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Mesogenic properties of single ring compounds: dipentyl derivatives of *p*-carboranes and bicyclo[2.2.2]octane

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The dipentyl derivatives of 10- and 12-vertex *p*-carboranes and bicyclo[2.2.2]octane have been prepared and studied in the pure state and in binary mixtures with a nematic host. Only 1,4-dipentylbicyclo[2.2.2]octane was found to exhibit a monotropic nematic transition. The extrapolated virtual nematic–isotropic transition temperatures provide the expected order of ring effectiveness in supporting the nematic mesophase: bicyclo[2.2.2]octane > 12-vertex *p*-carborane > 10-vertex *p*-carborane. The results for the single ring derivatives **[1]b** were compared with clearing temperatures for the two-ring mesogens **[2]c**.

Introduction

Single ring compounds very rarely exhibit thermotropic liquid crystal (LC) phases, and the vast majority crystallize before forming a mesophase.[1] Such compounds, particularly those with simple alkyl substituents, are of interest as additives which might reduce the viscosity of nematic mixtures without significantly reducing the device operating range.[2] From a more fundamental point of view, studies of simple single ring compounds provide an excellent way of understanding and comparing the effectiveness of the rings in promoting liquid crystalline behavior.

Our recent results indicate that *p*-carboranes, the 12-vertex **1[1]a** and the 10-vertex **2[1]a** (Fig. 1), are effective structural elements for LCs, promoting the nematic phase in preference to the smectic phases.[3–9] The clearing points of compounds containing *p*-carboranes are significantly lower than those for the analogous bicyclo[2.2.2]octane (**3[1]a**) derivatives and often lower than those containing a benzene ring (**4[1]a**). The actual ring effect on mesogenic behavior is often difficult to assess due to the complex molecular and electronic structures and conformational mobility of most mesogens. In an attempt to reduce the number of variables, we focused on simple nonpolar compounds with homostructural cores which provide the most direct comparison of ring effects on LC properties. For instance, our recent analysis of two ring compounds **[2]c** has established the following order of mesophase stabilization ability: $\mathbf{3} > \mathbf{1} > \mathbf{2} > \mathbf{4}$.[9] This structure–property relationship is inconsistent with the relative sizes of the cores (rings) and has been ascribed to differences in conformational preferences and intramolecular dynamics of the two ring compounds.[9]

Here we report the syntheses of single ring dipentyl derivatives **1[1]b**–**3[1]b** and their thermal properties in the pure state and as binary mixtures with the nematic host 1-(4-pentylbicyclo[2.2.2]octan-1-yl)-2-(4-methoxyphenyl)ethane. We compare these results with those obtained for the two ring analogs **[2]c**.

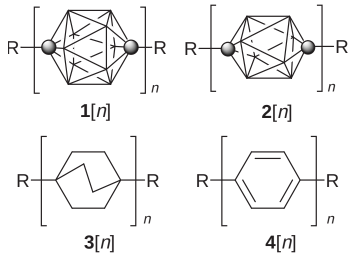
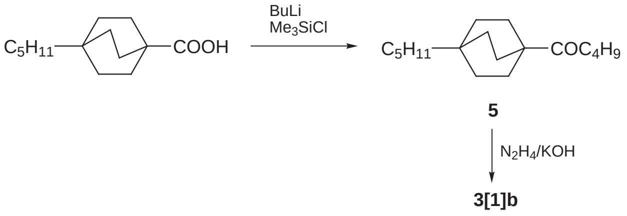


Fig. 1 Derivatives of 1,12-dicarbadodecaborane (**1[1]a**), 1,10-dicarbadecaborane (**2[1]a**), bicyclo[2.2.2]octane (**3[1]a**) and benzene (**4[1]a**). In **1** and **2** each vertex corresponds to a BH fragment and the sphere represents a carbon atom.

