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Synthesis and Photophysical Properties of Models for Twisted PRODAN and Dimethylaminonaphthonitrile

Brittany N. Davis and Christopher J. Abelt*

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187-8795

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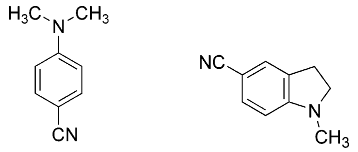
The synthesis and photophysical properties of 7-cyano-3,4-dihydro-2*H*-1,4-ethano-benzo[*g*]quinoline and 3,4-dihydro-2*H*-1,4-ethano-7-propionyl-benzo[*g*]quinoline are reported. These compounds possess a quinuclidine substructure that locks the tertiary amino group perpendicular to the naphthalene ring. Their excited states are models for the twisted excited states of 2-(dimethylamino)-6-naphthonitrile (DMANN) and 6-propionyl-2-(dimethylamino)naphthlene (PRODAN). In contrast to DMANN and PRODAN, the fluorescence of these twisted derivatives is strongly deactivated in polar solvents. Neither DMANN nor PRODAN likely emit from TICT excited states.

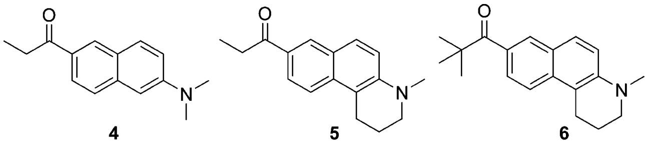
I. Introduction

Aromatic compounds with intramolecular charge-transfer states (ICT) are useful as probes of micropolarity.[1−3] Some of these compounds can achieve a large degree of charge transfer by twisting about a bond that connects the donor and acceptor portions. The archtypal molecule with a TICT excited state is 4-dimethylaminobenzonitrile (DMABN, Figure 1). The lowest energy absorption band in DMABN (^1L_b) produces a planar, locally excited (LE) state. A surface crossing generates the TICT state where the energy minimum occurs with a perpendicular arrangement of the dimethylamino group and the benzene ring. The TICT state is characterized by nearly complete electron transfer from the amino group to the cyanophenyl group. Fluorescence from the TICT state shows substantial Stokes shifts. The highly dipolar nature of the TICT state leads to a high sensitivity toward solvent polarity. Some of the strongest evidence for the TICT model has been the behavior of geometrically constrained model compounds. In these molecules, the nitrogen lone pair is forced to be parallel or perpendicular to the aromatic π-system (Figure 1).[4−8] Compound **2** shows only LE emission, whereas **3** shows TICT emission. It should be noted that the TICT model has not found universal acceptance.[9−12]



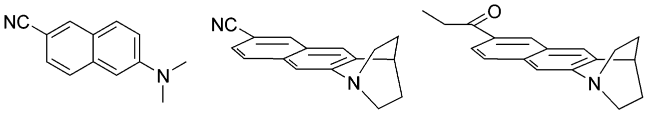
1
DMABN
2
3

Figure 1. Structures of DMABN and planar and twisted DMABN models **2** and **3**.



4
PRODAN
5
6

Figure 2. Structures of PRODAN, **4**, and derivatives **5** and **6**.



7
DMANN
8
9

Figure 3. Structures of DMANN, and models of twisted DMANN and PRODAN.

PRODAN (**4**, Figure 2), prepared in 1979 by Weber and Farris,[13] is another useful fluorescent probe of micropolarity. PRODAN possesses an electron-donating dimethylamino group just like DMABN. The electron-withdrawing propionyl group is positioned at maximal distance from the amino group. Transfer of electron density from the donor to the acceptor produces a substantial excited-state dipole moment that is sensitive to the polarity of the immediate environment. The similarities between PRODAN and DMABN in their structure and fluorescence properties suggest that PRODAN may also emit from a TICT state. Theoretical studies on PRODAN excited states support the amino-twisted geometry (TICT) as the lowest energy.[14−16] However, it was pointed out that this assignment is greatly dependent on the choice of the Onsager radius. The solvent stabilization by a radius of 4.6 Å favors the TICT state, whereas a slightly higher value (5.6 Å) gives the PICT (planar ICT) state as the lowest. [14] On the other hand, experimental evidence points to a PICT emitting state. Estimations of the excited-state dipole moment, either by solvatochromic studies[17−19] or by transient dielectric loss measurements,[20] show that it is only 4−7 D larger than that of the ground state. This difference is too small for a TICT state with nearly full charge transfer. In a previous report, we have shown that PRODAN derivatives **5** and **6** (Figure 2) fluoresce just like PRODAN.[21] In these compounds, the dialkylamino group is constrained to be coplanar with the naphthalene ring, so the TICT state is not possible. Because they still give strong CT emission, we concluded that twisting is not necessary for PRODAN's fluorescence behavior.

