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Induced Circular Dichroism in Cyanine Borate Penetrated Ion Pairs

David J. Owen and Gary B. Schuster*

Department of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

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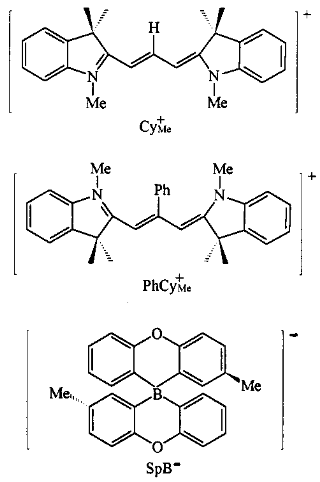
The induction of optical activity by a chiral environment acting on an achiral or racemic substrate is an important phenomenon that has been observed in several systems.[1] Optically active counterions in solutions of achiral ionic species can induce optical activity. Early examples of this include the Pfeiffer effect, in which a racemic complex perturbs the optical activity of a scalemic cosolute.[2,3] More recent reports reveal that solutions of achiral ketone-substituted carboxylic acids and optically active amines in nonpolar solvents give induced circular dichroism spectra (CD) in the absorption region of the acid.[4] Very recently, Whitten and co-workers have discovered chiral structures in aggregates of dyes and of aromatic molecules.[5] However, the most thoroughly studied of the chiral-inducing media are cyclodextrins.[6] Optical activity in ketones,[7] acids,[8] bilirubin,[9] hydrocarbons,[10] pyrazolium salts,[11] and anionic azo compounds[12] has been induced by their inclusion in cyclodextrin cavities. Of most relevance to the current work is the observation that a cyclodextrin host will induce a CD spectrum in an achiral cyanine dye dimer that has penetrated into the chiral channel of two γ-cyclodextrin molecules.[13]

We recently reported that solutions of cyanine cations and tetraarylborate anions in nonpolar solutions form penetrated ion pairs where the chemical and physical properties of the cyanine are controlled by the size and shape of cavities formed by the substituents of the borate.[14] These findings suggested that a chiral borate might induce optical activity in a penetrated, achiral cyanine dye which might have important applications as a nonlinear optical device for frequency doubling.[15] We report herein that solutions of certain cyanine dyes do exhibit CD spectra as penetrated ion pairs with chiral borates in nonpolar solvents.

We prepared and examined the salts of 1,3,3,1′,3′,3′-hexamethylindocarbocyanine ($\mathrm{Cy_{Me}^+}$) and 1,3,3,1′,3′,3′-hexamethyl-9-phenylindocarbocyanine ($\mathrm{PhCy_{Me}^+}$) with both enantiomers of the optically active spirobi[(3-methyl)borataxanthene] ($\mathrm{SpB^-}$) that are shown in Chart 1.[16] The absorption spectra[17] of these salts in benzene solution at room temperature are independent of whether the counterion is tetraphenylborate or $\mathrm{SpB^-}$. No electronic interaction between the cation and anion is apparent. The absorption spectrum of $\mathrm{Cy_{Me}^+}$ shows a structure typical of cyanine dyes that sharpens somewhat on cooling to 77 K; see Figure 1. In contrast, the absorption spectrum of $\mathrm{PhCy_{Me}^+}$ at room temperature is structureless, but features appear when the spectrum is recorded in a frozen glass. This finding suggests that averaging among several conformations of $\mathrm{PhCy_{Me}^+}$ occurs at room temperature. This was confirmed by examination of the temperature dependence of the ^{1}H NMR spectrum of $\mathrm{PhCy_{Me}^+I^-}$ in $\mathrm{CD_2Cl_2}$ and $\mathrm{CD_3OD}$ solutions. In both solvents the spectra broaden at low temperature and reach coalescence at -34 °C in $\mathrm{CD_2Cl_2}$ and at -44 °C in $\mathrm{CD_3OD}$. At -80 °C the ^{1}H NMR spectrum of $\mathrm{PhCy_{Me}^+I^-}$ sharpens to reveal paired sets of resonances. In $\mathrm{CD_2Cl_2}$ at -80 °C, negative cross-correlated peaks appear in ROSEY spectra[18] showing enhancements between the geminal methyl proton and vinyl proton resonances, suggesting a twisted *cis, trans, cis* (*Z,E,Z*) structure for $\mathrm{PhCy_{Me}^+}$. Similar observations have been reported previously for *meso*-substituted cyanine dyes.[19]

Chart 1. Structures of Cyanines and Borates



We attempted to observe the CD spectrum of $\mathrm{Cy_{Me}^+SpB^-}$ in benzene solution at room temperature and in toluene solution at -20 °C,[20] but only weak signals (artifacts[21,22]) independent of the enantiomer of $\mathrm{SpB^-}$ were measured. Evidently the induced circular dichroism of this penetrated ion pair is too small to detect spectroscopically. However significantly, as is shown in Figure 2, the induced CD spectrum of $\mathrm{PhCy_{Me}^+SpB^-}$ in benzene solution is readily measured, and it follows the absorption spectrum of $\mathrm{PhCy_{Me}^+}$ precisely. As a control, we demonstrated that the two enantiomers of $\mathrm{SpB^-}$ cause an induced CD of equal magnitude but opposite sign. Clearly, the

