

**Penetrated Ion Pairs: Structure and Properties of (*N,N'*-Dimethyl)dimethylindocarbocyanine Tetrakis(phenylethynyl)borate in Solution and in the Solid State**

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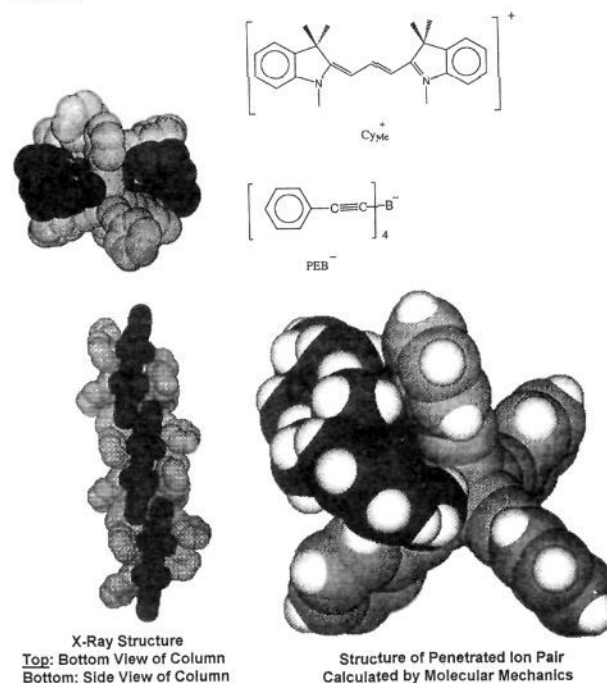
Received August 13, 1993

Revised Manuscript Received October 14, 1993

The unique properties of (*N,N'*-dimethyl)dimethylindocarbocyanine tetrakis(triptycenyphenyl)borate led us to suggest that this salt exists in benzene solution as a penetrated ion pair.<sup>1,2</sup> In this form, the relatively flat, plate-like cationic cyanine dye penetrates into crevices between the substituent groups of the borate anion so that the ion pair is smaller than the sum of the individual ions. Penetration inhibits isomerization of the cyanine in its electronically excited singlet state and slows intra-ion pair electron transfer. Molecular force field calculations revealed that the Coulombic attraction force pulls the cyanine into the borate and that the bulk of the triptycenyphenyl groups restricts the number of energetically accessible conformations of the dye. We report herein examination of the solution-phase properties and the solid-state structure of (*N,N'*-dimethyl)dimethylindocarbocyanine tetrakis(phenylethynyl)borate { $\text{Cy}_{\text{Me}}^+\text{PEB}^-$ }; see Chart I. This salt forms a penetrated ion pair in solution and has a unique, penetrated cylindrical motif in the solid state.

The unique properties of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  in benzene solution are easily recognized by comparison with the hexafluorophosphate ( $\text{PF}_6^-$ ) and tetraphenylborate ( $\text{Ph}_4\text{B}^-$ ) salts of this cyanine dye. The absorption spectrum of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  is independent of its concentration from  $10^{-7}$  to  $10^{-3}$  M, indicating that there is no aggregation over this concentration range. The shapes of the absorption and fluorescence spectra of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  are the same as those of the  $\text{PF}_6^-$  salt, but they are shifted to lower energy [ $\lambda_{00}^{\text{PEB}} = 570$  nm,  $\Delta\epsilon_{00}^{\text{(PEB-PF}_6\text{)}} = 173$  cm<sup>-1</sup>] by interaction with the counterion.<sup>3</sup> The fluorescence quantum yield ( $\Phi_{\text{F}}$ ) of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  is 0.1. Under identical conditions, the  $\Phi_{\text{F}}$  for the  $\text{PF}_6^-$  salt is 0.07, and the fluorescence efficiency of the  $\text{Ph}_4\text{B}^-$  salt is only 0.0035.<sup>4</sup> The  $\Phi_{\text{F}}$  of  $\text{Cy}_{\text{Me}}^+\text{Ph}_4\text{B}^-$  is reduced from that of the  $\text{PF}_6^-$  salt by intra-ion pair electron transfer.<sup>3,5</sup> The oxidation potential of  $\text{PEB}^-$  is  $>1.4$  V vs SCE as estimated by adaptation<sup>6</sup> of the kinetic method of Rehm and Weller,<sup>7</sup> so electron transfer to the excited singlet state of  $\text{Cy}_{\text{Me}}^+$  from this borate is calculated to be endogonic. The  $\Phi_{\text{F}}$  of  $\text{Cy}_{\text{Me}}^+\text{PF}_6^-$  depends on the viscosity of the solvent since its major mode of nonradiative relaxation is rotation about a carbon-carbon bond.<sup>8,9</sup> In contrast, the  $\Phi_{\text{F}}$  of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  is essentially unaffected as the hydrocarbon solvent is varied. The increase of  $\Phi_{\text{F}}$  for the  $\text{PEB}^-$  salt beyond that

Chart I



observed for the  $\text{PF}_6^-$  salt and its insensitivity to the solvent are indications that  $\text{Cy}_{\text{Me}}^+$  has penetrated the borate anion.

