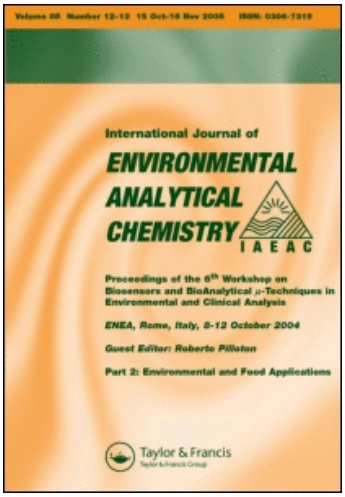

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The isomer-specific analysis of di-*iso*-propylnaphthalenes

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Di-*iso*-propylnaphthalenes (DIPN), frequently observed low-level contaminants of the aquatic environment, were analysed as the sum of isomers by GC/MS in Rhine and Lippe river sediments. For future isomer-specific trace analysis, linear retention indices of the components of a technical DIPN formulation were determined on six different GC-columns. Gas-phase infrared spectra aquired by GC/FT–IR analysis on GC capillaries coated with apolar and polar stationary phases showed characteristic patterns of C–H_{ar} out of plane deformation vibrations which allowed all DIPN isomers to be distinguished. Theoretical IR spectra of all DIPN were calculated with the B3LYP functional using 6-311G(d,p) and 6-311G+(d,p) standard triple zeta basis sets. The resulting frequencies were scaled by a factor derived emprically. Theoretical and experimental IR spectra allowed the structures of seven major DIPN isomers and two minor components to be assigned to the corresponding GC-peaks. All DIPN isomers of a technical formulation were resolved on polar GC capillaries, and the composition of the technical DIPN mixture was determined.

Keywords: Di-*iso*-propylnaphthalenes; Sediment; GC/MS; GC/FT–IR; Isomer-specific analysis; Retention index

1. Introduction

Di-*iso*-propylnaphthalenes (DIPN), produced and in use as a mixture of isomers, initially appeared in the aquatic environment when non-chlorinated replacement compounds for polychlorinated biphenyls were introduced for applications in open systems [1]. Studies on the environmental safety of DIPN date back to the 1970s, and oxygenated metabolites have been identified in biodegradation experiments with

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synthetic mixtures of ^{14}C-labelled DIPN without reference to single DIPN isomers [2, 3]. In vertebrates, the metabolism of one single DIPN isomer, 2,6-di-*iso*-propylnaphthalene [4–6] has been investigated.

Today, DIPN are frequently observed low-level contaminants of surface waters and aquatic sediments. Concentrations of the total of isomers ranged from 10 to 120 ng L^{-1} in Rhine river water between Bonn and Wesel [7] and reached 80 ng g^{-1} in Lippe river sediments. DIPN have been associated with tary off-flavours in drinking water [8], and migration of DIPN from paper and packaging materials into human foods is a matter of concern [9–12].

For the analysis of DIPN in environmental, biological, and food matrices, techniques of gas chromatography/mass spectrometry (GC/MS) are the most sensitive and selective presently available. However, the isomer-specific analysis of DIPN, needed to study migration processes, biodegradation, and metabolism in detail, has not been established fully. Isomer specifity in GC/MS relies on differences between the gas-chromatographic and/or mass-spectrometric properties of isomers and requires the assignment of the distinguished isomers to chemical structures on the basis of authentic reference compounds or reference data.

Technical DIPN consists mainly of seven of the 10 possible isomers (1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-), and may contain minor amounts of the sterically hindered *ortho*-(1,2- and 2,3-) compounds and at most traces of the most hindered *peri*-(1,8-) isomer. 2,6- and 2,7-DIPN are commercially available as single isomers only. 1,4-, 1,5-, and 1,8-DIPN have been prepared [13], but practicable isomer-specific laboratory syntheses depend on suitable starting materials for all isomers. Katayama *et al.* quantitatively analysed the composition of synthetic DIPN-mixtures by GC, and separated the seven main components of technical DIPN by distillation, crystallization, and preparative gas chromatography to confirm the identity of the isomers by ^{1}H- and ^{13}C-NMR spectroscopy, and GC/MS, but did not report the corresponding gas-chromatographic retention data [14]. GC/MS, HPLC with photo-diode array detection, and GC/Fourier-transform infrared spectroscopy (GC/FT–IR) of different synthetic mixtures of DIPN by Sturaro *et al.* [9] resulted in the assignment of the gas-chromatographic retention times of six DIPN isomers [9]. However, their IR data showed discrepancies with the results of Brzozowski *et al.*, who analysed partially purified DIPN isomers from synthetic mixtures by IR, NMR, and GC/MS, and assigned the retention times of 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-DIPN [15].