In this paper, we report the synthesis and photophysical properties of two compounds, **8** and **9** (Figure 3), where the dialkylamino group is constrained to be perpendicular with the naphthalene ring. Compound **8** is a model of twisted DMANN, which is a benzannulated derivative of DMABN. Compound **9** is a model of twisted PRODAN.

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* Corresponding author. E-mail: cjabel@wm.edu.

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II. Experimental Section

THF was dried by passage through an activated alumina column. NMR spectra were obtained with a Varian Mercury VX-400 spectrometer. Combustion analyses were conducted by Desert Analytics. UV/vis absorbance measurements were performed with an Ocean Optics Chem 2000 spectrometer. Fluorescence excitation/emission studies were performed using a SLM-Aminco SPF-500 spectrometer as the excitation source and the Ocean Optics system as the detector. All solvents were spectrophotometric grade from Acros. Quantum yield measurements were made using anthracene as a reference ($\Phi = 0.27$ in abs. EtOH) using the method of standard additions. The absorption of these solutions was kept below 0.05. Absolute EtOH for the quantum yield measurements was treated with sodium and distilled. AM1/SM5C semiempirical calculations were performed using AMPAC 6.7 from Semichem, Inc. Calculations incorporated the following keywords: AM1; C. I. = 14; singlet; qcscf; sm5c; solvnt = "ethanol"; tight; truste; micros = 0; root = 1 (or 2); gnorm = 0.2; scfcrt = 0. "Ethanol" is depicted through a set of seven parameters: dielectric constant, index of refraction, H-bonding donating ability, H-bonding accepting ability, surface tension, fraction of non-H atoms that are aromatic C atoms, and fraction of non-H atoms that are halogens. DMANN was prepared by modification of the method of Balo and co-workers.[22] PRODAN was made from DMANN using the phosphonate method described below for the conversion of **8** to **9**.

4-(3-Oxo-1-aza-bicyclo[2.2.2]oct-2-ylidenemethyl)-benzonitrile (10). Sodium metal (1.23 g of Na, 53.5 mmol) was added to absolute EtOH (200 mL). Quinuclidine hydrochloride (6.24 g, 38.6 mmol) was added, and the mixture was warmed to dissolve the quinuclidine. After the solution cooled to 40 °C, 4-cyanobenzaldehyde (5.23 g, 39.9 mmol) was added, and the reaction was heated to boiling for 10 min. The reaction was stirred at room temperature overnight. EtOH (300 mL) was added, and the mixture was heated to boiling and filtered. H_2O (200 mL) was added with continued heating, and the mixture was allowed to stand, yielding the aldol product as yellow needles (5.73 g): mp 158−9 °C. Another crop (1.08 g) was obtained from the mother liquor after recrystallization from EtOH−H_2O for a combined yield of 74%. ^{1}H NMR ($CDCl_3$): δ 8.13 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 6.97 (s, 1H), 3.19 (m, 2H), 2.99 (m, 2H), 2.67 (quin, $J = 2.6$ Hz, 1H), 2.07 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 205.8, 147.3, 138.4, 132.4, 132.1, 122.7, 118.9, 112.4, 47.5, 40.3, 25.8. Anal. Calcd for $C_{15}H_{14}N_2O{\cdot}0.02H_2O$: C, 75.49; H, 5.93; N, 11.74. Found: C, 75.21; H, 6.17; N, 11.70.