Laser flash photolysis (532 nm, 18 ps, 250  $\mu\text{J}$ ) of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  in benzene solution shows instantaneous bleaching of the ground-state absorption with appearance of new bands at 430 and 480 nm attributed to  $\text{S}_1 \rightarrow \text{S}_\text{N}$  absorption of the dye. Both the dye bleaching and the  $\text{S}_1 \rightarrow \text{S}_\text{N}$  absorption decay follow a first-order rate law with a lifetime of 340 ps. Spectra recorded 10 ns after the laser pulse show residual bleaching and a new absorption with an apparent maximum at 575 nm attributed to the *cis*-isomer of the cyanine dye.<sup>5</sup> The dynamic behavior of these features follows a first-order rate law that depends on the identity of the counterion. For the  $\text{PF}_6^-$  salt, the residual bleaching recovers and the absorption of the *cis*-cyanine decays with a lifetime of  $5 \pm 0.5$   $\mu\text{s}$ . For the  $\text{PEB}^-$  salt, the lifetime for this reaction is  $30 \pm 2$   $\mu\text{s}$ . The increased lifetime of the *cis*-isomer is another indication that the motions of  $\text{Cy}_{\text{Me}}^+$  are restricted and that it has penetrated the crevices of  $\text{PEB}^-$ .

The structure of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  calculated by molecular mechanics is shown in Chart I.<sup>10</sup> The predicted minimum energy structure shows penetration of  $\text{Cy}_{\text{Me}}^+$  into a crevice of  $\text{PEB}^-$ . In contrast to the penetrated structure predicted for  $\text{Cy}_{\text{Me}}^+$  tetrakis(triptycenyphenyl)borate,<sup>1</sup> inspection of the calculated structure of  $\text{PEB}^-$  shows that it does not completely lock the cation configuration, so its *trans* to *cis* isomerization is possible.

Single crystals of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  were grown from acetonitrile solution, and the solid-state structure shown in Chart I was determined by X-ray crystallography.<sup>11</sup> The structure of a series of cyanine halide salts was reported by Nakatsu and co-workers.<sup>12</sup> They recognize six columnar arrangements of cations organized into five two-dimensional patterns;  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  is similar to none

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(2) Unique behavior of related penetrated ion pairs has also been observed. Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 6714. Pochapsky, T. C.; Stone, P. M.; Pochapsky, S. S. *J. Am. Chem. Soc.* **1991**, *113*, 1460. Begum, M. K.; Grunwald, E. J. *J. Am. Chem. Soc.* **1990**, *112*, 5104. Abbott, A. P.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1449. Abbott, A. P.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1453.

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(4) These quantum yields are slightly different from those we reported in refs 1 and 5 due to correction of the standard. In the present work we set the  $\Phi_{\text{F}}$  of Rhodamine 6G in ethanol to 0.89 (see ref 8).

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(10) Molecular geometries and energies were calculated with the PC-MODEL interactive molecular modeling program supplied by Serena Software, Bloomington, IN, executed on a Silicon Graphics IRIS workstation. Since the force field parameters for anionic boron atoms bound to ethynyl carbon atoms are unavailable, this atom was modeled as a tetrahedral, anionic carbon atom.

(11) Two independent acetonitrile solvent molecules were located in the crystal lattice in cavities between cylindrical borate anion backbones parallel to the unique crystal axis. These cavities were bound by unfilled crevices in the borate anion backbone and neighboring methyl groups. Structure details are given in the supplementary material.

of these. This salt forms a unique cylindrical motif consisting of two cyanine ribbons that penetrate crevices along opposite sides of a zigzag backbone of borate anions. Ribbon structures are not uncommon for cyanine dyes, but no other penetrated cylinder motif of this sort was found in a search of the Cambridge Crystal Structure database.<sup>13</sup>

In summary, the solution behavior and solid-state structure of  $\text{Cy}_{\text{Me}}^+\text{PEB}^-$  reveal that it is a penetrated ion pair. Penetration into the borate anion affects the photophysics and photochemistry of the cyanine dye. Similarly, penetration in the solid state leads

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to a unique structure. The recognition of penetration within borate anions permits development of new strategies to control the properties of cyanine cations.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation, for which we are grateful.

**Supplementary Material Available:** Tables of crystal structure data, atomic coordinates, anisotropic displacement factors, hydrogen coordinates, and ORTEP plots of  $\text{Cy}_{\text{Me}}^+$  and  $\text{PEB}^-$  (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.