Mesogenic, optical, and dielectric properties of 5-substituted 2-[12-(4-pentyloxyphenyl)-*p*-carboran-1-yl] [1,3]dioxanes†

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Two homologous series of carborane-containing dioxanes **1**[*n*] and **2**[*n*] (*n* = 1–10) were prepared and their mesogenic properties investigated. All compounds exhibit nematic behavior and three members of series **2**[*n*] show an E phase. Numerical analysis of the clearing temperatures gave a limiting value $T_{NI}(\infty)$ of 89 °C for series **2**[*n*] and indicated conformational flexibility of the dioxane ring. Investigations of three-ring derivative **1**[4] gave Δn = 0.17, S = 0.53, and $\Delta\varepsilon$ = +0.4 ± 0.1 at 85 °C. Extrapolation of dielectric data for dilute solutions of **1**[4] in 6-CHBT gave $\Delta\varepsilon$ = +0.4 ± 0.25 at 24 °C. Modelling of dielectric results with the Maier–Meier equation demonstrated that conformers with a higher β angle are preferred, which is consistent with conformational selection for the most elongated conformers.

Introduction

The low polarizability anisotropy and a moderate molecular dipole moment[1] of 2.13 ± 0.03 *D*, oriented at 47° relative to the C2–C5 axes, make [1,3]dioxane an attractive structural element for the preparation of liquid crystals with positive dielectric anisotropy, low birefringence, and minimal absorption in the UV region.[2–6] Analysis of the available data[7] shows that the dioxane ring has a smectogenic character and even two-ring compounds often exhibit smectic phases.[2] While this property of [1,3]dioxane is useful for the development of SmC* materials,[6,8,9] it is undesirable for formulation of nematic materials. Our studies of liquid crystalline derivatives of *p*-carborane demonstrated their highly nematogenic behavior[10–12] and low birefringence.[13] Therefore, we were interested in combining these two structural elements, [1,3]dioxane and *p*-carborane, and investigating the properties of such new materials.

Here, we present the mesogenic properties of two homologous series of three- and four-ring compounds, **1**[*n*] and **2**[*n*], respectively (Fig. 1). In addition, we prepared several members of a third series **3**[*n*] to establish the effect of the linking oxygen atom on mesogenic behavior. We also performed detailed dielectric and optical studies of one of the compounds in the pure state and in nematic solutions. A combination of conformational analysis at the HF and DFT levels with analysis of the dielectric results using the Maier–Meier relationship yielded information about the origin of the observed small positive dielectric anisotropy and conformational properties of the compound.

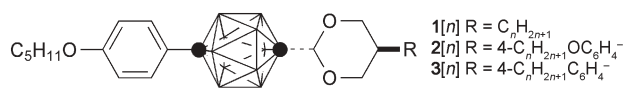


Fig. 1 Mesogenic derivatives **1**[*n*]–**3**[*n*]. In the carborane cage each vertex represents a BH fragment and each sphere is a carbon atom.

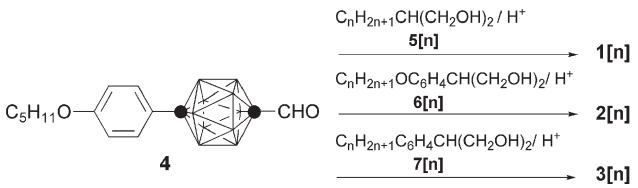
Results

Synthesis

All three series of dioxanes **1**[*n*]–**3**[*n*] were prepared from carborane-1-carboxaldehyde **4** and the appropriate 2-substituted propane-1,3-diols **5**[*n*]–**7**[*n*], according to a general literature method[2] (Scheme 1).

The required diols **5**[*n*]–**7**[*n*] were obtained from the corresponding malonates **8**[*n*]–**10**[*n*] by reduction with $LiAlH_4$ (Scheme 2). Monoalkyl malonates **8**[*n*] were prepared by alkylation of diethyl malonate under phase-transfer-catalysis conditions according to a general literature method.[14] Arylation of diethyl malonate with 4-substituted aryl iodides, **11**[*n*] and **12**[*n*], and preparation of **9**[*n*] and **10**[*n*] was accomplished using CuI according to a general method.[15] All intermediates **5**[*n*]–**10**[*n*] used in this work have been reported in the literature[16–20] but many lack analysis. For completeness of the work, ^{1}H and ^{13}C NMR data for all intermediates is reported in the ESI.

Aldehyde **4** was obtained in 74% yield by formylation of 1-(4-pentyloxyphenyl)-*p*-carborane[21] (**13**) with ethyl formate



Scheme 1

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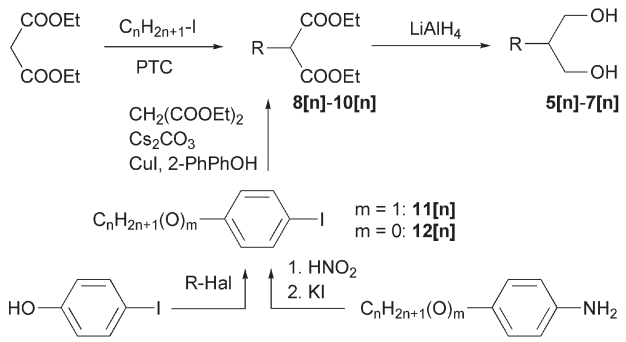
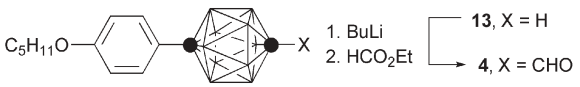
† Electronic supplementary information (ESI) available: Analytical data for derivatives **1**–**3** and intermediates **4**–**10**, complete optical and dielectric data, and also quantum-mechanical and Maier–Meier computational details. See DOI: 10.1039/b608012j