4-(3-Hydroxy-3-methyl-1-aza-bicyclo[2.2.2]oct-2-ylidenemethyl)-benzonitrile (11). Enone **10** (6.7 g, 28.1 mmol) was dissolved in THF (100 mL). The solution was cooled to −78 °C under N_2. MeLi (19 mL, 1.6 M in Et_2O) was added dropwise by syringe. The reaction was kept at −78 °C for 1 h, and then allowed to warm over several hours. Ammonium chloride (2 g, 37.4 mmol) was added, and the reaction was stirred for another 2 h. The solution was decanted from the undissolved salts and concentrated in vacuo. The residue was dried on a vacuum line and used without further purification.

4-(3-Methylene-1-aza-bicyclo[2.2.2]oct-2-ylidenemethyl)-benzonitrile (12). Unpurified **11** from the reaction above was dissolved in freshly distilled pyridine (43 mL). The solution was cooled in an ice−water bath while freshly distilled $POCl_3$ (8 mL) was added slowly dropwise under a $CaCl_2$ drying tube. The reaction was stirred overnight. The next day the reaction was cooled again in an ice−water bath. Water (150 mL) was added very slowly initially with vigorous stirring. A solid formed that was filtered and washed with ice-cold water leaving 3.33 g (50% from **10**) after drying for 1 day. A sample was recrystallized from EtOH−H_2O for analysis: mp 132−3 °C. ^{1}H NMR ($CDCl_3$): δ 7.99 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.6$ Hz, 2H), 6.45 (s, 1H), 5.38 (s, 1H), 4.91 (s, 1H), 3.06 (m, 2H), 2.87 (m, 2H), 2.61 (quin, $J = 2.9$ Hz, 1H), 1.73 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 151.9, 150.2, 141.1, 132.0, 130.2, 119.6, 115.3, 109.6, 105.5, 47.8, 34.2, 27.8. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.25; H, 7.12; N, 11.60.

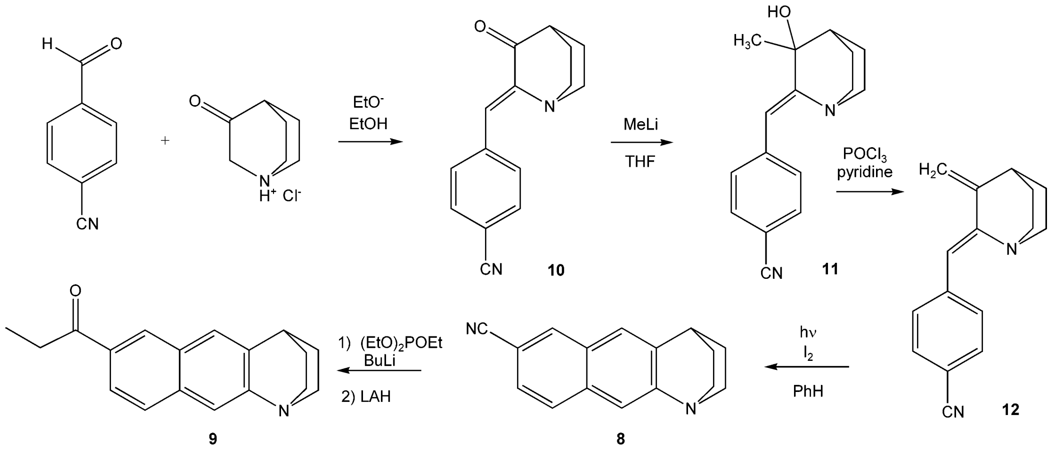
7-Cyano-3,4-dihydro-2*H*-1,4-ethano-benzo[*g*]quinoline (8). Diene **12** (460 mg, 1.9 mmol) was dissolved in freshly distilled benzene (300 mL), and the solution was passed through basic alumina. Iodine (450 mg, 1.8 mmol) and propylene oxide (10 mL) were added. The solution was sparged with Ar for 20 min, and then irradiated with a 450 W medium pressure Hanovia lamp for 3.5 h. After this time, the red iodine color was absent, and a dark red solid coated the immersion well. The solution was filtered, and the dark solid was dissolved in a minimum amount of acetone. The acetone solution was added dropwise to a rapidly stirring aqueous solution (500 mL) containing sodium bisulfite (2.5 g) and sodium bicarbonate (2.5 g). The solution was stirred overnight. Filtration gave a white solid. This procedure was repeated four more times giving a total product yield of 850 mg (37%). A portion was purified for analysis by sublimation under high vacuum followed by recrystallization from EtOH−H_2O: mp 172−3 °C. ^{1}H NMR ($CDCl_3$): δ 8.22 (s, 1H), 7.91 (d, $J = 8.4$, 1H), 7.68 (s, 1H), 7.65 (s, 1H), 7.57 (dd, $J = 8.4$, 1.6 Hz, 1H), 3.31 (m, 3H), 2.81 (m, 2H), 1.99 (m, 2H), 1.62 (m 2H). ^{13}C NMR ($CDCl_3$): δ 152.6, 145.1, 134.8, 133.6, 131.6, 129.4, 125.8, 122.6, 121.1, 119.7, 108.8, 49.8, 31.3, 28.2. Anal. Calcd for $C_{16}H_{14}N_2{\cdot}0.02H_2O$: C, 81.90; H, 6.03; N, 11.94. Found: C, 81.64; H, 6.32; N, 11.72.

