Energy Transfer in a Hydrogen-Bonded Carbazole–Benzophenone Complex

T. S. Spencer[1] and C. M. O'Donnell*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521. *Received October 28, 1971*

Abstract: In hydrocarbon solutions at 77°K, carbazole emission is quenched by benzophenone. Since quenching is not observed when polar solvents are used, the quenching is attributed to triplet–triplet energy transfer occurring only in the carbazole–benzophenone hydrogen-bonded complex. A large increase in the intersystem crossing rate in carbazole is proposed for the complex.

Hydrogen bonds formed between N-heterocyclics and carbonyl systems are believed to be important in biological systems such as those containing adenine–thymine and guanine–cytosine peptides.[2,3] Although a great deal of work has been published concerning energy transfer by the weak Förster type mechanism, little work has been published concerning energy transfer in hydrogen-bonded N-heterocyclic systems,[4,5] and none has been reported for N-heterocyclic–carbonyl systems. Our study of the carbazole–benzophenone system is designed to show that energy transfer occurs as a result of a hydrogen bond formed between a N-heteroaromatic and an aromatic carbonyl compound.

In 1961, El-Bayoumi and Kasha[4] proposed a singlet–singlet exciton transfer mechanism for the carbazole–acridine, hydrogen-bonded N-heterocyclic complex. Their proposal was based on the quenching of carbazole fluorescence by very small amounts of acridine and the large overlap of the emission and absorption bands of the strong singlet–singlet transitions in the two compounds. More recently, Mataga, *et al.*,[5] proposed a triplet–triplet energy-transfer mechanism for the carbazole–quinoline system. The singlet–singlet mechanism was ruled out on the basis that pyridine and other conjugated π systems quench carbazole fluorescence, even when energy transfer is energetically impossible, by causing an increase in the radiationless decay rate k_i from the singlet state.[6] Furthermore, they observed a concentration dependence for the energy transfer whereby higher concentrations of quinoline and carbazole in constant ratio caused greater quenching of carbazole fluorescence. This was attributed to favored orientation of carbazole molecules at higher concentrations of quinoline.

In the present paper we will show that energy transfer between carbazole and benzophenone (Figure 1) is due to formation of a hydrogen-bonded complex. Furthermore, we will show that the complex formed phosphoresces only through the benzophenone triplet state and that no energy transfer takes place at the concentrations studied unless the hydrogen-bonded complex is formed. The strength of the hydrogen bond has been determined through a temperature-dependent study of the equilibrium constant by monitoring carbazole fluorescence.

Experimental Section

Emission and excitation spectra were recorded routinely on a Perkin-Elmer Model MPF-2A fluorescence spectrophotometer at room temperature and at 77°K. Higher resolution spectra were recorded using a 200-W xenon lamp output passed through a 0.25-m Bausch and Lomb monochromator with a 7-54 Corning glass filter as an excitation source. The emission passed through a 0.75-m Spex 1700-11 monochromator and was detected by a system consisting of an EMI 6256-S phototube, a Keithley Model 414 picoammeter, and a Moseley 7100B strip chart recorder. Lifetimes were measured using a phosphoroscope with a variable speed motor, an AH-6 GE lamp with appropriate Corning filters for excitation, and an EMI 6256-S phototube detector. The phototube output was fed into a Tektronix 531-A oscilloscope and recorded on Polaroid film with a C-12 oscilloscope camera. Alternately, the lifetimes were run using an EG & G FX 12–0.25 flash lamp as excitation and a 1P28 RCA phototube as a detector. The lifetimes were plotted on a semilog paper to detect any nonexponential decay and run through a least-squares analysis to determine the best fit for $1/\tau$.

Carbazole, purchased from Aldrich Chemical Co., puriss grade, was recrystallized, vacuum sublimed, and zone-refined with 96 passes to mp 249–252°. Ethyl carbazole, Matheson Coleman and Bell, was twice recrystallized from ethanol and vacuum sublimed, mp 68–69°. Benzophenone was twice recrystallized, dried under Argon gas, and twice vacuum sublimed to a mp 48–49°.

3-Methylpentane (3MP), methylcyclohexane (MCH), and isopentane (IP) were prepared as in ref 7. Ethanol was prepared by drying 95% ethanol over a magnesium reflux for 20 hr, distilling off the ethanol keeping the middle portion, and redistilling over Ag_2O in a 90-cm fractional distillation column again keeping the middle portion. Ether was prepared by distilling anhydrous ether over $LiAlH_4$. All solvents were checked for purity by absorption and emission spectroscopy.

