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Low temperature spectroscopy of internally hydrogen-bonded 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole in a mixed crystal^{a)}

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Low temperature fluorescence and fluorescence excitation spectra of 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (MeHPB) in a single crystal biphenyl host are reported which exhibit sharp vibrational structure. The spectra are analyzed in terms of seven vibrational modes including three phenyl modes, three normal modes involving N-N and C-N stretching and bending motion, and a low frequency torsional vibration about the central C-N bond. The fluorescence exhibits a normal Stokes shift indicating that excited-state intramolecular proton transfer is precluded in this mixed crystal probably because the MeHPB molecule is held in a nonplanar conformation by molecular packing forces. A model of the MeHPB molecule based on semiempirical molecular orbital calculations is also presented which provides support for these conclusions.

I. INTRODUCTION

The emission properties of 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (MeHPB) in a variety of low temperature glasses¹⁻⁶ and in room temperature solutions^{4,7-9} have been studied by several investigators. In low temperature hydrocarbon glasses the emission consists almost entirely of a very broad, highly Stokes-shifted ("red") fluorescence band with its maximum intensity at ~ 600 nm.¹⁻⁶ This red fluorescence has been attributed to emission from an excited state proton transferred tautomer of MeHPB.¹⁻⁶ In hydrogen bonding glasses the emission characteristics of MeHPB are quite different. The fluorescence is only moderately (or "normally") Stokes shifted in an ethanol glass, having its intensity maximum in the blue at ~ 410 nm.^{3,4} Furthermore, this blue fluorescence is accompanied by fairly intense green phosphorescence.³ The lack of a highly Stokes-shifted fluorescence band in the emission spectrum of MeHPB in an ethanol glass has been attributed to an excited species of MeHPB for which excited state proton transfer does not occur.^{3,4} The formation of intermolecular hydrogen bonds between MeHPB and ethanol may prevent excited state proton transfer.³

In the present work, highly resolved vibrational structure is reported for the first time in both the fluorescence and fluorescence excitation spectra of MeHPB. In a single crystal host of biphenyl the fluorescence of MeHPB was measured and found to be entirely in the blue, normally Stokes-shifted region of the spectrum. The emission is indicative of a nonproton transferred

excited state of MeHPB. Molecular orbital calculations have also been undertaken that suggest that the molecular conformation of MeHPB plays a major role in determining whether or not excited state proton transfer is favored. Evidence is presented indicating that the crystal structure of biphenyl at low temperature requires that MeHPB adopt a nonplanar conformation which does not allow excited state proton transfer.

II. EXPERIMENTAL TECHNIQUES

Commercially available 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (MeHPB; Ciba-Geigy, Tinuvin P) and biphenyl (Alpha) were purified by zone refining. Single mixed crystals of biphenyl, containing less than 0.1% by weight of MeHPB, were grown by the Bridgman method. Samples used in the experiments were cleaved from the central portion of the crystal in order to avoid contamination from MeHPB crystallites that zone refine towards the top of the crystal growing tube and adhere to its wall. The dimensions of crystals used in these experiments were ~ 3 × 3 × 1.5 mm.

Samples were cooled to below 2.17 K by immersion in liquid helium which was maintained below the lambda point by reducing the He vapor pressure over the liquid. However, the temperature of the sample was not actually measured.

Fluorescence spectra were obtained using the 325 nm line of a HeCd laser (Liconix model 4050/4055) as the excitation source. Emission was collected and focused with a 4 cm focal length, 4 cm diam quartz lens onto the slit of a 1.0 m scanning monochromator (Hilger-Engis, model 1000), which was calibrated with an Ar discharge lamp. The dispersed emission was detected with a photomultiplier tube (Hamamatsu, R1104) which produced a signal current that was amplified with a picoammeter (Keithly, model 414A) and recorded with an X-Y recorder (Hewlett-Packard, model 7040A).

