Comparative Theoretical Study on Charge-Transfer Fluorescence Probes: 6-Propanoyl-2-(*N*,*N*-dimethylamino)naphthalene and Derivatives

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The efficient fluorescence probe 6-propanoyl-2-(*N*,*N*-dimethylamino)naphthalene (PRODAN) shows a significant Stokes shift in polar solvents. Neither experimental nor theoretical studies performed up to now yield a definitive description of the character of the emissive state. Results of the recently developed DFT/SCI method are compared to semiempirical calculations with the spectroscopic ZINDO/S parametrization and the AM1/CISD Hamiltonian which was not parametrized for computation of spectroscopic properties. The most reliable results are obtained with the DFT/SCI and AM1/CISD approaches. The absorption spectrum of PRODAN is excellently reproduced by the DFT/SCI calculations, and the AM1/CISD results are superior to ZINDO/S. These results allow the assignment of the red-shifted fluorescence band to both emission of a highly polar dimethylamino twisted intramolecular charge transfer state (N-TICT) and a geometrically unchanged planar intramolecular charge transfer (PICT) state. A comparison with 2-(*N*,*N*-dimethylamino)-naphthalene (DAN) and 2-propanoylnaphthalene (PRON) shows that each of the donor or acceptor substituents alone in combination with rotation about the naphthalene-substituent single bond is sufficient to generate a low lying charge-transfer state with a large dipole moment.

1. Introduction

Due to its extreme environmental sensitivity, the organic donor−acceptor compound PRODAN (see Figure 1) has been proposed as a highly efficient fluorescence probe by Weber et al. in 1979.[1] Several photophysical studies[2,3] revealed a large solvatochromic fluorescence shift with increasing solvent polarity. This behavior can be explained by the molecular composition of PRODAN, which is a typical representative of a wide class of chromophores: an electron donor (D) and an acceptor (A) unit are connected to the aromatic spacer by a single bond. Thereby, a charge-transfer (CT) excited state is formed after the excitation, characterized by its significant Stokes shift in polar solvents. The chromophore is widely used as a molecular probe in photobiology due to its unusual fluorescence behavior.[3] It is utilized, for example, in investigations of protein environments,[4] lipid research,[5,6] or cellular membranes studies.[7] A slightly modified derivative of PRODAN was used for estimates of hydrophobic cavity polarity by the labeling of the heme pocket in apomyoglobin.[8] The structure D−S−A also leads to enhanced molecular first hyperpolarizabilities β,[9] which are of common interest for electrooptic light modulators,[10] high-speed transportation and storage of data, and information processing on the basis of light.[11] PRODAN has been recently investigated with respect to this topic, and its high hyperpolarizability make this compound an attractive second-order nonlinear-optics chromophore.[12]

A lowest lying excited state of charge-transfer character in PRODAN has been deduced from fluorescence spectroscopy measurements.[1] The partial electron shift from the donor to the acceptor moiety results in a high excited-state dipole moment in comparison to the electronic ground state. For the simpler D−S−A compound 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN), an unusual fluorescence behavior is found as well.[13] In addition to the normal emission from the locally excited state (LE), in DMABN a second, red-shifted fluorescence is observed in polar solvents and attributed to a highly polar charge-transfer state. According to the so-called *twisted intramolecular charge transfer* (TICT) hypothesis,[13,14] this CT state is stabilized by rotation along the single bond connecting the donor and the acceptor subunits. The final perpendicular conformation is thus characterized by electronically decoupled donor and acceptor subunits and nearly complete charge separation.[15] There is still a vivid discussion about the origin of PRODAN fluorescence, and the question whether excitation into the highly polar state is connected with geometrical relaxation (i.e., TICT formation) is not settled yet. Several publications[2,3] deny the importance of any twisting motion and postulate an emissive, geometrically unchanged, so-called planar intramolecular charge transfer state (PICT[16]).

The question of which moieties can be assigned as the donor and acceptor units of PRODAN is not cleared definitely. According to the similar structures of PRODAN and DMABN, the dimethylamino group is widely interpreted as the donor and the propanoylnaphthalene subunit as the electron acceptor group. A “N-TICT” coordinate is defined therefore as the dimethylamino group rotation with respect to the naphthalene moiety. In 1986 Nowak et al.[17] suggested on the basis of CNDO/S

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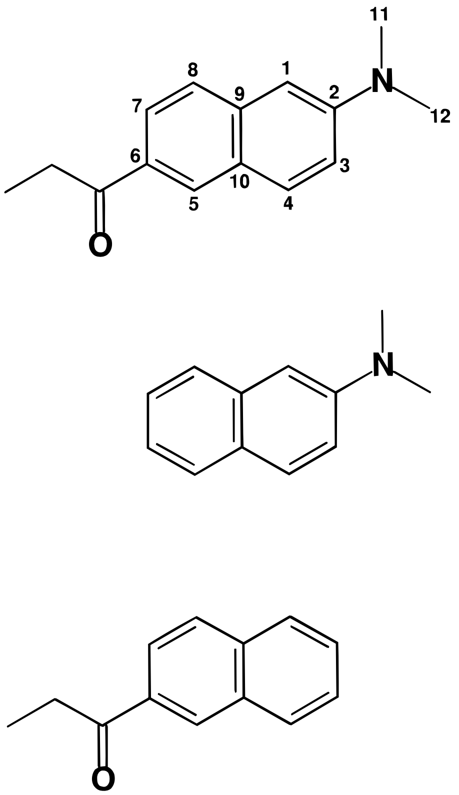

Figure 1. Structure and numbering of atoms for PRODAN (top), DAN (middle), and PRON (bottom).

calculations that the unusual spectral properties of PRODAN may be related to TICT state formation. Recently, ab initio HF computations including single excitations (HF/SCI[18]) have been published[19] in order to explain the fluorescence behavior. However, the excited-state properties were poorly reproduced because only single excitations and only small portions of electron correlation are taken into account by the HF/SCI method. On the other hand, it seems also possible that solely the propanoyl group acts as the acceptor so that a rotation about the keto-naphthalene single bond generates a so-called O-TICT state as the possible origin of the fluorescence. This relaxation mode has not been taken into account before, even though this mode could possibly be of great importance for the explanation of PRODAN emission spectra. According to the INDO/S computations of Ilich et al.,[20] the combination of the amino group twisting and antiquinoid distortions of the naphthalene ring leads to an energetically low lying and highly polar excited state necessary for the occurrence of red-shifted fluorescence. The geometrical relaxation modes and investigated conformations of PRODAN are summarized in Figure 2.

