Several electrically neutral, highly quadrupolar derivatives of the \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) cluster (I) substituted in the apical positions with onium fragments derived from 4-alkoxyypyridine, 4-pentylthiain, 4-pentylquinuclidine, or dinitrogen were synthesized from the parent cluster in 2–5 steps, and their thermal, structural, photophysical and dielectric properties were investigated. Only derivatives 2, containing thianium and alkyloxypyridinium substituents with linear alky chains, exhibit liquid crystalline behavior and form a nematic phase. \(\alpha\)-Branching of the alkoxy chain leads to marked destabilization of both crystalline and nematic phases, which suggests the importance of polar interactions in phase stabilization of these compounds. Derivatives 2 and 3 with one \(\pi\) and one \(\sigma\) substituent, \(Q^+\), exhibit a directional cluster-to-O charge transfer and increase of the net electric dipole moment to \(\mu_e = 17.9\) D for 2a upon photo-excitation. They are weak fluorophores \((\Phi_F = 2–7\%)\). Detailed investigation of 4-heptyloxypyridinium derivative 2b revealed that it exhibits a nematic phase above 100 °C with \(\Delta\tau = +1.3\) (130 °C), and a moderate negative solvatochromism. Hyper-Rayleigh scattering measurement gave \(\beta^{\text{HRS}} = 45 \pm 10 \times 10^{-30}\) esu at 1064 nm. In solutions, and presumably in the melt, it exists as a mixture of interconverting \(\text{trans}\) \& \(\text{cis}\) isomers at about 4 : 1 ratio with \(\Delta\Gamma_{298} = 0.82 \pm 0.06\) kcal mol \(^{-1}\) and \(\Delta\Gamma_{529} = 25.3 \pm 0.6\) kcal mol \(^{-1}\) established by VT NMR methods.

### Introduction

Despite a large number of liquid crystalline materials characterized to date,\(^1\) there are relatively few mesogenic betaines,\(^2-6\) and quadrupolar bis-betaine mesogens are practically unknown. Such compounds are of interest for studying of fundamental and applied aspects of liquid crystals. For instance, using betaines derived from \([\text{closo-1-CB}_3\text{H}_1\text{O}]^+\), we have demonstrated the effect of molecular dipole moment on phase stability,\(^7\) and prepared high \(\Delta\tau\) nematic materials, including one with a record high dielectric anisotropy \(\Delta\tau = 113.4\).\(^4\) Properly designed bis-betaines derived from the isoelectronic closo-decaboriane dianion, \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) (I, Fig. 1), could yield other information on the effect of polarity on phase stability,\(^5\) and materials exhibiting useful photophysical properties, such as NLO.\(^7\)\(^8\)

Decaborane dianion, \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) (I), is a 3-dimensional polarizable,\(^9\) \(\sigma\)-aromatic system\(^6,11\) with the \(D_{4d}\) molecular symmetry.\(^12\) Its FMOs are doubly degenerated with \(E_1\) (HOMO) and \(E_3\) (LUMO) symmetry, and the calculated HOMO–LOMO gap of 12.96 eV \((\text{HF/6-31G*})\).\(^13,14\) Consequently, the anion is transparent above 200 nm. The orbital symmetry allows for efficient electronic interactions between \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) and \(\pi\) substituents,\(^15\) and intense cage-to-substituent CT bands have been observed in pyridine,\(^16,17\) dinitrogen\(^18,19\) and other derivatives.\(^8,19\)

![Figure 1](https://example.com/figure1.png)

**Fig. 1** \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) anion (I) and its derivative II. Each unsubstituted vertex corresponds to the BH fragment. Groups \(Q^+\) and \(2Q^+\) are onium substituents such as ammonium, sulfonium or pyridinium.
Substitution of the \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) cluster (I) with two onium fragments, \(^1\text{Q}\) and \(^2\text{Q}\), at the apical positions (Fig. 1) leads to electrically neutral bis-betaines II with a large linear quadrupole and a small net ground state dipole moment \(\mu_g\), whose exact value depends on the nature of the onium groups. Several such parent compounds have been known,\(^{17,20,21}\) including two mesogenic bis-betaines II reported by us.\(^{16}\) The symmetric bis-pyridinium derivative 1 forms a nematic phase, exhibits a strong absorption band at 319 nm ascribed to cluster-symmetric bis-pyridinium derivative leads to electrically neutral bis-betaines II with a large linear quadrupole moment coincides with stabilization of the nematic phase by 100 K.\(^3\) Since both pyridine rings are involved in photoexcitation of 1 at 319 nm, the ground and excited state dipole moments are similar \((\mu_g \approx \mu_e)\). A directional CT in bis-betaines II and hence \(\mu_g < \mu_e\) could be achieved with two significantly different onium fragments, such as one of \(\pi\) type and the other of \(\sigma\) type. According to our previous calculations,\(^{13,22}\) the net molecular dipole moment in such unsymmetrical derivatives II markedly increases upon excitation \((\mu_g < \mu_e)\) due to vanishing only one of the local dipole moments, and the chromophores are expected to exhibit moderate second-order NLO properties. Quadrupolar NLO chromophores have the advantage over dipolar materials, in which \(\mu_g \gg \mu_e\), because their low \(\mu_g\) is more conducive to alignment of the molecules and higher stability of the requisite non-centrosymmetric material.\(^{23}\) Earlier we described an unsymmetric nematic bis-betaine belonging to series 2 with a 4-heptyloxy pyridine substituent 2b,\(^{16}\) and found that in a planar cell it forms a nematic glass that generates a weak SHG signal.\(^{24}\) This discovery provided a further impetus for investigation of this type of mesogenic materials.

Here we provide full synthetic details and also thermal, dielectric, structural and dynamic characterizations of 2b. Compounds 2a, 2b, 3b, and two intermediates are characterized for their photophysical properties. Experimental results are compared to DFT calculations. We investigate the effect of the chain-length (2a-c) and branching of the alkyo chain (2d and 2e) on mesogenic properties. We analyzed the effect of replacement of the sulfonium fragment with quinuclidinium, and we characterize derivatives 3b and 3e. Finally, we characterize symmetric bis-betains, bis-sulfonium 4 and bis-quinuclidinium 5.

**Results**

**Synthesis**

The preparation of hetero-dissubstituted \(\text{closo}\)-decaborane derivatives II involves a sequential introduction of the onium fragments \(^1\text{Q}\) and \(^2\text{Q}\) at the apical positions of the \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) cluster. The strategy takes advantage of a general method for selective preparation of monodinitrogen derivatives\(^{23}\) and substitution of the apical \(\text{N}_2^+\) group with nucleophiles\(^{17,20,21}\) (Fig. 2). The sequence of reactions from 6 through 7 to 8 was run without rigorous purification of the intermediate salt 7. The non-ionic compounds 8 were obtained in moderate overall yields, rigorously purified, and fully characterized.

The monodinitrogen salt 6\([\text{NMe}_4]\) was conveniently prepared according to the original procedure for a diazo-transfer reaction from arenediazonium to \([\text{closo-B}_{10}\text{H}_{10}]^{2-}\) (Scheme 1).\(^{23}\) Subsequent thermolysis of 6\([\text{NMe}_4]\) in Me_2NCHS gave the masked mercapto derivative 7a\([\text{NMe}_4]\),\(^{23}\) which was a precursor to series 2. Thermolysis of 6\([\text{NMe}_4]\) in the presence of dry NH_3 gave ammonium derivative 7b\([\text{NMe}_4]\), a precursor to series 3. This method represents a convenient alternative to the reported method for the preparation of 7b\([\text{NMe}_4]\).\(^{18}\)

**Synthesis of series 2.** The formation of the thiane ring in 7c \([\text{NMe}_4]\) was accomplished by alkylation cyclization of the masked mercaptan 7a\([\text{NMe}_4]\) with dibromide 9 (ref. 26) under hydrolytic conditions\(^{25,27}\) in the presence of \(\text{NMe}_4\)\(^+\)OH\(^-\)•H_2O (Scheme 2). The resulting salt 7c\([\text{NMe}_4]\) was diazotized using HNO_3 followed by treatment with zinc powder, according to a general method.\(^{26}\) The dinitrogen intermediate 8a was isolated in about 40–55% yield. Preparation of 8a using the tribromobenzenediazonium salt following a general procedure gave significantly lower yields, about 25%, of a yellow product, that was difficult to purify. \(^1\)C NMR spectroscopy of 8a demonstrated the presence of two isomers at approximately 4 : 1 ratio. Thermolysis of dinitrogen derivative 8a in 4-alkoxy-pyridine (10) at 120 °C gave the sulfonium derivatives 2.

![Fig. 2](image-url)
The quinuclidine ring in derivatives 3 was constructed by alkylative cyclization of amine 7b[\text{NMe}_4] with tribromide 11 (ref. 28) following our method reported earlier (Scheme 3). Without purification, crude 7d was substituted with dinitrogen following a general literature procedure\(^{29}\) to form 1-dinitrogen derivative 8b in 40% overall yield based on starting \([\text{NMe}_4]_6\). Thermolysis of dinitrogen derivative 8b in 4-alkoxy pyridine (10) at 120 °C gave the pyridinium derivatives 3.

