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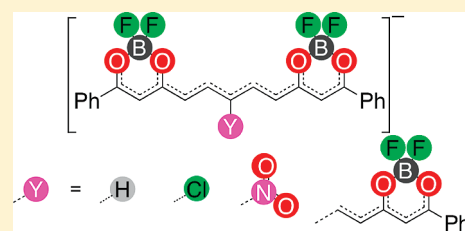
Dioxaborine- and Indole-Terminated Polymethines: Effects of Bridge Substitution on Absorption Spectra and Third-Order Polarizabilities

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Supporting Information

ABSTRACT: Cyanine-like dyes are promising candidates for third-order non-linear optical (NLO) applications such as all-optical switching. Here, we examine the consequences for linear and nonlinear optical properties of varying substituents on the central methine unit of bis(dioxaborine)-terminated anionic pentamethines and bis(indole)-terminated cationic heptamethines. The variation in absorption maxima and electrochemical potentials with structure can generally be rationalized using the Dewar–Knott rules, providing that mesomeric and inductive electron-withdrawal and donation are explicitly considered. In the case of nitro- and (dioxaborinyl)vinyl-substituted bis(dioxaborine) pentamethines, the low-energy transitions are significantly broadened, consistent with ^1H NMR spectra indicating deviation from cyanine-like geometry. Real and imaginary parts of the third-order polarizabilities, $\text{Re}(\gamma)$ and $\text{Im}(\gamma)$, were measured at $1.3\ \mu\text{m}$. The values of $\text{Im}(\gamma)$ indicate that the values of $\text{Re}(\gamma)$ are significantly resonantly enhanced, while the positive value of $\text{Re}(\gamma)$ found for a nitro-substituted dioxaborine example is atypical for a symmetrical polymethine and suggests that a two-state treatment is inadequate. The relevance of these results to chromophore design for third-order NLO applications is discussed.



INTRODUCTION

Cyanines and other symmetrical polymethines exhibit large third-order polarizabilities, γ , that are associated with the vanishing bond-length alternation found in the polymethine chains.^{1,2} Recently, we have shown that certain dioxaborine³ and selenopyrylium-terminated polymethines⁴ exhibit very large negative values of the real part of γ , $\text{Re}(\gamma)$, and large ratios of $|\text{Re}(\gamma)/\text{Im}(\gamma)|$ at telecommunications wavelengths, suggesting that, if these parameters can be translated into correspondingly attractive solid-state susceptibilities, they may be useful candidates for all-optical signal-processing (AOSP) applications^{5–7} at these wavelengths. The dependence of the optical properties on the conjugation length, L , is well-established; for a given charge-stabilizing end group, γ typically varies according to L^n ($n = 7–11$),^{5,8–10} at least up to a critical large value of L , beyond which symmetry-breaking phenomena,^{11–16} which adversely affect γ ,¹⁷ are anticipated. The linear and nonlinear optical properties of cyanines can also be modified by the choice of the charge-stabilizing end group; for example, polymethines with chalcogenopyrylium end groups give stronger and lower-energy transitions than analogues of the same length with many other types of end groups.⁴ We have also modified the properties of dioxaborine-terminated polymethines using functionalization beyond the dioxaborine end groups with substituted aryl groups¹⁸ or with bipyridine-bound transition-metal moieties;¹⁹ for example, we found that replacing post-terminal phenyl groups with stilbenyl groups led to a bathochromically shifted absorption with increased transition dipole moment, M_{ge} , and, thus, to an increased magnitude of $\text{Re}(\gamma)$,¹⁸ although this effect is much less dramatic

than that achieved by addition of an additional vinylene group to the polymethine chain.

An additional strategy for modification of the optical properties of polymethines is to introduce substituents onto the carbon atoms of the polymethine bridge. Substituent effects on the absorption maxima of cyanines and cyanine-like polymethines can often be predicted using the general color rules formulated by Dewar and Knott.^{20–22} The HOMO coefficients in cyanine-like polymethines alternate between vanishingly small and relatively large, while the LUMO coefficients also alternate, but such that those atoms with large coefficients in the HOMO will have negligible to zero LUMO coefficients and vice versa (as shown, for example, for simple streptomethines in Figure XII.2 of ref 22 and in Figure 5 of ref 23). For example, in the indole-terminated pentamethines, **1a–d**, shown in Figure 1, the HOMO has large coefficients on the nitrogen atoms and on the α and γ methine carbon atoms (“starred” atoms in the Dewar–Knott description), while the LUMO density is concentrated on the indole *ipso* carbon and β methine carbon atoms (“unstarred”). Representations of the frontier molecular orbitals of indole-terminated pentamethines consistent with this picture, obtained from quantum-chemical calculations, can be found in Figure 8 of ref 24. Accordingly, if the γ substituent, Y , is an electron-withdrawing group, the main effect will be to stabilize the HOMO relative to that of the $Y = \text{H}$ parent compound, with only a minor stabilizing

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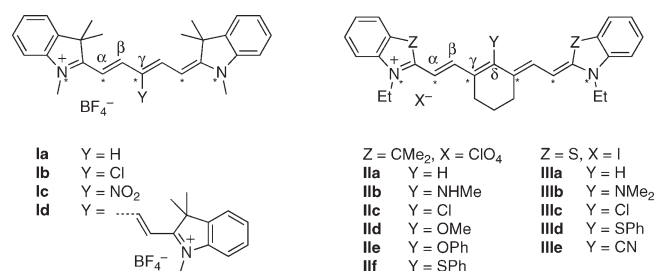


Figure 1. Examples of previously synthesized bridge-substituted pentamethine^{28,29} and heptamethine^{25–27} cyanines. “Starred” positions correspond to those at which significant HOMO coefficients are expected, while “unstarred” positions are those with significant LUMO coefficients.

