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The Mechanism of Photochromism, Thermochromism and Piezochromism of Dimers of Triarylimidazolyl

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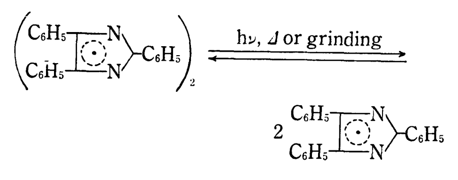
A stable free radical, 2,4,5-triphenylimidazolyl, which was produced by oxidation of 2,4,5-triphenylimidazole, dimerizes to yield two dimers, a photochromic dimer and a piezochromic dimer. The photochromic dimer shows thermochromism and photochromism at temperatures between −196°C and about 200°C both in solution and in solid state. The piezochromic dimer shows piezochromism in solid state and thermochromism both in solution and in solid state. Spectroscopic and kinetic studies showed that photochromism, thermochromism and piezochromism are caused by radical dissociation of the dimers of triphenylimidazolyl on irradiation, heating and grinding. Dimers of substituted triphenylimidazolyl also showed these phenomena which are due to the same mechanism as that of the dimers of triphenylimidazolyl.

In the study of the mechanism of chemiluminescence of 2,4,5-triphenylimidazole (lophine)[1] we obtained new compounds by oxidation of lophine.[2] One compound exhibited photochromism[2] and thermochromism both in solution and in solid state[3,4] with irradiation and change of temperature. The other isomeric compound which is convertible to the former by recrystallization exhibited piezochromism[5] on grinding at room temperature, showing a reddish-purple color reversibly. By spectroscopic and kinetic studies it was shown that the photochromic compound is a dimer of triphenylimidazolyl, and the photochromism, thermochromism and piezochromism of the two compounds are due to reversible dissociation of the dimers into triphenylmidazolyl radical which is shown by the following reversible reaction.



(1)

White and Sonnenberg[6] reported that the photochromic and piezochromic compounds are isomeric dimers which are different in the positions of combination of the 2,4,5-triphenylimidazolyl radical and are in equilibrium with the radical in solution.

We found that[7] besides photochromism at room temperature, showing a reddish-purple color, the photochromic dimer showed photochromism at low temperatures between about −150°C and −196°C, showing a violet color.

In the present paper, the mechanisms of photochromism, thermochromism and piezochromism of the dimers of triarylimidazolyl are reported. The photochromism at low temperatures was reported previously.[8]

Experimental

Materials. The Piezochromic Dimer of Triphenylimidazolyl.[2] To a solution of lophine (1 g) in 2 N ethanolic potassium hydroxide (100 m*l*) about 500 m*l* of 2% aqueous solution of potassium ferricyanide was gradually added for 1.5 hr with stirring by a stream of oxygen at 10°C. A reddish-purple color first appeared and then an almost colorless precipitate was formed gradually. The precipitate filtered was washed with water repeatedly and then dried *in vacuo*; 1 g of the piezochromic dimer (piezo-dimer) was obtained; almost colorless fine powder, mp 191—192°C.

Found: C, 84.73; H, 5.28; N, 9.19%. Calcd for $C_{42}H_{30}N_4$ (dimer of triphenylimidazolyl): C, 85.40;

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1) T. Hayashi and K. Maeda, This Bulletin, **35**, 2057 (1962); K. Maeda, H. Ojima and T. Hayashi, *ibid.*, **38**, 76 (1965).

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

3) T. Hayashi, K. Maeda and M. Morinaga, This Bulletin, **37**, 1563 (1964).

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

5) T. Hayashi and K. Maeda, *ibid.*, **38**, 685 (1965).

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

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

8) K. Maeda and T. Hayashi, *ibid.*, **42**, 3509 (1969); T. Shida, K. Maeda and T. Hayashi, *ibid.*, **42**, 3044 (1969).

TABLE 1. PHOTO- AND PIEZO-DIMERS OF TRIARYLIMIDAZOLYL

Imidazolyl radical	Molecular formula of dimer*1 (molecular weight)	Abbreviation of photo-chromic dimer	Mp °C	Molecular weight of photo-chromic dimer*2	Abbreviation of piezo-chromic dimer	Mp °C
2,4,5-Tri-phenyl-	$C_{42}H_{30}N_4$ (591)	photo-dimer	199—201	600	piezo-dimer	191—192
2,4,5-Tri-*p*-tolyl-	$C_{48}H_{42}N_4$ (633)	photo-dimer -CH_3	194—195	600	piezo-dimer -CH_3	148—150
2,4,5-Tri-*p*-chloro-phenyl-	$C_{42}H_{24}N_4Cl_6$ (695)	photo-dimer -Cl	213—214	680	piezo-dimer -Cl	140—142
2-*p*-Chloro-phenyl-4,5-diphenyl-	$C_{42}H_{28}N_4Cl_2$ (526)	photo-dimer -2-Cl	219—220	510	piezo-dimer -2 Cl	205—207

*1 Found: photo-dimer-CH_3: C, 84.78; H, 6.03; N, 8.30%
piezo-dimer-CH_3: C, 84.99; H, 6.17; N, 8.12%
Calcd for $C_{48}H_{42}N_4$: C, 85.43; H, 6.27; N, 8.30%.
Found: photo-dimer-Cl: C, 63.71; H, 3.04; N, 6.86; Cl, 26.95%
piezo-dimer-Cl: C, 62.44; H, 3.34; N, 6.62; Cl, 26.95%
Calcd for $C_{42}H_{24}N_4Cl_6$: C, 63.26; H, 3.03; N, 7.02; Cl, 26.68%.
Found: photo-dimer-2-Cl: C, 76.65; H, 4.18; N, 8.38; Cl, 10.40%
piezo-dimer-2-Cl: C, 76.49; H, 4.70; N, 8.00; Cl, 10.43%
Calcd for $C_{42}H_{28}N_4Cl_2$: C, 76.48; H, 4.28; N, 8.49; Cl, 10.75%.

