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Singlet Excitation Energy Migration in the Glassy and Single Crystalline States of 1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline

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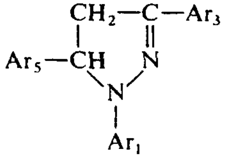
Comparative studies have been made of the singlet excitation energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline between the glassy and single crystalline states at near room temperature. The rate parameter for the singlet excitation energy migration, i.e., frequency of excitation hopping, was determined from the fluorescence quenching by the guest molecule, dimethylterephthalate, the quenching process being the migration controlled charge-transfer. The results are discussed in terms of both kinetic and random migration models. The results show that the singlet excitation energy migrates over 523 ± 9 molecules in the glassy state and (3.71 ± 0.06) × 10^5 molecules in the single crystalline state at 10°C within its lifetime which was found to be almost the same in both states. The rate parameter for the migration is slightly temperature dependent, the apparent activation energy being ~0.052 ev in the glassy state and ~0.012 ev in the single crystalline state. It is indicated that the difference of the two or three orders of magnitude in the efficiency of migration between the disordered and ordered system is mainly due to the difference of the preexponential frequency factor rather than of the activation energy.

INTRODUCTION

A great deal of information has been accumulated on the optical and electrical properties of organic solids in the single crystalline state. There has recently been growing interest in the transport phenomena in organic amorphous solids from both academic and practical viewpoints. Understanding of the charge carrier transport phenomena in organic amorphous solids are of importance in view of the application of these materials for electrophotography. Understanding of the excitation energy migration, which is involved as a precursory process of the photocarrier generation process, is also important for a basic understanding of the photoconduction mechanism. Numerous studies have been made of the excitation energy migration and charge carrier transport in polymeric materials[1–6] and in some low molecular weight organic amorphous solids in order to gain insight into the nature of the transport phenomena in the disordered system.[7,8] In this regard, it is most desirable to make direct comparison of the transport phenomena between the single crystalline and amorphous glassy states of the same material over the same temperature region; however, very few attempts have been made up to this time[9,10] because many organic materials do not form readily a glassy state, and even if they do, the glassy state is usually unstable except for at low temperature, changing easily into a crystalline state at around room temperature. To enable this sort of study, it is required to search for appropriate organic materials which readily give a glassy state at near room temperature and keep its state for quite a long period of time.

1,3,5-Triaryl-2-pyrazolines are a class of ideal compounds for these studies, since, as described in our previous papers,[11,12] they are easily supercooled and then change into a glassy state at near room temperature which is kept for quite a long period of time, and single crystals of these materials can also be grown by a Bridgeman method. In addition, they possess intense fluorescent characteristics and photoconductive properties which are suitable for the study of the transport phenomena. This paper describes the results of the first successful comparative studies of the singlet excitation energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline[13] between the glassy and single crystalline states over the same temperature region.



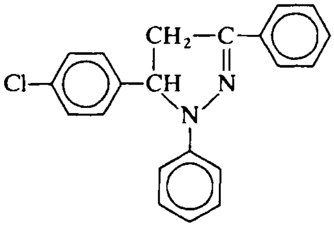
1,3,5-triaryl-2-pyrazoline

EXPERIMENTAL

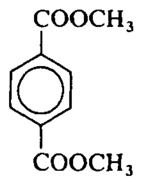
Materials

1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (glass transition point 16.5°C) was prepared from *p*-chlorobenzaldehyde, acetophenone and phenylhydrazine, according to the method described in the literature.[14] In order to obtain a highly purified material, 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline was purified by repeated recrystallizations from ethanol and column chromatography over neutral alumina, followed by zone refining.

Dimethylterephthalate was purified by repeated recrystallizations from ethanol and then by sublimation.



1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline



dimethylterephthalate

Apparatus

Zone refining was carried out with SHIMAZU Cryogenic Zone Refiner CZ-1. The electronic absorption spectra were recorded with a Hitachi 124 spectrophotometer. The fluorescence and excitation spectra were measured with a Hitachi MPF-3 spectrofluorometer fitted with a R446 photomultiplier, using a special sample holder which can keep the sample tube in a fixed position at constant temperature. The fluorescence lifetime was measured by means of a JASCO FL-10 phase fluorometer and a pulsed N_2 laser with a pulse width of *ca.* 1.5 nsec and repetition of *ca.* 3 Hz using a Tektronix 5103 N oscilloscope.

