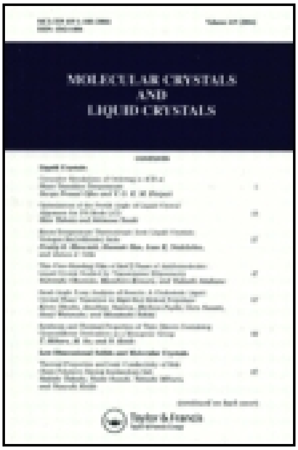


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Synthesis and Physical Properties of Some 1-n-Alkyl-4-(4-substituted phenyl) bicyclo(2.2.2)octanes

N. Carr [b] [a] , G. W. Gray [a] & S. M. Kelly [c] [a]

[a] Department of Chemistry, The University, Hull, HU6, 7RX, ENGLAND

[b] Allen Clark Research Centre, Plessey Research (Caswell) Limited, Caswell Towcester, Northants, NN12 8EQ

[c] Brown Boveri Research Centre, CH, 5405, Baden-Daettwil, Switzerland

To cite this article: N. Carr , G. W. Gray & S. M. Kelly (1985): The Synthesis and Physical Properties of Some 1-n-Alkyl-4-(4-substituted phenyl) bicyclo(2.2.2)octanes, Molecular Crystals and Liquid Crystals, 129:4, 301-313

To link to this article: http://dx.doi.org/10.1080/00268948508085036

Mol. Cryst. Liq. Cryst., 1985, Vol. 129, pp. 301–313
0026-8941/85/1294–0301/$20.00/0

The Synthesis and Physical Properties of Some 1-n-Alkyl-4-(4-substituted phenyl) bicyclo(2.2.2)octanes

N. CARR,† G. W. GRAY, and S. M. KELLY‡
Department of Chemistry, The University, Hull, HU6 7RX, ENGLAND

(*Received February 4, 1985*)

The preparation and mesomorphic properties of a number of 1-n-alkyl-4-(4-n-alkyl- and 4-n-alkoxy-phenyl)bicyclo(2.2.2)octanes and 1-n-alkyl-4-(4′-n-alkylbiphenyl-4-yl)bicyclo(2.2.2)octanes are described. The clearing temperatures reported emphasise the high thermal stability conferred upon liquid crystal phases by the presence of the bicyclo-octane ring in a mesogen. Some physical data relating to the use of such materials in mixtures for electro-optical displays have been obtained.

INTRODUCTION

The 4-n-alkyl- and 4-n-alkoxy-phenyl 4-n-alkylbicyclo(2.2.2)octane-1-carboxylates[1,2] in admixture with, for example, cyanobiphenyls exhibit advantageous properties for application in twisted nematic (and cholesteric-nematic phase-change) devices with multiplexed addressing.[3] The most significant features of these mixtures are the high degree of sharpness and the low temperature dependence of the threshold voltage, as well as their low smectic-nematic transition temperatures. The nematic-isotropic liquid transition temperatures (T_{N-I}) of the bicyclo-octane esters are also consistently higher than those of the corresponding benzoate[4] and cyclohexanoate[5] esters often used

---

†Present address: Allen Clark Research Centre, Plessey Research (Caswell) Limited, Caswell, Towcester, Northants, NN12 8EQ

‡Present address: Brown Boveri Research Centre, CH-5405, Baden-Daettwil, Switzerland

in commercial mixtures of this type, and this is an advantage for producing high clearing points for the mixtures.

One serious disadvantage of the above-mentioned bicyclo-octane esters is their relatively high viscosities (higher than those of the analogous benzoate and cyclohexanoate esters).[3] This can be attributed in part to the bicyclo-octane ring and in part to the ester function, which is known[3-7] to contribute significantly to the viscosities of nematic phases. Therefore, the 1-n-alkyl-4-(4-n-alkylphenyl)- and 1-n-alkyl-4-(4-n-alkoxyphenyl)-bicyclo(2.2.2)octanes—the analogues of the bicyclo-octane esters,[1,2] but without the ester linkage—were synthesised (Scheme 1). The corresponding compounds, with a cyclohexane ring[6,7] or a benzene ring[7,8] in place of the bicyclo-octane ring, are commercial additives used to induce low viscosities.

