyl)-bicyclo[2.2.2]octanes would be unlikely to have any

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* A full discussion of the strikingly higher N–I transition temperatures of the bicyclo-octane compounds (both those described here and also analogous esters) will be presented in a subsequent publication.

specially advantageous properties. However, one example of the series was prepared as a matter of interest. 1-(6-Cyano-2-naphthyl)-4-pentylbicyclo[2.2.2]octane has C–N 115 and N–I 159°. As would be expected, the compound gives a moderately wide-range nematic phase at temperatures intermediate between those of the pentyl homologues of compounds (8) and (12). The increases in the melting and clearing points of this naphthalene derivative, relative to 1-(4-cyanophenyl)-4-pentylbicyclo[2.2.2]octane, are approximately equal (50—60°), whereas the corresponding increase in the clearing point (170°) of 1-(4′-cyanobiphenyl-4-yl)-4-pentylbicyclo[2.2.2]octane is considerably greater than the increase in the melting point (100°) (see Tables 1 and 2). This is consistent with recent results of Gray and Kelly[10] for 4-cyanophenyl, 6-cyano-2-naphthyl, and 4′-cyanobiphenyl-4-yl esters of 1-n-alkyl-4-carboxybicyclo[2.2.2]octanes.

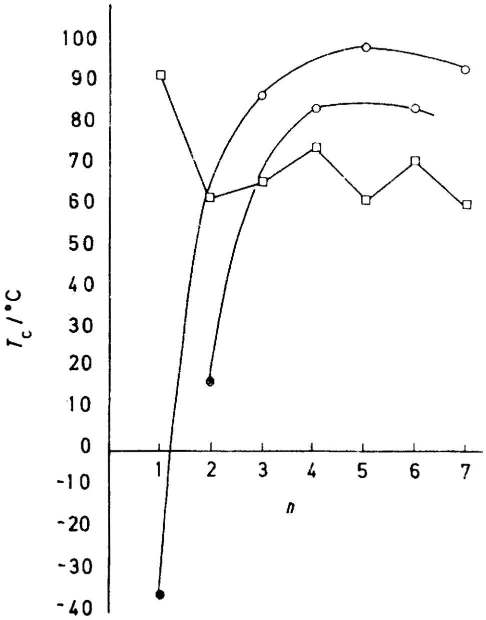

FIGURE 1 Variation in m.p. and nematic–isotropic liquid transition temperature T_c with the number of carbon atoms (*n*) in the alkyl chain for the 1-(4-cyanophenyl)-4-n-alkylbicyclo[2.2.2]octanes: □, m.p. (C–N or I); ○, nematic–isotropic liquid transition temperature (N–I); ●, virtual nematic–isotropic liquid transition temperature (N–I)

TABLE 1

Thermodynamic data for 1-(4-cyanophenyl)-4-n-alkylbicyclo[2.2.2]octanes (8)

n-Alkyl	C–N/I (°C)	N–I (°C)	ΔH/kJ mol^{-1}
CH_3	93	(−35) *	26.1
C_2H_5	62.5	(17) *	21.8
C_3H_7	66.5	88	17.4
C_4H_9	75.5	85	32.7
C_5H_{11}	62	100	20.7
C_6H_{13}	72	86	21.1
C_7H_{15}	61	95	32.7

* ' Virtual ' monotropic transition temperature determined by extrapolation (see Experimental section).

A large number of the aryl bromides (7) and (11) are themselves liquid crystalline in character and some exhibit enantiotropic nematic phases at high temperatures, *e.g.* 1-(4′-bromobiphenyl-4-yl)-4-hexylbicyclo[2.2.2]octane has C–N 158 and N–I 214°, and 1-(4-bromophenyl)-4-heptylbicyclo[2.2.2]octane has C–I 74 and (N–I) 59° (see Experimental section). In the latter example, (N–I) represents a monotropic nematic–isotropic liquid transition. These results again demonstrate the capacity of the 1,4-disubstituted bicyclo[2.2.2]octane ring to give rise to pronounced nematic liquid crystal properties when embodied in a suitable molecular environment.

