

PHOTOCHEMISTRY OF NON-CONJUGATED BICHROMOPHORIC SYSTEMS. PHOTOCYCLOMERIZATION  
OF 1,1' AND 2,2' LINKED DIANTHRACENES

F.C. De Schryver<sup>\*</sup>, M. De Brackeleire, S. Toppet and M. Van Schoor  
Dept. Scheikunde, Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Heverlee,  
Belgium

(Received in UK 15 February 1973; accepted for publication 2 March 1973)

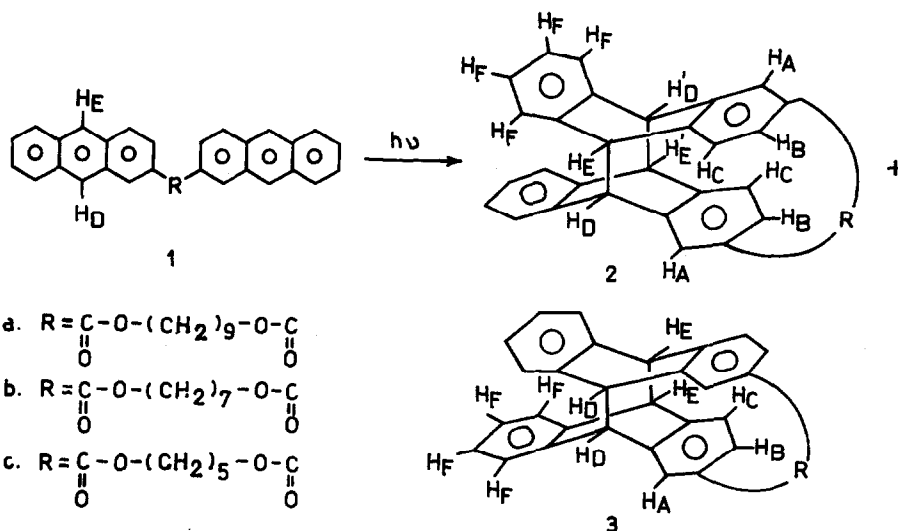
We recently <sup>(1)</sup> stated that the feasibility of an intramolecular photocycloaddition in a suitably chosen non-conjugated bichromophoric system depends on the probability of reaching, within the lifetime of the excited state involved, a conformation favorable for reaction, and on the stability of this conformation.

We wish to report the first example in which one of the factors influencing this stability is clearly demonstrated. It has been shown that 9,9'-linked dianthracenes react intramolecularly on irradiation only if the number of bonds in the link does not exceed three <sup>(2a-d)</sup>. 9,9' Linked dianthracenes with a longer chain do not react intra- but intermolecularly <sup>(3)</sup> even at high dilution. However dianthracenes linked at the 1 or 2 positions can be photochemically cyclomerized.

Compounds *1a-c* <sup>(4)</sup> were synthesized by condensation of equimolar amounts of 2-anthroylchloride and the respective diol in benzene in the presence of pyridine. After evaporation of the solvent the residue is purified by column chromatography (aluminum, CHCl<sub>3</sub> eluent) and subsequently by recrystallization from a CHCl<sub>3</sub>-MeOH mixture. (*1a* yield 60%, m.p. 156-157°C; *1b* yield 70%, m.p. 168°C; *1c* yield 70%, m.p. 172°C). In nmr (CDCl<sub>3</sub>) absorption of the meso protons was observed at 8.5δ (H<sub>d</sub>) and 8.4δ (H<sub>c</sub>) for *1a* and *1b* and at 8.4δ (H<sub>d</sub>) and 8.24δ (H<sub>c</sub>) for *1c*. Irradiation <sup>(5)</sup> of *1a* could in principle result in the formation of four cycloimers: the syn head-to-head, syn head-to-tail, anti head-to-head and anti head-to-tail adducts. The last possibility can, however, be excluded on the basis of molecular models. From the reaction mixture two products *2a* and *3a* were isolated (column chromat. florisil, dichloromethane) in 60% yield <sup>(6)</sup> for which the intramolecular nature of the addition was proved by mass spectroscopy (M<sup>+</sup> 568) and by vapor pressure osmometry in CHCl<sub>3</sub> (MW = 575). They were separated by preparative thin-layer chromatography on silica gel with CHCl<sub>3</sub> as eluent.