Results

Solutions of MP (methylcyclohexane–isopentane, 3:1 by volume) with carbazole concentrations of 8.4×10^{-5} *M* and benzophenone from 1×10^{-4} to 8×10^{-3} *M* were excited with a band of light from 300 to 328 nm. Both the phosphorescent and fluorescent emission of carbazole were quenched with increasing benzophenone concentration while benzophenone phosphorescence was enhanced. At 1.7×10^{-4} *M* in benzophenone, the quenching was noticeable and at 2.3×10^{-3} *M* in benzophenone carbazole was completely

(1) T. S. Spencer, part of a thesis submitted to the Graduate Faculty of Colorado State University in partial fulfillment of the requirements for the degree of doctor of philosophy, Dec 1971.

(2) J. D. Watson and F. H. C. Crick, *Nature (London)*, 171, 965 (1953).

(3) I. Isenberg, R. B. Leslie, S. L. Baird, R. Rosenbluth, and R. Bersohn, *Proc. Nat. Acad. Sci. U. S.*, 52, 379 (1964).

(4) M. A. El-Bayoumi and M. Kasha, *J. Chem. Phys.*, 34, 2181 (1961).

(5) F. Tanaka, M. Kato, and N. Mataga, *Z. Phys. Chem. Frankfurt am Main*, 70, 104 (1970).

(6) N. Mataga, F. Tanaka, and M. Kato, *Acta Physiol. Pol.*, 34, 733 (1968).

(7) C. M. O'Donnell, G. A. Knesel, T. S. Spencer, and F. R. Stermitz, *J. Phys. Chem.*, 74, 3555 (1970).

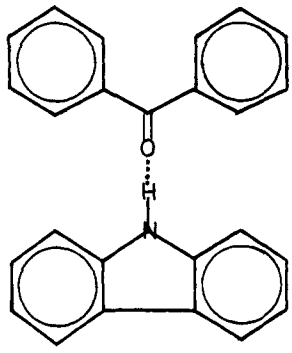

Figure 1. Proposed carbazole–benzophenone hydrogen-bonded structure.

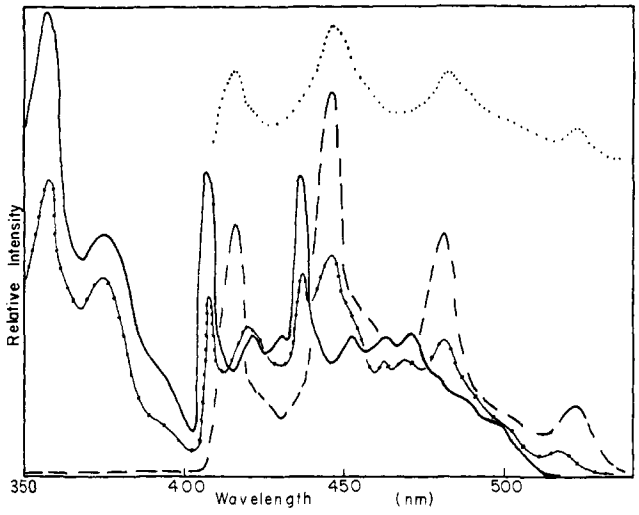

Figure 2. Phosphorescence of carbazole and benzophenone in a nonpolar solvent. Carbazole and benzophenone concentrations (M), respectively, are: 8.4×10^{-5}, 0.0 (——); 8.4×10^{-5}, 6.7×10^{-4} (-·-·-·-·-); 8.4×10^{-5}, 2.3×10^{-3} (- - - -); 0.0, 6.7×10^{-4} (· · · ·). Solvent is methycyclohexane–isopentane, 3:1 by volume.

quenched (Figure 2). On closer examination, using a phosphoroscope in conjunction with the 0.75-m monochromator, carbazole phosphorescence was detected in the solution containing 2.3×10^{-3} M benzophenone; however, the signal level was at least 100 times lower than the benzophenone signal. To ensure that what we were observing was not the formation of microcrystals in the solutions, solutions of 3.9×10^{-4} M benzophenone with carbazole concentrations down to 9.6×10^{-6} M were studied. The quenching effect on carbazole phosphorescence was approximately the same as in the more concentrated solutions; therefore, the phenomena observed was not energy transfer in microcrystals. When ethyl carbazole was used in place of carbazole, no decrease in the ethyl carbazole phosphorescence, increase in benzophenone phosphorescence, or change in fluorescence/phosphorescence ratio was observed. Therefore, a π-bonded dimer is not the probable cause of the decrease in carbazole emission, for the ethyl substitution would break up a hydrogen-bonded complex completely and make a π-bonded complex only slightly more difficult to form.