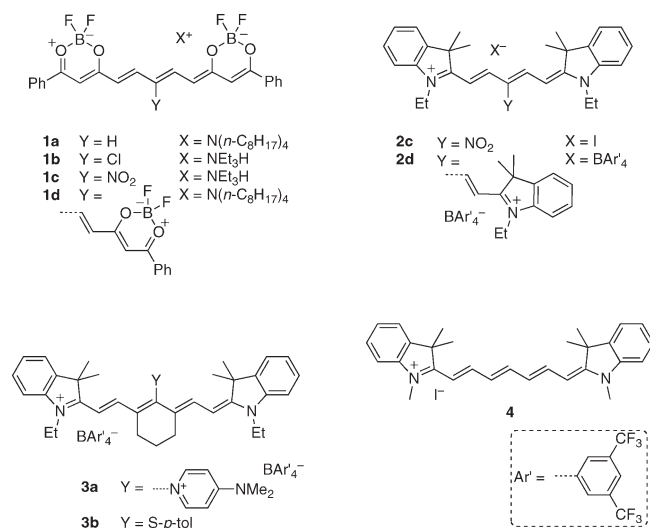


Figure 2. Polymethines for which data are reported in this work.

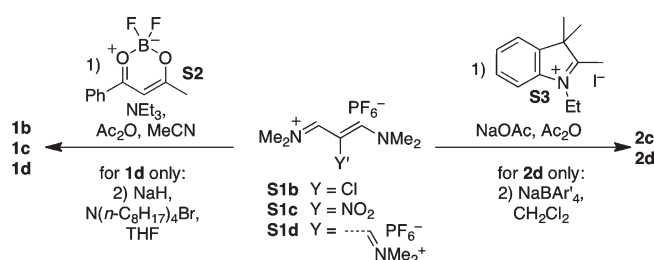
effect on the LUMO, thus causing a hypsochromic shift of the absorption maximum (assuming that, as is the case for many polymethines, the $S_0 \rightarrow S_1$ transition is well-described as a one-electron HOMO \rightarrow LUMO excitation). On the other hand, an electron-donating group will destabilize the HOMO much more significantly than the LUMO, resulting in a bathochromic shift. The opposite effects are anticipated when a substituent is introduced to one of the “unstarred” positions. Experimental optical data for a number of bridge-substituted cyanines, for example, the heptamethines **IIa–f** and **IIIa–e** shown in Figure 1,^{25–27} generally conform to these predictions. It is worth noting that often the distinction between inductive and mesomeric donor and acceptor properties is not explicitly considered by the Dewar–Knott treatment, although these two effects for many substituents act in opposition to one another (vide infra).

Here, we investigate the effects of bridge substitution of polymethines on the third-order polarizabilities in polymethine dyes, using both static (zero-frequency) values of $\text{Re}(\gamma)$, obtained from application of a two-state model to linear optical parameters, and values of $\text{Re}(\gamma)$ and $\text{Im}(\gamma)$ at 1300 nm obtained by Z-scan measurements. In particular, we focus on a series of dioxaborine-terminated pentamethine dyes, **1a–d** (Figure 2). Few studies have been performed on dioxaborine-terminated dyes that relate absorption data to bridge-substituent effects.^{30,31} Moreover, we have shown that a dioxaborine-terminated

Table 1. Modified Swain–Lupton Field and Resonance Parameters³⁵ for Some of the Substituents Discussed in This Work Arranged in Order of Increasing π Donor Strength

substituent	<i>F</i>	<i>R</i>
CN	0.51	0.15
NO ₂	0.65	0.13
H	0.03	0.00
Cl	0.42	−0.19
SPh	0.30	−0.23
OPh	0.37	−0.40
OMe	0.29	−0.56
NHMe	0.03	−0.73
NMe ₂	0.15	−0.98

Scheme 1



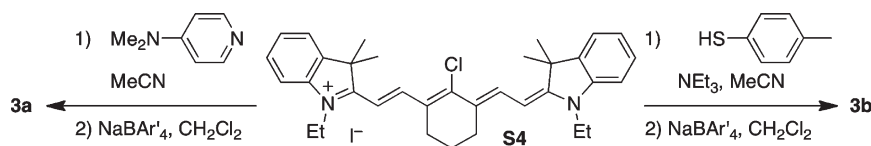
nonamethine is a promising candidate for AOSP applications;³ the Dewar–Knott rules^{20–22} predict that pentamethines and nonamethines should respond to substitution of the central bridge carbon in the same way, and so the pentamethines serve as more synthetically accessible and potentially more stable models for the nonamethines. One of the pentamethines examined, **1d**, bears a (dioxaborinyl)vinyl substituent; that is, it is an example of a branched triply terminated polymethine with 3-fold (or approximate 3-fold) symmetry.³² We have also included in our study comparisons to newly acquired optical data for the indole-terminated pentamethines, **2c–d**, and heptamethines, **3a–b** and **4**, also shown in Figure 2, and to literature optical data for the indole- and benzothiazole-terminated heptamethines, **IIa–f** and **IIIa–e**, shown in Figure 1.

RESULTS AND DISCUSSION

Substituents. The compounds synthesized (Figure 2) represent a compromise between the desire to examine a range of substituents with varying inductive and mesomeric electron-donating and -withdrawing properties, and synthetic practicalities. The inductive and mesomeric properties of substituents can be gauged using the field and resonance parameters defined by Swain and Lupton.³³ Values of modified Swain–Lupton³⁴ field and resonance parameters, F and R , respectively, available for groups used in this work or used in previous work discussed below, taken from ref 35 are summarized in Table 1. Positive values of F and R indicate inductive and mesomeric electron-withdrawing character, respectively, while negative values denote electron donation.

