Electronic Supplementary Information for

\textit{o}-Carborane derivatives for probing molecular polarity effects on liquid crystal phase stability and dielectric behavior

Jacek Pecyna,\textsuperscript{a,b} Aleksandra Jankowiak,\textsuperscript{a} Damian Pociecha\textsuperscript{c} and Piotr Kaszyński\textsuperscript{a,c,d}

\textsuperscript{a} Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN 37235
\textsuperscript{b} Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132, USA
\textsuperscript{c} Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland
\textsuperscript{d} Faculty of Chemistry, University of Łódź, 91403 Łódź, Poland

Table of content

1. Thermal analysis \hspace{100mm} \ldots S2
2. Powder XRD measurements \hspace{95mm} \ldots S3
3. Binary mixtures \hspace{90mm} \ldots S5
   \hspace{5mm} • Binary mixtures preparation \hspace{90mm} \ldots S5
   \hspace{5mm} • Thermal analysis \hspace{90mm} \ldots S5
   \hspace{5mm} • Dielectric measurements \hspace{90mm} \ldots S6
4. Background for calculations in the nematic phase \hspace{45mm} \ldots S8
5. Procedures for Maier-Meier analysis \hspace{40mm} \ldots S9
6. Quantum mechanical calculations \hspace{40mm} \ldots S9
7. Archive for DFT calculations \hspace{40mm} \ldots S11
8. References \hspace{40mm} \ldots S14
### 1. Thermal analysis

**Table S1.** Transition temperatures and enthalpies for compounds in series 1.\(^a\)

![Diagram](attachment:image.png)

<table>
<thead>
<tr>
<th>L</th>
<th>A</th>
<th>B</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 71 (SmA 45) N 149</td>
<td>20.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Cr 58 (SmC 38) SmA 121 N 144</td>
<td>37.8</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr 97 E 194 SmB 211 SmA 222</td>
<td>12.6</td>
<td>5.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

\(^a\) Cr-crystal, N-nematic, Sm-smectic, soft-crystalline phases B, E, G and possibly H. \(^b\) Ref. \(^1\). \(^c\) Ref. \(^2\). \(^d\) From XRD measurement.

**Table S2.** Transition temperatures and enthalpies for for compounds in series 2.\(^a\)

![Diagram](attachment:image.png)

<table>
<thead>
<tr>
<th>L</th>
<th>A</th>
<th>B</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 124 N 135</td>
<td>54.3</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Cr 121 N (101)</td>
<td>46.3</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Cr 72 X 209 G 254 SmC 258 SmA 281 N 285</td>
<td>7.7</td>
<td>5.4</td>
<td>11.8</td>
</tr>
</tbody>
</table>

\(^a\) Cr-crystal, N-nematic, Sm-smectic, soft-crystalline phases E and G, X-unidentified phase. \(^b\) Ref. \(^3\). \(^c\) Ref. \(^2\). \(^d\) Second heating: Cr 63 \((19.4)\) N 101 \((1.2)\) I. \(^e\) Second heating: Cr 69 \((17.8)\) N 77 \((1.1)\) I. \(^f\) Previously an E phase reported. Ref. \(^3\).
2. Powder XRD measurements

X-ray diffraction experiments in broad angle range were performed with Bruker D8 GADDS system (Cu Kα radiation, Göbel mirror, point collimator, Vantec 2000 area detector) equipped with a modified Linkam heating stage. For small angle diffraction experiments Bruker Nanostar system was used (Cu Kα radiation, cross-coupled Göbel mirrors, three pinhole collimation, Vantec 2000 area detector). Samples were prepared in a form of a thin film / droplet on heated surface or in thin-walled glass capillaries. Results are shown in Figures S1 – S4.

