How much can an electric dipole stabilize a nematic phase? Polar and non-polar isosteric derivatives of $[closo\text{-}1\text{-}CB_9H_{10}]^-$ and $[closo\text{-}1,10\text{-}C_2B_8H_{10}]$†

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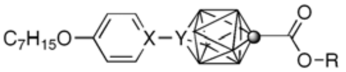
Replacement of a C–C fragment with an N^+–B^- fragment leads to pairs of isosteric non-polar/polar nematics with a difference in the calculated molecular dipole moment of about 12 D. Contrary to the expectations, the uniform increase of the dipole moment does not affect phase stability equally, and a strong dependence on the substituent structure is observed. For one of the polar derivatives (5b, $\mu = 20$ D) a record high dielectric anisotropy ($\Delta\varepsilon = 113$) was measured in dilute nematic solutions.

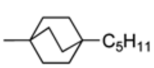
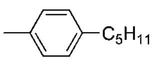
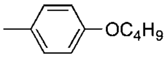
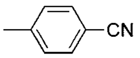
Dynamic shape anisotropy of molecules is considered to be the main factor responsible for the formation of the liquid crystalline state.[1] Earlier molecular theories of the nematic state included shape and electronic polarizability of the mesogens.[2] However, most liquid crystals of technological importance possess a dipole moment, which permits electro-optical switching[3] and applications in the display industry.[4] Therefore, the impact of the dipole moment on phase properties has been of intense interest, and numerous simulations[5] of the nematic phase have appeared over the past two decades.[6,7] These results suggest that for a given increase of the dipole moment there is certain degree of phase stabilization. Experimental verifications of these predictions are hampered by the lack of appropriate molecular models in which *only* polarity can be modified.

Typically, change of the molecular dipole moment is associated with alteration of the molecular geometry and conformational dynamics, which themselves affect phase behavior. Recently, we suggested that the N^+–B^- fragment can serve as an isosteric polar replacement for the C–C fragment in liquid crystalline molecules.[8] Such a replacement would have negligible impact on molecular geometry and dynamics, and the change in phase properties would be due solely to the molecular dipole. Therefore, we have focused on zwitterionic derivatives of $[closo\text{-}1\text{-}CB_9H_{10}]^-$ and their 10-vertex *p*-carborane, $[closo\text{-}1,10\text{-}C_2B_8H_{10}]$, analogues. Here we report the first experimental assessment of the dipole moment effect on phase stability in 5 pairs of *isosteric* and *isoelectronic* molecules using non-polar/polar mesogens **1–5** shown in Table 1.

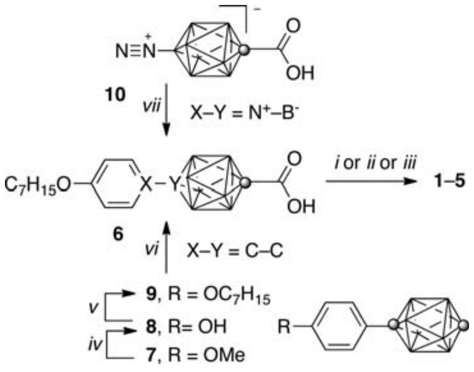
Analysis of molecular models for mesogens **1–5** at the B3LYP/6-31G(d,p) level of theory in gas phase demonstrated that replacement of C–C with N^+–B^- results in significant change of the molecular dipole moment and negligible change in electronic polarizability and geometry. Thus, the replacement increases the longitudinal component of the dipole $\mu_{\|}$ by about 12 D and the transverse component $\mu_{\perp}$ by an average of 1.7 D (Table 1).[9] At the same time electronic polarizability $\alpha_{\|}$ and $\Delta\alpha$ increase by about 1.8 Å^3 and 1.5 Å^3, respectively, or about 3%. The polar molecules are longer by 8.4 ± 2 pm or ~0.3% as a result of minor expansion of the aryl–cage bond and the $\{closo\text{-}1\text{-}CB_9\}$ cage by 3.8 ± 0.06 pm and 9.4 ± 0.08 pm, respectively, and contraction of the aryl ring and cage–COO bond by −2.7 ± 0.3 pm and −0.8 ± 0.04 pm, respectively.[10] Since the only significant change

Table 1 Calculated molecular dipole moment components for **1–5**[a]



	R	X–Y	$\mu_{\|}$/D	$\mu_{\perp}$/D
1		**a**: C–C	1.3	1.7
		b: N^+–B^-	13.2	3.2
2		**a**: C–C	1.5	1.5
		b: N^+–B^-	13.3	3.3
3		**a**: C–C	2.0	1.4
		b: N^+–B^-	14.0	3.3
4		**a**: C–C	1.3	1.9
		b: N^+–B^-	13.3	3.7
5		**a**: C–C	8.1	0.5
		b: N^+–B^-	20.2	1.8

[a] Obtained at the B3LYP/6-31G(d,p) level of theory in Gaussian standard orientation. In the cluster each vertex represents a BH fragment and the sphere is a carbon atom. For details see ESI†.