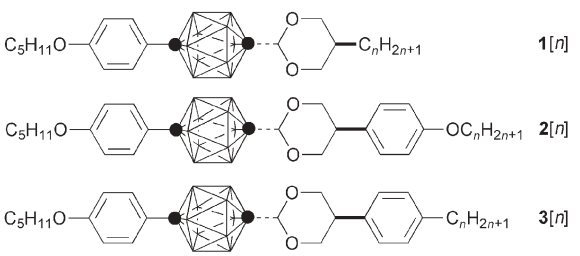
Scheme 2



Scheme 3

(Scheme 3). 4-Alkoxy-1-iodobenzenes[22] (**11**[*n*]) were prepared according to a literature procedure[23] by alkylation of 4-iodophenol. The three 4-alkyl-1-iodobenzenes **12**[5],[24] **12**[6],[25] and **12**[7][26] were obtained from the commercially available anilines according to a literature procedure for **12**[6].[25]

Table 1 Transition temperatures (°C) and enthalpies (kJ mol^{-1})[a]



n	**1**[*n*]	**2**[*n*]	**3**[*n*]
1	Cr[b] 139 (N 101)[c] I (27.7)	Cr_1 130 Cr_2 137 N 257.1 I (15.2) (12.2) (2.5)	—
2	Cr 116 (N 81.7) I (28.3) (1.6)	Cr_1 88 Cr_2 171 N 264.0 I (14.2) (21.4) (1.8)	—
3	Cr 90 N 105.8 I (21.1) (1.6)	Cr_1 121 Cr_2 161 N 247.1 I (8.2) (19.5) (2.5)	—
4	Cr 74 N 101.0 I (36.5) (1.5)	Cr 140 N 237.5 I (22.7) (2.6)	—
5	Cr 92 N 111.0 I (22,8) (1.9)	Cr 143 N 217.5 I (25.7) (1.9)	Cr 144 N 201.2 I (26.7) (2.0)
6	Cr[d] 66 N 105.0 I (21.1) (1.7)	Cr_1 117 Cr_2 144 N 210.1 I (10.1) (19.4) (2.3)	Cr 147 N 183.7 I (18.9) (1.7)
7	Cr 75 N 109.6 I (27.8) (1.9)	Cr_1 103 Cr_2 145 N 197.2 I (6.8) (19.4) (1.9)	Cr 155 N 177.7 I (23.5) (1.8)
8	Cr 64 N 101.9 I (25.0) (1.6)	Cr 127 E 131 N 190.1 I (15.7) (15.3) (2.3)	—
9	Cr 59 N 103.3 I (23.5) (1.8)	Cr 113 E 127 N 182.5 I (15.4) (17.1) (1.8)	—
10	Cr 58 N 96.6 I (40.2) (1.6)	Cr[e] 125 E 127 N 177.4 I (3.7) (8.7) (1.9)	—

[a] Cr: crystal, E: soft crystal E, N: nematic, I: isotropic. [b] Cr–Cr transition at 87 °C (3.0 kJ mol^{-1}). [c] Microscopic observations. [d] Cr–Cr transition at 49 °C (19.0 kJ mol^{-1}). [e] Cr–Cr transition at 112 °C (7.4 kJ mol^{-1}) and 120 °C (4.1 kJ mol^{-1}).

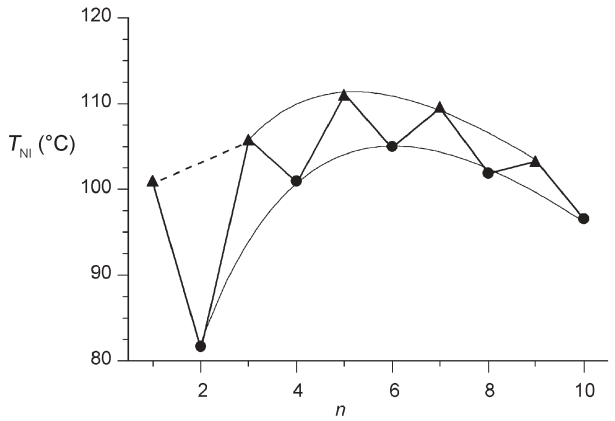


Fig. 2 Nematic–isotropic transition temperatures T_{NI} for **1**[*n*] as a function of the chain length *n*. Lines are guide for the eye.

Mesogenic properties

All investigated compounds in series **1**[*n*]–**3**[*n*] form nematic phases. Lamellar phases are observed only for higher members of series **2**[*n*] ($n \geqslant 8$), which exhibit relatively narrow range E phases. Most compounds in this series also show rich crystalline polymorphism. Phase transition temperatures and enthalpies are collected in Table 1.

