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Photochromic Color Change of the Dimer of Triphenylimidazolyl at Low Temperatures

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The photochromic dimer of triphenylimidazolyl which is one of two dimers obtained by oxidation of triphenylimidazole shows photochromism at temperatures between room temperature and −196°C in solutions and in a solid state. At temperatures higher than about −20°C the photochromic color in solutions is reddish-purple, at temperatures lower than about −150°C the color is bluish-purple and at intermediate low temperatures the photochromic color does not appear. Absorption spectrum and ESR measured with the change of temperature showed variations corresponding to the change of color. The photochromic color in a solid state was light reddish-purple above about −70°C and bluish-purple at −196°C. The mechanism of the color change was discussed in connection with that of the photochromism at room temperature and the results obtained from spectroscopic and ESR studies.

We obtained a photochromic compound¹⁾ and a piezochromic compound²⁾ by oxydation of 2,4,5-triphenylimidazole. The photochromic compound exhibited photochromism and thermochromism in solid state³⁾ as well as in solutions at temperatures near room temperature. It was confirmed by kinetic studies with absorption spectrum and ESR, that the compounds are dimers of triphenylimidazolyl⁴,⁵⁾ and that photochromism, thermochromism and piezochromism are due to the dissociation of the dimers into triphenylimidazolyl radical caused by irradiation, heating and grinding. White and Sonnenberg⁶⁾ reported that the photochromic and piezochromic dimers are isomers and the piezochromic dimer shows thermochromism at temperatures lower than room temperature, and discussed the interconversion between two dimers and radical.

We found that a solution of the photochromic dimer in benzene exhibited photochromism within a wide range of temperatures from room temperature down to −196°C, except for temperatures between about −20°C and −150°C.⁷⁾ At temperatures higher than about −20°C, the photochromic color is reddish-purple and at temperatures lower than about −150°C bluish-purple. In the present paper, the results of studies on a reversible color change of the photochromic dimer in solutions and in a solid state at temperatures between room temperature and −196°C under irradiation or in the dark are presented.

Experimental

Materials. The piezochromic dimer of 2,4,5-triphenylimidazolyl (piezo-dimer) $C_{42}H_{30}N_4$ and its isomer, the photochromic dimer (photo-dimer), were prepared according to the method given in a previous report.¹⁾ Piezo-dimer prepared by the oxidation of 2,4,5-triphenylimidazole was almost colorless fine powder, mp 191—192°C and photo-dimer obtained by recrystallization of piezo-dimer from benzene was light yellow fine crystals, mp 199—201°C.

The photochromic dimer of 2-*p*-chlorophenyl-4,5-diphenylimidazolyl (photo-dimer(Cl)), $C_{42}H_{28}N_4Cl_2$, almost colorless fine crystals, mp 219—220°C and its isomeric piezo-dimer (piezo-dimer (Cl)), almost colorless powder, mp 205—207°C, were prepared according to previous reports.¹,⁵⁾

Measurements. Absorption spectra were measured with a Hitachi recording spectrophotometer, EPS 2 type.

The electron spin resonance absorption was measured with an ESR instrument of the Japan Electron Optics Laboratory, JES 3B type (100 kc modulation), with a variable temperature controller, JES VT 2 type.

As an exciting source the 365 mμ light obtained from a Toshiba 100 watt super high-pressure mercury lamp combined with a Toshiba glass filter UV D1B was used.

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1) T. Hayashi and K. Maeda, This Bulletin, **33**, 566 (1960); T. Hayashi, K. Maeda, S. Shida and K. Nakada, *J. Chem. Phys.*, **32**, 1568 (1960).

2) T. Hayashi and K. Maeda, This Bulletin, **38**, 685 (1965).

3) T. Hayashi, K. Maeda and T. Kanaji, *ibid.*, **38**, 857 (1965).

4) T. Hayashi, K. Maeda and M. Morinaga, *ibid.*, **37**, 1563 (1964).