Scheme 1 (i): 2-Chloro-3,5-dinitropyridine (CDNP) and ROH, heat; (ii): (1) $(COCl)_2$, (2) ROH and Et_3N; (iii): (1) $(COCl)_2$, (2) ROH, heat; (iv): BBr_3; (v): $C_7H_{15}OTs$, K_2CO_3; (vi): (1) BuLi, (2) CO_2, (3) H_3O^+; (vii): 4-$C_7H_{15}OC_5H_4N$, heat.

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upon polar substitution is the increase of the dipole moment by about the same value, phase stability should be affected in a similar way in all five pairs of compounds.

Colorless esters **1–5** were prepared from acid **6** and appropriate phenol or alcohol either directly or through acid chloride (Scheme 1). Acid **6a** (X–Y = C–C) was prepared in three steps from 1-(4-methoxyphenyl)-*p*-carborane **7**, which was obtained by arylation of *p*-carborane according to a similar literature procedure[11] (Scheme 1). Acid **6b** (X–Y = N^+–B^-) was obtained in 88% yield by thermolysis of dinitrogen acid[12] **10** in excess 4-heptyloxypyridine.

Optical and thermal analysis demonstrated that all derivatives **1–5** exhibit exclusively the nematic phase (Table 2). The observed nematic behavior for the non-polar compounds **1a–5a** is consistent with results for other mesogens containing *p*-carborane.[13] The absence of smectic phases in **1b–5b**, typically observed in polar three-ring liquid crystals,[14] is surprising and highly unusual. This can be attributed to the presence of the carborane unit near the molecule's center, which destabilizes layered molecular organization.[13]

A comparison of transition temperatures for the two series of compounds demonstrates that the polar derivatives **1b–5b** have higher melting points than the non-polar analogues **1a–5a**, and the increase ranges from 49 K for **5** to 87 K for **1**. The most interesting aspect of the two series is, however, the comparison of the N–I transition temperatures (Fig. 1). For the polar alicyclic derivatives **1b** and **2b**, the nematic phase is stabilized by about 55 K relative to the non-polar analogues **1a** and **2a**. This effect is much smaller for the benzene derivatives **3–5**; the nematic phase is most stabilized in **4b** although by only $\Delta T_{NI} = 18$ K and *destabilized* by $\Delta T_{NI} = -4$ K in the nitrile **5b** relative to the *p*-carborane analogues. The trend in ΔT_{NI} for **3–5** follows the Hammett σ_p values and correlates well with the field parameters of the substituents.[15] Thus, results in Fig. 1 indicate that the effect of the dipole moment on phase stability is not only a function of its magnitude and orientation, but most importantly, the molecular structure.

Table 2 Transition temperatures for **1–5**[a]

	X–Y	Cr		N		I
1	**a**: C–C	•	74	•	174[b]	•
	b: N^+–B^-	•	161	•	231	•
2	**a**: C–C	•	64	•	107	•
	b: N^+–B^-	•	148	•	161	•
3	**a**: C–C	•	45	•	105	•
	b: N^+–B^-	•	120	(•	114)	•
4	**a**: C–C	•	64	•	138	•
	b: N^+–B^-	•	122	•	156	•
5	**a**: C–C	•	79	•	133	•
	b: N^+–B^-	•	128	(•	129)	•

[a] Cr—crystal, N—nematic, and I—isotropic. Temperatures obtained on heating at 5 K min^{-1}. Enthalpies are listed in the ESI†. [b] Recorded at 10 K min^{-1}.

