

THE UNIVERSITY OF MANITOBA  
STUDIES OF THE ELECTRONIC ABSORPTION AND  
LUMINESCENCE OF 2,1,3-BENZOTHIADIAZOLE

by

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TO MY WIFE, ELLEN, AND MY PARENTS

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## ABSTRACT

A study has been made of the spectral properties of 2,1,3-benzothiadiazole (BTD -  $d_0$ ) and of totally deuterated BTD -  $d_4$ . Absorption spectra have been obtained in polar and nonpolar solvents at room temperature and in an EPA rigid glass at 77°K. The complete loss of resolution of the first singlet absorption in ethanol at room temperature is explained in terms of the formation of weak solute-solvent electrostatic complexes. This solvent effect is taken as evidence that the heterocyclic ring portion of the molecule is involved in the electronic transition. The greatly enhanced resolution of  $S_2$  peaks compared to the slightly enhanced resolution of  $S_1$  peaks at 77°K is considered as suggesting evidence for  $^1n\pi^*$  vibronic coupling to the lowest  $^1\pi\pi^*$  singlet state.

Fluorescence and phosphorescence emission spectra have been obtained in polar, nonpolar and heavy atom rigid glasses at 77°K for both BTD -  $d_0$  and BTD -  $d_4$ . Triplet decay lifetimes have been obtained for BTD -  $d_4$  in polar and nonpolar solvents both by measuring directly the phosphorescence decay and by monitoring the decay of triplet-triplet (T-T) absorption. A triplet decay lifetime has been obtained for BTD -  $d_0$  in EPA only by monitoring the decay of T-T absorption. The T-T absorption spectrum of BTD -  $d_4$  has been obtained in EPA at 77°K in the region from 20 000  $\text{cm}^{-1}$  to 28 000  $\text{cm}^{-1}$ .

The deuterium effect on the triplet state lifetime and the external heavy atom effect on phosphorescence intensity are interpreted as providing evidence for  $\pi\pi^*$  character in the lowest triplet state. On the other hand, the phosphorescence energy and the triplet lifetime are considered as providing evidence for  $n\pi^*$

character in the same state. Similarly, the T-T absorption spectrum is suggestive of  $n\pi^* - \pi\pi^*$  interaction in the triplet manifold.

A difference in the triplet state lifetime obtained by the two measuring techniques is discussed in terms of oxygen quenching because of the experimental arrangement or the formation of a cationic photoproduct.

A preliminary study has been made of the spectral properties of 3- deazauridine (3 DAU). The room temperature absorption spectrum in ethanol and the total emission spectrum in a polar rigid glass at 77°K have been obtained. The phosphorescence decay lifetime has also been obtained. The preliminary results are considered as showing no signs of the presence of biprotonic phototautomerism.

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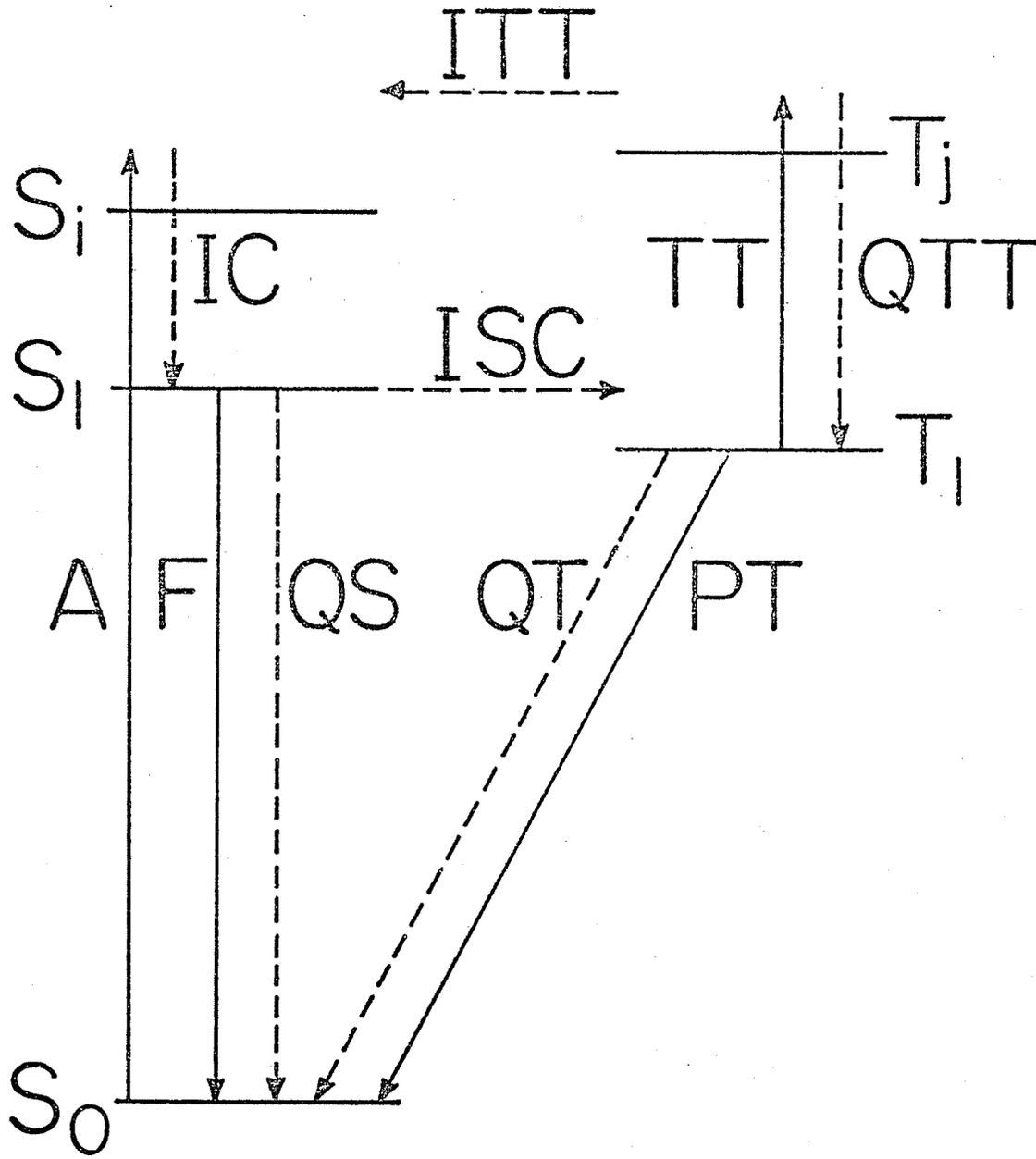
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## A. Photophysical Processes (1,2)

Absorption of a photon of light by a molecule causes many possible photophysical processes, both intramolecular and intermolecular. An energy level diagram showing the primary and secondary intramolecular processes is shown in Fig. 1. Starting with a molecule in its singlet ground state ( $S_0$ ), absorption (A) of a photon of energy,  $h\nu$ , greater than the energy separation between  $S_0$  and the first excited singlet state ( $S_1$ ), will excite the molecule to some upper vibrational level of an excited singlet state ( $S_1$ ). The excited molecule is nonradiatively deactivated to the lowest vibrational level of  $S_1$  by vibrational deactivation in  $10^{-11}$  -  $10^{-14}$  sec. The nonradiative decay from the lowest vibrational level of  $S_2$  to some upper vibrational level of  $S_1$  is called internal conversion (IC).

Deactivation of  $S_1$  is a competition between radiative decay to the ground state, i.e., fluorescence (F), nonradiative decay to the ground state (QS) and nonradiative intersystem crossing (ISC) to some excited vibrational level in the triplet manifold. Nonradiative decay to the ground state which generally occurs in  $10^{-5}$  -  $10^{-3}$  sec is usually the least important deactivation process of  $S_1$  because of the large energy gap between  $S_1$  and  $S_0$  which results in small Franck-Condon factors (i.e., small vibrational overlap integrals). The competition between the deactivation by fluorescence ( $10^{-7}$  -  $10^{-9}$  sec) and intersystem crossing ( $10^{-8}$  sec) generally determines the observed spectral properties of  $S_1$ .

Fig. 1. Energy level diagram of first and second order intramolecular processes.



After intersystem crossing the molecule nonradiatively decays via vibrational deactivation and internal conversion to the lowest vibrational level of the lowest triplet state ( $T_1$ ). If no secondary processes occur the molecule then returns to the ground state via non-radiative (QT) and/or radiative, i.e., phosphorescence (PT), processes. Since  $T_1 \rightarrow S_0$  processes are to a first order approximation spin forbidden they, therefore, occur more slowly ( $10^{-3}$  sec.). If, however, instead of  $T_1 \rightarrow S_0$  deactivation the molecule absorbs another photon while in  $T_1$  then secondary processes can occur. Excitation of the molecule from  $T_1$  to some upper triplet state  $T_j$  is called triplet-triplet absorption (TT). From  $T_j$  the molecule can either radiationlessly decay via vibrational deactivation and internal conversion back to the lowest vibrational level of  $T_1$  (QIT) or it can form a highly excited ionic species or photoproduct (ITT).

## B. Spin-Orbit-Vibronic Coupling

In conjugated molecules the states of spectroscopic importance are  $\pi\pi^*$ ,  $n\pi^*$ ,  $\sigma\pi^*$  and  $\pi\sigma^*$  states. Because aromatic hydrocarbons have no nonbonding electrons ( i.e., no  $n\pi^*$  states ), the  $\pi\pi^*$ ,  $\sigma\pi^*$  and  $\pi\sigma^*$  states are the only low lying states that need to be considered in perturbative approaches to intramolecular energy transfer processes. The energy separation between states is an important factor in these perturbative approaches. Thus in conjugated heterocyclic compounds,  $n\pi^*$  states, which are lower in energy than  $\sigma\pi^*$  and  $\pi\sigma^*$  states, play a greater role than these latter states in spin-orbit-vibronic coupling.

According to first order selection rules singlet-triplet transitions would be spin forbidden. But because the state description (i.e., pure singlet and triplet states) is inaccurate, these transitions are not completely forbidden. In heterocyclic compounds the  $\pi\pi^*$  and  $n\pi^*$  states are vibronically (vibrationally-electronically) coupled and spin-orbitally coupled to other states of the molecule. The following simple model of spin-orbit-vibronic coupling is based on that presented for polycyclic monoazines by Lim and Yu (3).

The total electronic Hamiltonian can be written for the zero order Born-Oppenheimer (BO) approximation as

$$H = H_0 + H_{SO} \quad (1)$$

where  $H_0$  contains the kinetic and potential energies for the electrons as well as the spin-energy operators and  $H_{SO}$  is the spin-orbit operator. Thus by applying the conventional Herzberg-Teller (HT) expansion about the equilibrium nuclear coordinate  $Q_0$ , the total first

order Hamiltonian becomes

$$H = H_0(Q_0) + H_{SO}(Q_0) + \sum_{k=1}^{3N-6} (\partial H_0 / \partial Q_k)_{Q_0} Q_k + \sum_{k=1}^{3N-6} (\partial H_{SO} / \partial Q_k)_{Q_0} Q_k \quad (2)$$

The use of second order perturbation theory leads to the approximate triplet wavefunction

$${}^3\psi_1 = {}^3\phi_1 + \sum_m \frac{\langle {}^1\phi_m | \hat{H}' | {}^3\phi_1 \rangle}{E_1 - E_m} + \sum_m \sum_n \frac{\langle {}^1\phi_m | \hat{H}' | r\phi_n \rangle \langle r\phi_n | \hat{H}' | {}^3\phi_1 \rangle}{(E_1 - E_n)(E_1 - E_m)} {}^1\phi_m \quad (3)$$

where  ${}^3\phi_1$  and  $E_1$  are the zeroth order wavefunction and energy of  $T_1$ ;  ${}^1\phi_m$  and  $E_m$  are the zeroth order wavefunction and energy of the singlet state which is spin-orbitally coupled to  ${}^3\phi_1$ ;  $r\phi_n$  and  $E_n$  are the zeroth order wavefunction and energy of the state (singlet or triplet) which is vibronically coupled to  ${}^1\phi_m$  or  ${}^3\phi_1$  respectively; and

$$\hat{H}' = H_{SO}(Q_0) + \sum_{k=1}^{3N-6} (\partial H_0 / \partial Q_k)_{Q_0} Q_k + \sum_{k=1}^{3N-6} (\partial H_{SO} / \partial Q_k)_{Q_0} Q_k \quad (4)$$

which can be rewritten as

$$\hat{H}' = H_{SO} + H_V + H_{SV} \quad (5)$$

At this level of approximation the mixing into the lowest triplet state by the ground state is omitted. This leads to a transition moment between  $T_1$  and  $S_0$  of

$$M_{01} = \sum_m \frac{\langle {}^1\phi_m | \hat{H}' | {}^3\phi_1 \rangle}{E_1 - E_m} M_{0m} + \sum_m \sum_n \frac{\langle {}^1\phi_m | \hat{H}' | r\phi_n \rangle \langle r\phi_n | \hat{H}' | {}^3\phi_1 \rangle}{(E_1 - E_n)(E_1 - E_m)} M_{0m} \quad (6)$$

where  $M_{0m}$  is the zeroth order transition moment of the perturbing transition  ${}^1\phi_m \leftarrow {}^1\phi_0$ . Expansion of the second term of (6) in terms of

(5) and keeping only the cross terms  $H_V H_{SO}$  and  $H_{SO} H_V$ , since in general  $H \gg H_{SO} \gg H_V$ , yields a transition moment

$$M_{01} = \sum_m \frac{\langle {}^1\phi_m | H_{SO} | {}^3\phi_1 \rangle M_{0m}}{E_1 - E_m} + \sum_m \sum_n \frac{\langle {}^1\phi_m | H_V | {}^1\phi_n \rangle \langle {}^1\phi_n | H_{SO} | {}^3\phi_1 \rangle M_{0m}}{(E_1 - E_n)(E_1 - E_m)} \\ + \sum_m \sum_n \frac{\langle {}^1\phi_m | H_{SO} | {}^3\phi_n \rangle \langle {}^3\phi_n | H_V | {}^3\phi_1 \rangle M_{0m}}{(E_1 - E_n)(E_1 - E_m)} \quad (7)$$

in which the spin-vibronic contributions to the first term in (7) have been neglected.

