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Anti – Syn Isomerization of Carbazole-3-carbaldehyde Hydrazone Derivative. Isolation and Characteristics of Syn Isomer

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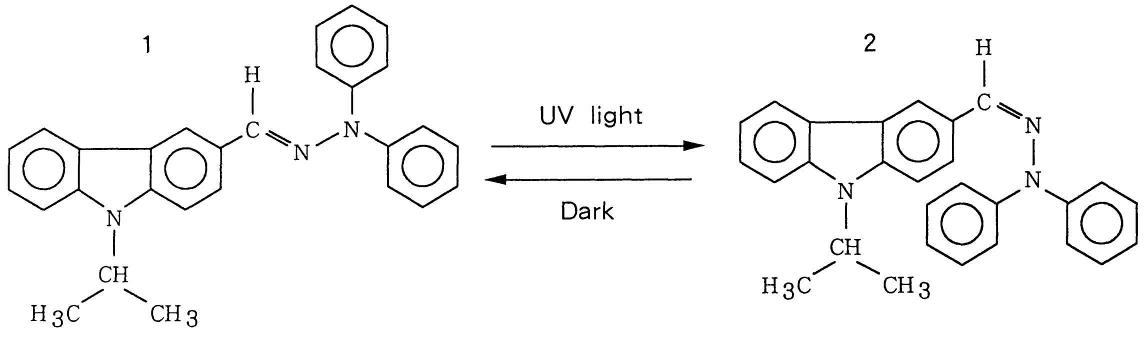
9-Isopropylcarbazole-3-carbaldehyde diphenylhydrazone (anti – form) isomerized to syn – form upon UV light irradiation both in solution and in solid polymer film. The syn – form was successfully isolated in crystalline state by extracting with hexane and recrystallization.

Photochemistry of carbon – nitrogen double bond (C = N) has been actively investigated.[1 – 8] Among others, photochemical behavior of aromatic hydrazones is very important. They are much used as charge transport material of organic photoconductive layer for electrophotography and their behavior connects closely with the so – called fatigue phenomenon of the layer.[9]

As Wettermark reviewed,[10] isolation of geometircal isomer of C = N compounds had not been certain till 1970 and as far as we know there have been no reports of the isolation.

We report here that 9-isopropylcarbazole-3-carbaldehyde diphenylhydrazone (1, anti – form) isomerizes



Scheme 1. Anti – syn isomerization of carbazole-3-carbaldehyde hydrazone derivative.

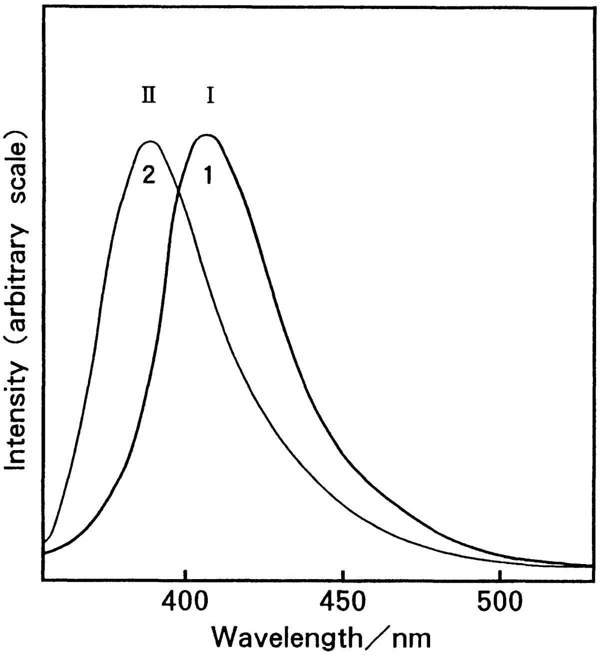


Fig. 1. I and II are fluorescence spectra of 1 and 2, in methanol respectively. (Ex. 332 nm)

