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EXCITON COUPLING IN MOLECULAR CRYSTALS

By

Robert L. Ake

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I. INTRODUCTION

An understanding of energy transfer is important if one is to utilize effectively the electrical and spectral properties of systems of organic molecules. For example, elucidation of the modes of triplet production and decay is essential to improving the performance of dye lasers. In addition, interpretation of the paths of energy degradation in chemiluminescent systems such as the ozone-rubrene system used to follow ozone concentrations would point the way toward improvements for this system and for the selection of other such systems of practical importance. An excellent path of research designed to provide an understanding of these mechanisms is the study of exciton coupling.

Study of exciton coupling in molecular crystals has been intensive over the last decade. This results from the wide ranging applicability of the concept to a diversity of scientific areas. Exciton coupling is thought to be responsible for the generation of enhanced triplet populations in certain molecules. Kasha (ref. 1) examined a series of phenylmethane derivatives and explained the increase in the phosphorescence yield relative to the fluorescence yield by an exciton mechanism. Little (ref. 2) has proposed an exciton type of model as a basis for the production of a room temperature superconductor. Recently Pope (ref. 3) described the production of two tetracene triplets from the "fission" of a singlet exciton. Alternatively, the migration of triplet excitons can result in triplet-triplet annihilation or "fusion" to give a singlet exciton.

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[1] Associate Professor, Department of Chemical Sciences, Old Dominion University, Norfolk, Virginia 23508.

The objective for this investigation was an understanding of the implications of perfect exciton coupling and molecular vibrations and the effect they have on the lifetime of singlet and triplet excitons coupled in a limiting geometry. Crystalline bibenzyl $C_{14}H_{14}$ provides a situation in which these mechanisms involving exciton coupling can be studied in the limit of perfect coupling between units. Such a limit is brought about by the crystal's geometry. The coupling is known to be perfect from a study of the crystal structure (ref. 4) which shows that the planes of the two phenyl rings and the C_1-C_4 and C_1'-C_4' axes in each bibenzyl molecule are parallel to each other. This geometry leads to a coupling between the two halves of the molecule resulting in a splitting of the molecular excited states. The lower energy component of the split lowest excited singlet is expected to be radiatively forbidden and was not seen by McClure (ref. 5) who studied the absorption spectrum of the crystal. He did, however, infer from vibrational splittings that the exciton splitting is 45 cm^{-1}. It is the forbidden character of the lower band, resulting from the perfect coupling in the crystalline environment, that is of interest here. The long radiative lifetime should increase the chances of intersystem crossing to the triplet manifold and produce an enhanced triplet population. Radiationless energy transfer processes become more important and thus the effect of vibronic coupling or damping on exciton migration is an important process. The long lifetime should increase "fusion" processes and the production of enhanced triplet populations should make exciton "fusion" likely.

In addition to the absorption work, McClure observed no fluorescence from bibenzyl crystals at 20 K (ref. 6). Vala, et al. (ref. 7) examined the UV-excited room temperature emission spectrum of a solution of bibenzyl in EPA and observed the expected benzene-like fluorescence. Phillips and Schug (ref. 8) excited the emission of crystalline bibenzyl at 143 K with 1 MeV electrons. They observed no fluorescence but they did see a band toward longer wavelengths of where the fluorescence might be expected to be seen which they ascribed to the phosphorescence of bibenzyl.

The present study of excitonic coupling in a limiting geometry involved an experimental approach. The approach, a spectroscopic one, begins with the purification of the bibenzyl. The purity criteria necessary for luminescence studies are very exacting. Commercially available zone refined materials are not pure enough; however, a number of techniques for improving purity are available.

The principal experimental apparatus employed was an emission spectrometer. A closed cycle cryogenic system was used to vary the temperature of the sample anywhere between 300 K and 20 K. This capability allowed a determination of temperature-dependent effects. The desired results are temperature-dependent emission spectra of the pure crystalline bebenzyl. In addition, the lifetimes and quantum yields measured at each temperature reveal the effect of competing radiationless processes.

