

## Short Communication

## Photochemical Diels-Alder dimerization of 9-phenylethynylantracene

HANS-DIETER BECKER and KJELL ANDERSSON

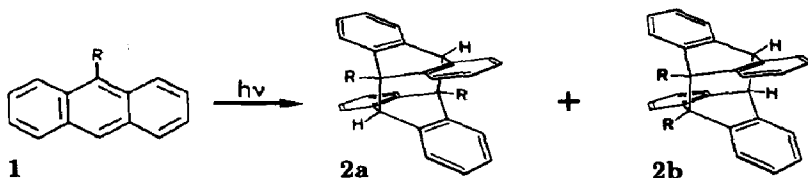
*Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg (Sweden)*

(Received December 21, 1983)

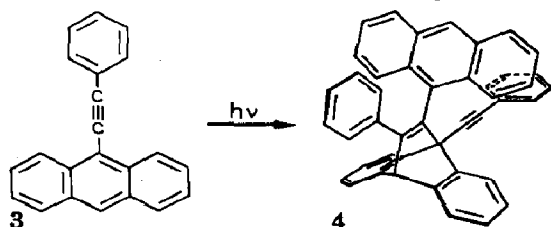
Irradiation of 9-phenylethynylantracene in benzene solution leads to a dimer whose formation involves the intermolecular Diels-Alder addition of an ethynyl moiety to the central ring of the anthracene system. The regiochemistry of the addition is governed by a centrosymmetric orientation complex.

*1. Results and discussion*

Anthracene and numerous 9-substituted anthracenes **1** readily undergo photochemical dimerization by  $4\pi + 4\pi$  cycloaddition to give dianthracenes **2** [1, 2] (e.g. R  $\equiv$  methyl):



We have now found, however, that the photochemical dimerization of 9-phenylethynylantracene **3** takes an unexpectedly different course. Irradiation of **3** in benzene solution ( $\lambda > 392$  nm) smoothly affords the Diels-Alder dimer **4** in about 70% yield:



The 270 MHz  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of the photoproduct (see Section 2) is in agreement with a Diels-Alder dimer resulting from the addition of the acetylenic bond to the anthracene moiety. Likewise, the electronic absorption spectrum of the photodimer is indicative of the presence of the 9-( $\beta$ -styryl)anthracene chromophore (Fig. 1) [3].

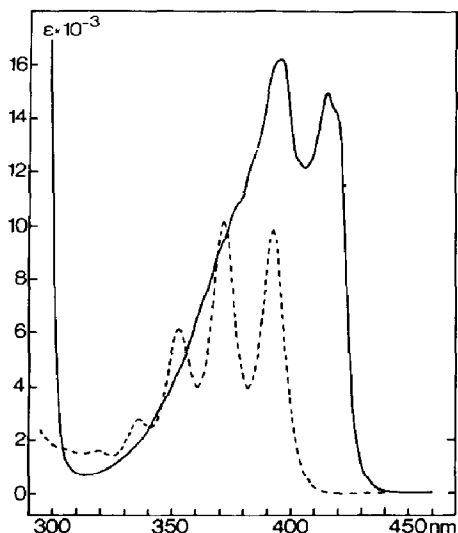
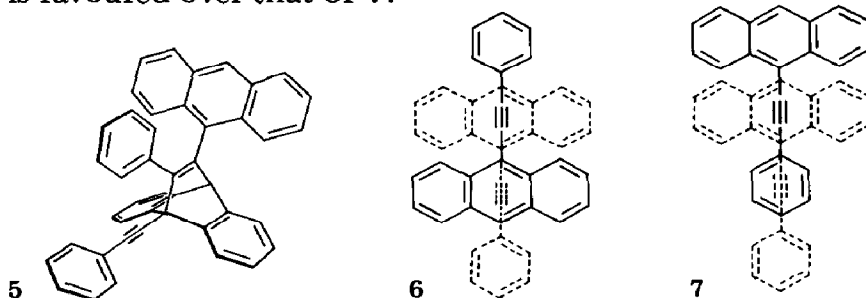


Fig. 1. Electronic absorption spectra of 9-phenylethynylantracene (—) and its photodimer (---) in cyclohexane.

However, as these data also agree with the regio-isomeric structure 5, the unambiguous decision in favour of 4 has been made by means of an X-ray diffraction analysis of the photodimer. The formation of 4, rather than 5, suggests that the formation of the centrosymmetric orientation complex 6 is favoured over that of 7:



The photochemical dimerization of 3 leading to 4 is remarkable in so far as photochemical additions of acetylenes to anthracenes appear to be unknown. Our own attempts to add acetylene or diphenylacetylene to photoexcited anthracene left the acetylenes unchanged and gave dianthracene (2;  $R \equiv H$ ) exclusively. We believe therefore that the photochemical dimerization of 9-phenylethynylantracene proceeds predominantly by  $4\pi + 2\pi$  rather than  $4\pi + 4\pi$  addition because electronic excitation is not limited to the anthracene chromophore but, by way of conjugation (*cf.* Fig. 1), also involves its dienophilic ethynyl substituent [4].

## 2. Experimental details: photochemical dimerization of 9-phenylethynylantracene

A solution of 9-phenylethynylantracene [3] (400 mg) in benzene (180 ml) was irradiated for 1.5 h with light of wavelengths greater than

392 nm (immersion well apparatus; 10 °C; nitrogen atmosphere; Philips HPK 125 W high pressure mercury lamp; filter solution of 150 g of potassium nitrite in 1000 ml of water of 1 cm path length). The solid yellowish brown residue obtained on vacuum evaporation of solvent was recrystallized from methylene chloride solution by addition of *n*-hexane to give 333 mg (83%) of pale yellow crystals which, according to <sup>1</sup>H NMR analysis, consisted mainly (90%) of the 4π + 2π dimer. Separation of the 4π + 2π dimer from the byproduct (10%) believed to be an intermolecular 4π + 4π cycloadduct was accomplished by slow recrystallization from warm methylene chloride solution containing methanol. The pure 4π + 2π dimer 4 forms almost colourless crystals (melting point, around 315 °C). 270 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>) gave the following results: δ = 5.71 ppm (singlet; 1 H); δ = 6.45 - 7.90 ppm (multiplet; 26 H); δ = 8.31 ppm (singlet; 1 H). The results of analysis were 94.62% C and 5.07% H. C<sub>44</sub>H<sub>28</sub> requires 94.93% C and 5.07% H.

We are gratefully indebted to Professor A. H. White, University of Western Australia, for the X-ray diffraction analysis of 4.

- 1 T. Wolff, N. Müller and G. von Büнау, *J. Photochem.*, 22 (1983) 61.
- 2 H. Bouas-Laurent, A. Castellan and J.-P. Desvergne, *Pure Appl. Chem.*, 52 (1980) 2633.
- 3 H.-D. Becker and K. Andersson, *J. Org. Chem.*, 48 (1983) 4542.
- 4 D. R. Maulding and B. G. Roberts, *J. Org. Chem.*, 34 (1969) 1734.