Zone refining of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline

Difficulty was encountered with zone refining of this compound because of the properties of forming readily a supercooled liquid and then a glassy state; however, zone refining of this compound was successfully accomplished by keeping the cooling zone above 80°C and the heating zone at 130°C (melting point) and by running at a very slow rate of 1.1 mm/hr.

Purity check of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline

The purity of the material was checked by the method of confirming the absence of any spectral dependence of the fluorescence lifetime as has been suggested by Kobayashi *et al.*[15] That the melt zones in the zone refining tube solidify as a transparent glassy state when the zone tube is taken out from the refiner and then allowed to cool down to room temperature enabled the measurement of the fluorescent lifetime of each transparent portion in the tube. With regard to samples of *ca.* 250 zones passed, no spectral dependence of the fluorescence lifetime was observed with each portion along the tube except for the lowest portion.

Single crystal growth of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline doped with dimethylterephthalate

Single crystals were grown from the melt in a Bridgeman type crystal-growing furnace. Pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline doped with 10^{-6} mole/mole order of dimethylterephthalate placed in pyrex glass capillary tubes of 1.5 mm in diameter were degassed at 3×10^{-6} torr and sealed. After melting the samples in the furnace with seed crystals left at the bottom end of the capillary, single crystals were grown very slowly at a rate of 0.2 mm/hr.

Preparation of glass

In the same way as described above, pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline doped with *ca.* 10^{-3}-10^{-2} mole/mole order of dimethylterephthalate placed in pyrex glass capillary tubes of 1.5 mm in diameter were degassed and sealed. The amorphous glassy state was prepared by melting these samples and then cooling down to 15°C.

Single crystals and glasses thus prepared were used for the measurement without taking them out from the pyrex glass capillary tubes so as to avoid exposure of the samples to oxygen.

RESULTS AND DISCUSSION

The method employed for the present study of the singlet excitation energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy and single crystalline states is to measure the quantity of the quenching of the fluorescence intensity of the host molecule, 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline, by the doped guest molecule, dimethylterephthalate, as a function of the amount of the guest molecule. The principle is discussed first in terms of simple kinetic and random migration treatments, and the experimental results analyzed will then be described and discussed.

Before going to description of the above two treatments, the followings must be mentioned. In the present host (1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline)—guest (dimethylterephthalate) system, trapping of the excitation

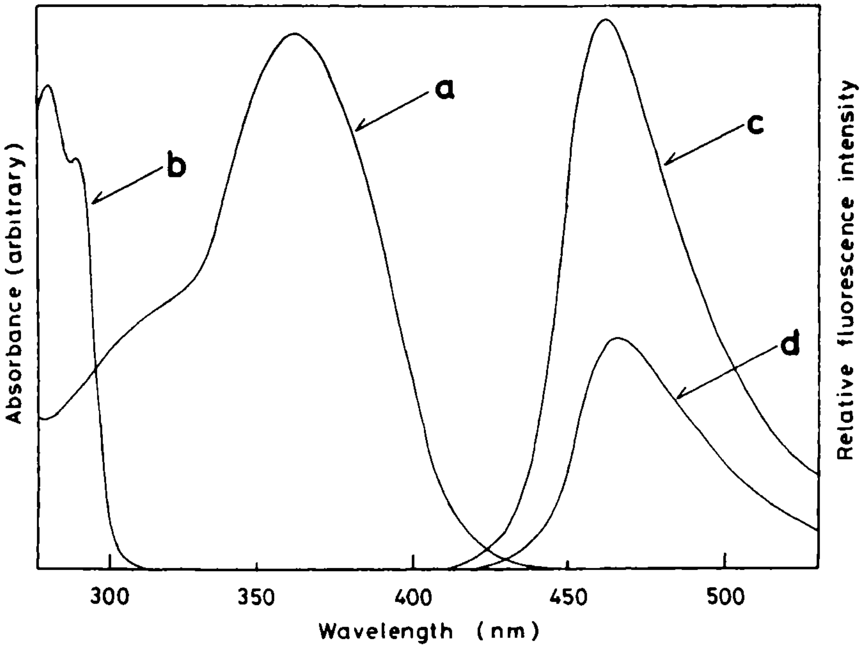


FIGURE 1 Absorption and emission spectra; (a) the absorption spectrum of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy state. (b) the absorption spectrum of dimethylterephthalate in tetrahydrofuran solution. (c) the fluorescence spectrum of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy state. (d) typical example of the fluorescence of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline partially quenched by the addition of dimethylterephthalate in the glassy state.