As an example of the application of the above coupling scheme, assume that a heterocyclic molecule has as its lowest triplet state, a  ${}^3\pi\pi^*$  state. The only direct first order coupling of the lowest triplet state to the perturbing singlet state is via the first term of equation (7). The perturbing singlet could be  $\pi\pi^*$ ,  $n\pi^*$ ,  $\sigma\pi^*$ , or  $\pi\sigma^*$ . Because the latter two types of states are of much less importance than  $n\pi^*$  states in heterocycles and because their matrix elements are similar to those of  $n\pi^*$  states, they will be omitted.

For heterocycles the  ${}^3\pi\pi^*$  and  ${}^1\pi\pi^*$  coupling matrix elements are similar to those for aromatic hydrocarbons. Therefore, this type of coupling can be omitted since it involves vanishingly small three centre terms (4). The matrix element,  $\langle {}^1n\pi^* | H_{SO} | {}^3\pi\pi^* \rangle$ , contains one centre terms. Thus the first order spin-orbit perturbation leads to a  $\pi^* \leftarrow n$  singlet-singlet transitions as the perturbing transition.

Of the second order terms, i.e., the second and third terms of equation (7), those matrix elements involving  $n\pi^*$  states as the perturbing states should be much smaller than the matrix elements of direct first order spin-orbit coupling. This statement only holds

if the perturbing singlet-singlet transition is not symmetry forbidden. Assuming that the transition is symmetry allowed, then the perturbing singlet of interest in second order coupling would be a  $^1_{\pi\pi^*}$  state. With a  $^1_{\pi\pi^*}$  perturbing singlet the intermediate spin-orbitally-vibronically coupled states would probably be  $^1,^3_{n\pi^*}$  since  $^1_{\pi\pi^*} - ^3_{\pi\pi^*}$  spin-orbit coupling is several orders of magnitude smaller than  $^1_{\pi\pi^*} - ^3_{n\pi^*}$  spin-orbit coupling (5). When the lowest triplet state is  $^3_{\pi\pi^*}$ , and when the singlet state in first order spin-orbit coupling is an  $^1_{n\pi^*}$  state, which in general has a weak transition moment, and the perturbing singlet states in second order coupling are  $^1_{\pi\pi^*}$  states with large transition moments then the second order mechanism can compete with the first order mechanism.

In the above vibronic coupling scheme two major assumptions were made. One assumption was that coupling between the lowest excited states and the ground state could be omitted. The other assumption was based on the conventional Herzberg-Teller expansion of the Hamiltonian about the ground or the lowest triplet state equilibrium nuclear coordinate  $Q_0$ . This implies that there is no change in the equilibrium nuclear coordinate upon excitation from the ground state to some upper excited state. In recent years several authors have questioned the validity of these assumptions in vibronic coupling.

Craig and Small (6) have considered the effect of the linear term in the dependence of the transition moment on normal coordinate for vibronic perturbations by totally symmetric vibrations. The authors found that when the dependence is significant, mirror symmetry can be lost between fluorescence and absorption spectra. This is because in the transition moment operator the "allowed"

and "forbidden" components will either add in absorption and subtract in fluorescence or vice versa resulting in a loss of the mirror image between the spectra.

The effects of anharmonicity and of the Duschinsky effect (7) on the totally symmetric vibronic perturbations in the phenanthrene spectrum have been considered by Craig and Small (6) to be negligible with respect to the previously discussed effect.

The Duschinsky effect (7) arises from an expansion of equation (2) to include the next higher order terms involving two or more modes (i.e., off diagonal Herzberg Teller coupling). This expansion results in a transformation between the normal coordinates for the ground and excited states' motions which includes a rotation of the eigenvectors of the two states in coordinate space. This rotation restricts Duschinsky mixing to modes of the same symmetry when the point group symmetries of the ground and excited states are the same.

Sharf and Honig (8) pointed out that it was theoretically inconsistent to apply HT theory with ground state normal coordinates and neglect the Duschinsky effect, since the vibronic coupling mechanism will induce rotations in normal coordinate space. They also predicted that a loss in mirror symmetry between emission and absorption will result from the vibronic interactions when several promoting modes are active.

The assumption that the difference in composition, in terms of symmetry coordinates, between the normal vibrational modes of the ground state and the first excited state (Duschinsky effect) can be neglected in the HT coupling theory of absorption and fluorescence

has been examined by Small (9). Inclusion of the Duschinsky effect in the HT coupling for two or more nontotally symmetric perturbing vibrations introduces a constructive-destructive interference problem, involving the "forbidden" transition moments, similar to the problem discussed previously (6) for totally symmetric perturbing modes. This interference can also lead to a breakdown in mirror symmetry. The sign problem, involving the "allowed" and "forbidden" components of the transition moment operator, introduces the possibility that, in a given vibronic transition to or from, for example, the lowest excited state, the higher energy states may collectively act as an intensity source or sink.

The conventional Herzberg-Teller theory of vibronic borrowing has been criticized by Orlandi and Siebrand (10) who stress the importance of the Born-Oppenheimer borrowing mechanism based on nuclear momenta integrals. (The HT mechanism is based on the dependence of the electronic transition dipole moment integrals on nuclear position. This dependence is neglected in the Condon approximation, so that the HT mechanism is based on deviations from the Condon approximation. The BO mechanism is based on deviations from the Born Oppenheimer approximation, i.e., coupling between adiabatic BO states caused by nonvanishing nuclear momenta.) If the transition is forbidden then Orlandi and Siebrand have shown that the linear terms in HT coupling are

$$M_{mn}^{HT} \approx \sum_i \{ \langle \phi_m | P | \phi_i \rangle \langle \phi_i | \partial/\partial Q | \phi_n \rangle - \langle \phi_m | \partial/\partial Q | \phi_i \rangle \langle \phi_i | P | \phi_n \rangle \}_{Q_0} \langle \Lambda_m | \Lambda_n \rangle \quad (8)$$

and the linear terms in BO coupling are

$$M_{mn}^{BO} \approx \sum_i \left\{ \frac{\hbar\omega}{\Delta E_{im}} \langle \phi_m | P | \phi_i \rangle \langle \phi_i | \partial/\partial Q | \phi_n \rangle - \frac{\hbar\omega}{\Delta E_{im}} \langle \phi_m | \partial/\partial Q | \phi_i \rangle \langle \phi_i | P | \phi_n \rangle \right\} \langle \Lambda_m | \Lambda_n \rangle \quad (9)$$

where the minus sign arises because  $\partial/\partial Q$  is an anti-Hermitian operator and  $\langle \Lambda_m | \Lambda_n \rangle$  are the vibrational overlap integrals. From equations (8) and (9) it can be seen that when the energy separation is of the order of  $\hbar\omega$ , then BO coupling is comparable to HT coupling.

Geldof et. al. (11) have also noted that for energy separations between the two interacting states of the order of the promoting vibrational modes that BO coupling was very important. They used the example of pyrene to show the importance of the BO coupling mode ( $\approx 1100 \text{ cm}^{-1}$ ). Orlandi and Siebrand (10) pointed out that for pyrene the energy separation between  $S_1$  and  $S_2$  is  $\approx 2700 \text{ cm}^{-1}$  which is much larger than the frequency of the promoting mode ( $\hbar\omega \approx 1100 \text{ cm}^{-1}$ ). These authors suggested that BO coupling is still important due to partial cancellation of the  $S_1$ - $S_2$  HT coupling term by a term representing HT vibronic coupling between  $S_0$  and some higher singlet state.

The assumption made in both HT and BO coupling schemes with regard to isotope dependence has been criticized by Orr and Small (12). They feel that the dynamics of vibrations are not necessarily invariant to isotope substitution, but that isotope dynamic mixing (IDM) may play an important role on the vibronic structure in observed spectra. In fact, depending upon the sign of the mixing cross terms, the heavy atom may decrease the observed intensity of some modes in absorption.

Orr and Small (13) have extended the theory of vibronic coupling to include BO coupling, and the Duschinsky and isotope dynamic mixing adiabatic corrections to the conventional HT theory. This theory is a first order approximation which is basically only applicable to molecules where the perturbing vibrational frequencies are small relative to the energies which separate the coupled electronic states. This is because in systems where this energy gap is larger than the geometries of coupled excited electronic states must be known (11).

### C. Phosphorescence Decay Lifetimes For $n\pi^*$ and $\pi\pi^*$ States

Assuming that in a heterocyclic molecule the states of interest can be considered as pure  $\pi\pi^*$  and  $n\pi^*$  singlets and triplets, then several different criteria can be used to distinguish between the two types of states. These criteria for differentiation are: phosphorescence decay lifetimes, polarization of absorption, fluorescence and phosphorescence 0-0 bands, the energy separation between singlet and triplet states, solvent effects, heavy atom effects, and isotope effects.

For phosphorescence decay lifetimes, in general, if the observed lifetime is  $> 1$  sec then the emitting state is  $^3\pi\pi^*$  and if the lifetime is  $< 10^{-2}$  sec then the triplet state is  $^3n\pi^*$ . In the intermediate lifetime range, this criteria is doubtful since the phosphorescing state is probably a hybrid state of the form

$$^3\psi = a^3\phi(\pi\pi^*) + b^3\phi(n\pi^*) \quad (10)$$

where  $a$  and  $b$  are mixing coefficients and  $^3\phi(\pi\pi^*)$  and  $^3\phi(n\pi^*)$  are orbitally pure states. It is important to realize that the phosphorescence decay lifetime observed is not the true triplet state radiative lifetime since

$$\tau_p = 1/(k_{PT} + k_{QT}) \quad (11)$$

where  $k_{PT}$  and  $k_{QT}$  are the radiative and nonradiative rates of deactivation of the triplet state respectively.

The longer lifetimes for pure  $^3\pi\pi^*$  states in comparison to  $^3n\pi^*$  states results from the spin-orbit-vibronic coupling involved. Since transitions involving a change of multiplicity are

forbidden, there must be spin-orbit coupling to some singlet state which has a non zero transition dipole moment. For  $T_1(^3\pi\pi^*)$  the possible coupling routes as shown by equation (7) are direct spin-orbit coupling to (i)  $S_i(^1n\pi^*)$  or (ii)  $S_i(^1\pi\pi^*)$ , or (iii) vibronic coupling in the singlet manifold  $S_i(^1n\pi^*) \rightarrow S_k(^1\pi\pi^*)$  with spin-orbit coupling to  $T_1$ , or (iv) vibronic coupling in the triplet manifold  $T_j(^3n\pi^*) \rightarrow T_1(^3\pi\pi^*)$  with spin-orbit coupling to  $S_i(^1\pi\pi^*)$ . The allowed transition dipole moment of an  $S_i(^1n\pi^*) \leftarrow S_0$  transition is low and, therefore, mechanism (i) would give little "allowed" transition dipole moment to the  $T_1(^3\pi\pi^*) \rightarrow S_0$  transition. This results in a long lived phosphorescence from  $T_1(^3\pi\pi^*)$ . Since mechanism (ii) requires three-centre matrix coupling terms it is not competitive and can be omitted. For mechanisms (iii) and (iv) the length of the observed lifetime is dependent on the strength of the vibronic coupling. Thus with increasing  $^1,^3n\pi^*$  character in  $T_1$  the phosphorescence lifetime decreases.

For a  $T_1(^3n\pi^*)$  state mechanism (i) is not competitive. For mechanism (ii), direct spin-orbit coupling to a  $^1\pi\pi^*$  state with a strong transition dipole moment would mean a strong "stolen" transition dipole moment for  $T_1(^3n\pi^*) \rightarrow S_0$  phosphorescence. Thus there would be a short observed phosphorescence decay lifetime. In mechanism (iii) and (iv) the states of interest are now  $S_i(^1\pi\pi^*)$ ,  $S_i(^1n\pi^*)$  and  $T_j(^3\pi\pi^*)$ . In these two mechanisms as the vibronic coupling to the  $^1,^3\pi\pi^*$  states increases, the observed lifetime increases.

### D. Polarization

After absorption of energy by a molecule the probability of a transition depends on the square of the transition dipole moment integral

$$\text{Probability} \propto | \langle \psi_i | M | \psi_j \rangle |^2 \quad (12)$$

where M is the transition moment operator. If the transition moment (or matrix element of the electric dipole moment) between two states is

$$R_{ij} = \langle \psi_i | M | \psi_j \rangle \quad (13)$$

then when  $R \neq 0$  the transition is electric dipole allowed.

Molecules whose absorption transition moments are parallel with the electric vector of the light will be excited. Because of the different symmetry characteristics of the n and  $\pi$  orbitals relative to the molecular plane, the "allowed"  $\pi^* \leftarrow n$  singlet-singlet transitions are out-of-plane polarized. For "allowed"  $\pi\pi^*$  transitions the polarization is in-plane. For "forbidden" but observed transitions, either  $n\pi^*$  or  $\pi\pi^*$ , the observed polarization will be that of the state with "allowed" transition probability which is vibronically mixed to the "forbidden" state.

For phosphorescence, the polarization is determined by that of the perturbing transition or state. Thus for  $^3n\pi^* \rightarrow S_0$ , the phosphorescence polarization is generally in-plane since the perturbing state is usually  $\pi\pi^*$ . Similarly a  $^3\pi\pi^* \rightarrow S_0$  transition will be out-of-plane polarized since the perturbing transition is usually  $n\pi^*$ .

### E. Singlet-Triplet Intervals

It has been shown (14) that for an  $lk$  electron configuration that the singlet-triplet interval is

$$E_s - E_t = 2K_{lk} \quad (14)$$

where  $K_{lk}$  is the electrostatic exchange integral and is given by

$$K_{lk} = \iint \psi_l(x_1)\psi_k(x_1)\psi_l(x_2)\psi_k(x_2) \left\{ \frac{e^2}{|x_1-x_2|} \right\} dx_1 dx_2 \quad (15)$$

where  $\int \psi_l(i)\psi_k(i)dx_i$  ( $i = 1$  or  $2$ ) are the overlap integrals. As can be seen from equation (15), the singlet-triplet interval is dependent upon the overlap between the initial and the final states.

