The differences between the single- and double-chain stilbenes is probably due to one of two factors. It is reasonable to expect that the anchoring of the chromophore by imbedding both ends into a nearly crystalline lattice should impose severe restrictions on twisting; this could in itself account completely for the limiting ϕ_f values rapidly attained below T_c. Another possibility is that the more effective "anchoring" provided by the second chain restricts the stilbene to an interior site and prevents any migration to or equilibration with the interface region. The observation of only a single component for fluorescence decay with 6S4A and 4S4 supports this as does a study of bromination rates of the stilbenes in DPL which shows extremely slow rates for 6S4A and 4S4 compared to the single-chain stilbenes;[73] since bromination rates are extremely sensitive to the "polarity" of the environment, the slow rate for these compounds supports a view that they are restricted to highly hydrophobic sites, most likely in an ordered hydrocarbon region of the vesicle.

The difference in behavior between 4S4 (di-*n*-butylstilbene) and S is especially striking; the apparent preference of S for an interface site is noteworthy and suggests that structurally related molecules such as 1,4-diphenylbutadiene could occupy similar sites and not the "interior" site often assumed.[40–42] It has been recently demonstrated that the extent of intramolecular excimer formation in 1,1'-dipyrenyl methyl ether can be correlated with T_c for several vesicles; in these studies it has been found that different Arrhenius parameters are obtained above and below T_c as is the case with the stilbenes.[75] However, for the dipyrenyl compound E_a obtained *below* T_c is much larger than that measured at higher temperatures—a finding opposite to those reported above for the stilbenes.[75] The most likely reason for this difference is a difference in the solubilization of the pyrene and stilbene probes. While the stilbene probes are probably very close to passive as far as interrupting the bilayer structure is concerned, it seems reasonable that a larger and non-rodlike molecule such as the dipyrenyl derivative cannot "fit" simply into a crystalline region of the bilayer. Whether this molecule resides at an interface or simply in an interrupted part of the bilayer interior cannot be ascertained; thus although its activation parameters suggest it is in a more solution-like environment as far as microviscosity is concerned, it must be close enough to "normal" areas of the bilayer to be sensitive to the bulk changes occurring near T_c. Along these lines Zachariasse[33] has concluded from a study of 1,3-dipyrenylpropane in vesicles (where similar results are obtained) that the probe must perturb the lipid structure in the ordered phase such that the vesicle is relatively fluid in the vicinity of the probe. It would seem reasonable that a melting or related perturbation probably occurs when other large aromatics, whose fluorescence depolarization behavior readily detects T_c, are "dissolved" in vesicles.

In conclusion, it must be acknowledged that virtually all fluorescent probes or molecules (e.g., spin-label probes)[80,81] having structures very different from the component lipids can produce structural changes in the assembly or occupy sites very different from the host. Knowledge of the microenvironment or solubilization site provided for different kinds of guests is of itself of great importance so studies using different kinds of solute-probes are of importance in any case. The surfactant stilbenes and other probes such as parinaric acid (octadecatetraenoic acid)[43–47] having structures similar to or compatible with the host lipids of vesicles or liposomes appear to offer useful information otherwise not accesible except through techniques involving studies of properties of the lipid hosts themselves; these kinds of probes offer particular use in investigating assembly–solute interactions with solutes which may not themselves serve as probes.

(80) Rothman, J. E.; Dawidowicz, E. A. *Biochemistry* 1975, *14*, 2809.
(81) Kornberg, R. D.; McConnell, H. M. *Biochemistry* 1971, *10*, 1111.

Dual Fluorescence of 4,4'-Dimethylamino- and 4,4'-Diaminophenyl Sulfone. Consequences of d-Orbital Participation in the Intramolecular Charge Separation Process

Wolfgang Rettig*† and **Edwin A. Chandross*‡**

Contribution from the Iwan N. Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin, D-1000 Berlin(W) 12, Federal Republic of Germany, and AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received August 7, 1984

Abstract: 4,4'-Dimethylaminophenyl sulfone (DMAPS) and 4,4'-diaminophenyl sulfone (APS) show multiple fluorescence in polar solvents without the strong diminution of fluorescence efficiency found for similar systems. Based on numerous similarities with the dual fluorescence of dimethylaminobenzonitrile (DMABN), a mechanism involving "twisted intramolecular charge transfer" (TICT) states is proposed. These states are mainly derived from geometries where one anilino or dimethylanilino group is rotated. Fluorescence lifetime and quantum yield data point to the forbidden nature of the radiative TICT transition. The sensitivity of the equilibrium between locally excited (LE) and TICT states to solvent polarity is related to the participation of sulfur d-orbitals which play a significant role in the symmetry reduction process necessary for TICT state formation. Solvatochromic measurements show this state to be of very high polarity, and the LE state of medium polarity. The LE → TICT transition thus involves a strong dipole moment increase accompanied by a directional flip of nearly 90°.

I. Introduction

The observation of dual fluorescence in dimethylaminobenzonitrile (DMABN)[1] stimulated the work of many research groups and eventually led to the notion of "twisted intramolecular charge transfer" (TICT) excited states.[2] These states are possible in

† Technical University of Berlin.
‡ AT&T Bell Laboratories.

(1) E. Lippert, W. Lüder, and H. Boos in "Advances in Molecular Spectroscopy", A. Mangini, Ed., Pergamon Press, Oxford, 1962, p 443.
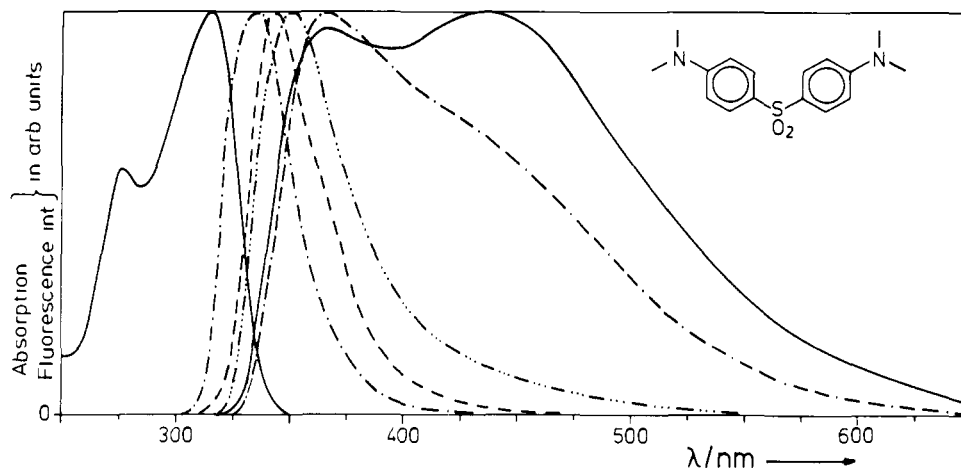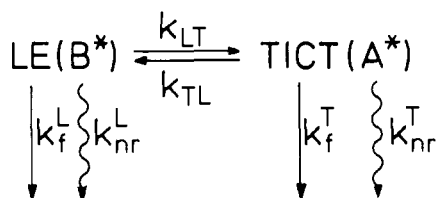
Figure 1. Corrected fluorescence spectra of DMAPS at room temperature in *n*-hexane (····), *n*-butyl chloride (---), tetrahydrofuran (-···-), acetonitrile (·-··) and ethanol (—), and absorption spectrum in ethanol.