II. EXPERIMENTAL

A. Chemicals

The chemicals used for this study were obtained from the sources listed, with the grade stated, and were used without further purification unless noted.

Toluene:	J.T. Baker Chemical Co., Analyzed Reagent Spectrophotometric.
Bibenzyl:	James Hinton, zone refined 99.7% purity Princeton Organics, PAR grade Eastman Kodak Co., Reagent grade (further purified by zone refining).
Ethanol:	U.S. Industrial Chemicals Co., Reagent grade.
2-methylbutane:	J.T. Baker Chemical Co., Baker grade.
Ethyl ether:	J.T. Baker Chemical Co., Anhydrous analyzed reagent.
EPA mixed solvent:	Matheson Coleman and Bell, phosphorimetric.
Hexane:	J.T. Baker Chemical Co., Baker analyzed reagent (further refined by distillation).

B. Equipment

1. Emission Spectrometer

The continuous wavelength excitation source was a cooled 1000-watt xenon lamp powered by a model C-72-50 regulated power supply (Oriel Corporation of America). Alternatively, a short-wave UV Pen Ray (Ultraviolet Products, San Gabriel, CA) was used because of its high intensity emission at 254 nm. Both the excitation and detection monochromator were model 82-410 .25-meter Ebert (Jarrell Ash Division, Fisher Scientific Company) with either 150-μm or 1-mm slits. The quartz optics, monochromators, and sample holder were manipulated on Ealing optical benches and accessories. The luminescence was detected by a Centronics Q4249B photomultiplier tube selected for low dark current and housed in a PR-1000 housing with a potted standard resistance chain (Products for Research). The tube was shielded with aluminum foil raised to the cathode potential and insulated with electrical tape. The phototube was powered by a Keithly 244 high voltage power supply and the photosignal was amplified by a Keithly 427 current amplifier. The signal was recorded on a Leeds & Northrup Speedomax X/L 680 potentiometric recorder or displayed on a Tektronix 5103N oscilloscope.

2. Crystal Growth Chamber

The chamber used was one designed and built at the National Bureau of Standards for growing large single crystals (ref. 9). It is based on the principle that since heat transfer between immiscible liquids is poor, a sharp temperature gradient can be developed at the liquid-liquid interface. The two liquids chosen were ethylene glycol (Eastman Kodak Co.) for the low temperature lower fluid and SF1093-inhibited dimethyl silicone oil (General Electric Co.) for the higher temperature upper fluid. A Briskheat flexible heating tape was wrapped around the upper portion to keep the silicone at about 348 K which is 20 K above the melting point of bibenzyl. The glycol was kept at room temperature which was some 30 K below the melting point of bibenzyl. The specially designed crystal growth tubes were lowered at the rate of 1 cm per day through the two liquids by a Cramer synchronous 1/3 rpd motor controlled by a percentage timer.

3. Modular Vacuum System

The vacuum system used for sample purification and loading of the crystal growth tubes was assembled from components made by Sentinel Glass Company, Hatboro, PA. Some sections were held together by Teflon gaskets and clamps while other more frequently moved sections were attached with Viton O rings and clamps. The modular arrangement gave a high degree of flexibility, employed a minimum volume to be evacuated, and allowed a minimum down time from breakage.

4. Cryogenic System

The basic cryogenic system is a Cryogenic Technology, Incorporated model Spectrum closed cycle helium refrigerator with VTR variable temperature control capable of producing a sample temperature at the cold head of 18 K to 373 K. The temperature was maintained at ± 1 K by a West temperature controller. The vacuum control system was modified to allow the input of an inert gas required for the cooldown of easily sublimed crystalline samples. A special holder was designed to hold the solution capsules and provide sufficiently good thermal contact to cool them to 20 K.

