Polymer Bulletin 1, 475-479 (1979)

Polymer Bulletin

Dimerization of 9-Isopropenyl Phenanthrene by $TiCl_4$
Structural Study of the Dimer

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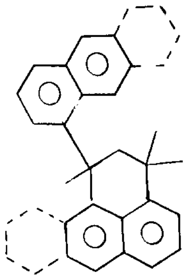
Summary

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

Introduction

In the preceeding articles [COUDANE et al. (1979) a,b] the cationic polymerization and dimerization ($TiCl_4$) of various isopropenyl aromatic monomers have been described and the structure of the dimer of 1-isopropenyl anthracene has been obtained from the study of its ^1H NMR spectrum. Dimers of 1-isopropenyl naphthalene and 1-isopropenyl anthracene have a similar structure :



Under the same conditions [COUDANE (1979)a] a dimer A is obtained in quantitative yield from 9-isopropenyl phenanthrene ; its melting point is 124°C. In this work the structure of A is determined by ^1H NMR spectroscopy.

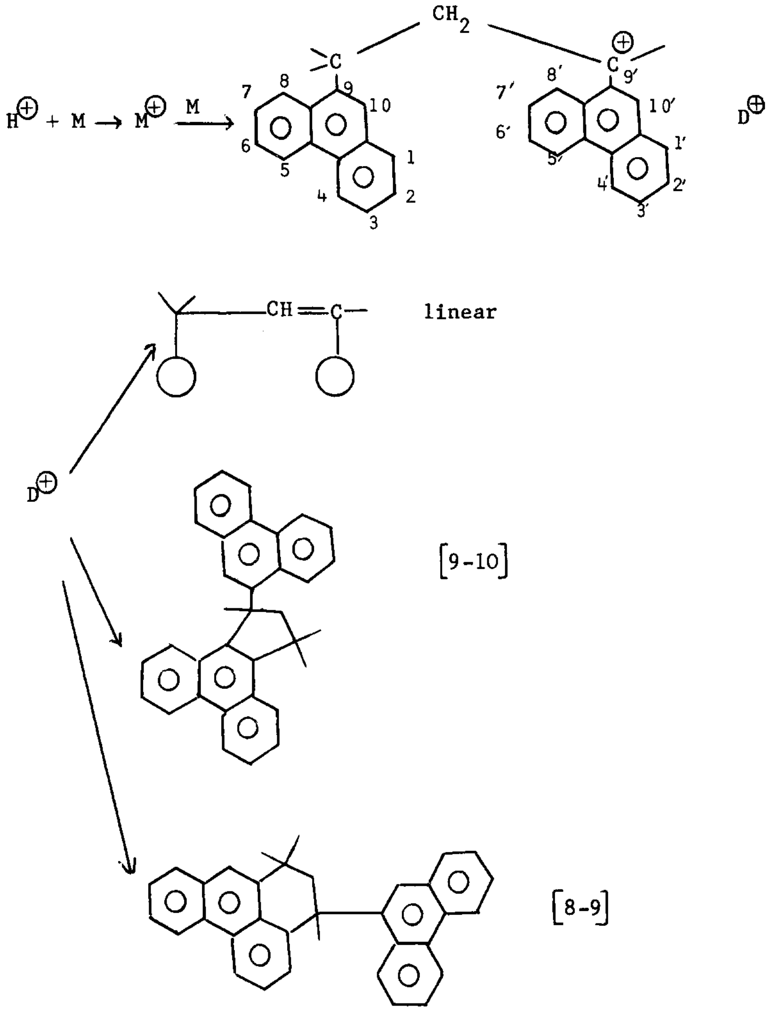
Experimental

Experimental and simulated spectra were obtained by the same technics as in our preceeding article [COUDANE (1979)a].

0170-0839/79/0001/0475/$01.00

Results and discussion

The dimerization of 9-isopropenyl phenanthrene can be described by one of the following reaction paths :



Linear structure cannot correspond to the ^{1}H NMR spectrum.

If structure is [9-10] 4 spin systems ABCD and 1 proton without short range homonuclear interaction will be found.

If the structure is [8-9] 3 spin systems ABCD, 1 spin system ABC and two protons without short range homonuclear interaction will be observed.

In the range 6.8 - 8.8 ppm the spectrum is complex (fig. 1) and is not completely first order. However a singlet completely separate from the rest of the spectrum can be seen at 8.25 ppm. Another singlet appears at 7.92 ppm but is part of a complex system of lines. Thus it will be possible to conclude that the structure is [8-9] only after the assignment of the various peaks.

The vicinal protons can be assigned by double resonance and the various spin systems can be identified (table 1).

