Squaraine Chemistry. A Study of the Solute–Solvent Complexation of Squaraine in Solvents by Proton NMR Spectroscopy

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The solute–solvent complexation process of squaraine in organic solvents has been studied by proton NMR spectroscopy using model compound bis(4-(dibutylamino)phenyl)squaraine (1). Two doublets of coupling constant of $\sim$9.5 Hz are observed for the aromatic protons of 1, and the difference in chemical shift ($\delta_\alpha - \delta_\beta$) between them is found to be sensitive to solvent. The solvent effect on $\delta_\alpha - \delta_\beta$ correlates not only with the solvent parameter π^*, but also with the absorption maximum (λ_{max}) and the fluorescence quantum yield (ϕ_f) of 1. Since the general bathochromic effect of π^* on the λ_{max} and the variation of the ϕ_f of 1 in different solvents are shown to be a result of the shift in equilibrium of the solute–solvent complexation process (equilibrium constant for the complex formation increases as π^* increases), the correlation of the NMR spectral data in this work with parallel electronic spectral data implies that the variation of $\delta_\alpha - \delta_\beta$ also originates from the solute–solvent complexation process. Because the ϕ_f of 1 is shown to be dependent on the planarity of the squaraine structure, the correlation between $\delta_\alpha - \delta_\beta$ and the ϕ_f of 1 leads us to propose that there is a conformational change in the squaraine structure associated with the complexation process; e.g., the squaraine structure becomes increasingly nonplanar as the solute–solvent association increases. This model is supported by the specific solvation effects observed in chlorinated and aromatic solvents and by variable-temperature NMR spectral data.

Introduction

Squaraines are 1,3-disubstituted products synthesized from squaric acid and N,N-dialkylanilines.[1,2] They are known to possess interesting semiconductive and photoconductive properties and have been found to be useful for electrophotographic photoreceptor applications,[3] organic solar cells,[4] ablative optical recording,[5] etc. While the technological uses of squaraines are extensive and a large number of squaraines have been synthesized and found to be useful,[6] very little is known about the fundamental properties of squaraines, however. Structural characterization of squaraines

squaric acid

squaraine
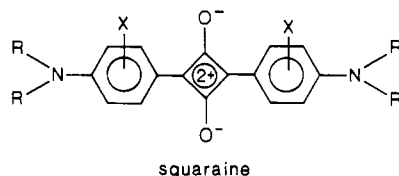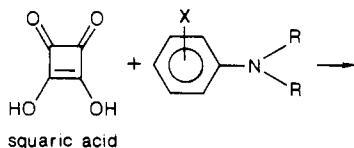
has been limited to elemental analysis, vis absorption and IR spectroscopy. Proton NMR spectroscopy, one of the basic tools for characterization of organic compounds, has only been applied very recently. In 1981, Kazmaier, Burt and Hamer reported[7] the 250-MHz proton NMR spectra of a number of squaraine pigments in chloroform solution. Two sets of aromatic signals, at $\delta \sim 7$ and ~ 8.5 ppm, were observed. From structure–property relationships, these authors assigned the signal at $\delta \sim 8.5$ ppm to the α-protons and the signal at $\delta \sim 7$ ppm to the β-protons.
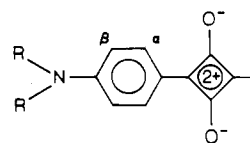
Recently we[8] reported an investigation on the electronic properties of squaraine in solution. In that study, we showed that squaraine exhibits as many as three emission bands in solvents. The composition of the multiple emission bands is sensitive to the solvent, the ambient temperature, and the structural variation of the squaraine chromophore. Through systematic study, the three emission bands are found to be emissions from the excited state of squaraine, the excited state of a solute–solvent complex, and a relaxed twisted excited state of the solute–solvent complex. Structural effect study and preliminary solvent effect study on the fluorescence quantum yield (ϕ_f) of squaraine revealed that the quantum yield of intersystem crossing, $S_1 \rightarrow T_1$, is very very low and that the major radiationless decay processes of these excited states are by rotation of the C–C bond between the central C_4O_2 unit and the phenyl ring. Structural effect study further showed that ϕ_f decreases as the size of the α-substituent increases. Since absorption spectral data suggest that bulky substituents induce nonplanarity between the phenyl ring and the central C_4O_2 unit, the decrease in ϕ_f for α-substituted squaraines indicates that the rate of rotation increases as the twist angle between the central C_4O_2 unit and the phenyl ring increases. Even though the details of the effect of solvent on the multiple emission of squaraines have yet to be totally unravelled, preliminary data in this paper reveal that the ϕ_f value of squaraine is solvent sensitive, implying that there exists a change in the geometry of the squaraine chromophore due to solute–solvent complexation. This observation has prompted us to examine the geometrical changes of squaraine in

(1) For nomenclature, see: West, R. *Oxocarbons*; Academic Press: New York, 1980; Chapter 10.

(2) For reviews on the synthesis of squaraines, see: (a) Schmidt, A. H. *Synthesis* **1980**, 961. (b) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530. (c) Maahs, G.; Hegenberg, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 888.

(3) (a) Law, K. Y. *J. Imaging Sci.* **1987**, *31*, 83. (b) Tam, A. C.; Balanson, R. D. *IBM J. Res. Dev.* **1982**, *26*, 186. (c) Wingard, R. E. *IEEE Industry Appl.* **1982**, 1251. (d) Tam, A. C. *Appl. Phys. Lett.* **1980**, *37*, 978. (e) Melz, R. J.; Champ, R. B.; Chang, L. S.; Chiou, C.; Keller, G. S.; Liclican, L. C.; Neiman, R. B.; Shattuck, M. D.; Weiche, W. J. *Photogr. Sci. Eng.* **1977**, *21*, 73.

