

APPLICATION OF CAPILLARY GC/MS TO THE ANALYSIS OF WASTES FROM CHEMICAL PLANTS.

II. IDENTIFICATION OF NAPHTHYL[b]THIOPHENES AND BINAPHTHYLS IN GASEOUS RELEASES FROM THE PRODUCTION OF 2-NAPHTHOL

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Naphthyl[b]thiophenes were identified in gaseous releases from the production of 2-naphthol based on the elucidation of their mass spectra. The identification was verified by comparison with mass spectra and retention data of the authentic compounds which were synthesized for this purpose. Three isomeric binaphthyls were also found in the industrial releases.

2-Naphthol is among the most important naphthalene intermediates. It finds application, e.g., in the production of tar dyes and serves as the starting raw material in the preparation of artificial tanning materials and other organic substances. Its production, however, burdens the environment considerably by its emissions. The substance is manufactured, following Technological Guidelines¹, by discontinuous sulfonation of naphthalene with sulfuric acid. The sulfonation mixture is subjected to hydrolysis and treatment by salting-out to isolate sodium 2-naphthalenesulfonate. The salt is then added portionwise to sodium hydroxide and converted to sodium 2-naphtholate by alkali fusion in a melting kettle at 280 – 335 °C. The final product is obtained by acidification, isolation and refining. The alkali fusion of sodium 2-naphthalenesulfonate in kettles is a key operation which gives rise to waste gases that are released into the environment. The gases are complex mixtures which contain appreciable quantities of naphthalene and other substances, among which dihydronaphthalene, tetralin, benzo[b]thiophene, methylnaphthalenes, quinoline, naphthol, some higher molecular weight components such as dinaphthyl ethers and dinaphthyl sulfides and other compounds have also been identified².

The present work was aimed at the identification of unknown substances in the releases by using the gas chromatography/mass spectrometry combination (GC/MS). In

addition to the various types of substances identified previously², an interesting group of isomeric compounds having the formula $C_{18}H_{12}S_1$ was found and attributed to the class of naphthylbenzo[*b*]thiophenes. In samples of the waste gases, this group was accompanied by three isomeric binaphthyls, whose formation in the existing conditions can be expected because they generally arise from naphthalene at 280 – 285 °C in the presence of various catalysts^{3,4}.

In contrast to binaphthyls, few data concerning naphthylbenzo[*b*]thiophenes have been found in available literature. 3-(1'-Naphthyl)benzo[*b*]thiophene was first synthesized by Schuetz and Ciporin⁵. 2-(2'-Naphthyl)benzo[*b*]thiophene was isolated from crude naphthalene in 1961 by Lamberton and Mc Grail⁶, who later examined additional procedures for the preparation of this isomer and studied its properties^{7 - 9}. 2- and 3-(1'-naphthyl)benzo[*b*]thiophenes have not been studied extensively and only mentions of their photochemical behaviour¹⁰ and UV and fluorescence spectra^{11,12} could be found. Mass spectra of naphthylbenzo[*b*]thiophenes, except for the 2-(1'-naphthyl) isomer, have been published in the collection¹³. In the present work, reference GC/MS analyses of the authentic compounds were also used for an unambiguous identification of the naphthylbenzo[*b*]thiophenes.

EXPERIMENTAL

Samples

Waste gas samples from the manufacture of 2-naphthol were taken at the VCHZ Synthesia Chemical Works in Pardubice-Semtin. The sampling site was after the melting kettle. An evacuated glass device of 1 litre volume was used for sampling the waste gases, which were trapped in 10 ml of hexane.

Reference Compounds

2-(1'-Naphthyl)benzo[*b*]thiophene was prepared¹⁰ by reduction of 2-(1'-naphthyl-3,4-dihydro)benzo[*b*]thiophene, which was obtained by reacting 2-benzothienyllithium¹⁴ and 1-tetralone. The product was purified by column chromatography (silica gel/petroleum ether).

2-(2'-Naphthyl)benzo[*b*]thiophene was prepared from benzothiophene, butyllithium and 1-chloronaphthalene⁹.

3-(1'-Naphthyl)benzo[*b*]thiophene^{5,10,15} was synthesized by reduction of 3-(1'-naphthyl-3,4-dihydro)benzo[*b*]thiophene, which was prepared by reacting 1-tetralone with benzo[*b*]thiophene-magnesium bromide.

3-(2'-Naphthyl)benzo[*b*]thiophene was prepared in the same manner as 3-(1'-naphthyl)benzo[*b*]thiophene, only 2-tetralone was used instead of 1-tetralone.