1-(*N*,*N*-Dimethylamino)naphthalene (1-DAN)[21] and 2-naphthalenecarboxylic acid (NCA)[22] (a compound comparable to 2-propanoylnaphthalene) are naphthalene derivatives which contain only donor or acceptor subunits, respectively. They exhibit significant Stokes shifts with increasing solvent polarity as well. For both compounds, the twisting motion about the naphthalene-substituent single bond, as described by the TICT model, can be applied to explain the large solvent shift. No definite arguments for or against this relaxation has been published yet. 2-(*N*,*N*-Dimethylamino)naphthalene (DAN) and 2-propanoylnaphthalene (PRON) are also studied in this paper due to their structural similarity to 1-DAN and NCA, respectively (for their structures, see also Figure 1). These model compounds should be helpful in revealing the nature of naphthalene-based fluorescence probes.

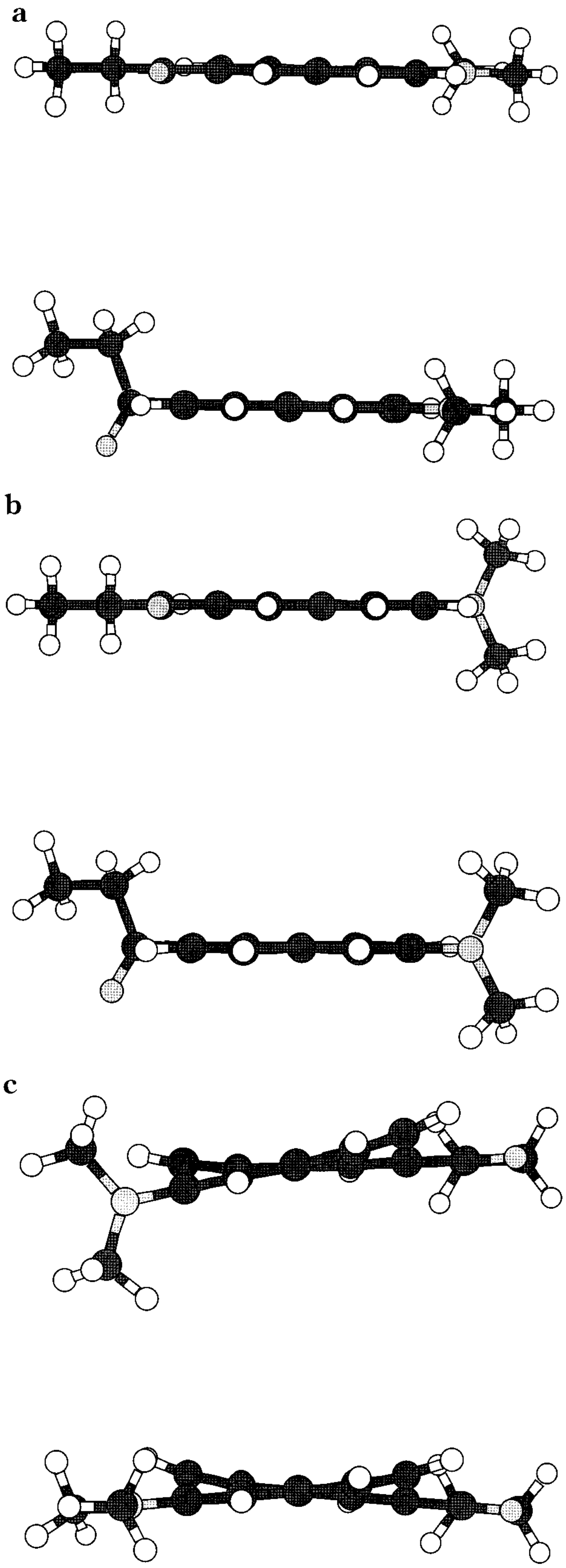

Figure 2. Model geometries used for PRODAN: planar geometry (P: a, top), propanoyl twisted (OT: a, bottom), dimethylamino twisted (NT: b, top), dimethylamino and propanoyl twisted (NOT: b, bottom), planar, ring distorted (D: c, bottom), and dimethylamino twisted, ring distorted (NTD: c, top) geometry. For abbreviations see Table 1.

In this work we present a series of calculations for excited singlet states of PRODAN with the aim to characterize its absorption and fluorescence spectra. Results for excited-state properties calculated with three different methods are compared, i.e., the spectroscopically parametrized ZINDO/S method,[23] the AM1[24] Hamiltonian in combination with configuration interaction including some single and double excitations (CISD), and the recently developed density functional theory approach combined with single configuration interaction (DFT/SCI). The AM1 Hamiltonian has not been parametrized for the calculation of spectroscopic but of ground-state properties of molecules. Nevertheless, several AM1 studies of the fluorescence properties of DMABN have been published recently.[25−28] The results are of surprisingly good quality, and we thus include this method in our work to check the reliability of this basically nonspectroscopic Hamiltonian for spectroscopic applications. The CISD approach is used in the AM1 data computations which is known to be sufficient in determination of ground-state correlation energies as well as properties of molecules in their excited states.

