

Nonphotochemical hole burning and antihole production in the mixed molecular crystal pentacene in benzoic acid

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(Received 22 March 1982; accepted 27 April 1982)

Results of narrowband hole burning experiments and picosecond photon echo experiments on pentacene in benzoic acid are presented. On burning, several new discrete pentacene absorptions (antiholes) are created. These spontaneously revert to the unburned form at low temperatures, but may also be induced to revert by optical excitation. Deuteration of the host acidic protons markedly changes the pentacene fluorescence lifetime and hole burning and recovery behavior, indicating the strong interaction of pentacene and the benzoic acid dimer hydrogen bonds. Hole burning and antihole formation are attributed to hydrogen bond tautomerism of benzoic acid dimers near excited pentacenes. Two mechanisms for this tautomerization are suggested. The homogeneous linewidth of the pentacene $S_0 \rightarrow S_1$ transition is measured by both photon echo and hole burning experiments. A preliminary study of the homogeneous linewidth measured by hole burning indicates the transition broadens with an 11 cm^{-1} thermal activation energy, which differs from measurements made by other methods.

I. INTRODUCTION

Nonphotochemical hole burning has been observed in a wide variety of glasses at low temperatures.¹ In those experiments, optical excitation of a chromophore, such as tetracene, induces a mechanical rearrangement of the local glass environment which changes the chromophore excitation energy. If an excitation laser with bandwidth much narrower than the inhomogeneously broadened chromophore absorption band is used, the optically induced rearrangement of the glass results in a decrease in the number of molecules resonant with the laser and an increase in the number of molecules in the rest of the inhomogeneously broadened band. The net result is that a hole is formed in the absorption band in the immediate spectral vicinity of the irradiating laser frequency, i.e., the absorbance is decreased at the laser frequency. The changes in absorbance, the holes, are persistent at low temperature. They have been observed to last many hours after cessation of irradiation and have depths 10%–20% of the total absorbance. Holewidths have been interpreted in terms of the chromophores' homogeneous linewidths.

In this paper, we report the results of narrowband cw dye laser hole burning experiments and picosecond photon echo experiments on the mixed molecular crystal system pentacene in benzoic acid (PC/BZA). Excitation of the pentacene $S_0 \rightarrow S_1$ transition results in hole burning in the pentacene inhomogeneous line.² This is a rare example of nonphotochemical hole burning in a crystalline system, i.e., hole burning involving a structural rearrangement of the matrix. This system also provides the opportunity to compare the results of hole burning experiments and photon echo experiments. In the PC/BZA system, spontaneous hole filling is observed at 1.5 K. The recovery of the hole absorbance occurs with a half-life on the order of one-half hour.

In PC/BZA, hole burning results in the creation of several distinct new pentacene sites in the crystal.

These are evidenced by the appearance of sharp new spectral features outside of the original pentacene inhomogeneous line. For convenience, these features will be called antiholes, although their width is considerably larger than the corresponding hole. A detailed discussion of their properties is presented below. Four new pentacene origins with associated vibrational progressions can be identified. This is in marked contrast to the situation found in glass systems, wherein antiholes are not observed. The spectrum associated with each antihole disappears with a characteristic rate as the sample spontaneously reverts to its unburned state. BZA exists as hydrogen bonded dimers in the crystalline state.³ In *d*-BZA (benzoic acid with the acidic protons replaced by deuteriums) burning and recovery are much slower than in *h*-BZA (the fully protonated form).² This, the discrete nature of the antiholes, and the known bistability of the BZA hydrogen bonds⁴ suggests that hydrogen bond tautomerization of the host is involved in the hole burning mechanism. Photochemical hole burning due to proton tautomerization of free base porphyrin has been extensively studied.⁵ In that case the host is inert, usually an alkane crystal, and the tautomerization occurs on the chromophore itself.

II. EXPERIMENTAL

Two different spectroscopic setups were used in the hole burning experiments. A Coherent model 599-21 single mode scanning cw dye laser pumped by 2.5 W of the 514 nm line of a Spectra Physics model 171 argon ion laser was used for hole burning. Maximum dye laser power was $\sim 40 \text{ mW}$ with $\sim 3 \text{ MHz}$ bandwidth. A Molelectron DL200 nitrogen-pumped dye laser was used for excitation and emission spectra. Holes and antiholes were monitored by fluorescence excitation using suitable filters and an EMI 9658 PMT. A Jarrel Ash 1 m scanning double monochromator was used for measuring fluorescence spectra.