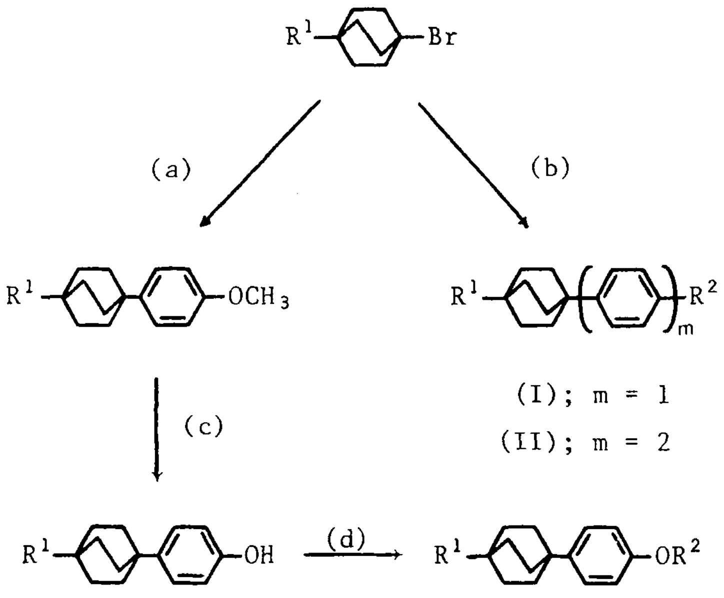
Several 1-n-alkyl-4-(4′-n-alkylbiphenyl-4-yl)bicyclo(2.2.2)octanes were also synthesised (Scheme 1). On the basis of previous results,[7,9] these compounds were expected to exhibit high T_{N-I} values which might make the compounds interesting as additives to induce high clearing points in nematic mixtures, without significantly increasing viscosity.[6]

RESULTS AND DISCUSSION

The liquid crystal transition temperatures for the 1-n-alkyl-4-(4-n-alkylphenyl)bicyclo(2.2.2)octanes [(I); m = 1] and the 1-n-alkyl-4-(4′-n-alkylbiphenyl-4-yl)bicyclo(2.2.2)octanes [(II); m = 2] are recorded in Table I. The liquid crystal transition temperatures for the homologous series of 1-(4-n-alkylphenyl)-4-pentylbicyclo(2.2.2)octanes (I) are plotted against the number of carbon atoms in the alkyl chain in Figure 1. A nematic phase (monotropic) could be observed directly for only one homologue (R^1, R^2 = C_5H_{11}; i.e., 5/5). For all the other homologues (I), virtual T_{N-I} values were obtained by extrapolation of data obtained from mixtures in the usual fashion.[10] The normal alternation of the nematic-isotropic liquid transition temperatures is observed.[9] No particular significance is attached to the shapes/trends of the T_{N-I} curves in Figure 1, since these are mainly determined by values of the nematic-isotropic transition temperatures that are virtual; however, since two reasonable curves can be drawn, this suggests that the virtual values can be considered as reasonably reliable. The melting points (C-I) also alternate, but not regularly. Monotropic smectic phases (S_B) were observed for homologues with longer alkyl chains at both termini of the molecules—

SCHEME 1

(R^1,R^2 = n-alkyl)



(I); m = 1

(II); m = 2

(III)

(a) .. $AlCl_3$ (or $FeCl_3$); $PhOCH_3$; $PhNO_2$

(b) .. $AlCl_3$; PhR^2 or 4-alkylbiphenyl

(c) .. HBr; CH_3CO_2H; H_2O

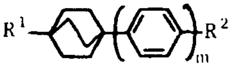
(d) .. R^2I/K_2CO_3/butanone

see Table I and Figure 1. The fact that the monotropic T_{S_B-I} value for the 5/7 homologue lies above the T_{N-I} value is again a consequence of the virtual nature of the latter value. It is noted that increasing the length of R^1 is more effective than lengthening R^2 for raising the T_{N-I} values of the compounds (I).