The effect of substitution of one of the linking oxygen atoms in **2**[*n*] with a methylene group was briefly investigated, and three members of a homologous series **3**[*n*] with $n = 5$–7 were prepared. All three compounds show nematic phases destabilized relative to the alkoxy analogs **2**[*n*] by an average of 34 °C, which is a typical value for such a substitution in other mesogenic series.[7]

The clearing temperatures in both series **1**[*n*] and **2**[*n*] exhibit the typical "odd–even" effect. The T_{NI} values in the first series have maxima at $n = 5$ and $n = 6$ for homologs with an odd and even number of carbon atoms in the chain, respectively (Fig. 2). Such behavior is typically observed for mesogenic series containing alkylcyclohexyl groups.[7] In contrast, the second series, **2**[*n*], exhibits a monotonous exponential decay of the T_{NI} values with increasing chain-length (Fig. 3). The observed behavior of the series is typical for mesogens with the alkoxyphenyl group.[10,11]

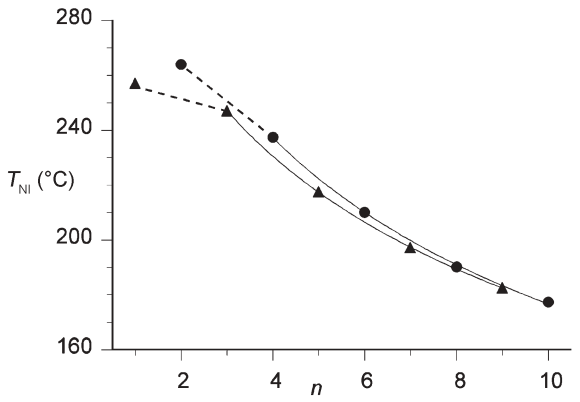


Fig. 3 Nematic–isotropic transition temperatures T_{NI} for **2**[*n*] as a function of the chain length *n*. Best fit functions are listed in the ESI.

Numerical analysis of series **2**[*n*] revealed that the T_{NI} data can be approximated by empirical three-parameter exponential function (F1)[10] and also by homographic function (F2).[27] Initial fitting of all five datapoints for either an odd or even series showed an unacceptably large error on all three parameters in both functions. Therefore, the first two homologs **2**[1] and **2**[2] were excluded from the analysis.

$$T_{NI}(n) = a + \exp\left(b - c\bullet\sqrt{n}\right) \quad \text{(F1)}$$

$$T_{NI}(n) = a\frac{n+b}{n+c} \quad \text{(F2)}$$

The limiting values $a \lim_{n\to\infty} T_{NI}(n) = a$ in function (F1) obtained for both odd and even *n*-series of **2**[*n*] were 86 $\pm$ 6 and 90 $\pm$ 37 °C, respectively, with the overall high correlation factor r^2 of >0.999 for each fit. Since both values should be the same for infinite *n*, the limit *a* in **2**[*n*] was constrained at 86 °C without significant change in r^2. Analogous analysis of series **2**[*n*] using function (F2), gave similar limiting values *a* with a significantly lower error (*n* = odd, *a* = 89 $\pm$ 0.5 °C, r^2 = 1; *n* = even, *a* = 88 $\pm$ 16 °C, r^2 = 0.9996).

Dielectric measurements

To assess the electro-optical properties of the carborane mesogens **1**[*n*], the butyl derivative **1**[4] was selected as a representative for the series and investigated in the pure state and also as a low concentration additive to 6-CHBT (*trans*-4-(4-hexylcyclohexyl)phenylisothiocyanate), a nematic host with positive dielectric anisotropy ($\Delta\varepsilon > 0$).

The measurements for the pure compound were performed in 3 cells and each was measured 3 times over the temperature range of 75–105 °C. The resulting values were averaged and are shown in Fig. 4. Dielectric constants for **1**[4] in 6-CHBT were obtained by linear extrapolation of data for three solutions and the pure host to mole fraction 1.0 (Fig. 5), and results are collected in Table 2. Each datapoint in Fig. 5 represents an average of 5 repetitive measurements in a single cell and has an associated error of <0.03. To lower the error for the extrapolated values, the intercept in the fitting functions was set at the appropriate value for the pure host. The extrapolated dielectric anisotropy $\Delta\varepsilon$ has a small positive value of +0.4 $\pm$ 0.25 which is practically the same as that obtained for pure **1**[4] at 85 °C. The individual components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are larger than those for pure **1**[4] which reflects the difference in the temperature and dielectric strength of the medium.

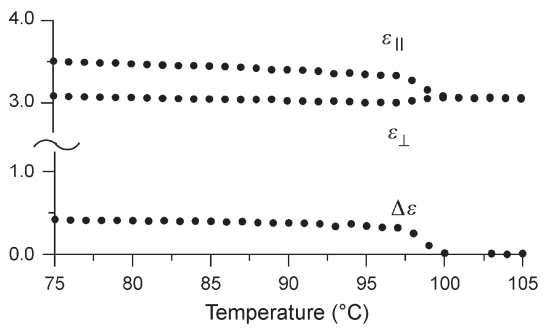


Fig. 4 Dielectric parameters for **1**[4] as a function of temperature. Estimated standard deviation for $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ is 0.1, and for $\Delta\varepsilon$ is 0.01.