In the second setup, a Coherent 599-21 single mode cw dye laser pumped by 2 W of the 514 nm line of a Lixel model 95 argon ion laser was used for hole burning with approximately the same power and bandwidth. A Spex 1 m monochromator and 150 W arc lamp were used for excitation and emission spectra.

The fast decay times of large molecules require high-energy, tunable, picosecond light pulses to perform photon echo experiments. These are provided by a mode-locked, cavity-dumped dye laser synchronously pumped by the frequency-doubled output of a cw-pumped, acousto-optically mode-locked and Q-switched Nd:YAG laser. This dye laser system provides a very stable source of 30 ps, 20 μ J pulses at a 400 Hz repetition rate. A dye laser single pulse passes through a network of beam splitters and a motorized optical delay line. This splits the pulse into a sequence of excitation pulses with appropriate intensities and variable temporal delays for the photon echo experiments. The excitation pulse sequence is then directed to the sample, located in a liquid-helium Dewar. The generated echo signal leaves the sample and is temporally, spatially, and frequency selected by summing with a single 80 ps IR pulse. The up-converted echo signal is then detected. Further details of the experimental procedures appear elsewhere.⁶

Pentacene fluorescence lifetimes were measured by exciting into the $S_0 - S_1$ origin with the pulsed picosecond dye laser described above. Very low concentration crystals were used to avoid reabsorption. A computer-interfaced Tektronix R7912 transient digitizer and a low noise, low ringing RCA 1P28A PMT⁷ were used to measure fluorescence decays. Several hundred decays were averaged in each case to remove noise.

The PC/BZA crystals were grown from the melt by the Bridgman technique. The pentacene, obtained from Aldrich, was used after vacuum sublimation. Benzoic acid (Baker analyzed reagent 0076) was recrystallized from deionized H₂O and extensively zone refined (~300 passes) before use. Monodeuterated benzoic acid (acid proton substitution, *d*-BZA) was prepared by refluxing a nearly saturated solution of zone-refined BZA in D₂O for ~24 h followed by recrystallization by slow cooling to 0 °C and filtering. The refluxing, recrystallization, and filtering procedure was repeated three or four times. Deuteration, measured by NMR, was ~95% complete.

Crystal samples were mounted such that the *a* axis polarized PC transition was parallel to the laser polarization. Liquid He temperatures were measured with calibrated pressure gauges.

III. RESULTS AND DISCUSSION

A. Photopopulated sites (antiholes)

An excitation spectrum of unburned PC/*h*-BZA is shown in the lower trace of Fig. 1(a). The PC zero-phonon line (ZPL) occurs at 5880 Å with a phonon sideband peaking +33 cm⁻¹ to the blue. The PC first vibration with its phonon sideband occurs +251 cm⁻¹ above the origin at 5794.5 Å. The lower trace of Fig. 1(b) is

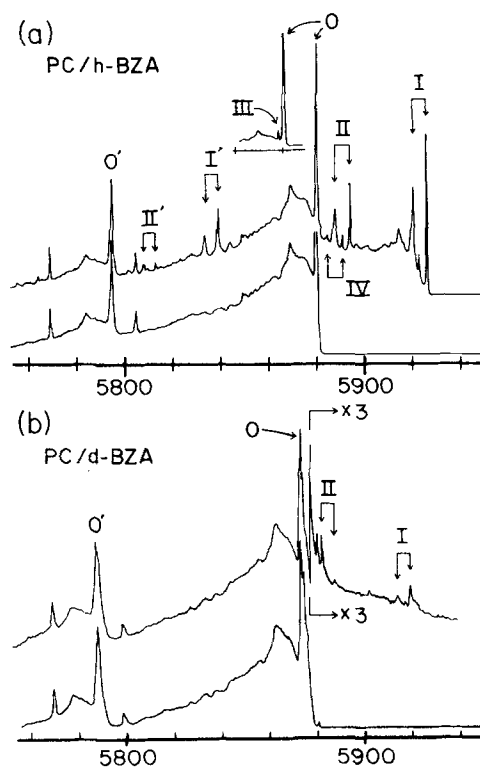


FIG. 1. (a) Excitation spectra of PC/*h*-BZA at 1.4 K recorded by monitoring fluorescence to the red of 640 nm. The PC singlet electronic origin and first vibration are labeled *o* and *o'*. The lower and upper traces were recorded before and after hole burning at *o'*, respectively. Hole burning creates several new distinct PC absorptions, labeled I–IV with primes indicating the associated vibronic transitions. The inset shows site III, which is absent in the main spectrum (see the text). (b) Excitation spectra of PC/*d*-BZA at 1.4 K. Note the blue PC spectral shift on deuteration and the much weaker antihole peaks due to low burning efficiency. The broader peaks are believed to result from incomplete deuteration.

