# Structure and Photophysical Properties of 2,6-Di-*tert*-Butyl-4-arylpyrylium 2-Naphthalenesulfonate Ion Pairs in Solution and in the Solid State

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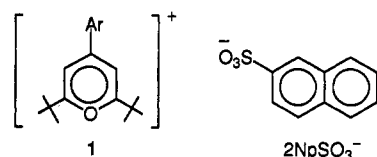
2,6-Di-*tert*-butyl-4-arylpyrylium 2-naphthalenesulfonate salts form ion pairs in dimethylcarbonate solution that exhibit charge-transfer absorptions and result in the rapid quenching of the pyrylium fluorescence. Molecular mechanics calculations predict that these ion pairs exist in a T-shaped orientation, but X-ray structural analysis reveals a π face-to-face arrangement in the solid state. Nuclear Overhauser effect and time-resolved spectroscopic experiments carried out in solution are consistent with a T-shape for the ion pair, but these experiments do not prove that this structural hypothesis is correct.

## Introduction

Since the pioneering work of Grunwald,[1] Winstein,[2] and Fuoss[3] 40 years ago, ion pairs in solution have generally been assigned to contact and solvent-separated structures. Contact (intimate) ion pairs are formed at short distances when the cation and anion actually touch each other. Solvent-separated ion pairs are metastable intermediates formed when the solvation shells of a cation and an anion overlap. This classification scheme for ion pairs in solution provides a satisfactory description of their structure when the ions have spherical shapes. However, when either or both of the ions in the ion pair have a more elaborate structure than a sphere, this simple scheme does not suffice. The unique, structure-dependent properties of complexly shaped ion pairs has recently been investigated by Pochapsky, Grunwald, and Abbott.[4] This topic became a focus of research in our laboratory when we realized that penetration of a cationic cyanine dye within the crevices of an anionic borate can modulate the photophysical and photochemical properties of the ion pair. Specifically, formation of a cyanine borate-penetrated ion pair alters the nature of the radiative and nonradiative relaxation pathways of the excited cyanine dye and can greatly affect the rate constant for intra-ion pair electron-transfer reactions.[5]

Ion pairs formed from complexly-shaped ions may adopt arrangements other than the penetrated structure seen for cyanine borates. For example, a flat, plate-like delocalized cation and an anion having charge localized on one end of a flat structure might adopt either a "T-shaped" or a face-to-face arrangement of their π-electron systems. It was anticipated that these two arrangements might have different properties that would be revealed by examination of their spectroscopic, photochemical, and

## Chart 1



Ar = (a) Ph–; (b) 4-MePh–; (c) 4-ClPh–;
(d) 4-CNPh–; (e) 4-CF$_3$Ph; (f) 4-MeOPh;
(g) 3,5-(Me)$_2$Ph; (h) 2,4,6-(Me)$_3$Ph

photophysical behavior. We report herein investigation of a series of 2,6-di-*tert*-butyl-4-arylpyrylium 2-naphthalenesulfonate ion pairs (Chart 1). Molecular mechanics calculations[6] predict that these salts will form T-shaped ion pairs in nonpolar solvents. The spectroscopic and photochemical studies are consistent with this prediction, but X-ray crystallography of 1e·2NpSO$_3^-$ reveals a solid-state structure with a slipped π face-to-face orientation of the ions.

## Results

**Molecular Mechanics Prediction of T-Shaped Ion Pairs.** Molecular mechanics calculations can predict the structure of some complexly-shaped ion pairs dissolved in a nonpolar solvent with reasonable reliability. In particular, we found that the minimum-energy structure calculated for *N,N'*-dimethylindocarbocyanine tetrakis-(phenyltriptycenyl)borate is consistent with the physical properties of this ion pair, and that the penetrated structure for this cyanine cation with tetrakis(phenyl-ethynyl)borate anion is in agreement with its solid-state structure revealed by X-ray crystallography.[7] We applied thes calculations to assess the structures of ion pairs formed from pyrylium cations and naphthalenesulfonate anions. The predicted structure was tested by experiments in the solid state and in solution.

Application of the PCMODEL molecular mechanics calculation to the ion pairs formed from the substituted

• Abstract published in *Advance ACS Abstracts*, February 15, 1994.
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(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. *J. Am. Chem. Soc.* **1990**, *112*, 6714. Pochapsky, T. C.; Stone, P. M.; Pochapsky, S. J. *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.
(5) Yang, X.; Zaitsev, A.; Sauerwein, B.; Murphy, S.; Schuster, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 793.

