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Solvent Effects on the UV−Vis Absorption Properties and Tautomerism of N-Confused Tetraphenylporphyrin

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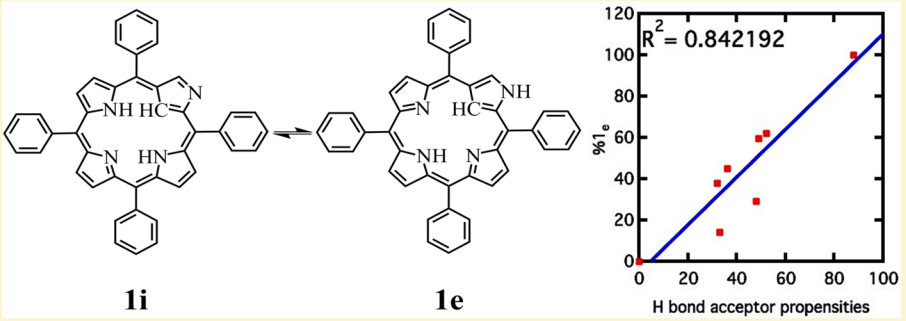

ABSTRACT: The two tautomeric forms of N-confused tetraphenylporphyrin (NCTPP) show distinctly different absorption spectra. The existence of each tautomer in solution has been shown to be strongly solvent-dependent. In the present work, we have studied the tautomerization using absorption spectroscopy in 15 different solvents. While changes in the two tautomers are not large in the Soret band region, the distinct spectral changes between the two tautomers in the Q-band region provide a convenient way to measure the concentration of each tautomer. The resulting data shows a strong correlation between the tautomer and the H-bond accepting ability of the solvent. The anomaly in this data is for the alcoholic solvents ethanol and methanol, for which we observe evidence for H-bonding, presumably between the exterior N2 nitrogen of the NCTPP and the O−H proton of the solvent.

INTRODUCTION

Photosynthesis is initiated by the absorption of light by the bacteriochlorophylls present in the light harvesting (LH) complexes of green plants and purple photosynthetic bacteria. The resulting excitation energy is subsequently transferred to the photosynthetic reaction center (RC), resulting in charge separation across the photosynthetic membrane that is localized between the cytoplasmic and periplasmic membranes.[1] The antenna complex[2] in purple photosynthetic bacteria consists of two types of LH complexes, LH1 and LH2, that surround the RC and together form the so-called photosynthetic unit (PSU).[3,4] The major light-absorbing species in all of these assemblies is bacteriochlorophyll *a* (Bchl *a*) and its derivatives. The near-unity conversion of solar energy into chemical potential in the LHCs and RC has inspired significant research toward the design and study of molecular systems that effectively mimic the energy- and electron-transfer processes in photosynthesis, with the ultimate goal of efficiently converting solar energy into electricity.

A detailed understanding of the photophysical properties of bacteriochlorophylls and more generally the parent porphyrins has been important for elucidating mechanisms such as energy and electron transfer in biological complexes, as well as artificial photosynthetic analogues, molecular electronics, and photonic devices.[5,6] Porphyrins contain an 18-electron aromatic ring with four nitrogen atoms in the core of the macrocycle. This conjugated π-system is the electronic "heart" of the macrocycle and is responsible for the intensity, color, and optical properties of porphyrins. Changes to the tetrapyrrolic macrocycle upon reduction of the pyrrole rings,[7,8] fusing different rings across the pyrrole rings of the macrocycle,[9−11] or exchanging, adding, or removing atoms or molecular groups in the macrocycle,[12−16] often result in substantial changes in the photophysical properties. The photophysical properties of free base tetraphenylporphyrin (**H_2TPP**, Scheme 1) are well understood, and the molecule, as a result, is often used as standard to study the photophysical properties of other porphyrins. The absorption spectra of free base tetraarylporphyrins typically show four relatively weak bands in the 480−800 nm region that are collectively called the Q-bands, and correspond to the forbidden $S_0 \rightarrow S_1$ transition. A more intense band is observed at higher energy (390−450 nm) that results from the strongly allowed $S_0 \rightarrow S_2$ transition (the B-band or Soret band).

N-Confused tetraphenylporphyrins **1e** and **1i** (Scheme 1) are isomers of tetraphenylporphyrin that have one pyrrolic nitrogen exchanged with one of the pyrrolic β-carbons so that one nitrogen faces outside the macrocycle.[17,18] Three possible

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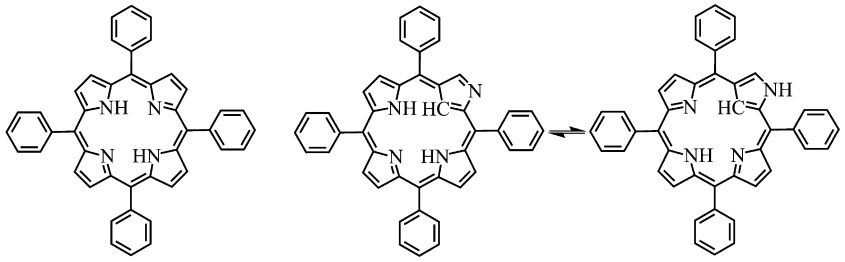
Scheme 1



H_2TPP 1i 1e

tautomers of NCTPP have been postulated to coexist in equilibrium,[19] although only two of the tautomers have been observed experimentally.[17,18,20] The most stable tautomeric form (**1i**) has three hydrogens inside the macrocycle, with the outer nitrogen unprotonated, while the second tautomer (**1e**) has two hydrogens inside the ring and one on the external nitrogen.