Fluorescence excitation spectra were also obtained from samples cooled to below the lambda point as above. Sample excitation was accomplished with a 450 W xenon

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lamp (Osram, XBO-450), the light from which was dispersed by the 1.0 m scanning monochromator described above. A portion ($\sim 10\%$) of this dispersed light was directed onto a quantum counter [a 1 cm path length quartz dye cell containing a concentrated solution of Rhodamine 6G (10 g/l) coupled to a photomultiplier tube (Hamamatsu, 1P28)]. The remainder of this quasimonochromatic light was used to excite the sample. Sample fluorescence was isolated from the excitation light with filters (Schott GG 400 \times 6 mm thick glass filters). The fluorescence was further isolated into a band between ~ 400 and ~ 500 nm with additional filters (Schott BG 3 and FG 10 glass filters). The broadband fluorescence was detected with a photomultiplier tube (Hamamatsu, R1104). The sample fluorescence signal (V_x) and the reference signal from the quantum counter (V_y) were amplified and fed into a ratiometer (Evans Associates, model 4122). The output from the ratiometer V_x/V_y was recorded with the X-Y recorder (H-P 7040A).

III. METHODS OF CALCULATION

Molecular orbital calculations were carried out for the parent molecule of MeHPB, 2-(2'-hydroxyphenyl)-benzotriazole (HPB). This molecule differs from MeHPB only in that the methyl group in the 5' position of MeHPB is replaced with hydrogen. This structural modification simplifies the calculations but should have little effect on the actual numerical results of interest.

An energy minimized geometry for HPB was obtained using the complete neglect of differential overlap (CNDO) formalism with Quantum Chemistry Program Exchange (QCPE) Program No. 312.⁴ This geometry, which is planar, was then used for the calculation of the ground and excited state properties of HPB using the intermediate neglect of differential overlap with configuration interaction (INDO/CI) approximation in another program.^{4,10-15} Potential energy surfaces were calculated with this method as a function of the dihedral angle (Φ) for torsional motion about the C-N bond joining the benzotriazole and phenol portions of the molecule (see Fig. 1). The hydroxy hydrogen—H(17)—was simulta-

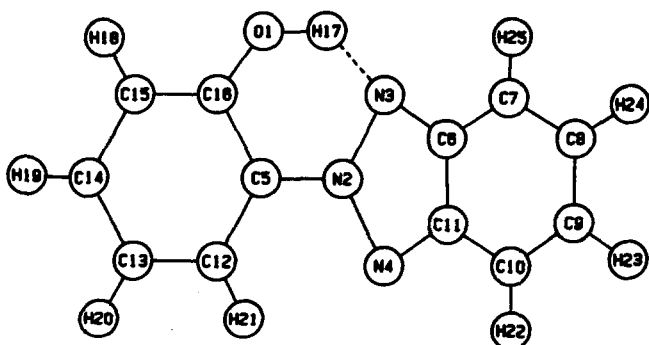


FIG. 1. Structure of 2-(2'-hydroxyphenyl)-benzotriazole (HPB). Molecular orbital calculations were performed on this molecule. The experiments reported were performed on the derivative 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (MeHPB) in which H(20) shown in this structure is replaced with a methyl group. The atoms are numbered for reference in the text.

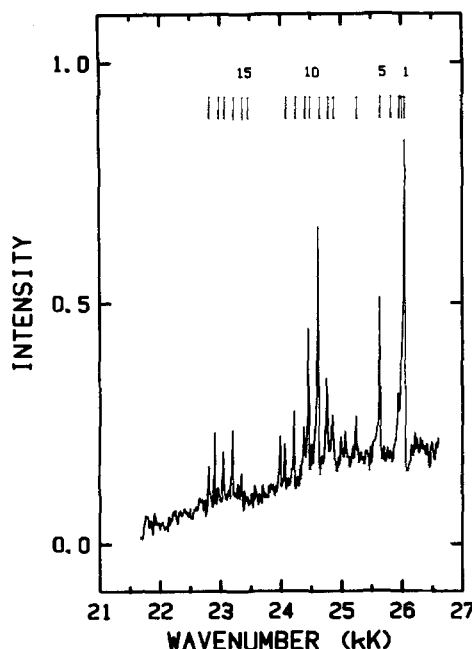


FIG. 2. Fluorescence spectrum of MeHPB in a single crystal of biphenyl held at a temperature below the λ point of liquid helium.

neously rotated out of the phenol plane as Φ was varied to minimize the H(17)...N(3) distance.

The potential energy surfaces thus generated for the torsional motion in the ground and excited states were used to calculate the torsional vibrational energy levels. The potential surfaces were approximated by Fourier cosine series. A detailed discussion of the techniques for calculating the eigenvalues for the potential surfaces is given in Ref. 14.