Synthesis. Compound **1a** was synthesized as previously described,¹⁸ while the remaining dioxaborine-terminated dyes, **1b–d**, were obtained in a similar manner from the Knoevenagel reaction between the appropriate vinamidinium salts, **S1b–S1d**,^{36–38} with

Scheme 2

Table 2. ^{13}C NMR Chemical Shifts (ppm) for the Methine Nuclei of **1a–d** and **1a–d** in CD_3CN and CDCl_3 , Respectively

Y	dye	α	β	γ	dye	α	β	γ
H	1a	110.6	152.6	121.5	1a ²⁹	103.3	154.0	125.2
Cl	1b	108.1	146.6	120.5	1b ²⁹	100.0	147.4	122.3
NO_2	1c	110.2	140.4	130.8	1c ²⁹	102.3	141.5	131.5
branched	1d	112.7	147.0	118.0	1d ²⁸	106.5	149.5	121.8

2,2-difluoro-4-phenyl-6-methyl-1,3,2(2*H*)-dioxaborine **S2**³⁹ in the presence of base (Scheme 1). Compound **1d** was isolated as a tetra-*n*-octylammonium salt to facilitate purification; as described previously for **1a** and related compounds, the corresponding triethylammonium salt was converted to a sodium salt by treatment with sodium hydride, which was then treated with tetra-*n*-octylammonium bromide.¹⁸ Compounds **2c** and **2d** were synthesized for comparison to **1c** and **1d**, respectively, by condensation of **S1c** and **S1d** with 1-ethyl-2,3,3-trimethylindolinium iodide **S3**,⁴⁰ followed in the case of **2d** by anion metathesis using NaBAr'_4 ($\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) to improve solubility and ease of purification. Compounds **3a** and **3b** were synthesized by reaction of 4-methylbenzenethiol or 4-(dimethylamino)pyridine with the iodide salt of the corresponding chloro-substituted cyanine, **S4**,^{26,27} followed by counterion metathesis with NaBAr'_4 (Scheme 2), and were compared to commercially available **4**. Experimental details and characterizing data are given in the Supporting Information.

Charge-Density Distribution. As discussed above, the HOMOs of cyanine-like polymethines exhibit alternating large and negligible coefficients along the polymethine chain; this results in the pattern of alternating electron density first proposed by König,⁴¹ and first shown experimentally using ^1H NMR spectroscopy by Dähne and Ranft.⁴² To examine the relationship of the present dioxaborine polymethines to more typical cyanines, we compared the ^{13}C NMR shifts for the polymethine carbon nuclei of **1a–d** to those of their indole-terminated analogues **1a–d** (Figure 2).^{28,29} In the case of **1a**, an HSQC spectrum was used to unambiguously assign the polymethine nuclei (see the Supporting Information). The chemical shift data are shown in Table 2,⁴³ and the variations in shift with substituent are illustrated graphically in the Supporting Information. Both classes of dye show very similar patterns in the chemical shifts; in particular, the α and γ methine carbons are generally shifted upfield relative to the β carbons, consistent with high positive charge densities on the α and γ positions. For **1a–d**, this is consistent with the expectation that a cyanine should exhibit significant HOMO coefficients on the donor nitrogen atoms and every second intermediate carbon atom (the “starred” positions shown in Figure 1). For **1a–d**, the data support the results of DFT calculations presented in Figure 6 of ref 18 that show the HOMO of **1a** to be primarily located on the dioxaborine moieties and on the α and γ positions of the bridge; thus, the dioxaborines,

Table 3. Electrochemical Potentials (V vs Ferrocenium/Ferrocene) for Dioxaborine-Terminated Pentamethines in $\text{THF}/0.1\text{ M }^n\text{Bu}_4\text{NPF}_6^a$

dye	Y	0/–	–/2–	2–/3–
1a	H	–0.12 ^b	–1.49	–2.62 ^c
1b	Cl	–0.08 ^c	–1.43	–2.09 ^c
1c	NO_2	+0.34 ^c	–1.41	–1.41 ^{c,d}
1d	branched	+0.08 ^c	–1.37 ^c	

^a Redox processes are reversible, and reported potentials are half-wave potentials, $E_{1/2}$, unless otherwise stated. Potentials corresponding to one-electron oxidation and reduction of the closed-shell polymethine dye defined by the compound numbers are in bold and italic, respectively. ^b Irreversible; peak potential, E_{ox} , at 50 mV s^{-1} reported. ^c EC-type process for which $I_{\text{red}} \ll I_{\text{ox}}$ (for 0/– couples) or $I_{\text{ox}} \ll I_{\text{red}}$ (for –/2– and 2–/3– couples). ^d First and second reduction overlap; a third reduction is observed at $E_{1/2} = \text{ca. } -2.00\text{ V}$.

1, show a pattern of “starred” and “unstarred” positions analogous to indole-terminated cyanines of comparable length,⁴⁴ **1** and **2**, and suggest that the HOMO of pentamethine (and non-amethine) examples will be primarily affected by substitution at the γ position.

Electrochemistry. As discussed above, NMR data and previously reported DFT results¹⁸ suggest that γ substitution of dioxaborine pentamethines should primarily affect the HOMO. Cyclic voltammetry confirms this hypothesis; the potentials shown in Table 3 indicate that there is a significant variation in the ease of oxidation of the anionic polymethine⁴⁴ to a neutral radical (i.e., removal of an electron from the HOMO), while the potentials for reduction to a radical dianion (addition of an electron to the LUMO) show less variation with Y. Moreover, **1c** is much less easily oxidized and somewhat more easily reduced than **1a**, consistent with the positive *F* and *R* values for NO_2 (Table 1). Comparison of **1b** and **1a** suggests that, in this series of compounds at least, the inductive electron-withdrawing properties of Cl dominate over its π -donor properties, although the overall differences are small. Finally, the (dioxaborinyl)vinyl substituent in **1d** appears to behave as an electron-withdrawing moiety, as is expected from the π -acceptor behavior of dioxaborines linked through their 4- or 6-positions found in other contexts.^{30,45,46}

Cyclic voltammetry was also performed on the indole-heptamethines **3a**, **3b**, and **4** (Table 4). Both **3a** and **3b** are less readily reduced and more readily oxidized than **4**, indicating that the δ substituents exert an overall electron-withdrawing effect. Both oxidation and reduction features for **4** are consistent with electrochemical-chemical (EC) processes in which reverse currents are considerably diminished due to instability of the radical dication and the neutral radical, respectively. However, both processes are reversible for **3a** and **3b**, the increased stability of the redox products likely arising from the effects of incorporating part of the polymethine chain into a ring.^{47,48}