The 1-n-alkyl-4-(4′-n-alkylbiphenyl-4-yl)bicyclo(2.2.2)octanes [(II); m = 2] possess higher melting points (*ca.* +60° – 100°) and higher clearing points (*ca.* +60° – 150°) than the analogous compounds [(I); m = 1]. The compounds (II) also exhibit high smectic-nematic tran-

TABLE I

Transition temperatures for compounds of structure

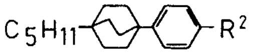


(I), m = 1
(II), m = 2

n-R¹	n-R²	m	C-S$_B$/N/I (°C)	S$_B$-N/I (°C)	N-I (°C)
C_3H_7	C_5H_{11}	1	57	-	[5]
C_3H_7	C_7H_{15}	1	49	-	[8]
C_4H_9	C_4H_9	1	42	-	[7]
C_5H_{11}	CH_3	1	64	-	[19]
C_5H_{11}	C_2H_5	1	44	-	[0]
C_5H_{11}	C_3H_7	1	50	-	[31]
C_5H_{11}	C_4H_9	1	34	-	[2]
C_5H_{11}	C_5H_{11}	1	52	-	(33)
C_5H_{11}	C_6H_{13}	1	47	(30)	[15]
C_5H_{11}	C_7H_{15}	1	52	(44)	[35]
CH_3	C_7H_{15}	2	107	(104)	-
C_2H_5	C_3H_7	2	124.5	(124)	155.5
C_4H_9	C_3H_7	2	160	179.5	208
C_5H_{11}	C_3H_7	2	175	191	210

( ) denotes a monotropic transition temperature

[ ] denotes a virtual transition temperature



(I, m = 1)

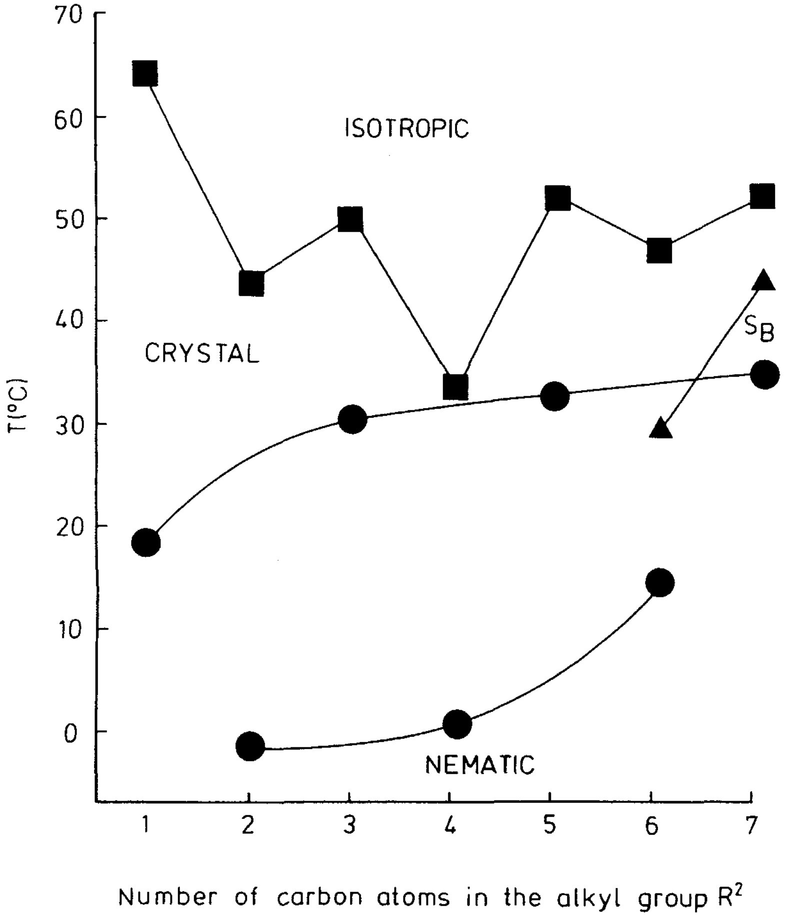


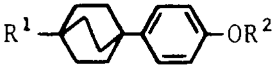
FIGURE 1 Plot of transition temperatures against number of carbon atoms in the alkyl chain R^2 of the compounds of structure [(I), m = 1]: ●, virtual nematic-isotropic liquid transition (monotropic for $R^2 = C_5H_{11}$); ▲, monotropic smectic B-isotropic liquid transition; ■, crystal-isotropic liquid transition. The occurrence of S_B-I points above N-I points is a consequence of the virtual nature of these T_{N-I} values.