To provide a basis for the isomer-specific analysis of DIPN in environmental samples, we determined linear retention indices of the components of technical DIPN on GC-columns of different polarity and aquired gas phase IR spectra of the major DIPN isomers by GC/FT–IR analysis. The C–H_{ar} out-of-plane deformation vibrations in the 1000–600 cm^{-1} range provide characteristic patterns of absorption bands that allow the assignment of DIPN isomers by comparison with theoretical IR spectra obtained by quantum chemical calculations [16, 17]. Methods based on density functional theory (DFT) show an excellent performance in predicting both the harmonic force field (frequencies) and dipole moment derivatives (intensities) in the IR region [18]. For calculations, we used Becke's three-parameter hybrid functional B3LYP [19] as implemented in the GAUSSIAN suite of programs [20].

2. Experimental

2.1 *Sediment analysis*

2.1.1 Sediment sampling. Sediment sampling campaigns at the Lippe river were performed between summer 1999 and spring 2001. Details on sampling locations, sampling procedure and sample characterstics were published elsewhere [21]. Rhine river sediment samples were taken in August 2000 at 14 sampling locations between Bonn and Xanten by the Environmental Protection Agency of North-Rhine Westphalia (Landesumweltamt NRW). The samples were grabbed with a simple gripper device, filled in glass vessels with Teflon seals and stored at 4°C until extraction.

2.1.2 Extraction and fractionation. Sediment extraction and fractionation followed a published procedure [21]. Briefly, the samples were treated by sequential dispersion extraction with acetone and hexane. Each extraction was followed by centrifugation and separation of the solvent. The raw extracts were dried with anhydrous granulated sodium sulphate, and elemental sulfur was removed with activated copper powder. The extracts were separated into six fractions by liquid chromatography on silica gel using mixtures of pentane, dichloromethane, and methanol as eluents. After fractionation, 50 µL of internal standard mixture containing d_{34}-hexadecane (5.0 ng µL^{-1}), d_{10}-anthracene (5.0 ng µL^{-1}), and d_{12}-chrysene (5.0 ng µL^{-1}) in hexane were added.

Recovery rates were determined by spiking of pre-extracted sediments with reference compounds and subsequent application of the analytical procedure. The recovery rate of DIPN was 51%. Analyses of method blank samples ($n = 3$) revealed no laboratory contamination.

2.1.3 GC/MS analysis of sediment fractions. GC/MS analysis was carried out with a Finnigan MAT 8222 mass spectrometer (Finnigan, Germany) linked to an HP 5890 gas chromatograph (Agilent, USA). A 30 m × 0.25 mm i.d. × 0.25 µm film BPX-5 fused silica capillary column was used (SGE, Australia). The GC conditions were 1 µL split/splitless injection at 60°C, splitless time 60 s, GC temperature programme: 3 min hold, 3°C min^{-1} to 300°C, helium carrier-gas velocity 40 cm s^{-1}. The mass spectrometer was operated in full-scan mode at a resolution of 1000 in (EI$^+$, 70 eV), source temperature 200°C, scanning from 35 to 700 amu with a rate of 1 s decade^{-1} and an inter-scan time of 0.1 s.

Quantitative data were obtained by integration of selected ion chromatograms extracted from the total ion current. The ions used for quantification were m/z 197 and 212. GC/MS response factors for quantification were determined from four-point linear regression functions based on calibration measurements with different compound concentrations. For correction of injection volume and sample-volume inaccuracies, the internal standard was used.

Limits of quantification (signal-to-noise ratio of approx. 10 : 1 in real samples) were calculated at 1 ng g^{-1} dry matter. All concentrations are recovery-corrected and normalized on dry-weight bases.

2.2 *Analysis of technical DIPN*

2.2.1 GC/MS analysis. Solutions of 5–10 ng μL^{-1} of technical DIPN in *n*-hexane were analysed on a VG 70-250 SE (Micromass, UK) mass spectrometer (EI^+, 70 eV, 200°C source temperature, RP 1000, m/z 35–500 at 0.7 s $decade^{-1}$) linked to a HP 5890 (Agilent, USA) GC using (a) a BPX-5 (SGE, Australia) fused silica capillary column, 50 m × 0.22 mm i.d. × 0.25 μm film, with 1 μL splitless injection, and a temperature programme of 60°C, 3 min hold, 3°C min^{-1} to 300°C; and (b) a DB-5MS (J&W, USA) fused-silica capillary column, 30 m × 0.25 mm i.d. × 0.25 μm film, with 1 μL on-column injection, and a temperature programme of 50°C, 3 min hold, 3° min^{-1} to 300°C, helium carrier gas at 35 cm s^{-1}.

