Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Czuprynski, Krzysztof and Kaszynski, Piotr(1999) 'Homostructural two-ring mesogens: a comparison of p-carboranes, bicyclo[2.2.2]octane and benzene as structural elements', Liquid Crystals, 26: 5, 775 — 778
To link to this Article: DOI: 10.1080/026782999204877
URL: http://dx.doi.org/10.1080/026782999204877

Liquid Crystals, 1999, Vol. 26, No. 5, 775–778

Homostructural two-ring mesogens: a comparison of *p*-carboranes, bicyclo[2.2.2]octane and benzene as structural elements

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(*Received 29 November 1998; accepted 29 December 1998*)

Mesogenic properties of diheptyl and diheptynyl derivatives of 12- and 10-vertex bi-*p*-carboranes have been studied in the pure state and as binary mixtures with a nematic host. The results are compared with those for analogous derivatives of bibicyclo[2.2.2]octane and biphenyl. The clearing temperature for 10,10′-diheptyl-bi-*p*-carborane **B2** is significantly lower than that for the 12-vertex analogue **B1** and still lower than that for the corresponding bicyclo[2.2.2]octane derivative **B3**. The observed order of mesophase stability is opposite to the trend expected from shape and polarizability anisotropy. Introduction of an acetylene link into bicarborane derivatives dramatically lowers the clearing temperatures by about 150°C. The results are rationalized in terms of molecular conformations and intramolecular rotational barriers.

1. Introduction

Current theories explain the existence of liquid crystalline phases as a balance between attractive and repulsive intermolecular interactions [1]. The attractive forces arise from anisotropy of the electronic polarizabilities [2] ($\Delta\alpha$) and multipolar interactions, while the more dominant repulsive forces result mainly from the shape anisotropy (length to width ratio, L/D) of the mesogen [3, 4]. Therefore, rod-like molecules [5] with a high $\Delta\alpha/\alpha_{avrg}$ ratio and a large number of low energy conformational minima corresponding to the most extended molecular shapes (high dynamic shape anisotropy, L/D) are expected to display calamitic mesophases with high isotropization transition temperatures T_I [6, 7].

According to these theories, one might predict that compounds containing 1,12-dicarbadodecaborane (**1**) should show lower mesophase stability than those based on the 10-vertex analogue **2** (figure 1). The calculated anisotropies of the electronic polarizability and the molecular dimensions for dimers **A1** and **A2** (table 1) are less favourable for the former than for the 10-vertex carborane dimer **A2**. Moreover, table 1 suggests that 1,10-dicarbadecaborane (**2**) may even be a better structural element for liquid crystals than bicyclo[2.2.2]octane (**3**)‡!

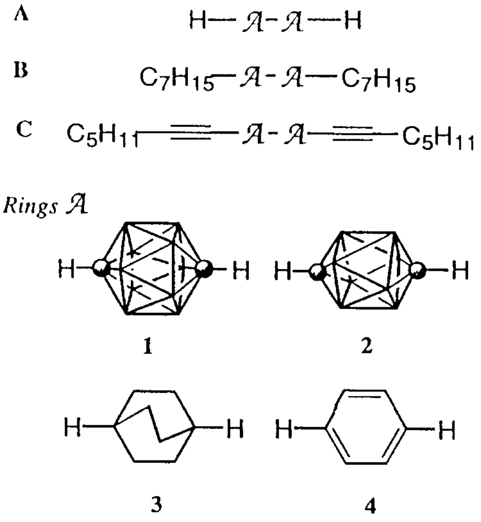

Figure 1. Three classes of compounds **A**, **B** and **C** containing rings **1**–**4**. In **1** and **2** each vertex corresponds to a BH fragment and the sphere represents a carbon atom.

Table 1. Calculated (HF/6-31G*) ratio of polarizability anisotropy $\Delta\alpha$ and average polarizability α_{avrg} and the length (L) to width (D) ratio for dimers **A**. L is the H ··· H end-to-end distance and D is the diameter of the cylinder of rotation described by the lateral hydrogen atoms.