sition temperatures (S_B-N) and consequently the nematic ranges are fairly short. One homologue (1/7) does not exhibit a nematic phase and a S_B-I transition is observed.

The transition temperatures for the 1-n-alkyl-4-(4-n-alkoxyphenyl)bicyclo(2.2.2)octanes (III) are collated in Table II and plotted

TABLE II

Transition temperatures for compounds of structure



(III)

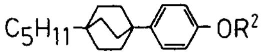
n-R^1	n-R^2	C-N/I ($^\circ$C)	S_B-N ($^\circ$C)	N-I ($^\circ$C)
C_3H_7	C_2H_5	81	-	(74)
C_4H_9	C_3H_7	69.5	-	[47]
C_5H_{11}	CH_3	64	-	70
C_5H_{11}	C_2H_5	73	-	86
C_5H_{11}	C_3H_7	72	-	(65)
C_5H_{11}	C_4H_9	65	-	77
C_5H_{11}	C_5H_{11}	75	(50)	(70.5)
C_5H_{11}	C_6H_{13}	66	(54)	79

( ) denotes a monotropic transition temperature

[ ] denotes a virtual transition temperature

against the number of carbon atoms in the terminal alkoxy chain for the homologous series of 1-(4-n-alkoxyphenyl)-4-pentylbicyclo(2.2.2)octanes in Figure 2. The T_{N-I} values exhibit the normal pattern of alternation, and it is interesting to note that both curves fall to minima before rising again. The T_{N-I} trends are therefore similar to those for the series of 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls.

The clearing points for the alkoxy-compounds (III) are higher (*ca.* +15° – 30°) than those of the corresponding alkyl-compounds [(I); m = 1], although the melting points are also higher (*ca.* +20°). Several homologues (e.g., $R^1 = C_5H_{11}$; $R^2 = CH_3$) exhibit enantiotropic nematic phases, and homologues with long chain lengths (e.g., R^1 and $R^2 = C_5H_{11}$) also possess monotropic smectic B phases.



(III)

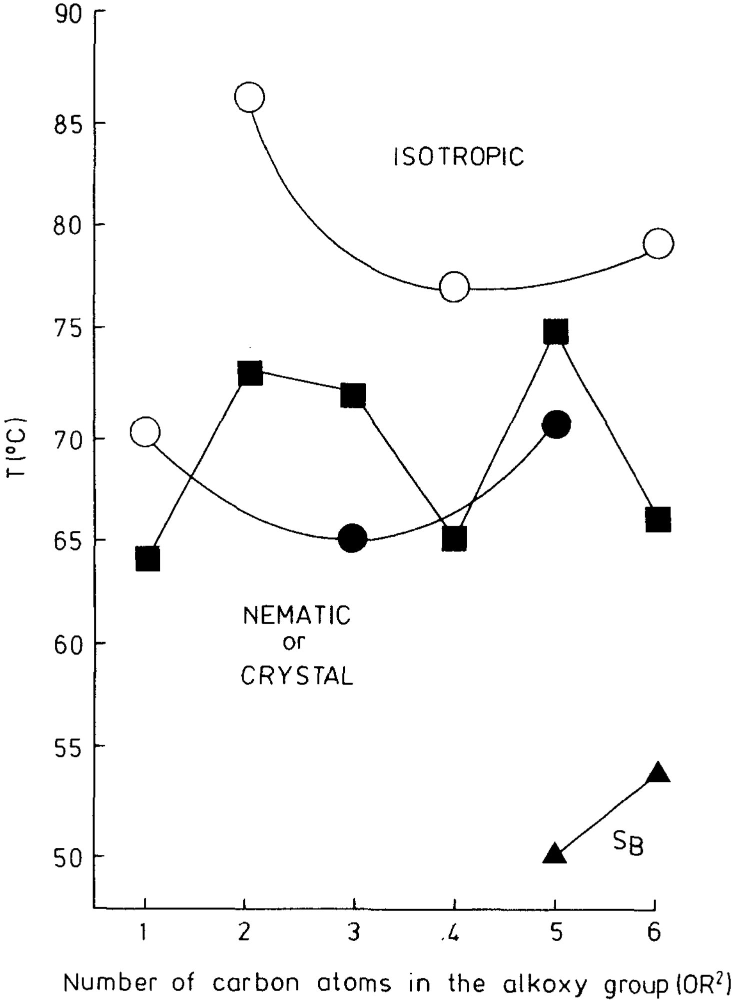
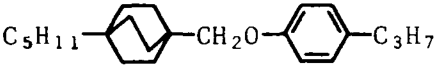