*2 Determined in a dim light by the cryoscopic method in solutions prepared in the dark.

H, 5.12; N, 9.48%.

Piezo-dimer is soluble in benzene, toluene and other aromatic hydrocarbons, carbon tetrachloride, chloroform, acetone, ethyl acetate and pyridine and slightly soluble in methanol, ethanol, ether and *n*-hexane.

As another method to prepare the piezo-dimer, 200 m*l* of 5% aqueous solution of sodium hydroxide containing 20 g of bromine was added to a solution of lophine (1 g) in 2 N ethanolic solution of potassium hydroxide (100 m*l*) with stirring by a stream of oxygen at 10°C during 1.5 hr. A reddish-purple color first appeared and then an almost colorless precipitate was formed gradually. The precipitate filtered was washed with water repeatedly and dried *in vacuo*; 1 g of piezo-dimer was obtained.

The Photochromic Dimer of Triphenylimidazolyl.[2] By slow recrystallization of piezo-dimer from benzene at 5°C in the dark light yellow crystals of the photochromic dimer (photo-dimer) were obtained.

Found: C, 85.20; H, 5.50; N, 9.41%. Calcd for $C_{42}H_{30}N_4$: C, 85.40; H, 5.12: N, 9.48%.

Photo-dimer is soluble in benzene, acetone, ethyl acetate, pyridine, chloroform and carbon tetrachloride and slightly soluble in ether and *n*-hexane, mp 199—201°C.

Photo-dimer was also prepared by oxidation of lophine according to the method of Khun and Kainer[9] who obtained tetraphenylpyrryl radical by oxidation of tetraphenylpyrrole with lead dioxide. When lophine (0.3 g) was heated in benzene (100 m*l*) with lead dioxide (10 g) for 2 hr at 80°C with stirring by a stream of nitrogen, a reddish-purple solution was obtained. After the solution was cooled to room temperature, lead dioxide was filtered. The reddish-purple filtrate was concentrated under nitrogen atmosphere at room temperature in the dark under reduced pressure. By standing the concentrated solution for 1 day in the dark, a small amount of photo-dimer was obtained.

The Dimers of Substituted Triphenylimidazolyl. Piezo-dimers of substituted triphenylimidazolyl, shown in Table 1, were prepared from the corresponding imidazoles by oxidation with potassium ferricyanide in ethanolic potassium hydroxide. Photo-dimer of these triarylimidazolyls were obtained by recrystallization of the corresponding piezo-dimers.

Spectroscopic Measurements. Measurements of the absorption spectra and kinetic studies were carried out with a Hitachi recording spectrophotometer, EPS 2 type. Temperatures between room temperature and 60°C were controlled within ±0.5°C by circulating hot water from a thermostat to the cell room of the spectrophotometer. Deaerated solutions were used in all spectroscopic measurements.

Electron Spin Resonance Absorption. Kinetic measurements by the ESR method were carried out by the Japan Electron Optics Laboratory JES 3B type ESR spectrometer (100 kc modulation) with deaerated solutions. Spin concentrations of piezochromic systems were measured by a Japan Electron Optics Laboratory JES P-10 type ESR spectrometer (100 kc modulation) which has a JES 1D-2 type integrator. The hyperfine structure of the ESR spectrum was measured by a Hitachi ESR spectrometer.

Irradiation. Sunlight or the 365 mμ light of a high pressure mercury lamp filtered through a Toshiba glass filter UV-D1B, was used.

Results and Discussion

Formation of Piezo-dimers and Photo-dimers. Lophine which showed an absorption maximum at 303 mμ in ethanol showed a red shift

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[9] R. H. Kuhn and H. Kainer, *Biochim. Biophys. Acta*, **12**, 325 (1953).

toward 326 mμ in 2N ethanolic potassium hydroxide, whereas *N*-methyl- and *N*-ethyl-lophine phenylimidazole anion in alkaline solution. When lophine was oxidized in a mixture of ethanolic potassium hydroxide and benzene with an aqueous solution of potassium ferricyanide, a reddish-purple substance was produced and transfered to a benzene layer which separated out from an aqueous layer when an excess of the potassium ferricyanide solution was added. The reddish-purple benzene solution showed absorption maxima at 347 and 554 mμ and an ESR signal (*g* 2.003), attributable to the triphenylimidazolyl radical. These facts show that on oxidation of lophine piezo-dimer was produced from triphenylimidazole anion through the triphenylimidazolyl radical.

Because oxidation of monophenylimidazoles did not give the corresponding radicals and diphenylimidazoles gave corresponding radicals only in a small amount, substitution of three phenyl groups in the imidazole ring seems to be favorable for formation of the radicals and their dimers.