5) T. Hayashi, K. Maeda and M. Takeuchi, *ibid.*, **37**, 1717 (1964).

6) D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 3825 (1966).

7) T. Hayashi and K. Maeda, This Bulletin, **36**, 1052 (1963); *ibid.*, **40**, 2990 (1967).

Results and Discussion

Reversible Changes of Color and ESR of Photo-dimer in Solutions with Temperature. Change of the color of photo-dimer in solutions with the temperatures from room temperature to −196°C was observed under irradiation and without irradiation. ESR signal intensity of the solution showed variation corresponding to the change of color.

When a reddish-purple benzene solution of photo-dimer obtained by irradiation of a light yellow solution at room temperature was cooled under irradiation, the color gradually faded and disappeared at about −20°C. When the resulting frozen solution was further cooled to about −150°C, it remained colorless. However, with further cooling to −196°C the solution showed a bluish-purple color which became more intense with the fall of temperature. When the bluish-purple solution was warmed from −196°C to room temperature under irradiation, a color change reverse to that on cooling was observed.

Figure 1 shows variation of the ESR signal intensity, which corresponds to the change of the color with temperature under irradiation.

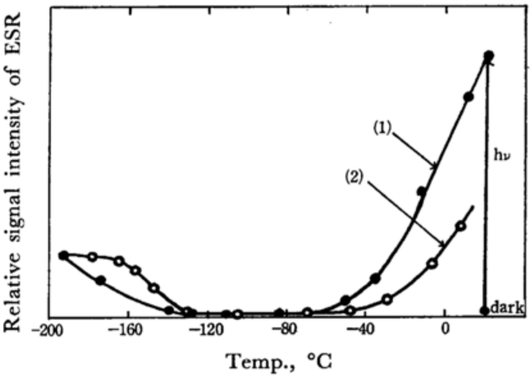


Fig. 1. Variation of the ESR signal intensity of photo-dimer in deaerated benzene under irradiation.
(1) with cooling from room temperature to −196°C
(2) with warming from −196°C to room temperature
Concn.: 6.8×10^{-5} mol/l

When the reddish-purple benzene solution of photo-dimer was cooled from room temperature without irradiation, the color gradually faded and disappeared at about −20°C. The resulting frozen solution remained colorless on further cooling to −196°C. When the colorless frozen solution was warmed from −196°C without irradiation, a color change reverse to that on cooling was observed. On irradiation at −196°C, the colorless frozen solution turned deep bluish-purple. By warming the solution to room temperature without irradiation, the color showed a change similar to that observed with warming under irradiation. Figure 2 shows variation of the ESR signal intensity which corresponds to the change of color with temperature in the dark.

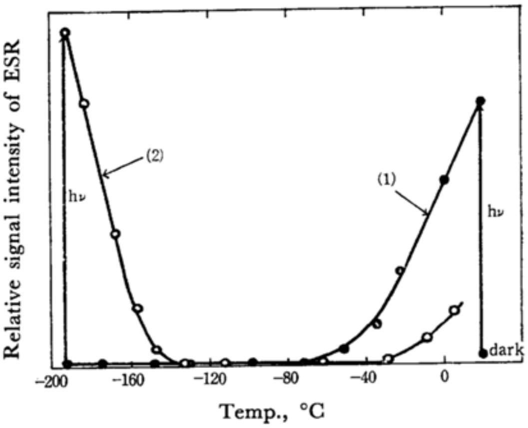


Fig. 2. Variation of the ESR signal intensity of photo-dimer in deaerated benzene.
(1) with cooling to −196°C in the dark after irradiation at room temperature
(2) with warming to room temperature in the dark after irradiation at −196°C
Concn.: 6.8×10^{-5} mol/l

When the light yellow solution of photo-dimer in benzene prepared in dim light at room temperature was cooled to −196°C without irradiation, color and ESR did not appear during cooling. On irradiation at −196°C, the frozen solution showed an intense bluish-purple color and a strong ESR signal.

