

Structure-retention relationships for polychlorinated biphenyls and polyaromatic hydrocarbons on different GC phases

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Abstract

The mechanistic interactions that occur between different GC phases (BP1, BP5, BPX5, HT8, BPX35 and BPX50) and PCB congeners are discussed in terms of silphenylene and carborane content relative to their sterically forced and electronically preferred conformations and the degree of steric hindrance around the less hindered aromatic ring.

Retention is found to respond to priorities that are weighted according to phase type. The factors are (1) forced conformation and restricted rotation determined by the ortho effect, (2) preferred conformation driven by electronic effects, (3) steric hindrance of the π/π^* orbitals by the substitution pattern of the less hindered ring, (4) electron density on the less crowded ring and (5) overall electron density.

Keywords: PCB congener resolution, GC phases, HT8, BP5, BPX5, BPX35, BPX50.

Introduction

The use of gas chromatography for the analysis of PCB mixtures is well established with most commercial approaches to column selection based on the dimensional tuning of a target phase. The mechanistic rationale for PCB retention on GC phases has been described previously in terms of conformation of the PCB under the influence of the number of ortho substituents. While this general rule provides a basis for describing some aspects of the unique selectivity and resolving power of the carborane based phase HT8, it cannot be invoked as readily to describe the variation in retention of such analytes on phases with embedded aromatic rings.

In this study, we examine the retention of closely eluting PCBs as a function of phase chemistry using identical column dimensions and chromatographic conditions. This approach allows the generation of a retention matrix based on phase chemistry and analyte structure that is a useful tool for describing retention mechanisms.

Material and methods

PCB standards 28 and 31, 71 and 72, 84, 89, 99 and 101 and 138, 158 and 160 were purchased from AccuStandard Inc. (New Haven, CT, USA) and diluted in acetone.

Gas chromatography Mass spectrometry was performed on a 6890GC-5973N MSD (Agilent Technologies, CA, USA) equipped with an ETP electron multiplier (SGE Analytical Science, VIC, Australia) and either a BP1, BP5, BPX5, HT8, BPX35 or BPX50 column (30 m x 0.25 mm i.d., 0.25 μ m film thickness, SGE). Injections of 0.1 μ L standards in acetone were fast and splitless at a temperature of 260°C. Purge flow was 50 mL/min and a nominal inlet pressure of 93kPa. The oven temperature was programmed from 40°C (hold for 4 min) to 300°C (hold for 10 min) at 10°C/min. The carrier gas was helium at a flow rate of 1.2 mL/min in constant flow mode. EI mass spectra were collected over the range 40-500 Da at 2 scan/sec. The transfer line temperature was 260°C, the quadrapole was 150 °C and the source was 230 °C.

Chromatographic data was acquired and processed using ChemStation software (Version 100 D.02.00.275, Agilent Technologies). Retention times were measured at the peak apex and reproducibility was confirmed by reanalysis of the same sample under identical conditions on a second day and by reanalysis on the same column after reinstallation.

Results and discussion

The major moieties that are responsible for the GC phases studied are shown in figure 1. The PCBs that were included in this study are shown in figure 2, along with their conformation derived from steric effects (enforced) or electronic effects (preferred). The extracted ion chromatograms that result from the separation of these compounds on each of the columns, under identical conditions, are shown in fig 3.

The separation of tri-CBs 28 and 31 shows the carborane retains the coplanar compound more than the planar one. Silphenylene dominant phases show no selectivity for the pair as the less hindered ring responsible for the interaction is the same for both compounds.

The tetra-CBs 71 and 72 differ in their preferred planarity as a result of electronic effects. PCB 71 is likely to adopt a coplanar configuration while PCB 72 is able to take up a low energy planar configuration. The HT8 phase shows the expected increase in retention for the coplanar congener while the opposite is observed for silphenylene imbedded phases where coplanarity presents a steric barrier to interaction.