Photochromism in Solutions. Light yellow solutions of photo-dimer in various organic solvents quickly turned reddish-purple on irradiation at room temperature and the color gradually reverted to the original color on standing in the dark at room temperature. The change in intensity of photochromic color with time of irradiation, shown in Fig. 1, was measured by the change in absorbance at absorption maximum (347 mμ in benzene, 346 mμ in *n*-hexane). The maximum absorbance at the photo-stationary state depended on the intensity of the irradiation light, concentration of solution, solvent and temperature. The rate of fading in the dark was not accelerated by irradiation with visible light.

Photo-dimer gradually lost photochromic activity in solutions with prolonged irradiation. Duration time of photochromic activity varied with the solvent and also with coexistence of oxygen. For example, in a deaerated benzene solution the duration time was one year or longer, whereas in ethanol and toluene it was very short even in a deaerated solution. The loss of activity is due to hydrogen abstraction from the solvent by triphenylimidazolyl radical which reverts to lophine or oxidation with dissolved oxygen.

A light yellow solution of photo-dimer in *n*-hexane which was prepared in a darkened room at room temperature showed an absorption maximum at 270 mμ (ε 1.6×10^4) which obeyed Beer's law. The reddish-purple solution obtained with

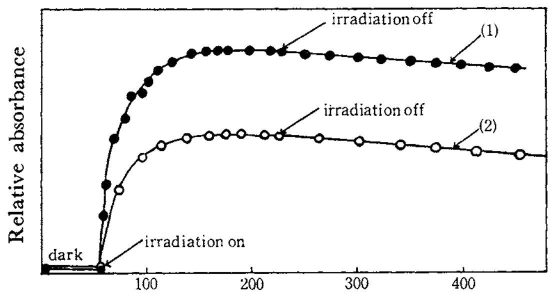

Fig. 1. Photochromic variation of the absorbance of photo-dimer.
(1) 5.28×10^{-5} mol/*l* in benzene; measured at 347 mμ, (2) 5.49×10^{-5} mol/*l* in *n*-hexane; measured at 346 mμ
Irradiation: 365 mμ light, Temp.: 16.0°C

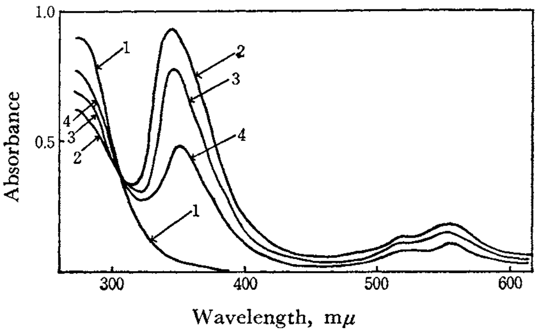

Fig. 2. Photochromic variation of absorption spectrum of photo-dimer in benzene.
(1) before irradiation, (2) immediately after irradiation, (3) 6 min after irradiation, (4) 24 min after irradiation.
Irradiation: 365 mμ light for 3 min, Temp.: 15.0°C. Concentration of photo-dimer: 3.38×10^{-5} mol/*l*.

TABLE 2. PHOTOCHROMIC CHANGES OF THE COLOR AND THE ABSORPTION MAXIMUM OF PHOTO-DIMER IN ETHANOL

Dimer	Before irradiation		After irradiation	
photo-dimer	light yellow	(270 mμ)	reddish-purple	(270, 348, 554 mμ)
photo-dimer -CH_3	light yellow	(280 mμ)	bluish-violet	(280, 365, 583 mμ)
photo-dimer -Cl	almost colorless	(274 mμ)	violet	(274, 368, 585 mμ)
photo-dimer -2-Cl	almost colorless	(268 mμ)	violet	(268, 366, 575 mμ)*

* Measured in benzene as the solubility of photo-dimer-2 Cl in ethanol is too low for measurement of the absorption spectrum of the colored form.

irradiation showed new absorption maxima at 346 and 548 mμ with decrease of absorbance at 270 mμ. When the reddish-purple solution was kept in the dark at room temperature, the absorbances of the new bands gradually decreased with recovering of the absorbance at 270 mμ. A similar photochromic variation was also observed in other solvents, for example in benzene, as shown in Fig. 2. Photo-dimers -CH_3, -Cl and -2-Cl also exhibited similar photochromism. The photochromic changes in color and absorption maxima are shown in Table 2.

The absorbances at 347 and 554 mμ of the reddish-purple benzene solution of photo-dimer at different concentrations (7×10^{-6}—5×10^{-5} mol/l) were measured immediately after irradiation. The results are shown in Fig. 3. As can be seen the absorbances of the photochromic absorption maxima did not obey Beer's law as the absorbances of absorption maxima at 347 and 554 mμ due to thermochromism of photo-dimer were negligibly small under the present conditions.

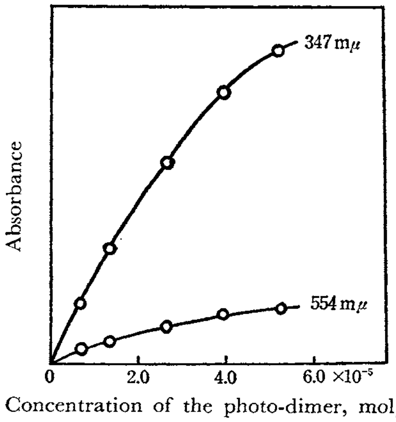

Fig. 3. Variation of the absorbance of the absorption maximum in a photochromic colored benzene solution of photo-dimer, measured immediately after irradiation.
Irradiation: 365 mμ light for 2 min. Temp.: 10.0°C.