In solutions of photo-dimer in other solvents, changes of color and ESR signal intensity similar to those in benzene were observed with the change of temperature between room temperature and −196°C. On cooling from room temperature, the temperature at which the reddish-purple color disappears differs to some extent with solvents, and the temperature at which a bluish-purple color appears seems to be about −150°C, irrespective of solvents. In a solvent of a relatively high melting point, such as benzene and dioxane, the temperature at which the reddish-purple color disappears is about −20°C and the solutions are frozen. However, in a solvent of a relatively low melting point, such as ethanol and toluene, the temperature at which the color disappears is about −70—−100°C, and the solutions mostly remain unfrozen. The fact suggests that freezing favors the disappearance of the reddish-purple color at a relatively high temperature.

Figure 3 shows the variation of the ESR signal measured in EPA with the change of temperature.

The ERS signal measured at −196°C in the intense bluish-purple solutions of benzene and EPA showed three pairs of signals at 3120—3375 gauss

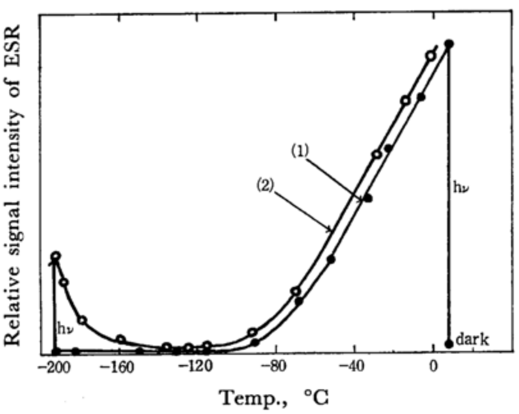


Fig. 3. Variation of the ESR signal intensity in deaerated EPA.

(1) with cooling to −196°C in the dark after irradiation at room temperature
(2) with warming to room temperature in the dark after irradiation at −196°C

Concn.: 4.5×10^{-5} mol/l

and a single peak signal at 1750 gauss as well as a strong signal at 3250 gauss.

The intensity of the bluish-purple color and the ESR siganls observed at −196°C did not diminish at −196°C after irradiation was cut off. With irradiation of an infrared light at −196°C the intensity of the ESR signal decreased.

The rate of formation of triphenylimidazolyl radical under irradiation with different intensities of light in benzene at −196°C was measured by means of ESR. As a signal intensity of the radical was assumed to be directly proportional to the concentration of the radical, the rate of formation of the radical was measured from the rate of the increase of the signal intensity under irradiation with different intensities. The signal intensity was proportional to irradiation time. In Fig. 4, the rate of the radical formation measured in benzene is plotted against the intensity of the irradiation.

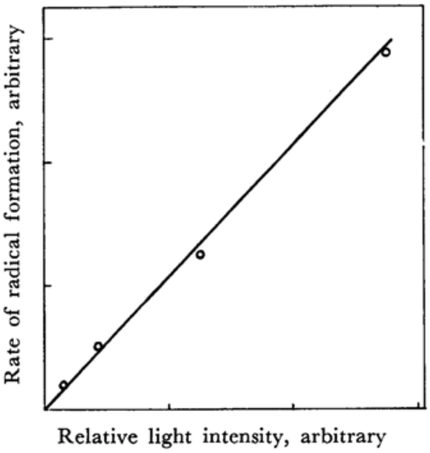


Fig. 4. Dependence of rate of the radical formation in benzene at −196°C, on light intensity.

From the dependence of the rate of the radical formation on the light intensity in Fig. 4, we see that the formation of the bluish-purple radical is a one-photon process.

