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PHOTOCYCLIZATION OF BIS(9-ANTHRYL) 1,1,3,3-TETRAMETHYLDISILOXANE, UNSYMMETRICAL PHOTODIMERIZATION OF THE ANTHRACENE RING.

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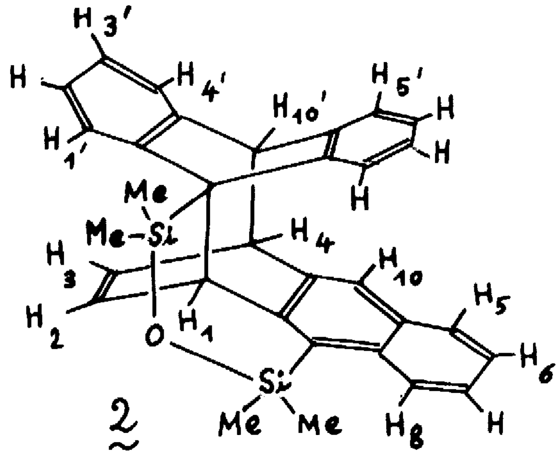
In a study of photochromic systems based on aromatic hydrocarbons photodimerization[1] we examined compounds of type A-a-b-c-A where A is 9-anthryl and a, b, c are atoms or groups of atoms[2] ; the three member chain was chosen as providing the best overlap between the two aromatic moieties in the sandwich excimer[3]. When a = c = CH_2 and b = O, the compound (bis(9-anthryl) methyl oxide) smoothly cyclomerizes under U.V. light but we could not clearly detect intramolecular excimer fluorescence emission at room temperature. We therefore prepared the title compound (1) with a chain 'a-b-c' crowded enough to allow the excimer fluorescence to compete with the photochemical reaction[4]. We report here the cyclomerization and fluorescence emission data of 1 as well as the structure determination of the cyclomer 2.

-PHOTOCYCLIZATION : An ether solution (100 cm^3) of 1 (100 mg : $\simeq 2 \times 10^{-3}$M) degassed by three freeze-pump-thaw cycles under high vacuum, was irradiated for 7 hr. in a Pyrex reactor with a 500 W high pressure mercury lamp. After solvent evaporation, addition of light petroleum precipitated 2 (white crystals, 80 % yield, m.p. $\simeq$ 180°C).

STRUCTURE OF THE CYCLOMER (2)



2

Nuclear magnetic resonance : proton NMR spectra were recorded with a BRUKER WH 270, ref TMS, at 20°C (50 scans), $CDCl_3$ being internal standard and solvent. Chemical shifts for aliphatic protons are as follows : δ ppm (apparent multiplicity) : H_1, 4.63 (d) ; H_2, 5.87 (t) ; H_3, 6.32 (t) ; H_4, 4.17 (t) ; $H_{10'}$, 4.34 (d) ; aromatic, 6.53-7.63 (m). In our case, precise assigment of the aromatic protons is not believed to be necessary.

The integrated area are in good agreement with formula 2. Due to lack of symmetry, the protons of the four methyl groups are not equivalent (δ(ppm) : 0.57 ; 0.58 ; 0.61 ; 0.74). By PMR double resonance experiments, successive irradiation of H_1, H_2, H_3, H_4 and $H_{10'}$ enabled to measure the following coupling constants : J (Hz) : H_1-H_2 (7.2) ; H_2-H_3 (7.6) ; H_3-H_4 (7.2) ; H_4-$H_{10'}$ (10.2) ; H_1-H_3 (0.5) ; H_2-H_4 (1.8).

The electronic absorption spectrum shows the presence of a naphthalene chromophore : λ_{max}(nm) (ε_{max}) in ether : 225 (4.67) ; 252 (4.56) ; 273 (8.82) ; 283 (3.75) ; 297 (3.71) ; 307 (3.54) ; 320 (2.98) ; 348 (2.82).

The mass spectrum (AEI, MS 12) exhibits the expected molecular peak at m/e : 486.

DISCUSSION Other bis anthracenes [1-2] photodimerize through meso bonds. The present result is the first example of photodimerization of the anthracene ring through vertices 1 and 4 ; this might be rationalized as follows : steric requirements of the bulky $SiMe_2$ groups prevent closure between the positions 9,10 and 9', 10' and probably also formation of a stable sandwich excimer; but the flexibility of the chain allow the formation of a staggered excimer (where the two aromatic rings are $\leqslant$4 Å apart) able to collapse to the cyclomer **2**. We observed that the reaction is slow compared to the cyclomerization of other bisanthracenes[2] ; it is in accordance with the existence of a structureless redshifted band (centered at λ = 500 nm) in addition to the normal anthracenic pattern in the fluorescence spectrum of **1** (in degassed ether, conc 10^{-5} M, 25°C) ; this emission, intense enough ($I_{obs.}$ (500 nm)/$I_{obs.}$ (400 nm) $\simeq$ 1 : 3.5), is likely to be due to the fluorescence of an intramolecular excimer. Very recent results by De Schryver[5] and Mataga[6] on closely related systems are also along these lines.

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