Photo-dimer and photo-dimers -CH_3, -Cl and -2-Cl also exhibited a similar photochromism in plastics, such as polystyrene and butyral resin.

A light yellow benzene solution of photo-dimer (1.48×10^{-4} mol/l) which was prepared in the dark gave no ESR in the dark at room temperature, whereas the reddish-purple benzene solution produced by irradiation at room temperature showed ESR with g 2.003 (a single peak singal with a line width about 9 gauss). On standing the colored solution in the dark at room temperature, the signal intensity of ESR gradually decreased. The decrease corresponded to the decrease of the absorbance in the visible region. The photochromic colored benzene solutions of photo-dimers -CH_3, -Cl and -2-Cl also showed ESR absorption.

A highly resolved hyperfine structure of an ESR spectrum shown in Fig. 4 was observed in benzene.[10]

Radical formation in the photochromic system was also confirmed by the following chemical evidence. When a light yellow solution of photo-dimer in carbon tetrachloride was brought into contact with oxygen under irradiation with sunlight at room temperature, a reddish-purple color produced on irradiation slowly faded with gradual absorption of oxygen. After about 20 hr the solution turned yellow. A brownish-yellow crystalline residue was obtained by evaporation of the solvent under reduced pressure. It was probably peroxide, because it melted with evolution of gas and liberated iodine from potassium iodide in an acetic acid solution. When nitrogen monoxide was passed into a reddish-purple solution of photo-dimer in oxygen-free benzene under irradiation at room temperature, the solution gradually turned light yellow and almost colorless crystals separated. As the crystals gave a positive Leibermann's test and decomposed at about 105°C with evolution of gas, the colorless crystals are likely to be an addition product of nitrogen monoxide with the radical. When an ethanolic solution of photo-dimer (0.12 g/300 ml) was irradiated for about 5 days with sunlight at room temperature, a reddish-purple color first appeared and then gradually faded. From the solution, lophine (0.11 g) and acetaldehyde which was identified as a dimedone derivative (0.057 g) were obtained. Acetaldehyde seems to arise from ethanol by reaction with the radical under irradiation. When an ethanolic solution of hydroquinone was added to the reddish-purple benzene solution of photo-dimer under irradiation, the color turned almost colorless and lophine was isolated from the solution.

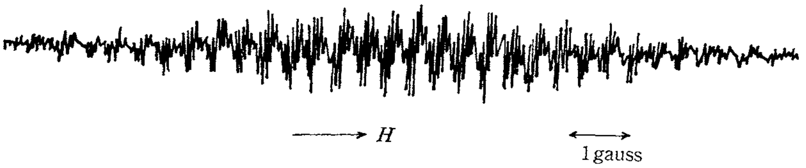

Fig. 4. The ESR spectrum of a photochromic colored benzene solution of photo-dimer.

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[10] The measurement was carried out by Dr. Koichi Ito of Osaka University.

By using the reaction with hydroquinone the degree of photo-dissociation of photo-dimer in reaction (1) was estimated in benzene at the photostationary state. To a reddish-purple benzene solution (4.7×10^{-5} mol/*l*, 10 m*l*) obtained by irradiation with the 365 mμ light for 3 min at room temperature, an ethanolic solution of hydroquinone (9.1×10^{-5} mol/*l*), was added under a stream of nitrogen. From the volume of hydroquinone solution added to extinguish the color, the degree of the photo-dissociation was estimated to be 0.15 by the following equation.

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2} + \underset{\substack{\text{triphenylimida-}\\\text{zolyl radical}}}{2C_{21}H_{15}N_2} \longrightarrow \underset{\text{benzoquinone}}{C_6H_4O_2} + \underset{\text{lophine}}{2C_{21}H_{16}N_2}$$

The degree of photo-dissociation of photo-dimer was also estimated from molecular weight determination. The molecular weight of photo-dimer determined in a benzene solution under a dim light by the cryoscopic method (0.1127 g in 20.13 g of benzene) was 600 which corresponds to the molecular weight 590 of the dimer $C_{42}H_{30}N_4$, whereas the apparent molecular weight measured immediately after irradiation for 5 min with sunlight at 6°C was 500 (freezing point depression $\Delta t = 0.057$°C). From the apparent molecular weight, the degree of photo-dissociation in benzene was estimated to be 0.18. The measurements of the weights of photo-dimers -CH_3, -Cl and -2-Cl in benzene before and after irradiation also showed decrease of the molecular weight on irradiation.

Kinetic Study of Photochromism in Solutions with ESR.[11] In order to confirm the mechanism of photochromism of photo-dimers represented by the reversible reaction (1), the rates of decrease of the radical concentration in the photochromic systems were measured by ESR. The rate of decrease of the radical concentration caused by recombination of the radical to the dimer was expected to obey the second order rate law.