(6) Molecular geometries and energies were calculated with the PCMODEL interactive molecular modeling program supplied by Serena Software, Bloomington, IN, executed on a Silicon Graphics IRIS workstation. The calculations were performed with the MM2 forcefield and with an SCF π-electron calculation.
(7) Koska, N. A.; Wilson, S. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1993**, *115*, 11628.
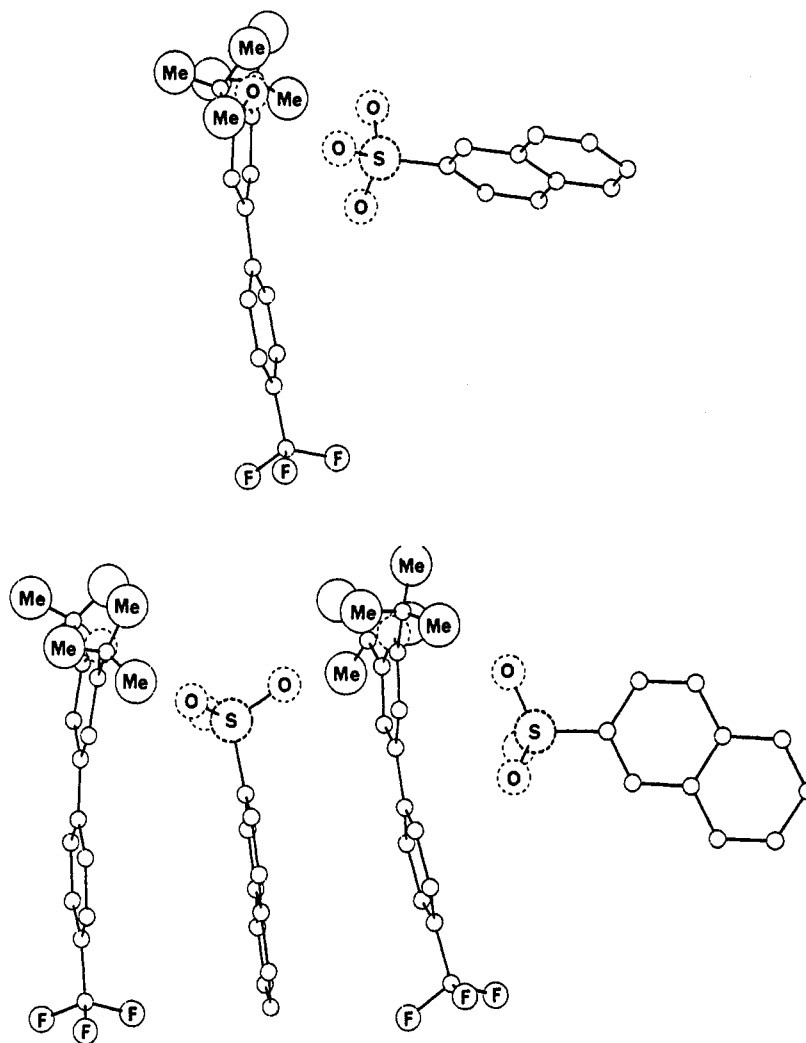
**Figure 1.** Upper part: Structural prediction from molecular mechanics calculation for a single ion pair of 1e·2NpSO₃⁻. Lower part: Structural prediction for a pair of ion pairs.

pyrylium cations with 2NpSO₃⁻ as the anion reveals a T-shaped orientation as an apparent global minimum when the "solvent" dielectric constant is set to its default value of 1.5 D. This predicted ion pair structure is shown in Figure 1. Clearly, the dominant factors controlling the relative orientation of these ions is a minimization of both the distance between opposite charges and the van der Waals repulsion between nonbonded atoms. The Coulomb stabilization energy for the ion pair in the T-shaped orientation, estimated by assuming that the sulfur atom of the sulfonate is the center of negative charge and that positive charge is centered in the pyrylium ring (a distance of ca. 3.4 Å), is more than 80 kcal/mol. Of course, this value is inversely proportional to the presumed dielectric constant of the medium, and the estimation of this quantity has considerable uncertainty. In particular, it is important to note here that the X-ray structure of 1e·2NpSO₃⁻ reveals a π face-to-face rather than a T-shaped orientation (see below). To test the sensitivity of the structural orientation prediction for the ion pair to the electric field of neighboring ion pairs, the molecular mechanics calculations were repeated for two ion pairs located at van der Waals distance. In this case, a π face-to-face orientation (see Figure 1) for the sandwiched 2NpSO₃⁻ is found as (at least) a local minimum. This finding suggests that the minimum energy structures in solution and in the solid state may be different, and that the solution structure for the ion

pair may be strongly dependent on the dielectric constant (local electric field) of the solvent.

**X-Ray Crystal Structure of [4-[p-(Trifluoromethyl)phenyl]-2,6-di-tert-butylpyrylium 2-Naphthalenesulfonate.** In contrast to the molecular mechanics calculation prediction for isolated ion pairs, X-ray analysis of 1e·2NpSO₃⁻ shows that the pyrylium cation and the naphthalenesulfonate anion are stacked in an almost parallel π face-to-face orientation, as is shown in Figure 2.

Single crystals of 1e·2NpSO₃⁻ were obtained from 95% ethanol solution by slow evaporation of the solvent.[8a,b] The ion pairs in these triclinic crystals are packed in a π face-to-face structure with each unit cell consisting of four ion pairs. Within the unit cell there are two slightly different conformations for the ion pairs, and each of these ion pairs is related by an inversion center to another ion pair. In the solid-state structure, the naphthalene rings and the aryl ring on the 4-position of the pyrylium group lie essentially parallel to each other with the anionic sulfonate group approximately centered over the pyrylium ring. In appears that this arrangement is stabilized by

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(8) (a) Structure details are given in the supplementary material. (b) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.
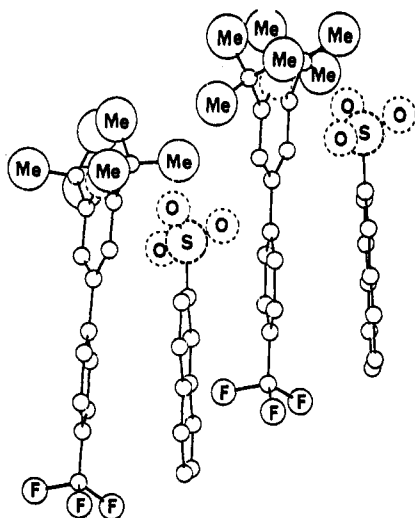
**Figure 3.** Absorption spectra recorded in DMC solution. The solid line is the spectrum of 1c·2NpSO$_3^-$, the dashed line is 1c·ClO$_4^-$, the dotted line is the difference spectrum obtained by subtracting the spectrum of 1c·ClO$_4^-$ and (*n*-Bu)$_4$N$^+$2NpSO$_3^-$ from 1c·2NpSO$_3^-$.



