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Optical and ESR Studies on Triphenylimidazolyl Radicals Produced by Photolysis and Radiolysis at Low Temperature[*1]

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The characteristic temperature-dependent behavior exhibited by the solution of the photochromic dimer of triphenylimidazolyl (photo-dimer) has been reinvestigated by means of optical and ESR spectroscopy. Assuming two conformations for triphenylimidazolyl radical, the spectral change at low temperatures has been elucidated in terms of a conformational isomerization of the radical and dimerization of the radical to a colorless dimer. Photo-dimer in γ-irradiated glassy solutions undergoes a dissociative electron attachment to produce triphenylimidazolyl radical and its anion.

UV-illumination of the photochromic dimer of triphenylimidazolyl in benzene at room temperature produced triphenylimidazolyl radical which was characterized by the absorption spectrum having absorption maxima of 347 and 554 mμ.1) Upon lowering the temperature of the solution under illumination the intensity of the absorption band diminished gradually, and at sbout −20—−150°C the absorption in the visible region disappeared. The phenomenon first studied by Hayashi and Maeda2) was later interpreted by White and Sonnenberg on the basis of a thermochemical equilibrium between the radical and the colorless piezochromic dimer.3),[*2] It was found that illumination at still lower temperatures gave a color slightly different from that observed at higher temperatures.4) We attributed the absorption observed at −196°C to the radical cation of photo-dimer produced by photoionization.4) Later work revealed, however, that the absorption should be associated with triphenylimidazolyl radical produced by the same mechanism as that in solutions at room temperature.5) Assuming two conformations for the radical, one stable at higher temperatures (>*ca.* −20°C), the other at lower temperatures (<*ca.* −150°C), we are able to explain the temperature dependence of photochemical reactions of the lophine system.

Experimental

Photo-dimer was dissolved in deaerated solvents in a dimmed room. Methyltetrahydrofuran (MTHF) was mainly used as a solvent, because it forms a clear glass at −196°C. For the optical measurement the solution was transferred in a vacuum to a thin quartz absorption cell. The absorption spectrum of the solution was measured at −196°C in a quartz Dewar with quartz windows using a Cary 14 RI spectrophotometer. Polymer films containing photo-dimer was prepared by dissolving the dimer in polystyrene-benzene gel and solidifying it by evaporation of benzene in nitrogen stream. A 500 W high-pressure mercury lamp in combination with a glass filter passing light of $240\ m\mu < \lambda < 400\ m\mu$ and a 12000 Ci Co 60 γ-ray source were for photolysis and radiolysis. ESR spectra were recorded on a JEOL 3B spectrometer with a 100 kc modulation.

Results and Discussion

Photolysis. When a colorless solution of photodimer in MTHF glass at −196°C was exposed to UV light, the glass colored immediately to reddish-

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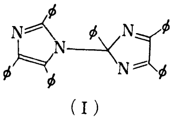
[*1] Presented at the Symposium on Photochemistry of the Chemical Society of Japan (T. Shida, K. Maeda and T. Hayashi, Oct., 1968, Sendai).

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

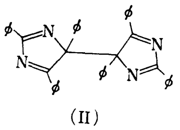
2) T. Hayashi and K. Maeda, *ibid.*, **36**, 1052 (1963).

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

[*2] The dimer of triphenylimidazolyl, called lophine dimer, has two isomeric forms, one of which is photochromic and is assumed to have structure I. The other is piezochromic presumably having structure II.3)



(I)



(II)

The two isomers will be designated photo- and piezodimers, respectively.

4) T. Hayashi and K. Maeda, This Bulletin, **40**, 2990 (1967).

5) T. Hayashi and K. Maeda, *Nippon Kagaku Zasshi*, **90**, 325 (1969).

purple. The absorption spectrum shown in curve 1 of Fig. 1 was almost the same as that of triphenylimidazolyl radical in solutions at room temperature (*e.g.*, the absorption maximum of the visible band at −196° was 556 mμ which corresponded to 552 mμ at room temperature). Apparently photo-dimer dissociates also in the rigid matrix at −196°C. Reaction (1) formulates the process with R· standing for triphenylimidazolyl radical.