Table 1

Study of the dimer of 1 isopropenyl phenanthrene by double resonance (↑ = irradiated protons. * = decoupled protons) and assignments of the peaks. Each column corresponds to a peak and each line to the irradiation of a proton.

δ (ppm)	Double resonance						Assignment	Multiplicity	Coupling constants (Hz)
8.69							4,4'	M	$J_{12} = 9$ $J_{13} = 1.5$ $J_{14} = 0$ $J_{23} = 7$ $J_{24} = 1.5$ $J_{34} = 9$
8.68							5'	D	
8.65	↑	*	*	*	*	*	4,4'	M	
8.58							5	D	
8.25							10,10'	S	
7.94							1,1'	M	
7.92		↑					10,10'	S	
7.65	*		↑				2,2' 3,3'	M	
7.63									
7.39	*			↑		*	6'	T	
7.30							6	T	
7,21				*	↑	*	8	D	
7,05							7'	D	
6.93				*		↑	7	T	

Figure 1: Dimer of 9-isopropenyl phenanthrene - ^1H NMR spectra.
1 : experimental 2 : simulated

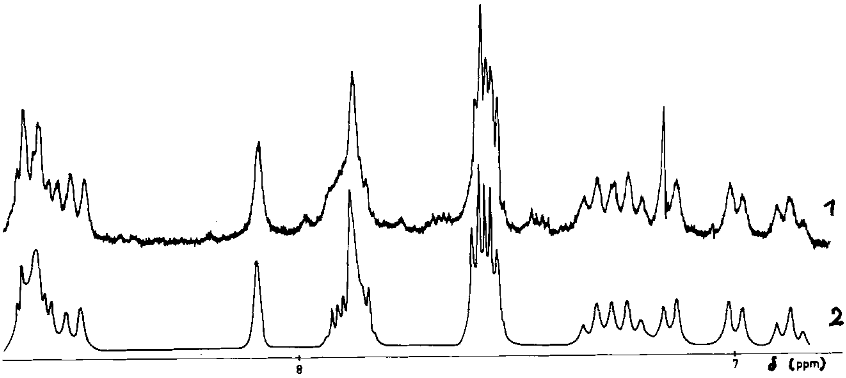
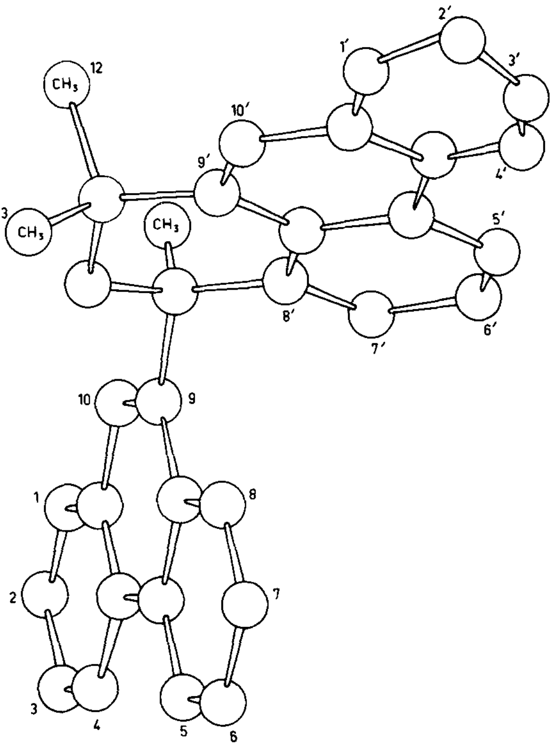


Figure 2: Dimer of 9-isopropenyl phenanthrene.
Spacial positions of the various atoms



The spectrum consists of three spin systems ABCD, 1 spin system ABC and 2 singlets. This result is in agreement with a structure [8-9] .

First order areas of the spectrum were simulated : $^3J_{H-H}$ couplings measured on the experimental spectrum are in the range 8 to 9 Hz which is analogeous to the values obtained for methyl phenanthrenes [BAVIN (1965), BARTHE (1967)] . On the other hand the frequencies and the coupling constants can be obtained from the simulation of the second order areas of the spectrum.

In order to assign the various peaks of the spectrum it is necessary to assume that in the molecules of dimer [8-9] of 9-isopropenyl phenanthrene and of dimer [1-2] of 1-isopropenyl naphthalene [BUNEL, in press] the spacial positions of the various atoms are the same. Examination of the molecular model built according to this structure (fig. 2) shows that atom H_7 is in the shielding cone of the monosubstituted ring and can be assigned to the doublet at 7.05 ppm. In the same way atom H_8 is in the shielding cone of the disubstituted ring and is more shielded than atom H_5 ; for this reason it has been assigned to the peak at 7.21 ppm.

References

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Received March 26, 1979