When 1 ml of EtOH was added to 10-ml portions of carbazole and benzophenone in MP at 77°K, the quenching of carbazole phosphorescence was no longer

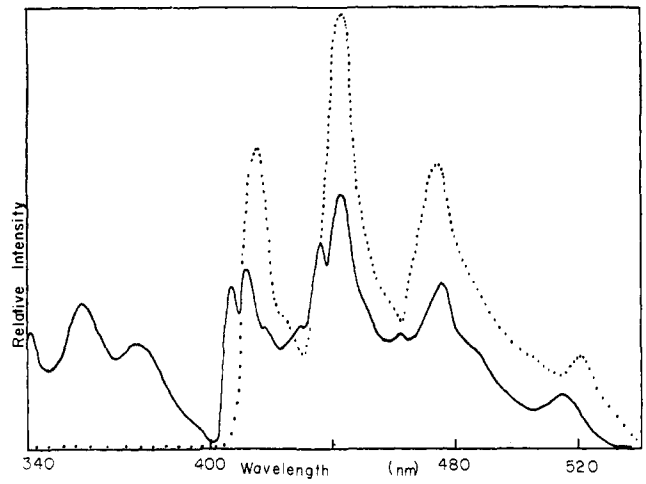

Figure 3. Comparison of total emission of carbazole–benzophenone in polar and nonpolar solvents. Carbazole and benzophenone concentrations (M) and solvent, respectively, are: 8.4×10^{-5}, 2.3×10^{-3}, methycyclohexane (· · · ·); 9.6×10^{-5}, 2.5×10^{-3}, EPA (ether, isopentane, ethanol, 5:5:2 by volume) (——).

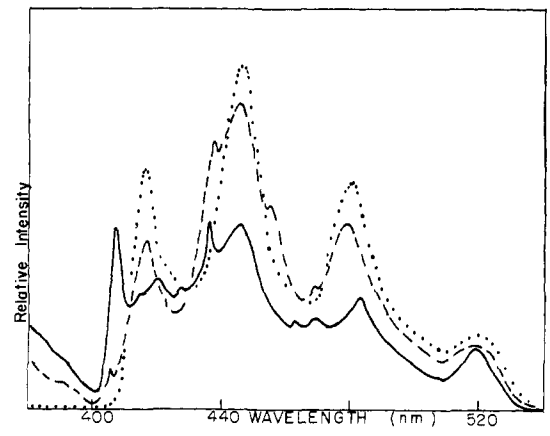

Figure 4. Carbazole–benzophenone phosphorescence corrected for emission from direct excitation of benzophenone: carbazole, 8.4×10^{-5} M; benzophenone, 6.7×10^{-4} M (——), 1.6×10^{-3} M (- - -), 2.3×10^{-3} M (· · · ·). Solvent is methycyclohexane–isopentane, 3:1.

observed. Furthermore, when EPA (isopentane–ether–ethanol, 5:5:2 ratio by volume) was used as a solvent, no quenching was observed even in solutions with benzophenone concentrations up to a 7.4×10^{-3} M (Figure 3). This indicates that the quenching is caused by the formation of a hydrogen-bonded dimer, for quenching is not observed when either ethyl carbazole or a hydroxylic solvent is present. An alternative long distance Förster type energy transfer can be eliminated on the basis of a forbidden S_0–S_1 acceptor transition in benzophenone, an $R_0 \simeq 100$ Å, and the absence of energy transfer in a polar solvent.[8]

The band of excitation light used slightly overlapped the weak singlet (n,π^*) absorption band of benzophenone; however, the ratio of the carbazole and benzophenone oscillator strengths in the region between 300 and 328 nm is approximately 40 so that carbazole absorbed most of the light. In Figure 4 we have corrected the emission spectrum of carbazole–benzophenone in a nonpolar solvent for absorption by benzo-

(8) Th. Förster, *Discuss. Faraday Soc.*, 27, 7 (1959).

phenone by taking into account their relative oscillator strengths and phosphorescence quantum yields. This corrected spectrum clearly shows the increase in the benzophenone phosphorescence brought on by energy transfer taking place in the hydrogen-bonded complex in a nonpolar solvent.

