Excited State Dipole Moment of PRODAN as Determined from Transient Dielectric Loss Measurements

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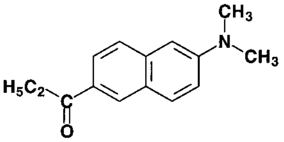
Time-resolved changes in microwave dielectric absorption have been studied to determine the excited state dipole moment of 6-propanoyl(*N*,*N*-dimethylamino) naphthalene (PRODAN), a molecule extensively used as a fluorescence probe for the study of microheterogeneous environments of a wide variety of chemical and biological systems. This study, which provides by far the most reliable value of the excited-state dipole moment of PRODAN, shows that the change in the dipole moment of the molecule upon excitation (4.4−5.0 D) is far less than the commonly mentioned value (∼ 20 D). The results imply that solvatochromism of the fluorescence band of PRODAN, the property that makes this system an ideal probe, cannot be attributed to an extraordinarily large magnitude of $\Delta\mu$. Other forces, such as a hydrogen-bonding interaction of the molecule with the solvent, must play a crucial role in determining the location of the fluorescent state of PRODAN. Furthermore, the results imply that internal rotation or twisting of the dimethylamino group in the excited state, if any occurs, does not influence the fluorescence properties of PRODAN and that the fluorescence originates from a locally excited state.

Introduction

Ever since it was introduced by Weber and Farris,[1] 6-propanoyl(*N*,*N*-dimethylamino)naphthalene (PRODAN, Chart 1) has generated considerable interest and has been extensively employed as a fluorescence probe for studying the microenvironments of various chemical and biological systems.[1−39] The property that makes PRODAN an ideal probe molecule is that its fluorescence band position is extremely sensitive to the polarity of the medium, which is evident from the fact that the fluorescence maximum shifts from 401 to 531 nm on changing the solvent from cyclohexane to water. Even though the utility of PRODAN in probing a wide variety of organized systems has been well documented,[1−32] the origin of the solvatochromic nature of the fluorescence band of the molecule is a subject of considerable debate.[33−39] To account for the solvatochromism, it was originally thought that the emitting state of this electron donor−acceptor molecule could be highly polar. The solvatochromic absorption and fluorescence data were analyzed using the Lippert−Mataga equation[40−42] to obtain the change in dipole moment ($\Delta\mu$) of the molecule on electronic excitation, and the value was estimated to be as large as 20 D.[1] A number of investigations, aimed at understanding the nature of the electron distribution and/or structural changes that might lead to such a polar excited state, have subsequently been carried out.[33−39] Semiempirical calculations based on CNDO/S, INDO/S and AM1 methods were undertaken[33,34] to find out whether the fluorescence originates from a highly dipolar twisted intramolecular charge transfer (TICT) state[43−45] of the molecule. However, because the TICT states were found to be located at higher energies, they were not expected to influence the photophysical properties of the probe molecule unless they are stabilized by a considerable amount as a result of solvation. Although Nowak et al. concluded that the TICT state could be the lowest state in polar media,[33] Ilich and Prendergast felt the need for specific solvation for the TICT state to be lower than the locally excited state.[34] A trivial error in the equation used by Weber and Farris was recognized by Balter et al., who reported a $\Delta\mu$ of only 8 D from an analysis of solvatochromic data in some selected solvents.[35] Using a modified Lippert equation and Onsager cavity radius of 4.2 Å, the excited-state dipole moment of PRODAN was measured to be 11.7 D.[36] Although a lower excited state dipole moment has been suggested in these reports, PRODAN continues to find applications in which it is assumed that its excited state dipole moment is unusually large,[13−15] and reports continue to appear in print describing whether or how the dipole moment of the molecule could be so large.[37−39] Interestingly, with more and more sophisticated calculations on the molecule, the issue has become somewhat confusing. This is apparent in that a gas phase ab initio calculation performed by Parusel et al. suggests a low-lying TICT state,[37] whereas the DFT/SCI and AM1/CISD calculations indicate that the emission originates from a highly polar dimethylamino twisted charge transfer state (N-TICT) and also, from a geometrically unchanged planar intramolecular charge transfer (PICT) state.[38] In a later paper, however, it has been reported that PRODAN fluoresces from the propanoyl TICT state.[39]