Experimentally it has been found that the energy separation between  $^1n\pi^*$  and  $^3n\pi^*$  states is approximately  $2\,000$ - $4\,000\text{ cm}^{-1}$ . For the energy separation between  $^1\pi\pi^*$  and  $^3\pi\pi^*$  states it has been found to be generally larger and with values between  $3\,000\text{ cm}^{-1}$  and  $20\,000\text{ cm}^{-1}$ . The difference in observed energy gaps is due to the difference in the overlap in  $n\pi^*$  states as compared to the overlap in  $\pi\pi^*$  states. In  $n\pi^*$  states the overlap is between an in-plane  $n$  orbital and an out-of-plane  $\pi^*$  orbital. This overlap is usually weak and thus  $K$  is small. For  $\pi\pi^*$  states there is the much stronger overlap between an out-of-plane  $\pi$  orbital and an out-of-plane  $\pi^*$  orbital. Therefore,  $K_{\pi\pi^*} \geq K_{n\pi^*}$ .

## F. Solvent Effects (15, 16, 17)

Pure  $\pi\pi^*$  and  $n\pi^*$  states are experimentally distinguishable in solution absorption spectroscopy. This is because  $n\pi^*$  states are blue shifted (to shorter wavelengths) and  $\pi\pi^*$  states are red shifted (to longer wavelengths) on going from a nonpolar to a polar solvent.

The blue solvent shift of  $n\pi^*$  states may be explained as follows. Because there are two nonbonding electrons in the ground state but only one in the excited state, stronger hydrogen bonds between the solute and polar solvent can be formed with the ground state molecules. These stronger hydrogen bonds would tend to stabilize the ground state more than the excited state. Also the ground state which is at equilibrium with the polar solvent cage is stabilized by the formation of solute-solvent electrostatic interaction complexes. After absorption, however, to the metastable excited state (i.e., Franck Condon state) there is less stabilization of this excited state with respect to the stabilization of the ground state because the solvent molecules are not necessarily oriented in their equilibrium positions about the solute molecule. This results in the formation of weaker electrostatic interaction complexes with the solute molecule. This would increase the energy separation between the ground and excited states in the polar solvent, as compared to the energy separation in the nonpolar solvent, resulting in a blue shift in the polar solvent.

The red solvent shift observed with  $\pi\pi^*$  states is a smaller shift than the blue shift observed for  $n\pi^*$  states. This smaller shift occurs because the interactions are the weaker dispersive forces, which are proportional to  $1/r^6$ , as compared to the stronger electrostatic interactions with  $n\pi^*$  states.

The strong  $n\pi^*$  blue shift and the weaker  $\pi\pi^*$  red shift have a new observable consequence in emission. The solvent shifts in certain cases, usually with carbonyl (C=O) containing molecules, are enough to reverse the order of the lowest singlet and/or triplet states.

Pownall and Huber (18) in a study of the luminescence of xanthone found that in the nonpolar solvent, 3-methylpentane (3MP), that the lowest triplet state was  $^3n\pi^*$ , whereas, in the polar solvent, EPA (diethyl ether, isopentane, ethanol, 5:5:2), the lowest triplet state was  $^3\pi\pi^*$ . The phosphorescence lifetimes observed, however, were nonexponential which lead the authors to conclude that there were two emissions due to different solvent cages in the rigid solvent glasses. They also noted that in the very highly polar glass, MW (methanol, water, 20:1), that xanthone fluoresced. This they considered as an indication of an interchange of the lowest singlet states from  $^1n\pi^*$  in the nonpolar solvent to  $^1\pi\pi^*$  in MW.

Another consequence of the solvent shifts in emission has been the observation of dual phosphorescence in molecules such as 1-indanone. Long and Lim (19) reexamined the dual phosphorescence of 1-indanone. They argued that the large blue shifting of the lowest  $^3n\pi^*$  from nonpolar to polar solvents was responsible for the observed dual emission. In 3MP they found that the emission was solely from  $^3n\pi^*$  and in the very polar solvent, MW (methanol, water, 9:1), that the emission originated from only the  $^3\pi\pi^*$  state. In the intermediate polar solvent, EPA, they found dual phosphorescence which they attributed to strong emission from the lowest triplet ( $^3n\pi^*$ ) and weaker, longer-lived emission from the close lying, higher energy (ca.  $30\text{ cm}^{-1}$ )  $^3\pi\pi^*$  state.

### G. External Heavy Atom Effects

The first external heavy atom effect was observed by Kasha (20). Since then it has been confirmed that the external heavy atom effect is due to increased spin-orbit coupling. The external spin-orbit coupling due to the heavy atom produces several observable effects: (2)

- (i) the  $T_1 \leftarrow S_0$  absorption transition is enhanced;
- (ii) the phosphorescence lifetime decreases;
- (iii) the fluorescence quantum yield decreases;
- (iv) the rate of intersystem crossing increases;
- (v) the phosphorescence quantum yield may increase.

The decrease in fluorescence quantum yield is thought to be due to the increase in the rate of intersystem crossing (20). There is also an increase in  $k_{PT}$  and  $k_{QT}$  because the spin-orbit matrix elements which are sensitive to the heavy atom perturbation are contained in the electronic integral for the probability of  $T_1 - S_0$  transitions (21). Often it can not be predicted whether  $k_{PT}$  or  $k_{QT}$  will increase the most. This also means that an increase or decrease in phosphorescence quantum yield can occur.

Since the observed phosphorescence decay lifetime is the reciprocal sum of  $k_{PT}$  and  $k_{QT}$ , an increase in these latter two rates will decrease  $\tau$ . Though the observed effects of the external heavy atom are well known, the reasons for these effects have not been generally accepted.

Giachino and Kearns (22, 23) examined the effects of the external heavy atom on the luminescence from aromatic hydrocarbons. They arrived at a number of conclusions:

- (i) Radiative  $T_1 - S_0$  transitions ( $k_{PT}$ ) are much more susceptible to a heavy atom effect than are the corresponding radiationless

transitions ( $k_{QT}$ ).

(ii) The important perturber states appear to be highly localized on the heavy atom rather than states which are essentially delocalized (eg.  $\pi\pi^*$  states).

(iii) The enhancement of the radiative  $T_1 - S_0$  transitions is due to mixing of excited singlet states associated with the perturber molecule into the triplet state of the perturbed molecule.

(iv) It is not necessary to invoke charge transfer interactions to account for the enhancement (22).

(v) Only totally symmetric modes of the molecule are enhanced by the external heavy atom. This implies that the effect is purely electronic and that there is no vibronic coupling (23).

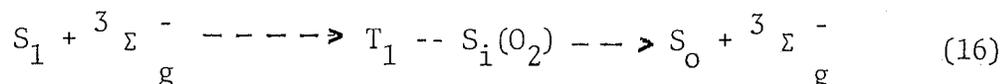
The fourth conclusion is in opposition to that of McGlynn *et. al.* (2) and Azumi (24) who consider the heavy atom effect to be a charge transfer interaction rather than an electron exchange mechanism.

The third conclusion above is also in opposition with the work of Azumi (24). Azumi has examined the effect of the external heavy atom perturbation on each of the three spin sublevels of the lowest triplet state of planar aromatics. He has concluded that the external spin-orbit enhancement is mainly due to the opening of new spin-orbit coupling channels, in which the mixing singlet state is of the charge transfer configuration from a  $\pi$  orbital of the molecule to a vacant  $\sigma^*$  orbital of the perturber. Azumi states that the locally excited states contribute to the total transmission probability, terms approximately proportional to the fourth power of the overlap, whereas, the contribution from charge transfer states is approximately proportional to the second power.

McGlynn et. al. (2) state that the heavy atom effect introduces no new spin-orbit coupling mechanisms but rather increases the spin-orbit coupling already present. Azumi's mechanism (24) introduces new spin-orbit coupling routes without increasing the already present spin-orbit coupling very much. Azumi uses the experimental results available for quinoxaline's three spin sublevels,  $T_x$ ,  $T_y$  and  $T_z$  (25, 26) as support for his mechanism. Spin-orbit coupling in quinoxaline is one-centre coupling from  $T_z$  to dipole allowed singlet states, one-centre and three-centre coupling from  $T_y$  to dipole forbidden singlet states, and three-centre coupling from  $T_x$  to a dipole allowed singlet state. The external heavy atom opens up new spin-orbit coupling routes from  $T_{x,y,z}$  via two-centre terms. This would increase the coupling from  $T_x$  and  $T_y$  much more than from  $T_z$ .

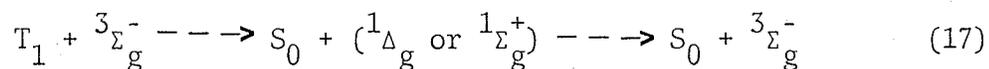
It is not conclusively known which transition rate ( $k_{ISC}$ ,  $k_{PT}$  or  $k_{QT}$ ) is increased the most by external spin-orbit coupling. According to McGlynn et.al. (27), it appears that the external heavy atom perturbation increases  $k_{ISC}$  more than  $k_{PT}$  or  $k_{QT}$ .

Another form of external heavy atom perturbation is quenching of fluorescence and phosphorescence by dissolved oxygen. Oxygen quenching is a diffusion controlled process and thus in frozen solvent glasses dissolved oxygen has little if any effect on fluorescence or phosphorescence. If quenching does occur it is a bimolecular collisional process which can be considered as a pseudo unimolecular process because the concentration of ground state oxygen molecules remains constant. Fluorescence quenching probably occurs via a mechanism such as (2)



where  $S_1$  and  $S_2$  are the first excited and ground singlet states respectively of the molecule being quenched,  ${}^3\Sigma_g^-$  is the triplet ground state of oxygen,  $T_1 \text{ -- } S_i(O_2)$  is some form of complex between the triplet state of the quenched molecule and an excited singlet state of oxygen, and  $\text{---}\rightarrow$  represent nonradiative deactivation processes.

Phosphorescence quenching is thought to be an energy transfer mechanism such as (17)



where  $T_1$  and  $S_0$  are the lowest triplet and ground states of the quenched molecule,  ${}^3\Sigma_g^-$  is the ground triplet state of oxygen and  ${}^1\Delta_g$  and  ${}^1\Sigma_g^+$  are upper excited singlet states of oxygen.

## H. Internal Deuterium Effect

Replacing the hydrogens by deuteriums in an aromatic hydrocarbon increases the observed phosphorescence lifetime  $\tau$ . The explanation of this effect was given by Robinson and Frosch (28, 29). In their theory of radiationless transitions, the nonradiative decay rate  $k_{QT}$  is proportional to the Franck-Condon factors (i.e., vibrational overlap integrals). Since the vibrational overlap integrals are smaller for deuterium than for hydrogen,  $k_{QT}$  is lowered and  $\tau$  is raised.

Siebrand (30) has shown that the primary accepting modes responsible for  $T_1 \rightarrow S_0$  radiationless decay in aromatic hydrocarbons are the anharmonic C-H stretching vibrations. Replacement of the hydrogens by deuteriums forms C-D vibrations which are of a lower frequency and have less anharmonicity than their corresponding C-H vibrations. Since C-D vibrations are of lower frequency more oscillators are required to accept the energy which causes a decrease in  $k_{QT}$ .

From the work of Robinson and Frosch (28, 29) and Siebrand (30) it has been shown that the increase in  $\tau$  for aromatic hydrocarbons is due almost solely to a decrease in  $k_{QT}$  with little if any change in  $k_{PT}$ .

For heterocyclics there is in general no clear distinction between the effects of deuteration on  ${}^3_{n\pi^*}$  and  ${}^3_{\pi\pi^*}$  states because in many heterocyclics there is strong vibronic coupling between the two different types of states. If the lowest triplet state, however, is primarily  $\pi\pi^*$  then deuteration is expected to increase  $\tau$  by about the same magnitude as the increase observed for aromatic hydrocarbons.

When the lowest triplet state is primarily  $n\pi^*$  there is only a small increase in  $\tau$  (1).

## I. Triplet-Triplet Absorption

In general the only way that the upper triplet states of conjugated molecules can be studied is by triplet-triplet (T-T) absorption techniques. Direct absorption  $T_j \leftarrow S_0$  is unlikely to be seen due to the low extinction coefficients of the spin forbidden  $T_j \leftarrow S_0$  transitions and due to the interference of overlapping  $S_1 \leftarrow S_0$  allowed transitions.

There are two general techniques for observing T-T absorption. The earliest technique is the steady-state technique developed by Lewis *et. al.* (31, 32). The more recent method is the synchronized flash technique first developed by Porter (33). A combination of both techniques which includes a steady-state light source and a flash excitation has also been commonly used. Recently, Henry and Charlton (34) used this technique to study the position-dependent deuterium effects on radiationless transitions in anthracene.

T-T absorption by either technique can be enhanced by deuteration of the molecule being studied. As discussed in the previous section, deuteration will increase the observed phosphorescence lifetime and the triplet state population which thus enhance T-T absorption.

## SPECTROSCOPIC STUDIES ON BENZOTHIADIAZOLE

Recently there has been considerable spectroscopic interest in 2,1,3-benzothiadiazole (BTD) and closely related molecules (35 -37). Christoffersen *et. al.* (35) have analyzed the rotational structure of the lowest energy singlet-singlet absorption band at  $3280 \overset{\circ}{\text{A}}$  and assigned the transition as  ${}^1\text{B}_2 \leftarrow {}^1\text{A}_1$ . A similar conclusion was reached by Hollas and Wright (36) through a vibrational analysis of this transition which was carried out along with an analysis of related transitions in the molecules benzofurazan and 2,1,3-benzoselenadiazole. These authors detected a significant amount of  $b_2$  vibrational activity in this transition which they explained on the basis of intensity stealing from a more intense  ${}^1\text{A}_1 \leftarrow {}^1\text{A}_1$  transition at  $3060 \overset{\circ}{\text{A}}$ . The assignments were confirmed by vapor and mixed crystal studies of BTD -  $d_0$  and BTD -  $d_4$  by Gordon and Yang (37). In contrast to Hollas and Wright (36), Gordon and Yang (37) assigned the sharp vibrational maxima beyond  $32\ 400 \text{ cm}^{-1}$  to the  $3060 \overset{\circ}{\text{A}}$  system and not to overlapping sharp bands of the  $3280 \overset{\circ}{\text{A}}$  system. These latter authors also indicated that the  $3280 \overset{\circ}{\text{A}}$  transition was not primarily a benzene transition, as suggested by Hollas and Wright (36), but that the heterocyclic ring portion of the molecule played a role in the electronic structure active in the transition.

