Liquid Crystalline Benzoic Acid Ester MIDA Boronates: Synthesis and Mesomorphic Properties

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Received: 3.06.2020
Accepted after revision: 9.07.2020
DOI: 10.1055/s-0040-1715900; Art ID: om-20-0021oa

Abstract Two series of N-methyliminodiacetic acid (MIDA) boronates were prepared and their mesomorphic properties were investigated. MIDA-substituted benzoic acid esters were synthesized via the Mitsunobu reaction. The second series of MIDA benzyl ether derivatives was prepared via Williamson etherification and subsequent borylation. Both series exhibit smectic A (SmA) phases. In the case of MIDA boronate esters, a substitution with perfluorinated side chains led to increased transition temperatures and broadening of the SmA phases. The phase geometries of the mesophases were determined by X-ray diffraction. Quantum-chemical calculations provided further insight into the packing model.

Key words boronate, MIDA, liquid crystals, mesophases, Mitsunobu reaction

Introduction

Boron-containing liquid crystals are an emerging class of soft matter materials. Particular emphasis has been put on borondipyrromethane (BODIPY) derivatives,1–12 borondifluoride β-diketonates and β-enaminoketonates,13–16 discotic borolanes,20 and boroxines.21,22 Boron clusters containing carbonates, closo-boranes, and closo-carborabates give rise to polar liquid crystals relevant for molecular electronic and nonlinear optical applications.23–28 Boron clusters such as 1 and 2 have been utilized to probe the stabilization of thermotropic mesophases by Coulomb and dipolar interactions (Scheme 1).23,26 For example, isosteric and isoelectronic replacement of the apical C–C bond in carbaborates 1a by N–B (1b) not only increased the longitudinal dipole moment by an order of magnitude, but also stabilized the nematic (N) phase by 55 K.23 However, reversal of the carbon position in the carbaborate cluster 2a increased the dipole moment but led to a very high melting point and disappearance of the smectic A (SmA) phase.26

Another powerful tool in the design of liquid crystals is perfluoroalkyl chains, which show higher polarity and rigidity than alkyl chains favoring nanosegregation and formation of mesophases.29 Terminal semifluorinated chains in combination with rod-like structures such as cyano-biphenyls,30 alkoxybenzoates,31 and Schiff’s base systems32 stabilize SmA and SmC phases and show high thermal

Scheme 1 Liquid crystalline boron clusters.23,26
stability. Furthermore, the successful application on bent-core structures such as naphthalene, viologen, and oxadiazolyl bipyridine was reported.

Previously, we disclosed that p-alkoxyphenyl boronates \( \text{PEth} \) carrying the \( N \)-methyliminodiacetic acid (MIDA) unit as a protecting group at boron displayed stable SmA mesophases in contrast to the corresponding boronic acids \( \text{3} \) with similar chain lengths (Figure 1).

Quantum-chemical calculations showed that the longitudinal dipole moment of the MIDA boronates \( \text{PEth} \) is three times larger than those of the boronic acids \( \text{3} \). Furthermore, the computational study in combination with solid-state structures yielded dipole distributions and provided a model for the liquid crystalline self-assembly of these MIDA boronates \( \text{PEth} \). In the previous work, mesophase induction was achieved by variation of the charge distribution in the “boron head group” and the phase type was governed mostly by the number of side chains, i.e. exclusion of free volume. We surmised that attaching a nonpolar (methylene) or polar (carboxylate) linker opposite to the MIDA unit at the aryl ring should affect both mesophase stability, i.e. clearing temperature, and temperature range of the mesophase. Furthermore, by utilizing the fluorophobic effect, i.e. replacing flexible alkyl side chains by more rigid and more polar partially fluorinated side chains, the mesomorphic properties should be modified as well. In the current manuscript, we describe the dipole moment variation via linkers and side chains by synthesizing MIDA boronates \( \text{BEth} \) and \( \text{Est} \).

Although protective group chemistry, subsequent functionalization and cross-coupling of MIDA boronates have been extensively studied, and both precursors, 4-MIDA boronato benzyl alcohol \( \text{4} \) (\( L = \text{CH}_2 \)) and 4-MIDA boronato benzoic acid \( \text{5} \) (\( L = \text{CO} \)) respectively, are known compounds; the corresponding ethers and esters are quite rare. Thus, we anticipated that the synthesis of compounds \( \text{BEth} \) and \( \text{Est} \) might not only lead to new insights from a materials perspective but also require new synthetic methods. Our results, which are reported below, show that this is indeed the case.

Results and Discussion

The synthesis of MIDA boronate benzyl ethers \( \text{BEth} \) is shown in Scheme 2. Commercially available 4-MIDA boronato benzyl alcohol \( \text{4} \) was treated with NaH and 1-bromodecane in DMF at room temperature following a method by Jin et al. (route A). However, after 16 h no trace of decylether \( \text{BEth10} \) could be detected. Thus, an alternative protocol was developed for the Williamson etherification (route B). 4-Bromobenzylbromide \( \text{6} \) was treated with NaH and the respective alcohol in DMF for 16 h at 0 °C and warmed to room temperature and the desired ethers \( \text{7a, b} \) were isolated in 73% and 69%, respectively. Subsequent reaction with n-BuLi and triisopropylborate in THF at ~78 °C, followed by addition of MIDA in DMSO at 125 °C, yielded the MIDA boronates \( \text{Beth9} \) and \( \text{BEth11} \) in 65% and 63%, respectively, without any event.