CHART 1



Considering the importance of PRODAN as a probe molecule and that the literature as confusing as it could be, we felt an

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urgent need of resolving the issue (the nature of the excited state of the molecule). The current $\Delta\mu$ values have been obtained either by theoretical calculation or experimental measurement from the solvatochromic absorption and fluorescence data using the Lippert−Mataga equation. Because the latter method requires the knowledge of an Onsager cavity radius that is most often chosen arbitrarily, the reported values may not be very reliable. Hence, for the determination of the excited state dipole moment of the molecule, we have resorted to a more direct method that involves measurement of time-resolved changes in microwave dielectric absorption and is known to be ideally suited for a species undergoing a change in dipole moment.[46−49]

Experimental Section

Methodology and Instrumentation. The microwave absorption is proportional to the dielectric loss, ϵ'', and is given by,[50]

$$\epsilon'' = A[\mathrm{S}]\mu^2 g(\omega\tau) \qquad (1)$$

where A is a combination of some fundamental constants and the absolute temperature, [S] is the solute concentration, μ is the dipole moment, and $g(\omega\tau)$ is a factor that takes into account the nature and rate of molecular reorientation (ω is the angular frequency of the microwaves, and τ is the molecular rotational relaxation time). In an ideal case, $g(\omega\tau) = \omega\tau/[1+(\omega\tau)^2]$, but usually, the factor departs somewhat from this form. The unknown values of $g(\omega\tau)$ were determined by measuring the loss at the desired frequency for known concentrations of the ground-state molecules in static experiments as done previously.[47]

The transient experiments use a comparison with the change in dielectric loss of a reference compound to eliminate all factors of the experimental setup. The final equation is

$$\Delta(\mu^2)_x = (V_\mathrm{x} g_\mathrm{r}/V_\mathrm{r} g_\mathrm{x})\ \Delta(\mu^2)_\mathrm{r} \qquad (2)$$

where the subscripts x, and r refer to the unknown and reference compounds, respectively, the g terms are $g(\omega\tau)$ as defined above, and V represents the amplitude of the transient signal.[47] The use of the ground state to measure the loss factor g assumes that the direction of the dipole in the ground and excited states is the same. This assumption is expected to be valid whenever the ground state is already quite polar as a result of electron donating and accepting groups, as is the case here.

The details of microwave measurements were described in earlier publications.[47,48] The microwave signal source was a 40-mW klystron with frequency in the range 9.0−9.2 GHz. The signal amplitudes of the sample were compared with those from diphenylcyclopropenone (DPCP), and necessary corrections were made for adjustments of cavity coupling. The usual response time of the apparatus, as determined by the cavity Q, was 36 ns, which was significantly higher than the fluorescence lifetime of PRODAN (3.3 ns in 1,4-dioxane and 2.7 ns in benzene). To better resolve the decay curves, the cavity Q was lowered by introducing a resistive plate in the cavity. The measured Q factor under these conditions gave a time constant of about 8.9 ns that still did not fully resolve the response but represented a better compromise between resolution and sensitivity. The shapes of the data curves were fitted by integrating a suitable differential equation taking into account the pulse shape of the excitation laser (12 ns full-width, half-maximum Gaussian), the response time of the apparatus from the Q factor, an additional 1 ns time constant for the subsequent amplifier, and the excited-state lifetime of the compound. The equation allowed for a fraction of the singlet to decay into a long-lived (on this time scale) triplet. This calculation was also used to model the rising portion of the data curves observed DPCP, which gives a step response as a result of the transformation of this compound into nonpolar photoproducts.[47] The response times so measured agreed with the value from the Q factor. Photolysis of the samples was achieved with 355 nm pulses (approximately 10 mJ/pulse over 1 cm^2) from a Quanta-Ray PRO 230−10 Nd:YAG laser. The laser dose was monitored while photolyzing the samples to allow correction for any fluctuation in laser intensity. Considerable care was given to verify, by experiments at several laser pulse energies, that there were no effects such as ground-state bleaching. The fluorescence lifetime of PRODAN was measured on a single photon counting spectrofluorimeter equipped with a N$_2$ laser (Photon Technology International, GL 3300) as the excitation source. Spectrophotometric measurements were made using a Shimadzu spectrophotometer (UV 3101PC).