Linear Optical Properties. Parameters (absorption maximum, λ_{\max} , peak absorptivity, ϵ_{\max} and transition dipole moment, M_{ge}) characterizing the strong low-energy absorptions of **1a–d**, assigned to the $S_0 \rightarrow S_1$ transitions, along with those of indole analogues **2c,d** (which differ only from **1c,d**, Figure 1, in the *N*-alkyl substituent and the counterion), are collected in Table 5, while the absorption spectra of **1a–d** are shown in Figure 3a. Comparison of the data for **1a** and **1b** shows that chloro substitution leads to only a very slight hypsochromic shift of λ_{\max} . The similarity of Y = H and Cl derivatives is consistent with previous work on indole-terminated pentamethines; absorption maxima of 641 and 647 nm have been reported for close analogues of **1a** (differing in having a ClO_4^- counterion) and **1b** (differing in having *N*-*n*-butyl substituents and a ClO_4^- counterion) in ethanol or methanol,⁴⁹ but can be contrasted to the case of indole- and benzothiazole-terminated heptamethines

Table 4. Electrochemical Potentials (V vs Ferrocenium/Ferrocene) for Indole-Terminated Heptamethines in THF/0.1 M $\text{N}^+\text{Bu}_4\text{NPF}_6^a$

	Y	3+/2+	2+/+	+/0
3a	$\text{N}^+\text{C}_5\text{H}_4\text{-4-NMe}_2$	+0.16	−0.95	
3b	<i>S-p</i> -tol		+0.11	−1.05
4	H	+0.04 ^b	−0.13 ^b	−1.12 ^b

^a Redox processes are reversible, and reported potentials are half-wave potentials, $E_{1/2}$, unless otherwise stated. Potentials corresponding to one-electron oxidation and reduction of the closed-shell polymethine dye defined by the compound numbers are in bold and italic, respectively. ^b EC-type processes ($I_{\text{red}} \ll I_{\text{ox}}$ for 3+/2+ and 2+/+ couple; $I_{\text{ox}} \ll I_{\text{red}}$ for +/0 couple).

(Figure 1, Table 6, vide infra), where chloro substitution in the central (unstarred) position leads to a much larger bathochromic shift. This can be understood in terms of the competing inductive and mesomeric effects of Cl (Table 1); presumably, the π -donor effect in the heptamethines is relatively minor due to the large energy mismatch between the LUMO of the heptamethine bridge and the Cl $p\pi$ orbital, allowing the inductive effect to dominate, lowering the LUMO more significantly, due to its large coefficient on the δ carbon. In contrast, in **1b**, the Cl $p\pi$ orbital interacts more strongly with the pentamethine HOMO, due to the smaller energy mismatch, the result of which is to largely cancel out the greater inductive stabilization of the HOMO versus the LUMO, as shown schematically in Figure 4 and consistent with the electrochemical data for **1a** versus **1b**. This result emphasizes the limitations of attempting to strictly define substituents as electron withdrawing or electron donating; not only is there an interplay of inductive and resonance effects in some cases, but the overall effect on the spectra may vary from system to system.

The large hypsochromic shift seen between **1a** and **1c** is more straightforwardly explained; NO_2 is both inductively and mesomerically electron withdrawing, thus leading to preferential stabilization of the HOMO (and, thus, to a larger effect on the oxidation potential than the reduction potential). The same hypsochromic shift is also seen on comparing **2c** with its unsubstituted analogue ($\lambda_{\max} = 641$ nm for the ClO_4^- analogue of **1a** in ethanol).⁴⁹ Nitro substitution in both dioxaborine- and indole-terminated systems also results in a considerable decrease in the peak absorptivity and in the transition dipole moment of the low-energy band. As shown in Figure 3a, the low-energy band of **1c** also has a somewhat different band shape from that of **1a**

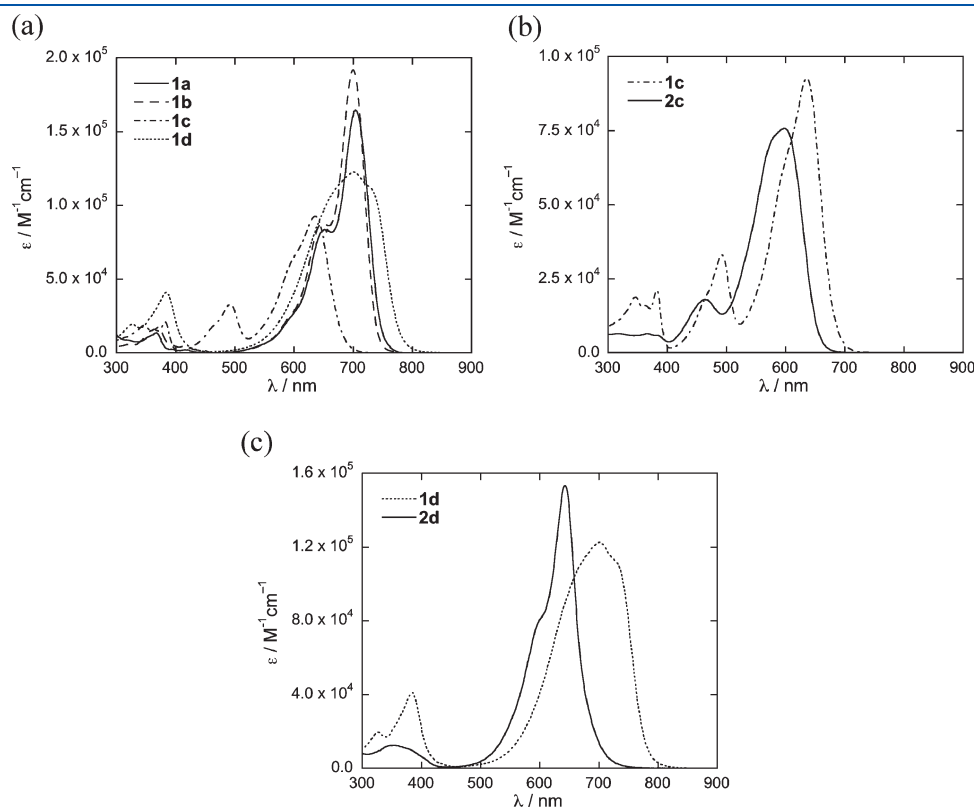


Figure 3. Absorption spectra in DMSO of (a) dioxaborine-terminated pentamethines **1a–d**, (b) γ -nitro-substituted dioxaborine- and indole-terminated pentamethines **1c** and **2c**, and (c) branched dioxaborine- and indole-terminated dyes **1d** and **2d**.

