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Evaluation of carborane-containing nematic liquid crystals for electro-optical applications

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Three new structurally similar compounds in series **1[2]** and **2** containing 12- and 10-vertex *p*-carborane units (**A** and **B**) were prepared. Their thermal properties were investigated in the pure state and compared to those of their carbocyclic analogues. Using several higher homologues in the series **1[n]**, clearing temperatures for the unknown **1[4]** and **1[10]** were predicted. Optical, dielectric and rotational viscosity parameters for carborane derivatives **1[2]** and **2** and their cyclohexane analogies were obtained by extrapolation of values measured for 10% solutions in a standard nematic host. The observed trends were rationalised using computed molecular parameters.

Keywords: nematics; carborane; fluorine; synthesis; dielectric

1. Introduction

Liquid crystals with partially fluorinated rigid cores are important materials for applications in flat panel displays (*1*, *2*). Strategic placement of fluorine atoms in benzene rings is an effective way to construct polar nematic materials with low viscosity and high resistivity (*3*–*9*). In this context, we recently began a systematic investigation of partially fluorinated mesogens containing *p*-carborane (**A** and **B**) and comparison of their properties with those of carbocyclic analogs containing bicyclo[2.2.2]octane (**C**), cyclohexane (**D**), and benzene (**E**) rings (Figure 1). One advantage of the carboranes is their reduced tendency to form smectic phases, which has been ascribed to the high conformational freedom of the carborane derivatives (*10*–*14*).

Our recent experimental investigation augmented with the Maier–Meier analysis of a series of laterally fluorinated mesogens **1[6]** and members of series **2** demonstrated the significance of the structure and electronegativity of the variable ring $\mathcal{A}$ to dielectric anisotropy (*13*, *15*). In continuation of our studies, we focused on evaluating the performance of four selected carborane derivatives as components of nematic materials and assessing their potential use in mixture formulation.

In this paper, the synthesis and properties of three new carborane-containing nematogens, **1[2]A**, **1[2]B** and **2B** are described. We investigate the properties of these three new mesogens and also **2A** in the pure form and as additives to a standard ZLI nematic host, and compare the results to those for the cyclohexyl analogs **1[2]D** and **2D**. The trends in the extrapolated clearing point (T_{NI}), viscosity and dielectric and optical parameters are rationalised with results of molecular modelling.

2. Results and discussion

Synthesis

Compounds **1** and **2** were obtained from pentylcarboranes **3** and aryl iodides **4** and **5**, respectively,

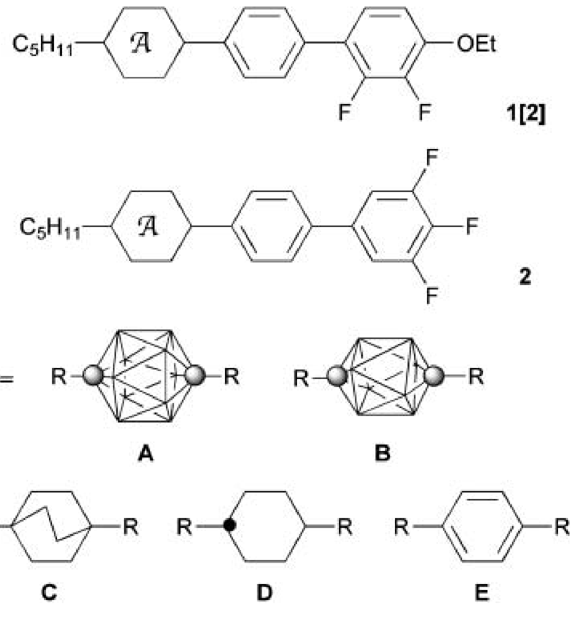

Figure 1. Molecular structures for **1[2]** and **2**, and five-ring systems: 1,12-dicarba-*closo*-dodecaborane (12-vertex *p*-carborane, **A**), 1,10-dicarba-*closo*-decaborane (10-vertex *p*-carborane, **B**), bicyclo[2.2.2]octane (**C**), cyclohexane (**D**) and benzene (**E**). In **A** and **B**, each vertex represents a BH fragment and each sphere is a carbon atom.