Scheme I

$$LE(B^*) \underset{k_{TL}}{\overset{k_{LT}}{\rightleftharpoons}} TICT(A^*)$$

$$\Big\downarrow k_f^L \Big\} k_{nr}^L \qquad\qquad \Big\downarrow k_f^T \Big\} k_{nr}^T$$

molecules that can have perpendicular π-systems, and involve a full intramolecular charge separation. If the groups involved are not perpendicular in the ground state, an intramolecular rotational relaxation in the excited state can lead to TICT geometry. For DMABN and related dialkylamino compounds, the twisting donor moiety has been shown to be the dialkylamino group.[2,3] Other known donor groups[2] range from the anilino,[4] anthryl,[5] or carbazole groups[6] to a variety of substituted pyrrole groups.[7] DMAPS is related to DMABN by its donor–acceptor properties, but possesses two different rotational possibilities which can lead to TICT states, namely, the rotation of a dimethylamino group as donor, or of an entire dimethylanilino group. In this respect it is very similar to the diphenylmethane dye Michler's ketone (MK), which also shows dual fluorescence,[8,9] but it differs strongly from MK in its ground-state geometry. X-ray analysis of APS,[10] the antileprosy and antimalarial drug Dapsone, established that both phenyl rings are approximately perpendicular to the N···S···N plane. Similar conclusions follow from the UV spectra of sterically hindered sulfones[11] and are rationalized by the participation of sulfur d-orbitals in the mesomeric interaction. d-Orbital participation is also possible in an all-planar arrangement of the two phenyl rings as suggested by ESR data.[12]

The d-orbital participation has significant consequences regarding the properties of the TICT state and its formation and decay kinetics. This is shown by comparison with the TICT

properties of other compounds where d-orbital participation is not possible.

II. Experimental Section

4,4'-Dimethylaminophenyl sulfone (DMAPS) was prepared by treatment of the commercially available diamino compound (APS) with excess trimethyl phosphate in boiling diglyme (16 h). The product was
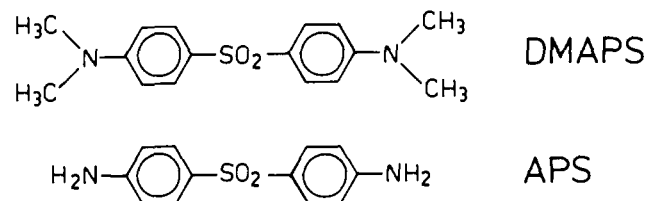
heated with aqueous sodium hydroxide to remove traces of methyl phosphate to give an off-white powder, mp 255–260° (uncor) lit. 266–268° (cor)[13]). Further purification by thin layer chromatography did not change the absorption and fluorescence spectra in ethanol. APS (EGA-Chemie) was repeatedly recrystallized. Solvents used were of Merck Uvasol quality or Fluka puriss (higher alcohols) or were purified by column chromatography and fractional distillation. They showed no luminescence at the sensitivity levels used.

Quantum-corrected fluorescence spectra were measured on a Perkin-Elmer 650-60 spectrofluorimeter with excitation near the maximum of the long-wavelength absorption band. For the determination of fluorescence quantum yields, solutions with optical density ≤0.1 were used and compared to *p*-terphenyl in cyclohexane ($\phi_f = 0.93$) as described.[14] In the case of multiple fluorescence, band decomposition was carried out by subtracting the scaled pure short-wavelength band.[15] Emission maxima were determined according to Mathias' rule[16] from the spectra corrected[17] by multiplication with λ^2 for the solvatochromic plots.

Single photon counting equipment (Edinburgh Instruments) was used for the fluorescence decay times. A good fit was obtained for a single exponential decay law in all cases. For small deviations in alcohols, see the Discussion.

III. Results

DMAPS shows a multiple fluorescence (Figure 1) in strongly polar solvents like alcohols or alkylnitriles. In weakly or moderately polar solvents, however, a second fluorescence band is absent or can hardly be detected. Similarly, a second fluorescence band is absent in a rigid polar solvent like ethanol at 77 K. Figure

(2) Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann, *Nouv. J. Chim.*, **3**, 443 (1979), and references therein.

(3) W. Rettig, *J. Phys. Chem.*, **86**, 1970 (1982).

(4) A. Siemiarczuk, Z. R. Grabowski, A. Krówczyński, M. Asher, and M. Ottolenghi, *Chem. Phys. Lett.*, **51**, 315 (1977).

(5) W. Rettig and M. Zander, *Ber. Bunsenges. Phys. Chem.*, **87**, 1143 (1983).

(6) W. Rettig and M. Zander, *Chem. Phys. Lett.*, **87**, 229 (1982).

(7) W. Rettig and F. Marschner, *Nouv. J. Chim.*, **7**, 425 (1983).

(8) E. Kirkor-Kaminska, Ph.D. Thesis, Warszawa.

(9) W. Rettig, contribution to the 8th Vortragstagung Fachgruppe Photochemie of the Gesellschaft Deuterscher Chemiker, Tübingen, Nov 1983.

(10) Ch. Dickinson, J. M. Stewart, and H. L. Ammon, *J. Chem. Soc., Chem. Commun.*, 920 (1970).

(11) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **72**, 1292 (1950); V. Baliah and V. Ramakirshnan, *J. Indian Chem. Soc.*, **35**, 151 (1958).

(12) E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963).

(13) H. Heyman and L. F. Fieser, *J. Am. Chem. Soc.*, **67**, 1979 (1945).

(14) W. Rettig, G. Wermuth, and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **83**, 692 (1979). W. Rettig and G. Wermuth, *J. Photochem.*, **28**, 351 (1985).

(15) G. Wermuth, W. Rettig, and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **85**, 64 (1981).

(16) R. Brdicka, "Grundlagen der Physikalischen Chemie", 7th ed., VEB Deutscher Verlag der Wissenschaften, Berlin, 1968, p 252.

(17) C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, 1968.
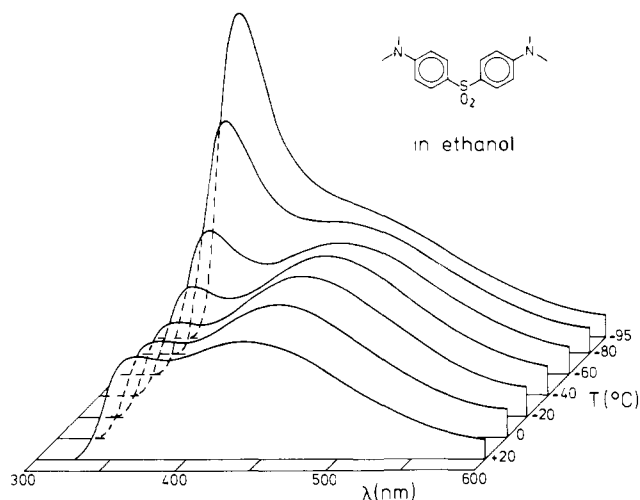
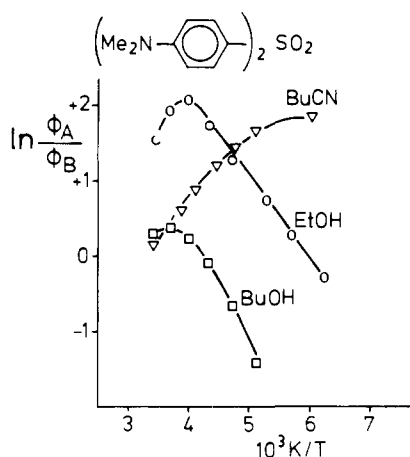**Figure 2.** Temperature dependence of the dual fluorescence of DMAPS in ethanol.