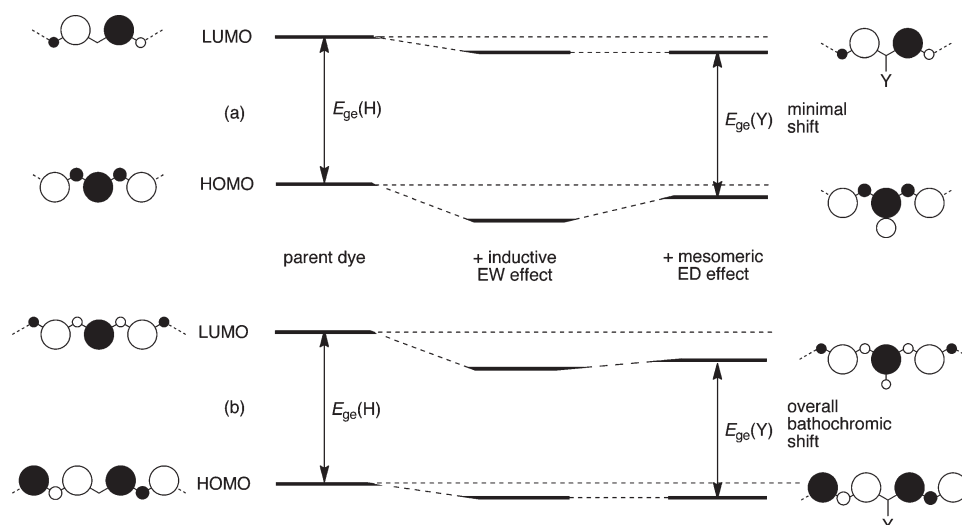


Figure 4. Schematic showing how a substituent Y with opposing inductive and mesomeric effects (such as Cl or SAR) affects the energy of the frontier molecular orbitals and can lead to (a) little change in the absorption spectrum when present in a “starred” position and (b) a bathochromic shift when present in an “unstarred” position. The phase and relative magnitude of contributions from atomic orbitals for the central polymethine portions of (a) pentamethines and (b) heptamethines with end groups such as indole or dioxaborine (end groups not shown) are shown schematically; these representations are based on figures published elsewhere showing the results of quantum-chemical calculations for various polymethines (for example, see refs 18,22–24).

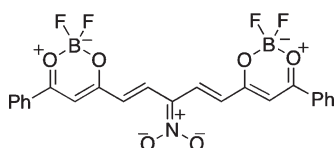


Figure 5. Resonance structure responsible for increased $C_{\alpha}-C_{\beta}$ double-bond character seen in **1c**.

and **1b** with a more significant vibronic shoulder. The band shape of **2c** (as compared to that of **1c** in Figure 3b) also differs from that of typical indole-terminated cyanine; in both cases, these bandshapes are consistent with a larger geometric change between ground and excited states than is typical for cyanine-like polymethines. Indeed, ^1H NMR spectroscopy suggests that the ground-state structures of the nitro-substituted chromophores deviate significantly from the ideal cyanine-like case in which the $C-C$ bonds of the polymethine chain are all approximately equal. Thus, while the coupling constant between the α and β protons of **1b** is ca. 12.5 Hz, the corresponding value in **1c** is 14.5 Hz, suggesting that the $C_{\alpha}-C_{\beta}$ bond exhibits increased double-bond character, as represented by contributions from the valence-bond structure shown in Figure 5. The spectra of both **1c** and **2c** also show a second band at higher energy, with vibronic structure similar to the low-energy band, occupying a region where typical polymethine dyes have a window of high transparency;^{3,4,9,24} this band may be associated with a transition from the HOMO to a low-lying nitro-localized orbital. This assignment is fully consistent with results obtained from steady-state fluorescence excitation anisotropy measurements (see the Supporting Information), which indicate a markedly different polarization for this higher energy band as compared to the energetically lowest lying band, specifically that the two transition dipole moments are oriented ca. 64° with respect to one another.

The low-energy transitions of the branched polymethine dyes with three termini, **1d** and **2d**, are at energies similar to their linear analogues with two termini, but are broader; in particular,

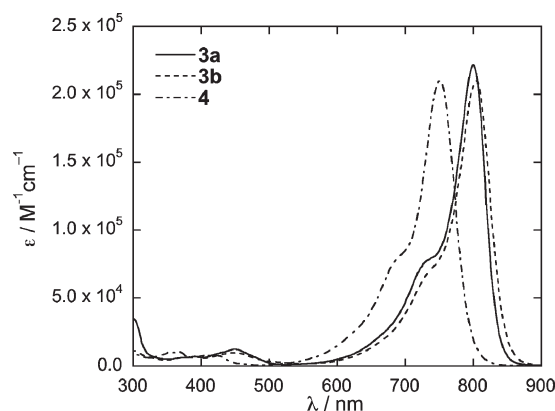


Figure 6. Absorption spectra of indole-terminated heptamethines **3a**, **3b** and **4**, in DMSO.