**Figure 2.** Lower part: Solid state structure for 1c·2NpSO$_3^-$. View is along a plane approximately parallel to the pyrylium ring. Hydrogen atoms are not shown, and the crystal contains one H$_2$O per ion pair thought to be bridging two sulfonate groups by hydrogen bonding ($r_{H-O-SO_3}$ = 2.8 Å). The parallelogram outlines a unit cell containing four unique ion pairs. Upper part: X-ray structure showing $\pi$ face-to-face arrangement of the ion pairs.

both dispersive $\pi$-electron interactions and by Coulombic attraction of the ions. The distance between the overlapping aromatic rings is 3.5 Å in both conformers. Also, the distance between the closest oxygen atom of the sulfonate and the ring-oxygen atom of the pyrylium is 2.9 Å.

**Properties of Pyrylium Naphthalene Sulfonate Ion Pairs in Solution.** The solid-state structure and the structure of these ion pairs in solution clearly need not be identical. A series of experiments was performed in an attempt to decide if either a T-shaped orientation or the solid state $\pi$ face-to-face arrangement are the structure of the pyrylium naphthalenesulfonate ion pairs when they are dissolved in a nonpolar solvent.

**(1) Absorption Spectra and C-T Complex Formation.** The absorption spectra of 1c·2NpSO$_3^-$ in dimethylcarbonate[9] (DMC) solution reveals evidence for the

formation of ion pairs. The difference absorption spectrum shown in Figure 3 is the result of subtracting the absorptions of 1c·ClO$_4^-$ and tetra-*n*-butylammonium salt (*n*-Bu$_4$N$^+$) of 2NpSO$_3^-$ from 1c·2NpSO$_3^-$ in DMC solution (all spectra were recorded at 2.4 × 10$^{-4}$ M). The difference spectrum shows a charge-transfer absorption band with an apparent maximum at 364 nm. Significantly, the charge-transfer absorption band of 1c·2NpSO$_3^-$ in DMC solution is the same at 2.4 × 10$^{-6}$ M as it is at the higher concentration. This observation seems to indicate that there is no aggregation beyond the formation of ion pairs over this concentration range.

The appearance of a charge-transfer band in the spectrum of 1c·2NpSO$_3^-$ in DMC solution indicates that these ions are associated in this solvent. The association must be a consequence of Coulombic attraction since in acetonitrile, where this force is much weaker, there is no detectable charge-transfer band. Similarly, with naphthalene, a better electron donor but lacking a negative charge, no charge-transfer absorption is detectable even in DMC solution. The appearance of the charge-transfer band under these circumstances demonstrates that 1c·2NpSO$_3^-$ probably exists as an intimate ion pair, but it does not provide clear evidence for the structure of the ion pair.

**(2) NOE Experiments.** Clear evidence for the structure of an ion pair in solution can sometimes be obtained from intra-ion nuclear Overhauser experiments. In the present case, $^1$H NOE experiments were performed on 1g·2NpSO$_3^-$ in CDCl$_3$ solution. No intra-ion NOE effects were observed. This finding is more consistent with the T-shaped structure for the ion pair than the $\pi$ face-to-face orientation, but a negative result of this sort must be interpreted with caution.

**(3) Photoinitiated Electron Transfer of Freely Solvated Ions.** In acetonitrile solution at low concentration, the 2,6-di-*tert*-butyl-4-arylpyrylium cations, as their BF$_4^-$ or ClO$_4^-$ salts, are expected to exist as independently solvated ions.[10] Under these conditions the pyrylium cations studied in this work are fluorescent,

(9) DMC was selected because it does not quench the excited singlet states of the pyrylium cations, and its low dielectric constant insures formation of ion pairs, see below. Ion pairs should be present. Pawlak, Z.; Robinson, R. A.; Bates, R. G. *J. Solution Chem.* **1978**, *7*, 631.
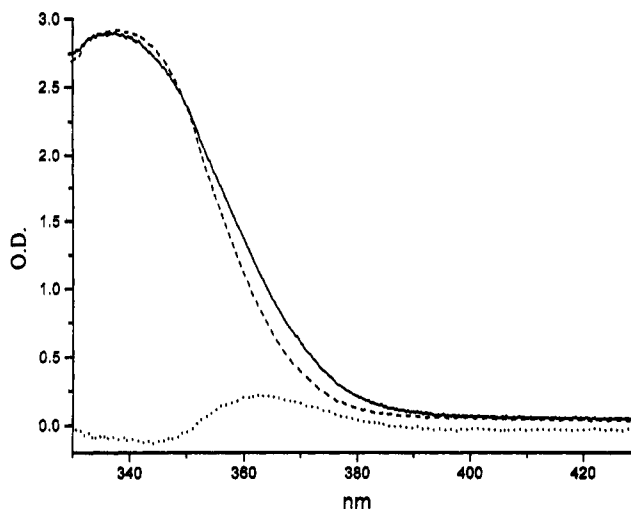
(10) Barthel, J. *Angew. Chem. Int. Ed.* **1968**, *7*, 260.