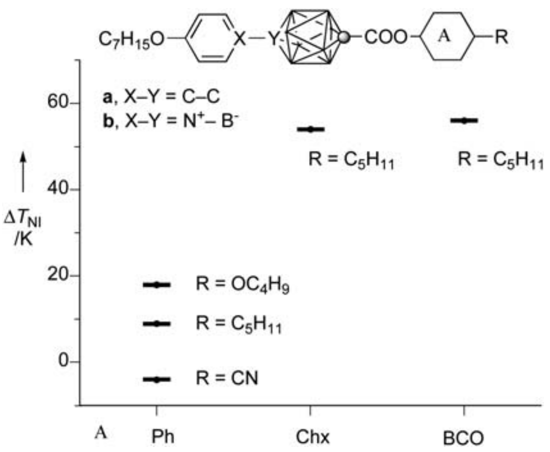
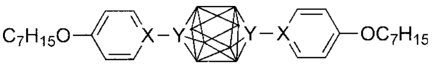


Fig. 1 A plot of the ΔT_{NI} between polar (**1b–5b**) mesogens and their non-polar analogues (**1a–5a**).

The observed variation of the electric dipole effect on phase relative stability (ΔT_{NI}) in the isosteric pairs can be due to the difference in the mean distance *r* between the molecules or to the magnitude of the effective dipole moment μ_{eff} in the nematic phase, since both quantities define the dipole–dipole interaction energy E_{dip}.[16,17] If considering intermolecular separation only, the largest mean distance *r* and consequently lowest E_{dip} in the series are expected for **1** and **2** with the most voluminous groups; conversely smallest *r* and largest E_{dip} are expected for the nitrile **5**. The trend in E_{dip} is opposite to that observed for ΔT_{NI} in the pairs of mesogens.

In general, the magnitude of the dipole moment depends on the dielectric strength of the medium; it is largest in gas phase ($\varepsilon = 1$) and diminishes with increasing ε.[18] For instance, the dipole moment for MeCN is smaller in CS_2 solutions ($\varepsilon = 2.63$) than in gas phase by 22% and for nitrobenzene the difference is 13%.[18] This suggests that alicyclic substituents, bicyclo[2.2.2]octane in **1** and cyclohexane in **2**, have a lower screening effect on the molecular dipole than the benzene ring in **3–5** in the condensed phase. Consequently, E_{dip} is larger for **1** and **2**, which, in turn, leads to greater stabilization of the parallel alignment of the molecules (the Keesom orientation[16]) and higher relative stability of the nematic phase in these pairs of molecules. In the isostructural derivative **3**, the dielectric screening of the benzene ring reduces the strength of the dipole moment, which results in lower phase stabilization. It appears that the substituent on the benzene ring further modulates the strength of this dielectric screening, and its field impacts stabilization of the nematic phase.[17]

While this report concentrates on polar nematic, it should also be mentioned that the isosteric replacement of C–C with N^+–B^- can lead to liquid crystals with large linear quadrupole. An example is the pair **11a**[19] and **11b**.[20] Analysis revealed that the most significant difference between these two C_2-symmetric molecules is in their longitudinal component of the primitive quadruple moment: $Q_{xx} = -172$ D Å for the non-polar **11a** and $Q_{xx} = -61$ D Å for the polar **11b**.[21] The calculated nearly 3-fold change in Q_{xx} corresponds to the observed 120 K higher T_{NI} for the polar **11b** than for the non-polar analogue **11a**. This surprisingly strong nematic phase stabilization is consistent with the results of Gay–Berne modeling[22] and presumably occurs by interaction of local dipole moments.



11 **a**, X-Y = C-C
b, X-Y = N^+- B^-

Polar nematics, such as **1b–5b**, are of interest as high $\Delta\varepsilon$ additives in formulation of mixtures for LCD applications.[4] Low concentration solution studies of **3b** in a weakly polar nematic host[23] at 24 °C gave an extrapolated $\Delta\varepsilon$ of 42. The same measurements for the pair **5a** and **5b** show that the replacement of C–C in the former with N$^+$–B$^-$ in **5b** results in an increase of dielectric anisotropy $\Delta\varepsilon$ by 98 to a record value of *113*! There are very few materials with $\Delta\varepsilon > 40$,[24] and to our knowledge, the extrapolated value of $\Delta\varepsilon$ for **5b** is the highest ever recorded for a nematic material.[25]

We have demonstrated that the isosteric polar replacement of the C–C fragment with the N$^+$–B$^-$ fragment in pairs of mesogenic compounds is a new and powerful tool in addressing fundamental and applied aspects of liquid crystal research. The substitution in compounds **1–5** introduces a substantial longitudinal dipole moment, whose effect on phase properties depends on the nature of the substituent that is distant from the zwitterion. This suggests that simulation of a realistic nematic phase requires atomistic models.[26] The present findings constitute an important contribution to the understanding of the role of an electric dipole on phase stability, offer experimental verification of current theoretical models, and guide development of new high $\Delta\varepsilon$ materials for electro-optical applications.

Acknowledgements

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