The results obtained by the recently developed DFT/SCI method[29] are presented and compared to the data obtained from the semiempirical calculations. This new scheme for the theoretical description of excited states is based on a combination of density functional theory (DFT, for a survey see, for example, ref 30) and the singles excitation configuration interaction method (SCI). The method is clearly superior to standard ab initio HF/SCI theory,[18] as it takes dynamical electron correlation effects implicitly into account. Especially for the prediction of UV and CD spectra of aromatic compounds, where correlation effects are very important, good results have been obtained with this approach.[29,31−33] Its accuracy for closed-shell systems is in most cases comparable to that of much more elaborate CASPT2 or MRSD-CI calculations. The DFT/SCI approach has been applied successfully to describe the TICT state formation in DMABN.[33]

In the first part of the paper ground-state properties and frontier molecular orbitals are analyzed within an active space from the five highest occupied to the five lowest unoccupied orbitals. Second, the absorption spectrum and characteristic properties of the excited states of PRODAN are calculated by all three methods. The results are compared with the experimental spectrum. In the third part, the excited states are characterized for the model geometries shown in Figure 2. In the last part we compare the results for PRODAN with those of solely donor (DAN) or acceptor (PRON) substituted naphthalene derivatives.

2. Computational Methods

The ground-state geometries of all compounds are optimized using the AM1[24] Hamiltonian as implemented in the VAMP(6.1) program package.[34] No electron correlation is taken into account in the ground-state optimizations. A small pyramidalization angle of 18° is computed for the amino group of PRODAN. The pyramidalization angle is defined as half of the sum of the dihedral angles ω_1(C11−N−C2−C1) and ω_2(C12−N−C2−C3) with the numbers of the atoms given in Figure 1. This structural property has a small influence on the photophysical behavior which was proven by a set of calculations performed with and without pyramidalization of the dimethylamino group. The results differ only marginally. Thus, we employ here a planar conformation with C_s symmetry, which was also deduced from X-ray analysis[20] and found in ab initio HF-SCF calculations.[19] In the calculations with the spectroscopic parametrization of ZINDO/S, the INSIGHT II program package[35] is used with variation of the original INDO/S method.[23] Mataga−Nishimoto repulsion integrals are employed,[36] and 100 selected singly excited configurations are taken into account. The excited-state properties with the AM1 Hamiltonian are obtained from configuration interaction including all single and double excitations (AM1/CISD) within an active space of 10 orbitals (i.e., from the HOMO−4 to the LUMO+4), yielding 876 configurations. All DFT calculations have been performed with the TURBOMOLE suite of programs.[37,38] Valence double-ζ Gaussian AO basis sets (C, N, O: [3s2p]; H: [2s])[39] augmented with d-polarization functions at the carbon, nitrogen, and oxygen atoms (VDZd) and Beckes hybrid exchange−correlation functional[40,41] (B3LYP) have been used throughout. All possible single excitations from the occupied valence MOs to the virtual space (i.e., 9284 without symmetry for PRODAN) have been considered in the DFT/SCI calculations. The oscillator strengths in the DFT/SCI treatments were calculated in the dipole lengths form from the SCI wave functions and the Kohn−Sham orbitals. Also for both the ZINDO/S and AM1/CISD method the dipole lengths form was used considering the complete active space. The simulations of the UV spectra were performed by summing Gaussian curves with an exponential half-width of 0.2 eV for each electronic transition i:

$$\epsilon(E) = \sum_i^t \frac{1.6196 \times 10^4}{\sigma} f_i \exp\left(-\left[\frac{E - E_i}{\sigma}\right]^2\right)$$

where E and the bandwidth σ are given in eV, f_i is the oscillator strength, and the molar extinction coefficient is obtained in l/(mol cm).

For a characterization of PRODAN and derivatives in their excited states the planar C_s geometry of the ground state is considered first. Furthermore, a wagged geometry (W) is calculated with a pyramidalization of the nitrogen atom, defined by a dihedral angle $C_{12}-N-C_2-C_3$ and $C_{11}-N-C_2-C_1$ of 20°, respectively. A 90° twisted dimethylamino group conformation (NT) is examined for PRODAN and DAN, and the corresponding propanoyl twisted geometry (OT) for PRODAN and PRON. Twisting of both groups by 90° leads to the NOT model structure. In addition, a ring distorted structure (D) is investigated with the bond lengths, C_1-C_9 and C_3-C_4 elongated by 0.1 Å and the dihedral angles $C_1-C_9-C_{10}-C_4$ and $C_4-C_{10}-C_9-C_8$ twisted by 10° out of the aromatic plane (for a numbering of atoms see Figure 1, and for a sketch of the distorted molecule see Figure 2).

3. Results and Discussion

3.1. Ground-State Properties of PRODAN. The optimized AM1 ground-state geometry is in good agreement with available X-ray data.[20] The critical parameters, describing the partial conjugation of the amino and the carbonyl group with the naphthalene unit, are discussed in more detail. The bond length of the nitrogen atom to the adjacent aromatic carbon atom is calculated only 0.019 Å too long in comparison to experimental data (d_{N-C}(exp) = 1.387 Å; d_{N-C}(AM1) = 1.406 Å). The maximum deviation from experiment with 0.028 Å is found for the keto C=O bond length (d_{C-O}(exp) = 1.211 Å; d_{C-O}(AM1) = 1.239 Å). All other structural parameters are calculated with smaller deviations from X-ray data, and we can therefore safely use the AM1 optimized geometry of PRODAN for further computations. Hereinafter, all conformations investigated were obtained from a geometry optimization with solely the changed parameters kept fixed. All other coordinates are optimized.

