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Gas chromatographic–mass spectrometric, high-performance liquid chromatographic–UV and gas chromatographic–Fourier transform IR responses to an industrial mixture of diisopropylnaphthalenes

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Abstract

GC and HPLC parameters and mass spectrometric, ultraviolet and infrared responses of the diisopropylnaphthalene isomers are reported in order to allow their analytical determination. The interest in these compounds, widely used in the manufacture of special paper, is linked to their appearance as environmental and food pollutants due to recycling and waste processes.

1. Introduction

A recent GC–MS investigation showed the presence of a mixture of diisopropylnaphthalene (DIPN) isomers in some kinds of food (rice and pasta) and in their containers [1]. These naphthalene derivatives, with general formula $C_{16}H_{20}$, may give rise, theoretically, to ten positional isomers, i.e., 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- and 2,7-derivatives. Because of steric hindrances, their real number could be lower, considering that the isomers having adjacent substituents are not favoured under non-specific synthesis conditions [2].

These compounds are widely used in the manufacture of special paper, such as carbonless and thermal copy paper, ink for jet printers and similar commercial products [3–7]. There is a great deal of interest in these special papers because, being pure cellulose, they can be used as starting materials to obtain high-quality recycled paper. The recycling process does not involve any specific treatment for the removal of DIPN from the paper, therefore significant amounts of these compounds are put back into the environment as waste or in the form of material used in the production of container board. In this way the useless presence of diisopropylnaphthalenes may lead to environmental pollution and food contamination with, consequently, new implications even of a toxicological nature [8]. Samples of carbonless copy paper have shown that the average amount of these naphthalene derivatives is about 1% of their total mass. Until now, only some Japanese researchers have investigated the presence of these molecular species in the environment, realising their harmful effects due to their pos-

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sible accumulation. Rivers, sea water and sediments have been investigated [9–12]. In spite of the widespread use and the large number of isomers, their analytical characteristics are almost unknown. Only two mass spectra of the 2,6-isomer, one obtained with an old spectrometer [11] and the other under 20 eV electron impact ionization conditions [13], have been reported. This paper reports the GC and HPLC parameters and UV, mass and Fourier transform (FT) IR spectra of the diisopropylnaphthalene isomers, as reference data for their analytical determination.

2. Experimental

2.1. Materials

All the chemicals, 1,3-, 1,6-, 1,4-, 1,5-, 2,6- and 2,7-dimethylnaphthalenes (DMN) and solvents of HPLC grade were purchased from Aldrich Chimica (Milan, Italy). 2,6-Diisopropylnaphthalene, 1- and 2-isopropylnaphthalene mixture (1:1) and 2-isopropylnaphthalene were supplied by Aldrich (Milwaukee, WI, USA). A sample of DIPN mixture was kindly furnished by a European manufacturer of carbonless copy paper.

2.2. Preparation of the samples

Mixtures of some diisopropylnaphthalene isomers were synthesized according to the literature procedure [14]. To a naphthalene solution (0.4 g) in 2-propanol (6 ml), used as the solvent and reagent, was added aluminium chloride catalyst. The mixture was maintained under agitation at room temperature for 5 h. After pouring off the crude reaction into water, the products were extracted with dichloromethane and injected into the GC–MS instrument. The analogous Friedel–Crafts reaction was also performed using separately the two monoisopropyl derivative samples (100 mg), isopropyl bromide (80 mg) in the presence of the same Lewis acid and light petroleum (10 ml) as a solvent [15]. The above reaction conditions and sample treatment were also applied to this second synthesis procedure.

An alternative Friedel–Crafts alkylation was carried out using naphthalene (150 mg) and 2-propanol (130 μl) in the presence of 80% sulfuric acid solution (1 ml) at 80°C for 3 h. Extraction of the products with *n*-hexane allowed the GC–MS analysis of DIPN obtained.

The complete DIPN mixture was obtained from carbonless copy paper (6.3 g) by extraction with CH_2Cl_2 (200 ml) by means of ultrasonic equipment for 30 min. Successive purification of the crude extract was performed applying flash chromatography on silica gel (Kieselgel 60, 70–230 mesh; Merck, Darmstadt, Germany) with *n*-hexane as the mobile phase. The compounds investigated showed an R_F value of 0.9. A further DIPN enrichment was obtained by the Bjorseth procedure by extraction with dimethylformamide–water (9:1) and back-extraction into cyclohexane to eliminate the aliphatic components of the sample [16]. The various steps of purification were checked with the available analytical techniques. All the data obtained from the DIPN extract were confirmed with an authenticated mixture used in carbonless copy paper production.