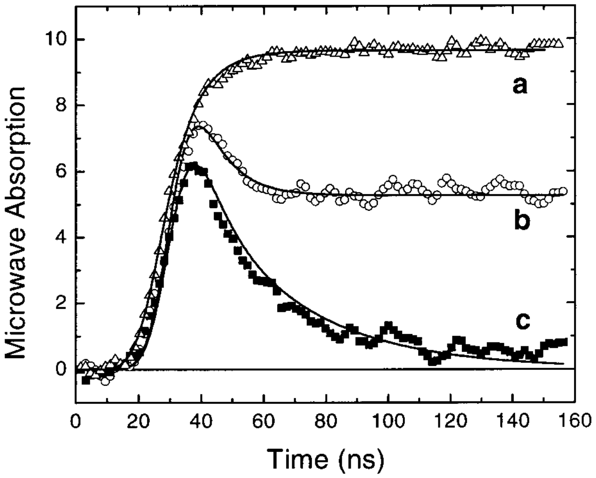

Figure 1. Transient changes in dielectric loss for (a) deoxygenated 3 mM DPCP in benzene (average of 4 pulses), (b) deoxygenated 0.2 mM PRODAN in benzene (average of 50 pulses), and (c) the solution of (b) after bubbling oxygen (average of 50 pulses). The curve for DPCP has been inverted and multiplied by 1/3 for presentation. The solid curves are calculated by the method described in the text.

PRODAN was used as received from Molecular Probes. Diphenylcyclopropenone (Aldrich) was recrystallized several times from an ethanol−water mixture before photolysis. 1,4-dioxane (Merck, Uvasol) and benzene (Fischer Scientific, spectranalyzed) were used without any further purification. The solutions were deoxygenated by bubbling with argon.

Theoretical Calculation. The ground-state dipole moment of PRODAN was obtained by theoretical calculations based on AM1 method, which consists of modified MNDO Hamiltonian.[51−53] The calculations were performed on a DEIL microVAX 3300 computer. Unrestricted geometry optimization at the semiempirical level was performed following initial optimization of the geometry by MMX molecular mechanics program. The gradient norms were monitored to test for successful convergence.

Results and Discussion

Time dependent variation of the dielectric loss signals observed upon photolysis of benzene solutions of PRODAN and the reference compound, DPCP are shown in Figure 1. It should be noted that the curve for DPCP represents a decrease in dielectric loss and would normally be shown as a signal in the negative direction, but this curve has been inverted for comparison with the signal for PRODAN that shows an increase

TABLE 1. Excited State Dipole Moment of PRODAN along with Some Data Involved in Its Estimation

solvent	sample	amplitude[a]	$g(\omega t)$	μ_g	$\Delta(\mu^2)$	μ_e
Benzene	**DPCP**	21.03	0.288	5.1	$(5.1)^2$	0
	PRODAN	40.91	0.190	5.2	76.8	10.2
Dioxane	**DPCP**	13.50	0.193	5.1	$(5.1)^2$	0
	PRODAN	17.00	0.098	5.2	64.7	9.6

[a] Value from curve fitting corrected for differences in dose, cavity *Q*, and absorbances.

in loss on excitation. The data shown for DPCP have been multiplied by a factor of 1/3 for display purposes. The relatively weak signal observed for PRODAN and its sign immediately suggest that even though the dipole moment of PRODAN increases on electronic excitation, the magnitude of change is not large. Second, the decay of the loss signal for PRODAN is found to consist of a fast and a slow component. Although the fast component represents the decay of the singlet state, the long-lived one arises due to the triplet state of the molecule. This suggestion is substantiated by the observation that in the presence of oxygen this long-lived component disappears almost completely (lower curve in Figure 1). That the signals do not arise from any spurious effect, such as the heating of the solution or the cavity, has been verified by performing blank experiments on benzene. Furthermore, we have confirmed that only the dipole moment change gives rise to the dielectric loss by the absence of any signal from a benzene solution of anthracene (with a similar absorbance), a molecule for which $\Delta\mu$ is known to be negligible. Curves representing the response calculated as described in the Experimental Section are shown as solid curves in Figure 1. The curve for DPCP provides an amplitude and shows that the response time matches the data. With PRODAN, the amplitude is smaller because the excited-state lifetime is shorter than the excitation pulse width and response time. The actual amplitude is larger than that for DPCP as shown in Table 1, which also shows some of the steps in the calculation. The effect of the formation of the triplet state is also included. If the triplet state has the same dipole moment as the singlet excited state, then the amplitude of the long-lived portion corresponds to a triplet yield of 0.12. The dipole moments so obtained for PRODAN in benzene and 1,4-dioxane are given in Table 1.