In all these studies, as well as in the recent quasiline emission studies of the related molecules naphthothiadiazole (38) and anthrathiadiazole (39), there has been no evidence concerning the presence and activity of  $n\pi^*$  states. Thus we began a study of the fluorescence, phosphorescence, triplet-triplet absorption, and phosphorescence lifetime of both BTD -  $d_0$  and BTD -  $d_4$  in an attempt to discover if  $n\pi^*$  states played any role at all in the properties of the low lying excited singlet and triplet states of this molecule.

## EXPERIMENTAL

Benzothiadiazole- $d_0$  (BTD -  $d_0$ ) obtained from the Aldrich Chemical Co. was purified by zone-refining. Benzothiadiazole- $d_4$  (BTD -  $d_4$ ) was prepared by a modified method of Khaletskii et. al. (40). The starting material for the synthesis was o-phenylenediammine (Eastman, practical grade) which after recrystallization from water was added to 100 gm  $D_2O$  and a trace of hydrochloric acid and refluxed. Every twenty-four hours for one week the  $D_2O$  and  $H_2O$  were removed and fresh  $D_2O$  was added until the o-phenylenediammine was  $\approx 98\%$  totally deuterated as determined by low voltage mass spectrometry (Finnigan 1015, 8eV). The deuterated material was refluxed with N-thionylaniline (Aldrich, analyzed quality) in benzene. After acidification and evaporation, the resulting impure BTD -  $d_4$  was recrystallized from ethanol/water. The recrystallized product was dissolved in n-pentane and dried. After vacuum sublimation there was an  $\approx 19\%$  yield of BTD -  $d_4$  with an isotopic purity of  $95 \pm 2\%$  as determined by low voltage mass spectrometry.

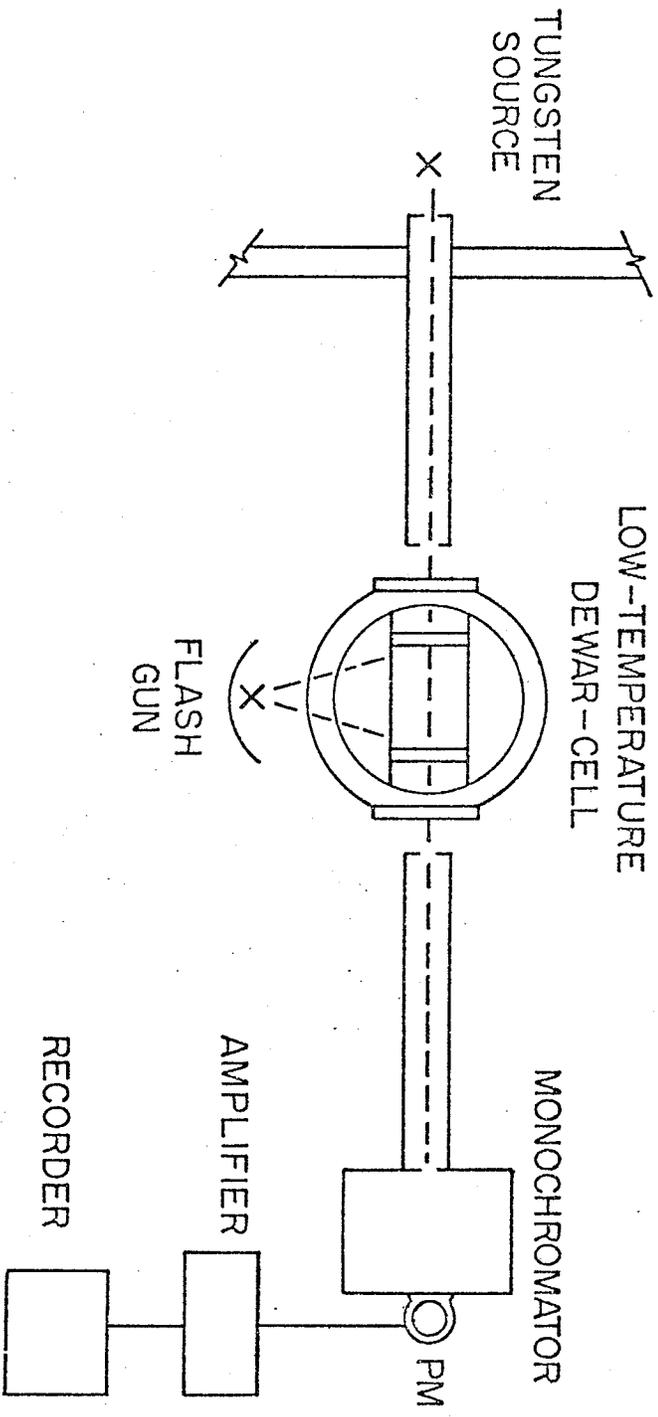
EPA (ether, isopentane, ethanol, 5:5:2) was used as received from the American Instrument Co. 3-Methylpentane (3MP) was obtained from the Phillips Petroleum Co. and was purified by the procedure of Potts (41). Absolute ethanol (Canadian Industrial Alcohols and Chemicals Ltd.) was purified by refluxing over CaO for 24 hours and then was distilled using a reflux head. Absolute ether (McArthur Chemical Co., reagent grade), ethyl iodide (Eastman, white label grade), isopentane, methylcyclohexane (Matheson, Coleman and Bell, spectro-quality) and cyclohexane (Fisher, spectroanalyzed) were used as received. The solvent mixtures used to form rigid, clear glasses at

77°K were EPA, 3MP, IM4 (isopentane, methylcyclohexane, 1:4) and EAI4 (ether, ethanol, ethyl iodide, 1:1:4).

The  $S_i \leftarrow S_0$  room temperature absorption spectra were determined with a Cary 14 spectrophotometer using approximately  $10^{-4}$ M solutions in either ethanol or cyclohexane in a 1 cm quartz cell. The  $S_i \leftarrow S_0$  absorption spectrum at 77°K was obtained on the Cary 14 in an approximately  $5 \times 10^{-6}$ M solution in EPA using a quartz sample cell about 8 cm long built into an all quartz dewar (#203908, H.S. Martin Co., Evanston, Ill.).

The steady-state cross illumination technique originally described by Henry and Kasha (42) was used in the first attempts to observe the  $T_j \leftarrow T_1$  low temperature absorption spectrum of  $\text{BTD} - d_0$  and of  $\text{BTD} - d_4$ . However, due to the low population of  $T_1$  achieved, the observed  $T_j \leftarrow T_1$  spectrum was too weak to interpret. The  $T_j \leftarrow T_1$  absorption spectrum of  $\text{BTD} - d_4$  was observed using the flash apparatus of Henry and Charlton (34). This experimental arrangement as seen in Fig. 2 was a modification of the apparatus originally described by Porter (43). The analyzing light source was an unfiltered tungsten bulb (General Electric CPR 18A, 6V) powered by a six volt storage battery. The collimated beam from the light source was passed through the sample contained in the quartz cell and dewar described for the low temperature  $S_i \leftarrow S_0$  absorption. The sample was prepared as an approximately  $10^{-4}$ M solution of  $\text{BTD} - d_4$  in EPA and was cooled to a clear glass at 77°K. The transmitted light then entered a 0.25 m Jarrell-Ash grating monochromator and was detected by a Hamamtsu 1P28 phototube. The amplified signal from the phototube was recorded photographically on an oscilloscope (Fairchild 766 H/F) at 50 Å intervals from 3500 Å to 5500 Å before and after flashing with an electronic flash gun

Fig. 2. Flash apparatus used to obtain the T-T absorption spectrum and the triplet state lifetime from the decay of T-T absorption.



(Honeywell, model Strobonar 780) with the polystyrene filter removed.

In measuring T-T absorption and the decay of T-T absorption it was found advantageous to offset the dewar so that the incident, analyzing light beam passed through the edge of the sample nearest to the flash. By off-centering the dewar the number of triplet molecules produced by the flash in the path of the analyzing beam would be increased because of the existence of a concentration gradient of excited molecules across the absorption cell.

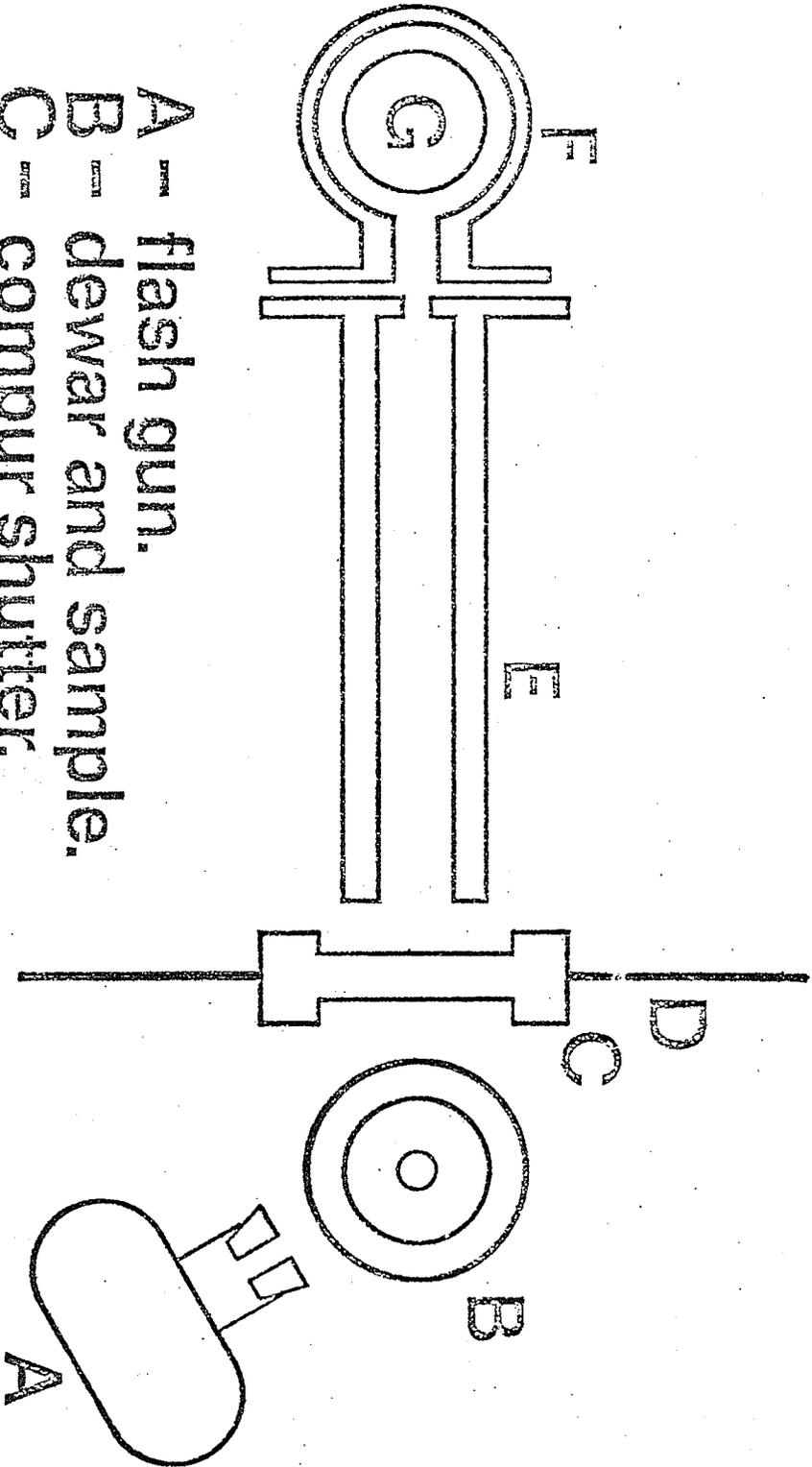
The emission spectra were measured at 77°K in approximately  $10^{-3}$  -  $10^{-4}$ M clear glassy solutions of EPA, 3MP or EAI4. The sample cell was a 5 mm i.d. quartz tube with ~2 mm i.d. finger, housed in a quartz liquid nitrogen vessel. The emission spectrophotofluorometer was a modified Aminco spectrophotofluorimeter (4-8401 A motor driven monochromator with an A11-61041 grating, 3000 Å blaze at the excitation position; and a 4-8401 A motor driven type monochromator with an A248-61041 grating, 5000 Å blaze at the analyzing position). The excitation source was either a high pressure Mercury-Xenon lamp (200 watt Hanovia 901-B) which was used for all the phosphorescence studies as well as for the fluorescence of BTD -  $d_0$  in all solvents except EAI4, or a high pressure Xenon lamp (150 watt Hanovia 901-C) which was used for the fluorescence studies of BTD -  $d_4$  in all solvents and the fluorescence of BTD -  $d_0$  in EAI<sub>4</sub>. The detector was a Hamamtsu R446S photomultiplier tube with a solid state photomultiplier microphotometer (Aminco 10-280) as a high voltage power supply and amplifier for the photomultiplier tube or with a Fluke 412B high voltage power supply and a Gencom Nanoammeter model 911 amplifier for the phototube. The amplified signal was recorded on an X-Y recorder (Photamatic model 814

or Houston Instrument X-Y recorder). The spectra were calibrated using lines from the mercury arc and the wavelength error was approximately  $\pm 30 \text{ \AA}$  which was principally due to electronic noise and the inherent broadness of the peaks. No correction was made for the varying spectral sensitivity of the analyzing monochromator and the photomultiplier tube. The phosphorescence signal was isolated from the scattered exciting light and the fluorescence by placing a Corning CS3-75 glass cut off filter between the analyzing monochromator and the photomultiplier tube.

