Fresenius' Journal of Analytical Chemistry
December 1997, Volume 359, Issue 7–8, pp 561–564
DOI: 10.1007/s002160050632

Capillary gas chromatography of polychlorinated benzonitriles (PCBN)

Bernhard Mittermaier, Karlheinz Ballschmiter
Department of Analytical and Environmental Chemistry,
University of Ulm, D-89069 Ulm, Germany

Results partly presented at ANAKON ’97 in Konstanz, Germany, 6–8 April 1997

Abstract

Polychlorinated benzonitriles (PCBN) are products of combustion chemistry and can be emitted from municipal waste incinerators. Their possible relevance to environmental chemistry has not previously been described, with the exception of the herbicide 2,6-dichlorobenzonitrile. The isomer-specific separation and detection of the 19 PCBN congeners is performed by HRGC-ECD and HRGC-MSD. Commercially unavailable congeners were synthesized from chlorinated anilines and benzaldehydes. Retention data on three different stationary phases are given. Structure-retention relationships are discussed. A structure-specific systematic numbering of the 19 PCBN congeners is suggested.

1 Introduction

Polychlorinated benzonitriles are among the possible products in combustion chemistry [1]. They have recently been detected in the flue gas of a municipal waste incinerator: Unpublished results from H. Schimmel, K. Hauff, G. Kaiser, K. Ballschmiter. Except for the herbicide 2,6-dichlorobenzonitrile (Dichlobenil) [2], this class of compounds has not previously been described as substances of environmental concern. 3,4,5-Trichlorobenzonitrile is not even mentioned in “Beilstein”, which emphasizes the novelty of this group of compounds. A herbicidal function in analogy to Dichlobenil can be expected for other congeners of this group [3].

Only 10 out of 19 possible PCBN congeners were commercially available. We have synthesized the remaining nine congeners, as far as possible free of other isomers. By means of a Sandmeyer-reaction, chlorinated anilines were transformed into the corresponding nitriles. Chlorinated benzaldehydes were converted into nitriles in a one-pot reaction with hydroxylamine hydrochloride. 2,3,4,6-Tetrachlorobenzonitrile was synthesized by chlorination of 2,4,6-trichlorobenzonitrile with the BMC-reagent. A mixture of all congeners was analyzed with HRGC-ECD and HRGC-MSD on non-polar and semi-polar stationary phases.

2 Systematic numbering of PCBNs

A systematic numbering for the PCBN is introduced in Table 1, analogous to the established system for the halogenated anisoles [4].

No.	Structure
B 0	
PCB 1	2-Cl
PCB 2	3-Cl
PCB 3	4-Cl
PCB 4	2,3-Cl_2
PCB 5	2,4-Cl_2
PCB 6	2,5-Cl_2
PCB 7	2,6-Cl_2
PCB 8	3,4-Cl_2
PCB 9	3,5-Cl_2

PCB 10	2,3,4-Cl_3
PCB 11	2,3,5-Cl_3
PCB 12	2,3,6-Cl_3
PCB 13	2,4,5-Cl_3
PCB 14	2,4,6-Cl_3
PCB 15	3,4,5-Cl_3
PCB 16	2,3,4,5-Cl_4
PCB 17	2,3,4,6-Cl_4
PCB 18	2,3,5,6-Cl_4
PCB 19	2,3,4,5,6-Cl_5

Table 1 Systematic numbering of PCBN compounds.
The number is used as a synonym for the corresponding PCBN compound throughout this paper. The numbers correspond to the respective numbering of the polychlorinated anisoles [5]

3 Materials and instruments

Chemicals

Benzonitrile and PCBN 1, 2, 3, 4, 5, 6, 7, 8, 9 and 14 were purchased from ABCR (Karlsruhe, Germany), Aldrich (Steinheim, Germany), Fluka (Buchs, Switzerland) and Merck-Schuchardt (Hohenbrunn, Germany), respectively. 2,3,4-Trichloroaniline, 2,4,5-trichloroaniline, 3,4,5-trichloroaniline, 2,3,4,5-tetrachloroaniline, 2,3,5,6-tetrachloroaniline and pentachloroaniline were purchased from Aldrich, Fluka and Ventron (Karlsruhe, Germany), respectively. 2,3,5-Trichlorobenzaldehyde and 2,3,6-trichlorobenzaldehyde were obtained from Aldrich. Isooctane (solvent for gas chromatographic analysis) was obtained nanograde from Promochem (Wesel, Germany). The other chemicals used for syntheses were purchased from Fluka and Merck. Gas chromatography was performed as shown in Table 2.