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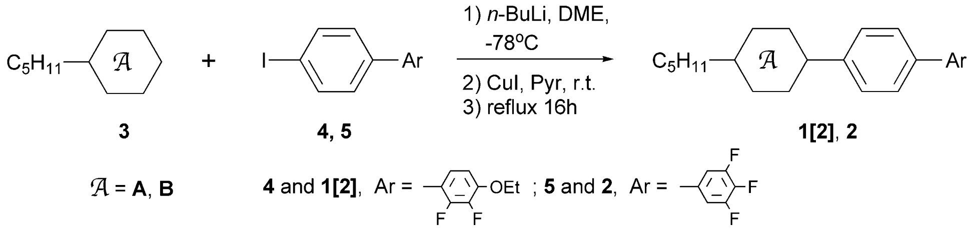
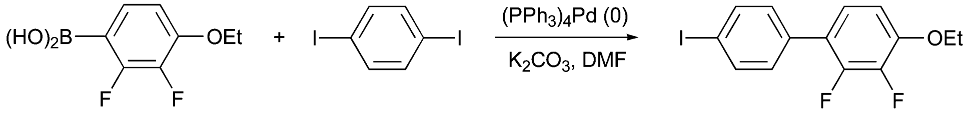


Scheme 1. Synthesis of compounds **1** and **2**.



6 **4**

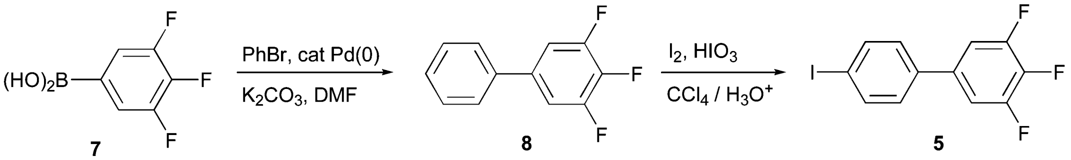
Scheme 2. Preparation of the iodide **4**.

according to a general method for arylation of 12-vertex carboranes (*16*) extended (*17*) to 10-vertex carborane **B** (Scheme 1). The conversion of the reactants was low, about 20% after 24 h. Therefore, the reaction mixture was separated into starting carborane **3** and a mixture of the starting iodide and the product. The recovered carborane was used to generate the carboranylcopper reagent, which was reacted with the isolated mixture. In the synthesis of compound **1[2]A** and **1[2]B**, two or three such processes were applied and the products were isolated in 52% and 59% overall yields, respectively.

The iodide **4** was prepared as shown in Scheme 2 from 4-ethoxy-2,3-difluorophenylboronic acid (**6**) and 1,4-diiodobenzene using an analogous literature procedure (*18*) The reaction proceeded slowly, and the separation of **4** from byproducts required column chromatography.

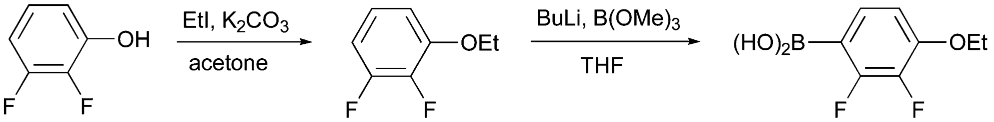
The preparation of iodide **5** by coupling of 3,4,5-trifluorophenylboronic acid (**7**) and 1,4-diiodobenzene, according to the procedure described for **4**, proved impractical. Under these conditions, a complex reaction mixture was formed containing significant amounts of 3,4,5,3′,4′,5′-hexafluorobiphenyl, 3,4,5-trifluorobiphenyl, 4-iodobiphenyl and 4,4′-diiodobiphenyl in addition to the expected iodide **5**, according to GCMS analysis. Chromatography, crystallisation, and sublimation methods were ineffective in purification of the desired iodide **5**. Therefore, iodide **5** was prepared in two steps, as shown in Scheme 3. Coupling of boronic acid **7** with bromobenzene under Suzuki–Miyaura cross-coupling conditions (*19*) gave 3,4,5-trifluorobiphenyl (**8**) in a good yield. Subsequent iodination of biphenyl **8** with a mixture of I_2 and HIO_3 under acidic conditions (*20*) gave the desired iodide **5** in 80% yield. Traces (<5%) of an isomer of **5**, presumably the product of *ortho*-substitution, were also detected in the reaction mixture.

Boronic acid **6** was obtained from 2,3-difluoroethoxybenzene (**9**) according to a general literature procedure (*8*) (Scheme 4). Ether **9** was prepared in 78% yield from 2,3-difluorophenol by alkylation with ethyl iodide.



7 **8** **5**

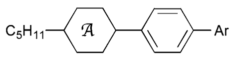
Scheme 3. Preparation of the iodide **5**.

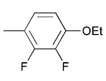
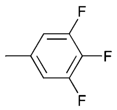
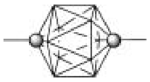
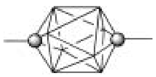
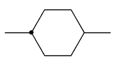
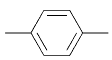


9 **6**

Scheme 4. Synthesis of boronic acid **6**.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for selected compounds determined by DSC (heating rate 5 K min^{-1}) (Cr=crystal; Sm=smectic; N=nematic; I=isotropic).