1d shows a markedly different vibronic structure from **1a**, with the 0,0 transition no longer being the strongest. This behavior qualitatively resembles that seen for other symmetrically branched polymethines,^{49–52} where differences in bandshapes have been attributed to increased vibronic coupling associated with increased $C_{\alpha}-C_{\beta}$ double bond character and increased (end-group)- C_{α} and $C_{\beta}-C_{\gamma}$ single bond character in the ground-state geometry, although the presence of multiple conformers may also play a role.⁴⁹ ^1H NMR coupling constants ($J_{\alpha\beta} = 15.6$ Hz for **1d**) provide evidence for this structural feature, which is consistent with equal contributions from three equivalent valence-bond structures, in each of which two of the $C_{\alpha}-C_{\beta}$ bonds are double and one single. This situation is similar to that proposed for the nitro-substituted examples above in which, however, one of the three principal valence-bond structures (that shown in Figure 5) is somewhat higher in energy than the other two. The similarity in absorption maxima for branched and unbranched compounds, which is consistent with observations for other branched and unbranched dyes,^{49–52} is not readily rationalized

Table 5. Absorption Maxima, Peak Absorptivities, and Transition Dipole Moments for the Low-Energy Transitions of Dioxaborine- and Indole-Terminated Pentamethines in DMSO

	Y	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/10^5 \text{ M}^{-1} \text{ cm}^{-1a}$	$M_{\text{ge}}/D^{a,b}$
1a	H	705	1.65	13.9
1b	Cl	700	1.92	14.4
1c	NO ₂	636	0.93	12.9
1d	branched	701	1.23	15.7
2c	NO ₂	598	0.76	12.3
2d	branched	643	1.54	13.6

^a Experimental uncertainties were estimated to be $\pm 4\%$ in ϵ_{max} and ca. $\pm 2\%$ in M_{ge} . ^b Obtained from integration of the low-energy absorption feature according to $M_{\text{ge}} = 0.09584(\int \epsilon \, dv/v_{\text{max}})^{0.5}$, where ϵ is in $\text{M}^{-1} \text{ cm}^{-1}$ and v is in cm^{-1} .

within the framework of the Dewar–Knott rules in that the substituent “Y” in both **1d** and **2d** is anticipated to be predominantly electron-withdrawing in character, both inductively and mesomerically. However, both of these substituents introduce additional conjugation, the bathochromic shift associated with which presumably more-or-less cancels the expected hypsochromic effect associated with electron withdrawal; that is, effectively there is a π -donor interaction between the substituent and the bridge, and so classification of the mesomeric properties of these particular substituents as either acceptor or donor is overly simplistic.⁵³ In some respects, the nitro-substituted dyes discussed above are related to **1d** and **2d** in that they can both be described as three strong π -acceptors (two dioxaborinylvinyl groups plus either a nitro or a third dioxaborinylvinyl group) stabilizing a negative charge on a central carbon. The impact of three significant valence-bond structures on the geometry, and, therefore, band shapes, is similar. The three-site systems considered here should exhibit a doubly degenerate LUMO (at least in conformers with C_{3h} or C_3 symmetry, in principle lifted in lower symmetry conformers);^{49,52,54} in **1c** and **2c**, the reduced symmetry leads to a breaking of this degeneracy and the presence of two low-energy transitions.

Absorption data from the literature for a number of heptamethines with indole and benzothiazole termini in ethanol are summarized in Table 6, along with newly acquired data for three examples **3a**, **b** and **4** (Figure 6). As expected, the absorption maximum for **4** (for which very similar values of $\lambda_{\text{max}} = 750 \text{ nm}$, $\epsilon_{\text{max}} = 2.03 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ have been reported in the literature⁵⁵) is close to that for its ring-locked analogue **IIa**, while the *p*-tolylsulfanyl group of **3b** leads to similar bathochromic shift in the absorption maximum as the phenylsulfanyl group of **IIIc**. As indicated in Figure 1, the Y substituent in these dyes is an “unstarred” (δ) position. Thus, the bathochromic shifts observed on substitution with chloro, alkoxy, aryloxy, or arylsulfanyl groups indicate these groups act here as electron-withdrawing groups in the Dewar–Knott sense; values of *F* and *R* (Table 1) indicate all these groups to be inductive acceptors and mesomeric donors, and so the former effect is evidently dominant. The effect can be contrasted to the pentamethines (vide supra), for which, for example, little measurable effect on λ_{max} is observed on chloro substitution, due to the approximate cancellation of competing effects (Figure 4).⁵⁶ The bathochromic shift seen on CN substitution (**IIIe** vs **IIIa**) is consistent with the positive values of both *F* and *R* for CN. Although the hypsochromic shift seen for

Table 6. Absorption Maxima, Peak Absorptivities, and Transition Dipole Moments for some Indole- and Benzothiazole-Terminated Heptamethines

	Y	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/10^5 \text{ M}^{-1} \text{ cm}^{-1a}$	$M_{\text{ge}}/D^{a,b}$
3a ^c	N ⁺ C ₅ H ₄ -4-NMe ₂	800	2.22	15.0
3b ^c	S- <i>p</i> -tol	804	2.10	14.8
4 ^c	H	751	2.10	16.0
IIa ^d	H	747	2.62	
IIb ^d	NHMe	615	0.84	
IIc ^d	Cl	778	2.19	
IId ^d	OMe	753	1.82	
IIe ^d	OPh	764	2.06	
IIIf ^d	SPh	790	1.68	
IIIa ^e	H	770		
IIIb ^f	NMe ₂	698	1.11	
IIIc ^g	Cl	799	2.10	
IIId ^f	SPh	805	2.64	
IIIe ^f	CN	884	1.80	

^a Experimental uncertainties were estimated to be $\pm 4\%$ in ϵ_{max} and ca. $\pm 2\%$ in M_{ge} for **3a**, **3b**, and **4**. ^b Obtained from integration of the low-energy absorption feature according to $M_{\text{ge}} = 0.09584(\int \epsilon \, dv/v_{\text{max}})^{0.5}$, where ϵ is in $\text{M}^{-1} \text{ cm}^{-1}$ and v is in cm^{-1} . ^c DMSO. ^d In methanol; from ref 27. ^e In ethanol; from ref 57. ^f In methanol; from ref 25. ^g In ethanol, from ref 26.

amino groups in **IIb** and **IIIb** is consistent with these groups acting as net donors, the dramatically decreased peak absorptivity is perhaps indicative of a loss of cyanine-like character, perhaps due to the amino donor acting as stronger donor than the indole/benzothiazole end groups, leading to the dominance of a resonance structure in which the positive charge is primarily localized on the amino nitrogen atom. Although *F* and *R* values for the 4-(dimethylamino)pyridine substituent are not available, one would expect it to act primarily as a strongly inductive electron acceptor (consistent with *F* values for other pyridinium substituents³⁵), consistent with the observed bathochromic shift.