3,4-Dihydro-2*H*-1,4-ethano-7-propionyl-benzo[*g*]quinoline (9). Diethylethylphosphonate (360 mg, 2.2 mmol) was dissolved in THF (30 mL), and the solution was cooled to −78 °C under Ar. MeLi (1.25 mL, 1.6 M in Et_2O) was added dropwise by syringe. After the reaction had been stirred for 15 min, nitrile **8** (450 mg, 1.9 mmol) was added in one portion. The reaction was stirred and allowed to warm over 1 h. $LiAlH_4$ (240 mg, 6.3 mmol) was added, and stirring was continued for 4 h. H_2O was added carefully followed by 10% aqueous H_2SO_4 (50 mL), and the mixture was stirred overnight. H_2O (200 mL) was added, and Na_2CO_3 was added until the solution was basic, and then it was extracted with CH_2Cl_2 (2 × 100 mL). The combined CH_2Cl_2 layers were dried over $CaCl_2$ and concentrated in vacuo. The product was sublimed under high vacuum giving **9** (220 mg, 43%). A portion was purified for analysis by recrystallization from EtOH−H_2O: mp 173−4 °C. ^{1}H NMR ($CDCl_3$): δ 8.48 (s, 1H), 8.00 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.89 (d, $J = 8.6$ Hz, 1H), 7.74 (s, 1H), 7.63 (s, 1H), 3.30 (m, 3H), 3.15 (q, $J = 7.2$ Hz, 2H), 2.83 (m, 2H), 1.97 (m, 2H), 1.64 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 200.9, 151.7, 143.7, 135.5, 133.9, 131.8, 129.1, 128.6, 123.7, 123.3, 120.7, 49.9, 32.2, 31.4, 28.4, 8.8. Anal. Calcd for $C_{18}H_{19}NO{\cdot}0.02H_2O$: C, 81.42; H, 7.21; N, 5.27. Found: C, 81.12; H, 7.51; N, 5.06.

III. Results and Discussion

Synthesis. The synthesis of the models for twisted DMANN and PRODAN is shown in Scheme 1. The crossed-aldol reaction between quinuclidinone and benaldehyde derivatives has been reported.[23] The *E*-isomer forms exclusively in agreement with

SCHEME 1: Synthesis of Models of Twisted DMANN and PRODAN



the literature. The carbonyl group in **10** was converted to the exocyclic methylene group in **12** by adding methyllithium followed by dehydration. The addition of methyllithium was selective for the carbonyl group over both conjugated addition and nitrile addition. Formation of the naphthalene ring in **8** was accomplished by photochemical cis−trans isomerization and then photoelectrocyclization-oxidation. Following the procedure of Katz et al., a full equivalent of I_2 was used to oxidize the initially formed dihydronaphthalene.[24] Propylene oxide was used to scavenge the resulting HI; however, much of the product precipitated out of solution as the hydroiodide salt. Conversion of the nitrile to the ethyl ketone **9** was done by phosphonate addition-reduction.[25] As compared to a Grignard addition, which we used in the preparation of **5** and **6**, this method is milder, results in better conversion, and shows fewer side products.

Photophysical and Computational Studies. The absorption spectra of **8** and **9** are shown together with DAMNN and PRODAN, respectively, in Figure 4. Two effects are apparent. First, the molar absorptivity of the longest wavelength bands of **8** and **9** is reduced by an order of magnitude as compared to those of their planar analogues. Second, the long wavelength bands are blue shifted, whereas the short wavelength bands are red shifted. The smaller absorptivity is a result of the deconjugation of the N lone pair. The spectral shifts also result from the deconjugation; however, the effect here is to change the amino group from a resonance electron-donating group into an inductively electron-withdrawing group.