(4) (a) Loutfy, R. O.; Hsiao, C. K.; Kazmaier, P. M. *Photogr. Sci. Eng.* **1983**, *27*, 5. (b) Morel, D. L.; Stogryn, E. L.; Ghosh, A. K.; Feng, T.; Purwin, P. E.; Shaw, R. F.; Fishman, C.; Bird, G. R.; Piechowski, A. P. *J. Phys. Chem.* **1984**, *88*, 923. (c) Piechowski, A. P.; Bird, G. R.; Morel, D. L.; Stogryn, E. L. *J. Phys. Chem.* **1984**, *88*, 934. (d) Merritt, V. Y.; Hovel, H. J. *Appl. Phys. Lett.* **1976**, *29*, 414.

(5) (a) Gravesteijn, D. J.; Steenbergen, C.; van der Veen, J. *Proc. SPIE* **1983**, *420*, 327. (b) Jipson, V. P.; Jones, C. R. *J. Vac. Sci. Technol.* **1981**, *18*, 105. (c) Jipson, V. P.; Jones, C. R. *IBM Tech. Discl. Bull.* **1981**, *24*, 298.

(6) Kampfer, H.; Verhille, K. E. U.S. Patent 3,617,270 (1971). Champ, R. B.; Shattuck, M. D. U.S. Patent 3,824,099 (1974). Haley, N. F.; Ott, R. J. U.S. Patent 4,175,956 (1979). Yanus, J. R. U.S. Patent 4,486,520 (1985). Law, K. Y.; Bailey, F. C. U.S. Patent 4,508,803 (1985).

(7) Kazmaier, P. M.; Hamer, G.; Burt, R. A. 11th Northeast Regional Meeting, Rochester, New York, October 18–21, 1981; p 140.

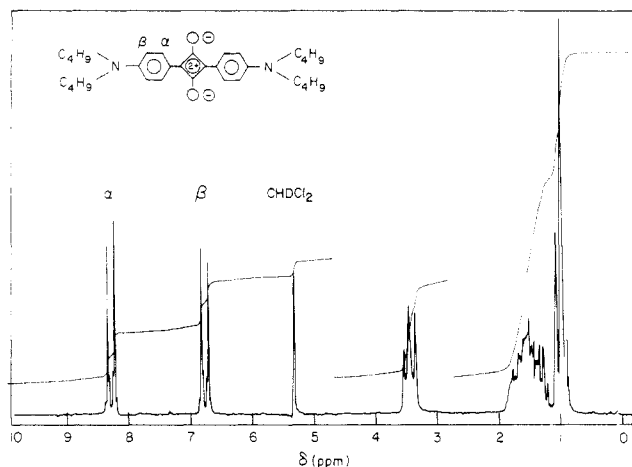(8) Law, K. Y. *J. Phys. Chem.* **1987**, *91*, 5184.

Figure 1. Proton NMR spectrum of **1** in CD_2Cl_2.

different solvents by NMR spectroscopy. Here we report the effect of solvent on the chemical shifts of the α- and the β-proton of bis(4-(dibutylamino)phenyl)squaraine (**1**). Special focus will be placed on the differences in chemical shift between these two protons, $\delta_\alpha - \delta_\beta$, as the recording solvent varies. From results obtained in parallel studies on the effects of solvent and temperature on the absorption and fluorescence emission of **1**, we have been able to correlate $\delta_\alpha - \delta_\beta$ with the solvent parameter π^* and the absorption maximum as well as the fluorescence quantum yield of **1**. These correlations lead us to propose that the variation of $\delta_\alpha - \delta_\beta$ is a conformational effect induced by the solute–solvent complexation. This hypothesis is further supported by the results obtained from the temperature effect and the structural effect studies of the ^1H NMR spectra of squaraines **1–4**.

	X	R
1	H	n-C_4H_9
2	OH	n-C_4H_9
3	CH_3	n-C_4H_9
4	C_2H_5	C_2H_5
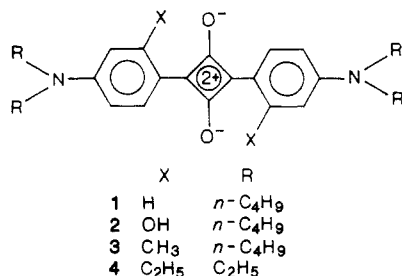
Experimental Section

Materials. Squaraine dyes **1–4** were synthesized from squaric acid and the corresponding N,N-dialkylaniline derivatives. Details on the synthesis have been reported earlier.[9] (p-(N,N-Di-methylamino)benzylidene)malononitrile, **6**, was synthesized and purified as previously described.[10] Deuteriated solvents were the highest isotopic grade from Merck and were used as received.

Technique. Proton NMR spectra were recorded on a Brucker WP-80 spectrometer at 298 K at a squaraine concentration of about 10^{-3}–10^{-4} M.

Results and Discussion

Proton NMR Spectrum of 1. Figure 1 shows the proton NMR spectrum of **1** in CD_2Cl_2. The chemical shifts of the N-butyl protons are at δ 3.46 (N–CH_2), 1.1–1.9 (–CH_2–CH_2–) and 0.98 ppm (–CH_3) and are comparable to those of N,N-dibutylaniline (in CD_2Cl_2) where they are at δ 3.28, 1.15–1.85, and 0.97 ppm, respectively. In the aromatic region, two doublets centered at δ 6.76 and 8.29 ppm with a coupling constant of 9.5 Hz are observed. On the basis of structure–property relationships, we have previously assigned the low-field doublet to the α-protons and the high-field doublet to the β-protons.[9]

Effect of Solvent on the Proton NMR Spectra of 1. The effect of solvent on the proton NMR spectra of **1** was studied. No

(9) Law, K. Y.; Bailey, F. C.; Bluett, L. J. *Can. J. Chem.* **1986**, *64*, 1607.
(10) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2803.