The bis-quinuclidinium 5 was prepared in an analogous manner starting from 1,10-bis-dinitrogen derivative \([\text{closo-B}_{10} \text{H}_8 \cdot 1,10-(\text{N}_2)_2]\) (12). Thermolysis of 12 in NH\(_3\) gave the bis-ammonium derivative \([\text{closo-B}_{10} \text{H}_8 \cdot 1,10-(\text{NH}_3)_2]\) (13),\(^{17}\) which upon treatment with tribromide 11 in the presence of a base gave the bis-quinuclidine derivative 5 (Scheme 4). Similarly, thermolysis of 12 in 4-pentylthian\(^{26}\) (14) gave bis-sulfonium derivative 4 in 18% yield (Scheme 4).

4-Alkoxy pyridines 10 were conveniently prepared by a reaction of 4-chloropyridine with sodium alkoxide in DMSO (Scheme 5).\(^{30}\)

**Chemical and thermal stability**

The chemical and thermal stabilities of compounds in series 2 were tested using samples of 2b. The pyridinium derivative 2b was found to be stable in anhydrous solvents, and it could be recrystallized from alcohol. However, a solid sample of 2b kept under ambient conditions, exposed to light and moisture, underwent decomposition to the extent of 10–15% after several days, and up to 40% after a year. Minimal decomposition was observed when compound 2b was kept in the dark and under dry Ar.

The structure of the decomposition product of 2b is unclear. The \{B\(_{10}\)\} cage lacks symmetry, as is evident from the \(^{11}\)B NMR spectrum. The most downfield signals of the pyridine ring are shifted upfield by 0.9 ppm. Mass spectrum is consistent with the incorporation of an oxygen atom to the molecule, however, no O–H stretching absorption was found in the infrared spectrum of the product.
Compound 2b was also tested for thermal stability. No changes were observed in $^1$H and $^{13}$B NMR spectra after heating a neat sample of 2b at 160 °C for 6 h under Ar. The DSC trace was practically unaffected by heating another sample of 2b at 180 °C for 2 h.

Thermal analysis of quinuclidinium derivative 3b demonstrated that it undergoes a partial decomposition at 280 °C, while bis-quinuclidinium 5 melts above 360 °C with complete decomposition.

**Liquid crystalline properties**

Transition temperatures and associated enthalpies for compounds in series 2–5 were determined by differential scanning calorimetry (DSC) and the results are shown in Table 1. Phases were identified by microscopic textures observed in polarized light.

Among all derivatives reported here, only four containing the pyridinium ring exhibit mesogenic behavior. This includes bis-pyridinium derivative 1 (ref. 16) and three derivatives 2a–c containing the sulfonium ring. Compound 2b, with the heptyloxypyridinium substituent, exhibits a relatively broad-range enantiotropic nematic phase with the $T_{NI}$ of 160 °C (Fig. 3).

Surprisingly, substituting a methyl group in the alpha position of the heptyl chain in 2b to form chiral (S)-1-methylheptyl derivative 2e eliminates the mesogenic behavior and dramatically lowers the melting point by >90 K. Extending of the heptyl chain in 2b by 2 carbon atoms to C$_9$H$_{19}$ in 2c has marginal effect on liquid crystalline properties, however both phase transitions are lower by 6 K. On the other hand, shortening of the heptyl chain in 2b by 2 carbon atoms to C$_7$H$_{15}$ in 2a markedly increases the melting point by 62 K with little impact on the N–I transition temperature (Table 1).

Replacement of the sulfonium ring in 2b with quinuclidinium in 3b increases the melting point by 161 K and eliminates mesogenic behavior. Substitution of a methyl group into the heptyl ring in 3b only moderately lowers the melting point (by 19 K), but no mesophase was detected even upon supercooling. Replacement of the pyridinium ring in series 3 with quinuclidinium leads to a further increase of the melting point by about 100 K to over 360 °C in bis-quinuclidinium 5. In contrast, the melting point of bis-sulfonium analogue 4 is lower by about 170 K relative to 5 and by at least 75 K relative to its longer non-mesogenic analogue 15.**

**Molecular and crystal structures**

Colorless, monoclinic crystals of 2b and 8a, and triclinic crystals of 8b were grown from a CH$_2$Cl$_2$–hexane mixture by slow evaporation. Their solid-state structures were determined by X-ray diffraction$^{17}$ and pertinent interatomic dimensions are shown in Fig. 4 and Table 2.

Crystallographic analysis of a single crystal of 2b revealed two molecules, both trans isomers (Fig. 4), in the asymmetric unit cell, which constitute about 80% of the sample. The remaining material was disordered and not refined. In both molecules, the thian ring adopts a nearly ideal chair conformation, while the pyridine ring is essentially planar and has a staggered orientation relative to the borane cluster. The pentyl chain adopts the gauche conformation with the dihedral angle of 70.4(8)$^\circ$ in molecule A of 2b, while in molecule B the pentyl chain is disordered at a 0.62 : 0.38 ratio. In contrast, the heptyl chain was found in all-trans conformation and approximately co-planar with the pyridine ring in both molecules. The total length of the rigid core is about 12.5 Å, and the whole molecule 27.7 Å.

The dinitrogen derivative 8a also contains two unique molecules of the trans isomer in the asymmetric unit cell. No positional disorder was found and the pentyl chain adopts all-trans conformation in both molecules (Fig. 4).

There is only one unique molecule in the unit cell of quinuclidine derivative 8b. Analysis demonstrated that the quinuclidine ring is slightly twisted by 2.7° (avg.) and has smaller cylinder of rotation than that of the {closo-B$_{10}$} cluster (4.14 Å vs. 4.3 Å).
4.72 Å. The total length of the rigid core in 8b (B(1)···C(4)quin) is 7.76 Å (Fig. 4).

The B(1)–N2 bond distance in dinitrogen derivatives 8a (d_B–N = 1.486(4) Å) and 8b (d_B–N = 1.479(3) Å) is similar to that found in [closo-B_10H_10-N_2] anion\(^{\text{23}}\) and 0.02 Å shorter than that reported for [closo-B_10H_8·1,10-(N_2)_2] (d_B–N = 1.499(2))\(^{\text{13}}\) (Table 2).

The S–B distances in 2b and 8a, averaged for two unique molecules in each compound, are similar, 1.850(5) Å and 1.870(3) Å, respectively. They are close to d_S–B = 1.866(3) Å reported for [closo-B_10H_8·1,10-(SMe)_2]\(^{\text{24}}\) and fall into a range of d_S–B = 1.83 Å reported\(^{\text{26}}\) for anion [closo-B_10H_8·1-SMe] and 1.89(1) Å found in ruthenium complex [closo-B_10H_8·1-SMe·10-N_2-RuL].\(^{\text{28}}\) In all these derivatives the lone pair of the S atom eclipses the B–B bond. A similar S–B(10) bond length was found in a [closo-1-CB_9H_7] derivative.\(^{\text{27}}\)

A comparison of dinitrogen derivatives in Table 2 suggests that substitution of the [closo-B_10H_8·1-N_2] anion at the B(10) position with electron withdrawing groups decreases pyramidalization at the B(10) position from 100.6° to 105.8° and the average deck-to-deck separation from 1.687 Å to 1.678 Å, which results in an overall contraction of the [closo-B_10] cage from 3.585 Å in [closo-B_10H_8·1-N_2] to 3.494 Å in [closo-B_10H_8·1,10-(N_2)_2].

**Molecular modeling and conformational analysis**

For a better understanding of molecular and bulk properties of compounds 1–5, their molecular geometries and electronic structures were modeled using DFT methods. Detailed comparison of equilibrium geometries obtained at the B3LYP/6-31G(d,p) level of theory with experimental bond lengths for 2b, 8a and 8b revealed that the DFT method generally overestimates interatomic distances by an average of 0.011 ± 0.014 Å, with the B–B distances being reproduced most accurately.

Computational analysis of model compounds 8c–e was used to establish conformational preference of the heterocycles relative to the [closo-B_10] cluster. The DFT calculations demonstrated that the lone pair of the sulfur atom in the thian ring eclipses the B(1)–B bond of the [closo-B_10] cluster in a conformational minimum in 8c, while the staggered orientation of the lone pair was found in the rotational TS (Fig. 5). The quinoline ring in 8d is slightly twisted (\(\Theta_{N-C-C-C} = 8^\circ\)) and adopts a pseudo-eclipsed conformation relative to the cage in the conformational minimum (\(\Theta_{C-N-B(10)-B} = 5.6^\circ\)). Similar analysis for 8e revealed that the pyridine ring adopts an ideal staggered orientation with respect to the cage in the conformational minimum, and eclipsed in rotational TS. Analysis of the activation parameters for rotational about the X–B bond revealed a rather flat potential energy surface with the enthalpy of activation essentially 0 kcal mol\(^{-1}\) and \(\Delta G^\ddagger_{298}\) due to entropy change (1.6 kcal mol\(^{-1}\) for 8c and 1.9 kcal mol\(^{-1}\) for 8e). A rotational transition state for the quinuclidine derivative could not be located.