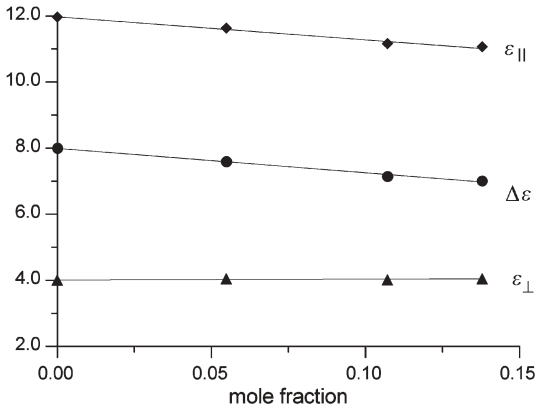


Fig. 5 Plot of dielectric parameters *vs.* concentration for **1**[4] in 6-CHBT at 24 °C. Correlation parameters for $\varepsilon_{\|}$ and $\Delta\varepsilon$ are $r^2 > 0.98$.

Table 2 Dielectric parameters for **1**[4] extrapolated from 6-CHBT solutions at 24 °C and measured for pure compound at 85 °C

	In 6-CHBT	Neat at T = 85 °C
$\varepsilon_{\|}$	4.5 $\pm$ 0.3	3.45 $\pm$ 0.1
$\varepsilon_{\perp}$	4.1 $\pm$ 0.2	3.05 $\pm$ 0.1
$\Delta\varepsilon$	0.4 $\pm$ 0.25	0.4 $\pm$ 0.01

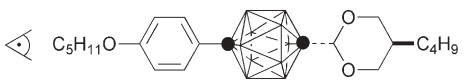
Computation of molecular parameters

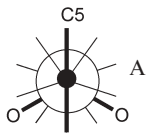
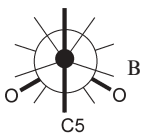
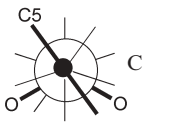
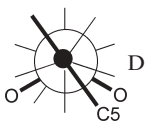
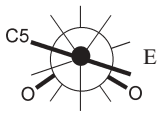
To better understand the experimental results, the molecular structure for each of the principal conformers of **1**[4] was optimized, and dipole moments μ and electronic polarizabilities α were calculated at Gaussian standard orientation (in which the molecular axes are defined by the nuclear charge distribution) using the HF and the B3LYP methods, respectively.

Conformational analysis. The HF calculations show that the dioxane and benzene rings prefer conformations in which the ring's C–H bond eclipses the carborane B–H bond. In compounds **1**[*n*], this conformational preference results in three relative orientations of the two rings. The presence of the polar pentyloxy group results in six orientations of its dipole moment with respect to the dipole moment of the dioxane ring (A–F, Table 3). Finally, the butyl chain on the dioxane ring may assume either a *syn* or *anti* position relative to the pentyloxy group. This gives rise to 10 distinct conformers (and 10 of its enantiomers) as shown in Table 3.

Inspection of the conformers revealed that the relative orientation of the alkyl chains varies significantly from roughly co-planar in E(*anti*) and C(*anti*), F(*syn*), and D(*syn*) (θ = 16–20°) to nearly orthogonal in D(*anti*) and C(*syn*) (θ = 88°). The former conformers are expected to be favored by the nematic phase, particularly the most extended C(*anti*) and E(*anti*). Less compatible with the nematic phase are expected to be F(*anti*)

Table 3 Calculated molecular parameters for the conformers of **1**[4][a]



Conformer	A	B	C		D		E		F	
										
			syn	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*
θ [b] (deg)	56	56	88	19	20	88	53	16	16	53
$\mu_{\parallel}$[c]/D	1.55	1.77	1.60	1.54	1.82	1.76	1.69	1.60	1.74	1.66
$\mu_{\perp}$/D	1.83	0.78	1.58	1.59	1.07	1.09	1.58	1.60	1.14	1.17
μ/D	2.39	1.93	2.25	2.21	2.11	2.07	2.31	2.26	2.08	2.03
β[d] (deg)	50	24	45	45	30	32	43	45	33	35

[a] Dipole moments were obtained with the HF/6-31G(d) method. Extended Newman-type projections along the long molecular axes show the relative orientation of the dioxane (in back) and the 4-pentyloxyphenyl ring (in front). The benzene ring is represented by the black bar and is coplanar with the pentyloxy substituent. In the *syn* conformer, the butyl chain (not shown) propagates on the same side as C_5, and in the *anti* form the two alkyl chains are on the opposite sides of the molecule. [b] The dihedral angle between the pentyl and butyl chains is measured as C1–C2–C3···C1–C2–C3. [c] Dipole moment vector is oriented from the phenyl (positive) to the dioxane ring (negative). [d] Angle between the net dipole vector μ and long molecular axes calculated from the vector components.

and A, B and E(*syn*), with an intermediate dihedral angle θ of about 55°. The least favorable conformers are predicted to be C(*syn*) and D(*anti*) for which the dihedral angle θ between the alkyl group planes is about 88°.