HRGC-MSD
Gas chromatograph: HP 5890, Hewlett Packard (Palo Alto, USA)
Stationary phase I: DB 5 MS, J & W Scientific (Folsom, USA) 60 m, 0.32 mm i.d., film thickness 0.25 µm
Carrier gas: Helium 4.6, Linde (Munich, Germany), 135 kPa
Detector: HP 5970, Hewlett Packard (Palo Alto, USA)
Injector: On column
Integrator: HP Chemstation for Windows 3.11
Temperature program I: 80°C (3 min), 2.5° C/min, 190°C
SIM indicator ions: Cl_0: 103.05/104.05; Cl_1: 137.00/139.05; Cl_2: 170.95/173.00; Cl_3: 206.95/209.00; Cl_4: 238.90/240.90; Cl_5: 274.90/276.90 amu

HRGC-ECD
Gas chromatograph: HP 5890 Series II plus, Hewlett Packard (Palo Alto, USA)
Stationary phase II: DB 5, J & W Scientific (Folsom, USA) 60 m, 0.32 mm i.d., film thickness 0.1 µm
Stationary phase III: DB 1701, J & W Scientific (Folsom, USA) 30 m, 0.25 mm i.d., film thickness 0.25 µm
Carrier gas: Helium 4.6, Linde (Munich, Germany), constant mass flow 1.3 mL/min
Make-up gas: Ar/CH_4 (90:10), flow 40 mL/min
Detector: ^{63}Ni-ECD, T = 280°C
Injector: On column
Integrator: HP 3396 A, Hewlett Packard (Palo Alto, USA)
Temperature program II: 80°C (3 min), 2° C/min, 170°C
Temperature program III: 80°C (3 min), 2° C/min, 180°C

Table 2 Gas chromatography instrumentation

4 Syntheses

4.1 Sandmeyer reaction [5, 6]

0.01 mol of the respective aniline was dissolved in 25 mL glacial acetic acid at 80° C. This solution was added dropwise under ice cooling and stirring to a solution of 1.0 g sodium nitrite in conc. sulfuric acid. Stirring was continued for another 30 min. The diazonium sulfate was precipitated by dropwise adding of 50 mL ether under vigorous stirring. The precipitate was filtered off, washed with 25 mL glacial acetic acid/ether (1:1 by volume) and finally washed with 50 mL ether.

The solid was dissolved in water and dropped into 8 mL of an aqueous solution of 1.1 g cuprous cyanide and 2.4 g potassium cyanide. (CAUTION: Hydrogen cyanide may be evolved.) The precipitated nitrile was filtered off, washed with 20 mL of saturated aqueous sodium carbonate solution, and finally washed with 50 mL of water.

According to this procedure, PCBN 10, 13, 15, 16, 18 and 19 were synthesized in typical yields of 30%.

Fig. 1 HRGC of chlorobenzonitriles on DB 5 MS (GC-MSD), DB 5 (GC-ECD) and DB 1701 (GC-ECD)

4.2 Conversion of aldehydes to nitriles [7]

0.025 mol of the respective aldehyde and 0.035 mol hydroxylamine hydrochloride were dissolved in 5 g formic acid (95–98%) refluxed for 1 h, and then allowed to cool. The mixture was poured onto 50 g crushed ice, neutralized under ice cooling with 10% sodium hydroxide solution, and extracted with ether (3 × 30 mL). The combined extracts were dried over sodium sulfate and concentrated using a rotary evaporator.

According to this procedure, PCBN 11 and PCBN 12 were synthesized in quantitative yield.

4.3 Chlorination with BMC-reagent [8]

For 2,3,4,6-tetrachlorobenzonitrile (PCBN 17) no suitable starting materials were available for any of the possible conversion reactions. Therefore, chlorination with the BMC-reagent starting from 2,4,6-trichlorobenzonitrile (PCBN 14) was carried out. The BMC-reagent is a mixture of aluminium chloride, disulfur dichloride, and sulfuryl chloride in an approximate molar ratio of 1:1:100 [8].

0.5 mmol PCBN 14, 100 mg $AlCl_3$ and 0.1 mL S_2Cl_2 were dissolved in 8 mL SO2Cl2 and refluxed for 2 h. After removal of excess SO_2Cl_2, 20 mL of saturated aqueous sodium carbonate solution were added and the mixture was refluxed for 1 h, allowed to cool, neutralized with hydrochloric acid (20%), and extracted with ether (3 × 30 mL). The combined extracts were washed with water and dried over sodium sulfate.

PCBN 17 and 19 were yielded in a ratio of approx. 1:4 (GCMSD); no unchanged PCBN 14 remained.

	PCBN	PCBN	PCBN	Anisole	Anisole
	DB 5 MS	DB 5	DB 1701	DB 1701	DB 1701
	GC-MSD/He	GC-ECD/He	GC-ECD/He	GC-MSD/He	GC-ECD/N_2
1	0.328	0.306	0.362	0.316	
2	0.289	0.270	0.300	0.276	
3	0.306	0.282	0.319	0.289	
4	0.511	0.479	0.546	0.559	0.567
5	0.477	0.442	0.495	0.496	
6	0.472	0.435	0.490	0.490	0.498
7	0.521	0.491	0.567	0.370	0.376
8	0.472	0.436	0.486	0.504	0.505
9	0.409	0.372	0.400	0.428	0.435
10	0.690	0.663	0.714	0.802	0.806
11	0.619	0.586	0.621	0.711	0.719
12	0.691	0.663	0.720	0.576	0.585
13	0.631	0.600	0.638	0.708	0.713
14	0.633	0.601	0.640	0.504	0.511
15	0.628	0.594	0.627	0.711	0.718
16	0.824	0.806	0.826	0.981	0.979
17	0.826	0.809	0.831	0.757	0.766
18	0.815	0.800	0.822	0.756	0.762
19	1.000	1.000	1.000	1.000	1.000