FIGURE 2 Plot of transition temperatures against number of carbon atoms in the alkyl chain R^2 *of the compounds of structure (III):* ○, *enantiotropic nematic-isotropic* liquid transition; ●, monotropic nematic-isotropic liquid transition; ▲, monotropic smectic B-nematic transition; ■, crystal-nematic/isotropic liquid transition.

Although it is difficult to arrive at definite conclusions from the data available, the bicyclo-octane materials [(I); m = 1 and (III)] would seem to possess higher clearing points than the corresponding *trans*-1-n-alkyl-4-(4-n-alkylphenyl) and -4-(4-n-alkoxyphenyl) cyclohexanes (e.g., 3/2: C-I, −1.5°; N-I, (−75°) and 3/02: C-I, 41°;

N-I, (37°)).[6,7] A similar clearing point relationship exists between the three-ring compounds [(II); m = 2] and the analogous *trans*-1-n-alkyl-4-(4'-n-alkylbiphenyl-4-yl)cyclohexanes (e.g., 5/2: C-S, 34°; S-N, 146°; N-I, 164°).[6,7] The analogous 4-n-alkyl-4'-alkoxybiphenyls appear to be predominantly smectic (e.g., 5/02: C-S_B, 70°; S_B-I, 81° and 5/06: C-S_B, 82°; S_B-I, 84°)[7,8] like the corresponding 4,4'-dialkylbiphenyls and 4,4''-dialkyl-*p*-terphenyls.[7] Thus, on the basis of this limited information, it would seem that the order of decreasing T_{N-I} value for these types of system, differing only in the presence of one of the three rings below, is that normally observed[9] for many other types of compound.

The T_{N-I} values for the di-pentyl homologues of five types of compound, each containing a 1,4-disubstituted bicyclo(2.2.2)octane ring, a 1,4-disubstituted benzene ring, and a central linking unit (—X—), are collated in Table III. It is clear from the T_{N-I} values that a central linking unit is not necessary for mesophase formation. However, the compounds incorporating a central —CH_2CH_2—, —O.CO—, or —CO.O— linkage all exhibit higher clearing points than the hydrocarbon without a central linking unit. The markedly low T_{N-I} of −88° for the compound† with X = —OCH_2— is a further instance of the adverse influence on T_{N-I} of separating polar/polarisable centres (—O— and —C_6H_4—) by units of low polarisability (—CH_2—). Data for the homologous ether with the ether linkage reversed (—CH_2O—) are not available, but the compound



has[11] C-N, 56° and a monotropic T_{N-I} at (30°).

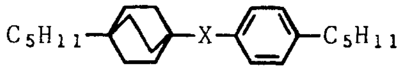
The values recorded in Table III and the other two Tables serve to demonstrate once again that the presence of the 1,4-disubstituted bicyclo(2.2.2)octane ring system in a compound gives rise to high N-I transition temperatures, permitting very simple molecular structures to exhibit liquid crystal properties (albeit monotropic in the case of the simple hydrocarbons of structure (I), m = 1). When a central linking unit (e.g., —CO.O—) is present which also promotes high clearing points, then very good T_{N-I} values can be obtained for simple esters with two terminal alkyl groups.[12]

---

†This compound could not be obtained with purity > 95%, but the 5/1 homologue was obtained pure and its low virtual T_{N-I} of [−210°] bears out the trend indicated.