The fluorescence decay curves of PRODAN in benzene and 1,4-dioxane were found to be single exponential with lifetimes of 3.3 and 2.7 ns, respectively. Even though the fluorescence lifetime of PRODAN in these solvents has not been measured previously, the single-exponential nature of the fluorescence decay as well as the lifetime values are found to be consistent with those measured in other aprotic solvents.[35]

The excited-state dipole moment of PRODAN as obtained by the analysis of the dielectric loss data is found to lie between 9.6 (± 0.5) and 10.2 (± 0.5) D in 1,4-dioxane and benzene, respectively (the error limits are based on those found between replicate experiments). These values are obtained assuming the ground-state dipole moment of the molecule to be 5.2 D. Although no experimental value of μ_g is available for PRODAN, we note that its crystal structure suggests a planar geometry of the molecule and the same could be predicted by AM1 calculations.[34] Taking into consideration these observations and the superiority of the AM1 method (over other semiempirical methods such as CNDO or MNDO) in predicting the ground-state structure and dipole moment of a molecule,[51−53] a μ_g of 5.2 D has been obtained by AM1 calculation. It is to be noted that the value of μ_g so calculated is in close agreement with that obtained recently for the planar form of the molecule[38] by other methods. Therefore, we conclude that the change in the dipole moment of PRODAN on electronic excitation lies between 4.4 and 5.0 D. It should be noted that the corresponding value of the excited-state dipole moment, 9.6−10.2 D, is only slightly less than that reported (11.7 D) in ref 36.

Because the dielectric loss measurements have to be made in relatively nonpolar solvents such as those used here, one might argue that in polar solvents such as in acetonitrile, the emitting state could be a more polar TICT state. However, a number of points argue against this.

The emission data for PRODAN in benzene and 1,4-dioxane can be plotted as peak energy against the solvent $E_T(30)$ value and fit well on a straight line that includes aprotic solvents from benzene to acetonitrile. (The point for dioxane lies near that for chlorobenzene.) This behavior suggests that the same state is involved. In addition, the fluorescence decay of PRODAN has been found to be single-exponential in nonpolar as well as in polar aprotic solvents such as in acetonitrile. In this context, it is to be noted that the fluorescence lifetime in 1,4-dioxane as measured here is almost identical with that in acetonitrile.[16,35] Because the dielectric constants of 1,4-dioxane (2.21) and acetonitrile (35.94) differ considerably,[54] had there been a close-lying TICT state, one would have observed a change in the decay pattern and/or a difference in the fluorescence lifetime in these two solvents. However, that is not the actual case, and one can rule out the possibility of a highly polar state contributing to fluorescence in polar media. Next, the measured values of the excited-state dipole moment are 10.2 and 9.6 D in benzene and 1,4-dioxane, respectively. Taking into consideration of the error involved in the measurements, we can conclude that the measured dipole moments in the two solvents are fairly close if not the same. That the measured μ_e of PRODAN is not higher in the more polar 1,4-dioxane (as compared with benzene) indicates clearly that no other dipolar state comes into the picture as the polarity of the medium is increased.

In light of the above, we can conclude that no matter what the polarity of the media the fluorescence of PRODAN occurs neither from a dimethylamino group twisted (N-TICT) nor from a propanoyl group twisted (O-TICT) charge transfer state.[37−39] Quite obviously, the fluorescence originates from a solvated excited state of the molecule in which the structure of PRODAN is not very different from that in the ground state.

