Cyanine Borate Penetrated Ion Pair Structures in Solution and the Solid State: Induced Circular Dichroism

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Abstract: An induced circular dichroism (CD) spectrum is observed for 1,1′,3,3,3′,3′-hexamethyl-9-phenylindocarbocyanine, 1,1′-diethyl-2,2′-cyanine, 1,1′-di-(3,5-di-*tert*-butyl)benzyl-2,2′-cyanine, or 1,1′-di-(4-*tert*-butyl)benzyl-2,2′-cyanine when penetrated into a chiral cavity of either spirobi[(2-methyl)borataxanthene] or spirobi[(3-methyl)borataxanthene]. Within the ion pair, the cyanine dye exists in two (or more) interconverting conformations of unequal energy. Solid-state structural evidence suggests that a nitrogen-forward mode for penetration by the cyanine dominates the solution behavior. A critical feature for the observation of induced circular dichroism is that the dye is twisted in the ground state. The free energy difference between the diastereomers with right- and left-handed twist in the chiral cavity of the borate is less than 1 kcal/mol, but this is sufficient to induce the CD spectrum. The magnitude of the observed CD spectrum is dependent on the structure of both the cyanine and borate.

Introduction

Cyanines are a class of organic dyes discovered in 1856 by Williams[1] that are used today in numerous applications over wide areas of chemistry and technology. One of the earliest and most important uses of the cyanines was as photosensitizers for silver halide photography.[2−4] Cyanines are also used as saturable absorbers for lasers.[2,5−8] Chiral examples of these dyes have been used to test helicity rules for optical rotation.[9,10] Paired with borates, reactive electron donors, cyanines are used to photoinitiate acrylate polymerization.[11] Cyanine borates have also been used as probes of lipid bilayer membranes [12−14] where their spectroscopic perturbation reports on the microenvironment.

One particularly sensitive means to probe a microenvironment is by induced circular dichorism (CD) spectroscopy. An induced CD spectrum results when a chiral environment creates an asymmetry or causes an excess population of rapidly interconverting enantiomers.[15] The extent of the symmetry breaking perturbation is recordable and quantifiable by measurement of the CD spectrum. For example, cyanines[16] and other intercalators[17] have been used extensively to probe the DNA helix through measurement of induced CD spectra. The chiral environment of cyclodextrins has been investigated through measurement of induced CD spectra of dimer and higher cyanine aggregates in β and γ cyclodextrins.[18−20]

Cyanines, as a class, are cationic dyes typically consisting of two heterocyclic rings connected by an odd number of methine carbons. In most cases, the dyes adopt an "all-trans" geometry that minimizes steric interactions. Bond lengths, determined by X-ray analysis, indicate that the positive charge resonates across the chain extending to each hetereocycle.[21,22] Solid-state structures determined for several of the cyanines reveal complex organizations which may parallel those that are formed in solution when these dyes aggregate.[21,22] These solid-state structures generally have the two heterocyclic rings parallel to those in neighboring dye molecules forming macrostructures that are characterized as having brickwork, staircase, herringbone, or ladder type arrangements, depending on the identity of the cyanine. Solid-state structures[21−25] and solution absorp-

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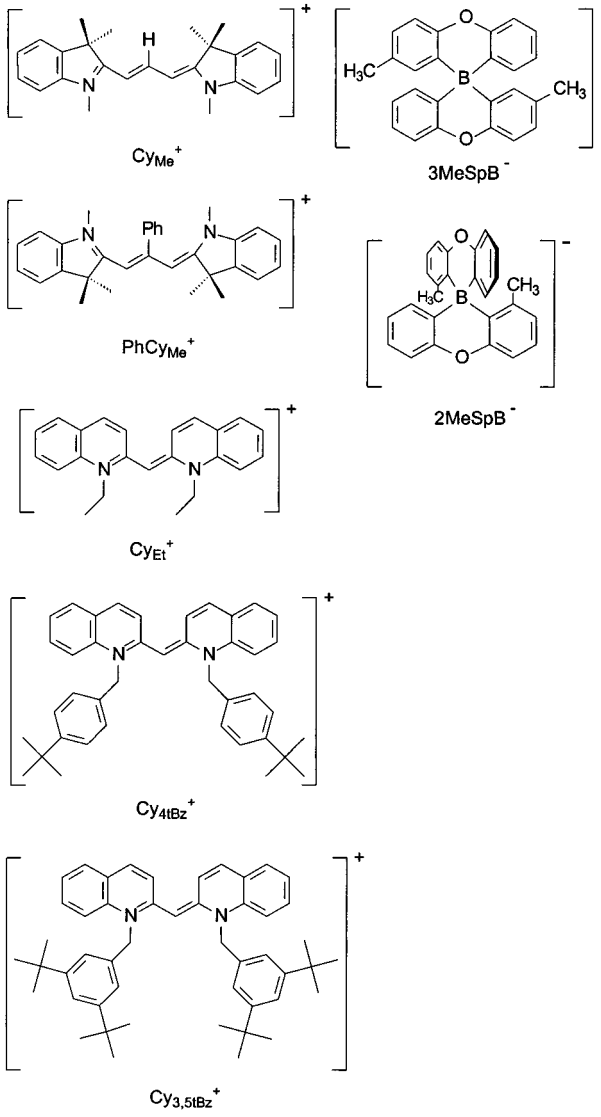
tion measurements[26] of cyanines indicate that steric interactions lead to twisting about the methine group. Similarly, crystal structures of *meso*-substituted (the central atom of the methine chain) carbocyanines dyes,[22,27,28] show that steric crowding leads to twisting of the methine chain. Examination of variable temperature ^{1}H NMR spectra,[29] absorption spectra,[30−32] and room temperature ^{13}C NMR spectra [33] indicate that theses dyes are also twisted in solution.

Borates are tetravalent, tetracoordinate anionic boron-containing species.[34] Torssell verified the tetrahedral structure of borates by synthesizing a chiral example and recording its optical activity.[35] More recent work has shown that tetraarylborates have significant voids or "crevices" between their substituents which permit occupation by suitably small cations such as planar cyanine dyes.[36,37] Occupation of the crevice by the cyanine dye gives a structure whose radius is less than the sum of the radii of the individual ions. Intimate ion pairs of this nature are identified as penetrated ion pairs.[38,39]

Pochapsky and Stone[40−42] and Abbot and Schriffrin[38] have investigated penetrated ion pairs. Abbot and Schriffrin explain the very short and relatively invariant distances between ion pairs calculated from conductivity measurements of tetraalkylammonium borate salts on this basis. They directly observe penetration through interionic ^{1}H{^{1}H} and ^{11}B{^{1}H} nuclear Overhauser effects (NOEs) in tertabutylammonium tetrahydroborate.[41] Their results suggest the BH_4^- resides in the crevice between the alkyl substituents, close to the center of cationic charge at the nitrogen atom. Similar interionic NOE effects were observed in solutions of cyanine borates in nonpolar solvents.[37] The rates of photoinduced electron transfer for a cyanine dye paired with a series of *para*-substituted phenyl- and biphenylylborates show no correlation with the borate anion radius, indicating that the cyanine has penetrated within the borate radius.[37]

The photophysical properties of cyanine borate penetrated ion pairs are dependent on the nature and structure of the anionic and cationic components. For example, the primary pathway

Chart 1



for relaxation of electronically excited cyanines is by rotation about a carbon−carbon bond in the methine chain. This motion is slowed in viscous solvents, and, consequently, the excited-state lifetime is lengthened. A similar effect is observed for the penetrated cyanine in a borate cavity. Rotation is hindered, and there is a significant increase in the singlet lifetime of the dye. In benzene solution, the singlet lifetime for 1,1′,3,3,3′,3′-hexamethylindocarbocyanine tetrakis(triptycenylphenyl)borate (Cy_{Me}^+ TRPB$^-$) (see Chart 2) is twice that of the nonpenetrating Cy_{Me}^+ PF_6^-.[37,43] Rotation to generate the mono-cis isomer is completely inhibited in the three-dimensional crevice of Cy_{Me}^+TRPB$^-$. With the less crowded 1,1′,3,3,3′,3′-hexamethylindocarbocyanine tetrakis(phenylethynyl)borate (Cy_{Me}^+ PEB$^-$) (see Chart 2), some mono-cis isomer is formed by irradiation, but its lifetime is longer than *cis*-Cy_{Me}^+ PF_6^- due to the restrictions to isomerization to the lower energy all-trans form imposed by the environment. Similarly, the constrained environment of the penetrated ion pair enhances the fluorescence quantum yield for Cy_{Me}^+ PEB$^-$ compared to Cy_{Me}^+ PF_6^-.[36]

Recent work has shown that polymethine dyes have potential

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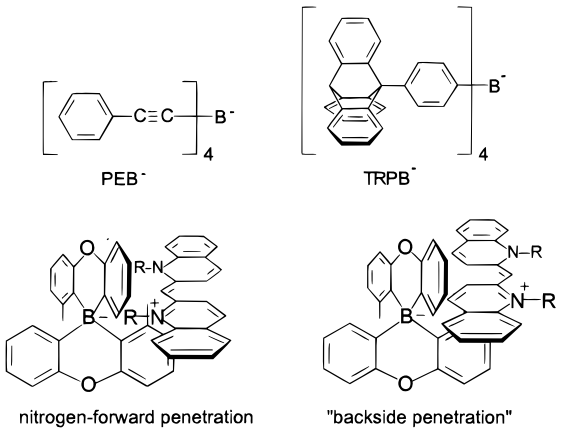
Chart 2



as nonlinear optical materials.[44] Requirements for such materials include optimal bond length alternation in the polyene chain, which is typically achieved through suitable substitution of donor and acceptor functionalities,[45] and that the structures must not be centrosymmetric.[46] The latter requirement is often met by polling the material in a polymer matrix.[46,47] Molecular crystals are also suitable if they are not formed in a centrosymmetric space group. In pioneering work, Tomaru and co-workers [48] used β-cyclodextrin as a chiral host to convert a normally centrosymmetric nitroaniline derivative into a crystal of a 1:1 complex which exhibited appreciable nonlinear polarizability. This finding suggests that achiral cyanines in chiral hosts may lead to a material with interesting nonlinear optical properties.

We recently reported that solutions of cyanine dyes with chiral borate anions in nonpolar solvents exhibit induced circular dichroism spectra which were attributed to formation of a twisted dye in the penetrated ion pair.[49] We report herein a study of the structural dependence of the induced CD spectra for a series of cyanine dyes and chiral borates.

Results

The borates, spirobi[(3-methyl)borataxanthene] (3MeSpB$^-$) and spirobi-[(2-methyl)borataxanthene] (2MeSpB$^-$) studied in this work are shown in Chart 1. While initially developed to prove the tetrahedral structure of the borate anion,[35] the chiral spiroborate 3MeSpB$^-$ has advantages for our purposes by limiting the approach of cationic species. In addition, the oxygen bridge provides a barrier to rotation about the four boron−carbon bonds, limiting the number of degrees of freedom and conformational isomers. The role of the position of the methyl group in the properties of the borate was examined through synthesis of the 2MeSpB$^-$ isomer.

The cyanine dyes examined in this work are shown in Chart 1. Previous studies of 1,1′,3,3,3′,3′-hexamethyl-9-phenylindocarbocyanine ($PhCy_{Me}^+$) have suggested that the lowest energy conformer for the cyanine is a twisted cis, trans, cis (*Z*, *E*, *Z*) structure,[49] while 1,1′,3,3,3′,3′-hexamethylindocarbocyanine exists in an all-trans conformation.[22,30] Previously reported solid-state structures of 1,1′-diethyl-2,2′-cyanine (Cy_{Et}^+) also show twisting about the central methine group.[21,24,25] Steric hindrance between the 3 and 3′ hydrogen atoms preclude a ground state planar structure. The *N*-benzyl derivatives, 1,1′-di-(3,5-di-*tert*-butyl)benzyl-2,2′-cyanine ($Cy_{3,5tBz}^+$) and 1,1′-di-(4-*tert*-butyl)benzyl-2,2′-cyanine (Cy_{4tBz}^+), are expected to have a similarly twisted ground state conformation while also providing measures of the effect of larger substituents at the 1 and 1′ positions.