**Fig. 5** Extended Newman projection along the long molecular axes of 8. The bars represent the substituent ring and the circle is the nitrogen or sulfur atom.

**Table 2** Comparison of selected interatomic distances and angles for several derivatives of 1-dinitrogen-closo-dodecaborate(1–)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>8b R = Quin</th>
<th>8a R = Thian</th>
<th>R = N_2</th>
<th>R = H</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1)–N_2</td>
<td>1.479(3)</td>
<td>1.486(4)</td>
<td>1.499(2)</td>
<td>1.489(6)</td>
</tr>
<tr>
<td>B(10)–R</td>
<td>1.5567(6)</td>
<td>1.870(3)</td>
<td>1.499(2)</td>
<td>1.208</td>
</tr>
<tr>
<td>B(1)–B(2–5) avg</td>
<td>1.674(3)</td>
<td>1.677(4)</td>
<td>1.678(3)</td>
<td>1.662(7)</td>
</tr>
<tr>
<td>B(2–5)–B(6–9) avg</td>
<td>1.805(4)</td>
<td>1.810(4)</td>
<td>1.799(3)</td>
<td>1.805(7)</td>
</tr>
<tr>
<td>B(6–9)–B(10) avg</td>
<td>1.687(3)</td>
<td>1.682(4)</td>
<td>1.678(3)</td>
<td>1.687(7)</td>
</tr>
<tr>
<td>B–B(10) avg</td>
<td>104.6(2)</td>
<td>104.9(2)</td>
<td>105.8</td>
<td>104.9(4)</td>
</tr>
<tr>
<td>B–B(10)–B avg</td>
<td>101.9(2)</td>
<td>105.0(2)</td>
<td>105.8</td>
<td>100.6(4)</td>
</tr>
<tr>
<td>B(1)–B(10)</td>
<td>3.584</td>
<td>3.563</td>
<td>3.494</td>
<td>3.585</td>
</tr>
<tr>
<td>N–N</td>
<td>1.101(2)</td>
<td>1.103(3)</td>
<td>1.091(2)</td>
<td>1.097(6)</td>
</tr>
</tbody>
</table>

\(^a\) This study, \(^b\) Ref. 33, \(^c\) Ref. 32.
The observed preferences for the orientation of the heterocyclic ring relative to the \{closo-B\}_{10}\} cluster are consistent with XRD results and appear to be common for all 10-vertex closo-boranes. The same types of conformational ground state were found for derivatives of the \{closo-1-CB_{10}\} cluster.\(^5,37\)

As a consequence of the orientation of substituents in 8 relative to the \(D_{4d}\)-symmetric boron cage, all conformers for bis-pyridinium 1, bis-sulfonium 4, and bis-quinuclidinium 5 are chiral. In series 2 there is a conformer in which the core is \(C_{s}\) symmetric. This \(C_{s}\) symmetry of the core is lost in series 3 due to the twisted conformation of the quinuclidine ring. Considering the orientation of all-trans alkyl chains attached to the heterocyclic substituents, more linear ground state conformers are found for compounds in series 3 than in series 2.

### Configurational mobility

The high concentration of the isomer 2b-trans in the solid sample of 2b indicated by X-ray analysis was confirmed by low temperature NMR spectroscopy, which showed only one set of \(^1\)H and \(^{13}\)C signals for a freshly dissolved crystalline sample of 2b in toluene-d\(_{8}\) or CDCl\(_{3}\) at –40 °C. The second set of signals belonging to the cis isomer slowly grew in at ambient temperature. Toluene was found to be a particularly convenient solvent for NMR analysis, since the pyridine ring \(^1\)H signals were separated by approximately 16 Hz (low field signals, Fig. 6) and 8 Hz (high field signals) in the two isomers. In CDCl\(_{3}\), these signals superimpose. Interestingly, pyridine hydrogen atoms are more shielded at lower temperature due to the change of the dielectric constant of the solvent (Fig. 6). Some of the \(^{13}\)C signals for 2b are well separated in both solvents.

Sufficient separation of the low field signals in toluene was used to establish thermodynamics of the isomerization process (Fig. 7). Thus, measurements of the ratio of the signals at equilibrium in the temperature range 50–100 °C allowed us to calculate the enthalpy and entropy difference, \(\Delta H = 1.06 \pm 0.06\) kcal mol\(^{-1}\) and \(\Delta S = +0.82 \pm 0.06\) cal mol\(^{-1}\) K\(^{-1}\), between the two isomers 2b-trans and 2b-cis shown in Fig. 7.\(^{37}\) Equilibrium data extrapolated to lower temperatures were used to calculate rates for isomerization. It was found that the trans-to-cis conversion is a first-order process with rate constants \(k = 8.7 \pm 0.2 \times 10^{-4}\) s\(^{-1}\) at 25 °C. Measurements in the range of 0–25 °C allowed us to calculate activation parameters, \(\Delta H^\ddagger = 23.5 \pm 0.6\) kcal mol\(^{-1}\) and \(\Delta S^\ddagger = -6.2\) cal mol\(^{-1}\) K\(^{-1}\) for the process.\(^{27}\)

DFT calculations for 2b in toluene dielectric medium are consistent with experimental results and show similar theoretical values for the equilibrium (\(\Delta H = 1.31\) kcal mol\(^{-1}\) and \(\Delta S = +0.3\) cal mol\(^{-1}\) K\(^{-1}\)) and isomerization process (\(\Delta H^\ddagger = 20.5\) kcal mol\(^{-1}\) and \(\Delta S^\ddagger = 6.4\) cal mol\(^{-1}\) K\(^{-1}\)).

### Photophysical properties

**Absorption/emission.** Electronic spectra for pyridinium 2a, 2b and 3b, and dinitrogen derivatives 8a and 8b, were recorded in MeCN and selected data are presented in Fig. 8 and Table 3.

**Fig. 6** Low field portion of the \(^1\)H NMR spectrum of 2b in toluene-d\(_{8}\).

**Fig. 7** Interconversion of the trans and cis isomers of 2b. Two major conformers are shown with the diagnostic aromatic H atoms.

**Fig. 8** Absorption spectra for 2b and 8a and emission spectrum for 2b in MeCN.
instance, the pentyloxy derivative exhibited a substantial Stokes shift at 466 nm (quinine bisulfate reference (Table 3 and Fig. 8). Comparison of compounds 8a and 2% was measured for calculations (Table 3).

The position of maxima for the quinuclidinium derivatives are slightly shifted to lower energies and have lower molar extinction coefficients relative to the sulfonium analogues. These findings are consistent with results of TD-DFT calculations (Table 3).

All pyridinium derivatives exhibit moderate absorption with maxima in a region of about 300 nm and 230 nm, while the absorption bands for the dinitrogen 8a and 2b are in a region of about 255 nm. The position of maxima for the quinuclidinium derivatives are slightly shifted to lower energies and have lower molar extinction coefficients relative to the sulfonium analogues. These findings are consistent with results of TD-DFT calculations (Table 3).

Solutions of pyridinium derivatives 2 and 3 fluoresce at ambient temperature with a substantial Stokes shift. For instance, the pentyloxy derivative 2a has a maximum of emission at 466 nm ($\lambda_{em} = 301$ nm), which corresponds to a Stokes shift of 1.46 eV (Table 3). Similar results were obtained for 2b (Table 3 and Fig. 8). Comparison of compounds 2 and 3 with quinine bisulfate reference demonstrated that they are inefficient fluorophores. Thus, a fluorescence quantum yield, $\Phi_f$, of 4% and 2% was measured for 2a and 3b, respectively, in MeCN, while in CH$_2$Cl$_2$, $\Phi_f = 7$% was found for 2a. The dinitrogen compounds 8 do not fluoresce under these conditions.

TD-DFT calculations in MeCN dielectric medium indicate that the observed lowest energy absorption bands in pyridinium derivatives 2b and 3b involve transition from the HOMO, localized primarily on the {closo-B$_{10}$} cluster, to the LUMO, localized on the pyridine substituent, as shown for 3b in Fig. 9. In the dinitrogen derivative 8b excitation at about 255 nm involves nearly double degenerate MOs constituting the HOMO and HOMO-2 localized on the {closo-B$_{10}$} cage and the LUMO localized mainly on the N$_2$ substituent. In the sulfonium derivatives such as 2b and 8a the orbital energies are more differentiated due to the involvement of the sulfur atom lone pair.

**Solvatochromism and excited state dipole moment.** Low energy absorption bands in compound 2, 3 and 8 exhibit a moderate negative solvatochromic effect, and they are shifted to higher energies with increasing solvent polarity expressed by normalized $E^N_f$ parameter (Fig. 10). The observed trend in $\lambda_{max}$ was reproduced with TD-DFT calculations in dielectric media of appropriate solvents. In contrast, emission bands weakly depend on solvent polarity and their energies decrease with increasing solvent polarity (small positive solvatochromic effect).