Next, the synthesis of the esters \( \text{Est} \) was examined (Scheme 3). Jones oxidation of \( \text{4} \) provided the known MIDA boronate benzoic acid \( \text{5} \). Attempted esterification of \( \text{5} \) with 1-decanol under Steglich conditions with \( \text{N,N-dicyclohexylcarbodiimide (DCC)} \) or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI) and DMAP did not meet with any success, even when different solvents were tested (for details, see Table S1, Supplementary Information). Also, the reaction of \( \text{5} \) with thionyl chloride followed by treatment with sodium decanolate did not give the desired product \( \text{Est10} \). Next, Yamaguchi conditions were tested, but no trace of the ester \( \text{Est10} \) could be detected. After these unsuccessful trials, we turned our attention to the Mitsunobu esterification (Scheme 3 and Table 1). Thus, acid \( \text{5} \) was treated with 1-decanol, triphenylphosphine, and diethyl azodicarboxylate (DEAD) in THF. Reaction monitoring by \( ^1 \text{H NMR} \) revealed 20% conversion to the ester \( \text{Est10} \) after 14 h at room temperature (entry 1). Replacement of DEAD by disisopropyl azodicarboxylate (DIAD) and an increase of the temperature to 60 °C gave an increased yield of 40% of \( \text{Est10} \), albeit with only 85% purity due to contamination with triphenylphosphine oxide, which could not be separated by column chromatography (entry 2). Despite variations of the workup procedure, complete removal of triphenylphosphine oxide was not possible. Next, we tested a method by Boger employing tri-n-butylphosphine, which gave 43% yield of the product \( \text{Est10} \) but still with low purity (80%; entry 3). In a final attempt, trimethylphosphine was employed together with DIAD in THF at room temperature. Luckily, this procedure provided the desired ester \( \text{Est10} \) in 53% yield in the pure form (entry 4). In order to prevent oxidation of the trimethylphosphine, special
precautions, e.g., a rigorous Schlenk technique, must be taken to exclude oxygen. By using this optimized protocol, the homologous ester derivatives \textit{Est12}, \textit{Est14}, and \textit{Est16} as well as the esters with fluorinated side chains \textit{Est2.6F}, \textit{Est2.8F}, and \textit{Est4.8F} could be obtained in 43–65\% yield (Scheme 3).

Liquid crystalline properties of compounds \textit{BEth} and \textit{Est} were analyzed by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction [small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS)]. The DSC results are summarized in Table 2. Benzylc ethers \textit{BEth9} and \textit{Beth11} showed enantiotropic mesomorphism in the DSC. Upon heating of benzylc ether \textit{BEth9} with C\textsubscript{9}H\textsubscript{19} chains, an endothermal melting transition at 105 °C followed by isotropization at 147 °C were observed (Table 2).

Upon cooling, the mesophase reappeared at 146 °C and the glass transition at 102 °C was hardly visible. The derivative \textit{BEth11} with C\textsubscript{11}H\textsubscript{23} chains behaved similarly. In the series of esters \textit{Est10–Est16}, the derivative \textit{Est10} with C\textsubscript{10}H\textsubscript{21} chains was nonmesomorphic and showed an isotropic melting transition at 131 °C (Table 2). In contrast, esters \textit{Est12} and \textit{Est14} displayed enantiotropic mesophases, e.g., for homologue \textit{Est12} a crystallization at 74 °C, an endothermal melting transition at 134 °C, and an endothermal clearing transition at 152 °C were detected upon heating. In the cooling cycle, only isotropic to mesophase transitions at 152 °C and a glass transition at 62 °C were detected.

For all fluorinated derivatives \textit{Est2.6F}, \textit{Est2.8F}, and \textit{Est4.8F}, decomposition was observed during the first heating cycle. Melting transitions into the liquid crystalline phase were visible at 160 °C for the shortest chain-length \textit{Est2.6F}. The longer perfluoro derivative \textit{Est2.8F} melted at 176 °C, whereas \textit{Est4.8F} melted at 169 °C. Upon further heating, additional endothermal decomposition peaks were observed at 240 °C for \textit{Est2.6F}, 287 °C for \textit{Est2.8F}, and 268 °C for \textit{Est4.8F}. During subsequent heating and cooling cycles, no transitions were observed.

During our investigation using a polarizing optical microscope of benzyl ether \textit{Beth9}, we observed uncharacteristic textures (Figure 2a); however, \textit{Beth11} showed large
areas of homeotropic alignment with small maltese cross-defects (Figure S6), despite the use of silylated slides. Furthermore, we observed a similar behaviour for MIDA boronates Est12–16, Est2.6F, Est2.8F, and Est4.8F. While compounds Est12 (Figure 2b) and perfluoro esters Est2.6F, Est2.8F, and Est4.8F (Figure 2e, f) showed uncharacteristic textures, compounds Est14 and Est16 showed large areas of homeotropic alignment with small defects (Figure 2c).

