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C. Bunel[a]; M. Brigodiot[b]; E. Marechal[b]
[a] Laboratoire de Chimie Macromoleculaire, Institut National Superieur de Chimie Industrielle de Rouen, Mont Saint Aignan, France [b] Laboratoire de Synthèse Macromoléculaire, Université Pierre et Marie Curie, Paris, France

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Dimerization of 1-Isopropenylnaphthalene: Structural Study of the Dimer

C. BUNEL

Institut National Supérieur de Chimie Industrielle de Rouen
Laboratoire de Chimie Macromoléculaire
76130 Mont Saint Aignan, France

and

M. BRIGODIOT and E. MARECHAL

Laboratoire de Synthèse Macromoléculaire
Université Pierre et Marie Curie
4 Place Jussieu
75230 Paris, France

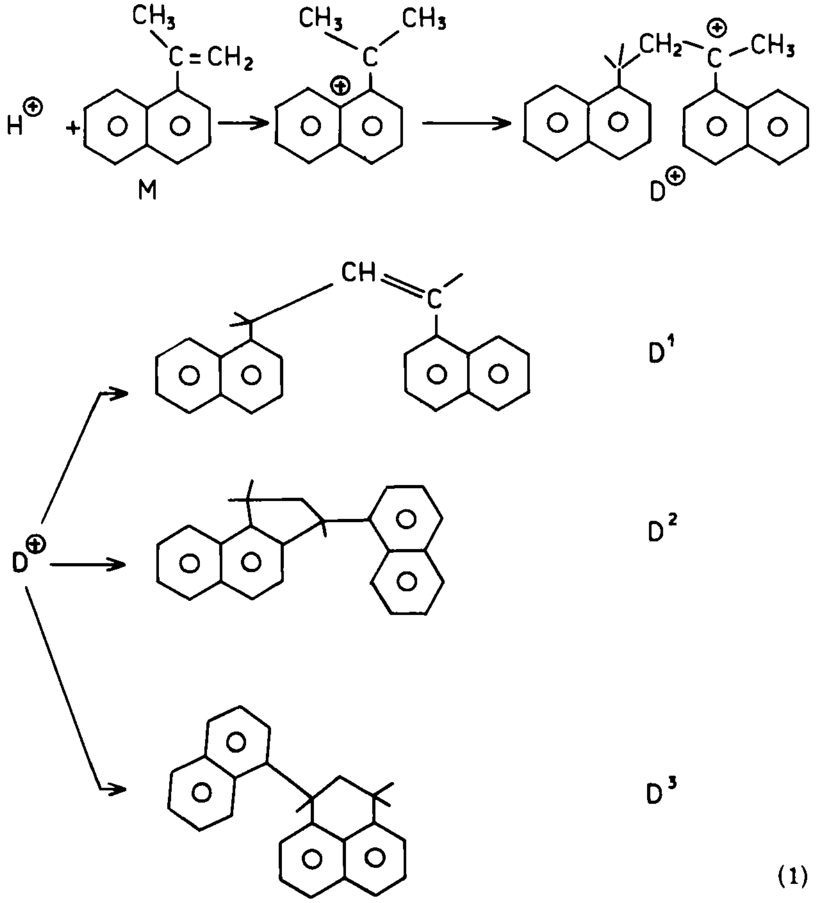
ABSTRACT

1-Isopropenylnaphthalene has been dimerized by cationic initiation. The structure of the dimer does not depend on the initiator. The cyclization of the dimeric ion takes place on carbon 8 (peri). The structure has been established both by x-ray diffractometry and by NMR. The complete crystallographic structure has been determined. The dimers of various substituted isopropenylnaphthalenes have been obtained in the same way and have the same structure.

INTRODUCTION

Over the past few years we have published a series of articles [1-3] devoted to the cationic polymerization of various vinylnaphthalenes. In order to increase the reactivity of 1-vinylnaphthalene towards carbocations we prepared its α-methyl derivative, 1-isopropenylnaphthalene.