Parameter	A1	A2	A3	A4
$\Delta\alpha/\alpha_{avrg}$	0.26	0.31	0.23	0.78
L/D	1.97	2.16	2.10	2.17

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[‡] Bicyclo[2.2.2]octane is generally accepted as superior over other rings in promoting highly stable nematic phases.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
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2. Results

In order to verify this prediction and also to compare the effectiveness of *p*-carboranes as mesogenic core elements with bicyclo[2.2.2]octane (**3**) and benzene (**4**), we examined simple non-polar molecular systems **B**, which contain two rings and have limited conformational flexibility. Such systems are particularly attractive since spherocylindrical molecules like **B1**-**B3** are generally assumed in theories of the liquid crystalline state [8].

Thermal and microscopic analyses of the diheptyl derivatives **B** revealed narrow temperature range nematic phases for the carborane dimers **B1** and **B2**, while the bibicyclo[2.2.2]octane [9] **B3**, and biphenyl [10] **B4**, compounds are reported to display smectic phases exclusively (table 2). The most surprising finding, however, is that the 10-vertex carborane dimer **B2** becomes an isotropic liquid at about 60°C *below* the clearing point (T_I) of the 12-vertex analogue **B1** and far below that reported for the bicyclo[2.2.2]octane derivative **B3**. This is consistent with results for other pairs of mesogens containing **1** and **2** [11–13]. Typically, the observed differences in the T_I are much lower than in the present case, but for the single ring analogues of **B1** and **B2** the difference is about 90°C [13].

Inspection of molecular models of **B1** and **B2** initially suggested that the difference in the mesophase stability may have a conformational origin. The symmetry of the 12-vertex carborane **1** allows for a conformational minimum of **B1** with antiperiplanar alkyl chains (similar to that in **B3**), while the chains in **B2** are off-set from coplanarity by 45°, forming chiral conformers (figure 2). The computational analysis is supported by single crystal X-ray structures for both dimers **B1** and **B2** [14].

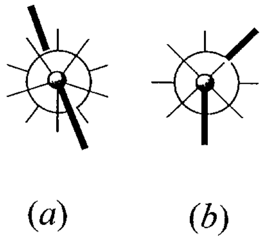

Figure 2. Extended Newman projections along the molecular long axes of (*a*) the 12-vertex and (*b*) the 10-vertex derivatives **B1** and **B2**. The bar represents the alkyl substituent plane.

If the difference in the thermal behaviour of the heptylcarboranes **B** is related to their conformations, then one might expect a drastic improvement in the mesophase stability in the 10-vertex derivative relative to the 12-vertex analogue when the rotational barriers are completely removed. To examine this hypothesis, the $–C1H_2C2H_2–$ groups in each terminal alkyl chain of **B** were replaced with acetylene –C≡C– links in **C1** and **C2**. As expected, single crystal X-ray diffraction analysis of acetylene derivatives **C1** and **C2** reveals that the arrangements of the alkyl chains in the crystal structures of the acetylenes are similar to those found in analogous dimers **B**, but more ordered structures and closer packing are observed [14]. Surprisingly, this structural change completely removed the liquid crystalline behaviour of the carborane derivatives despite the fact that a similar transformation in 4,4′-diheptylbiphenyl (**B4**) to form 4,4′-di(heptyn-1-yl)biphenyl (**C4**) [15] considerably increased both clearing and melting points (table 2).

The mesogenic properties of the acetylene dimers **C1** and **C2** and also **B1** and **B2** were examined in a weakly polar nematic host (figure 3) and their virtual clearing points [T_I] were extrapolated from five data points including that of the pure host (T_I = 89.1°C). The

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}). Observed phases are denoted by bullets and the monotropic transition of **B2** is in parentheses. Cr = crystal, Sm = smectic, N = nematic, I = isotropic.