A phenomenon we observed for all samples was the formation of filament-like textures after shearing of the cover glasses, indicating an SmA phase (Figure 2d). These observations are similar to the behavior of the previously published MIDA boronates. With the observations under the polarizing microscope and the structural resemblance to our previously published boronates, we surmised a smectic mesophase. The findings of DSC experiments for perfluorinated derivatives Est2.6F, Est2.8F, and Est4.8F are in accordance with observations under the polarizing microscope. We observed uncharacteristic textures for the perfluorinated derivatives Est2.6F, Est2.8F, and Est4.8F upon heating and slow fading at higher temperatures. No textures were observed during later heating and cooling cycles. This was another indication for decomposition of the samples at high temperatures.

To obtain a deeper insight into the mesophase geometries, for one member of each series, SAXS and WAXS measurements were conducted (Table 3). The diffractogram of BEth9 is shown in Figure 3a. In the small-angle area, the (011) reflection is displayed. Moreover, in the wide-angle area, a broad halo was visible. To clarify the phase geometries, temperature-dependent SAXS measurements were conducted. From the (001) X-ray diffractions for derivatives BEth9 and Est16, the layer spacing d was calculated. The layer spacings with the corresponding temperatures are shown in Figure 3b.

During cooling, a gradual increase in the layer spacing was observed. This is a typical phenomenon observed for SmA phases, presumably due to decreasing interdigitation of side chains. During DSC measurements for perfluorinated derivatives, we observed a decomposition of the compounds. Therefore, we were not able to gather sufficient data for evaluation from the SAXS measurement of Est2.6F. Fortunately, it was possible to conduct temperature-dependent WAXS experiments before decomposition started. Similar to the above-discussed experiments, an increase of the layer spacing d during cooling was observed.

To compare the layer spacings among each series, we calculated the reduced layer spacing d_red from the layer spacing trend lines at the reduced clearing temperature (0.95 × T_c). For comparison, the molecular lengths in the all-trans-configuration were estimated using the Avogadro program46 (molecular mechanics, force field: MMFF94s). The molecular length of nonyl ether BEth9 was determined between the outer most atoms to be 20.8 Å and the reduced layer spacing to be d_red = 29.6 Å. d_red is larger than the molecular length (L) but shorter than the twofold molecular length (2L), indicating an interdigitation of the side chains. However, the calculated layer spacing for full interdigitation is in good agreement with d_red (d_red = 31.5 Å). For the alkxy ester Est16, the reduced layer spacing d_red is 39.3 Å, which is in good agreement with the calculated value for fully interdigitated side chains (d_cal = 38.1 Å). Furthermore, the molecular length of perfluoro ester Est2.6F was determined to be 21.1 Å and the reduced layer spacing d_red to be 36.9 Å.

To rationalize the large volume d_red, we propose that the fluorophobic effect as well as the steric demand of the fluorinated tails leads to nanosegregation and an unfavorable interdigitation of the chain as observed for derivatives with alkyl ethers (BEth9) and alkoxy esters (Est16), respectively (Figure 4a). Instead the core fragments are stacked as shown in Figure 4b.

### Table 1: Esterification of 5 under Mitsunobu reaction conditions* to decyl ester Est10

| Entry | Reagents | Temp. | Method | Yield (purity%) |
|-------|----------|-------|--------|----------------|
| 1     | DEAD, PPh3 | t.t.  | A      | 20% (-85%)     |
| 2     | DIAD, PPh3 | 60 °C | B      | 40% (85%)      |
| 3     | DIAD, PbU3 | t.t.  | C      | 43% (80%)      |
| 4     | DIAD, PMe3 | t.t.  | D      | 53% (-99%)     |

*1-Decanol, THF, 14 h.
*2 Determined by 1H NMR.
*3 Schlenk conditions were applied.

### Table 2: DSC results of different MIDA boronates: Phase transition temperatures T are given in °C and the transition enthalpies in kJ/mol

| Compound | Cycle | Cr1 | Tm(ΔH) | Cr2 | T(ΔH) | SmA | Tc(ΔH) | t |
|----------|-------|-----|--------|-----|--------|-----|--------|---|
| BEth9    | 2nd heat | 105 (14.7) | 147 (1.3) |     |        |     |        |   |
|          | 2nd cool | 102 (-)   | 146 (-1.7) |     |        |     |        |   |
| BEth11   | 2nd heat | 110 (-)   | 161 (1.4)  |     |        |     |        |   |
|          | 2nd cool | 108 (-)   | 158 (-1.7) |     |        |     |        |   |
| Est10    | 1st heat | 131 (-)   |          |     |        |     |        |   |
|          | 2nd heat | 74 (-32.2) | 134 (46.8) |  152 (3.7) |     | |   |
|          | 2nd cool | 62 (-)    |          |     |        |     |        |   |
| Est12    | 2nd heat | 71 (6.3)  | 145 (12.4) |  176 (1.0) |     | |   |
|          | 2nd cool | 63 (-5.1) | 77 (-4.1)  |  176 (-1.0) |     | |   |
| Est14    | 2nd heat | 74 (12.4) | 140 (11.6) |  183 (0.9) |     | |   |
|          | 2nd cool | 64 (-14.5)|          |     |        |     |        |   |
| Est2.6F  | 1st heat | 160 (24.9)| 240 (6.7)  | b  |        |     |        |   |
|          | 1st heat | 176 (27.1)| 287 (7.2)  | b  |        |     |        |   |
| Est2.8F  | 1st heat | 169 (82.8)| 268 (5.2)  | b  |        |     |        |   |
| Est4.8F  | 1st heat | 169 (82.8)| 268 (5.2)  | b  |        |     |        |   |