C. Methods

1. Sample Preparation

For solution spectra taken at low temperature the sample must be mounted in the vacuum shroud of the cryostat which requires that the sample be encapsulated. In order to fit the specially designed sample holder the capsule can be no longer than 5.5 cm. The capsules were made from Spectrosil tubing 4 mm (inside diameter) × 6 mm (outside diameter) (Thermal American Fused Quartz Co., Montville, NJ). One end was closed off, the tube filled with the solution, immersed in a Dewar of liquid nitrogen, evacuated, and sealed off with a H_2/O_2 torch just above the level of the liquid to insure that the sample filled the excitation beam. Th[illegible]cedure was carried out behind a safety shield.

Crystals were mounted on a copper mounting plate attached to the coldhead of the cryostat. Silicone high vacuum grease was used to insure good thermal contact. The crystal was aligned for front face luminescence studies.

2. Sample Purification and Crystal Growth

Commercially available crystalline bibenzyl was loaded into a long pyrex tube. The tube was connected to the vacuum system, the sample melted to release gases, the tube was evacuated and closed off. The tube was transferred to a zone refiner where the sample was subjected to over 100 passes. The sample tube was returned to the vacuum system where the upper third of the sample containing the impurities was removed. The middle third of the sample was transferred to a specially designed crystal growth tube whose transfer arms were then sealed. The growth tube was attached to the cable from the lowering motor and was lowered slowly through the crystal growing apparatus.

3. Absorption Spectroscopy

All absorption spectra were recorded on a Cary 14 spectrophotometer. The low temperature absorption spectra were obtained using the Spectrum cryostat with its specially designed sample holder for solution vials. The sample holder of the cryostat was positioned in the center of the sample chamber of the spectrophotometer. All low temperature absorption spectra were obtained in the single-beam mode as no reference was used. To obtain low temperature solution spectra in a glassing solvent the temperature of the cold head was lowered as quickly as possible after insertion of the sample.

4. Fluorescence and Phosphorescence Spectroscopy

All emission spectra were obtained with the spectrometer described in section II.B.1. The slit size was 150 μm. The wavelength readings are accurate to ± 1 nm. The sample was positioned for each spectrum by maximizing the intensity of the emission signal. Phosphoresence spectra were not recorded independently. Instead, a rotating sector interrupted the excitation beam, rapidly decreasing the signal since the fluorescence decay is too rapid to be followed, leaving the long-lived phosphorescence as the residual signal.

5. Lifetime Determination

The fluorescence lifetimes were too fast to record. On the other hand, the phosphorescence lifetimes were extremely slow; so slow, in fact, that conventional choppers could not be used. Instead, a simple shutter was manually inserted in the excitation beam and the decay was followed either on an oscilloscope with storage capability or on a strip chart recorder, the latter being preferred. Opening the shutter allowed the rise time to be determined.

III. RESULTS

The work of Phillips and Schug (ref. 8) was repeated. The long wavelength emission was found to belong to an impurity, trans stilbene, present in the bibenzyl crystal at a concentration of less than 1 ppm. The stilbene served as an emission trap apparently prohibiting the bibenzyl phosphorescence. The lifetime of the emission was too fast to be that of the sought after bibenzyl phosphorescence. Attempts to further purify the crystals were unsuccessful.

To establish a basis from which to proceed, solution spectra of bibenzyl and the related molecule toluene were obtained. In such a dilute environment energy transfer between possible luminescent centers is unlikely and contamination by minor components is essentially eliminated. Absorption and emission spectra of both toluene and bibenzyl dissolved in ethanol, EPA, and n-hexane were recorded as a function of temperature. It should be noted that when the mercury pen lamp was used as an excitation source a substantial amount of photolysis was observed to occur. Because of this the mercury lamp was used only for phosphorescence lifetime determinations. Further, as the ethanol solution capsules were cooled the phosphorescence seemed to appear rather suddenly at temperatures below 90 K. This might be explained by a phase change in the ethanol glass at about that temperature.

The lifetimes of phosphorescence were measured as a function of temperature and the results were analyzed assuming a first order decay represented by

$$I_p = I_p^o\, e^{-k_p t} = I_p^o\, e^{-t/\tau}$$

where I_p is the phosphorescent intensity at time t, I_p^o is the intensity when $t = 0$, k_p is the phosphorescence decay rate constant, and τ is the phosphorescence lifetime. The results are given in Table 1. At the higher temperatures most phosphorescent decays became decidedly nonexponential.