The spectral distribution of intensity in the Mercury-Xenon and Xenon lamps as well as the effects of the excitation monochromator were such as to render light of  $3140 \text{ \AA}$  wavelength maximally effective in inducing luminescence of  $\text{BTD} - d_0$  and  $\text{BTD} - d_4$ . To isolate the shape of the fluorescence spectra from the broadness of the exciting light, the excitation wavelength was shifted to  $2960 \text{ \AA}$ .

The phosphorescence decay lifetimes in dilute glassy solutions of  $\text{BTD} - d_4$  in EPA, 3MP or IM4 at  $77^\circ\text{K}$  were measured with the apparatus shown in Fig. 3. The phosphorescence decay lifetime of  $\text{BTD} - d_0$  in any solvent could not be measured because the lifetime is of the order of the decay of the tail of the flash which then resulted in nonexponential decay curves being recorded. The apparatus consisted of a Honeywell, Strobonar 780, electronic flash gun with the plastic protective plate removed. The collimated light from the flash excited the sample in the  $\sim 2 \text{ mm}$  i.d. finger part of a  $5 \text{ mm}$  i.d. quartz tube immersed in liquid nitrogen in a quartz dewar. The emitted light was passed through a synchro compur shutter and down a brass collimating tube (i.d.  $5 \text{ mm}$ ) to a housed Hamamtsu 1P21 photomultiplier tube. The amplified signal was

Fig. 3. Phosphorescence lifetime decay measurement apparatus.



- A - flash gun.
- B - dewar and sample.
- C - compour shutter.
- D - mounting plate and baffle.
- E - collimating tube.
- F - photomultiplier housing.
- G - photomultiplier.

fed to an oscilloscope (Fairchild 766 H/F) and the resultant signal was photographically recorded. To excite only the BTD -  $d_4$  molecules a Corning glass filter CS7-54 was placed between the sample and the light source. To isolate the phosphorescence from scattered light a Corning glass filter CS3-71 was placed between the shutter and the collimating tube to the photomultiplier tube. In a typical measurement the flash gun was electronically coupled to the shutter which was set to 'M' synchronization. Triggering the shutter mechanism caused the flash to fire, the oscilloscope sweep to trigger, and the shutter to open after a delay of approximately 15 msec. Since all but the very weak, extreme tail of the flash has decayed, the phosphorescence decay of BTD -  $d_4$  could be recorded by keeping the shutter open.

The rate of triplet state deactivation was also measured by monitoring the decay of T-T absorption following flash excitation. The apparatus used was the same as shown in Fig. 2 and described previously for T-T absorption. The only differences were that the samples were BTD -  $d_0$  in EPA or BTD -  $d_4$  in EPA or IM4 and that the monochromator was set at the benzothiadiazole T-T absorption maximum at  $4100 \overset{\circ}{\text{A}}$ .

The phosphorescence decay lifetimes for BTD -  $d_4$  were calculated by fitting  $\ln$  intensity vs time to a straight line using a least mean squares analysis. The negative reciprocal of the slope of the line yielded the lifetime. The triplet state deactivation from the decay of T-T absorption was recorded as the intensity of light transmitted by the sample versus time. The relative concentrations of triplet molecules will then be given by  $\log (X_0/X_t)$  where  $X_0$  is the transmittance prior to flash excitation and  $X_t$  is the transmittance at time  $t$  after the flash. A plot of  $\ln \log (X_0/X_t)$  vs.  $t$  was fitted to

a straight line using a least mean squares analysis. The negative reciprocal of the slope of the line equalled the lifetime. The correlation coefficient  $r$  (44) which is a measure of the fit of the data to a straight line was calculated for both the phosphorescence and the T-T decays from

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\left\{ \sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2 \right\}^{1/2}} \quad (18)$$

where the  $x_i$  correspond to values of  $t$  and the  $y_i$  correspond to values of either the function  $\ln I$  or the function  $\ln \log (X_0/X_t)$ . A perfect correlation will be indicated if  $r = -1$  and no correlation if  $r = 0$ .

## RESULTS

In this study the spectral properties of 2,1,3-benzothiadiazole (BTD -  $d_0$ ) and of the totally deuterated BTD -  $d_4$  have been examined. The structure and numbering of BTD is shown in Fig. 4.

The room temperature absorption spectra of the first two observable transitions in BTD -  $d_4$  in cyclohexane and ethanol are presented in Fig. 5. Except for a slight wavelength shift towards the red, the room temperature absorption spectra of the first two transitions in BTD -  $d_0$  in the same solvents show the same general characteristics. The near ultraviolet room temperature absorption spectrum of BTD -  $d_0$  in cyclohexane agrees with the published spectrum of Gordon and Yang (37). The low temperature absorption spectrum at 77°K of the same bands as shown in the room temperature absorption spectra is presented in Fig. 6. The primary feature of the room temperature absorption spectra of BTD -  $d_0$  and BTD -  $d_4$  is the complete loss of resolution of the bands of the lower energy singlet state ( $S_1$ ) on going from nonpolar to polar solvent. At the same time there is also a slight loss of resolution of the peaks and shoulders of the second lowest energy observable singlet state ( $S_2$ ).

The energies of the major observable bands in the absorption spectrum of the second excited singlet state of BTD -  $d_0$  and BTD -  $d_4$  in different solvents are listed in Table I. The uncertainties represent the limits of a range of values determined from several spectra. The observed blue shift on going from BTD -  $d_0$  to BTD -  $d_4$  is in accord with the slight blue shift between BTD -  $d_0$  and BTD -  $d_4$  noted by Gordon and Yang (37) in their vapor absorption studies.

Fig. 4. Structure and numbering of 2,1,3,-benzothiadiazole.

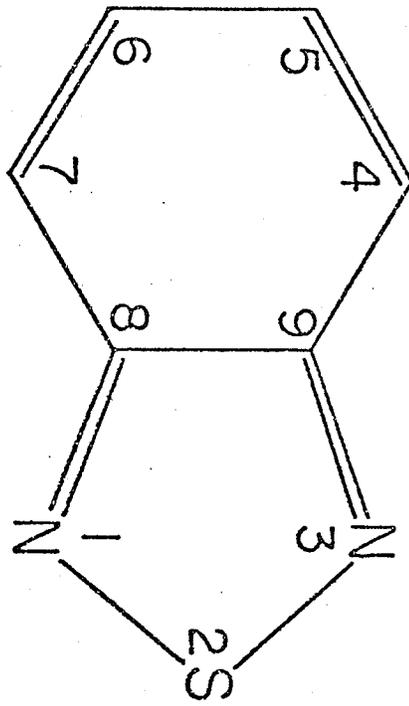


Fig. 5. Absorption spectrum of BTD-d<sub>4</sub> at room temperature in ethanol (top) and cyclohexane (bottom).

# ABSORBANCE UNITS

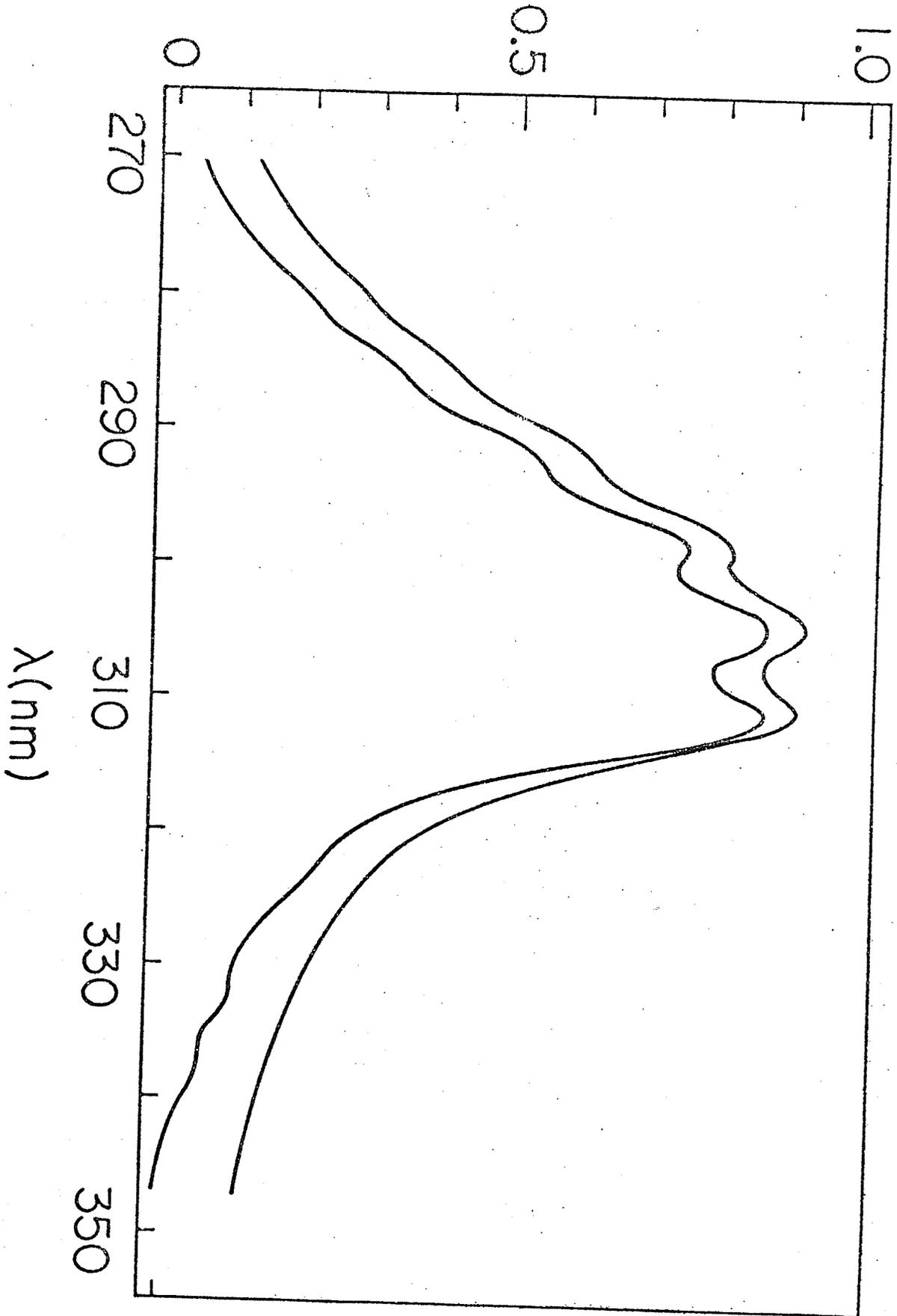


Fig. 6. Absorption spectrum of BTB-d<sub>4</sub> at 77°K in EPA rigid glass.

# ABSORBANCE UNITS

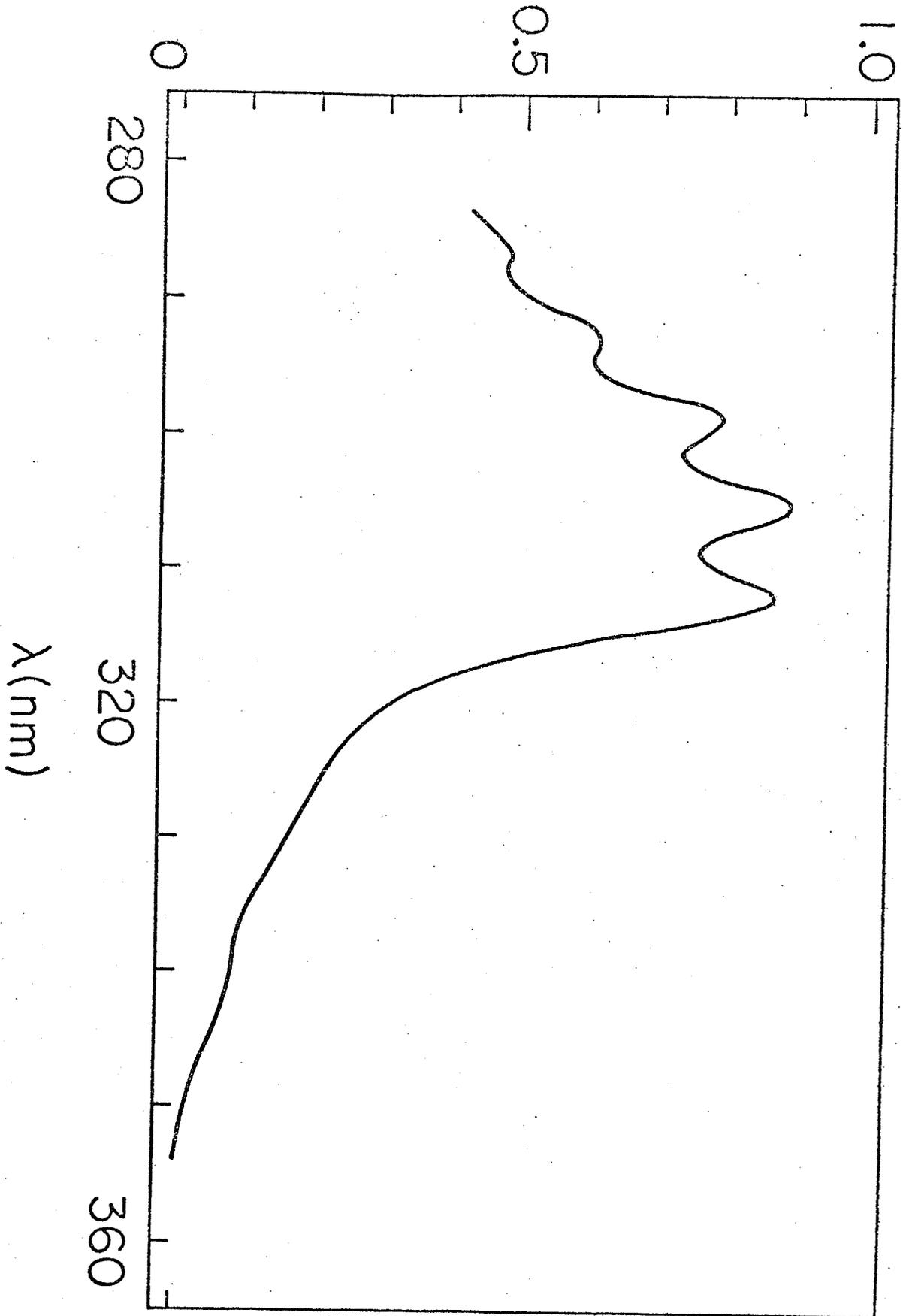


TABLE I.