2.2.2 GC/FT–IR analysis. Solutions at concentrations of 300, 750, 1500, and 3000 ng μL^{-1} of technical DIPN in *n*-hexane were analysed on a HP5890 II/HP5965A IRD (Agilent, USA; Biorad, USA) GC/FT–IR combination with FID in line with the IRD flow cell by splittless injections (1 μL, 1 s) on fused-silica capillary columns with H_2 carrier gas at 35–40 cm s^{-1} linear velocity: (a) BPX-5 (SGE, Australia) 50 m × 0.32 mm i.d. film 0.5 μm, 80°C, 3 min isoth., 10°C min^{-1} to 150°C, 3°C min^{-1} to 250°C; and (b) Innowax (J&W, USA) 30 m × 0.25 mm i.d. film 0.25 μm, 80°C, 3 min isoth., 3°C min^{-1} to 220°C. FT–IR spectra were aquired in the range of 4000–550 cm^{-1} at 4 cm^{-1} optical resolution and 250°C flow cell temperature.

2.2.3 Gas-chromatographic retention indices. Retention indices of DIPN were determined by analysing *n*-hexane solutions containing 5–10 ng μL^{-1} of technical DIPN and *n*-alkanes (C_{11}–C_{26}, 2 ng μL^{-1} each) as reference using an HP6890 (Agilent, USA) GC with programmable temperature vapourizer (PTV) and flame ionization detector (FID). Gas chromatography was performed on the following fused-silica capillary columns with hydrogen as carrier gas at 35 cm s^{-1} linear velocity: HP-5 (Agilent, USA) 30 m × 0.32 mm, film 0.25 μm, 40°C, 2 min isoth., 30°C min^{-1} to 120°C, 1°C min^{-1} to 300°C, Innowax (J&W, USA) 30 m × 0.25 mm, film 0.25 μm, 40°C, 2 min isoth., 30°C min^{-1} to 80°C, 3 min isoth., 3°C min^{-1} to 220°C, SolGel-Wax (SGE, Australia) 30 m × 0.25 mm, film 0.25 μm, 40°C, 2 min isoth., 30°C min^{-1} to 80°C, 3 min isoth., 3°C min^{-1} to 220°C, Optima-FFAP (Macherey & Nagel, Germany) 50 m × 0.25 mm, film 0.25 μm, 40°C, 2 min isoth., 30°C min^{-1} to 80°C, 3 min isoth., 3°C min^{-1} to 220°C, SP-2331 (Supelco, USA) 60 m × 0.32 mm, film 0.20 μm, 40°C, 2 min isoth., 30°C min^{-1} to 60°C, 3 min isoth., 3°C min^{-1} to 180°C, and CP-Sil-88 (Chrompack, The Netherlands) 50 m × 0.26 mm, film 0.20 μm, 40°C, 2 min isoth., 30°C min^{-1} to 60°C, 3 min isoth., 3°C min^{-1} to 210°C.

3. Results and discussion

GC/MS screening analyses of surface water and freshwater sediments frequently showed the presence of a group of compounds, easily identified by their mass spectra as the isomers of di-*iso*-propylnaphthalenes (DIPN). However, the mass spectra of DIPN isomers are virtually identical (see figure 1), and the small differences in the relative