(1) Synthesis. (A) Optically Active Borates. The synthesis and resolution of (3MeSpB$^-$) follows Torssell's method (see Scheme 1).[35] We prepared 2MeSpB$^-$ by the route, shown in Scheme 1, starting with 2-bromo-3-methylphenol **3a**. Coupling of the phenol with 2-chloronitrobenzene followed by reduction of the nitrodiphenyl ether gives aniline **5a**. Diazotization and bromination of **5a** forms the key dibromodiphenyl ether **6a**. Treatment of the di-Grignard reagent formed from **6a** with BF_3 etherate gives the racemic borate as its magnesium bromide salt. This salt was resolved by addition of one enantiomer of **7**.[50] Recrystallization, to constant rotation, of the diastereomer that precipitates gives the optically active borate as its methyl-*n*-propylbenzylphenylammonium salt **8a**.

(B) Cyanine Dyes. The synthesis of 1,1′,3,3,3′,3′-hexamethylindocarbocyanine iodide ($Cy_{Me}^+ I^-$) has been reported previously.[37,51] The synthesis of the *meso* substituted $PhCy_{Me}^+ I^-$ (**10**) is shown in Scheme 2.[52] The indolinium iodide was deprotonated to give the crude "Fischer" base which was treated with benzoyl chloride to give the ketone **9**. Additional Fischer base was coupled with the ketone **9** and dehydrated in the presence of phosphorus oxychloride to give the crude cyanine. After quenching with water and addition of excess potassium iodide, the cyanine was obtained as its iodide salt **10**.

The synthesis of $Cy_{3,5tBz}^+$ is shown in Scheme 3. Both the 2-methyl and 2-chloroquinolinium tetrafluoroborates were prepared by benzylation of the 2-methylquinoline and 2-chloroquinoline, respectively, with 3,5-di-*tert*-butylbenzyl iodide in the presence of silver tetrafluoroborate. Deprotonated benzyl 2-methylquinolinium, readily formed with triethylamine, was coupled with the 2-chloroquinolinium to give the cyanine as its tetrafluoroborate salt.

The synthesis of Cy_{4tBz}^+ is shown in Scheme 4. As direct benzylation was not successful, the precursor 1-(4-*tert*-butyl)-benzyl-2-methylquinolinium was prepared in a three step process wherein quinoline is treated with 4-*tert*-butylbenzyl bromide to give the 1-(4-*tert*-butyl)benzylquinolinium bromide, **14**. Methylation with methylmagnesium iodide gives 1-(4-*tert*-butyl)benzyl-2-methylquinoline, **15**, which was oxidized with iodine to form the quinolinium iodide salt **16**. Treatment of 2-chloroquinoline with 4-*tert*-butylbenzyl iodide in the presence of silver tetrafluoroborate gives the 2-chloroquinolinium **17**. Coupling with triethylamine gives the cyanine as the tetrafluoroborate salt **18**.

(C) Optically Active Cyanine Borates. The general route for the preparation of the optically active cyanine borates is shown in Scheme 5. The borate, as its methyl-*n*-propylbenzylphenylammonium salt **8**, was debenzylated and exchanged with $Me_4N^+Cl^-$ to form the Me_4N^+ salt **19**. In this process, the more hydrophobic chiral ammonium cation is replaced by the more hydrophilic Me_4N^+, thus facilitating the exchange and crystallization of the product cyanine borates from acetonitrile/water solutions.

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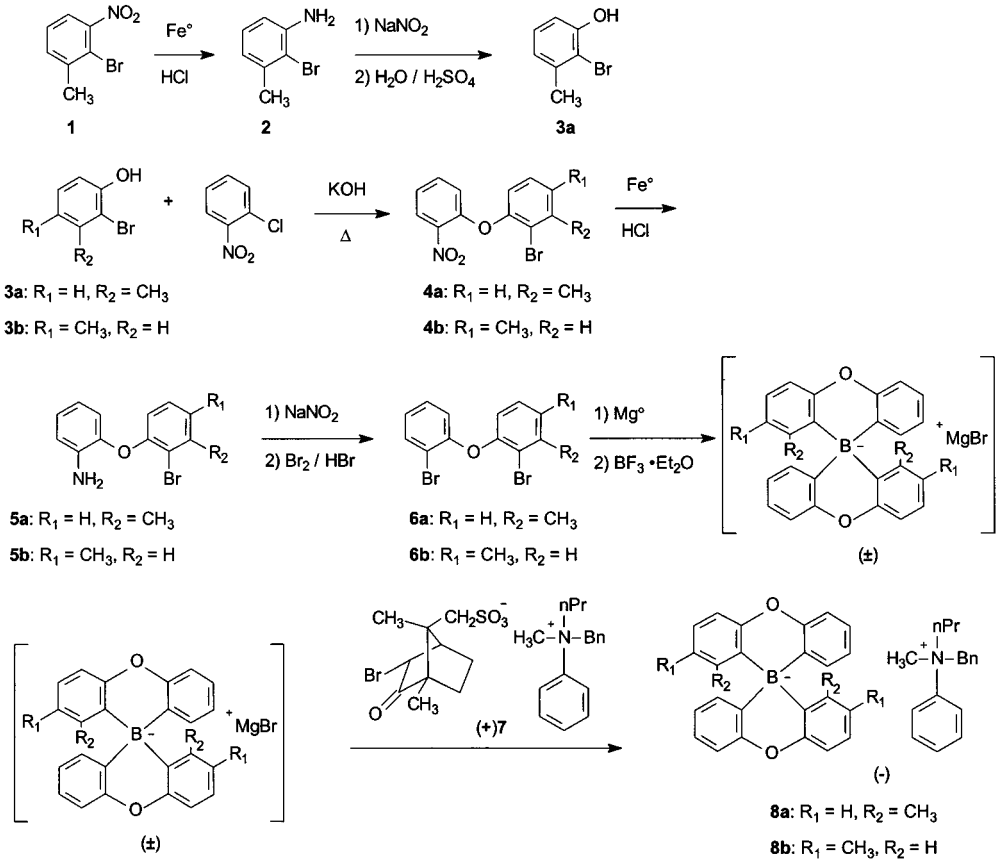
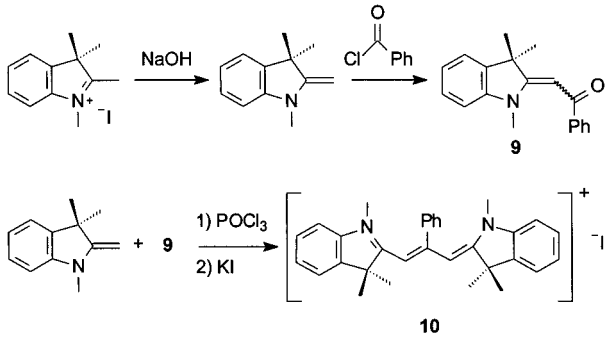
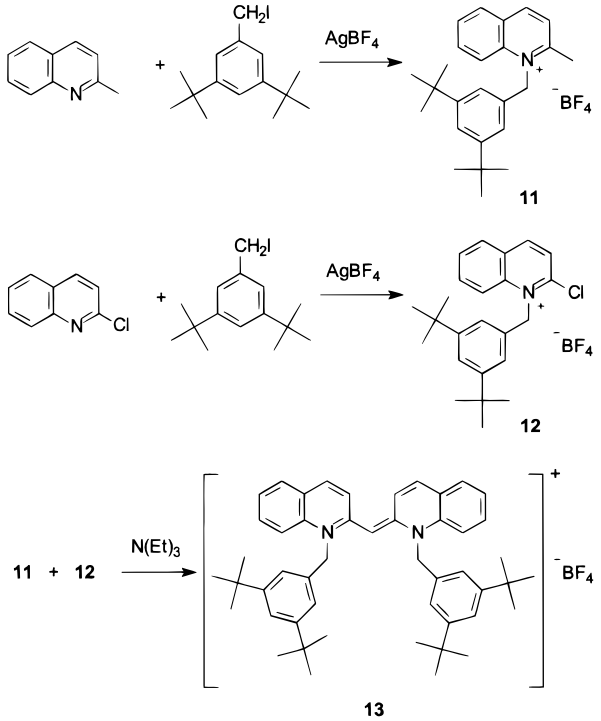
Scheme 1



Scheme 2



Scheme 3



(2) Characterization of Dyes and Borates. (A) NMR Spectroscopy of the Cyanine Dyes. The structures of both the *N*-benzyl and the *meso*-phenyl cyanines were probed in solution by variable temperature NMR spectroscopy. Their spectra in CD_3CN solution reveal a coalescence temperature for the benzyl protons at −10 °C for $Cy_{3,5tBz}^{+}$ BF_4^- and 20 °C for Cy_{4tBz}^{+} BF_4^-. The coalescence temperature of $Cy_{3,5tBz}^{+}$ BF_4^- in CD_2Cl_2 is −9 °C. The vinyl and *N*-methyl protons of $PhCy_{Me}^{+}$ I^- exhibit a coalescence temperature of −34 °C in CD_2Cl_2 and −44 °C in CD_3OD. This small effect of solvent dielectric constant indicates that coalescence is a result of conformational exchange and is not due to association with the counterion.

To examine the energy barrier between these conformers, line shape analysis was performed on the low temperature ^1H NMR spectra of $PhCy_{Me}^{+}$ I^- in CD_2Cl_2. The exchange simulated spectra for $PhCy_{Me}^{+}$ were generated and fit using DNMR5[53] at each of the recorded temperatures (Figure 2). From the calculated rates (Table 1), an Arrhenius plot was constructed for $PhCy_{Me}^{+}$ I^- (Figure 3) giving $E_a = 3.6 \pm 0.5$ kcal/mol. Similar low temperature measurements of the benzyl cyanines lead only to an observed slowing of the rotation of the benzyl groups about the nitrogen phenyl bond.

The structure of the low energy conformers of Cy_{35tBz}^{+} BF_4^-

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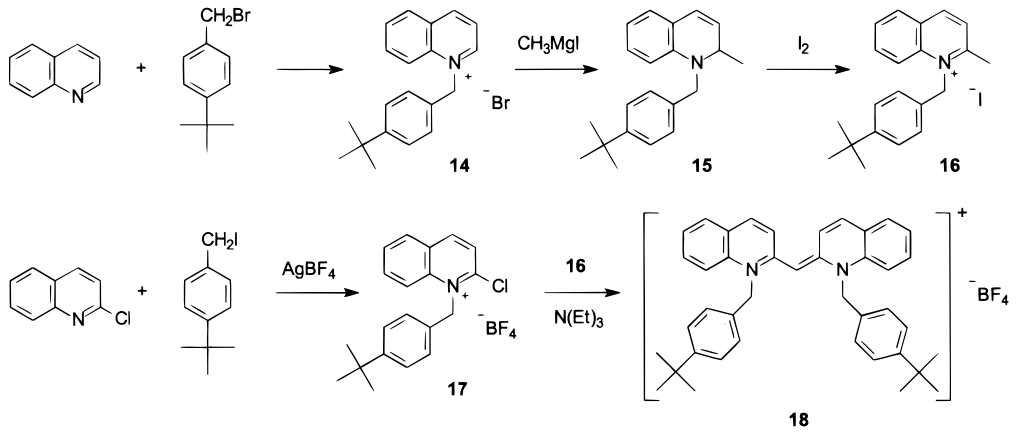
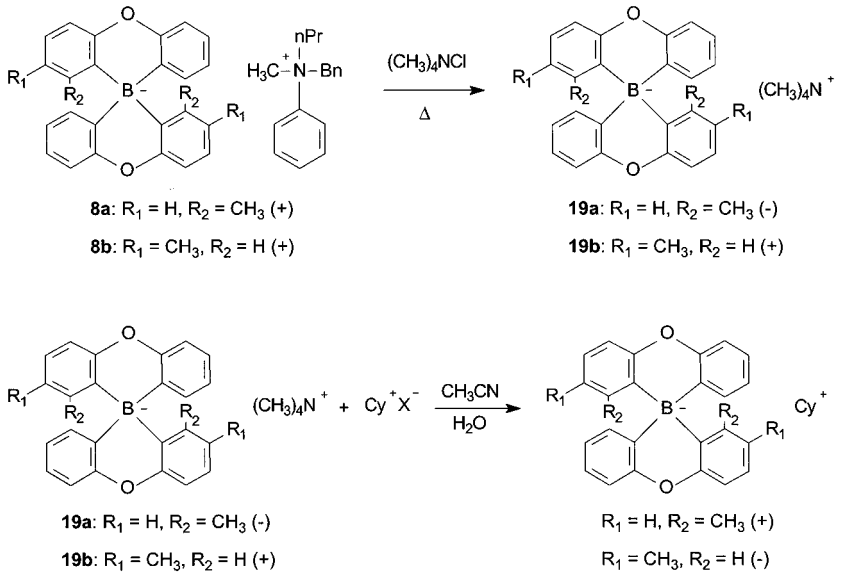
Scheme 4



Scheme 5



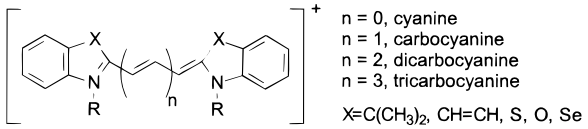


Figure 1. Structure typical of cyanine dyes.

and $PhCy_{Me}^{+}$ I^{-} were explored through measurement of ROESY spectra in CD_2Cl_2 at −56 °C and −80 °C, respectively, where conformational exchange is slow on the NMR time scale. For Cy_{35tBz}^{+} BF_4^{-}, the negative cross-correlated peaks indicate intramolecular enhancements[54] between one set of benzyl resonances and the vinyl proton. A similar enhancement is present between the other set of benzyl protons and the H_8 protons (Figure 8) on the quinonyl ring. No significant enhancements appear between the benzyl and the H_3 protons, suggesting an all-trans geometry. For $PhCy_{Me}^{+}$ I^{-}, the only measurable enhancements are between the geminal methyl protons and vinyl protons, suggesting a cis, trans, cis geometry.

