Penetrated Ion Pairs: Photochemistry of Cyanine Dyes within Organic Borates

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The pioneering work of Grunwald,[1] Winstein,[2] and Fuoss[3] led to the division of ion-pair structures in solution into two broad categories. Intimate ion pairs occur at very short distances when a cation and anion touch each other. Solvent-separated ion pairs are considered to be metastable intermediates formed when the solvation shells of oppositely charged ions overlap. Recent studies of complex ion pairs in solution by Pochapsky and Stone,[4] Grunwald,[5] and Abbott and Schiffrin[6] indicate more elaborate structures for these species. Our experimental results on the photochemistry of cyanine borate salts [$Cy^+(Ar_4B)^-$; see Chart I] led us to consider their existence in a third structural category for ion pairs in solution. Penetrated ion pairs result when the size of the ion pair is notably smaller than that of the sum of their individual ions.[6] Penetration markedly affects the chemical and physical properties of cyanine borate ion pairs.

In solution[7] and in the solid phase,[8] Cy^+ exists exclusively as the "all-trans" isomer. Irradiation of $Cy^+[(C_6F_5)_4B^-]$ in benzene solution with visible light (532 nm, 18 ps, 250 μJ) generates the excited singlet state of the cyanine. Under these conditions the lifetime of the excited cyanine is 340 ± 10 ps. It decays along two paths: to a small extent by fluorescence, and primarily by rotation to a presumed intermediate perpendicular excited state[9] which, in part, relaxes to form a metastable "mono-cis" isomer. The mono-cis isomer is detected spectroscopically by its apparent absorption maximum at 580 nm.[10] Electron transfer (k_{et}) occurs in the excited state of related cyanine borate salts,[10,11] but is prohibited energetically in this case because of the high oxidation potential of the perfluorophenyl borate (E_{OX} = 2.38 V vs SCE).[12] Since the singlet lifetimes of $[(Cy^+)^{*1}PF_6^-]$ and $[(Cy^+)^{*1}(C_6F_5)_4B^-]$ are determined primarily by bond rotation, they depend on the nature of the solvent.[13] These findings and those of the other experiments are summarized in Table I.

The spectroscopic and chemical properties of the cyanine borate ion pairs depend on the character of the borate. The absorption maxima of the $[(TRPPh)_4B^-]$ and PF_6^- salts occur at 563 nm; for $Cy^+[(C_6F_5)_4B^-]$ this peak is found at 553 nm.[14] The cyanine fluorescence quantum yields are solvent and anion dependent. In most solvents the singlet lifetime increases as the counterion is altered from PF_6^- to $[(C_6F_5)_4B^-]$ and $[(TRPPh)_4B^-]$, but decreases considerably when the anion is $[(C_6H_{11}Ph)_4B^-]$.