**Table 1. Physical Properties of 1 in Acetonitrile at Room Temperature**

| [Py]+: Ar = | $\Phi_{FL}$ (%) | $\tau$ (ns) | $k_{FL} \times 10^{-6}$ s$^{-1}$ | $E^*_{oo}$ (eV) | $-E_{Red}$ (vs SCE) | $-E^*_{Red}$ (eV) |
|---|---|---|---|---|---|---|
| Ph | 14.0 | 10.0 | 14.0 | 3.31 | 0.63 | 2.68 |
| 4-MePh | 33.0 | 6.0 | 55.0 | 3.22 | 0.64 | 2.58 |
| 4-ClPh | 20.0 | 2.4 | 83.0 | 3.32 | 0.60 | 2.72 |
| 4-CNPh | 3.0 | 1.8 | 17.0 | 3.35 | 0.57 | 2.78 |
| 4-CF$_3$Ph | 4.0 | 8.6 | 4.7 | 3.50 | 0.54 | 2.97 |
| 4-MeOPh | 0.3 | 3.0 | 1.1 | 2.84 | 0.73 | 2.11 |
| 3,5-(Me)$_2$Ph | 9.0 | 25.0 | 3.6 | 3.05 | 0.68 | 2.37 |
| 2,4,6-(Me)$_2$Ph | 3.0 | 7.9 | 3.8 | 3.02 | 0.73 | 2.29 |

and their singlet energies ($E_{oo}$) depend on the specific substitution of the 4-aryl group. Similarly, the fluorescence quantum yields ($\Phi_{FL}$) and fluorescence lifetimes ($\tau_{FL}$) of these pyrylium cations vary with the nature of the substituent. These data are summarized in Table 1. Interestingly, analysis of the $\Phi_{FL}$ and $\tau_{FL}$ data shows that the radiative rate constants ($k_{FL}$) of the pyrylium cations also depend on the substituent. This may indicate that these cations have two excited singlet states with similar energies and that the substituent determines which of these has the lowest energy. In this regard, Markovitisi and co-workers recently reported that theoretical calculations and spectroscopic measurements show that there are two close-lying excited states for triarylpyrylium cations.[11]

The reduction potentials ($E_{red}$) of the pyrylium cations were determined in order to assess the free energy change for electron transfer ($\Delta G_{ET}$) to their excited singlet states. These cations show quasireversible cyclic voltammetric waves in deoxygenated acetonitrile solution at room temperature. The reduction potentials reported in Table 1 are the midpoints between reduction and reoxidation waves with ferrocene as an internal standard.

Unfortunately the oxidation potential ($E_{ox}$) of 2NpSO$_3^-$ cannot be measured directly. In acetonitrile solution, only an irreversible oxidation wave with a peak at 1.2 V vs ferrocene ($E_{ox}$ = 1.5 V vs SCE) is observed. In support of this estimate, we find that $n$-Bu$_4$N$^+$2NpSO$_3^-$ quenches the fluorescence 9-cyanoanthracene[12,13] in acetonitrile solution with $k_q \approx 7 \times 10^8$ M$^{-1}$ s$^{-1}$. Another estimate of $E_{ox}$ for 2NpSO$_3^-$ comes from a plot of the oxidation potentials of substituted naphthalenes against the Hammett $\sigma$ constants of the substituent.[14,15] This approach yields a linear relationship and an estimate of $E_{ox}$ for 2NpSO$_3^-$ of 1.7 V. Despite consistency in the indirect determinations of $E_{ox}$ for 2NpSO$_3^-$, the true thermodynamic value is unknown, and this limitation dictates caution in the interpretation of results that rely on this quantity.

The fluorescence of 1g·ClO$_4^-$ in acetonitrile solution is quenched by naphthalene and $n$-Bu$_4$N$^+$2NpSO$_3^-$ with rate constants ($k_q$) = 1.4 × 10$^{10}$ and 2.8 × 10$^{10}$ M$^{-1}$ s$^{-1}$, respectively. These rate constants are close to the usual

estimate for the diffusion-limited rate constant ($k_{diff}$) in acetonitrile solution. Interestingly, despite the fact that 2NpSO$_3^-$ is more difficult to oxidize than naphthalene, its quenching rate constant has the greater value. This may be due to Coulombic attraction, which will affect the relative motion of the ions when they are close together. Or it might indicate some contribution from static quenching of preassociated ions in the acetonitrile solution. Since $k_q$ is nearly at the diffusion value, the rate constant for electron transfer ($k_{ET}$) is much faster than the escape from the solvent cage ($k_{diff}$).[16] This approach indicates a minimum value for $k_{ET}$ of 2.8 × 10$^{10}$ M$^{-1}$ s$^{-1}$ for 2NpSO$_3^-$.

**(4) Intra-Ion Pair Electron Transfer in Nonpolar Solvent.** The excited state reduction potentials ($E_{Red}^{1*}$) of the pyrylium cations can be calculated from the $E_{Red}$ and $E_{oo}$ values that are reported in Table 1. These singlet excited states are extraordinarily powerful oxidants and are expected to oxidize solvents such as benzene and THF. Measurements of their fluorescence properties support this prediction. For example, both the fluorescence yield and lifetime of 1g·ClO$_4^-$ in benzene solution are one-third of their values in acetonitrile solution. And, for 1c, a stronger oxidant than 1g, the fluorescence is completely quenched in benzene solution. Irradiation of 1g in benzene gives biphenyl, a product indicating the likely formation of benzene radical cation. The fluorescence of 1g is also quenched by THF, presumably also be electron transfer. For these reasons we examined the properties of these pyrylium naphthalenesulfonate salts in DMC solution.

The fluorescence quantum yields of the pyrylium ClO$_4^-$ or BF$_4^-$ salts in DMC are essentially the same as they are in acetonitrile solution, a fact indicating that DMC does not quench the excited singlet states. Also, the absorption and fluorescence spectra of these pyrylium salts in DMC are nearly identical to those recorded in acetonitrile solution. These observations indicate that there is little perturbation of the ground or excited state of the cations when the solvent is changed from acetonitrile to DMC.