The absorption and emission spectra for **8** and **9** are modeled using the AM1 semiempirical method. The results for the lowest two absorption bands and the lowest emission band are shown in Table 1. Incorporated into these calculations are a large CI level (14) and a COSMO dielectric screening emulation of ethanol. Of particular interest is the involvement of the N lone pair in any of these transitions. The lone pair comprises a significant fraction of the third highest HOMO. However, this orbital is not involved in any of the CI microstates for any of these transitions. Thus, the calculations indicate that the first two absorption bands and the LE emission band for **8** and **9** are π,π^* in nature.

TABLE 1: Calculated Peak Absorption and Peak Emission Bands (nm), *x*,*y*-Components of the Transition Moment (au), and Oscillator Strengths (*f*) for 8 and 9 in Ethanol[a]

	8				9			
transition	band	x	y	f	band	x	y	f
$S_0 \rightarrow S_1$	352	401	−5	14	338	541	32	26
$S_0 \rightarrow S_2$	305	548	−184	33	309	461	−224	26
$S_1 \rightarrow S_0$	377	379	−43	12	378	630	35	32

[a] Transition moments and oscillator strengths × 10^3.

TABLE 2: Fluorescence Quantum Yields for DMANN, PRODAN, 8, and 9 in Ethanol

compound	ϕ_f
DMANN	0.99 ± 0.02
PRODAN	0.71 ± 0.03
8	$(55 \pm 4) \times 10^{-4}$
9	$(8 \pm 2) \times 10^{-4}$

The emission spectra of **8** and **9** also differ significantly from DMANN and PRODAN. DMANN shows only LE emission,[26] whereas PRODAN shows only CT emission.[13] While DMANN and PRODAN show strong emission, **8** and **9** emit only very weakly. The emission strength for these compounds is characterized by their fluorescence quantum yields in absolute ethanol (Table 2). The quantum yields for **8** and **9** are reduced by 2−3 orders of magnitude as compared to DMANN and PRODAN.

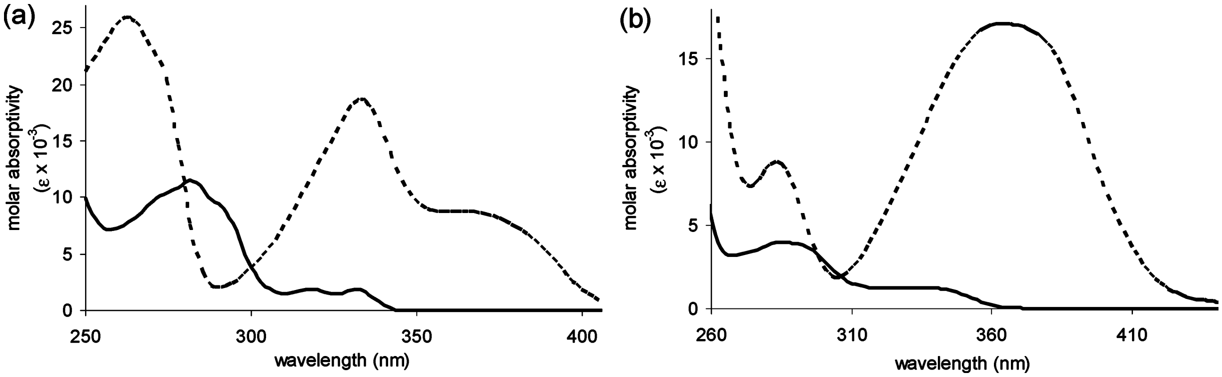


Figure 4. Absorption spectra (EtOH) of (a) **8** (−) and DMANN (- - -), (b) **9** (−) and PRODAN (- - -).