2.3. GC–MS apparatus and conditions

The GC–MS data were obtained with a Hewlett-Packard system consisting of a Model 5890 II gas chromatograph equipped with a PONA fused-silica capillary column (50 m × 0.2 mm I.D.; film thickness 0.5 μm) and a Model 5971 A mass spectrometer. An HP 59970 C data system was used for data acquisition and elaboration. Owing to the difficulty of isomer separation, the temperature programme chosen for the GC run was isothermal at 120°C for 0.5 min followed by a temperature increase of 3°C min^{-1} up to a final temperature of 260°C, maintained for 10 min. The helium flow into the column was constant at 0.528 ml min^{-1}.

The transfer line and injector temperatures were 280 and 250°C, respectively. The quadrupole conditions were electron energy 70 eV, emission current 300 μA and ion source tem-

perature 250°C. Mass spectra were recorded by cyclically scanning from 50 to 270 mass units with a cycle time of 0.51 s and a solvent delay of 9 min. A 1-μl volume from 150 ppm DIPN solution was injected into the GC–MS system under splitless conditions for 0.2 min.

2.4. HPLC apparatus and conditions

The measurements were performed using a Waters (Milford, MA, USA) HPLC system consisting of a Model 600 MS pump, a Model U6K injector, a Model 990 plus photodiode-array (PDA) detector and a Model 990 plotter. The acquisition and elaboration of the data were carried out with a NEC APC IV computer (Boxborough, MA, USA). The compounds under investigation were separated using a Delta-Pak RP-18 100 Å column (150 mm × 3.9 mm I.D. and spherical particles of 5 μm) and methanol–water (76:24) as the mobile phase at a flow-rate of 0.7 ml min^{-1}. The PDA detector recorded in the range 210–400 nm with a scan rate of 1 cycle s^{-1} and resolution of 1.4 nm. A 20-μl volume of 50 ppm DIPN solution was injected in the instrumental system.

2.5. GC–FT-IR apparatus and conditions

A Hewlett-Packard Model 5890 II gas chromatograph was coupled to a Model 5865 A FT-IR detector. The IR spectrometer recorded the transmittance/absorbance in the range 4000–750 cm^{-1} with a scan resolution of 4 cm^{-1}. The GC separation was performed by using an SPB-1 capillary column (Supelchem, Milan, Italy) (60 m × 0.32 mm I.D.; 1.0 μm film thickness) with a constant head pressure of 100 kPa. The oven temperature programme started from 150°C with a ramp rate of 5°C min^{-1} up to 230°C, maintained for 20 min. The flow-cell injector and transfer line were heated to 250°C. A helium