an excitation spectrum of unburned PC/*d*-BZA. The PC first vibration energy is +249 cm⁻¹ in this host. The inhomogeneous broadening in *d*-BZA is much greater than in *h*-BZA. Incomplete deuteration (~95%) is the probable cause of this, with successive maxima (from blue to red) in the PC/*d*-BZA spectrum, corresponding to decreasing numbers of deuterated BZA molecules in the immediate PC environment. A very weak peak of PC surrounded by protonated BZA dimers is also observed in the PC/*d*-BZA spectrum at the same frequency as the PC/*h*-BZA ZPL.

Hole burning in *d*-BZA was performed at the maximum of the inhomogeneous line at ~5873 Å, +21 cm⁻¹ from the PC/*h*-BZA ZPL. The blue shift of the PC lowest singlet transition upon host deuteration is probably due to lattice expansion. The hydrogens in the BZA dimer hydrogen bond experience a double-well tautomerization potential.^{4,6} In double-well systems, the hydrogen bond length is known to increase upon deuteration.⁹ Lattice expansion was observed in 1939 by examination of x-ray single crystal rotation photographs of *h*-BZA and *d*-BZA.¹⁰ Lattice expansion in *d*-BZA destabilizes (due to decreased van der Waals interactions) the more

polarizable PC S_1 state more than the S_0 state, causing the blue spectral shift.

Excitation spectra of burned PC in both BZA hosts are shown in the upper traces of Figs. 1(a) and 1(b). In each case, several new distinct spectral features appear. The two most prominent antiholes, site I at -131 cm^{-1} and site II at -40 cm^{-1} , each clearly exhibit a phonon sideband and an $\sim 250 \text{ cm}^{-1}$ vibration, much like the unburned line. A third site, shown in the inset of Fig. 1(a), is located $+7 \text{ cm}^{-1}$ to the blue of the unburned ZPL. It was observed only in PC/*h*-BZA and only after burning with full dye laser intensity at the origin. No vibration or phonon sideband was observed for this antihole, presumably due to its small population and occlusion by the phonon sideband of the unburned PC line. Site IV is very weakly populated but has a long recovery time and is located at -31 cm^{-1} . A small, possibly fifth site appears beneath site I at -122 cm^{-1} .

Fluorescence spectra of sites I and II have the same structure as the fluorescence spectrum of the unburned origin. This, the similarity in the absorption spectra and the relatively small spectral shifts of the antiholes, indicates that the new sites are PC molecules in an environment which is altered only slightly from that of unburned PC. The narrowness and discrete nature of the antiholes observed here indicates that very distinct and well defined environmental changes have occurred.

Sites I and II each exhibit a very noticeable absorption peak 16 and 18 cm^{-1} , respectively, to the blue of the ZPL. That these peaks are not independent PC antiholes is demonstrated by the fact that fluorescence spectra taken by exciting into these absorption peaks are identical to those taken by exciting into the respective antihole ZPLs. This suggests that a burned PC has a double-well excited-state potential energy surface. Interaction between states in the two sides of the well produces an excited state splitting giving rise to the $\sim 17 \text{ cm}^{-1}$ pseudolocal phonon. None of the fluorescence spectra exhibit the 17 cm^{-1} splitting, however, suggesting that the ground state potential surface has only a single minimum. This description is similar in spirit to the recent calculations of Craig and co-workers¹¹ which demonstrated that an excited state can have a double-well potential surface while the ground state has a single minimum.

The absorbance of each of the antiholes decays exponentially with time. In *h*-BZA at 1.4 K sites I–III exhibit ~ 45 , ~ 6 , and ~ 18 min reversion times, respectively. Site IV exhibited a very long reversion time, greater than an hour. The reversion rates in *d*-BZA are much slower; ~ 130 min for site I, >3 h for sites II and IV. Some variation in antihole decay times was observed for different samples and a sample cycled from room to liquid He temperatures on successive days exhibited different antihole decay times on different cycles.