TABLE 2

Thermodynamic data for 1-(4′-cyanobiphenyl-4-yl)-4-n-alkylbicyclo[2.2.2]octanes (12)

n-Alkyl	C–N/I (°C)	N–I (°C)	ΔH/kJ mol^{-1}
CH_3	198	(170) *	24.8
C_2H_5	188	221	50.5
C_3H_7	180.5	276	33.9
C_4H_9	173	271.5	34.8
C_5H_{11}	159	269	36.8
C_6H_{13} ‡	133	259	28.6 †
C_7H_{15}	141	250.5	41.4

* ' Virtual ' monotropic transition temperature determined by extrapolation (see Experimental section). † Value for fusion of the higher temperature crystal form (C_2). ‡ This material has a crystal to crystal transition (C_1–C_2; 95 °C).

It is notable that none of the mesogens prepared in this work exhibits smectic properties. Only nematic phases have been observed microscopically and compounds with the structures (8) and (12) containing longer carbon chains than C_7 will have to be synthesised in order to obtain the relative smectic tendencies of these compounds, the PCH–BiCH materials, and the biphenyls and *p*-terphenyls. All that can be said at present is that, when observed microscopically, 1-(4′-cyanobiphenyl-4-yl)-4-heptylbicyclo[2.2.2]octane (C–N 141, N–I 250.5°) can be supercooled to temperatures below 125.5° without observing a smectic phase before crystallisation occurs. This latter value is the temperature at

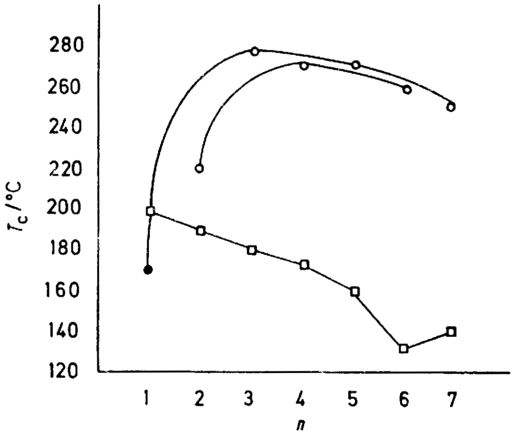

FIGURE 2 Variation in m.p. and nematic–isotropic liquid transition temperature T_c with the number of carbon atoms (*n*) in the alkyl chain for 1-(4′-cyanobiphenyl-4-yl)-4-n-alkylbicyclo[2.2.2]octanes: □, m.p. (C–N or I); ○, nematic–isotropic liquid transition temperature (N–I); ●, virtual nematic–isotropic liquid transition temperature (N–I)

which an S_A–N transition occurs in the corresponding fully aromatic material, *i.e.* 4-cyano-4″-heptyl-*p*-terphenyl [C–N 134, (S_A–N) 125.5, N–I 222°]. Transition temperatures are not at present available for the corresponding BiCH material.

The physical properties of the 1-(4-cyanophenyl)-4-n-alkylbicyclo[2.2.2]octanes (8) have been investigated both in this department and at the Royal Signals and Radar Establishment at Malvern.[12] Both single compounds and mixtures, sometimes incorporating 1-(4-cyanobiphenyl-4-yl)-4-n-alkylbicyclo[2.2.2]octane (12) or other mesogens, have been used. All these results show that the compounds (8) and (12) have a strong physical resemblance to the PCH and BiCH materials respectively; for example the nematic phase of the bicyclooctane (8) with R = n-C_5H_{11} has a birefringence (Δn) of 0.14 and a dielectric anisotropy ($\Delta\varepsilon$) of *ca.* +10 at 25°. The corresponding values for the analogous PCH material are Δn 0.12—0.13 and $\Delta\varepsilon$ +10.