BAND ENERGIES FOR  $S_2 + S_0$  IN BTD

Molecule	Solvent	Temp (°K)	$\bar{\nu} \times 10^{-3}$ ( $\text{cm}^{-1}$ )					
BTD-d <sub>4</sub>	EPA	77	32.06 ± 0.01	32.77 ± 0.03	33.47 ± 0.01	34.19 ± 0.03	34.90 ± 0.06	
-d <sub>4</sub>	ETOH	300	32.25 ± 0.03	32.92 ± 0.04	33.53 ± 0.04			
-d <sub>0</sub>	ETOH	300	32.16 ± 0.03	32.86 ± 0.03	33.47 ± 0.04			
-d <sub>4</sub>	Cyclohexane	300	32.19 ± 0.05	32.87 ± 0.04	33.52 ± 0.03			
-d <sub>0</sub>	Cyclohexane	300	32.11 ± 0.02	32.81 ± 0.04	33.44 ± 0.03			

The total emission spectrum of BTd - d<sub>0</sub> in 3MP is presented in Fig. 7. The total emission spectrum of BTd - d<sub>0</sub> in EPA matches that of BTd - d<sub>0</sub> in 3MP apart from a slight red shift. The phosphorescence appears unstructured because of the weakness of the phosphorescence signal which necessitated its analysis at maximum monochromator slit widths.

The total emission spectrum of BTd - d<sub>4</sub> in 3MP is presented in Fig. 8. The general structure of the total emission spectra of BTd - d<sub>4</sub> in EPA and EAI4 and of BTd - d<sub>0</sub> in EAI4 are the same as in Fig. 8. The lower wavelength part of the fluorescence spectra in Figs. 7 and 8 are represented by dashes because of the uncertainty due to the interference from exciting light. The ordinates represent arbitrary intensity units and are not directly comparable from spectrum to spectrum. Also to observe the shape of the fluorescence band, the exciting light wavelength was lowered from 3140 Å to 2960 Å thus preventing an exact comparison of fluorescence and phosphorescence peak heights within the same spectrum since the phosphorescence spectra were recorded at the wavelength for maximum signal (3140 Å). The energies of the fluorescence maxima and the energies of the phosphorescence maxima, or the highest energy phosphorescence maxima are listed in Table II for BTd - d<sub>0</sub> and BTd - d<sub>4</sub> in various solvents at 77°K.

In the low temperature absorption spectrum of BTd - d<sub>4</sub> in EPA, the spacing between the peaks is approximately 710 cm<sup>-1</sup>. For the phosphorescence spectrum of BTd - d<sub>0</sub> in EAI4, the average spacing is approximately 640 cm<sup>-1</sup>. For the phosphorescence spectra of BTd - d<sub>4</sub> in all three solvents, the total average spacing is approximately

Fig. 7. Total emission spectrum of BTD-d<sub>0</sub> at 77°K in 3MP rigid glass.

# RELATIVE INTENSITY

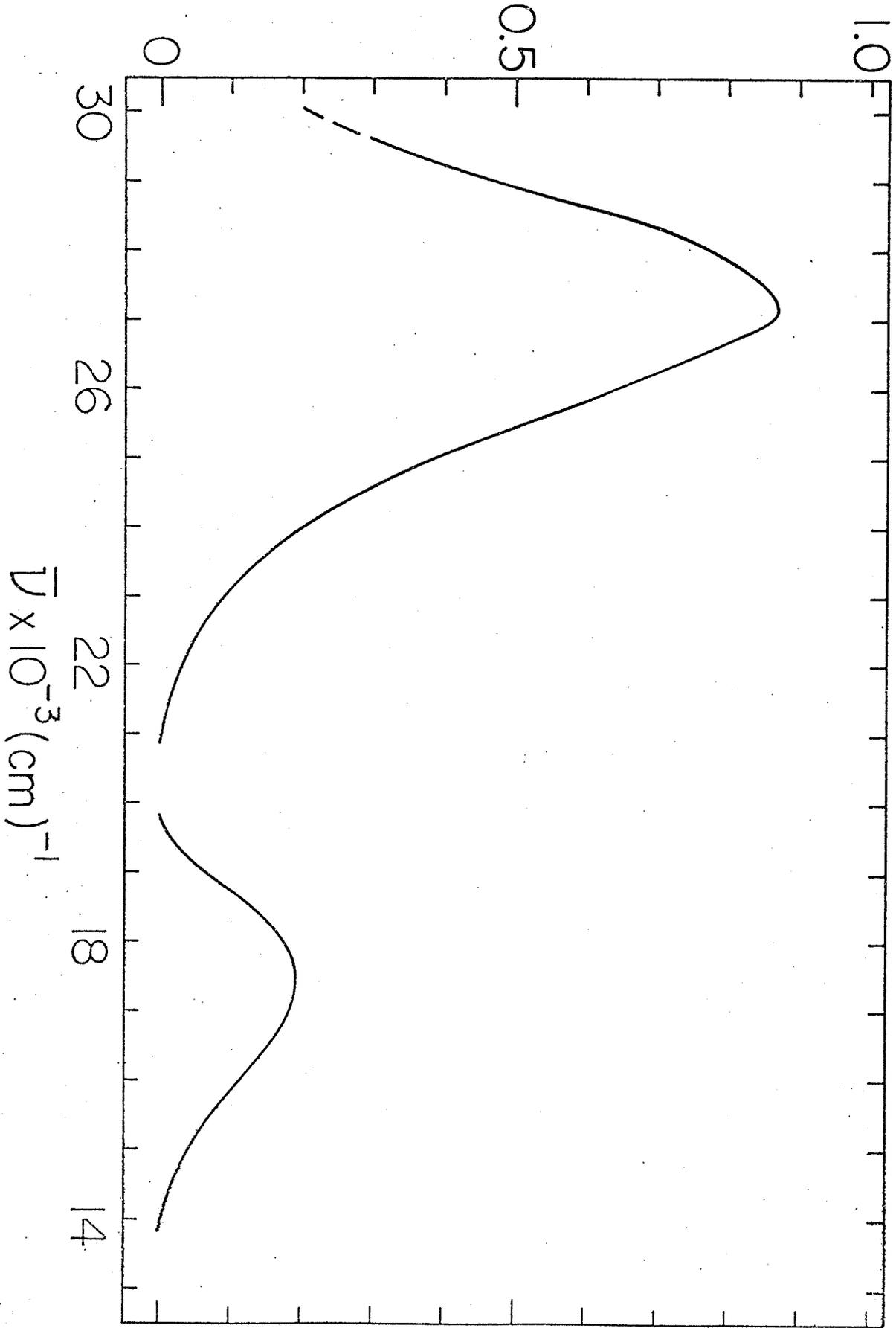


Fig. 8. Total emission spectrum of BTD-d<sub>4</sub> at 77°K in 3MP rigid glass.

# RELATIVE INTENSITY

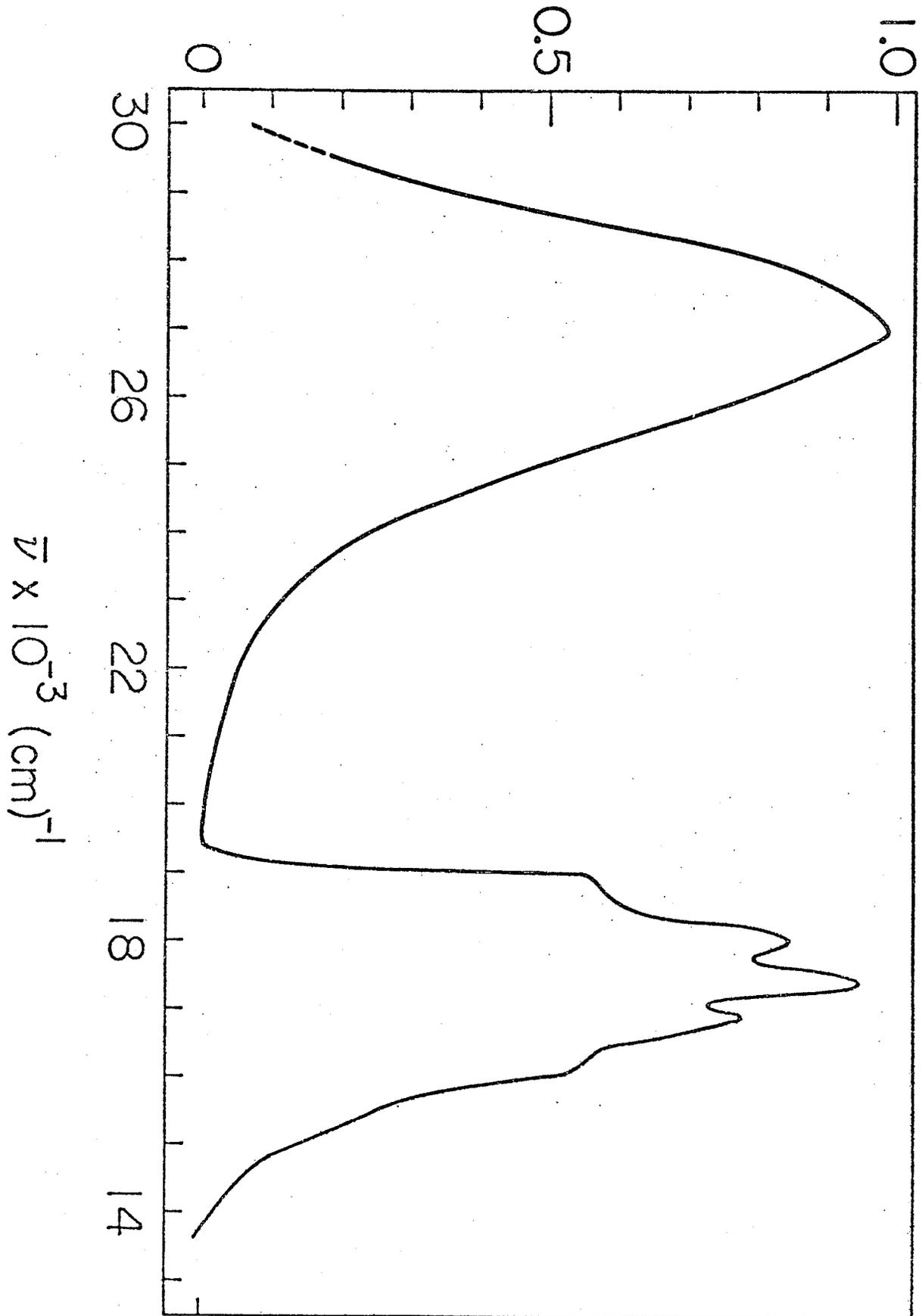


TABLE II.

## CHARACTERISTICS OF BTB EMISSION AT 77° K.

Molecule	Solvent	Fluorescence $\bar{\nu} \times 10^{-3} (\text{cm}^{-1})^a$	Phosphorescence $\bar{\nu} \times 10^{-3} (\text{cm}^{-1})$	$\tau^p^d$ (msec)	$\tau^{T-T}^e$ (msec)
BTB-d <sub>0</sub>	3MP	27.3	17.5 <sup>b</sup>		
	EPA	26.7	17.2 <sup>b</sup>		25 ± 4
	EAI4		18.5 <sup>c</sup>		
BTB-d <sub>4</sub>	IM4			153 ± 5	138 ± 8
	3MP	27.0	18.8 <sup>c</sup>	151 ± 3	
	EPA	26.9	18.6 <sup>c</sup>	144 ± 4	113 ± 7
	EAI4	26.8	18.5 <sup>c</sup>		

- a). Fluorescence maximum
- b). Phosphorescence maximum.
- c). Highest energy phosphorescence maximum.
- d). Triplet lifetime from direct phosphorescence decay measurements.
- e). Triplet lifetime from T-T absorption decay measurements.