1-Isopropenylnaphthalene has been polymerized by free-radical initiators under high pressure (5000-10,000 atm) at 125°C [4] but even after 30 hr only low polymers were obtained. No polymer was obtained by anionic initiation [5]. According to Hardy [6] poly-1-isopropenylnaphthalene has been prepared by cationic initiation. However, whatever the experimental conditions, we obtained only a dimer. Dimer formation by cationic initiation has been reported in the case of isopropenylstyrene [7], 2-vinyl- [8] and 2-isopropenylnaphthalene [9, 10].



(1)

In the case of 1-isopropenylnaphthalene the formation of a dimer has been reported; it has been obtained as a by-product in the preparation of the monomer [11]. The dimer of 4,7-dimethyl isopropenylnaphthalene has been obtained in the same way [12]. However it has not been possible to determine the structure of these two compounds [13].

In the case of 1-isopropenylnaphthalene three structures can be considered according to the schemes (1).

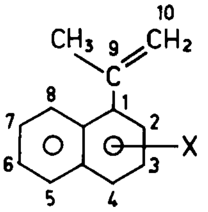
Dimers similar to D^1 and D^2 have been obtained by cationic dimerization of α-methylstyrene [14]; their structures have been established by direct synthesis.

^{1}H-NMR and infrared spectroscopy studies of the compound enable us to eliminate D^1 but are not sufficient to permit a choice between D^2 and D^3. We have been able to determine the complete structure of the dimer by using both crystallographic data and ^{1}H-NMR.

EXPERIMENTAL

Reagents

The monomers reported in Table 1 have been prepared and studied.



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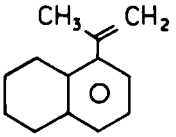

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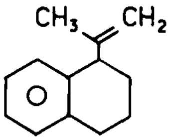


C

The monomers were prepared according to the scheme (2).

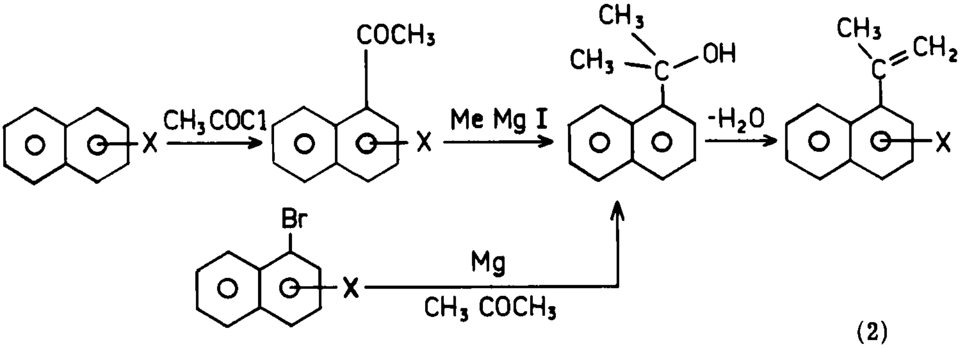
Solvent (CH_2Cl_2) was purified as described in our previous report [15].

Dimerizations were carried out under dry nitrogen. NMR spectra of $CDCl_3$ solutions were recorded at room temperature on a CAMECA 250 MHz high-field spectrometer (TMS internal reference).

TABLE 1. Monomers Prepared

Compound	X	C number	Ref.
A 1	H	4	[11]
A 2	CH_3	4	[12]
A 3	CH_3	2	a
A 4	CH_3O	4	[21]
A 5	Cl	4	[22]
B	-	-	[23]
C	-	-	[16]

[a] No reference to this compound has been found in chemical literature.



