Solvent Polarity Effect on *trans–cis* Photoisomerization and Fluorescence of Methyl 2-Naphthylacrylate

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Summary With increase of solvent polarity, the quantum yield of *trans* to *cis* isomerization of methyl 2-naphthylacrylate increased while the fluorescence quantum yield decreased.

SOLVENT polarity effects on *trans–cis* isomerizations have not been demonstrated except for 'push–pull' substituted stilbenes.[1–4] For such molecules having a large dipole moment in the ground state, the quantum yield of *trans* to *cis* isomerization was extremely small in polar solvent owing to stabilization of excited *trans* isomers. We found the opposite tendency for the isomerization of methyl 2-naphthylacrylate in polar solvents.

Figure 1 shows the quantum yield of *trans* to *cis* isomerization (ϕ_{t-c}) and fluorescence (ϕ_f) of methyl 2-naphthylacrylate in various solvents. In cyclohexane, ϕ_{t-c} is fairly small (0·22) and increases with increase of the solvent polarity (0·37 in methanol). The reverse is observed for ϕ_f; ϕ_f is large in cyclohexane (0·61) and decreases with increase of the solvent polarity (0·19 in acetonitrile)

Oxygen in the air had very little effect on the isomerization although it quenched the fluorescence strongly (Figure 1). However, saturation with pure oxygen increased ϕ_{t-c} from 0·22 to 0·30 in cyclohexane. Enhancement of isomerization by oxygen has been observed in the case of styrylnaphthalenes.[5] There it was considered that O_2 ($^3\Sigma^-_g$) increased the population of the triplet state by quenching the singlet state, owing to direct intermolecular

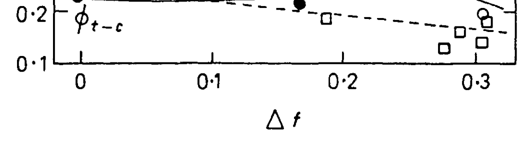

FIGURE 1. Effect of solvent polarity on the quantum yield of *trans–cis* isomerization and fluorescence of methyl 2-naphthylacrylate. ●, ϕ_{t-c}, *trans* to *cis* isomerization. Concentration *ca.* 8×10^{-5} mol/l, conversion <3%. (Isomerization is the only photochemical process at this concentration. Other reactions were not observed, even after the *trans–cis* photostationary state was attained.) Irradiation with 313 nm light in air; potassium ferrioxalate was used for actinometry. ○, ϕ_f in argon-saturated solution. □, ϕ_f in the air. 2-(1-naphthyl)-5-phenyloxazole was used as a standard (J. B. Birks, 'Photochemistry of Aromatic Molecules,' Wiley, New York, p. 136). Δf is the solvent polarity parameter: $(\epsilon-1)/(2\epsilon+1)-(n^2-1)/(2n^2+1)$, where ϵ and n are dielectric constant and refractive index of the solvent respectively. a: cyclohexane, b: Et_2O, c: EtOAc, d: tetrahydrofuran, e: Pr^iOH f: EtOH, g: MeCN, h: MeOH.

exchange interaction or the inhomogeneous field of O_2 ($^3\Sigma^-_g$). The heavy atom solvent n-propyl bromide quenched the fluorescence strongly and enhanced the isomerization.[6] The triplet quencher, ferrocene (8×10^{-4} mol/l), quenched the isomerization.[3,7]† These facts suggest that the isomerization takes place from the triplet state.

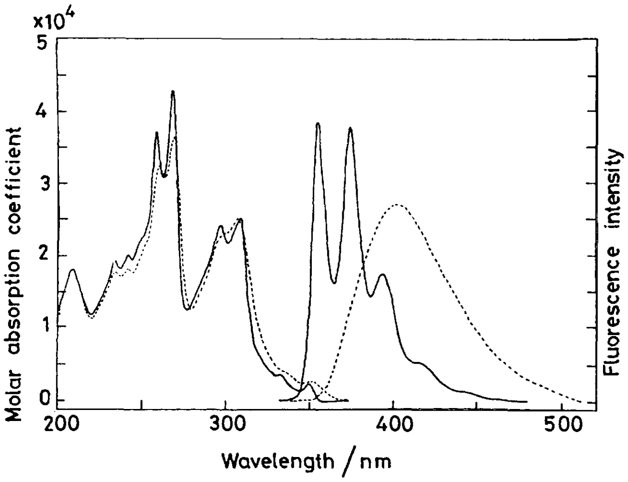

FIGURE 2. Absorption and fluorescence spectra of methyl 2-naphthylacrylate. —— in cyclohexane, - - - - - - in MeOH.

Figure 2 shows the absorption and fluorescence spectra in cyclohexane and in methanol. Since the fluorescence spectrum in cyclohexane is a good mirror image of the absorption spectrum, the lowest singlet state is thought to be near 353 nm (28,400 cm^{-1}). It resembles the ^1L_b state of naphthalene in the weakness of the absorption and in the long-lifetime of the fluorescence (107 ns in cyclohexane from quenching of the fluorescence by aerobic oxygen).

In methanol and other polar solvents, a large Stokes' shift is observed. The fluorescence maximum is shifted to 400 nm. This indicates that the dipole moment of the fluorescence state in polar solvents is larger than that in cyclohexane and that the separation between singlet and triplet states may be small in polar solvents.

The above solvent effect leads to the conclusion that the efficiency of intersystem crossing may be larger in polar solvents than in non-polar solvents for this molecule, in contrast to molecules having a large dipole moment in the ground state such as the 'push-pull' substituted stilbenes and *p*-dimethylaminocinnamonitrile.[8] For these molecules the efficiency of intersystem crossing was considered to be small in polar solvents.[2]

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† The stability of ferrocene was confirmed by monitoring its absorption at 440 nm during the irradiation.

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