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ARTICLES

Excitation, Hole-Burning, and Stark Spectroscopy of Free Base Isobacteriochlorin in an *n*-Octane Matrix at Liquid Helium Temperatures

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Excitation spectra of trans-free base isobacteriochlorin in an *n*-octane Shpol'skii matrix at liquid helium temperatures have been obtained. Upon rapid cooling, the guest isobacteriochlorin molecule inhabits two sites (A and B). In the 0−0 region of the lowest lying optical transition, each site displays a series of spectral peaks, which are investigated by photochemical hole burning. This radiant saturation technique confirms pairings of spectral peaks in site A and higher order connectivity of spectral lines and photophysically induced lines in site B. Application of an electric field to the system, while scanning the excitation spectrum, results in an irreversible reduction in intensity of the photophysically formed lines of site B. Evidence is also presented in which molecules inhabiting site B can interconvert to site A by optical means.

Introduction

Free base isobacteriochlorin (H_2iBC) is an isomeric form of bacteriochlorin. In the latter molecule, two pyrrole rings with reduced exterior double bonds are opposite each other, but H_2iBC consists of two pyrrole rings with reduced double bonds that are adjacent to one another. At room and cryogenic temperatures, H_2iBC exists in two stable tautomeric forms, cis and trans (Figure 1).[1] The trans form of H_2iBC readily undergoes photochemical hole burning by a 90° rotation of the inner protons of the molecule.[2] When a dilute solution of H_2iBC in *n*-octane is slowly grown into a single crystal, the excitation spectrum of the system displays several peaks belonging to a single site (A).[2] When H_2iBC is rapidly cooled in an *n*-octane Shpol'skii matrix, as with our experiment, the subsequent excitation spectrum yields a different group of lines assigned to a second site (B). Site A and B for H_2iBC in the *n*-octane Shpol'skii matrix appear in the 0−0 optical transition region for this molecule (580 nm region).[1]

The observation of both sites in our excitation spectrum for H_2iBC in a *n*-octane Shpol'skii matrix is in keeping with experimental results obtained by S. Voelker et al.[3,4,5] and G. Jansen et al.[6] Their experiments documented that porphyrin type molecules can inhabit two sites when rapidly cooled in certain n-paraffins. Note that, Jansen et al.[6] observed a photophysical change of site B in the fluorescence spectrum of palladium porphin in a heptane single crystal. During the course of their experiment, they observed the gradual formation of new spectral lines associated with site B, which they denote as site B′. It was unknown to them at the time whether these lines were formed by a thermally activated process, or whether they were created due to the absorption of light.

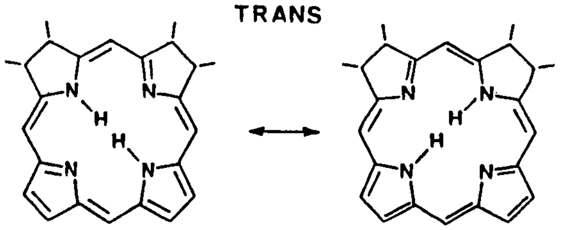

Figure 1. Trans-tautomers of free base isobacteriochlorin. Note that for the trans form, the inner hydrogens can inhabit two identical positions.

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In this work, we examine changes in the excitation spectrum of H_2iBC in an *n*-octane Shpol'skii matrix by way of photochemical hole burning and the Stark effect. In our excitation spectrum, each site (A and B) consists of four intense spectral lines. The hole burning spectra for H_2iBC gives evidence that site A in the *n*-octane single crystal[2] is identical to site A in the *n*-octane Shpol'skii matrix. For H_2iBC in the *n*-octane single crystal, only site A persists. It is only upon rapid cooling of the H_2iBC/*n*-octane matrix that site B forms.