When a benzene solution of photo-dimer (Cl) which showed a violet color with irradiation at room temperature was cooled under irradiation, the color gradually faded and disappeared at about −20°C. A light bluish-violet color appeared at about −150°C and became deeper with further cooling to −196°C. When the deep bluish-violet solution was warmed from −196°C to room temperature under irradiation, a change of color reverse to that with cooling was observed. Similar to the case of photo-dimer, the violet benzene solution of photo-dimer (Cl) obtained by irradiation at room temperature and the bluish-violet solution obtained by irradiation at −196°C showed ESR ($g=2.003$).

Change of Absorption Spectrum of Photo-dimer in EPA. Disappearance of the photochromic color at the intermediate low temperature range and appearance of the bluish-purple color by irradiation at temperatures below about −150°C were also studied by means of absorption spectrum.

An almost colorless solution of photo-dimer in

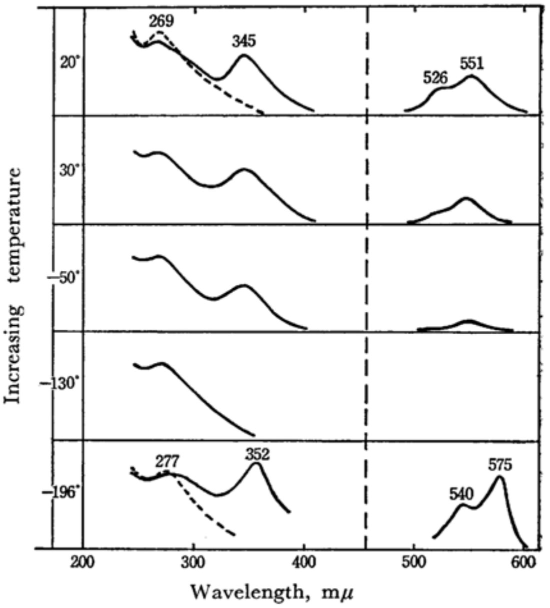


Fig. 5. Absorption spectra of photo-dimer in EPA at temperatures from −196°C to room temperature.

- - - Before irradiation
—— After irradiation by a mercury lamp without a filter for 2 min at −196°C

Concn.: 2.54×10^{-5} mol/l for shorter than 400 mμ; 4.48×10^{-4} mol/l for longer than 400 mμ

EPA (4.48×10^{-4} mol/l) which was prepared in dim light at room temperature was frozen into a glassy state in a quartz cell (1 cm thick) by immersing it in liquid nitrogen in a Dewar provided with quartz windows. On irradiation of the glassy solution with a mercury lamp for 2 min from outside the Dewar, a bluish-purple color appeared. Absorption spectra were measured at several temperatures between −196°C and room temperature obtained by evaporation of liquid nitrogen. In Fig. 5, absorbance at a wavelength region shorter than 400 mμ is shown on a reduced scale.

A red shift of the absorption maxima at 345 and 551 mμ at room temperature to 352 and 575 mμ at −196°C corresponded to the change of color from reddish-purple to bluish-purple. With the fading of the bluish-purple color, the absorption band with $\lambda_{\max}$ 352 and 575 mμ gradually decreased to vanish at about −150°C, and the absorption band with $\lambda_{\max}$ 345 and 551mμ appeared at about −50°C. The band increased with further rise of temperature to room temperature. The maxima at 345 and 551 mμ agreed with those of a reddish-purple solution obtained by irradiation of photo-dimer in EPA at room temperature.

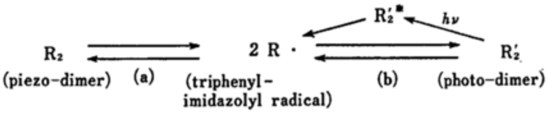
The violet solution of photo-dimer (Cl) in EPA obtained with irradiation showed absorption maxima at 356 and 568 mμ at room temperature. The bluish-violet solution obtained with irradiation at −196°C showed absorption maxima at 361 and 580 mμ. At temperatures between about −60 and −150°C, the absorption band in the visible region disappeared as in the case of photo-dimer.