The magnitude of the Stokes shift ($r_{ab} - r_{0}$) in 2a was solvent dependent and was treated with the Lippert–Mataga formalism (eqn (1)) to estimate the excited state dipole moment, $\mu_e$. A plot of Stokes shift $r$ vs. solvent parameter $D$ gave the slope 17.85 ± 1.6 × 10$^3$ cm$^{-1}$ (Fig. 11), from which the change of the dipole moment $\Delta \mu = 21 \pm 1$ D was obtained. The radius of the...
solvent cavity \(a_0\) used in eqn (1) was obtained from DFT calculations.

\[
\left( v_{ab} - v_0 \right) = \frac{2(\mu_x - \mu_y)^2}{4\pi\epsilon_0hc\omega_0^2} \Delta f + \text{const} \tag{1}
\]

Analysis of the orientation and magnitude of the calculated molecular dipole moment for parent dinitrogen compounds \(8e\) (\(\mu_x = 8.68\) D), \(8d\) (\(\mu_x = 9.39\) D), \(8e\) (\(\mu_x = 10.36\) D), [Fig. 5] and the 4-methoxy analogue of \(8e\), derivative \(8f\) (\(\mu_x = 12.55\) D) in \(\text{CH}_2\text{Cl}_2\) dielectric medium indicates that the effectiveness of the substituents in inducing local dipole moment increases in the order \(N_2^- < R_2S^- < R_3N^- < \text{C}_6\text{H}_5\text{N}^- < 4\text{-MeOC}_2\text{H}_4\text{N}^-\). With the dipole moment contribution for the \(N_2^+\) estimated from DFT results for two isomeric derivatives \([\text{closo-1-CB}_9\text{H}_9\text{-1-N}_2]\) (\(\mu_x = 7.74\) D) and \([\text{closo-1-CB}_9\text{H}_9\text{-10-N}_2]\) (\(\mu_x = 3.04\) D) in \(\text{CH}_2\text{Cl}_2\) dielectric medium, absolute values for other substituents were calculated as follows: \(\text{C}_6\text{H}_5\text{O}^+\) (14.1 D), \(\text{C}_6\text{H}_5\text{N}^-\) (14.8 D) \(\text{C}_6\text{H}_5\text{N}^-\) (15.8 D), and \(4\text{-MeOC}_2\text{H}_4\text{N}^-\) (17.9 D), assuming additivity of the local dipole moments in derivatives \(8\). Using the calculated values for substituents, the ground state dipole moment for compound \(16\) was estimated at 3.8 D, while the DFT calculated value was 4.3 D, which represents a reasonably good agreement (Fig. 12).

Upon cluster-to-pyridine excitation, the larger of the two local dipole moments essentially vanishes leaving the smaller local dipole as the major contributor to the net molecular dipole moment \(\mu_z\) of \(16^*\). As a result the molecule becomes more polar and the change \(\Delta\mu = \mu_x - \mu_y\) is 17.9 D, since the two dipoles have opposite orientation.

Results obtained for \(2a\) from the Lippert–Mataga analysis are consistent with this model. Thus, the dipole moment for \(2a^*\) can be estimated at about \(\mu_z = 16\) D using a DFT-computed value for \(2a\) of \(\mu_y = 4.8\) D in \(\text{CH}_2\text{Cl}_2\) dielectric medium.

**Molecular hyperpolarizability.** First hyperpolarizability \(\beta_{(\text{0,0,0})}\) was calculated for selected molecules in \(\text{CH}_2\text{Cl}_2\) dielectric medium at two frequencies \(\omega\) with the DFT method, and compared to results for standard NLO materials such as \(p\text{-nitroaniline}\), \(4\text{-bis(N,N-dimethylamino)nitrobenzene}\) (DMANB), and \(4\text{-methoxy-4\text{'-nitrostilbene}}\) (MONS, Table 4).

Results demonstrate that values of the \(\beta_{(\text{0,0,0})}\) calculated for \([\text{closo-B}_{10}\] derivatives are comparable with those for single-ring organic reference chromophores, and an order of magnitude lower than those obtained for stilbene MONS, a two-ring chromophore. Values of \(\beta_{(\text{0,0,0})}\) comparable with MONS were calculated for stilbazole derivative \(17\) (Table 4). The results also show that the dinitrogen derivatives \(8\) are half as efficient chromophores as the pyridinium derivatives \(2b\) and \(3b\).

NLO properties of the cluster derivatives were also compared with those for pyridine and stilbazole complexes with \(\text{BH}_3\), \(18\) and \(19\), respectively, in which borane acts only as Lewis acid. Data in Table 4 show that the complexes are significantly less efficient than \([\text{closo-B}_{10}\] derivatives and standard organic NLO chromophores. These results are in agreement with our original calculations at the AM1 level of theory and later experimental and computational studies\(^{46}\) of \(\text{BF}_3\) and \(\text{B(C}_9\text{F}_5)_3\) complexes.

**Table 4** Calculated first hyperpolarizability and molecular dipole for selected compounds in \(\text{CH}_2\text{Cl}_2\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\omega = 0) (esu)</th>
<th>(\omega = 1064) (esu)</th>
<th>Exp.</th>
<th>(\mu_x) (D)</th>
<th>(\mu_z) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2b^*)</td>
<td>17.5</td>
<td>20.0</td>
<td>45 (\pm 10)</td>
<td>4.85</td>
<td>4.11</td>
</tr>
<tr>
<td>(3b)</td>
<td>28.0</td>
<td>31.2</td>
<td>—</td>
<td>3.40</td>
<td>3.17</td>
</tr>
<tr>
<td>(8a^*)</td>
<td>12.2</td>
<td>10.0</td>
<td>—</td>
<td>8.92</td>
<td>8.88</td>
</tr>
<tr>
<td>(8b)</td>
<td>14.2</td>
<td>11.9</td>
<td>—</td>
<td>9.64</td>
<td>9.57</td>
</tr>
<tr>
<td>(17)</td>
<td>293.1</td>
<td>164.0</td>
<td>—</td>
<td>7.45</td>
<td>7.26</td>
</tr>
<tr>
<td>(18)</td>
<td>0.75</td>
<td>0.59</td>
<td>—</td>
<td>10.22</td>
<td>9.03</td>
</tr>
<tr>
<td>(19)</td>
<td>79.6</td>
<td>81.3</td>
<td>—</td>
<td>12.59</td>
<td>12.59</td>
</tr>
<tr>
<td>PNA</td>
<td>20.0</td>
<td>17.9</td>
<td>23 (\pm 3)</td>
<td>8.98</td>
<td>8.93</td>
</tr>
<tr>
<td>DMANB</td>
<td>26.1</td>
<td>23.5</td>
<td>26 (\pm 8)</td>
<td>9.71</td>
<td>9.66</td>
</tr>
<tr>
<td>MONS</td>
<td>203.7</td>
<td>231.5</td>
<td>105 (\pm 35)</td>
<td>9.59</td>
<td>9.56</td>
</tr>
</tbody>
</table>

\(a\) Obtained with the B3LYP/6-31G(d,p)||B3LYP/6-31G(d,p) method in \(\text{CH}_2\text{Cl}_2\) dielectric medium. \(b\) \(\beta\) is the vector part of hyperpolarizability tensor projected along the dipolar axis of the molecule. \(c\) For trans isomer only. \(d\) HRS method. \(e\) This work. \(f\) In \CHCl\_3, ref. 41; \(g\) in \CHCl\_3, ref. 42. \(h\) In CHCl\_3, ref. 43. \(i\) In CHCl\_3, ref. 41; \(j\) in CHCl\_3, ref. 41; \(k\) in CHCl\_3, ref. 41. This work.

Fig. 12 Local and net dipole moments estimated for ground and excited states of \(16\). For details see text.
was generated upon classification of the nematic phase below 90 °C.24 Analysis of the efficiency of the main component of the second-order nonlinear susceptibility \(\chi_{zzz} = 2.3 \pm 0.3 \text{ pm V}^{-1}\) along the nematic director \(z\), demonstrated that it corresponded to about 0.3% of molecules exhibiting spontaneous polar order. The origin of this effect remains unclear.