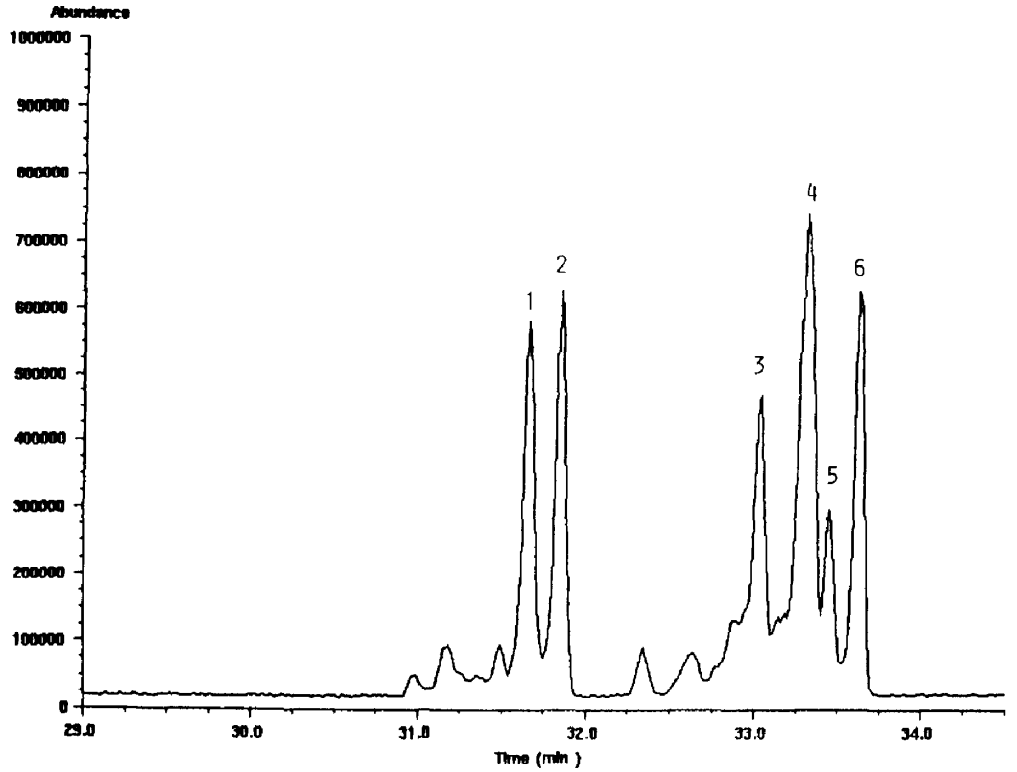

Fig. 1. GC–MS chromatograpic fingerprint of the industrial mixture of diisopropylnaphthalenes.

Table 1
Fragment ions and relative abundances (%) of six DIPN isomers, corresponding to GC peaks

Ion	m/z	Peak					
		1	2	3	4	5	6
$[M]^{+\cdot}$	212	57	52	43	54	63	45
$[M-CH_3]^+$	197	100	100	100	100	100	100
$[M-C_3H_7]^+$	169	12	9	10	8	9	7
$[C_{13}H_9]^+$	165	12	14	14	11	14	9
$[M-C_4H_9]^+$	155	39	45	24	42	56	26
$[C_{12}H_9]^+$	153	18	23	18	20	25	14
$[M-C_5H_{11}]^+$	141	14	13	13	12	15	8
$[C_{10}H_8]^{+\cdot}$	128	7	7	6	6	8	5
$[C_9H_7]^+$	115	7	5	6	5	6	5
$[C_7H_7]^+$	91	2	4	2	4	5	3
$[C_6H_5]^+$	77	3	3	3	2	4	2

pressure of 35 kPa was forced to feed the make-up flow. A 1-μl injection of a 2000 ppm DIPN solution was made in the splitless mode.

3. Results and discussion

All the samples containing the industrial mixture of diisopropylnaphthalenes showed by GC–MS analysis a characteristic total ion current distributed in six principal peaks as reported in Fig. 1. The lower peaks, recognized as DIPN, have not been attributed to any configuration owing to their low concentration in the mixture. The corresponding chromatogram may be considered as the fingerprint indicating the probable presence of such isomers. Under our experimental conditions the detection limit for the DIPN mixture was about 3.5 μg ml^{-1}.

The mass spectra corresponding to six peaks are reported in Table 1 and Fig. 2 shows the analog spectrum of the 2,6-isomer. The base peak for all was at m/z 197 due to CH_3 radical loss. The molecular ions (m/z 212) were very similar, in terms of relative intensity, for all the isomers. Another significant mass spectrometric peak was attributed to the loss of 57 and 59 mass units corresponding to the $[M-C_4H_9]^+$ and $[C_{12}H_9]^+$ fragment ions, leading to ionic species at m/z 155 and 153. All the other fragment ions had low relative intensities (<15%). The only mass spectrum found in the literature on these compounds was assigned to the 2,6-isomer [11], but it shows a significant difference in comparison with that above (see Fig. 2), as confirmed also by Peterman and Delfino [17]. In the old spectrum, the fragment ion at m/z 78 was probably due to the partial pyrolytic process, frequently occurring in old mass spectrometers. Therefore, this current MS response represents