	Ar	
𝒜	 **1[2]**	 **2**
 **A**	Cr 145 N 167 I (42.2) (1.2)	Cr 94 (N 72)[a] I [b] (24.0) (0.2)[c]
 **B**	Cr 104 N 157 I (32.2) (1.0)	Cr 46 (N 42)[a] I (17.6) (0.2) [c]
 **C**	[d]	Cr 78 N 105 I [b] (20.5) (0.3)
 **D**	Cr 74 SmA 86 N 171 I [e]	Cr 30 N 56 I [b] (18.9) (0.2)
 **E**	Cr 105 SmC 135 N 185 I [f]	Cr$_1$ 57 Cr$_2$ 94 SmA 97 I [b] (5.1) (7.9) (4.8)

[a] Monotropic transition. [b] Ref (*15*). [c] Recorded on cooling. [d] Not known. [e] Ref (*22*). [f] Ref (*5*).

Pentylcarboranes **3A** and **3B** were prepared as described previously (*17*, *21*).

Thermal analysis

Transition temperatures and associated enthalpies for compounds in series **1[2]** and **2** were obtained by differential scanning calorimetry (DSC) and mesophases were identified by optical microscopy. The results are presented in Table 1, which, for comparison purposes, also includes data for the known carbocyclic analogues (*5*, *15*, *22*).

All carborane derivatives in series **1[2]** and **2**, the three newly prepared derivatives, **1[2]A**, **1[2]B** and **2B**, and also **2A** (*15*), show only nematic behaviour, which includes monotropic phases observed for the latter two compounds. In contrast, the carbocyclic analogs in series **1[2]** show enantiotropic smectic A (SmA) phases in addition to the nematic phases. In series **2** the bicyclo[2.2.2]octane and cyclohexane derivatives, **2C** and **2D**, display only nematic behaviour. Surprisingly, the terphenyl analog **2E** exhibits only a narrow range SmA phase.

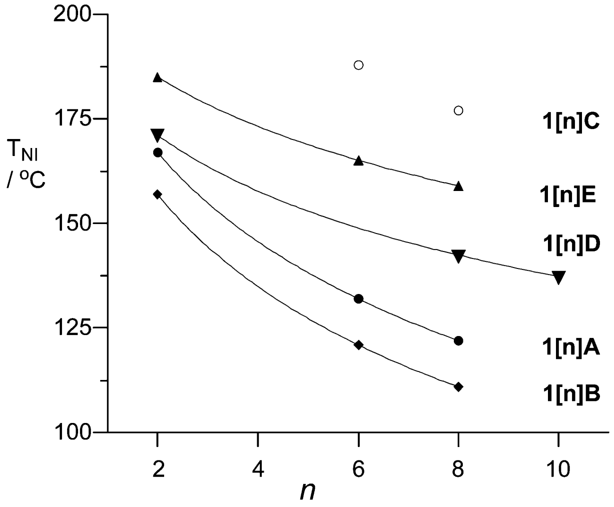


Figure 2. Clearing temperature, T_{NI}, for series of mesogens as a function of the chain length, *n*.

In general, the stability of the mesophase in both series **1[n]** and **2** is higher for the carbocycles than for carboranes, and clearing temperatures for the 12-vertex carborane derivatives **A** are higher than those for the 10-vertex analogues. This is consistent with general trends in other series of isostructural compounds (*23*, *24*). A rare exception from this general trend is the higher T_{NI} observed for **2A** than for the cyclohexane analogue **2D** (Table 1).

Several higher homologues in series **1[n]A** (*13*, *25*), **1[n]B** (*13*), **1[n]C** (*13*), **1[n]D** (*26*) and **1[n]E** (*13*) that have been reported in the literature, were used for numerical analysis of each series **1[n]**. Literature search found two additional members of each series, which makes the quantitative analysis difficult albeit possible (Figure 2). Fortunately, the high sensitivity of the three-parameter fitting function,

$$T_{NI} = a + \exp\left(b \times \sqrt{n} + c\right), \tag{1}$$

to the quality and self-consistency of the data, permits the estimation of T_{NI} for **1[4]** and **1[10]** with a reasonably high certainty even using three data points for fitting. The fitting function given by Equation (1) was previously used in a similar analysis of other homologous series (*23*), and in this investigation, initial poor fit to data points of **1[n]A** prompted us to re-examine transition temperatures for the three compounds (*25*).