### Dielectric measurements

Dielectric parameters for 2b were obtained in a planar cell at 130 °C by the single cell method.48 Analysis of capacitance as a function of applied voltage (Fig. 13) gave dielectric parameters \(\varepsilon_{||} = 6.1 \pm 0.1, \varepsilon_{\perp} = 4.8 \pm 0.1\) and \(\Delta \varepsilon = +1.3 \pm 0.1\). The positive dielectric anisotropy of the material is consistent with a calculated moderate molecular dipole moment of 4.33 D oriented at \(\beta = 30°\) relative to the long molecular axis in the trans isomer, while in the cis isomer the net dipole moment is larger (6.25 D) and the \(\beta\) is 44° in a vacuum. The dielectric results were analyzed using the Maier–Meier relationship connecting molecular and bulk parameters of the material.49,50 Assuming that at 130 °C the single cell method.48 Analysis of capacitance as a function of applied voltage (Fig. 13) gave dielectric parameters \(\varepsilon_{||} = 6.1 \pm 0.1, \varepsilon_{\perp} = 4.8 \pm 0.1\) and \(\Delta \varepsilon = +1.3 \pm 0.1\). The positive dielectric anisotropy of the material is consistent with a calculated moderate molecular dipole moment of 4.33 D oriented at \(\beta = 30°\) relative to the long molecular axis in the trans isomer, while in the cis isomer the net dipole moment is larger (6.25 D) and the \(\beta\) is 44° in a vacuum. The dielectric results were analyzed using the Maier–Meier relationship connecting molecular and bulk parameters of the material.49,50

### Discussion

The chemistry of the \(\{\text{closo-}1-\text{CB}_{10}\}\) cluster permits the preparation of unsymmetric derivatives 2 and 3 by sequential introduction of the onium fragments \(Q^+\). The overall yield of the 5 step synthesis is only about 5% based on \(\text{[closo-}2b\text{-}H_{10}]^+\) (I), with the last step, substitution of the pyridinium fragment for \(N_2\) in 8, being particularly inefficient. The mechanism for this transformation involves thermally induced heterolysis of the B–N bond and formation of boron ylide 20, which is trapped with a Lewis base \(L\) (Scheme 6). DFT calculations for model compound 16 demonstrate that the energetics of this \(S_{N1}\) substitution reaction are similar to those found for analogous derivatives of the \(\{\text{closo-}1-\text{CB}_{10}\}\) cluster.25 Thus, the formation of the ylide 20c from 8e (Q = thian) is moderately endothermic by \(\Delta H = 37.9 \pm 1\) kcal mol\(^{-1}\), while trapping of 20c with 4-methoxy-pyridine and formation of 16 is significantly exothermic (\(\Delta H \approx -67.4 \pm 1\) kcal mol\(^{-1}\)). Ylide 20 is a reactive intermediate, and besides reacting with the Lewis basic center (N in pyridines), also inserts to the C–H bonds.37 Thus, for larger molecules, the yield of the desired product diminishes due to higher ratio of C–H bonds to the Lewis center.

Bis-onium derivatives exhibit some hydrolytic and thermal instability. For instance, pyridine derivatives 2, and to a lesser extent 1 and 3, appear to be sensitive to light and moisture. This is presumably related to an increased susceptibility of the \(\{\text{closo-}B_{10}\}\) cluster to attack and cage opening by nucleophiles, such as water, upon photoexcitation. Support for this is provided by \(^1\)H NMR spectroscopy, which shows loss of symmetry by the cage and upfield shift of the pyridine H atoms in solid 2b that was exposed to ambient conditions for several weeks.

The \(\{\text{closo-}B_{10}\}\) cluster substituted with onium fragments is configurationally unstable above 200 °C and 1,10-disubstituted derivatives rearrange to other isomers.20–24 For instance \(\{\text{closo-B}_{10}H_8\}10\text{-(SMe}_2\text{)}_2\) gave nearly 3% of the \(\{\text{closo-B}_{10}H_8\}2\text{-(8)-(SMe}_2\text{)}_2\) isomer after 45 min at 230 °C.20 This is consistent with the observed partial decomposition and possible rearrangement of e.g. 3b upon melting at 285 °C.

Despite limited stabilities, quinuclidinium, thianium, and 4-alkoxypyridinium substituents investigated in this work appear to be most suitable for the formation of liquid crystalline derivatives of the \(\{\text{closo-B}_{10}H_8\}^{2-}\) cluster. Other types of onium fragments, are less suitable for structure 11 due to their low thermal stability (–N\(_2\)) or hydrolytic instability (–CO, –NCR).37

The effectiveness of the ring in promoting crystalline phase in 1–5 appears to follow the order: thian < pyridine < quinuclidine. The pyridine ring is also more effective than thian in stabilizing the nematic phase. However, on the basis of the ring size and fill fraction, pyridine is expected to be the least effective in phase stabilization. The lowest effectiveness of the thian is presumably related to its facile epimerization at the S center similar to that reported for 21, a B(10)-sulfonium derivative of the \(\{\text{closo-}1-\text{CB}_{10}\}^{2-}\) cluster, and with the cis isomer. The relatively low activation energy of the isomerization in 2b \(\Delta H^\ddagger = 23.5 \pm 0.6\) kcal mol\(^{-1}\) is nearly identical to that measured for sulfonium ylide 22,52,53 and involves pyramidal inversion44 with the participation of the adjacent \(\pi\)-symmetry electron manifold of the \(\{\text{closo-}B_{10}\}\) cluster. For comparison, the barrier to epimerization in sulfoxide 23 is significantly higher.53

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**Fig. 13** Capacitance C vs. applied voltage measured for an electrooptic cell containing 2b at 130 °C.
The rather small value of the steric factor $A$ (0.82 kcal mol$^{-1}$) for the $\{\text{closo-}B_{10}\}$ cluster in thian derivatives such as 2 and 8a results in a significant population of the $\text{cis}$ isomer in equilibrium, which destabilizes the nematic phase and inhibits crystallization. However, a comparison with other groups substituted at the sulfur atom in the thian demonstrates that the $\{\text{closo-}B_{10}\}$ cluster is relatively big, and its factor $A$ is nearly 3 times larger than that for the Me group$^{56,57}$ (Table 5). The generally low values of steric factors $A$ in thian derivatives, when compared to cyclohexane analogues (Table 5), are due to relatively long bonds to the sulfur atom (about 1.85 Å vs. 1.54 Å) and consequently lesser contact between the substituent and the 1,3-axial hydrogen atoms. For instance, the B–S bond in 2b-trans is $d_{B-S} = 1.850$ Å (Fig. 4). For comparison, the B(10)–S bond in a similar derivative of the iso electronic and nearly isosteric $\{\text{closo-}1\text{-CB}_{10}\}$ cluster ([closo-1-CB$_{10}$H$_{12}$-10-SC$_{6}$H$_{13}$-1-COOH])$^{27}$ is slightly longer ($d_{B-S} = 1.858$ Å), and consequently the $A$ factor of the boron cage in ester 21 is lower by 0.05 kcal mol$^{-1}$. The difference in the B–S bond distance in the two mesogens is also reproduced computationally for the $\text{cis}$ isomers in which the boron cluster is in the axial position: $d_{B-S} = 1.879$ Å for 2b-cis and $d_{B-S} = 1.886$ Å for 21-cis. In derivatives of $\{\text{closo-}1\text{-CB}_{10}\}$ in which the cluster is connected to the thian through the carbon atom, the C(1)–S distance is shorter$^4$ than in 2b, and $\text{cis}$ isomers are not observed experimentally.$^2$

Thus, thian derivatives 2 exist as a mixture of interconverting $\text{cis}$ and trans isomers, which impacts the stability of the nematic phase and ability to crystallize. This situation is even more complicated for bis-sulfonium 4, which exists as a mixture of 3 isomers, and consequently does not exhibit liquid crystalline properties. The two isomers in 2 interconvert slowly at ambient temperature (half-life of the trans isomer is $\tau = 13$ min), while above 100 °C the interconversion between linear and bent forms of the same molecule is fast ($\tau = 20$ ms at 130 °C, extrapolated from solution data). The existence of the mixture causes supercooling and glassification of the nematic phase of 2b, however, during crystallization configurational selection takes place and only the trans isomer forms the crystalline phase, according to NMR analysis.

The effect of the alkoxy group structure on phase transition temperatures in 2 is surprisingly large. For instance, branching of an alkyl chain causes phase destabilization, which can be estimated by comparison of pairs of structurally similar compounds. According to a correlation of $T_{NI}$ for mesogens containing 4-C$_{6}$H$_{13}$OPh$^-$ with those with the 4-C$_{4}$H$_{9}$CHMeOPh$^-$ fragment ($T_{NI} = 0.78 \times T_2 + 105$; $r = 0.97$, $n = 13$),$^1$ the expected N–I transition for 2e is 71 °C, and the melting point around 110 °C. However, the observed temperatures are lower than predicted by more than 50 K! Such a significant difference suggests that intermolecular polar interactions are important for phase stability, which are weakened by $z$-branching of the alkyl chain and shielding access to the pyridine ring. These interactions are evident from the single crystal structure of 2b in which the distance between the B–N bonds of neighboring molecules is 6.3 Å and the closest B–C intermolecular distance is 3.75 Å (Fig. 14). This analysis implies that the appearance of a broad-range nematic phase in 2b and also in 2c results, in part, from strong intermolecular polar interactions.