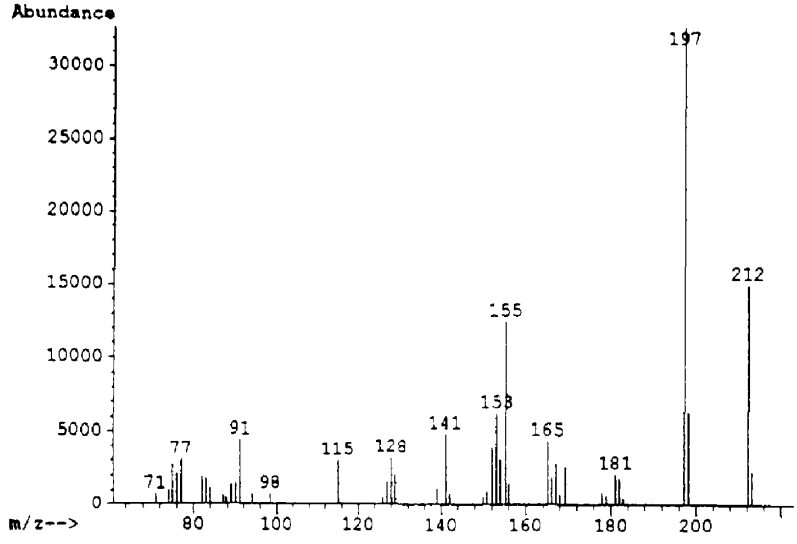

Fig. 2. Mass spectrum of 2,6-DIPN isomer.

an important update of the mass spectrometric behaviour of these naphthalene derivatives under the usual 70 eV electron impact ionization.

The HPLC analysis using PDA detection allowed the DIPN chromatographic peaks to be recorded together with UV information, as reported in Fig. 3. The UV spectra of all the HPLC peaks showed the same absolute absorption maxima at 227 nm, while lower absorption in the region 270–290 nm occurred at different wavelengths, probably owing to the positions of substituents on the naphthalene ring. The UV spectrum of the 2,6-isomer is reported in Fig. 4. Six isomers of dimethylnaphthalenes used as reference compounds were analysed separately with the HPLC–PDA system. These measurements highlighted three isomer pairs, having analogous positions of substituents with an absorption maximum at 279 nm for the α,β-, 286 nm for α,α- and 272 nm for β,β-configurations (Table 2). An analogous behaviour has been observed also for DIPN isomers where tentatively the maximum UV absorption at 280 nm was assigned to α,β-, 288 nm to α,α- and 271 nm to β,β-configurations. The comparison between the found values for DMN with respect to those for DIPN showed, in both instances, a red shift from β,β- to α,β- and α,α-substituted compounds. According to these data, the HPLC peaks of DIPN Nos. 1, 2 and 4 could be α,β-isomers, the third peak α,α- and the others (5 and 6) β,β-substituted (Table 2). The 2,6-isomer was confirmed by GC–MS and HPLC–PDA runs using an authenticated standard. This compound was eluted, under GC conditions, with the highest retention time, whereas in the HPLC sequence it occupied the fifth position (Table 3). From the relative abundance of each peak, obtained by both analytical techniques, a different position in the respective chromatogram was detected also for the other isomers, except for peaks 1 and 2 (Table 3).