The dielectric constant of DMC is 3.11 D at room temperature.[17] Consequently, on the basis of the Fuoss equation,[18] we expect that the pyrylium naphthalene-sulfonate salts will be essentially completely associated into ion pairs at normal concentrations in DMC solution. This prediction was tested experimentally by examination of the fluorescence properties of the pyrylium salts in DMC solution. The fluorescence intensity of 1c·ClO$_4^-$ in DMC increases as expected over the concentration range form 1.2 × 10$^{-6}$ to 1.1 × 10$^{-5}$ M as the absorbance at the excitation wavelength, 340 nm, increases from 0.05 to 0.45. Similarly, the fluorescence intensity of 1g·2NpSO$_3^-$ in acetonitrile solution over this concentration range is approximately the same as it is in DMC solution. In contrast, only a small residual (ca. 1%) fluorescence intensity is observed for 1g·2NpSO$_3^-$ in DMC solution even at the lowest concentration examined. These findings are summarized in Figure 4. Clearly, 1g and 2NpSO$_3^-$ are associated as an ion pair in DMC solution, and 2NpSO$_3^-$ quenches the excited singlet state of the pyrylium cation.

The rate constants for intra-ion pair quenching for the pyrylium naphthalenesulfonates can be calculated from their fluorescence intensities with the assumption that the radiative rate constant of the pyrylium is unaffected by the counterion. This seems likely since the absorption

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(12) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(13) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker, Inc.: New York, 1978; Vol. XI.

(14) Jaffe, H. H. *Chem. Rev.* **1953**, *112*, 6329.

(15) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

(16) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. Weller, A. *Z. Physik. Chem. Neue Folge* **1982**, *133*, 93. Chen, J. M.; Ho, T. I.; Mou, C. Y. *J. Phys. Chem.* **1990**, *94*, 2289. Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403. McClesky, T. M.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1992**, *114*, 6935. Kikuchi, K.; Niwa, T.; Takahashi, Y.; Ikeda, H.; Miyashi, T. *J. Phys. Chem.* **1993**, *97*, 5070.

(17) The dielectric constant of DMC was measured in our laboratory by application of standard capacitance techniques.
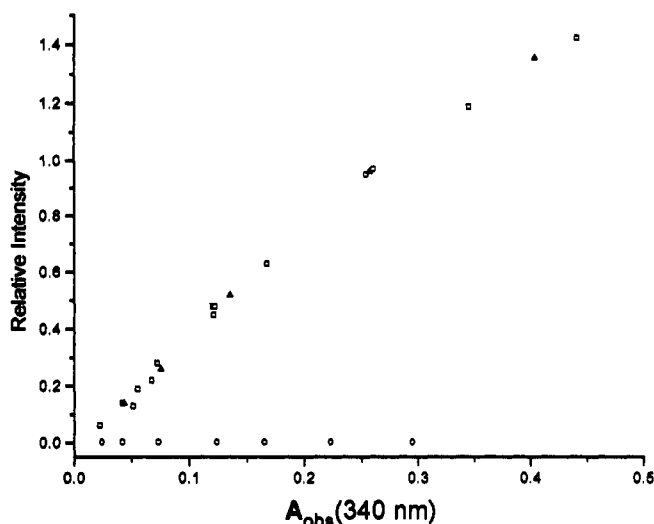
**Figure 4.** The solvent and counterion fluorescence behavior of the pyrylium salts. The solid circles are for $1g \cdot 2NpSO_3^-$ in DMC solution, the open squares are for $1g \cdot ClO_4^-$ in acetonitrile solution, and the solid triangles are for $1g \cdot 2NpSO_3^-$ in acetonitrile solution.

spectrum does not change with the counterion. However the fluorescence intensity observed from the pyrylium $2NpSO_3^-$ salts in DMC solution is only a few per cent, or less, of the value obtained for their $ClO_4^-$ or $BF_4^-$ salts. Such weak fluorescence emission makes it difficult to rule out the possibility that the observed emission is due, at least in part, to the presence of an impurity despite a satisfactory elemental analysis of the salt. Nevertheless, assumption that the residual fluorescence is from the $2NpSO_3^-$ salt provides a lower limit for the intra-ion pair quenching rate constants of $1.2 \times 10^9$ s$^{-1}$ and $2.8 \times 10^{10}$ s$^{-1}$ for $1g$ and $1c$, respectively. These data indicate that the rate constant for quenching of the excited pyrylium cation by the naphthalene sulfonate anion for the ion pair in DMC solution is slower than it is in acetonitrile solution.

**(5) Transient Absorption Spectra of Pyrylium Naphthalenesulfonates.** The mechanism for intra-ion pair quenching was probed by time-resolved absorption spectroscopy. Irradiation of $1g \cdot ClO_4^-$ in an acetonitrile solution with a 20-ps laser pulse at 355 nm instantaneously generates a transient absorption band with $\lambda_{max} = 483$ nm. The lifetime of this transient species is too long to determine precisely within the 10-ns time window of the spectrometer, but estimates are in agreement with fluorescence lifetime (25 ns) measured under these conditions for the singlet excited state of $1g$. Further, the lifetime of the 483-nm transient is shortened by addition of electron donors, such as tetramethylammonium $n$-butyltriphenylborate, known to quench the fluorescence of $1g$. On the basis of these experiments, this species is assigned to the excited singlet state of $1g$. Irradiation of an acetonitrile solution of $1g \cdot ClO_4^-$ at 308 nm with a 25-ns laser pulse reveals a second transient species with $\lambda_{max} = 450$ nm and a lifetime of 3.4 $\mu$s. This longer lived species is quenched by $O_2$—its lifetime is shortened in air saturated solution, and saturation with $O_2$ results in the further decreases of this value. On the basis of these experiments, the long-lived 450-nm absorbing transient is assigned to excited triplet state of $1g$.