IV. RESULTS

A. Experimental observations

1. Fluorescence spectrum

The fluorescence spectrum of a sample of MeHPB in a single crystal of biphenyl held at $T < 2.17$ K is shown in Fig. 2. The spectrum was recorded with a spectral resolution of 0.08 nm (i.e., about 5 cm^{-1} in this wavelength region). The observed linewidth of the sharpest band in this spectrum is 26 cm^{-1} . The electronic origin occurs at 26 046 cm^{-1} . The peak positions of 19 bands in the fluorescence spectrum were measured and are presented in Table I.

2. Excitation spectrum

The fluorescence excitation spectrum of the biphenyl crystal doped with MeHPB and held at $T < 2.17$ K is shown in Fig. 3. The band peak positions of 21 lines were measured in the excitation spectrum and are presented in Table I.

B. Molecular orbital calculations

The potential energy surfaces for the ground and lowest $^1\pi\pi^*$ excited states, calculated as a function of the

TABLE I. Fluorescence and fluorescence excitation spectral peak positions of MeHPB in a single crystal of biphenyl at $T < 2.17$ K. Band peak positions are reported in vacuum wave numbers. Estimated errors in the peak positions are ± 10 cm^{-1} . Deviations refer to the difference between the assigned combination position and the measured position.

| Peak No. (See Fig. 2) | Fluorescence | | | | Peak No. (See Fig. 3) | Excitation | | | |
|--------------------------|-------------------------------------|----------------------------------|------------------|-----------------------------------|--------------------------|-------------------------------------|----------------------------------|-----------------|------------------------------|
| | Wave number (cm^{-1}) | Δ (cm^{-1}) | Assignment | Deviation (cm^{-1}) | | Wave number (cm^{-1}) | Δ (cm^{-1}) | Assignment | Dev. (cm^{-1}) |
| 1 | 26 046 | 0 | 0-0 | | 1 | 26 048 | 0 | 0-0 | |
| 2 | 26 004 | 42 | lattice | | | | | | |
| 3 | 25 962 | 84 | ν_1 | | 2 | 26 146 | 98 | ν_1 | |
| 4 | 25 822 | 224 | | | 3 | 26 428 | 380 | ν_2 | |
| 5 | 25 647 | 399 | ν_2 | | 4 | 26 608 | 560 | | |
| | | | | | 5 | 26 767 | 719 | | |
| 6 | 25 261 | 785 | $2\nu_2$ | +14 | 6 | 26 812 | 764 | $2\nu_2$ | -4 |
| 7 | 24 880 | 1166 | ν_3 | | 7 | 27 036 | 988 | | |
| 8 | 24 787 | 1259 | ν_4 | | 8 | 27 194 | 1146 | ν_3 | |
| 9 | 24 646 | 1400 | ν_5 | | 9 | 27 209 | 1161 | ν_4 | |
| 10 | 24 486 | 1560 | ν_6 | | 10 | 27 431 | 1383 | ν_5 | |
| | | | | | 11 | 27 467 | 1419 | ν_6 | |
| 11 | 24 409 | 1637 | ν_7 | | 12 | 27 507 | 1459 | | |
| 12 | 24 249 | 1797 | $\nu_2 + \nu_5$ | +2 | 13 | 27 539 | 1491 | ν_7 | |
| 13 | 24 087 | 1959 | $\nu_2 + \nu_6$ | 0 | 14 | 27 584 | 1536 | $\nu_2 + \nu_3$ | -10 |
| | | | | | 15 | 27 812 | 1764 | $\nu_2 + \nu_5$ | -1 |
| 14 | 23 467 | 2579 | $\nu_3 + \nu_5$ | -13 | 16 | 27 915 | 1867 | $\nu_2 + \nu_7$ | +4 |
| 15 | 23 371 | 2675 | $\nu_4 + \nu_5$ | -16 | 17 | 28 585 | 2537 | $\nu_3 + \nu_5$ | -8 |
| 16 | 23 228 | 2818 | $2\nu_5$ | -18 | 18 | 28 616 | 2568 | $\nu_3 + \nu_6$ | -3 |
| | | | | | 19 | 28 821 | 2773 | $2\nu_5$ | -7 |
| 17 | 23 075 | 2971 | $\nu_6 + \nu_5$ | -11 | 20 | 28 916 | 2868 | | |
| 18 | 22 982 | 3064 | $\nu_7 + \nu_5$ | -27 | 21 | 28 954 | 2916 | | |
| 19 | 22 821 | 3225 | $2\nu_5 + \nu_2$ | -28 | | | | | |

dihedral angle (Φ) for the torsional motion about the C-N bond joining the benzotriazole and phenol portions of HPB are presented in Fig. 4. Changes in atomic