Table 1. Phosphorescence decay parameters.

	Temperature (K)	Lifetime τ (sec)	Rate Constant k_p (sec^{-1})
Toluene in ethanol	20	8.17	0.122
(10^{-3} M)	32	8.28	0.121
	40	8.10	0.123
	50	5.70	0.175
Bibenzyl in Ethanol	20	8.15	0.123
(7.5×10^{-4} M)	25	7.75	0.129
	30	7.48	0.134
	35	7.50	0.133
	40	7.53	0.133
	60	<6.45	<0.155
Bibenzyl (solid)	21	6.45	0.155
	21	6.21	0.161
	27	6.49	0.154
	27	5.92	0.169
	27	6.13	0.163
	29	6.06	0.165
	34	5.46	0.183
	39	6.54	0.153

The ratio of fluorescence to phosphorescence at each temperature was also calculated from the spectra. The ratios were corrected for the wavelength dependence of the monochromator and phototube sensitivities. No correction was made for fluorescence reabsorption. The fluorescence/phosphorescence ratios are given in Table 2.

Table 2. Fluorescence/phosphorescence intensity ratios.

	Temperature (K)	Ratio
Toluene in ethanol (10^{-3} M)	20	3.34
	54	3.40
	70	6.65
Bibenzyl in ethanol (7.5×10^{-4} M)	20	1.49
	40	2.94
Bibenzyl (solid)	21	2.08
	21	2.46
	27	2.30
	29	2.65
	34	2.96
	39	6.61

The emission spectrum of the zone refined crystalline bibenzyl showed that it contained an impurity of unknown identity. A highly structured set of emission bands appeared in a spectrum taken at 15 K in the wavelength region of the expected phosphorescence but the emission lifetime was short. However, fluorescence was detected from the crystalline bibenzyl and it matched that recorded by McClure (ref. 6).

Close inspection of the impurity fluorescence revealed an abnormal Franck-Condon profile for some of the bands. An examination of the emission lifetime in the wavelength region of the abnormalities showed a long-lived component hidden beneath the emission of the impurity. A chopping technique allowed separation of the two overlapping emissions. A spectrum taken of the long-lived emission using the chopping technique proved to be that of the long-sought phosphorescence of crystalline bibenzyl when compared to the phosphorescent spectrum of solid toluene (ref. 10). Phosphorescence lifetimes and the ratio of fluorescence to phosphorescence were measured for the crystalline sample as a function of temperature (see tables 1 and 2).

IV. DISCUSSION

Examination of the lifetimes of table 1 reveals that for each sample they remain rather constant with increasing temperature until a certain temperature is reached. At higher temperatures the lifetimes decrease sharply. Recall that at the higher temperatures the phosphorescence decay becomes nonexponential. If the rate constant of phosphorescent decay is analyzed by Arrhenius theory, the rate constant k_p is given by

$$k_p = Ae^{-E/kt}$$

where A is the Arrhenius pre-exponential factor, E is the activation energy, and k_p is the Boltzmann constant. If one takes the natural logarithm of both sides of the equation, the equation becomes

$$\ln k_p = \ln A - \frac{E}{kT}$$

A plot of $\ln k_p$ versus the inverse temperature should reveal a straight line with slope $-E/k$. Such a plot of the low temperature points in table 1 yields an activation energy which is very small. Hence no process competes with the phosphorescence at low temperature in each of the three cases. As the temperature is raised a competing process with a substantial activation energy begins to influence the decay pattern.

The fluorescence/phosphorescence ratios of table 2 show a different pattern. The toluene solution phosphorescence maintains a constant ratio until the temperature is raised above 54 K. On the other hand, both the bibenzyl solution and the crystalline bibenzyl showed a constantly decreasing fluorescence/phosphorescence ratio with increasing temperature. How can the phosphorescence lifetime remain constant with increasing temperature and the fluorescence/phosphorescence ratio decrease?