The relative differences in energy between the various conformations are presented in Table 1 together with the electric

TABLE 1: Dipole Moments μ (in D) and Energy Differences ΔE (in kcal/mol) for PRODAN between the Planar (P) C_s Conformation and the Pyramidal (W) Dimethylamino Twisted (NT), Propanoyl Twisted (OT), Dimethylamino and Propanoyl Twisted (NOT), Ring Distorted (D), and Dimethylamino Twisted and Ring Distorted (NTD) Geometries with DFT and AM1 Methods

	P	W	NT	OT	NOT	D	NTD
				μ			
DFT	5.7	5.6	3.4	5.0	3.1	6.0	3.8
AM1	5.0	5.1	3.0	4.9	3.3	5.3	3.6
				ΔE			
DFT		0.9	11.3	7.7	18.0	32.7	42.8
AM1		−1.5	5.0	−0.3	6.8	27.6	34.1

dipole moments. Only the results of DFT and AM1 are compared due to the well-known fact that the ZINDO/S method is not applicable for relative energy calculations. The flat energy surface for the amino group wagging mode (ΔE_W) is well represented by both methods, although AM1 predicts a pyramidal geometry to be more stable by 1.5 kcal/mol. The planar DFT global minimum fits excellently to experiment. The propanoyl group rotation is energetically unfavorable with the DFT method and AM1 localizes a minimum for the OT conformation in the ground state, but with a negligible rotational barrier. The general tendency in the dipole moment evolution is about the same for all methods. Twisting of the dimethylamino or propanoyl group leads to a decrease in μ, and the NOT conformation shows the lowest dipole moment due to the missing long-range conjugation from the amino to the propanoyl group. On the contrary, the distortion of the naphthalene system leads to a disturbance of the π-system, detected by a small increase in dipole moment. Summarizing, the DFT method represents the ground-state properties satisfactorily. The AM1 method underestimates the conjugation effects of the propanoyl and dimethylamino group to the naphthalene π-system. The pyramidalization of the nitrogen atom becomes the predominant effect in comparison to an expansive conjugation over the complete molecule and leads thereby to a nonplanar geometry of PRODAN. The ground-state rotational barriers are thus calculated too low by the AM1 Hamilatonian. The DFT/SCI rotational barrier of 11.3 kcal/mol represents a more realistic number, compared to the experimental activation energy for rotation of e.g. DMABN in an alkane solvent (8.0 ± 0.7 kcal/mol[42]).

3.2. Analysis of PRODAN Frontier Molecular Orbitals. The energetic ordering of the highest occupied MOs is the same within the semiempirical methods. The HOMO, HOMO-1, and HOMO-2 of a″ symmetry are of π character with a significant contribution from the amino group. The HOMO-3 of *a*′ symmetry is characterized as a free electron pair at the carbonyl group (n_O). This orbital is destabilized with the DFT approach and becomes the HOMO-2. In ab initio HF-SCF calculations[19] a further destabilization is observed, where the n_O becomes the occupied orbital next to the HOMO. By rotation of the donor group an orbital of a′ symmetry with free electron pair character at the nitrogen atom increases in energy. For a twisting angle of 90° this orbital is of pure N p_z (n_N) character. It is completely decoupled from the aromatic naphthalene moiety and becomes the HOMO (AM1 and DFT) or the HOMO-1 (ZINDO/S). The character of the lowest unoccupied MOs remains almost unchanged for all geometrical variations. The unoccupied orbitals are of π^* type with significant contributions from the propanoyl oxygen atom. The rotation of the propanoyl group yields a pure π^*_O orbital at the keto C=O group which is no longer in conjugation with the aromatic naphthalene moiety. This orbital is the LUMO+1 for DFT and AM1 and the LUMO+2 for the ZINDO/S method. An analysis of the MOs in distorted conformations shows that no significant deviations in orbital character compared to the planar structure occur. Complete decoupling is not achieved for the twisted dimethylamino group of the distorted geometry. Independent from the rotational angle a partial conjugation with the distorted aromatic π-system is possible. This effect stabilizes the N p_z orbital in comparison to the nondistorted system.

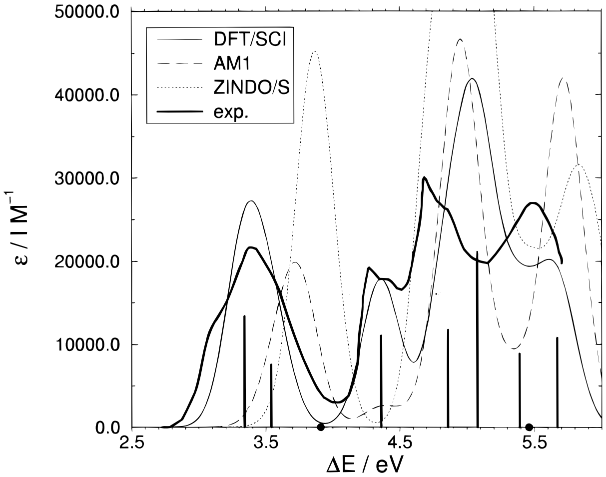

Figure 3. Comparison of experimental and theoretical absorption spectra of PRODAN. The solid lines and filled dots refer to the position of the calculated states with the DFT/SCI method.

3.3. Interpretation of the Absorption Spectrum of PRODAN. The calculated absorption spectra of PRODAN (which refer to gas-phase conditions) are compared to a spectrum recorded in the solvent cyclohexane[17] (see Figure 3). The simulations of the absorption bands have been performed by summing Gaussian curves with an exponential half-width of 0.2 eV for each calculated transition. The computational details are summarized for DFT/SCI (see Table 2a), ZINDO/S (see Table 2b), and AM1/CISD (see Table 2c). The absorption spectrum as simulated from the DFT/SCI data is in excellent qualitative and quantitative agreement with the experiment, with a mean absolute deviation for the excitation energies of less than 0.1 eV and a maximum deviation of about *0.2* eV. The first broad absorption band consists of two $\pi\pi^*$ transitions at 3.34 and 3.54 eV with significant charge-transfer character from the highest occupied donor orbital of dimethylamino−naphthalene π character to the π^* LUMO for S_1 and π^* LUMO+1 for S_2. Both unoccupied MOs are localized within the naphthalene−propanoyl moiety. These two close lying excited states of A′ symmetry are strongly coupled. The S_1 consists mainly of a HOMO → LUMO transition with a partial HOMO → LUMO+1 contribution. This HOMO → LUMO+1 transition is the main one-electron contribution to the second excited state, and a small HOMO → LUMO character is admixed. The calculated dipole moments (DFT/SCI) are 16.0 D for S_1 and S_2, respectively, which underlines this state-mixing effect. An orbital analysis and the dipole moment mainly characterize both S_1 and S_2 as intramolecular charge transfer states, which explains the experimental red shift of this band in polar solvents.[3] The third excited state of A″ symmetry at 317 nm (3.91 eV) is of $n_O\pi^*$ character and not observed in the experiment, which can be explained with the low calculated oscillator strength of $f = 3 \times 10^{-5}$. At 5.46 eV the DFT/SCI calculations find a second $n_O\pi^*$ state, again with nearly zero oscillator strength. The S_4 state shows an enhanced charge-transfer character with a calculated dipole moment of 16.4 D. The large dipole moment