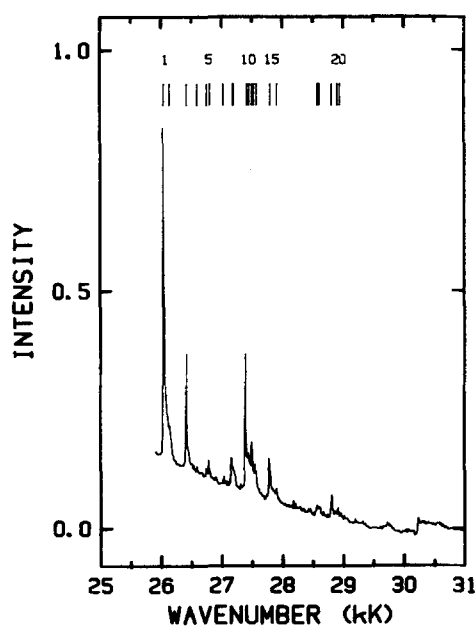


FIG. 3. Fluorescence excitation spectrum of MeHPB in a single crystal of biphenyl held at a temperature below the λ point of liquid helium.

charges on the oxygen and nitrogens of HPB resulting from electronic excitation to the lowest $^1\pi\pi^*$ electronic state as a function of the dihedral angle between the phenol and benzotriazole portions of HPB are presented in Fig. 5.

A listing of the electron densities and atomic charges on the oxygen and nitrogens for the planar configuration

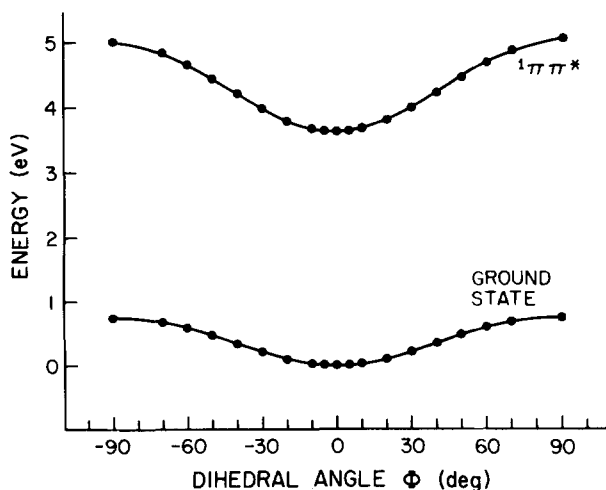


FIG. 4. Calculated ground state and excited state ($^1\pi\pi^*$) potential energies as a function of the dihedral angle for rotation about the C(5)-N(2) bond of HPB.

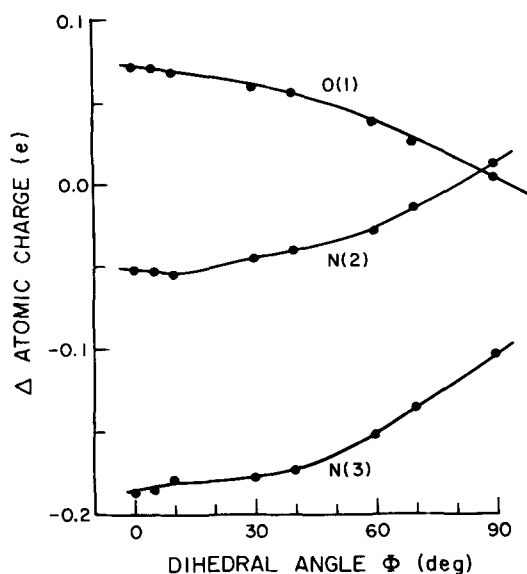


FIG. 5. Calculated changes in the atomic charge (e^-) on the oxygen [O(1)] and nitrogen [N(2) and N(3)] atoms upon excitation from the ground state to the lowest energy $1\pi\pi^*$ state as a function of the dihedral angle in HPB. Calculated charge changes were essentially identical for N(3) and N(4). Positive values indicate that the electron density decreases on the atom in the excited state.