TABLE I: Effect of Solvent on the Chemical Shift of the Aromatic Protons of 1

solvent	π^{*a}	$\delta_\alpha^{\ b}$	$\delta_\beta^{\ b}$	$\delta_\alpha - \delta_\beta$
toluene-d_8	0.535	8.82_8	6.32_3	2.50_5
benzene-d_6	0.588	8.95_4	6.32_3	2.63_1
ether-d_{10}	0.272	8.40_0	6.76_6	1.63_4
1,4-dioxane-d_8	0.553	8.30_8	6.78_8	1.52_0
THF-d_8	0.576	8.32_3	6.83_1	1.49_2
CD_2Cl_2	0.802	8.29_2	6.76_6	1.52_6
$CDCl_3$	0.760	8.36_0	6.70_8	1.65_2
acetone-d_6	0.683	8.27_7	6.92_6	1.35_1
CD_3CN	0.713	8.14_8	6.87_7	1.27_1
DMF-d_7	0.875	8.24_6	7.00_0	1.24_6

$^a \pi^*$ values are taken from ref 11. ^{b} Spectra were recorded at an ambient temperature of 305 ± 2 K.

TABLE II: Effect of Solvent on the Chemical Shift of the Aromatic Protons of Model D–A Compound 6

solvent	π^{*a}	$\delta_\alpha^{\ b}$	$\delta_\beta^{\ b}$	$\delta_\gamma^{\ b}$	$\delta_\alpha - \delta_\beta$
benzene-d_6	0.588	7.41_5	5.95_4	6.68_0	1.46_1
ether-d_{10}	0.272	7.90_5	6.77_2	7.61_8	1.13_3
1,4-dioxane-d_8	0.553	7.83_1	6.76_9	7.67_7	1.06_2
THF-d_8	0.576	7.87_7	6.80_0	7.70_8	1.07_7
CD_2Cl_2	0.802	7.82_8	6.71_4	7.50_8	1.11_4
$CDCl_3$	0.760	7.80_0	6.66_5	7.44_6	1.13_5
acetone-d_6	0.683'	7.92_3	6.86_2	7.83_1	1.06_1
CD_3CN	0.713	7.83_1	6.80_0	7.69_2	1.03_1
DMF-d_7	0.875	~7.95	6.91_3	~8.0	~1.04

$^a \pi^*$ values are taken from ref 11. ^{b} Spectra were recorded at an ambient temperature of 305 ± 2 K, and chemical shift data are reported in ppm from TMS.

specific solvent effect on the chemical shifts of the aliphatic protons of **1** was observed. On the other hand, interesting results are obtained in the aromatic region. Partial proton NMR spectra are presented in Figure 2 and the chemical shift data are tabulated in Table I. Results show that the difference in chemical shift between the α- and the β-proton, $\delta_\alpha - \delta_\beta$, is very sensitive to the recording solvent. Relatively large differences are observed in aromatic solvents (e.g., benzene-d_6 and toluene-d_8); and they appear to decrease as the solvent polarity constant π^{*11} increases. A plot of the $\delta_\alpha - \delta_\beta$ value of **1** as a function of π^* is given in Figure 3.[12] With the exceptions of the data taken in chlorinated and aromatic solvents where specific solvation effects are occurring (see later for discussion), a good linear relationship (cor. 0.95) between $\delta_\alpha - \beta_\beta$ and π^* is obtained.

To establish that the spectral results in Figures 2 and 3 are specific for squaraines, two series of experiments were performed. In the first series, we studied the effect of solvent on the chemical shifts of the aromatic protons of N,N-dibutylaniline. Since no solvent effect on the aromatic protons of N,N-dibutylaniline is evident, our results suggest that the solvent dependence of the $\delta_\alpha - \delta_\beta$ value of **1** is not due to the solvation effect on the N,N-dibutylanilino moiety of **1**.

The ground-state electronic structure of bis(4-(dimethyl-amino)phenyl)squaraine (**5**) has recently been studied by Bigelow and Freund using MNDO and CNDO semiempirical molecular orbital approximations.[13] These authors showed that the electronic distribution in squaraine is highly polarized, with the anilino moiety and the oxygen atom being electron donors (D) and the central C_4O_2 unit an electron acceptor. The ground state of squaraine can thus be considered as an intramolecular D–A–D charge-transfer state. In the second series of experiments, we attempted