We have previously investigated the photophysical properties of unsubstituted and substituted NCTPPs **1i** and **1e** in solution using a combination of computations,[21] steady-state fluorescence, time-resolved fluorescence, and ultrafast absorption spectroscopies.[22,23] These properties are of great interest because of the potential for incorporation of NCTPPs into applications for which porphyrins are normally considered. The absorption spectra of the tautomers are quite different from one another. Tautomer **1i** (in CH_2Cl_2) exhibits a Soret band at 437 nm and has a Q-band structure similar to that observed for free-base tetraphenylchlorin (H_2TPC),[7] with a maximum Q-band absorption at 724 nm. Tautomer **1e** (in DMAc), on the other hand, has a Soret band absorption at 442 nm and Q-band profile which gains in intensity with increasing wavelength to a maximum at 699 nm.

Furuta[20] and Latos-Grazynski[17] presented the first direct evidence for the tautomerization of **1i** and **1e**, and Furuta suggested the equilibrium was possibly dependent on solvent polarity.[20] Absorption experiments showed a dramatic change in both the color and the spectra of solutions of NCTPP in CH_2Cl_2 (red) and DMF (green). Using ^1H NMR and X-ray diffraction analysis, Furuta and co-workers determined that the tautomeric form **1e** predominates in DMF, while **1i** is observed in CH_2Cl_2.[20] Furuta also observed the presence of both tautomers in pyridine, resulting in a proposed mechanism for the transition from **1i** to **1e** wherein the confused pyrrole ring buckles toward the opposing core nitrogen, leading to proton exchange and subsequent tautomerization.[20,24,25]

A variety of subsequent experiments support the solvent dependent tautomerization, and several groups have used this information to study the various properties of **1e** vs **1i**, as well as the tautomeric forms of other NCTPP derivatives.[22,23,26−28] Recently, the construction of self-assembled supramolecular systems was investigated as a function of NCTPP tautomer, and a proposed mechanism of tautomeric structures in a combination of four protic and aprotic solvents using SEM and AFM analysis was described.[29] Computational work by Marchand and Jacquemin,[30] and separately by us,[21,31] using the polarization continuum model in Gaussian09 and density functional theory (DFT), confirmed energetic differences as a function of solvent polarity, but also showed a switch in tautomer preference did not occur under these conditions. We previously examined the solvent dependent nature of the tautomerization by UV−vis spectroscopy, confirming Furuta's observations that both NCTPP tautomers can exist simultaneously in certain solvents, presumably in equilibrium with one another.[32] In the present work, we extend this original analysis and present a more detailed photophysical investigation of the **1i**/**1e** tautomerism using a wide range of solvents in order to correlate the dependence of the NCP tautomerism with one or more of the following solvent properties: polarity/dipolarity, H-bond donor propensity, H-bond acceptor propensity, dipole moment, and dielectric constant.[33,34]

RESULTS AND DISCUSSION

Gu et al.[34] have previously applied a mathematical model to scale the parameters for solvent polarity/dipolarity (π), the H-bond donor ($\Sigma\alpha$), and the H-bond acceptor ($\Sigma\beta$) properties to a common scale of zero to one. These values are shown in Table 1, together with the literature values for dipole moment and dielectric constant for each solvent.[34] Because previous descriptions of this tautomerism have invoked solvent polarity as the main factor governing the direction of the equilibrium, we have organized this table so the other parameters are tabulated relative to the solvent polarity function, π.

Table 1. Solvent Parameters for the Solvents Used To Study the NCTPP Tautomerism[33,34]

solvent	π^a	$\Sigma\alpha^b$	$\Sigma\beta^c$	dipole moment (D)	dielectric constant
DMSO	1.00	0.00	0.88	3.96	46.83
Benzonitrile	0.90	0.00	0.33	4.18	25.59
DMAc	0.88	0.00	0.78	3.70	37.78
Pyridine	0.87	0.00	0.52	2.22	12.98
Dichloromethane	0.82	0.10	0.05	1.60	8.93
Dichloroethane	0.81	0.10	0.11	1.80	10.13
Acetonitrile	0.75	0.07	0.32	3.92	35.69
Acetone	0.71	0.04	0.49	2.88	20.49
Butyronitrile	0.71	0.00	0.36	4.07	24.29
Methanol	0.60	0.43	0.47	1.70	32.61
Chloroform	0.58	0.15	0.02	1.04	4.71
THF	0.58	0.00	0.48	1.75	7.43
Ethanol	0.54	0.37	0.48	1.69	24.85
Toluene	0.54	0.00	0.14	0.38	2.37
Cyclohexane	0.00	0.00	0.00	0.00	2.02

