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The Photochromism, Thermochromism, and Piezochromism of Dimers of Tetraphenylpyrryl

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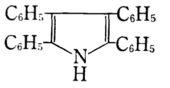
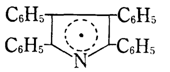
By the oxidation of tetraphenylpyrrole, two types of dimers of tetraphenylpyrryl were obtained. One dimer showed piezochromism and thermochromism, while the other showed photochromism and thermochromism. These phenomena were found to correspond to those of the piezochromic and photochromic dimers of triphenylimidazolyl obtained from triphenylimidazole. The photochromism, thermochromism, and piezochromism of the dimers of tetraphenylpyrryl are determined to be due to the radical dissociation caused by irradiation, heating, and grinding, the same machanism as that in the case of the dimers of triphenylimidazolyl.

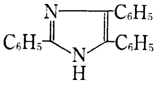
Kuhn and Kainer reported[1] that 2,3,4,5-tetraphenylpyrrole (I) was partially oxidized to the tetraphenylpyrryl radical (II) (about 4%). From spectroscopic and ESR studies Blinder *et al.* reported[2] that the oxidation product of I exhibits photochromism and thermochromism in solutions and that the phenomena are due to the dissociation of the oxidation product into the radical II caused by irradiation and heating. These results corresponded to the photochromism and thermochromism of the photochromic dimer of triphenylimidazolyl (IV) obtained by the oxidation of triphenylimidazole (III).[3] The existence of the photochromic and piezochromic dimers for IV suggests the presence of similar dimers for II. This paper will deal with the preparation of two isomeric dimers of II and with the radical mechanism of photochromism, thermochromism, and piezochromism exhibited by these dimers.



(I)



(II)



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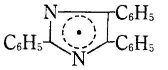

(IV)

Experimental

Materials. *Oxidation with Lead Dioxide.* A photochromic compound was obtained according to the method Kuhn and Kainer.[1] A solution of I (1 g) in benzene (50 m*l*) was refluxed with lead dioxide (10 g) for about 7 hr in a nitrogen atmosphere. The solution gradually turned pink. By the evaporation of the solvent in a dimmed room under reduced pressure in a nitrogen atmosphere, 0.7 g of a light pink powder (PH), mp 197—204°C, was obtained. PH was slightly soluble in benzene, ethanol, and *n*-hexane.

Found: C, 90.26; H, 5.62; N, 3.70%. Calcd for $C_{56}H_{40}N_2$ (dimer of II): C, 90.77; H, 5.44; N, 3.79%.

PH showed an infrared absorption spectrum similar to that of I. An almost colorless ethanolic solution of PH which was prepared in dim light at room temperature showed absorption maxima at 264 and 317 mμ, maxima which agreed with those of I. The solution turned pink on irradiation at room temperature. The pink solution showed new absorption maxima at 365, 525, and 563 mμ and an ESR signal (g=2.003). From these experimental results, PH was determined to be a mixture of I and a dimer of II. The dimer is called the photochromic dimer (photo-dimer). The concentration of the photo-dimer in PH was determined to be 13% by means of a hydroquinone titration according to the following reaction (1):

$$\underset{\text{(hydroquinone)}}{C_6H_4(OH)_2} + \underset{\text{(II)}}{2C_{28}H_{20}N} \longrightarrow \underset{\text{(benzoquinone)}}{C_6H_4O_2} + \underset{\text{(I)}}{2C_{28}H_{21}N} \qquad (1)$$

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

[2] S. M. Blinder, M. L. Peller, N. W. Lord, L. C. Aamodt and N. S. Ivanchukov, *J. Chem. Phys.*, **36**, 540 (1962).

[3] a) T. Hayashi, K. Maeda, S. Shida and K. Nakada, *ibid.*, **32**, 1568 (1960); b) T. Hayashi and K. Maeda, This Bulletin, **33**, 566 (1960); c) **38**, 685 (1965); d) **42**, 3509 (1969); e) T. Hayashi, K. Maeda and M. Morinaga, *ibid.*, **37**, 1563 (1964); f) T. Hayashi, K. Maeda and M. Takeuchi, *ibid.*, **37**, 1717 (1964); g) T. Hayashi, K. Maeda and T. Kanaji, *ibid.*, **38**, 957 (1965).