TABLE 2: Excitation Energies ΔE in eV (nm Values Given in Parentheses), Oscillator Strength f, Dipole Moments μ (in D), and Main Contributions of Single Excitations to the Excited-State Wavefunction of PRODAN According to (a) DFT/SCI, (b) ZINDO/S, and (c) AM1/CISD Methods

	state	ΔE	f	μ	character[a]
			a		
S_1	2A′	3.34 (371)	0.267	16.0	0 0
S_2	3A′	3.54 (351)	0.151	16.0	0 1
S_3	1 A″	3.91 (317)	0.000	1.0	2 0
S_4	4 A′	4.36 (285)	0.220	16.4	1 0
S_5	5 A′	4.86 (255)	0.234	7.0	1 1
S_6	6 A′	5.08 (244)	0.422	11.4	0 2
S_7	7 A′	5.39 (230)	0.177	13.9	3 0
S_8	2 A″	5.46 (227)	0.000	13.1	2 1
S_9	8 A′	5.67 (219)	0.215	13.9	3 1 and 0 3
S_{10}	9 A′	5.80 (214)	0.004	10.4	1 2 and 4 0
			b		
S_1	1 A″	3.11 (399)	0.000	2.5	3 0
S_2	2 A′	3.66 (339)	0.014	8.6	0 1
S_3	3 A′	3.87 (320)	0.554	15.0	0 0
S_4	4 A′	4.78 (260)	0.591	12.9	1 0
S_5	5 A′	5.08 (244)	0.695	9.3	1 1 (0 2 / 0 3)
S_6	6 A′	5.14 (241)	0.108	11.7	0 2
S_7	7 A′	5.46 (227)	0.218	13.1	1 1 (2 0 / 0 3)
S_8	2 A″	5.66 (219)	0.000	5.2	0 5
S_9	8 A′	5.77 (215)	0.272	7.1	1 2
S_{10}	9 A′	5.96 (208)	0.205	12.2	2 0
			c		
S_1	2 A′	3.58 (346)	0.070	8.3	0 0 and 0 1
S_2	3 A′	3.75 (331)	0.207	9.2	0 0 and 0 1
S_3	4 A′	4.37 (284)	0.031	2.7	0 4
S_4	1 A″	4.50 (276)	0.000	2.0	3 0
S_5	5 A′	4.73 (262)	0.030	8.1	0 2
S_6	6 A′	4.91 (252)	0.149	10.8	1 0
S_7	7 A′	4.97 (250)	0.426	8.4	1 1
S_8	8 A′	5.32 (233)	0.068	7.5	1 2
S_9	9 A′	5.40 (230)	0.022	8.2	0 3 (0 2)
S_{10}	10 A′	5.72 (217)	0.516	9.4	0 3

[a] 0 0 corresponds to a HOMO → LUMO transition, 1 1 to a HOMO-1 → LUMO+1 transition and so forth.

is mainly explained by an one-electron transition from the HOMO-1 with a large contribution at the nitrogen into the π^* LUMO. All absorption maxima are very well reproduced by our DFT/SCI calculations, as can be seen in Figure 3 with the exception of the absorption shoulder at 4.5 eV, which does not correspond to a computed excitation. Experimental difficulties in resolving electronic spectra in this high-energy region are well-known. Vibrational features of the close lying S_3 band are possible as well as vibrational intensity borrowing.

Second, we interpret the ZINDO/S results (see Table 2b and Figure 3). The overall agreement with the experimental spectrum is not very good, so that we give here only a brief description of the results. The first band is shifted by ~0.5 eV to higher energies, while the second band at 4.4 eV is not found at all. Furthermore, all computed intensities are too high by a factor of 1.5−2. A low lying $n_O\pi^*$ first excited state is computed at 3.11 eV. Comparison with experimental or DFT/SCI data shows that a lowest lying $n\pi^*$ state is very unlikely, so that this result is interpreted as a serious error of ZINDO/S (i.e., this method predicts the wrong character of the lowest state).

The AM1/CISD spectrum is presented in Figure 3 and Table 2c. The first two excited states of $\pi\pi^*$ character are blue shifted by 0.3 eV in comparison to experiment. For AM1/CISD both the absolute excitation energies and relative energy differences between both states are reproduced better than by the spectroscopic parametrization of ZINDO/S. The small energy gap between both states of less than 0.2 eV leads to a coupling of S_1 and S_2 states which is deduced from large contributions of the HOMO → LUMO and HOMO → LUMO+1 excitations to both states (both with $\pi\pi^*$ character). The dipole moments of 8.3 and 9.2 D for S_1 and S_2, respectively, are further signs for mixing of close lying states of the same symmetry. This effect is also not observed in ZINDO/S. In contrast to the ZINDO/S results the $n_O\pi^*$ transition is attached to the fourth excited state at 4.50 eV (HOMO-3 → LUMO transition of A″ symmetry). Also within AM1/CISD a second $n\pi^*$ transition is computed at higher energy (5.92 eV), but on top of that, all experimental excitations are assigned fairly well by the nonspectroscopic AM1 Hamiltonian. This indicates as well that the overall description of the absorption spectrum using AM1/CISD is better than ZINDO/S. The oscillator strengths are calculated too low in general, but the intense $\pi\pi^*$ maxima at long wavelengths are represented quite well.