The unique structure of the cyanine borate penetrated ion pair was probed by comparison of NMR spectra in acetonitrile, where the salt exists predominantly as separate ions, and in benzene or toluene, where the salt exists as an ion pair. The chemical shift of the borate methyl group of 2MeSpB^{-} and 3MeSpB^{-} as their $PhCy_{Me}^{+}$ and $Cy_{3,5tBz}^{+}$ salts provides a useful probe of the interactions. The data, shown in Table 2, reveal that the cyanine clearly affects the field experienced by the borate methyl groups.

(B) Solid-State Structure of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-}. Single crystals of racemic $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} were grown from a 2-butanone solution, and its solid-state structure was determined by X-ray crystallography. After solution and optimization, a small degree of disorder remains in some carbon atoms of one xanthyl ring of the three ion pairs that make up the asymmetric unit. Also, the positions of some methyl groups on the *tert*-butyl groups of the cyanines show residual disorder. The structure, shown in Figure 4, is the best approximation for the positions of the atoms affected; the relative positions of the borate and cyanine structures are not affected.

The structure reveals a repeating subunit consisting of a parallelogram-like arrangement of two borates along opposing sides of two cyanines. This subunit repeats in bands throughout the crystal. Where the corners of these subunits meet, significant overlap occurs with inter-ring distances ranging from 3.5 to 4.0 Å, permitting π stacking between adjacent cyanines and borates of adjacent subunits.

Vertical stacks of the subunits produce a ladder-like structure with the borates forming the "rails" and the cyanines acting as horizontal "rungs" (Figure 5). In this structure it is apparent that the closest approach of the cyanines to the borates occurs

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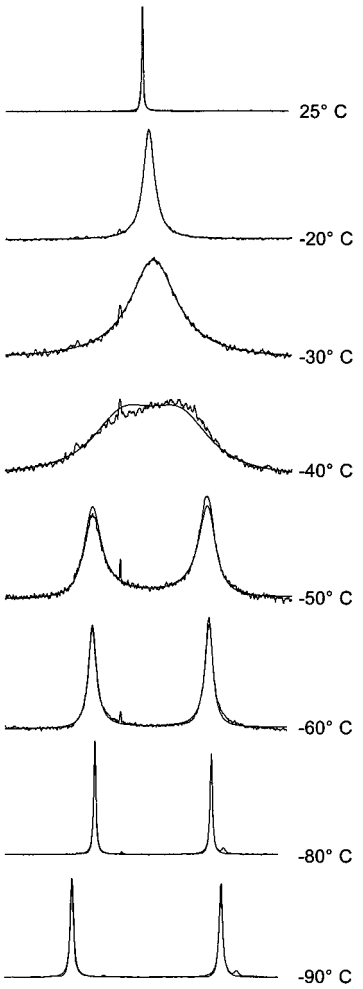

Figure 2. Low temperature ^{1}H NMR and exchange simulated spectra of *N*-methyl protons of $PhCy_{Me}^+$ I^- in CD_2Cl_2.

Table 1. Calculated ^{1}H NMR Exchange Rates for $PhCy_{Me}^+I^-$ in CD_2Cl_2

T (°C)	k (s^{-1})	T (°C)	k (s^{-1})
25	575	−50	143
−20	301	−60	60
−30	220	−80	10
−40	158	−90	14

with the quinonyl ring of the former canted such that its nitrogen atom is pointed toward the central boron atom. This arrangement is likened to a canted front-side penetration of the cyanine dye.

The structure of the cyanine of one subunit, shown in Figure 6, reveals a trans geometry with a twist about the central methine group that is similar to the structures previously reported for Cy_{Et}^+. The angle between the mean planes of the two quinonyl rings of the cyanine is 40 ± 1°. The benzyl rings are perpendicular to the respective quinonyl planes residing on opposing sides of the cyanine molecule relative to the plane formed from the central methine and the 2 and 2′ carbons of the rings.

(C) Induced Circular Dichroism (CD) of Cyanine Borates. The cyanine dyes we prepared are achiral or exist as a pair of rapidly converting enantiomers. In solutions of nonpolar solvent they form an ion pair with the borate, and, if the borate is chiral and optically enriched, then it is possible that the cyanine borate ion pair will show an induced CD spectrum. The CD spectra of the cyanine with the chiral borates, recorded in benzene

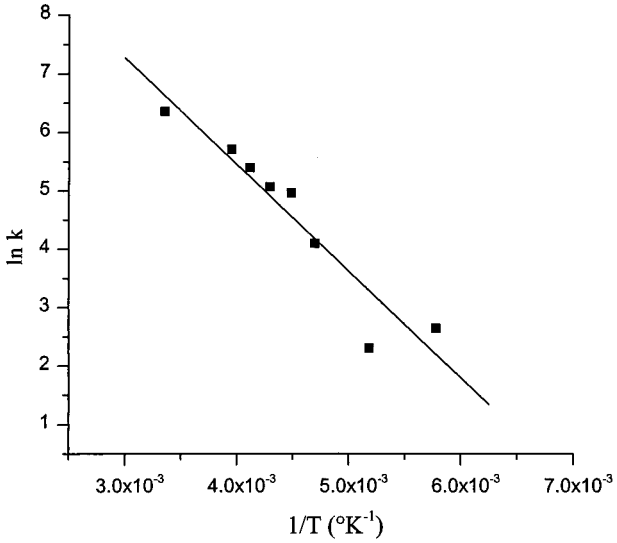

Figure 3. Arrhenius plot from the ^{1}H NMR line shape analysis of $PhCy_{Me}^+$ I^- in CD_2Cl_2 solution from −90 °C to 25 °C. See text for analysis of the temperature dependence of the molecular motion

solutions (optical densities ≈ 1 at λ_{max}), are shown in Figure 7. Attempts to measure the CD spectrum of Cy_{Me}^+ 3MeSpB$^-$ at room temperature in benzene solution and at −20 °C in toluene solution lead only to weak signals (artifacts[55−59]) that are independent of the enantiomer of the borate used. In all other cases, the sign of the induced CD spectrum parallels the enantiomer of the camphor salt used as the resolving agent. In all cases, except for $PhCy_{Me}^+$ 2MeSpB$^-$, the observed CD spectrum of the cyanine matches its UV absorption spectrum precisely. However, the enantiomers of $PhCy_{Me}^+$ 2MeSpB$^-$ give CD spectra in benzene solution with opposite sign and identical maxima (λ_{max} = 598 nm), that are red-shifted from their absorption maxima (581 nm). The location and shape of the CD spectrum is independent of concentration over a range from 4.1×10^{-5} M to 4.1×10^{-6} M, thus eliminating aggregation as the cause of the shifted spectrum. The magnitude of the chiral induction by the borates on the cyanines was quantified by calculation of asymmetry factors ($\Delta\epsilon/\epsilon$), Table 3. Using this measure, the "most" optically active of the cyanine borates is $Cy_{3,5tBz}^+$ 2MeSpB$^-$.

The free energy differences between the two equilibrating diastereomeric cyanine borate ion pairs in solution can be estimated by measurement of the temperature dependence of the CD spectra. The CD signal was averaged over a wavelength range about the absorption maximum (532−536 nm) for $Cy_{3,5tBz}^+$ 2MeSpB$^-$ in toluene. The data, shown in Table 4, reveal that at higher temperatures the population difference between the diastereomers is decreased, reducing the observed CD intensity. The free energy difference between the diastereomeric pairs was determined from the slope of a plot of CD intensity vs $1/[1+e^{(-\Delta G/RT)}]$ by varying ΔG to find the best linear fit.[60] This procedure gives ΔG < 1 kcal/mol for both $Cy_{3,5tBz}^+$ 2MeSpB$^-$ and $PhCy_{Me}^+$ 3MeSpB$^-$.

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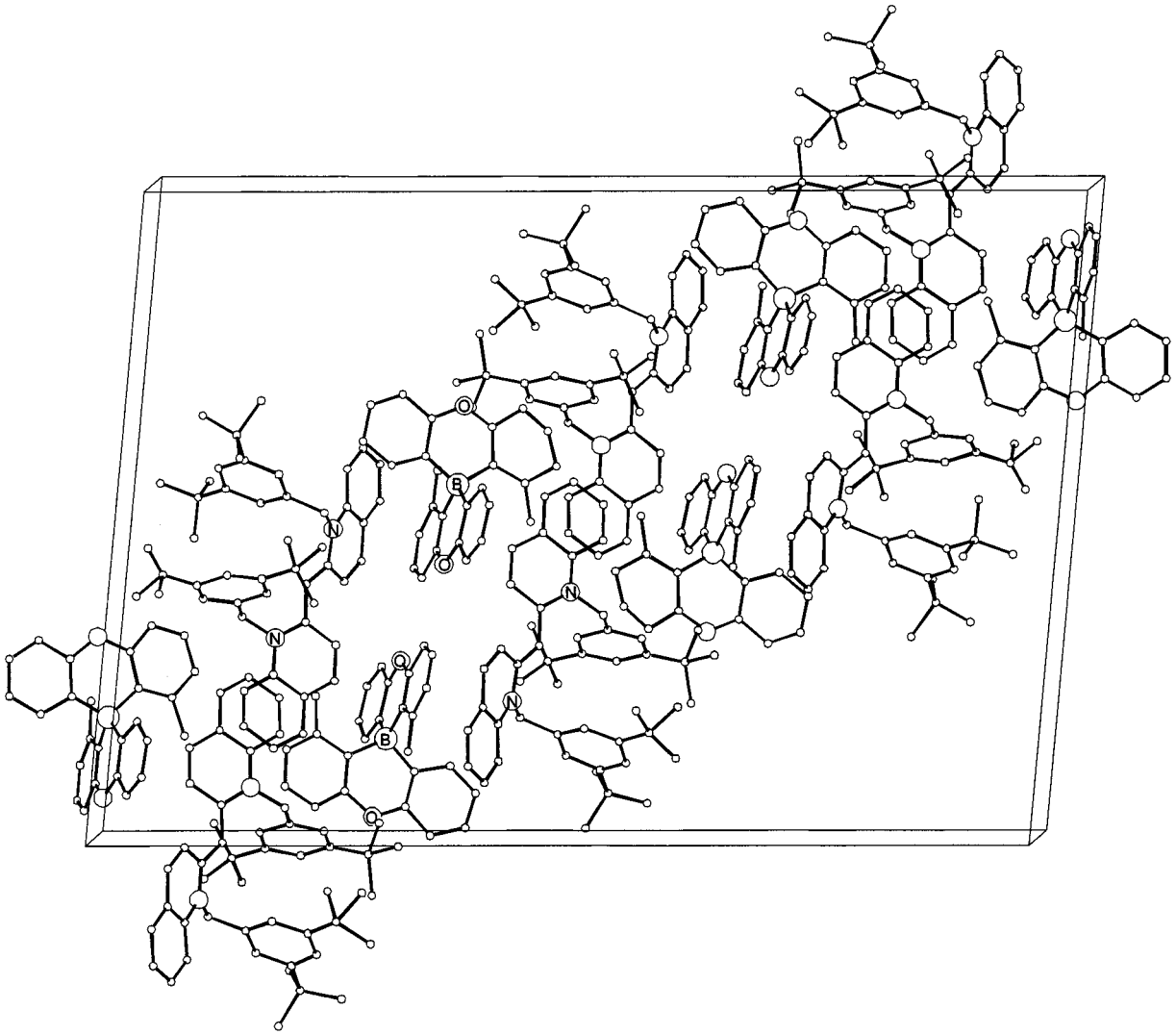

Figure 4. Unit cell from X-ray crystal structure of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-}.