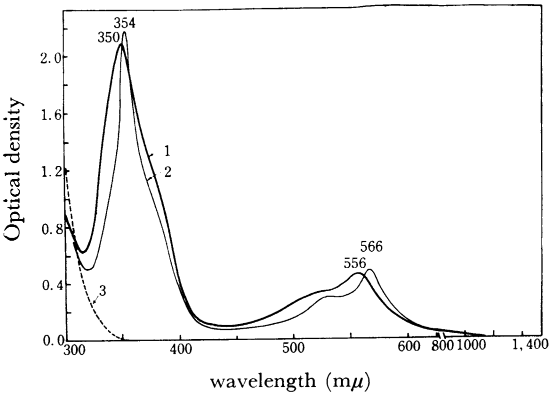


Fig. 1. Absorption spectra of photo-dimer in MTHF UV-illuminated at −196°C. Curve 1: immediately after illumination (R bands). Curve 2: the preceding solution after limited warming (S bands). Curve 3: before illumination. Concentration = 6.7×10^{-4}M. Cell thickensss = 0.5 mm.

$$R_2 \xrightarrow{h\nu} 2R\cdot \qquad (1)$$

In the rigid glass the bulky radicals must be confined in a cage. Strong evidence for the formation of radical pair is a broad ESR spectrum shown in Fig. 2. Since the monomeric triphenylimidazolyl radical in solutions at room temperature gives a singlet ESR spectrum of a line width of $\Delta H_{\mathrm{msl}} = 9.1$ gauss,[6] the spectrum of the width of about 200 gauss must be attributed to the fine structure of the two-spin system. The three pairs of bands connected by leading lines in Fig. 2 were also observed for solutions in several other solvents. The intensity of the central singlet (arrowed) varied with the solvent, illumination time and wavelengths of the exciting light, and was more easily saturated with the microwave power. Following Kommandeur's discussion on the photolyzed tetraphenylhydrazine[7] we identified the outermost pair of a small intensity with the separation of $2D$ and the inner two sets with $D \pm 3E$. In view of complexity of the molecules we used a simple relation, $D = 3g\beta r^{-3}/2$ to estimate the approximate distance between the two radicals.[8] From the observed $D = 112.6$ gauss we obtain $r = 6.3$ Å. As in the case of an EPA solution[4] a weak half-field absorption was detected also for the MTHF solution which confirms the triplet state of the two-spin system. The central singlet in Fig. 2, on the other hand, may be due to unknown species produced as byproducts of photolysis.

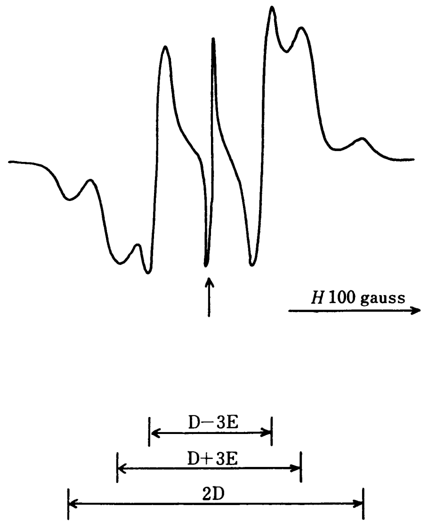


Fig. 2. ESR spectrum of photo-dimer in MTHF UV-illuminated at −196°C.

When the solution photolyzed at −196°C was taken out of the liquid nitrogen, the color of the sample faded with the rise of temperature. Before the rapid fading started, a very subtle color change from reddish-purple to purple took place. The purple solution, quickly dipped again in liquid nitrogen to quench the fading, exhibited the absorption spectrum shown in curve 2 of Fig. 1 which differs from the spectrum in curve 1: (1) the absorption maxima shifted towards red, (2) the bands became narrower with the increase of absorbance at λ_{max}, (3) the band structure manifested slightly. Hereafter we will denote the spectra before and after the heat treatment by R and S bands, respectively. A change from R to S bands was also observed invariably in other glass-forming solvents such as 3-methylpentane, decalin-cyclohexane 3 : 1 mixture, isobutyl chloride. In all cases tested only R and S bands appeared and no intermediate spectrum was observed as long as the temperature was controlled to ensure the color change from reddish-purple to purple. In alcoholic glasses such as EPA and ethanol the absorption maxima of both R and S bands shifted further to red probably because of the general dielectric solvent effect (*e.g.*, the absorption maximum of S bands in EPA was

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

[7] D. A. Wiersma and J. Kommandeur, *Mol. Phys.*, **13**, 241 (1967).