The penta-CBs will all have a preferred coplanar configuration with congener 89 influenced by both steric and electronic effects. Congeners 84, 99 and 101 show restricted rotation through ortho, ortho'-disubstitution and as a result of electronic effects (o,o,o'; o,p,o'; o,p,o',p'). Because all analogues prefer the coplanar conformation, the carborane phase does not show a significant influence on retention order over a non-polar (BP1) phase. In contrast, strongest retention for the silphenylene phases is observed for PCB 89 due to the relatively low steric barrier posed by diortho substituents on the less hindered ring.

The hexa-CBs exhibit electronically induced coplanarity (PCB 158), weakly steric and electronic coplanarity (PCB 138) and planar conformation (PCB 160). The very low degree of substitution on the unhindered ring of PCB 160 maximises the interactions of the analyte with silphenylene containing phases BPX35 and BPX50. The high level of substitution on the more hindered ring is sufficient to prevent any significant intercalation characteristic to be displayed by the BP5 phase.

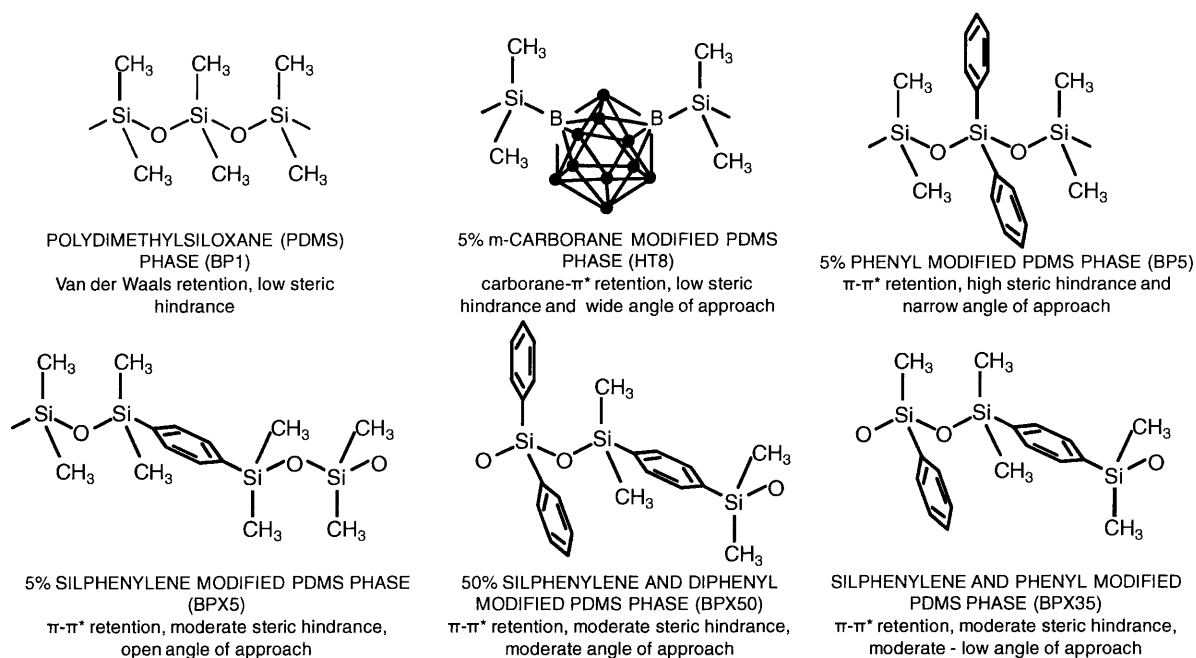


Figure 1: Functionally significant repeating units in phases that are useful for the separation of aromatic analytes.