(2)

RESULTS AND DISCUSSION

Dimerizations

The dimerizations were initiated by various Lewis acids; in all cases the same compound was obtained from the same monomer. The melting points of the various dimers are the following (-H, 202°C; 4-Cl, 176°C; 4-CH_3, 174°C; 4-CH_3O, 177°C). The values of the yield of dimerization for 1-isopropenylnaphthalene and with various experimental conditions are reported in Table 2.

Unlike the case of other initiators, no coloration appeared when $SnCl_4$ was added to the monomer solution.

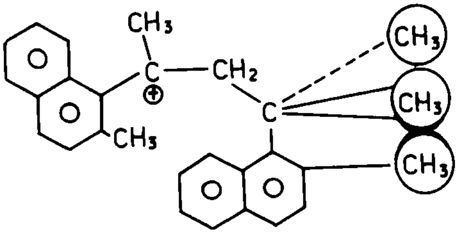
TABLE 2. Value of the Yield R in Dimerization of 1-Isopropenylnaphthalene for Various Experimental Conditions[a]

Lewis acid	Temperature (°C)	R (%)
$TiCl_4$	-72	84
	-40	78
	15	76
BF_3	15	56
$AlCl_3$	15	78
$SnCl_4$	15	4

[a] [M] = 0.1 mole/liter; solvent, CH_2Cl_2; [Lewis acid] = 2.3×10^{-2} mole/liter.

The influence of the initiator concentration was examined but was shown to be very small. The evolution of the yield after a 5 min contact between the Lewis acid and the monomer is almost asymptotic; after 30 min at 15°C the yield is 85%.

Whatever the substituent on carbon 4, a dimer is obtained; however in the case of compounds A3, B, and C no dimer is produced, and the monomer remains unchanged. In the case of A3, the failure to dimerize is probably due to steric hindrance between the methyl group on carbon 2 and the two methyl groups on carbon 10. The molecular models are in agreement with this assumption.



Monomer C does not polymerize because there is no stabilization of the carbocation by the phenyl group. The case of B is more difficult to explain; however it is reasonable to mention that the available amount of monomer allowed only very few experiments.