Lifetimes for both long-lived carbazole and short-lived benzophenone species were taken in polar and nonpolar solutions (Table I). In the polar solutions

Table I. Triplet Lifetimes for Carbazole–Benzophenone Solutions at 77°K

Solvent	Concentrations: Benzophenone, mol/l. × 10^3	Concentrations: Carbazole, mol/l. × 10^5	Lifetimes: Benzophenone, msec	Lifetimes: Carbazole, sec
MP[a]	2.3	8.4	5.5 ± 0.2	
	0.67	8.4	5.2 ± 0.2	6.4 ± 0.2
	0.39	7.5	5.2 ± 0.2	6.5 ± 0.1
	0.39	0.0	5.2 ± 0.2	
3MP[b]	1.1	0.0	5.56 ± 0.1	
3MPIP[c]	0.77	6.0	5.58 ± 0.2	6.8 ± 0.1
	0.50	6.0	5.55 ± 0.1	6.9 ± 0.1
	0.33	9.6	5.2 ± 0.2	
	0.0	6.0		6.9 ± 0.1
AE[d]	0.0	9.6		7.78 ± 0.1
	0.17	9.6	6.2 ± 0.5[e]	7.76 ± 0.1
	0.52	9.6	5.2 ± 0.5[e]	7.70 ± 0.1
	2.5	9.6	5.3 ± 0.2[e]	7.62 ± 0.1
	7.4	9.6	5.9 ± 0.5[e]	7.51 ± 0.1

[a] Methylcyclohexane–isopentane, 3:1 by volume. [b] 3-Methylpentane. [c] 3-Methylpentane–isopentane, 4:1 by volume. [d] Ethanol–ethyl ether, 1:1 by volume. [e] The short-lived lifetimes in the polar solvent were difficult to measure due to interference from the intensity of carbazole phosphorescence.

there was no effect on the carbazole lifetime except at very high concentrations of benzophenone (8×10^{-3} *M*), and even at these concentrations the effect was very small. In the nonpolar solvents, there was likewise no decrease in the carbazole lifetime with increasing benzophenone concentration. There was no change in the short-lived benzophenone lifetime within the series of solutions in either the polar or nonpolar solvents within experimental error. From these results we conclude that the carbazole emission observed is solely from free carbazole, since there was no decrease in the carbazole lifetime to indicate collisional quenching which is not expected in a rigid glass at 77°K. Moreover, the energy-transfer step in the complex must be rapid compared to k_p (Figure 5) since no increase is detected in the benzophenone lifetime when the complex is formed, that is, $k_{ET} \gg k_p^H$ of the complex or k_p of carbazole. Superscript H refers to rates of processes in the complex. All lifetimes were observed to decay exponentially over at least 2 half-lives.

The room temperature absorption spectra of benzophenone and carbazole in MP are additive. The lowest S_{n,π^*} band of carbazole red shifts about 80 cm^{-1} at 8.0×10^{-3} *M* in benzophenone at room temperature. At this concentration of benzophenone we should have been able to detect any large spectral shift due to hydrogen bond formation, unless either the hydrogen-bond shift is small or more likely the ground-state equilibrium is shifted away from complex formation at room temperature.

