

STRUCTURAL CONFIRMATION OF LEGACY HALOGENATED FLAME RETARDANTS DERIVED FROM HEXACHLOROCYCLOPENTADIENE

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Introduction

The environmental concerns associated with halogenated flame retardants have been primarily linked to high profile brominated compounds such as polybrominated diphenyl ethers (PBDEs). The production, use, and fate of chlorinated or mixed chlorinated/brominated flame retardants has not elicited as much attention and, as such, many of these compounds have not been fully characterized in the literature. In order to fully understand the behaviour of these compounds in biotic and abiotic systems or accurately model their toxicological potential, it is vital to have the correct chemical structure.

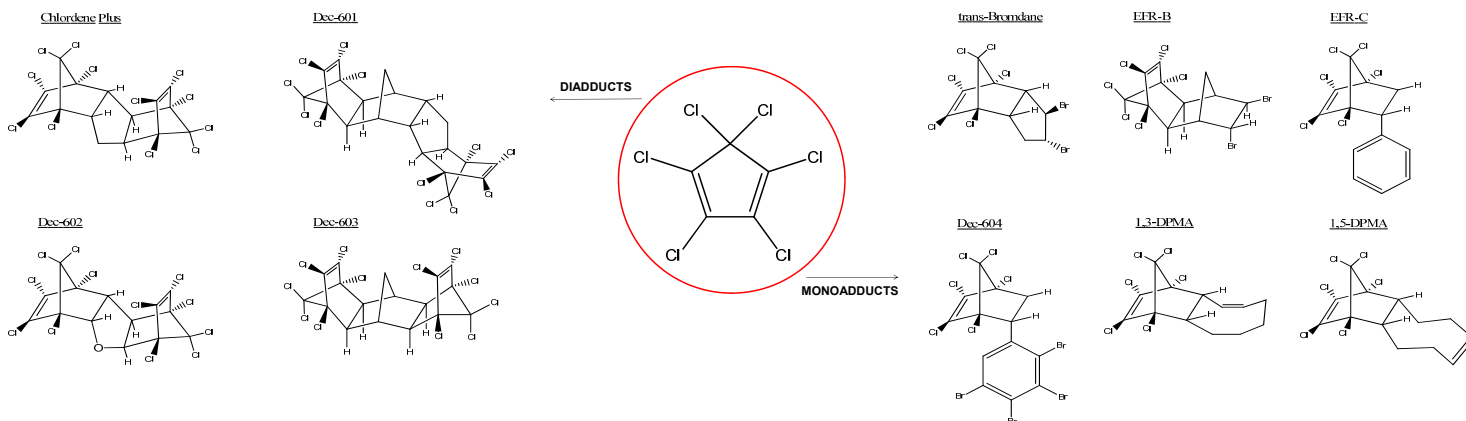
Objective
This work details the structural confirmation through GCMS and NMR analysis, as well as x-ray crystallography in some cases, of the following legacy halogenated flame retardants: Dec-601¹, Dec-602¹⁻⁵, Dec-603¹⁻⁵, Dec-604^{1-5,7}, 1,3-DPMA⁴, 1,5-DPMA⁴, EFR-B⁹, EFR-C⁹, trans-Bromdane, and Chlordene Plus²⁻⁴. All of these compounds belong to the family of flame retardants arising from Diels-Alder reactions of hexachlorocyclopentadiene.

Materials and Methods

All GCMS experiments were conducted on an Agilent 7890A GC/5975C MS using a DB-5HT column (15m x 0.25mm x 0.1µm) and all injections were done in splitless mode. A full scan range of 50-1000 amu was used in positive ion electron impact mode (EI+). ¹H-NMR analyses were performed on a 400 MHz Bruker instrument using CD₂Cl₂ (CDN Isotopes) as the solvent. Crystals submitted for x-ray structure determination were grown from either 1,2-dichloroethane (Dec-601) or dichloromethane/hexane (Dec-604).

