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Photochemical Conversion of anti-9-Methylcarbazole-3-carbaldehyde Diphenylhydrazone to Its syn-Isomer and an Indazole [1)]

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Under irradiation, the compound in the title, which is frequently used as a charge transport material in electrophotography, undergoes reversible isomerization into its syn-isomer and cyclization to the corresponding indazole. These reactions will affect the characteristics in the practical electrophotographic process using this compound.

Diphenylhydrazone derivatives have frequently been employed as charge transport materials in layered organic receptors for electrophotography.[2)] To reveal the mechanism of light fatigue during practical electrophotographic process using these compounds we undertook to investigate their photochemical reactions. Recent report by Pacansky on the photochemical cyclization of 4-(dimethylamino)-benzaldehyde diphenylhydrazone to the corresponding indazole [3)] prompted us to report our result that 9-methylcarbazole-3-carbaldehyde diphenylhydrazone (S), on irradiation, reversibly isomerizes to its syn-isomer (X) aliving for a certain lifetime to be characterized, and finally irreversibly cyclizes to an indazole (P).

X-Ray crystallographic analysis showed that the starting material S has anti-C=N configuration and one phenyl group in the hydrazone is almost coplanar to, and another phenyl is nearly vertical to the carbazole ring as illustrated in Fig. 1.

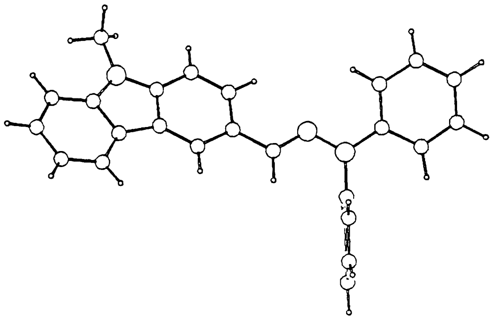
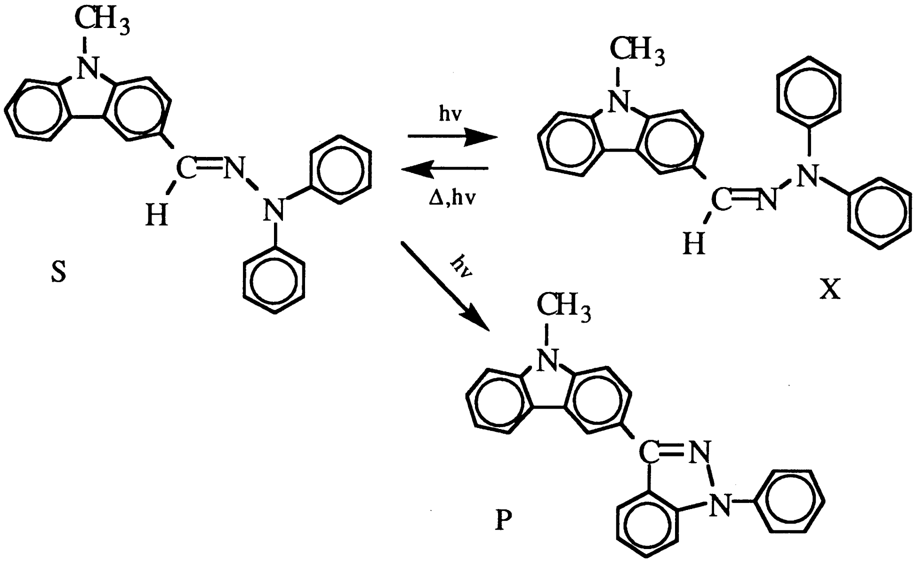


Fig. 1. Structure of S determined by X-ray analysis.

S was irradiated in deaerated acetonitrile solution (1 x 10^{-5} mol dm^{-3}) with light of wavelength longer than 310 nm from a medium pressure mercury lamp through a Toshiba UV-31 filter. With irradiation, the absorption peak of S at 345 nm was decreased accompanied by growth of an absorption at 290 nm (due to species X) with isosbestic point at 303 nm. When the irradiation was interrupted, the newly resulted absorption was reversibly reverted at room temperature to that before the irradition. However, further irradiation (longer than 2 hrs.) led to irreversible change of the absorption to give a new maximum at 329 nm (due to species P).



The first species (X) appeared in the initial stage of the irradiation is reasonably assigned to syn-isomer of S. The reaction mixture was subjected in the dark to inverted phase HPLC (column: ODP90) with acetonitrile as an eluent to separate X in acetonitrile solution. X was eluted with a much shorter retention time than P and S. X was reverted to S with a halflife of ca. 13 hours in acetonitrile at -10°C in the dark. Irradiation (>331 nm) quickly reverted X into S.