There are however some notable dissimilarities, but the results illustrating such effects will be reported in detail elsewhere, with a strong emphasis on the utilisation of compounds (8) and (12) in commercial electro-optical display devices, especially with respect to the cholesteric–nematic phase-change mode of operation. The detailed results of measurements of birefringence, viscosity, dielectric anisotropy, elastic constants, and electro-optical characteristics wlll be recorded in this publication.[12]

Conclusions.—The preparation of 1-n-alkyl-4-(4-cyanophenyl)bicyclo[2.2.2]octanes (8), 1-(6-cyano-2-naphthyl)-4-pentylbicyclo[2.2.2]octanes (10), and 1-n-alkyl-4-(4′-cyanobiphenyl-4-yl)bicyclo[2.2.2]octanes (12) has yielded a new range of colourless, chemically and photochemically stable compounds giving nematic phases of low birefringence and high positive dielectric anisotropy. Suitable mixtures of the new mesogens are directly advantageous for use in electro-optical display devices and their discovery represents a significant development in the preparation of stable nematogens incorporating alicyclic components.

EXPERIMENTAL

The liquid crystal transition temperatures recorded in Tables 1 and 2 were determined by optical microscopy, utilising a Nikon L-Ke polarising microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. In those instances when it was not possible to observe the liquid crystal transitions directly, ' virtual ' nematic–isotropic liquid crystal transition temperatures were determined. This is done by making up a series of binary mixtures (of known composition) of each compound in question with a standard nematic material such as E8 (a commercial mixture of cyanobiphenyls and a 4-n-alkyl-4″-cyano-*p*-terphenyl supplied by B.D.H. Chemicals Limited, having C–N −10 and N–I 60.5°). The N–I transition temperatures of each mixture are measured in the usual way for as wide a range of compositions as possible. The N–I temperatures are then plotted against the percentage composition of the mixture. Assuming a regular (usually linear) trend in the N–I temperatures, extrapolation to 100% of the test compound gives the ' virtual ' monotropic N–I value.

Enthalpies of melting were measured using a Stanton–Redcroft (model 671) low temperature differential thermal analyser. Indium was used as a standard for calibration, and the degree of error for the quoted enthalpy values is estimated as ±10%.

Purity of Materials.—I.r., ^{1}H n.m.r., and mass spectra of compounds (1)—(6) were obtained and compared with those given by the known methyl and ethyl homologues previously made by Holtz and Stock;[8] they were found to be identical in all essential aspects. The purities of the alcohols (5) and the bromides (6) were established as at least 99% by g.l.c. The bromides (6) did not give mass ions, but gave signals at values representing the mass ion minus bromine; the alcohols (5) gave mass ions in all cases.

The ^{1}H n.m.r., i.r., and mass spectra obtained for the aromatic compounds (7)—(12) were consistent with the required structures, and each material gave a single spot on t.l.c. The g.l.c. analyses of the aromatic bromides (7) and nitriles (8) indicated purities of 99%, and values of 99.9% were common for the nitriles (8).

Satisfactory analytical data for precursors of the cyano-compounds (8), (10), and (12) were obtained; satisfactory mass measurements and analytical data for nitrogen were also obtained for the final cyano-compounds. These data, together with the CN stretching frequencies of the cyano-compounds are in Supplementary Publication No. SUP 22901 (12 pp.).*

1-*n-Alkyl*-4-*bromobicyclo*[2.2.2]*octanes*.— 3-*Acetyl*-1,5-*dicyano*-3-*pentylpentane* (1). Cyanoethylene (158 g, 3.0 mol) was added dropwise to a stirred solution of octan-2-one (192 g, 1.5 mol) and a 40% w/v solution of benzyltrimethylammonium hydroxide in methanol (6 g) in 2-methylpropan-2-ol (300 g), while the temperature of the solution was maintained between 10 and 15°. The solution was stirred overnight and allowed to reattain room temperature. The solution was evaporated under reduced pressure, the pH of the residue was adjusted from 9 to 7 by the addition of a small volume of concentrated hydrochloric acid, and anhydrous magnesium sulphate was added as drying agent. After filtration, distillation of the crude product under reduced pressure yielded 3-*acetyl*-1,5-*dicyano*-3-*pentylpentane* (163 g, 46%), b.p. 210—215° at 1.5 mmHg; *m/e* 234, m.p. 47—48°.