(11) π^* values used in this work are taken from: Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.
(12) The effect of solvent on the absorption and the multiple fluorescence emission of **1** have been studied in over 30 organic solvents. Attempts were made to correlate these electronic data with a number of solvent parameters, such as ϵ, Z, E_T, δ, π^*, Py, etc. Good correlations can only be obtained between λ_{max} of **1** and solvent parameter π^*. The exceptions are in alcoholic solvents. π^* is therefore used to correlate the NMR data in this work.
(13) Bigelow, R. W.; Freund, H. J. *Chem. Phys.* **1986**, *107*, 159.
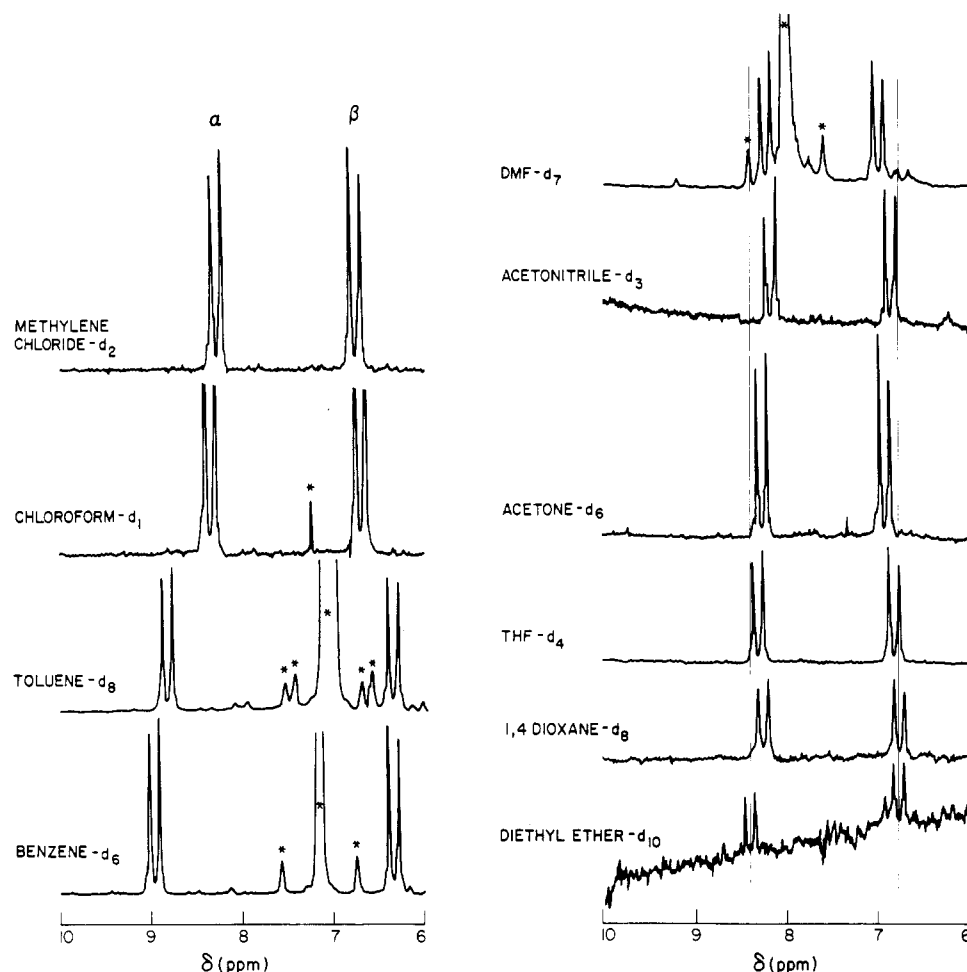
Figure 2. Effect of solvent on the chemical shift of the aromatic protons of **1** (*denotes solvent peaks).

to mimic the effect of solvent polarization on the chemical shifts of the aromatic protons in **1** using model D–A molecule **6**. The proton NMR spectrum of **6** in acetone-d_6 was reported earlier by Safarzadeh-Amiri where he found that δ_α, δ_β, and δ_γ are at 7.923, 6.862, and 7.831 ppm, respectively.[14] In the present work,
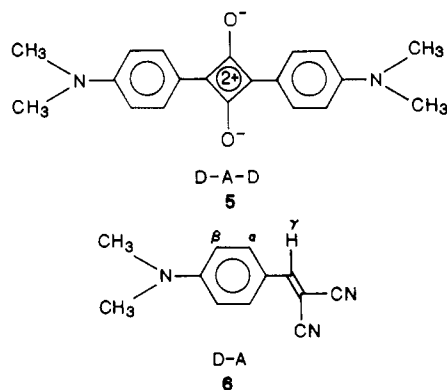
we concentrate on the effect of solvent on the δ_α, δ_β, and δ_γ values. With the exception of the spectral result obtained in benzene-d_6 where the entire spectrum is shifted to higher field due to special solvation effects,[15] our results (Table II) show that δ_γ is quite sensitive to the polarity of the solvent. δ_γ increases from 7.61 ppm in diethyl-d_{10} ether to ~8 ppm in DMF-d_7. This result suggests that solvent molecules do polarize the D–A structure in **6**, which in turn generates the deshielding effect on the γ-proton. On the other hand, solvent polarization of the D–A structure in **6** produces very little changes in the δ_α and the δ_β values which are ~7.9 ± 0.1 ppm and 6.8 ± 0.1 ppm, respectively. The plot of the δ_α –

δ_β of **6** against π^* is included in Figure 2. By comparison of the plots in Figure 2, we conclude that the variation of the δ_α – δ_β value of **1** as solvent changes is specific for squaraine and is not due to any solvent polarization of the D–A–D structure.

In a recent study, we[8] showed that the absorption maximum (λ_{max}) of **1** shifts to longer wavelengths as the polarity of the solvent increases. Plot of λ_{max} of **1** as a function of solvent parameter π^* yields a linear relationship (cor ~0.95) in ~20 non-hydroxylic solvents. The bathochromic shift of λ_{max} is accompanied by a gradual change in the composition of the multiple emission and by a small decrease in the total fluorescence quantum yield (ϕ_f). In conjunction with further electronic spectral data at low temperature and in mixed solvents, we have been able to show that *the solvent-induced bathochromic shift of* **1** *originates from the solute–solvent complex* where the equilibrium constant for the complex formation increases as the π^* value increases. Since results from structural effect study on the ϕ_f of **1** suggest that the major radiationless decay process of the excited state of squaraine is by rotation of the C–C bond between the phenyl ring and the C_4O_2 unit, and that the rate of rotation increases as the twist angle

(14) Safarzadeh-Amiri, A. *Can. J. Chem.* **1984**, *62*, 1895.