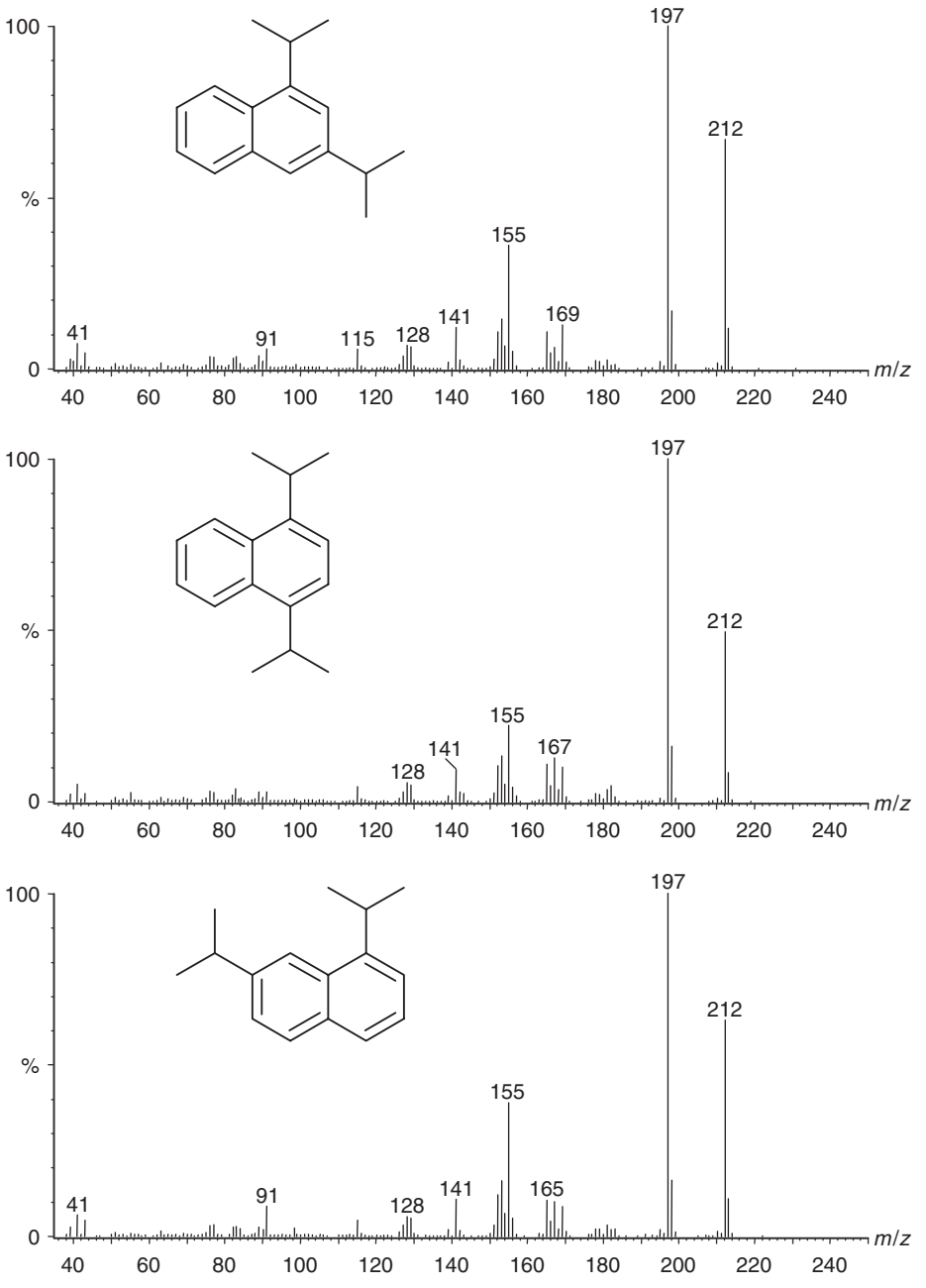


Figure 1. Mass spectra of DIPN from a GC/MS analysis (DB-5MS, see section 2.2.1) do not allow to differentiate isomers (upper 1,3-DIPN, middle 1,4-DIPN, lower 1,7-DIPN).

intensities of molecular and fragment ions observed between isomers [9] are not sufficient to assign structures. In addition, gas chromatography on capillary columns coated with apolar stationary phases which are often used in environmental analysis resolves technical DIPN incompletely into five or six major and one or two minor peaks

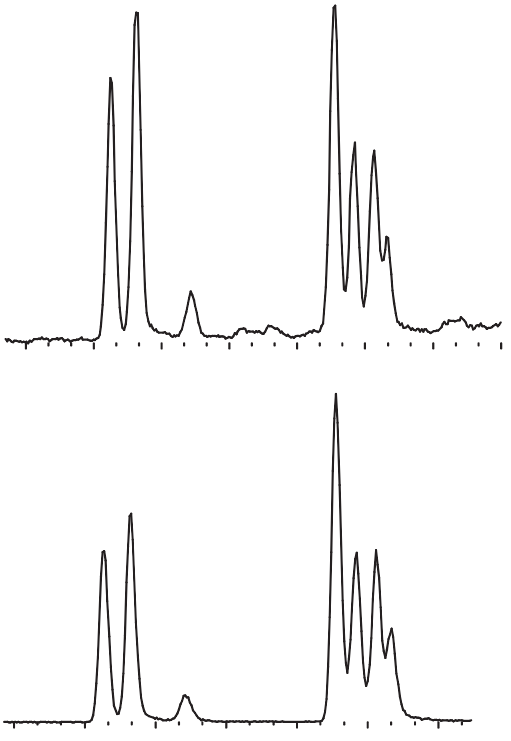


Figure 2. Fragment ion chromatograms (m/z 212) of Lippe river sediment (upper) and technical DIPN (Ruetasolv DI®, lower) showing the pattern of DIPN isomers on a BPX-5 capillary column under the conditions of sediment analysis.

(see figure 2), whereas it consists of seven major and two (or three) minor components of the 10 possible isomers.

3.1 *DIPN in Rhine river and Lippe river sediments*

DIPN were analysed in Lippe and Rhine river sediments by GC/MS using a non-polar (BPX-5) GC column. The amounts, therefore, given as the totals of all detected DIPN-peaks (see table 1) are generally low ranging from the limit of detection up to 80 ng g^{-1} dry matter. This concentration range corresponds well with data by Peterman and Delfino [1], who analysed DIPN in sediments and biota of the Fox river, Wisconsin, USA, and concluded that the origin of the sediment contamination by DIPN was a result of a source-point emission related to activities of the paper industry in this region. On the contrary, a low but widespread contamination of sediments in the Rhine river system can be assumed on the basis of our data. Since DIPN are not only common PCB substituents but also used in serveral different technical products and applications, this wide-ranging distribution is not surprising.

By comparing the quantitative data in Rhine river sediments with those published for Rhine river water samples derived from the same area [7], an accumulation in the particulate matter as a result of the lipophilicity of DIPN is obvious. However, notable

Table 1. Total concentrations ($ng\,g^{-1}$) of di-*iso*-propylnaphthalenes in sediments of the Lippe and Rhine rivers in 1999–2001.

Sampling locations, Lippe river	August 1999	February 2000	August 2000	March 2001	Sampling locations, Rhine river	August 2000
Wesel	83	2	3	30	Harbour Oberwinter	6
Hervest-Dorsten	< 1	5	5	< 1	Harbour Mondorf	9
Hüls AG	< 1	16	< 1	29	Harbour Köln-Deutz	13
Haltern	12	3	< 1	6	Petroleum Harbour Köln-Niehl	17
Datteln	37	< 1	38	3	Harbour Neuss	36
Lünen-Buddenburg	29	51	19	19	Harbour Düsseldorf	61
Hamm-Nordheringen	< 1	70	< 1	< 1	Harbour Krefeld	39
Lipperode	19	20	< 1	1	Harbour Wanheimerort	24
Bad Lippspringe	9	7	9	2	Harbour Duisburg	26
					Xanten	19
					Harbour Wesel	18
					Harbour Wesel	28
					Harbour Niedermörmter	37
					Keeken-Bimmen	< 1

amounts of DIPN with concentrations of up to $120\,ng\,L^{-1}$ remain in the water phase and, therefore, remain available for bioaccumulation by aquatic organisms.

3.2 *Isomer-specific analysis of DIPN*

Treating a whole group of isomeric compounds analytically as a sum paramter 'DIPN' is certainly not adequate if detailed information on the environmental fate is questioned. IR spectroscopy in conjunction with other spectroscopic methods has been used to assign single DIPN from mixtures by comparison with IR spectra of dimethylnaphthalenes [9] and with calculated IR spectra [16, 17]. However, in a GC/FT–IR-study [9], some isomers were separated incompletely on a non-polar GC column, and by the use of a narrow band IR-detector ($750–4000\,cm^{-1}$), spectral information in the $750–550\,cm^{-1}$ region could not be obtained. A good separation of the isomers on a polar GC column was achieved in another study [15], but IR spectroscopy was applied offline to isomerically enriched mixtures of DIPN leading to mixture IR spectra for some isomers.

3.2.1 GC/FT–IR analysis and computational chemistry. To provide a basis for the isomer-specific analysis of DIPN, we re-investigated the GC/FT–IR responses of a technical DIPN-mixture on BPX-5 (apolar, incomplete separation) and Innowax (polar, good separation) GC columns and obtained IR spectra of the seven main compontents with a broad band IR-detector in the $550–4000\,cm^{-1}$ wavenumber range. Unambiguously assigning the IR spectra to structures with reference to the published IR-data was not straightforward, because of differences between the literature data [9, 15, 16] and our experimental IR spectra.

Therefore, IR spectra of all DIPN isomers were calculated using density functional therory (DFT) with Becke's three-parameter exchange functional [19] in combination with the Lee–Yang–Parr correlation functional [22] (B3LYP).