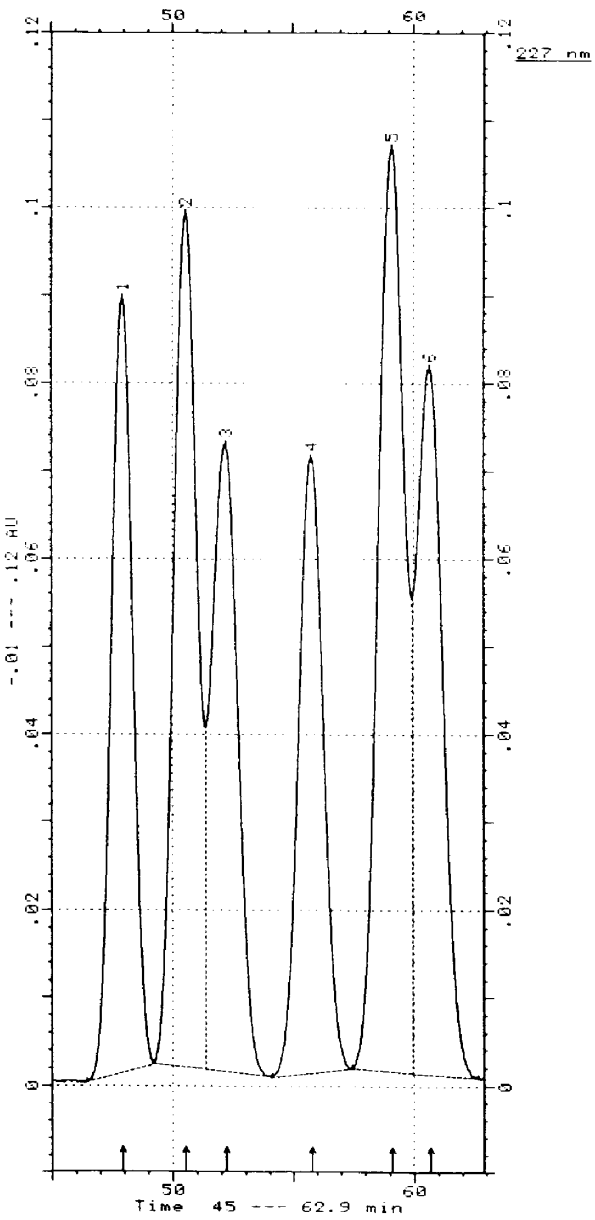

Fig. 3. HPLC fingerprint at 227 nm of the industrial mixture of diisopropylnaphthalenes.

The GC–FT-IR analysis confirmed the presence of CH_3 and =CH stretching in the range 3090–2880 cm^{-1} and specific bands in the 1000–700 cm^{-1} range, corresponding to CH bending out the plane due to different substituent positions (Table 4). Using the IR literature data for DMN isomers [18,19] the attribution of positions to the DIPN mixture was tried. The absorptions of chromatographic peaks 4, 5 and 6 in Fig. 1 were similar to those of 2,7-, 1,5- and 2,6-DMN, respectively (Table 4). Such a correspondence was not fully satisfied for the other peaks, but nevertheless the whole aspect of the spectra led