Results

The dipentylcarboranes **1[1]b**[10] and **2[1]b** were each obtained from the appropriate *p*-carborane as by-products in the syntheses of the corresponding pentylcarboranecarboxylic acids.[8,10] 1,4-Dipentylbicyclo[2.2.2]octane[2,11] (**3[1]b**) was prepared from 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid, which was converted to the butyl ketone **5** using the method of Rubottom and Kim[12] and was subsequently transformed to **3[1]b** by the Huang-Minlon reduction.[13]



Scheme 1

The pentyl derivatives **1[1]b**–**3[1]b** and also 1,4-dipentylbenzene[14] (**4[1]b**) are isotropic liquids at room temperature and their melting points range from $-49\,^{\circ}$C for **4[1]b**[14] to 18.6 °C for the 12-vertex derivative **1[1]b** (Table 1). Upon cooling, 1,4-dipentylbicyclo[2.2.2]octane (**3[1]b**) forms a narrow temperature range mesophase at $-24.5\,^{\circ}$C, as evident from the DSC (Fig. 2). Optical microscopy revealed a nematic schlieren texture at the transition point, which rapidly transforms to the homeotropic nematic texture. The formation of a nematic phase by **3[1]b** is reported for the first time and is a surprising finding for any single ring hydrocarbon. The crystallization processes for the carboranes show a hysteresis of about 12 and 25 °C for **1[1]b** and **2[1]b** respectively, at a cooling rate of 10 °C min^{-1}. Microscopic observations of droplets of the 12-vertex derivative **2[1]b** revealed no mesophase formation upon supercooling to $-35\,^{\circ}$C (instrument limit).

The ability of the three derivatives **1[1]b**–**3[1]b** to support a nematic phase was examined in a weakly polar nematic host (Fig. 3) which has been shown to perform well for non-polar

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Table 1 Transition temperatures and enthalpies for the **[1]b** series[a]

		Cr1	Cr2		N	
		$T/°C$	$T/°C$	$\Delta H/\text{kJ mol}^{-1}$	$T/°C$	I
[1]b	**1**	• 17.1	• 18.6	22.7[b]	[• −18]	•
	2	• −3.5		14.7	[• −109]	•
	3	• −13.7	• −9.8	20.4[b]	(• −24.5), [-6]	•
	4	• −49		[c]	[• −163][d]	•

[a] Observed phases are denoted by bullets, the monotropic transition in parentheses and virtual transitions in brackets. Cr-crystal, S-smectic, N-nematic, I-isotropic. Temperatures obtained at 1 °C min^{-1} heating rates and enthalpies 10 °C min^{-1} heating rates. [b] Total enthalpy of melting. [c] A. D. Petrov, G. I. Nikishin and V. D. Vorob'ev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1960, 675. Enthalpy not reported. [d] Estimated based on T_{NI} 157 °C lower relative to **3[1]b** in E7 host. H. M. Abdullah, G. W. Gray and K. Toyne, *J. Mol. Cryst. Liq. Cryst.*, 1985, **124**, 105.

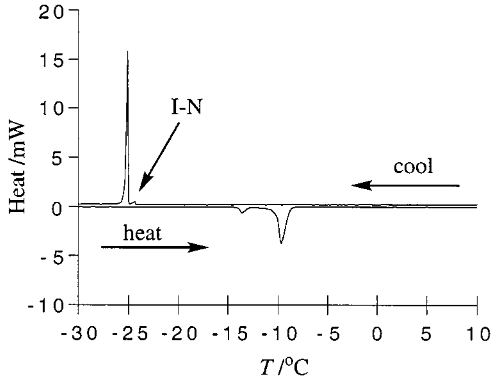

Fig. 2 Phase transitions for **3[1]b** as measured by DSC on heating (lower trace) and on cooling (upper trace) at a scanning rate of 1 °C min^{-1}.

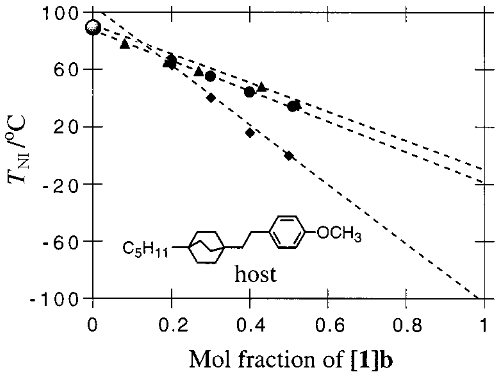

Fig. 3 Nematic–isotropic transition temperatures (T_{NI}) as a function of concentration of dipentyl derivatives **1[1]b** (circles), **2[1]b** (squares) and **3[1]b** (triangles) in the host shown in the diagram. Best fit lines are **1[1]b**, $y = 86 - x \cdot 104$ ($r = 0.999$); **2[1]b**, $y = 104 - x \cdot 213$ ($r = 0.996$); **3[1]b**: $y = 84 - x \cdot 90$ ($r = 0.993$). The circle on the vertical axis represents the N–I transition temperature for the pure host (89 °C).