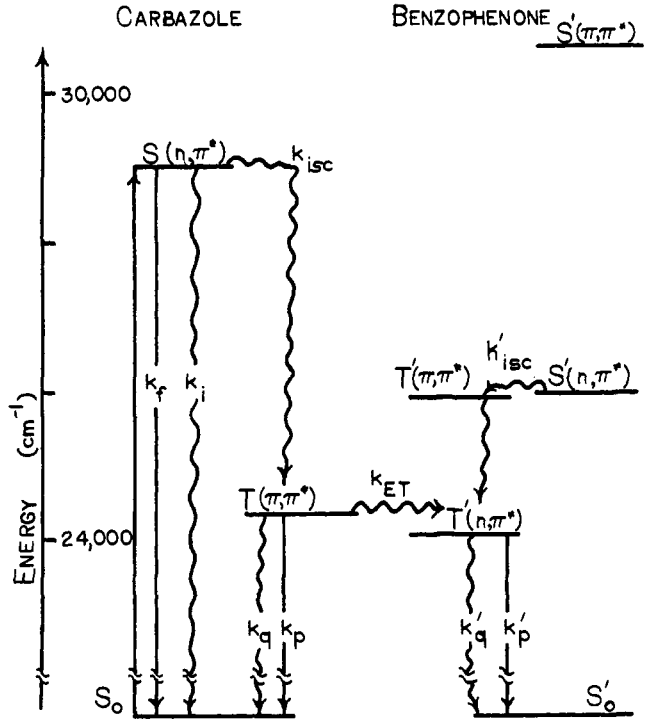

Figure 5. Carbazole–benzophenone Jablonski diagram. S_0 = ground state. S and S′ are the lowest excited singlets. k_f is the fluorescence rate constant. k_i is the rate of radiationless deactivation of the lowest excited singlet of carbazole. k_{ISC} is the intersystem crossing rate. k_p and k_p' are the phosphorescence rate constants. k_q and k_q' are the rates of radiationless deactivation of the triplet states. k_{ET} is the rate of triplet–triplet energy transfer.

Room temperature fluorescence was not quenched completely by concentrations of benzophenone up to 8×10^{-3} *M*, indicating an equilibrium between the hydrogen-bonded complex and free carbazole which is shifted toward the free species at higher temperature. The equilibrium constant is not necessarily the same in the ground and excited states;[9] therefore, the excited state equilibrium constant determined from fluorescence intensity of free carbazole is

$$K_{eq} = [CB]/[C][B] \quad (1)$$

where [C], [B], and [CB] are the carbazole, benzophenone, and complex concentrations, respectively, and K_{eq} is the excited state equilibrium constant[9] at 300°K. The observed fluorescence will be that of the free carbazole with a correction factor for the absorption of benzophenone. Using a solution of carbazole to obtain intensity I_f for free carbazole fluorescence we get

$$I_f = k[C] \quad (2)$$

where k is a proportionality constant taking into account the quantum yield of fluorescence for carbazole.

From the stoichiometric equation

$$[C \cdot B] = [C]_0 - [C] \quad (3)$$

where $[C]_0$ is the carbazole concentration at [B] = 0, one can rearrange (1) and substitute (2) and (3) to obtain the Stern–Volmer relationship

$$I_0/I_f - 1 = [B]K_{eq} \quad (4)$$

where I_0 is the intensity of carbazole fluorescence at [B] = 0. It is assumed that $[B]_0 \gg [C_0 \cdot B]$ which is reasonable assumption at room temperature where the

(9) A. Weller, *Z. Electrochem.*, 61, 956 (1957).

equilibrium tends toward the free species. Then a plot of $(I_0/I_f - 1)$ *vs.* [B] at 300°K yields the approximate excited state equilibrium constant[9] for the dissociation of the hydrogen-bonded complex. $K_{eq} \simeq 220$ l./mol. One should note that at 77°K, absence of mobility in the rigid glass prevents significant change in the equilibrium of the complex between the ground and excited state.

Using the Arrhenius expression of K_{eq}

$$K_{eq} = A \exp(-\Delta H/RT) \quad (5)$$

where ΔH is the hydrogen bond strength and the entropy factors are included in A. A plot of ln K_{eq} *vs.* $1/T$ (°K), over the range of 140–300°, yields an approximation of -2.9 ± 0.5 kcal/mol for the strength of the hydrogen bond in the carbazole–benzophenone complex, which is about the same as the -2.2 kcal/mol observed for the ground-state hydrogen bond strength of the benzophenone–ethanol system.[10]

Discussion

The quenching of carbazole emission in a nonpolar solvent by benzophenone and the absence of quenching in hydroxylic solvents or with ethyl carbazole indicate the formation of a hydrogen-bonded complex rather than a long distance energy-transfer process which might sensitize benzophenone phosphorescence. Two alternative energy-transfer mechanisms are possible in the hydrogen-bonded carbazole–benzophenone complex, singlet–singlet (S–S) and triplet–triplet (T–T). Although a singlet–singlet energy-transfer mechanism will explain the experimental results, we prefer the triplet–triplet mechanism for the following reasons.

(1) Quenching of carbazole fluorescence has been observed in the carbazole–pyridine hydrogen-bonded complex where energy transfer (S–S or T–T) is energetically impossible;[6] therefore, it was concluded by Mataga, *et al.*, that k_i for carbazole undergoes a large increase when carbazole is hydrogen bonded to a conjugated π system. Thus, in the carbazole benzophenone complex it is reasonable to assume that in the complex $k_i^H \gg k_i$ for free carbazole and that carbazole fluorescence will be quenched whether energy transfer is S–S or T–T. Also, if $k_{ET} \gg k_p$ or k_q (Figure 5) in the complex, T–T energy transfer will occur more rapidly than triplet quenching.