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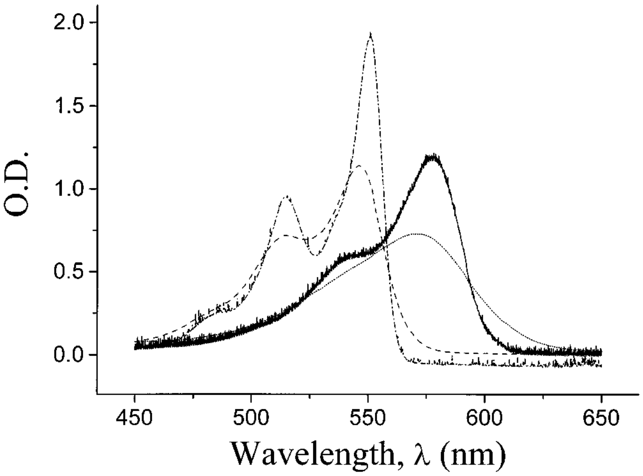

Figure 1. UV absorption spectra of $\mathrm{Cy_{Me}^{+}I^{-}}$ at ambient temperature in benzene (— — —) and at 77 K in 4:1 ethanol/methanol glass (—•—). UV spectra of $\mathrm{MsPhCy_{Me}^{+}I^{-}}$ at ambient temperature in benzene (•••) and at 77 K in 4:1 ethanol/methanol glass (—).

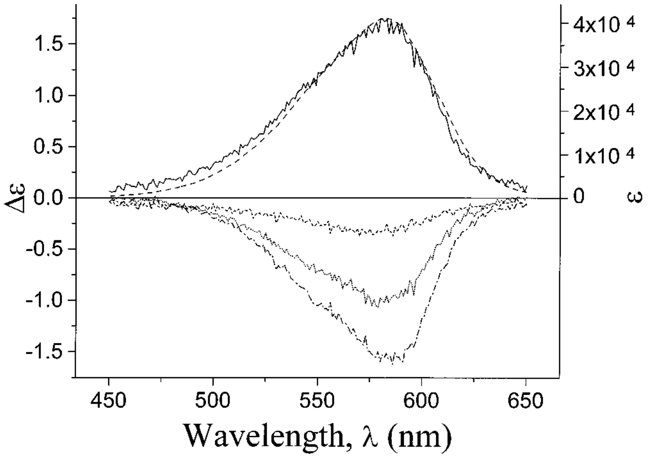

Figure 2. UV spectra of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ in benzene (— — —). CD of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ (+) in benzene at ambient temperature (—); CD of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ (−) in benzene at ambient temperature (•••), in toluene at −20 °C (—•—), and in xylenes at 80 °C (- - -).

structural differences between $\mathrm{Cy_{Me}^{+}}$ and $\mathrm{PhCy_{Me}^{+}}$ result in different interactions with $\mathrm{SpB^{-}}$. In toluene or xylene solution the temperature dependence of the induced CD spectrum of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ reveals a free energy difference between the two diastereomers[23] of less than 1 kcal/mol.

There are several kinds of intermolecular interactions that have been found to cause induced circular dichroism spectra.[24] These may be divided crudely into electronic and structural effects. The former is due to asymmetry in the local field experienced by the perturbed chromophore. This interaction is expected to depend strongly on distance, for example, but to be independent of fine structural detail. If this were the mechanism operating for these penetrated cyanine borates, then both $\mathrm{Cy_{Me}^{+}SpB^{-}}$ and $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ should behave identically. Since this is not the case, we attribute the induced circular dichroism of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ to a distortion of the structure of the dye caused by steric interactions with the borate.

Structural distortions that cause induced circular dichroism have been divided into two groups: association and diastereomeric equilibration.[25] The former requires different association constants of the cyanine with each of the borate enantiomers and a mixture of free ions and ion pairs, which in the present case seems unlikely since the cyanine borates are present essentially exclusively as ion pairs in benzene solution.[26] On the other hand, the penetrated $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ ion pair can clearly exist in two (or more) interconverting conformations of slightly unequal energy that are required to induce circular dichroism by diastereomeric equilibration. The presence of unique conformations of unequal energy is revealed experimentally by the temperature dependence of the CD spectrum.

The dissimilar temperature dependence of the NMR spectra of $\mathrm{Cy_{Me}^{+}}$ and $\mathrm{PhCy_{Me}^{+}}$ reveals the critical structural difference that leads to induced CD in the latter but not the former. $\mathrm{Cy_{Me}^{+}}$ exists in a planar *all-trans* configuration, while $\mathrm{PhCy_{Me}^{+}}$ is twisted in the ground state. Evidently, the interaction energy of the chiral cavity and cyanine is sufficient to select between right- and left-handed twists of $\mathrm{PhCy_{Me}^{+}SpB^{-}}$ but is insufficient to cause a normally planar cyanine to twist.

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