

STRUCTURAL CHARACTERIZATION OF 1,1,3-TRIMETHYL-4,5,6,7-TETRABROMO-3-(2,3,4,5-TETRABROMOPHENYL)INDANE

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INTRODUCTION

Octabromotrimethylphenyl**i**ndane (OBIND or OctaInd) is a commercial brominated flame retardant (BFR) used in styrenic and engineering thermoplastics.¹ The major component in the commercial mixture is believed to be 1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane (**1**). BFRs have been used in a variety of products to protect human life and property against fires. However, there is a growing concern that these BFR compounds are becoming significant environmental contaminants because of their widespread presence in the environment (including in human and wildlife samples²) and their potential threat to human health. However, obtaining a thorough understanding of the toxicological profile of BFRs is a daunting task, partly because of the wide range of possible effects and partly because of their structural diversity. To facilitate progress, an initial screening procedure has been suggested. Although very little is known about OBIND and, to the best of our knowledge, it has not been reported in the environmental literature, it was one of the top ten persistent brominated or chlorinated compounds identified by QSPR screening that deserve greater attention.³ It was also included in a recent modeling study⁴ aimed at identifying representative BFRs for toxicological research. In this study it was assigned structure **2** because its structure was not specified by the Chemical Abstracts Service. We have now completed GC/MS and NMR studies and an x-ray structure determination which proves that OBIND has the structure **1**. This information is important to researchers wishing to analyze for, or model the behaviour of, OBIND.

MATERIALS & METHODS

2.1 *Synthesis of 1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane (OBIND)*
(3R/S)-1,1,3-Trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane (**1**) was obtained by bromination of 1,1,3-trimethyl-3-phenylindane using proprietary methods.

2.2 GC/MS

Analyses were performed on a Shimadzu GC/MS-QP2010 using a J&W 30m DB-5 column (0.25 mm ID, 0.25 μ m film). All injections were done in splitless mode. All experiments were done with the following GC conditions: helium carrier gas flow at 1.0 ml/minute, injector temperature at 250°C, temperature program set to the following parameters: initial oven temperature at 100°C, hold for 5 minute, ramp at 10°C/minute to 325°C, hold for 20 minutes. Spectra (50 to 1000 u) were obtained in positive ion, electron impact mode (EI+).

2.3 ¹H NMR Spectroscopy

¹H-NMR analyses were performed on a 400 MHz Bruker instrument using deuteriochloroform (CDN Isotopes) as the solvent and TMS as an internal standard.

Heteronuclear **M**ultiple **B**ond **C**orrelation (HMBCGP) is an experimental procedure that correlates proton nuclei with carbon nuclei that are separated by more than one bond. The pulse sequence utilizes zero and double quantum coherence between J-coupled protons and carbons to label each proton with the frequency of a remote carbon in the F1 dimension of a two dimensional experiment.

RESULTS & DISCUSSIONS

3.1 NMR analysis

The ^1H NMR spectrum of OBIND (Fig. 2a) shows a signal (7.92 ppm) for an aromatic proton, three singlets (1.92, 1.70 and 1.63 ppm) for the three methyl groups and an AM doublet (2.70 and 2.12 ppm) for the CH_2 moiety since the geminal protons being non-equivalent. However, this information alone does not make a distinction between structures **1** from **2** (Fig. 1). A Nuclear Overhauser Enhancement (NOE) NMR experiment should be able to discriminate between structures **1** and **2** since the former ought to produce a through space interaction between the ortho aromatic proton and the neighboring methyl group while a through space interaction should not exist for the latter structure since the proton on the phenyl ring is at the meta position. