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Isolation and identification of diisopropylnaphthalene isomers in the alkylation products of naphthalene

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Abstract

GC analysis of diisopropylnaphthalene (DIPN) isomers is presented. Naphthalene was repeatedly alkylated with propylene over an amorphous aluminosilicate catalyst under different preparation conditions, and then pure isomers or at least DIPN fractions enriched in individual isomers were isolated from the alkylates and analysed using GC–MS, IR and NMR techniques. Eight of the ten possible isomers appeared in the chromatograms; seven of them (1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6- and 2,7-) were separated and identified, while the eighth one was indirectly proved to be 2,3-DIPN. The remaining two isomers (1,2- and 1,8-DIPN) were not found in the products.

Keywords: Naphthalenes; Diisopropylnaphthalenes

1. Introduction

Diisopropylnaphthalene (DIPN) isomers can be more and more frequently encountered in the environment and their analytical determination becomes more and more important. For example, DIPN mixtures are used as solvents in manufacturing of printing materials (e.g. carbonless copying papers) [1–3], or in agriculture as plant growth regulators [4].

Lately, 2,6-DIPN synthesis using shape-selective catalysts is of considerable interest, and so there is a need for the identification and determination of individual isomers in the product. Unfortunately, in most of the papers, where results of such catalytic tests are discussed, only the total content of β,β-isomers and the 2,6-DIPN/2,7-DIPN mole ratio are considered. Only a few papers have been published, where other DIPN isomers in an alkylation product are described [5–7]. Seven isomers (see Fig. 1) were detected, namely 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6- and 2,7-. Products of alkylation were analysed by gas chromatography with a 50-m OV-17 capillary column at 180 °C [5] or with a 30-m TC-17 capillary

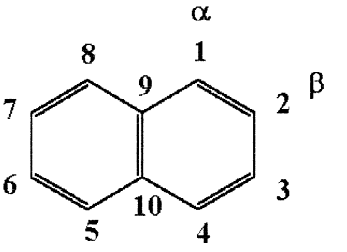

Fig. 1. Scheme of naphthalene nucleus with substitution positions.

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column at 170 °C [6]. However, neither particulars of identification nor assignment of individual peaks in the chromatogram have been published.

Sturaro et al. [8] detected and assigned DIPN isomers to the peaks of GC and HPLC fingerprints. They used GC–MS, HPLC and GC–Fourier transform (FT) IR. However, they were able to identify only six DIPN isomers both in GC and HPLC chromatograms. 1,4-DIPN appeared in the HPLC chromatogram together with 1,5-DIPN as a single peak. They did not detect 1,4-DIPN by GC, neither, although it could be present in the mixtures in concentrations as high as 40% [5,6].

In this paper, we present our studies on the detection and identification of diisopropylnaphthalenes by GC, using a capillary column of relatively high polarity. Such a column enabled us to resolve and detect more DIPN isomers than others did. We either isolated pure components or mixtures enriched in individual isomers, and then analysed them by ^{13}C-NMR and IR. NMR analysis as well as comparison of IR spectra of DIPN mixtures with spectra obtained by subtracting them one from the other (and/or subtracting spectra of pure isomers) let us isolate and identify signals characteristic for each isomer.

2. Experimental

2.1. Gas chromatography

Several samples of products, containing DIPN mixtures with different proportions of individual isomers, were analysed by GC using capillary columns with different stationary phases. Three Hewlett-Packard columns were tested: HP-1 with nonpolar dimethylpolysiloxane phase, HP-1701 with cyanopropylphenylmethylpolysiloxane phase of intermediate polarity, and HP-INNOWax with polar polyethylene glycol phase. Each column was 60 m×0.25 mm I.D., 0.25 μm film thickness. All columns were tested under the same analytical conditions on the HP-5890 II apparatus equipped with a flame ionization detector. The temperature programme was as follows: starting temperature of 120 °C for 3 min; rate of temperature increase of 8 °C/min; upper temperature of 220 °C for 30 min.

Injector and detector temperatures were 250 and 320 °C, respectively. Hydrogen was used as carrier gas at 0.4 m/s linear flow.

The electrical response from the GC apparatus was transformed with an analogue-to-digital interface and processed with aid of a personal computer.

2.2. Preparation of diisopropylnaphthalene fractions

Diisopropylnaphthalenes were isolated from two alkylates which had been prepared by the alkylation of naphthalene with propylene in a fixed bed reactor over amorphous aluminosilicate catalyst (PK-200, Solvay Catalysts, Germany) at considerably different preparation conditions. The first product was prepared at low reaction temperature of 160 °C and at high mass hourly space velocity (WHSV=14 h^{-1}); the diisopropylated product was relatively rich in α,α-isomers and the mono product was rich in 1-isopropylnaphthalene. The other one was prepared at higher temperature of 250 °C and at lower space velocity WHSV=4 h^{-1}; it was rich in 2-isopropylnaphthalene and β,β-diisopropylnaphthalenes and the concentration of α-substituted alkylnaphthalenes was low. Both alkylations were carried out under 3 MPa pressure and at a naphthalene-to-propylene mole ratio of 1.5.

GC chromatograms of the alkylates (the retention time range of mono- and diisopropylnaphthalenes) are shown in Fig. 2a,b.

Seven DIPN fractions differing one from the other in concentrations of particular isomers—including pure 2,6-DIPN and 1,3-DIPN fractions—were isolated from the alkylates by proper sequences of distillation and crystallisation as follows.

Two DIPN fractions, namely 1,3-DIPN crude fraction (302.5–303.5 °C) and 1,7-DIPN fraction of 61.8% purity (303.5–305 °C) were carefully distilled off from both alkylation products. The former fraction was cooled to 0 °C and the slurry was filtered off and recrystallised with methanol to give pure 1,3-DIPN with melting point 46.2 °C. It contained 97.7% of the pure isomer and its main contamination was 1,7-DIPN (2.1%).

A 2,6- and 2,7-DIPN rich fraction was isolated from the alkylation product rich in the β,β-isomer by distillation in the range of 196–197.5 °C under 40

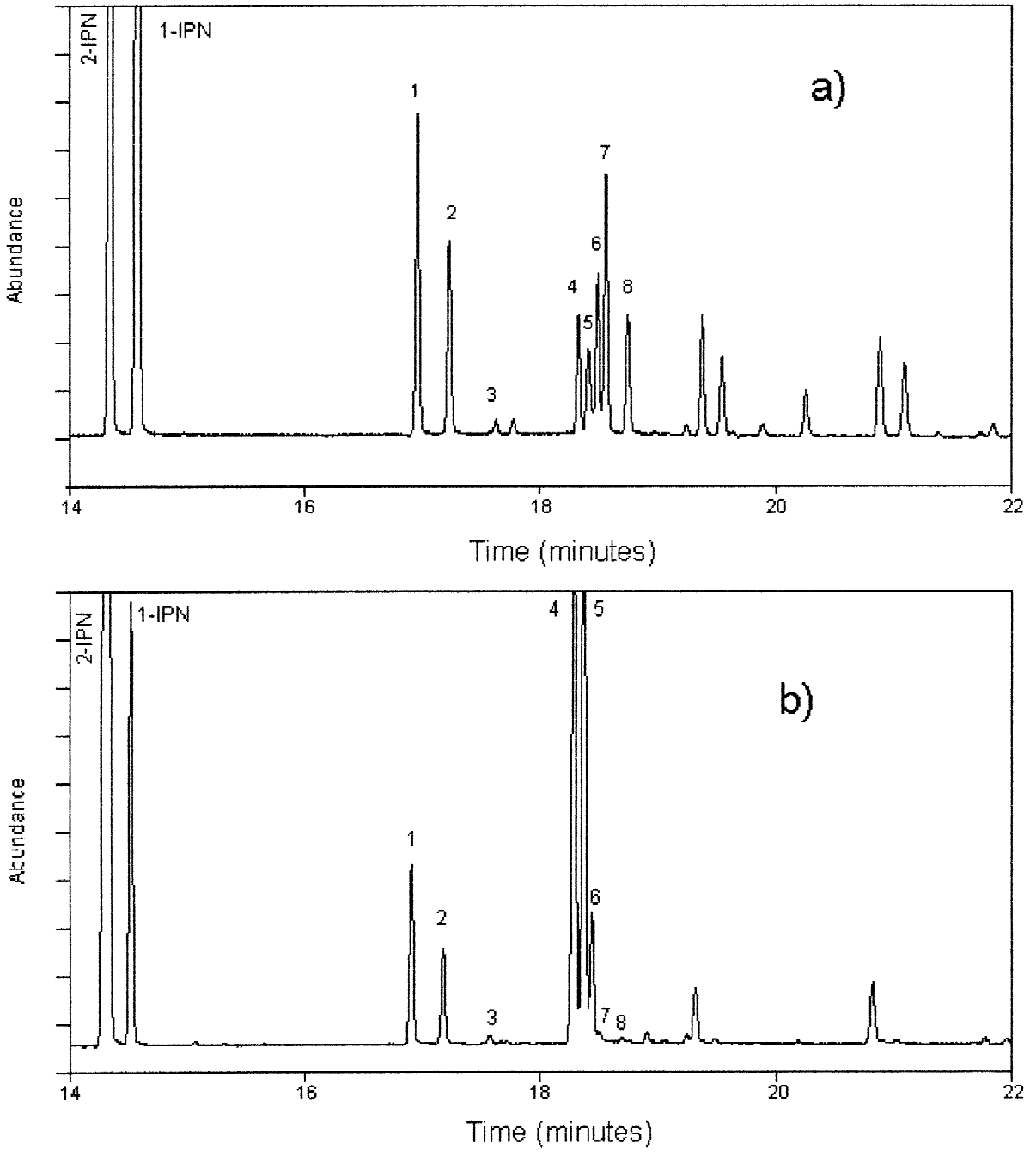

Fig. 2. Gas chromatograms of products of alkylation of naphthalene with propylene carried out at lower reaction temperature of 160 °C (a) and at higher temperature of 250 °C and at lower space velocity (b).

mmHg (1 mmHg=133.322 Pa). The fraction was cooled to −6 °C and crystals of crude 2,6-DIPN were filtered off. Mother liquor was 2.7-DIPN (64.3%) fraction whereas 2,6-DIPN crystals were recrystallised with methanol. The 2,6-DIPN fraction was 99.92% pure and revealed the same melting point as that published, i.e. 68.5 °C [9]. It contained 0.08% of 2,7-DIPN as the main impurity.

A fraction in the range 190–200 °C was distilled off under vacuum (40 mmHg) from the alkylation product rich in α,α-isomers. Next it was cooled to −15 °C and crystals of 2,6- and 1,5-DIPN were filtered off. The crystals were recrystallised with methanol and 313–315.5 °C fraction was distilled off to give 79.8% 1,5-DIPN fraction.

We did not succeed, however, in isolating fractions with high content (over 60%) of 1,6- and 1,4-diisopropylnaphthalenes—in particular, we were not able to remove 2,6-, 2,7- and 1,5-isomers. However, we prepared two fractions considerably differing in the 1,6- to 1,4-DIPN ratio.

2.3. GC–MS, IR and NMR analyses

The GC–MS analyses of DIPN fractions and starting alkylates were performed with a Hewlett-Packard mass spectrometer MS Engine HP-5890 B connected with a HP-5989 gas chromatograph equipped with 30 m×0.32 mm, 0.25 μm HP-INNOWax capillary column. Standard conditions (see Section 2.1) were applied except for helium carrier gas used instead of hydrogen. The helium flow was 0.5 cm^3/min, the ionising electron energy was 70 eV and the ion source temperature was 200 °C.

Infrared spectra were recorded in the range 4000–370 cm^{-1} with a FT-IR Perkin-Elmer System 2000 spectrometer with resolution 1 cm^{-1}.

A total of 25 MHz ^{13}C-NMR spectra of samples dissolved in C^2HCl_3 with tetramethylsilane (TMS) as an internal chemical shift standard were acquired with a Bruker WP-100SY spectrometer. Assignments of signals were made with the help of DEPT (Distortionless Enhancement by Polarization Transfer) and GASPE (Gated Spin Echo) subspectra editing techniques; chemical shift values for signals of individual carbon atoms in each isomer were also predicted with ACD/CNMR software of Advanced Chemistry Development (Toronto, Canada).

3. Results and discussion

Two gas chromatograms of alkylates, obtained on an HP-INNOWax column, are shown in Fig. 2. The time range corresponds to the retention times of mono-, di- and triisopropylnaphthalenes; peaks assigned to diisopropylnaphthalenes are marked with numbers 1–8. Their retention times were 1018, 1034, 1057, 1099, 1104, 1109, 1113 and 1125 s, respectively. Eight DIPN isomers (with molecular mass of 212 and suitable mass spectra) were detected by GC–MS; the mass spectra were very similar to those presented by Sturaro et al. [8]. For each DIPN isomer the base peak of ionic fragmentation was at m/z 197; other significant MS peaks were at m/z 212, m/z 155, m/z 153 and m/z 141, successively. An ionic fragment at m/z 183, which could be expected for dipropylnaphthalene molecules with at least one *n*-propyl substituent, was either very small or was absent.

We tested three capillary columns: HP-INNOWax (polar), HP-1 (non-polar) and HP-1701 (intermediately polar); the best resolution of DIPN isomers was achieved with the first of them. Although the eight peaks of diisopropylnaphthalene isomers could be distinguished also with the HP-1701 column, two of them overlapped with each other. Not more than seven peaks of diisopropylnaphthalenes could be detected with the HP-1 column; probably two of DIPN isomers appeared in the chromatogram as a single peak.

In order to assign GC peaks to appropriate isomers, we analysed seven DIPN fractions by IR spectroscopy. The spectra were compared in the 1000–680 cm^{-1} range. In each analysed fraction, one of the DIPN isomers was the most abundant and was present as a main GC peak. Thorough comparison of IR spectra recorded for the fractions and subtraction of already assigned bands from the given DIPN fraction spectrum enabled us to indicate bands characteristic for each DIPN isomer. IR bands for diisopropylnaphthalene isomers (marked in Fig. 2 with numbers) are shown in Table 1. They are compared with literature data [8] and also the best matching DIPN isomers are assigned to GC peaks.

Bands for diisopropylnaphthalenes corresponding to peaks 1 (1,3-DIPN) and 4 (2,6-DIPN) were obtained using pure compounds. In case of 1,5-, 1,7-

Table 1
IR absorption wavenumbers in the region 1000–680 cm^{-1} of DIPN fractions

Peak No. in the GC spectrum	IR absorption bands (cm^{-1}) [in parentheses: relative intensity (%)]	IR bands according to [8] (cm^{-1})	Assigned DIPN
1	750–754[a] (93), 784 (100), 857 (22), 885 (89), 940 (20)	780, 878, 942	1,3-DIPN
2	751 (ca. 50), 832 (100), 883 (ca. 20)	830	1,7-DIPN
4	685 (65), 817–822[a] (65), 883 (100), 892[a] (48), 931 (13)	810, 884, 924	2,6-DIPN
5	840 (100), 899 (38), 954 (19)	837, 899, 953	2,7-DIPN
6[c]	758 (100), 884 (ca. 80)	758, 835	1,6-DIPN
7	760 (100), 833 ? (ca. 75)	–	1,4-DIPN
8	774[b] (<30), 786 (100), 821 ? (36), 885 (65)	778	1,5-DIPN

[a] Doublet.
[b] On the slope.
[c] There are also bands in the region 830–790 cm^{-1}, however, overlapped by the ''ghosts'' of non-compensated 2,6-DIPN and 2,7-DIPN.

and 2,7-isomers, determination of IR band parameters was also simplified by the fact that although a given DIPN fraction was not highly pure, it frequently contained only one other DIPN isomer as a main impurity. For example, fraction of isomer 2 (1,7-DIPN) contained 61.8% of the 1,7-isomer and 30.7% of the 1,3-isomer. Subtraction of the IR spectrum of pure 1,3-DIPN from that of the 1,7-DIPN fraction enabled us to isolate three IR bands in the range 1000–680 cm^{-1} that derived from the 1,7-isomer. Similarly, subtraction of the IR spectrum of pure 2,6-DIPN from that of 1,5-DIPN fraction (peak 8), which contained 79.8% of the main isomer and 18.8% of the 2,6-DIPN impurity, allowed us to isolate bands characteristic for the 1,5-isomer.

Some difficulties appeared when we considered IR bands observed for GC peaks 6 and 7 (1,6-DIPN and 1,4-DIPN, respectively). It was necessary to compensate 2,6-, 2,7- and 1,5-DIPN occurring in the fractions in quite high concentrations and also to subtract both spectra from each other.

We did not succeed to determine IR bands for GC peak 3 because we were unable to prepare a fraction with relatively high concentration of this diisopropylnaphthalene isomer.

Our IR bands attributed to diisopropylnaphthalene isomers are generally consistent with those described by Sturaro et al. [8]; however, some discrepancies appeared. Moreover, we are able to distinguish some additional bands with significant intensity, not indicated by Sturaro et al. For 1,3-DIPN we can assume that our 784, 885 and 940 cm^{-1} bands correspond to literature bands 780, 878 and 942 cm^{-1}, respectively. However, we have also observed an intensive split band at 750–754 and a weak band at 857 cm^{-1}. Furthermore, the conformity of our 817–822 (split), 883 and 931 cm^{-1} bands with Sturaro et al.'s bands at 810, 884 and 924 cm^{-1} for the 2,6-DIPN can be recognised. Nevertheless, we were able to observe two additional bands: 685 and 892 cm^{-1} on slope of 883 cm^{-1} band. Our IR spectrum seems to be more precise, because we have tested highly pure (99.92%) 2,6-diisopropylnaphthalene which contained only a small admixture of 2,7-DIPN.

Quite good conformity of our and Sturaro et al.'s IR bands occurred in the case of 2,7-DIPN.

For 1,5-DIPN, apart from a very strong band at 786 cm^{-1} with a much smaller 774 cm^{-1} band on its slope (probably corresponding to the literature 778 cm^{-1} band), we could also distinguish bands at 821 and 885 cm^{-1}.

Both 1,4- and 1,6-isomers have very strong and very close bands (758 and 760 cm^{-1}, respectively). However, appropriate compensation of both spectra indicates the presence of the bands. We could also attribute the 884 cm^{-1} band to 1,6-DIPN. We observed also some bands in the region 830–790 cm^{-1} but they could be overlapped by non-compensated remains of the bands derived from 2,6- and 2,7-DIPN. The 835 cm^{-1} band observed for 1,6-DIPN by Sturaro et al. [8] was probably one of the bands from that region. The band at 833 cm^{-1}, attributed to 1,4-DIPN, is marked with a question mark because it can be strongly influenced by 2,6-, 2,7-, 1,5- and 1,6-DIPN bands.

IR bands have also been calculated by the quantum chemistry method. The parameters of theoretically calculated bands were in very good conformity

with the experimentally detected bands for DIPN isomers [10].

The individual fractions were also analysed with ^{13}C-NMR spectroscopy. Their spectra were compared with those predicted for individual DIPN isomers with the ACD/CNMR program, and thus their main components have been identified. Carbon atoms in isopropyl substituents, quaternary aromatic carbon atoms at the substitution positions, as well as the C_9 and C_{10} atoms in naphthalene rings have been recognised as most diagnostic (those last ones in spite of relatively slow longitudinal relaxation process). The observed (δ_{obs}), predicted ($\delta_{pr.}$) and—if available—literature ($\delta_{lit.}$) chemical shifts values are compiled in Table 2.

Observed chemical shifts for 1,4- and 1,6-diisopropylnaphthalenes were found by comparing ^{13}C-NMR spectra of two DIPN fractions with relatively high total content of both isomers, but considerably differing in their ratio. Although there were some difficulties in observing the C_9 and C_{10} atom signals (probably due to high longitudinal relaxation time T_1 values), the other δ values clearly indicated the substance 6 to be an α,β-isomer, i.e. 1,6-DIPN, and the substance 7 to be an α,α-isomer, i.e. 1,4-DIPN.

Comparison of gas chromatograms obtained for mixtures synthesised at two different alkylation conditions (Fig. 2a,b, respectively) also confirms that peaks 7 and 8 are α,α-isomers and peaks 4 and 5 are β,β-isomers. At mild reaction conditions, where high α-selectivity could be expected, the product contained relatively high concentrations of isomers 7 and 8, while at conditions favouring high β-selectivity, the diisopropylnaphthalene mixture was rich in isomers 4 and 5, whereas peaks 7 and 8 almost disappeared.

