Polymer Bulletin 1, 469–473 (1979)

Polymer Bulletin

Dimerization of 1-Isopropenyl Anthracene by $TiCl_4$

Structural Study of the Dimer

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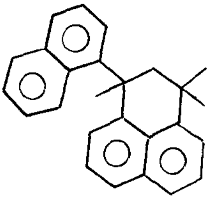
Summary

1-isopropenyl anthracene was dimerized by reaction with $TiCl_4$ in CH_2Cl_2 and the structure of the dimer studied by ^1H NMR spectroscopy. The spectrum was assigned and is in agreement with simulation. The structure results from the attack of carbocation on carbon 9.

Introduction

In the preceeding article [COUDANE et al. (1979)] the polymerization and the dimerization of various isopropenyl aromatic monomers have been described. When 1-isopropenyl anthracene is reacted with $TiCl_4$ in methylene chloride, a dimer A is obtained in quantitative yield, no matter what the monomer and initiator concentration and the temperature may be. Its melting point is 205°C. In the same way a dimer has been obtained from 1-isopropenyl naphthalene and its structure has been described in a preceeding article [BUNEL et al., in press] it has been found that the cyclisation takes place on carbon 8 leading to the following structure :



B

In the present work the structure of A is obtained by NMR spectroscopy.

Experimental

NMR spectra of $CDCl_3$ solutions were recorded at room temperature on a high field spectrometer CAMECA 250 MHz (internal reference TMS).

Simulated spectrum was obtained from a WP 80 Brücker using an IRCAL Listing.

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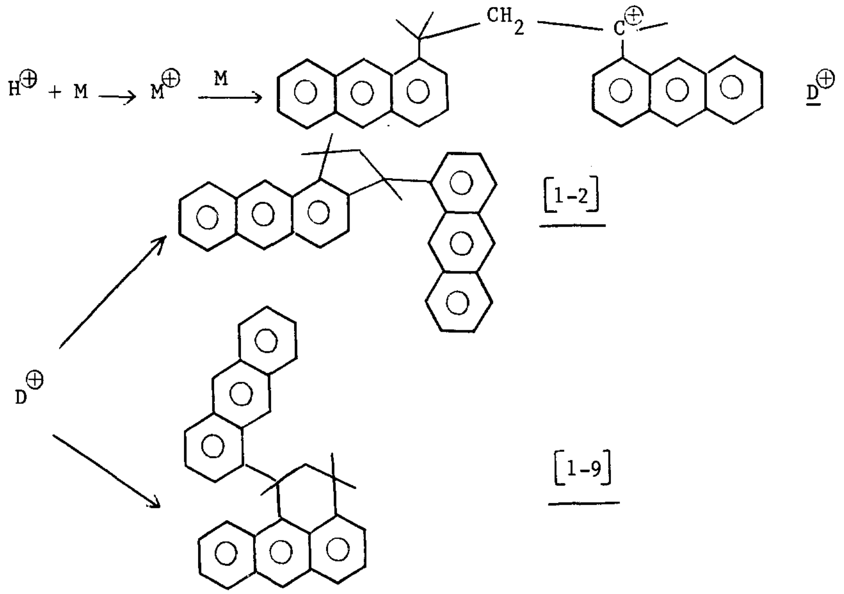
Results and discussion

The dimerization of 1-isopropenyl anthracene M can occur according to the following scheme :



^{1}H NMR spectroscopy study of A enable us to exclude the formation of a linear dimer.

In structure [1-2] 2 spin systems ABCD, 1 spin-system ABC, 1 spin-system AB and 4 protons without short range homonuclear interaction will be observed.

If structure is [1-9] 2 spin systems ABCD, 2 spin system ABC and 3 non coupled protons will occur.

The aromatic coupling constants have been determined for various methyl anthracenes [CASPAR et al. (1975)]. $3J_{H-H}$ are close to 8.5 Hz the others are below 1-5 Hz.

If it is a first order spectrum it will exhibit the following peaks : structure [1-2] : 8 doublets, 5 triplets and 4 singlets ; structure [1-9] : 8 doublets, 6 triplets and 3 singlets.

Between 6.5 and 8.3 p.p.m. the spectrum is first order and 3 singlets can be distinguished from the other peaks. However this is not enough to conclude that the structure is [1-9] since in the complex system of lines at 7.85 p.p.m. there is a peak whose intensity is of the same order of magnitude as that of a singlet. Consequently it is necessary to identify each spin system.

Table 1

Study of the dimer of 1-isopropenyl anthracene by double resonance (↑ = irradiated protons ; × = decoupled protons) and assignments of the peak. Each column corresponds to a peak and each line to irradiation of one proton.