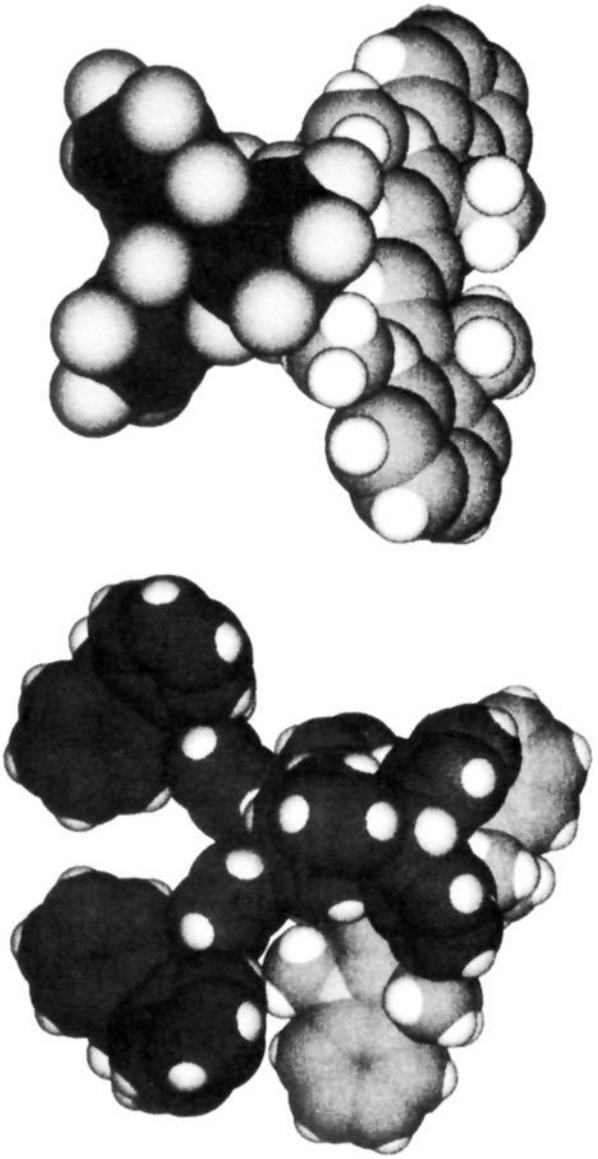
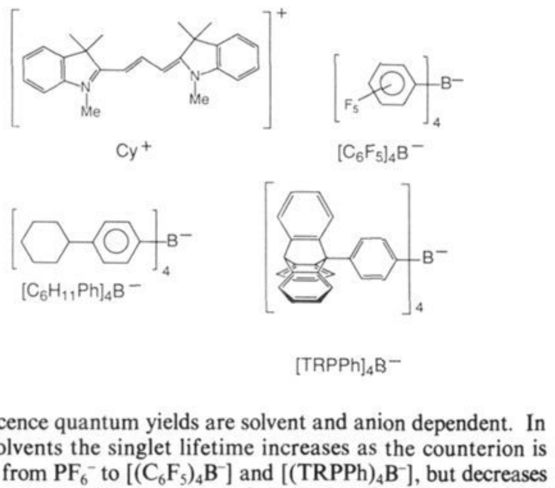


Figure 1. Top: Minimum-energy structure calculated for $[Cy^+(C_6F_5)_4B^-]$. This compound appears to be a contact ion pair. Bottom: Minimum-energy structure calculated for $[Cy^+(TRPPh)_4B^-]$. This compound appears to be a penetrated ion pair.

Chart I



Cy^+

$[C_6F_5]_4B^-$

$[C_6H_{11}Ph]_4B^-$

$[TRPPh]_4B^-$

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(1) Grunwald, E. *Anal. Chem.* **1954**, *26*, 1696.

(2) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597.

(3) Fuoss, R. M.; Sadek, H. *J. Am. Chem. Soc.* **1954**, *76*, 5897. Fuoss, R. M.; Sadek, H. *J. Am. Chem. Soc.* **1954**, *76*, 5905.

(4) Pochapsky, T. C.; Stone, P. M.; Pochapsky, S. *J. Am. Chem. Soc.* **1990**, *112*, 6714. Pochapsky, T. C.; Stone, P. M.; Pochapsky, S. *J. Am. Chem. Soc.* **1991**, *113*, 1460.

(5) Begum, M. K.; Grunwald, E. *J. Am. Chem. Soc.* **1990**, *112*, 5104.

(6) 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.

(7) Allman, R.; Anis, H.-J.; Benn, R.; Grahn, W.; Olejenek, S.; Waskowska, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 876.

(8) Allmann, R.; Waskowska, A.; Olejenek, S. *Cryst. Struct. Commun.* **1982**, *11*, 213.

(9) Rulliere, C. *Chem. Phys. Lett.* **1976**, *43*, 303. Momicchioli, F.; Baraldi, I.; Bertheir, G. *Chem. Phys.* **1988**, *123*, 103.

(10) Chaterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326.

(11) Chatterjee, S.; Davis, P. D.; Gottschalk, Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329. Significantly, k_{et} is only slightly affected by the alkyl substituent at the 4-position when it is a methyl or 2-adamantyl group.