The fitting equations permitted an estimation of the clearing temperatures for unknown derivatives **1[4]** and **1[10]** in each homologous series, and also **1[6]D**. Thus, the N–I temperatures for **1[4]** are estimated as 143°C (**A**), 135°C (**B**), 157°C (**D**) and 173°C (**E**). For the decyloxy derivatives the predicted clearing temperatures are: 114°C (**A**), 103°C (**B**), 137°C (**D**) and 154°C (**E**). Derivative **1[6]D** has an estimated T_{NI} of 148°C. The clearing temperature for $n=\infty$, $T_{\mathrm{NI}}(\infty)$ [parameter a in equation (1)], is about 100°C for the carbocycles **1[n]D** and **1[n]E**, about 80°C for **1[n]A** and about 50 °C for the carborane derivatives **1[n]B**. The faster descent of the T_{NI} values (the lower a parameter) in the carborane series than in the carbocyclic analogs is consistent with our previous findings (*23*) and has been attributed to the symmetry of the carborane clusters and conformational properties of their derivatives.

Electro-optical properties in a nematic host

Electro-optical properties for compounds in series **1[2]** and **2** were obtained by linear extrapolation of data measured for their 10% w/w solutions in appropriate nematic host. The only exception is the 12-vertex carborane derivative **1[2]A**, which due to its lower solubility, was investigated as 5% w/w solution. The results are shown in Table 2.

A comparison of the virtual T_{NI} of the additive extrapolated from solutions with T_{NI} obtained for the pure compound (ΔT_{NI} in Table 2) provides a means to assess its compatibility with the host and its impact on host order parameter. Results show that derivatives **1[2]** generally better stabilise the nematic phase of the host (higher ΔT_{NI}) than their more bulky (less anisometric) trifluoro analogues **2**. Further analysis of the data shows that the ΔT_{NI} of the additive and hence its compatibility with the host follows the same trend, **D**>**B**>**A**, in both series. Particularly poor compatibility is observed for the trifluoro derivative **2A** for which the virtual T_{NI} is lower by 36 K than the actual clearing temperature. The trend observed for both series in the ZLI host is consistent with our other findings for series **1[6]** (*13*) and **2** (*15*), which were investigated in another nematic host, 6-CHBT and fully analysed using the Maier–Meier formalism. Thus, similar to results in Table 2, the difference between the impact of **1[6]A** and **1[6]B** on the order parameter of the solution is small (*13*), whereas it is significant for **2A** and **2B** (*15*).

In general, dielectric properties obtained for **1[2]** and **2** in the ZLI host are consistent with our results for **1[6]** and **2** investigated in 6-CHBT (*13*, *15*). Dielectric data in Table 2 show that the extrapolated longitudinal dielectric component, $\varepsilon_{\parallel}$, is generally smaller for the carborane derivatives than for the cyclohexane analogues in both series. The trend in $\varepsilon_{\parallel}$ observed in series **2** (**2D**>**2B**>**2A**) parallels the trend in the calculated dipole moment component $\mu_{\parallel}$ (Table 3). This is in agreement with expectations (since $\varepsilon \sim \mu^2$) and it reflects the electron withdrawing ability of the ring $\mathcal{A}$. In series **1[2]**, however, the trend in $\varepsilon_{\parallel}$ is opposite to the trend in $\mu_{\parallel}$ (shown for **1[6]** in Table 3). This is surprising yet consistent with our results for series **1[6]** (*13*). In consequence, $\varepsilon_{\parallel}$ for carboranes **1[2]A** and **1[2]B** is lower than for the cyclohexane derivative **1[2]D** by nearly 2, which gives rise to their abnormally large extrapolated negative anisotropy $\Delta\varepsilon$. This unusual behaviour originates from the low order parameter of these carborane derivatives in solutions, as evident from the Maier–Meier theory analysis (*13*). This unfavourable impact on the host order parameter of **1[2]A** and **1[2]B** relative to **1[2]D** is also apparent from their ΔT_{NI} values shown in Table 2. In contrast to series **1[2]**, dielectric behaviour of series **2** is in agreement with the expectations, and also with results obtained in another host and for pure compounds (*15*). With the approximately constant extrapolated transverse dielectric component $\varepsilon_{\perp}$ of about 4, variation in the value of $\varepsilon_{\parallel}$ results in a similar variation in the dielectric anisotropy giving the highest value of $\Delta\varepsilon=11.3$ for **2D**.

In comparison to other measurements, the $\Delta\varepsilon$ values extrapolated from the ZLI host are larger by up to 2.6 (**2A**) than those obtained from 6-CHBT, and larger by over 3 than those measured for pure **2B** and **2D** at $T=T_{\mathrm{NI}}-15$ (*15*).