The ZPLs of the antiholes are themselves inhomogeneously broadened, even when the holes burned to create them are quite narrow. For example, a 1 GHz wide hole burned in the unburned 5.6 cm^{-1} wide ZPL of PC/*h*-BZA produced an ~ 12 GHz wide ZPL at site I into

which a 35 MHz wide hole could be burned. Similar behavior was observed for site III. This demonstrates that the 12 GHz width is an inhomogeneous broadening. This 12 GHz width is only a fraction of the full, $\sim 3.5 \text{ cm}^{-1}$ inhomogeneous width of site I.

When two 1 GHz wide holes were burned 20 GHz apart in the unburned ZPL, two site I antiholes were observed with about 10 GHz separation between their maxima and each having an ~ 12 GHz width (see Fig. 2). The lower energy hole was found to be responsible for the lower energy antihole. Thus, there is a strong correlation between the position of the hole burned in the inhomogeneous line and the position of the resulting antihole.

The above facts give some insight into the nature of the lattice perturbations responsible for inhomogeneous broadening. Burning causes a local lattice change, e.g., tautomerization of the BZA hydrogen bonds (see Sec. III C), large enough to significantly alter the PC transition energy. At the same time, additional lattice disorder is introduced, resulting in an antihole which has inhomogeneous broadening (12 GHz) greater than the associated hole (1 GHz). However, other sources of inhomogeneous broadening exist which are not greatly altered by the hole burning. Hence, a correlation exists between the spectral positions of the holes and the antiholes as depicted in Fig. 2. Thus, a local mechanical perturbation, i.e., hole burning, can produce inhomogeneous broadening, presumably local in nature, independent of long range influences such as crystal strains formed during crystal growth or handling. However, the type of local mechanical change which arises from hole burning in this system does not completely erase memory of inhomogeneous broadening originally present in the unburned system. These results indicate that inhomogeneous broadening has both local and nonlocal components.

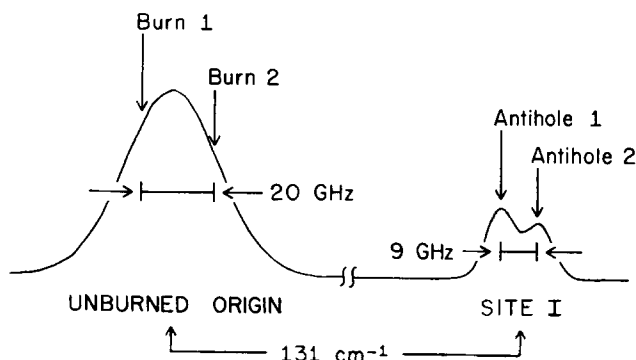


FIG. 2. Diagram depicting the effect of burning multiple holes in the unburned origin inhomogeneous line. A single 1 GHz wide hole (burn 1) produces an inhomogeneously broadened 12 GHz wide antihole (antihole 1) at site I. The broader antihole indicates that additional local inhomogeneity is introduced by burning. Burning a second 1 GHz wide hole (burn 2) 20 GHz from the first produces another inhomogeneously broadened antihole (antihole 2) 9 GHz from antihole 1. The correlation between hole position and antihole position indicates a nonlocal source of inhomogeneous broadening which is unaffected by the local changes due to hole burning.

TABLE I. Summary of fluorescence decay, photon echo, and hole burning results for penta-cene and deuterated benzoic acid.

	$2T_1$	T_2 (photon echo)	T_2 (hole burning)	Relative hole burning efficiency	Relative hole recovery rate
PC/ <i>h</i> -BZA	40 ns	39 ns	32 ns	1	1
PC/ <i>d</i> -BZA	18 ns	17 ns	15 ns	1/100	1/3

B. Lifetimes, photon echoes, and hole behavior

In *h*-BZA the PC fluorescent lifetime T_1 is 20.0 ± 0.5 ns. Photon echo experiments performed at low concentration and under appropriate low optical density conditions¹² yielded $T_2 \sim 40$ ns. Although there is some uncertainty in this result due to signal loss from hole burning during echo experiments, within experimental error $T_2 = 2T_1$ at 1.4 K. Thus, the homogeneous linewidth is due to lifetime broadening. The PC fluorescence lifetime in *d*-BZA (5873 Å peak) is dramatically shortened to 8.9 ± 0.5 ns. Here, the photon echo experiment did not suffer from signal loss, due to the low hole burning efficiency, and it was found that $T_2 = 18$ ns, again within experimental error of $2T_1$.