(15) The δ_α, δ_β, and δ_γ values of **6** in benzene-d_6 are 7.415, 5.954, and 6.68 respectively. The upfield shift of these protons is attributable to specific solvation of **6** by benzene.[16] The δ_α – δ_β value of **6** in benzene is 1.46 ppm and is ~35% larger than expected. Although an increase in δ_α – δ_β value is also observed for **1** in benzene-d_6, we believe that the increase in δ_α – δ_β value in **6** is generated by an entirely different mechanism. This is because both α- and β-protons of **6** shifts to higher field in benzene-d_6 whereas the α- and the β-proton of **1** shift in different directions in the same solvent. The increase in δ_α – δ_β value in **6** is likely a result of the stronger shielding effect provided by benzene toward the β-proton due to proximity effect, because benzene molecules are known to form complex with N,N-dimethylamino function when the nitrogen atom is partially positive.[17]

(16) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: New York, 1978; p 111.

(17) Hatton, J. V.; Richards, R. E. *Mol. Phys.* **1960**, *3*, 253; **1962**, *5*, 139.

Figure 3. Plots of $\delta_\alpha - \delta_\beta$ as a function of π^* (**1**, ■; **6**, $--\bullet--$).
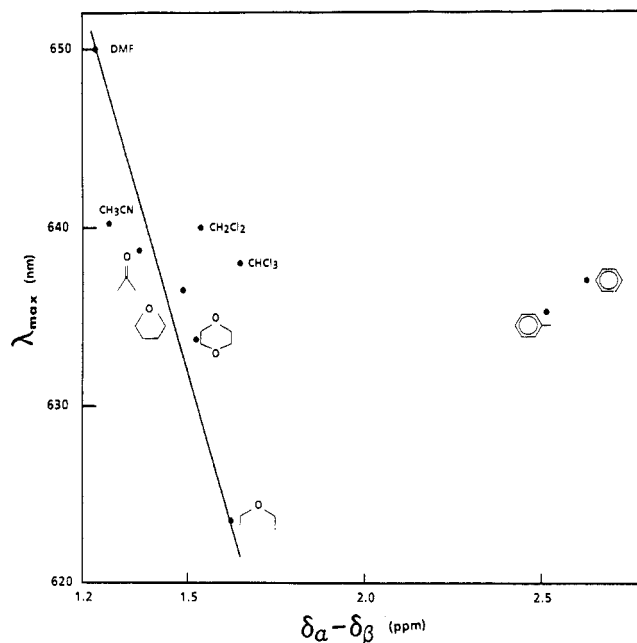
Figure 4. Plot of $\delta_\alpha - \delta_\beta$ of **1** as a function of λ_{max} of **1**.

increases,[8,18] the decrease in ϕ_f suggests that the coplanarity of the D–A–D structure of **1** is distorted during the complex formation and that the twist angle increases as the association between **1** and solvent molecules increases. The general correlation between the electronic spectral data of **1** with π^* prompted us to relate the proton NMR results in this work with our electronic spectral data. For example, λ_{max} of **1** is found to correlate reasonably well with $\delta_\alpha - \delta_\beta$ (Figure 4), except in chlorinated and aromatic solvents where specific solvations are known to occur. Since the bathochromic shift of λ_{max} is shown to originate from the shift of equilibrium for the solute–solvent complex formation, the plot in Figure 4 suggests that the variation of $\delta_\alpha - \delta_\beta$ also originates from the same source.

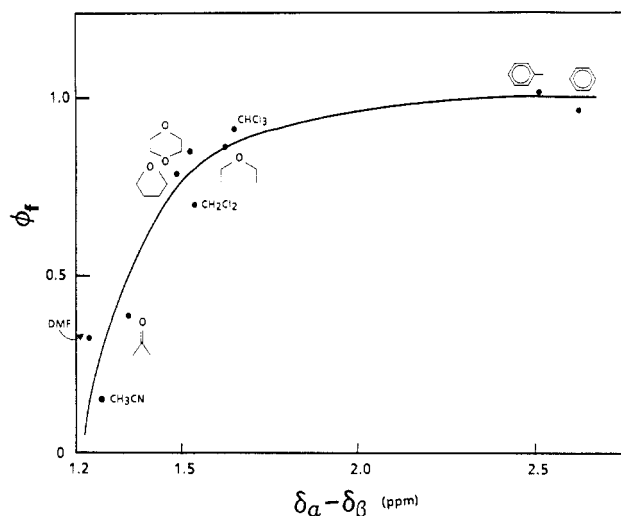(18) Rettig, W.; Gleiter, R. *J. Phys. Chem.* **1985**, *89*, 4676.

Figure 5. Plot of $\delta_\alpha - \delta_\beta$ of **1** as a function of the ϕ_f of **1**.