Discussion

Structure of Cyanine Borate Ion Pairs in the Solid State and in Solution. The solid-state structure of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} provides some insight into the nature of this ion pair. One possibility was that the large substituents on the nitrogen atoms of the cyanine might prevent nitrogen-forward penetration (see Chart 2) of the cyanine species into the borate for steric reasons. Using this logic, $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} should prefer a "backside penetration" motif whereby approach by the cyanine occurs with the quinonyl rings forward and the nitrogen atoms pointing away from the borate center, minimizing steric repulsion caused by the 3,5-di-*tert*-butylbenzyl groups. The solid-state structure shows both of these orientations with the quinonyl ring of a cyanine closest to the borate oriented with the nitrogen atom canted forward and the other more distant quinonyl ring positioned with the ring nitrogen atom pointed away from the borate. The solution behavior seems to suggest that the nitrogen-forward orientation is dominant in determining the sign of the CD spectrum. If backside penetration is dominant, then the sign of the CD might reverse when the structure of the paired cyanine changes.[61] This does not occur, as changing the nitrogen substituent from ethyl to 3,5-di-*tert*-butylbenzyl groups does not cause a change in the sign of the CD spectrum when paired with the same borate enantiomer.

The steric bulk of the 3,5-di-*tert*-butylbenzyl groups does appear to play a role in the macrostructure of the crystal. This is apparent from comparison of the structure of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} with that of the Cy_{Me}^{+} PEB^{-}.[36] Both cyanine borates have distinct subunit cell species consisting of two pairs of cyanine borates that form the basis of a repeating macrostructure. In Cy_{Me}^{+} PEB^{-}, this macrostructure takes the form of a cylindrical motif with the planar cyanine dye forming ribbons along the long axis of the cylinder. Conversely, the four molecule subunits of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} form a ladder structure in which the long axis of the cyanine is perpendicular to the long axis of the macrostructure.

Other parallels may be drawn between the structure of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} and that of other quinonyl cyanines. The solid-state structures determined for $Cy_{Et}^{+}Cl^{-}$, $Cy_{Et}^{+}Br^{-}$, and $Cy_{Et}^{+}I^{-}$ reveal twist angles of 50.6°,[21] 49°,[25] and 41° between rings units for the chloride, bromide, and iodide salts, respectively.[62] The three cyanines of the asymmetric unit give an average twist angle of 40.5° for the more sterically congested $Cy_{3,5tBz}^{+}$ 2MeSpB^{-}. These values suggest that the larger substituents on nitrogen and the larger counterion produce a flatter solid-state structure.

The twisted trans solid-state structure of $Cy_{3,5tBz}^{+}$ is in good agreement with its observed solution state properties. The

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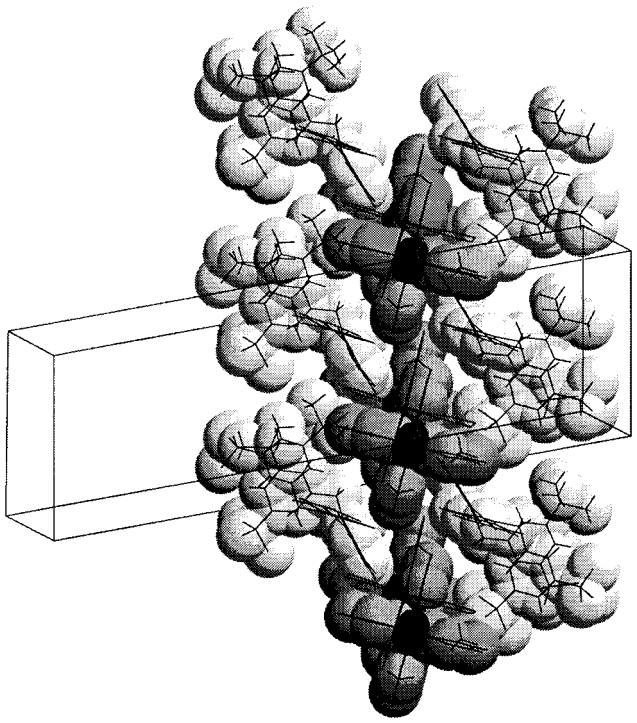

Figure 5. Ladder-like structure from X-ray crystal structure of (±)-54.

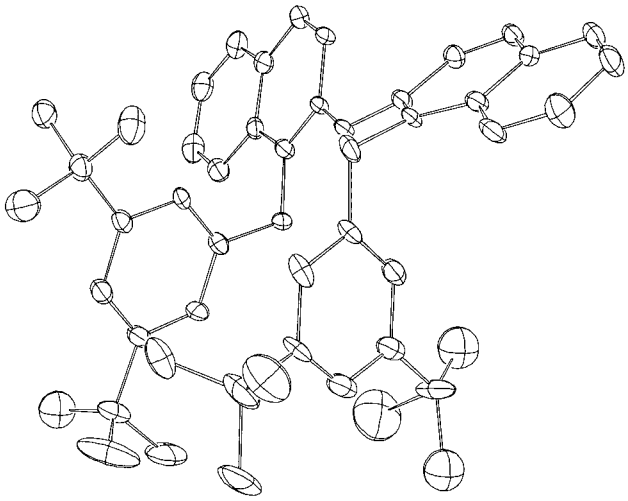

Figure 6. Solid-state structure of the cyanine of one unit cell subunit of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-}.

ROESY data give enhancements which are consistent with the structure shown in Figure 8. Similar enhancements would be observed from the cyanine with both benzyl rings coplanar; however, both steric effects and the solid-state structure suggest that the lowest energy conformer is the twisted periplanar arrangement that is depicted.

The variable temperature absorption and ^{1}H NMR spectra of the indocarbocyanines indicate the nature of their structure in solution. The featureless ambient temperature absorption spectrum of $PhCy_{Me}^{+}I^{-}$ exhibits new features in a frozen ethanol methanol glass at 77 K, indicating that solutions of the cyanine consist of a mixture of twisted forms.[49] However freezing solutions of all-trans Cy_{Me}^{+} I^{-}, which is planar, leads only to minor sharpening in its spectrum. The reduction in population of twisted forms revealed by the low-temperature absorption spectrum of $PhCy_{Me}^{+}I^{-}$ was also observed in its variable temperature ^{1}H NMR spectrum.

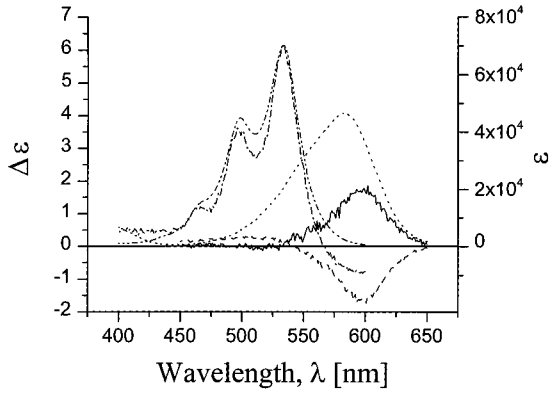

Figure 7. Induced CD of (+)$Cy_{3,5tBz}^{+}$ 2MeSpB^{-} (- · -), (+)$PhCy_{Me}^{+}$ 2MeSpB^{-} (—), (−)$PhCy_{Me}^{+}$ 2MeSpB^{-} (- -) in benzene. UV spectrum of $Cy_{3,5tBz}^{+}$ 2MeSpB^{-} (- · · -), $PhCy_{Me}^{+}$ 2MeSpB^{-} (···). The maximum absorbance of each solution was adjusted to equal ca. 1.0 (the optimum operating range of the spectrometer); this corresponds to a concentration of approximately 2×10^{-5} M in each case. Absorption data are summarized in Table 3.

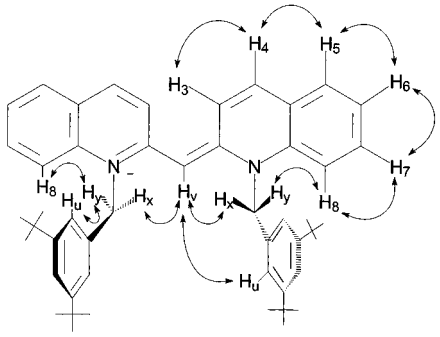

Figure 8. Observed negative cross correlated peaks in ROESY (NOEs) for $Cy_{3,5tBz}^{+}$ BF_4^{-}.

Table 2. ^{1}H NMR Chemical Shift of Cyanine Spiroborates[a]

compd	solvent	δ ^{1}H B_{Me}[b] (ppm)
$PhCy_{Me}^{+}$3MeSpB^{-}	toluene-d_8	1.87
	CD_3CN	2.01
$(n\text{-}Bu)_4N^{+}$	toluene-d_8	2.06
3MeSpB^{-}	CD_3CN	2.03
$Cy_{3,5tBz}^{+}$3MeSpB^{-}	toluene-d_8	1.95
	CD_3CN	2.01
$PhCy_{Me}^{+}$2MeSpB^{-}	benzene-d_6	2.23
	CD_3CN	1.59
$(n\text{-}Bu)_4N^{+}$2MeSpB^{-}	benzene-d_6	2.26
	CD_3CN	1.60
$Cy_{3,5tBz}^{+}$2MeSpB^{-}	benzene-d_6	2.35
	CD_3CN	1.59

[a] For identification of the structures see Chart 1. [b] ^{1}H chemical shift of borate methyl group (relative to TMS).

Induced Circular Dichroism in Cyanine Borate Ion Pairs. The twisted structure of the quinoline based and *meso*-substituted indocarbocyanine appears to be a critical feature for observation of an induced CD. The chiral borate is apparently incapable of twisting the planar all-trans Cy_{Me}^{+}. Significant interactions exist, however, as the chiral borate is capable of selecting between the two twisted enantiomers of $PhCy_{Me}^{+}$, Cy_{Et}^{+}, Cy_{4tBz}^{+}, and $Cy_{3,5tBz}^{+}$ and generating a CD spectrum. This selectivity is sensitive since the energy differences in the diastereomeric pairs is less than 1 kcal/mol.

The mechanisms for induction of a CD spectrum may be divided into two general groups: electronic and structural effects. Cyanine borates exist as penetrated ion pairs in nonpolar solvents[36,37,43] where the chiral borate should affect the sym-

Table 3. Circular Dichroism Data for Cyanine Borates

compd	λ_{max} (nm)	ϵ_{max} ($\times 10^3$)	av $\lvert\Delta\epsilon/\epsilon\rvert$[a] ($\times 10^{-5}$)	sd[b] ($\times 10^{-5}$)
$Cy_{Et}{}^+3MeSpB^-$	533	54	0.68[c]	0.17
$PhCy_{Me}{}^+3MeSpB^-$	581	47	4.2[d]	0.21
$Cy_{3,5tBz}{}^+3MeSpB^-$	533	69	4.4[c]	0.39
$Cy_{4tBz}{}^+2MeSpB^-$	532	70	5.7[c]	0.52
$Cy_{Et}{}^+2MeSpB^-$	533	57	7.0[c]	0.32
$Cy_{3,5tBz}{}^+$ $2MeSpB^-$	533	70	7.8[c]	0.58

[a] Average calculated from wavelength range determined from peak width at half-height. [b] Standard deviation of av $\lvert\Delta\epsilon/\epsilon\rvert$. [c] Calculated over 489−549 nm wavelength range. [d] Calculated over 538−611 nm wavelength range.