The substantial shortening of the PC lifetime in *d*-BZA is remarkable; presumably arising from a large increase in the molecule's nonradiative relaxation rate as is the case, e.g., for two of the four PC sites in *p*-terphenyl.¹³ Deuteration of the BZA's acidic hydrogens does not alter the BZA crystal structure, save for a slight lattice expansion resulting in a small, 20 cm^{-1} PC blue spectral shift (*vide supra*). However, the change in lifetime on deuteration of BZA is comparable to the variation observed among the PC sites in *p*-terphenyl, which have sizable site-to-site structural variations.¹³ These considerations indicate that the PC electronic states are extremely sensitive to subtle changes in the hydrogen bond structure of the BZA, i.e., there is sizable interaction between PC and the lattice hydrogen bonds.

In the limits of low intensity and short burn time,¹⁴ the widths of the holes burned in PC/BZA gave approximately the homogeneous linewidths determined by photon echo experiments (see Table I). In *h*-BZA (*d*-BZA), the narrowest holes burned yielded homogeneous linewidths of ~ 10 MHz (~ 22 MHz), while $(\pi T_2)^{-1}$, measured by photon echo, is 8 MHz (18 MHz). Such a discrepancy is not unusual in hole burning, due to the combined effects of laser bandwidth and low signal to noise in the limits of low intensity and short burn time.

As reported in Ref. 2, the hole burning efficiency in PC/*h*-BZA is 10^{-5} to 10^{-6} per PC excitation. Hole burning in PC/*d*-BZA was observed to be roughly 1% as efficient as in *h*-BZA. In both hosts, however, antiholes were more readily produced when the PC first vibration $\sim 250 \text{ cm}^{-1}$ above the origin was excited. It was not possible to burn narrow holes in this vibration and burning uniformly decreased absorption of the origin. Thus, the homogeneous linewidth of the vibration is comparable to the origin's inhomogeneously broadened width

($\sim 3 \text{ cm}^{-1}$). This is consistent with experiments measuring the dephasing time of this vibration in the mixed crystal PC in naphthalene in which T_2 was found to be 4–7 ps.¹⁵ The significant homogeneous width of the PC first vibronic transition allows essentially all PC molecules to be simultaneously excited with a narrowband source. This is in marked contrast to the PC origin, wherein the very narrow homogeneous linewidth permits only a small fraction of the PCs to be excited with a narrowband source. This consideration is probably responsible for the difference in antihole production of the two transitions.

Preliminary measurements of the pure dephasing contribution to the homogeneous linewidth, i.e., the linewidths determined by hole burning with the (presumably temperature independent) lifetime contribution removed, are displayed in Fig. 3 as a function of inverse temperature. The pure dephasing T_2^* was found to have a thermal activation of the form

$$(\pi T_2^*)^{-1} = \Gamma e^{-\Delta E/kT}$$

for $\Gamma \approx 9 \text{ GHz}$ and $\Delta E = 11 \text{ cm}^{-1}$ over the range 1.4–4.2

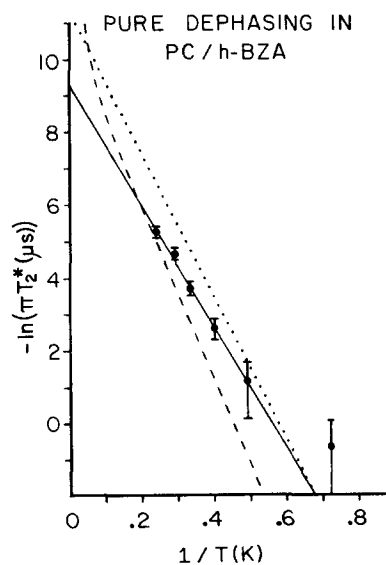


FIG. 3. Plot of the pure dephasing contribution to the homogeneous linewidth as a function of inverse temperature. The hole burning data, indicated by the large dots and fit by the solid line, were obtained by removing the contributions of both the excited state lifetime and 3 MHz laser bandwidth from the measured holewidths. The error bars are $\pm 15\%$ error limits. The dashed line is a representation of the results of Wiersma and co-workers (Ref. 16) and the dotted line those of Andrews and Hochstrasser (Ref. 17).