The plot of the ϕ_f of **1** as a function of $\delta_\alpha - \delta_\beta$ is shown in Figure 5. ϕ_f increases as $\delta_\alpha - \delta_\beta$ increases and levels off when $\delta_\alpha - \delta_\beta \geq 2$ ppm. The ability of the $\delta_\alpha - \delta_\beta$ value to correlate with ϕ_f (which is dependent of the coplanarity of the D–A–D structure of squaraine) not only supports our previous conclusion that the radiationless decay of the excited state of squaraine (by C–C bond rotation) is controlled by the ground-state conformation of squaraine[8] but also suggest that $\delta_\alpha - \delta_\beta$ probes any conformational changes of the D–A–D structure induced by the ground-state complexation. Complexation processes between solvent molecules and compounds having intramolecular charge-transfer states are known. For example, Wang[19] observed very similar solute–solvent complexation in the ground state as well as the excited state in his study of the photophysics of polarized enones. Wang[20] recently also reported a study of the exciplex formation between p-(dimethylamino)benzonitrile (DMABN) and alkylamines where a steric effect on the exciplex formation was observed. The steric effect reported in Wang's paper is actually very similar to the "squaraine–alcohol" solute–solvent complexes observed in our work.[21] In a similar context, Varma and co-workers[22,23] reported extensive evidence for the exciplex formation between DMABN and polar molecules. In one of their papers, Visser and Varma[22] actually demonstrated the formation of a 1:1 exciplex between DMABN and an alkanonitrile in cyclohexane using a mixed solvent experiment analogous to our work. The dipole moment of the excited state of DMABN is $\sim$14 D.[24] Assuming that the polarized charges in the excited state are localized in the dimethylamino group and the cyano group, each of these groups will bear $\sim$0.42e of opposite charges. The formation of an exciplex is presumably due to interactions between these polarized charges and dipoles of solvent molecules. According to MNDO calculations, the charges at the oxygen atom, the C_4O_2 unit, and the nitrogen atom are $\sim$0.35e, +0.37e, and −0.4e. Thus, interactions between the polarized charges in squaraine with dipoles of solvent molecules in the ground are really not irrational. Since previous structural effect study showed that the solute–solvent complexation process is only sensitive to steric factors around the α-position, the site of complexation for **1** would be in the central C_4O_2 unit. As the solvent molecule approaches to the C_4O_2 unit, the aniline

(19) Wang, Y. *J. Phys. Chem.* **1985**, *89*, 3799.

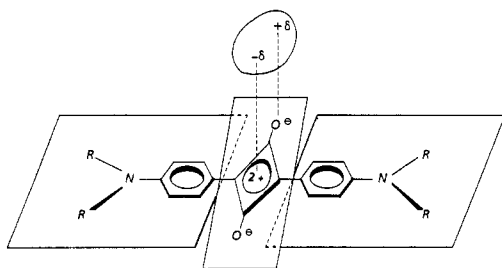(20) Wang, Y. *Chem. Phys. Lett.* **1985**, *116*, 286.

(21) Law, K. Y. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, **1987**; Chapter 13.

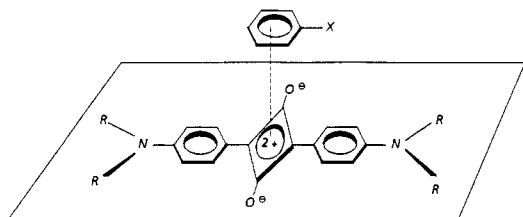(22) Visser, R. J.; Varma, C. A. G. O *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 453.

(23) (a) Visser, R. J.; Weisenborn, P. C. M.; Varma, C. A. G. O *Chem. Phys. Lett.* **1985**, *113*, 330. (b) Visser, R. J.; Varma, C. A. G. O.; Konijnenberg, J.; Weisenborn, P. C. M. *J. Mol. Struct.* **1984**, *114*, 105. (c) Visser, R. J.; Varma, C. A. G. O.; Konijnenberg, J. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 347.

(24) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczwk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

SCHEME I

SCHEME II

SCHEME III

SCHEME IV

TABLE III: Effect of Temperature on the Chemical Shift of the Aromatic Proton of 1

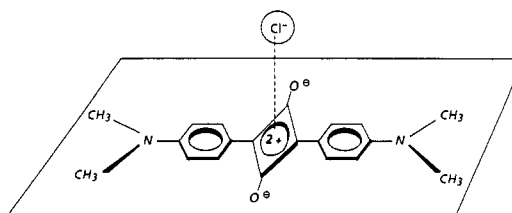| solvent	temp, K	$\delta_\alpha{}^a$	$\delta_\beta{}^a$	$\delta_\alpha - \delta_\beta$
THF-d_8	303	8.32_3	6.83_1	1.49_2
	263	8.28_6	6.86_1	1.42_5
	222	8.28_0	6.91_4	1.36_6
	203	8.26_1	6.93_8	1.32_3
	193	8.25_5	6.96_9	1.28_6
	183	8.25_5	6.98_2	1.27_3
toluene-d_8	333	8.84_7	6.41_9	2.42_8
	307	8.88_8	6.32_3	2.56_5
	283	8.90_7	6.31_2	2.59_5
	273	8.91_0	6.31_0	2.60_0
	263	8.93_7	6.30_4	2.63_3
	253	8.97_0	6.28_2	2.68_8

^{a} In ppm from TMS.

moiety will be twisted from planarity due to steric repulsion. A schematic illustration of the interactions between the dipole of a solvent molecule and squaraine is depicted in Scheme I.