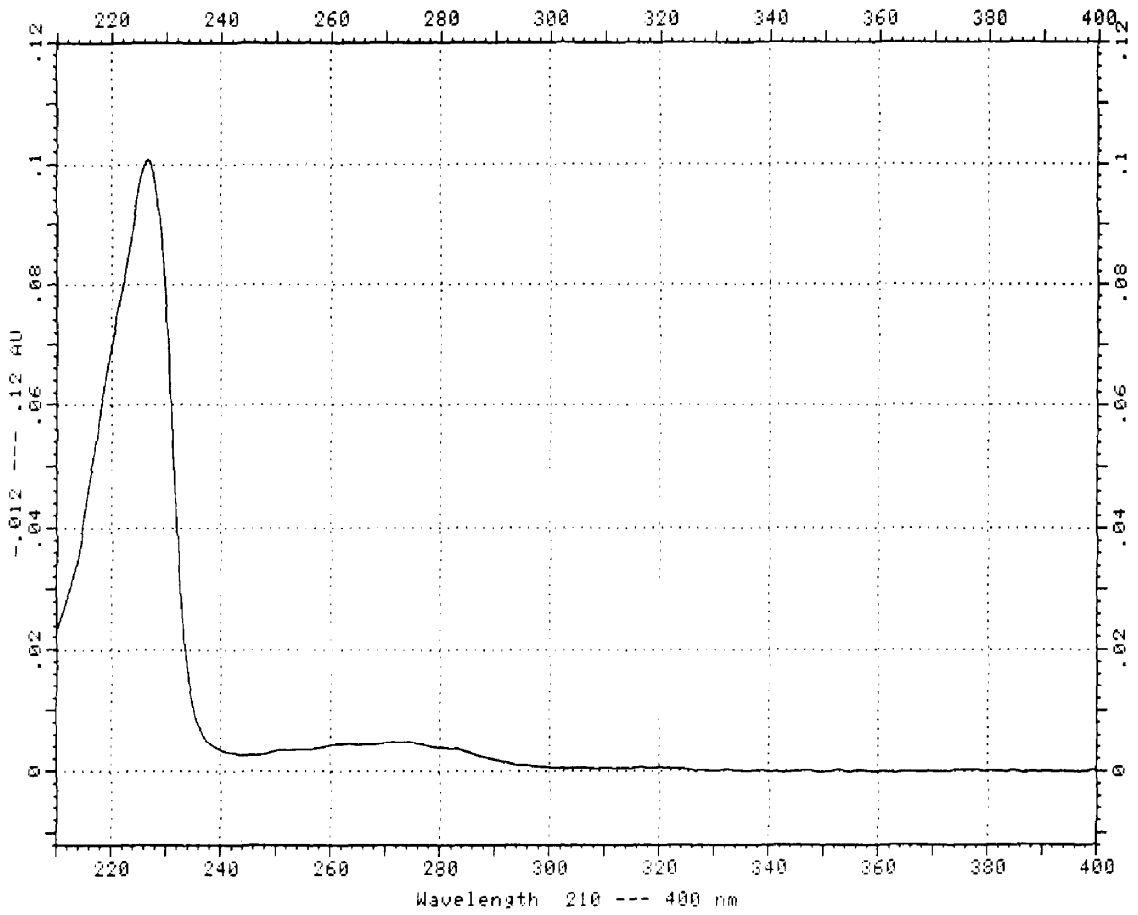

Fig. 4. UV spectrum of 2,6-DIPN isomer.

to the attribution of peaks 1, 2 and 3 to an α,β-configuration represented by the 1,3-, 1,6- and 1,7-isomers.

Friedel–Crafts synthesis was used to identify each isomer of the DIPN mixture. The products obtained starting from 2-isopropylnaphthalene and a 1- and 2-isopropylnaphthalene mixture showed the same isomers represented by the GC peaks 1, 2, 4 and 6 in Fig. 1. Probably this phenomenon is explained by an internal rearrangement due to the influence of aluminium chloride [15]. On the other hand, aromatic

Table 2
UV absorption wavelengths (nm) of six DMN isomers used as reference and the corresponding values found for DIPN isomer mixture

DMN isomer	Configuration	UV absorption (nm)	DIPN peak	UV absorption (nm)	Configuration
1,3-; 1,6-	α,β-	279	1,2,4	280	α,β-
1,4-; 1,5-	α,α-	286	3	288	α,α-
2,6-; 2,7-	β,β-	272	5,6	271	β,β-

Table 3
Elution sequence of DIPN isomers, from a commercial mixture, obtained by GC–MS, GC–FT-IR, HPLC and from synthesis, analysed by GC–MS

Method	Peak					
	1	2	3	4	5	6
GC–FT-IR GC–MS	1,3-	1,7-	1,6-	2,7-	1,5-	2,6-[a]
HPLC–PDA	1,3-	1,7-	1,5-	1,6-	2,6-[a]	2,7-
Synthesis	1,3-	1,7-	–	2,7-	–	2,6-[a]

Each chromatographic peak is assigned to a specific positional isomer.
[a] Confirmed by comparison with an authenticated reference compound.

substitution in the 2-position gives rise to the most stable alkyl derivative also under our experimental conditions. In fact, a similar synthesis procedure using naphthalene and 2-propanol as reagents produced the identical chromatographic pattern. Fig. 5 shows the HPLC trace of DIPN isomers obtained when Friedel–Crafts alkylation of naphthalene was carried out in presence of sulfuric acid as catalyst. The first evidence is the negligible amount of β,β-isomers (peaks 5 and 6) identified on the basis of their retention times and UV spectra as 2,6- and 2,7-derivatives, respectively. Moreover, as the naphthalene is first transformed into 1-naphthalenesulfonic acid,

Table 4
IR absorption wavenumbers in the region 1000–745 cm^{-1} of reference DMN isomers and the corresponding values detected from DIPN isomer mixture

DMN	IR absorption (cm^{-1})	DIPN peak	IR absorption (cm^{-1})
1,3-	745[a], 772, 859	1	780, 878[a], 942
1,7-	820[b]	2	830[a]
1,6-	748, 785, 812[a], 871	3	758[a], 835
2,7-	831[a], 890, 956	4	837[a], 899, 953
1,5-	787	5	778
2,6-	821[a], 889, 963	6	810, 884[a], 924

[a] More intense peak.
[b] The analog IR spectrum was reported by Schneider et al. [19].