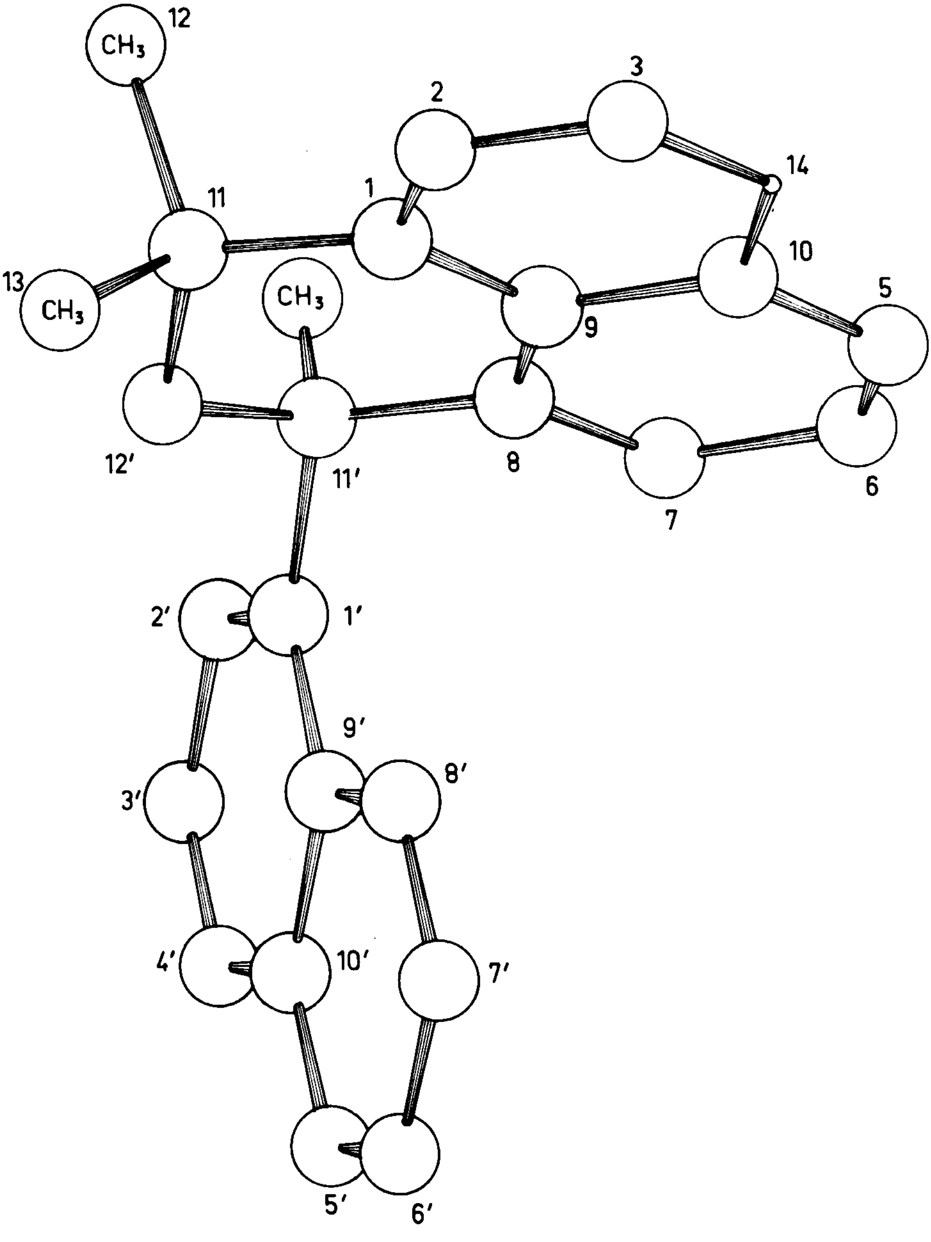


FIG. 1. Structure of the dimer of 1-vinylnaphthalene as obtained from the crystallographic study. The bond lengths and bond angles are reported in Tables 3 and 4.

TABLE 3. Crystallographic Structure of the Dimer of 1-Isopropenylnaphthalene

Bond	Bond length (A)[a]	Bond	Bond length (A)[a]
C(1)-C(2)	1.374(3)	C(1')-C(2')	1.371(3)
C(1)-C(9)	1.422(3)	C(1')-C(9')	1.434(3)
C(1)-C(11)	1.520(3)	C(1')-C(11')	1.543(3)
C(2)-C(3)	1.396(5)	C(2')-C(3')	1.415(3)
C(3)-C(4)	1.339(5)	C(3')-C(4')	1.336(5)
C(4)-C(10)	1.415(4)	C(4')-C(10')	1.406(4)
C(10)-C(9)	1.433(3)	C(10')-C(9')	1.430(3)
C(10)-C(5)	1.403(3)	C(10')-C(5')	1.413(3)
C(5)-C(6)	1.351(4)	C(5')-C(6')	1.344(5)
C(6)-C(7)	1.416(3)	C(6')-C(7')	1.394(4)
C(7)-C(8)	1.368(3)	C(7')-C(8')	1.370(3)
C(8)-C(9)	1.423(3)	C(8')-C(9')	1.418(3)
C(8)-C(11')	1.525(3)		
C(11)-C(12)	1.534(4)	C(11')-C(12')	1.543(3)
C(11)-C(13)	1.539(3)	C(11')-C(13')	1.545(3)
C(11)-C(12')	1.535(3)		

[a] Standard deviations in parentheses. Data of Jeannin and Stora [17].

Structure of the Dimer

X-Ray Diffractometry. The crystallographic structure of the dimer was established by Jeannin and Stora [17] to whom we entrusted some monocrystals obtained by slow crystallization in methylene chloride. The complete crystallographic study has been published elsewhere [17]. The structure resulting from this study is shown in Fig. 1, and the bond lengths and bond angles are reported in Tables 3 and 4.