![Fig. S1. Wide angle data for azo ester 1[Ph]d.](image)

![Fig. S2. Layer spacing $d$ as a function of temperature for 1[Ph]d.](image)

Thermal expansion coefficients of the SmA phase:

- $\kappa_{1[B]a} = -5.11 \pm 0.06$ pm K$^{-1}$ (95 – 130 °C)
- $\kappa_{1[B]b} = -9.65 \pm 0.08$ pm K$^{-1}$ (70 – 95 °C)
- $\kappa_{1[B]c} = -7.00 \pm 0.02$ pm K$^{-1}$ (60 – 140 °C)

![Fig. S3. Layer spacing $d$ as a function of temperature for selected compounds.](image)
Fig. S4. Wide angle XRD data for Schiff base 1[Ph]c.
3. Binary mixtures

Preparation of binary mixtures for dielectric studies. Solutions of compounds 1[A]a or 1[B]a in host 6CHBT (15-20 mg) in dry CH₂Cl₂ (~0.5 mL) were heated at ~60 °C for 2 hr in an open vial to ensure homogeneity of the sample. The sample was degassed under vacuum (0.2 mmHg), left at ambient temperature for 2 hr and analyzed by polarized optical microscopy (POM). After a minimum of several days, the mixtures were inspected again and no inhomogeneity or partial crystallization was found.

Thermal analysis Virtual N-I transition temperatures \([T_{NI}]\) were determined for selected compounds in 6CHBT host. The clearing temperature for each homogenous mixture, prepared as above, was determined by DSC as the peak of the transition using small samples (~0.5 mg) and a heating rate of 5 K·min⁻¹. The results are shown in Tables S3 and S4. The virtual N-I transition temperatures, \([T_{NI}]\), were determined by linear extrapolation of the data for peak of the transition to pure substance \((x = 1)\). To minimize the error, the intercept in the fitting function was set as the peak \(T_{NI}\) for the pure host.

Table S3. \(T_{NI}\) for solutions of 1[A]a in 6CHBT.

<table>
<thead>
<tr>
<th>(T_{NI} / °C)</th>
<th>Mole fraction, (x)</th>
<th>0.00 (host)</th>
<th>0.0413</th>
<th>0.0751</th>
<th>0.1774</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset</td>
<td>43.59</td>
<td>47.83</td>
<td>52.94</td>
<td>67.85</td>
<td></td>
</tr>
<tr>
<td>Peak</td>
<td>43.76</td>
<td>48.51</td>
<td>54.47</td>
<td>69.36</td>
<td></td>
</tr>
</tbody>
</table>

\([T_{NI}] = 187±3 °C, r^2 = 0.996\)
Dielectric measurements. Dielectric properties of solutions of selected esters in $\text{6CHBT}$ were measured by a Liquid Crystal Analytical System (LCAS - Series II, LC Vision, Inc.) using GLCAS software version 0.13.14, which implements literature procedures for dielectric constants. The instrument was calibrated using a series of capacitors (11.30 pF – 3292 pF). The homogenous binary mixtures were loaded into ITO electrooptical cells by capillary forces with moderate heating supplied by a heat gun. The cells (about 10 $\mu$m thick, electrode area 1.00 cm$^2$ and anti-parallel rubbed polyimide layer) were obtained from LC Vision, Inc. The filled cells were heated to an isotropic phase and cooled to room temperature before measuring of dielectric properties. Default parameters were used for measurements: triangular shaped voltage bias ranging from 0.1-20 V at 1 kHz frequency. The threshold voltage $V_{\text{th}}$ was measured at a 5% change. For each mixture the measurement was repeated 10 times manually for two cells. The results were averaged to calculate the mixture’s parameters. Results are shown in Tables S5 and S6. All measurements were run at 25 °C. Error in concentration is estimated at about 1.5%. The dielectric values obtained for each concentration were fitted to a linear function in which the intercept was set at the value extrapolated for the pure host. The resulting extrapolated values for pure additives are shown in Table 3 in the main text.
Table S5. Dielectric parameters for 1[A]a in 6CHBT at 25 °C.

![Chemical structure]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mole fraction, x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00 (host)</td>
</tr>
<tr>
<td>ε</td>
<td></td>
</tr>
<tr>
<td>ε⊥</td>
<td>3.99±0.01</td>
</tr>
<tr>
<td>Δε</td>
<td>8.06±0.01</td>
</tr>
<tr>
<td>K_{11}</td>
<td>7.0</td>
</tr>
<tr>
<td>K_{22}</td>
<td>4.22</td>
</tr>
<tr>
<td>γ</td>
<td>81</td>
</tr>
</tbody>
</table>

Table S6. Dielectric parameters for 1[B]a in 6CHBT at 25 °C.