*Heating/cooling rate 10 K/min. Phase transitions were determined during 1st heating cycle for Est10, Est2.6F, Est2.8F, and Est4.8F, and during 2nd heating/cooling for BEth9, BEth11, Est12, Est14, and Est16.

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Upon comparison of MIDA boronate benzyl ethers BEth9 and BEth11 with the corresponding MIDA boronate aryl ethers Peth,\textsuperscript{35} the additional methylene group did not affect the melting transition but decreased the clearing point considerably (compare, e.g., PEth10 vs. BEth9 and PEth12 vs. BEth11) by 30 K.

In contrast, the additional “anti-periplanar” dipole introduced by the carboxylate moiety resulted in a slightly reduced longitudinal dipole moment. However, the slightly bent ester led to the appearance of a second crystalline phase (temperature range: 60–70 K) and an SmA phase (phase widths: 18–43 K) for Est12–Est16. However, the known tendency of

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Figure 2 Observed POM textures of nonyl ether BEth9 at 152 °C (a); dodecyl ester Est12 at 150 °C (b); hexadecyl ester Est16 at 165 °C (c); and after shearing (d); perfluorodecyl ester Est2.8F at 230 °C (e, f) (200× magnification).
fluorinated or partially fluorinated side chains to reduce the conformational mobility significantly stabilized the SmA phase up to the thermal decomposition at 240–287 °C.

In addition, melting points also increased by 80–100 K and thus the overall mesophase widths increased up to 37 K as compared to the nonfluorinated analogues.

To obtain further insight into the packing model, we performed quantum-chemical calculations (for details, see the Experimental Section, quantum chemical calculations). In our previous studies, a negligible impact of chain length on the electronic core structure of MIDA boronates PEth8–PEth14 was observed. This prompted us to use MIDA boronates with ethoxy side chains as model systems in the calculations. Here, we use the compound BEth2 as a model for all compounds with a methylene linker and Est2 as a model for all compounds with a carboxylate linker. One of the first findings of our computations was that the overall dipole moment of the two compounds was not strongly affected by the linker group. We calculated a value of 7.1 D for both BEth2 and Est2, which is only slightly smaller than the dipole moment of alkoxy ether PEth2 (7.6 D; Figure 5). More insight was provided by plotting the electrostatic potential of BEth2, Est2, and PEth2 (Figure 6). The plot of PEth2 (Figure 6c) indicates that there is no strong variation of the electrostatic potential in the vicinity of the phenyl oxygen, whereas BEth2 and Est2 (Figure 6a, b) show a strong contribution of the negatively charged oxygen atoms to the electrostatic potential. This will likely induce repulsive interactions between neighboring side chains and lead to decreased interdigitation of these.

Furthermore, ester Est2 and ether BEth2 exhibit a slightly bent structure of the side chain in comparison to nearly linear compound PEth2. This bending of BEth2 and Est2 leads to a larger occupied volume fraction and an unfavorable space filling in the liquid-crystalline phase, resulting in decreased clearing temperatures for benzyl

Table 3 XRD data of derivatives BEth9, Est16, and Est2.66

| Compd. | Mesophase | d Values (Å), expt. (calcld.) | Miller indices |
|--------|-----------|-----------------------------|----------------|
| BEth9  | SmA at 140 °C | 30.2 (–) | (001) |
|        |           | 4.9   | Halo |
| Est16  | SmA at 150 °C | 39.0 (–) | (001) |
|        |           | 4.40  | Halo |
| Est2.66 | SmA at 225 °C | 38.6 (–) | (001) |
|        |           | 19.2 (19.3) | (002) |
|        |           | 12.8 (12.9) | (003) |
|        |           | 5.7    | Halo |

Figure 3 (a) WAXS diffractogram of Beth9 at 140 °C and 2D X-ray pattern (inset). (b) Temperature-dependent layer spacing d of Beth9, Est16, and Est2.66.