Compound		Cr$_1$		Cr$_2$		Sm		N		I
B1	$T/\Delta H$	•	92.4/19	•	142.5/19			•	143.2/1.5	•
B2	$T/\Delta H$	•	20.3/1.6	•	82.5/22			(•	81.7/1.4)[a]	•
B3[b,c]	T	•	47			•	226			•
B4[d]	$T/\Delta H$	•	< 20			•	61.0/13.0			•
C1	$T/\Delta H$	•	93.5	•	96.5/28.5[e]			[•	– 31][f]	•
C2	$T/\Delta H$	•	77.3/25					[•	– 73][f]	•
C4[c, g]	T	•	67.5			•	86			•

[a] Monotropic transition.
[b] Ref. [9].
[c] Unidentified smectic phases, enthalpies not reported.
[d] Smectic phases E, E′ and B_{cryst}, ref. [10].
[e] Total enthalpy of melting.
[f] Virtual transition temperatures in square brackets were obtained using as host 1-(4-pentylbicyclo[2.2.2]oct-1-yl)-2-(4-methoxyphenyl)ethane.
[g] Ref. [15].

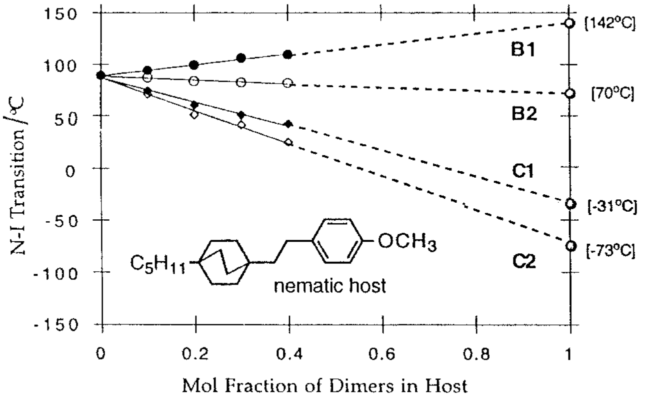

Figure 3. Nematic–isotropic transition temperatures (T_I) as a function of concentration of **B1,2** (circles) and **C1,2** (diamonds) in the host shown in the diagram.

observed correlation for the linear regression is excellent for all ($r > 0.993$) except for **B2** ($r = 0.961$), and the extrapolated [T_I] values for **B1** and **B2** agree well with the clearing points of the pure materials. This once again demonstrates excellent miscibility of the carborane derivatives with organic mesogens [12, 16, 17], which is remarkable considering that the former are composed of 50% inorganic elements.

3. Discussion and Conclusions

The introduction of the acetylene link and removal of the conformational bias in **B** results in a dramatic depression of the clearing points in both carborane derivatives **C**, but the 12-vertex derivative still shows a higher virtual mesophase stability (table 2). These and other results [11–13] indicate that 12-vertex *p*-carborane (**1**) performs better as a structural element for liquid crystals than its 10-vertex analogue **2** regardless of the conformational bias and despite the calculated *less favourable aspect ratio* and *polarizability anisotropy* of the former. In a broader context, the observed trend of mesophase stability **B3** > **B1** > **B2** is found for other sets of structurally similar compounds [12, 13, 16, 18], and is different from what might be expected based on theories and the data in table 1 (**B2** > **B3** > **B1**).

The significant difference in mesophase stabilization displayed by carboranes and bicyclo[2.2.2]octane can be rationalized on the grounds of fundamental structural differences between the two types of cages: while bicyclo[2.2.2]octane is a small and compact aliphatic hydrocarbon, the carboranes are relatively large [12], σ-aromatic inorganic boron hydrides characterized by three-centre two-electron bonds. The reason, however, for the generally poorer performance of the 10-vertex carborane as compared with the 12-vertex analogue is not obvious.

In an attempt to shed some light on the origin of the observed trends in mesophase stability, we have examined some molecular properties of the three mesogens **B1–B3**. In particular, we focused on intramolecular dynamics, which affects the dynamic aspect ratio of the mesogenic molecules and has been postulated to be a factor in mesophase stability [19]. According to our *ab initio* calculations [14], the combined heights of the barriers to internal rotation in the structurally similar spherocylindrical derivatives **B1–B3** correlate well with their isotropization temperatures T_I. This is also consistent with the dramatic ~150°C depression of the clearing temperature in acetylenes **C1** and **C2**, but disagrees, in part, with our recent results obtained for the series of single ring compounds [13].