![Chemical structure]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mole fraction, x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00 (host)</td>
</tr>
<tr>
<td>ε</td>
<td></td>
</tr>
<tr>
<td>ε⊥</td>
<td>3.99±0.01</td>
</tr>
<tr>
<td>Δε</td>
<td>8.06±0.01</td>
</tr>
<tr>
<td>K_{11}</td>
<td>7.0</td>
</tr>
<tr>
<td>K_{22}</td>
<td>4.22</td>
</tr>
<tr>
<td>γ</td>
<td>81</td>
</tr>
</tbody>
</table>
4. Background for calculations in the nematic phase

The equations derived from the Maier-Meier theory\textsuperscript{4} used in this work were adopted from literature\textsuperscript{5} and had the following form:

\[
\Delta \varepsilon = \frac{NFh}{\varepsilon_0} \left\{ \Delta \alpha - \frac{F\mu_{\text{eff}}^2}{2k_B T} (1 - 3\cos^2 \beta) \right\} S \tag{1}
\]

\[
\varepsilon_{\parallel} = 1 + \frac{NFh}{\varepsilon_0} \left\{\bar{\alpha} + \frac{2}{3} \Delta \alpha S + \frac{F\mu_{\text{eff}}^2}{3k_B T} [1 - (1 - 3\cos^2 \beta)S] \right\} \tag{2}
\]

\[
\varepsilon_{\perp} = 1 + \frac{NFh}{\varepsilon_0} \left\{\bar{\alpha} - \frac{1}{3} \Delta \alpha S + \frac{F\mu_{\text{eff}}^2}{3k_B T} [1 + \frac{1}{2} (1 - 3\cos^2 \beta)S] \right\} \tag{3}
\]

All quantities were in SI units as defined in the ESI in previous publications.\textsuperscript{6}

- Dielectric permittivity of vacuum:

\[\varepsilon = 1.114 \times 10^{-10} / 4\pi = 8.865 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}\]

- The diagonalized values of the electronic polarizabilities tensors matrix $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$ expressed in a.u. units were converted to F·m\textsuperscript{2} units by multiplying with $1.482 \times 4\pi \varepsilon \times 10^{-31} = 1.651 \times 10^{-41}$

- Computed dipole moments $\mu_x$, $\mu_y$, $\mu_z$ in Debye were converted to dipole moments in C·m units using the conversion 1D = 3.3356 $10^{-30}$ C·m

- Number density $N$ is expressed in molecules per m\textsuperscript{3}

Field parameters $F = 1.34806$ and $h = 1.394366197$ in equations 1–3 were assumed to be of pure host, 6CHBT, and obtained from literature dielectric and optical data\textsuperscript{7} according to equation 4 and 5. Permittivity $\varepsilon_s$ was assumed to be experimental average permittivity ($\varepsilon = 6.70$) for the
pure host, **6CHBT**. The density of the hosts **6CHBT** at 25 °C was taken as 1.02 g/cm³ according to a literature report.\(^7\)

\[
F = \frac{1}{1 - \alpha \cdot f} \quad \text{where} \quad f = \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1} \frac{N}{3\varepsilon_0}
\]

\[h = \frac{3\varepsilon_s}{(2\varepsilon_s + 1)}\]  

5. Procedures for Maier-Meier analysis.

The apparent order parameter \(S_{app}\) and the Kirkwood factor \(g\) for the additives were obtained by solving simultaneously equations for \(\Delta \varepsilon\) and \(\varepsilon \parallel\) (equation 1 and 2, letting \(S = S_{app}\)). The unknown \(g\) from the expression for \(\Delta \varepsilon\) (equation 1) was substituted into the expression for \(\varepsilon \parallel\) (equation 2) and solved for \(S_{app}\) (equation 6). In this form, apparent order parameter \(S_{app}\) does not depend on the dipole moment \(\mu\), but depends on the dielectric permittivity components \(\varepsilon \parallel\) and \(\varepsilon \perp\). The obtained value \(S_{app}\) was substituted to the expression for parameter \(g\) (equation 7).