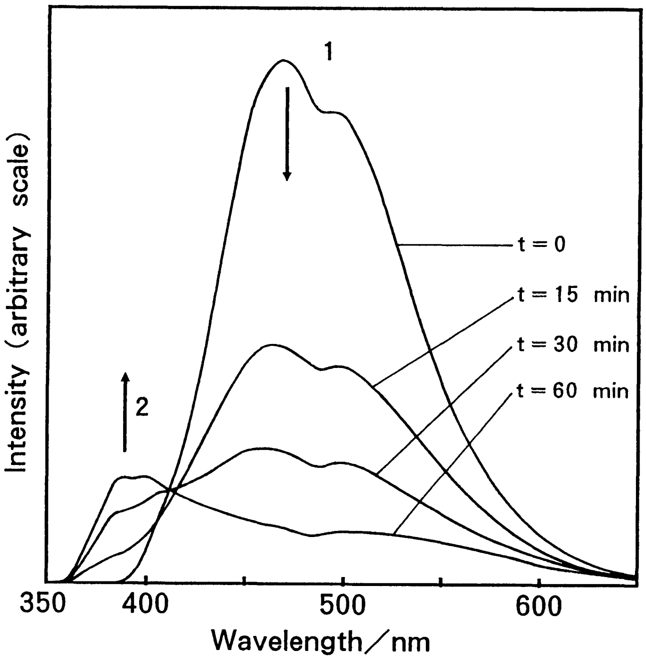


Fig. 2. Solid line shows fluorescence spectrum of 1 in solid polymer film. (Ex. 332 nm)[15] Dotted lines show change of the spectrum upon UV light irradiation (0.5 mW/cm^2). t : irradiation time.

to 2 (syn − form) upon UV light irradiation not only in solution but also in solid polymer film and 2 is successfully isolated in crystalline state. In both isomers, as evidenced by NMR spectra, carbazole part and hydrazone double bond seem to be coplanar. Although syn − form 2 has some stability, thermal back reaction to 1 proceeds naturally, which is most conveniently followed by fluorescence spectrum.

Isomerization of 1 to 2 was carried out typically in methanol solution.[11] Isolation of syn − form (2) was achieved by evaporating the irradiated solution below 40 ℃ of bath temperature and extracting with hexane, 2 being soluble in hexane in contrast to almost complete insolubility of 1.[12] The MS data and elemental analysis of 2 were the same with 1.[13] Conversion of 1 to 2 upon UV irradiation for 2 h in methanol solution was ca. 18%.

Most remarkable differences between 1 and 2 are the solubility in hexane and the fluorescence spectrum (Ex. 332 nm).[14] As shown in Fig. 1, fluorecence peak of 1 and 2 in methanol are at 407 nm and 388 nm, respectively. Figure 2 shows fluorescence of 1 in solid polymer film[15] and change of the spectrum upon UV light irradiation. When 1 is irradiated in the film, fluorescence peaking at 472 nm of 1 decreases with the increase of peak of 2, having isoemissive point at about 415 nm. After 60min, peak of 2 becomes clear.

The back reaction of 2 to 1 is confirmed with fluorescence and NMR spectra. After preparation of the saturated solution of 2 in methanol at room temperature, deposition of difficultly soluble 1 begins within 1 h. Thermal back reaction of 2 to 1 completes practically after 12 h at room temperature in both solution 16) and polymer film. In crystals of 2, 100% change of 2 to 1 needs ca. 80 h at room temperature.

As evidenced by ^{1}H NMR Nuclear Overenhauser Enhancements (NOEs) of carbazole protons, in both isomers 1 and 2, carbazole part and C = N double bond are on the same or nearly the same plane, the methine proton of hydrazone being adjacent to 4 - proton of carbazole part in both 1 and 2.17)

The cause of fatigue phenomenon of the photoconductive layer having 1 as charge transport material has been confirmed to be due to the formation of 2, as to be reported in detail elsewhere : (1) decrease of photocurrent of the film upon UV light irradiation is observed, (2) isomer 2 is produced in the film with this irradiation, (3) ionization potential of 2 is lower by about 0.1 eV than that of 1, (ionization potential of 1 and 2 being 5.29 and 5.20 eV respectively 18)), (4) 2 produced in photoconductive layer upon UV irradiation can, therefore, function as hole trapping sites leading to film fatigue.