[8] H. van Willigen and S. I. Weissman, *ibid.*, **11**, 175 (1966).

575 mμ compared with 566 mμ of the corresponding band in MTHF).

Since a simple heat treatment transforms the radical R· at −196°C to a species giving rise to the S bands which resemble the R bands in general appearance, we presume that the species responsible for the S bands is a similar radical to R· with the conformation slightly modified, and will designate the species S· radical. The features of S bands enumerated above in relation to the R bands may be associated with the enhancement of planarity in the radical; as the radical becomes more planar, the extent of conjugation would increase to result in a red shift of the absorption band. The variance in the twist angle between the planes of phenyl groups and of imidazole ring would produce a number of potential energy curves for both the ground and the excited electronic states of the radical, and the electronic absorption band would be broadened on account of the Franck-Condon principle.[9] Thus the observed sharpening of the absorption band may be an indication of the enhancement of planarity.

The phenyl groups in the crowded photo-dimer must be twisted considerably from the plane of imidazole ring. The phenyl groups in a monomeric R· radical at room temperature are also considered to be twisted by analogy with orthoterphenyl and hexaphenylbenzene.[10] The rotatory displacement of the phenyl group, however, must have been attained at the sacrifice of conjugation, and at low temperatures a planar conformation might be favored. On the basis of this inference we account for the R· to S· transition in the following way; the radical produced by reaction (1) in a rigid cage is forced to retain the same conformation of twisted phenyl groups as in photo-dimer. However, as soon as the original cage is relaxed by softening the matrix, the radical assumes a more or less planar conformation presumed to be stable at −196°C.

Upon warming the solution the S bands disappeared at about −100——150°C. This can be explained by dimerization of S· radicals to a colorless dimer S_2. When the temperature was further raised to room temperature, the solution regained a reddish-purple color attributable to the regeneration of R· radical.

The R bands also appeared when the MTHF solution containing photo-dimer was illuminated first at room temperature. Upon lowering the temperature, however, the bands diminished and disappeared at temperatures below about −20°C. This phenomenon is essentially the same as reported before for benzene and EPA solutions.[5,11] For the latter systems White *et al.* constructed an energy diagram reproduced in the solid curve of Fig. 3.[3]

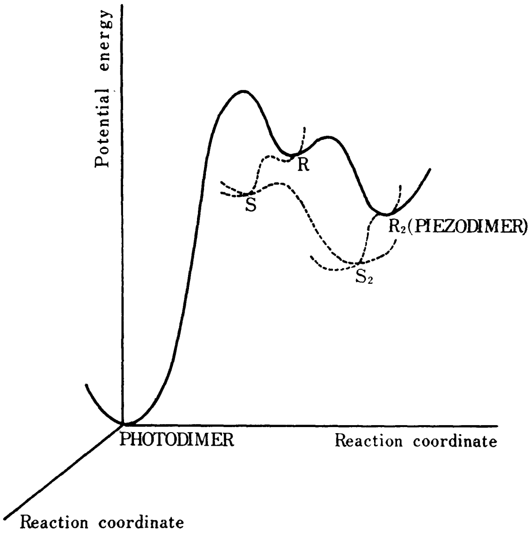

Fig. 3. Possible potential surface of the system of triphenylimidazolyl radicals and dimers.

To incorporate the newly proposed S· and S_2 we modify the diagram as shown in Fig. 3 and account for the processes throughout the whole temperatures; photo-dimer in the matrix at −196°C is "pumped up" by photons to dissociate into R· radicals in a cage. By raising the temperature slightly above −196°C radical R· overcomes a small barrier to become radical S· which successively dimerizes to piezo-dimer R_2 *via* S_2. Dimer S_2 assumed here may be less substantive than S·, because dimerization of S· radicals could lead directly to piezo-dimer, in which case the paths of S· to S_2 and S_2 to R_2 should be replaced by a single path of S· to R_2. Since piezo-dimer is thermochemically unstable in relation to photo-dimer, the former eventually isomerizes to the latter through the thermal dissociation to R· radicals.[3]

The polymer film illuminated at room temperature also exhibited the R bands. In contrast with the MTHF solution the color of the polymer did not fade on cooling, and the bands measured at −196°C showed a spectral change indicative of the transition from R to S. The change is not due to a mere temperature shift of the R bands, because the polymer film illuminated at −196°C produced the same R bands as those obtained by the illumination at room temperature. These results of film samples are also consistent with the diagram of Fig. 3; R· radical produced in the film at room temperature may be prevented from dimerization in the rigid polymer network, and on lowering the temperature the radical may undergo the isomerization to S· radical without the intervention of the formation of piezo-dimer.