Table 4. Variable Temperature CD of $Cy_{3,5TBz}{}^+2MeSpB^-$

T (°C)	CD[a] (mdeg)	T (°C)	CD[a] (mdeg)
−13.1	3.97	19.2	3.23
−10.4	3.92	38.7	2.84
−0.8	3.82	58.0	2.51
9.3	3.50	77.0	2.16

[a] Average of measured CD over 532−536 nm range.

metry of local field experienced by the cyanine. These electronic effects could affect the electronic transition of the cyanine chromophore. They do not. The lack of an observed induced CD spectrum for $Cy_{Me}{}^+$ $3MeSpB^-$ excludes this mechanism.

Structural effects generating induced CD spectra may be divided into two groups: association and diastereomeric equilibration. Association equilibration requires significant concentrations of solvated ions along with different association constants for the two diastereomers in equilibrium. This is unlikely in the current case because cyanine borates exist almost exclusively as ion pairs in benzene solutions.[63] Diastereomeric equilibration, on the other hand, is an attractive explanation because of the low energy barrier separating twisted forms of the cyanine and the small, but measurable, energy difference between the diastereomers.

The longer, more conformationally flexible structure of $PhCy_{Me}{}^+$ appears to reduce its response to the chiral borate structure. In benzene solution, $PhCy_{Me}{}^+$ $3MeSpB^-$ [49] has a slightly larger induced CD with $\Delta\epsilon_{max} = 1.9$ cm^{-1} M^{-1} compared with $PhCy_{Me}{}^+2MeSpB^-$ which has $\Delta\epsilon_{max} = 1.7$ cm^{-1} M^{-1}. The symmetry reducing methyl group is apparently closer to the indole rings of the cyanine in $PhCy_{Me}{}^+$ $3MeSpB^-$, leading to greater selectivity and a stronger induced CD. This is supported by the observed shifts in their ^1H NMR spectra. In the presence of $PhCy_{Me}{}^+$, the $3MeSpB^-$ methyl group resonance is shifted upfield, indicating that the methyl group is located in the interior, deshielding, region of the cyanine ring system. With the shorter, more compact $2MeSpB^-$, however, there is no significant shift of the borate methyl group in the presence of the cyanine, indicating a greater distance between the ring and the methyl group. The chemical shifts of the borate methyl groups for the tetrabutylammonium salts of $3MeSpB^-$ and $2MeSpB^-$ in acetonitrile solution support the suggestion of a more compact structure in $2MeSpB^-$. The methyl protons of $2MeSpB^-$ clearly reside in more of the shielding region of the borate ring system, closer to the boron center, as indicated by their 0.4 ppm upfield shift compared with $3MeSpB^-$.

The more compact structure of $PhCy_{Me}{}^+$ $2MeSpB^-$ has interesting effects on the structure of the observed CD spectrum. Apparently those conformations responsible for generating the CD represent a small fraction of those present in solution as evidenced by the difference in maxima between absorption and circular dichroism spectra (Figure 7). The narrower band of the CD spectrum indicates that fewer conformations are present, and the conformations present in this population appear to have a greater twist as evidenced by the shift to longer wavelengths.[64]

The quinoline based cyanines appear to be much more sensitive to borate structure. In the penetrated ion pairs formed with either $Cy_{Et}{}^+$ or $Cy_{3,5tBz}{}^+$, the $2MeSpB^-$ isomer appears to be far more selective than $3MeSpB^-$, as reflected by the strength of their CD spectra. The reduced methine chain length brings the cyanine rings closer to the symmetry reducing element of the borate methyl group. In general, the asymmetry factor (Table 3) and direct CD (Figure 7) measurements indicate these quinoline-based cyanines are more disposed to exhibiting an induced CD than are the indocarbocyanines.

While measurement of an induced CD indicated promise for nonlinear optical properties of these cyanine borates, unfortunately, neither $Cy_{Et}{}^+$ $2MeSpB^-$ nor $PhCy_{Me}{}^+$ $2MeSpB^-$ yielded any measurable second harmonic generation.

Conclusion

In solutions of nonpolar solvents, cyanine dye cations paired with chiral borate anions form penetrated ion pairs where this association leads to an induced CD spectrum in the cyanine dye. The borate interacts with the penetrated cyanine through selection of a twisted form but does not twist a planar dye. Solid-state structures support the twisted nitrogen-forward penetrating cyanine structure. The mechanism for generation of the induced CD spectrum involves a diastereomeric equilibration with energy differences of less than 1 kcal/mol. The strength of the induced CD spectrum is tunable through the structure of both the borate and the cyanine.

Experimental Section

General Methods. ^1H, ^{11}B, and ^{13}C NMR spectra were obtained on a Bruker DRX 500 (500 MHz), Bruker AMX 400 (400 MHz), Varian Unity 400 (400 MHz), Varian Gemini 3000 (300 MHz), General Electric QE−300 (300 MHz), or General Electric GN300 Narrow Bore (300 MHz) spectrometers. Chemical shifts are reported in parts per million (δ) downfield from Me_4Si. The ^{11}B NMR spectra are referenced to boron trifluoride diethyl etherate (external reference) at δ 0.0. Absorption spectra were recorded on a Varian Cary 1E UV−vis spectrophotometer. Infrared Spectra (IR) were recorded on a Mattson Galaxy 3000 FTIR as thin films. A Hewlett-Packard 5970 Series Mass Selective Detector was used for low resolution mass spectrometry. A Varian 3700 GC equipped with a flame ionization detector and an HP 3390A electronic integrating recorder was used for analytical separations. GC analyses were performed with 0.25 mm × 6 m HP-1 column. Optical rotation measurements were recorded on a Jasco DIP 360 Digital Polarimeter. Elemental analyses were performed by the University of Illinois Microanalysis Laboratory or Atlantic Microlab, Inc. Melting points were taken in open capillary tubes in a Büchi or Mel-Temp melting point apparatus and are uncorrected. For reactions requiring dry solvent diethyl ether (Et_2O) or tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under nitrogen atmosphere. Dry acetonitrile was obtained by distillation from calcium hydride under nitrogen atmosphere. Flash chromatography was conducted according to the method of Still[65] and performed with Merck silica gel 0.40−0.63 mm, 230−400 mesh. The synthesis and characterization of precursors and previously reported compounds is described in the Supporting Information accomanying this paper.

Circular dichroism spectra were acquired with a Jasco Model J-720 spectropolarimeter. The concentrations of all solutions used for acquiring circular dichroism measurements were adjusted such that optical densities ≈ 1 at λ_{max}. The measured CD spectra of the optically

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active cyanine borates were corrected for artifacts by subtracting CD spectra of the racemic tetrafluoroborate salt of the measured cyanine. The resulting spectra were corrected to 100% enantiomeric excess based on the optical rotations of the precursor tetramethylammonium spiroborate.

General Method for Synthesis of Cyanine Borates. Equimolar amounts of the cyanine as the iodide or tetrafluoroborate salt and the borate as the tetramethylammonium salt were dissolved in hot acetonitrile. Water was slowly added to the hot solution until the small amount of precipitate formed persisted. A small amount of acetonitrile was added to clarify the solution which was allowed to cool in the dark. A gentle stream of nitrogen was passed over the solution to evaporate the acetonitrile. The product cyanine borate was collected from the aqueous solution.

X-ray Structure Determination. $(\pm)Cy_{3,5tBz}^{+}$ 2MeSpB^{-} crystallizes as hexagonal plates from 2-butanone. The crystal selected had the dimensions 0.75 × 0.40 × 0.20 mm. Data were collected on a Siemens SMART/CCD diffractometer at 173 K. Cell constants were determined from a least-squares refinement of the strongest 8192 reflections from the data frames: triclinic; *P*1; $a = 11.0925(2)$ $b = 24.5561(5)$ $c = 34.9827(1)$ $\alpha = 94.513(1)$ $\beta = 98.346(1)$ $\gamma = 95.208(1)$; volume = 9348.2(3) Å^3; $Z = 6$. A total of 1261 frames of 120 s were collected. The total number of reflections collected was 42 832 of which 27 542 were unique ($R_{int} = 0.056$). The structure was solved using direct methods. All non-hydrogen atoms, including disordered methyl carbon atoms, were refined anisotropically. Hydrogen atoms for the ordered carbon atoms were refined using a riding model. The final *R* factor was 0.120 with w$R^2 = 0.312$; GooF = 1.011. All calculations were performed using SHELXTL.

(−)-Methyl-*n*-propylbenzylphenylammonium Spirobi[(2-methyl)-borataxanthene], (−)-8a. The synthesis was carried out following the guidelines given by Torssell.[35] An oven dried condenser, addition funnel, and stopper were affixed to a similarly dried three-necked round-bottom flask. Magnesium turnings (0.30 g, 12.2 mmol) were added, and the apparatus was flame dried while purging with nitrogen. The magnesium was stirred vigorously for 40 h under nitrogen to aid in activation.[66] To this, 2 mL of a solution of freshly distilled dibromide **6a** (1.92 g, 5.6 mmol) in dry THF (17 mL) was added with stirring and gentle heating. Within 10 min the reaction was initiated as indicated by the presence of yellow color. The remaining solution of the dibromide was added dropwise over a period of 30 min, and it was stirred and heated at reflux for 5 h. To the suspension of the di-Grignard reagent, chilled in an ice bath, a solution of boron trifluoride diethyl etherate (309 μL, 2.5 mmol) in dry diethyl ether (1.8 mL) was added dropwise with stirring over a period of 2 min. The resulting cloudy green suspension was heated at mild reflux for 15 min. After cooling, the solution was filtered. The solvent was removed in vacuo to leave a yellow oil which was dissolved in ethanol (15 mL). To the solution of this crude salt was added a solution of the (+)-methyl-*n*-propylbenzylphenylammonium [(1*R*)-(*endo*,*anti*)]-3-bromocamphor-9-sulfonate **(+)-7**[67] (0.93 g, 1.7 mmol) in ethanol (10.7 mL). The solution was chilled, and the resulting crystals were collected. The solid was further recrystallized from nitromethane/ethanol (1:3 vol:vol) until 0.15 g (29%) of white crystals with a constant optical rotation were obtained: mp 200−201 °C; $[\alpha]_D = -8.6°$ (*c* 1.00, NO_2Me); ^{1}H NMR (CD_3CN, 300 MHz) δ 7.59−7.57 (m, 3H), 7.51−7.48 (m, 2H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.32−7.27 (m, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.88−6.83 (m, 2H), 6.78 (d, $J = 6.6$ Hz, 2H), 6.74−6.70 (m, 4H), 6.68−6.62 (m, 2H), 6.55 (t, $J = 6.7$ Hz, 2H), 6.47 (d, $J = 7.7$ Hz, 2H), 4.86 (d, $J = 12.5$ Hz, 1H), 4.71 (d, $J = 13.5$ Hz, 1H), 4.01 (td, $J = 12.3$, 4.6 Hz, 1H), 3.64 (td, $J = 11.8$, 5.5 Hz, 1H), 3.29 (s, 3H), 1.74−1.62 (m, 1H), 1.59 (s, 6H), 1.26−1.11 (m, 1H), 0.89 (t, $J = 7.3$, 3H); ^{13}C NMR (CD_3CN, 300 MHz) δ 158.16, 156.47, 144.90, 137.61, 134.17, 132.16, 132.02, 131.83, 130.17, 128.45, 125.88, 125.82, 125.18, 124.53, 123.44, 122.02, 121.99, 114.37, 113.43, 75.24, 69.59, 47.59, 23.06, 17.35, 10.64.

