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# Photochemistry and Hole-Burning of Free-Base Porphin and Chlorin in *n*-Alkane Hosts at 4.2 K

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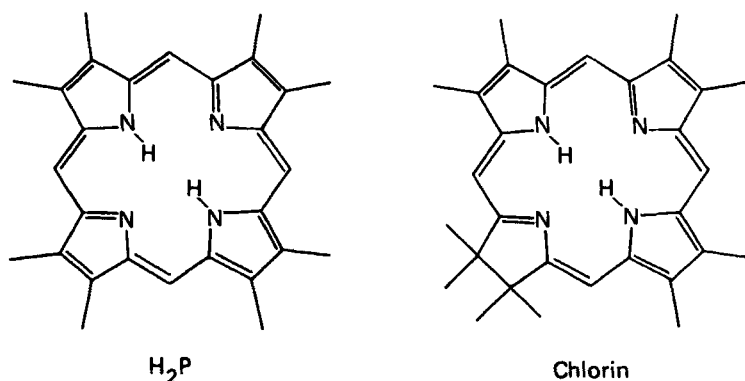
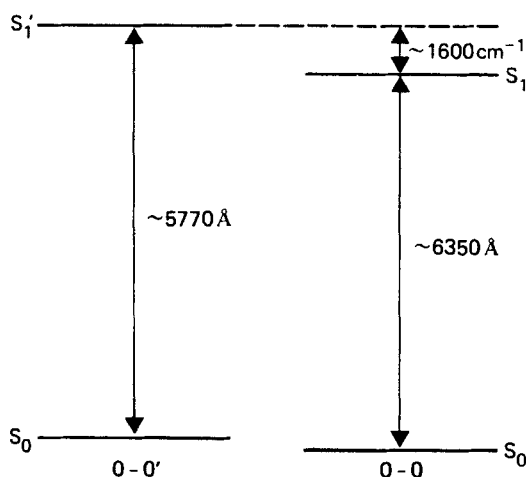
(Received July 2, 1978)

It is known that the porphyrin free-base ( $H_2P$ ) is incorporated in an *n*-octane crystal in an oriented fashion in at least two different sites (*A*, *B*).<sup>1,2</sup> In each of these sites two tautomeric forms occur (1, 2) which have their  $N-H \cdots H-N$  axes at right angles. Due to a difference in interaction with the crystalline host for the two orientations, the optical spectra show a doublet structure for each site.<sup>1</sup> The separation between the doublet components depends both on the *n*-alkane host and on the site occupied.<sup>2</sup>

By selective excitation into the  $S_1 \leftrightarrow S_0$  transition of a given site, one tautomer can be transformed into the other.<sup>3,4</sup> Holes can be burnt into these inhomogeneously broadened lines at low temperatures,<sup>3,5</sup> and in this way the homogeneous linewidths can be obtained.<sup>5</sup> From a study of the broadening and frequency shift of holes in the 0–0 lines as a function of temperature, the dephasing mechanism was proposed.<sup>6</sup>

Here we compare the mechanism of phototautomerization of  $H_2P$  and chlorin (an asymmetric  $H_2P$  with a reduced pyrrole ring) [Figure 1].

The measurements were made at 4.2 K in *n*-alkane hosts using single vibronic level excitation. The spectral positions of both tautomers, and the relative rates of their isomerizations show remarkable differences between the two molecules. Because of the symmetry, in  $H_2P$  the two tautomeric forms are only distinguished by the crystal field of the *n*-alkane host. Here the energy difference between the two 0–0 lines is in the range of 0 to  $100\text{ cm}^{-1}$ .<sup>2</sup> On the other hand, in chlorin this separation is around  $1600\text{ cm}^{-1}$  and arises from the intramolecular asymmetry. This asymmetry leads to one tautomer being preferred over the other. The most stable tautomer absorbs at  $\sim 6350\text{ Å}$  and

FIGURE 1 Molecular geometry of free-base porphyrin ( $\text{H}_2\text{P}$ ) and chlorin.FIGURE 2 Energy level diagram for the  $S_1 \leftarrow S_0$  transition of the two tautomers of chlorin at  $\sim 5770 \text{ \AA}$  ( $0-0'$ ) and  $\sim 6350 \text{ \AA}$  ( $0-0$ ).