only of HPB in the ground and lowest $1\pi\pi^*$ excited states is presented in Table II. The calculated π bond orders for the planar configuration in the ground and lowest $1\pi\pi^*$ excited state and the change in bond order accompanying excitation are presented in Table III. The calculated energy separations of the vibrational states in the ground state and in the lowest $1\pi\pi^*$ excited state for the torsional potential surfaces are $\Delta\bar{\nu}'(S_0) = 74 \text{ cm}^{-1}$ and $\Delta\bar{\nu}'(1\pi\pi^*) = 89 \text{ cm}^{-1}$, respectively. These surfaces are both essentially harmonic for at least the ten lowest vibrational states.

V. DISCUSSION

A. Spectra

The nineteen peaks observed in the fluorescence spectrum of MeHPB (Fig. 2 and Table I) can be analyzed in terms of a lattice mode, seven molecular fundamental vibrations, and various combinations of these fundamentals. The assignments and the deviations from the assignments are presented in Table I. Similarly, the

TABLE III. Calculated π bond orders for the ground and lowest $\pi\pi^*$ excited state of HPB in the planar conformation. (See Fig. 1 for atom numbering.)

| Atom pair | Type | π bond order ground state (P_g) | π bond order excited state (P_e) | Bond order change ($P_e - P_g$) |
|-----------|------|---|--|-----------------------------------|
| 2-5 | C-N | 0.26 | 0.43 | +0.17 |
| 16-1 | C-O | 0.33 | 0.42 | +0.09 |
| 2-3 | N-N | 0.53 | 0.33 | -0.20 |
| 2-4 | N-N | 0.55 | 0.35 | -0.20 |
| 3-6 | N-C | 0.59 | 0.53 | -0.06 |
| 4-11 | N-C | 0.59 | 0.53 | -0.06 |
| 6-7 | C-C | 0.51 | 0.53 | +0.02 |
| 7-8 | C-C | 0.77 | 0.72 | -0.05 |
| 8-9 | C-C | 0.53 | 0.51 | -0.02 |
| 9-10 | C-C | 0.77 | 0.72 | -0.05 |
| 10-11 | C-C | 0.51 | 0.53 | +0.02 |
| 5-12 | C-C | 0.64 | 0.60 | -0.04 |
| 12-13 | C-C | 0.68 | 0.69 | +0.01 |
| 13-14 | C-C | 0.65 | 0.57 | -0.08 |
| 14-15 | C-C | 0.68 | 0.68 | 0.00 |
| 15-16 | C-C | 0.63 | 0.61 | -0.02 |
| 16-5 | C-C | 0.61 | 0.50 | -0.11 |

peaks observed in the excitation spectrum were analyzed in terms of seven fundamentals and combinations of these fundamentals. These assignments are also presented in Table I. The rows of Table I are lined up so that the corresponding modes in the fluorescence and excitation spectra can be compared. The vibrational analysis shows that the fluorescence in the region $0-2000 \text{ cm}^{-1}$ is heavily influenced by combinations of the 399 cm^{-1} (ν_2) mode. The higher energy region is built upon combinations involving the 1400 cm^{-1} (ν_5) mode. The entire emission spectrum is contained in the $26000-22000 \text{ cm}^{-1}$ region, and no highly Stokes-shifted emission is observed.

Only a few of the ($3N-6=78$) normal modes of MeHPB were observed in the optical spectra. The identification of these modes can be aided by drawing analogies to spectra of molecules having similar structural features. In addition, results from the molecular orbital and torsional calculations provide clues as to the origin of the observed modes. For example, changes in bond order between the ground and excited state should be reflected in differences between the ground and excited state fundamental frequencies.

A comparison of the fundamental modes observed in the fluorescence and fluorescence excitation spectra of

TABLE II. Electron densities and atomic charges on selected atoms for the ground and lowest $1\pi\pi^*$ excited state of HPB in the planar conformation. (See Fig. 1 for atom numbering).

| Atom | Ground state | | $1\pi\pi^*$ excited state | |
|------|------------------|------------|---------------------------|------------|
| | Electron density | Net charge | Electron density | Net charge |
| O | 6.2896 | -0.2896 | 6.2178 | -0.2178 |
| N(2) | 4.7673 | 0.2327 | 4.8198 | 0.1802 |
| N(3) | 5.2764 | -0.2746 | 5.4500 | -0.4500 |
| N(4) | 5.2767 | -0.2767 | 5.4634 | -0.4634 |