Figure 3. Quantum yield ratio of long-wavelength to short-wavelength fluorescence bands ϕ_A/ϕ_B for DMAPS in protic and aprotic polar solvents as a function of temperature.

1 also shows the long-wavelength absorption bands, which are very similar to those of Michler's ketone (MK), but somewhat blue shifted.

The multiple emission is independent of concentration over a wide range (10^{-6}–10^{-4} M) and does not depend on the excitation wavelength. In ethanol, the excitation spectra for the short- and long-wavelength fluorescence bands are identical and coincide with the absorption spectrum at room temperature as well as at low temperature (−120 °C).

In highly viscous solvents, however, such as glycerol at room temperature, the two excitation spectra are somewhat different. In these high-viscosity conditions, solute and/or solvent relaxation are slowed down to such an extent, that the decay to the ground state competes with equilibration in the excited state, and part of the fluorescence occurs from unrelaxed sites. This is known to lead to red edge excitation effects.[18]   In order to evaluate whether the long-wavelength band is due to specific solute–solvent interaction or to possible traces of water in the solvent, doping experiments were carried out. Addition of one drop of 95% ethanol to 2 mL of either acetonitrile or n-butyl chloride solution failed to change the fluorescence spectrum. Thus the spectral behavior, as shown in Figure 1, is dependent upon the bulk properties of the solvent and not on trace amounts of added protic component (alcohol and water).

Figure 2 shows the characteristic temperature dependence of the two bands. The intensity of the short-wavelength, B, band

Table I. Temperatures, T_{max}, for Which $\ln \phi_A/\phi_B$ Attains a Maximum, Indicative of the Changeover from Irreversible to Reversible Excited-State Reaction Mechanisms

| | T_{max}/K | |
solvent	DMAPS	DMABN
n-butyl chloride	~150	196[a]
n-butyronitrile	<170	>280[a,b]
ethanol	300	283[c]

[a] Reference 20. [b] By comparison with diethylaminobenzonitrile in n-butyl chloride and nitriles. [c] Reference 21.

Table II. Relative Fluorescence Quantum Yields ϕ_A/ϕ_B at Room Temperature of the Decomposed Dual Fluorescence of DMAPS, DMABN, and 9,9'-Bianthryl (BA) as a Function of Solvent Polarity

| | | $\ln \phi_A/\phi_B$ | | |
solvent	Δf^a	DMAPS	DMABN[b]	BA[c]
n-butyl chloride	0.209	≲−2.3	−0.2	−0.1
tetrahydrofuran	0.210	−1.2		0.9
n-butyronitrile	0.275	0.0	2.5	1.7
acetonitrile	0.305	1.1	3.2	2.4

[a] Polarity function[1] $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$. [b] Reference 20 and 53. [c] Reference 5.

is minimal at a certain temperature and increases on cooling or heating; that of the long-wavelength, A, band shows only a small dependence on temperature. This behavior is very similar to that observed for the dual fluorescence of DMABN and related compounds[2,19,20] and can be interpreted using a kinetic scheme (Scheme I) which involves the equilibrium of two emitting species, B* and A*.[2,19] The long-wavelength (A) fluorescence band, in this case, is unusually broad (bandwidth $\Delta\bar{\nu}_{1/2}$ 7200 ± 200 cm^{-1} in ethanol or acetonitrile at room temperature). The entire spectrum (A and B band) has a bandwidth of 9800 cm^{-1} in EtOH.

Figure 3 shows the ratio of the fluorescence quantum yields, ϕ_A/ϕ_B, given by the ratio of the areas of the two fluorescence bands. It exhibits a maximum at a temperature, T_{max}, close to the temperature where the B band has minimal intensity (Figure 2). Increasing the viscosity and reducing the polarity somewhat from ethanol to 1-butanol strongly increases the relative amount of B fluorescence, shifting the curve to lower values of $\ln\phi_A/\phi_B$. For aprotic polar solvents such as n-butyronitrile, T_{max} is shifted to considerably lower temperatures. Thus, the observable temperature region above the melting point of this solvent covers the "high-temperature" range where B* and A* states establish an equilibrium during the excited-state lifetime. The main portion of the temperature dependence in alcohols depicted in Figure 3, on the other hand, corresponds to the "low-temperature" range, where the excited-state reaction follows the irreversible mechanism, and the back reaction A* → B* does not take place during the excited-state lifetime.[9]

The changeover from one predominant reaction mechanism to the other at T_{max} occurs at significantly lower temperatures for DMAPS than for DMABN. Relevant T_{max} values are given in Table I. As is apparent from Figure 1, only the strongly polar solvents produce a readily discernible A band. The presence of a weak A band in medium polarity solvents can be inferred from the increased fluorescence band (half) widths. Detailed band decomposition leads to the relative fluorescence quantum yields, ϕ_A/ϕ_B, which are shown in Table II. For comparison, this table also contains the data for other dual fluorescence compounds forming TICT states. For these compounds, even weakly polar solvents produce a sizable TICT fluorescence band. In a large variety of solvents, the $\ln (\phi_A/\phi_B)$ values for DMABN are approximately linearly related to the solvent polarity function,[1]

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

although with a large scatter. On closer inspection, they can be

(18) K. A. Al-Hassan and M. A. El-Bayoumi, *Chem. Phys. Lett.*, **76**, 121 (1980).

(19) W. Rettig and E. Lippert, *J. Mol. Struct.*, **61**, 17 (1980).
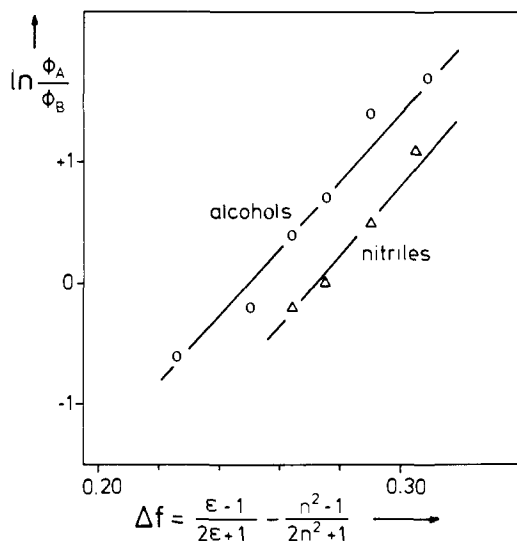(20) W. Rettig, *J. Lumin.* **26**, 21 (1981).

