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Photochromism of 2,2,4,6-Tetraphenyl-1,2-dihydro-1,3,5-triazine

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Synopsis. 2,2,4,6-Tetraphenyl-1,2-dihydro-1,3,5-triazine shows temperature dependent photochromism only in a solid state at temperatures above *ca.* −70 °C under UV(320—380 nm) irradiation, giving several absorption maxima in the visible region, but no change in the IR spectrum. *N*-Substituted derivatives show no photochromism.

It was briefly reported by Lottermoser[1] that 2,2,4,6-tetraphenyl-1,2-dihydro-1,3,5-triazine (TPDT) exhibits photochromism in a solid state. No investigation has been made since the phenomenon was confirmed by von Walthers.[2] In this note the specificity of the photochromism of TPDT is reported.

TPDT turned brownish pink on irradiation in a solid state with the light 320—380 nm of sunlight or a Xenon lamp, the coloration reaching a limit with continual irradiation. TPDT which showed λ_{max} 257 and 325 nm (broad; assigned to an n,π^*-transition[3]) in a solid state before irradiation showed λ_{max} 430, 447, 487, 502, 533, 565, and 584 nm in a solid state after irradiation (Fig. 1).

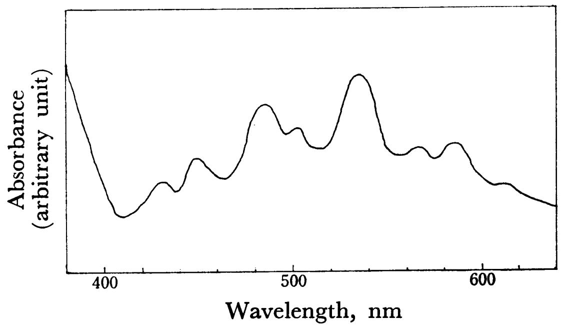

Fig. 1. The electronic absorption spectrum of TPDT measured in a solid state after irradiation at room temperature (the paraffin paper method).

It seems that the absorption at 325 nm indicates the start of photochromism. The color hardly faded at all at room temperature in the dark and also under irradiation with visible light, but it reverted thermally to the original colorless state in the dark slowly at temperatures above room temperature, somewhat rapidly with a rise in temperature. TPDT showed no change in the IR spectrum in the range 650—4000 cm^{-1} on irradiation in solid state, showing no ESR signal in both solid state not irradiated and solid state irradiated. The photochromic characteristic was lost by repetition of photochromic treatment.

It was found that TPDT exhibits photochromism only in solid state, since TPDT exhibits photochromism neither in solutions at various temperatures nor in rigid glasses in mixed solvents such as isopentane–methylcyclohexane(1 : 1) at *ca.* −196 °C. In addition, no absorption of the light in the visible region was recorded at room temperature on high density excitation by the 337 nm light of a nitrogen laser pulse with a nanosecond time-resolved spectrosco pytechnique.[4] The result indicates that TPDT does not yield even a transient colored species with a short lifetime on irradiation in solution. Very few compounds have been reported[5,6] which exhibit photochromism only in a solid state.

The photochromism of TPDT is temperature dependent. It was not observed at low temperatures below *ca.* −70 °C down to *ca.* −196 °C. A weak photochromic coloration was first observed at *ca.* −70 °C, deepening with a rise in temperature to about room temperature. No such temperature dependence seems to have been reported.[6]

TPDT containing a solvent of crystallization, such as acetone, benzene and chloroform, exhibited photochromism accompanied by the absorption of light in visible region, similar to that of TPDT free from a solvent of crystallization. TPDT containing methanol or ethanol as a solvent of crystallization, in which formation of a hydrogen bond between the alcohol and NH of TPDT was confirmed by IR analysis, exhibited no photochromism. Salts of TPDT, such as hydrochloride, and *N*-substituted TPDT, such as *N*-methyl-, *N*-ethyl-, and *N*-nitroso-TPDT, exhibited no photochromism. This shows that the photochromism of TPDT requires the presence of free H in NH.