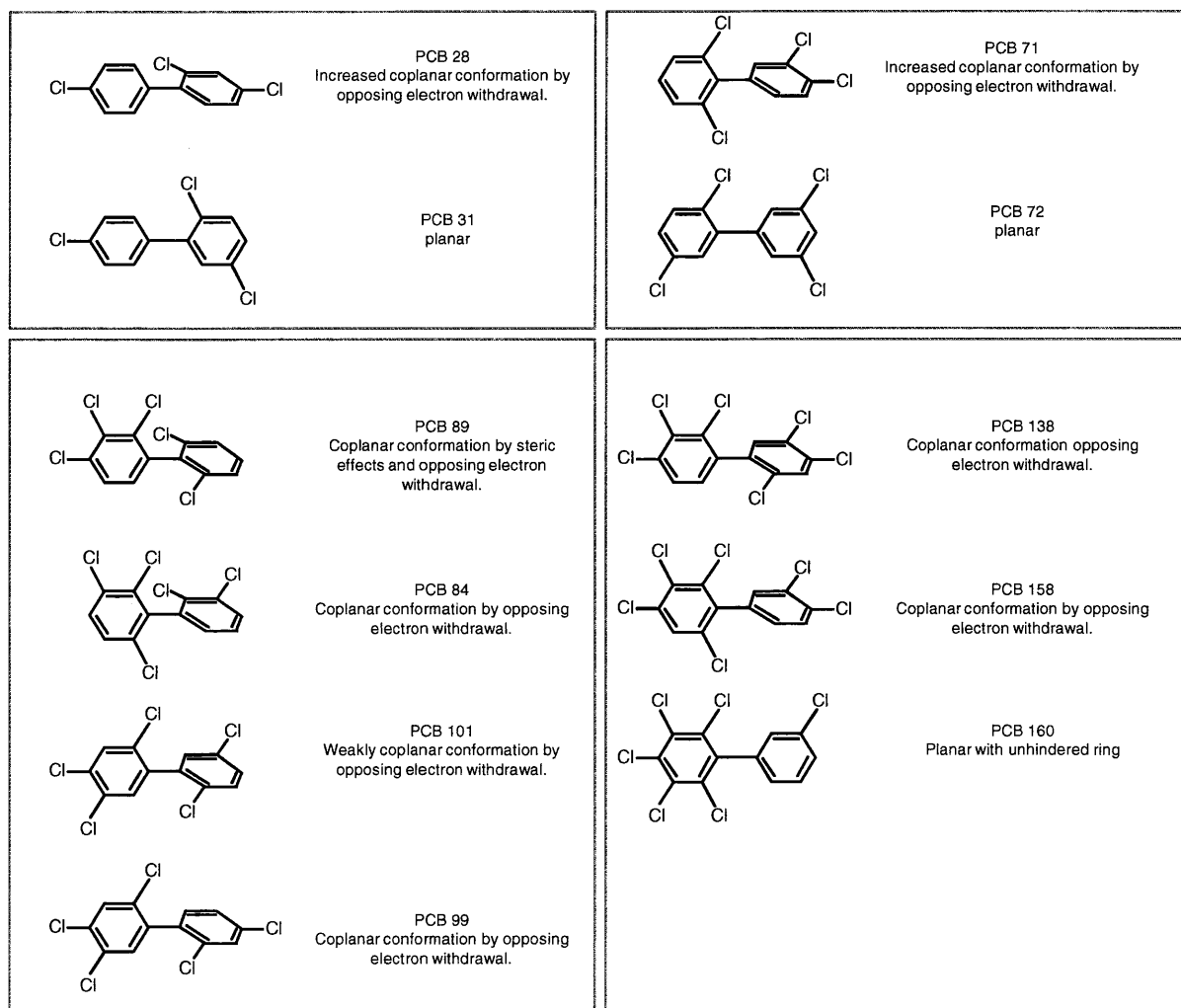


Figure 2: Structure and conformational influences on PCB congeners included in this study.