Figure 4. Quantum yield ratio ϕ_A/ϕ_B for DMAPS as a function of solvent polarity for homologous alcohols and nitriles.
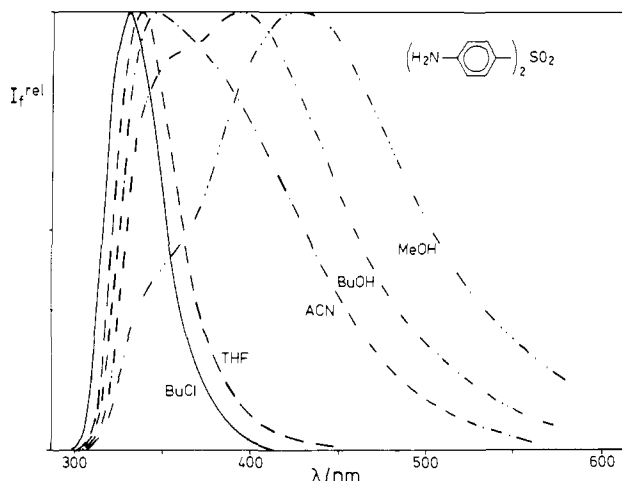

Figure 5. Corrected fluorescence spectra of APS in different polar solvents: *n*-butyl chloride (—), tetrahydrofuran (- - -), acetonitrile (- · · ·-), butanol (- ·· -), and methanol (- ···· -).

divided into two families, one for aprotic and the other for protic solvents.[21]

A similar relationship is observed for DMAPS as shown in Figure 4, where the data for the homologous alcohol and nitrile series are compared. The two solvent families are clearly different. The slopes are considerably steeper than for DMABN or BA (Table II).

The compound with the free amino group, APS, also shows dual fluorescence; cf. Figure 5.[22] In medium polarity solvents such as *n*-butyl chloride, virtually no long-wavelength component can be detected.

In more polar solvents, the ratio ϕ_A/ϕ_B is increased more than for DMAPS; it is twice that of DMAPS in ethanol, and slightly smaller in acetonitrile. Replacing the amino group with the *N*-pyrrolo group, a much better donor, leads to the corresponding pyrrolophenyl sulfone (prepared from APS in the manner described in ref 7). This compound also exhibits dual fluorescence with a considerably stronger A component than APS and DMAPS in *n*-butyl chloride and ethanol.

The fluorescence quantum yields and lifetimes for DMAPS in different solvents are compiled in Table III. Both quantum yields and lifetimes decrease in alcohols, relative to those in strongly polar

Table III. Fluorescence Lifetimes and Quantum Yields of Aerated Room-Temperature Solutions of DMAPS, the Derived LE ↔ TICT Equilibrium Constant K_e, and the Radiative and Nonradiative Decay Rates of LE and TICT States

	τ_f/ns	ϕ_f^{LE}	ϕ_f^{TICT}	K_e	$k_f/10^7$ s^{-1}	$k_{nr}/10^7$ s^{-1a}
n-hexane	1.7	0.16	0	0	9.4 (LE)	49 (LE)
acetonitrile	3.5	0.03	0.09	10	2.9 (TICT)	23 (TICT)
ethanol	3.0	0.02	0.08	13	2.9 (TICT)	28 (TICT)

^{a} Including oxygen quenching.

aprotic solvents. Similar behavior was observed in the case of DMABN[23] and a planar model compound.[24] Fluorescence decay times were also measured for DMAPS in ethanol and 1-butanol at two different wavelengths, 360 nm (B band) and 490 nm (A band). In accordance with the ln ϕ_A/ϕ_B plots in Figure 3, which indicate equilibrated states, the decay times were identical at the two observation wavelengths (3.0 ± 0.1 ns for both solvents). The observation of a slight deviation from monoexponential behavior at very short times is discussed below.

Figure 6 shows the dual fluorescence of DMAPS in the series of homologous alcohols and nitriles. This figure and Figure 4 show clearly that the A band increases with increasing solvent polarity. By separating the spectra into the two individual bands, polar solvent shifts of these bands can be measured. They are displayed in Figure 7 against a solvatochromic parameter which takes into account polarity effects of the solvent and a mean solute polarizability.[25] Thus, the much higher solvatochromic slope for the A band points to a much larger dipole moment for the A* state as compared to the B* state (ref 25 and references cited therein). Figure 8 shows the solvatochromic red shifts of the TICT band in homologous alcohol solvents. DMAPS and APS have similar solvatochromic slopes, but the TICT band of the latter is blue shifted by 1390 ± 100 cm^{-1}.

In view of the sizable fluorescence quantum yield and the extremely broad fluorescence spectrum of DMAPS in ethanol, experiments were undertaken for the possible use of DMAPS as a laser dye. No lasing action could be detected, however, under conditions where commercial laser dyes showed strong laser emission. This observation is similar to Mataga's observation[26] for ADMA (4-(9-anthryl)-*N*,*N*-dimethylaniline) which does not show any lasing action in polar solvents despite its high fluorescence quantum yield, presumably as a consequence of the electronic nature of the TICT states populated.

IV. Discussion

A. Evidence for TICT State Formation. The long-wavelength (A) fluorescence band in DMAPS and APS is connected with an adiabatic photoreaction that takes place primarily in strongly polar solvents. This can be concluded from the similarity of the excitation spectra for the B and A bands. The lack of concentration dependence precludes a bimolecular excimer mechanism, and the doping experiments with 95% ethanol/5% water suggest that specific solute–solvent interactions involving hydrogen bonds do not play a major role for the occurrence of the A band. These experiments also exclude the possibility that the A band might be due to traces of water in the solvent leading to solute–water complexes in the ground and/or excited states.

The excitation spectra of the A and B bands are identical with the UV absorption spectrum, establishing a common precursor. The temperature dependence of the two fluorescence bands (Figure 2 and 3) indicates that the two emitting states can be in an equilibrium which is highly solvent polarity and solvent viscosity dependent. The solvatochromy experiments indicate the very different polarities of the emitting species; the A band is associated with a very large dipole moment change. All these facts are very similar to the observations of TICT fluorescence in DMABN,[2,19]

(21) O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *J. Lumin.*, 6, 229 (1973).

(22) E. Lippert, A. A. Ayuk, W. Rettig, and G. Wermuth, *J. Photochem.*, 17, 237 (1981).

(23) E. M. Kosower and H. Dodiuk, *J. Am. Chem. Soc.*, 98, 924 (1976).

(24) G. Wermuth and W. Rettig, *J. Phys. Chem.*, 88, 2729 (1984).

(25) W. Rettig, *J. Mol. Struct.*, 84, 303 (1982).