(12) Oxidation of the borates gives irreversible waves; these potentials were determined by the kinetic method described in ref 11.

(13) Åkesson, E.; Sundström, V.; Gillbro, T. *Chem. Phys.* **1986**, *106*, 269.

(14) McRae, E. G. *J. Chem. Phys.* **1956**, *61*, 562.

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Table I. Photochemical and Photophysical Data for Cyanine Borates

solvent	cyanine lifetime,[a] ps; $[\phi_{fl}]$[b] PF_6^-	$(C_6F_5)_4B^-$	$(TRPPh)_4B^-$	$(C_6H_{11}Ph)_4B^-$	k_{et},[d] 10^{10} s^{-1} $(C_6H_{11}Ph)_4B^-$	$(TRPPh)_4B^-$
toluene	300; [0.048]	350; [0.05]	490; [0.04]	13;[c] [0.002]	7.1	<0.20
benzene	250; [0.047]	340; [0.05]	520; [0.05]	28;[c] [0.005]	2.6	<0.20
p-xylene	350; [0.066]	410; [0.06]	400; [0.03]	8;[c] [0.001]	13	<0.25
tetralin	435; [0.066]	580; [0.11]	670; [0.04]	6;[c] [0.001]	20	<0.15
p-cymene	*e*; [*e*]	520; [0.11]	520; [0.02]	13;[c] [0.003]	7.5	<0.20

[a] Determined by monitoring the rate of ground state absorption recovery or excited state absorption decay following laser excitation. Standard deviations from independent measurements are ±20 ps. [b] Quantum yield of fluorescence determined by excitation at 532 nm for PF_6^- salts and 526 nm for the others. [c] The lifetime of the excited cyanine is too short to measure with an 18-ps laser pulse. These values were computed from the fluorescence yields and the assumption that the radiative and nonradiative rates are the same as for the $(C_6H_5)_4B^-$ salt. [d] Rate constant for electron transfer calculated from the ratio of fluorescence efficiencies of $Cy^+[(C_6F_5)_4B^-]$ and $Cy^+[(C_6H_{11}Ph)_4B^-]$ and the lifetime of $Cy^+[(C_6F_5)_4B^-]$ as described in ref 8. [e] The solubility is too low for accurate measurement of the lifetime and fluorescence yield.

The decrease in fluorescence efficiency and lifetime for $Cy^+[(C_6H_{11}Ph)_4B^-]$ (borate E_{OX} = 1.14 V vs SCE) compared with those for the perfluorophenyl borate is attributed to electron transfer from the borate to the excited cyanine in accord with observations in related systems.[10,11] Obviously, electron transfer in $[(Cy^+)^{*1}(TRPPh)_4B^-]$ is inhibited by the change in the substituent on the phenyl groups of the borate from a cyclohexyl to a triptycenyl group. Since this change will have little effect on E_{OX} of the borate, the inhibition of electron transfer must have a steric origin.

The formation of the mono-cis isomer from irradiation of cyanine dyes is generally solvent dependent.[13] We investigated the isomerization of the cyanine borates described in Chart I to probe the microscopic environment of the medium surrounding the cyanine dye. The absorption due to the mono-cis isomer 100 ns after irradiation of the cyanine ion pair in benzene solution (532 nm, 25 ns, 20 mJ) is readily apparent when the anion is $[(C_6F_5)_4B^-]$ or PF_6^-, but is completely absent for the $[(C_6H_{11}Ph)_4B^-]$ and $[(TRPPh)_4B^-]$ salts. Inhibition of isomer formation for the $[(C_6H_{11}Ph)_4B]^-$ salt is easily explained since rapid electron transfer competes with bond rotation in the excited singlet state of this compound. Surprisingly, both electron transfer and bond rotation are inhibited in $[(Cy^+)^{*1}(TRPPh)_4B^-]$.