Tables 3 and 4 show unambigously that the structure is D^3; it results from an attack of carbon 8 by carbocation.

TABLE 4. Crystallographic Structure of the Dimer of 1-Isopropenylnaphthalene

Bond angle	Bond angle (degrees)[a]	Bond angle	Bond angle (degrees)[a]
C(2)-C(1)-C(11)	119.5(2)	C(2')-C(1')-C(11')	119.8(2)
C(2)-C(1)-C(9)	118.9(2)	C(2')-C(1')-C(9')	117.8(2)
C(9)-C(1)-C(11)	121.5(2)	C(9')-C(1')-C(11')	122.4(2)
C(1)-C(2)-C(3)	121.7(3)	C(1')-C(2')-C(3')	122.0(2)
C(2)-C(3)-C(4)	120.7(3)	C(2')-C(3')-C(4')	121.0(3)
C(3)-C(4)-C(10)	121.0(3)	C(3')-C(4')-C(10')	120.3(3)
C(4)-C(10)-C(9)	118.7(2)	C(4')-C(10')-C(9')	119.6(2)
C(4)-C(10)-C(5)	121.3(2)	C(4')-C(10')-C(5')	120.8(2)
C(9)-C(10)-C(5)	120.0(2)	C(9')-C(10')-C(5')	119.6(2)
C(10)-C(5)-C(6)	121.0(2)	C(10')-C(5')-C(6')	121.5(3)
C(5)-C(6)-C(7)	120.0(2)	C(5')-C(6')-C(7')	119.9(3)
C(6)-C(7)-C(8)	121.1(2)	C(6')-C(7')-C(8')	120.8(3)
C(7)-C(8)-C(9)	120.2(2)	C(7')-C(8')-C(9')	121.4(2)
C(7)-C(8)-C(11')	119.3(2)		
C(9)-C(8)-C(11')	120.4(2)		
C(8)-C(9)-C(10)	117.8(2)	C(8')-C(9')-C(10')	116.8(2)
C(8)-C(9)-C(1)	123.2(2)	C(8')-C(9')-C(1')	123.9(2)
C(1)-C(9)-C(10)	119.0(2)	C(1')-C(9')-C(10')	119.4(2)
C(1)-C(11)-C(13)	108.5(2)	C(1')-C(11')-C(13')	111.5(2)
C(1)-C(11)-C(12)	111.9(2)	C(1')-C(11')-C(12')	107.0(2)
C(1)-C(11)-C(12')	110.9(2)	C(1')-C(11')-C(8)	110.8(2)
C(12)-C(11)-C(13)	107.0(2)	C(12')-C(11')-C(8)	111.7(2)
C(12)-C(11)-C(12')	105.9(2)	C(13')-C(11')-C(8)	104.8(2)
C(13)-C(11)-C(12')	112.7(2)	C(13')-C(11')-C(12')	110.2(2)

[a] Standard deviations in parentheses. Data of Jeannin and Stora [17].