Results for other homologues were: methyl, *m/e* 178, 66%, m.p. 66—67° (lit.,[8] 67°); ethyl, *m/e* 192, 57%, m.p. 108—110° (lit.,[8] 109°); *propyl, m/e* 206, 48%, b.p. 188—189° at 0.4 mmHg, m.p. 65—66°; *butyl*, *m/e* 220, 61%, b.p. 180—181° at 0.7 mmHg, m.p. 58—59°; *hexyl*, *m/e* 248, 49%, b.p. 215—220 °C at 0.5 mmHg; *heptyl*, *m/e* 262, 45%, b.p. 225—227 °C at 0.3 mmHg. The methyl and ethyl homologues could be crystallised from methanol.

3-*Acetyl*-3-*pentylpentane*-1,5-*dicarboxylic acid* (2). A mixture of 3-acetyl-1,5-dicyano-3-pentylpentane (163 g, 0.7 mol), sodium hydroxide (84.1 g, 2.1 mol), and water (280 cm^3) was stirred and heated under reflux until the evolution of ammonia had ceased (10 h) and all of the organic material had gone into solution. Concentrated hydrochloric acid was added carefully to the cooled solution (Congo Red) and the precipitated *acid* was collected by filtration, washed several times with small volumes of water, pressed dry, and

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

crystallised (134.8 g, 71%) from water–ethanol, *m/e* 272, m.p. 75—76°.

Results for other homologues were: methyl, *m/e* 216, 74%, m.p. 122—123° (lit.,[8] 125°); ethyl, *m/e* 230, 74%, m.p. 111—112° (lit.,[8] 112—113°); *propyl*, *m/e* 244, 92%, m.p. 89—90°; *butyl*, *m/e* 258, 90%, m.p. 66—67°; *hexyl*, *m/e* 286, 94%; *heptyl*, *m/e* 300, 86%. The hexyl and heptyl homologues could not be obtained crystalline.

4-*Acetyl*-4-*pentylcyclohexanone* (3). 3-Acetyl-3-pentylpentane-1,5-dicarboxylic acid (130 g, 0.478 mol) and acetic anhydride (750 cm^3) were heated (14 h) under anhydrous conditions. The acetic acid formed in the reaction was continuously distilled from the mixture at 122—126° at atmospheric pressure, and an addition of acetic anhydride (250 cm^3) was made after 8 h. At the end of the reaction period, residual acetic anhydride was distilled off and water (250 cm^3) was added to the solid residue. The resultant mixture was shaken with ether (3 × 50 cm^3) and the combined organic extracts were washed with brine (2 × 250 cm^3) and dried ($MgSO_4$). Distillation of the crude product under reduced pressure yielded 4-*acetyl*-4-*pentylcyclohexanone* (70 g, 71%), b.p. 129—130° at 2.5 mmHg, *m/e* 210.

Results for other homologues were: methyl, *m/e* 154, 63%, b.p. 133—135° at 15 mmHg (lit.,[8] 133° at 15 mmHg); ethyl, *m/e* 168, 52%, b.p. 145—147° at 15 mmHg (lit.,[8] 144° at 18 mmHg); *propyl*, *m/e* 182, 62%, b.p. 91—92° at 0.65 mmHg; *butyl*, *m/e* 196, 67%, b.p. 132—134 °C at 1.7 mmHg; *hexyl*, *m/e* 224, 65%, b.p. 139—140° at 2.0 mmHg; *heptyl*, *m/e* 238, 59%, b.p. 160° at 0.8 mmHg.