In contrast to the findings for $1g$, laser irradiation of $1c \cdot ClO_4^-$ (355 nm, 20 ps) in acetonitrile solution did not

instantaneously generate an absorbing species in the detectable spectral region (400 to 700 nm). However, a transient species having an absorption with $\lambda_{max} = 475$ nm grows into the spectrum with a first-order rate constant $= 3.4 \times 10^8$ s$^{-1}$. This rate constant agrees well with the rate constant for the decay of the fluorescence of $1c$, and, on this basis, we conclude that the undetected excited singlet state of $1c$ is the precursor to the 475-nm absorbing transient species. This transient absorption is also formed when $1c$ is irradiated at 308 nm with a 20-ns laser pulse. Under these conditions this species has a lifetime of 5 $\mu$s. This lifetime is shortened in $O_2$-saturated solution. On the basis of these results, the 475-nm transient species is assigned to the excited triplet state of $1c$. Similar experiments were carried out for the other pyryliums investigated. In some cases both the singlet and triplet excited states could be detected, in others cases only one excited state was observed.

Irradiation of $1g \cdot 2NpSO_3^-$ in DMC solution at 355 nm with a 20-ps laser pulse gives a transient spectrum with bands at 485 and at 650 nm. The decay rate constants for these two absorption bands are the same, within experimental error, and correspond to a lifetime for the transient species of 330 ps. Laser irradiation of $1a$, and $1b$, as the $2NpSO_3^-$ salt in DMC solution gives similar results (the position of the ca. 485-nm band depends somewhat on the specific pyrylium cation). The decay rates for these species are the same within experimental error.

The mesitylsulfonate ($MesSO_3^-$) salts of the pyrylium cation $1g$ was prepared to help assign the transient species detected in the laser irradiation experiments. With this anion, the spectrum recorded after laser flash photolysis of the pyrylium in DMC solution shows only the absorption band with a maximum at 485 nm.

The radical cation of $2NpSO_3^-$ [19] was generated independently by irradiation of a DMC solution containing tetracyanoethylene (TCNE) and $n$-$Bu_4N^+$ $2NpSO_3^-$. Neither TCNE or $n$-$Bu_4N^+$ $2NpSO_3^-$ absorbs at 355 nm; however, the mixture of the two shows a maximum at 360 nm. Irradiation of this mixture at 355 nm with a 20-ps laser pulse gives a transient spectrum consisting of bands at 435 and 650 nm. The 430-nm band is attributed to the absorption of the TCNE radical anion,[20] and the 650-nm band is assigned to the radical cation. Additional support for this assignment comes from the observation that many 2-substituted naphthalene radical cations have absorptions in the range from 600 to 700 nm.[21]

On the basis of these experiments, the transient species detected in the irradiation of the pyrylium naphthalenesulfonate ion pairs in DMC solution are assigned to the pyrylium radical ($\lambda_{max} \approx 485$ nm) and the naphthalenesulfonate radical cation ($\lambda_{max} \approx 650$ nm) formed by intra-ion pair electron transfer. Consequently, the intra-ion pair quenching mechanism is electron transfer from the naphthalenesulfonate anion to the excited singlet state of the pyrylium cation.

## Discussion

A major objective of this work was an attempt to identify the structure of the pyrylium naphthalenesulfonate salts

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(19) Oxidation of the $2NpSO_3^-$ will lead formally to neutral radical. However, we prefer to think of this species as the radical cation of the naphthalenesulfonate anion.

(20) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

(21) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

in the solid state and in solution. In the first case this is a straightforward task since 1e·2NpSO₃⁻, which is presumed to be typical of the others, forms crystals suitable for X-ray examination. From analysis of these results it is clear that in the solid state these salts adopt a head-to-head, π face-to-face structure. In contrast, molecular mechanics calculations predict that the isolated ion pair in a simulated low dielectric environment will adopt a T-shape. Additional confidence in the prediction of the ion pair structure comes from the calculation for a pair of ion pairs which yields a π face-to-face orientation that resembles the X-ray result. In fact, the major differences between the structure predicted by the molecular mechanics calculation and the solid-state structure may be readily attributed to effects of nearby ion pairs that are not included in the calculation. Thus, despite the solid-state structure, it seems possible that the ion pair in solution may adopt the T-shaped predicted by the calculation. It is a difficult task to establish the structure of an ion pair in solution since only indirect evidence can be obtained.

Analysis of the absorption and emission spectra of the pyrylium naphthalenesulfonate salts in DMC solution shows conclusively that ion pairs are formed under these conditions. The evidence supporting this conclusion comes primarily from the appearance of a charge-transfer absorption band and from the nearly complete quenching of the pyrylium fluorescence at low concentrations of the salt. If the pyrylium cation and the naphthalenesulfonate anion were dissociated in DMC solution, then fluorescence quenching, even with a rate constant at the diffusion limit, would be modest. It comes as no surprise that ion pairs are formed in DMC solution and is a clear prediction from analysis of conductivity dependence on solvent dielectric constant. However, it is a difficult task to decide if these ion pairs are T-shaped, π face-to-face, or a set of equilibrating structures.

In principle, NOE experiments can reveal the structure of an ion pair in solution. Close contact between non-bonded atoms of the two ions should lead to enhancements. This is seen in cyanine borates which form penetrated ion pairs.[22] However, no inter-ion NOE is seen for the pyrylium naphthalenesulfonates. Since the distance between relevant atoms is greater in the T-shaped structure than in π face-to-face, this finding is seemingly consistent with the molecular mechanics prediction. However, since it is negative, this result must be interpreted with special caution. It could be that the NOE enhancements for the π face-to-face orientation are simply too small to be detected under the experimental conditions.