Lines representing site B in the Shpol'skii system are also examined by photochemical hole burning. When specific peaks of site B are illuminated with strong laser radiation, four new lines form in the subsequent excitation spectrum. Upon burning the initial excitation lines of site B and forming the four new lines, we further observe that burning in spectral lines of site B increases the intensities of certain spectral lines attributed to site A. The H_2iBC Shpol'skii system is also subjected to an external electric field while scanning the excitation source. From the Stark effect, we observe minimal broadening for spectral lines in site A, but site B exhibits a lowering of intensities of the four new lines. We examine the implications of photochemical hole burning and Stark spectra of sites A and B for the orientations of H_2iBC in the *n*-octane matrix.

Experimental Section

Free base isobacteriochlorin (H_2iBC) was synthesized using the methods of Egorova et al.[7] A dilute solution (~10^{-6} M) of H_2iBC in *n*-octane is rapidly cooled in a liquid nitrogen bath, while contained in a square quartz cell, and quickly transferred into a tank of liquid helium. The excitation spectrum of trans-H_2iBC is garnered using a Molectron DL II tunable dye laser (with a bandwidth 0.30 cm^{-1} and an average laser power of $\leq$ 180 mW), which is pumped by a Molectron UV 14 nitrogen laser. The laser emission from the dye laser is focused onto a quartz fiber optic strand obtained from Newport Inc., which transports the excitation radiant to the sample. During scanning, the laser emission from the Molectron DL II dye laser is reduced by ~10^{-3} of the full laser power via optical density filters, to prevent photo bleaching the sample trans-isobacteriochlorin. For photochemical hole burning, the optical density filters are removed for 60 to 120 s, while the dye laser is fixed at the maximum of the spectral line of interest. The irradiated sample area is ~6.38 mm^2.

Fluorescence from the excited trans-H_2iBC is collimated by a quartz lens and focused onto a fiber optic bundle. The H_2iBC fluorescence is the passed through an ~600 nm high pass filter, which is detected by a Hamamatsu 1P28 side-on photo multiplier tube. After which, the data is collected in real time by LabView 4.1 software.

A Stark cell is constructed for application of an external electric field to the system. The Stark cell consists of a thin quartz slide, ~0.25 cm thick, coated on one side with tin oxide, which is optically transparent for collection of fluorescence. The effective area of irradiation in the Stark cell is ~5.25 mm^2. The electric field is generated by a Glassman high voltage power supply, where the maximum voltage output is 5 kV.

Results

The excitation spectrum of trans-H_2iBC in an *n*-octane Shpol'skii matrix at 4.2 K is shown in Figure 2(a). The excitation spectrum displays two sets of spectral peaks labeled site A and B. Both sites are examined by photochemical hole burning to obtain a better understanding of how the guest H_2iBC molecules orient in the host *n*-octane Shpol'skii matrix.