The question that follows immediately is, why is the emitting state of PRODAN so sensitive to the solvent if the change in the dipole moment is not extraordinarily large? Balter et al. came to the conclusion that a specific solute−solvent interaction such as hydrogen bonding is responsible for the solvent induced dramatic shift of the fluorescence band of PRODAN,[35] and it was subsequently found that the fluorescence properties of PRODAN in hydrogen bond donating solvents such as methanol are different from those in aprotic solvents.[13,14,16] However, not much attention has been paid to these observations, presumably due to the fact that no convincing and reliable measurement of the excited state dipole moment of the molecule has been available. The present study shows clearly that the change in the dipole moment of PRODAN is moderate, and the photophysical behavior of the molecule is not complicated. Therefore, it must be the hydrogen-bonding interaction that is primarily responsible for the sensitivity of the location of the fluorescence maximum to the nature of the solvent. That the photophysical behavior of PRODAN is not complex, but very similar to that of other electron donor acceptor molecules, is evident from a comparison with 4-aminophthalimide. This system exhibits as large a shift in the fluorescent state as is shown by PRODAN and the excited-state dipole moment is also not large.[55−57]

Conclusion

We have determined the excited state dipole moment of PRODAN, a molecule of considerable interest, by a direct method that is far more reliable than any other previous method. The change in the dipole moment of the fluorescent state of the molecule is found to be much lower than that which is is commonly believed. The results clearly indicate that PRODAN does not fluoresce from a TICT state but from a state in which the geometry of the molecule need not be different from that in the ground state. We have also arrived at the conclusion that solvent induced Stokes shift of the fluorescence of PRODAN, the property which makes PRODAN as an attractive probe molecule, cannot be attributed to the polar nature of the fluorescent state but on the contrary, the same must be interpreted as being largely due to the stabilization of the fluorescent state by hydrogen bonding interaction with the solvent molecules.