(2) In the hydrogen-bonded complex of carbazole and quinoline where only T–T energy transfer is possible, Mataga, *et al.*,[5] observed T–T energy transfer from carbazole to quinoline and simultaneous quenching of carbazole fluorescence. Hence, k_{ISC} and possibly k_i must be much greater in a hydrogen-bonded complex as opposed to free carbazole, $k_{ISC} \gg k_f$, so that quenching of fluorescence (k_{ISC} or $k_f \gg k_f$) and T–T energy transfer ($k_{ISC} \gg k_f$) can both occur. In the carbazole–benzophenone system energy transfer occurred in a hydrogen-bonded complex such that one might propose the k_{ISC}^H and $k_i^H \gg k_f^H$.

(3) Finally, in the hydrogen-bonded carbazole–acridine system where the S–S energy transfer has been proposed, El-Bayoumi and Kasha[4] observed quenching of carbazole emission with no corresponding increase in acridine emission. Moreover, since the acridine–carbazole complex quenched carbazole emission out of proportion to the amount of complex formed, the complex was said to form an energy sink; this effect was not observed in the carbazole–benzophenone system. In addition, the acceptor singlet state in acridine is a stronger transition than that in benzophenone; therefore, the energy sink and singlet–singlet transfer are more probable in the carbazole–acridine case.

Since the experimental results are more similar to the carbazole–quinoline than the carbazole–acridine system, we propose that triplet–triplet energy transfer occurs from carbazole to benzophenone in a hydrogen-bonded complex. Since $k_{ISC} \simeq k_i$ in free carbazole,[11,12] and since intersystem crossing occurs prior to T–T energy transfer, k_{ISC} must increase enough in the complex, k_{ISC}^H, to be competitive with k_i or no energy transfer will be observed. Thus, $k_{ISC}^H \gg k_f^H$ and $k_i^H \gg k_f^H$ to explain the absence of carbazole fluorescence.

Since k_{ISC} is dependent on the spin–orbit coupling between the carbazole singlet and triplet states, changes in spin–orbit coupling due to hydrogen bond formation must be considered. The energy of the lowest excited singlet state in carbazole (Figure 5) is lowered on the order of 600–1000 cm^{-1} by the formation of a hydrogen bond, making the carbazole S–T energy gap smaller. Hence, an increase in the spin–orbit coupling is expected from changes in the vibronic coupling resulting from the smaller S–T energy gap.[13]

At higher concentrations ($\sim 10^{-3}$ M) of donor and acceptor, Mataga observed an increased quenching effect in the carbazole–quinoline system. Since no significant concentration dependence on the quenching effect of benzophenone was observed so long as carbazole concentrations are kept well below the solubility limits at 77°K, the increased quenching effect observed by Mataga[5] at higher concentrations could possibly be caused by microcrystal formation as well as the proposed favored orientation.

In summary, we propose that triplet–triplet energy transfer occurs in the carbazole–benzophenone complex, a hydrogen-bonded nitrogen-heterocyclic aromatic–carbonyl system. As a result of complex formation, radiationless deactivation from the first excited donor singlet and intersystem crossing in the donor are increased so that donor fluorescence is quenched. The T–T mechanism is made possible by a large increase in k_{ISC} resulting from increased vibronic overlap and spin–orbit coupling between the carbazole singlet and triplet states. A similar energy-transfer mechanism should be possible in any hydrogen-bonded complex containing molecules with appropriately spaced energy levels. The strength of the hydrogen bond has been calculated as approximately -2.9 kcal/mol.

Acknowledgments. Support for this work came from the Biomedical Sciences Support Grant, Colorado State University, Fort Collins. Partial support was provided by the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation. Also, thanks go to Dr. P. F. Jones and Dr. J. P. Guillory for helpful discussions during the course of the work. Finally, we appreciate the careful reviewing of this paper by one of the referees.

(10) G. J. Brealey and M. Kasha, *J. Amer. Chem. Soc.*, 77, 4462 (1955).

(11) V. L. Ermolaev, *Opt. Spektrosk.*, 11, 266 (1961).

(12) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, London, 1970, pp 122–123.

(13) E. C. Lim and J. M. H. Yu, *J. Chem. Phys.*, 47, 3270 (1967).