The structures of these salts shown in Figure 1 were computed using PCMODEL.[15] The calculations indicate that energy minimization requires striking a balance between the strong electrostatic attraction of the oppositely charged ions and steric repulsion. For $[Cy^+(TRPPh)_4B^-]$, movement of the phenyltriptycenyl groups away from the symmetrical structure of the free ion opens a cavity that accommodates penetration by the cyanine cation. In this ion pair the central methylene chain and the heteroaryl groups of the cyanine are encased in the borate. For the smaller $Cy^+[(C_6F_5)_4B^-]$, the cyanine cation does not penetrate the interior of the borate anion significantly. The chemical and physical properties of this salt are consistent with the contact ion pair structure depicted in Figure 1. Further experiments are required to test the validity of these predictions, which provide, at least, a guide to selection of additional structures.

When the cyanine is within the anion, as in $[Cy^+(TRPPh)_4B^-]$, it cannot rotate to form the mono-cis isomer without cooperative motions in the borate. For the smaller borates, cyanine bond rotation remains operational and the singlet lifetime shows a solvent dependence since formation of the mono-cis isomer requires movement of solvent molecules. The magnitude of k_{et} similarly is strongly dependent on the structural details of the penetrated ion pair since it is much smaller for $[Cy^+(TRPPh)_4B^-]$ than it is for $[Cy^+(C_6H_{11}Ph)_4B^-]$. Clearly, penetrated cyanine borate ion pairs have unique, experimentally observable properties that depend on the structural details.

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[15] The structures were calculated with the PCMODEL 4.0 program available from Serena Software, Bloomington, IN. The cyanine dye and the borate were independently minimized and then minimized as the ion pair in a variety of geometries. In this process the cationic dye was positioned within the borate at a distance closer than the van der Waals contact. Minimization results in an ion-pair structure of lower energy than the free ions. A range of possible starting structures was examined, and the minimized structures shown in Figure 1 represent the lowest energy obtained. However, these structures reflect only steric and Coulombic interactions; they ignore effects of solvation and possible kinetic prohibition to their formation.

Distinction of Symmetric Lithium Dialkylamide Dimers from Higher Oligomers by Inverse-Detected ^{15}N Homonuclear Zero-Quantum NMR Spectroscopy

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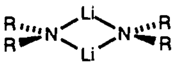
^6Li and ^{15}N NMR spectroscopy have played a prominent role in the characterization of solvation, aggregation, and mixed aggregation equilibria of lithium dialkylamides.[1-8] It has been suggested that a range of lithium amide cyclic oligomers can exist in hydrocarbon solutions, but that only cyclic dimers are observable in donor solvents.[9] Despite mounting indirect spectroscopic,[2-5] kinetic,[7,10] and theoretical[9,11,12] evidence in support of this model, however, the high symmetry of the more synthetically important lithium dialkylamides has precluded a direct distinction of cyclic dimers (**1**) from other cyclic oligomers (e.g., trimer **2**). We report herein a simple NMR experiment in which indirectly detected homonuclear zero-quantum coherence[13] unambiguously differ-



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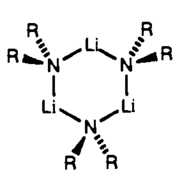

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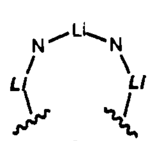

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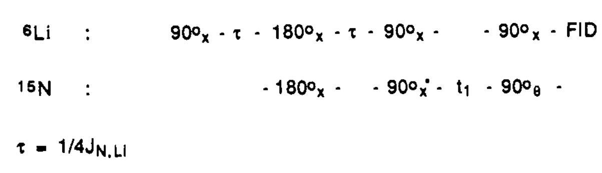

Figure 1. Pulse sequence used to measure ^6Li-detected ^{15}N zero-quantum NMR spectra. Zero-quantum coherence was selected by cycling the third ^{15}N pulse through four phases (0°, 90°, 180°, 270°) and adding the resulting free induction decays.

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