The single peak signal shown by a reddish-purple benzene solution of photo-dimer (1.48×10^{-4} mol/*l*) gradually decreased with time in the dark. The rate of decrease of the relative signal intensity was successively measured by the height of a signal, *h* (cm), according to the following procedure. When the recording of the first signal was completed, the sweeping direction of the magnetic field was reversed and the second signal was recorded immediately. Similar procedures were repeated about 20 times for about 15 min at 23.0°C. Since the line width of the signals was 9.3 gauss during the measurement, the height *h* is assumed to be proportional to the radical concentration. The height *h* was used in place of the concentration of the radical in the reaction rate expression for the recombination of the radical. The differences between the reciprocals of *h* at time *t* and h_0 at $t=0$, $(1/h - 1/h_0)$, were plotted against time *t*. The plots gave a straight line, as shown by (1) in Fig. 5, showing that the rate of decrease of ESR signal intensity obeyed the second order rate law, expressed by $1/h - 1/h_0 = k't$.[12]

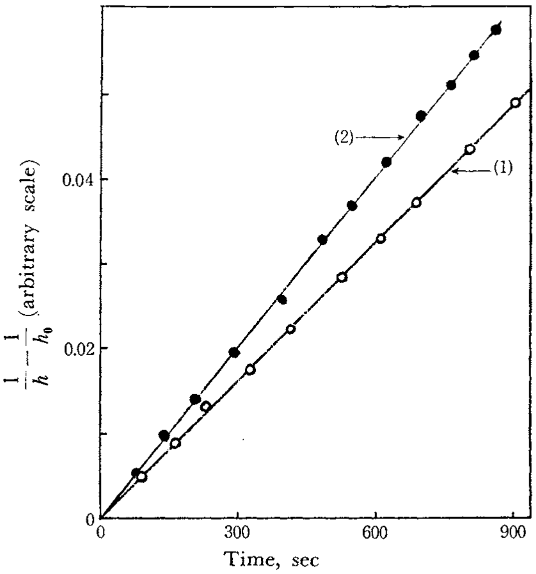

Fig. 5. Plot of $\left(\frac{1}{h} - \frac{1}{h_0}\right)$ against time *t* in the fading process of photochromism in benzene.
(1) Photo-dimer, (2) Photo-dimer-CH_3
Concentration: Photo-dimer; 1.48×10^{-4} mol/*l*, Photo-dimer-CH_3; 1.46×10^{-4} mol/*l*.
Temp.: 23.0°C. Irradiation: 365 mμ light for 3 min.

A similar result was obtained for photo-dimer –CH_3 as shown by the straight line (2) in Fig. 5.

Kinetic Study of Photochromism in Solutions by the Spectroscopic Method.[3] The radical mechanism shown by the reversible reaction (1) is also supported by spectroscopic measurements. The degree of photo-dissociation α of photo-dimer at a photo-stationary state in benzene ($c = 3.38 \times 10^{-5}$ mol/*l*) at 15.0°C was estimated to be about 0.30 from the change of absorbance at 280 mμ (ε 2.6×10^4) measured before and after irradiation for 3 min (thickness of the solution layer; 1 cm). The degree of photo-dissociation of photo-dimers in the photo-stationary state, shown in Table 3, was estimated in a similar way.

From the absorbances at 347 and 554 mμ and the degree of photo-dissociation α of photo-

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[11] T. Hayashi, K. Maeda and M. Takeuchi, This Bulletin, **37**, 1717 (1964).

[12] M. A. J. Wilks and M. R. Willis, *J. Chem. Soc.*, *B*, **1968**, 1526, reported a result, different from that of the present authors.

Table 3. The degree of photo-dissociation of photo-dimer in the photo-stationary state in benzene at 15.0°C.

Dimer	Concentration (mol/l)$\times 10^5$	Degree of dissociation α
photo-dimer	3.38	0.30
photo-dimer-CH_3	1.60	0.35
photo-dimer-Cl	1.61	0.25
photo-dimer-2-Cl	1.45	0.25

Table 4. Molar absorptivitiy ε of triarylimidazolyl radical at absorption maxima in benzene

Imidazolyl radical	λ_{max}, mμ	($\varepsilon\times 10^{-4}$)
2,4,5-Triphenyl-	347(4.8)	554(0.84)
2,4,5-Tri-*p*-tolyl-	366(6.3)	587(1.6)
2,4,5-Tri-*p*-chlorophenyl-	367(6.5)	588(1.8)
2-*p*-Chlorophenyl-4,5-diphenyl-	366(7.4)	575(1.6)

dimer in benzene, the molar absorptivities of triphenylimidazolyl radical at 347 and 554 mμ were estimated to be about 4.8×10^4 and 8.4×10^3 respectively. The molar absorptivities of other radicals estimated by a similar method are shown in Table 4.

From the measurements of decrease of absorbances at absorption maxima of the triarylimidazolyl radicals the rate of recombination of the radicals was obtained. Absorbance at the absorption maximum, A_λ, is the sum of the absorbance A_p due to photochromism and A_t due to thermochromism. A_p was obtained by subtraction of A_t measured before irradiation from A_λ. The concentration of triarylimidazolyl radicals, C_r, at time t were calculated from the relation, $A_p=\varepsilon C_r l$. The values of $(1/C_r-1/C_{r_0})$ increased linearly with time, as shown in Fig. 6 (photo-dimer) and 7 (photo-dimer-CH_3).