Specific Solvation Effects. Aromatic Solvents. The proposed conformational effect on the $\delta_\alpha - \delta_\beta$ value also gains supports from the specific solvation effect observed. For instance, the $\delta_\alpha - \delta_\beta$ values of **1** in benzene-d_6 and toluene-d_8 are 2.34 and 2.20 ppm, respectively, and are $\sim$50% larger than that in diethyl-d_{10} ether (1.63 ppm), the weakest complexing solvent for **1**.[25] Fluorescence spectral results show that there exists a rapid equilibrium between **1** and solute–solvent complexes in benzene and in toluene,[26] and that the ϕ_f values of **1** are 0.96 and 1.0, respectively. Since rotation of the C–C bond between the phenyl ring and the four-membered ring of squaraine is shown to be the major radiationless decay process, the unity ϕ_f values suggest that the D–A–D structure in **1** is rigidized in the solute–solvent complex in these two solvents. This leads us to propose that the complexation sites of the solute–solvent complexes in aromatic solvents are the four-membered ring of squaraine and the π-orbital of the aromatic solvent molecules (Scheme II). Because aromatic molecules are planar, any rocking or wiggling motions around the C–C bond would be slowed down significantly. The high ϕ_f values in these solvents are therefore a result of the decrease in rate of C–C rotation due to the rigidized structure in the complex. The large $\delta_\alpha - \delta_\beta$ values in benzene-d_6 and toluene-d_8 as compared to diethyl ether are thus attributable to the "perfect planar" geometry adopted in the solute–solvent complex. Our results also suggest that the slightly lower $\delta_\alpha - \delta_\beta$ value in diethyl ether is probably a result of the wiggling motion of the phenyl ring around the C–C bond. Although the time-average geometry of **1** is planar, the protons in ether are actually experiencing an environment equivalent to a small distortion due to the wiggling motion. The ϕ_f of **1** in diethyl ether is 0.85 and is lower than those in benzene or toluene. The slightly lower ϕ_f value in diethyl ether is thus consistent with the wiggling motion proposed above.
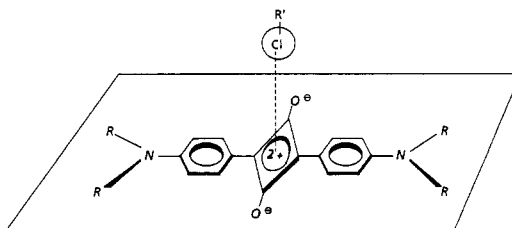
Chlorinated Solvents. The $\delta_\alpha - \delta_\beta$ values of **1** in CH_2Cl_2 and $CHCl_3$ are 1.553 and 1.65 ppm, respectively, and are 10–20% larger than expectation (see Figure 3). Since electronic spectral results show that **1** primarily exists as solute–solvent complexes in CH_2Cl_2 and $CHCl_3$,[8] the large $\delta_\alpha - \delta_\beta$ values suggest that the perturbation on the planarity is relatively small when the solute–solvent complex is formed in these two solvents.

In our earlier study on the mass spectrometric behavior of squaraines,[9] we studied the chemical ionization mass spectrum

of bis(4-(dimethylamino)phenyl)squaraine (**5**) using CH_2Cl_2 as ionization gas. In the negative mass spectrum, ion peaks at m/z 355 and 675, which can be assigned to the complexes between the monomer and the dimer of **5** with Cl^-, respectively, were observed. Since complexation does not occur with any other fragments, the binding of the chloride ion to the monomer or the dimer of **5** appears to be specific, probably through the four-membered ring of squaraine (Scheme III). On the basis of this observation, we propose the complexes between **1** and CH_2Cl_2 or $CHCl_3$ also through the chlorine atom (Scheme IV). Due to the complexing geometry, the distortion of the planarity of **1** upon complexation is greatly reduced. Consequently, anomalously large $\delta_\alpha - \delta_\beta$ and high ϕ_f values are obtained.

Effect of Temperature. As noted earlier, ϕ_f of **1** is twist angle dependent. Since the variation of $\delta_\alpha - \delta_\beta$ is shown to be a result of the shift in equilibrium for the formation of the solute–solvent complex, the correlation in Figure 5 indicates that as the association of the solute–solvent increases, a greater nonplanarity and consequently a smaller $\delta_\alpha - \delta_\beta$ value will result. From results obtained from previous study, we know that the association between the solute and the solvent can also be enhanced by lowering the ambient temperature. If the model on the origin of the variation of the $\delta_\alpha - \delta_\beta$ value is correct, a decrease in $\delta_\alpha - \delta_\beta$ is anticipated. Using **1** in THF-d_8 as a model, the effect of temperature on the $\delta_\alpha - \delta_\beta$ value was studied. Results are summarized in Table III and show that $\delta_\alpha - \delta_\beta$ decreases steadily as the recording temperature is lowered. The decrease of $\delta_\alpha - \delta_\beta$ confirms that the variation of $\delta_\alpha - \delta_\beta$ reflects conformational changes of the squaraine structure induced by solute–solvent complexation.

On the other hand, complexation of **1** with aromatic solvents rigidizes the D–A–D squaraine structure, resulting in large $\delta_\alpha - \delta_\beta$ and high ϕ_f values. If the above interpretation were correct, stabilization of the solute–solvent complex between **1** and aromatic solvent by lowering the temperature should further rigidize the squaraine structures and consequently increase the $\delta_\alpha - \delta_\beta$ value.

(25) Fluorescence emission spectrum of **1** in ether shows that **1** primarily exists as noncomplexing species in ether.[8]

(26) The excitation spectra of **1** in benzene and in toluene are independent of the monitoring emission wavelengths, indicating that the solute–solvent complexation process is in very rapid equilibrium, probably on a subnanosecond time scale.
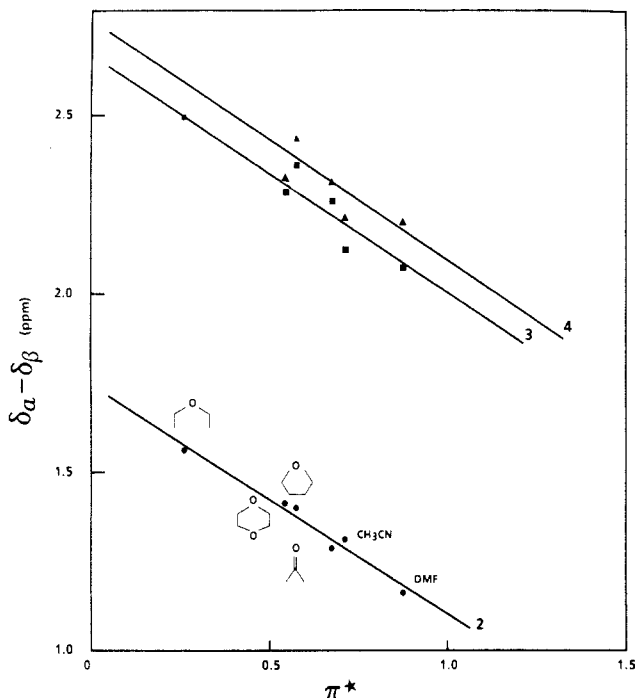
Figure 6. Plots of $\delta_\alpha - \delta_\beta$ values of **2**, **3**, and **4** as a function of π^*.