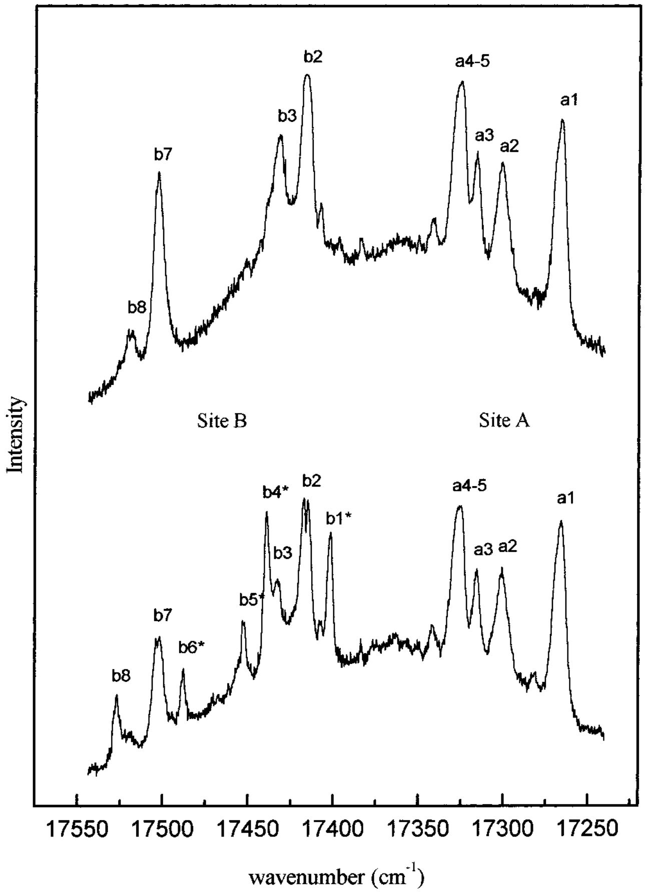

Figure 2. Excitation spectrum of free base isobacteriochlorin in an *n*-octane Shpol'skii matrix before (a) and after (b) probing spectral peak b2 via photochemical hole burning.

TABLE 1: Spectral Peak Positions of Site A

spectral peaks	frequency (cm^{-1})
a1	17 224
a2	17 259
a3	17 275
a4−5	17 284

The excitation spectrum of site A displays four intense spectral peaks in the spectral range of ~17 300 cm^{-1} to 17 200 cm^{-1} (Figure 2a). In the direction of increasing wavenumbers, these four peaks are labeled a1, a2, a3, and a4−5. The maxima of these peaks are given in Table 1. From the frequencies at which the four spectral peaks reside in our excitation spectrum, it is assumed that these peaks are analogous to the five spectral peaks acquired by Johnson et al. for trans-H_2iBC in the single crystal form of *n*-octane.[2] The only discrepancy is that the fourth and fifth peaks of the previous work were partially resolved. These lines in our excitation spectrum are, most likely, unresolved due to an increase in inhomogeneous broadening brought on by greater guest host interactions in the Shpol'skii lattice.

Upon illuminating spectral peak a1, spectral peak a4−5 increases in intensity and vice versa. Molecules that are in resonance with the hole burning frequency appear in the subsequent excitation spectrum as a dip in the a1 spectral line. The hole in spectral line a1 is roughly the same as the bandwidth of the dye laser, ~0.3 cm^{-1}, which is possible because the width of spectral peak a1 is ~7.3 cm^{-1}. The hole created in spectral line a1 is "filled in" when the burning procedure is performed at the peak of the a4−5 spectral line. This reversible relationship is also exhibited between spectral lines a4−5 and a3. The

TABLE 2: Spectral Positions of Site B[a]

spectral lines	frequency (cm^{-1})
b1*	17 360
b2	17 374
b3	17 390
b4*	17 397
b5*	17 411
b6*	17 445
b7	17 460
b8	17 485

[a] *b** Lines appear after burning unstarred lines.

spectral lines of site B are unaffected when probing site A by photochemical hole burning. Because of the coincidence of the spectral positions and separation distance of the photochemically paired lines and the hole burning patterns exhibited for site A, we believe that our site A of H_2iBC in the *n*-octane Shpol'skii matrix is identical to that of site A in the *n*-octane single-crystal acquired by Johnson et al.[2]

Because the environment of the molecules in site A is symmetric, Johnson et al.[2] argued that there would be distinct spectral lines for the two trans tautomers. They also reasoned that the photochemically paired lines were due to specific molecular orientations of H_2iBC in the crystal lattice. Spectral peak a2 does not show any visible effects from the photochemical hole burning process. The inability to burn spectral peak a2 was also observed by Johnson et al. for this molecule in the single crystal.[2] They raised the possibility that spectral peak a2 displays no hole burning features due to the coincidence of several spectral lines caused by a totally symmetric environment experienced the guest molecule in the host lattice.[2] Because of the previous hole burning results of site A for H_2iBC in the single crystal, our experimentation will focus on H_2iBC molecules in site B and their unique relationship to H_2iBC molecules in site A.

