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Ground- and Excited-State Tautomerism in Porphycenes

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ABSTRACT

Owing to short distances between the inner nitrogen atoms and, therefore, strong intramolecular hydrogen bonds, porphycenes display completely different tautomeric properties than porphyrins, their constitutional isomers. Tunneling splitting caused by delocalization of two inner hydrogen atoms is observed for porphycenes isolated in supersonic jets. The barrier to tautomerization is higher in the lowest excited singlet state than in the ground state. Still, rapid exchange of inner hydrogen atoms is detected in S_1 . The mechanism of tautomerization involves synchronous double hydrogen tunneling, activated by excitation of a low-frequency mode, which modulates the $NH\cdots N$ separation. This separation can also be strongly altered by peripheral substitution. In porphycenes with alkyl substituents on the ethylene bridges, the $NH\cdots N$ distances become extremely small. For these derivatives, both *trans* and *cis* tautomeric forms are detected. Tautomerism in porphycenes was also monitored on a single-molecule level.

Introduction

Among the enormous diversity of hydrogen-bonded systems, a unique class is formed by those for which the transfer of proton(s) along the hydrogen bond(s) leads to a chemically equivalent structure. A representative example is provided by free-base porphyrins, “pigments of life”.¹ In these molecules, two inner hydrogen atoms can migrate between four nitrogen atoms that form the inner cavity. Strong interest in the tautomerism in porphyrins has many causes. On one hand, such studies probe basic chemical notions, such as coupling between vibrations of the protons and heavy atoms, role of tunneling, and cooperativity. On the other hand, tautomerization, especially when induced by light, can be exploited for practical purposes, e.g., in information storage.² Moreover, porphyrins constitute important models for theoretical treatment of tautomerization, because the process occurs in a reaction center of well-defined geometry, located inside a molecule, and isolated from the environment.

The mechanism of ground-state tautomerization in porphyrin that emerged after extensive, mainly nuclear

magnetic resonance (NMR), studies^{3–5} is that of a stepwise mechanism (Figure 1). The first stage involves conversion of a *trans* species, with hydrogen atoms located on the opposite nitrogen atoms, into a *cis* form, with the two hydrogens on adjacent nitrogen atoms. This step requires thermal activation to a level from which *trans* \rightarrow *cis* tunneling occurs. The *cis* structure can either go back to the substrate or, via the transfer of the second hydrogen, end up in the other *trans* tautomeric form. Interestingly, the *cis* structure of porphyrin, a crucial transient in this mechanism, has never been experimentally detected.

Porphycene (**1**),⁶ the first constitutional isomer of porphyrin (**2**), synthesized by the group of E. Vogel, provided a molecule with an inner cavity of different symmetry and geometry (Scheme 1). Already the initial NMR studies revealed major differences between the two systems.⁷ The ground-state tautomerization in porphycene turned out to be extremely rapid even at 107 K, well below the temperature at which this process in porphyrin becomes frozen. Our studies by various electronic spectroscopy techniques, described below and recently discussed in more detail elsewhere,⁸ confirm these differences, also for excited states, and indicate a synchronous, concerted mechanism of tautomerization. A completely different behavior in the two isomeric systems is due to much stronger hydrogen bonds in porphycene, caused by favorable topology of the inner cavity.

Excited-State Tautomerism in Condensed Phases

In a rigid environment, where the reorientation of an excited chromophore is hindered, the directions of the S_0 – S_1 transition moments should coincide in absorption and emission, resulting in the fluorescence anisotropy value of 0.4. Contrary to this expectation, fluorescence of porphycene embedded in rigid media is depolarized, both at room temperature in a polymer film and at low temperatures in glassy matrices.^{9–11} The observed values barely exceed 0.1 at 293 K, gradually increase with lowering the temperature, and finally, reach the “normal” value of 0.4 at about 20 K (Figure 2). An analogous pattern of changes of anisotropy with temperature is observed for S_0 – S_2 excitation. According to calculations, the S_0 – S_2 transition moment should be nearly orthogonal to that of the emitting S_0 – S_1 transition; therefore, the anisotropy should be close to –0.2. A value of –0.18 is indeed observed but only at the lowest temperatures. Upon heating, the anisotropy changes sign and, at high temperatures, reaches the value of about 0.10, similar to the value obtained when exciting to S_1 .

Depolarization of fluorescence, even at temperatures as low as 77 K, was also observed for 2,7,12,17- and 9-, 10,19,20-tetra-*n*-propyl-substituted porphycenes **1a** and **1c**, but not for the 2,3,6,7,12,13,16,17-octaethyl derivative **1d**.¹⁰ In the latter, the “textbook” anisotropy values were

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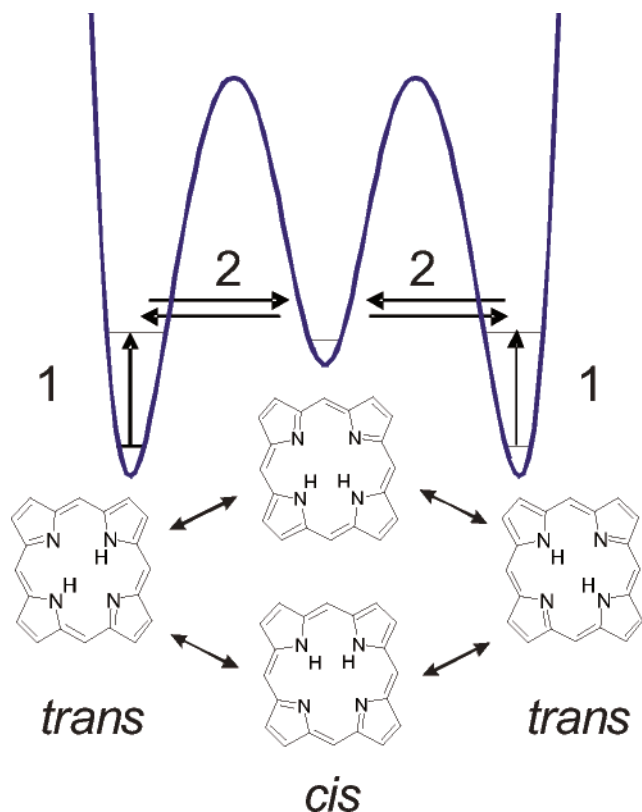
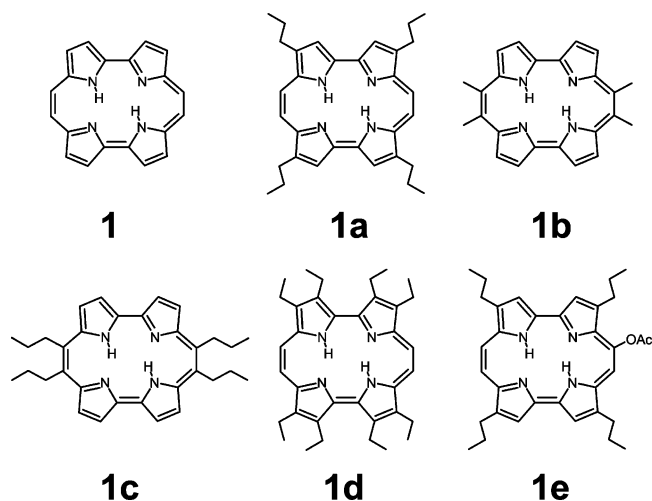