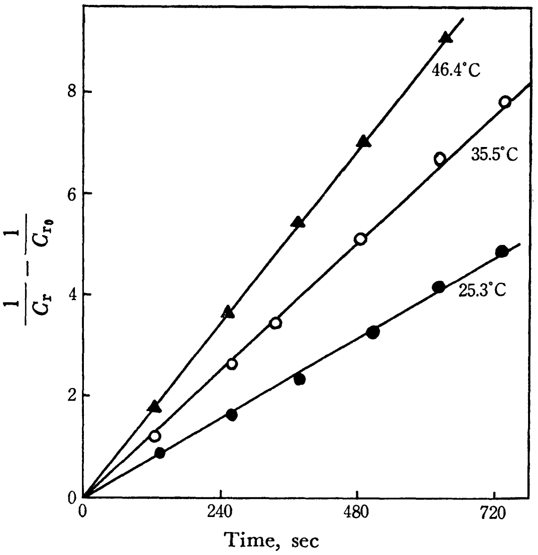

Fig. 6. Plot of $\left(\frac{1}{C_r}-\frac{1}{C_{r_0}}\right)$ against time t in the fading process of photochromism of photo-dimer in benzene.
Concentration of photo-dimer: 1.44×10^{-5} mol/l.
C_r: radical concentration at time t
C_{r_0}: radical concentration at time $t=0$
Irradiation: 365 mμ light for 3 min.

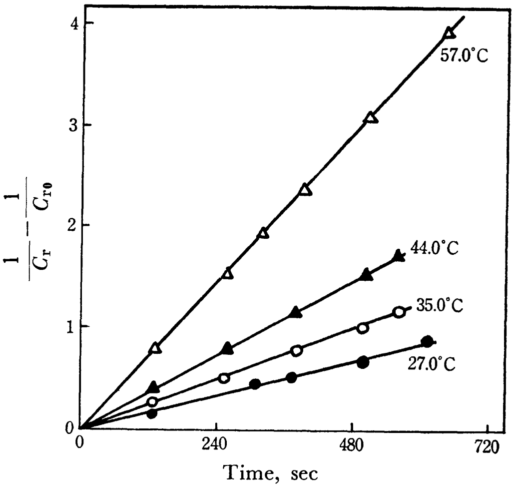

Fig. 7. Plot of $\left(\frac{1}{C_r}-\frac{1}{C_{r_0}}\right)$ against time t in the fading process of photochromism of photo-dimer-CH_3 in benzene.
Concentration of photo-dimer-CH_3: 2.25×10^{-5} mol/l.
Irradiation: 365 mμ light for 3 min.

Rate constants, activation energies and pre-exponential factors of the Arrhenius equation for the recombination reaction of the triarylimidazolyl radicals in the photochromic systems of photo-dimers are shown in Table 5.

Photochromism of Photo-dimer in Solid State.[4] On irradiation of light yellow fine crystals of photo-dimer at room temperature the color of the crystals turned light reddish-purple. The color hardly faded in the dark at room temperature, whereas the rate of reversion to the original color was accelerated by heating above 40°C. The color rapidly disappeared when the colored solid was subjected to contact the vapor of organic solvents, such as ether, acetone or benzene, at room temperature. This indicates that photo-dimer exhibits photochromism also in solid state. The light reddish-purple crystals also exhibited a strong ESR signal of a single peak (*g* 2.003) at 20°C at which the signal intensity hardly decreased in the dark. On standing in the dark at 45°C the signal intensity gradually decreased with fading of the photochromic color. The absorption spectrum of the photochromic colored crystals was measured in solid state by both the opal-glass

Table 5. Rate constant, activation energy and pre-exponential factor of the recombination of triarylimidazolyl radical in the photochromic system in benzene

Imidazolyl radical	Temp. °C	k l mol^{-1} sec^{-1}	E_a kcal	A l mol^{-1} sec^{-1}
2,4,5-Triphenyl-	25.3	66	7.4	1.7×10^7
	35.5	103		
	46.4	146		
2,4,5-Tri-*p*-tolyl	27.0	14	9.5	1.1×10^8
	35.0	22		
	44.0	30		
	57.0	61		
2,4,5-Tri-*p*-chlorophenyl-	29.0	200	6.9	1.9×10^7
	35.3	253		
	46.0	354		
2-*p*-Chlorophenyl-4,5-diphenyl-	16.5	62	7.2	1.7×10^7
	28.0	108		
	44.0	183		

Table 6. Photochromic change of color and absorption maximum in the visible region measured in solid state

Dimer	Color		λ_{max} (mμ) after irrdiation
	before irradiation	after irradiation	
photo-dimer	light yellow	light reddish-purple	563
photo-dimer-CH_3	light greenish-yellow	light greenishblue	590
photo-dimer-Cl	light greenish-yellow	light blue	591
photo-dimer-2-Cl	almost colorless	light violet	580

* Measured by the opal-glass transmission method.

transmission method and the potassium bromide disk method which gave the same spectrum. The spectrum showed an absorption maximum at 563 mμ as shown in Fig. 8. Although the maximum shifted 9 mμ to wavelengths longer than 554 mμ in the benzene solution, a reddish-purple solution obtained by dissolution of the reddish-purple crystals in benzene in a dim light showed a maximum at 554 mμ immediately after dissolution. These findings indicate that the photochromic color appeared in a solid state is also attributed to triphenylimidazolyl radical produced by dissociation of photo-dimer with irradiation.

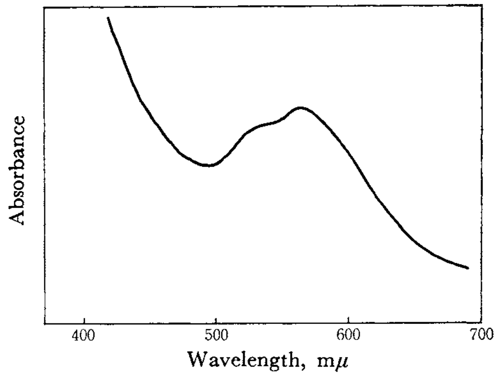

Fig. 8. Absorption spectrum of the photochromic colored solid of photo-dimer, measured by the opal-glass transmission method.