\[S_{app} = \frac{2\Delta \varepsilon \varepsilon_0}{NFh[2\Delta \alpha + 3\beta(1 - 3\cos^2 \beta)] - 3(\varepsilon - 1)\varepsilon_0(1 - 3\cos^2 \beta)}\]  

\[g = \frac{[\varepsilon_1 - \varepsilon_0 - \frac{2\Delta \alpha NFhS_{app}}{NF^2 \mu^2[1 - (1 - 3\cos^2 \beta)S_{app}]^T}}{NFK_B T}}\]  

The protocol was verified by substituting the computed parameters \(S = S_{app}\) and \(g\) into equation 1–3 and calculating back the dielectric parameters.

6. Quantum mechanical calculation

Quantum-mechanical calculations were carried out using Gaussian 09 suite of programs.\(^8\) Geometry optimizations for unconstrained conformers of **1a – 1c** with most extended molecular shapes were undertaken at the B3LYP/6-31G(2d,p) level of theory using default convergence limits. Vibrational frequencies were used to characterize the nature of the stationary points and to
obtain exact polarizabilities in vacuum. The alkyl groups were in all-\textit{trans} conformation. No conformational search was attempted. Final coordinates for each molecular model are provided below and the calculated molecular lengths are listed in Table S7.

\textbf{Table S7.} Molecular length (the H–H distance) for selected compounds.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{d}</td>
<td>30.74</td>
<td>31.01</td>
<td>30.13</td>
<td>33.27</td>
<td>33.28</td>
<td>32.60</td>
<td>33.05</td>
<td>33.01</td>
<td>32.38</td>
</tr>
<tr>
<td>\textit{d+VDW\textsuperscript{b}}</td>
<td>33.14</td>
<td>33.41</td>
<td>32.53</td>
<td>35.67</td>
<td>35.68</td>
<td>35.00</td>
<td>35.45</td>
<td>35.41</td>
<td>34.78</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured for equilibrium geometry at the B3LYP/6-31G(2d,p) level of theory. \textsuperscript{b} Hydrogen atom van der Waals radius of 1.20 Å.

Dipole moments and exact electronic polarizabilities of \textbf{I[A]a} and \textbf{I[B]a} used in the Maier–Meier data analysis were obtained in 6CHBT dielectric medium using the B3LYP/6-31+G(2d,p)//B3LYP/6-31G(2d,p) method and the PCM solvation model\textsuperscript{9} requested with SCRF(Solvent=Generic, Read) keywords and “eps=6.70” and “epsinf=2.4623” parameters (single point calculations). Exact polarizabilities were obtained with the POLAR keyword and are listed in Table S8. The reported values for dipole moment components and dielectric permittivity tensors are at Gaussian standard orientation of each molecule (charge based), which is close to the principal moment of inertia coordinates (mass based).

Dipole moment components and polarizability tensors for selected molecules in \textbf{vacuum}

All molecules are in Gaussian standard orientation with their long molecular axes oriented along the x axis. Dipole moments in Debye and polarizability in au (1Å\textsuperscript{3} = 0.1482 au)

\textbf{1[A]a}

\begin{align*}
X &= -1.9511 & Y &= 0.5738 & Z &= -0.3127 & \text{Tot}= 2.0576 \\
\text{Exact polarizability:} & & 683.502 & 9.561 & 340.985 & -2.455 & -0.897 & 279.741
\end{align*}

\textbf{1[B]a}

\begin{align*}
X &= -7.5745 & Y &= -1.6777 & Z &= 1.1333 & \text{Tot}= 7.8404 \\
\text{Exact polarizability:} & & 693.573 & -12.208 & 338.614 & 4.005 & 9.398 & 283.316
\end{align*}

Dipole moment components and polarizability tensors for selected molecules in \textbf{6CHBT dielectric medium}