Dipole moment. The HF calculation showed that the total molecular dipole moment varies in the series of conformers of **1**[4] from 1.93 D in B, in which the dioxane oxygen atoms and the pentyloxy group point in opposite directions, to 2.39 D in A, in which the two local dipole moments are parallel. These two conformers also define the extreme orientations of the dipole moment with respect to the long molecular rotational axes, and hence the range of the angle β (24–50°). In two groups of conformers, D and F, the longitudinal component of the dipole moment $\mu_{\parallel}$ is substantially larger than the transverse $\mu_{\perp}$, which results in a relatively low β ($\sim$33°). In contrast, the two dipole moment components are comparable in conformers C and E, and the resulting β is about 45°.

Electronic polarizability. Calculations of the electronic polarizability components for 6 selected conformers showed that the average polarizability α_{avrg} is about 49.7 Å^3. The anisotropy of polarizability $\Delta\alpha$ also varies little between conformers and approximately is 35.5 Å^3 for *anti* and 34.5 Å^3 for the *syn* conformers.

Orientational order parameter from optical data

Refractive indices for **1**[4] were measured at 589 nm as a function of temperature using an Abbe-type refractometer and the results are shown in Fig. 6. The resulting experimental birefringence and calculated electronic polarizabilities were used to derive order parameter S according to a transformed Lorenz–Lorentz equation [eqn (1)].[28] The resulting order parameter was 0.52 for *anti* conformers and 0.54 for the *syn* conformers at 85 °C. Similar values (0.53 and 0.55) were obtained at 71.5 °C suggesting that the order parameter changes little in the investigated temperature range. The order parameters S obtained using the Vuks model[29] were about 15% higher (*e.g.*, 0.60 and 0.62 at 85 °C) presumably due to an underestimation of the calculated polarizability by about 10% and assumption of density 1.0 g cm^{-3} for **1**[4]. Experimental optical values and computational details are listed in the ESI.

$$S = \frac{\alpha}{\Delta\alpha} \bullet \frac{n_e^2 - n_o^2}{n_{avrg}^2 - 1} \quad (1)$$

Dielectric data analysis

The experimental dielectric data were analyzed quantitatively using the Maier–Meier relationship[30] which relates the dielectric anisotropy of the nematic phase and molecular parameters [eqn (2)].[31] Using this equation, the dielectric behavior of compound **1**[4] was evaluated in the pure state and also in 6-CHBT solutions in a similar way to the recently described analysis for another series of mesogens.[12]

In all calculations, **1**[4] was treated as a mixture of individual conformers shown in Table 3. For this purpose, the Maier–Meier equation [eqn (2)] was simplified, and $\Delta\varepsilon$ was expressed

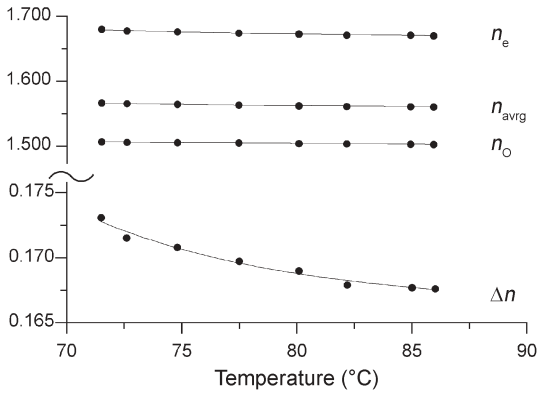


Fig. 6 Refractive indices and birefringence measured for **1**[4] at 589 nm as a function of temperature.

as a product of the molecular parameter C and order parameter S. Consequently, the ideal additivity of $\Delta\varepsilon$ for a mixture's components can be presented as eqn (3), in which x_i represents the mole fraction and S_i is the individual order parameter. In a homogenous mixture, all individual order parameters S_i have close values, and the assumption of their equality leads to eqn (4). Thus, for the purpose of this work, it was assumed that all the conformers considered have the same order parameter.

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_0}\left\{\Delta\alpha - \frac{F\mu_{\mathrm{eff}}^2}{2k_{\mathrm{B}}T}\left(1-3\cos^2\beta\right)\right\}S \quad (2)$$

$$\Delta\varepsilon = \Sigma\Delta\varepsilon_i x_i = \Sigma C_i S_i x_i \quad (3)$$

$$\Delta\varepsilon = S\Sigma C_i x_i \text{ where } \Sigma x_i = 1 \quad (4)$$

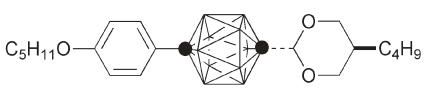
For calculations involving pure **1**[4] the order parameter S was set at the experimentally established average value of 0.53. The reaction field factor F and the cavity factor h in eqn (2) were obtained from the experimental average refractive index n_{avrg} = 1.561 and permittivity $\varepsilon_{\mathrm{avrg}}$ = 3.18 at 85 °C. For calculations involving binary mixtures of **1**[4] in 6-CHBT, the medium was assumed to be the pure host, and the effect of the additive was ignored. Therefore, parameters F and h were calculated for pure 6-CHBT using experimental optical and dielectric data.[32] With these assumptions, the dielectric properties of pure **1**[4] were modelled at 85 °C by varying the Kirkwood factor[33] g, which relates μ^2 and μ_{eff}^2, in such a way that the calculated $\varepsilon_\parallel$ was consistent with the experimental value of 3.45. In the analysis of dielectric data extrapolated from binary mixtures, the g factor and also the overall apparent order parameter[34] S_{app} were varied systematically in such a way that the reverse calculations reproduced the extrapolated dielectric parameters $\varepsilon_\parallel$ and $\varepsilon_\perp$ for **1**[4]. Changes in the Kirkwood factor g mostly affected the $\varepsilon_\parallel$ and $\varepsilon_\perp$ values, while the variation of S_{app} mainly controlled the magnitude of the dielectric anisotropy $\Delta\varepsilon$.