Table 3 Relative retentions of PCBN and chlorinated anisoles (pentachlorobenzonitrile and pentachloroanisole = 1) on DB 5 MS, DB 5 and DB 1701 in temperature programmed capillary gas chromatography. The respective detector and carrier gas is indicated.

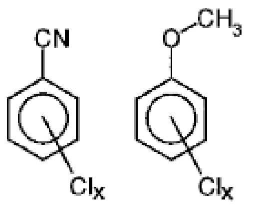

Fig. 2 Molecular formulas of chlorinated benzonitriles (*left*) and chlorinated anisoles (*right*)

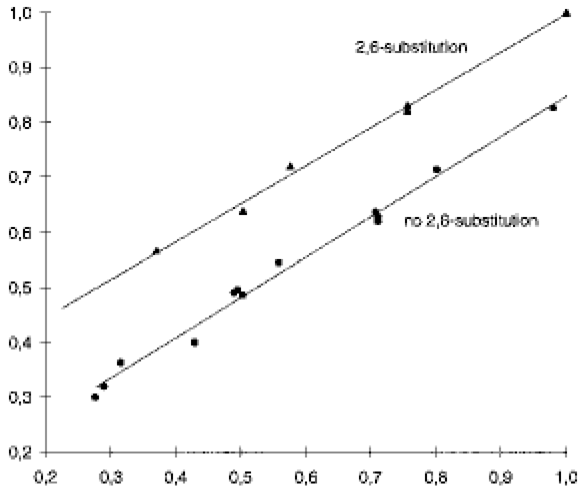

Fig. 3 Relative retention of chlorinated benzonitriles vs. chlorinated anisoles on DB 1701 (GC-ECD/He, GC-MSD/He)

5 Results and discussion

By means of the described reactions, all but one commercially unavailable compounds were obtained congener-free. Although PCBN 17 was synthesized in a mixture with PCBN 19, no problems occurred concerning peak assignment, since the tetrachlorobenzonitriles (e.g. PCBN 17) are well separated in HRGC from pentachlorobenzonitrile and because pure PCBN 19 was obtained.

Chromatograms of the separations on DB 5 MS, DB 5, and DB 1701 are shown in Fig. 1. Compared with the non-polar phases DB 5 MS and DB 5, resolutions are generally enhanced on the semi-polar phase DB 1701.

On each stationary phase, all PCBN are eluted strictly according to the number of chlorine atoms. It was found that, within a given grade of chlorination, compounds with chlorine substitution at positions 3 and 5 always elute before the compounds without chlorine at these positions on DB 1701. This effect might be due to polarity of the PCBN contributing to retention on this phase. By a symmetric substitution with electron-attracting groups (-CN and -Cl) in the positions 1, 3 and 5 a quite uniform distribution of electrons in the molecule is achieved, which reduces the dipole moment, increases the respective volatility, and reduces thereby the required retention time.

Table 3 summarizes the relative retention (pentachlorobenzonitrile= 1.000) of all PCBN congeners in temperature programmed capillary gas chromatography on these three stationary phases and allows a comparison to the relative retention of chloroanisoles on DB 1701 from (pentachloroanisole = 1.000) [4, 9].

A comparison of the relative retention times of benzonitriles and anisoles (Fig. 2) on DB 1701 (Fig. 3) reveals a significant increase of retention from 2,6-chlorosubstituted anisoles to the respective benzonitriles (# 7, 12, 14, 17, 18 and 19 in Table 3). In case of the anisoles, the –*I*-effect of the chlorine substituents is partially compensated by the *+M*-effect of the neighboring methoxy group, which leads to reduced polarity of the molecule and therefore reduced retention. Concerning the benzonitriles, the dipole moment is even enlarged due to an additional –*I*-effect of the cyano group. Hence, 2,6-chlorosubstituted PCBN show longer retention times than the respective anisoles.

6 Conclusions

Several syntheses were adapted to the requirements of the congener specific preparation of polychlorinated benzonitriles. Congener-specific analysis can be performed by high resolution capillary gas chromatography, preferably on a semi-polar stationary phase.

Investigations of structure – retention relationships showed shorter retention times for 3,5-chlorosubstituted compounds, presumably due to a more uniform distribution of electrons in the ring system. A comparison between chlorinated anisoles and chlorinated benzonitriles revealed increased retention times for 2,6-chlorosubstituted benzonitriles as compared to the respective anisoles. This is caused by the *+M* – effect of the methoxy group, which reduces the dipole moment of the molecule and hence reduces retention.

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