Site B of the excitation spectrum of trans-H_2iBC initially displays four spectral peaks, which do not appear in the single-crystal spectrum. In the direction of increasing wavenumbers the spectral lines are designated b2, b3, b7, and b8, in the spectral range of ~17 475 cm^{-1} to 17 330 cm^{-1} (Figure 2a). The wavenumbers at which these peaks appear are given in Table 2. The spectral lines of site B are probed via photochemical hole burning in an identical manner to the hole burning process used to probe site A. Fixing the dye laser emission at ~17 374 cm^{-1}, peak b2, and exposing the sample to the full laser power for 60 s, yields an excitation spectrum that contains four new lines (Figure 2b). Burning any of the spectral lines of site B forms the new spectral lines, but they display greater intensity when formed by burning at line b2. In the direction of increasing wavenumbers the four new spectral lines are designated b1*, b4*, b5*, and b6*. Note that, spectral line b8 appears weakly in the initial excitation spectrum but increases upon the formation of the b* spectral lines, which causes this line to shift in spectral position.

The formation of the b* lines for H_2iBC in an *n*-octane Shpol'skii matrix is similar to a phenomenon observed by Jansen et al.[6] While studying the Zeeman shifts of excited palladium porphin in a heptane single crystal, they initially detected two sites in their single-crystal system, site A and B. During the course of their experimentation, they observed the gradual formation of new spectral peaks associated with site B. They assigned the new lines as belonging to a different site, B′, that is coplanar to site B, and the formation of the lines is due to an in plane 20° rotation of the trapped molecule. It was unknown to them at the time whether these new lines were formed via a thermally activated process, or were created by the absorption of light.[6]

TABLE 3: Summary of the Photochemical Relationships for Lines in Site B. B8″ Indicates No Increase or Decrease of the Line after Burning

peaks probed via hole burning	peaks for which intensity increases or [decreases]							
b1*		b2	b3	[b4*]	[b5*]	[b6*]	b7	b8
b2	b1*		[b3]	b4*	b5*	b6*	[b7]	b8
b3	b1*	[b2]		b4*	b5*	b6*	[b7]	b8″
b4*	[b1*]	b2	b3		[b5*]	[b6*]	b7	b8
b5*	[b1*]	b2	b3	[b4*]		[b6*]	b7	[b8]
b6*	[b1*]	b2	b3	[b4*]	[b5*]		b7	[b8]
b7	b1*	[b2]	[b3]	b4*	b5*	b6*		b8
b8	b1*	[b2]	[b3]	b4*	b5*	b6*	[b7]	

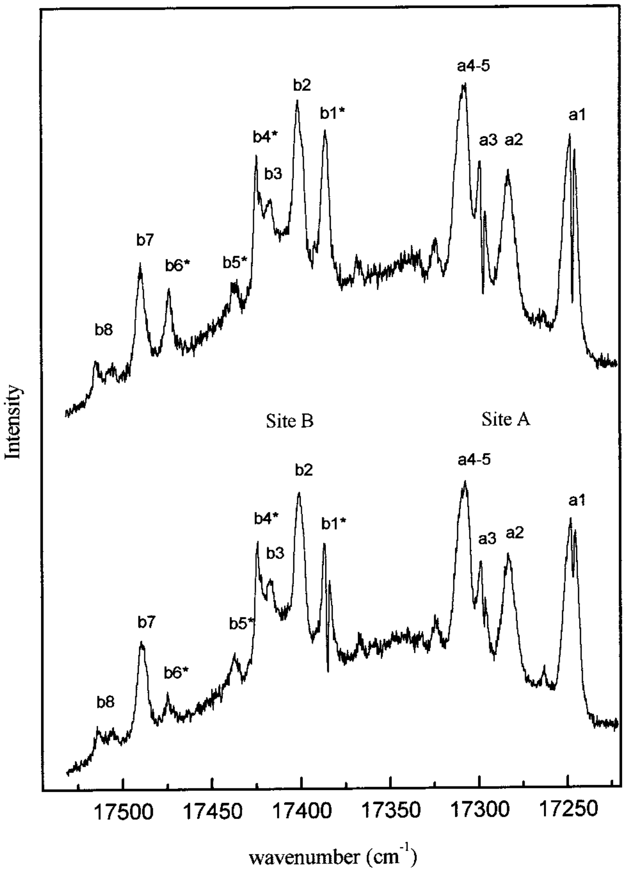

Figure 3. Resulting excitation spectrum after burning spectral peaks a1, a3, and b8 (a) and after burning spectral peak b1′ (b).