Analysis of the dielectric results was conducted either for all conformers A–F, which were assumed to be present in equal concentration (x_i = 0.1), or only for the most anisometric C(*anti*) and E(*anti*) for which x_i = 0.5. Exclusion of the least anisometric conformers C(*syn*) and D(*anti*) from the calculations had marginal effect on S_{app} and g. For each group of conformers the angle β between μ and $\mu_\parallel$ was either taken as calculated (Table 3) or adjusted for all considered conformers to fit the experimental data. The resulting g, S_{app} and computed permittivity values are listed in Table 4, and details of calculations are described in the ESI.

Results in Table 4 for pure **1**[4] show that the dielectric anisotropy $\Delta\varepsilon$ calculated from molecular parameters and the experimental order parameter is about twice larger than the experimental value when all conformers A–F are included. Calculations of the experimentally established value of $\varepsilon_\parallel$ require the g parameter to be set at 0.51. Increasing the value of angle β decreases the computed $\Delta\varepsilon$, and the experimental dielectric values are reproduced for β + 19° and g = 0.79. When only the most anisometric conformers C(*anti*) and E(*anti*) are considered, the computed $\Delta\varepsilon$ is lowered by 0.1. Upon increasing the β by 13° and setting g = 0.74 the resulting $\Delta\varepsilon$ is equal to the experimental value (0.40).

Similar analysis was performed for the binary mixtures of **1**[4] in 6-CHBT using extrapolated dielectric parameters. In general, the resulting trends are similar to those obtained for neat **1**[4] (Table 4). Thus, the required value of parameter g is generally about 1.0 and the apparent order parameter[34] S_{app} is low, <0.2, even when only the most extended conformers C(*anti*) and E(*anti*) are considered. If all conformers assumed the matrix's order parameter S = 0.67, then the value of $\Delta\varepsilon$ for **1**[4] would be 2.0. Increasing the angle β by 19° for all conformers A–F had practically no effect on g, but significantly improved the S_{app} to a reasonable value of 0.54. The experimental dielectric values for **1**[4] in 6-CHBT with S_{app} = 0.67 can be reproduced if β is increased by 20° for all conformers or by 14° for an equimolar mixture of C(*anti*) and

Table 4 Bulk parameters for **1**[4] calculated using the Maier–Meier equation[a]



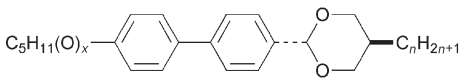
Computed values[a] for	All conformers	All conformers β + 19°	C(*anti*) + E(*anti*)	C(*anti*) + E(*anti*) β + 13°
Pure compound		**For S = 0.53, ε_s = 3.18, T = 358 K**		
g	0.51 ± 0.07	0.78 ± 0.1	0.54 ± 0.07	0.74 ± 0.1
$\varepsilon_\parallel$	3.45 ± 0.1	3.45 ± 0.1	3.45 ± 0.1	3.45 ± 0.1
$\varepsilon_\perp$	2.61 ± 0.06	3.04 ± 0.1	2.71 ± 0.07	3.05 ± 0.1
$\Delta\varepsilon$	0.84 ± 0.04	0.41 ± 0.01	0.74 ± 0.03	0.40 ± 0.02
6-CHBT solution		**T = 297 K**		
g	1.04	1.03	0.97	0.97
S_{app}	0.13 ± 0.09	0.54 ± 0.15	0.17 ± 0.1	0.60 ± 0.15
$\varepsilon_\parallel$	4.51 ± 0.2	4.50 ± 0.08	4.51 ± 0.15	4.50 ± 0.06
$\varepsilon_\perp$	4.11 ± 0.1	4.10 ± 0.04	4.10 ± 0.1	4.10 ± 0.04
$\Delta\varepsilon$	0.40 ± 0.28	0.40 ± 0.10	0.39 ± 0.25	0.40 ± 0.10
		For S_{app} = 0.67, g = 1.0, T = 297 K		
$\varepsilon_\parallel$	5.5	4.5	5.4	4.6
$\varepsilon_\perp$	3.5	4.0	3.8	4.15
$\Delta\varepsilon$	2.0	0.5	1.6	0.45

[a] Computed using molecular parameters listed in Table 3 and experimental $\Delta\varepsilon$ in Table 2. For details see text and the ESI.

E(*anti*). Increase of the angle β in the latter pair by +13°, the same value as obtained for the pure material, gives $S_{app} = 0.60$.

Discussion

All compounds in series **1**[*n*] and **3**[*n*], and most in series **2**[*n*] exhibit only nematic phases. This observed highly nematogenic behavior is consistent with our findings for other series of compounds containing *p*-carborane including an analogous series of Schiff bases[10] and diesters.[11] Typically, the mesophase stability of the *p*-carborane derivatives is lower than that of their benzene analogs. Therefore, it can be expected that clearing temperatures in series **14**[*n*] would be significantly higher than those in **1**[*n*]. A literature search revealed that direct analogs for these series of carborane derivatives are not known, and homologous series[6] **15**[*n*] is structurally closest to the *p*-carborane series **1**[*n*].