TABLE III

Transition temperatures for some related compounds of structure



X	C-S_B/N/I (^oC)	S_B-N (^oC)	N-I (^oC)	Ref
-	52	-	(33)	-
$-CH_2CH_2-$	45	58	[62]	14
$-OCH_2-$	-5	-	[-88]	11
-CO.O-	31	-	64.5	12
-O.CO-	68	-	(59)	12

( ) denotes a monotropic transition temperature

[ ] denotes a virtual transition temperature

PHYSICAL PROPERTIES

A mixture of three homologues (3/5, 25 wt %; 3/7, 25 wt %; 5/7, 50 wt %) of the l-n-alkyl-4-(4-n-alkylphenyl)bicyclo(2.2.2)octanes [(I); m = 1] exhibits an enantiotropic nematic phase of low birefringence ($\Delta n_{20°}$, 0.05) and reasonably low viscosity ($\eta_{20°}$, 35 cP; $\eta_{0°}$, 52 cP). The viscosity is considerably greater than that of a typical *trans*-1-n-alkyl-4-(4-n-alkylphenyl)cyclohexane (3/2; $\eta_{20°}$, 4 cP; $\eta_{0°}$, 10 cP; both values are extrapolated values for the nematic phase).[6,7]

Mixtures (40 wt %) of either the 1-n-alkyl-4-(4-n-alkylphenyl)bicyclo(2.2.2)octanes [(I); m = 1, e.g., 5/3] or the 1-n-alkyl-4-(4-n-alkoxyphenyl)bicyclo(2.2.2)octanes (III); e.g., 5/01 with cyano-substituted compounds (60 wt %; primarily cyanobiphenyls and a cyano-*p*-terphenyl) exhibit almost identical electro-optic responses at 20° (1.59 and 1.16 volts for $V_{10}(0°)$ and $V_{90}(45°)$ respectively). The sharpness of the threshold voltage, again at 20°, is however poor (M_{20}, 1.84 and M'_{20}, 1.37), the temperature dependence of the threshold voltage at 20° is quite high ($-1/V(dV/dT)$ at $V_{10}(0°)$ is in the range 0.62 to 0.84% °C^{-1}), and the multiplexing properties are weak (1:3 margin, 5%). The rise and decay times at 20° of the mixture containing the alkyl compound [(I); m = 1] are lower (3 V; 59 ms and 48 ms, respectively) than those (3 V; 84 ms and 50 ms, respectively) of the mixture containing the alkoxy compound (III).

EXPERIMENTAL

Structure and purity of materials

Infra-red, ^{1}H n.m.r., and mass spectra were obtained for the compounds synthesised and found to be consistent with the required structures. Infra-red spectra were determined using a Perkin Elmer 457 spectrometer, ^{1}H n.m.r. spectra using a Jeol JNM-4Hx60 spectrometer, and mass spectra using an AEI MS 902 mass spectrometer. Each final product [(I), (II), and (III)] gave a single spot on thin layer chromatography (t.l.c.) and was at least 99.7% pure as determined by gas-liquid chromatography (g.l.c.) and values of 99.9% were common.

Transition temperatures

The transition temperatures for the compounds [(I), (II), and (III)] reported in Tables I and II were determined by optical microscopy using either a Nikon L-Ke polarising microscope or a Vickers M72c polarising microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit. The Mettler stage could be cooled (to $<-20°$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage. In those cases when it was not possible to observe the nematic-isotropic liquid transition directly, virtual values were determined in the usual way.[10] Some transition temperatures, particularly crystal to smectic (C-S_B) transition temperatures, were checked using a Perkin-Elmer DSC-2C differential scanning calorimeter.