Photochemical hole burning experiments on the newly formed lines of site B display photochemical relationships that seem, on first inspection, chaotic. Burning at the maximum of any unstarred spectral line, meaning line b2, b3, b7, or b8, readily forms the four new lines of site B. Forming the new lines burning line b2, we observe a spectral hole in line b2 as well as an overall decrease in intensity of all unstarred lines in site B. This phenomenon is also observed for the new lines of site B as well. By this we mean burning any starred spectral line in site B will decrease the intensity of all starred lines but will increase the intensity of all unstarred lines in site B. A summary of the burning relationship for all lines in site B is given in Table 3.

Once all starred lines are formed by hole burning, certain spectral lines of site B could photochemically interconvert with spectral lines of site A. This is shown in Figures 3a and 3b. In

TABLE 4: Summary of Hole Burning Relationships for Lines of Site A and B

peaks burned in site B	lines that increased in intensity in site A
b1*, b4*	a1, a4−5
b2, b7	a1, a3, a4−5

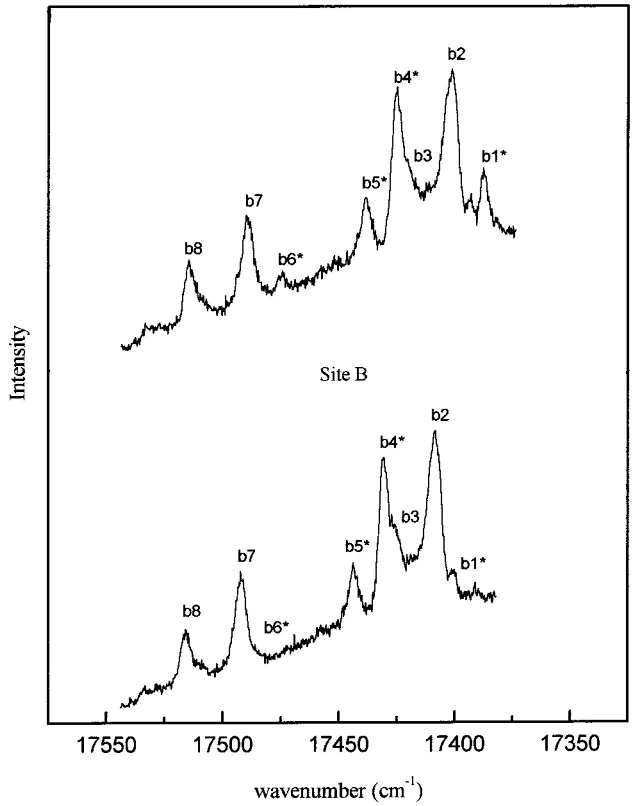

Figure 4. B site spectra before applied external electric field (a) and B site spectrum obtained while applying an external electric field of 11.8 kV/cm (b).

Figure 3(a), spectral lines a1, a3 and b8 are photochemically burned. This is evident by the spectral holes in spectral lines a1 and a3 and of the burning down of line b8. Figure 3b illustrates the “filling” in of these holes after burning spectral line b1*. The spectral lines that have this unique ability are given in Table 4.

Site B is further examined by applying an external electric (Stark) field across the H_2iBC/Shpol’skii system while scanning the dye laser. The result of the Stark effect is an overall reduction in intensity of all starred lines in site B with a concomitant increase in intensity of unstarred lines. Surprisingly, line b8 also decreases in intensity upon experiencing the external electric field, which leads to ambiguities as to whether this spectral line is truly a b or b* line. The reduction in intensity of the starred lines only occurs while the electric field is active with the dye laser scanning. Note that after the formation of the starred lines, Stark experiments are performed with no further hole burning in site B. The spectral lines of site A only exhibit minimal Stark broadening.