14[*n*] *x* = 1, **15**[*n*] *x* = 0

A comparison of **1**[*n*] with **15**[*n*] showed that nematic–isotropic transition temperatures T_{NI} for the *p*-carborane derivatives are lower by an average of 56 °C (±4 °C) than for the benzene analogs. Considering that incorporation of a linking oxygen atom generally increases the T_{NI} by about 30 °C,[7] the destabilization of the nematic phase by the replacement of the central benzene ring in **14**[*n*] by carborane can be estimated as nearly 90 °C. This significant destabilization of the mesophase is also consistent with the lack of smectic behavior in series **1**[*n*]. In comparison, a SmA phase appears in **15**[5] and completely replaces the nematic phase in **15**[10]. Also the B_{cr} phase is present in all members of the series.

Numerical analysis of the T_{NI} in dioxanes **2**[*n*] allows for assessment of transition temperatures for the higher homologs, provides insight into conformational behavior of the compounds, and also is a useful means of verification of sample purity and quality of DSC analysis.[11] As we demonstrated elsewhere, both empirical fitting functions (F1) and (F2) well describe the T_{NI} transitions of a long homologous series up to at least $n = 22$.[11] The limit of the functions for $n = \infty$ has limited physical meaning since for an infinitely long alkyl chain, the compounds would not be mesogenic. However, the $T_{NI}(\infty)$ provides a measure of series mesogenicity and allows for the comparison of closely related series of compounds. Thus, the $T_{NI}(\infty)$ of approximately 90 °C obtained for series **2**[*n*] indicates a rather low mesophase stability as compared to $T_{NI}(\infty) = 155$ °C calculated for another four-benzene-ring homologous series.[35] The T_{NI} values for the first two homologs, **2**[1] and **2**[2], that were not used in the analysis, can be estimated from the fitting functions. Thus, the extrapolated value for **2**[1] is 321 °C [function (F1)] or 315 °C [function (F2)], while the observed value is 257 °C. For **2**[2] both functions predict 268 °C which is only 4 °C higher that the experimental T_{NI}. This discrepancy for **2**[1] and **2**[2] is presumably related to the conformational flexibility of the dioxane ring and the presence of the non-mesogenic diaxial conformer (in addition to the mesogenic diequatorial conformer) at higher temperatures.[11]

Among the three series of compounds, only in series **1**[*n*] are transition temperatures low enough to conduct optical and dielectric studies of neat substances. For detailed investigations, the butyl derivative **1**[4] was selected as a compromise of temperature range (74–101 °C) and molecular size (a smaller molecular size saves computation time). Optical measurements for the three-ring mesogen **1**[4] showed that the average refractive index and the birefringence are relatively low and similar to those found in biphenyls (*e.g.*, nCB). This, in part, is due to the lack of electronic conjugation between the rings and also to the relatively low orientational order parameter *S*.

Analysis of the dielectric results was significantly complicated by the complex conformational properties of the dioxane derivatives. Even without various conformational forms of the alkyl chains, the relative orientation of the three rings and two substituents in **1**[4] results in 10 pairs of chiral conformers A–F. Their overall shapes vary significantly from the most extended in C(*anti*) and E(*anti*), through bow-type shapes of the *syn* forms, to C(*syn*) and D(*anti*) in which the alkyl chains propagate in nearly orthogonal planes. Therefore, their compatibility with the nematic phase varies significantly. It can be anticipated that the conformers are differentiated energetically in the nematic phase, and the more anisometric forms, such as C(*anti*) with low angle θ, are more populated in the nematic phase. It is possible that this multitude of available conformers and shapes is responsible for the lack of the lamellar phases in carborane derivatives and the relatively low T_{NI} values observed in this work.

Molecular geometry is not directly recognized in the Maier–Meier relationship. Instead, it is expressed indirectly by polarizability anisotropy $\Delta\alpha$ and order parameter *S*. For **1**[4] however, all conformers have very similar values of $\Delta\alpha$ and individual order parameters, S_i, are unattainable. The only quantity that differentiates the conformers to some degree is the angle β which defines the orientation of the net dipole moment with respect to the main rotational axes. However, the trend in β does not correspond to the trend in the conformer's anisometry defined by the dihedral angle θ between the planes of the two terminal alkyl chains (Table 3). Therefore, our rational choice of the conformers to be included in calculations is based solely on the type of conformer (*syn* or *anti*) and the value of angle θ: it is assumed that the *anti* conformers are preferred over the *syn*, and the smaller the angle θ the more compatible conformer is with the nematic phase. Thus, the most favorable conformers are C(*anti*) and E(*anti*), which also have a relatively large value for the angle β.