Reversible Color Change of Piezo-dimer in Solutions with Temperature. A benzene solution of piezo-dimer which was prepared under dim light at room temperature showed an intense reddish-purple color due to triphenylimidazolyl radical formed by the dissociation of dimer.⁶⁾ When the reddish-purple solution was allowed to stand at room temperature without irradiation, the reddish-purple color gradually turned light yellow¹⁾ by dimerization of triphenylimidazolyl radical to photo-dimer. The resulting solution is an equilibrium mixture of photo-dimer and a small amount of piezo-dimer.⁶⁾ When the temperature of the solution changed between room temperature and −196°C under irradiation, the solution showed a color change similar to that of the solution of photo-dimer.

When the reddish-purple solution of piezo-dimer in benzene was cooled without irradiation immediately after preparation, the reddish-purple color faded with the fall of temperature and disappeared at temperatures lower than about −20°C. The colorless solution showed no change of color even with irradiation at −196°C. When the colorless solution was warmed with or without irradiation from −196°C, a light reddish-purple color due to thermochromism of piezo-dimer appeared above about −20°C and became more intense at room temperature.

In other solvents piezo-dimer showed a color change similar to that in benzene observed with the change of temperature between room temperature and −196°C, with or without irradiation. The temperature at which the reddish-purple color disappeared was to some extent different with solvents, as the case of photo-dimer which was cooled under irradiation.

Mechanism of Riversible Color Change of Photo-dimer in Solutions. Disappearance of the photochromic reddish-purple color and ESR signal in benzene at temperatures between about −20 and −150°C is interpreted as follows. In solutions the following equilibria (a) and (b) take place between piezo-dimer, triphenylimidazolyl radical and photo-dimer.⁶⁾ Equilibrium (a) lies far on the side of the radical at room temperature and shifts toward piezo-dimer at temperatures lower than about −20°C,⁶⁾ while the position of equilibrium (b) lies far on the side of photo-dimer at room temperature and shifts further toward photo-dimer at low temperatures.



Under irradiation, the reddish-purple triphenylimidazolyl radical produced by photo-dissociation of photo-dimer dimerizes quickly to piezo-dimer at temperatures lower than about −20°C owing to a low activation energy for the dimerization of the radical to piezo-dimer.⁶⁾ As a result, the reddish-purple color and ESR signal do not appear within the temperatures between about −20 and −150°C.

Appearance of the photochromic bluish-purple color and ESR signal at temperature slower than about −150°C with irradiation is interpreted by means of the following mechanism.⁸⁾ At temperatures lower than −150°C, a part of the radicals produced by photo-dissociation remains unchanged in the solution, because it becomes difficult for the radical to surmount the barrier of the activation energy of dimerization at such low temperatures, although equilibria (a) and (b) lie very far on the sides of the two dimers. The concentration of the radical increases with the fall of temperature to −196°C, because the difficulty in surmounting the energy barrier increases at low temperatures. The intensity of ESR signal appearing at −196°C when the solution was cooled under irradiation, was weaker than that in the solution which was

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8) T. Hayashi and K. Maeda, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **90**, 325 (1969).

irradiated after cooling from room temperature in the dark, because photo-dimer isomerizes to piezo-dimer through the radical during cooling under irradiation.

The bluish-purple color appearing at temperatures lower than about −150°C is attributed to triphenylimidazolyl radical S·[9] which has a conformation different from that of the reddish-purple triphenylimidazolyl radical, R·. The red shift of the absorption maxima shows an increase in resonance stability due to the increase in coplanarity of a conjugated system in the radical S·. ESR signals at 3120—3375 gauss and 1750 gauss ($\Delta m=\pm 1$ and ± 2) in frozen solutions of photo-dimer irradiated at −196°C is likely to be a radical pair[9] of triphenylimidazolyl radical. On warming the deep bluish-purple benzene solution of photo-dimer from −196°C, the bluish-purple radical S· gradually surmounts the barrier of the activation energy for dimerization to a colorless dimer S_2 and the solution turns colorless above about −150°C. From the thermochromic behavior of the solution warmed near room temperature without irradiation, the structure of the dimer S_2 is likely to be the same as that of piezo-dimer. With the rise of temperature to about −20°C the dimer S_2 seems to be transformed into piezo-dimer.