FIGURE 1. Scheme of ground-state tautomerization in porphyrin. Step 1 corresponds to thermal activation, while step 2 corresponds to a single hydrogen transfer via tunneling.

Scheme 1. Porphycene (1) and the Derivatives Discussed in This Account: 2,7,12,17-tetra-*n*-propylporphycene (1a), 9,10,19,20-tetramethylporphycene (1b), 9,10,19,20-tetra-*n*-propylporphycene (1c), 2,3,6,7,12,13,16,17-octaethylporphycene (1d), and 9-acetoxy-2,7,12,17-tetra-*n*-propylporphycene (1e)



obtained, about 0.4 and -0.2 for excitation into S_1 and S_2 , respectively. Significantly, the octaethyl derivative has the largest separation between the nitrogen atoms and should thus exhibit the slowest tautomerization kinetics. Therefore, it was concluded that the reduced anisotropy values are caused by excited-state tautomerization occurring on the time scale faster or comparable to the lifetime

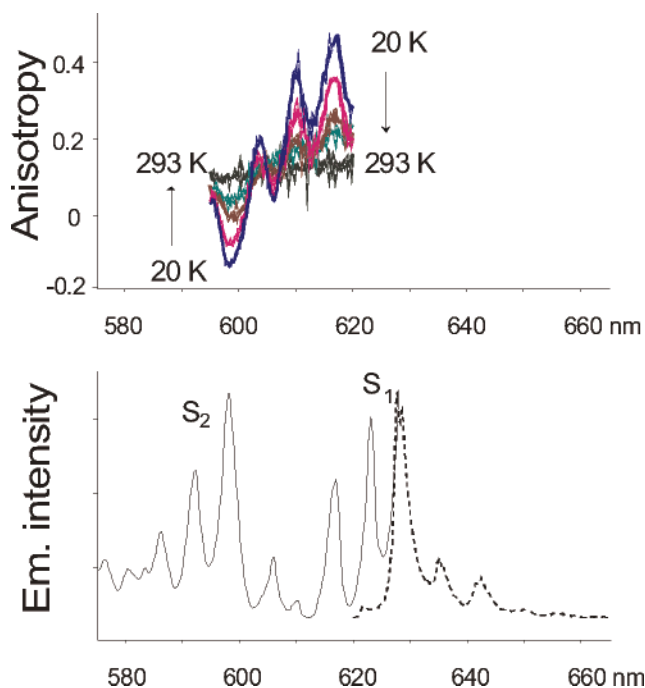


FIGURE 2. (Bottom) Fluorescence (---) and fluorescence excitation spectrum of porphycene in poly(vinyl butyral) film at 20 K. (Top) Anisotropy of fluorescence excitation to S_1 and S_2 states as a function of temperature (20, 70, 120, 160, and 293 K, respectively).

of the lowest excited singlet state, about 10 ns for the parent porphycene at 293 K and picoseconds for 9,10,-19,20-tetraalkylporphycenes.

Not many techniques are available that enable studying chemical reactions in systems where the substrate and product are chemically indistinguishable. NMR is usually applied for such cases, naturally limited to the ground-state processes. For the investigations of excited-state reactions, an invaluable tool is provided by quantitative analysis of the emission anisotropy values. When applied to porphycenes, such methodology leads to information about (i) dominant tautomeric structures in both S_0 and S_1 states, (ii) transition-moment directions, and (iii) tautomerization rates. Double hydrogen transfer in a “narcissistic”, degenerate, type of reaction (*trans*–*trans* or *cis*–*cis*) is equivalent to a rotation of each in-plane transition-moment direction by an angle α that is twice that of the angle formed by this moment with the horizontal (or vertical) in-plane axis (Figure 3). In a high-temperature regime, when the excited-state reaction is much faster than the S_1 lifetime, equal populations of both tautomers are established and the measured fluorescence anisotropy r can be expressed by eq 1

$$r(\alpha, \beta) = \{3[\cos^2(\beta - \alpha/2) + \cos^2(\beta + \alpha/2)] - 2\}/10 \quad (1)$$

where β and $\alpha/2$ are the angles between the molecular horizontal axis and the transition moment in absorption and emission, respectively.