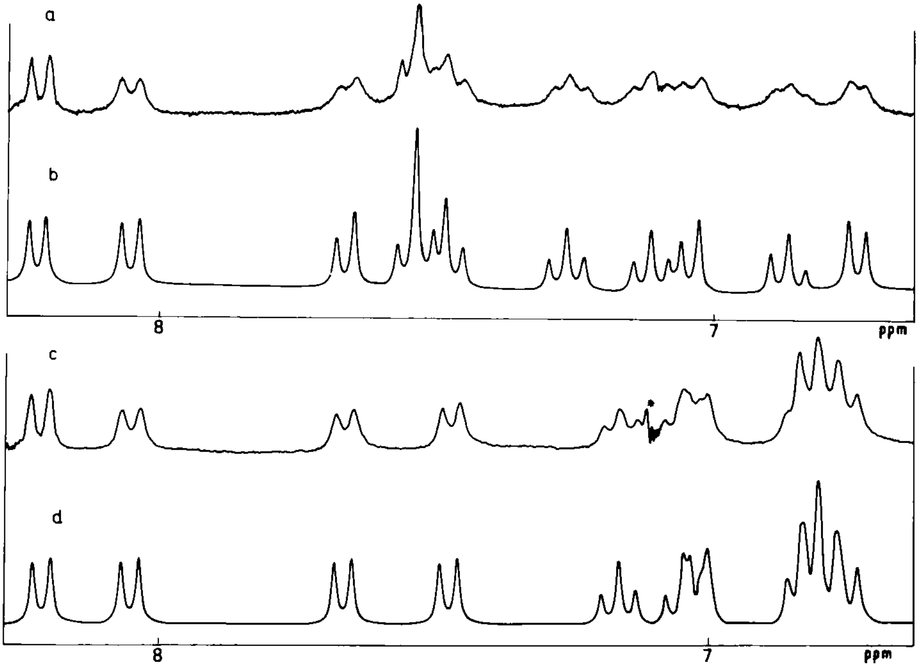


FIG. 2. ^{1}H-NMR spectra (250 MHz) of various dimers: (a) chlorinated dimers, experimental; (b) chlorinated dimers, simulated; (c) methoxy-substituted dimer, experimental; (d) methoxy-substituted dimer, simulated.

^{1}H-NMR Spectrum. There are as many aromatic protons in D^3 as in D^2; however, it can be expected that the part of the spectrum corresponding to these protons will be different, since in structure D^3 there are three ABC spin systems and one ABCD spin system, and in structure D^2 one AB, one ABC, and two ABCD spin systems.

Between 7 and 8 ppm the spectra of the dimers of A1 and A2 are extremely complex because of a very important overlapping of the peaks. The substitution by a chlorine atom or a methoxy group shifts the proton 8 strongly towards low fields and clarifies the spectra to a large extent, so the analysis of the NMR spectrum has been possible only in these cases.

The frequencies corresponding to the protons in the ortho position of the substituent largely depends on its nature [18]. Comparison of the spectra in the region of aromatic protons leads to assign the protons in the position *α* to the chlorine around 7.5 ppm and the protons

TABLE 5. Chemical Shifts

	Chemical shift (ppm)	
	4-Cl	4-OCH_3
5'D	8.22	8.21
6'T	7.25	7.15
7'T	6.85	6.82
8'D	7.03	7.01
5 D	8.05	8.04
6 T	7.1	7.04
7 D	6.73	6.74
3'D	7.46	6.78
2'D	7.54	7.46
3D	7.52	6.81
2D	7.65	7.65

in the position α to the methoxy around 6.5 ppm. The frequencies relative to the other protons depend only very little on the nature of the substituent.

The J_{H-H} couplings have been determined by Emsley et al. [18] for some substituted naphthalenes. The $^3J_{H-H}$ are close to 8 Hz; the other J_{H-H} couplings are below 1 Hz, and they will be neglected because on a high field spectrum small splittings are not detected.

In this case, if the protons in the ortho position to the substituent are not taken into consideration the spectrum should consist of three triplets and six doublets if the structure is D^3 and of four triplets and five doublets if the structure is D^2.

Comparison of the spectra (Fig. 2a) clearly shows three triplets and six doublets (3 and 3' being excepted).

By double resonance the vicinal protons were identified and, step by step, the frequencies relative to the protons of a same ring were assigned. Chemical shifts and multiplicity of peaks are reported on Table 5.

Close agreement can be observed between the experimental and the simulated spectra (Fig. 2b).obtained from the suggested attributions. This proves that the structure is undoubtedly D^3.

The same mode of cyclization has been observed by Fieser [19] in the case of (1-naphthyl)propionic acid and A. Ur Rahman [20] in the case of (1-naphthyl)butyric acid.

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