[a]The solute dipolarity−polarizability term reported by Abraham represents the dipole−dipole or dipole-induced−dipole plus some polarizability interaction in the solute-condensed phase interaction.[33] [b]Hydrogen bond donor propensities of the solvent. [c]Hydrogen bond acceptor propensities of the solvent.

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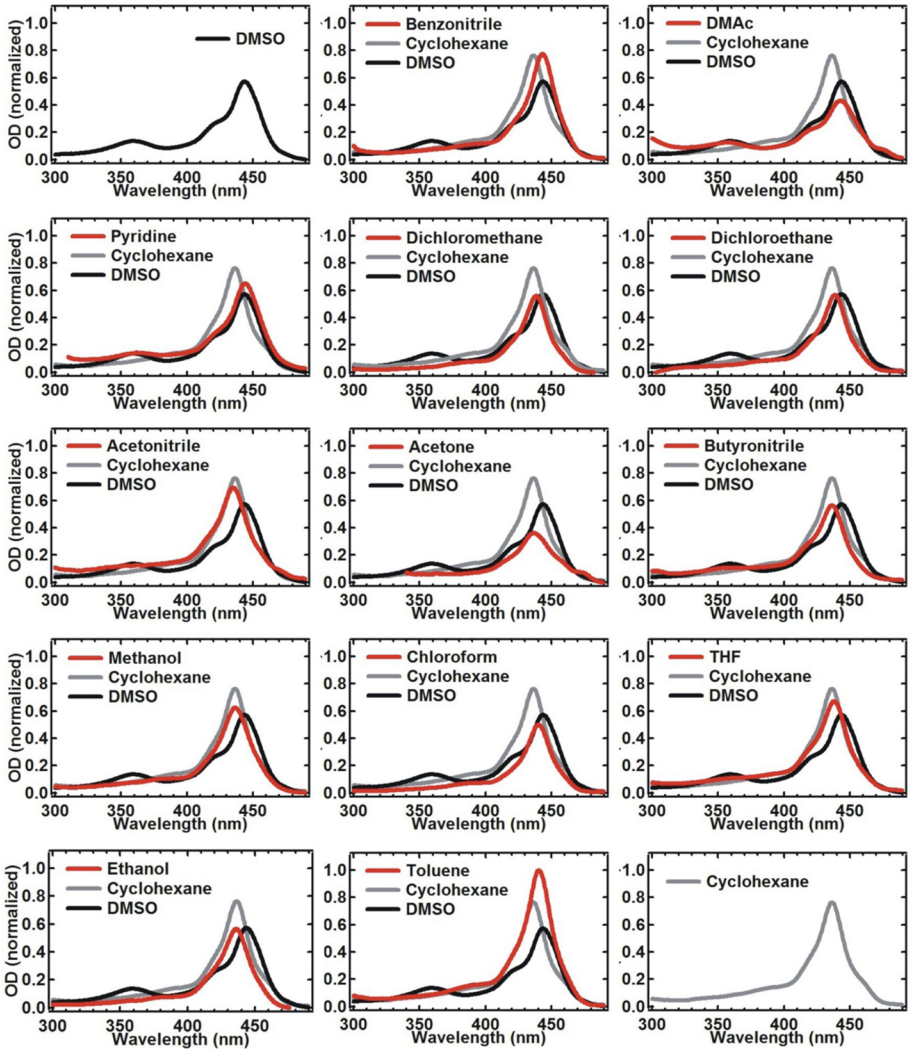

Figure 1. Steady-state absorption spectra of NCTPP tautomers **1i** and **1e** in the 300−500 nm range in a series of solvents. The spectra of NCTPP in DMSO (black) and in cyclohexane (gray) are shown together with the spectrum in the solvent (red) under investigation.