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9) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, N. Y. (1967).

10) Ref. 9, p. 292.

11) K. Maeda and T. Hayashi, to be published.

Radiolysis. When γ-irradiated at −196°C, pure MTHF glass yields an absorption band in the near IR region ($\lambda_{max} \cong 1.2\ \mu$) which is known as due to the electron trapped by the matrix and is designated $(e^-)_t$.[12] In the presence of photo-dimer (0.67 mM) the $(e^-)_t$ band was suppressed to about 70% and new absorption bands identifiable with the R bands appeared (curve 1 of Fig. 4). The remaining $(e^-)_t$ band was easily photobleached with light of λ—620 mμ. The bleaching enhanced the R bands as shown in curve 2 of Fig. 4. The decrease of the $(e^-)_t$ band with the concomitant enhancement of R bands indicates that the formation of R· radical in the radiolysis is related with electron and not with photon as in the photolysis.

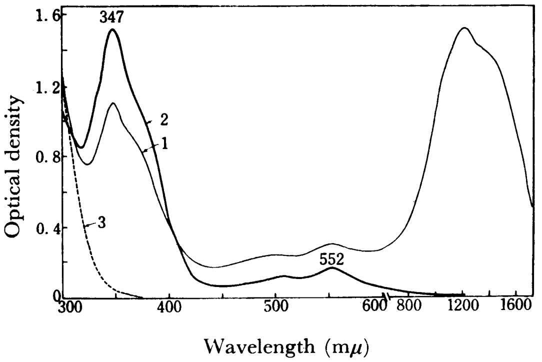

Fig. 4. Absorption spectra of photo-dimer in MTHF γ-irradiated at −196°C. Curve 1: immediately after irradiation. The absorption at λ—600 mμ is due to the trapped electron. Curve 2: the preceding solution after optical bleaching with light of λ—620 mμ. Curve 3: before irradiation.
Concentration=6.7×10^{-4}M. Cell thickness=0.5 mm. Dose=6.3×10^{19} eV/g.

In a study of tetraphenylhydrazine in MTHF we have found that UV-illumination induces the homolysis,

$$(C_6H_5)_2NH(C_6H_5)_2 \xrightarrow{h\nu} 2(C_6H_5)_2N\cdot \qquad (2)$$

while γ-irradiation leads to the heterolytic dissociation,[13]

$$(C_6H_5)_2NN(C_6H_5)_2 + e^- \longrightarrow (C_6H_5)_2N\cdot + (C_6H_5)_2N^- \qquad (3)$$

By analogy with reaction (3) we may assume that the γ-irradiated photo-dimer induces the following reaction.

$$R_2(\text{photo-dimer}) + e^- \longrightarrow R\cdot + R^- \qquad (4)$$

A criterion for this type of reaction is the exothermicity of the reaction; if the electron affinity of the radical exceeds the dissociation energy of the central bond of the dimer, reaction (4) is possible.[14] Although the electron affinity of triphenylimidazolyl radical is not known, reaction (4) may be exothermic owing to the extremely small dissociation energy of photo-dimer(~1 eV[1,5]). If the excess energy is utilized to excite R· or R^- to a luminescent state, reaction (4) should accompany the emission of light which was, in fact, observed; when γ-irradiated solutions corresponding to curve 1 of Fig. 4 was thawed in the dark, a bright yellow light was emitted. However, if, prior to thawing, the $(e^-)_t$ band was photobleached (see curve 2 of Fig. 4), the solution did not luminesce on thawing. Thus electrons released from the trap by thawing seem to produce excited R· or R^-.