Measuring anisotropy upon excitation into S_1 leads to the determination of $\beta_1 = \alpha/2$. In turn, the knowledge of α enables us to obtain the directions of the moments of transitions to higher excited states. The determination of

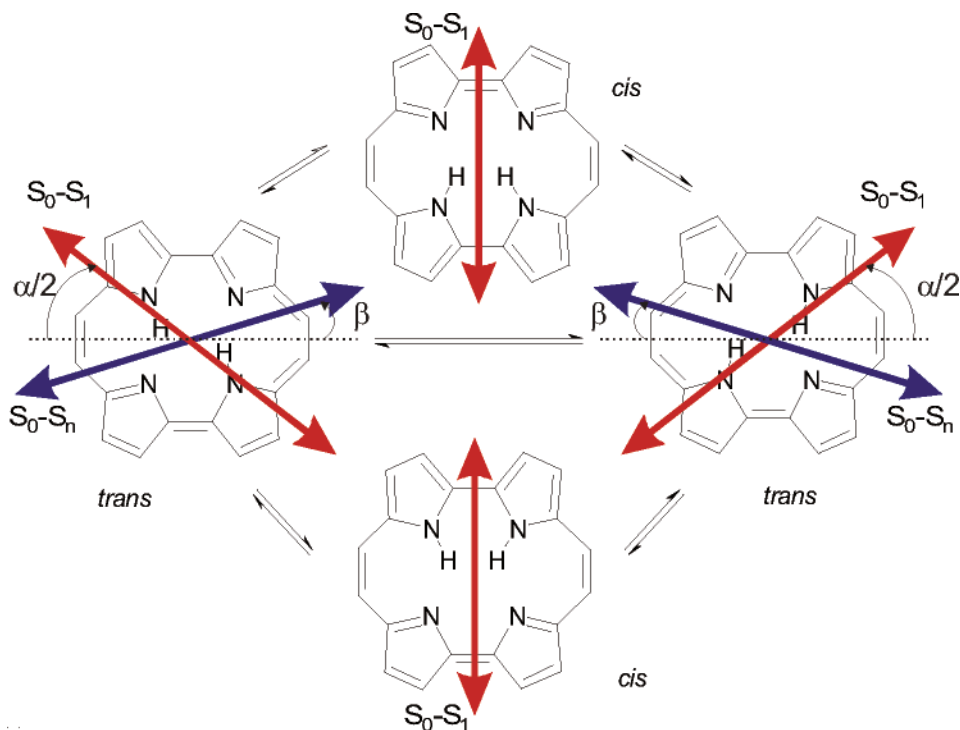


FIGURE 3. *Trans* and *cis* tautomeric forms of porphycene and changes of transition moment directions accompanying *trans*–*trans* conversion. See the text for details.

the absolute values of the angles requires the sign of at least one of them. It can readily be provided, even by approximate calculations.

Equations 2 and 3 are obtained for a general case, when the simultaneous presence of both *trans* and *cis* tautomers is allowed, with each form differently populated in S_0 and S_1

$$r(\alpha, \beta, \gamma, \delta) = (1 - e)r(\alpha, \beta) + g r(\delta - \gamma) + (e - g)r(\beta - \gamma), \quad g < e \quad (2)$$

$$r(\alpha, \beta, \gamma, \delta) = (1 - g)r(\alpha, \beta) + e r(\delta - \gamma) + (g - e)r(\beta - \gamma), \quad g > e \quad (3)$$

where g is the fraction of ground-state *cis* tautomers being excited, e is the fraction of the *cis* form in the excited state, and δ and γ are the angles between the horizontal axis and the transition moments in absorption and emission, respectively, in the *cis* form. Because of symmetry, these angles can only assume values of 0° or 90° . We do not consider another possible *cis* structure, with the inner hydrogen atoms located on different bipyrrrole units. Calculations predict a very high energy for such species.

The anisotropy values observed for porphycene not only prove the occurrence of the excited-state reaction, but they also demonstrate that the tautomerization involves mostly *trans*–*trans* interconversion. A small fraction of *cis* structures can also be present, but is not dominant. The same is true for the ground state, for which the fluorescence polarization experiments reveal the dominance of *trans* forms. It should be noted that *cis*–*cis* tautomerization does not change the transition-moment direction and thus cannot lead to depolarization. *Cis*–*trans* conversion, in turn, would result in much

smaller anisotropy changes than observed. Finally, a hypothetical structure with the inner protons equidistant from both nitrogen atoms involved in the hydrogen bond can also be excluded.

The determination of the *trans* structure as the most stable tautomeric form of porphycene was an important result, not easy to obtain using other techniques. Previous structural assignments were based on calculations,¹² whereas the X-ray data⁶ as well as NMR,^{7,13} IR, and Raman measurements¹⁴ were not unequivocal.

Using eq 1, excited-state tautomerization in **1** could be applied as a tool for the determination of electronic transition-moment directions,¹⁰ not a trivial task in the case of low-symmetry molecules: C_{2h} symmetry of the *trans* form of porphycene dictates that any direction in the molecular plane is possible. The transition moments were determined for the four lowest $\pi\pi^*$ transitions, responsible for Q and Soret bands. The transition moment for the transition to the lowest excited singlet state is approximately parallel to the line connecting the protonated nitrogen atoms, whereas the S_0 – S_2 transition moment is nearly orthogonal to this direction. This pattern of transition moments is similar to that of free-base porphyrin, where the molecular symmetry (D_{2h}) dictates that only these two in-plane transition-moment directions are allowed.

Fluorescence anisotropy measurements can also be used to obtain the rates of the excited-state tautomerization. Two approaches are possible. The first is based on the analysis of time-resolved anisotropy curves. The anisotropy decay reflects the movement of the transition moment and, thus, the migration of inner hydrogens. The experiments should be carried out in rigid media, to avoid

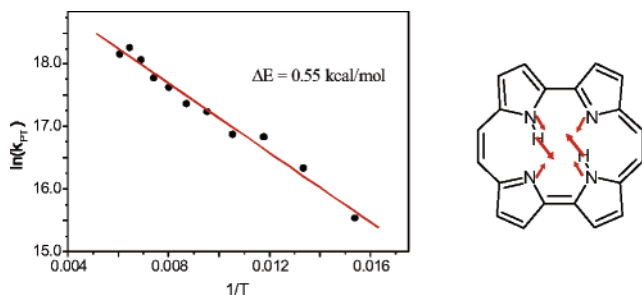


FIGURE 4. (Left) Arrhenius plot for the rate of *trans*–*trans* conversion in the lowest excited singlet state of porphycene. (Right) Inner-cavity atom displacements involved in the 180 cm^{−1} mode.