TABLE 3: Experimental Ground-State Dipole Moments μ_g and Emissive Excited State Dipole Moments μ_e (in D), with Differences (in D) and Ratio μ_g/μ_e

	Weber et al.[1]	Catalan et al.[2]	Bunker et al.[3]	Balter et al.[44]	Baumann et al.[47]
μ_g	5−7	4.7	2.9	3.0	4.7
μ_e	25	11.7	9.8	10.9	12.4
$\Delta\mu_{ge}$	20	7	7	8	8
μ_g/μ_e	1:5	1:2.5	1:3.5	1:3.6	1:2.6

3.3. Interpretation of PRODAN Fluorescence Spectrum. The large Stokes shift for PRODAN in polar solvents has been investigated by time-resolved[43,44] and temperature-[45] and pressure[46]-dependent fluorescence spectroscopy as well as electro-optical absorption and emission measurements,[47] and the general conclusion of all investigations clearly votes for the existence of an intramolecular charge transfer state. In addition, dual fluorescence is observed at low temperatures and in a highly viscous environment.[43] Nevertheless, the discussion on the origin of this ICT state as well as the correct assessment of ground- and excited-state dipole moments is not finished yet.

Weber and Farris postulate in their original hypothesis[1] an excited-state dipole moment 5 times larger than the ground-state dipole moment (see Table 3). This ratio is ruled out in the meantime,[2,3,44,47] but neither the ground- nor excited-state dipole moments are ascertained yet, as can be seen in Table 3. The measurement of excited-state dipole moments is quite difficult and depends also on several assumptions, e.g., an arbitrary Onsager radius and the continuum dielectric model of the solvent. Nevertheless, the estimation by Weber and Farris[1] gives a value much too high ($\mu_g = 5$ D, $\mu_e = 25$ D), whereas the dipole moments postulated by Bunker et al.[3] seems to be too low ($\mu_g = 2.9$ D and $\mu_e = 9.8$ D) in comparison to further experiments (see Table 3) and to our calculations. The difference between ground- and excited-state values of about 7−8 D seems to fit into the general interpretation.

In Table 4 we show the computed dipole moments and differences in dipole moments between ground and excited states for the polar charge-transfer state of planar PRODAN. In addition we present several other highly polar states and differences in total energy with respect to the first excited state of PRODAN. The energies in Table 4 are achieved by calculating the differences between ground-state energies and excited-state energies as obtained in each method separately. A low lying $n\pi^*$ S_1 is assumed to be an artifact of the INDO/S and CNDO/S methods (which has been pointed out by Nowak et al.[17]). The difference in dipole moment between the ground and the first (for ZINDO/S second) excited state is computed

TABLE 4: Dipole Moments of the Ground State and Highly Polar Charge-Transfer States of Excited PRODAN (in D) and the Energy Differences (in kcal/mol) between the Planar Intramolecular Charge Transfer State (PICT) and Dimethylamino (N-TICT) or Propanoyl (O-TICT) Twisted Intramolecular Charge Transfer States

	DFT/SCI	ZINDO/S	AM1/CISD
S_0	5.7	6.8	4.5
PICT	16.0	8.5	8.3
N-TICT	22.6	17.8	23.0
O-TICT	30.5	21.7	30.8
ΔE(N-TICT-PICT)	11.8	16.8	17.7
ΔE(O-TICT-PICT)	39.0	27.0	48.9

to be 10 D (DFT/SCI), 2 D (ZINDO/S), and 4 D (AM1/CISD), respectively. The DFT/SCI dipole moment of 16.0 D is indicative of CT character of the first planar excited state, and the AM1/CISD dipole moment of 8.3 D (*8.5* D for ZINDO/S) accounts barely for partial charge transfer. According to these results an energetically low lying singlet state with partial charge-transfer character is found without any changes in geometry for S_1. Although the dipole moments from DFT/SCI are usually at the upper limit of experimental data,[29] the calculated difference between S_0 and S_1 of 10 D fits much better to experiment (7−8 D) than the semiempirical results.

Twisting and distortion of PRODAN should increase this charge-transfer character and should generate a highly polar excited state with partial diradical character. According to the results presented in Table 4, the twisting coordinate of the dimethylamino group supplies a highly polar TICT state with a dipole moment of 22.6 D (DFT/SCI), 17.8 D (ZINDO/S), and 23.0 D (AM1/CISD), respectively. The formation of the TICT state for DMABN[15,33] is not exothermic in the gas phase; that is the energy of the final TICT state is higher than the energy of the primary excited planar S_1 state. Thereby, no dual fluorescence is observed in the isolated molecule. Nevertheless, the TICT state is stabilized in energy in contrast to the PICT state (planar S_2 excited state). This has been shown in numerous calculations for the isolated molecule on a high computational level. The TICT state for DMABN becomes the first excited state in polar solvents, as has been shown by computations with consideration of solvent effects.[15,25−27,33] In contrast, the energy for the N-TICT state in PRODAN increases and is 11.8 kcal/mol (DFT/SCI) higher in energy than the planar S_1 conformation.

We have estimated the solvent stabilization dependence on the cavity radius for solvents of different polarity. The solvent shifts of electronic transitions are calculated according to the crude Amos−Burrows theory[48] by

$$\Delta E_{ge} = -\left(\frac{2}{a_0^{\ 3}}\right)(\vec{\mu}_e - \vec{\mu}_g)\vec{\mu}_g\left(\frac{\mathrm{D}-1}{\mathrm{D}+2} - \frac{n^2-1}{n^2+2}\right) - \frac{\mu_e^{\ 2} - \mu_g^{\ 2}}{\mathrm{a}_0^{\ 3}}\,\frac{n^2-1}{n^2+2}$$