The decay rate of the ESR intensity of the photochromic colored crystals was measured in solid state at 46.0°C and 63.0°C. Differing from the rate in a benzene solution, the decay rate of the signal intensity did not obey the second order rate law.

Photo-dimers -CH_3, -Cl and -2-Cl also exhibited photochromism in solid state. Photochromic changes of the color and absorption maxima measured in solid state by the opal-glass transmission method are shown in Table 6. Benzene solutions prepared by dissolving the photochromic colored crystals in a dim light showed the same absorption maxima as those in the photochromic benzene solutions.

Thermochromism of Photo-dimer in Solutions. When a light yellow benzene solution of photo-dimer was heated in a dim light, a light reddish-purple color and an ESR signal were observed at 40°C and were enhanced with the rise of temperature. On cooling in the dark, the color reverted to the original color with diminution of ESR signal intensity. The fact shows that photo-dimer exhibits thermochromism in solutions above room temperature. Photo-dimer-CH_3, -Cl and -2-Cl also showed thermochromism in solutions. The color and absorption maxima due to thermochromism are the same as those thermochromism of photo-dimers in solutions is also the same as that of photochromism.

The equilibrium constanst for the thermal dissociation of photo-dimer in benzene were estimated at different temperatures from the variation of the absorbance at 554 mμ with the concentration of the dimer. The measurement was carried out at high concentrations, such as 10^{-3}—10^{-2} mol/l, because coloration due to thermochromism is relatively weak, and at such concentrations the absorption band of $\lambda_{\max}$ 347 mμ overlapped with the tail of the band of the dimer ($\lambda_{\max}$ 273 mμ) but the absorption band of $\lambda_{\max}$ 554 mμ which has a relatively small molar absorptivity did not. The equilibrium constants K shown in Table 7 were calculated by the relation $K=2A^2/\varepsilon(2C\varepsilon-A)$, where ε is the molar absorptivity of $\lambda_{\max}$ at 554 mμ of the radical.

TABLE 7. EQUILIBRIUM CONSTANT OF PHOTO-DIMER OF THE THERMOCHROMIC SYSTEM IN BENZENE

Concn. mol/l	$K\times10^7$		
	49.0°C	53.8°C	60.4°C
1.05×10^{-2}	1.2	2.1	4.9
8.39×10^{-3}	1.3	1.9	5.1
6.29×10^{-3}	1.3	2.0	5.4
5.24×10^{-3}	1.2	1.6	4.8
3.35×10^{-3}	1.2	1.9	4.5
mean $K\times10^7$	1.2	1.9	4.9

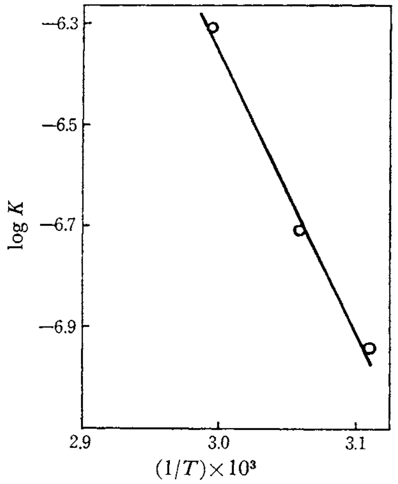

Fig. 9. Plot of logarithm of the equilibrium constant for the thermal dissociation of photo-dimer in benzene against reciprocal of absolute temperature.

From the slope of the straight line shown in Fig. 9, ΔH for the dissociation of photo-dimer in benzene was estimated approximately to be 26 kcal/mol.

Thermochromism of Photo-dimer in Solid State.[4] When light yellow fine crystals of photo-dimer were heated in a dim light, a light reddish-purple color appeared at about 170°C and a deep reddish-purple melt was obtained on melting. On cooling the colored crystals from about 180°C, the light reddish-purple color rapidly reverted to the original light yellow color. A light reddish-purple solution prepared by dissolving a small amount of the reddish-purple crystals in benzene in a dim light showed a weak absorption maximum 554 mμ of triphenylimidazolyl radical immediately after dissolution. When the crystals of photo-dimer which show no ESR signal at room temperature were heated in the dark, a weak signal of a single peak (g 2.003) began to appear at about 50°C and was enhanced with rise of temperature as shown in Fig. 10. On cooling the reddish-purple crystals from about 170°C to room temperature, the signal intensity rapidly decreased to vanish at room temperature.

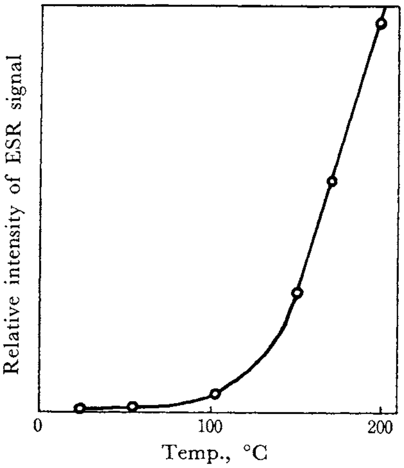

Fig. 10. Variation of the signal intensity of ESR due to thermochromism of photo-dimer in solid state.

This indicates that the mechanism of thermochromism of photo-dimer in solid state is also the same as that of photochromism and thermochromism in solutions. Photo-dimers -CH_3, -Cl and -2-Cl also showed thermochromism in solid state.