The extrapolated optical anisotropy Δn decreases in both series in the order **B**>**D**>**A**. In contrast, the ordinary and isotropic refractive indices, n_{o} and $\tilde{n}$, follow the order **A**>**B**>**D**. Both of these orders are consistent with the trends in molecular polarisability α_{avrg} and its anisotropy $\Delta\alpha$ calculated for the three parent ring systems (*10*) and reflected in the molecular polarisabilities of **1[6]** and **2** (Table 3).

Analysis of rotational viscosity data in Table 2 shows that derivatives in series **1[2]** increase the host viscosity by a factor of nearly 2 relative to compounds in series **2**. The extrapolated γ_1 values follow the order **A**>**B**>**D** in each series reaching a surprisingly high value of 1.07 P s for **2A**. For 10-vertex carborane derivatives (**B**) values of γ_1 are greater by a factor of about 2.5 than those for the cyclohexane analogs (**D**), and γ_1 for the 12-vertex carborane derivatives (**A**) is higher nearly 4 times for series **2** and almost 6 times for series **1[2]**. The relative values of γ_1 for compounds **B** and **D** are consistent with rotational viscosity values of 0.10 P s and 0.18 P s measured at 36°C for pure **2B** and **2D**, respectively (*15*).

3. Conclusions

The presented investigation of two series **1[2]** and **2** in the ZLI host allowed for a detailed comparison of their properties with those obtained in another host (series **2**) and also for their higher homologues (series **1[6]**).

Table 2. Extrapolated phase parameters measured by electro-optical methods in 10% w/w mixtures at T=25°C. With the exception of dielectric data measured for series **1[2]** in ZLI-2857, all other parameters for both series were obtained from ZLI-4792 solutions. The estimated error for the extrapolated values is about 10%.

Compound	ΔT_{NI}[a] /K	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	n_o	n_e	Δn	$\tilde{n}$	γ_1[b] /P s
1[2]A[c]	−2	4.1	8.7	−4.6	1.5284	1.6919	0.1635	1.5848	1.07
1[2]B	+1	4.2	8.9	−4.7	1.5164	1.7073	0.1909	1.5826	0.88
1[2]D	+30	5.9	8.4	−2.5	1.5000	1.6670	0.1670	1.5577	0.35
2A	−36	12.7	4.0	8.7	1.5360	1.6550	0.1190	1.5767	0.74
2B	−16	13.6	4.1	9.5	1.5226	1.6640	0.1414	1.5711	0.43
2D	+9	15.4	4.1	11.3	1.5000	1.6310	0.1310	1.5449	0.19

[a] Difference between the extrapolated molar T_{NI} and observed for the pure compound. [b] Measured at 20°C. [c] 5% w/w solution.

Results obtained for **1[2]** and **2** in the ZLI host are consistent with those previously obtained for **1[6]** and **2** in 6-CHBT host and showed once again significant differences between carborane-containing mesogens and their carbocyclic analogues. Thus, carborane additives **1[2]A** and **1[2]B** show excessively negative extrapolated dielectric anisotropy, $\Delta\varepsilon$, which is presumably due to the negative impact on the host order parameter. The electron-deficient nature of the carborane groups lowers the longitudinal component of the dipole moment $\mu_{\parallel}$ and gives rise to the lower positive dielectric anisotropy $\Delta\varepsilon$ in series **2** relative to the carbocyclic mesogens. The electronic structure of the carborane ring gives rise to a relatively high average refractive index of the carborane-containing mesogens. The birefringence, Δn, is highest for the 10-vertex carborane **B**, which deviates more from the spherical electron distribution than the 12-vertex cluster **A**. Overall, results presented here can be summarised as follows: values of ΔT_{NI} and $\varepsilon_{\parallel}$ follow the order **A**<**B**<**D**, whereas values of n_o, $\tilde{n}$ and γ_1 follow the opposite order **A**>**B**>**D** in both series of compounds. Considering their negative impact on host order parameters and viscosity, these carborane derivatives are less attractive for mixture formulation than their cyclohexane analogues.

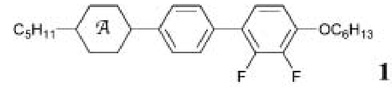
4. Experimental section

NMR spectra were taken in $CDCl_3$ or acetone-d_6 on Bruker instruments operating at 300 MHz or 400 MHz (^1H) and referenced to the solvent. Mass spectrometry was performed using Hewlett-Packard 5890 Series II instrument (GCMS) using a 30 m 5%-phenylmethylpolysiloxane column. Melting points were measured in opened capillary. Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia.