Oxidation with Potassium Ferricyanide. A piezochromic compound was obtained from I by means of a modification of the oxidation method of III.[3b)] To a solution of I (1.5 g) in ethanol (280 m*l*), a 2% aqueous solution of potassium ferricyanide (400 m*l*) and a 5% ethanolic solution of potassium hydroxide (15 m*l*) were added[4)] over about a 30-min period at about 50°C in a nitrogen atmosphere. The pink color of II first appeared, and then a light pink precipitate was formed. After the reaction mixture was cooled to room temperature, the precipitate was filtered in a nitrogen atmosphere, washed repeatedly with water, and dried at room temperature under reduced pressure. A light pink powder (PI) (1.3 g), mp 160—165°C, was thus obtained. PI is soluble in ethanol, benzene, and *n*-hexane.

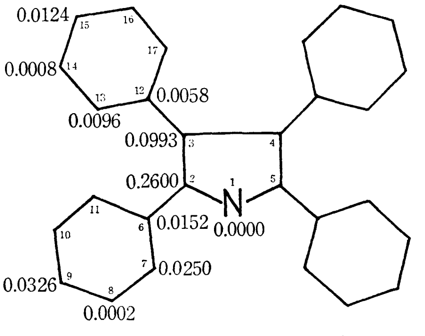
Found: C, 90.16; H, 5.20; N, 3.67%. Calcd for $C_{56}H_{40}N_2$ (dimer of II): C, 90.77; H, 5.44; N, 3.79%.

The infrared absorption spectrum of PI was rather different from that of I, although it showed a weak N–H band at 3420 cm^{-1}, thus indicating the presence of I. PI showed a weak ESR absorption (g=2.00) and exhibited piezochromism which showed a pink color. A pink solution which was prepared by dissolving PI in ethanol at room temperature showed absorption maxima at 365, 525, and 563 mμ. From these experimental results, PI was determined to be a mixture of I, a dimer of the radical II, and a small amount of II. The dimer is called the piezochromic dimer (piezo-dimer). The concentration of the piezo-dimer in PI was determined to be 23% by means of hydroquinone titration according to Reaction (1).

PH and PI were used for the present study because I itself did not exhibit photochromism, thermochromism, and piezochromism and caused no disturbance in studies of these phenomena.

Spectroscopic Measurements. The absorption spectra were measured with a Hitachi EPS 2 recording spectrophotometer. The absorption spectra at temperatures from −196°C to room temperature were measured by the method described in a previous paper.[3d)] The absorption spectrum in the solid state was measured by means of an opal-glass transmission method.

Electron Spin Resonance Absorption. The ESR measurements were carried out in a deaerated state with a Japan Electron Optics Laboratory JES-P-10-type ESR spectrometer (100 kc modulation) which had, as attachments, a 1D-2 integrator and a VT-2 variable temperature controller. The ESR spectra of the triplet state at −196°C were measured with a Japan Electron Optics Laboratory 3B-type ESR spectrometer (100 kc modulation).



$\alpha_N=\alpha+0.5\beta,\ \beta_{2,6}=\beta_{3,12}=0.5\beta$

Fig. 1. Spin density of tetraphenylpyrryl radical.

Irradiation. The 365-mμ light of a high-pressure mercury lamp (Toshiba SHL-100 UV), filtered through a Toshiba UV-D1B glass filter, was used.

Results and Discussion

Structures of Photo-dimer and Piezo-dimer. The structures of the dimers of IV[5,6)] suggest that two tetraphenylpyrryl radicals in the photo-dimer and the piezo-dimer combine at N, C2, or C3 of the pyrryl rings. The HMO calculation of the spin density of II (given in Fig. 1) shows a high probability of the dimerization of II to the piezo-dimer at C2.

The fact that 2,3,4,4-tetrachloro-1,4-dihydronaphthalene-1-one,[7)] tetraphenylhydrazine,[8)] and the photochromic dimer of IV exhibit photochromism due to a radical dissociation of C–Cl, N–N, and C–N respectively suggests a high probability of linking between the N of one pyrryl ring and the C of another ring in the photo-dimer.

Photochromism of PH in Solutions. An almost colorless solution of PH in benzene, ethanol,

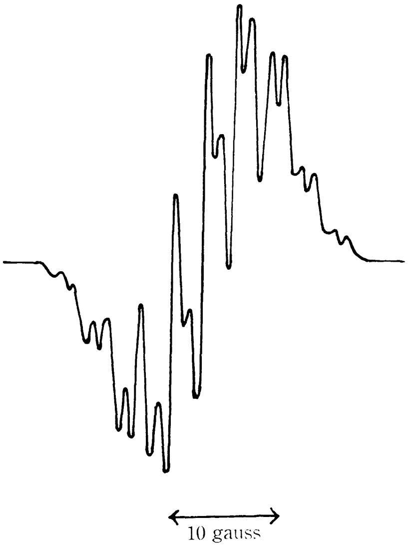


Fig. 2. ESR spectrum of PH in benzene.