energy of the host molecule by the guest molecule will occur by the charge-transfer mechanism which requires close approach of the excited state host and ground state guest molecules, the excited state host molecule functioning as an electron donor and the guest molecule as an electron acceptor. Energy transfer from the host to the guest molecule by either the long-range resonance-excitation or the short-range electron exchange mechanism is improbable since, as shown in Figure 1, the lowest excited singlet energy level of the guest molecule is much higher than that of the host molecule. Consequently, the fluorescence quenching of the host molecule by the guest molecule will take place through the excitation energy migration over the host molecules, followed by trapping of the excitation energy by the nearby guest molecule.

Kinetic treatment

Generation and dissipation of the singlet excitation energy of the host molecule involve the processes as shown in Scheme 1, where k_f, k_i, and k_q

represent the rate parameter for radiative deactivation, radiationless deactivation, and quenching of the excitation energy by the guest molecule, respectively.

$$\mathrm{H} \xrightarrow{h\nu} {}^1\mathrm{H}^* \qquad \text{(a)}$$

$$ {}^1\mathrm{H}^* \xrightarrow{k_f} \mathrm{H} + h\nu_f \quad \text{(fluorescence)} \qquad \text{(b)}$$

$$ {}^1\mathrm{H}^* \xrightarrow{k_i} \mathrm{H} \qquad \text{(c)}$$

$$ {}^1\mathrm{H}^* + \mathrm{G} \xrightarrow{k_q} (\mathrm{H}^+\mathrm{G}^-) \qquad \text{(d)}$$

$$ {}^1\mathrm{H}^* + \mathrm{H} \xrightarrow{k_m} \mathrm{H} + {}^1\mathrm{H}^* \xrightarrow{k_m} \cdots \; \mathrm{H} + {}^1\mathrm{H}^* \qquad \text{(e)}$$

$$ {}^1\mathrm{H}^* + \mathrm{G} \xrightarrow{k_t} (\mathrm{H}^+\mathrm{G}^-) \qquad \text{(f)}$$

Scheme 1

Schematically, a particular host molecule is electronically excited to the excited singlet state (process a), and the singlet excitation energy is quenched by the guest molecule in competition with radiative and non-radiative dissipations of the excitation energy (processes b, c, and d). Simple kinetic treatment of the quenching behavior of the host molecule fluorescence by the guest molecule gives Eq. (1) which correlates the quantity of F_0/F with the concentration of the guest molecule $N_g/(N_h + N_g)$, where F_0 and F are the fluorescence intensity of the host molecule without and with the guest molecule, N_h and N_g are the number of the host and guest molecules in the solid.

$$\begin{aligned} \frac{F_0}{F} &= 1 + \frac{k_q}{k_f + k_i}\frac{N_g}{N_h + N_g} \\ &\fallingdotseq 1 + \frac{k_q}{k_f + k_i}\frac{N_g}{N_h} \qquad (1) \\ &\qquad\qquad (\because N_h \gg N_g) \end{aligned}$$

Equation (1) is a Stern–Volmer type equation which has been widely accepted for analyzing energy transfer in the solid state.[16–19] The important notion involved in the quenching process (d) in Scheme 1 is that the process consists of the two processes (e) and (f), that is, the singlet excitation energy migrates over the host molecules (process e) coming to near the guest molecule during radiative and non-radiative dissipations of the excitation energy, followed by trapping of the excitation energy by the guest molecule via the charge-transfer process (process f). Hence if k_t is much larger than k_m, k_q represents k_m, and conversely if k_m is much larger than k_t, k_q represents k_t.