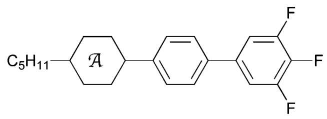
Electro-optical measurements

T_{NI}, Δn and γ_1 for **1[2]** and **2** were determined by linear extrapolation from a 10% w/w solution (5% w/w for **1[2]A**) in the commercially available Merck mixture ZLI-4792 (T_{NI}=92.8°C, $\Delta\varepsilon$=5.3, Δn=0.0964) at 25°C (T_{NI} and Δn) or 20°C (γ_1). Dielectric parameters for **1[2]** were extrapolated from ZLI-2857 (T_{NI}=82.3°C, $\Delta\varepsilon$=−1.4, Δn=0.0776), whereas for series **2** from ZLI-4792. The clearing temperatures, T_{NI}, for the additives were extrapolated from

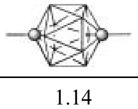
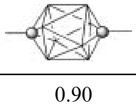
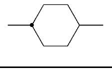
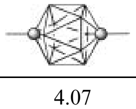
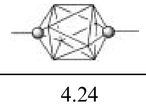
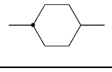
Table 3. Calculated molecular parameters for **1[6]** and **2**. Dipole moments were obtained with the HF/6-31G(d) method and electronic polarisabilities at the B3LYP/3-21G level. Data for **1[6]A** and **1[6]B** are taken from Januszko *et al.* (*13*) and data for **2** from Kaszynski *et al.* (*15*).



1[6]



2

	A	B	D	A	B	D
						
$\mu_{\parallel}$ /D [a]	1.14	0.90	0.78	4.07	4.24	4.41
$\mu_{\perp}$ /D	3.63	3.76	3.78	0.12	0.18	0.57
μ /D	3.80	3.86	3.86	4.07	4.24	4.45
β /° [b]	73	77	78	2	2	7
$\Delta\alpha$ / Å^3	50.4	52.0	42.3	36.2	37.7	29.1
α_{avrg} / Å^3	57.1	55.1	46.8	44.7	42.6	34.9

[a] The dipole moment vector is orientated from $\mathcal{A}$ (negative) to OC_6H_{13} (positive). [b] Angle between the net dipole vector μ and long molecular axes calculated from the vector components. For details see Januszko *et al.* (*13*).

solution using mole fractions. All parameters for the solutions were measured in a single cell with an accuracy of 1%. Therefore, an estimated error for the extrapolated values is about 10%.

Syntheses

*1-(4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)-12-pentyl-1,12-dicarba-*closo*-dodecaborane (**1[2]A**).*

The compound was obtained according to the procedure described for **2B** using carborane **3A** (*21*) (0.84 g, 3.9 mmol) and iodide **4** (1.40 g, 4.0 mmol). The reaction was repeated twice using the recovered **3A** and isolated mixture **1[2]A** and **4**. The crude product was purified by column chromatography (hexane followed by hexane/CH_2Cl_2, 4:1) and recrystallised from isooctane followed by MeCN giving 0.92 g (52% yield) of **1[2]A** as colourless crystals. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.84 (t, J=7.1 Hz, 3H), 1.10–1.26 (m, 6H), 1.47 (t, J=6.9 Hz, 3H), 1.66 (t, J=8.1 Hz, 2H), 1.5–3.5 (br m, 10H), 4.14 (q, J=6.9 Hz, 2H), 6.76 (td, J_1=8.1 Hz, J_2=1.3 Hz, 1H), 7.01 (td, J_1=8.3 Hz, J_2=2.2 Hz, 1H), 7.26 (d, J=8.6 Hz, 2H), 7.31 (d, J=8.8 Hz, 2H). Elemental analysis: calculated for $C_{21}H_{32}B_{10}F_2O$, C 56.48, H 7.22; found, C 56.64, H 7.22%.

*1-(4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)-10-pentyl-1,10-dicarba-*closo*-decaborane (**1[2]B**).*

The compound was obtained according to the procedure described for **2B** using carborane **3B** (*17*) and iodide **4**. The reaction was repeated using the recovered carborane **3B** and isolated mixture of **1[2]B** and **4**. The product was purified by crystallisation from MeCN followed by gradient sublimation giving 0.76 g (59% yield) of **1[2]B** as colourless crystals. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.98 (t, J=7.1 Hz, 3H), 1.41–1.57 (m, 4H), 1.50 (t, J=6.9 Hz, 3H), 1.97 (quint, J=7.8 Hz, 2H), 3.21 (t, J=8.3 Hz, 2H), 1.5–3.5 (br m, 8H), 4.18 (q, J=7.0 Hz, 2H), 6.83 (td, J_1=8.1 Hz, J_2=1.8 Hz, 1H), 7.15 (td, J_1=8.3 Hz, J_2=2.1 Hz, 1H), 7.58 (dd, J_1=8.2 Hz, J_2=1.5 Hz, 2H), 7.85 (d, J=8.2 Hz, 2H). Elemental analysis: calculated for $C_{21}H_{30}B_8F_2O$, C 59.64, H 7.15; found, C 59.65, H 7.21%.

