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One-way Photoisomerization of the C=N Double Bond. Isomerization of (*Z*)-*N*-Methoxy-1-(2-anthryl)ethanimine

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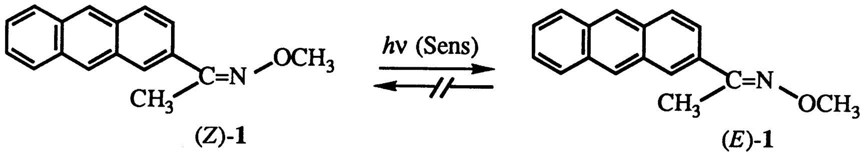
On triplet sensitized excitation *N*-methoxy-1-(2-anthryl)ethanimine underwent Z→E one-way isomerization, while no reverse isomerization took place. Photostationary state isomer compositions, quantum yields, and transient absorption spectra indicate an adiabatic quantum chain process in the isomerization as proposed for 2-anthrylethylenes.

Despite the active interest in photoisomerization of the carbon nitrogen double bond, only a few molecules were studied.[1)] Oxime ethers of aromatic ketones such as *N*-methoxy-1-phenyl- and *N*-methoxy-1-(2-naphthyl)ethanimine were reported to undergo mutual isomerization in the triplet state, therefore, giving a photostationary mixture of E and Z isomers.[2)] Our findings that substituents on the ethylenic carbons of aromatic olefins strongly affect the mode of isomerization, one-way or two-way,[3)] led us to investigate the effects of aromatic substituents on the photoisomerization of C=N double bonds.

The E and Z isomers of *N*-methoxy-1-(2-anthryl)ethanimine (**1**) are stable at room temperature in the dark.[4)] However, on benzil (2.0×10^{-2} M, M=mol dm^{-3})-sensitized irradiation with 435-nm light[5)] in degassed benzene (*Z*)-**1** (2.1×10^{-3} M) isomerized to the corresponding E isomer, while the E isomer gave no Z isomer after prolonged irradiation. The quantum yield for Z→E isomerization of **1** was determined as high as 11 (quantum chain process)[3)] at a (*Z*)-**1** concentration of 2.0×10^{-3} M.



(*Z*)-**1** (*E*)-**1**

Laser flash photolysis[6)] of **1** (1.1×10^{-2} M) in benzene in the presence of benzil (2.1×10^{-2} M) under argon at room temperature afforded transient absorption spectra consisting of strong bands at 445 and 420 nm and broad bands at 540 and 580 nm, as shown in Fig. 1. All bands decayed single-exponentially to give a lifetime of ca. 10 μs. Rates for energy transfer from triplet benzil to (*Z*)- and (*E*)-**1** were determined to be 4.1×10^{9} and 4.8×10^{9} M^{-1} s^{-1}, respectively, by monitoring the decay of T-T absorption of benzil in the presence of varying amounts of **1**. Under the present conditions the energy transfer from the benzil triplet to **1** will be completed within ca. 20 ns and, therefore, the spectrum observed at 0.8 μs after a laser pulse is ascribable to the **1** triplet. The same absorption spectra and decay profiles were observed for the Z and E isomers.

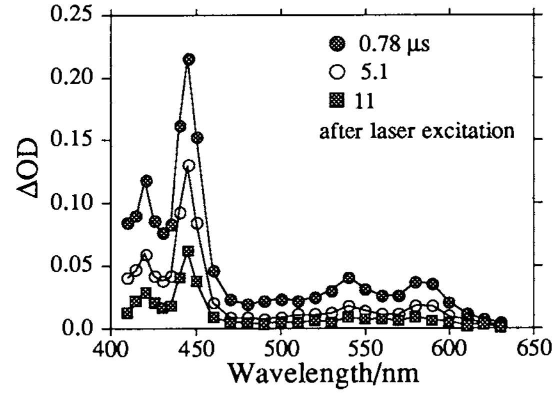


Fig. 1. Transient absorption spectra on laser excitation of (*E*)-**1**.

Taking into account the isomerization mode and the long triplet lifetime comparable with one-way isomerizing olefins,[3)] we can reasonably assign the observed transient to triplets with a planar E geometry.[7)] Thus, the triplet potential energy curve for twisting the C=N double bond is also modified by aromatic groups resulting in a change in the isomerization mode from two-way for *N*-methoxy-1-(2-naphthyl)ethanimine (**2**) to one-way for **1**. Lack of transient-spectroscopic evidence has made it difficult to determine the detailed mechanisms for photoisomerization of oxime ethers; however, the present compound provided clear evidence of T-T absorption with a very long lifetime assigned to the E triplets. The mutual isomerization of imino compounds such as **2** may proceed through twisting of the C=N double bond to give a perpendicular triplet ($^3P^*$) which will deactivate to the Z and E isomers. The deactivation from $^3P^*$ to the ground state must be faster than the detection limit of our nanosecond laser photolysis instrument, suggesting that the lifetime of $^3P^*$ is shorter than 20 ns. However, it is clear that the deactivation rate constant of the E triplet is similar to those of aromatic olefins, indicating no strong hetero-atom effects on the deactivation process.

It should be noted that the T-T absorption of a simple oxime ether was successfully observed for the first time and this observation strongly supports the rotational mechanism for isomerization of the C=N double bond.

References

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4) The structure was identified on the basis of ^1H and ^{13}C NMR spectra; see, G. W. Buchanan and B. Dawson, *Can. J. Chem.*, **55**, 1437 (1977).

5) The 435-nm light was isolated from a 400-W high pressure mercury lamp through a filter solution of $CuSO_4+NaNO_2+NH_4OH$ in water.

6) Laser flash photolyses were performed by using an excimer laser(XeCl)-pumped dye laser exciting at 425 nm (Stilbene 3).

7) The spectrum was quenched by oxygen with a rate constant of 2.8×10^9 M^{-1} s^{-1} and resembles T-T absorption spectra of 2-acetyl- and 2-vinylanthracene.[3b)]

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