Nonlinear Optical Properties. Zero-frequency (static) values of the real part of the third-order polarizability, $\text{Re}(\gamma)_{\text{static}}$, can be estimated from the transition energies, *E*, transition dipole moments, *M*, and changes in state dipole moment, $\Delta\mu$, linking ground, first excited, and higher-lying excited states (denoted by *g*, *e*, and *e'* subscripts, respectively) according to the perturbation-theory derived eq 1.^{58–60}

$$\text{Re}(\gamma)_{\text{static}} \propto -\frac{M_{\text{ge}}^2}{E_{\text{ge}}^3} + \frac{M_{\text{ge}}^2 \Delta\mu_{\text{ge}}^2}{E_{\text{ge}}^3} + \sum_{\text{T}} \frac{M_{\text{ge}}^2 M_{\text{ee}'}^2}{E_{\text{ge}}^2 E_{\text{ee}'}^2} \quad (1)$$

In cyanine-like polymethines, the presence of a strong low-energy transition results in a large negative “N” term. Vanishing $\Delta\mu_{\text{ge}}$ is expected to lead to negligible positive “D” terms. More significant positive contributions to $\text{Re}(\gamma)_{\text{static}}$ can be expected from the “T” term. However, although values of $M_{\text{ee}'}$ approaching those of M_{ge} have been reported for some polymethines, the *e'* states in question are associated with values of $E_{\text{ee}'}$ over twice those of E_{ge} ,⁶¹ while values of $M_{\text{ee}'}$ for lower lying *e'* states are typically fairly small.^{4,62} Thus, even though the “T” term can, in general, significantly affect the value of $\text{Re}(\gamma)_{\text{static}}$, this term is often small relative to the “N” term in cyanine-like polymethines so that values of $\text{Re}(\gamma)_{\text{static}}$ for such systems are generally negative.^{1,2} Moreover, consideration of only the “N” term can

Table 7. Third-Order Polarizabilities of Dioxaborine- and Indole-Terminated Polymethines Obtained from Z-Scan Measurements at 1300 nm in DMSO along with Estimates of Static Values Estimated from Linear Absorption Data

	Y	$\text{Re}(\gamma)/10^{-33}$ esu	$\text{Im}(\gamma)/10^{-33}$ esu	$ \gamma ^a/10^{-33}$ esu	ϕ^a/deg	$\text{Re}(\gamma)_{\text{static,2-level}}^b/10^{-33}$ esu
1a	H	−3.5	2.9	4.6	141	−1.3
1b	Cl	−2.6	3.7	4.5	125	−1.5
1c	NO ₂	0.50	0.27	0.57	29	−0.73
1d	branched	−3.3	3.2	4.6	136	−2.1
3a	N ⁺ C ₅ H ₄ -4-NMe ₂	−8.9	2.7	9.3	163	−2.6
3b	S- <i>p</i> -tol	−8.1	2.3	8.4	164	−2.5
4	H	−10.1	5.9	11.7	150	−2.8

^aThe magnitude and phase of γ are defined as $|\gamma|^2 = \text{Re}(\gamma)^2 + \text{Im}(\gamma)^2$ and $\phi = \arctan[\text{Im}(\gamma)/\text{Re}(\gamma)]$, respectively. Experimental uncertainties were estimated to be $\pm 10\%$ in $|\gamma|$ and $\pm 14\%$ in ϕ . ^bEstimated from the “N”-term of eq 1 using values of M_{ge} and E_{ge} from the data of Tables 5 and 6.

often account for the evolution of $\text{Re}(\gamma)$ with chemical structure. Accordingly, values of $\text{Re}(\gamma)_{\text{static,2-level}}$ for **1a–d**, **3a,b**, and **4** were estimated using the “N” term of eq 1, taking values of M_{ge} and E_{ge} from Tables 5 and 6, and are presented in Table 7. In addition, the third-order nonlinear optical properties of **1a–d**, **3a,b**, and **4** were investigated experimentally using open- and closed-aperture femtosecond Z-scan measurements of $\text{Im}(\gamma)$ and $\text{Re}(\gamma)$, respectively, at 1.3 μm .^{63,64}

$\text{Re}(\gamma)_{\text{static,2-level}}$ values for **1a**, **1b**, and **1d** are similar, while that for **1c** is considerably lower, due to the higher transition energy and lower transition dipole moment found for this compound.⁶⁵ The experimental values of $\text{Re}(\gamma)$ for **1a**, **1b**, and **1d** are negative in sign, as expected, and are fairly similar to one another. A major factor contributing to the overall increase in the magnitude of the $\text{Re}(\gamma)$ values as compared to the $\text{Re}(\gamma)_{\text{static,2-level}}$ values is the frequency dependence of γ , specifically one-photon near-resonance enhancement, that is not taken into account in eq 1. The Z-scan measurements also indicate significant values of $\text{Im}(\gamma)$ at 1300 nm for **1a**, **1b**, and **1d**, which can be attributed to two-photon absorption (2PA). This is consistent with results for many other cyanine-like polymethines,^{18,24,66} in which a 2PA peak is typically observed at a transition energy corresponding to that observed for the vibronic shoulder of the lowest energy one-photon absorption; in particular, the one-photon absorption (1PA) spectra of **1a** and **1b** (Figure 3a) show a pronounced vibronic shoulder at ca. 650 nm, corresponding to a degenerate 2PA wavelength of 1300 nm. The presence of a 2PA resonance at ca. 1300 nm may also contribute to deviation of the observed $\text{Re}(\gamma)$ values from the $\text{Re}(\gamma)_{\text{static,2-level}}$ values, although minimal dispersion is expected at the peak of a 2PA transition (the 1PA spectra suggest that the peaks of the vibronically assisted 2PA transitions may indeed be close to a 2PA photon wavelength of 1300 nm). It is interesting to note that, although the branched structure of **1d** leads to a 1PA spectrum that deviates somewhat from that of typical cyanine-like molecules (see above), the third-order nonlinear optical properties, at least at 1300 nm, remain characteristically cyanine-like.