K. Wiersma and co-workers¹⁶ have measured the temperature dependence of the homogeneous line broadening by accumulated photon echo and absorption experiments from 1.4–25 K. At low temperature, their data is of the above form with $\Gamma = 45$ GHz and $\Delta E = 16.7$ cm⁻¹. Andrews and Hochstrasser¹⁷ also have measured the line broadening from 4.5–10 K by coherent Stokes Raman scattering, finding $\Gamma = 93$ GHz and $\Delta E = 13.8$ cm⁻¹. It is seen from Fig. 3 that the three measurements do not agree. The reason for the discrepancies is not known at this time. A detailed analysis of the relationship of the various experimental observables to the homogeneous linewidth has begun¹⁸ and additional experiments are in progress.

Nonphotochemical hole burning in glasses at low temperature creates holes which are stable as long as the temperature is not raised.¹ The holes burned in the PC/BZA origin recover completely at low temperature. The recovery is nonexponential, as would be expected for the reversion of several types of antiholes, each at a different rate. This in itself does not fully explain the observed hole recovery, however. The holes universally exhibit an initial, fast recovery (a few seconds) followed by a slower recovery on the time scale of the antihole recoveries. The fast recovery is burn intensity dependent, being ~ 4 s at 4 mW/mm² intensity and ~ 20 s at 0.4 mW/mm² intensity. It may be due to the fast recovery of relatively unstable antiholes and may involve bulk crystal heating effects at higher intensities. The nonexponential long hole recovery occurs on a 10–30 min time scale and is independent of burning conditions.

An intensity dependence was observed for the depth and width of the long-lived portion of the holes. At low burning intensities, relatively narrow deep holes were burned, whereas for the same fluence at higher intensity, a broader, more shallow hole of approximately the same total area was formed. The increased width at high intensity could partly result from power broadening. At the highest laser intensity used ~ 40 mW/mm², the Rabi frequency ω_1 is 120 MHz, easily sufficient to produce a power broadening contribution to the hole-width.

Burning an antihole can cause reversion to the unburned state, i. e., erasure of the antihole. Antiholes were created by burning into the PC first vibronic transition. The site I antihole was then burned on successive trials at various positions in its phonon sideband. The phonon sideband was illuminated to excite all site I PC molecules with the narrow band laser. In each trial, excitation spectra recorded before and after burning revealed that the site I peak height had decreased and the unburned origin peak height had increased. The reversion efficiency was roughly constant at each position in the phonon sideband that was tested (every 7.5 cm⁻¹ from 2.5 to 47.5 cm⁻¹ to the blue side of the site I ZPL). Burning a narrow hole in the inhomogeneously broadened site I ZPL (see Sec. III A) presumably also causes reversion.

Similar antihole disappearance was observed when the sites II and IV phonon sidebands in the region just to the

red of the unburned ZPL were illuminated. The overlap of these phonon sidebands with the unburned ZPL gives rise to the interesting observation that hole burning can cause hole filling. A 1 GHz wide hole was first burned at the center of the unburned ZPL. When an identical second hole was burned a few GHz away, the first hole was $\sim 25\%$ filled by the burning of the second. This phenomenon was found to be independent of hole separation. The laser, in burning the second hole, overlaps with the phonon sidebands of PCs in sites II and IV and causes partial hole filling by forcing the sites II and IV environments to revert to the unburned state. Because burning causes only partial alteration of the environment about a PC (see Sec. III A), PCs in sites II and IV environments which revert to the unburned state can be expected to return to that part of the unburned inhomogeneous line from which they originated, filling the first hole. The small population of sites II and IV relative to site I ($\sim 1:3$) might be explained in part by the fact that, even in burning a single hole in the unburned inhomogeneous line, their phonon sidebands are resonant with the burning laser. Hence, an equilibrium between simultaneous creation and reversion of these antiholes exists.

Note that the hole filling behavior described here is distinctly different from that observed in glasses.^{1,19} Nonphotochemical hole burning in glasses results from environmental changes, which cause some molecules originally resonant with the burning laser, to be shifted slightly off resonance. The degree of filling of a hole by burning a second nearby hole yields information about the size of the resonance shift experienced by molecules during the second burn. For example, when Hayes and Small¹⁹ burned two holes 3 cm⁻¹ apart in the tetra-cene $S_0 \rightarrow S_1$ absorption in an ethanol-methanol glass, no hole filling was observed. For a 1.5 cm⁻¹ hole separation, however, hole filling was observed, allowing them to conclude that roughly 45% of the spectral shifts were less than 2 cm⁻¹. The hole filling behavior in PC/BZA crystals is due to antihole reversion caused by burning in the antihole phonon sideband.