Dimethyl sulfoxide (DMSO) and cyclohexane represent the two extremes in terms of polarity, hydrogen bond acceptor value, and dielectric constant. DMSO has the highest polarity ($\pi \sim 1.00$), the highest hydrogen bond acceptor value ($\Sigma\beta \sim 0.88$), and the greatest dielectric constant (46.83) of the solvents examined in this work, while cyclohexane has the lowest polarity (0.00), hydrogen bond acceptor value (0.00), and dielectric constant (2.02). To compare the tautomerism of **1i**/**1e** in each solvent used, it was assumed that the steady-state absorption spectrum in DMSO corresponded to 100% of tautomer **1e**, while the spectrum in cyclohexane corresponded to 100% of tautomer **1i**. The other solvents in Table 1 represent a range intermediate between these two extremes, allowing the analysis of several criteria that might inform what solvent-related factor(s) specifically influence the interconversion between the two tautomers. The steady-state absorption spectra of NCTPP in each of the solvents used, compared to the spectra of DMSO and cyclohexane, are shown in Figure 1 (Soret or B-band) and Figure 2 (the significantly more diagnostic Q-band region), while the absorption data from these experiments in both the 300−500 nm (B-band) and 500−850 nm (Q-band) ranges are listed in Tables 2 and 3, respectively. The log of the apparent extinction coefficients (log ε) for each wavelength, which correspond to either one tautomer or a contribution from both tautomers absorbing at that wavelength, are also shown in Tables 2 and 3.

The B-band region (300−500 nm) in DMSO displays a maximum absorption wavelength (λ_{max}) at 444 nm (log ε = 5.20), while in cyclohexane a value of 436 nm (log ε = 5.32) is observed. In general, the maximum absorption wavelengths in this region for solvents with very high polarities (>0.80) and high hydrogen bond acceptor values (>0.50) were observed in the range of 442−444 nm (DMSO, benzonitrile, DMAc, and pyridine). In solvents such as dichloromethane (CH_2Cl_2) and dichloroethane ($EtCl_2$) that have high polarity constants (0.80) but low H-bond acceptor values (<0.11), λ_{max} was blue-shifted to 437 and 439 nm, respectively. In acetonitrile, acetone, and butyronitrile, which have high polarity constants (0.71−0.75) and medium of H-bond acceptor values (0.20−0.49), the NCTPP B-band absorption wavelength was very similar to that observed in cyclohexane. In toluene and chloroform, which have low polarities (0.54 and 0.58) and low H-bond acidities (0.00 and 0.15), absorption maxima at wavelengths in between DMSO and cyclohexane were observed.

Methanol and ethanol differ from the previously mentioned solvents because they are the only solvents examined that have

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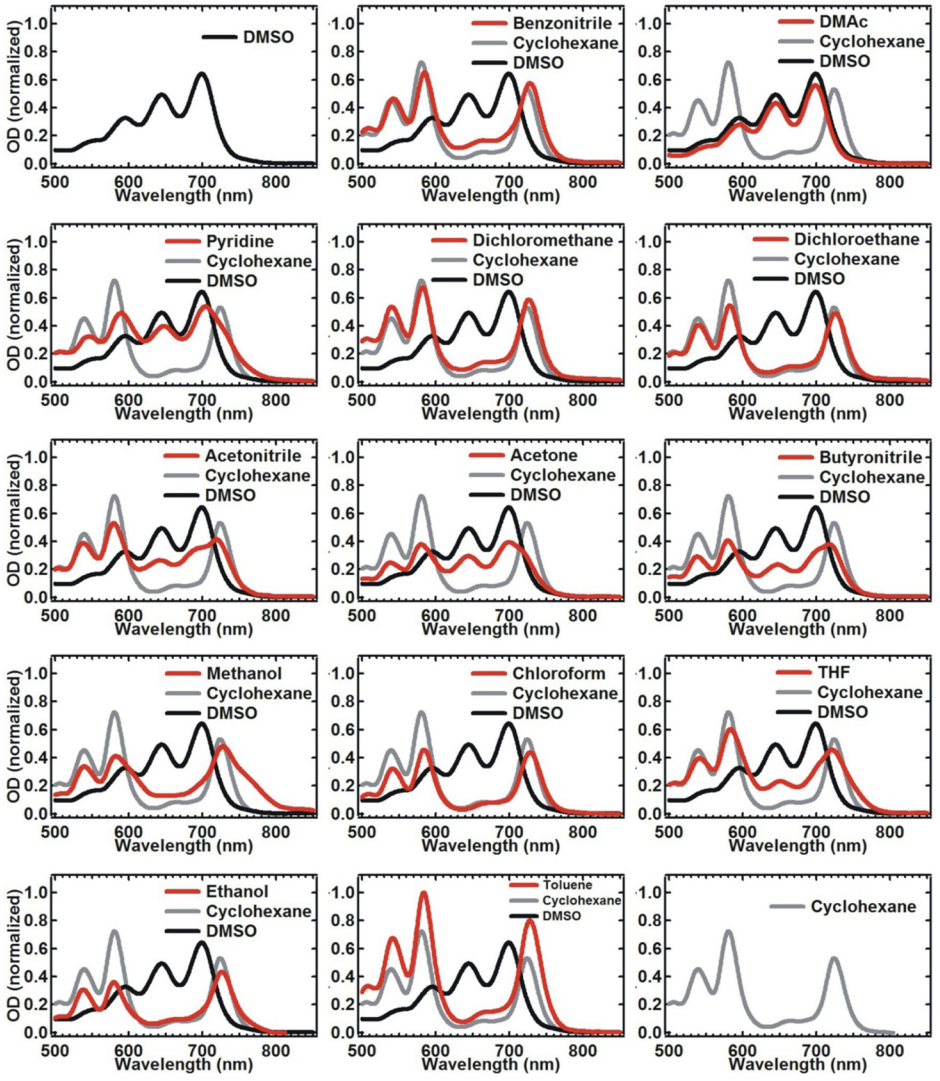

Figure 2. Steady-state absorption spectra of NCTPP tautomers **1i** and **1e** in the 500−850 nm range in a series of solvents. The spectra of NCTPP in DMSO (black) and in cyclohexane (gray) are shown together with the spectrum in the solvent (red) under investigation.