Analysis shows that the calculated angle β has an insufficient value to reproduce the experimental dielectric parameters neither for pure **1**[4] nor for solutions in 6-CHBT. It was found that the angle β must be increased by 19°, when all conformers are considered, or by 13° when only C(*anti*) and E(*anti*) are used for analysis of the pure material. Using similar values for analysis of the extrapolated dielectric parameters leads to a reasonably high apparent order parameter $S_{app} > 0.5$. Without this correction of β, the calculated S_{app} is very small <0.2, which implies a significant destabilization of the binary mixture. The difference of ~13° between the value of

the angle β obtained from the fit to the experimental data and the calculated value is reasonable. The disagreement may be due, in part, to the computed dioxane ring geometry and dipole moment, and the different orientations of the main molecular rotational axis in the condensed and gas phases. However, a difference of nearly 20° is more difficult to account for. Thus, the expectation that the calculated β should be close to the experimental value indicates that conformers with higher value of angle β are required. Among five conformers with $\beta \geqslant 43°$ (Table 3) two, C(*anti*) and E(*anti*), are the most anisometric with the smallest dihedral angle θ of $<20°$. This is strongly suggestive that conformational selection takes place in the nematic phase and those with higher anisometry are preferred.

Summary and conclusions

Results demonstrate that a combination of carborane and dioxane rings give rise to a highly nematogenic materials with relatively low transition temperatures, low Δn, and small positive $\Delta\varepsilon$. The clearing temperatures of series **2**[*n*] can be fitted with two asymptotic functions that predict the T_{NI} for higher members of the series, and give the limiting T_{NI} value for $n = \infty$ about 90 °C.

Conformational analysis of **1**[4] showed 10 principal conformers, which differ in shape and in the orientation of the molecular dipole moment with respect to the main rotational axes. Analysis of dielectric results demonstrated that the experimental values require higher orthogonality of the dipole moment, which is consistent with higher fraction of the more anisometric conformers. This suggests that conformational selection may be taking place in the nematic phase in preference for those with most elongated shapes. These results indicate that the Maier–Meier relationship can provide insight into conformational properties of liquid crystals, if sufficient difference in $\Delta\alpha$ or β exists.

Experimental

Synthesis of liquid crystals and their analytical data are provided in the ESI. Optical microscopy and phase identification was performed using a PZO "Biolar" polarized microscope equipped with a HCS250 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (1–2 mg) and a heating rate of 5 °C min^{-1} under a flow of nitrogen gas. Enthalpies for isotropic transitions were obtained by integration of the zoomed-in DSC transition peak in the range ± 2.5 °C (for **1**[*n*]) or ± 5 °C (or **2**[*n*] and **3**[*n*]) from the peak. For DSC and microscopic analyses, each compound was rigorously purified by dissolving in CH_2Cl_2, filtering to remove particles, evaporating and repeated recrystallization (typically EtOH and pentane for **1**[*n*], and *i*-octane for **2**[*n*] and **3**[*n*]) till constant transition temperature. The resulting crystals were dried in vacuum overnight at ambient temperature. For such purified samples, the clearing transitions were typically less than 0.3 °C wide.

trans-4-(4-Hexylcyclohexyl)phenylisothiocyanate (6-CHBT) was purified by vacuum distillation before use. The measurements for the pure host in three SiO_2 planar cells at 24 °C: $V_{TH} = 1.55 \pm 0.02$ V; $\varepsilon_{\parallel} = 12.0 \pm 0.1$; $\varepsilon_{\perp} = 4.0 \pm 0.1$; $\Delta\varepsilon = 8.0 \pm 0.1$. Literature values:[36] $V_{TH} = 1.63$; $\varepsilon_{\parallel} = 12.0$; $\varepsilon_{\perp} = 4.0$; $\Delta\varepsilon = 8.0$ at 25 °C.

Dielectric measurements

The properties of dioxane **1**[4] were measured by a liquid crystal analytical system (LCAS - Series II, LC Vision®) using GLCAS software version 0.59 which implements literature procedures for dielectric constants.[37]

Solutions of 5.5, 10.7, and 13.8 mol% of **1**[4] in 6-CHBT were prepared and conditioned for 1–2 h at 50 °C. The mixtures were loaded into ITO electro-optical cells by capillary forces at ambient temperature. The cells (about 5 μm thick, electrode area of 0.28 cm^2 and antiparallel SiO_2 with the pretilt $\sim 0°$) were obtained from LC Vision®, and their precise thicknesses (± 0.05 μm) was measured by optical methods. The filled cells were heated to an isotropic phase and were left for an hour at room temperature before measurement.

Default parameters were used for measuring dielectric constants of the mixtures: triangular shaped voltage bias ranging from 0.1–20 V at 1 kHz frequency. The threshold voltage V_{th} was measured as a 10% of change. Each mixture was measured at least 5 times in a single cell, and results were averaged giving the dielectric values with an associated error of <0.03. Since cell parameters vary slightly, reproducibility of the measurement from cell-to-cell and hence uncertainty of a single cell measurement is about 0.08. This relatively high uncertainty for the measured values is partially eliminated in the fitting process of three datapoints from three different cells. Values for dielectric permittivity ε were plotted as a function of concentration and extrapolated to pure **1**[4]. The intercept in the fitting functions was fixed at the appropriate value for the pure host (*vide supra*). The results are presented in Table 2.

Temperature-dependent dielectric permittivity of neat **1**[4] was measured in three SiO_2 cells. Measurements were repeated three times for each cell and averaged. Estimated standard deviation for the single cell measurement was about 0.01. The resulting mean values for each of the three cells were averaged to give the final dielectric permittivities. Standard deviation for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ was approximately 0.1, while $\Delta\varepsilon$ differed little between the cells (std 0.01).

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