Addition of 10 vol% of carbon tetrachloride to the solution of photo-dimer in MTHF prevented the formation of R· radical in the radiolysis, whereas in the photolysis the chloride caused no effect on the production of R· radicals. This can

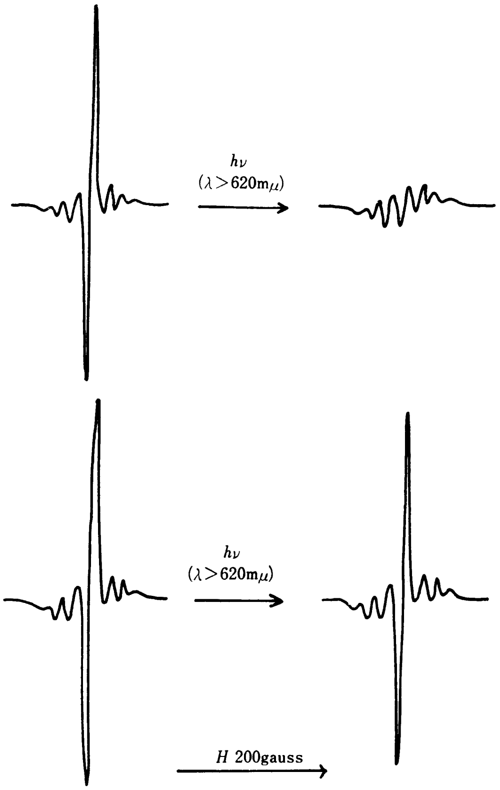

Fig. 5. ESR spectra of pure MTHF and photo-dimer in MTHF both γ-irradiated at −196°C. Upper: pure MTHF. The singlet is due to the trapped electron. Lower: photo-dimer in MTHF. Concentration=5 mM. Dose=6.3×10^{19} eV/g for both.

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12) F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc., Part A*, **285** 319 (1965).

13) T. Shida and A. Kira, *J. Phys. Chem.*, **73**, 000 (1969).

14) J. B. Gallivan and W. H. Hamill, *Trans. Faraday Soc.*, **61**, 1960 (1965).

be accounted for by the competition for electron between photo-dimer and the chloride which is known to react with electron as follows.[15]

$$CCl_4 + e^- \longrightarrow \cdot CCl_3 + Cl^- \quad (5)$$

ESR measurements also support reaction (4): Fig. 5 shows the ESR spectra of γ-irradiated pure MTHF and a solution of photo-dimer (5 mM) in MTHF. The singlet in pure MTHF having $\Delta H_{msl}=4.6$ gauss disappears on photobleaching and is attributed to the $(e^-)_t$.[12] The spectrum remaining after the bleaching is due to the MTHF radical.[12] On the other hand, the singlet in the photo-dimer solution, though similar to the $(e^-)_t$ singlet, has a width of $\Delta H_{msl}=8.1$ gauss and did not disappear on the same optical bleaching. It was more resistive against the microwave power saturation than the $(e^-)_t$ singlet. Contrary to the photolysis, the spectrum of the radiolyzed photo-dimer solution showed no sign of radical pairs. These results indicate that the singlet of photo-dimer solution is due to the singlet R· radical produced by reaction (4). The line width of the singlet, $\Delta H_{msl}=8.1$ gauss, is comparable with that of the R· radical in solutions at room temperature.[6]

Closer examination of the absorption spectra of photolyzed (curve 1, Fig. 1) and radiolyzed (curve 2, Fig. 4) rigid solutions reveals that the absorption maxima of R bands in the γ-irradiated solution are slightly blue-shifted, compared with the photolyzed solution (347 and 552 mμ for the former and 350 and 556 mμ for the latter). Although the shift is admittedly small, it was reproducible. This shift may reflect the weak interaction between the paired radicals in the photolyzed solution as manifested by the ESR fine structure. The R bands of the radiolyzed solution at −196°C coincide with those of the R· radical in MTHF at room temperature ($\lambda_{max}=552$ mμ). This coincidence may be attributed to the fact that in both media R· radicals are not paired as in the photolyzed rigid solution.

