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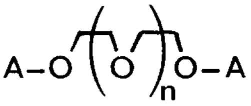
SYNTHESIS OF NEW MACROCYCLIC POLYOXA [X.X] AND [X] (9,10)-ANTHRACENOPHANES FROM 9,10-BISTRIMETHYLSILOXYANTHRACENE

Alain CASTELLAN, Michèle DANEY, Jean-Pierre DESVERGNE, Marie-Hélène RIFFAUD
and Henri BOUAS-LAURENT

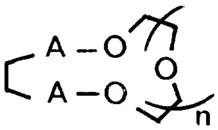
Laboratoire de Photophysique et Photochimie Moléculaire (LA n° 348)
Université de Bordeaux I, 33405 TALENCE

SUMMARY : The synthesis of new crown (9,10) anthracenophanes designed to combine cation complexing and photochemical properties is described. It is based on the use of 9,10-bis trimethylsiloxyanthracene as convenient starting material.

The first photochemical synthesis of crown-ethers[1] from bis-9-anthryl-α,ω - polyoxaalkanes (I_n) was realized in order to develop photochemical systems sensitive to ion complexation. In the same manner, independently[2], the cyclophanes II_2 and II_3 were prepared. But the photochemical properties of I_n or II_{2-3} do not seem to be modified in the presence of salts. We considered that new macrobicyclic polyoxaanthracenophanes such as IV_n should be more appropriate to display cation-induced photophysical and photochemical properties ; of note is the presence of dual hard-soft basic sites and the potential generation of a double complexing cavity on irradiation.



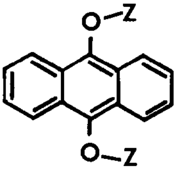
I_n ;



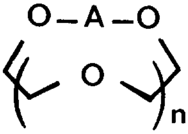
II_n

A = 9-anthryl **A = 9,10-anthrylidene**

"Photoresponsive" complexing systems monitored by azobenzene isomerization were successfully prepared[3] but fluorescence studies were not considered. One advantage of anthracenophanes is the intense dual fluorescence (locally excited and excimer) of the anthracene ring in addition to its well known photoreactivity[2a]. A number of anthracenophanes are known[4] but they do not show an interplay between complexing and photochemical properties, expected for IV_n. Among other cyclophanes[5], some macrotricyclic compounds[6a], which exhibit outstanding complexing properties are of interest in photophysics[6b].



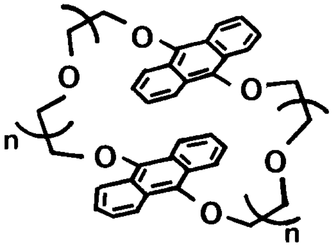
III { a $Z = H$; b $Z = SiMe_3$ }



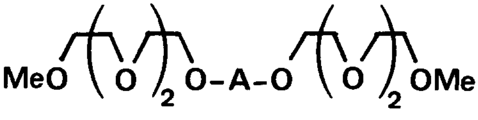
V_n (2,3)

A = 9,10-anthrylidene

We report the synthesis of compounds $IV_{n(1-3)}$ as well as cyclophanes V_n and the reference (monochromophoric) compound VIII.

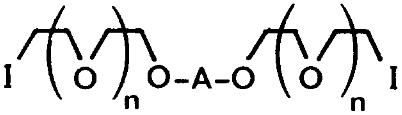


IV_n (1-3)

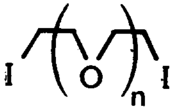


VIII (m.p. 50°C)

The principle of the method, first stated by Pedersen[7] and adopted by others[8] consists of the reaction of a diphenol in a basic medium with polyethylenoxyditosylates or dihalides. We observed that using 9,10-dihydroxyanthracene (IIIa) prepared in situ[9a] does not readily work; moreover, it is very reactive[9b] towards oxygen. It was then considered to mask



VI_n ;



VII_n (1-3)

the two OH by protective groups easily removable to generate phenate anions during the course of the reaction and found that 9,10-bistrimethylsiloxyanthracene (IIIb) fulfills the requirements. The preparation of IIIb (yellow-green crystals m.p. 132°C) has been described elsewhere[10]. Scaling up is possible. From anthraquinone (150 g), we obtained 96g of <u>pure</u> IIIb which can be stored under inert gas. The synthesis of IV_n, outlined below, can be performed in one step (procedure 1) or two steps (procedure 2).

PROCEDURE 1

$$IIIb + VII_n \xrightarrow[ii]{K_2CO_3/acetone^{i}} IV_n + V_n + VI_n$$

	IV_n m.p.	% yield	V_n m.p.	% yield	VI_n m.p.	% yield
n = 1	240 °C	3		*	140 °C	2,5
n = 2	175 °C	10	oil	16		*
n = 3	156 °C	3	140 °C	6		*

* not isolated

PROCEDURE 2

a) $\mathrm{IIIb} + \mathrm{VII}_n \xrightarrow[\text{iii}]{K_2CO_3/\text{acetone}^{\text{i}}} \mathrm{VI}_n$

	m.p.	% yield
n = 2	78°C	35
n = 3	50°C	36

b) $\mathrm{VI}_n + \mathrm{IIIb} \xrightarrow[\text{ii}]{K_2CO_3\ -\ CsCO_3/\text{acetone}^{\text{i}}} \mathrm{IV}_n$

	% yield
n = 2	29
n = 3	16

i = under reflux and bubbling argon
ii = very slow addition of stoicheiometric mixtures of VII_n or VI_n and III_b ($\simeq 10^{-3}$M) in acetone to the carbonate suspension.
iii = III_b and VII_n (n = 2,3) (5 mol. equiv.) are reacted with the carbonate suspension ; no attempt was made at preparing VI_1 by procedure 2a.

In both cases, the use of the diiodo derivatives VII_n gave a better fractionation of the products by flash chromatography on silica ; these were prepared from the corresponding ditosylates[11] according to a method used by Morawetz from the dichlorides[12]. Derivative VIII results from reaction of IIIb with 1-iodo-3,6,9-trioxadecane (procedure 2a ; 18% yield). The purification of compounds IV_n proved easier with procedure 2. Yields are in isolated pure compounds. The fluorescence of phanes IV_n, presently under study, appears to be, as anticipated, solvent and cation dependent.

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