Table 2. Steady-State Absorption Data for NCTPP in the 300−500 nm Range in a Series of Solvents

	Absorption/nm (log ε)			
solvent	N-band	shoulder[a]	B-band	shoulder[b]
DMSO	359 (4.58)	425 (4.89)	444 (5.20)	-
Benzonitrile	393 (4.51)	427 (5.00)	443 (5.33)	-
DMAc	357 (4.54)	423 (4.81)	442 (5.08)	476 (4.31)
Pyridine	362 (4.60)	426 (4.96)	444 (5.26)	-
Dichloromethane	393 (4.36)	422 (4.86)	438 (5.21)	-
Dichloroethane	383 (4.37)	424 (4.90)	439 (5.20)	-
Acetronitrile	359 (4.52)	-	435 (5.28)	469 (4.45)
Acetone	363 (4.23)	-	437 (5.01)	471 (4.27)
Butyronitrile	360 (4.46)	421 (4.93)	436 (5.19)	-
Methanol	388 (4.46)	416 (4.86)	437 (5.24)	-
Chloroform	393 (4.30)	-	440 (5.14)	-
THF	363 (4.48)	423 (5.02)	438 (5.27)	-
Ethanol	383 (4.33)	419 (4.86)	436 (5.20)	-
Toluene	390 (4.64)	-	441 (5.44)	-
Cyclohexane	393 (4.60)	423 (5.06)	436 (5.32)	-

[a]The shoulder to the blue of the B-band. [b]The shoulder to the red of the B-band.

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Table 3. Steady-State Absorption Data in the Range of 500−850 nm of NCTPP in a Series of Solvents

solvent	Q-Bands Absorption/nm (log ε)					
DMSO	-	556 (3.55)	596 (3.86)	645 (4.04)	699 (4.16)	-
Benzonitrile	509 (3.75)	543 (4.02)	585 (4.16)	665 (3.58)	-	728 (4.11)
DMAc	-	550 (3.30)	595 (3.79)	644 (3.98)	699 (4.09)	-
Pyridine	509 (3.66)	546 (3.82)	591 (4.04)	648 (3.94)	704 (4.08)	~ 720
Dichloromethane	507 (3.80)	540 (4.05)	580 (4.15)	672 (3.46)	-	726 (4.09)
Dichloroethane	508 (3.71)	540 (4.01)	582 (4.13)	671 (3.44)	-	725 (4.08)
Acetonitrile	504 (3.65)	538 (3.94)	580 (4.07)	643 (3.76)	698 (3.90)	719 (3.97)
Acetone	503 (3.46)	539 (3.74)	580 (3.93)	644 (3.81)	699 (3.94)	719 (3.86)
Butyronitrile	506 (3.51)	538 (3.80)	580 (3.95)	648 (3.72)	703 (3.89)	718 (3.93)
Methanol	512 (4.52)	540 (3.89)	582 (3.97)	-	-	728 (3.74)
Chloroform	509 (3.49)	542 (3.86)	584 (4.00)	677 (3.23)	-	729 (3.99)
THF	509 (3.70)	541 (3.95)	583 (4.13)	651 (3.72)	706 (3.92)	721 (4.01)
Ethanol	507 (3.40)	538 (3.84)	580 (3.90)	669 (3.33)	-	726 (3.99)
Toluene	508 (3.87)	542 (4.18)	584 (4.35)	675 (3.52)	-	728 (4.25)
Cyclohexane	506 (3.70)	540 (4.01)	581 (4.21)	665 (3.29)	-	724 (4.07)

moderately high H-bond donor values (0.43 and 0.37, respectively). As a result, if solvent acidity plays any kind of role in the tautomerization, it should show the most dramatic influence in these solvents. In addition, these two solvents have polarity values similar to chloroform and H-bond acceptor values comparable to acetone. Despite the relatively high H-bond donor and polarity values of these solvents, the observed B-band of NCTPP is the same as that observed in cyclohexane (**1i**), indicating the H-bond donor ability ($\Sigma\alpha$) of the solvent does not seem to influence the equilibrium. In THF, which is similar in polarizability and H-bond accepting ability to methanol and ethanol, the B-band absorption wavelength occurs at ~438 nm, similar to the absorption band energy observed in cyclohexane. These results indicate that tautomer **1i** is favored in solvents with H-bond acceptor values lower than 0.50. When NCTPP is dissolved in a solvent having a higher H-bond acceptor value, such as DMSO or DMAc, the band absorption maxima is red-shifted to that of **1e**. The outlying data point in this analysis is benzonitrile, which has a high polarity value (0.90) and low H-bond acceptor value (0.33), and for which a value of λ_{max} of 443 nm was observed. However, the shape of the B-band in benzonitrile is similar to that in cyclohexane, which suggests the red-shift in the B-band in this solvent is related to other factors, such as refractive index,[35] that are not considered in this analysis. In general, the ratio of the two tautomeric forms does not appear to appreciably depend on solvent polarity.[20]