The former case corresponds to the frequently observed diffusion-controlled energy or charge-transfer processes in solutions. Consequently, Eq. (1) is represented by Eq. (2) when k_t is much larger than k_m, and by Eq. (3) when k_m is much larger than k_t.

$$\frac{F_0}{F} \fallingdotseq 1 + \frac{k_m}{k_f + k_i}\frac{N_g}{N_h} \qquad (2)$$

(when $k_m \ll k_t$)

$$\frac{F_0}{F} \fallingdotseq 1 + \frac{k_t}{k_f + k_i}\frac{N_g}{N_h} \qquad (3)$$

(when $k_m \gg k_t$)

The efficient fluorescence quenching will be observed in the former case, i.e., when k_t is much larger than k_m, and information on the excitation energy migration in solids can be obtained in this case. The present system was found to be this case as described later.

Random migration treatment

Essentially the same equation as Eq. (2) can be derived by the treatment of the random excitation energy migration as schematically shown in Figure 2 based on the following three assumptions. (1) The singlet excitation energy is localized on a particular host molecule and migrates over the host molecules by a randomly hopping process from one host molecule to another neighboring host molecule coming to near the guest molecule. (2) Excitation energy undergoes radiative (fluorescence emission, process k_f) and non-radiative (process k_i) deactivations during migration. (3) Trapping of the excitation energy occurs when the excitation energy comes to host molecules nearest to the guest molecules through migration in competition with the k_f, k_i and k_m processes. Using the same notation as described in the section of kinetic treatment, the probability of the excitation energy at some site to migrate to the next site in competition with the energy dissipation processes is expressed as $k_m/(k_f + k_i + k_m)$, and the probability of guest molecules existing in the solid is $N_g/(N_h + N_g)$. The probability (p_1) of the excitation energy of the host

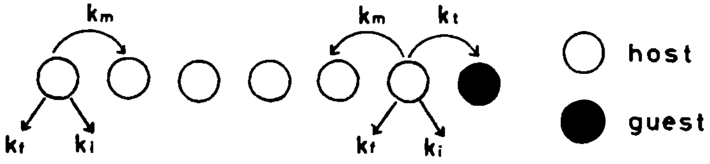


FIGURE 2 Simple random migration model of singlet excitation energy.

molecule being trapped by the guest molecule through only one step is given by Eq. (4).

$$p_1 = \frac{k_t}{k_f + k_i + k_m + k_t} \frac{N_g}{N_h + N_g} \tag{4}$$

Therefore, the probability (p_n) of the excitation energy of the host molecule being trapped by the guest molecule through n steps, i.e., through the excitation energy migration over ($n - 1$) host molecules is given by Eq. (5).

$$p_n = \left(\frac{k_m}{k_f + k_i + k_m}\right)^{n-1} \left(1 - \frac{N_g}{N_h + N_g}\right)^{n-1} \times p_1 \tag{5}$$

Hence, the total probability (P_m) of the excitation energy of the host molecule being trapped by the guest molecule is $P_m = \sum_{n=1}^{\infty} p_n$. Then, the probability (P_f) with which the singlet excitation energy dissipates its energy as fluorescence emission will be

$$P_f = (1 - P_m) \frac{k_f}{k_f + k_i} \tag{6}$$

Since the fluorescence intensity is proportional to the probability P_f, the quantity of F_0/F is given by Eq. (7).

$$\frac{F_0}{F} = 1 + \frac{(k_f + k_i + k_m)k_t N_g}{(k_f + k_i)(k_f + k_i + k_m + k_t)N_h + (k_f + k_i + k_m)^2 N_g} \tag{7}$$

The efficient quenching of the host molecule fluorescence by the guest molecule will occur when the singlet excitation energy is efficiently trapped by the guest molecule, i.e., when k_t is much larger than k_m, and k_m is much larger than k_f and k_i. In this case, Eq. (7) is expressed as Eq. (8). Information on the excitation energy migration can be obtained in terms of this equation.

$$\begin{aligned} \frac{F_0}{F} &\fallingdotseq 1 + \left(1 + \frac{k_m}{k_f + k_i}\right) \frac{N_g}{N_h} \\ &\fallingdotseq 1 + \frac{k_m}{k_f + k_i} \frac{N_g}{N_h} \end{aligned} \tag{8}$$

$$(\because N_h \gg N_g)$$

If, on the other hand, k_m is much larger than k_t, the efficient fluorescence quenching would not occur as is shown from Eq. (7); in this case F_0/F becomes nearly unity.

As described in the following section, the efficient fluorescence quenching was observed for the present system, which indicates that the fluorescence quenching for the present system occurs via the migration-controlled energy trapping. This is reasonable in view of much stronger interaction between the host (electron donor) and guest (electron acceptor) molecules than that between the host molecules.