1-*Hydroxy*-4-*pentylbicyclo*[2.2.2]*octan*-3-*one* (4). A mixture of 4-acetyl-4-pentylcyclohexanone (70 g, 0.33 mol), potassium hydroxide (56 g, 1.00 mol), and water (560 cm^3) was stirred and heated at 70° (6 h). The cooled mixture was shaken with ether (3 × 100 cm^3) and the combined ethereal extracts were washed with brine (2 × 250 cm^3) and dried ($MgSO_4$). The crude 1-*hydroxy*-4-*pentylbicyclo*[2.2.2]*octan*-3-*one* was crystallised (39.5 g, 56%) from cyclohexane, *m/e* 210, m.p. 36—38°.

Results for other homologues were: methyl, *m/e* 154, 71%, m.p. 57° (lit.,[8] 60°); ethyl, *m/e* 168, 81%, m.p. 49—51° (lit.,[8] 49—51°); *propyl*, *m/e* 182, 58%, m.p. 88—90°; *butyl*, *m/e* 196, 64%, m.p. 59—60°; *hexyl*, *m/e* 224, 49%, m.p. 47—48°; *heptyl*, *m/e* 238, 42%, m.p. 50—51°.

1-*Hydroxy*-4-*pentylbicyclo*[2.2.2]*octane* (5). A mixture of 1-hydroxy-4-pentylbicyclo[2.2.2]octan-3-one (21.5 g, 0.10 mol) and hydrazine hydrate (128 cm^3) was heated under reflux (5 h). Potassium hydroxide (28.9 g, 0.52 mol) and diethylene glycol (178 cm^3) were added to the cooled mixture and the temperature of the solution was raised to 230—240°, in the process of distilling off the excess of hydrazine hydrate. The solution was then heated at this temperature until the evolution of nitrogen had ceased (20 h). The cooled mixture was added to water (1 700 cm^3) and the resultant mixture shaken with ether (3 × 200 cm^3). The combined organic extracts were washed with 15% hydrochloric acid (2 × 150 cm^3), with brine (2 × 500 cm^3), and dried ($MgSO_4$). The crude 1-*hydroxy*-4-*pentylbicyclo*[2.2.2]*octane* (16.6 g, 82.7%) was crystallised from cyclohexane, *m/e* 196, m.p. 55—56°.

Results for other homologues were: methyl, *m/e* 140, 87%, m.p. 101—102° (lit.,[8] 103—104°); ethyl, *m/e* 154, 72%, m.p. 103—104° (lit.,[8] 105—106°); *propyl*, *m/e* 168, 65%, m.p. 83—84°; *butyl*, *m/e* 182, 54%, m.p. 85—86°; *hexyl*, *m/e* 210, 70%, m.p. 67—68°; heptyl, *m/e* 224, 68%, m.p 60—61°.

1-*Bromo*-4-*pentylbicyclo*[2.2.2]*octane* (6). A well stirred mixture of 1-hydroxy-4-pentylbicyclo[2.2.2]octane (20 g, 0.10 mol), anhydrous zinc bromide (99 g, 0.44 mol), and 48—50% hydrobromic acid (200 cm^3) was heated at 60—70° (16 h). The cooled mixture was added to water (300 cm^3) and shaken with ether (3 × 80 cm^3). The combined organic extracts were washed with brine (2 × 500 cm^3) and dried ($MgSO_4$). The crude reaction product was distilled under reduced pressure and 1-*bromo*-4-*pentylbicyclo*[2.2.2]*octane* (25.0 g, 95%), b.p. 104—105° at 1.4 mmHg, was collected.

