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# Photochromism of *N*-3-Pyridylsydnone

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Except for a few qualitative studies[1-4] the photochromism (PC) of *N*-3-pyridylsydnone (3PS) has been little investigated, the only mechanism proposed thus far being that of Mill *et al.*[3] who assumed the formation of a color center. However, the experiments described seem somewhat inexact and the mechanim has several drawbacks. The substance is very liable to decompose and available information is scanty. The present note attempts to contribute to the understanding of the PC of 3PS.

*Radiolysis of 3PS.* Mill's mechanism requires that the electron in the color center should be supplied from the molecule and leaves a $3PS^+$ cation radical. It is known that 3PS acts as an electron donor to form complexes with $Cu^{2+}$, $Ni^{2+}$ or $I_2$.[5,6] This, however, does not necessarily mean that 3PS ionizes easily to form a cation radical. To clarify the mode of ionization of 3PS, γ-radiolysis was tried in a rigid matrix at 77°K.[7] It gave only $3PS^-$ (Fig. 1) and no cation radical was formed. This is against the color center mechanism.

*Flash Photolysis of Solutions.* Metz[2] has concluded from a solution experiment by steady irradiation that the PC of 3PS was restricted only to solid state. Solutions of 3PS ($10^{-2}$ to $10^{-5}$ mol/l) in various solvents were subjected to flash photolysis (500 J, 5 μsec) in either the presence or absence of addenda (NaCl, KBr, $O_2$ or TCNE) which might affect the stability of 3PS ionic structures. In all cases no PC was observed down to the lifetime of 5 μsec. There were no effects of temperature, solvent polarity, solvent viscosity or presence of any electron acceptor. As the solution PC due to unimolecular reactions usually has a much longer lifetime under similar conditions, it is hard to regard PC of 3PS as an intramolecular process. Experiments in PVA or polystyrene also failed to show the PC.

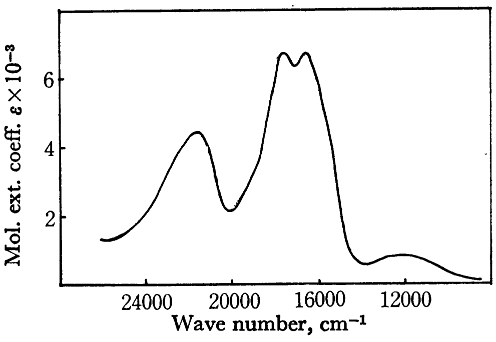

Fig. 1. Spectrum of $3PS^-$ in 2-methyltetrahydrofuran (Courtesy of Dr. T. Shida)

However, the effect of TMPD in an ethanol solution was remarkable. Although the solution showed no PC, 3PS seemed to stabilize in its stead the $TMPD^+$ radical. It was found that for a $4.0\times10^{-4}$ mol/l TMPD solution, the presence of either $5.1\times10^{-5}$ or $4.0\times10^{-4}$ mol/l 3PS made 48.9 or 100%, respectively, of the recombination of $TMPD^+$ take place by way of electronated 3PS. Hence, the acceptor property of 3PS seemed to be manifest.

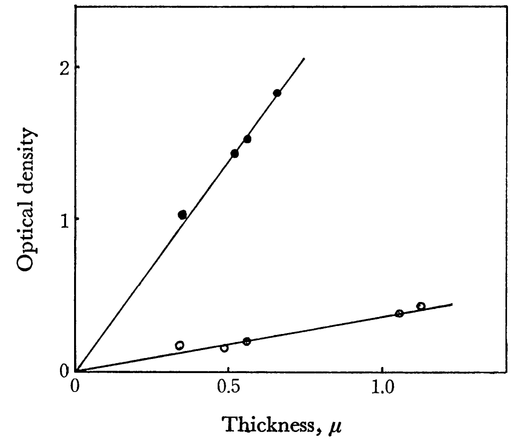

Fig. 2. Plots of OD against the thickness of the film (in μ): ○ at 605 nm, ● at 290 nm

*PC in Crystal Films.* Tien[1] could not decide whether the PC was confined to the surface of the crystals or it extended to within. We thus measured the maximum absorption intensity of the blue form obtained by constant irradiation of the oxygen-free evaporated crystal film. The thickness was determined from the interference pattern. The good linearity in Fig. 2 shows that the PC is distributed almost uniformly within the crystal entity. The plots were compared with those for the absorption by 3PS itself at 290 nm. Assuming tentatively that the extinction coefficient of the blue absorption was 10000 (double the value at 290 nm), the extent to which the PC took place amounted to 7.5%.

The dielectric constant of the crystal film was also measured. It did not change on irradiation until decomposition took place.