The phosphorescence lifetime stays constant over the low temperature range because the processes deactivating the excited triplet state are not altered as the temperature is raised. However, the processes producing the excited triplet states are changing with temperature. Suppose the triplet states are being populated from the lowest excited singlet state of bibenzyl and raising the temperature activates a process that increases fluorescence at the expense of the phosphorescence. The fluorescence/phosphorescence ratio should show a temperature dependence. If I_P is the phosphorescence intensity and I_F the fluorescence intensity, then

$$\frac{I_F}{I_P} = \frac{k_F n_F \, e^{-E/kT}}{k_P n_P}$$

where k_F and k_P are the fluorescence and phosphorescence decay rate constants, n_F and n_P are the populations of the lowest excited singlet and the phosphorescent triplet, and E is the activation energy for the fluorescence enhancing process. In logarithmic form the equation becomes

$$\ln I_F/I_P = \ln \left(\frac{k_F n_F}{k_P n_P}\right) - \frac{E}{kT}$$

Thus a plot of the natural logarithm of the fluorescence/phosphorescence ratio versus the inverse temperature should yield a straight line if this equation is obeyed. The slope of the line is equal to $-E/k$. A plot of the crystalline bibenzyl data of table 2 can be fit to this equation with an activation energy of 30 to 50 cm^{-1}, a range of values very close to those McClure found for the exciton splitting between the lower forbidden excited singlet state and the upper allowed excited singlet state (ref. 5). There is evidence therefore that exciton coupling in bibenzyl does influence the production of excited triplet molecules. The bibenzyl solution data shows the same trend as the crystalline bibenzyl, supporting the idea that the geometry assumed by bibenzyl molecules in ethanol glass allows some intramolecular exciton coupling.

The role played by the fluorescent impurity in the crystalline bibenzyl is uncertain. The energy of the impurity fluorescent state is 1000 cm^{-1} higher than that of the phosphorescent bibenzyl triplet state. It is unlikely therefore that the impurity is being pumped from the bibenzyl triplet. It is more likely that excitation of the impurity occurs directly by illumination from the lamp or by energy transfer from the excited singlet states of bibenzyl. If the latter mode is the operational mode of excitation of the impurity, then any alteration in the fluorescence quantum yield of bibenzyl should affect the emission intensity of the impurity. A quantitative study of impurity emission yields has not been conducted.

In conclusion, this study reports the temperature-dependent fluorescence and phosphorescence spectra of crystalline bibenzyl. Lifetimes of phosphorescence and fluorescence/phosphorescence intensity ratios are analyzed in an attempt to decide if intramolecular exciton coupling influences the energy transfer in crystalline bibenzyl. Constancy of phosphorescence lifetimes over the temperature range 20 K to 40 K while phosphoroscence quantum yields decrease in the same temperature range seems to indicate an exciton influence.

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REFERENCES

1. Kasha, M., Rawls, H.R., and El-Bayoumi, M.A.: Pure and Applied Chem., 11, 371, 1965.
2. Little, W.A.: Phys. Rev., A134, 1416, 1964.
3. Pope, M., Geacintov, N.E., and Vogel, F.: Mol. Cryst., 6, 83, 1959.
4. Cruickshank, D.W.J.: Acta Cryst., 2, 65, 1949.
5. McClure, D.S.: Can. J. Chem., 36, 59, 1958.
6. Coffman, R., and McClure, D.S.: Can. J. Chem., 36, 48, 1958.
7. Vala, M.T., Haebig, J., and Rice. S.A.: J. Chem. Phys., 43, 886, 1966.
8. Phillips, D.H., and Schug, J.C.: J. Chem. Phys., 50, 3297, 1969.
9. Horton, A.T., and Glasgow, A.R. J. Res. Nat. Bur. Stand., 69C, 195, 1965.
10. Kanda, Y., and Sponer, H.: J. Chem. Phys. 28, 798, 1958.