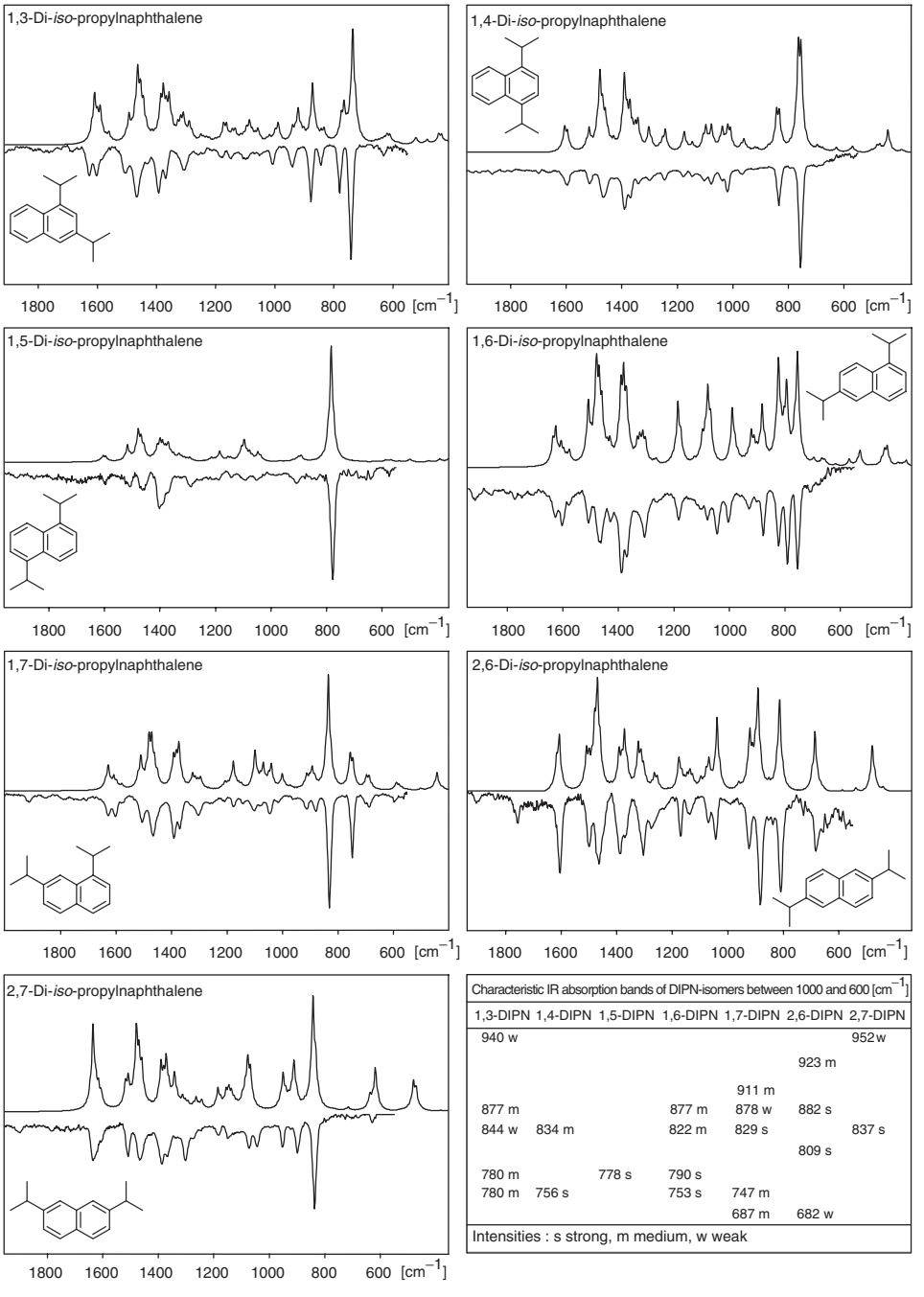
All equilibrium geometries, force fields, and dipole moment derivatives were computed using a standard triple zeta basis set augmented with polarization functions on carbon and hydrogen. Diffuse functions were added on all carbon atoms (6-311+G(d,p)) in order to predict reliable IR intensities [23]. Force constants and dipole moment derivatives were calculated using analytical second derivatives. Since no scaling factors are available for this relatively large basis set, the resulting vibrational frequencies were scaled by a factor of 0.9752 derived from fitting calculated frequencies of strong absorption bands to the experimental in the 1000–600 cm^{-1} range (the factor originally developed for the 6-31G(d) basis set [24] is 0.9613). A normal coordinate analysis was carried out using Wilson's GF Method [25]. A 6-311G(d,p) basis set gave excellent matches of theoretical and experimental spectra of 1,3-, 1,4-, 1,7-, and 2,6-DIPN after scaling the vibrational frequencies. However, for the 1,5-, 1,6-, and 2,7-isomers, better fits to the experimental data were obtained after reoptimizing the geometry with a 6-311+G(d,p) basis set, and the spectra calculated finally allowed the structures of seven major DIPN isomers to be assigned to the corresponding GC peaks (see figure 3).

As the sensitivity of GC/FT–IR is about two orders of magnitude less than that of GC/MS, relatively high amounts of DIPN had to be used to aquire infrared spectra of sufficient quality. With 1 μL, injected concentrations of 750 and 1500 ng μL^{-1} gave the best results. At 3000 ng μL^{-1}, serious peak broadening caused by column overload deteriorated the chromatographic resolution. However, at this high concentration, a mixed IR spectrum of the minor components of DIPN could be obtained with bands at wavenumbers 883, 813, and 742, and relative intensities of 30, 50, and 100, respectively. Corresponding bands were present in the theoretical spectra of 2,3-DIPN at wavenumbers 887 (60) and 740 (100), and of 1,2-DIPN at 814 (80) and 737 (100) but absent in the calculated spectrum of 1,8-DIPN with bands at 820 (35) and 769 (100) cm^{-1}. Therefore, the observed mixture spectrum is considered to be composed of roughly equal amounts of 2,3- and 1,2-DIPN. By gas-chromatographic analysis, a 2,3-DIPN/1,2-DIPN ratio of $\approx 3/2$ was found (see table 2).

Jamroz *et al.* [16] predicted IR bands for 2,3-DIPN at 880 (66) and 749 (100), 1,2-DIPN at 819 (100) and 750 (90), and 1,8-DIPN at 828 (66) and 776 (100) cm^{-1}. The calculated frequencies are in reasonable agreement with our data, but the relative intensities differ in the theroretical spectra of 1,2- and 1,8-DIPN.