Figure 4 Packing model of MIDA boronates BEth9, Est16 (a), and Est2.66 (b).
ethers B Eth 9 and B Eth 11 and a second crystalline phase for alkyl esters E st 1 2–E st 1 6. The bending of MIDA boronate ester E st 2 formed in the calculations also explains why compounds E st 1 2–E st 1 6 with alkyl side chains have lower melting and clearing points together with smaller phase widths as compared with the derivatives E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 f with partially fluorinated side chains. The fluorinated tails of E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 are stiffer and more rigid than the alkyl chains of E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 , and they tend to pack more tightly due to fluorine–fluorine interactions. Thus, even a short fluorinated tail and an overall shorter total chain length can outperform a much longer alkyl chain; see for example E st 1 6 vs. E st 2 . 6.

Conclusions

In conclusion, a convenient synthetic access to both MIDA-boronate benzyl ethers B Eth 9 and B Eth 11 and MIDA boronate esters E st 1 0–E st 1 6, E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 f, respectively, has been developed. Key steps were Williamson etherification of 4-bromobenzyl bromide and late-stage borylation in the case of B Eth 9 and B Eth 11, while MIDA boronate carboxylic acid 5 could be successfully esterified under Mitsunobu conditions to E st 1 0–E st 1 6, E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 f.

Except for compound E st 1 0, all other MIDA boronates showed Sm A phases, with particularly broad phases for MIDA boronate esters E st 2 . 6 , E st 2 . 8 , and E st 4 . 8 with partially fluorinated tails. Their packing mechanisms and different mesomorphic properties were compared with those of the known MIDA boronate alkoxy ethers PE th 8–PE th 1 4 and rationalized by quantum-chemical calculations. Our results show that even unfavorable dipolar and electrostatic interactions as well as bending of a calamitic core can be overruled by attachment of fluorine tails resulting in the formation of broad mesophases. Thus the current work broadens the scope of MIDA boronates with respect to organic materials.

Experimental Section

NMR spectra were recorded on Bruker Avance 500 (1H, 500 MHz; 13C, 126 MHz), Bruker Avance 400 (1H, 400 MHz; 13C, 100 MHz), and Bruker Avance 300 (1H, 300 MHz; 13C, 75 MHz). All NMR spectra were recorded at room temperature and the calibration was done on the residual solvent peaks. For calibration of NMR spectra, the residual solvent peaks were used. FT-IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with a MKII golden gate single reflection Diamond ATR system, at room temperature. POM was performed using an Olympus BX50 polarizing microscope with a Linkam TP93 central controller. DSC measurements were performed on a Mettler Toledo DSC 822e device in aluminum pans (40 µL) from Mettler Toledo. X-ray diffraction measurements (SAXS and WAXS) were conducted on a Bruker Nanostar C device with a HI-STAR detector using CuKα radiation (α = 1.5418 Å) calibrated to silver behenate. TLC was done on aluminum plates precoated with silica gel 60 F254 from Merck. Flash chromatography was conducted with silica gel from Fluka (grain size: 40–63 µm).

Materials

All commercial chemicals were used as received. Dry solvents were distilled under a nitrogen atmosphere using common drying agents prior to use. Moisture- and/or oxygen-sensitive reactions were conducted using common Schlenk techniques. Prior to use. Moisture- and/or oxygen-sensitive reactions were conducted using common Schlenk techniques. The synthesis of MIDA, 48 4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl) benzoic acid, 49 trimethylphosphine, 49,50 and ethyl 3-butenolate 51 were performed according to literature procedures.

Esterification: General Procedure

MIDA acid 5 (0.10 g, 0.36 mmol), DIAD (0.09 mL, 0.47 mmol), and the respective alcohol (0.47 mmol) were dissolved in dry THF (10 mL). Trimethylphosphine (0.05 mL, 0.47 mmol) was added and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexanes/ethyl acetate 1:3; Rf: 0.2) and Soxhlet extraction (hexane).
Decyl-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)benzoate (Est10)

The general esterification procedure was followed with 5 and 1-decanol to give Est10 as a white solid (80 mg, 53%).

1H NMR (400 MHz, CDCl3): \(\delta = 8.05\) (d, \(J = 8.2\) Hz, 2H, 3-H), 7.61 (d, \(J = 8.2\) Hz, 2H, 2-H), 4.32 (t, \(J = 6.7\) Hz, 2H, OCH2), 3.95 (d, \(J = 16.4\) Hz, 2H, 1′-H), 3.78 (d, \(J = 16.4\) Hz, 2H, 1′-H), 2.55 (s, 3H, NC\(_3\)H3), 1.71–1.82 (m, 2H), 1.20–1.49 (m, 14H, CH2), 0.84–0.93 (m, 3H, C\(_3\)H3), ppm. 13C NMR (101 MHz, CDCl3): \(\delta = 166.7\) (C=O), 166.52 (C-5), 132.25 (C-2), 132.04 (C-4), 129.29 (C-3), 65.32 (O\(_{C\_H2}\)), 61.90 (C-1′), 47.45 (N\(_{C\_H3}\)), 31.89, 29.53, 29.30, 29.21, 28.72, 26.03, 22.67 (CH2), 14.10 (CH3) ppm.