The reactivity of the ion pairs might provide some evidence for their structure in solution. The excited singlet states of the pyrylium cations are powerful oxidants. In acetonitrile solution, where they exist as freely solvated ions, 2NpSO₃⁻ quenches these excited states rapidly by single electron transfer. The same reaction occurs when the pyrylium naphthalenesulfonate ion pairs are irradiated in DMC solution. The time-resolved laser spectroscopy experiments reveal the formation of the singlet and triplet excited states of the pyrylium cations in acetonitrile solution, but irradiation of the ion pairs in DMC gives only the pyrylium radical and the naphthalenesulfonate radical cation. Thus, intra-ion pair electron transfer is a very rapid reaction for the photoexcited pyrylium naphthalenesulfonate in DMC solution. However, if the residual weak fluorescence is not due to impurities, this reaction is slower than it is for the encounter complex in acetonitrile solution. The structure of the encounter complex of the cation and anion formed in acetonitrile presumably depends less on minimization of the distance between positive and negative charges than it does in DMC because of the much higher dielectric constant of the former. Consequently, the structure of the contact ion pair may be different in acetonitrile and DMC solution. Since the charges are closer in a T-shape than in the π face-to-face structure, the former is more likely in DMC than in acetonitrile solution. This result supports the molecular mechanics prediction of a T-shape for the pyrylium naphthalenesulfonate in low dielectric constant solvents. The smaller rate constant for electron transfer in DMC is consistent with poorer overlap in the T-shaped ion pair than in the π face-to-face arrangement that might be formed in acetonitrile. However, this evidence for the structure of these ion pairs is indirect and must be considered highly speculative.

## Conclusions

Pyrylium naphthalenesulfonate salts form ion pairs in DMC solution that exhibit charge-transfer absorptions and result in the rapid quenching of the pyrylium fluorescence. Molecular mechanics calculations predict that these ion pairs will exist in a T-shaped orientation but X-ray structural analysis reveals a π face-to-face arrangement in the solid state. Experiments carried out in solution are consistent with a T-shape, but do not prove that this is the structure for the ion pair.

## Experimental Section

**General.** Melting points were measured with capillaries and were not corrected. UV-vis absorption spectra were recorded with a Varian Instruments Cary-1E spectrometer at room temperature. NMR spectra were recorded on General Electric QE300 or a Varian XL 200 instruments. The chemical shifts are relative to CHCl₃ (δ = 7.26 ppm). The NOE experiments were carried out with a Varian Unity 400 spectrometer. A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC-MS analyses. Fluorescence quantum yields were measured with a SPEX Fluorolog spectrofluorometer at room temperature. Fluorescence lifetimes were determined on a PTI LS-1 spectrometer at room temperature. The dimethyl carbonate was distilled from P₂O₅. Acetonitrile was spectroscopic grade (Aldrich) and was distilled from CaH₂. The time-resolved absorption apparatus has been described previously.[23] Elemental analyses were performed by the Microanalytical laboratory of the University of Illinois.

**Synthesis of the Pyrylium Perchlorates.[24]** Methyl 4,4-dimethyl-3-oxo-pentanoate (50 g) was placed in a 100-mL round-bottom flask equipped with a Vigreaux column and a distillation head. The temperature was adjusted so that volatile material distilled leaving a high boiling residue that was distilled under vacuum. The portion boiling at ca. 110 °C (0.01 mmHg) was collected (9 g, 24%). This material was added to a mixture of acetic acid (25 mL) and concentrated HCl (25 mL) and heated overnight. The reaction mixture was diluted with water and the organic layer was extracted with ether. The ethereal solution was washed with water and then dried over MgSO₄. Removal of the solvent gave 2,6-di-*tert*-butyl-4*H*-pyran-4-one. The crude product was purified by column chromatography (silica gel, CH₂-

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**Table 2. Analytical and Spectroscopic Data for Pyrylium ClO₄⁻ and BF₄⁻ Salts**

| compd | mp, °C | ¹H NMR | anal. found (calcd), % |
|---|---|---|---|
| 1a·BF₄⁻ | 223 | 8.0 (s, 2H), 8.1–7.5 (m, 5H), 1.6 (s, 18H) | For C₁₉H₂₅BF₄O: C 64.07; H 7.08 (C 64.07; H 7.07) |
| 1b·BF₄⁻ | 222 | 8.0 (d, *J* = 8 Hz, 2H), 8.0 (s, 2H), 7.4 (d, *J* = 8 Hz, 2H), 2.4 (s, 3H), 1.6 (s, 18H) | For C₂₀H₂₇BF₄O: C, 64.84; H, 7.36 (C, 64.88; H, 7.35) |
| 1c·ClO₄⁻ | 246 | 8.1 (d, *J* = 9 Hz, 2H), 8.0 (s, 2H), 7.6 (d, *J* = 9 Hz, 2H), 1.6 (s, 18H) | For C₁₉H₂₄Cl₂O₅: C, 56.72; H, 5.98 (C, 56.59; H, 6.00) |
| 1d·BF₄⁻ | 283 | 8.3 (d, *J* = 8 Hz, 2H), 8.2 (s, 2H), 8.1 (d, *J* = 8 Hz, 2H), 1.6 (s, 18H) | For C₂₀H₂₄BF₄NO· H₂O:C, 60.06; H, 6.61; N, 3.34 (C, 60.17; H, 6.56; N, 3.51) |
| 1e·BF₄⁻ | 228 | 8.2 (d, *J* = 8 Hz, 2H), 8.0 (s, 2H), 7.8 (d, *J* = 8 Hz, 2H), 1.6 (s, 18H) | For C₂₀H₂₄BF₇O: C, 56.23; H, 5.68 (C, 56.23; H, 5.70) |
| 1f·BF₄⁻ | 210 | 8.2 (d, *J* = 9 Hz, 2H), 8.0 (s, 2H), 7.2 (d, *J* = 9 Hz, 2H), 3.9 (s, 3H), 1.6 (s, 18H) | For C₂₀H₂₇BF₄O₂: C, 62.20; H, 7.09 (C, 62.20; H, 7.05) |
| 1g·ClO₄⁻ | 211 | 8.0 (s, 2H), 7.4 (s, 2H), 7.3 (s, 1H), 2.4 (s, 6H), 1.6 (s, 18H) | For C₂₁H₂₉ClO₅: C, 63.57; H, 7.35 (C, 63.55; H, 7.36) |
| 1h·ClO₄⁻ | 213ᵃ | 7.9 (s, 2H), 7.1 (s, 2H), 2.4 (s, 3H), 2.2 (s, 6H), 1.6 (s, 18H) | |

ᵃ A satisfactory elemental analysis was not obtained. Spectra are included in the supplementary material.

