Introduction

The use of gas chromatography for the analysis of PCB structures is well established with most commercial approaches having 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 confirmation of the PCB retardation character and the number of ortho substituents on the less hindered ring. In this general approach to explaining the characteristic selectivity of silphenylene based phases over non-polar or aromatically modified phases, the latter are often used as a control but do not display strong selectivity for the PCB analytes. This is due, in part, to the nature of the aromatic analyte interactions which is sensitive to steric hindrance. Because interaction with aromatic analytes is not dependent on an intercalation mechanism, these types of phases are capable of providing greater selectivity over phenyl modified PDMS phases and carborane phases (HT8) for PCBs. The inclusion of non-polar (BP1) phases in this study allows for comparisons to be made between the relative selectivity of the different phases and those observed in previous studies. 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 71, 72, 84, 89, 99 and 101 and 138, 158 and 160 were purchased from AccustandardInc. (New Haven, CT, USA) and diluted in acetone. Gas Chromatography-Mass Spectrometry was performed on a 6890N/5973N MSD (Agilent Technologies). The GC phases used were, Silphenylene (BPX5, BX50 and BPX 35) phases and carborane phases (HT8). The hexa-CBs exhibit electronically induced coplanarity (PCB 158), weakly steric hindrance (PCB 160), and electronic coplanarity (PCB 138) and planar conformation (PCB 160). The very low degree of substitution on the unhindered ring of PCB 160 maximizes the significant intercalation characteristic to be displayed by the BP5 phase. The pent-CBs will all have a preferred coplanar configuration with congener 89 influenced by both steric and electronic effects. Congeners 84, 99 and 101 are shown in figure 1. The PCBs that were included in this study are shown in figure 3. The separation of tri-CBs 28 and 31 shows the carborane retains the coplanar arrangement for the pair as the less hindered ring responsible for the interaction is the 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.

Results and discussion

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) functional substitution on the unhindered ring of the PCB, (2) electronic effects, (3) steric hindrance of the less hindered ring, (4) electron density tuning of a target phase. The mechanistic rationale for PCB retention on GC phases has been described previously in terms of confirmation of the PCB retardation character and the number of ortho substituents on the less hindered ring. In this general approach to explaining the characteristic selectivity of silphenylene based phases over non-polar or aromatically modified phases, the latter are often used as a control but do not display strong selectivity for the PCB analytes. This is due, in part, to the nature of the aromatic analyte interactions which is sensitive to steric hindrance. Because interaction with aromatic analytes is not dependent on an intercalation mechanism, it cannot be invoked as a major factor in the 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 columns under identical 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.

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) functional substitution on the unhindered ring of the PCB, (2) electronic effects, (3) steric hindrance of the less hindered ring, (4) electron density tuning of a target phase. The mechanistic rationale for PCB retention on GC phases has been described previously in terms of confirmation of the PCB retardation character and the number of ortho substituents on the less hindered ring. In this general approach to explaining the characteristic selectivity of silphenylene based phases over non-polar or aromatically modified phases, the latter are often used as a control but do not display strong selectivity for the PCB analytes. This is due, in part, to the nature of the aromatic analyte interactions which is sensitive to steric hindrance. Because interaction with aromatic analytes is not dependent on an intercalation mechanism, it cannot be invoked as a major factor in the 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 columns under identical 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.