depolarization because of molecular rotation. However, when the *S*₁ lifetime is short compared to that of rotational diffusion, tautomerization rates can be determined even in solutions. This situation occurs in 9,10,19,20-tetra-*n*-propylporphycene **1c**, for which time-resolved anisotropy measurements have been performed in liquid solutions at 293 K. Fluorescence was found to be depolarized from the very onset of the signal, which implies that the tautomerization rate is larger than 10¹¹ s^{−1}. Such a high rate is due to very strong hydrogen bonds in this molecule, as can be deduced from extremely small NH⋯N distances (2.53 Å) in porphycenes alkylated on the ethylene bridges. Moreover, for 9,10,19,20-methyl- and *n*-propyl-substituted porphycenes **1b** and **1c**, biexponential fluorescence decays were observed, providing evidence for the presence of two forms, even at low temperatures. Fluorescence remains depolarized, implying that the rate of excited-state *trans*–*trans* tautomerization may be faster than that of the *cis*–*trans* conversion. Thus, simultaneous transfer of two hydrogen atoms may be more favorable than a single hydrogen-transfer process.

A related technique, experimentally much more expedient, is based on the steady-state anisotropy values. For the *trans*–*trans* interconversion, the observed fluorescence anisotropy *r* and the reaction rate *k*_{PT} are related by eq 4

$$k_{\text{PT}} = \frac{1}{\tau} \left[\frac{r(0) - r}{2r - r(\alpha) - r(0)} \right] \quad (4)$$

where *τ* is the fluorescence decay time and *r*(0) and *r*(α) are the anisotropies of the initially excited and tautomeric species, respectively. Applying this formula to the results obtained for porphycene dissolved in rigid media, such as poly(vinyl butyral) film at various temperatures, results in an Arrhenius type of behavior (Figure 4). The apparent activation energy extracted from the plot is 0.55 ± 0.05 kcal/mol (192 ± 20 cm^{−1}). This value is surprisingly small when compared with several kcal/mol, the barrier estimated from calculations. On the other hand, it agrees perfectly with the frequency of a well-assigned *a*_g vibration of porphycene, observed both in absorption (181 cm^{−1} in an argon matrix) and emission (182 cm^{−1}).^{14,15} This mode corresponds to an in-phase modulation of NH⋯N distances and angles (Figure 4) and, therefore, should be crucial for the reaction barrier. It can therefore be

concluded that the double hydrogen exchange in porphycene occurs as a thermally activated synchronous tunneling process, gated by the vibration that lowers the barrier. Such interpretation allows us to understand differences in the tautomerization mechanism in porphycene and porphyrin. For the latter, the *cis*–*trans* energy difference is much smaller than the barrier for *trans*–*trans* conversion. This barrier remains significant even when the molecule acquires the energy sufficient to populate the *cis* tautomer. On the contrary, for porphycene, the *trans*–*trans* barrier is low and becomes further reduced when the energy of about 0.5 kcal/mol is deposited into the gating mode. This energy is about 4 times lower than the calculated *cis*–*trans* energy difference.¹² Thus, efficient double *trans*–*trans* hydrogen transfer in porphycene is possible even under conditions when the *cis* form cannot be populated. Even in cases when it can, as discussed above for **1b** and **1c**, *trans*–*trans* conversion may be faster than the *cis*–*trans* reaction.

This mechanism of tautomerization, proposed for the lowest excited singlet state, can probably operate also in the ground electronic state of porphycenes. However, the barrier for tautomerization in *S*₀ is lower than in *S*₁, as demonstrated by the results obtained for porphycenes isolated in supersonic jets, discussed below. Therefore, double hydrogen tunneling in the ground-state may be possible even from the lowest vibrational level. Indeed, the results obtained for 9-acetoxy-2,7,12,17-tetra-*n*-propylporphycene **1e** indicate ground-state tunneling between two *trans* forms, even at cryogenic temperatures.¹⁶ It is noteworthy that in this compound the two *trans* tautomers are no longer chemically equivalent.

Porphycenes in Supersonic Jets: Ground- and Excited-State Tunneling Splittings

Differences between porphyrin and porphycene with respect to tautomerization barriers are clearly revealed in the fluorescence excitation spectra recorded in supersonic jets. Porphyrin shows a usual pattern, with single peaks corresponding to particular vibronic transitions.¹⁷ In contrast, the spectrum of porphycene¹⁸ consists of doublets, separated by 4.4 cm^{−1} (Figure 5). Upon replacing one or two inner protons with deuterons, the splitting disappears (which means that it becomes smaller than the experimental resolution, i.e., 0.1 cm^{−1}). Also, complexes with water or alcohol do not reveal the doublet structure. The splitting observed for isolated, nondeuterated porphycene has been attributed to the ground-state tunneling of two inner hydrogen atoms. In singly and doubly deuterated porphycenes, fluorescence excitation spectra are shifted to the red, roughly by the same amount per each substituted proton. Thus, the lowering of zero-point energies in the deuterated species is larger in *S*₁ than in *S*₀, which indicates that the hydrogen bonds become weaker in the excited state. Most likely, the molecule expands upon excitation, and the cavity (or, at least, the shorter side of the rectangle) becomes larger. This hypothesis has been confirmed by TD-DFT B-P86/TZVP

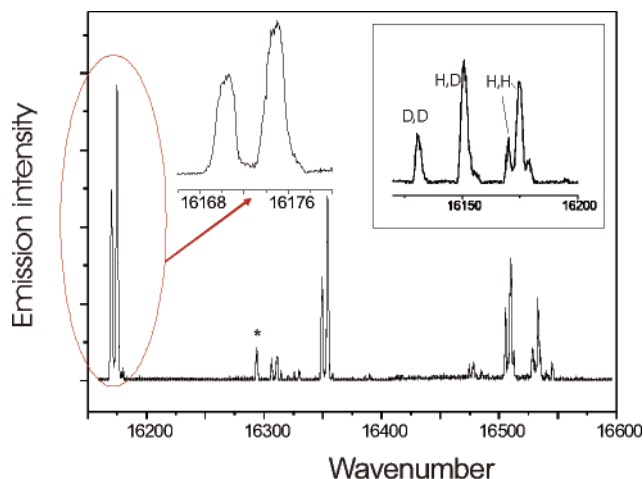


FIGURE 5. Fluorescence excitation spectra of porphycene isolated in a supersonic jet. The peak marked with an asterisk corresponds to the complex with water. (Inset) Region of 0–0 transition in undeuterated (H,H) and singly (H,D) and doubly deuterated (D,D) **1**.