Experimental results and discussion

Figure 1 shows the absorption spectra of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and dimethylterephthalate and the fluorescence spectra of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline. When 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline is doped with dimethylterephthalate no new absorption due to charge transfer complex formation in the ground state was observed. The fluorescence of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline was quenched significantly when doped with a small amount of dimethylterephthalate. No new emission due to the exciplex was observed.

The results obtained show that the fluorescence quenching of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in both the glassy and single crystalline

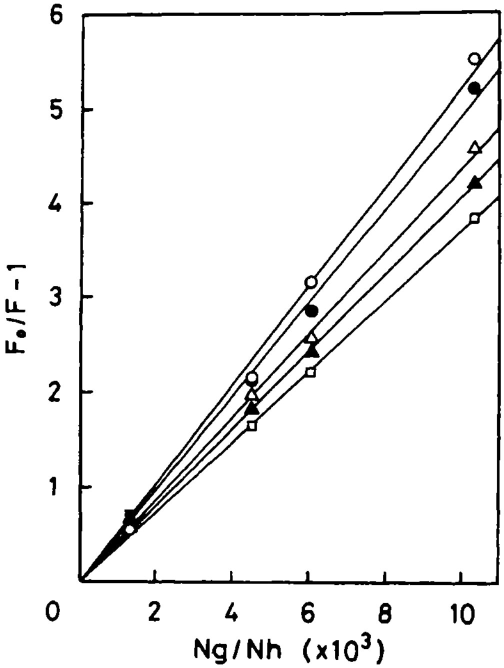


FIGURE 3 Quenching of the fluorescence of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline by the addition of guest molecule (dimethylterephthalate) in the glassy state at −30°C (□), −20°C (▲), −10°C (△), 0°C (●), and 10°C (○). F_0 and F are the fluorescence intensities of the pure and the doped materials, respectively, and N_h and N_g are the number of the host and guest, respectively.

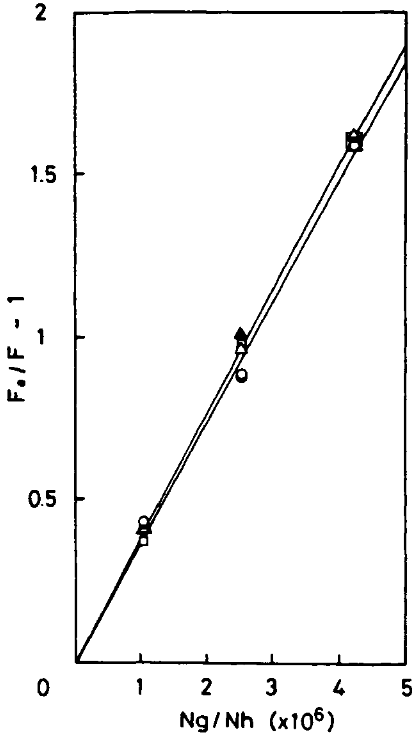


FIGURE 4 Fluorescence quenching of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline by the addition of guest molecule (dimethylterephthalate) in the single crystalline state at 10°C (○), 15°C (●), 20°C (△), 25°C (▲), and 30°C (□). F_0 and F are the fluorescence intensities of the pure and the doped materials, respectively, and N_h and N_g are the number of the host and guest, respectively.

states by the guest molecule, dimethylterephthalate, is migration-controlled, fitting with Eq. (2) or (8) (the same equation). Consequently, the experimental results are analyzed and discussed in terms of this equation, which is again given here as Eq. (9), where *n* represents the number of hops of singlet excitation energy within its lifetime ($\tau = 1/(k_f + k_i)$).

$$\begin{aligned}\frac{F_0}{F} &= 1 + \frac{k_m}{k_f + k_i}\frac{N_g}{N_h}\\ &= 1 + n\frac{N_g}{N_h} \qquad (9)\\ &\left(n = \frac{k_m}{k_f + k_i}\right)\end{aligned}$$

More strictly, it would be necessary to take into account the probability (f) of the excitation energy returning to the starting point during its random migration, i.e., the value of nN_g/N_h should be modified by a factor of $(1 - f) \approx 0.66$;[20–22] however, this is not taken into consideration in the discussion which follows for the sake of simplicity.[23]