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4) When a larger amount of potassium hydroxide was added, a piezochromic compound which contained oxygen was obtained.

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

6) Presented by A. Fukuoka, H. Fukatsu, T. Kondo and T. Goto at the Annual Meeting of the Chemical Society of Japan (April, 1969, Tokyo); Preprint, p. 1379.

7) G. Scheibe and F. Feichtmayr, *J. Phys. Chem.*, **66**, 2449 (1962).

8) G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 2801 (1942); D. A. Wiersma and J. Kommandeur, *Mol. Phys.*, **13**, 241 (1967).

or another solvent, prepared in dim light and at room temperature, showed no ESR absorption. On irradiation at temperatures between room temperature and about −20°C, the benzene solution rapidly turned pink and showed a strong ESR signal (shown in Fig. 2) ($g=2.003$). The color and ESR hardly faded at all[9] over several days in the dark at room temperature. However, in solutions of PH in decaline and naphthalene, which turned pink on irradiation at 80—90°C, the color faded after the irradiation was cut off. This fact shows that PH exhibits photochromism at 80—90°C, above which exhibits thermochromism.

At temperatures between about −20°C and −100°C, the benzene solution showed no color change on irradiation. At temperatures lower than about −100°C, a purple color appeared on irradiation. The color became deeper with a decrease in the temperature. Such changes in the color were investigated by means of the absorption and the ESR spectra.

An EPA solution of PH, which turned purple on irradiation at −196°C, showed the absorption bands shown in Fig. 3. The bands corresponded to those of the pink solution obtained by irradiation at room temperature. The absorption maxima at −196°C showed a red shift of about 10 mμ compared with those of the pink solution. The change in the absorption spectra was measured at temperatures from −196°C to room temperature. The change corresponded to the dependence of the color change on the temperature.

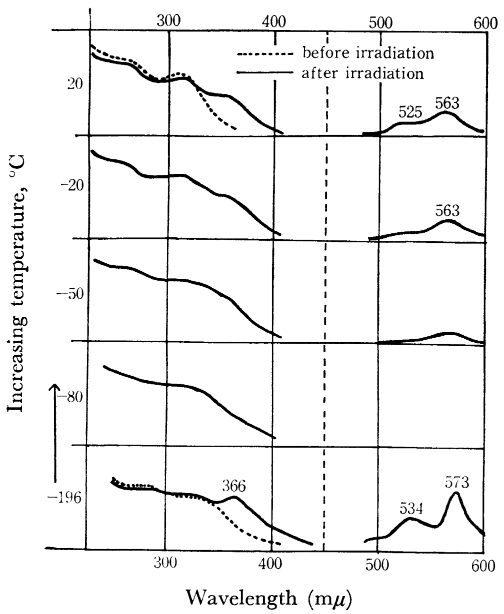


Fig. 3. Absorption spectra of PH in EPA at temperatures from −196°C to room temperature.

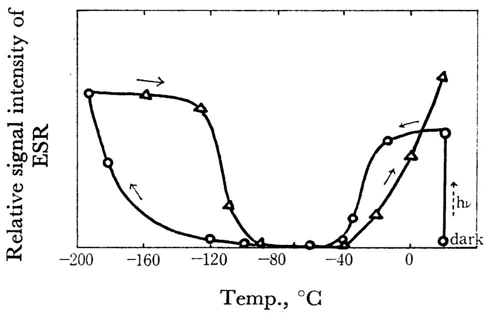


Fig. 4. Dependence of the ESR signal intensity on the temperature under irradiation in benzene.

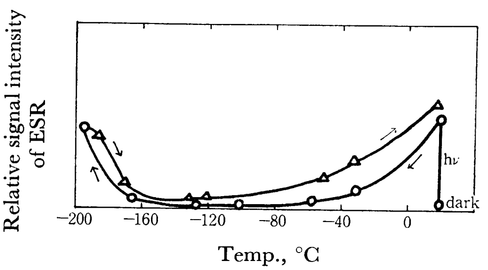
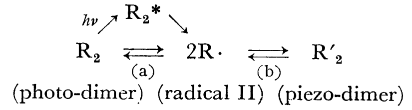


Fig. 5. Dependence of the ESR signal intensity on the temperature under irradiation in EPA.

The dependence of the relative signal intensity of ESR on the temperature under irradiation is shown in Figs. 4 and 5.