3.2.2 Gas-chromatographic analysis and retention indices of DIPN. With the assignment of the gas-chromatographic peaks on apolar (BPX-5) and polar (Innowax) stationary phases to the corresponding structures, the elution pattern of the DIPN isomers on six different GC columns was determined (apolar: HP-5, carbowax-type: Innowax, SolGel-Wax and FFAP, cyanopropylsilicone: SP-2331 and CP-Sil-88). Linear retention indices (RI, see table 3) were calculated by scaling linearly the retention time (t) distance between a DIPN component and the preeluting n-alkane (carbon number n) with the distance between the post- (carbon number $n+1$) and the pre-eluting n-alkane, according to

$$\mathrm{RI} = 100 \times \left[n + \frac{(t - t_n)}{(t_{n+1} - t_n)} \right].$$



Characteristic IR absorption bands of DIPN-isomers between 1000 and 600 [cm^{-1}]

1,3-DIPN	1,4-DIPN	1,5-DIPN	1,6-DIPN	1,7-DIPN	2,6-DIPN	2,7-DIPN
940 w						952 w
					923 m	
				911 m		
877 m			877 m	878 w	882 s	
844 w	834 m		822 m	829 s		837 s
					809 s	
780 m		778 s	790 s			
780 m	756 s		753 s	747 m		
				687 m	682 w	

Intensities : s strong, m medium, w weak

Figure 3. Calculated (upper traces) and measured (lower traces) infrared spectra of the seven major DIPN isomers in the range of 400–1800 cm^{-1} and isomer-specific C–H_{ar} out-of-plane deformation vibrations.

Table 2. Composition of a technical DIPN formulation determined by GC/FID on Innowax and CP-Sil-88 capillary columns.

Innowax	*t* (min)	Area (%)	CP-Sil-88	*t* (min)	Area (%)
1,3-DIPN	35.38	14.5	1,3-DIPN	33.54	14.5
1,7-DIPN	35.82	17.7	1,7-DIPN	33.86	17.7
1,2-DIPN	36.49	1.2	2,6-DIPN	34.67	14.1
2,3-DIPN	36.66	1.7	2,3-DIPN	34.97	1.7
2,6-DIPN	37.57	14.1	2,7-DIPN	35.06	11.6
2,7-DIPN	37.72	11.6	1,2-DIPN	35.19	1.2
1,6-DIPN	37.90	14.2	1,6-DIPN	35.35	14.2
1,4-DIPN	38.10	17.8	1,4-DIPN	35.70	17.8
1,5-DIPN	38.39	7.2	1,5-DIPN	35.96	7.2

Table 3. Linear retention indices of DIPN isomers on six different capillary columns.

Apolar		Carbowax-type				Cyanopropylpolysiloxane		
	HP-5		Innowax	SolGel	FFAP		SP-2331	CP-Sil-88
1,3-DIPN	1662.1	1,3-DIPN	2139.4	2092.4	2162.1	1,3-DIPN	2368.7	2406.2
1,7-DIPN	1666.8	1,7-DIPN	2154.2	2106.4	2177.7	1,7-DIPN	2382.8	2421.1
1,2-DIPN	1676.1	1,2-DIPN	2176.9	2127.6	2200.0	2,6-DIPN	2420.2	2458.7
2,3-DIPN	1676.1	2,3-DIPN	2182.8	2132.8	2210.0	2,3-DIPN	2431.3	2472.6
1,4-DIPN	1703.5	2,6-DIPN	2214.1	2164.1	2241.5	2,7-DIPN	2436.5	2477.0
2,7-DIPN	1706.6	2,7-DIPN	2219.2	2168.6	2246.3	1,2-DIPN	2441.7	2482.8
1,6-DIPN	1706.6	1,6-DIPN	2225.8	2175.1	2253.6	1,6-DIPN	2451.0	2490.3
2,6-DIPN	1709.1	1,4-DIPN	2256.7	2181.5	2260.4	1,4-DIPN	2467.4	2506.9
1,5-DIPN	1714.8	1,5-DIPN	2234.6	2190.7	2271.2	1,5-DIPN	2479.9	2519.4

On HP-5, like DB-5MS and BPX-5 a methylpolysiloxane with 5% phenyl groups, DIPN eluted between *n*-hexadecane and *n*-octadecane with complete separation of 1,3-, 1,7-, and 1,5-DIPN from other isomers, partial separation of 1,4- and 2,6-DIPN, and coelution of the pairs 1,2-, 2,3- and 1,6-, 2,7-DIPN. However, 1,2- and 2,3-DIPN can be partially separated on this stationary phase, at the expense of the resolution of other isomers. Under different GC conditions, 1,4- and 2,7-DIPN may coelute, while 1,6-DIPN is better and 1,5-DIPN less resolved from 2,6-DIPN (compare figure 2 and table 3).

The good separation of DIPN achieved with polar columns is shown exemplarily for Innowax and CP-Sil-88 in figure 4. With the carbowax-type stationary phases tested (Innowax, SolGel-Wax and FFAP), retention times shifted to higher RI in the range of *n*-heneicosane to *n*-tricosane, and nine DIPN isomers were completely separated. Compared with the elution on HP-5, the elution order on the carbowax stationary phases of 2,6- and 1,4-DIPN is reversed.