δ (ppm)	Double resonance											Assignment	Multiplicity
8.27												10,10'	S
8.04													S
7.91	↑					×						4,4'	2D
7.83		↑								×		5'	D
7.78			↑			×						2	D
7.64				↑				×				8'	D
7.58					↑	×	×					2'	D
7.54												5	D
7.46	×		×			↑						3,3'	2T
7.21												9	S
7.04					×		↑		×			6	T
6.94				×				↑				7'	T
6.88							×		↑		×	7	T
6.70								×		↑		6'	T
6.54									×		↑	8	D

The spectrum includes 8 doublets, 6 triplets and 3 singlets which is in agreement with structure [1-9].

The spectrum was simulated (fig. 1) using data of table 2. $^3 J_{H-H}$ coupling constants were obtained from experimental spectrum and are in range 8-9 Hz ; the other coupling constants which are below 1.5 Hz were not taken into consideration because in a first order high field spectrum such coupling can hardly be seen.

Even if it is not possible to assign experimentally all the peaks, it is reasonable to assume that the molecular structure of A is analogeous to that of the dimer B obtained from 1 isopropenyl naphthalene. Its structure has been determined by both X.Ray diffractometry [JEANNIN et al., (1978)] and ^1H NMR spectroscopy [BUNEL et al., (in press)].

Figure 1: Dimer of 1-isopropenyl anthracene - ^1H NMR spectra.
1 : experimental 2 : simulated

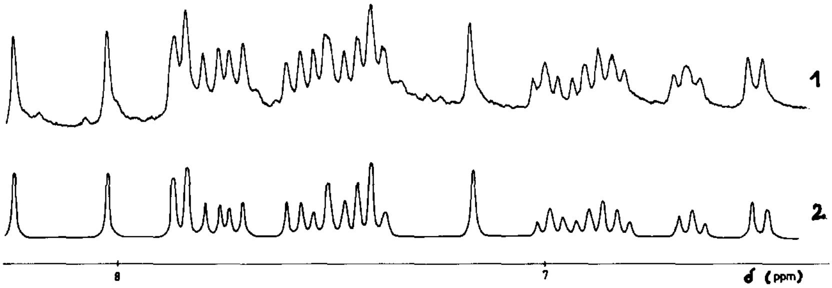
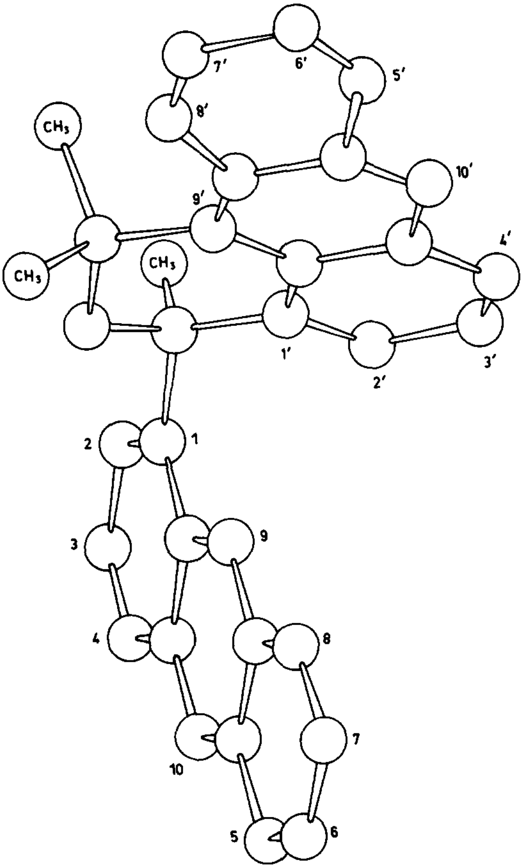


Figure 2: Dimer of 1-isopropenyl anthracene.
Spacial positions of the various atoms



A molecular model (fig. 2) of this structure shows that atom H_9 is in the shielding cone of the disubstituted anthracenic ring and is very close to the ring. Thus, atom H_9 is probably much more shielded than meso atoms of an anthracenic derivative. For this reason the singlet at 7.21 ppm was assigned to proton H_9.

From the respective positions of proton H_8 and $H_{8'}$, it can be inferred that H_8 is more shielded than $H_{8'}$ and for this reason it is assigned to the triplet at 6.54 ppm. Atoms H_5 and $H_{5'}$, being much less under the influence of these field effects they can be expected at frequencies close to those of H_5 atoms of methylated anthracenes.

References

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Received March 26, 1979