Results for other homologues were: methyl, 69%, b.p. 88—90° at 12 mmHg, m.p. 91—92° (lit.,[8] b.p. 70° at 1 mmHg, m.p. 92—94°); ethyl, 81.5%, b.p. 59—60° at 12 mmHg, m.p. 35° (lit.,[8] b.p. 70° at 1 mmHg, m.p. 34—35°); *propyl*, 92%, b.p. 98—99° at 0.8 mmHg, m.p. 28—29°; *butyl*, 80%, b.p. 92—93° at 0.7 mmHg; *hexyl*, 92%, b.p. 125—126° at 1.4 mmHg; *heptyl*, 84%, b.p. 145—146° at 1.0 mmHg.

1-*Substituted* 4-*n*-*Alkylbicyclo*[2.2.2]*octanes*.— 1-(4-*Bromophenyl*)-4-*pentylbicyclo*[2.2.2]*octane* (7). A solution of 1-bromo-4-pentylbicyclo[2.2.2]octane (6 g, 0.023 mol) in sieve-dried nitrobenzene (100 cm^3) was added dropwise to a stirred solution of sieve-dried bromobenzene (97 cm^3, 0.930 mol) and anhydrous aluminium chloride (1.2 g, 0.009 mol) in sieve-dried nitrobenzene (100 cm^3) maintained at 80° throughout the addition and overnight. The cooled solution was added to a small volume of 15% hydrochloric acid and stirred (20 min). The organic layer was separated off and steam-distilled to yield a solid residue. This was taken up in chloroform and dried ($MgSO_4$). The crude product was stirred with hot ethanol and the supernatant solution was decanted off and allowed to crystallise to yield 1-(4-*bromophenyl*)-4-*pentylbicyclo*[2.2.2]*octane* (6.2 g, 80%), *m/e* 334 and 336, m.p. 95—96°.

Data for the other homologues prepared were: *methyl*, *m/e* 278 and 280, 53%, m.p. 85—86°; *ethyl*, *m/e* 292 and 294, 47%, C–I 49—50°; *propyl*, *m/e* 306 and 308, 74%, C–I 92—93°; *butyl*, *m/e* 320 and 322, 71%, C–I 75—76°; *hexyl*, 348 and 350, 57%, C–I 60°, (N–I) 42.5°; *heptyl*, *m/e* 362 and 364, 70%, C–I 74°, (N–I) 59°.

1-(4-*Cyanophenyl*)-4-*pentylbicyclo*[2.2.2]*octane* (8). A solution of 1-(4-bromophenyl)-4-pentylbicyclo[2.2.2]octane (6.1 g, 0.018 mol) and anhydrous copper(I) cyanide (4.1 g, 0.046 mol) in 1-methyl-2-pyrrolidone (18 cm^3) was heated at 185° (3 h) under anhydrous conditions. The cooled mixture was added to a solution of anhydrous iron(III) chloride (4.1 g, 0.025 mol) and concentrated hydrochloric acid (2 cm^3) in water (40 cm^3) and stirred (20 min) at 50—60°. This mixture was shaken with ether (3 × 80 cm^3) and the combined organic layers were washed with brine (2 × 250 cm^3) and dried ($MgSO_4$). The crude product was purified by column chromatography using silica gel and chloroform–light petroleum (b.p. 40—60°) (1.5 : 1) as eluant. Fractions giving only one spot on t.l.c. were collected and evaporated to yield a solid which was crystallised from methanol to yield 1-(4-*cyanophenyl*)-4-*pentylbicyclo*[2.2.2]*octane* (3.3 g, 64%), *m/e* 281 (see Table 1 and Figure 1 for the liquid crystal transition temperatures of ths and the other homologues of this series).

Data for the other homologues prepared were: *methyl*, *m/e* 225, 54%; *ethyl*, *m/e* 239, 45%; *propyl*, *m/e* 253, 73%; *butyl*, *m/e* 267, 56%; hexyl, *m/e* 295, 59%; *heptyl*, *m/e* 309, 70%.