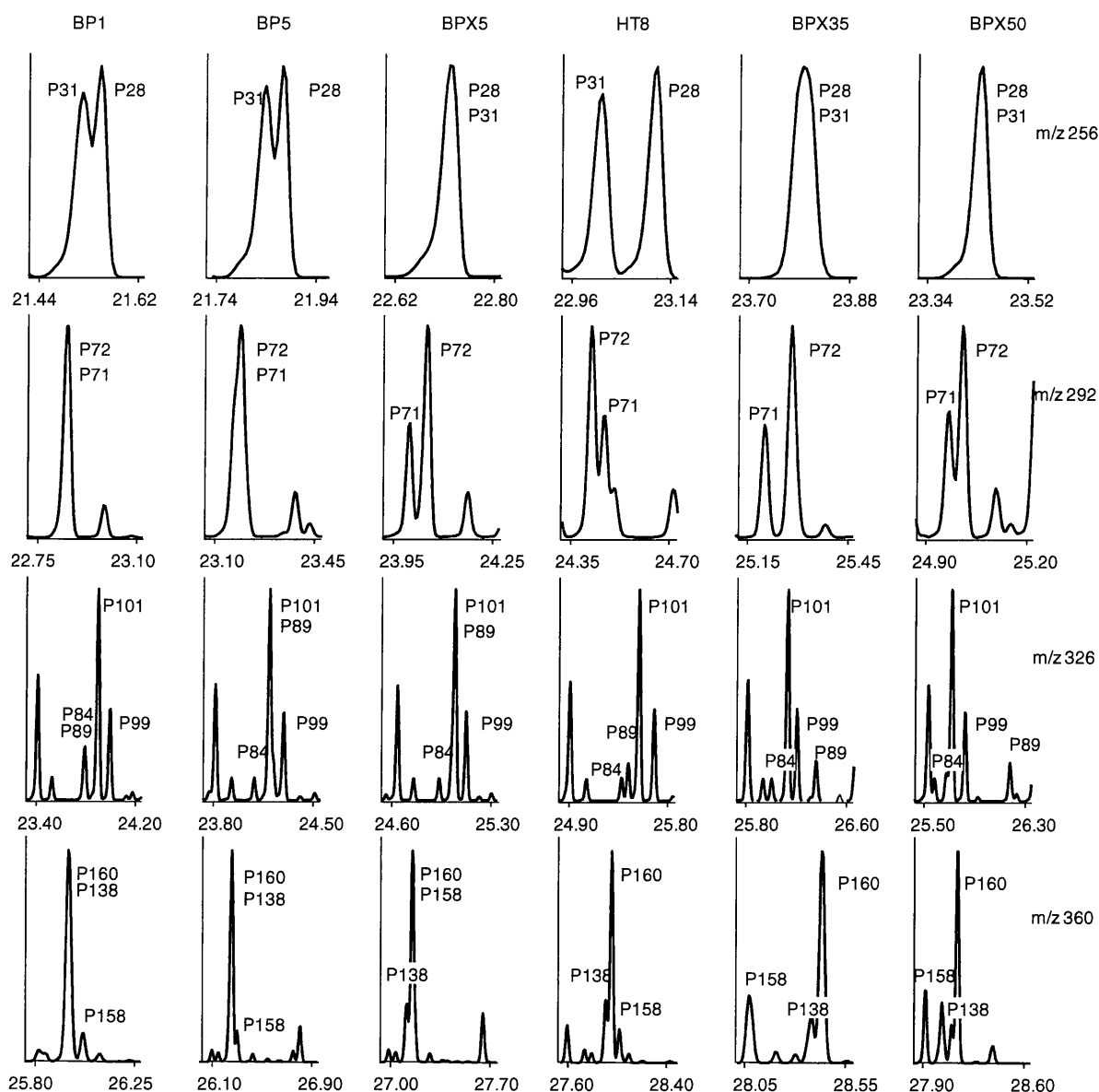


Figure 3: Extracted ion chromatograms for the PCBs included in this study on each column.

Conclusion

Retention is based on priority rules that are weighted according to phase chemistry. In order of importance to retention on a simple gradient are (1) forced conformation and restricted rotation determined by the ortho effect, (2) preferred conformation by electronic effects, (3) steric hindrance of the π/π^* orbitals by the substitution pattern of the less hindered ring, (4) electron density on the less crowded ring and (5) overall electron density.

Silphenylene (BPX5, BX50 and BPX 35) phases and carborane phases (HT8) are capable of providing greater selectivity over phenyl modified PDMS phases because interaction with aromatic analytes is not dependent on an intercalation mechanism that is sensitive to steric hindrance.