Apparatus and Measurement Conditions

An MS 25 RFA mass spectrometer (Kratos) was used. The EI mass spectra were recorded at 70 eV and an ionization current of 100 μ A under low resolution conditions ($R_{10\%} = 600$). The ion source temperature was 250 °C. The calibration region for routine measurements was 28 – 480 daltons. The mass spectrometer was directly interfaced to an HP 5890 gas chromatograph (Hewlett-Packard),

equipped with capillary columns and working in the splitless mode. The capillary column used was an HP Ultra-2 (25 m \times 0.20 mm, 0.11 μ m film thickness, fused silica, 5% phenylmethylsilicone) and was directly introduced into the MS ion source. The temperature programme was as follows: 60 $^{\circ}$ C for 1 min, 10 $^{\circ}$ C min^{-1} rise up to 280 $^{\circ}$ C, then isothermally, injector temperature 250 $^{\circ}$ C. Helium served as the carrier gas. The junction between the GC system and the MS ion source was held at 250 $^{\circ}$ C.

RESULTS AND DISCUSSION

Figure 1 shows a segment of a chromatogram of the gas effluent after the melting kettle, corresponding to higher boiling compounds (retention times 18.5 to 26 min). Curve *a* pertains to the total ionic current (TIC), whereas curves *b* and *c* represent ionic currents of the molecular ions of binaphthyls and naphthylbenzo[*b*]thiophenes. The chromatograms demonstrate that the actual sample contains all the four naphthylbenzo[*b*]thiophene isomers (M^+ 260, chromatographic peaks Nos 2, 4, 5 and 7) and three binaphthyl isomers (M^+ 254, peaks Nos 1, 3 and 6). The two types of compound belong to the group of polyaromatic hydrocarbons, whose EI mass spectra are usually relatively simple: generally, the signal of the molecular ion M^+ is very intense and

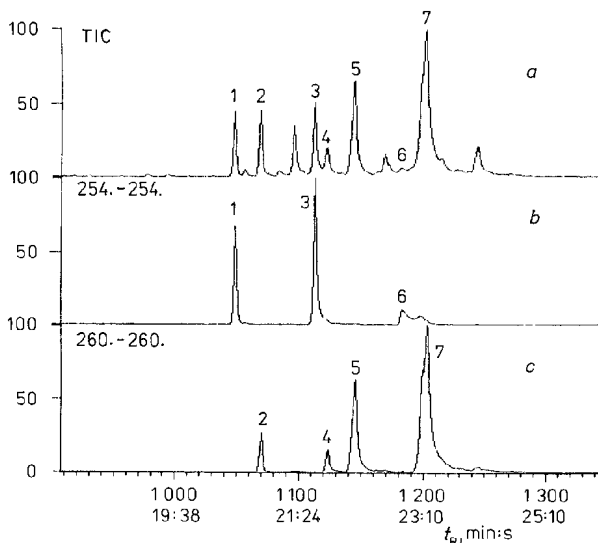


FIG. 1

Chromatogram of a sample of industrial releases from the production of 2-naphthol taken after the melting kettle; *a* total ionic current, *b* molecular ions M^+ of binaphthyls (254), *c* molecular ions M^+ of naphthylbenzo[*b*]thiophenes (260)

fragmentation is poor. Because of the absence of fragment ions, isomeric compounds usually fail to be discriminated based on their EI spectra solely.

The mass spectral patterns (EI, 70 eV) of the isomeric binaphthyls (Fig. 2) and naphthylbenzo[*b*]thiophenes (Fig. 3) are very similar. The high stability of the molecular ions (254 and 260 daltons, respectively) is also borne out by the occurrence of peaks of the doubly charged ions M^{2+} and $(M - 2)^{2+}$ with a medium abundance.

The loss of hydrogen atoms from the molecular ion, which occasionally can contribute some structural information, is documented by the presence of the ions $(M - 1)^+$ and $(M - 2)^+$ with a high abundance. For instance, the steric arrangement of 1,1'-binaphthyl and 1,2'-binaphthyl facilitates the loss of two hydrogen atoms, which gives rise to a structure whose arrangement probably corresponds to perylene. A similar situation apparently occurs during the elimination of hydrogen atoms from 3- and 2-(1'-naphthyl)benzo[*b*]thiophene. The presence of one sulfur atom in the molecule is manifested by the peak of the ion $(M + 2)^+$ with an intensity corresponding to the natural abundance of ^{34}S . The signals of the ion $(M - 32)^+$ (elimination of the sulfur atom, $m/z = 228$) and of the ion $(M - 45)^+$ (elimination of the $-\text{CHS}$ group, $m/z = 215$) are very low intensity but their importance from the constitutional analysis point of view is appreciable because they also confirm the presence of sulfur in the aromatic system of the molecule.