carborane-containing mesogens.[9] As expected, extrapolation from four data points, excluding that of the pure host, gives the highest virtual nematic–isotropic transition for the bicyclo[2.2.2]octane derivative **3[1]b** ($[T_{NI}] = -6$ °C) and the lowest for the 10-vertex analog **2[1]b** ($[T_{NI}] = -109$ °C). Interestingly, the extrapolated transition for **3[1]b** is almost 20 °C higher than the actually observed monotropic T_{NI}. The $[T_{NI}]$ obtained for the 12-vertex carborane derivative **1[1]b** (−18 °C) is surprisingly close to that obtained for **3[1]b** (Table 1). 1,4-Dipentylbenzene (**4[1]b**) has not been studied in this work, but its $[T_{NI}]$ can be estimated to be about −160 °C based on the 157 °C lower virtual clearing temperature relative to that of bicyclo[2.2.2]octane **3[1]b** measured in an E7 nematic mixture.[2]

The values extrapolated to zero concentration of **1[1]b** and **3[1]b** (84 and 86 °C, respectively) are in good agreement with that measured for the pure host ($T_{NI} = 89.1$ °C); however, the value obtained from the data for the 10-vertex **2[1]b** is 15 °C higher. Such a discrepancy has been observed before[9] for another derivative of 10-vertex *p*-carborane **2[2]c** and in both cases the correlation factors for the extrapolations are the lowest in the series.

Discussion

The stability order **3**>**1**>**2**>**4** in series **[1]b** is identical with that previously observed for the two ring compounds **[2]c**, but appears inconsistent with the intramolecular dynamic model proposed for the latter series.[9] The observed trend in stability is, however, in general accord with our other results for compounds with heterostructural cores *e.g.* biphenyl esters.[7] In the latter case, the role of the ring is not as pronounced as in series **[1]b** and **[2]c** presumably mostly due to the influence of other molecular components and conformational flexibility.

The observed virtual T_{NI} for 1,4-dipentylbicyclo[2.2.2]-octane (**3[1]b**) is higher than that previously reported in more polar nitrile (−36 °C) and aliphatic ester (−47 °C) hosts[2,15] but it is still not as high as would be expected based on comparison with the T_I for the two ring compounds **3[2]**.[16]

Since rigid cores stabilize the liquid crystal order, an increase in mesophase stability upon addition of another homostructural ring to the core should be approximately proportional to the mesophase stability of the lower homolog. This assumption should be generally true providing that the stereochemical and electronic properties are not abruptly altered in the homologous series.

Addition of another homostructural ring to the core and a $\text{-CH}_2\text{CH}_2\text{-}$ fragment to each alkyl chain of **[1]b** leads to the structurally analogous series of two ring diheptyl derivatives **[2]c**. A plot of the virtual isotropic transition temperatures of the former series **[1]b** against the clearing temperatures (N–I for the carboranes and S–I for the hydrocarbons) for the two ring series **[2]c**[9] is shown in Fig. 4. It demonstrates that the points obtained for the three rings $\mathcal{A} = $ **1**, **2** and **4** are approximately collinear while that for bicyclo[2.2.2]octane dramatically deviates from the three-point trend. Although there are several assumptions built in the plot in Fig. 4,[17] the resulting difference of about 80 °C between the expected and experimental clearing temperature for **3[2]c** cannot be explained based on the effect of different hosts or the $\text{-C}_5\text{H}_{11}$ as opposed to

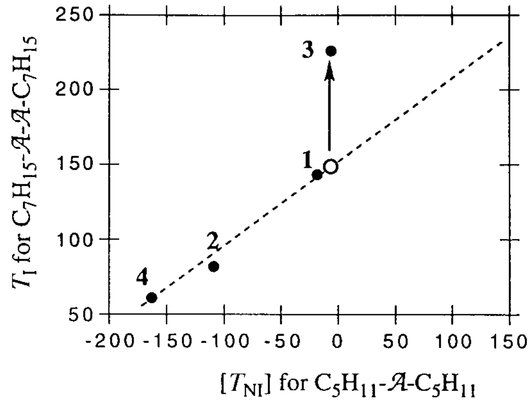

Fig. 4 Plot of virtual nematic–isotropic transition temperatures T_{NI}/ °C for single ring compounds *vs.* isotropic transitions for two ring compounds containing rings **1a**–**4a**. The open circle represents the expected data point. The three point line (**1**, **2** and **4**) best fit; $T_I = 0.576 \times [T_{NI}] + 151$; ($r = 0.992$).