SP-2331 and CP-Sil-88 coated with 100% cyanopropylpolysiloxane as stationary phase eluted the DIPN isomers in the range of *n*-tricosane to *n*-pentacosane (because *n*-alkanes are relatively fast eluting on this type of column). As with carbowax columns, the DIPN isomers were fully resolved on cyanopropylpolysiloxane stationary phases. The relative amounts of DIPN isomers in the mixture determined on Innowax and CP-Sil-88 (see table 2 and figure 4) clearly showed the different elution order on

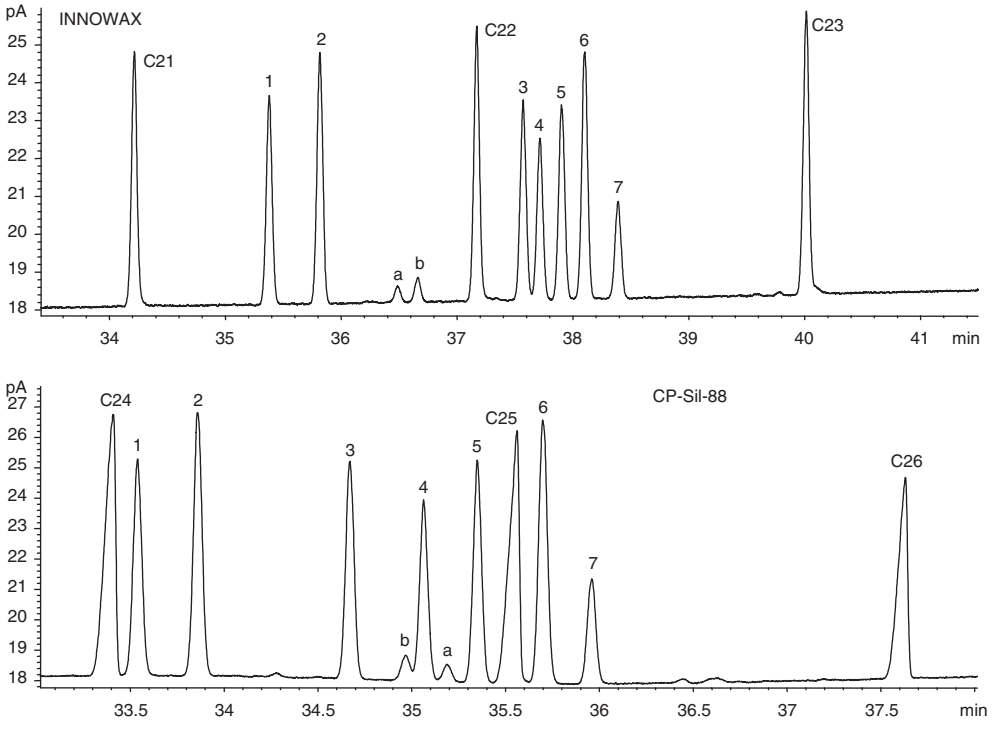


Figure 4. Gas-chromatographic separation of DIPN isomers on polar carbowax-type (upper chromatogram Innowax) and cyanopropylpolysiloxane (lower chromatogram CP-Sil-88) stationary phases. 1: 1,3-DIPN; 2: 1,7-DIPN; 3: 2,6-DIPN; 4: 2,7-DIPN; 5: 1,6-DIPN; 6: 1,4-DIPN; 7: 1,5-DIPN; a: 1,2-DIPN; b: 2,3-DIPN (a and b assigned from a mixture IR).

carbowax-type and 100% cyanopropylpolysiloxane capillaries. CP-Sil-88 and SP-2331 eluted 2,6- earlier than 2,3-DIPN, 2,7- earlier than 1,2-DIPN, and the pair 1,2- and 2,3-DIPN appeared in reversed order.

4. Conclusion

Di-*iso*-propylnaphthalene isomers are most efficiently separated by gas chromatography on polar stationary phases. Assigned by GC/FT–IR analysis and calculated vibrational spectra, the elution order of DIPN was established on methyl-(5% phenyl)-polysiloxane, carbowax type, and 100% cyanopropylpolysiloxane fused silica capillary columns. The seven main isomers of technical DIPN, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-, account for 97% of the composition of the mixture. Of the sterically hindered *ortho*-isomers, 1.2% (1,2-) and 1.7% (2,3-) were present. The most hindered *peri*-isomer (1,8-) was not detected. The elution order of DIPN isomers determined on an Innowax capillary column is in agreement with Brzozowski *et al.* [15], who indirectly assigned the 2,3- but not the 1,2- isomer. In the analysis of Sturaro *et al.* [9], 1,4-DIPN was erroneously assigned as the 1,6-isomer [9].

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