(+)-Methyl-*n*-propylbenzylphenylammonium Spirobi[(2-methyl)-borataxanthene], (+)-8a. The synthesis was carried out in the same manor as that for the (−) enantiomer **(−)-8a** with the exception that (−)-methyl-*n*-propylbenzylphenylammonium [(1*S*)-(*endo*,*anti*)]-3-bromocamphor-9-sulfonate **(−)-7** was used to resolve the racemic magnesium salt of the borate. After recrystallization from nitromethane/ethanol (1:3 vol:vol) to constant optical rotation was obtained 0.30 g (47%) of a white powder: $[\alpha]_D = +7.3°$ (*c* 1.00, NO_2Me); mp 190−193 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 7.59−7.57 (m, 3H), 7.51−7.48 (m, 2H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.32−7.27 (m, 2H), 6.99 (d, $J = 7.2$ Hz, 2H), 6.87−6.82 (m, 2H), 6.78 (d, $J = 6.5$ Hz, 2H), 6.73−6.70 (m, 4H), 6.67−6.61 (m, 2H), 6.54 (t, $J = 7.1$ Hz, 2H), 6.46 (d, $J = 7.2$ Hz, 2H), 4.86 (d, $J = 12.4$ Hz, 1H), 4.72 (d, $J = 12.9$ Hz, 1H), 4.01 (td, $J = 12.1$, 3.9 Hz, 1H), 3.65 (td, $J = 12.2$, 4.2 Hz, 1H), 3.30 (s, 3H), 1.72−1.61 (m, 1H), 1.59 (s, 6H), 1.25−1.10 (m, 1H), 0.89 (t, $J = 7.4$, 3H).

(±)-Tetra-*n*-butylammonium Spirobi[(3-methyl)borataxanthene]. The synthesis was carried out following the guidelines given by Torssell.[35] An oven dried condenser, addition funnel, and stopper were affixed to a similarly dried three-necked round-bottom flask. Magnesium turnings (0.22 g, 9.1 mmol) were added, and the apparatus was flame dried while purging with nitrogen. The magnesium was stirred vigorously for 24 h under nitrogen to aid in activation.[66] To this was added 3 mL of a solution of freshly distilled dibromide **6b** (1.53 g, 4.5 mmol) in dry THF (15 mL) with stirring and gentle heating. Within 10 min, the reaction was initiated as indicated by the presence of yellow color. The remaining solution was added dropwise over a period of 20 min, and it was stirred and heated at reflux for 5 h. To the suspension of the di-Grignard reagent, chilled in an ice bath, a solution of freshly distilled boron trifluoride diethyl etherate (226 μL, 1.5 mmol) in dry diethyl ether (1.5 mL) was added dropwise with stirring over a period of 7 min. The resulting green solution was heated at mild reflux for 20 min. The solvent was removed in vacuo to leave a yellow oil which was dissolved in acetonitrile (300 mL)/water (80 mL) and washed with hexane (2 × 40 mL). The aqueous layer was filtered to remove any undissolved material. To this crude solution of the magnesium salt of the racemic spiroborate was added excess tetrabutylammonium chloride (2.02 g, 7.3 mmol), and the acetonitrile was removed with a stream of nitrogen to leave a brown oil which was recrystallized from ethanol to give 0.65 g (58%) of a tan solid: mp 173−174 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 6.90−6.81 (m, 4H), 6.77−6.63 (m, 8H), 6.56 (s, 2H), 3.02 (t, $J = 8.8$ Hz, 8H), 2.03 (s, 6H), 1.60−1.52 (m, 8H), 1.38−1.28 (m, 8H), 0.95 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.52, 155.55, 137.09, 136.87, 130.26, 125.72, 125.00, 123.17, 121.89, 121.85, 114.74, 114.64, 59.22, 24.22, 20.91, 20.27, 13.77; ^{11}B NMR (CD_3CN, 300 MHz) δ −18.51. Anal. Calcd for $C_{42}H_{56}NO_2B$: C, 81.66; H, 9.14; N, 2.27; B, 5.18. Found: C, 81.33; H, 9.11; N, 2.17; B, 5.06.

(±)-Tetra-*n*-butylammonium Spirobi[(2-methyl)borataxanthene]. The synthesis was performed in the same manner as (±)-tetra-*n*-butylammonium spirobi[(3-methyl)borataxanthene] with the exception that the dibromodiphenyl ether **6a** was used to give 0.14 g (29%) of the tetra-*n*-butylammonium spiroborate as fine needles: mp 166−168 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 6.85 (t, $J = 7.7$ Hz, 2H), 6.78 (d, $J = 6.6$ Hz, 2H), 6.73−6.70 (m, 4H), 6.68−6.61 (m, 2H), 6.55 (td, $J = 7.1$, 1.3 Hz, 2H), 6.47 (d, $J = 7.1$ Hz, 2H), 3.05 (t, $J = 8.5$ Hz, 8H), 1.63−1.53 (m, 14H), 1.40−1.27 (m, 8H), 0.95 (t, $J = 7.4$ Hz, 12H). Anal. Calcd for $C_{42}H_{56}NO_2B$: C, 81.66; H, 9.14; N, 2.27. Found: C, 81.06; H, 9.19; N, 2.23.[68]

(±)-Tetramethylammonium Spirobi[(2-methyl)borataxanthene]. The synthesis was performed in the same manner as (±)-tetra-*n*-butylammonium spirobi[(2-methyl)borataxanthene] with the exception that tetramethylammonium chloride was used in place of tetra-*n*-butylammonium chloride to give 0.88 g (83%) of the tetramethylam-

(66) Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis *J. Org. Chem.* **1991**, *56*, 698−703.

(67) The synthesis and characterization of this material is available as Supporting Information.

(68) Elemental analysis of organonboron compounds can lead to low observed values for carbon from incomplete combustion due to the formation of boric oxides. (a) Crompton, T. R. *Comprehensive Organometallic Analysis*; Plenum Press: New York, 1987; pp 34−44. (b) Mizukami, S.; Ieki, T. *Micrchem. J.* **1963**, *7*, 485−492. (c) Arthur, P.; Annino, R.; Donahoo, W. P. *Anal. Chem.* **1957**, *29*, 1852−1854. (d) Kainz, G.; Chromy, G. *Mikrochim. Acta* **1966**, *16*, 1140−1147. (e) Butterworth, D. E. *Analyst* **1961**, *86*, 357−358.

monium spiroborate as needles: mp > 250 °C ^{1}H NMR (CD_3CN, 300 MHz) δ 6.85 (t, J = 7.7 Hz, 2H), 6.78 (dd, J = 6.6, 1.7 Hz, 2H), 6.73−6.70 (m, 4H), 6.67−6.61 (m, 2H), 6.55 (td, J = 7.1, 1.5 Hz, 2H), 6.47 (d, J = 7.2 Hz, 2H), 3.04 (s, 12H), 1.59 (s, 6H).

1,1′-Di-(3,5-di-*tert*-butyl)benzyl-2,2′-cyanine tetrafluoroborate, 13. To a solution of the 1-(3,5-di-*tert*-butyl)benzyl-2-methylquinolinium tetrafluoroborate **11** (0.33 g, 0.77 mmol) and the 1-(3,5-di-*tert*-butyl)-benzyl-2-chloroquinolinium tetrafluoroborate **12** (0.35 g, 0.77 mmol) in acetonitrile (10 mL) was added triethylamine (215 μL, 1.5 mmol). The resulting red solution was heated at reflux for 45 min. Upon cooling, crystals formed and were collected by vacuum filtration to afford 0.48 g (82%) of the cyanine **13** as orange crystals: mp > 300 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.13 (d, J = 9.3 Hz, 2H), 7.96 (d, J = 9.3 Hz, 2H), 7.87 (d, J = 7.7 Hz, 2H), 7.65 (t, J = 7.1 Hz, 2H), 7.51−7.45 (m, 4H), 7.26 (s, 2H), 6.87 (s, 4H), 6.76−6.70 (m, 4H), 6.67−6.61 (m, 2H), 6.56−6.54 (m, 1H), 5.62 (s, 1H), 5.45 (s, 4H), 2.02 (s, 6H), 1.14 (s, 36H). ^{13}C NMR (CD_3CN, 400 MHz) δ 156.38, 152.72, 140.69, 139.76, 133.70, 133.40, 130.30, 126.43, 126.25, 122.84, 120.58, 117.72, 117.64, 91.26, 55.14, 35.45, 31.52.

1,1′-Di-(4-*tert*-butyl)benzyl-2,2′-cyanine Tetrafluoroborate, 18. To a solution of the 1-(4-*tert*-butyl)benzyl-2-methylquinolinium iodide **16** (0.13 g, 3.1 mmol) and the 1-(4-*tert*-butyl)benzyl-2-chloroquinolinium tetrafluoroborate **17** (0.12 g, 3.1 mmol) in acetonitrile (3.8 mL) was added triethylamine (87 μL, 6.2 mmol). The resulting red solution was heated at reflux for 40 min before the acetonitrile was removed in vacuo to give a red oil which was purified by recrystallization from a small amount of methanol to give 0.14 g (67%) of the cyanine **18** as green metallic crystals: mp 280−281 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.12 (d, J = 9.3 Hz, 2H), 7.92−7.87 (m, 4H), 7.69 (t, J = 8.0 Hz, 2H), 7.55−7.48 (m, 4H), 7.27 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.4 Hz, 4H), 5.28 (s, 4H), 5.21 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (CD_3CN, 300 MHz) δ 155.38, 151.67, 140.99, 139.60, 134.00, 130.71, 130.33, 127.10, 126.41, 126.20, 126.08, 122.41, 117.61, 91.99, 54.20, 35.18, 31.55; ^{11}B NMR (CD_3CN, 400 MHz) δ −0.73. Anal. Calcd for $C_{41}H_{43}BF_4N_2 \cdot H_2O$: C, 73.65; H, 6.78; N, 4.19. Found: C, 73.64; H, 6.82; N, 4.15.

(+)-Tetramethylammonium Spirobi[(2-methyl)borataxanthene], (+)-19a. To a solution of the resolved chiral quaternary ammonium spiroborate **(−)-8a** (0.096 g, 0.16 mmol) in benzene/acetonitrile (7 mL, 3:1 vol:vol) was added excess tetramethylammonium chloride (0.17 g, 1.6 mmol). The suspension formed was stirred and heated at a gentle reflux in a 74 °C bath under argon atmosphere for 9 h. The solvent was removed in vacuo to leave a white solid which was dissolved in acetonitrile/water (40 mL, 1:1 vol:vol) and washed with hexane (2 × 20 mL). The acetonitrile was removed by placing the aqueous layer under a stream of nitrogen which facilitated the precipitation of the tetramethylammonium borate **(+)-19a** as fine white needles, 54 mg (77%): mp > 360 °C; $[\alpha]_D$ = +42.4° (*c* 1.00, NO_2Me); ^{1}H NMR (CD_3CN, 300 MHz) δ 6.85 (t, J = 7.7 Hz, 2H), 6.79 (d, J = 6.6 Hz, 2H), 6.74−6.70 (m, 4H), 6.68−6.62 (m, 2H), 6.55 (t, J = 7.1 Hz, 2H), 6.47 (d, J = 7.1 Hz, 2H), 3.03 (s, 12H), 1.60 (s, 6H); ^{13}C NMR (CD_3CN, 300 MHz) δ 158.14, 156.46, 145.19 (q, J = 47 Hz), 144.89, 140.90 (q, J = 49 Hz), 137.59, 125.88, 125.18, 124.55, 122.05, 114.36, 113.42, 56.28, 23.05.

(−)-Tetramethylammonium Spirobi[(2-methyl)borataxanthene], (−)-19a. The synthesis was carried out in the same manner as that for the (+)-enantiomer, **(+)-19a**, with the exception that the (+) enantiomer of the chiral quaternary ammonium spiroborate **(+)-8a** (0.35 g, 0.56 mmol) was used to give 0.23 g (91%) of the tetramethylammonium spiroborate **(−)-19a** as white needles: mp > 340 °C; $[\alpha]_D$ = −46.4° (*c* 1.00, NO_2Me); ^{1}H NMR (CD_3CN, 300 MHz) δ 6.85 (t, J = 7.8 Hz, 2H), 6.78 (d, J = 6.5 Hz, 2H), 6.73−6.70 (m, 4H), 6.67−6.61 (m, 2H), 6.55 (t, J = 7.1 Hz, 2H), 6.47 (d, J = 7.3 Hz, 2H), 3.04 (s, 12H), 1.59 (s, 6H).