(26) N. Nakashima, N. Mataga, C. Yamanaka, R. Ide, and S. Misumi, *Chem. Phys. Lett.*, 18, 386 (1973).
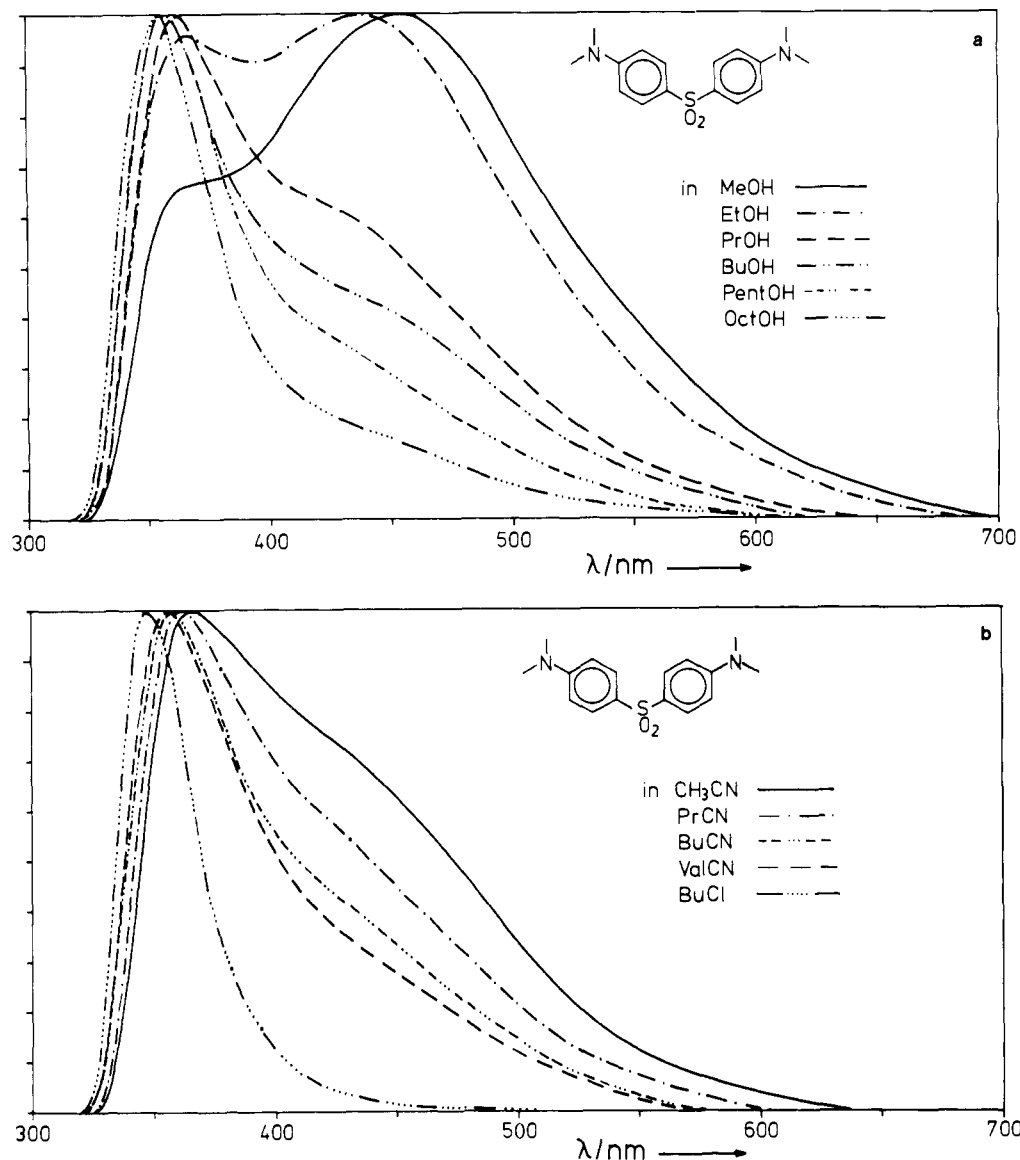
Figure 6. Dual fluorescence of DMAPS in (a) homologous alcohol solvents and (b) homologous nitriles (PrCN, propionitrile; BuCN, butyronitrile; ValCN, valeronitrile). As reference, the spectrum in *n*-butyl chloride (BuCl), which contains only a trace of the long-wavelength band, is also given.
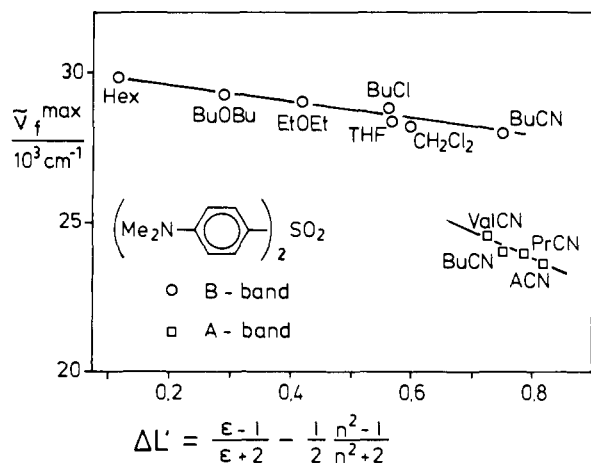
Figure 7. Solvatochromic plot for DMAPS in aprotic polar solvents. The two fluorescence bands have strongly differing solvatochromic slopes.

and therefore the A band in these sulfones is assigned to a TICT state.

We specifically eliminate the possibility that TICT state formation is connected not only with two mutually perpendicular
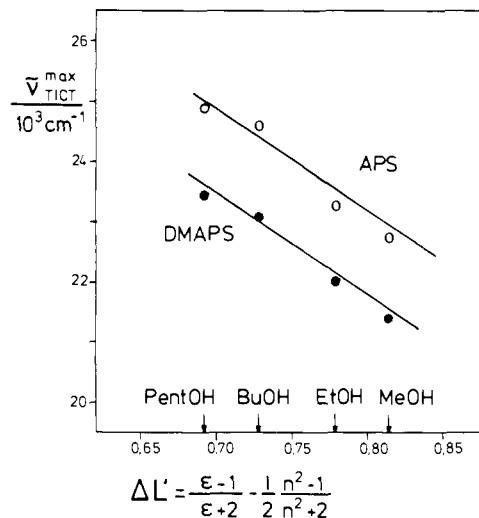
Figure 8. Solvatochromic plot for DMAPS (●) and APS (○) in homologous alcohols.

π-systems, but also with the formation of an excited-state complex (exciplex) of solute and polar solvent.[27-30] The occurrence of

5622 *J. Am. Chem. Soc., Vol. 107, No. 20, 1985*

Rettig and Chandross
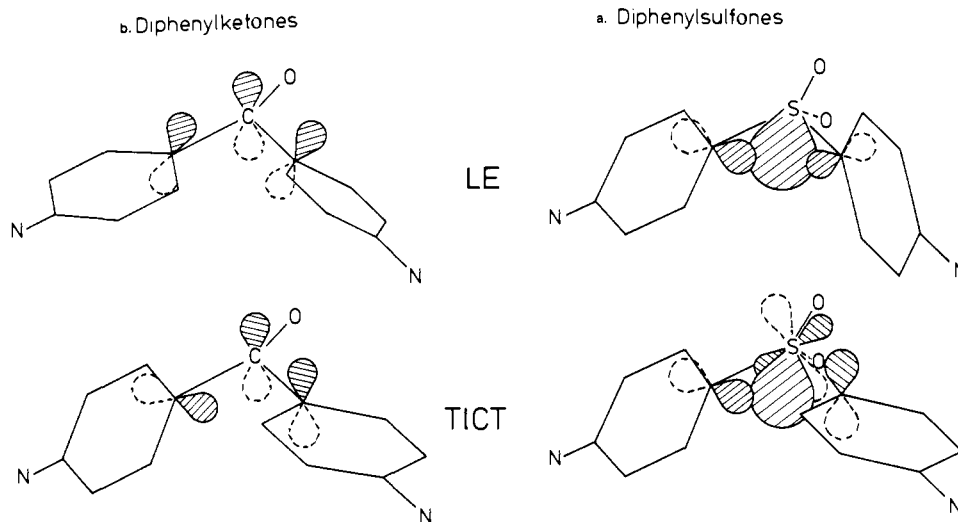
b. Diphenylketones

a. Diphenylsulfones

LE

TICT

Figure 9. π- and d-orbital participation in (a) diphenyl sulfones and (b) diphenyl ketones. The geometries for ground state and locally excited state (LE) possess phenyl ring planes perpendicular to the N···S···N plane for the sulfones, but near planar (twisted by $\sim 30°$) for the ketones. The TICT state possesses two mutually perpendicular phenyl rings in both cases. Whereas in the sulfones, both phenyl rings can interact with the center group (SO_2, π- and d-orbitals), one phenyl ring is blocked off from the center (C=O, π-orbitals only) in the TICT geometry of the diphenyl ketones.