These experimental results can be interpreted by a mechanism similar to that used in the case of the dimer IV.[3,5,10]



$$\begin{array}{c} h\nu \nearrow R_2{}^{*} \searrow \\ R_2 \underset{(a)}{\rightleftarrows} 2R\cdot \underset{(b)}{\rightleftarrows} R'_2 \end{array}$$

(photo-dimer) (radical II) (piezo-dimer)

The equilibrium (a) is likely to lie far to the side of R_2 at temperatures near room temperature. However, because the dimerization of $R\cdot$ produced by the photo-dissociation of R_2 is very slow, the photochromic color faded hardly at all at temperatures, near room temperature. With the elevation of the temperature, dimerization was accelerated and photochromism was exhibited at 80—90°C. At temperatures between about −20°C and −100°C the photochromic color does not appear, for the equilibrium (b) lies far to the side of R'_2 and the dimerization of $R\cdot$ is rapid. The purple color observed at temperatures lower than about −100°C is due to a tetraphenylpyrryl radical, which has more coplanarity than the pink radical. At low temperatures the equilibrium (b) lies far to the side

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9) Blinder *et al.* reported[2] that a reversible, rapid color change was observed at room temperature in a benzene solution of the oxidation product of I. We could not observed such a reversible phenomenon at room temperature.

10) T. Shida, K. Maeda and T. Hayashi, This Bulletin, **42**, 3044 (1969).

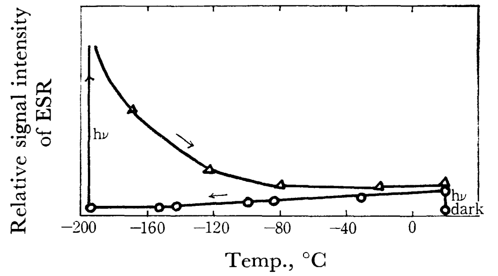

Fig. 6. Dependence of the ESR signal intensity of PH on the temperature in the solid state.
-○- in the dark

of R'_2. However, because the dimerization of the purple radical is slow at such low temperatures, the purple color was observed.

The ESR spectrum observed at −196°C showed a strong signal at 3296 gauss, three pairs of weak signals at 3358—3231 gauss, and a weak signal at 1762 gauss. These signals suggest the formation of a radical pair similar to that of the photochromic dimer of IV.[3d,10)]

Photochromism of PH in the Solid State. PH exhibits photochromism in the solid state at temperatures near room temperature and near −196°C. With intense irradiation at room temperature, a pink color and a weak ESR signal were observed. On heating to about 50°C after irradiation was cut off, the color and ESR faded very slowly. On irradiation at −196°C, a deep bluish-purple color and a strong ESR signal were immediately observed. The color and ESR signal hardly faded at all at −196°C in the dark, but they rapidly faded on slight warming from −196°C, even under irradiation. The dependence of the signal intensity on the temperature was measured under irradiation, as is shown in Fig. 6.

These phenomena, which correspond to those shown by the photochromic dimer of IV in the solid state,[3g)] suggest a radical mechanism similar to that of the photochromism of the latter. The ESR absorption at −196°C showed a strong signal at 3127 gauss and a weak signal at 1762 gauss which is likely to be due to the formation of a radical pair, as in solutions.

Thermochromism of PH and PI. PH and PI showed thermochromism in solutions and in the solid state. In solutions PH showed a thermochromic pink color and an ESR signal (g=2.00) when heated above 90°C without irradiation. In the solid state PH showed a pink color and an ESR signal (g=2.00) when heated to temperatures higher than about 180°C, and the deep pink melt formed on melting showed a strong ESR signal. When PH which had been heated to about 190°C in the solid state without irradiation was rapidly cooled to room temperature in the dark, the thermochromic color rapidly faded.

A benzene solution of PI prepared at room temperature showed a deep pink color due to the radical II (λ_{max} 365, 525 and 563 mμ) produced by the dissociation of the piezo-dimer present in PI. The color did not change with irradiation. When the pink solution was cooled, the color gradually faded until it disappeared at temperatures lower than about −20°C. The absorption and ESR spectra showed variations corresponding to the change in the color. In the solid state PI showed a thermochromic pink color on heating to about 130°C. PI heated in the solid state *in vacuo* at about 100°C for 1 hr showed photochromism both in solutions and in the solid state. This fact shows that the piezo-dimer isomerizes to the photodimer upon heating, probably through the radical II.

Piezochromism of PI. PI showed piezochromism in the solid state. PI, which turned pink with grinding, showed absorption maxima at 535 (sh) and 570 mμ; these maxima can be attributed to the radical II. The piezochromis of PI is due to a radical dissociation similar to that of the piezochromic dimer of IV.[3g)] The change in the spin concentration caused by piezochromism was measured by means of ESR. The spin concentration increased from 7.8×10^{18} spin/g to 7.6×10^{19} spin/g when grinding was continued for about 1 min. The spin concentration of the PI ground gradually decreased at room temperature. It became about one third after 1 week.

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