optimization of S_1 , which predicts for the *trans* tautomer of **1** the $\text{NH}\cdots\text{N}$ distances of 2.68 Å, compared to 2.64 Å for the ground state. These results and the observation that all S_1 vibronic peaks reveal the same separation of the doublet components suggest that the observed value of 4.4 cm^{-1} can be assigned to ground-state tunneling splitting, whereas the S_1 splitting should be much smaller. The ongoing studies of fluorescence in nanohelium droplets fully confirm this conclusion.¹⁹

The fluorescence and fluorescence excitation spectra of unsubstituted porphycene in the jet revealed vibrations of a_g symmetry that could be safely assigned to the *trans* tautomer. There was no evidence for the presence of *cis* species. For 9,10,19,20-alkyl-substituted porphycenes **1b** and **1c**, which have smaller N–N separation and thus stronger hydrogen bonds, the situation is different.²⁰ A complicated pattern is observed in the fluorescence excitation spectra. Two features lying 12.5 cm^{-1} apart (parts A and B in Figure 6) are observed in the 0–0 region. Both A and B are composed of doublets split by about 2 cm^{-1} . The A and B features are still observed for singly and doubly deuterated compounds, but their doublet structure disappears. Each A and B peak is associated with a different vibronic structure. Two low-frequency modes (32 and 38 cm^{-1}) are associated with the upper peak, B, whereas only one vibration (38 cm^{-1}) related to the lower component A is detected. Hole-burning experiments in the jets were performed to secure these assignments.

The features attributed to A disappear when the spectrum is recorded at further distances from the nozzle, i.e., for better cooled molecules. However, these peaks cannot be assigned to ordinary hot bands: these are also observed but disappear much earlier (Figure 6).

These findings were interpreted as evidence for the presence of two different ground-state structures, *trans* and *cis* tautomers, in agreement with the results of B3LYP/6-31G(d,p) calculations, which suggest that the two forms should have very similar energies [$\Delta E(\text{cis} - \text{trans}) = 0.7$ kcal/mol, after including zpve correction]. The A and B

spectral features were assigned to *cis* and *trans* tautomers, respectively. These conclusions from supersonic jet studies nicely correspond to the results obtained for both **1b** and **1c** in condensed phases: biexponential fluorescence decays were observed in solutions, glasses, polymers, and rare gas matrices, indicating the presence of two forms.

Dispersed fluorescence spectra recorded in the jet for both A and B forms revealed peaks that could not be readily associated with ground-state vibrations. These features were assigned to transitions ending on the upper components of ground-state tunneling doublets. The values of about 15 cm^{-1} were found for both *cis* (A) and *trans* (B) tautomers in S_0 . The ground-state splitting is larger than in **1**, because of much shorter $\text{NH}\cdots\text{N}$ distances (2.53 Å for both **1b** and **1c**, about 0.1 Å less than in the parent compound). Also the excited-state (S_1) splitting could now be estimated: the value of about 2 cm^{-1} is smaller than that of S_0 , but much larger than that of the parent molecule. Finally, the analysis of intensity patterns led to the conclusion that the double minimum potentials for *trans*–*trans* and *cis*–*cis* conversion are not symmetrical (Figure 6), as they were in bare porphycene. The reason for the asymmetry is the coupling between the movement of inner hydrogen atoms and low-frequency motions of alkyl substituents.

In summary, the results obtained from the jet studies not only corroborate the conclusions drawn from investigations in condensed phases (dominance of *trans* tautomers and presence of two forms in bridge-alkylated porphycenes), but they also provide important quantitative information concerning double hydrogen tunneling. These studies are now continued, supplemented by measurements in nanohelium droplets.¹⁹ Of particular interest is the determination of tunneling splittings for the vibrations that can promote or hinder tautomerization. As discussed above, condensed-phase studies of parent porphycene suggest the 180 cm^{-1} mode as the most prominent representative of the former. Indeed, the ground-state tunneling splitting associated with this vibration, determined from fluorescence spectra, turns out to be much larger than 4.4 cm^{-1} , the value observed for the 0–0 transition and for many other “neutral” modes.

While comparing the results obtained in the jets with those from condensed phase studies, one should bear in mind that the tunneling mechanisms are different in these two regimes. For an isolated molecule, tautomerization occurs as a coherent double hydrogen transfer. This leads to tunneling splittings. In the condensed phase, the coherence is lost or, at most, preserved only for very short time periods. Therefore, the reaction can be described as a rate process.

Tautomerization in Single Molecules of Porphycene

The realization that *trans*–*trans* tautomerization in porphycene leads to changes in transition-moment directions suggested this molecule as a promising object for single-molecule studies. Various single-molecule spectroscopy