FT-IR (ATR): 2956 (w), 2924 (s), 2854 (w), 2178 (w), 2039 (w), 1761 (s), 1718 (s), 1562 (w), 1507 (w), 1458 (w), 1430 (w), 1396 (w), 1337 (w), 1272 (s), 1221 (s), 1186 (w), 1112 (s), 1039 (w), 997 (s), 890 (w), 843 (s), 803 (w), 767 (s), 711 (w), 648 (w), 594 (w), 547 (w), 513 (w), 482 (w) cm\(^{-1}\). MS (ESI): \(m/z = 440\) [M + Na]\(^+\). HRMS (ESI): [M + Na]\(^+\) calcd. for C\(_{22}\)H\(_{32}\)BNO\(_6\)Na: 440.2219, found: 440.2210. CHN analysis calcd. (%) for C\(_{22}\)H\(_{32}\)BNO\(_6\) (417.31): C 63.32 H 7.73, N 3.36; found: C 62.34, H 7.47 N 2.83.

Dodecyl-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)benzoate (Est12)

The general esterification procedure was followed with 5 and 1-dodecanol to give Est12 as a white solid (73 mg, 45%).

1H NMR (500 MHz, CDCl3): \(\delta = 8.05\) (d, \(J = 8.2\) Hz, 2H, 3-H), 7.61 (d, \(J = 8.2\) Hz, 2H, 2-H), 4.31 (t, \(J = 6.7\) Hz, 2H, OCH2), 4.02 (d, \(J = 16.4\) Hz, 2H, 1′-H), 3.80 (d, \(J = 16.4\) Hz, 2H, 1′-H), 2.55 (s, 3H, NC\(_3\)H3), 1.72–1.80 (m, 16H, CH2), 1.39–1.47 (m, 2H, OCH2CH2), 0.87 (t, \(J = 6.9\) Hz, 3H, C\(_3\)H3) ppm. 13C NMR (126 MHz, CDCl3): \(\delta = 167.4\) (C=O), 166.8 (C-5), 132.5 (C-2), 132.2 (C-4), 129.5 (C-3), 65.6 (OCH2), 62.1 (C-1′), 47.8 (NCH3), 32.1, 29.89, 29.87, 29.83, 29.79, 29.59, 29.54, 28.94, 26.2, 22.8 (CH2), 14.38 (CH3) ppm. FT-IR (ATR): 2955 (w), 2923 (s), 2854 (s), 1763 (s), 1719 (s), 1562 (s), 1508 (s), 1459 (w), 1430 (w), 1396 (w), 1397 (w), 1337 (w), 1272 (s), 1221 (s), 1186 (w), 1112 (s), 1039 (w), 997 (s), 890 (w), 843 (s), 803 (w), 767 (s), 711 (w), 648 (w), 594 (w), 547 (w), 513 (w), 482 (w) cm\(^{-1}\). MS (ESI): \(m/z = 460\) [M + Na]\(^+\). HRMS (ESI): [M + Na]\(^+\) calcd. for C\(_{22}\)H\(_{32}\)BNO\(_6\)Na: 460.234, found: 460.234. CHN analysis calcd. (%) for C\(_{22}\)H\(_{32}\)BNO\(_6\) (443.39): C 63.32 H 7.73, N 3.36; found: C 62.34, H 7.47 N 2.83.

Figure 6: Visualization of the electrostatic potential of MIDA boronates BEth2, Est2, and PEth2. The electrostatic potential is color-coded (red = −1.9 eV to blue 1.9 eV) on an isosurface of the electron density (0.0067 Å\(^{3}\)).
Tetradecyl-4-(6-methyl-4,8-dioxo-1,3,6,2-diazodioxaborocan-2-yl) benzoate (Est14)

The general esterification procedure was followed with 5 and 1-tetradecanol to give Est14 as a white solid (96 mg, 56%).

1H NMR (700 MHz, CDCl3): δ = 8.06 (d, J = 7.7 Hz, 2H, 3-H), 7.61 (d, J = 7.7 Hz, 2H, 2′-H), 4.32 (t, J = 6.7 Hz, 2H, -OCH2), 3.95 (d, J = 16.3 Hz, 2H, 1′-H), 3.79 (d, J = 16.3 Hz, 2H, 1′-H). 2.56 (s, 3H, -NCH3), 1.74–1.80 (m, 2H, -OCH2CH2), 1.40–1.46 (m, 2H, -OCH2CH2C2H5), 1.21–1.38 (m, 20H, CH2). 0.88 (t, J = 7.1 Hz, 3H, CH3) ppm. 13C NMR (176 MHz, CDCl3) δ = 166.8 (C-O), 166.5 (C-5), 132.3 (C-2), 132.0 (C-4), 129.3 (C-3), 65.3 (OCH2), 61.9 (C-1′), 47.5 (NCH3), 31.92, 29.70, 29.66, 29.60, 29.60, 29.55, 29.36, 29.30, 28.72, 26.04, 22.70 (CH2), 14.13 (C3H3) ppm. FT-IR (ATR): 2922 (vs), 2853 (w), 1762 (s), 1719 (s), 1562 (w), 1450 (s), 1396 (w), 1337 (w), 1275 (s), 1221 (w), 1186 (w), 1114 (w), 1040 (s), 996 (w), 890 (w), 843 (w), 767 (w), 711 (w), 595 (w) cm⁻¹. MS (ESI): m/z = 496 [M + Na]⁺. HRMS (ESI) (m/z): [M + Na]⁺ calcd. for C22H40BNO17Na 496.2876, found: 497.2877. CHN analysis calcd. (%) for C22H40BNO17Na: 46.84, H 6.02, N 2.47; found: C 46.84, H 6.02, N 2.47.