The conformational preferences and intramolecular dynamics certainly affect intermolecular interactions and, in turn, the stability of the molecular order in the condensed phase. Further calorimetric and dilatometric studies of the mesogens are required to better understand the extent of conformational effects on the bulk structure and to elucidate structure–property relationships using, for example, the Eidenschink model [20, 21].

This project was funded by the National Research Council under the Collaboration in Basic Science and Engineering Program (KC), The Petroleum Research Fund (28742-G1), and NSF CAREER grant (DMR-9703002).

References

[1] For recent overviews of nematic theories see: Demus, D., and Hauser, A., 1990, in *Selected Topics in Liquid Crystal Research*, edited by H.-D. Koswig (Berlin: Akademie-Verlag), p. 19; also Madhusudana, N. V., 1990, in *Liquid Crystals, Applications and Uses*, Vol. 1, edited by B. Bahadur (Singapore: World Scientific), p. 37.

[2] Maier, M., and Saupe, A., 1959, *Z. Naturforsch.*, **14A**, 882.

[3] Onsager, L., 1949, *Acad. Sci.*, **51**, 627.

[4] Flory, P. J., 1956, *Proc. Roy. Soc. (London)*, **234A**, 73.

[5] For general discussions see: Demus, D., 1988, *Mol. Cryst. liq. Cryst.*, **165**, 54; Toyne, K. J., 1987, in *Thermotropic Liquid Crystals*, edited by G. W. Gray (New York: Wiley), p. 28; Collings, P. J., and Hird, M., 1997, *Introduction to Liquid Crystals, Chemistry and Physics* (London: Taylor & Francis).

[6] Osman, M. A., 1983, *Z. Naturforsch.*, **38A**, 693 and 779.

[7] Deutscher, H. J., Frach, R., Tschierske, C., and Zaschke, H., 1990, in *Selected Topics in Liquid Crystal Research*, edited by H.-D. Koswig (Berlin: Akademie-Verlag), p. 1–18.

[8] Toriumi, H., and Samulski, E. T., 1983, *Mol. Cryst. liq. Cryst.*, **101**, 163.

[9] Reiffenrath, V., and Schneider, F., 1981, *Z. Naturforsch.*, **36A**, 1006.

[10] Czuprynski, K., Przedmojski, J., and Baran, J. W., 1995, *Mol. Cryst. liq. Cryst.*, **260**, 435.

[11] Kaszynski, P., Lipiak, D., Bairamov, K. A., Brady, E., Patel, M. K., and Laska, J., 1997, in *Advances in Boron Chemistry*, edited by W. Siebert (Bodmin, UK: The Royal Society of Chemistry), p. 507.

[12] Douglass, A. G., Czuprynski, K., Mierzwa, M., and Kaszynski, P., 1998, *Chem. Mater.*, **10,** 2399.

[13] Douglass, A. G., Both, B., and Kaszynski, P., 1999, *J. mater. Chem.*, **9,** 683.

[14] Kaszynski, P., Tesh, K. F., and Young, V. G. Jr., *Inorg. Chem.* (submitted).

[15] Adomeniene, O., Adomenas, P., Velyvis, A., Paskoniene, R., and Goto, Y., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 269.

[16] Czuprynski, K., Douglass, A. G., Kaszynski, P., and Drzewinski, W., 1999, *Liq. Cryst.*, **26,** 261.

[17] Douglass, A. G., Czuprynski, K., Mierzwa, M., and Kaszynski, P., 1998, *J. Mater. Chem.*, **8,** 2391.

[18] Kaszynski, P., Huang, J., Jenkins, G. S., Bairamov, K. A., and Lipiak, D., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 315.

[19] Kleinpeter, E., Kohler, H., Lunow, A., Tschierske, C., and Zaschke, H., 1988, *Tetrahedron*, **44,** 1609.

[20] Eidenschink, R., 1980, *Kontakte* (E. Merck, Darmstadt), p. 12; Eidenschink, R., 1987, *Kontakte* (E. Merck, Darmstadt), p. 15.

[21] Asahina, S., Sorai, M., and Eidenschink, R., 1998, *Liq. Cryst.*, **24,** 201.