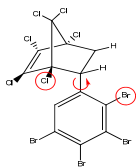
Results

The constitution and stereochemistry of all of the legacy flame retardants were determined definitively (see below). In two instances (Dec-601 and Dec-604), stereochemistries could not be assigned on the basis of ¹H-NMR analysis alone. These two compounds were therefore characterised by x-ray crystallography.



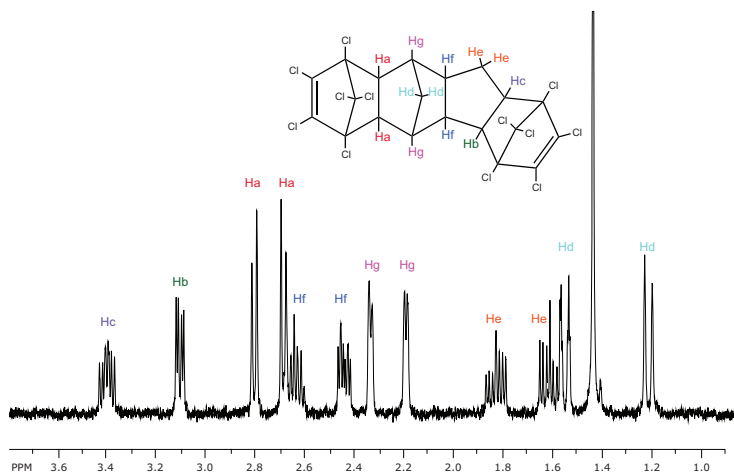
Results continued...

It had been previously reported in the literature⁷ that Dec-604 (also known as Dechlorane D) was not brominated in the para position of the phenyl ring. However we found that because the ortho position is sterically hindered by the chlorine atom in position 5 of Dec-604, it is one of the ortho sites that is being left unbrominated. We believe that bromination of the first ortho position results in the phenyl ring rotating so that interaction between the ortho bromine and chlorine atom on the norbornene substituent is minimized. The resulting restricted rotation leaves the second ortho position sterically hindered.



All of the compounds were analyzed using proton NMR and GC/MS analysis. For the most part, these techniques allowed for the definitive determination/verification of the compounds' structure. This was not the case for Dec-601 and Dec-604 so crystalline samples were sent for x-ray structure determination. The resulting x-ray structures are given on the right.

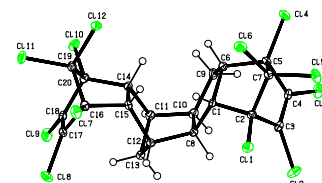
The norbornene framework and high degree of halogenation common to all of these compounds made interpretation of their proton NMR spectra relatively easy in most cases. In fact, the symmetry of Dec-603 resulted in a very simple spectrum with only 3 singlets observed. The most complicated NMR spectrum to interpret was Dec-601. The assignments for this compound are shown on the partial spectrum reproduced below.



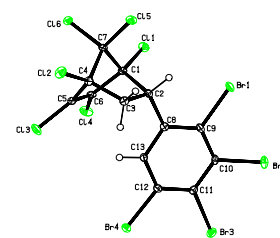
The GCMS analyses of these compounds also afforded some interesting results. Surprisingly, hexachlorocyclopentadiene (HCCP; formed from a retro-Diels Alder reaction) was not always observed in the positive EI spectra of these flame retardants. Specifically, it was not observed for EFR-B, 1,3-DPMA, and Dec-603. Also, in most cases, the molecular ion cluster of the adducts gave lower responses than the [M-Cl]⁺ and HCCP clusters. This could be important for identifying related or dechlorinated compounds in real samples.

Conclusions

It is well known that the chemical structure of a compound can have a large effect on its impact on, or role in, biochemical processes. The toxicity differences observed between enantiomers or positional isomers has been well-documented and emphasizes the importance of fully characterizing both emerging and legacy organic pollutants.



Dec-601



Dec-604

References

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