The results suggest that the mechanism of the photochromism of TPDT is of a new type[6] attributed to an intermolecular interaction in a crystalline structure, presumably an interaction between free H in NH and excited C=N, rather than an intramolecular change of the molecular structure.

Experimental

The crystals of 2,2,4,6-tetraphenyl-1,2-dihydro-1,3,5-triazine(TPDT), $C_{27}H_{21}N_3$, were prepared according to the method of von Walthers;[2] colorless fine crystalline powder, mp 197—198 °C; $\lambda_{max}^{C_2H_5OH}$ 242(ε=3.62×10^4), 307(ε=1710), 330 nm (ε=1100), $\lambda_{max}^{C_6H_6}$ 274(ε=6.84×10^4), 310(sh)(ε=1170), 333 nm (ε=884); IR(KBr) 3405(m, ν_{NH}), 1685(w), 1612 cm^{-1}(m, ν_{CN}); NMR(δ ppm) 6.12 (1H, NH; missing on treatment with D_2O), 7.20—8.60 (aromatic protons). TPDT exhibits no thermochromism both in solid state and in solution. TPDT containing methanol, ethanol, benzene, acetone, or chloroform as solvent of crystallization was obtained as colorless fine crystals by recrystallization of TPDT from the solvents respectively; $C_{27}H_{21}N_3 \cdot CH_3OH$(IR 3190 cm^{-1}, m, ν_{NH} (hydrogen-bonded)), $C_{27}H_{21}N_3 \cdot C_2H_5OH$ (IR 3155 cm^{-1}, m,) $C_{27}H_{21}N_3 \cdot CH_3COCH_3$(IR 3420 cm^{-1}, m, ν_{NH}), $C_{27}H_{21}N_3 \cdot 1/3\ C_6H_6$ (IR 3415 cm^{-1}, m), $C_{27}H_{21}N_3 \cdot 1/5\ CHCl_3$ (IR 3415 cm^{-1}, m). *N*-Methyl-TPDT, mp 198—200 °C, and *N*-ethyl-TPDT, mp 218—219 °C, were prepared[7] from alkyl iodide and TPDT-potassium which was obtained by heating TPDT with metallic potassium in dioxane. *N*-Nitroso-TPDT, $C_{27}H_{20}ON_4 \cdot 2H_2O$, mp 171—173 °C, was prepared by a reaction of an aqueous solution of sodium nitrite with TPDT-hydrochloride, $C_{27}H_{21}N_3 \cdot HCl$, obtained from TPDT and 2M HCl.

The electronic absorption spectra were measured with a Cary 14 spectrophotometer. The spectrum in a solid state was recorded with a thin layer of the specimen on paraffin paper obtained by rubbing crystals of the specimen on paraffin paper with an agate pestle and also with KBr disk. The infrared spectra were recorded with a Hitachi 215 grating spectrophotometer. The nuclear magnetic resonance spectrum was recorded with a Varian HA 100D spectrometer. The electron spin resonance was recorded with a JES 3B electron spin resonance spectrometer of Japan Electron Optics Laboratory.

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References

1) A. Lottermoser, *J. Prakt. Chem.*, [2], **54**, 113 (1896).

2) R. von Walthers, *J. Prakt. Chem.*, [2], **67**, 446 (1905).

3) The absorption λ_{max} 325 nm is reasonably assigned to an n,π^*-transition in C=N, since $\lambda_{max}^{C_2H_5OH}$ 307, 330 nm and $\lambda_{max}^{C_6H_6}$ 310, 333 nm measured in the solutions are assigned to an n,π^*-transition in C=N.

4) The nanosecond time-resolved spectroscopic measurement was carried out by Drs. K. Kobayashi and R. Nakagaki, Institute of Physical and Chemical Research.

5) J. M. Tien and I. M. Hunsberger, *J. Am. Chem. Soc.*, **79**, 6604 (1955).

6) "Photochromism," ed by G. H. Brown, Wiley-Interscience, New York (1971) and literatures subsequently published.

7) *N*-Methyl- and *N*-ethyl-TPDT were supplied by Dr. K. Maeda, Ochanomizu University.