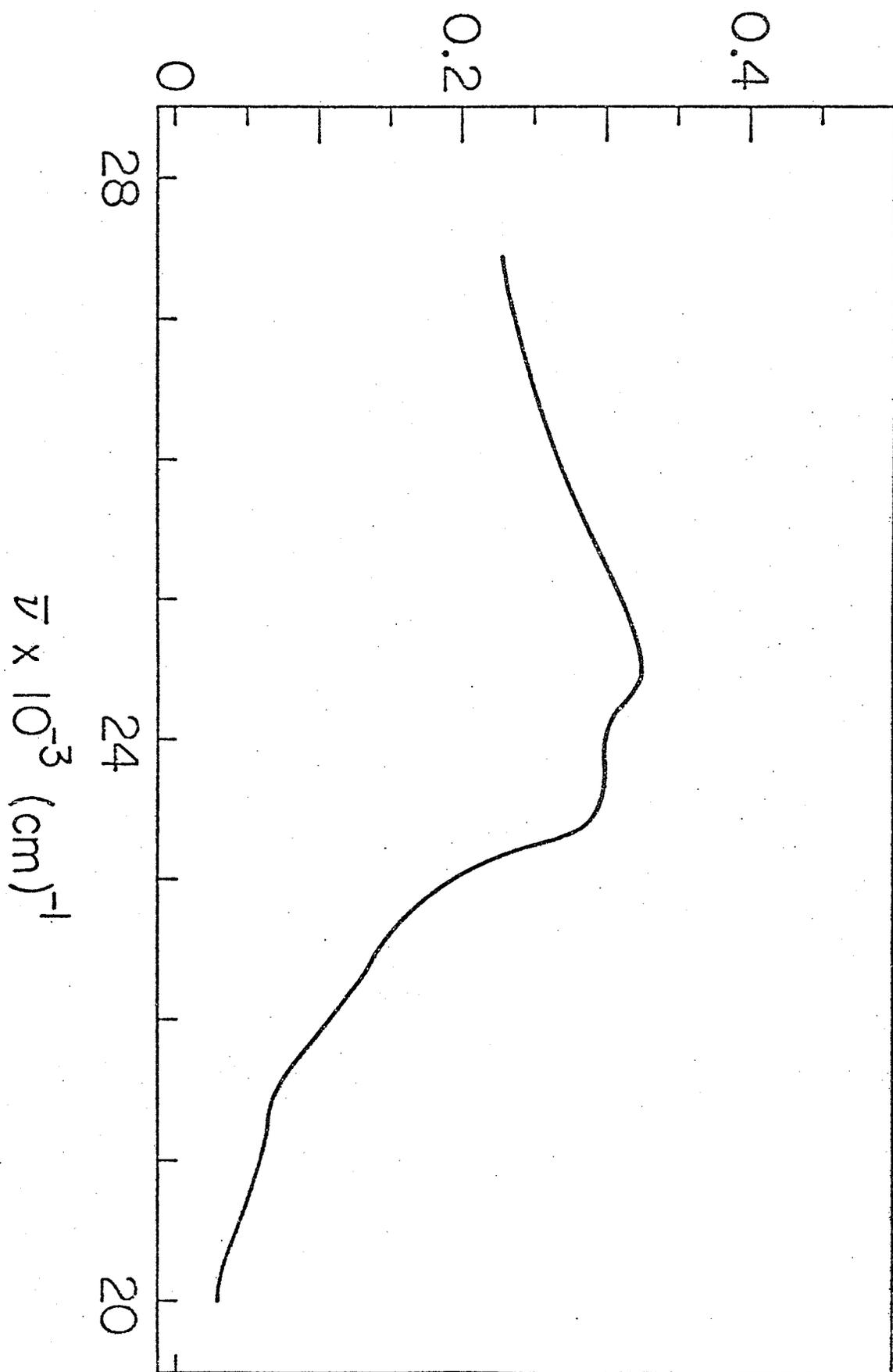
$620 \text{ cm}^{-1}$ . Only approximate vibrational band spacings can be obtained from the phosphorescence spectra because the noise present in the phosphorescence signals gave rise to an uncertainty of  $20\text{-}50 \text{ \AA}$  in measuring the peak maxima.

The T-T absorption spectrum of BTD - $d_4$  in EPA at  $77^\circ\text{K}$  is presented in Fig. 9. The spectrum is very diffuse with a hint of two peaks and two shoulders. The peaks have an approximate separation of  $750 \text{ cm}^{-1}$ .

The phosphorescence decay lifetimes for BTD -  $d_4$  in various solvents are listed in Table II. With the exception of the lifetime in 3MP, the results are the average of 10 or more measurements and the quoted errors represent the range of values obtained. For the lifetime in 3MP, the result is the average of 7 trials. The phosphorescence lifetimes for BTD -  $d_0$  and BTD -  $d_4$  from the decay of T-T absorption are listed in Table II. For these results the values listed are the average of 10 or more trials and the quoted errors represent the range of values obtained. IM4 was used as the nonpolar glass for the T-T decay measurements because it forms a more transparent glass than 3MP in the large cells used for the T-T lifetimes. With the exception of the decay of T-T absorption in BTD -  $d_0$ , the absolute values of the average of the correlation coefficients were all  $\geq 0.9989$ . For the case of BTD -  $d_0$  the absolute values of the correlation coefficients fell in the range 0.990 to 0.999 because of the weaker signal and possible interference from the decay of the tail of the flash. The phosphorescence decay lifetime of BTD -  $d_0$  could not be reliably measured because of the weakness of the signal and because of the interference due to the decay of the residual light from the flash.

Fig. 9. T-T absorption spectrum of BTD-d<sub>4</sub> in EPA rigid glass at 77°K in the range 20 000 to 28 000 cm<sup>-1</sup>: (ordinate) arbitrary linear absorption units.

# RELATIVE INTENSITY



## DISCUSSION

In the absorption spectra of Fig. 5, the  $S_1$  bands which are resolved in cyclohexane are not resolved in ethanol and the  $S_2$  bands are also slightly less resolved in ethanol. Band contour analysis has shown that the  $S_1 \leftarrow S_0$  transition is primarily a long-axis, in-plane polarized transition with some stolen intensity from a short-axis, in-plane polarized transition, assumed to be the  $S_2 \leftarrow S_0$  allowed transition (35). Because both  $S_2$  and  $S_1$  are in-plane polarized these states should be  $\pi\pi^*$  states. This makes the solvent effects on the absorption spectra observed in this study surprising. In attempt to understand these results, a band fit analysis using a Gaussian product function was run on an IBM 370 computer. It was found that the total loss of  $S_1$  resolution and the partial loss of  $S_2$  peak resolution in the observed spectra could be accounted for by a  $200 \text{ cm}^{-1}$  increase in the bandwidths at half height of  $S_2$  and  $S_1$  on going from a nonpolar ( $600 \text{ cm}^{-1}$ ) to a polar ( $800 \text{ cm}^{-1}$ ) solvent. This increase in bandwidth in polar medium is probably associated with the formation of weak solute-solvent electrostatic interaction complexes which undergo reorganization upon transition. This increase in bandwidth arises because the ground and the excited states have different equilibrium solvent cages and the solvent molecules around the ground state give rise to many different complexes of varying energies which cause broadening. The formation of these weak complexes is due to the greater hydrogen bonding capabilities of the polar solvent.

In EPA at  $77^\circ\text{K}$  there are two unresolved shoulders in the  $S_1$  region. Thus the resolution here appears to be intermediate

between the resolution in cyclohexane and ethanol at room temperature. The increased resolution observed in  $S_1$  at low temperature, as compared with room temperature ethanol, may be because the hydrogen bonding capabilities of EPA are less than ethanol. However, the peaks in  $S_2$  at 77°K are even more resolved than those in cyclohexane at room temperature. This suggests that there is increased sharpness due to the stabilization of the solvent environment at low temperature. The decreased sharpness of the  $S_1$  peaks, as compared to the  $S_2$  peaks, could be due to  $^1n\pi^*$  coupling to the  $^1\pi\pi^*$  ( $S_1$ ) state since stronger solute-solvent interactions would be expected between  $n\pi^*$  states and a polar solvent than between  $\pi\pi^*$  states and a polar solvent. This observed solvent effect on what is basically a  $^1\pi\pi^*$  electronic transition suggests, as postulated by Gordon and Yang (37), that the heterocyclic ring portion of the molecule is indeed involved in the electronic transition and the transition is not localized solely on the hydrocarbon ring as considered by Hollas and Wright (36).

The lack of definite signs of  $^1n\pi^*$  in the absorption spectra of BTD -  $d_0$  and BTD -  $d_4$  is not surprising. With the exception of the study by Korobkov et.al. (45) all the absorption studies of which we are aware on five-membered heterocyclic rings with adjacent heteroatoms show no absorption due to  $^1n\pi^*$  transitions. Korobkov et.al. (43) in an absorption study of a number of 4- or 5- position monosubstituted benzothiadiazoles attributed the weak bands at  $3300 \overset{\circ}{\text{Å}}$  -  $3700 \overset{\circ}{\text{Å}}$  to  $^1n\pi^*$  transitions. The lack of observable  $^1n\pi^*$  transitions support the predictions of Mason (46). Mason predicted that an  $n\pi^*$  transition involving a lone pair electron on a nitrogen atom in a five-membered heterocyclic ring should be stronger and occur at higher energies

relative to the  $\pi\pi^*$  bands than the corresponding transition involving nitrogen in a six-membered ring. Since it is no longer the lowest singlet state, an  $^1_{n\pi}$  transition would lose its characteristic sharpness (47) and would easily be buried under the more intense  $^1_{\pi\pi}$  transitions.

The weakness of the emission from  $\text{BTD} - d_0$  in 3MP and EPA suggests that the most important processes of deactivation are likely to be radiationless decays from  $S_1$  and/or  $T_1$ . The weakness of the fluorescence is to be expected since the  $S_1 \leftarrow S_0$  absorption transition has a low extinction coefficient. It is also expected that the most important radiationless deactivation process will be the nonradiative decay from  $T_1$  since there are probably  $^1,^3_{n\pi}$  and  $^1,^3_{\pi\pi}$  states available for spin-orbit-vibronic coupling between  $S_1$  and  $T_1$  which should make  $k_{ISC} > k_{QS}$ . For  $\text{BTD} - d_4$  in 3MP and EPA, the increased phosphorescence intensity, as compared to that of  $\text{BTD} - d_0$  in the same solvents is undoubtedly due to a decrease in the efficiency of the radiationless transition from  $T_1$  to  $S_0$ . This is the expected deuterium effect (48). The magnitude of the increase in triplet lifetime from 25 msec to 113 msec is about the same as the increase in the triplet lifetime observed for anthracene (36 msec to 117.8 msec) (34). The similar increase in lifetimes suggests that the lowest triplet state is primarily a  $^3_{\pi\pi}$  state. This assignment is also suggested by the large external heavy atom effect on the phosphorescence intensity observed for  $\text{BTD} - d_0$  (2) and the singlet-triplet interval of approximately  $9\,000\text{ cm}^{-1}$ .

Kulberg *et al.* have used the Shpol'skii method to observe the quasi-line emission spectra of anthra(2,3-d)2,1,3-thiadiazole (ATD) (38)

and naphtho(2,3-d)2,1,3-thiadiazole (NTD) (39) in nonpolar solvents at 77°K. They observed fluorescence origins in ATD and NTD at 24 940 cm<sup>-1</sup> (38) and 27 940 cm<sup>-1</sup> (39) respectively. Due to the broadness of the fluorescence spectrum of BTD-d<sub>0</sub> in all solvents an origin cannot be identified, however, the high energy onset of fluorescence occurs at approximately 29 500 cm<sup>-1</sup>. Thus as the number of hydrocarbon aromatic rings attached to the heterocyclic ring system decreases, the fluorescence blue shifts. This is the same trend observed for the fluorescence of the linear aromatic hydrocarbons, benzene, naphthalene and anthracene (1) and suggests that the lowest energy excited singlet states involved are primarily  $\pi\pi^*$  states.

However, in the series benzimidazole (1,3-benzodiazole) (BID), benzotriazole (BT) and BTD the fluorescence maxima is red shifted. For BID which has an -NH-CH=N- heterocyclic ring attached to a benzene ring the fluorescence maximum wavelength ( $\lambda_{\text{max}}^{\text{F}}$ ) is 3100 Å in H<sub>2</sub>O and 3150 Å in 95% ethanol at room temperature (49). For BT which has an -NH-N=N- heterocyclic ring attached to a benzene ring,  $\lambda_{\text{max}}^{\text{F}}$  is 3500 Å in H<sub>2</sub>O (49, 50) and in 95% ethanol (49) at room temperature. BTD whose  $\lambda_{\text{max}}^{\text{F}}$  is 3750 Å in EPA at 77°K is, however, an o-quinoid type structure (51-53) which probably has less delocalized  $\pi$  character in the ground state than the benzenoid structures of BID and BT. The red shift in  $\lambda_{\text{max}}^{\text{F}}$  through the series BID, BT and BTD suggests that the heterocyclic ring in BT and especially in BTD plays an important role in the observed transitions.

The phosphorescence of BTD occurs at a lower energy than the phosphorescence of NTD (20 062 cm<sup>-1</sup>) (39). Also the observed phosphorescence lifetime of NTD in hexane is 1.3 sec (39), whereas,

BTD-d<sub>0</sub> in EPA has a lifetime of 25 msec. This is opposite to the results observed for aromatic hydrocarbons. The phosphorescence of benzene occurs at higher energy than the phosphorescence of naphthalene, and the triplet lifetime of benzene (7.0 sec) is about three times as long as the triplet lifetime of naphthalene (~ 2.25 sec) (1). These results suggest that there is a significant amount of nπ\* character in the lowest triplet state of BTD and that this character is increased in BTD relative to NTD.

Considering the series benzimidazole, benzotriazole and BTD there is a decrease in the energy of the phosphorescence 0-0 band and in the phosphorescence lifetime. Benzimidazole ( $\lambda_{0-0}^P = 25\ 100\ \text{cm}^{-1}$  and  $\tau \sim 1\ \text{sec}$ ) (2) and benzotriazole ( $\lambda_{0-0}^P = 24\ 700\ \text{cm}^{-1}$  and  $\tau \sim 1\ \text{sec}$ ) (2) show little effect due to the extra heteroatom in BT. However, with the increased nπ\* character with respect to ππ\* in BTD-d<sub>0</sub>, as compared to BID and BT, the phosphorescence onset is at approximately  $19\ 000\ \text{cm}^{-1}$  and the triplet lifetime is 25 msec in EPA at 77°K. This suggests that there is significant nπ\* vibronic coupling to the lowest <sup>3</sup>ππ\* triplet state. Another possible explanation for the observed decrease in τ for BTD, as compared to BID and BT, is that this decrease may be due to increased spin-orbit coupling which results from the higher atomic number of the sulphur atom, as compared to the atomic numbers of the carbon atom and the nitrogen atom in the 2-position of BID and BT respectively.

The observed T-T absorption spectrum of BTD-d<sub>4</sub> in EPA is broad with little resolved structure. A similar T-T spectrum has been observed in phthalazine (54) where it was suggested that the breadth of the peaks was a reflection of nπ\* - ππ\* interactions in the triplet

manifold. A similar explanation would seem to be appropriate for BTB.

Thus it would seem that from the results observed for BTB-d<sub>0</sub> and BTB-d<sub>4</sub> that the lowest singlet and triplet states are primarily  $\pi\pi^*$  but, especially in the lowest triplet state, with  $n\pi^*$  character via coupling to higher energy  $^1n\pi^*$  and  $^3n\pi^*$  states.