with a_0 the cavity radius, $\vec{\mu}_\mathrm{g}$ and $\vec{\mu}_\mathrm{e}$ being the ground- and excited-state dipole moment vectors, respectively, D is the dielectric constant, and n is the refractive index. The Onsager cavity radius (a_0) is estimated to 4.6 Å as used by Nowak et al.[17] (this is larger than the original estimation of 4.2 Å by Weber et al.[1]). In addition, half the distance between both the amino methyl and the most distant propanoyl carbon atom of 5.6 Å is considered also for this value. We have employed the ground- and excited-state dipole moments from the DFT/SCI calculations. The N-TICT state shows an additional solvent stabilization compared with the PICT state ($\Delta\mu = 6.6$ D) for $a_0 = 4.6$ Å of 19.6 kcal/mol in acetonitrile and approximately 14 kcal/mol in the apolar solvent benzene. This definitely overweighs the increase in total energy upon rotation (ΔE(N-TICT-PICT) = 11.8 kcal/mol), and this state is strongly stabilized in polar solvents and becomes the emissive first excited state. On the contrary, the N-TICT state energy is 0.7 kcal/mol higher in total energy compared to the PICT state even in strongly polar acetonitrile, enlarging the cavity radius by 1 Å to 5.6 Å. The planar form remains the lowest excited state, although the difference in energy is close to zero and this radius represents thus a sort of limiting case for the PICT/TICT question. The crude estimates of solvent effects indicate the possibility of TICT emission in polar solvents, but the fluorescence out of the planar PICT state cannot be ruled out employing the DFT/SCI dipole moments and total energies. In principle no twisting mode is required to explain the solvent sensitivity of PRODAN, since even the planar intramolecular CT state is quite polar with respect to the ground state.

In contrast, the difference in dipole moments are computed to be 9.3 D (ZINDO/S) and 14.7 D (AM1/CISD), respectively, which favors a lowering of the N-TICT state below the PICT state. The twisting coordinate of the propanoyl group leads to an excited state with an extremely large dipole moment. μ is increased significantly, for the DFT/SCI results 14.5 D with respect to the PICT state ($\mu_\mathrm{OT} = 30.5$ D), 6.7 D according to ZINDO/S ($\mu_\mathrm{OT} = 21.7$ D), and 22.5 D for AM1/CISD ($\mu_\mathrm{OT} = 30.8$ D). However, this conformational change is also energetically disfavored because the total energy for the propanoyl twisted (OT) charge transfer states is about 40 kcal/mol larger than the planar S_1, and this difference in energy cannot be compensated by solvent stabilization. The Amos−Burrows calculation using the DFT/SCI data yields a energy lowering of approximately 56 kcal/mol ($a_0 = 4.6$ Å for acetonitrile), which locates this state just a few kcal/mol above the solvent-stabilized PICT state. A further highly polar excited state is investigated, shown by the DFT/SCI results. For the geometry of PRODAN with both the propanoyl and the dimethylamino group twisted perpendicular to the naphthalene plane neither the donor nor the acceptor subunit is in conjugation with the aromatic π-system. The resulting seventh excited state with charge-transfer character is described by an electron flow from the dimethylamino to the propanoyl group with a dipole moment of 40.5 D. This so-called "NO-TICT" state is 49.0 kcal/mol higher in energy than the planar first excited state. The calculated stabilization by polar solvent is also not enough to lower the energy of this state sufficiently, and this state is therefore excluded as a candidate for the emissive state.

The proposed distortion of the aromatic ring system in combination with twisting the dimethylamino group orthogonal to the naphthalene as a possible relaxation mode is investigated as well.[20] This hypothesis cannot be supported by our calculations. A common tendency is found for all three methods and will be presented for the DFT/SCI results. Upon twisting and distortion of PRODAN the N-TICT state partly loses charge-transfer character. The free electron pair at the nitrogen is no longer completely decoupled. An increase in conjugation is found, discernible by a smaller dipole moment for S_1 ($\mu_\mathrm{P} = 22.6$ D and $\mu_\mathrm{D} = 20.6$ D). The distorted N-TICT state is energetically destabilized and becomes the second excited state (S_1 in the nondistorted TICT state). The destabilization in energy is slightly more distinct for the ground state than for the excited state. We therefore compute a small decrease of

TABLE 5: Dipole Moments (in D) of the Ground State and Highly Polar Planar (PICT) and Twisted Intramolecular Charge Transfer (TICT) States of Excited DAN and PRON and the Energy Differences ΔE between the PICT and TICT State (in kcal/mol)

	DAN			PRON		
	DFT/ SCI	ZINDO/ S	AM1/ CISD	DFT/ SCI	ZINDO/ S	AM1/ CISD
S_0	2.4	1.7	2.4	3.3	4.9	3.2
PICT	9.5	4.2	7.1	9.7	6.6	4.0
TICT	16.0	11.9	16.3	17.3	17.8	19.2
ΔE(TICT-PICT)	16.6	34.7	24.9	45.2	35.3	56.2

the energy gap between S_0 and S_1 for the distorted form ($\Delta E_P(S_1-S_0) = 3.34$ eV and $\Delta E_D(S_1-S_0) = 3.20$ eV). This decrease is of no photophysical consequence due to the fact that for both ground and excited states the total energies increase by about 30 kcal/mol when the distorted ring system is examined. The distortion motion is therefore definitely excluded as being of any importance to the fluorescence behavior.

3.4. Excited States of DAN and PRON. In continuation of the investigation of the large Stokes shift of PRODAN in polar solvents the spectroscopic properties of 2-(*N*,*N*-dimethylamino)naphthalene (DAN) and 2-propanoylnaphthalene (PRON) are of interest. The formation of a fluorescent charge-transfer state is reported for compounds with both electron donor and acceptor subunits united in one single molecule (DMABN, PRODAN), but the presence of only one of these subunits should also show a significant effect on the emission spectra. Indeed, 1-(*N*,*N*-dimethylamino)naphthalene (1-DAN) has been investigated in a variety of solvents by fluorescence spectroscopy,[21] and a significant red shift of emission was found for solvents with high polarity. Moving from the apolar cyclohexane (3.26 eV, 26 300 cm^{-1}) to the polar solvent water (2.74 eV, 22 100 cm^{-1}), a shift of 73 nm ($\Delta E = 0.52$ eV, corresponding to 4200 cm^{-1}) was found. This is a surprisingly large value in comparison to PRODAN, where 133 nm ($\Delta E = 0.81$ eV, corresponding to 6500 cm^{-1}) has been measured.[3] A former semiempirical study on pyrrole and dimethylamino derivatives of naphthalene[49] also postulated the formation of a twisted intramolecular charge transfer state for 1-DAN. 2-Naphthalenecarboxylic acid (NCA) can be interpreted as a compound related to 2-propanoylnaphthalene, where dual fluorescence in water−organic mixtures is observed. The two fluorescence bands are assigned to the locally excited and an intramolecular charge transfer state, and solvent shifts up to 50 nm (0.42 eV, 3400 cm^{-1}) are obtained for polar solvents.[22]