TABLE IV. Comparison of the predominant fundamentals observed in the fluorescence and fluorescence excitation spectra of MeHPB in a single crystal of biphenyl.

| Mode | Fluorescence (cm ⁻¹) | Excitation (cm ⁻¹) | Description |
|---------|----------------------------------|--------------------------------|------------------------------------|
| | 42 | ... | Lattice |
| ν_1 | 84 | 98 | Torsion C-N |
| ν_2 | 399 | 380 | Benzene ν_{6a-11b} |
| ν_3 | 1166 | 1146 | Benzene ν_{17-11b} C-H bend |
| ν_4 | 1259 | 1161 | N-N mode |
| ν_5 | 1400 | 1383 | Benzene ν_{13-11b} C-C stretch |
| ν_6 | 1560 | 1419 | C-N stretch |
| ν_7 | 1637 | 1491 | N-N stretch |

MeHPB is presented in Table IV. The rows in Table IV are lined up for comparison of the corresponding fundamental vibrational modes in the ground and excited states. The correspondence was based on the relative intensities and the positions of the peaks as well as the combination bands formed in the fluorescence and fluorescence excitation spectra.

Most of the fundamentals exhibit the typically expected decrease in frequency upon excitation into the $^1\pi\pi^*$ state. The only fundamental showing an increase in frequency in the excited state is ν_1 . This fundamental was assigned to the torsional vibration about the C-N bond joining the phenol and benzotriazole portions of the MeHPB molecule. The molecular orbital calculations on planar HPB predict an increase in bond order for this C-N bond, following excitation, from 0.26 to 0.43 (see Table III), indicating an increase in the torsional mode force constant upon electronic excitation. The torsional energy calculations based on the potential energy surfaces for this motion thus predict an increase in this frequency. The increase in frequency upon electronic excitation predicted by the torsional calculations on HPB was 15 cm⁻¹ (see Sec. IV B) while that observed from the spectroscopic data for MeHPB was 14 cm⁻¹ (Table IV).

The remainder of the spectroscopically observed fundamentals decrease in frequency in the excited state. The largest changes in frequency involve ν_4 , ν_6 , and ν_7 . A survey of Table III shows that the largest changes in bond order involve the N-N bonds N(2)-N(3) and N(2)-N(4). It is expected that similar bond order changes would occur in a slightly twisted HPB molecule. Nitrogens N(3) and N(4) also exhibit large changes in electron density following excitation, a situation which has been implicated as an important factor in the excited state relaxation pathway which involves excited state proton transfer.¹ The decrease in the π bond order for the N-N bonds suggests that the normal modes identified with ν_4 , ν_6 , and ν_7 may involve vibrations which include the N-N bonds. C-N stretching modes have been identified for a number of nitrogen containing heterocycles. The C-N stretching frequencies in imidazole and benzimidazole have been reported to range from

1520-1560 cm⁻¹.¹⁶ This fits well with the ground state frequency observed for ν_6 (1560 cm⁻¹). ν_6 was therefore assigned to a C-N stretch in HPB. ν_4 and ν_7 are tentatively assigned to modes involving the N-N bonds.

The 399 cm⁻¹ mode ν_2 is similar in frequency to the benzene ν_{6a} -like band observed in the benzoic acid hydrogen-bonded dimer (311 cm⁻¹).¹⁷ ν_2 is also similar in frequency to a mode observed at 347 cm⁻¹ for methyl salicylate.^{18,19} The 399 cm⁻¹ mode is found in various combinations throughout the spectrum as was observed for the corresponding mode in methyl salicylate.^{18,19} The 1166 cm⁻¹ mode ν_3 is similar to a benzene ν_{17} C-H bend.²⁰ The 1400 cm⁻¹ mode ν_5 is found in strong combinations throughout the spectrum. This mode is similar in frequency to the benzene ν_{13} C-C stretch.²⁰ The last fundamental to be identified is at 42 cm⁻¹. This mode is buried in the phonon wing of the origin band and is likely due to a lattice mode.

A summary of the mode assignments and descriptions is presented in Table IV.