The close overlap between the Soret absorption maxima of the two tautomers in different solvents makes it difficult in solvents intermediate between cyclohexane and DMSO to definitively identify the ratio of tautomers. The Q-band region (500−750 nm), in which each tautomer has a distinct absorption pattern, was therefore used to determine quantitatively the amount of each **NCTPP** tautomer in each solvent. In cyclohexane, two high-energy Q-bands for **1i** are observed as very intense absorptions at 540 and 581 nm, respectively, whereas a third, lower-energy Q-band at 665 nm is quite weak. An intense low energy Q-band for **1i** is observed at 724 nm. In DMSO, the high-energy, low intensity Q-bands for **1e** at 556 and 596 nm overlap the 540 and 581 nm Q-bands of **1i**, and cannot easily be used to distinguish between the tautomers. However, the low-energy Q-bands for **1e** at 645 and 699 nm are both quite intense, and conveniently occur in a region of the spectrum where **1i** does not have a strong absorption. As a result, this region of the spectrum provides a window where quantitative comparisons between **1i** and **1e** are possible. The red side of the 699 nm band of **1e** overlaps somewhat the blue side of the 724 nm band of **1i**, and analysis of these bands to quantify the amount of each tautomer in those solvents where both tautomers coexist was accomplished using eqs 1 and 2. Because the differences in the H-bond donor values are quite small, except in the case of methanol and ethanol, we have largely limited the following discussion to just examine the Q-band ratios of **1i** and **1e** as a function of the H-bond acceptor values and polarity values.

The Q-band region in the absorption spectra in DMSO and DMAc are very similar to one another, indicating the same tautomer (**1e**) is present in both solvents. In solvents such as pyridine, acetonitrile, acetone, and butyronitrile, which have high polarity values but lower H-bond acceptor values, the absorption spectra showed evidence of the presence of both tautomers. To approximate the quantity of each tautomer, it was assumed that the changes in the extinction coefficients of the Q-bands for **1e** and **1i** as a function of solvent were minor.[36,37] By measuring the absorption at ~581 nm (where **1i** absorbs significantly more strongly than **1e**) and ~645 nm (where **1e** absorbs more intensely than **1i**), the relative percent of each tautomer in solution was estimated as follows (eqs 1 and 2):

$$\frac{n_{\mathbf{1i}}}{V_T} = \frac{\begin{vmatrix} A_{645} & A_{581} \\ \varepsilon^{\mathbf{1e}}_{645} & \varepsilon^{\mathbf{1e}}_{581} \end{vmatrix}}{\begin{vmatrix} \varepsilon^{\mathbf{1i}}_{645} & \varepsilon^{\mathbf{1i}}_{581} \\ \varepsilon^{\mathbf{1e}}_{645} & \varepsilon^{\mathbf{1e}}_{581} \end{vmatrix}} \qquad \frac{n_{\mathbf{1e}}}{V_T} = \frac{\begin{vmatrix} A_{645} & A_{581} \\ \varepsilon^{\mathbf{1i}}_{645} & \varepsilon^{\mathbf{1i}}_{581} \end{vmatrix}}{\begin{vmatrix} \varepsilon^{\mathbf{1i}}_{581} & \varepsilon^{\mathbf{1i}}_{645} \\ \varepsilon^{\mathbf{1e}}_{581} & \varepsilon^{\mathbf{1e}}_{645} \end{vmatrix}} \quad (1)$$

$$\%\mathbf{1i} = \frac{n_{\mathbf{1i}}}{n_{\mathbf{1i}} + n_{\mathbf{1e}}} \times 100 \qquad \%\mathbf{1e} = \frac{n_{\mathbf{1e}}}{n_{\mathbf{1i}} + n_{\mathbf{1e}}} \times 100 \quad (2)$$

where A_x corresponds to the absorption at a given wavelength (x) in each solvent, ε_x is the extinction coefficient determined at that same wavelength for **1e** in DMSO and **1i** in cyclohexane, and n represents the moles of each tautomer in solvents where both NCTPP tautomers are present simultaneously. With this analysis, the amount of the externally protonated tautomer **1e** in pyridine (~69%), acetone (~64%) and butyronitrile (~51%), and acetonitrile (~46%) shows a better correlation