According to quantum chemistry calculations,

Table 2
Observed ($\delta_{obs.}$), predicted ($\delta_{pr.}$) and literature ($\delta_{lit.}$) values of ^{13}C-NMR chemical shifts in DIPN isomers (towards TMS)

GC peak No./DIPN isomer		Chemical shift δ (ppm)							
		Isopropyl substituents				Quaternary carbon atoms in naphthalene ring			
		CH[a]		CH_3 [a]		At the substitution positions[a]		Shared by aromatic rings	
								C_9	C_{10}
1 (1,3-DIPN)	$\delta_{obs.}$	28.67	34.41	23.61	23.91	145.94	144.52	130.27	134.48
	$\delta_{pr.}$	28.60	34.40	23.70	23.89	149.19	145.06	135.93	135.63
	$\delta_{lit.}$ [11]	28.62	34.37	23.61	23.90	145.85	144.54	130.26	134.47
2 (1,7-DIPN)	$\delta_{obs.}$	28.61	34.75	23.53	24.08	145.87	144.07	131.74	123.89
	$\delta_{pr.}$	28.50	34.20	23.70	23.89	145.99	144.47	130.34	137.30
4 (2,6-DIPN)	$\delta_{obs.}$	34.23	34.23	23.96	23.96	145.52	145.52	132.54	132.54
	$\delta_{pr.}$	34.20	34.20	23.89	23.89	145.91	145.91	136.37	136.37
	$\delta_{lit.}$ [12]	34.18	34.18	23.98	23.98	145.53	145.53	132.26	132.26
5 (2,7-DIPN)	$\delta_{obs.}$	34.31	34.31	23.95	23.95	146.28	146.28	131.01	134.13
	$\delta_{pr.}$	34.20	34.20	23.89	23.89	144.54	144.54	132.54	139.81
6 (1,6-DIPN)	$\delta_{obs.}$	28.45	34.02	23.58	23.66	146.17	145.29	134.46	?
	$\delta_{pr.}$	28.50	34.20	23.70	23.89	146.06	144.54	135.93	135.63
7 (1,4-DIPN)	$\delta_{obs.}$	28.65	28.65	23.58	23.58	146.17	146.17	?	?
	$\delta_{pr.}$	28.50	28.50	23.70	23.70	145.99	145.99	123.82	123.82
8 (1,5-DIPN)	$\delta_{obs.}$	28.83	28.83	23.66	23.66	145.31	145.31	131.93	131.93
	$\delta_{pr.}$	28.50	28.50	23.70	23.70	145.99	145.99	123.82	123.82

[a] Values in the first and the second column correspond to carbon atoms with the lower and the higher number, respectively.

40% of each of 2,6- and 2,7-diisopropylnaphthalenes can be expected in an isomeric mixture at the thermodynamic equilibrium, while any α,β-isomer can contribute several percents and an α,α-isomer below 1% [13]. Comparison of DIPN peaks in the alkylate obtained at severe conditions (Fig. 2b), i.e. a product with a composition close to thermodynamic equilibrium, clearly indicates that diisopropylnaphthalenes 4 and 5 are 2,6- and 2,7-isomers, diisopropylnaphthalenes 1, 2 and 6 are α,β-isomers, and 7 and 8 are α,α-isomers.

We were unable to identify directly peak 3. Theoretically three diisopropylnaphthalenes can be attributed to this peak—these are 1,2-DIPN, 1,8-DIPN and 2,3-DIPN. However, 2,3-DIPN is the most probable. First, according to theoretical calculations, a diisopropylnaphthalene mixture at thermodynamic equilibrium at temperature 150–300 °C should contain 0.7–1.9% 2,3-isomer [13], whereas no more than 0.008% 1.2-DIPN and 0.0002% 1,8-DIPN can be expected. Second, the presence of 2,3-dihydro-1,1,3-trimethyl-1H-benz[*f*]indene in the products of alkylation of naphthalene with propylene [14,15] can be a good evidence for the existence of 2,3-DIPN in the alkylation mixtures. Such indene-type species can be formed by dehydrogenation of 2,3-diisopropylnaphthalene. Also consideration of steric hindrances connected with the presence of two adjacent isopropyl substituents indicates that 2,3-DIPN can be expected in higher concentrations than 1,2-DIPN in which two adjacent isopropyl groups are additionally influenced by the neighbour naphthalene ring.

The above considerations indicate that the eighth DIPN isomer detected by GC–MS is 2,3-DIPN. Amounts of 1,2-DIPN and 1,8-DIPN in the naphthalene alkylation product are expected to be rather out of range of the GC analysis.

Better resolution of DIPN isomers was achieved with a polar capillary column than with a non-polar one. Eight of the ten DIPN isomers were identified in the alkylation products. The 1,2- and 1,8-DIPN were not found in the products.

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