B. Emission characteristics

The low temperature fluorescence observed for MeHPB in the biphenyl host is entirely contained in the blue region of the spectrum 26 000-22 000 cm⁻¹. No highly Stokes shifted fluorescence was observed. The energies of the fluorescence and fluorescence excitation origins are identical within experimental error (Table I). A very low intensity blue-green phosphorescence was observed visually but was not photoelectrically recorded. The observation of very weak phosphorescence compared to the fluorescence intensity supports an assignment of the lowest excited singlet state to a $^1\pi\pi^*$ type transition. The assignment of the lowest energy singlet to a $^1\pi\pi^*$ type transition is based on the high oscillator strength for the transition and the short fluorescence lifetime ($\tau = 10^{-9}$ s).⁴ The phosphorescence lifetime is on the order of 1 s, a value which also indicates a lowest $^3\pi\pi^*$ level. If the lowest singlet state were $^1n\pi^*$ one would have expected very rapid intersystem crossing, resulting in very weak fluorescence, contrary to observations on low temperature samples.

Previous studies of the low temperature emission from MeHPB in frozen hydrocarbon solutions yielded only a highly Stokes-shifted emission which was attributed to the excited state proton transferred form of the molecule.¹⁻⁶ Blue, moderately Stokes-shifted fluorescence was observed in frozen solutions of MeHPB in hydrogen bonding solvents such as ethanol and methanol.^{3,4} This blue fluorescence has been attributed to nonplanar forms of the molecule.⁴ The molecular orbital calculations of the changes in electron density on the oxygen and nitrogens following excitation predict that excited state proton transfer is less favorable for nonplanar forms of HPB. For example, Fig. 5 shows that the maximum difference in the electron density upon excitation between O(1) and N(3) [or N(4)] occurs for the planar configuration. This difference is presumably the driving force for proton transfer in the planar form, but may be insufficient in twisted nonplanar forms to cause proton transfer. The observation of blue fluorescence from

MeHPB in the biphenyl host suggests that the structure of MeHPB may be nonplanar in the biphenyl host.

There has been a considerable amount of work done on low temperature mixed crystals using biphenyl as host. Most of the work has been done on planar molecules such as phenanthrene²¹⁻²³ and naphthalene²³ as well as neat crystals of biphenyl²⁴ and biphenyl-*h*₁₀ doped into a host of biphenyl-*d*₁₀.²⁵⁻²⁸ A number of these studies show a site splitting on the order of 10–20 cm⁻¹.^{24,25,27} The site splitting is attributed to a phase transition which occurs in biphenyl crystals below 75 K. In the room temperature crystal, the biphenyl molecules are planar.²⁸ As the temperature is lowered below 75 K there is a continuous change in the crystal and molecular structure of biphenyl.²⁴ The change in molecular structure is associated with a long axis twist between the two halves of the biphenyl molecule.²⁴ The torsional angle between the two rings has been measured by neutron diffraction to be ~10° at 4.2 K.²⁹ The twist of the rings is in opposite directions for two neighboring molecules.²⁹ The fluorescence spectra of MeHPB in biphenyl show no indication of site splitting. This suggests that either there is a single orientation of the MeHPB molecule in this host or that the site splitting is less than the line-width of the bands. The observation of only blue fluorescence from MeHPB in the biphenyl host suggests a molecular conformation for MeHPB that is twisted by molecular packing forces.

VI. SUMMARY AND CONCLUSIONS

The low temperature fluorescence and fluorescence excitation spectra of MeHPB in a single crystal of biphenyl exhibit sharp vibrational structure which has not been previously observed. A low frequency mode observed in the spectra was assigned to the torsional vibration involving motion about the C–N bond joining the phenol and benzotriazole portions of the molecule. This assignment was supported by calculations of the energy levels for this vibration in potential wells modeled from molecular orbital calculations on HPB. The two major modes upon which much of the spectrum is built were assigned to a benzene-like C–C bend and a C–C stretch at 399 and 1400 cm⁻¹, respectively. Three modes may be associated with normal vibrations involving the N–N or C–N bonds based on the observed decrease in frequency and the calculated decrease in bond order in the excited state. The observation of blue, nonproton-transferred type fluorescence indicates that MeHPB exists in a nonplanar form in the low temperature, single crystal, biphenyl host. The nonplanar conformation is dictated by the crystalline and molecular structure of biphenyl at low temperature. The observation of a very weak phosphorescence compared to the blue fluorescence intensity supports the assignment of the lowest excited state to a ¹ππ* state.

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