**Table 3. Analytical and Spectroscopic Data for the Pyrylium Naphthalenesulfonate Salts**

| compd | mp, °C | ¹H NMR | anal. found (calcd), % |
|---|---|---|---|
| 1a·NpSO₃⁻ | 87ᵃ | 8.1 (s, 2H), 8.2–7.3 (m, 5H), 1.6 (s, 18H) | |
| 1b·NpSO₃⁻ | 177 | 8.2 (s, 2H), 8.2–7.2 (m, 11H), 2.4 (s, 3H), 1.6 (s, 18H) | For C₃₀H₃₄O₄S: C, 73.35; H, 7.07 (C, 73.44; H, 6.98) |
| 1c·NpSO₃⁻ | 196 | 8.2 (s, 2H), 8.2–7.3 (m, 11H), 3.2 (br, 2H), 1.6 (s, 18H) | For C₂₉H₃₁ClO₄S· H₂O: C, 65.79; H, 6.36 (C, 65.83; H, 6.29) |
| 1e·NpSO₃⁻ | 187 | 8.2 (s, 2H), 8.3–7.3 (m, 11H), 3.7 (br 2H), 1.6 (s, 18H) | For C₃₀H₃₁F₃O₄S· H₂O: C, 64.18; H, 5.82 (C, 64.04; H, 5.91) |
| 1g·NpSO₃⁻ | 143 | 8.2 (s, 1H), 8.1 (s, 2H), 7.8–7.1 (m, 9H), 2.3 (s, 6H), 1.6 (s, 18H) | For C₃₁H₃₆O₄S: C, 73.84; H, 7.20 (C, 73.78; H, 7.19) |
| 1g·MesSO₃⁻ | 165 | 8.2 (s, 2H), 7.9 (s, 2H), 7.3 (s, 1H), 6.6 (s, 2H), 2.4 (s, 6H), 2.2 (s, 3H), 1.6 (s, 18H) | For C₃₀H₄₀O₄S: C, 72.46; H, 8.15 (C, 72.54; H, 8.12) |
| (*n*-Bu)₄N⁺ NpSO₃⁻ | 116 | 8.2–7.4 (m, 7H), 3.0 (t, *J* = 8 Hz, 8H), 1.6 (m, 8H), 1.3 (m, 8H), 0.9 (t, *J* = 8 Hz, 12H) | For C₂₆H₄₃NO₃S: C, 69.48; H, 9.67 (C, 69.44; H, 9.64; N, 3.11) |

ᵃ A satisfactory elemental analysis was not obtained. Spectra are included in the supplementary material.

triphenylmethyl tetrafluoroborate in boiling glacial acetic acid for 30 min. The pyrylium tetrafluoroborates were precipitated from solution by addition of ether (yields 72–87%). NMR spectral data and elemental analyses for these compounds are summarized in Table 2.

**Synthesis of Pyrylium 2-Naphthalenesulfonates.[26]** A mixture prepared from the pyrylium perchlorate (or tetrafluoroborate) salt in 95% ethanol and an equal volume of an aqueous 20% sodium acetate solution was heated at reflux for 10 min, cooled to room temperature, and then placed in a freezer for 12 h. The white solid that precipitated, 5-aryl-2,2,8,8-tetramethylnon-5-ene-3,7-dione, was collected and purified by recrystallization from hexane (yields ~ 90%). The nonenedione was dissolved in ethanol, and a 20% molar excess of 2-naphthalenesulfonic acid was added. Removal of the solvent gave the crude pyrylium sulfonates, which were purified by recrystallization from methylene chloride and ether (yields 60–92%). NMR spectral data and elemental analyses for these compounds are summarized in Table 3.

**Supplementary Material Available:** Copies of ¹H NMR spectra of 1h·ClO₄⁻ and 1a·NpSO₃⁻ (2 pages). This material is contained in 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.

Cl₂) to yield 3.2 g (49%) of pure material. The appropriate Grignard reagent was prepared from the aryl halide and magnesium and was added to an equal molar amount of the pyran-4-one in dry THF solution at 0 °C. The solution was warmed to room temperature and stirred for 30 min, and then the mixture was poured into a dilute HClO₄ solution. The solid that precipitated was collected and then redissolved in CHCl₃. The chloroform solution was dried (MgSO₄) and recrystallized by addition of ether to the CHCl₃ solution. The yields of the pyrylium perchlorates obtained by this procedure ranged between 70 and 80%. NMR spectral data and elemental analyses for these compounds are summarized in Table 2.

**Synthesis of Pyrylium Tetrafluoroborates.[25]** Equimolar amounts of pinacolone and the appropriately substituted benzaldehyde were added to a solution of NaOCH₃ (10%) in methanol. The reaction mixture was heated at reflux for 4 h and then added to a saturated Me₄NCl solution in water. The aqueous solution was extracted with CHCl₃ and the CHCl₃ layer was washed with water and brine and then dried (MgSO₄). Removal of the solvent gave 1-aryl-4,4-dimethylpent-1-en-3-ones (yields > 90%). A mixture was prepared containing the penten-3-one, NaNH₂ suspended in benzene, and pinacolone in a molar ratio of 1:1.5:1. The mixture was heated at reflux for 20 h and worked up as described above to give 5-aryl-2,2,8,8-tetramethylnonane-3,7-diones (yields 80–96%). The diketones were converted into pyrylium cations by reaction with equal molar amounts of

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