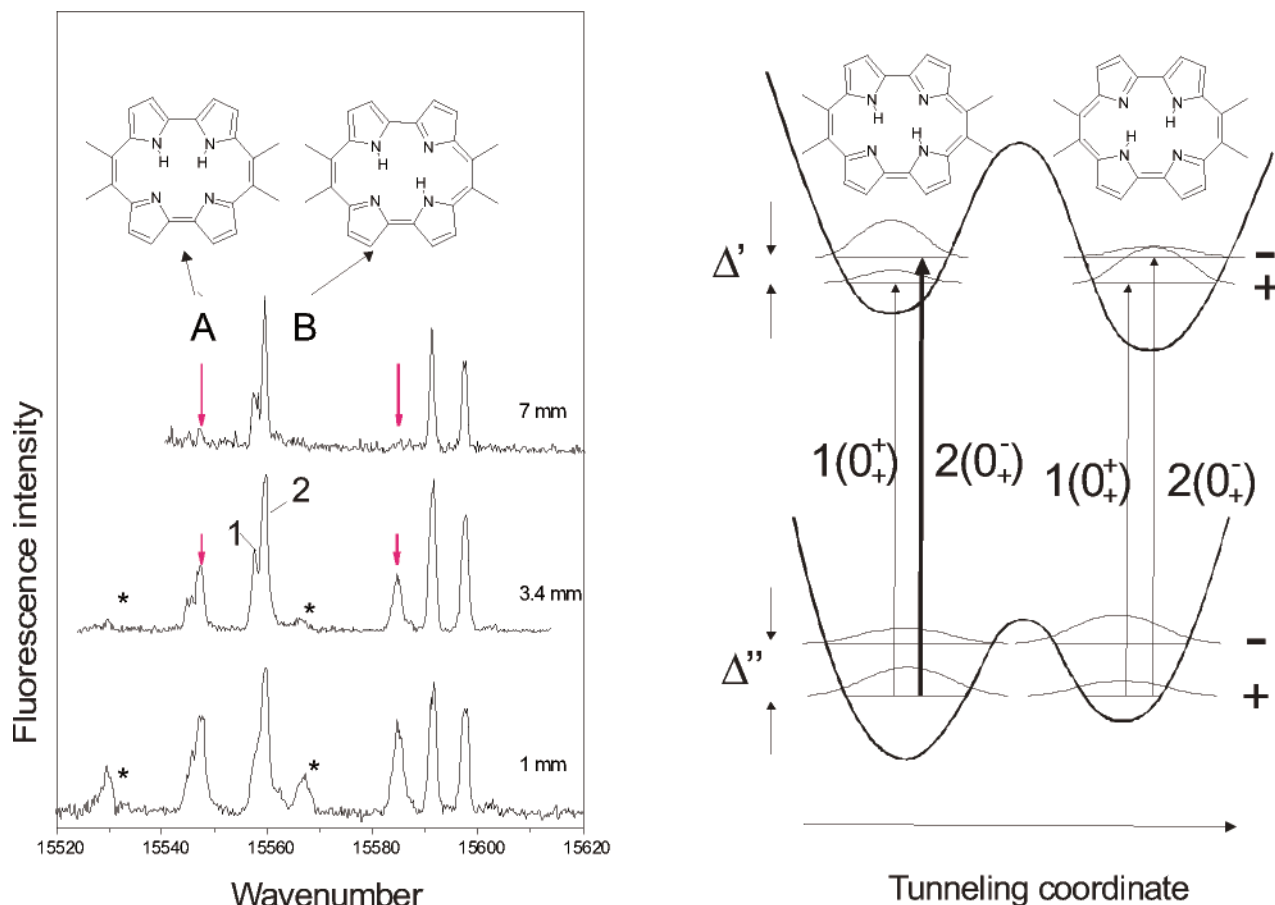


FIGURE 6. (Left) Fluorescence excitation spectra of 9,10,19,20-tetramethylporphycene in a supersonic jet. From bottom to top, the spectra recorded at increasing distances from the nozzle and thus corresponding to a higher degree of cooling. The vertical arrows show the features assigned to the *cis* tautomer. "Normal" hot bands are indicated by asterisks. (Right) Proton potentials for the S_0 and S_1 tunneling splittings in the two states, labeled as Δ'' and Δ' , respectively.

techniques combine excitation with polarized light with the analysis of the spatial patterns of the emission, in order to determine the orientation of the chromophore in three dimensions or to study energy-transfer processes. The emitting molecule is treated as a dipole. It is obvious that, for a porphycene molecule that undergoes tautomerization, this approximation is not valid, and the fluorescence can be envisaged as occurring from two nearly orthogonal dipoles (cf. Figure 3). Thus, finding an intensity pattern that cannot be reproduced by a single dipole would provide a strong argument for observing tautomerization in a single molecule. The experiments carried out for single molecules of porphycene²¹ and its alkylated derivatives confirmed this prediction. Using the so-called azimuthal polarization mode of the exciting light, various spatial patterns were observed for the fluorescence of single molecules embedded in poly(methyl metacrylate) (PMMA) film at room temperature (Figure 7). Particularly interesting were those consisting of a nearly perfect ring, a pattern impossible to obtain in the case of a single dipole. The simulations assuming two equally emitting dipoles yielded $72 \pm 3^\circ$ for the angle between them, in perfect agreement with $71 \pm 5^\circ$, the value provided by fluorescence anisotropy studies of bulk porphycene in polymer films. Several molecules revealed different emission intensity patterns, corresponding to double lobes

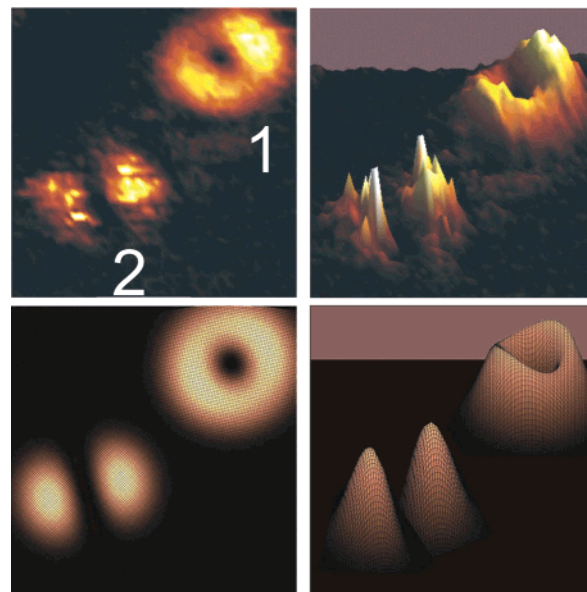


FIGURE 7. Spatial patterns of fluorescence from two single molecules of porphycene embedded in PMMA film at 293 K. (Top) Experiment. (Bottom) Simulation. The ring pattern in molecule 1 is due to two emitting dipoles, resulting from *trans-trans* conversion.

