CHEMISTRY LETTERS, pp. 1811-1812, 1993.

Effect of Acetonitrile Completely Suppressing Trans-to-cis Photoisomerization of Styrylpyrene Substituted with a Nitro Group

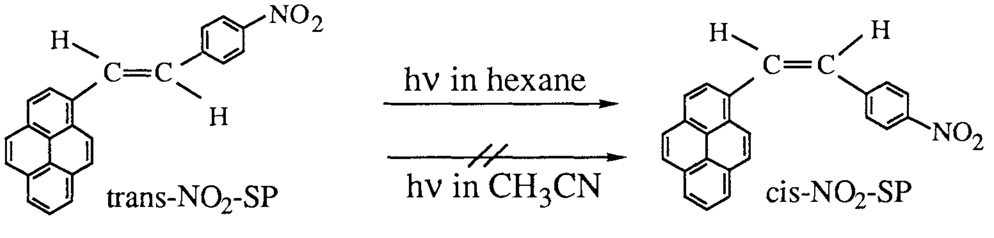
Yoshihiko KIKUCHI, Hiroaki OKAMOTO, Tatsuo ARAI,* and Katsumi TOKUMARU*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Acetonitrile completely suppresses trans-to-cis isomerization of 1-[2(4-nitrophenyl)ethenyl]pyrene.

Previously we have shown that on triplet sensitization 1-styrylpyrene (SP) and its derivatives substituted with 4-methoxy, methyl, cyano, and nitro groups on the benzene ring undergo isomerization between the cis and trans isomers in the triplet excited state by a dual mechanism comprising from the mechanisms for the conventional mutual isomerization and the one-way isomerization. [1,2]

We now wish to report anomalous behavior of trans-1-[2(4-nitrophenyl)ethenyl]pyrene (trans-NO_2-SP) in acetonitrile, not undergoing at all detectable isomerization on direct irradiation.

trans-4-NO_2-SP (2×10^{-5} mol dm^{-3}) was irradiated without any sensitizer in several organic solvents with 436 nm light filtered from a 400 W high pressure mercury lamp, and the quantum yields for the isomerization from the trans to cis isomer, $\Phi_{t\rightarrow c}$, were determined as 0.11 in hexane, 0.09 in diethyl ether, and essentially nil (at most 10^{-5}) in acetonitrile.



In hexane, the quantum yield for the intersystem crossing from the initially resulting trans singlet state ($^1t^*$) to the trans triplet state ($^3t^*$), Φ_{isc} ($^1t^*\rightarrow{}^3t^*$), was determined as 0.28.[3] Thus, on direct irradiation of trans-NO_2-SP in hexane, the $^3t^*$ produced by the intersystem crossing will isomerize to cis-NO_2-SP with a quantum yield of nearly half of Φ_{isc} as in isomerization of various olefins in the triplet state.[1,2] In acetonitrile, however, Φ_{isc} of trans-NO_2-SP was only 0.036.

The above facts suggest that in acetonitrile $^1t^*$ rapidly deactivates to the ground state (^1t) before undergoing intersystem crossing to $^3t^*$.

In the absorption spectra, trans-NO_2-SP exhibits bathochromic shift with increasing solvent polarity (λ_{max}: 386.5, 389 and 393.5 nm in hexane, diethyl ether, and acetonitrile, respectively), while unsubstituted trans-SP showed almost the same absorption among the above solvents (λ_{max}: 370.0, 370.5, and 372.5 nm, respectively). The fluorescence spectra display more remarkable bathochromic shift with increasing solvent polarity. The fluorescence maximum of trans-NO_2-SP shifts from 452 nm in hexane to 534 nm in diethyl ether and further to ca. 700 nm in acetonitrile. Thus, the Stokes shift between the absorption and fluorescence is very much larger in acetonitrile (nearly 11000 cm^{-1}) than in hexane (nearly 3800 cm^{-1}) to show that $^{1}t^{*}$ of NO_2-SP is highly stabilized in acetonitrile. The quantum yields of fluorescence were 0.040 and 0.001 in hexane and acetonitrile, respectively. The difference of the dipole moment between the lowest singlet excited state (S_1) and the ground state (S_0) of NO_2-SP is estimated as large as 29 D by Mataga-Lippert plots[4)] assuming the cavity radius as 750 pm.[5)] Therefore, the above findings indicate that in the singlet excited state of trans-NO_2-SP intramolecular charge transfer (ICT)[5,6)] occurs from the pyrene ring to the NO_2-C_6H_4 group.

As to the effect of polar solvents on the isomerization of nitro-substituted arylethenes on direct irradiation, $\Phi_{t\rightarrow c}$ for 4-nitrostilbene is slightly decreased from 0.50 in benzene to 0.39 in methanol, [7a)] and that for 1-[2(4-nitrophenyl)ethenyl]naphthalene (1-naphthyl-CH=CH-C_6H_4-NO_2) is reduced from 0.45 in cyclohexane to 0.08 in acetonitrile.[7b)] Therefore, the effect of acetonitrile is extraordinarily remarkable in the present NO_2-SP to suppress completely the isomerization from trans to cis.

These facts strongly suggest that in acetonitrile $^{1}t^{*}$ of trans-NO_2-SP quickly relaxes to ICT state situated only nearly 40 kcal mol^{-1} (assumed from the fluorescence maximum at ca. 700 nm) over the ground state of the corresponding configuration, which suppresses either twisting of the double bond to $^{1}p^{*}$ or the intersystem crossing to $^{3}t^{*}$ and reduces the efficiency of trans-to-cis isomerization.

The present dramatic effect of acetonitrile is attributable to higher degree of intramolecular charge transfer in the singlet excited state of trans-NO_2-SP than in those of nitro-derivatives of stilbene and styrylnaphthalene, reflecting the magnitude of the extension of the conjugated systems composing from aromatic rings of different size.

The authors thank Ministry of Education, Science and Culture for their Grant-in-Aid for Specially Promoted Research No. 03101004 (K. T. and T. A.) for the support of this work.

References

1) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, H. Furuuchi, H. Zeng, H. Sakuragi, and K. Tokumaru, *Pure Appl. Chem.*, **60**, 989 (1988); K. Tokumaru and T. Arai, *J. Photochem. Photobiol. A: Chem.*, **65**, 1 (1992); T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993).

2) H. Okamoto, T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **63**, 2881 (1990); Y. Kikuchi, H. Okamoto, T. Arai, and K. Tokumaru, *Chem. Lett.*, **1993**, 833.

3) NO_2-SP exhibited broad T-T absorption spectra at 500-720 nm with peaks at 640 nm in hexane and 680 nm in CH_3CN. Φ_{isc} values were determined by comparing the initial absorbance of T-T absorption on direct excitation as well as camphorquinone sensitization using anthracene as a reference.[2)]

4) N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **29**, 465 (1956); E. Lippert, *Z. Elektrochem.*, **61**, 962 (1957).

5) Y. Maeda, T. Okada, and N. Mataga, *J. Phys. Chem.*, **88**, 2714 (1984).

6) W. Rettig, W. Majenz, R. Lapouyade, and G. Haucke, *J. Photochem. Photobiol. A: Chem.*, **62**, 415 (1992).

7) a) D. Schulte-Frohlinde and H. Görner, *Pure Appl. Chem.*, **51**, 279 (1979); b) H. Görner, F. Elisei, U. Mazzucato, and G. Galiazzo, *J. Photochem. Photobiol. A: Chem.*, **43**, 139 (1988).

(Received July 19, 1993)