Tetrahedron Letters No. 31, pp 2815 - 2818.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/0729-2815$02.00/0

PHOTOCHEMISTRY OF NON CONJUGATED BICHROMOPHORIC SYSTEMS

PHOTOCYCLOMERIZATION OF DI-(α-NAPHTHYLMETHYL)ETHER

R. Todesco, J. Gelan, H. Martens, J. Put *
Limburgs Universitair Centrum, Universitaire Campus, B 3610 Diepenbeek, Belgium

N. Boens, F.C. De Schryver *
Department of Chemistry, University of Leuven, Celestijnenlaan 200 F, B 3030 Heverlee, Belgium

(Received in UK 25 May 1978; accepted for publication 2 June 1978)

During a study of the fluorescence of various α,ω-dinaphthylalkanes designed to yield information about the geometrical requirements for intramolecular excimer formation, Chandross and Dempster(1,2) showed that irradiation of 1,3-di(α-naphthyl)propane resulted in only one intramolecular cycloaddition product. This cyclomer underwent thermal Cope-rearrangement to a cyclobutane isomer. The authors assumed that the intramolecular cyclomerization occured via an excimer. Davidson and Whelan(3) reported further evidence for this assumption.

In the intermolecular photodimerizations of naphthalene derivatives, reported up to now, endo- as well as exo-dimers are formed(4-11).

In the present paper we wish to report the results of a study of the fluorescence behavior and the intramolecular photocycloaddition of di-(α-naphthylmethyl)ether, I. This photoreaction leads to both the endo-cyclomer, IIa, and the exo-cyclomer, III, (figure 1).

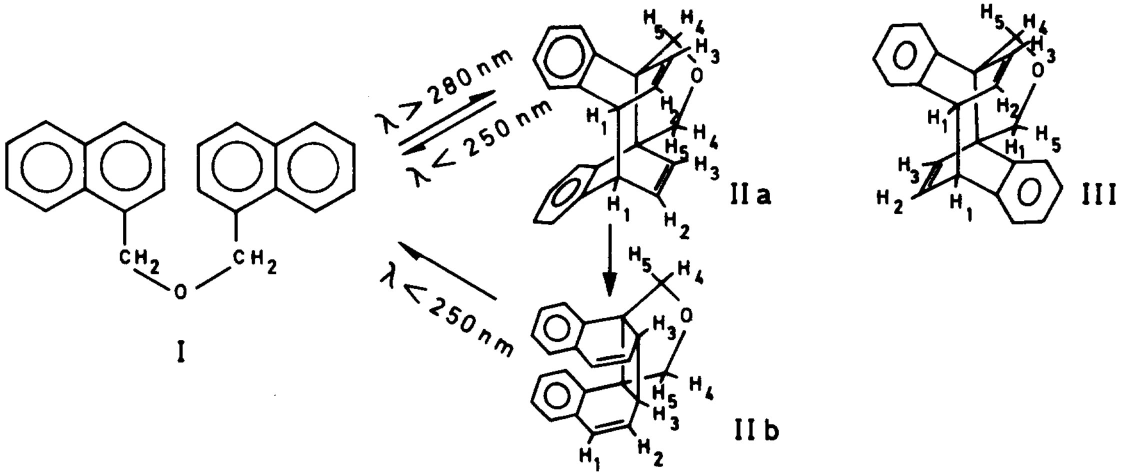

figure 1

IIa is thermally unstable at room temperature and undergoes a Cope-rearrangement to IIb, while III is stable under the reaction conditions(12).

The photocycloaddition was performed by irradiation of a degassed dilute solution (10^{-3}M) of I in iso-octane, dichloromethane or acetonitrile, for 10 hours at room temperature in a Rayonet RS preparative photochemical reactor equipped with 8 RUL-3000 Å lamps. No attempt was made to separate the isomers IIa and III. After irradiation, the solution was refluxed for two hours, and evaporated under reduced pressure. The residue was chromatographed on silica using benzene as eluent. A mixture of IIb and III was collected and after fractional crystallization from benzene pure IIb (colorless needles, M.P. 178-180°C) was obtained. Upon addition of pentane to the filtrate colorless needles of III (M.P. 144-146°C) precipitated. By irradiation of the original unheated reaction mixture at wavelengths below 254 nm, the reverse photoreaction occurs, yielding I. The same observation is made on irradiation of III and IIb in ethanol or chloroform. Both IIb and III revert to I upon melting.