The spectra indicating the lowering of the overall intensity for the starred lines while experiencing the external electric field are shown in Figure 4, parts a and b. Figure 4(a) is a truncated version of site B from the entire excitation spectrum. Figure 4b is the same truncated spectrum experiencing an electric field of 11.8 kV/cm. Upon comparison, Figure 4b displays a drop in spectral intensity for all starred lines in site B. A minimum electric field of 7.87 kV/cm is needed to initiate this effect.

Discussion

Because of molecular similarities in H_2iBC and porphin, we discuss the orientation of H_2iBC in an *n*-octane matrix with respect to porphin. In a Monte Carlo calculation of porphins embedded in an *n*-octane matrix, Koehler[8] presented evidence that in site A the guest porphin displaces two host *n*-octane molecules, and the plane of the molecule is positioned in the b−c plane of the crystal (Figure 5). Site B involves displacement of three *n*-octane molecules, with the molecular plane positioned in the crystal a−c plane (Figure 6).

In each of these sites, there are four likely minimum orientations of the molecule corresponding to successive rotations by 90° about the z (out of plane) axis. In site A, the appearance of only five lines, one (a2) which does not burn, can be explained if one orientation is sufficiently symmetric that two orientations are identical, resulting in the coincidence

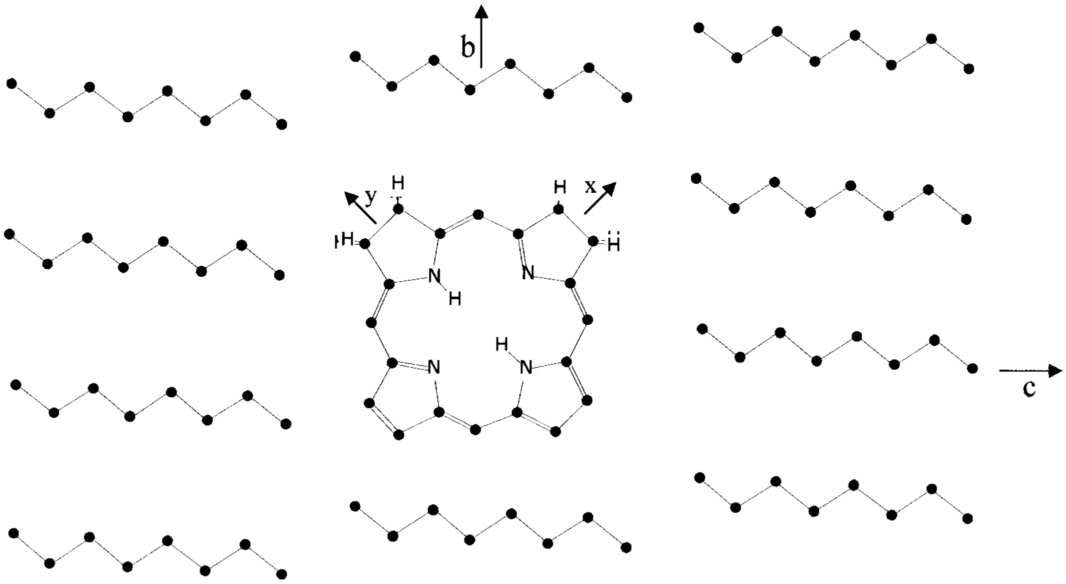

Figure 5. Diagram of H_2iBC in site A. The *n*-octane crystal is shown in the b−c plane perpendicular to crystal axis a. The *c* axis is horizontal. The H2iBC molecule is shown in the x−y in plane perpendicular to the molecular *z*-axis.