Preparation of materials

The 4-n-alkylphenyl compounds [(I) and (II)] were prepared by a Friedel-Crafts reaction[10] involving the known 1-n-alkyl-4-bromo-bicyclo(2.2.2)octane,[10] the appropriate n-alkylbenzene or 4-n-alkylbiphenyl, and anhydrous aluminium chloride in nitro-benzene. This method was suitable for the preparation of the 4-n-alkoxyphenyl compounds (III) when the alkoxy chain of the required alkoxybenzene was shorter than propyloxy; with longer chain alkoxy groups, cleavage of the oxygen-aliphatic carbon bond occurs, although this is reduced to some extent by the use of iron(III)chloride instead of aluminium(III)chloride. In order to prepare the higher homologues in better yield, it was necessary to alkylate the corresponding substituted phenol, prepared by demethylating the analogous 1-n-alkyl-4-(4-methoxyphenyl)bicyclo(2.2.2)octane.

The compounds [(I)–(III)] were purified in the usual way by column chromatography using silica-gel as the stationary phase and a 1:5 (v/v) mixture of chloroform and light petroleum (b.p. 40–60°) as eluant, followed by crystallisation until constant liquid crystal transition temperatures were obtained.

1-Pentyl-4-(4-propylphenyl)bicyclo(2.2.2)octane. A solution of 1-bromo-4-pentylbicyclo(2.2.2)octane (1.5 g, 0.0058 mol) in sieve-dried nitrobenzene (35 cm^3) was added dropwise to a stirred solution of propylbenzene (28 g, 0.23 mol), anhydrous aluminium chloride (1.2 g, 0.2 mol), and sieve-dried nitrobenzene (100 cm^3) maintained at 80° throughout the addition and thereafter for 18 h. 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 remove the solvent. The residual oil was taken up in chloroform and dried ($MgSO_4$). The crude product was purified by column chromatography (silica-gel), eluting with a 1.5:1 (v/v) mixture of chloroform/light petroleum (b.p. 40–60°). Appropriate fractions giving a single-spot on t.l.c. were combined to yield a solid residue which was crystallised from methanol until constant transition temperatures were obtained (see Table I for the transition temperatures for this compound and other homologues prepared using this method).

1-(4-Methoxyphenyl)-4-pentylbicyclo(2.2.2)octane. This may be prepared by Friedel-Crafts alkylation using $AlCl_3$, following the procedure given above for the preparation of 1-pentyl-4-(4-propylphenyl)bicyclo(2.2.2)octane.

As mentioned earlier, some evidence exists to show that the use of $FeCl_3$ causes less dealkylation, particularly with alkoxy groups larger than methoxy or ethoxy. An example of the $FeCl_3$ procedure, applied in this instance to a methoxy system, is given below.

A solution of 1-bromo-4-pentylbicyclo(2.2.2)octane (5 g, 0.019 mol) in sieve-dried nitrobenzene (80 cm^3) was added dropwise to a solution of anisole (84 g, 0.775 mol), anhydrous iron(III)chloride (1.3 g, 0.008 mol), and sieve-dried nitrobenzene (80 cm^3) maintained at an oilbath temperature of 80° throughout the addition and overnight. The reaction mixture was worked-up and the crude product purified, as described in the preparation of 1-pentyl-4-(4-propylphenyl)bicyclo(2.2.2)octane, to yield the desired substituted anisole (3.4 g, 61%), m/e, 286 (see Table II for the liquid crystal transition temperatures of this compound).

1-(4-Hydroxyphenyl)-4-pentylbicyclo(2.2.2)octane. A solution consisting of 1-(4-methoxyphenyl)-4-pentylbicyclo(2.2.2)octane (3.3 g, 0.0115 mol), 48–50% aqueous hydrobromic acid (12 cm^3), 45% (w/v) hydrogen bromide in glacial acetic acid (40 cm^3), and glacial acetic acid was heated under reflux for 18 h. The cooled solution was added to water (100 cm^3), and the mixture shaken with chloroform (3 × 100 cm^3). The combined organic extracts were washed with water (2 × 250 cm^3), 10% aqueous sodium carbonate (2 × 500 cm^3), and water (2 × 500 cm^3), and dried ($MgSO_4$). The crude product was purified by crystallisation from ethanol to yield the pure phenol (2.4 g, 76%, m.p. 123–124° (lit.[13] m.p. 124°); m/e, 272.