All molecules are in Gaussian standard orientation with their long molecular axes oriented along the x axis. Dipole moments in Debye and polarizability in au (1Å\textsuperscript{3} = 0.1482 au)

\textbf{1[A]a}
### Dipole moment (field-independent basis, Debye):

\[ X = 1.6346 \quad Y = 1.0371 \quad Z = -0.4279 \quad \text{Tot} = 1.9826 \]

Exact polarizability: 786.959 \quad 15.517 \quad 506.351 \quad -2.475 \quad -0.961 \quad 419.284

Diagonalized: 787.80 \quad 505.50 \quad 419.25

### 1[A]a

Dipole moment (field-independent basis, Debye):

\[ X = 8.2405 \quad Y = -2.5073 \quad Z = 1.5168 \quad \text{Tot} = 8.7460 \]

Exact polarizability: 798.600 \quad -19.533 \quad 503.265 \quad 7.500 \quad 12.271 \quad 425.370

Diagonalized: 800.00 \quad 504.04 \quad 423.19

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#### Table S8. Calculated molecular parameters for selected compounds in 6CHBT dielectric medium.\(^a\)

|          | \(\mu||/D\) | \(\mu_/D\) | \(\mu_/D\) | \(\beta\) \(^b\) | \(\Delta\alpha/\AA^3\) | \(\alpha_{\text{avg}}/\AA^3\) |
|----------|------------|------------|------------|-----------------|-----------------|-----------------|
| 1[A]a    | 1.63       | 1.12       | 1.98       | 34.5            | 48.23           | 84.60           |
| 1[B]a    | 8.24       | 2.93       | 8.75       | 19.6            | 49.85           | 85.33           |

\(a\) Dipole moments and polarizabilities obtained at the B3LYP/6-31+G(2d,p)// B3LYP/6-31G(2d,p) level of theory in 6CHBT dielectric medium. Polarizability values calculated from diagonalized polarizability tensors were converted from a.u. to \(\AA^3\) using the factor 0.1482. \(b\) Angle between the net dipole vector \(\mu\) and \(\mu_/D\).

#### 7. Archive for DFT calculations

1[A]

1\1\GINC-OCTOPUS\SP\RB3LYP\6-31+G(2d,p)\C7H46B10O1\PIOTR\02-Mar-2015\0\#P B3LYP/6-31+G(2d,p) SCF=tight POLAR SCRF(Solvent=Generic,Read)\para-C5-C2B10-PPh-OC8,Cl at the B3LYP/6-31G(2d,p) geom in 6CHBT\0,\1C\0,0,1.0911990212,1.7960382736,5.596676029\B,0,-0.832077823,0.328063481,5.53785307\B,0,-1.7713695687,1.20155137,4.0497926611,0,0.048813025,1.803112364,4.172387157\B,0,1.6543518583,5.575081333,4.0892606742\B,0,1.048927933,0.39842412.59,4.2804412237\B,0,0.047723071,1.075029203,4.2264047578\C,0,0.40020732,3.337685331\C,0,0.254057209,0.321304423,1.82854863\C,0,0.136892461,0.477914187,1.019900374\C,0,0.718468364,1.107074378,1.198526782\C,0,0.916646554,0.489617102,0.3614679968\C,0,0.865228877,1.0970725808,0.182413218\C,0,0.051825948,0.2981959035,0.9984693308\C,0,0.210315312,0.2846206526,2.4698780159\C,0,1.4799868564,0.3991877883,3.065286772\C,0,1.6347246023,0.383137478,4.44231374\C,0,0.5185851554,0.2529608125,5.278973611\C,0,0.752360688,0.1396454203,4.704022763\C,0,0.895086823,0.1559789951,3.321461986\C,0,0.775013416,0.2485000254,6.6132725865\C,0,0.3126286677,0.0843095151,7.5182137219\C,0,0.2513349213,0.0854701777,8.9307385967\C,0,0.8347688736,0.1095345825,9.9934009447\C,0,0.2856968005,0.108617823,0.4241630795\C,0,1.3656666477,0.3224839275,12.4896449305\C,0,0.8213
8. References