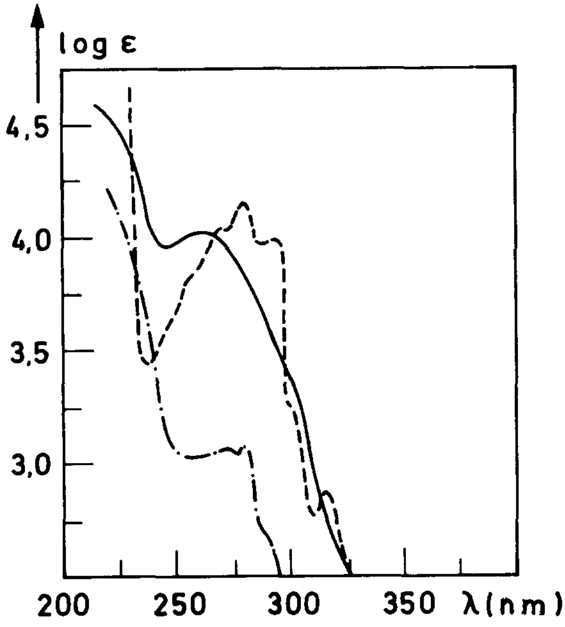

figure 2 : Ultraviolet absorption spectra of I (---), IIb (——) and III (.-.-.-) in 95% ethanol.

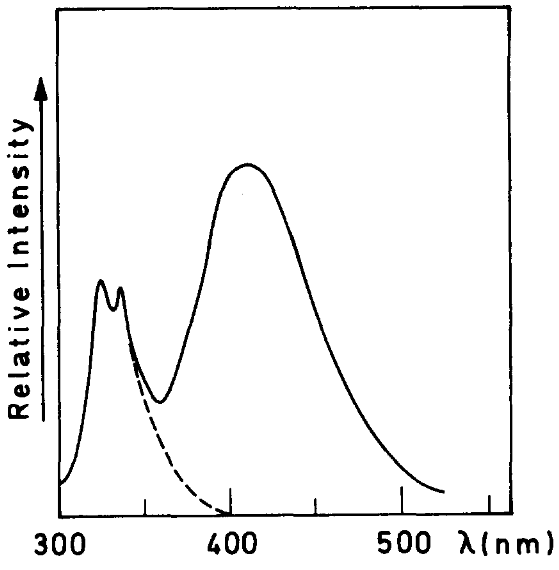

figure 3 : Emission spectra of (α-naphthylmethyl)ethyl ether ($2\text{x}10^{-4}$M) (---) and I (10^{-4}M) (——) in iso-octane solution ($\lambda_{excit.}$ = 305 nm).

The mass spectrum of IIb shows a molecular ion peak at m/e 298, indicating the intramolecular character of the photoreaction. The ultraviolet spectrum (figure 2) is similar to that of 1,2-dihydronaphthalene(13)(14). The hypochromism(15) is attributed to interactions between the two chromophores.

The mass spectrum of III has a molecular ion peak at m/e 298 and the UV spectrum (figure 2) resembles closely that of 2,3-dihydronaphthalene. Further evidence for the structure of IIa, IIb and III was obtained from the nmr spectra which are summarized in table 1. As no attempt was made to separate IIa from III, the spectrum of the mixture was recorded. Knowing the spectrum of pure III, the remaining peaks could be assigned to IIa.

table 1 : nmr data (δ values) for IIa, IIb and III ($CDCl_3$/TMS)

	H_1	H_2	H_3	H_4 H_5	Aryl
IIa	3.8;m;2H	6.5;m;2H	6.2;d;2H;J=8Hz	3.8;d;2H;J=10Hz 4.78;d;2H;J=10Hz	6.70;m;8H
IIb	6.31;d;2H;J=10Hz	5.71;d of d;2H J_{2-3}=6Hz;J_{2-1}=10Hz	3.6;m;2H	4.23;s;4H	6.93;m;8H
III	3.85;m;2H	6.0;d of d;2H J_{2-3}=8Hz;J_{2-1}=8Hz	5.63;d;2H;J=8Hz	3.92;d;2H;J=10Hz 4.70;d;2H;J=10Hz	7.23;m;8H

s = singulet; d = doublet; m = multiplet

The spectra of IIa and IIb are comparable with those of the photodimer of 1,3-di-(α-naphthyl)propane and its Cope-rearranged product(1,2), as far as the ring protons are concerned. For the elucidation of the structure of III, it is particularly interesting to compare its nmr spectrum with that of IIa. As expected the more highly shielded H_2 and H_3 protons of III appear upfield as compared with the corresponding protons of IIa. On the other hand there is a striking difference between the peaks associated with the aryl protons in the exo- and endo-forms. In the endo isomer, these protons are rigidly held in the field of the transannular arylgroup and are shifted significantly upfield, while in the exo isomer, these aryl protons experience less shielding. It is worth noting that the aryl protons in IIb are less shielded than those in IIa.