the other at  $\sim 5770 \text{ \AA}$  [Figure 2]. In *n*-hexane there are four principal  $0-0$  lines for each tautomer corresponding to different orientations of the molecules in the host lattice [Figure 3a]. Each of the lines in Figure 3a can be reversibly interconverted to each of the lines of the other tautomer by selective irradiation [Figures 3b,c,d]. It was found that the  $6350 \text{ \AA}$  form is produced  $10^3$  times faster than the  $5770 \text{ \AA}$  form. This result is in contrast to  $\text{H}_2\text{P}$  where the rates of transformation between both forms are equal. Exciting into the Soret band of  $\text{H}_2\text{P}$  and chlorin restores the equilibrium distribution of the tautomers.

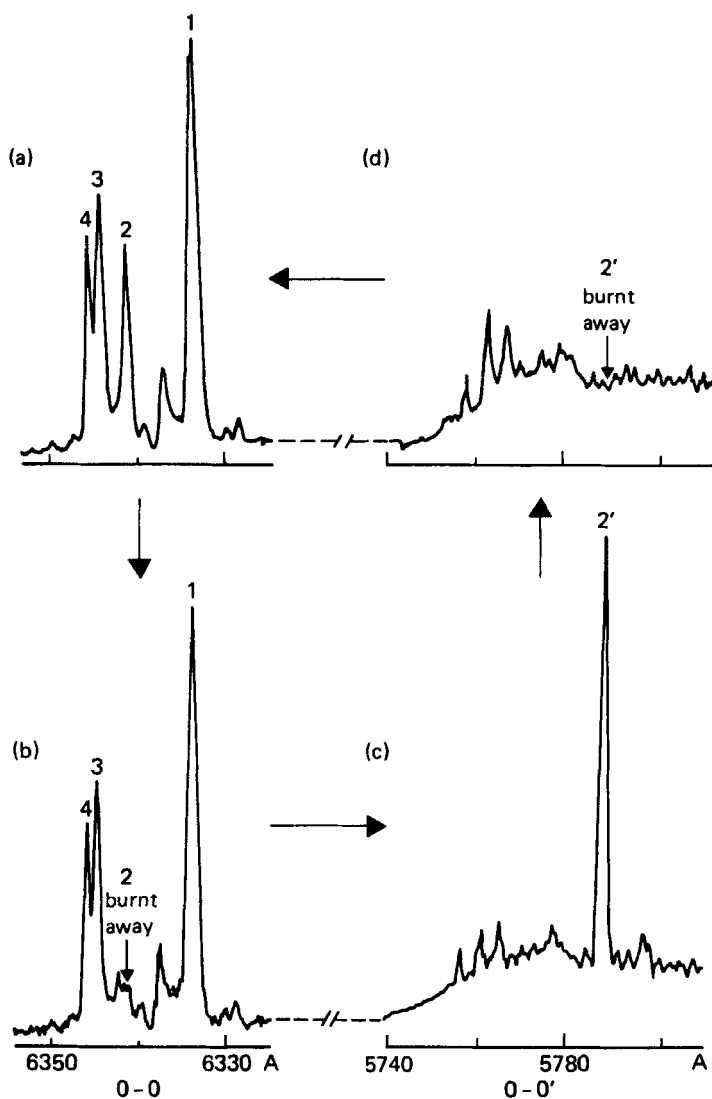


FIGURE 3a Excitation spectrum of the 0-0 transition ( $S_1 \leftarrow S_0$ ) of chlorin in *n*-hexane at 4.2 K.

FIGURE 3b The same as a after irradiation in line 2.

FIGURE 3c Excitation spectrum of the 0-0' transition ( $S'_1 \leftarrow S_0$ ) of chlorin in *n*-hexane at 4.2 K after burning line 2, showing the appearance of line 2'.

FIGURE 3d The same as c after irradiation in line 2'.

Thermally induced tautomerism was observed in both sites of  $\text{H}_2\text{P}$  in *n*-octane. In the *B*-site the low energy line ( $B_2$ ) is completely transformed to the high energy line ( $B_1$ ) when the temperature is increased to  $\sim 100$  K. The *A*-site behaves very differently. At temperatures of  $\sim 200$  K the intensities of  $A_1$  and  $A_2$  are approximately equal and no burning is observed.

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