The experimental value of $\text{Re}(\gamma)$ for compound **1c** is rather small in magnitude as compared to molecules **1a**, **1b**, and **1d** and, uncharacteristically for a cyanine-like polymethine, is positive in sign. This can, in part, be attributed to contributions from the dispersion of $\text{Re}(\gamma)$: the hypsochromic shift of the absorption maximum of **1c** relative to those of **1a** and **1b** should result in a similar shift of the 2PA band, and so 1300 nm is expected to correspond to excitation on the low-energy side of the 2PA resonance, where a strong positive peak in $\text{Re}(\gamma)$ is expected that may compensate for a static negative value of $\text{Re}(\gamma)$. This

positive $\text{Re}(\gamma)$ value may also be related to the deviation from a typical polymethine structure and the corresponding spectral changes discussed above. In particular, contributions from the resonance structure shown in Figure 5 suggest significant dipolar character,⁶⁷ in which case the “N” term alone will not adequately describe the contributions of the lowest lying excited state to the static value of $\text{Re}(\gamma)$, and may be partially compensated for by a positive “D”-type contribution.⁶⁸ Moreover, in all of these polymethines in which low-energy 2PA, corresponding to a vibronically assisted transition into a higher lying vibronic sublevel for the first electronic excited state, is observed, the positive “T”-term contributions may be larger than anticipated if the only e' states considered are higher lying electronically excited states.

As discussed above, two-photon excitation at 1300 nm falls on the low-energy side of the vertical 1PA state for **1c**, and thus well below the energy expected for a typical cyanine-like vibronically assisted 2PA peak. This is consistent with the relatively small value of $\text{Im}(\gamma)$ found for **1c**. Indeed, the $\text{Im}(\gamma)$ observed at 1300 nm may be associated with direct 2PA into the lowest 1PA-allowed state, which will be allowed if the molecule possesses significant dipolar character.

The indole-terminated heptamethines show larger calculated and experimental magnitudes of $\text{Re}(\gamma)$ than the dioxaborine pentamethines. $\text{Re}(\gamma)_{\text{static,2-level}}$ for **4** was calculated to be slightly larger than that for **3a,b**, the larger transition dipole moment more than compensating for the higher transition energy. The trends in $\text{Re}(\gamma)_{\text{static,2-level}}$ follow well those in the experimental values of $\text{Re}(\gamma)$, although the latter values are considerably larger in magnitude, likely due to resonance enhancement associated with the significant 2PA revealed by the values of $\text{Im}(\gamma)$; the situation differs from that observed for **1c** in that the excitation wavelength of 1300 nm now falls on the short wavelength side of the 2PA resonance, at which there is expected to be a strong dip in $\text{Re}(\gamma)$, augmenting the intrinsically negative value of $\text{Re}(\gamma)$. The larger magnitude of $\text{Im}(\gamma)$ for **4** indicates stronger 2PA at 1300 nm (consistent with closer proximity of 1300 nm to the vibronically allowed 2PA transition), which may also lead to greater resonance enhancement of $\text{Re}(\gamma)$.

CONCLUSION

The effects of bridge substitution on the linear spectra of polymethine dyes can be understood within the general framework of the Dewar–Knott rules, although for many substituents one must explicitly consider both the inductive and the mesomeric donor/acceptor properties of a substituent (as quantified, for example, by modified Swain–Lupton coefficients). While the

specific chromophores examined here are unsuitable for all-optical switching applications at 1300 nm, due to the relatively small values of $\text{Re}(\gamma)$ and to significant two-photon absorption leading to unacceptable nonlinear loss figures-of-merit,⁶⁹ the study has some implications for the use of bridge substitution in the development of more extended chromophores, such as bis(dioxaborine)-terminated nonamethines, for these applications. Bridge substituents can be used to fine-tune the absorption maxima and, therefore, to maximize near-resonant enhancement at a given wavelength, while avoiding linear loss. Specific substitution patterns, however, are problematic. The presence of strong π -acceptors in the γ position of pentamethines (and, therefore, presumably at the central carbon of nonamethines) leads to broadened and weakened one-photon absorption and thus to diminished values of the estimated two-state value of $\text{Re}(\gamma)_{\text{static}}$; partial dipolar character and the presence of other low-lying excited states may have additional adverse effects on $\text{Re}(\gamma)_{\text{static}}$ while reducing the wavelength range over which nonlinear transparency can be achieved. The broader absorption features of triply terminated branched polymethines may also lead to reduced linear and/or nonlinear transparency.

■ ASSOCIATED CONTENT

S Supporting Information. Full experimental details and characterizing data, HSQC spectrum for **1a**, graphical presentation of data from Table 2, figures showing cyclic voltammograms, and steady-state excitation fluorescence anisotropy data for **1a** and **1c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (67) This dipolar character will be heightened further if the chromophore adopts a more “V-shaped” conformer related to those shown in Figures 2 and 5 by rotation of 180° around the $C_\beta-C_\gamma$ bonds.
- (68) In addition, the presence of an additional low-energy band for **1c** may mean that more excited states than the lowest-energy state may be required to adequately describe γ .
- (69) Stegeman, G. I.; Stolen, R. H. J. *Opt. Soc. Am. B* **1989**, 6, 652.