The fluorescence spectrum of a 10^{-4}M iso-octane solution of I (figure 3) shows, besides the emission from a locally excited naphthalene, a new structureless red-shifted band, attributed to an excimer(3). Quantum yields of monomer fluorescence, Φ_{FM}, excimer fluorescence, Φ_{FE} and photocyclomerization, Φ_R, as well as the endo/exo ratio in different solvents at 20°C are summarized in table 2. The ratio of the excimer to monomer emission is temperature dependent. An energy of activation for the formation of the excimer I of 17.6 kJ can be obtained from the plot of ln Φ_{FE}/Φ_{FM} as a function of 1/T.

The quantum yield for exo cyclomerization is the same in all solvents, while $\Phi_{R\ endo}$ on the contrary increases with solvent polarity. This increase is accompanied by a decrease in the quantum yield of excimer fluorescence. This further supports the view that the excimer lies on the reaction pathway(16)(3).

table 2 : quantum yields in various solvents at 20°C

Solvent	$\Phi_{FM}^{(a)}$	$\Phi_{FE}^{(a)}$	$\Phi_{R}^{(b)}$	endo/exo	$\Phi_{R\ endo}$	$\Phi_{R\ exo}$	$\Phi_{FE} + \Phi_{R\ endo}$
Iso-octane	0.010	0.037	0.030	1.00	0.015	0.015	0.052
CH_2Cl_2	0.011	0.027	0.033	1.70	0.021	0.012	0.048
CH_3CN	0.010	0.023	0.037	1.85	0.024	0.013	0.047

(a) $[I] = 10^{-4}M$, degassed (b) $[I] = 2\times10^{-4}M$, conversion < 10%, degassed

The sum of the measured relaxation pathways of the excimer, $\Phi_{FE} + \Phi_{R\ endo}$, is nearly constant. This suggests that the change in the endo/exo ratio reflects an influence of solvent on the relaxation behavior of the excimer.

The detailed study of the dynamics of the system will be published separately.

Acknowledgements

The Ministry of Scientific Programming, the University of Leuven Research Fund and the Belgian National Science Foundation are thanked for financial assistance. N.B. is indebted to the N.F.W.O. for a post-doctoral fellowship.

References

1. E.A. Chandross and C.J. Dempster, J. Amer. Chem. Soc. 92, 3586 (1970).
2. E.A. Chandross and C.J. Dempster, J. Amer. Chem. Soc. 92, 703 (1970).
3. R.S. Davidson and T.D. Whelan, J. Chem. Soc. Chem. Comm., 11, 361 (1977).
4. J.S. Bradshaw and G.S. Hammond, J. Amer. Chem. Soc. 85, 3953 (1963).
5. J.S. Bradshaw, N.B. Nielsen and D.P. Rees, J. Org. Chem., 33, 259 (1968).
6. M. Sterns and B.K. Selinger, Aust. J. Chem. 21, 733 (1968); 21, 2131 (1968).
7. W.H.F. Sasse, P.J. Collin, D.D. Roberts and G. Sugawolz, Aust. J. Chem., 24, 2339 (1971).
8. B.K. Selinger and M. Sterns, Chem. Comm., 978 (1969).
9. T. Teitei, D. Wells and W.H.F. Sasse, Tetrahedron Lett., 367 (1974).
10. T. Teitei, D. Wells and W.H.F. Sasse, Aust. J. Chem. 29, 1783 (1976).
11. T. Teitei, D. Wells and W.H.F. Sasse, Aust. J. Chem. 31, 85 (1978).
12. W.E. von Doering and W.R. Roth, Tetrahedron, 18, 67 (1962).
13. W. Hückel, E. Venera and U. Worffel, Chem.Ber. 90, 901 (1957).
14. D.J. Cram, N.L. Allinger and H. Steinberg, J. Amer. Chem. Soc., 76, 6132 (1954).
15. J.N. Murell, "The Theory of the Electronic Spectra of Organic Molecules", J. Wiley and Sons, New York, N.Y. 1963, chapter 7.
16. N. Boens, M. De Brackeleire, J. Huybrechts and F.C. De Schryver, Zeit.für Phys. Chem., Neue Folge, Bd. 101, 427 (1976).