The results of the fluorescence quenching as a function of the concentration of the guest molecule in the glassy state is shown in Figure 3. Figure 4 shows similar results obtained for the single crystalline state. As shown in the figures, a good linearity was observed for both states as expected from Eq. (9). Noteworthy is the fact that while the quenching becomes appreciable with the doping level of $\sim 10^{-3}$ mole/mole guest molecule in the glassy state, the doping level of $\sim 10^{-6}$ mole/mole is sufficient for the same order of magnitude quenching in the single crystalline state, which indicates that the excitation energy migration is much more rapid in the ordered single crystalline state. Tables I and II summarize the number of hops (n) of singlet excitation energy within its lifetime (τ) at various temperatures in the glassy and single crystalline states, respectively.

TABLE I

Number of hops (n) of singlet excitation energy within its lifetime (τ) and the rate parameter of its migration (k_m) in the glassy state at various temperatures.

T(°C)	n	τ(nsec)	k_m(sec^{-1})*
−30	371 ± 6	9.80 ± 0.28	(3.94 ± 0.09) × 10^{10}
−20	407 ± 4	9.04 ± 0.16	(4.33 ± 0.08) × 10^{10}
−10	438 ± 4	9.15 ± 0.10	(4.66 ± 0.08) × 10^{10}
0	493 ± 7	9.02 ± 0.17	(5.24 ± 0.11) × 10^{10}
10	523 ± 9	10.04 ± 0.19	(5.56 ± 0.13) × 10^{10}

* k_m was calculated from the mean value of τ, 9.41 ± 0.14 nsec.

TABLE II

Number of hops (n) of singlet excitation energy within its lifetime (τ) and the rate parameter of its migration (k_m) in the single crystalline state at various temperatures.

T(°C)	n	τ(nsec)	k_m(sec^{-1})*
10	(3.71 ± 0.06) × 10^5	9.71 ± 0.16	(3.73 ± 0.07) × 10^{13}
15	(3.70 ± 0.07) × 10^5	9.78 ± 0.17	(3.73 ± 0.07) × 10^{13}
20	(3.82 ± 0.00) × 10^5	9.93 ± 0.10	(3.85 ± 0.03) × 10^{13}
25	(3.81 ± 0.05) × 10^5	10.30 ± 0.24	(3.84 ± 0.06) × 10^{13}
30	(3.80 ± 0.03) × 10^5	9.93 ± 0.20	(3.83 ± 0.04) × 10^{13}

* k_m was calculated from the mean value of τ, 9.93 ± 0.07 nsec.

As is evident from the tables, the *n* values obtained for the glassy state are about 1/700 of those obtained for the single crystalline state. Obviously, this difference is due to the difference of k_m between the glassy and single crystalline states since the lifetime (τ) of the singlet excitation energy of the host molecule is nearly equal in both states. It is therefore indicated that the efficiency of the excitation energy migration in the disordered glassy state is much smaller as compared with that in the ordered single crystalline state, resulting in a much smaller probability of the excitation energy encountering the guest molecules in the glassy state.

It was observed that the *n* values and hence the values of k_m show a slight temperature dependence as is shown in Figure 5. Apparently, the temperature dependence of k_m will be expressed as Eq. (10).

$$k_m \approx k'_m \exp\left(\frac{-\Delta E}{kT}\right) \tag{10}$$

The values of the apparent activation energy (ΔE) obtained are listed in Table III. Although the ΔE values are very small in both states, being of the order of magnitude of the room temperature kT value, the value obtained for the glassy state is a little bit larger than that of the crystalline state. This apparent activation energy observed for the excitation energy migration process is suggested to be due to the presence of shallow traps in the host molecules. The difference of only *ca.* 0.04 ev in ΔE values between the glassy