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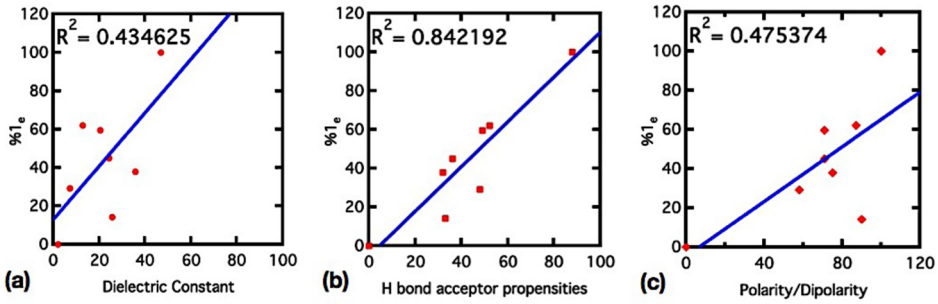

Figure 3. Correlation of **1e** formation with the solvent properties (a) diaelectric constant, (b) H-bond acceptor propensities, and (c) polarity/dipolarity.

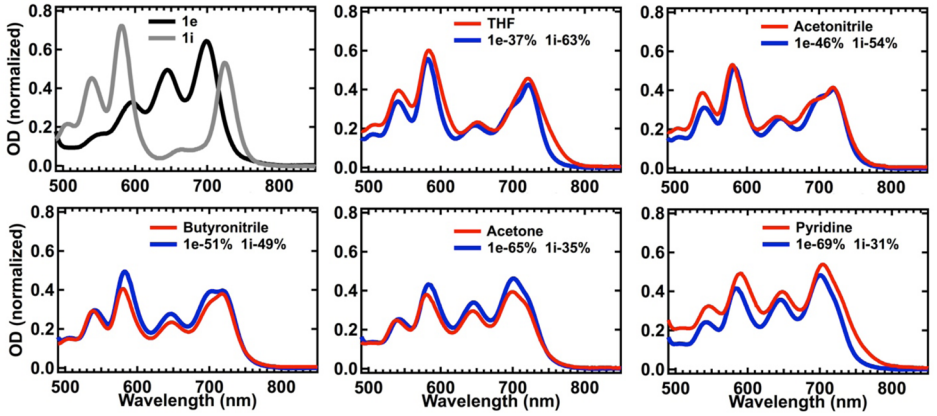

Figure 4. Simulated steady-state absorption spectra of NCTPP tautomers **1i** and **1e** in the 500−850 nm range in a series of solvents. The spectra of NCTPP in DMSO (black) and in cyclohexane (gray) are shown to compare the simulated spectrum in the solvent (red) under investigation. The simulated spectra (blue) were plotted as a function of the percent contribution of each tautomer.

with the trend in the H-bond acceptor value (pyridine (0.52) > acetone (0.49) > butyronitrile (0.36) > acetonitrile (0.32)) than with the trend in polarity (pyridine (0.87) > acetonitrile (0.75) > acetone (0.71) ∼ butyronitrile (0.71)). In pyridine and acetone, which have similar H-bond acceptor values (0.52 and 0.49) but relatively larger differences in polarity (0.87 and 0.71), the ratio of **1e** to **1i** is nearly equivalent. However, a different ratio of **1e** to **1i** is observed in acetone (64% **1e**) and butyronitrile (51% **1e**), both of which have the same polarity values (0.71) but different H-bond acceptor values (0.49 and 0.36). This data is summarized in Figure 3.

The Q-band regions in the absorption spectra of NCTPP in CH_2Cl_2 and $EtCl_2$, both of which have very high polarities (0.82 and 0.81) and very low H-bond acceptor values (0.05 and 0.11), are near-perfect matches with the absorption spectrum of NCTPP in cyclohexane. Similarly, the Q-band region in $CHCl_3$ and toluene, both of which have a very low H-bond acceptor value (0.02 and 0.14) but moderate polarity (0.58 and 0.54), indicates the major tautomer in either solvent is **1i**. In benzonitrile, which has a very high polarity value (0.90) and a low-to-moderate H-bond acceptor value of 0.33, analysis of the absorption spectrum indicates the concentration of **1i** is quite high (81%) but that the equilibrium does not completely favor its formation, as is observed for the halogenated solvents or toluene. THF has a significantly lower polarity value of 0.58 but a higher H-bond acceptor value (0.48) than benzonitrile. The change in the H-bond acceptor value is to push the equilibrium more toward **1e**, thereby decreasing the concentration of **1i** in this solvent to ∼63%. From these results, the tautomerism of NCTPP in solution apparently shows a strong dependence on the H-bond acceptor of the solvent and very little dependence on the polarity (Figure 3). The absorption spectra were simulated[38] in the Q-band region with good correlation using the relative amount of each tautomer, shown in Figure 4 as the percent contribution relative to the standard spectra of DMSO and cyclohexane.