^{1}H-NMR of X in CD_3CN solution at -30 °C (Fig.2) exhibited that the numbers of protons are the same as in S, however two singlet peaks of S, 7.3 ppm for the imidoyl hydrogen and 8.2 ppm for hydrogen at 4-position of carbazole ring, were shifted to 8.2 and 8.65 ppm as identified by their NOE on mutual irradiation; the two phenyl groups appeared at 7.2 ppm which indicates that they take magnetically nearly equivalent conformation. Molecular orbital calculation of X by MOPAC program (AM1) and INDO/S-CI gives the structure of X as illustrated in Fig. 3, which suggests that the N-N bond is twisted about 60° from the C=N plane and the unpaired electron pair is in parallel to the bond between the imidoyl carbon and the carbazole ring.

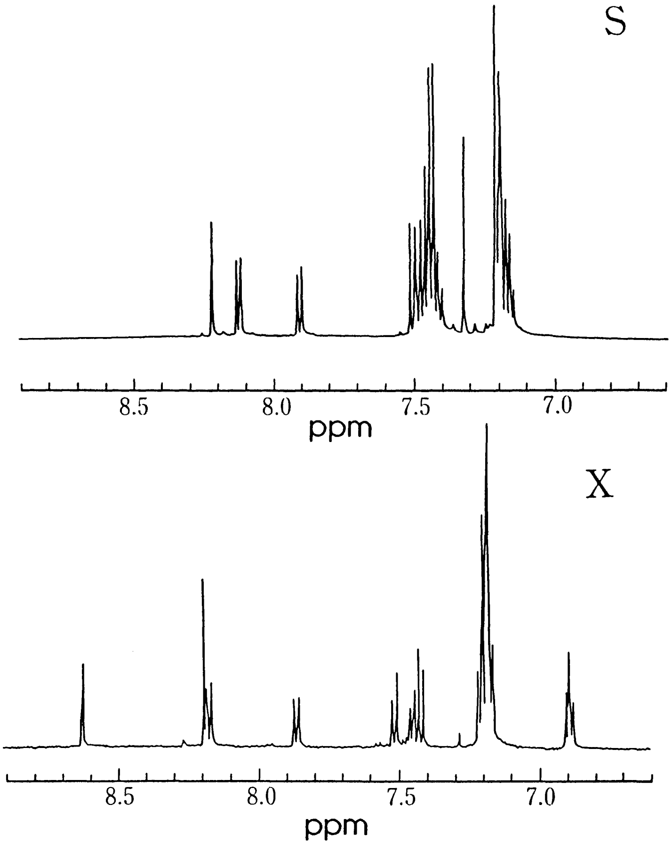


Fig. 2. ^{1}H-NMR spectra of S and X in CD$_3$CN at -30 °C.

The final reaction mixture was worked up to isolate a product. The product is identified as an indazole (P), mp 170.5-171 °C, by MS (M$^+$, 373, C$_{26}$H$_{19}$N$_3$) corresponding to the decrease of two hydrogen atoms from S, and NMR.4) In ^{1}H-NMR, only one singlet peak (8.9 ppm) appeared whereas S exhibited two singlet peaks. Irradiation of the 8.9 ppm signal afforded NOE on two doublet peaks at 8.4 ppm, which shows 8.9 ppm to be the hydrogen at 4-position of the carbazole ring and 8.4 ppm to be those at 5-position of the carbazole ring and 4-position of the indazole ring.

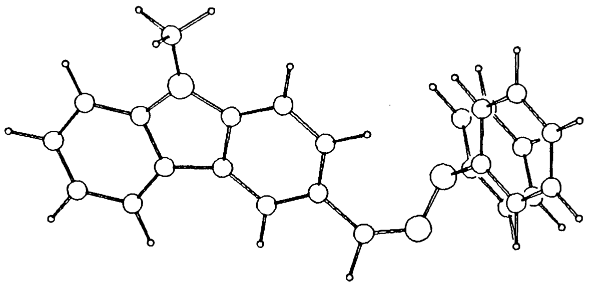


Fig. 3. Structure of X based on MO calculation.

It is noted that the substitution of Ph_2N group on the nitrogen atom of C=N bond can stabilize its syn-isomer to be seperated in solution at -10 °C whereas substitution of MeO group very much stabilizes syn-isomers to be isolated as stable compounds.5)

The above results suggest that the reduction of the efficiency of charge transport during electrophotographic process employing hydrazones like S could be attributed to their conversion into their syn-isomers as well as cyclized products which have different electronic properties in the hole transport.

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References

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2) for example, S. Ishikawa, I. Kajita, and E. Kondo, "Fine Chemicals for the Electronics Industry," ed by P. Bamfield, The Royal Society of Chemistry Special Publication, No. 60 (1986), p.82.
3) J. Pacansky, R. J. Waltman, R. Grygier, and R. Cox, Chem. Mater., 3, 454 (1991).
4) Production of P from S is accompanied by loss of two hydrogen atoms. However, irradiation of S in thoroughly degassed solution still afforded P. At moment, the fate of the eliminated hydrogens is not clear.
5) For example, H. Ohta and K. Tokumaru, Yuki Gosei Kagaku Kyokaishi, 30, 1006 (1972); A. Padwa, Chem. Rev., 77, 37 (1977); A. C. Pratt, Chem. Soc. Rev., 1977, 63.

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