The reddish-purple color which appeared as the solution was warmed above about −20°C under irradiation is attributed to triphenylimidazolyl radical, produced by the thermal dissociation of piezo-dimer isomerized from photo-dimer and also by the photo-dissociation of photo-dimer remaining unchanged in the solution.

The mechanism of the changes of color and ESR shown by the solutions of photo-dimer (Cl) with temperatures from room temperature to −196°C is similar to that of photo-dimer.

Changes of Photochromic Color and ESR of Photo-dimer in Solid State. When a light yellow solid of photo-dimer was irradiated at low temperatures such as −20°C or −70°C, it showed a light reddish-purple color similar to that of the photochromism[3] at room temperature. On irradiation, after cooling to −196°C without irradiation, the solid showed an intense bluish-purple color which scarcely faded after irradiation was cut off.

The color change of the solid with the change of temperature was studied with ESR. With cooling from room temperature to −196°C in the dark, no ESR signal appeared. On irradiation at room teaperature a weak ESR signal corresponding to the light reddish-purple color was observed. When the solid was cooled after irradiation was cut off, a small increase in signal intensity was observed at temperatures near −196°C as shown in Fig. 6. On irradiation of the solid at −196°C a very strong ESR signal (Fig. 6) appeared. It corresponds to the intense bluish-purple color. The signal intensity increased with the time of irradiation and scarcely decreased after irradiation was cut off. However, it decreased on warming a little in the dark or under irradiation, as shown in Fig. 6. With cooling of the solid from room temperature under irradiation, the small ESR signal increased slightly at temperatures below about −80°C, and with further cooling the signal increased considerably near −196°C.

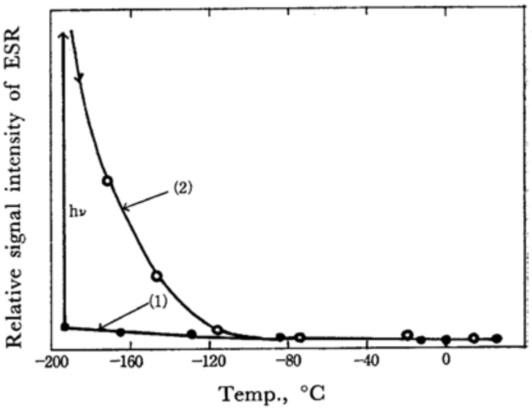

Fig. 6. Variation of ESR of the solid of photo-dimer.
(1) with cooling in the dark after irradiation at room temperature
(2) with warming in the dark after irradiation at −196°C

The light reddish-purple color appearing at temperatures above about −70°C is attributed to triphenylimidazolyl radical produced by photo-dissociation of photo-dimer.[3] The light color which corresponds to a small concentration of the radical seems to result from the recombination of the radical owing to difficulty of diffusion in the solid. Differing from the change in solutions, the color does not disappear at the intermediate low temperatures, because photo-dimer is not transformed into piezo-dimer owing to the retarded thermal motion of the radical. The bluish-purple color appearing at temperatures near −196°C is considered to be due to the triphenylimidazolyl radical S·, as in the solutions. Three pairs of ESR signals at 3160—3400 gauss and a single peak signal at 1750 gauss observed at −196°C are considered to be due to a radical pair similar to that formed in solutions. The large concentration of the radical corresponding to the strong ESR signal and deep bluish-purple color near −196°C might be attributed to a very small rate of dimerization at the low temperatures.

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[9] Presented at the Symposium on Photochemistry of the Chemical Society of Japan (Oct., 1968, Sendai) by T. Shida, K. Maeda and T. Hayashi; T. Shida, K. Maeda and T. Hayashi, This Bulletin, **42**, 3044 (1969).

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