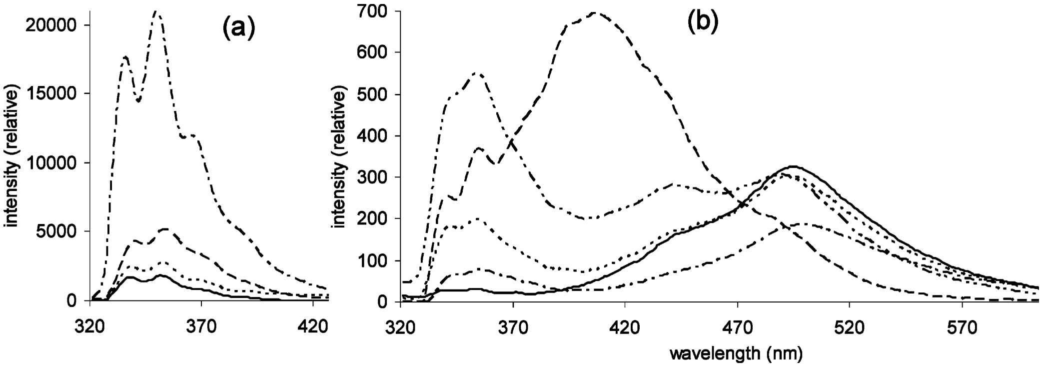


Figure 5. Emission spectra of **8** in (a) cyclohexane (— - —), chlorobenzene (— — —), dichloromethane (- - - -), and chloroform (—), and in (b) 2-propanol (— - - —), toluene (— — —), methanol (- - - -), dimethyl sulfoxide (— - —), and acetonitrile (—).

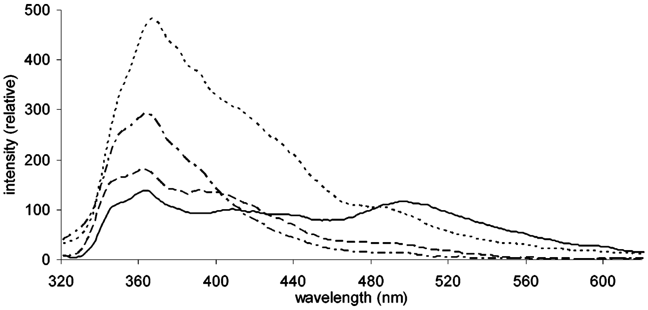


Figure 6. Emission spectra of **9** in dimethyl sulfoxide (- - - -), chlorobenzene (— - —), methanol (— — —), and acetonitrile (—).

The emission spectra of **8** and **9** vary with the solvent (Figures 5 and 6). With **8**, strong LE emission is seen in cyclohexane. This emission decreases very rapidly with increasing solvent polarity (Figure 5a). As the LE emission nearly extinguishes, the existence of a red-shifted band becomes apparent (Figure 5b). The red-shifted band has two maxima, and the intensity of these maxima, both absolute and relative, depends on the solvent but not directly on the solvent polarity. The longest wavelength band does not show much variation in its position except in toluene. In the toluene emission spectrum, the LE bands are discernible as shoulders on the strong red-shifted band, whose maximum is at a much shorter wavelength than in the other solvents.

The results seen in **8** aid in the interpretation of the behavior of **9**. The dominant feature in the emission of **9** is the LE emission (Figure 6). The intensity of this weak band varies with the solvent. In most solvents, the existence of a red-shifted band is not readily apparent; however, in acetonitrile and DMSO, both very polar but aprotic solvents, this band is discernible.

We interpret these results as follows. Both **8** and **9** show dual emission from LE and CT states. The intensity of the LE band is modulated by the solvent. Increasing solvent polarity favors internal conversion from the LE state to the CT state. The CT state suffers efficient nonradiative deactivation. The existence of the CT state is revealed by the weak long wavelength emission. By necessity, the CT state is a TICT state. The LE band owes its existence to the slow internal conversion that results from the poor overlap factor between the states. Likewise, the poor overlap factor between the CT state and the ground state favors radiationless deactivation.

IV. Conclusions

We conclude that PRODAN's emission is from a planar intramolecular charge-transfer state. Not only do constrained planar analogues behave just like PRODAN, but twisted analogues behave very differently. It is appropriate to point out that these models for the twisted excited states have a pyramidal amino group rather than one that is planar. Calculations have indicated that pyramidalization plays a role in the photophysical behavior of DMABN.[27] However, the photophysical behavior of **3**, which also has a pyramidal amino group, shows only CT emission and, as such, is taken as strong evidence for a TICT state in DMABN.

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