Compound **2a** (m.p. 235°C) showed the following nmr characteristics in  $\text{CDCl}_3$  :  $H_A$  7.65 $\delta$  d,  $H_B$  7.51 $\delta$  q,  $H_C$  7.01 $\delta$  d,  $H_F$  6.8-7.10 $\delta$  m,  $H_E$  and  $H_D$  4.64 $\delta$  s. The absence of the typical absorptions for the meso protons in nmr indicated that the reaction occurred at the 9,9', 10,10' positions.

On addition of Eufod the following shifts were observed :  $H_A$  11.95 $\delta$ ,  $H_B$  10.45 $\delta$ ,  $H_C$  8.1 $\delta$ ,  $H_F$  6.4-7 $\delta$ ,  $H_D$  and  $H_E$  4.82 $\delta$  and 4.50 $\delta$ . AA'BB' pattern with  $[J_{ED} + J_{ED'}] = 11$  cps.



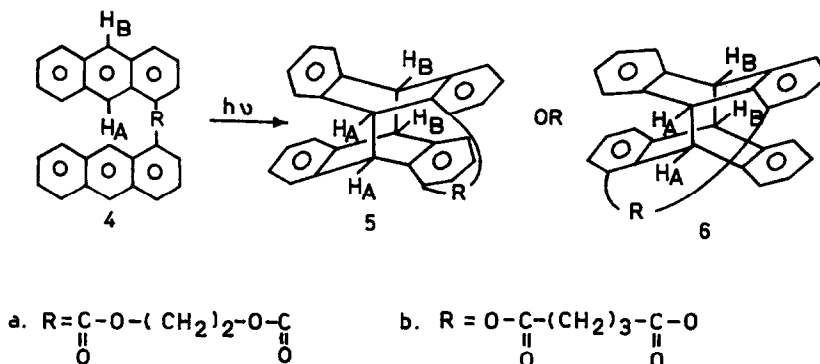
The coupling observed between  $H_E$  and  $H_D$  upon addition of Eufod indicated a head-to-tail structure which has to have a syn stereochemistry (vide supra). Compound **3a** (m.p. 211°C); in  $\text{CDCl}_3$   $H_A$  7.57 $\delta$  d,  $H_B$  7.55 $\delta$  q,  $H_C$  7.01 $\delta$  d,  $H_F$  6.7-7 $\delta$  m,  $H_D$  4.66 $\delta$  s,  $H_E$  4.61 $\delta$  s) must have a head-to-head regiochemistry since on addition of Eufod no coupling between adjacent bridgehead protons was observed ( $H_A$  8.65 $\delta$ ,  $H_B$  8.8 $\delta$ ,  $H_C$  7.25 $\delta$ ,  $H_F$  6.7-7 $\delta$ ,  $H_D$  4.92 $\delta$ ,  $H_E$  4.78 $\delta$ ). A syn stereochemistry is proposed since the  $H_F$  protons, in analogy with **2a**, do not shift to a lower field upon addition of Eufod.

Irradiation of **1b** resulted in the quantitative formation of cyclomers **2b** and **3b** ( $M^{\ddagger}$  540) in 1:3 ratio <sup>(7)</sup>, based upon the tertiary bridgehead protons in nmr, while photolysis of **1c** led to the exclusive formation of **3c** (m.p. 263°C; nmr in  $\text{CDCl}_3$   $H_D$  4.64 $\delta$  s,  $H_E$  4.58 $\delta$  s;  $M^{\ddagger}$  512).