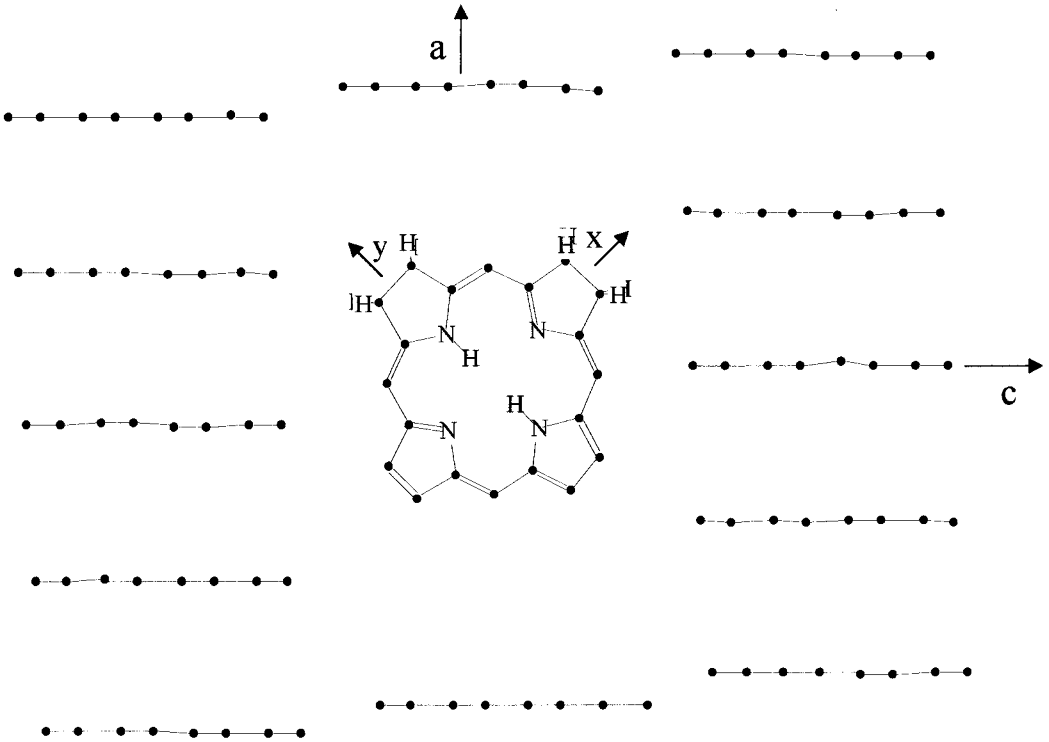

Figure 6. Diagram of H_2iBC in site B. The *n*-octane molecule is shown in the a−c plane perpendicular to crystal axis b. The *c* axis is horizontal.

of four lines. In site B, the fact that only four lines appear initially indicates that either only two of the orientations are occupied on cooling, with both phototautomers present, or that all four orientations are occupied with only one phototautomer in each orientation. The latter would most likely result in pairwise burning patterns. However, we observe that burning in any of the initial four lines results in four new lines. This can be explained only if molecules can be photophysically rotated in plane by 90° upon burning. This indicates that only two orientations, with both phototautomers, are initially occupied, and that burning causes tranformation among all eight possible configurations.

Koehler's[8] analysis was based on crystallographic data for *n*-octane obtained by Mathisen et al.[9] at 90° K. Using these results alone, it is difficult to explain our results upon burning site B. However, recent findings Neumann et al.,[10] via neutron diffraction studies, confirm the *n*-octane structure obtained by Mathisen et al. for temperatures greater than 55 K, but below this temperature they observed a phase change for the crystal lattice that led to a doubling of the (longitudinal) *b* axis of the unit cell.[10] The existence of this phase change provides a reasonable explanation for our results. Because the unit cell is doubled along the crystal *b* axis below 55° K, the molecular environment is somewhat of lower symmetry than above 55° K, allowing for more distinct orientational sites. Furthermore, on burning at these laser powers, some local heating is inevitable, resulting in possible elevation of the local temperature above the phase transition. This would allow rotation of molecules and most likely reorientation of molecules in site B, which would lead to transformation among the configurations.

The phase change for *n*-octane, prompted by localized heating during excitation, also explains the ability to burn from lines in site B to lines in site A. During excitation, localized heating causes a softening of the *n*-octane lattice. The relaxed environment of, the normally rigid matrix, allows for molecules in site B to photophysically transform into lines of site A, even with the sites being perpendicular in the *n*-octane lattice. We leave for later experimentation the observations of the Stark effect results.

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