C. Burning mechanisms

The observed hole burning behavior in PC/BZA is related to the hydrogen bonds of the host dimers as evidenced by the dramatically different behavior of PC/*h*-BZA and PC/*d*-BZA and the absence of hole burning in PC in other hosts such as naphthalene and *p*-terphenyl. The discrete nature of the hydrogen bond bistability and the appearance of discrete antihole spectra give strength to the idea that hydrogen bond tautomerization in the vicinity of a PC is responsible for the hole burning. With this in mind, we discuss two mechanisms for the occurrence of optically induced tautomerization.

For an isolated BZA dimer, the two tautomers have identical energies. In BZA crystals, the dimer site symmetry destroys this identity. NMR data suggest that the energies of the two forms are split by ~ 35 cm⁻¹ with an ~ 400 cm⁻¹ activation energy between them.⁸ The BZA lattice consists of parallel stacks of plane-parallel BZA dimers.³ The vector normal to the plane of a BZA dimer makes an angle of 49° to the stacking

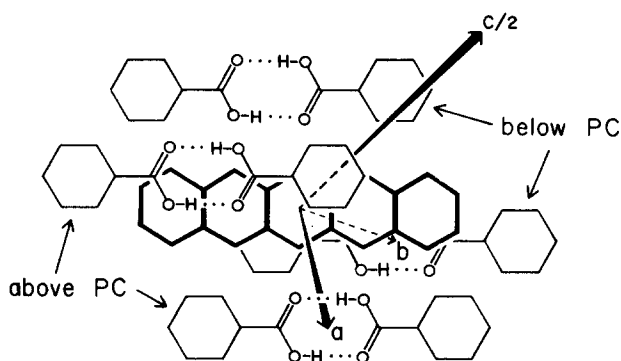


FIG. 4. View of a PC molecule occupying the site of a BZA dimer in the BZA lattice. The PC is shown lying in the plane of the figure with its four nearest neighbor dimers $\sim 3 \text{ \AA}$ above or below the plane. The BZA dimer hydrogen bonds are shown in the stabler form. Tautomerization of any dimer hydrogen bond would alter the electronic interactions of PC. For example, the carboxyl group double bond above the second ring of PC would shift to a position above the first PC ring. The unit cell axes are indicated.

direction.³ Thus, the stacks of dimers are tilted significantly.

Consider a PC molecule in the BZA lattice (see Fig. 4). Since PC and BZA dimers are approximately the same size, PC most probably replaces one dimer in the stack, with its molecular plane parallel to the other BZA dimers in the stack. The PC is surrounded by several differently oriented BZA dimers in neighboring stacks. The van der Waals interactions between PC and the BZA lattice determine an equilibrium position for the PC molecule. At 1.4 K, very little motion of the PC about its equilibrium position is expected.

When a tautomerization occurs, not only are the hydrogens exchanged, but the electronic interactions of the PC with the BZA dimer are also altered (see Fig. 4). This is most clearly evident in the changed positions of the carboxyl group double bonds. If PC occupies the site of a displaced BZA dimer, as depicted in Fig. 4, the site inversion symmetry is lost upon tautomerization. The PC ground and first excited singlet states are of different point symmetries (A_{1g} and B_{2u} , respectively) and differ with respect to inversion. Thus, the tautomerization could affect the ground and excited states quite differently, leading to the antihole spectral shifts. These considerations are consistent with the observed different transition energies of the antiholes, each different peak resulting from tautomerization of a BZA dimer which is oriented differently with respect to PC.

The question of what causes the tautomerization still remains. The first hole burning mechanism to consider involves changes in lattice configuration upon PC optical excitation. When a PC is electronically excited, its polarizability increases, altering its van der Waals interactions with its neighbors. As in the calculations of Craig and co-workers for other systems,¹¹ this could cause the PC equilibrium lattice configuration to be dynamically unstable when PC is electronically excited,

i. e., the excited PC prefers a different equilibrium lattice configuration. The excited PC and neighboring BZA dimers would relax to new equilibrium positions. Graf *et al.*²⁰ have recently presented calculations demonstrating that, in carboxylic acid dimers, tautomerization can have a greatly reduced activation energy, if cooperative motion of the heavy atom molecular framework occurs, rather than simple hydrogen transfer without heavy atom motion. Local lattice relaxation about an electronically excited PC might provide a sufficiently large impetus to drive hydrogens on a neighboring BZA dimer to the energetically unfavorable tautomeric form. Whether the less stable tautomer is formed could depend intimately upon the lattice dynamics at the moment of excitation of the PC, in a manner similar to that suggested for excimer and photodimer formation by Collins and Craig.¹¹ Thus, tautomerization might require the lattice to sample a particular region of its vibrational phase space during relaxation around an excited PC. Additionally, return of the excited PC to its ground state and concomitant lattice relaxation might cause the tautomerized BZA to revert to its stabler unburned form. This could result in low hole burning efficiency.