Measurement of the triplet lifetime of BTB-d<sub>4</sub> by two different methods has resulted in two different values for  $\tau$  in both EPA and IM4, although this difference is greater in the polar solvent. One possible reason for this may be experimental in origin. In the T-T apparatus the analyzing light was an unfiltered tungsten bulb which contains a significant amount of IR radiation. Thus some local heating and softening of the solvent glass may occur in the region where the lifetime is being determined. This could allow mobility by dissolved oxygen and thus lead to some triplet quenching. The depletion of the triplet state would still appear to proceed via a process which was first order in BTB-d<sub>4</sub> triplets although, in reality, the sum of the rates of the intramolecular and intermolecular processes would be observed. The greater difference in lifetime observed in EPA as compared with IM4 would be due to the high solubility of oxygen in diethyl ether which is two to three times its solubility in most other organic solvents (55).

Another possible reason for this difference in lifetime could be due to the formation of a photoproduct from the excited terminal state in T-T absorption. Thus if  $I_0$  is the intensity of the transmitted light through the sample in the absence of triplets,  $I$  is the intensity in the presence of triplets, and  $\alpha$  is the fraction of excited triplet states that produce the photoproduct, then the number

of molecules reacting to give photoproduct in unit volume in unit time ( with  $I$  in einsteins/sec  $\text{cm}^3$  ) is

$$\alpha( I_0 - I ) = \alpha I_0 ( 1 - e^{-\epsilon C_T l} ) \quad (19)$$

Now if  $\epsilon$ , the extinction coefficient for T-T absorption, is taken to be  $10^4$  and it is assumed that 1/100 of the molecules present are excited to the triplet state by the flash, then  $\epsilon C_T l = (10^4) (10^{-6}) (8) \approx 0.1$  and the exponential can be approximated by the linear term. ( These estimates are reasonable since the minimum value of  $I/I_0$  is not less than 80% in these experiments. ) Thus rewriting equation (19) to the linear term

$$\alpha( I_0 - I ) \approx \alpha I_0 \epsilon C_T l \quad (20)$$

shows that photoproduct formation could compete with intramolecular triplet decay as a process also first order in triplet concentration. A probable candidate for photoproduct formation would be the radical cation  $(\cdot\text{BTD})^+$ . Such a process has been shown to occur in phenoxazine (42) and is more prevalent in polar than in nonpolar solvents due to the stabilization afforded the cation by solvation. Thus the greater lifetime difference observed in EPA as compared with IM4 is also to be expected if this mechanism is operative.

## APPENDIX

Biprotonic phototautomerism has been reported for 7-azaindole (56, 57). The results for 7-azaindole suggested the occurrence of an intermolecular double proton transfer reaction in the lowest excited singlet state. Some preliminary studies were done on the molecule, 3-deazauridine (3DAU), in an effort to detect the presence of biprotonic phototautomerism. 3 DAU was chosen because the replacement of the nitrogen atom in the 3-position of uridine by a carbon atom to form 3 DAU allows the possibility of intermolecular phototautomerism.

3 DAU was used as received from Dr. M.P. Schweizer (ICN Nucleic Acid Research Institute, Irvine, California ). The room temperature  $S_1 \leftarrow S_0$  absorption spectrum was determined with the Cary 14 spectrophotometer using approximately  $10^{-4}$  M solutions in ethanol. The low temperature emission apparatus was the same as that used for BTD except that for the measurement of the phosphorescence of 3 DAU, the excitation monochromator was removed and a filter system, consisting of a 1 cm path of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (500 g/l  $\text{H}_2\text{O}$ ) and a Corning glass filter CS7-54, was used to select the excitation wavelength band. Both the fluorescence and phosphorescence spectra were recorded using the Mercury-Xenon lamp as the excitation source and EA4 (ether, alcohol, 1:4) as the solvent for 3 DAU. The phosphorescence spectrum was isolated from the rest of the total emission spectrum by using a rotating can phosphoroscope. To record the phosphorescence lifetime decay curves of 3 DAU, the phosphorescence decay apparatus described for BTD was used with two modifications. An X-Y recorder replaced the oscilloscope and camera and instead of the glass filters CS7-54 and CS3-71 one Corning glass filter CS7-39 was used between the flash

gun and the sample dewar.

The structure and numbering of 3 DAU is presented in Fig. 10. The room temperature near-ultraviolet  $S_i \leftarrow S_0$  absorption spectrum in ethanol and the total emission spectrum of 3 DAU in EA4 at 77°K are presented in Fig. 11. The wavelengths of the maximum and minimum in the  $S_i \leftarrow S_0$  absorption spectrum,  $\lambda_{\max}^A = 2821 \pm 6 \text{ \AA}$  and  $\lambda_{\min}^A = 2451 \pm 1 \text{ \AA}$ , are in good agreement with the results of Currie et al (58) for 3 DAU in 50% aqueous ethanol ( $\lambda_{\max}^A = 281 \text{ nm}$  and  $\lambda_{\min}^A = 249 \text{ nm}$ ). The uncertainties represent a range of values obtained from several spectra. As in the emission spectra of BTD there is an uncertainty in the maximum wavelengths of fluorescence ( $\lambda_{\max}^F = 3500 \text{ \AA}$ ) and of phosphorescence ( $\lambda_{\max}^P = 4400 \text{ \AA}$ ) of  $\pm 30 \text{ \AA}$ . The observed phosphorescence decay lifetime of 3 DAU in EA4 at 77°K is  $0.72 \pm 0.02 \text{ sec}$  with a correlation coefficient,  $r = 0.9993 \pm 0.0004$ . The quoted uncertainties are standard deviations calculated from 20 trials.

In these preliminary results there is no observable evidence for the occurrence of biprotonic phototautomerism. This lack of observable biprotonic phototautomerism may be due to the low solubility of 3 DAU in the solvents available for the emission studies. Also it is possible that if biprotonic phototautomerism does occur in the rigid glasses at 77°K as was observed for 7-azaindole (57) that the long wavelength fluorescence peak which should be present would be hidden under the phosphorescence band.

The presence of the nitrogen heteroatom in the 3-position (i.e. uridine) causes a blue shift in the absorption maximum ( $2615 \text{ \AA}$  in  $\text{H}_2\text{O}$ ) and in the fluorescence maximum ( $3280 \text{ \AA}$  in  $\text{H}_2\text{O}$ ) (59) as compared to the respective maxima of 3 DAU. The phosphorescence of

Fig. 10. Structure and numbering of 3-deazauridine.

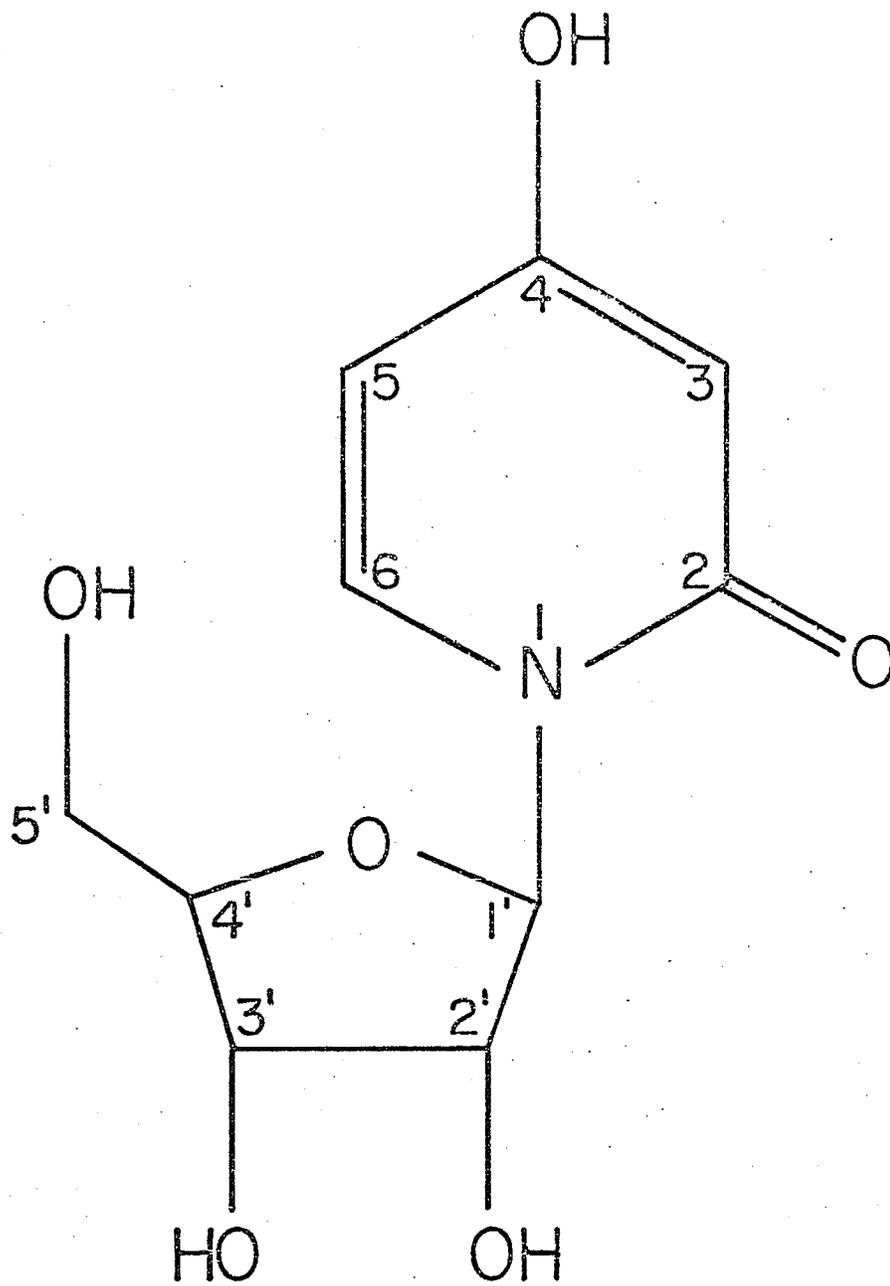
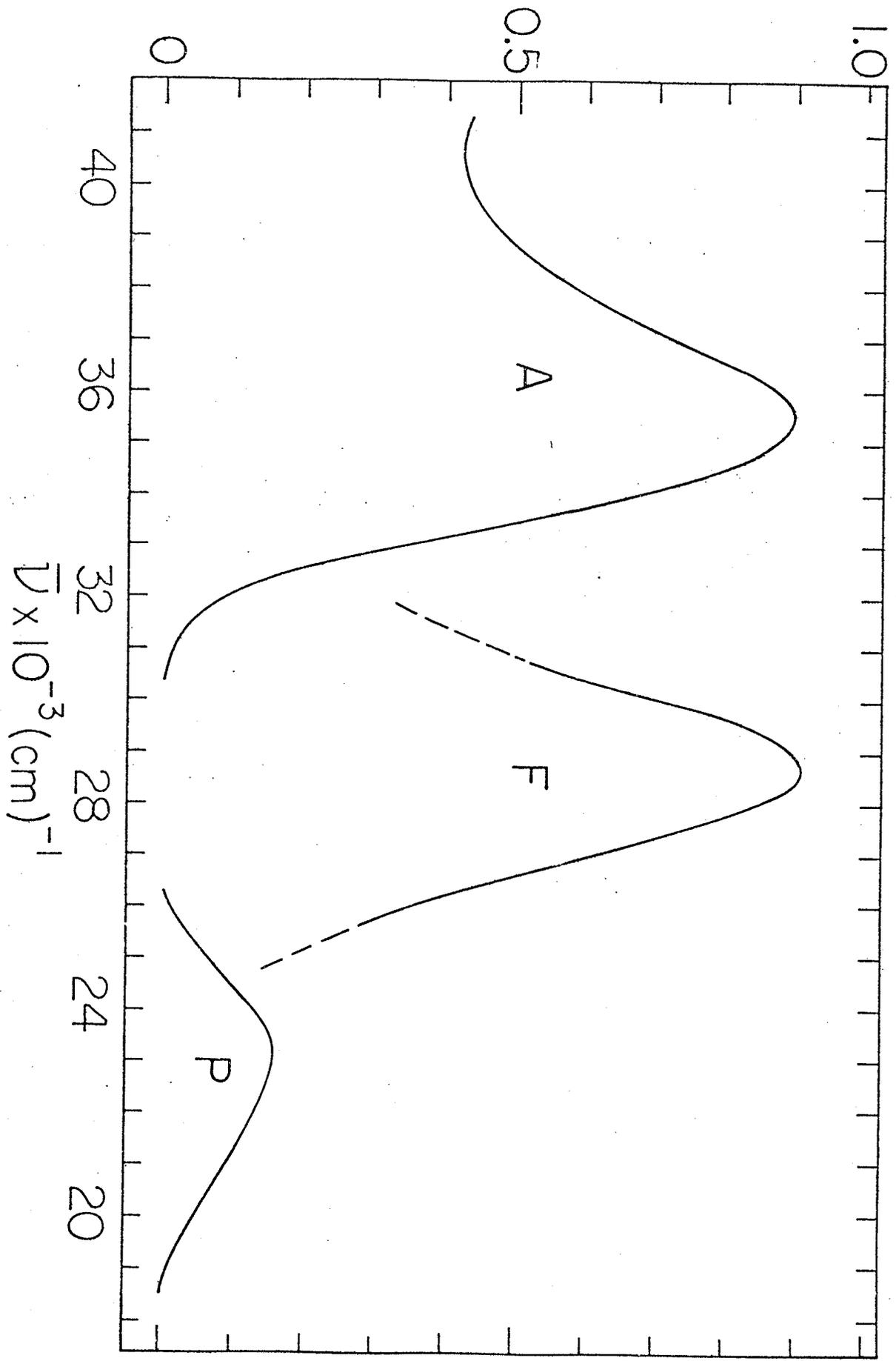


Fig. 11. The absorption spectrum of 3DAU in ethanol at room temperature and the total emission spectrum of 3DAU in EA4 at 77°K.

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uridine was observed to be very weak (59). The observed blue shift suggests that the singlet-singlet transitions are involved with the base and not the sugar part of the nucleoside

We would like to express our thanks to Dr. M.P. Schweizer, presently at the National Science Foundation, Washington, D.C., for the gift of 3DAU.

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