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References and Notes

(1) Weber, G.; Farris, J. F. *Biochemistry* **1979**, *18*, 3075.
(2) Torgerson, P. M.; Drickamer, H. G.; Weber, G. *Biochemistry* **1979**, *18*, 3079.
(3) Rollinson, A. M.; Drickamer, H. G. *J. Chem. Phys.* **1980**, *73*, 5981.
(4) Macgregor, R. B.; Weber, G. *Ann. NY Acad. Sci.* **1981**, *366*, 140.
(5) Macgregor, R. B.; Weber, G. *Nature* **1986**, *319*, 70.
(6) Cowley, D. J., *Nature* **1986**, *319*, 14.
(7) Warshel, A.: Russel, S. T.; Churg, A. K. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 4785.
(8) Chong, P. L. G. *Biochemistry* **1988**, *27*, 399.
(9) Massey, J. B.; She, H. S.; Pownall, H. J. *Biochemistry* **1985**, *24*, 6973.
(10) Lakowicz, J. R.; Balter, A. *Biophys. Chem.* **1982**, *16*, 117.
(11) Lakowicz, J. R.; Balter, A. *Biophys. Chem.* **1982**, *16*, 223.
(12) Heisel, F.; Miehe, J. A.; Szemik, A. W. *Chem. Phys. Le*tt. **1987**, *138*, 321.
(13) Zurawsky, W. P.; Scarlata, S. F. *J. Phys. Chem.* **1992**, *96*, 6012.
(14) Zurawsky, W. P.; Scarlata, S. F. *Photochem. and Photobiol*. **1994**, *60*, 343.
(15) Narang, U.; Jordan, J. D.; Bright, F. V.; Prasad, P. N. *J. Phys. Chem*. **1994**, *98*, 8101.
(16) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem*. **1995**, *99*, 4811.
(17) Yamashita, M.; Kikuma, S.; Yamaoka, Y.; Murakami, H.; Morita, R.; Shigekawa, H. *Appl. Phys. Lett*. **1999**, *75*, 28.
(18) Lissi, E. A.; Abuin, E. B.; Rubio, M. A.; Ceron, A. *Langmuir* **2000**, *16*, 178.
(19) Toshiaki, H. *J. Biol. Chem*. **1999**, *274*, 29 156.
(20) Wong, J. E.; Duchscherer, T. M.; Pietraru, G.; Cramb, D. T. *Langmuir* **1999**, *15*, 6181.
(21) Hutterer, R.; Parusel, A. B. J.; Hof, M. *J. Fluoresc.* **1998**, *8*, 389.
(22) Parasassi, T.; Krasnowska, E. K.; Bagatolli, L.; Gratton, E. *J. Fluoresc*. **1998**, *8*, 365.
(23) Bondar, O. P.; Rowe, E. S. *Biophys*. J. **1999**, *76*, 956.
(24) Moreno, F.; Cortijo, M.; Gonzalez-Jimenz, J. *Photochem. Photobiol.* **1999**, *69*, 8.
(25) Hutterer, R.; Schneider, F. W.; Hermens, W. Th.; Wagenvoord, R.; Hof, M. *Biochim. Biophys. Acta* **1998**, *1414*, 155.
(26) Karukstis, K. K.; Frazier, A. A.; Loftus, C. T.; Tuan, A. S. *J. Phys. Chem. B* **1998**, *102*, 8163.
(27) Hiratsuka, T. *Biochemistry* **1998**, *37*, 7167.
(28) Krasnowska, E. K.; Gratton, E.; Parasassi, T. *Biophys. J*. **1998**, *74*, 1984.
(29) Karukstis, K. K.; Frazier, A. A.; Martula, D. S.; Whiles, J. A. *J. Phys. Chem*. **1996**, *100*, 11 133.
(30) Karukstis, K. K.; Suljak, S. W.; Waller, P. J.; Whiles, J. A.; Thompson, E. H. Z. *J. Phys. Chem*. **1996**, *100*, 11 125.
(31) Sheffield, M. J.; Baker, B. L.; Li, D.; Owen, N. L.; Baker, M. L.; Bell, J. D. *Biochemistry* **1995**, *34*, 7796.
(32) Gvishi, R.; Narang, U.; Bright, F. V.; Prasad, P. N. *Chem. Mater*. **1995**, *7*, 1703.
(33) Nowak, W.; Adamczak, P.; Balter, A.; Sygula, A. *J. Mol. Struct. THEOCHEM* **1986**, *39*, 13.
(34) Ilich, P.; Prendergast, F. G. *J. Phys. Chem*. **1989**, *93*, 4441.
(35) Balter, A.; Nowak, W.; Pawelkiewicz, W.; Kowalczyk, A. *Chem. Phys. Lett*. **1988**, *143*, 565.
(36) Catalan, J.; Perez, P.; Laynez, J.; Blanco, F. G. *J. Fluores*. **1991**, *1*, 215.
(37) Parusel, A. B. J.; Schneider, F. W.; Köhler, G. *J. Mol. Struct. THEOCHEM* **1997**, *398*−*399*, 341.
(38) Parusel, A. B. J.; Nowak, W.; Grimme, S.; Köhler, G. *J. Phys. Chem. A* **1998**, *102*, 7149.
(39) Parusel, A. *J. Chem Soc. Faraday Trans*. **1998**, *94*, 2923.
(40) Lippert, E. *Z. Elektrochem*. **1957**, *61*, 962.
(41) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465.
(42) Mataga, N. *Bull. Chem. Soc. Jpn*. **1963**, *36*, 654.
(43) Rotkiewicz, K.; Grellman, K. H.; Grabowski, Z. R. *Chem. Phys. Lett*. **1973**, *19*, 315.
(44) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim*. **1979**, *3*, 443.
(45) Rettig, W. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 971.
(46) Fessenden, R. W.; Carton, P. M.; Paul, H.; Shimamori, H. *J. Phys. Chem*. **1979**, *83*, 1676.
(47) Fessenden, R. W.; Carton, P. M.; Shimamori, H.; Scaiano, J. C. *J. Phys. Chem*. **1982**, *86*, 3803.
(48) Fessenden, R. W.; Hitachi, A. *J. Phys. Chem*. **1987**, *91*, 3456.
(49) Toublanc, D. B.; Fessenden, R. W.; Hitachi, A. *J. Phys. Chem*. **1989**, *93*, 2893.
(50) For example, see: Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill, New York, 1955; p. 64. Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1952, eq 10.102.
(51) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc*. **1985**, *107*, 3902.
(52) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc*. **1986**, *108*, 8075.
(53) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc*. **1977**, *99*, 4899−4907.
(54) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.
(55) Soujanya, T.; Krishna, T. S. R.; Samanta, A. *J. Photochem. Photobiol. A: Chem.* **1992**, *66*, 185.
(56) Soujanya, T.; Krishna, T. S. R.; Samanta, A. *J. Phys. Chem*. **1992**, *96*, 8544.
(57) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem*. **1996**, *100*, 3507.