(molecule 2 in Figure 7). They were interpreted as a result of molecules that are oriented approximately perpen-

dicular to the sample surface. In such a situation, even the fluorescence produced by several in-plane transition dipoles looks like the emission generated by a single dipole.

The feasibility of studying tautomerization in single molecules permits us to devise completely new experimental schemes. For instance, one can exploit the possibility to distinguish between the molecules lying flat on a particular support and the molecules perpendicular to the surface. The external potential experienced by the two inner hydrogen atoms should be the same in the former case but not necessarily so in the latter. Such nonequivalent potential could induce switching from the synchronous to the stepwise mechanism of tautomerization.

Our current efforts focus on the detection of *cis* and *trans* forms in selected porphycenes and on separately monitoring ground- and excited-state reactions within a single molecule.

Conclusions and Outlook

The studies of tautomerization in porphycenes have thus far permitted quite an extensive characterization of this process for both ground and the lowest excited singlet states. The dominant forms were determined to be the *trans* tautomers, but the *cis* species were also detected in the derivatives with ultrashort NH...N separation. The tunneling splittings caused by double hydrogen delocalization were determined. The barrier to tautomerization is lower in the ground electronic state, because of smaller NH...N separation and, in consequence, stronger hydrogen bonds. For porphycene in condensed phases, it was demonstrated that the excited-state process is gated by a low-frequency vibration that simultaneously strengthens both hydrogen bonds by bringing the hydrogen donor and acceptor atoms closer together and making the hydrogen bonds more linear.

The porphycenes constitute an ideal series of compounds for testing the computational methods dealing with hydrogen bonds, tautomerization, and tunneling. Their ability to undergo significant changes in the dimensions of the inner cavity under the influence of mild substituents, such as alkyl groups, provides an opportunity for systematic studies of the tautomerization rate versus hydrogen-bond topology (distances and angles) relationship. The crucial role of tunneling is illustrated by the data accumulated from the lowest excited singlet state studies of several porphycenes: a change of 0.25 Å in the N...N separation leads to orders of magnitude variation in the tautomerization rates. A challenge for theoretical studies would be to properly describe the correlation between the inner protons or even provide a model for their quantum entanglement.

Equally as important, the results obtained for porphycene allow for understanding of the mechanism of tautomerization in the parent isomer, free-base porphyrin. In principle, the origin for dissimilarities between the two isomers may be due to either different electronic structure or distinct geometries. It seems that the latter is more

important. Strong, nearly linear hydrogen bonds in porphycenes result in drastically lower barriers to tautomerization. In consequence, the energy required for *trans*→*trans* conversion in porphycene is lower than the *cis*→*trans* separation. Therefore, the synchronous double hydrogen transfer in porphycene is the preferred path, contrary to the case of porphyrin, where it is energetically more favorable to populate the *cis* tautomer, which can subsequently transfer the second hydrogen atom.

Differences in the electronic structure in the two isomers seem to play a less important role. This is suggested by similar values of NMR chemical shifts of peripheral hydrogen atoms and by analogies in the electronic spectra. For a definitive assessment of the contributions of geometry and electronic structure, the experiments are planned for porphyrins in which the pattern of peripheral substitution produces an inner cavity with similar geometry to that of porphycenes.

Previous studies of tautomerization in porphyrins^{3–5,22–23} could not detect the presence of the *cis* tautomeric species, even though this form is a crucial intermediate in the process. It was postulated that the too short lifetime of the *cis* tautomers makes their detection impossible. The findings for porphycenes do not support such a conclusion, because *cis* tautomers are observed, separated from *trans* forms by barriers much smaller than those expected for porphyrins. We propose instead that the difficulties in the detection of *cis* tautomers in porphyrins are due to their very small concentration, because of large *cis*→*trans* energy separation. Chances are that, if the *cis* tautomers of porphyrins could be efficiently populated, i.e., via an excited state, they should be amenable to detection, particularly at low temperatures.

Finally, it should be mentioned that the results of photophysical studies of porphycenes can be applied in a completely different field: photodynamic therapy. Numerous studies have demonstrated that derivatives of porphycene are very efficient in the photoinduced destruction of tumors^{24–26} and inactivation of bacterial strains.²⁷ The photophysical data obtained for various porphycenes indicate that the derivatives with the strongest hydrogen bonds (**1b** and **1c**) reveal an efficient $S_0 \leftarrow S_1$ internal conversion process. In consequence, the triplet state is not populated, and these molecules cannot act as efficient singlet oxygen sensitizers, which excludes them as potential phototherapeutic agents. On the other hand, parent porphycene and 2,7,12,17-alkylated derivatives (e.g., **1a**) reveal high yields of triplet formation and singlet oxygen generation. Because the NH...N distance in porphycenes is very sensitive to peripheral substitution, the knowledge of the relationship between the hydrogen-bond strength and triplet-formation efficiency may be crucial for the design of new phototherapeutic substances.