TICT fluorescence for DMABN in alcohols, nitriles, esters, chlorides, and ethers[1] would imply formation of very similar exciplexes with all of these solvents, even though they possess very different nucleophilic and electronic properties. This is highly unlikely because the TICT state shows very specific behavior in quenching experiments with inorganic anions.[31] Moreover, there are several cases of TICT fluorescence in saturated hydrocarbon solvents, which cannot act as exciplex partners,[15,32] and even in the gas phase.[33] The role of the polar solvent thus seems to be a nonspecific bulk polarity effect, mainly energetically favoring the TICT state.

Having established that aminophenyl sulfones form TICT states, we were interested in studying compounds with a stronger acceptor group. Replacing the sulfone by a carbonyl group, Michler's ketone (MK), and its amino analogue,[34] leads to red-shifted absorption spectra, thus pointing to a higher degree of charge transfer. Indeed, recent results indicate that for both compounds, TICT state formation in polar solvents is the major excited-state pathway.[8,9] In contrast to DMAPS, MK in ethanol exhibits excitation wavelength dependent fluorescence spectra.[35] This is coupled with the much shorter fluorescence lifetime of MK in ethanol (<0.1 ns[35] vs. 3.0 ns for DMAPS). Both the excitation wavelength dependence of MK in ethanol and of DMAPS in glycerol can be explained by incomplete equilibration during the excited-state lifetime, either with respect to the surrounding solvent cage[18] or intramolecular rotational relaxation. Because of the short lifetime of MK, these effects are discernible in ethanol at room temperature, whereas for the longer lived DMAPS, they appear only in highly viscous solvents.

B. The Rotating Moieties: Comparison to the TICT State in DMABN. Both static[2] and dynamic evidence[3] lead to the conclusion that the dialkylamino group twists for the formation of the TICT state in DMABN and related compounds. In compounds with two rotational degrees of freedom, as in p-(9-

anthryl)-N,N-dimethylaniline (ADMA), only one possibility is apparently important for the TICT formation process. Model compounds for ADMA suggest that the entire aniline group rotates relative to the anthryl group for TICT formation, i.e., that dimethylamino group rotation apparently is not important.[36] DMAPS also has both rotational possibilities. In APS, on the other hand, the ionization potential of the NH_2 group is too high for a low-lying TICT state involving NH_2 rotation.[37] Thus, the occurrence of TICT fluorescence in APS implies that, similar to ADMA, the entire anilino group is rotating.[22] The same then may be assumed for the dimethylanilino group in DMAPS.

The dimethylamino group rotation is much facilitated if the cyano group in DMABN is replaced by an ester group.[22] This is one of the reasons why the ester shows sizable TICT fluorescence even in nonpolar solvents. Fluorescence polarization studies established[14] that in the ester compound, the lowest excited singlet state is a ^1L_a-type state (symmetry species A in the C_2 point group) possessing the same symmetry as the TICT state. In DMABN, on the other hand, the TICT state and B* are of different symmetry, necessitating an excited-state crossing,[3,14] which reduces the observed rate constant. In Michler's ketone, the first absorption band is due to a transition to a strongly absorbing state, polarized in the direction of the N···N axis,[34,38] which can be described by a linear combination of the ^1L_a-type states of the benzene units. From the similarity of the absorption spectra of many diphenylmethane derivatives,[38] we may assume the same for DMAPS. The S_1 state in DMAPS thus has the appropriate symmetry properties for facilitated rotation of the dimethylamino group. It is thus possible that both processes take place; i.e., the TICT band in DMAPS could be due to two different TICT species, one with a rotated dimethylanilino, the other with a rotated dimethylamino group. On the other hand, the TICT band halfwidths for DMAPS and APS in ethanol are similar (ca. 7000 cm^{-1}), a fact which indicates the involvement of only one rotational degree of freedom, as discussed below.

C. d-Orbital Participation: Steric and Kinetic Consequences. The possible importance of sulfur d-orbitals for the conjugational properties of the sulfone group has been discussed for decades. Based on theoretical arguments, Koch and Moffitt[39] concluded that in the sulfone group two types of d-orbital hybrids with

(27) E. A. Chandross in "The Exciplex", M. Gordon and W. R. Ware, Academic Press, New York 1975, p 187.

(28) R. J. Visser and C.A.G.O. Varma, *J. Chem. Soc., Faraday Trans. 2* **76**, 453 (1980).

(29) R. J. Visser, C. A. G. O. Varma, J. Konijenberg, and P. Bergwerf, *J. Chem. Soc., Faraday Trans. 2*, 347 (1983).

(30) Y. Wang and K. B. Eisenthal, *J. Chem. Phys.*, **77**, 6076 (1982).

(31) R. Kołos and Z. R. Grabowski, *J. Mol. Struct.*, **84**, 251 (1982).

(32) G. Wermuth, *Z. Naturforsch., Teil A*, **38**, 641 (1983).

(33) K. Rotkiewicz and W. Rubaszewska, *J. Lumin.*, **27**, 221 (1982).

(34) E. J. J. Groenen and W. N. Koelman, *J. Chem. Soc., Faraday Trans. 2*, **75**, 58 (1979).

(35) W. Liptay, H.-J. Schumann, and F. Petzke, *Chem. Phys. Lett.*, **39**, 427 (1975).

(36) W. Baumann, F. Petzke, and K.-D. Loosen, *Z. Naturforsch., Teil A* **34**, 1 (1979).

(37) W. Rettig and V. Bonačić-Koutecký, *Chem. Phys. Lett.*, **62**, 115 (1979).

(38) W. Th. Van der Lugt, H. M. Buck, and L. J. Oosterhoff, *Ind. Chim. Belge*, **32**, 161 (1967).