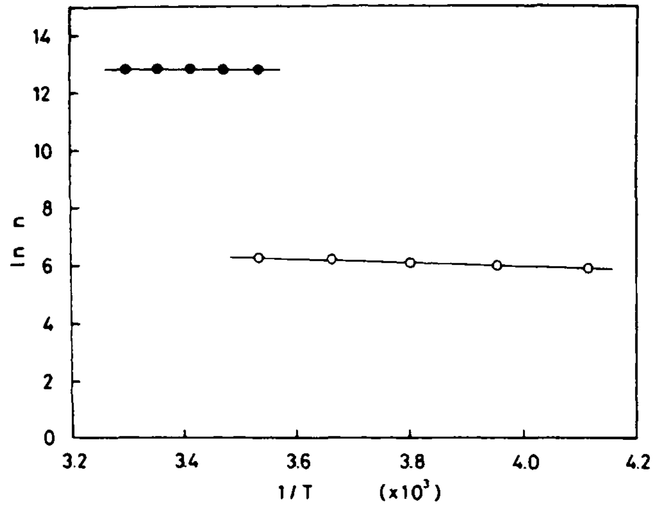


FIGURE 5 Temperature dependence of the number of hops (*n*) of singlet excitation energy in the glassy (○) and single crystalline (●) states of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline within its lifetime.

TABLE III
Apparent activation energy (ΔE) and frequency factor (k_m') of singlet excitation energy migration in the glassy and single crystalline states.

state	ΔE(ev)	k_m'(sec^{-1})
glass	0.052 ± 0.002	$(4.72 \pm 0.07) \times 10^{11}$
crystal	0.012 ± 0.003	$(6.08 \pm 0.04) \times 10^{13}$

and single crystalline states corresponds to the difference in the Boltzmann factor $\exp(-\Delta E/kT)$ only by a factor of 5–6 between the two states, and hence difference of nearly two orders of magnitude will be seen with regard to the k_m' value between the two states. These results tell that the difference of the disordered and ordered structures is reflected mainly on k_m' rather than on ΔE.

The average radial displacement ($\bar{r}$) of the excitation energy was calculated according to the Eq. (11)

$$\bar{r} = dn^{1/2} \tag{11}$$

where, d is the intermolecular distance of host molecules. From the crystal structure data of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (Figure 6),[24]

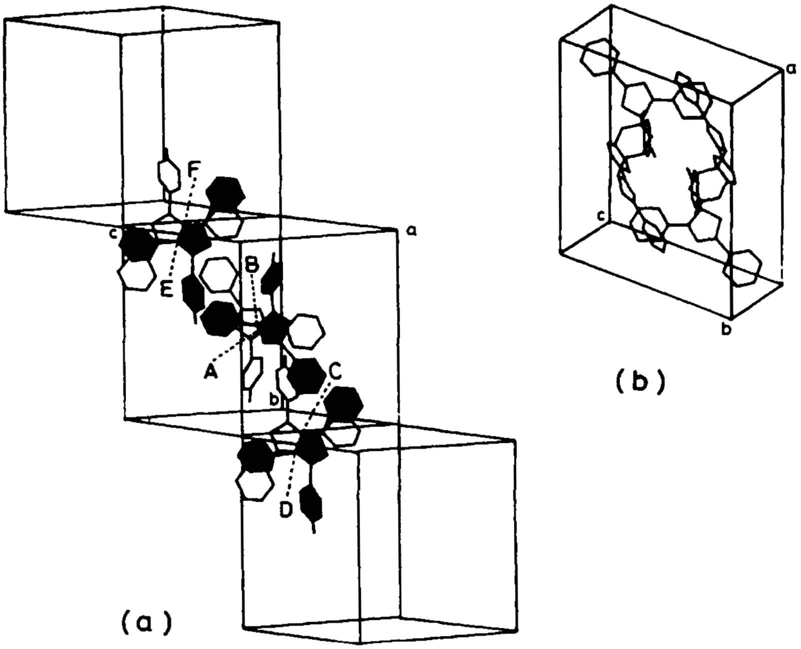


FIGURE 6 Crystal structure of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline. (a) α form. The distance between number 1 nitrogen atoms A and B is 4.2 Å. C–D and E–F are also the same. A–C and B–E are 8.6 Å. (b) β form.

the intermolecular distance d is estimated to be *ca.* 6.4 Å.[25] This distance may be fluctuated to some extent in the glassy state; however, the same value was used for the calculation for both crystal and glass. As a result, $\bar{r}$ was estimated to be 150 Å and 3900 Å for the glassy and single crystalline states, respectively.