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References

- (1) Battersby, A. R.; Fookes, C. J. R.; Matcham, G. W. J.; McDonald, E. Biosynthesis of the pigments of life: Formation of the macrocycle. *Nature* **1980**, *285*, 17–21.
- (2) Renn, A.; Wild, U. P.; Rebane, A. Multidimensional holography by persistent spectral hole burning. *J. Phys. Chem. A* **2002**, *106*, 3045–3060.
- (3) Braun, J.; Limbach, H. H.; Williams, P. G.; Morimoto, H.; Wemmer, D. E. Observation of kinetic tritium isotope effects by dynamic NMR. The tautomerism of porphyrin. *J. Am. Chem. Soc.* **1996**, *118*, 7231–7232.
- (4) Braun, J.; Schlabach, M.; Wehrle, B.; Köcher, M.; Vogel, E.; Limbach, H. H. NMR study of the tautomerism of porphyrin including the kinetic HH/HD/DD isotope effects in the liquid and the solid state. *J. Am. Chem. Soc.* **1994**, *116*, 6593–6604.
- (5) Schlabach, M.; Wehrle, B.; Rumpel, H.; Braun, J.; Scherer, G.; Limbach, H. H. NMR and NIR studies of the tautomerism of 5,10,15,20-tetraphenylporphyrin, including kinetic HH/HD/DD isotope and solid state effects. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 821–833.
- (6) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. Porphycene—A novel porphin isomer. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257–259.
- (7) Wehrle, B.; Limbach, H. H.; Köcher, M.; Ermer, O.; Vogel, E. ¹⁵N-CPMAS-NMR study of the problem of NH tautomerism in crystalline porphine and porphycene. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 934–936.
- (8) Waluk, J. Tautomerization in porphycenes. In *Handbook of Hydrogen Transfer, Volume 1: Physical and Chemical Aspects of Hydrogen Transfer*; Hynes, J. T., Limbach, H. H., Eds.; Wiley-VCH: Weinheim, Germany, 2006.
- (9) Waluk, J.; Müller, M.; Swiderek, P.; Köcher, M.; Vogel, E.; Hohlneicher, G.; Michl, J. Electronic states of porphycenes. *J. Am. Chem. Soc.* **1991**, *113*, 5511–5527.
- (10) Waluk, J.; Vogel, E. Distance dependence of excited-state double proton-transfer in porphycenes studied by fluorescence polarization. *J. Phys. Chem.* **1994**, *98*, 4530–4535.
- (11) Kyrychenko, A.; Herbich, J.; Izydorak, M.; Gil, M.; Dobkowski, J.; Wu, F. Y.; Thummel, R. P.; Waluk, J. Photoinduced double proton transfer: Inter- and intramolecular cases. *Isr. J. Chem.* **1999**, *39*, 309–318.
- (12) Kozłowski, P. M.; Zgierski, M. Z.; Baker, J. The inner-hydrogen migration and ground-state structure of porphycene. *J. Chem. Phys.* **1998**, *109*, 5905–5913.
- (13) Langer, U.; Hoelger, C.; Wehrle, B.; Latanowicz, L.; Vogel, E.; Limbach, H. H. N-15 NMR study of proton localization and proton transfer thermodynamics and kinetics in polycrystalline porphycene. *J. Phys. Org. Chem.* **2000**, *13*, 23–34.
- (14) Malsch, K.; Hohlneicher, G. The force field of porphycene: A theoretical and experimental approach. *J. Phys. Chem. A* **1997**, *101*, 8409–8416.
- (15) Starukhin, A.; Vogel, E.; Waluk, J. Electronic spectra of porphycenes in rare gas and nitrogen matrices. *J. Phys. Chem. A* **1998**, *102*, 9999–10006.
- (16) Gil, M.; Jasny, J.; Vogel, E.; Waluk, J. Ground and excited state tautomerization in 9-acetoxy-2,7,12,17-tetra-*n*-propylporphycene. *Chem. Phys. Lett.* **2000**, *323*, 534–541.
- (17) Even, U.; Jortner, J. Isolated ultracold porphyrins in supersonic expansions. III. Free-base porphine. *J. Chem. Phys.* **1982**, *77*, 4391–4399.
- (18) Sepioł, J.; Stepanenko, Y.; Vdovin, A.; Mordziński, A.; Vogel, E.; Waluk, J. Proton tunneling in porphycene seeded in a supersonic jet. *Chem. Phys. Lett.* **1998**, *296*, 549–556.
- (19) Vdovin, A.; Waluk, J.; Dick, B.; Slenczka, A. Manuscript in preparation.
- (20) Vdovin, A.; Sepioł, J.; Urbańska, N.; Pietraszkiewicz, M.; Mordziński, A.; Waluk, J. Evidence for two forms, double hydrogen tunneling, and proximity of excited states in bridge-substituted porphycenes: Supersonic jet studies. *J. Am. Chem. Soc.* **2006**, *128*, 2577–2586.
- (21) Piwoński, H.; Stupperich, C.; Hartschuh, A.; Sepioł, J.; Meixner, A.; Waluk, J. Imaging of tautomerism in a single molecule. *J. Am. Chem. Soc.* **2005**, *127*, 5302–5303.
- (22) Korotaev O. N.; Personov, R. I. Reversible transformations of luminescent impurity centers in *n*-paraffin matrix upon laser irradiation. *Opt. Spectrosc.* **1972**, *32*, 479–480.
- (23) Völker, S.; van der Waals, J. H. Laser-induced photochemical isomerization of free base porphyrin in an *n*-octane crystal at 4·2 K. *Mol. Phys.* **1976**, *32*, 1703–1718.
- (24) Fickweiler, S.; Abels, C.; Karrer, S.; Bäuml, W.; Landthaler, M.; Hofstädter, F.; Szeimies, R. M. Photosensitization of human skin cell lines by ATPn (9-acetoxy-2,7,12,17-tetrakis-(β -methoxyethyl)-porphycene) in vitro: Mechanism of action. *J. Photochem. Photobiol., B* **1999**, *48*, 27–35.
- (25) Cañete, M.; Ortiz, A.; Juaranz, A.; Villanueva, A.; Nonell, S.; Borrell, J. I.; Teixidó, J.; Stockert, J. C. Photosensitizing properties of palladium–tetraphenylporphycene on cultured tumour cells. *Anti-Cancer Drug Des.* **2000**, *15*, 143–150.
- (26) Karrer, S.; Abels, C.; Bäuml, W.; Ebert, A.; Landthaler, M.; Szeimies, R. M. Topical photodynamic therapy of psoriasis using a novel porphycene dye. *J. Invest. Dermatol.* **1996**, *107*, 112–112.
- (27) Lauro, F. M.; Pretto, P.; Covolo, L.; Jori, G.; Bertoloni, G. Photo-inactivation of bacterial strains involved in periodontal disease sensitized by porphycene–polylysine conjugates. *Photochem. Photobiol. Sci.* **2002**, *1*, 468–470.

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