(39) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

different symmetry properties are available for conjugation with adjacent π-systems. Conjugation with a phenyl group in DMAPS is thus possible whether the ring is in the N···S···N plane or rotated perpendicular to it. Mesomeric stabilization is expected to be stronger for the fully planar arrangement,[40] but steric interaction disfavors this geometry. It is thus understandable why an X-ray analysis of APS finds both rings twisted nearly perpendicular[10] and why steric hindrance by ortho substituents does not produce the effects normally expected for UV absorption maxima and extinction coefficient.[11] The twist angles of the two phenyl rings in DMAPS can thus be assumed to be distributed around the perpendicular conformation, with maximum overlap between the π-orbitals of the phenyl rings and the unoccupied sulfur d-orbital symmetrical with respect to the N–S–N plane,[39] as depicted in Figure 9. On the other hand, MK which has no similar possibility tends to have an all planar geometry, but is twisted because of steric repulsions (Figure 9b). The TICT geometry necessitates an orbital decoupling, i.e., two mutually orthogonal π-systems achieved by rotation of one phenyl group. In MK, both phenyl rings are twisted by ~30° in the ground-state equilibrium geometry. One of the phenyl rings thus has to cross an angular gap of only 60° on the way toward the perpendicular TICT geometry. In DMAPS, on the other hand, one of the phenyl rings twists from the perpendicular geometry toward a planar one in the TICT state. No pretwisted situation is present (angular gap ~90°).

Nanosecond kinetic data regarding the TICT formation rate constant in DMABN and related compounds[3] suggest that pretwisting due to steric hindrance is a very important factor substantially increasing this rate constant. Accordingly, the TICT formation rate can be expected to be considerably faster for MK than for DMAPS.

D. Requirements for Symmetry Reduction. The d-orbital participation in DMAPS not only has important implications for ground-state geometry and TICT state formation rate, but also affects fluorescence quantum yields and TICT state decay rates.

In Table II, a steep increase of ln (ϕ_A/ϕ_B) can be observed for DMAPS in strongly polar solvents. This increase is considerably diminished for 9,9′-bianthryl (BA) and DMABN.

Compounds with two identical halves like BA, MK, DMAPS, etc., have to undergo symmetry reduction in order to reach the TICT state.[5,41] This symmetry breaking is possible only if the interaction between locally excited (LE) and charge-transfer (CT) states is weaker than the solvent-induced energetic fluctuations of the CT states.[5] This is possible for a twisted or space separated "minimal overlap geometry" of the two chromophores and is also one of the reasons for the "minimal overlap rule" governing TICT state formation.[42] In bichromophoric symmetrical compounds with a large π-overlap, the symmetry cannot be broken even in strongly polar solvents because LE and TICT states are coupled too strongly.[5] This coupling can be accounted for theoretically by the off-diagonal element between LE and TICT configurations in the configuration interaction(CI) matrix. This matrix element can be expressed as a sum of Coulomb and exchange integrals[43] which, in a simple CI treatment, approaches zero for a strictly perpendicular arrangement of the two chromophores. A non-vanishing interaction is still possible, however, as a result of electron correlation as suggested by a recent calculation on the related phenomenon of "sudden polarization" applying extended CI.[44] It is conceivable that electron correlation effects are more important for systems where the π-electron orbitals of donor and acceptors overlap. The central SO₂ group in the sulfones investigated can conjugate with both phenyl rings even if they are mutually per-

pendicular because d-orbital hybrids of different symmetry species are available.[39] Thus donor and acceptor π-orbitals carrying the positive and negative charge distribution in the TICT state both extend to the SO₂ group and penetrate each other at the sulfur atom. The consequence is predicted to be a somewhat reduced charge separation (i.e., TICT state dipole moment) and an increased TICT/LE interaction as compared to a case where this overlap is not possible (MK, BA).

The larger interaction for DMAPS and APS is probably one of the reasons why the TICT state is appreciably populated only in strongly polar solvents. There the fluctuations of the solvent dielectric field are strong enough to overcome the TICT–LE coupling and to induce symmetry reduction. For BA, with a smaller interaction, this symmetry reduction is easily possible in solvents of medium to weak polarity. In fact, it seems that for some perpendicular biaromatic hydrocarbon systems this interaction can be so small that symmetry reduction is induced even in a nonpolar solvent.[45] These TICT systems with very small exchange interaction can be described as biradicaloid zwitterions[37] with very close lying singlet and triplet states.

The small singlet–triplet splitting should be increased in the sulfones owing to the increased interaction and consequently lead to a reduced nonradiative singlet to triplet transition $[k_{isc}^{TICT}]$ in the TICT state.[46] Heavy atom quenching experiments of TICT fluorescence[47] in carbazole derivatives[47] are consistent with k_{isc}^{TICT} being the main nonradiative TICT deactivation pathway in these systems $[k_{nr}^{TICT} \approx k_{isc}^{TICT}]$. Reduction of k_{isc}^{TICT} relative to the other TICT depopulation rate constants $(k_{TL}, k_f^{TICT}$; see Scheme I) will then lead to an overall increase of ϕ_f. This may be one of the reasons for the relatively high fluorescence quantum yield of DMAPS as compared to MK ($\phi_f = 3 \times 10^{-3}$ in ethanol at room temperature) or DMABN ($\phi_f \lesssim 0.02$ in ethanol at room temperature). Favorable competition between k_{TL} and k_{isc}^{TICT} will, moreover, be possible at lower temperatures, which explains why T_{max} is at considerably lower temperatures in DMAPS as compared to DMABN and related compounds.[20] In alcohols where k_{TL} has to compete with an additional TICT deactivation process,[48] T_{max} shifts to higher temperatures.

The activation energy, E_{LT}, for the TICT formation process, k_{LT}, can be calculated from the low-temperature slope (Figure 3)[1,2,19] and amounts to ~9.3 kJ/mol in ethanol, a value somewhat less than the activation energy of macroscopic solvent viscosity (16.6 kJ/mol[49]). From the high-temperature slope in *n*-butyronitrile, $E_{TL} - E_{LT}$, the energetic stabilization of the TICT state relative to the B* state, is found to be ~9.6 kJ/mol in this solvent.

E. TICT Kinetics: Formation Rate and Radiative Decay. The single photon counting data in butanol and ethanol at room temperature show identical decay times (3.0 ± 0.1 ns) for the B* fluorescence (observed at 360 ± 11 nm) and the A* fluorescence (observed at 490 ± 11 nm), which points to the rapid equilibration of B* and A* states on this time scale. Within the time resolution of the single photon counting experiment (~0.2 ns), no risetime for the A fluorescence could be observed. The B* decay, however, exhibited some slight deviations from the monoexponential decay law for very short times. Recently, a model of "time-dependent rate constants" to explain pico- and nanosecond kinetic results on DMABN has been proposed.[50] The above observations seem to indicate that this model applies to DMAPS as well. Picosecond kinetic measurements should clarify this point.

For the two equilibrated states LE(B*) and TICT(A*), the observed decay constant is a weighted average of the individual LE and TICT decay constants in Scheme I and follows the equation[51]

(40) G. Jeminet, C. Pigenet, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 3631 (1966).
(41) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.* **49**, 854 (1976).
(42) Z. R. Grabowski and J. Dobkowski, *Pure Appl. Chem.*, **55**, 245 (1983).
(43) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, Reading, MA, 1966.
(44) R. J. Buenker, V. Bonačič-Koutecký, and L. Pogliani, *J. Chem. Phys.*, **73**, 1836 (1980).