*Polarization of Crystal Spectra.* Spectra of two

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[1] J. M. Tien and I. M. Hunsberger, *J. Amer. Chem. Soc.*, **77**, 6604 (1955); **83**, 181 (1961).

[2] F. I. Metz, W. C. Servoss, and F. E. Welsh, *J. Phys. Chem.*, **66**, 2246 (1962).

[3] T. Mill, A. V. Roggen, and C. F. Wahlig, *ibid.*, **34**, 1139 (1961).

[4] H. S. Gutowsky, R. L. Rutledge, and I. M. Hunsberger, *ibid.*, **29**, 1183 (1958).

[5] S. M. Lee, U. S. 3549639 (1971).

[6] H. Yamada and K. Kozima, *J. Amer. Chem. Soc.*, **82**, 1543 (1960).

[7] We are very much indebted to Dr. T. Shida, the Institute of Physical and Chemical Research, for the experiment of γ-radiolysis.

kinds of sample film, one evaporated in a vacuum and the other precipitated from a nitromethane solution, are shown in Fig. 3. They differ considerably, which seems to be due to the preferred orientation in the crystal films rather than to polymorphism, since there is no indication of the latter. Assuming that the crystals mainly have their axes of growth (assigned later to the *b* axis) almost perpendicular to the quartz plate in an evaporated film, as is often the case, but parallel or at random in a precipitated film, the difference may be accounted for in terms of the factor group splitting. Comparison of the spectra of 3PS with the corresponding spectra of *N*-phenylsydnone (PhS), which is non-photochromic, shows that the splitting in the former is far more greater (1700 cm$^{-1}$ compared with 750 cm$^{-1}$ of PhS for the lowest band), and that the direction of the splitting is reversed (see arrows in Fig. 3).

The anisotropy in the blue band is astonishingly large. A single crystal was placed under a polarizing microscope and was observed visually. It was blue when the polarizer was perpendicular to the *b* axis, but pale yellow-green when the polarizer was parallel to the *ac* plane.

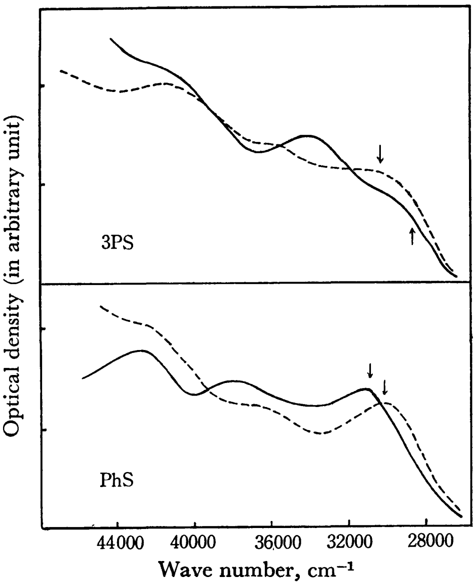

Fig. 3. Crystal spectra of 3PS and PhS.
——: evaporated film, ------: precipitated film.

*Crystal Structure.* In view of the large anisotropy in the crystal spectrum and the failure of observing solution PC, the crystal analysis of 3PS was carried out. The crystal of 3PS has orthorhombic structure with $a=22.9$, $b=7.0$, $c=8.6$ Å and $Z=8$. Three space groups conformed to the extinction rule, P2$_1$ma, Pm2a, and Pmma. Comparison with the crystal of PhS[8] (P2$_1$/a, $a=22.06$, $b=3.75$, $c=9.58$, $\beta=103°10'$, and $Z=4$) suggests that the space group of 3PS is possibly Pm2a (or Pmma) and that both structures do not differ greatly except that the crystal of 3PS consists of molecular layers stacked along the *b* axis, whereas in the crystal of PhS the molecules are stacked alternatively by a screw axis.

*Discussion.* Under suitable conditions every kind of organic PC except for that of 3PS was found to take place in solution. The absence of solution PC in 3PS suggests that it is not a unimolecular process such as ionization, isomerization or dissociation. Absence of an ESR signal in oxygen-free samples[4] shows that it does not involve radical formation. The marked polarization of the blue band in the *ac* plane suggests that the absorption is an intermolecular transition which is of CT type in nature, and that the interaction took place between the molecules in the same layer. The homoionic structure and the donor-acceptor property of sydnones seem to favor the complex formation. If this is the case, the formation of the complex may be invoked by some change in the molecular structure or in the molecular disposition in the crystal, which is induced photochemically. Metz[2] reported that the blue form was bleached by the application of e.m.f. Mill[3] observed that a surge of electric current occurred when the blue crystal was thermally bleached. Although the observations do not seem to be exact, they conform to the present mechanism.

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[8] G. M. J. Schmidt, *Bull. Res. Council, Israel*, **1**, 121 (1951).