Hexadecyl 4-(6-methyl-4,8-dioxo-1,3,6,2-diazodioxaborocan-2-yl) benzoate (Est16)

The general esterification procedure was followed with 5 and 1-hexadecanol to give Est16 as a white solid (98 mg, 54%).

1H NMR (700 MHz, CDCl3): δ = 8.05 (d, J = 8.0 Hz, 2H, 3-H), 7.61 (d, J = 8.0 Hz, 2H, 2′-H), 4.32 (t, J = 6.7 Hz, 2H, -OCH2), 4.01 (d, J = 16.3 Hz, 2H, 1′-H), 3.80 (d, J = 16.4 Hz, 2H, 1′-H). 2.56 (s, 3H, NCH3), 1.73–1.80 (m, 18H, CH2), 1.39–1.47 (m, 2H, OCH2CH2), 1.21–1.38 (m, 24H, CH2), 0.87 (t, J = 7.0 Hz, 3H, CH3) ppm. 13C NMR (176 MHz, CDCl3) δ = 167.1 (C-O), 166.5 (C-5), 132.3 (C-2), 132.0 (C-4), 129.3 (C-3), 65.3 (OCH2), 61.9 (C-1′), 47.6 (NCH3), 39.21, 31.93, 29.70, 29.69, 29.66, 29.62, 29.56, 29.37, 28.72, 26.04, 22.70 (CH2), 14.14 (C3H3) ppm. FT-IR (ATR): 2917 (vs), 2850 (s), 2165 (w), 1762 (s), 1719 (w), 1647 (w), 1277 (w), 1114 (w), 1041 (w), 995 (w), 842 (w), 767 (w), 711 (w) cm⁻¹. MS (ESI): m/z = 501 [M]⁺, HRMS (ESI) (m/z): [M + Na]⁺ calcd. for C28H44BNO18Na 524.3159, found: 524.3165. CHN analysis calcd. (%) for C28H44BNO18Na: 46.84, H 8.84, N 2.79; found: C 46.81, H 8.70 N 2.70.
The general esterification procedure was followed with 5 and 10 to give Est4.8′ as a white solid (116 mg, 43%).

1H NMR (500 MHz, (CD3)2CO): δ = 8.01 (d, J = 8.3 Hz, 2H, 2-H), 7.69 (d, J = 8.3 Hz, 2H), 4.37–4.43 (m, 4H, 1′-H, OCH2), 4.19 (d, J = 17.1 Hz, 2H, 1′-H), 2.77 (s, 3H, NCH3), 2.37 (tt, J = 19.6 Hz, 8.0 Hz, 2H, 4′-H), 1.92–2.00 (m, 2H, 2″-H), 1.79–1.89 (m, 2H, 3″-H) ppm. 13C NMR (126 MHz, (CD3)2CO): δ = 179.5 (C-3′), 167.4 (C-4′), 164.3 (C-5′), 130.0 (C-6′), 108.8 (C-7′), 53.4 (OCH2), 15.3 ppm.

The general etherification procedure was followed with 6 and 1-undecanol to give 7b as a white solid (2.49 g, 65%).

1H NMR (400 MHz, CDCl3): δ = 7.43–7.49 (m, 2H, 2-H), 7.17–7.25 (m, 2H, 3-H), 4.44 (s, 2H, 5-H), 3.45 (t, J = 6.6 Hz, 2H, -OCH2), 1.51–1.66 (m, 2H, -OCH2CH2), 1.19–1.41 (m, 16H, CH2), 0.83–0.92 (m, 3H, CH3), ppm. 13C NMR (101 MHz, CDCl3): δ = 137.8 (C-4′), 131.4 (C-2′), 129.2 (C-3′), 121.3 (C-1′), 72.1 (C-5′), 70.7 (C-6′) ppm. FT-IR (ATR): 1765 cm⁻¹ (C=O) ppm. MS (ESI): m/z = 340 [M+Na]+. HRMS (ESI) (m/z): [M + Na]+ calcd. for C34H36BrNO3Na: 597.0130, found: 597.0128.

**Benzyl Ether Boronate Preparation: General Procedure**

The respective alkoxy-bromo-benzene 6 (2.93 mmol) was dissolved in dry THF (20 mL) and cooled to –78 °C. n-Butyllithium (1.9 mL, 4.69 mmol, 2.5 M) was added and the mixture was stirred for 30 min. Triisopropyl borate (1.1 mL, 4.69 mmol) was added and the reaction was allowed to warm up to room temperature over 2 h. A solution of MIDA borane (1.3 g, 8.79 mmol) in abs. DMSO (18 mL, 0.5 M) was added and the mixture was refluxed for 2 h. The reaction mixture was poured into water and extracted with CH2Cl2 (3 x 50 mL). Combined organic layers were washed with brine (50 mL), dried with MgSO4, and the solvent was evaporated. Benzyl ether boronate was obtained as a crude product which was used without further purification.