A second possible hole burning mechanism does not depend upon motion induced by optical excitation but rather upon lattice heating. An electronically excited PC will sometimes radiationlessly relax to the ground state or triplet state, even under intense cw illumination. In doing so, thousands of wave numbers of energy are converted to intramolecular vibrations and eventually to lattice phonons. The releasing of this large amount of energy into the local lattice might also cause BZA tautomerization if it were channeled into the appropriate vibrational modes of the BZA dimer. In other words, depending on the pathways and time scale of non-radiative electronic relaxation, the lattice around a PC may become "hot" enough to trigger BZA tautomerization. Of course, if a hole burning tautomerization is allowed, the reverse process is also likely. This type of process could also affect burning if the initial tautomerization occurred by the first burning mechanism proposed.

Regardless of the correct hole burning mechanism, antihole recovery is consistent with the tautomerization model for the nature of the holes. Because the BZA tautomer created upon burning is not in its most stable form, slow tunneling through the barrier in the double-well tautomerization potential to the stabler form would occur naturally, resulting in the eventual disappearance of the antiholes. The recovery rate in *d*-BZA is presumably reduced for reasons related to considerations of the tunneling process. Generally, heavier isotopes will tunnel at slower rates.²¹ Additionally, if the low temperature hydrogen bond length in *d*-BZA is longer than in *h*-BZA, as is the case at room temperature,¹⁰ the additional width of the tautomerization potential barrier will substantially reduce the tunneling rate.²²

As shown in Table I, deuteration of the BZA host shortens the PC fluorescence lifetime by more than a factor of 2. This is most likely due to an increased non-radiative relaxation rate. The ratio of site I antihole

recovery rates in *h*-BZA and *d*-BZA is about 3:1. Since recovery occurs in a thermally equilibrated low-temperature lattice in the absence of an excited PC molecule, this ratio indicates the relative tunneling rates for reversion to the stable tautomer. The ratio of hole burning efficiencies in the two hosts is about 100:1; much greater than the recovery rate ratio. This suggests that, for *d*-BZA, (1) the tautomerization involved in burning is relatively much more difficult than that involved in recovery or (2) once this tautomerization has occurred, there is an increased likelihood of rapid reversion to the stable form, decreasing the overall burning efficiency. This uncertainty about the cause of the 100:1 burning efficiency ratio makes it of little value in evaluating burning mechanisms since the effect of increased radiationless relaxation is not isolable from other effects of isotopic substitution, such as the kinetic effects of tunneling or thermal activation. Further experiments to determine the burning mechanism are under way.

IV. SUMMARY

Results of narrowband hole burning experiments and picosecond photon echo experiments on pentacene (PC) in benzoic acid (BZA) were presented. Hole burning was found to form a discrete set of antiholes which were well separated from the PC/BZA inhomogeneous $S_0 \rightarrow S_1$ absorption. Burning of the antiholes caused reversion to the original, unburned state. A frequency correlation between holes and their associated antiholes suggests a way to separate local and nonlocal contributions to inhomogeneous broadening.

Comparison of hole burning and photon echo measurements of the PC low temperature homogeneous linewidths showed that the two methods agreed. A temperature dependent study of the homogeneous linewidth measured by hole burning did not yield the same results as studies by other researchers who used other experimental methods.

Deuteration of the BZA acidic hydrogens resulted in a greatly reduced PC fluorescence lifetime and much reduced hole burning efficiency. The hole burning was attributed to tautomerization of the BZA dimer hydrogen bonds. Two hole-burning mechanisms were suggested; one involves tautomerization during lattice relaxation around an electronically excited PC; the other involves tautomerization from local lattice heating during radiationless relaxation of PC to the ground state. Available evidence has not permitted a definitive choice between the two mechanisms to be made.

ACKNOWLEDGMENTS

We wish to thank D. A. Wiersma for many helpful discussions. This work was supported by the National

Science Foundation through grant NSF DMR 79-20380 and by IBM Research Laboratories, San Jose, CA. We would also like to acknowledge the NSF San Francisco Laser Center for making available the argon ion laser and narrowband dye laser equipment used in the portion of the hole burning work conducted at Stanford.

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