The R bands of the radiolyzed solution also changed to S bands with the heat treatment (Fig. 6). Since the change occurring in the softened matrix was transient, the signal of S bands was liable to disappear by the successive dimerization. However, the disappearance was less rapid in the radiolyzed solution than in the photolyzed and the spectral change is seen more distinctly in Fig. 6 than in Fig. 1 (curve 2). This may be because in the photolyzed solution the radical pairs are ready to recombine geminately whereas in the radiolyzed solution the R· radical from reaction (4) has more chances for the isomerization to S·. Contrary to the R bands which show a slight shift between the radiolyzed and photolyzed rigid solutions, the S bands derived from both photolysis and radiolysis were identical with $\lambda_{max}=566$ mμ. This indicates that the R· radicals in a cage in photolyzed solutions separate from each other upon softening the matrix and the resulting S· radicals are no longer paired to exhibit any spectral shift due to the pairing.

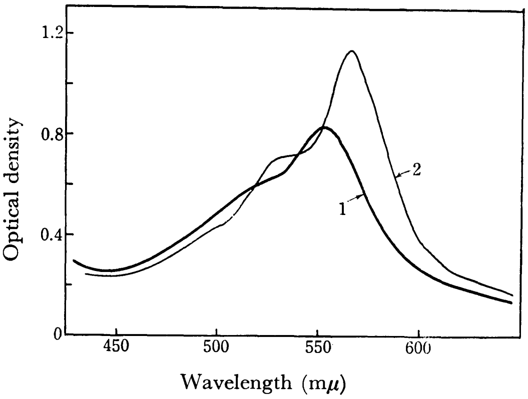

Fig. 6. Absorption spectra of photo-dimer in MTHF γ-irradiated at −196°C. Curve 1: corresponding to curve 2 of Fig. 4. Concentration=5 mM. Cell thickness=1.5 mm. Dose=3.1×10^{19} eV/g. Curve 2: the preceding solution after limited warming.

The absorption at 300—400 mμ of the R· radical in the radiolyzed solution (curve 2, Fig. 4) is disproportionately high compared with the spectrum of the photolyzed solution (curve 1, Fig. 1). Since the lophine anion, R^-, produced by reaction (4) is known to have $\lambda_{max}=326$ mμ with $\varepsilon_{326}=2.48\times$

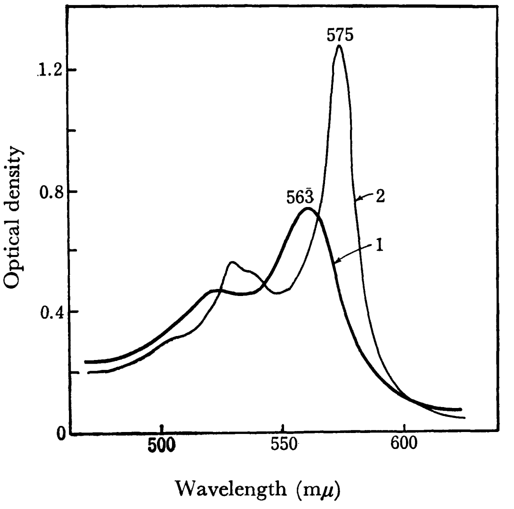

Fig. 7. Absorption spectra of photo-dimer of 2,3,4,5-tetraphenylpyrryl in MTHF UV-illuminated at −196°C. Curve 1: immediately after illumination. Curve 2: the same solution after limited warming. Concentration=1 mM. Cell thickness=1.5 mm.

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[15] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

10^4,[5] the anion should contribute to the absorption in the near UV region. This contribution can be subtracted by using the known molar extinction coefficients of R bands at 552 mμ (8.4×10^3) and 347 mμ (4.8×10^4).[5] Even after the subtraction, however, the absorption at 300—400 mμ is still high compared with the spectrum of the photolyzed solution. The reason for this discrepancy is not clear at present.

Additional Remark

As in the case of triphenylimidazole, 2,3,4,5-tetraphenylpyrrole produces two isomeric dimers on oxidation, one photochromic and the other piezochromic.[5,16] We have carried out parallel studies on these dimers also and obtained quite analogous results. One example is shown in Fig. 7 where the spectrum in curve 1 was observed immediately after UV-illumination at −196°C, and that in curve 2 was obtained after the limited warming. The two spectra are regarded as corresponding to the R and S bands in the case of lophine dimer.

The authors wish to thank Dr. Masashi Imamura and Dr. Hiroshi Midorikawa of The Institute of Physical and Chemical Research for their helpful discussion.

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16) K. Maeda, A. Chinone and T. Hayashi, to be published.