1-(6-*Bromo*-2-*naphthyl*)-4-*pentylbicyclo*[2.2.2]*octane* (9). A solution of 1-bromo-4-pentylbicyclo[2.2.2]octane (3.0 g, 0.011 6 mol) in sieve-dried nitrobenzene (80 cm^3) was added dropwise to a well stirred solution of 2-bromonaphthalene (7.2 g, 0.034 9 mol) and crushed, anhydrous aluminium chloride (0.6 g, 0.004 6 mol) in sieve-dried nitrobenzene (50 cm^3); anhydrous conditions were maintained at 80° during the addition and overnight. The reaction mixture was worked up as for 1-(4-bromophenyl)-4-pentylbicyclo[2.2.2]octane and the crude product was crystallised from ethanol to yield 1-(6-*bromo*-2-*naphthyl*)-4-*pentylbicyclo*[2.2.2]*octane* (1.3 g, 23%), *m/e* 384 and 386, m.p. 134—135°.

1-(6-*Cyano*-2-*naphthyl*)-4-*pentylbicyclo*[2.2.2]*octane* (10). The cyanation of 1-(6-bromo-2-naphthyl)-4-pentylbicyclo-[2.2.2]octane (1.3 g, 0.003 mol) was achieved as described previously and the crude product was crystallised from ethanol to yield 1-(6-*cyano*-2-*naphthyl*)-4-*pentylbicyclo*[2.2.2]-*octane* (0.6 g, 53%), *m/e* 331 (see the Results and Discussion section for the liquid crystal transition temperatures).

1-(4′-*Bromobiphenyl*-4-*yl*)-4-*pentylbicyclo*[2.2.2]*octane* (11). A solution of 1-bromo-4-pentylbicyclo[2.2.2]octane (1.0 g, 0.003 9 mol) in sieve-dried nitrobenzene (15 cm^3) was added dropwise (30 min) to a well stirred solution of crushed, anhydrous aluminium chloride (0.2 g, 0.001 6 mol) and 4-bromobiphenyl (2.7 g, 0.011 6 mol) in sieve-dried nitrobenzene (25 cm^3); anhydrous conditions were maintained at 80° throughout the addition and overnight. The reaction mixture was worked up as for 1-(4′-bromophenyl)-4-pentylbicyclo[2.2.2]octane and the crude product was crystallised from ethylene glycol monomethyl ether to yield 1-(4′-*bromobiphenyl*-4-*yl*)-4-*pentylbicyclo*[2.2.2]*octane* (1.0 g, 63%), *m/e* 410 and 412, C–N 192°, N–I 233°.

Results for the other homologues were: *methyl*, *m/e* 354 and 356, 67%, C–I 207—208°; *ethyl*, *m/e* 368 and 370, 67%, C–I 178—179°; *propyl*, *m/e* 382 and 384, 69%, C–I 204—205°; *butyl*, *m/e* 396 and 398, 63%, C–N 188°, N–I 189°; *hexyl*, *m/e* 424 and 426, 51%, C–N 158°, N–I 215°; *heptyl*, *m/e* 438 and 440, 66%, C–N 154°, N–I 206°.

1-(4′-*Cyanobiphenyl*-4-*yl*)-4-*pentylbicyclo*[2.2.2]*octane* (12). The cyanation of 1-(4′-bromobiphenyl-4-yl)-4-pentylbicyclo[2.2.2]octane (0.8 g, 0.001 9 mol) was carried out as previously described and the crude product was crystallised from ethylene glycol monomethyl ether to yield 1-(4′-*cyanobiphenyl*-4-*yl*)-4-*pentylbicyclo*[2.2.2]*octane* (0.35 g, 54%), *m/e* 357 (see Table 2 and Figure 2 for the liquid crystal transition temperatures for this and other homologues of this series).

Data for the other homologues prepared were: *methyl m/e* 301, 49%; *ethyl*, *m/e* 315, 43%; *propyl*, *m/e* 329, 57%; *butyl*, *m/e* 343, 72%; *hexyl*, *m/e* 371, 51%; *heptyl*, *m/e* 385, 45%.

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