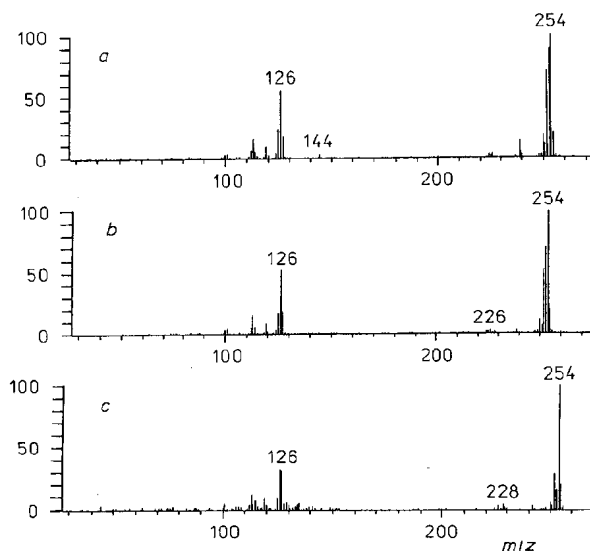


FIG. 2

Mass spectra of binaphthyls (EI, 70 eV); *a* 1,1'-binaphthyl, *b* 1,2'-binaphthyl, *c* 2,2'-binaphthyl

Since the presence of naphthylbenzo[*b*]thiophenes in the releases from the production of 2-naphthol is a novelty, and in view of the similarity of the EI mass spectra of the isomers, reference samples 3- and 2-(1'-naphthyl)benzo[*b*]thiophene and 3- and 2-(2'-naphthyl)benzo[*b*]thiophene were prepared and employed for an unambiguous identification.

The GC/MS analyses of the actual sample and of a mixture of the reference compounds, performed under identical conditions, are compared in Fig. 4. Owing to the marked differences in the retention times of the naphthylbenzo[*b*]thiophenes, the compounds could be identified unambiguously, even in the case of 3- and 2-(1'-naphthyl)benzo[*b*]thiophene (Fig. 3*a*, 3*b*) whose MS spectra are nearly identical.

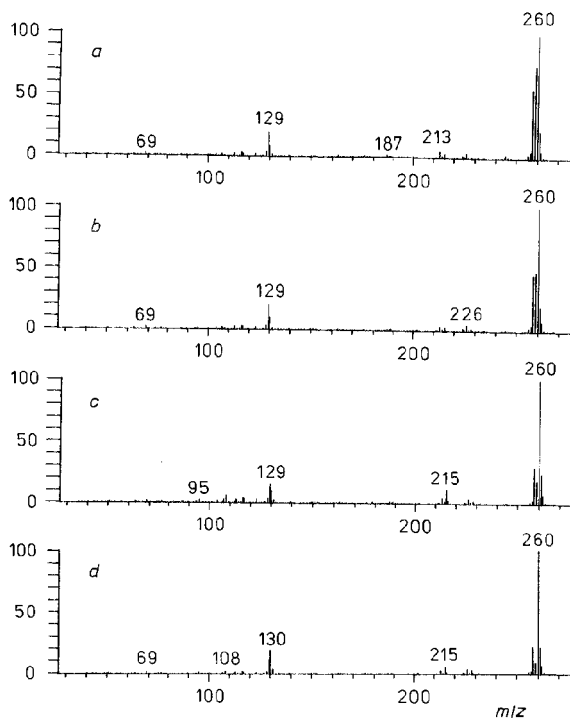


FIG. 3

Mass spectra of naphthylbenzo[*b*]thiophenes (EI, 70 eV); *a* 3-(1'-naphthyl)benzo[*b*]thiophene, *b* 2-(1'-naphthyl)benzo[*b*]thiophene, *c* 3-(2'-naphthyl)benzo[*b*]thiophene, *d* 2-(2'-naphthyl)benzo[*b*]thiophene

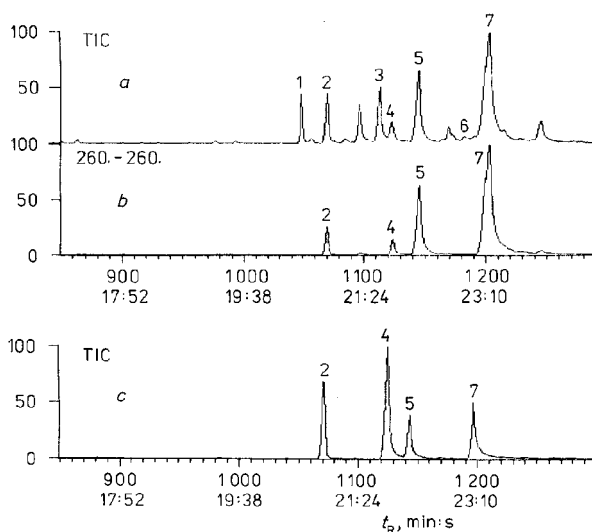


FIG. 4

Comparison of GC/MS analyses of a sample of industrial releases from the production of 2-naphthol (a, b) and of a reference mixture of naphthylbenzo[b]thiophenes (c). Total ionic current: a, c; M^+ = 260 b. Compounds (peak No., t_R (min), M, name): 1, 20.50, 254, 1,1'-binaphthyl; 2, 20.87, 260, 3-(1'-naphthyl)benzo[b]thiophene; 3, 21.65, 254, 1,2'-binaphthyl; 4, 21.82, 260, 2-(1'-naphthyl)benzo[b]thiophene; 5, 22.22, 260, 3-(2'-naphthyl)benzo[b]thiophene; 6, 22.87, 2,2'-binaphthyl; 7, 23.22, 260, 2-(2'-naphthyl)benzo[b]thiophene

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