Not much attention has been paid to the phenomena of twisted intramolecular charge transfer in compounds with either donor or acceptor subunits. We therefore calculated the excited-state properties of DAN and PRON in order to settle the question whether donor *or* acceptor substituents exclusively are able to form high polar, low lying charge-transfer states with (TICT) or without (PICT) twisted conformations. The results are summarized in Table 5 for both compounds. The relatively small ground-state dipole moment (DFT/SCI 2.4 D, ZINDO/S 1.7 D, and AM1/CISD 2.4 D) of DAN is opposed to a higher value of μ_e for the first excited state with partial charge-transfer character (DFT/SCI 9.5 D, ZINDO/S 4.2 D, and AM1/CISD 7.1 D). This state is described mainly by a HOMO → LUMO transition: a large dimethylamino free electron pair contribution in the highest occupied molecular orbital is combined with a π^* acceptor MO of naphthalene type. After rotation of the dimethylamino moiety perpendicular to the naphthalene group, the dipole moment reaches its maximum value of 16.0 D (DFT/SCI), 11.9 D (ZINDO/S), and 16.3 D (AM1/CISD), respectively. The N-TICT state is still the S_1 according to the DFT/SCI method, but one locally excited (LE) state in the naphthalene moiety is close below this N-TICT state for ZINDO/S and two LE-like states are energetical favored against the twisted charge-transfer state for AM1/CISD. This state is destabilized in total energy in comparison to the PICT state by all methods. Nevertheless, a significant increase of the dipole moment upon rotation (DFT/SCI 6.5 D, ZINDO/S 7.9 D, AM1/CISD 9.2 D) is found, which accounts for an additional solvent stabilization. We therefore postulate for DAN as well as for PRODAN and by its similarity also for 1-DAN that the TICT state becomes of photophysical significance in polar solvents.

The situation is quite similar in PRON. Using the ZINDO/S method a low lying $n\pi^*$ first excited state is computed which is neglected in our further investigations as for PRODAN. The S_1 state is characterized by a partial electron shift from the naphthalene donor moiety to the propanoyl acceptor group. The S_1 dipole moment for PRON is similar to DAN in the DFT treatment (9.7 D), whereas 4.0 D is found for AM1/CISD and 6.6 D for the ZINDO/S method. Nevertheless, all three methods give a first excited state of partial intramolecular charge transfer character. We also localize a CT state with a significantly increased dipole moment for the propanoyl twisted conformation (O-TICT state). This state is characterized by a large dipole moment: 17.3 D (DFT/SCI) and 17.8 D (ZINDO/S) for the S_4 state and 19.2 D for the S_{10} state (AM1/CISD). Again, the situation is similar to DAN and PRODAN. The TICT state is about 45 kcal/mol (DFT/SCI) higher in energy (see Table 5) than the planar first excited state and therefore accessible on the excited-state hypersurface solely in very polar solvents.

4. Conclusions

The extensive theoretical study on the photophysics of PRODAN by semiempirical (ZINDO/S, AM1/CISD) and density functional methods (DFT/SCI) results in a satisfactory interpretation of the absorption spectrum. The DFT/SCI method has been proven as the qualitatively and quantitatively best quantum mechanical method used in our work for assignments of excited singlet states up to 6.0 eV. Excited-state calculations with the AM1 method are suitable for the interpretation of absorption and fluorescence spectra, although it is parametrized only for the ground state. In contrast to experimental observation, ZINDO/S computes a low lying $n\pi^*$ S_1 state, which is not found by AM1/CISD and DFT/SCI. The red-shifted fluorescence is most likely assigned to emission from a highly polar N-TICT state in polar solvents but to a planar PICT state in apolar solvents. The low lying excited states in the planar geometry have significant charge-transfer character. The formation of an intramolecular charge transfer state by twisting of either the dimethylamino (N-TICT) or the propanoyl group (O-TICT) leads to an excited state with a significantly enlarged dipole moment, in agreement with experiment. Nevertheless, the total energy increases upon twisting. This can only be compensated in highly polar solvents by the comparatively large dipole moment of the N-TICT state. In contrast, solvent stabilization cannot counteract the increase in energy even in a polar environment for the rotation about the naphthalene−propanoyl single bond. This difference in behavior is deduced from the significant larger increase in total energy for the O-TICT state compared to the N-TICT state. In addition to the donor *and* acceptor substituted naphthalene (PRODAN) also the donor (DAN) *or* acceptor (PRON) substituted derivatives are investigated. According to the present results either a donor or acceptor substituent is sufficient to create a low lying intramolecular charge transfer state with a twisted conformation. The CT character is not as marked as for PRODAN in the PICT geometry, which is, for example, seen by the smaller S_1 dipole moment. We estimate that the increase in the dipole moment for DAN and PRON is sufficient to balance the increase in energy upon twisting about the donor−acceptor single bond at least in polar solvents. This is clearly an argument for the TICT hypothesis for donor and/or acceptor substituted naphthalene derivatives. It was also proposed[20] that twisting of the amino group should be combined with a distortion of the aromatic ring system. Such an additional stabilization was not found in our calculations. The distorted TICT state loses part of its CT character. The possibility of distortion as an indispensable relaxation coordinate for excited PRODAN is not supported by our calculations. Further calculations that explicitly include solvent effects are necessary in order to explain the strong solvent dependencies of PRODAN. A semiempirical work considering the solvent by self-consistent reaction field (SCRF) calculations is to be published.[50]

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