*1-(3′,4′,5′-Trifluorobiphenyl-4-yl)-10-pentyl-1,10-dicarba-*closo*-decaborane (**2B**).*

1-Pentyl-1,10-dicarba-*closo*-decaborane (*17*) (**3B**, 0.925 g, 4.8 mmol) was dissolved in dry DME (25 ml) and treated with a hexane solution of *n*-BuLi (2.4M, 2.1 ml, 5.0 mmol) at −78°C. The mixture was warmed up to room temperature, stirred for 20 min and dry CuI (1.37 g) was added in one portion. After 30 min, to the resulting black solution dry pyridine (3.2 ml) was added, followed by 3,4,5-trifluoro-4′-iodobiphenyl (**5**, 1.55 g, 4.6 mmol). The resulting mixture was stirred, gently refluxed overnight, cooled and poured into 5% HCl (20 ml). The mixture was filtered through Celite, washed with hexanes and layers were separated. The aqueous layer was extracted with hexanes (20 ml) and then with CH_2Cl_2 (10 ml), organic layers were combined, dried (Na_2SO_4), and the solvents were removed. The oily residue was passed through a silica gel plug (hexane) giving the starting carborane derivative **3B** (324 mg) as the first fraction and a mixture of product **2B** and unreacted iodide **5** (1.41 g). The reaction was repeated with the recovered carborane **3B** and the isolated mixture of **2B** and **5**. Finally, the unreacted iodide **5** was removed from the crude reaction mixture under reduced pressure (90°C/0.1 mmHg) and the residue was crystallised repeatedly from a MeCN/EtOH (~4:1) mixture to give 0.90 g (49% yield) of **2B** as colourless crystals. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.98 (t, J=7.1 Hz, 3H), 1.41–1.58 (m, 4H), 1.5–3.5 (br m, 8H), 1.99 (quint, J=7.8 Hz, 2H), 3.23 (t, J=8.3 Hz, 2H), 7.25 (dd, J_1=8.8 Hz, J_2=6.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.87 (d, J=8.4 Hz, 2H). ^{11}B NMR ($CDCl_3$, 128 MHz): δ −11.9 (d, J=172 Hz). Elemental analysis: calculated for $C_{19}H_{27}B_8F_3$, C 57.21, H 6.82; found, C 57.43, H 6.44%.

*4-Ethoxy-2,3-difluoro-4′-iodobiphenyl (**4**).*

A mixture of 1,4-diiodobenzene (7.2 g, 22.0 mmol), boronic acid **6** (2.91 g, 14.5 mmol), $Pd(Ph_3P)_4$ (0.420 g, 0.36 mmol) and K_2CO_3 (3.0 g, 22 mmol) in DMF (35 ml) was degassed, backfilled with nitrogen and heated at 90°C overnight. The mixture was cooled and another portion of the catalyst was added (ca. 400 mg), degassed and heated at 90°C. After this procedure was repeated once more, the resulting deep-red mixture was vigorously stirred with aq. HCl (5%, 15 ml), filtered through Celite, and organic products were extracted with EtOAc (3 × 20 ml). Combined extracts were dried (Na_2SO_4) and passed through a silica gel plug (hexanes). The solvent was evaporated and the residue was purified by column chromatography (SiO_2, hexane followed by hexane/CH_2Cl_2, 4:1) to give 1.70 g (33% yield) of iodide **4** as a colourless solid. M.p. 74–75 °C (hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.48 (t, J=7.0 Hz, 3H), 4.16 (q, J=7.0 Hz, 2H), 6.79 (td, J_1=8.2 Hz, J_2=1.6 Hz, 1H), 7.05 (td, J_1=8.4 Hz, J_2=2.2 Hz, 1H), 7.24 (dd, J_1=8.7 Hz, J_2=1.5 Hz, 2H), 7.76 (d, J=8.3 Hz, 2H). GCMS, rt 17.7 min, m/z 361 (90, M), 333 (100). Elemental analysis: calculated for $C_{14}H_{11}F_2IO$, C 46.69, H 3.08; found, C 46.89, H 3.07%.

3,4,5-Trifluoro-4′-iodobiphenyl (27) (**5**).