1-n-Pentyl-4-(4-propyloxyphenyl)bicyclo(2.2.2)octane. A mixture of 1-(4-hydroxyphenyl)-4-pentylbicyclo(2.2.2)octane (1.0 g, 0.0037 mol), 1-iodopropane (1.0 g, 0.0059 mol), anhydrous potassium carbonate (2.0 g, 0.0147 mol), and sieve-dried butanone (50 cm^3) was heated under reflux for 18 h. The cooled reaction mixture was added to water (250 cm^3) and the whole shaken with chloroform (3 × 50 cm^3). The combined organic extracts were washed with water (2 × 500 cm^3) and dried ($MgSO_4$). After removal of the solvent, the crude product was chromatographed on a column of silica-gel, eluting with a 1.5:1 (v/v) mixture of chloroform and light petroleum (b.p. 40–60°). The solid obtained was crystallised from methanol until constant transition temperatures were obtained (see Table II for the transition temperatures for this compound and other homologues prepared using this method).

CONCLUSION

Two homologous series [(I) and (III)] of 1-n-alkyl-4-n-alkyl- or -4-n-alkoxy-phenylbicyclo(2.2.2)octanes have been prepared. These new compounds, without a central molecular linking unit, exhibit nematic phases (often monotropic) of moderate viscosity, low birefringence, and low dielectric anisotropy. The T_{N-I} values for these bicyclooctane compounds [(I) and (III)] are significantly higher than those of the corresponding cyclohexane materials. The electro-optical properties of mixtures of these new materials with, for example, cyanobiphenyls are not exceptional and show no real advantages for use in mixtures for electro-optical display devices.

The compounds (II), m = 2, containing a biphenyl ring system have much higher T_{N-I} values, but are strongly smectic (S_B).

Acknowledgments

This work was carried out under a contract from the Ministry of Defence (U.K.), and the authors gratefully acknowledge the associated research grant. This paper is published by permission of the Director H.M.S.O. The authors thank colleagues at R.S.R.E. (Malvern) for their permission to publish the recorded electro-optical data.

References

1. G. W. Gray and S. M. Kelly, *J. Chem. Soc., Chem. Commun.*, 465 (1980).
2. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **75**, 95 (1981).
3. J. Constant and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **70**, 105 (1981).
4. R. Steinstraesser, *Z. Naturforsch.*, **27b**, 774 (1972); M. E. Neubert, L. T. Carlino, R. D'Sidocky, and D. L. Fishel, '*Liquid Crystals and Ordered Fluids*,' (J. F. Johnson and R. S. Porter, eds.), Vol. 2, p.293, Plenum Press, New York, 1974.
5. H. -J. Deutscher, B. Laaser, W. Doelling, and H. Schubert, *J. prakt. Chem.*, **320**, 194 (1978).
6. R. Eidenschink, J. Krause, and L. Pohl, *German Patent Application*, DE 2636684 C3 (1979).
7. R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **94**, 119 (1983); W. H. de Jeu and R. Eidenschink, *J. Chem. Phys.*, **78**, 4637 (1983).
8. R. Skubatz, Diplomarbeit, Halle (1978); E. Merck, Darmstadt, *Data Sheet*, S 1009 and S 1010 Licristal (1977); M. A. Osman and T. Huynh-Ba, *Z. Naturforsch.*, **38b**, 1221 (1983).
9. N. Carr, G. W. Gray, and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **66**, 267 (1981).
10. G. W. Gray and S. M. Kelly, *J. Chem. Soc., Perkin Trans. II*, 26 (1981).
11. N. Carr and G. W. Gray, Proc. 10th International Liquid Crystal Conference, York (1984), *Mol. Cryst. Liq. Cryst.*, in press.
12. G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **75**, 95 (1981); N. Carr, G. W. Gray, and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, to be published.
13. P. Adomenas, D. Girdzhyunaite, and G. Mazunaites, *Zhurnal Organicheskoi Khimii*, **19**, 2366 (1983).
14. N. Carr, Ph.D. Thesis, University of Hull, 1984.