**6-Methyl-2-[4-((nonyloxy)methyl)phenyl]-1,3,6,2-dioxazaborocane-4,8-dione (BETH9)**

The general esterification procedure was followed for benzyl ether boronate preparation with 7a to give BETH9 as a white solid (741 mg, 65%).

1H NMR (400 MHz, CDCl3): δ = 7.42–7.50 (m, 2H, 2-H), 7.17–7.25 (m, 2H, 3-H), 4.44 (s, 2H, 5-H), 4.11 (d, J = 16.8 Hz, 2H, 1′-H), 3.78 (d, J = 16.7 Hz, 2H, 1′-H), 3.48 (t, J = 6.7 Hz, 2H, CH2O), 2.51 (s, 3H, NCH3), 1.57–1.67 (m, 2H, CH2CH2O), 1.21–1.40 (m, 12H, CH2), 0.83–0.92 (m, 3H, CH3), ppm. 13C NMR (101 MHz, CDCl3): δ = 167.4 (C-O), 140.7 (C-4′), 132.3 (C-2′), 127.5 (C-3′), 72.7 (C-5′), 70.9 (C-6′), 61.8 (C-1′), 47.49 (NCH3), 29.77, 29.57, 29.52, 29.28, 26.20, 22.67 (CH3), 14.11 (CH3) ppm. FT-IR (ATR): 2924 (w), 2853 (w), 1746 (vs), 1613 (w), 1457 (w), 1697 (w), 1338 (w), 1292 (s), 1229 (s), 1115 (w), 1099 (w), 1037 (s), 934 (w), 792 (m), 689 (w), 631 (w) cm⁻¹.
6-Methyl-2-[4-[(undecyloxy)methyl]phenyl]-1,3,6,2-dioxazaborocarbox-4,8-dione (BEth11)

The general etherification procedure was followed for benzyl ether boronate preparation with 7b to give BEth11 as a white solid (770 mg, 63%).

1H NMR (400 MHz, CDCl3): δ = 7.48 (d, J = 7.7 Hz, 2H, 2-H), 7.36 (d, J = 7.7 Hz, 2H, 3-H), 4.49 (s, 2H, 5-H), 3.94–4.10 (m, 2H, 1'-H), 3.77 (d, J = 16.1 Hz, 2H, 1'-H), 3.48 (t, J = 6.7 Hz, 2H, –OCH₂), 2.53 (s, 3H, –CH₃), 1.54–1.67 (m, 2H, –OCH₂CH₂), 1.19–1.42 (m, 16H, C –CH₂), 0.91 (m, 3H, C –CH₃), 1.42 (m, 1H, CH₂), 1.67 (m, 2H, CH₂), 0.84–0.91 (m, 3H, CH₃), ppm. 13C NMR (101 MHz, CDCl₃): δ = 167.2 (C=O), 140.7 (C-4), 132.3 (C-2), 127.5 (C-3), 72.7 (C-5), 70.9 (–OCH₂), 61.8 (–C=O), 47.4 (NCH₃), 31.92, 29.77, 29.63, 29.52, 29.34, 26.21, 22.69, (CH₂), 14.12 (CH₃) ppm. FT-IR (ATR): 2922 (s), 2853 (w), 1761 (vs), 1612 (w), 1457 (w), 1397 (w), 1338 (w), 1293 (s), 1230 (s), 1151 (w), 1000 (s), 991 (w), 989 (w), 807 (w), 710 (w), 653 (w), 593 (w), 548 (w), 491 (w), 458 (w) cm⁻¹. MS (ESI): m/z = 440 [M + Na]⁺. HRMS (ESI) (m/z): [M + Na]⁺ calcld. for C₂₁H₃₂BNO₅Na: 440.2579, found: 440.2596. CHN analysis calcld. (%) for C₂₁H₃₂BNO₅Na: 440.2579, found: 440.2596. CHN analysis calcd. (%) for C₂₃H₃₆BNO₅Na (417.35): C 66.19 H 8.69, N 3.27. CHN analysis for C₂₃H₃₆BNO₅Na: 66.19, 8.69, 3.27.

Quantum Chemical Calculations

We employed Müller–Plesset second-order perturbation theory (MP2) and a def2-TZVPB basis set and appropriate auxiliary basis sets for efficient two-electron integral evaluation.⁵²⁻⁵⁴ Full-structure optimizations were carried out at this level of theory and dipole moments and electrostatic potentials were evaluated from the relaxed one-electron density. The TURBOMOLE program package⁵⁵,⁵⁶ was used throughout; graphical representations were generated by the TmolX program (Version 4.5.2).⁵⁷

Funding Information

Generous financial support by the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg, the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Carl-Schneider-Stiftung Aalen (shared instrumentation grant) is gratefully acknowledged.

Supporting Information

Supporting information for this article is available online at http://doi.org/10.1055/s-0040-1715900.

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