(45) M. Zander and W. Rettig, *Chem. Phys. Lett.* **110**, 602 (1984).
(46) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970.
(47) W. Rettig and M. Zander, *Z. Naturforsch., Teil A.* **39**, 41 (1984).
(48) Dialkylamines seem to undergo a reversible photoaddition in alcoholic solvents: K. Rotkiewicz, private communication, 1983.
(49) E. R. Pantke and H. Labhart, *Chem. Phys. Lett.*, **23**, 476 (1973).
(50) F. Heisel and J. A. Miehé, *Chem. Phys. Lett.*, **100**, 183 (1983).

$$\tau^{-1} = \frac{k^{LE} + k^{TICT} K_e}{1 + K_e} \qquad (1)$$

where $K_e = k_{LT}/k_{TL}$, $k^{LE} = k_f^{LE} + k_{nr}^{LE}$, $k^{TICT} = k_f^{TICT} + k_{nr}^{TICT}$

The corresponding fluorescence quantum yields, ϕ_B and ϕ_A, are given by eq 2 and 3 ("high-temperature range" $T > T_{max}$)[52]

$$\phi_B = k_f^{LE}/[k^{LE} + k^{TICT} K_e] \qquad (2)$$

$$\phi_A = k_f^{TICT} K_e/[k^{LE} + k^{TICT}K_e] \qquad (3)$$

Thus, the "apparent" radiative rate constants ϕ_f/τ_f are dependent on the equilibrium constant

$$K_e = k_{LT}/k_{TL} = [A^*]/[B^*]$$

and

$$\phi_B/\tau = k_f^{LE}/(1 + K_e) \qquad (4)$$

$$\phi_B/\tau = k_f^{TICT}/(1 + K_e^{-1}) \qquad (5)$$

Assuming a solvent-independent k_f^{LE} value as determined in hexane, K_e, k_{nr}, and k_f^{TICT} values are derived from the lifetimes and quantum yields in polar solvents (Table III). Noticeable is the reduction by a factor of 3 of k_f^{TICT} as compared to k_f^{LE} (forbidden radiative TICT transition[2]) as well as the increase in k_{nr}^{TICT} for ethanol as compared to acetonitrile as discussed above. On the other hand, even in ethanol, k_{nr}^{TICT} is remarkably small compared to k_{nr}^{LE}.

F. TICT Fluorescence Bandwidths. The unusually broad TICT band of DMAPS ($\Delta\bar{\nu}_{1/2} = 7200$ cm^{-1} in ethanol or acetonitrile at room temperature) could be due to the presence of two TICT states, one formed by rotation of the anilino group, and the other by rotation of the dimethylamino group. A reduced bandwidth would then be expected for the TICT band of APS which is, however, not observed ($\Delta\nu_{1/2} = 7000$ cm^{-1} in ethanol at room temperature). Both molecules have an increased degree of freedom of the TICT state (two relevant intramolecular rotational coordinates) as compared to DMABN. Both phenyl groups can be angularly distributed around the perpendicular TICT geometry. This will lead to an effectively broader angular distribution around this geometry and to an increased fluorescence band halfwidth, because the FC ground state possesses an energy maximum at the TICT geometry.[2] In the case of DMABN or related *p*-cyanodialkylanilines with only one rotational degree of freedom, $\Delta\nu_{1/2}$ for the TICT band is only 5300 ± 200 cm^{-1} in acetonitrile.[53]

G. Dipole Moments of Near-Perpendicular Excited States. The solvatochromic slopes in Figure 7, which differ strongly for the B and A bands (2800 vs. 9000 cm^{-1}/$\Delta L'$ in aprotic polar solvents), are evidence that the dipole moment difference between excited state and FC ground state, $\Delta\mu = \mu_e - \mu_g^{FC}$, is much larger for the A band (TICT state) because the radiative TICT transition involves a back electron transfer. By comparison with DMABN and consideration of molecular shape and charge distribution,[25] μ_e(TICT) for DMAPS is estimated to be in excess of 16 D, the value for DMABN in dioxane.[2] The B band also shows considerable solvatochromy, as opposed to the virtual insensitivity of the B band of DMABN to solvent polarity.[1] This is in agreement with the assignment of S_1 (first absorption band and B fluorescence band) as a combination of the rather polar ^1L_a-type states of the two symmetry equivalent halves in DMAPS, whereas in DMABN,

Locally Excited State   TICT State
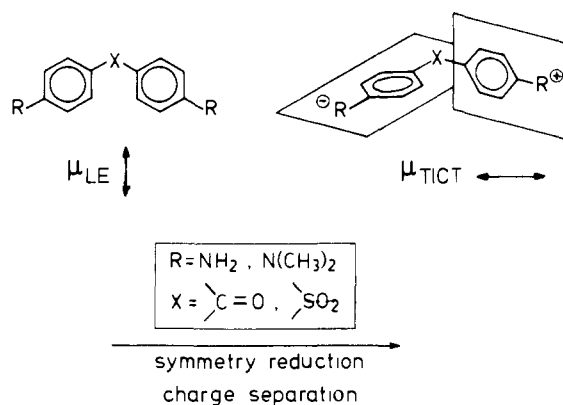

symmetry reduction

charge separation

Figure 10. Schematic representation of dipole moment changes in diphenyl sulfones and diphenyl ketones. The formation of the TICT state is accompanied by a strong increase of the dipole moment μ, and an angular change of nearly 90°. At the same time, the molecular charge is effectively separated in two molecular parts which have lost their symmetry equivalence.

S_1 (B fluorescence band) is a less polar ^1L_b-type state.[14] The direction of the dipole moment of the B* state is given as the vector sum of the individual ^1L_a dipole moments and is pointed perpendicular to the N···N axis (Figure 10) for reasons of symmetry. In the TICT state where the two molecular halves are neither electronically nor sterically symmetry equivalent, the center of the separated charges makes the dipole moment flip to a nearly perpendicular direction close to the N···N axis as depicted in Figure 10.

APS shows a solvatochromic slope similar to DMAPS for the TICT band, 16500 cm^{-1}/$\Delta L'$ in homologous alcohols, Figure 8. This points to a similar large charge separation. However, compared to DMAPS, the TICT emission band is blue shifted by 1380 cm^{-1}. As the TICT energy is related to donor ionization potential, IP(D), and acceptor electron affinity, EA(A), by eq 6[37]

$$E(\text{TICT}) = \text{IP(D)} - \text{EA(A)} + C + \Delta E_{solv} \qquad (6)$$

where C is the Coulomb stabilization, and ΔE_{solv} that brought about by the solvent, and because C and ΔE_{solv} can be considered equal for DMAPS and APS because of their similar charge distributions, most of this blue shift is due to the change of IP(D) − EA(A). If, in a crude approximation, the change of IP(D) for aniline and dimethylaniline is taken as ΔIP(D) = −5500 cm^{-1},[54] then the electron affinity for −SO$_2$C$_6$H$_4$N(CH$_3$)$_2$ should be around 4400 cm^{-1} less positive than for −SO$_2$C$_6$H$_5$NH$_2$.

(51) D. J. S. Birch and J. B. Birks, *Chem. Phys. Lett.*, **38**, 432 (1976).
(52) Z. R. Grabowski, K. Rotkiewicz, W. Rubaszewska, and E. Kirkor-Kaminska, *Acta Phys. Pol.* **A54**, 767 (1978).
(53) W. Rettig, unpublished results.

(54) T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn*, **47**, 2563 (1974).