Compound **4a** was synthesized by condensation of an equimolar amount of 1-anthroyl-chloride and ethylene-1,2-diol in benzene in the presence of pyridine, while **4b** was obtained by condensation of 1-anthrol and propaan-1,3-diacidchloride in analogous reaction conditions. The products were isolated and purified as mentioned above. (**4a** yield 70%, m.p. 151°C; **4b** yield 60%, m.p. 166.5°C). The nmr absorptions of the meso protons occurred at 9.58 $\delta$  ( $H_A$ ) and 8.45 $\delta$  ( $H_B$ ) for **4a** and at 8.45 $\delta$  ( $H_A, H_B$ ) for **4b** in  $CDCl_3$ .

Irradiation of **4a** gives in quantitative yield one product for which structure **5a** or **6a** can be proposed (m.p. > 350°C,  $M^+$  470, vapor pressure osmometry 474). Nmr analysis indicated a head-to-head regiochemistry (in  $CDCl_3$   $H_A$  5.55 $\delta$  s,  $H_B$  4.55 $\delta$  s) but did not give clear cut evidence for anti or syn addition although the latter is more probable on the basis of molecular models.

Irradiation of **4b** led to exclusive formation of one product (m.p. 279°C,  $M^+$  498, vapor pressure osmometry 499) with a head-to-head regiochemistry ( $CDCl_3$   $H_A$  5 $\delta$  s,  $H_B$  4.55 $\delta$  s) for which structure **5b** or **6b** is proposed. Again no definite choice between syn and anti addition could be made to date.



Preliminary quantitative measurements of the photochemical properties of **1c** in  $CH_2Cl_2$  gave a value for the quantum yield of cyclomerization,  $\phi_c$ , equal to  $0.107 \pm 0.003$ , and the quantum yield of fluorescence,  $\phi_f$ , is  $0.16 \pm 0.01$ . The cyclomer **3c** could be converted back into **1c** upon irradiation at 310 nm with a quantum yield,  $\phi_r$ , of  $0.98 \pm 0.03$ .

These results indicate that, in accord with the statement above, intramolecular cyclomerization is possible, even for long chains, if the link separating the two chromophores is not attached to a carbon that is going to form a bond.

*Acknowledgements : The financial aid of the Nationaal Fonds voor Wetenschappelijk Onderzoek is gratefully acknowledged.*

#### References

- (1) J. Put and F.C. De Schryver, J.Amer.Chem.Soc. 93, 137 (1973)
- (2) a. F.D. Greene, J.L. Misnock and J.R. Wolfe, J.Amer.Chem.Soc. 77, 3852 (1955)  
b. F.D. Greene, Bull.Soc.Chem.France, 1356 (1960)  
c. D.E. Applequist, M.A. Lintner and R. Searle, J.Org.Chem. 33, 254 (1968)  
d. I. Roitt and W. Waters, J.Chem.Soc. 2695 (1967)  
e. N. Wenschuker and F.D. Greene, J.Amer.Chem.Soc. 90, 506 (1968)  
f. J.H. Golden, J.Chem.Soc. 3741 (1961)  
g. R. Livingston and Kei Sin Wei, J.Amer.Chem.Soc. 89, 3098 (1967)  
h. S. Kaupp, Angew.Chem. Int.Ed. 11, 394 (1972)
- (3) F.C. De Schryver, L. Anand, G. Smets and J. Switten, J.Pol.Sci. 9, 777 (1971)
- (4) All new compounds gave correct elemental analyses.
- (5) All preparative irradiations are carried out at  $5 \cdot 10^{-3}$  molar concentrations in degassed  $\text{CH}_2\text{Cl}_2$  in a Rayonet Reactor using RUL 3500 Å lamps with a cut-off filter at 340 nm.
- (6) 40% of the starting material did react intermolecularly under the reaction conditions.
- (7) The two isomers were not separated.