(+)-Tetramethylammonium Spirobi[(3-methyl)borataxanthene], (+)-19b. To a solution of the optically active chiral quaternary ammonium spiroborate **(+)-8b**[67] (75 mg, 0.12 mmol) in benzene/acetonitrile (5 mL, 3:1 vol:vol) was added excess tetramethylammonium chloride (0.13 g, 1.2 mmol). The suspension formed was stirred and heated at a gentle reflux in a 74 °C bath under nitrogen for 17 h. The solvent was removed in vacuo to leave a white solid which was dissolved in acetonitrile/water (20 mL) and washed with hexane (2 × 10 mL). The acetonitrile was removed by placing the aqueous layer under a stream of nitrogen which facilitated the precipitation of the tetramethylammonium borate **(+)-19b** as fine white needles, 94 mg (86%): $[\alpha]_D$ = −6.3° (c 1.0, CH_3CN); mp > 225 °C (lit. mp > 300 °C);[35] ^{1}H NMR (CD_3CN, 300 MHz) δ 6.87 (t, J = 7.2 Hz, 2H), 6.82 (d, J = 8.1 Hz, 2H), 6.76−6.71 (m, 4H), 6.70 (dd, J = 8.3, 2.2 Hz, 2H), 6.65 (td, J = 7.0, 1.3 Hz, 2H), 6.57−6.54 (m, 2H), 3.02 (s, 12H), 2.03 (s, 6H).

(−)-Tetramethylammonium Spirobi[(3-methyl)borataxanthene], (−)-19b. To a solution of the optically active chiral quaternary ammonium spiroborate **(−)-8b**[67] (0.15 g, 0.25 mmol) in benzene/acetonitrile (11 mL, 3:1 vol:vol) was added excess tetramethylammonium chloride (0.27 g, 2.4 mmol). The suspension formed was stirred and heated at a gentle reflux in a 74 °C bath under nitrogen for 11 h. The solvent was removed in vacuo to leave a white solid which was dissolved in acetonitrile/water (50 mL) and washed with hexane (3 × 10 mL). The acetonitrile was removed by placing the aqueous layer under a stream of nitrogen which facilitated the precipitation of the tetramethylammonium borate **(−)-19b** as fine white needles, 94 mg (86%): $[\alpha]_D$ = −4.28° (c 1.0, CH_3CN); mp > 225 °C (lit. mp > 300 °C);[35] ^{1}H NMR (CD_3CN, 300 MHz) δ 6.88 (t, J = 7.2 Hz, 2H), 6.83 (d, J = 7.7 Hz, 2H), 6.78−6.73 (m, 4H), 6.70 (dd, J = 8.2, 2.2 Hz, 2H), 6.65 (td, J = 6.9, 1.7 Hz, 2H), 6.59−6.55 (m, 2H), 3.02 (s, 12H), 2.03 (s, 6H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.52, 155.54, 144.27 (q, J = 47 Hz), 144.02 (q, J = 47 Hz), 137.06, 136.85, 130.33, 125.75, 125.03, 121.90, 114.75, 114.66, 56.06, 20.89; ^{11}B NMR (CD_3CN, 300 MHz) δ −18.75.

1,1′,3,3,3′,3′-Hexamethylindocarbocyanine Spirobi[(3-methyl)-borataxanthene], Cy_{Me}^+ 3MeSpB$^-$. To a hot solution of the (+)-tetramethylammonium spiroborate **(+)-19b** (32 mg, 0.07 mmol) and 1,1′,3,3,3′,3′-hexamethylindocarbocyanine iodide[69] (40 mg, 0.07 mmol) in acetonitrile (5 mL) was added enough water to cause precipitation of a white solid to begin. Additional acetonitrile (2 mL) was added to clarify the solution, and it was allowed to cool. The resulting solid was collected by vacuum filtration to give 46 mg (88%) of the cyanine spiroborate Cy_{Me}^+ 3MeSpB$^-$ as metallic green crystals: mp > 225 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.43 (t, J = 13.4 Hz, 1H), 7.50 (d, J = 7.3 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.28 (q, J = 8.3 Hz, 4H), 6.88−6.80 (m, 4H), 6.75−6.62 (m, 8H), 6.55 (s, 2H), 6.25 (d, J = 13.7 Hz, 2H), 3.54 (s, 6H), 2.02 (s, 6H), 1.70 (s, 12H); ^{13}C NMR (CD_3CN, 400 MHz) δ 176.08, 157.51, 155.53, 143.87, 141.74, 137.09, 136.88, 130.31, 130.26, 129.64, 126.32, 125.72, 125.00, 123.20, 123.17, 121.90, 121.85, 114.74, 114.66, 112.05, 103.19, 50.20, 32.07, 27.96, 20.89; ^{11}B NMR (CD_3CN, 300 MHz) δ −18.73. Anal. Calcd for $C_{43}H_{42}NO_2B$: C, 83.89; H, 6.88; N, 2.28; B, 1.76. Found: C, 83.83; H, 6.86; N, 2.38; B, 1.67. The synthesis was repeated with the (−)-tetramethylammonium spiroborate **(−)-19b** yielding a cyanine borate with identical properties.

(−)-1,1′,3,3,3′,3′-Hexamethyl-9-phenylindocarbocyanine Spirobi-[(3-methyl)borataxanthene], (−)$PhCy_{Me}^+$ 3MeSpB$^-$. To a hot solution of the (−)-tetramethylammonium spiroborate **(−)-19b** (25 mg, 0.4 mmol) and 1,1′,3,3,3′,3′-hexamethyl-9-phenylindocarbocyanine iodide **10**[67] (20 mg, 0.4 mmol) in acetonitrile (6 mL) was added enough water to cause precipitation of a solid to begin. A small portion of ethanol (2 mL) and methanol (2 mL) was added. The solution was allowed to cool and solvent evaporate for 1 day. The resulting solid was collected by vacuum filtration and dried under vacuum to afford 30 mg (85%) of the cyanine spiroborate (−)-$PhCy_{Me}^+$ 3MeSpB$^-$ as metallic green crystals: mp 150−154 °C; $\Delta\epsilon_{max(581\ nm)}$ = −1.3 cm^{-1} M^{-1} (benzene); ^{1}H NMR (CD_3CN, 300 MHz) δ 7.59−7.53 (m, 1H), 7.51 (d, J = 1.7 Hz, 1H), 7.49−7.46 (m, 5H), 7.41 (td, J = 7.7, 1.1 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 6.89−6.80 (m, 4H), 6.77−6.71 (m, 4H), 6.69 (dd, J = 8.2, 2.2 Hz, 2H), 6.63 (td, J = 6.6, 1.1 Hz, 2H), 6.58−6.54 (m, 2H), 5.66 (s, 2H), 2.98 (s, 6H), 2.01 (s, 6H), 1.55 (s, 12H); ^{13}C NMR (CD_3CN, 400 MHz) δ 178.81, 165.41, 157.54, 155.57, 145.42, 144.35 (q, J = 47 Hz), 144.03 (q, J = 47 Hz), 143.02, 141.01, 137.11, 136.90, 132.29, 130.49, 130.38, 130.29, 129.56, 126.62,

(69) The synthesis of the cyanine has been reported previously: (a) Hamer, F. M. *J. Chem. Soc.* **1927**, 2796−2804. (b) Murphy, S.; Yang, X.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2411−22.

125.73, 124.99, 123.61, 121.87, 114.75, 114.66, 112.52, 100.30, 51.70, 37.50, 26.88, 20.91.

(+)-1,1′,3,3,3′,3′-Hexamethyl-9-phenylindocarbocyanine Spirobi-[(3-methyl)borataxanthene], (+)PhCy$_{Me}^+$ 3MeSpB$^-$. The cyanine spiroborate was synthesized in the same manner as that for the (−)-enantiomer, with the exception that the (+)-enantiomer of the tetramethylammonium spiroborate **(+)-19b** (98 mg, 0.22 mmol) was used to give 0.15 g (85%) of the cyanine spiroborate (+)-PhCy$_{Me}^+$ 3MeSpB$^-$ as a purple solid: $\Delta\epsilon_{max(581\ nm)} = +1.9\ cm^{-1}\ M^{-1}$ (benzene); mp 150−154 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 7.58−7.54 (m, 1H), 7.51−7.44 (m, 6H), 7.40 (td, J = 7.7, 1.2 Hz, 2H), 7.29 (td, J = 7.3, 0.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 6.86 (td, J = 7.4, 1.8 Hz, 2H), 6.81 (d, J = 7.9 Hz, 2H), 6.75−6.71 (m, 4H), 6.68 (dd, J = 8.2, 2.1 Hz, 2H), 6.63 (td, J = 7.0, 1.3 Hz, 2H), 6.57−6.54 (m, 2H), 5.66 (s, 2H), 2.98 (s, 6H), 2.01 (s, 6H), 1.55 (s, 12H). Anal. Calcd for $C_{57}H_{53}BN_2O_2$: C, 84.64; H, 6.60; N, 3.46. Found: C, 84.49; H, 6.69; N, 3.44.

(+)-1,1′,3,3,3′,3′-Hexamethyl-9-phenylindocarbocyanine Spirobi-[(2-methyl)borataxanthene], (+)PhCy$_{Me}^+$ 2MeSpB$^-$. To a hot solution of the (−)-tetramethylammonium spiroborate **(−)-19a** (23 mg, 0.5 mmol) and 1,1′,3,3,3′,3′-hexamethyl-9-phenylindocarbocyanine iodide **10**[67] (29 mg, 0.4 mmol) in acetonitrile (15 mL) was added enough water to cause precipitation of a solid to begin. A small portion of acetonitrile (5 mL) was added, and the homogeneous solution was allowed to cool. Over a period of 2 days in the dark the solvent partially evaporated resulting in precipitation of a solid which was collected by vacuum filtration and dried under vacuum to afford 34 mg (84%) of the cyanine spiroborate (+)PhCy$_{Me}^+$ 2MeSpB$^-$ as purple crystals: $\Delta\epsilon_{max(589\ nm)} = +1.7\ cm^{-1}\ M^{-1}$ (benzene); mp 150−153 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 7.60−7.53 (m, 1H), 7.52 (d, J = 1.1, 1H), 7.49−7.45 (m, 5H), 7.41 (td, J = 7.7, 1.1 Hz, 2H), 7.30 (td, J = 7.1, 1.1 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 6.84 (t, J = 7.7 Hz, 2H), 6.81−6.76 (m, 2H), 6.73−6.70 (m, 4H), 6.67−6.61 (m, 2H), 6.54 (td, J = 7.1, 1.1 Hz, 2H), 6.46 (d, J = 7.1 Hz, 2H), 5.66 (s, 2H), 2.99 (s, 6H), 1.59 (s, 6H), 1.55 (s, 12H). Anal. Calcd for $C_{57}H_{53}BN_2O_2{\cdot}CH_3CN$: C, 83.38; H, 6.64; N, 4.94. Found: C, 83.23; H, 6.58; N, 5.06.

(−)-1,1′,3,3,3′,3′-Hexamethyl-9-phenylindocarbocyanine Spirobi-[(2-methyl)borataxanthene], (−)PhCy$_{Me}^+$ 2MeSpB$^-$. The cyanine spiroborate was synthesized in the same manor as that for the (+)-enantiomer**,** with the exception that the (+)-enantiomer of the tetramethylammonium spiroborate **(+)-19b** (98 mg, 0.22 mmol) was used to give 45 mg (98%) of the cyanine spiroborate (−)-PhCy$_{Me}^+$ 2MeSpB$^-$ as a purple solid: $\Delta\epsilon_{max(589\ nm)} = -1.7\ cm^{-1}\ M^{-1}$ (benzene); mp 150−153 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 7.58−7.54 (m, 1H), 7.51 (t, J = 0.7, 1H), 7.50−7.45 (m, 5H), 7.41 (td, J = 7.9, 1.3 Hz, 2H), 7.30 (td, J = 6.9, 0.7 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.84 (t, J = 7.6 Hz, 2H), 6.80−6.71 (m, 2H), 6.73−6.69 (m, 4H), 6.66−6.61 (m, 2H), 6.54 (td, J = 7.1, 1.4 Hz, 2H), 6.46 (d, J = 7.2 Hz, 2H), 5.66 (s, 2H), 2.99 (s, 6H), 1.59 (s, 6H), 1.55 (s, 12H); ^{13}C NMR (CD_3CN, 400 MHz) δ 178.84, 165.44, 157.56, 145.45, 144.64 (q, J = 46 Hz), 144.36, 143.03, 141.03, 140.42 (q, J = 49 Hz), 137.10, 132.27, 130.44, 130.39, 126.62, 125.40, 124.70, 124.08, 123.62, 121.58, 113.91, 112.99, 112.52, 100.31, 51.72, 37.51, 26.87, 22.98, 22.93.