In series 3 this effect of polar interactions appears to be less important, and the difference of 19 K in the melting point between 3b, containing the heptyloxy chain, and 3e with the 1-methylheptyloxy substituent is within expectations. Instead, efficient space filling with rigid cylindrical quinuclidine and the

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**Table 5** Steric parameter $A = -\Delta G_{sw}$ for selected substituents in cyclohexane and thiane

<table>
<thead>
<tr>
<th>R</th>
<th>$\Delta G_{sw}$/kcal mol$^{-1}$</th>
<th>$X = \text{CH}$</th>
<th>$X = \text{S}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^-$</td>
<td>(1.04)$^a$</td>
<td>0.68$^b$</td>
<td>$-0.75^b$</td>
</tr>
<tr>
<td>NH$^-$</td>
<td>(1.47)$^a$</td>
<td>0.075$^d$</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>1.34$^e$</td>
<td>0.77$^f$</td>
<td>0.82$^f$</td>
</tr>
<tr>
<td>PhCON</td>
<td>(1.6)$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Value for OH in CS$_2$, ref. 58. $^b$ At 183 K, ref. 59. $^c$ Value for NH$_3$ in toluene-d$_8$, ref. 60. $^d$ At 188 K, CH$_2$Cl$_2$/CHCl$_2$, ref. 61. $^e$ Ref. 62. $^f$ At 373 K in CDCl$_3$, ref. 56 and 57. $^g$ Value for PhCONH, ref. 63. $^h$ At 201 K in CH$_2$Cl$_2$/acetone-d$_6$, ref. 64. $^i$ Ref. 4.$^j$ This work.

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**Fig. 14** Molecular packing in the unit cell of 2b.
closo-B\textsubscript{10}H\textsubscript{10}\) cluster becomes the dominant factor stabilizing the crystalline phase. The stability of the crystalline phase increases further upon substitution of the pyridinium ring with the second quinuclidinium substituent in 5.

Branching at the \(\beta\)-carbon atom of the alkoxy chain typically lowers the melting point, as is evident from a comparison of a number of pairs with isomeric pentloxy and 2-methylbutoxy substituents.\(^2\) Instead, experiments show that the \(\beta\)-branched derivative 2d has higher stability of the solid phase by 25 K than 2a, which is 40 K higher than expected. A correlation of \(T_{\text{m}}\) for pairs containing either 4-C\textsubscript{5}H\textsubscript{11}OPh– or 4-C\textsubscript{5}H\textsubscript{11}CH\textsubscript{2}MeCH\textsubscript{2}OPh– fragment (\(T_{\text{m}} = 0.90 \times T_{\text{m}} + 44; r = 0.99, n = 69\)) predicts the N–I transition for 2d at 131 °C, which is significantly below melting.

Bis-betains of structure II have high longitudinal quadrupole moment \(q\) arising from two opposing each other strong local dipoles associated with the cluster–onium bonds. For instance, in 1a the longitudinal component of the quadrupole moment \(q_{xx} = 118.3\) D Å and in 2b-trans \(d_{xx} = 86.5\) D Å. The local dipole moments only partially cancel out, and even in symmetric derivatives there is a residual net ground state dipole moment related to the \(D_{4d}\) symmetry of the boron cluster. For instance, in 1a with the \(D_{2}\) point group symmetry, the transverse dipole moment component is \(\mu_{T} = 1.20\) D. In dissymmetric derivatives II the net ground state dipole moment depends on the substituents and varies from 3.40 D for 3b to 9.64 D for 8b and is oriented along the long molecular axis. Consequently such compounds have \(\Delta \mu > 0\) and undergo electrooptical switching, as was demonstrated for 2b.

Computational and experimental results for selected derivatives of the \([\text{closo-B}_{10}\text{H}_{10}]\)^\(2^–\) cluster (I) in Table 4 demonstrated that compounds 2 and 3 are moderately efficient NLO chromophores. Their molecular hyperpolarizability \(\beta\) values are similar to those of carborane and ionic \([\text{closo-B}_{10}\text{H}_{10}]\)^\(2^–\)–derivatives\(^a\) and comparable with simple organic NLO chromophores with the classical architecture Donor–\(\pi\) Linker–Acceptor. However, derivatives 2 and 3 appear to be more efficient NLO chromophores than their closest structural analogues, ylide \([\text{closo-1-CB}_{11}\text{H}_{11}-12-C_{6}H_{6}]\) (\(\beta_{\text{HRS}} = 7.2 \times 10^{-30}\) esu),\(^\text{67}\) and \(N\)-phenoxido-pyridinium betaines (\(\beta_{\text{xxx}} = 8.8–34 \times 10^{-30}\) esu).\(^\text{48}\) Much higher \(\beta\) values are predicted for systems in which the boron cluster is a bridge between a strong donor and acceptors, such as tropylidium and cyclopentadienyl, and the cluster acts as a conduit of electron transfer in the excitation process.\(^\text{67}\)

In chromophores derived from I, the boron cluster serves a dual role: the electron donor and a Lewis acid directly bonded to the acceptor, the pyridinium ring (Donor–Accepter). In compounds derived from mono-boranes, such as BR\textsubscript{3},\(^\text{44}\) the borane serves only as a Lewis acid and, consequently, the molecular hyperpolarizability \(\beta\) is lower than for cluster derivatives such as 2 and 3. In spite of the moderate \(\beta\) values, it appears that derivatives of \([\text{closo-B}_{10}\text{H}_{10}]\)^\(2^–\), such as 2 and 3, may have advantage over conventional molecular NLO systems by having low ground state dipole moment and being transparent above 400 nm, providing that non-centrosymmetric bulk structure could be obtained.

### Conclusions

We have demonstrated that substitution of the \([\text{closo-B}_{10}\text{H}_{10}]\)^\(2^–\) cluster at the apical positions with appropriate onium groups \(Q\) leads to bis-betains II in which polar and photophysical properties (solvatochromism, absorption/emission energy, hyperpolarizability) can be adjusted and liquid crystalline behavior can be induced. Besides bis-pyridinium 1, only \(n\)-alkoxy-pyridinium derivatives 2 exhibit mesophase and they form a nematic phase above 100 °C. Results of structure–property relationship studies aided by the LiqCrys database suggest that polar intermolecular interactions play an important role in the stability of both crystalline and nematic phases.

Molecules of compounds containing the thian ring (2) are conformally and configurationally labile, and they exist as a mixture of interconverting isomers in a fluid phase. It is estimated that up to 30% of the cis isomer co-exists with the trans form in the liquid crystal phase (120–160 °C), which affects the crystallization process and results in glass formation. Interestingly, crystallization proceeds with configurational selection for the trans isomer.

Electronic structure of the 10-vertex \textit{closo}-boranes permits efficient electronic communication with \(\pi\)-substituents such as pyridinium in 1–3 and dinitrogen in 8. In heterodisubstituted derivatives, in which one onium group has a \(\pi\) and another \(\sigma\) character, directional photoexcitation eliminates one of the local dipole moments and increases the net molecular dipole moment. Such compounds exhibit a negative solvatochromic effect and have a moderate value for the first hyperpolarizability \(\beta\), similar to those of conventional organic NLO materials of comparable size.

### Computational details

Quantum-mechanical calculations were carried out with the B3LYP\textsuperscript{30,31} method with 6-31G(d,p) basis set using Gaussian 09 package.\(^\text{2a}\) Details of ground and transition state geometry optimization, electronic excitation energies and hyperpolarizability calculations, and solvation effects are provided in the ESL.\(^\ddagger\)

### Experimental part

**General**

NMR spectra were obtained at 300 or 400 MHz (\(^1H\)), 75 MHz (\(^1C\)), and 128 MHz (\(^13B\)) respectively, in CD\textsubscript{3}CN or CDCl\textsubscript{3}. Chemical shifts were referenced to the solvent (\(^1H,\) \(^13C\)) or to B(O\textsubscript{3}Me\textsubscript{3})\textsubscript{4} (external sample). IR spectra were recorded by deposition of a thin film from solution onto sodium chloride disks. Dry DMSO was prepared by using molecular sieves that were activated in a microwave oven. Thermal analysis was performed on TA 2920 DSC using a typical heating rate of 5 K min\textsuperscript{−1}. Fluorescence quantum yield was established according the literature protocol using quinine bisulphate solution in 0.1 N H\textsubscript{2}SO\textsubscript{4} as a reference.\(^\text{28}\) Details are described in the ESL\(^\ddagger\).
Trans–cis equilibrium measurements

A solution of 2b in toluene-\textit{d}_8 was equilibrated at a constant temperature for 2 h before each measurement in the range of 50–100 °C every 10 K. The mole fraction \( \alpha \) of the cis isomer was obtained at each temperature by integration of low field \(^1\)H NMR signals as described below. Thermodynamic parameters were calculated by plotting \( \ln(\alpha) \) vs. \( 1/T \). For details see ESL†

Isomerization of 2b–trans. Kinetic measurements

A crystalline sample of 2b (~10 mg) was dissolved in toluene-\textit{d}_8 (0.6 mL) in an NMR tube at ice bath temperature and inserted into a precooled NMR instrument (400 MHz). Spectra were referenced to the Ph-CD\(_2\)H quintet at 2.09 ppm. The sample was kept at a constant temperature (0–25 °C) and \(^1\)H NMR spectra were taken at regular time intervals until little change was observed (>3 × half-life). The low field portion of the NMR spectrum was processed in MestReC program version 4.3.6.0: (http://www.MestReC.com) the partially overlapping pseudo-doublets of the AAXX' patterns for both isomers were deconvoluted and areas were calculated using the Line Fitting tool. The areas of the downfield wing of the major pseudo-doublet and the upfield wing of the minor pseudo-doublet were used for calculation of the mole fraction \( \alpha \) of the cis isomer 2b–cis.