The effect of solvent on the related tautomerization within a series of keto−enol pairs has been previously investigated by Mills and Beak[39] using a similarly wide range of solvents. In their work, the keto−enol equilibrium was also found to primarily be determined by the hydrogen-bonding basicity (H-bond accepting ability) of the solvent. The enol forms were observed to be preferentially stabilized by H-bonding-acceptor solvents, and when the correlations were calculated, the whole weight of the correlations were carried by the β term, which corresponds to the H-bonding accepting property of each solvent. The same correlations were obtained when the dielectric constant term was deleted in the analysis. Therefore, the major interaction of the isomers with the surrounding is the ability of the enolic forms to act as a hydrogen-bond donor to a basic solvent. We believe the same effect is operational in the NCTPP tautomerization.

Furuta et al. have previously proposed[24] a mechanism for the tautomerization wherein the outer nitrogen (N2) on the A-ring, which the crystal structure shows[20] is already rotated out-of-plane toward the two interior N−H groups in the B- and D-rings, initiates the tautomerization in an intramolecular fashion by removing one of the inner N−H protons. The formation of tautomer **1e** in the Furuta mechanism results from the preferred stability of this tautomer in a polar solvent. The

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Furuta mechanism is also consistent with the H-bond accepting solvent results described here, where **1e** is more stable in H-bond accepting solvents, biasing the equilibrium in this direction. A second alternate mechanism can also be proposed for the tautomerization that involves two or more solvent molecules. In this mechanism, one H-bond accepting solvent molecule is hydrogen bonded to one of the inner N−H bonds in the B- or D-rings, and, together with a second solvent that adds a proton to the external nitrogen, catalyzes the tautomerization. This reaction would occur in a concerted or near-concerted process similar to many deprotonation−protonation reactions present in biological systems. Furuta et al. have examined the equilibrium in pyridine-d_5 and observed $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values of 14.94 kcal mol^{-1}, 1.93 kcal mol^{-1}, and −47.6 eu, respectively.[20] The low activation enthalpy is consistent with a concerted reaction, and the rather negative entropy of activation with the highly ordered transition state predicted by an intramolecular mechanism. For reference, Abraham and co-workers reported values of 13.5 kcal mol^{-1}, 9.2 kcal mol^{-1}, and −10 eu for the NH shift in H_2TPP. Importantly, the transition state for the H_2TPP isomerization is not likely to involve the out-of-plane distortion/rotation required by Furuta's NCTPP mechanism.[40]

Interestingly, the absorption spectra acquired in methanol and ethanol are also consistent with the presence of **1i** (i.e., in cyclohexane). These solvents, which have the highest H-bond donor values (0.43 and 0.37, respectively) and moderate H-bond acceptor values (0.47 and 0.48), shift the equilibrium toward **1i**, consistent with a mechanism involving H-bonding of the alcohol to the lone pair of electrons on the external nitrogen. Several groups[17,18,26] have determined the absorption spectra of NCTPP under acidic conditions, and have shown both tautomers undergo sequential mono- and diprotonations, a process that is accompanied by new absorption bands at ∼790 nm for the monocation and ∼840 nm for the dication in $CHCl_3$, and ∼840 nm in DMF.[18,26,27] The absorption spectra in both solvents, and in particular methanol, show a low energy tail to the red of the $Q_y(0,0)$ band that extends toward 800 nm. We suggest this tail results from H-bonding from the solvent to the exterior nitrogen (N2). From the absorption spectra, it is clear the proton is not fully shifted to the nitrogen, a result that is not surprising given the expected difference in pK_a values between the alcohols and protonated **1i**. Nonetheless, the high H-bond acidity in methanol and ethanol may result in H-bonding interactions between the solvent molecules and the external nitrogen of **1i** that stabilizes this tautomer, and in any case influences the tautomerization more than the H-bond accepting capacity of the solvent.

CONCLUSIONS

The tautomerization of NCTPP was studied in a series of 15 solvents, and the dependence of the equilibrium was examined as a function of several solvent parameters, including polarity/dipolarity (π), H-bond donor ($\Sigma\alpha$), and H-bond acceptor ($\Sigma\beta$) values; dielectric constant; and dipole moment. The absorption spectra of NCTPP observed in these solvents indicated the tautomerization correlated most strongly with the H-bond acceptor properties of the solvent. In the case of methanol and ethanol, the opposite effect is observed, with evidence of hydrogen-bonding between the exterior N2 nitrogen and the solvent observed.

EXPERIMENTAL SECTION

Absorption spectra were measured on a double-beam spectrophotometer. All solvents used for spectroscopic measurements were either HPLC or spectophotometric grade and were used as received, except chloroform, dichloromethane, and dichloroethane, which were passed through a short column of silica gel prior to use to remove HCl. Every experiment was performed at least three times for reproducibility.

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Notes

The authors declare no competing financial interest.

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