(+)-1,1′-Diethyl-2,2′-cyanine Spirobi[(3-methyl)borataxanthene], (+)Cy$_{Et}^+$ 3MeSpB$^-$. The 1,1′-diethyl-2,2′-cyanine iodide (Aldrich) was recrystallized from methanol prior to use. To a hot solution of the (+)-tetramethylammonium spiroborate **(+)-19b** (23 mg, 0.5 mmol) and 1,1′,-diethyl-2,2′-cyanine iodide (23 mg, 0.5 mmol) in acetonitrile (8 mL) was added enough water to cause precipitation of a solid to begin. A small portion of acetonitrile (2 mL) was added, and the homogeneous solution was allowed to cool and solvent evaporate in the dark. The resulting solid was collected to afford 0.29 g (79%) of the cyanine (+)-Cy$_{Et}^+$ 3MeSpB$^-$ spiroborate as a red solid: $\Delta\epsilon_{max(533\ nm)} = +0.5\ cm^{-1}\ M^{-1}$ (benzene); mp 130−133 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 7.92 (d, J = 9.6 Hz, 2H), 7.83−7.76 (m, 6H), 7.71 (d, J = 9.6 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 6.85 (t, J = 7.2 Hz, 2H), 6.80 (d, J = 7.5 Hz, 2H), 6.75−6.70 (m, 4H), 6.67 (dd, J = 8.1, 2.2 Hz, 2H), 6.62 (td, J = 6.9, 1.4 Hz, 2H), 6.56−6.53 (m, 2H), 5.55 (s, 1H), 4.47 (q, J = 7.2 Hz, 4H), 2.00 (s, 6H), 1.55 (t, J = 7.4 Hz, 6H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.55, 155.57, 154.83, 144.34 (q, J = 47 Hz), 144.03 (q, J = 47 Hz), 140.20, 138.95, 137.10, 136.89, 133.74, 130.46, 130.33, 126.13, 125.75, 125.02, 122.60, 121.90, 121.86, 117.21, 114.76, 114.66, 86.63, 45.79, 20.89, 12.24. Anal. Calcd for $C_{49}H_{43}BN_2O_2$: C, 83.75; H, 6.17; N, 3.99. Found: C, 83.13; H, 6.32; N, 4.10.[68]

(−)-1,1′-Diethyl-2,2′-cyanine Spirobi[(2-methyl)borataxanthene], (−)-Cy$_{Et}^+$ 2MeSpB$^-$. The cyanine spiroborate was synthesized in the same manner as that used for Cy$_{Et}^+$ 3MeSpB$^-$ with the exception that (+)-tetramethylammonium spiroborate **(+)-19a** (0.22 mg, 5 mmol) was used to afford 29 mg (82%) of the cyanine spiroborate (−)-Cy$_{Et}^+$ 2MeSpB$^-$ as pink needles: $\Delta\epsilon_{max(532\ nm)} = -3.1\ cm^{-1}\ M^{-1}$ (benzene); mp 220−221 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 7.95 (d, J = 9.6 Hz, 2H), 7.84−7.77 (m, 6H), 7.73 (d, J = 9.3 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 6.83 (t, J = 7.6 Hz, 2H), 6.83 (t, J = 7.6 Hz, 2H), 6.78 (t, J = 7.2 Hz, 2H), 6.72−6.69 (m, 4H), 6.65−6.61 (m, 2H), 6.53 (td, J = 7.2, 1.4 Hz, 2H), 6.45 (d, J = 7.2 Hz, 2H), 5.56 (s, 1H), 4.49 (q, J = 7.2 Hz, 4H), 1.58 (s, 6H), 1.57 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.55, 155.86, 154.80, 144.62 (q, J = 46 Hz), 144.35, 140.47 (q, J = 49 Hz), 140.17, 138.90, 137.08, 133.70, 130.29, 126.11, 125.39, 124.68, 124.05, 122.73, 122.56, 121.57, 117.19, 113.90, 112.97, 89.61, 45.78, 22.97, 12.23. Anal. Calcd for $C_{49}H_{43}BN_2O_2$: C, 83.75; H, 6.17; N, 3.99. Found: C, 82.06; H, 6.21; N, 4.24.[68]

(+)-1,1′-Di-(4-*tert*-butyl)benzyl-2,2′-cyanine Spirobi[(2-methyl)-borataxanthene], (+)Cy$_{4tBz}^+$ 2MeSpB$^-$. To a hot solution of the (−)-tetramethylammonium spiroborate **(+)-19a** (23 mg, 0.5 mmol) and 1,1′-di-(4-*tert*-butyl)benzyl-2,2′-cyanine tetrafluoroborate **18** (27 mg, 0.5 mmol) in acetonitrile (15 mL) was added enough water to cause precipitation of a solid to begin. A small portion of acetonitrile (2 mL) was added to reform a homogeneous solution. Over a period of 2 days in the dark the solvent partially evaporated resulting in precipitation of a solid which was collected by vacuum filtration and dried under vacuum to yield 36 mg (75%) of the cyanine spiroborate (+)-Cy$_{4tBz}^+$ 2MeSpB$^-$ as red needles: $\Delta\epsilon_{max(533\ nm)} = +4.0\ cm^{-1}\ M^{-1}$ (benzene); mp 249−251 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.07 (d, J = 9.5 Hz, 2H), 7.87−7.86 (m, 2H), 7.85−7.84 (m, 2H), 7.66 (t, J = 8.0 Hz, 2H), 7.48 (t, J = 7.8 Hz, 4H), 7.26 (d, J = 8.4 Hz, 4H), 6.82 (t, J = 7.6 Hz, 2H), 6.76 (t, J = 7.4 Hz, 2H), 6.72−6.67 (m, 8H), 6.65−6.60 (m, 2H), 6.50 (td, J = 7.0, 1.4 Hz, 2H), 6.43 (d, J = 7.3 Hz, 2H), 5.22 (s, 4H), 5.18 (s, 1H), 1.57, (s, 6H), 1.33 (s, 18H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.55, 155.88, 155.34, 151.68, 144.63 (q, J = 46 Hz), 144.36, 141.98, 140.42 (q, J = 49 Hz), 139.68, 137.70, 134.00, 130.70, 130.34, 127.11, 126.43 126.21, 126.07, 125.40, 124.70, 122.38, 121.56, 117.63, 113.93, 112.99, 92.01, 54.17, 35.20, 31.58, 22.97. Anal. Calcd for $C_{67}H_{63}BN_2O_2$: C, 85.70; H, 6.76; N, 2.98. Found: C, 85.14; H, 6.78; N, 2.96.[68]

(+)-1,1′-Di-(3,5-di-*tert*-butyl)benzyl-2,2′-cyanine Spirobi[(3-methyl)borataxanthene], (+)Cy$_{3,5tBz}^+$ 3MeSpB$^-$. To a hot solution of the tetramethylammonium spiroborate **(−)-19b** (17 mg, 0.4 mmol) and 1,1′-di-(3,5-*tert*-butyl)benzyl-2,2′-cyanine tetrafluoroborate **13** (30 mg, 0.4 mmol) in acetonitrile (15 mL) was added enough water to cause precipitation of a solid to begin. A small portion of acetonitrile (2 mL) was added, the homogeneous solution was allowed to cool, and evaporation of solvent under a stream of nitrogen in the dark caused precipitation. The resulting solid was collected to afford 40 mg (98%) of the cyanine spiroborate (+)-Cy$_{3,5tBz}^+$ 3MeSpB$^-$ as orange needles: $\Delta\epsilon_{max(533\ nm)} = +3.2\ cm^{-1}\ M^{-1}$ (benzene); mp 181−183 °C; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.11 (d, J = 9.3 Hz, 2H), 7.94 (d, J = 9.3 Hz, 2H), 7.86 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.1 Hz, 2H), 7.50−7.44 (m, 4H), 7.26 (s, 2H), 6.87−6.80 (m, 8H), 6.76−6.61 (m, 8H), 6.56−6.54 (m, 2H), 5.62 (s, 1H), 5.45 (s, 4H), 2.02 (s, 6H), 1.14 (s, 36H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 156.16, 154.75, 154.22, 150.90 143.23 (q, J = 47 Hz), 142.78 (q, J = 48 Hz), 139.22, 138.65, 135.96, 135.74, 132.83, 129.31, 128.43, 125.33, 124.80, 124.50, 123.70, 121.16, 120.64, 119.48, 118.10, 116.87, 113.63, 113.48, 90.43, 53.07, 53.04, 34.39, 31.03, 20.69. Anal. Calcd for $C_{75}H_{79}BN_2O_2{\cdot}CH_3CN$: C, 84.67; H, 7.57; N, 3.85. Found: C, 84.12; H, 7.49; N, 3.52.[68]

(+)-1,1′-Di-(3,5-di-*tert*-butyl)benzyl-2,2′-cyanine Spirobi[(2methyl)borataxanthene], (+)Cy$_{3,5tBz}^+$ 2MeSpB$^-$. The cyanine spiroborate was synthesized in the same manner as that used for (+)-Cy$_{3,5tBz}^+$ 3MeSpB$^-$ with the exception that tetramethylammonium spiroborate **(−)-19a** (0.22 mg, 5 mmol) was used to afford 49 mg (93%) of the cyanine spiroborate (+)-Cy$_{3,5tBz}^+$ 2MeSpB$^-$ as orange crystals: $\Delta\epsilon_{max(533\ nm)} = +6.1\ cm^{-1}\ M^{-1}$ (benzene); mp 272−274 °C; ^{1}H NMR (CD_3CN,

400 MHz) δ 8.10 (d, $J = 9.5$ Hz, 2H), 7.93 (d, $J = 9.5$ Hz, 2H), 7.86 (dd, $J = 7.7$, 1.5 Hz, 2H), 7.63 (t, $J = 8.0$ Hz, 2H), 7.49−7.45 (m, 4H), 7.26 (t, $J = 1.8$ Hz, 2H), 6.87−6.86 (m, 4H), 6.83 (t, $J = 7.6$ Hz, 2H), 6.78 (t, $J = 7.5$ Hz, 2H), 6.72−6.69 (m, 4H), 6.66−6.61 (m, 2H), 6.53 (td, $J = 7.0$, 1.1 Hz, 2H), 6.45 (d, $J = 7.3$ Hz, 2H), 5.61 (s, 1H), 5.45 (s, 4H), 1.59 (s, 6H), 1.14 (s, 36H); ^{13}C NMR (CD_3CN, 400 MHz) δ 157.56, 156.37, 155.88, 152.72, 144.63 (q, $J = 46$ Hz), 144.36, 140.69, 140.41 (q, $J = 48$ Hz), 139.69, 137.10, 133.40, 130.30, 126.43, 126.25, 125.40, 124.70, 124.07, 122.86, 121.57, 120.58, 117.74, 117.64, 113.91, 112.98, 91.25, 55.15, 35.46, 22.97. Anal. Calcd for $C_{75}H_{79}BN_2O_2$: C, 85.69; H, 7.57; N, 2.66. Found: C, 85.64; H, 7.64; N, 2.73.

General Method for Synthesis of Cyanine Tetraphenylborates. Equimolar amounts of ammonium tetraphenylborate (Aldrich) and the cyanine as the iodide or tetrafluoroborate salt were dissolved in hot acetonitrile. Water was slowly added to the hot solution until the small amount of precipitate formed persisted. A small amount of acetonitrile was added to clarify the solution which was allowed to cool in the dark. A gentle stream of nitrogen was passed over the solution to evaporate the acetonitrile. The product cyanine borate was collected from the aqueous solution.

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Supporting Information Available: Synthesis of the precursors to the cyanine borates, ROESY NMR spectra and crystal structure data (71 pages). See any current masthead page for ordering and Web access instructions.

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