The variable-temperature proton NMR spectra data of **1** in toluene-d_8 are also given in Table III. Results show that $\delta_\alpha - \delta_\beta$ in toluene-d_8 increases as the ambient temperature decreases. *The direction of increasing the $\delta_\alpha - \delta_\beta$ value is opposite to that seen in THF-d_8.* This result not only reaffirms our previous conclusion about the special rigidization effect experienced by the squaraine structure upon complexation with aromatic solvent molecules, but also reaffirms the correctness of using $\delta_\alpha - \delta_\beta$ as a measure of the planarity of the squaraine structure in solution.

Structural Effect Study. Among squaraines **1–4**, **2** is expected to be the most planar and rigid molecule because of the intra-molecular H bonding between the OH group in the phenyl ring and the C–O group in the four-membered ring. On the other hand, the coplanarity of **3** and **4** should be distorted due to the steric repulsion between the alkyl and the C–O groups. The nonplanarity of **3** and **4** is confirmed by absorption spectral data where significant decreases in absorption coefficients are observed.[8] Because of this structural variation, the solvent-induced chemical shift changes of the aromatic protons of **2–4** are expected to give further insight regarding the use of $\delta_\alpha - \delta_\beta$ as a measure for any conformational changes in squaraines.

Plots of $\delta_\alpha - \delta_\beta$[27] as a function of solvent parameter π^* for **2**, **3** and **4** are given in Figure 6. Good linear relationships are obtained for all compounds studied. Data from aromatic and chlorinated solvents, which are known to give specific solvation effects, are deleted for clarity. It is worth noting that the $\delta_\alpha - \delta_\beta$ values of **3** and **4** are in the range of $\sim$2–2.4 ppm and are much larger than those of **1** and **2** ($\sim$1.2–1.6 ppm). The large $\delta_\alpha - \delta_\beta$ value is believed to be an electronic effect induced by the α-substituents in **3** and **4** because very similar downfield shifts had

(27) There are two β-protons in **2–4**. $\delta_\alpha - \delta_\beta$ denotes to the chemical shift difference of the adjacent α- and β-proton, where the latter proton is usually identifiable by the characteristic coupling constant (9–10 Hz).

TABLE IV: Effects of Solvent and Structural Changes on the $\delta_\alpha - \delta_\beta$ Values

$\delta_\alpha - \delta_\beta$, ppm	1	2	3	4
in benzene-d_6				
obsd	2.63$_1$	2.33$_8$	3.50$_5$	3.68$_6$
calcd^a	1.43$_4$	1.37$_2$	2.28$_2$	2.38$_0$
Δ	1.19$_7$	0.96$_6$	1.22$_3$	1.30$_6$
in toluene-d_8				
obsd	2.50$_5$	2.20$_3$	3.35$_7$	
calcd^a	1.47$_1$	1.40$_6$	2.31$_9$	
Δ	1.03$_4$	0.79$_7$	1.03$_8$	

^{a}Obtained by extrapolation from the π^* values of benzene and toluene in Figures 3 and 6.

also been observed in other α-substituted squaraines.[9] The surprising result in Figure 6 is that, despite the structural variation, the slopes of all the plots are very similar. This probably indicates that the magnitude of the conformational change induced by solute–solvent interactions among **1–4** is very similar. The most useful information obtained in the structural effect study comes from the spectral data in benzene-d_6 and toluene-d_8. As noted earlier, the larger $\delta_\alpha - \delta_\beta$ values obtained in these solvents are due to the rigidization effect provided by solvent molecules in the solute–solvent complex. Assuming that there exists hypothetic solvents with π^* values identical with those of benzene and toluene, except that the specific solvation effects are absent, one can calculate the $\delta_\alpha - \delta_\beta$ values of **1–4** in these hypothetic solvents from the plots in Figures 3 and 6. The differences between the calculated values and the observed values, Δ, will thus be a measure of the rigidization effect imposed on the squaraine in question by benzene or toluene solvent molecules; the larger the nonplanarity induced by the complexation process, the larger the Δ value is expected. These Δ values are summarized in Table IV. The smallest differences are observed in **2**, and this is consistent with the H-bonding effect. From the Δ values, the direction of increasing nonplanarity is **2** $\to$ **1** $\to$ **3** $\to$ **4**. These results are in agreement with our electronic spectral data where we observed significant decreases in absorption coefficient and ϕ_f for **3** and **4** due to the nonplanarity. These results also provide further support that $\delta_\alpha - \delta_\beta$ is a valid measure of the planarity of the D–A–D structure of squaraine in solution.

Concluding Remarks

This work reports the effect of solvent on the chemical shift of the α- and the β-proton of squaraine **1**. The difference in chemical shift between these protons, $\delta_\alpha - \delta_\beta$, are found to correlate with solvent parameter π^* and λ_{max} of **1**, as well as the composition variation in the multiple emission and the fluorescence quantum yield of **1**. From these correlations, we are able to show that the variation of $\delta_\alpha - \delta_\beta$ in solvents originates from solute–solvent complexation and the coplanarity of the D–A–D structure of squaraine becomes increasingly distorted as the solute–solvent association increases. This model is supported by the specific solvation effects observed in aromatic and chlorinated solvents, the results obtained in variable-temperature experiments, and structural effect studies.

Registry No. **1**, 121289-35-8; **2**, 121289-36-9; **3**, 121314-06-5; **4**, 121289-37-0; **6**, 2826-28-0.