Thermochromism of Piezo-dimer in Solid State. When the solid of piezo-dimer was heated, the color turned light reddish-purple at about 180°C. The color rapidly faded on cooling. A deep reddish-purple melt was obtained on melting. When the solid of piezo-dimer which shows a weak ESR signal at room temperature was heated, the signal intensity increased with the rise of temperature. This fact shows that piezo-dimer exhibits thermochromism in solid state above about 180°C. The weak ESR signal observed at room temperature is due to a small amount of triphenylimidazolyl radical produced by the oxidation of lophine and remained without dimerization.

Table 8. Piezochromic change in color and absorption maximum

Dimer	Color		λ_{max} (mμ) after grinding
	before grinding	after grinding	
piezo-dimer	almost colorless	reddish-purple	563
piezo-dimer-CH_3	light violet	greenish-blue	589
piezo-dimer-Cl	light violet	dark blue	591
piezo-dimer-2-Cl	almost colorless	light violet	580

Piezochromism of Piezo-dimer.[5] The solid of piezo-dimer turned deep reddish-purple by grinding in a mortar or pressing at a pressure of about 10—50 kg/cm² at room temperature. The colored solid reverted very slowly to the original almost colorless solid on standing for several days in the dark at room temperature. The rate of fading of the color was accelerated by heating to 50°C. These facts show that piezo-dimer exhibits piezochromism. When the solid was ground at 80°C, it showed a reddish-purple color during grinding, but when grinding was stopped, the color quickly disappeared. When the piezochromic colored solid was subjected to contact the vapor of organic solvents, such as ether, ethanol, acetone or benzene at room temperature, the reddish-purple color rapidly disappeared. Since the rate of fading of the piezochromic color at room temperature was very slow and the temperature at which the thermochromic color was first observed was 180°C in solid state, piezochromism is not due to a rise of temperature which may occur by grinding or pressing.

A very intense ESR signal (g=2.003) appearing by grinding piezo-dimer decreased very slowly at room temperature, but rapidly at a higher temperature such as 50°C.

The absorption spectrum of the piezochromic colored solid was measured by both the opal-galss transmission method and the potassium bromide disk method which gave a similar spectrum to that of the photochromic colored solid of photo-dimer shown in Fig. 8. The absorption maximum at 563 mμ agreed with that of the photochromic colored solid which showed a red shift of about 9 mμ, as compared with the absorption maximum in the photochromic colored benzene solution.

Piezo-dimers -CH_3, -Cl and -2-Cl also exhibited piezochromism. The changes in color and absorption maxima due to piezochromism are shown in Table 8. These results indicate that the mechanism of piezochromism is due to dissociation of the bond between the imidazolyl radicals into the triarylimidazolyl radicals caused by mechanical work.

The spin concentration of piezo-dimer after grinding for 5 min in an agate mortar was measured with ESR. The spin concentration and the degree of piezochromic dissociation are shown in Table 9. The spin concentration increased with the time of grinding.

Table 9. Spin concentration and degree of piezochromic dissociation of piezo-dimer

Piezo-dimer	Spin concentration (spin/g) (degree of piezochromic dissociation)*1	
	before grinding	after grinding*2
Sample 1	7.2×10^{16} (3.6×10^{-3}%)	3.3×10^{19} (1.6%)
Sample 2	4.3×10^{16} (2.1×10^{-3}%)	5.2×10^{19} (2.6%)

*1 $\frac{1}{2}\times\frac{\text{spin concentration}}{\left(\text{number of molecules in 1 g of piezo-dimer}\right)}\times100$

*2 ground in an agate mortar for 5 min at room temperature.

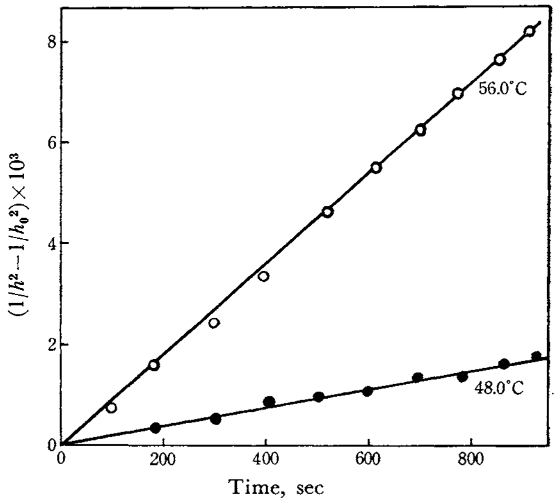

Fig. 11. Plot of $(1/h^2-1/h_0^2)$ against time t in the fading process of piezochromism of piezo-dimer.
h: height of a signal at time t
h_0: height of a signal at time t=0

The decay rates of the signal intensity of ESR due to piezochromism of piezo-dimer were measured at 48.0 and 56.0°C. The decrease of the relative signal intensity, h, with time virtually obeyed the relation $1/h^2-1/h_0^2=k't$, as shown in Fig. 11. As the line widths of the signals were almost constant during the measurement, h could be assumed to be approximately proportional to the concentration of triphenylimidazolyl radical. Differing from the case of photochromism in benzene, the result seems to show that the rate of recombination of the radical in the fading process of piezochromism obeys the third order rate law.

Also in the case of piezo-dimer-CH_3, the decay rates of the signal intensity due to piezochromism, measured at 52.0, 58.0 and 65.0°C were found to obey the third order rate law.

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