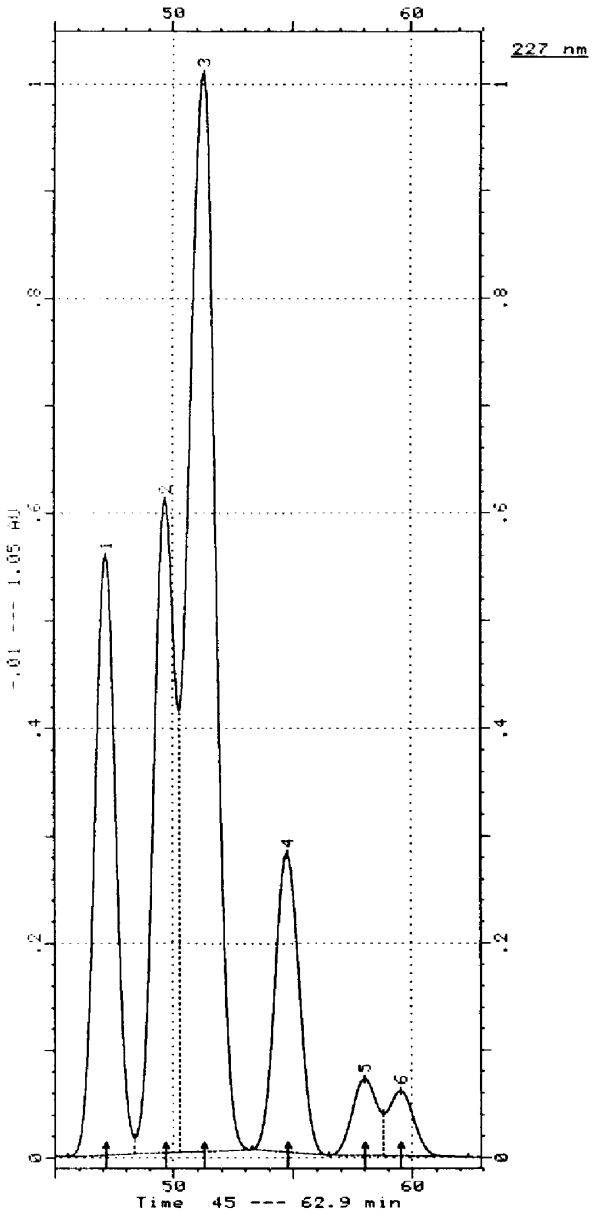

Fig. 5. HPLC of DIPN isomers obtained by Friedel–Crafts alkylation using sulfuric acid as catalyst.

the final products must be all considered 1-substituted [15]. The most abundant peak (3) having the α,α-configuration, is attributed to co-eluted 1,5- and 1,4-isomers. The presence of the 1,4-derivative is deduced by comparison of the relative abundances of GC and HPLC chromatographic peaks.

The GC–MS, HPLC–PDA and GC–FT-IR measurements together with reference compound and synthesis data allowed us to assign, with sufficient matching, the structures 2,7-, 1,5- and 2,6- to the last three GC peaks in Fig. 1, respectively (Tables 2, 3 and 4). Peak 1, having a α,β-configuration as emphasized by HPLC data, could be the 1,3- or 1,7-isomer. On the other hand, the GC–FT-IR and synthesis information led to the attribution of the 1,3-structure to this peak. This attribution was also supported by the analysis of the shape parameters [20]. In fact, the criteria used in the molecular shape determinations of DMN have been applied on a planar representation of DIPN (Table 5). These values were obtained by drawing the smallest rectangle enveloping the planar representation of each isomer which maximized the length-to-breadth ratio (L/B). Such data showing the lowest shape value for 1,3-compound confirmed our hypothesis, as this isomer is eluted first in both chromatographic techniques. Concerning the attribution of the GC peaks 2 and 3, the HPLC–PDA data (peaks 2 and 4) suggested an α,β-configuration. The IR information confirmed this, assigning the 1,7- and 1,6-structures, respectively.

NMR analysis constitutes a fundamental means to establish the certain configuration of substitution isomers. However, this technique requires for each isomer a few milligrams of pure sample, which could not be obtained for the studied DIPN mixture owing to insufficient HPLC resolution. Moreover, the selective synthesis of pure isomers was very difficult and with uncertain results. In contrast, the less specific HPLC–PDA technique supplied an unexpected and useful aid to assigning the positions of two isopropyl substituents in the naphthalene ring. The study of the UV spectra allowed us to distinguish the different isomers on the basis of the maximum absorption wavelength in the range 270–290 nm, working with analytical amounts. The responses of diisopropylnaphthalenes in the principal analytical techniques may be useful as references for their identification in different matrices and with respect to the choice of the most suitable analytical system.

Table 5
Molecular shape parameter values calculated for each DIPN isomer

Isomer	L/B (max)
1,3-	1.166
1,7-	1.237
1,5-	1.420
1,6-	1.443
2,7-	1.710
2,6-	1.867

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