Data analysis. The mole fraction of the cis isomer at the infinite time (\( \alpha_\infty \)) was calculated at each temperature \( T \) from the extrapolated equilibrium constant \( K_T \) (vide supra). Rate constants were obtained from plots of \( \ln(\alpha_\infty - \alpha) \) against \( 1/T \) and are listed in the ESL†

Dielectric measurements

Dielectric parameters were obtained from Liquid Crystal Analytical System – Series 1 (LCAS). A sample of 2b was placed into a 9.1 μm thick cell (optical measurements) with a rubbed SiO\(_2\) layer. Ten scans were taken for each of three different cells at a 1 kHz triangular shape voltage applied with an amplitude between 0.1 V and 20 V, and the results were averaged. Each empty cell was measured by LCAS (“cell nulling”) before filling with 2b by capillary forces at about 140 °C. Subsequently, the filled cells were heated to the isotropic phase for a short time, and quickly cooled to 130 °C for dielectric measurements.

General procedure for the preparation of pyridine derivatives 2 and 3

A solution of dinitrogen derivative 8 (1.0 mmol) in appropriate 4-alkoxy pyridine 10 (5 mL) was stirred at 120 °C overnight. Excess pyridine was distilled off under reduced pressure and the semicrystalline residue was passed through a silica gel plug (hexane–CH\(_2\)Cl\(_2\), 1 : 2) giving crude product in about 30% yield. Further purification was accomplished by column chromatography (hexane–CH\(_2\)Cl\(_2\)) followed by repeated recrystallization.

1-(4-Heptyloxyphenyl)-10-(4-pentyl-1-thiacyclohexyl)-closo-decaborane (2b)

Yellowish crude solid product was purified by chromatography (SiO\(_2\), hexanes–CH\(_2\)Cl\(_2\), 2 : 1) and recrystallized from EtOH followed by an iso-octane–toluene mixture giving white crystals: \(^1\)H NMR (400 MHz, CDCl\(_3\)) major signals \( \delta 0.5–2.0 \) (br m, 8H), 0.91 (t, \( J = 7.0 \) Hz, 3H), 0.97 (t, \( J = 8.0 \) Hz, 3H), 1.25–1.35 (m, 8H), 1.36–1.53 (m, 6H), 1.56–1.75 (m, 3H), 1.91 (quint, \( J = 7.0 \) Hz, 2H), 2.32 (br d, \( J = 13.8 \) Hz, 2H), 3.44 (t, \( J = 13.1 \) Hz, 2H), 3.68 (br d, \( J = 13.0 \) Hz, 2H), 4.23 (t, \( J = 6.5 \) Hz, 2H), 7.13 (d, \( J = 7.3 \) Hz, 2H), 9.29 (d, \( J = 7.3 \) Hz, 2H); \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \( \delta -25.8 \) (4B), -25.0 (4B), 4.2 (1B), 21.3 (1B).

Distinct signals ascribed to the 2a-cis isomer (23% int): \(^1\)H NMR \( (400 \) MHz, CDCl\(_3\)) \( \delta 1.98–2.07 \) (m, 3.41, 3.34 (ddd, \( J_1 \) = 13.6 Hz, \( J_2 \) = 10.5 Hz, \( J_3 \) = 3.3 Hz), 3.52–3.58 (m).

Anal. calcd for C\(_{202}\)H\(_{51}\)B\(_{10}\)N\(_{10}\): C, 56.54; H, 10.08; N, 2.75.

Found: C, 53.20; H, 9.38; N, 3.07%.

1-(4-Nonyloxyphenyl)-10-(4-pentyl-1-thiacyclohexyl)-closo-decaborane (2c)

Distinct signals ascribed to the 2b-cis isomer: \(^1\)H NMR \( \delta 3.52–3.59 \) (m, 3.34 (ddd), 2.41–2.52 (m), 1.98–2.06 (m)); \(^{13}\)C NMR \( \delta 26.1, 26.6, 33.9, 34.6, 36.0; \) \(^{11}\)B NMR \( \delta 1.4 \).

UV (MeCN) \( \lambda_{max} \) (max e) 301 nm (4.12), 232 (4.19); HRMS, calcd for C\(_{22}\)H\(_{47}\)B\(_{10}\)N\(_{10}\): m/z 483.4339; found: m/z 483.4337.

Found: C, 55.08; H, 9.89; N, 2.98, S, 6.59%.
1.45–1.73 (m, 4H), 1.94–2.07 (m, 1H), 2.30 (d, J = 13.5 Hz, 2H), 3.44 (t, J = 13.0 Hz, 2H), 3.68 (d, J = 13.0 Hz, 2H), 4.01 (dd, J1 = 9.1 Hz, J2 = 6.6 Hz, 1H), 4.09 (dd, J1 = 9.1 Hz, J2 = 6.0 Hz, 1H), 7.14 (d, J = 7.4 Hz, 2H), 9.30 (d, J = 7.3 Hz, 2H).

Distinct signals ascribed to the 2cis isomer: 1H NMR δ 3.52–3.59 (m), 3.34 (ddd), 2.42–2.52 (m).


1-(4-[(S)-2-Octyloxyprydinyl])-10-(4-pentyl-1-thiacyclohexyl)-closo-decaborane (2e)

Chromatography (SiO22, CH2Cl2–hexane, 1:2) gave 2d as a viscous oil: 1H NMR (400 MHz, CDCl3) major signals δ 0.5–2.0 (m, 8H), 0.90 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), 1.22–1.38 (m, 14H), 1.44 (d, J = 6.1 Hz, 3H), 1.56–1.76 (m, 6H), 1.80–1.91 (m, 1H), 2.30 (br d, J = 13.6 Hz, 2H), 3.44 (br t, J = 13.0 Hz, 2H), 3.67 (br d, J = 12.9 Hz, 2H), 4.67 (sex, J = 6.2 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 9.27 (d, J = 7.3 Hz, 2H).

Distinct signals ascribed to 2cis isomer: 1H NMR δ 3.52–3.59 (m), 3.33 (ddd), 2.42–2.52 (m). 11B NMR δ 0.85–0.89 (t, 2.00–2.09 (m), 2.39–2.50 (m) 3.28–3.39 (m), 3.52–3.60 (m).

Anal. calcd for C20H48B10S2: C, 52.13; H, 10.50. Found: C, 52.20; H, 10.41%.

1,10-Bis(4-pentyl-1-thiacyclohexyl)-closo-decaborane (4)

A solution of bisdinitrogen [closo-B10H4-1,10-[N2]2] (12, 86 mg, 0.50 mmol) in 4-pentylthian (4, 2 mL) was stirred at 120 °C for 18 h. Excess than was removed under reduced pressure, and the residue was passed through a silica gel plug (CH2Cl2). Pure product 4 was isolated by column chromatography (first hexane, then CH2Cl2–hexane, 1:1, 42 mg, 18% yield) followed by repeated recrystallization (hexane/EtOAc). 1H NMR (400 MHz, CDCl3) major signals δ 0.5–2.5 (brm, 8H), 0.91 (t, J = 7.0 Hz, 6H), 1.25–1.40 (m, 18H), 1.60–1.75 (m, 4H), 2.32 (br d, J = 13.8 Hz, 4H), 3.44 (t, J = 12.8 Hz, 4H), 3.69 (br d, J = 12.5 Hz, 4H); 11B NMR (128 MHz, CDCl3) δ −24.4 (8B) 10.2 (B).

Distinct signals ascribed to 4cis isomer present in about 25%: 1H NMR δ 0.85–0.89 (t, 2.00–2.09 (m), 2.39–2.50 (m) 3.28–3.39 (m), 3.52–3.60 (m).

Anal. calcd for C20H48B10S2: C, 52.13; H, 10.50. Found: C, 52.20; H, 10.41%.