A mixture of 3,4,5-trifluorobiphenyl (**8**, 2.94 g, 14.1 mmol), HIO_3 (1.06 g, 6.0 mmol), I_2 (2.72 g, 10.7 mmol), CCl_4 (2.15 ml), acetic acid (17 ml) and conc. H_2SO_4 (0.9 ml) was stirred and heated at 80°C under gentle reflux for 5 h. The red solution was cooled, crushed ice (30 g) and sodium thiosulfate (1M in water, 50 ml) were added and organic products were extracted with CH_2Cl_2 (× 2). Combined organic layers were dried (Na_2SO_4) and solvents were removed. The residue was passed through a silica gel plug (hexane) and the solvent was removed. The resulting yellowish oil was short-path distilled (Kugel-rohr, 160°C/0.05 mmHg) to give 3.76 g (80% yield) of iodide **5** as an oil, which solidified upon standing. Recrystallisation from heptane gave colourless crystals. M.p. 47–49°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.15 (dd, J_1=8.6 Hz, J_2=6.6 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.78 (d, J=8.4 Hz, 2H). GCMS, rt 14.0 min, *m/z* 335 (100, M), 207 (87). Elemental analysis: calculated for $C_{12}H_6F_3I$, C 43.14, H, 1.81; found, C 42.94, H 1.70.

4-Ethoxy-2,3-difluorophenylboronic acid (6).

A hexane solution of *n*-buthyllithium (2.5M, 5.2 ml, 13.0 mmol) was added dropwise to a stirred, cooled (−78°C) solution of 2,3-difluoroethoxybenzene (**9**, 1.95 g, 12.0 mmol) in dry THF (20 ml) under inert atmosphere. The reaction mixture was stirred for 3 h and than a cooled (−78°C) solution of freshly distilled $B(OMe)_3$ (2.9 ml, 2.65 g, 24 mmol) in dry THF (10 ml) was added dropwise at −78°C. The reaction mixture was left overnight at room temperature, quenched with 10% aq. HCl (25 ml), and organic products were extracted with Et_2O (3 × 30 ml). Combined organic layers were washed with water (10 ml), dried (Na_2SO_4) and solvents were removed. The residue was washed with hot hexane (20 ml) and dried under reduced pressure giving 1.94 g (78% yield) of acid **6** as a colourless solid, which was recrystallised from toluene. M.p. 135–136°C. ^{1}H NMR (acetone-d_6, 300 MHz): δ 1.40 (t, J=7.0 Hz, 3H), 4.18 (q, J=7.0 Hz, 2H), 6.93 (ddd, J_1=8.5 Hz, J_2=7.1 Hz, J_3=1.6 Hz, 1H), 7.45 (ddd, J_1=8.5 Hz, J_2=6.7 Hz, J_3=2.3 Hz, 1H). Elemental analysis: calculated for $C_8H_9BF_2O_3{\cdot}H_2O$, C 43.68, H 5.04; found, C 42.55, H 4.54%.

3,4,5-Trifluorobiphenyl (28) (**8**).

A mixture of bromobenzene (3.4 g, 21.6 mmol), 3,4,5-trifluorophenylboronic acid (**7**, 3.8 g, 21.6 mmol), $Pd(Ph_3P)_4$ (624 mg, 0.54 mmol) and K_2CO_3 (6.0 g, 43.5 mmol) in DMF (50 ml) was degassed, backfilled with nitrogen and heated at 80°C overnight. H_2O (50 ml) was added, the mixture was vigorously stirred. Organic products were extracted with hexane, extracts were dried (Na_2SO_4) and filtered through a silica gel plug (hexane). The solvent was evaporated and the resulting product was short-path distilled (Kugel-rohr, 110°C/0.15 mmHg) to give 2.94 g (65% yield) of biphenyl **8** as colourless solid (~90% purity by ^{1}HNMR, m.p. 50–53°C), which was used in next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (dd, J_1=8.4 Hz, J_2=6.6 Hz, 2H), 7.37–7.52 (m, 5H). GCMS, rt 9.0 min, *m/z* 209 (100, M), 189 (19).

2,3-Difluoroethoxybenzene (9).

A mixture of 2,3-difluorophenol (2.72 g, 21.0 mmol), ethyl iodide (4.05 g, 26.0 mmol), anhydrous K_2CO_3 (6.1 g, 44 mmol) and acetone (20 ml) was stirred and refluxed for 16 h. Most of the solvent was removed and the residue was passed through a silica gel plug (CH_2Cl_2). The filtrate was concentrated giving 2.58 g (78% yield) of **9** as a colourless liquid used directly in the next step. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.46 (t, J=7.0 Hz, 3H), 4.11 (q, J=7.0 Hz, 2H), 6.70–6.83 (m, 2H), 6.96 (dtd, J_1=5.9 Hz, J_2=8.5 Hz, J_3=2.3 Hz, 1H). GCMS, rt 4.3 min, *m/z* 158 (32, M), 130 (100).

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