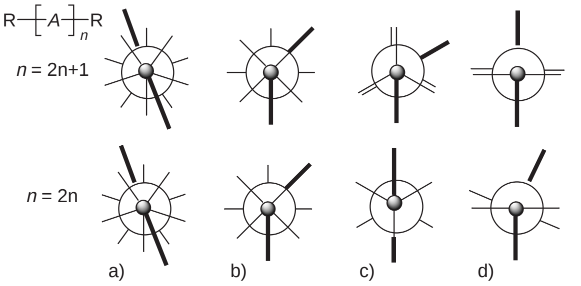

Fig. 5 Extended Newman projection along the long molecular axes of odd- (upper row) and even-membered (lower row) oligomers of (a) 12-vertex *p*-carborane **1[*n*]**, (b) the 10-vertex *p*-carborane **2[*n*]**, (c) bicyclo[2.2.2]octane **3[*n*]**, and (d) *p*-phenylene **4[*n*]**. The bar represents the alkyl substituent plane.

-C_7H_{15} chains alone. One can speculate, however, that the difference in stereochemistry between the single ring **3[1]** and the two ring **3[2]** bicyclo[2.2.2]octane derivatives must be responsible, in part, for the discrepancy.

Inspection of molecular models for the bicyclo[2.2.2]octane oligomers **3[*n*]** [Fig. 5(c)] shows that while the alkyl chains can adopt an antiperiplanar orientation in the two ring compounds **3[2]** (in general, n = even number), the conformational minima force the alkyl substituents to assume a pseudo-*gauche* arrangement in **3[1]b** (in general, n = odd number). The *gauche* conformation would be expected to unfavorably affect the mesophase stability and this prediction is consistent with the apparently low clearing point observed for **3[1]b** as compared with **3[2]c**. Unlike series **3[*n*]**, *p*-carborane derivatives **1[*n*]** and **2[*n*]** retain the same relative ground state orientation of the terminal alkyl chains throughout the homologous series and no 'odd–even' effect is expected (Fig. 5). Although anticipated for oligophenylenes **4[*n*]**, the effect may be much less pronounced than in **3[*n*]** due to the low energy of planarization for biphenyl **[4]2a**, which is about 1/3 of that for conformational interconversion in **3[2]a**.

Conclusions

Simple dipentyl derivatives of bicyclo[2.2.2]octane and 12-vertex *p*-carborane exhibit similar mesogenic properties in a nematic host and sub 0 °C virtual nematic–isotropic transition temperatures. The discovery of a nematic phase in the bicyclo[2.2.2]octane derivative opens the possibility of finding low temperature thermotropic phases in other single ring hydrocarbons and derivatives of 12-vertex *p*-carborane.

A comparison of mesogenic properties of compounds in series **[1]b** and **[2]c** indicates that ring stereochemistry may influence the stability of liquid crystal phases. Further detailed studies of the remaining compounds in both series in the same host are required to complete the comparison and interpretation of the results. Expansion of these studies to higher homologs **[3]** and other rings such as bicyclo[1.1.1]pentane and cubane is needed to explore the role of the ring stereochemistry and the distribution and depth of conformational minima on mesophase stability.

Experimental

Binary mixtures were prepared using CH_2Cl_2 distilled from CaH_2 as the solvent. The phase transition points of the compounds and their mixtures were determined using a PZO 'Biolar' polarized microscope with a HCS250 Instec hot stage. Melting points were obtained using a Mettler DSC 30 instrument. For mixtures the transition temperature was taken as the upper limit of the biphasic region as observed by optical microscopy. The phase diagrams were determined by the single concentration method. ^{1}H, ^{13}C and ^{11}B NMR spectra were obtained in $CDCl_3$ on Bruker instruments operating at 300, 75.4 and 64.2 MHz respectively and referenced to the solvent (^{1}H and ^{13}C) or to $B(OMe)_3$. IR spectra were recorded using an ATI Mattson Genesis FT-IR by deposition of a thin film from solution onto sodium chloride disks. Mass spectrometry was performed using a Hewlett-Packard 5890 instrument (GCMS). Elemental analysis was provided by Atlantic Microlabs, Norcross, Georgia.