SUMMARY

Comparative studies of the excitation energy migration between the disordered glassy state and the ordered single crystalline state of the same material over the same temperature region was achieved for the first time by using 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline. It was shown that the efficiency of the singlet excitation energy migration is about three orders of magnitude larger in the ordered system in comparison with the disordered system, which is attributable mainly to the preexponential frequency factor rather than to the activation process which is probably caused by the detrapping of the excitation energy during migration. The principle of the method of the quenching of the host molecule by the guest molecule doped, which was employed for studying the excitation energy migration in solids, is discussed in terms of simple random migration model with reference to the previously accepted kinetic model.

References and Notes

1. P. J. Rosenberger, *Photochem. Photobiol.*, **8**, 429 (1968).
2. D. M. Pai, *J. Chem. Phys.*, **52**, 2285 (1970).
3. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
4. D. J. Williams, W. W. Limburg, J. M. Pearson, A. O. Goedde, and J. F. Yanus, *J. Chem. Phys.*, **62**, 1501 (1975).
5. W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
6. G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
7. W. Hofberger and H. Bässler, *Phys. Stat. Sol.*, **B69**, 725 (1975).
8. K. P. Seefeld, H. Müller, and H. Bässler, *J. Lumin.*, **16**, 395 (1978).
9. Mobility of the charge carrier is compared between the single crystalline and glassy states.
10. W. D. Gill, *Amorphous and Liq. Semicond.*, **2**, 901 (1974).
11. K. Kato, M. Yokoyama, Y. Shirota, H. Mikawa, M. Sorai, H. Suga, and S. Seki, *Energy and Charge Transfer in Organic Semiconductors*, Ed. by K. Masuda and M. Silver, Prenum Publishing Corp., pp. 77 (1972).
12. Y. Sano, K. Kato, M. Yokoyama, Y. Shirota, and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **36**, 137 (1976).
13. The X-ray analysis of the crystal of this compound shows that the crystal has two modifications α and β depending upon the crystallization method[24]. When crystallized from *n*-hexane or grown from the melt, the crystal has α-form structure.
14. R. H. Wiley, C. H. Jarboe, F. N. Hayes, E. Hansbury, J. T. Nielsen, P. X. Callahan, and M. C. Sellars, *J. Org. Chem.*, **23**, 732 (1958).
15. T. Kobayashi, S. Nagakura, S. Iwashima, and H. Inokuchi, *J. Mol. Spectry.*, **41**, 44 (1972).
16. D. C. Northrop and O. Simpson, *Proc. Roy. Soc.*, **A234**, 136 (1956).
17. A. Schmillen, *Z. Physik.*, **150**, 123 (1958).

18. K. W. Benz and H. C. Wolf, *Z. Naturforsch.*, **19a**, 177 (1964).
19. V. L. Zima and A. N. Faidysh, *Opt. Spectrosc.*, **20**, 566 (1966).
20. M. Rudemo, *SIAM. J. Appl. Math.*, **14**, 1293 (1966).
21. H. B. Rosenstock, *J. Chem. Phys.*, **48**, 532 (1968).
22. W. Klöpffer, *J. Chem. Phys.*, **50**, 1689 (1969).
23. It was pointed out by a referee that the probability (f) will be different between the glassy and single crystalline states. However, no information is available at present regarding this point, and in the present study the comparison of the efficiency of the singlet excitation energy migration is made based on the assumption that the dimensionality of the excitation energy migration tensor is the same in the crystalline as well as the glassy state. We appreciate the referee for his comments.
24. T. Kimura, Y. Kai, N. Yasuoka, and N. Kasai, *Acta Cryst.*, **B33**, 1786 (1977).
25. 1,3-Diphenyl-5-(p-chlorophenyl)-2-pyrazoline crystallizes in α form and β form. α form is obtained from n-hexane solution and melt-grown single crystal has also α form. β form is easily obtained from ethanol or xylene solution. Both forms belong to the monoclinic system, space group $P2_1/c$. The unit-cell parameters are: α form, $a = 11.365(3)$ Å, $b = 13.854(3)$ Å, $c = 12.026(4)$ Å, $\beta = 112.26(3)$; β form, $a = 18.836(4)$ Å, $b = 5.494(3)$ Å, $c = 16.569(4)$ Å, $\beta = 96.38(3)$. The distance between number 1 nitrogen atoms belonging to the pyrazoline molecules in the nearest and the next nearest positions are 4.2 Å and 8.6 Å, respectively, in α form crystal. Therefore, mean hopping distance d (in equation (11)) is estimated to be 6.4 Å.