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References

1) A. Padwa, *Chem. Rev.*, 77, 37 (1977).

2) A. C. Pratt, *Chem. Soc. Rev.*, 1977, 63.

3) H. Ohta and K. Tokumaru, *Yuki Gosei Kagaku Kyokaishi*, 30, 1006 (1972).

4) W. G. Herkstroeter, *J. Am. Chem. Soc.*, 98, 6210 (1976).

5) M. Yoshida and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 54, 2395 (1981).

6) A. Okami, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, 1984, 289.

7) Y. Takeda, H. Misawa, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, 62, 2213 (1989).

8) L. F. Clarke, F. O'Sullivan, and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1649.

9) J. Packansky, R. J. Waltman, R. Grygier, and R. Cox, *Chem. Mater.*, 3, 454 (1991).

10) G. Wettermark, "The chemistry of carbon - nitrogen double bond", S. Patai, Wiley, New York, (1970), p. 565 - 596.

11) Typically, methanol solution of 1 (0.01 M) was irradiated with the light power of 0.5 mW/cm^2 with ultra - violet source (Type FI - 31L, Tokyo Optical Machines. Spectral range 300 - 405 nm, spectral peak

365 nm). The photochemical isomerization was also observed in acetonitrile tetrahydrofuran, benzene, toluene, ethyl acetate, and methylene dichloride.

12) Solubility of 1 in hexane is less than 10^{-5} wt%, and the solubility of 2 is more than 1.0 wt%.

13) For 1 : mp 158 ℃, $\lambda_{max} = 343$ nm (in methanol, ε 4.15×10^4), MS m/z 403 (M^+), Found : C, 83.31 ; H, 6.30 ; N, 10.39 %. Calcd for $C_{28}H_{25}N_3$: C, 83.34 ; H, 6.24 ; N, 10.41 %. ^1H NMR (CD_3CN) ; δ = 1.67 (6H, d, $J = 7.3$ Hz), 5.06 (1H, m), 7.18 – 7.65 (15H, Ar), 7.83 (1H, d, $J = 9.8$ Hz), 8.13 (1H, d, $J = 7.9$ Hz), 8.27 (1H, s).

For 2 : mp 156 ℃ (change of 2 to 1 is considered). $\lambda_{max} = 342$ nm (in methanol, ε 1.76×10^4), MS m/z 403 (M^+), Found : C, 83.45 ; H 6.35 ; N, 10.20 %. Calcd for $C_{28}H_{25}N_3$: C, 83.34 ; H, 6.24 ; N, 10.41 %. ^1H NMR (CD_3CN) ; $\delta = 1.68$ (6H, d, $J = 7.3$ Hz), 5.07 (1H, m), 7.19 – 7.65 (15H, Ar), 7.84 (1H, d, $J = 9.8$ Hz), 8.14 (1H, d, $J = 7.9$ Hz), 8.28 (1H, s).

14) Fluorescence measurement of 2 was carried out with freshly made solution immediately after the isolation and recrystallization of 2.

15) Polymer film : Tetrahydrofuran solution of one to one mixture of 1 and vinyl chloride – vinyl acetate copolymer (S – lec C, Sekisui Chemical Inc.) was casted onto a quartz plate and heated at 100 ℃ for 30 min.

16) In the back reaction, methanol, hexane, acetonitrile, and chloroform afforded the same results.

17) In measurement of NOEs, the methine proton of hydrazone group was enhanced in 7.40 ppm by NOEs of 4 – proton of carbazole in each case of 1 and 2, but there was no enhanced peak of methine proton by NOEs of 2 – proton of carbazole in each case.

18) The ionization potentials of the compounds were measured by atmospheric photo – electron emission spectroscope (Riken Keiki Co., Ltd. Japan, Model AC – 1). See the references in 19 and 20 on the principle of this measurement.

19) H. Kirihara and M. Uda, *Rev. Sci. Instrum.*, 52, 68 (1981).

20) E. Miyamoto, Y. Yamaguchi, and M. Yokoyama, *Denshi – shashin Gakkaishi*, 28, 364 (1989).

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