4-Pentylbicyclo[2.2.2]octan-1-yl butyl ketone 5

4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid (460 mg, 2.05 mmol) was dissolved in dry THF (15 mL) and cooled to 0 °C. The stirred solution was treated rapidly (~15 s) with *n*-butyllithium in hexanes (1.6 M, 5.1 mL, 8.2 mmol) forming a yellow solution. After 2 h at 0 °C chlorotrimethylsilane (4.45 g, 41.0 mmol) was added *via* syringe and the resulting white suspension was allowed to reach room temperature. Then hydrochloric acid (1 M, 15 mL) was added and the resulting two-phase system was stirred for 30 min at room temperature. The mixture was then transferred to a separatory funnel and extracted with ether (3 × 20 mL). The organic layer was washed with water (3 × 20 mL) and then dried over magnesium sulfate. The solvent was evaporated to yield 539 mg of crude material containing 86% of the product based on GCMS. Analytical sample was obtained by using Chromatotron (silica, petroleum ether–ethyl acetate, 10 : 1) giving a colorless oil: bp 145 °C/0.1 torr; ^{1}H NMR δ 0.85 (t, J = 6.9 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H), 1.02–1.52 (m, 18H), 1.62–1.67 (m, 6H), 2.37 (t, J = 7.3 Hz, 2H); ^{13}C NMR δ 13.92, 14.05, 22.43, 22.66, 23.32, 25.78, 27.93, 30.51, 30.72, 32.79, 36.78, 41.34, 44.96, 216.16; (EIMS) *m/e* 264 (4, M), 222 (25), 179 (100), 123 (30), 109 (38), 95 (41); IR 2928, 2860, 1700, 1456 cm^{-1}.

1,4-Dipentylbicyclo[2.2.2]octane 3[1]b

Crude 4-pentylbicyclo[2.2.2]octan-1-yl butyl ketone (**5**, 539 mg, 86% pure) was dissolved in diethylene glycol (30 mL). Potassium hydroxide (3.0 g, 0.05 mol) and 85% hydrazine hydrate (6.12 mmol, 0.36 mL) were added at once and the resulting mixture refluxed for 30 min. The condenser was removed and the aqueous layer evaporated. After reconnecting the condenser the reaction mixture was heated and stirred for 2 h at 200 °C. The reaction mixture was cooled, diluted with water and extracted with hexanes (5 × 20 mL). The combined organics were washed with water (5 x 50 mL) and then dried over magnesium sulfate. The solvent was evaporated to yield 313 mg crude product which was purified using Chromatotron (silica–hexanes) yielding 241 mg (47% overall yield based on the acid) of a colorless oil: bp 145 °C/1.2 torr; ^{1}H NMR δ 0.84 (t, J = 6.8 Hz, 6H), 0.96–1.07 (m, 4H), 1.12–1.25 (m, 12H), 1.28 (s, 12H); ^{13}C NMR δ 14.10, 22.72, 23.37, 30.59, 31.46, 32.94, 41.86; (EIMS) *m/e* 221 (59, M − Et), 179 (100), 109 (40), 95 (61); IR 2955, 2926, 2857, 1456 cm^{-1}. Anal. calcd. for $C_{18}H_{34}$: C, 86.32; H, 13.68. Found: C, 86.40; H, 13.68%.

1,10-Dipentyl-1,10-dicarbadecaborane 2[1]b

^{1}H NMR δ 0.93 (t, J = 8.0 Hz, 6H), 1.0–3.0 (br m), 1.37–1.51 (m, 8H), 1.84–1.94 (m, 4H), 3.10 (t, J = 8.3 Hz, 4H); ^{13}C NMR δ 14.05, 22.52, 31.57, 31.81, 34.22, 77.20; ^{11}B NMR δ −12.8 (d, J_{BH} = 162 Hz); (EIMS) *m/e* 263–258 (max at *m/e* 261, 17, M), 235–225 (max at *m/e* 232, 100), 57 (74); IR 2957, 2932, 2861, 2590, 1464 cm^{-1}; Anal. calcd. for $C_{12}H_{30}B_8$: C, 55.25; H, 11.59. Found: C, 55.20; H, 11.64%.

Acknowledgements

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Dabrowski of the Military University of Technology, Warsaw for the gift of the nematic host, and Dr Eike Poetsch of E. Merck, Darmstadt for the gift of 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid.

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17 Correlation in Fig. 4 should be treated semiquantitatively at best at this point of investigations. Additional assumptions include a) virtual [T_{NI}] for 1,4-dipentylbenzene (**4[1]b**) in the host, b) equal treatment of N–I and S–I transitions for **[2]c**, c) equal effect of extending pentyl chain to the heptyl chain on mesogenic properties in the series.

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