1,10-Bis(4-pentyl-1-quinuclidinyl)-closo-decaborane (5)

A mixture of crude diamine [closo-B10H4-1,10-[NH2]2] (13, 57 mg, 0.37 mmol), 3,3-bis(2-bromoethyl)-1-bromooctane28 (11, 305 mg, 0.75 mmol), dicyclohexyl-18-crown-6 (7 mg, 0.03 mmol), anhydrous K2CO3 (280 mg, 2.0 mmol) and dry MeCN (5 mL) was stirred under reflux for 5 days under Ar. The suspension was filtered and the solid was washed with MeCN. The crude product was purified on a silica gel plug (CH2Cl2–hexane, 1:1) to give 34 mg (28% yield) of 5 as white crystals, which was recrystallized from iso-octane–toluene and then toluene: 1H NMR (400 MHz, CDCl3) δ 0.5–2.3 (brm, 8H), 0.91 (t, J = 6.9 Hz, 6H), 1.26–1.38 (m, 16H), 1.83 (t, J = 7.9 Hz, 12H), 4.02 (t, J = 7.9 Hz, 12H); 13C NMR (75 MHz, CDCl3) δ 14.0, 22.6, 23.1, 27.9, 29.6, 30.3 (3C), 32.4, 40.3, 58.6 (3C); 11B NMR (128 MHz, CDCl3) δ −29.1 (d, J = 124 Hz, 8B), 18.2 (s, 2B). Anal. calcd for C22H35B2S2N2: C, 60.20; H, 11.37; N, 5.85. Found: C, 60.18; H, 11.21; N, 5.73%.

1-(4-Pentyl-1-thiacyclohexyl)-closo-decaborate[NMe4+] (7c[NMe4+])

A mixture of crude [closo-B10H4-1-SCHNMe4+][NMe4+] (7a[NMe4+], 9.0 g, 31.4 mmol), 1,5-dibromo-3-pentylpentane29 (9, 9.3 g, 31.4 mmol), NMe2OH·5H2O (14 g, 85 mmol), and MeCN (100 mL) was stirred for 24 h at room temperature. The mixture was filtered to remove inorganic solids and the filtrate was evaporated. The residue was treated with CH2Cl2 and the mixture was filtered through a silica gel plug, which was washed well with MeCN–CH2Cl2 (2:1). The eluate was evaporated, the residue extracted into warm hexane–CH2Cl2 (1:10), and the extract was evaporated to give 6.20 g (53% yield) of a pale yellow solid material: 1H NMR (400 MHz, CD3CN) major signals δ −0.6 to 1.4 (br m, 8H), 0.91 (t, J = 6.8 Hz, 3H), 1.26–1.40 (m, 6H), 1.60–1.68 (m, 3H), 2.25–2.32 (m, 2H), 3.07 (s, 12H), 3.25–3.40 (m, 4H), 3.60 (br d, J = 12.5 Hz, 2H), 3.9 (br q, J = 154 Hz, 1H); 11B NMR (128 MHz, CD2CN) δ −27.7 (d, J = 131 Hz, 4B), −25.3 (d, J = 125 Hz, 4B), 0.1 (s, 1B), 8.4 (d, J = 154 Hz, 1B).
Distinct signals ascribed to 7e[NMe4]− closo isomer present in about 25%: 1H NMR δ 0.85–0.89 (m), 2.41–2.50 (m); 11B NMR δ −1.9 (s).
Anal. calc'd for C14H14B10NSC: C, 46.24; H, 11.36; N, 3.85. Found: C, 46.46; H, 10.85; N, 3.77%.

1-(4-Pentyl-1-quinuclidinyl)-closo-decaborate [NMe4]−

A mixture of crude [closo-B10H12Z-1-NH2] [NMe4]− (7b[NMe4], 495 mg, 2.40 mmol),27 3,3-bis(2-bromoethyl)-1-bromoocotan-28a (11, 96.7 mg, 2.44 mmol), diphenylethanol-18-crown-6 (44.7 mg, 0.12 mmol), anhydrous K2CO3 (994 mg, 7.2 mmol) and dry MeCN (25 mL) was stirred under reflux for 7 days under Ar. The suspension was filtered and the solid was washed with MeCN. The filtrate was evaporated and dispersed in an aqueous solution of NMe4Cl. The brown precipitate was filtered, washed with cold water and dried. The resulting solid was washed with boiling hexanes (50 mL) to yield 889 mg (99% yield) of crude salt 7d[NMe4]− that was approx. 90% pure based on 1H NMR: 1H NMR (300 MHz, CD3CN) δ −0.6 to 1.4 (br m, 8H), 0.90 (t, J = 6.9 Hz, 3H), 1.22–1.40 (m, 8H), 1.79 (t, J = 7.9 Hz, 6H), 3.09 (s, 12H), 3.89 (t, J = 7.9 Hz, 6H); 1H NMR (300 MHz, CDCl3) δ 0.5–2.0 (m, 8H), 0.91 (t, J = 6.8 Hz, 3H), 1.25–1.35 (m, 8H), 1.82 (t, J = 7.9 Hz, 6H), 3.28 (s, 12H), 4.01 (t, J = 7.9 Hz, 6H); 11B NMR (64 MHz, CD3CN) δ −30.0 (d, J = 122 Hz, 4B), −28.3 (d, J = 122 Hz, 4B), −0.6 (d, J = 124 Hz, 1B), 15.3 (br s, 1B); 13C NMR (75 MHz, CD3CN) major peaks δ 14.2, 23.1, 23.6, 28.5, 30.6 (3C), 33.1, 40.9, 56.1 (4C), 59.1 (3C).

1-Dinitrogen-10-(4-pentyl-1-thiaclohexyl)-closo-decaborate

Salt 7e[NMe4]− (6.0 g, 16.5 mmol) was dissolved in a biphasic mixture of water (60 mL) and THF (60 mL) containing NaN3 (13.0 g, 188 mmol). Acetic acid (8 mL) was slowly added, while the temperature was maintained below 5 °C. The mixture was stirred for 1.5 h during which the THF layer became dark red. Zinc powder (12 g) was added and the mixture was stirred for 1 h. The resulting light yellow mixture was extracted with CH2Cl2, the organic layer was dried (Na2SO4) and then solvent removed. The yellow solid residue was passed through a silica gel plug (hexane–CH2Cl2, 1:1) yielding 2.40 g (46% yield based on starting borane 7a[NMe4]). An analytical sample was isolated by chromatography (hexane–CH2Cl2, 1:1); mp 133 °C decomp.; 1H NMR (400 MHz, CDCl3) major signals δ 0.6–2.0 (br m, 8H), 0.91 (t, J = 6.9 Hz, 3H), 1.26–1.40 (m, 6H), 1.63–1.76 (m, 5H), 3.24 (br d, J = 12.3 Hz, 2H), 3.42 (br t, J = 13.2 Hz, 2H), 3.68 (br d, J = 12.8 Hz, 2H); 13C NMR (100 MHz, CDCl3) major isomer: δ 14.0, 22.5, 26.0, 26.1, 31.0, 31.8, 35.6, 36.0, 36.4, 41.1; 11B NMR (128 MHz, CDCl3) δ −22.0 (d, J = 143 Hz, 4B), −17.3 (d, J = 149 Hz, 4B), −3.9 (s, 1B), 18.6 (s, 1B).
Distinct signals ascribed to 8a-cis isomer present in 25%: 1H NMR δ 0.86–0.89 (t), 2.03–2.10 (m), 3.32–3.38 (m) 3.53–3.56 (m); 13C NMR δ 26.2, 33.6, 34.7; 11B NMR δ 16.9.
IR υβH = 2529 and υβB = 2223 cm−1; UV (MeCN) λmax (log ε) 253 (4.44); FAB m/z, 313–318 (mass at 316, M+), 275–290 (mass at 283). Anal. calc'd for C10H8B10N2S: C, 37.95; H, 8.92; N, 8.85. Found: C, 38.28; H, 9.02; N, 8.81%.

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References


39 Crystal data for 2b (CCDC no. 875509): C_{22}H_{47}B_{10}NOS triclinic, P-1, a = 9.7645(12) Å, b = 15.716(2) Å, c = 20.148(3) Å, α = 77.516(2)°, β = 83.823(2)°, γ = 86.823(2)°, V = 29489.96(9) Å³, Z = 4, T = 173(2) K, λ = 0.70173 Å, R(F²) = 0.0905 or R_w(F²) = 0.2374 (for 6251 reflections with I > 2σ(I)). Crystal data for 8a (CCDC no. 875508): C_{10}H_{22}N_{5}S monoclinic, P2_1/n, a = 10.7989(2) Å, b = 21.0221(4) Å, c = 17.1320(4) Å, β = 99.468(1)°, V = 3836.25(14) Å³, Z = 8, T = 173(2) K, λ = 0.70173 Å, R(F²) = 0.0594 or R_w(F²) = 0.1066 (for 4514 reflections with I > 2σ(I)). Crystal data for 8b (CCDC no. 875507): C_{12}H_{24}N_{10} monoclinic, P2_1/c, a = 11.1832(7) Å, b = 11.4422(7) Å, c = 16.2022(10) Å, β = 109.272(1)°, V = 1957.1(2) Å³, Z = 4, T = 173(2) K, λ = 0.70173 Å, R(F²) = 0.0578 or R_w(F²) = 0.1296 (for 2458 reflections with I > 2σ(I)). For details see ESL.†
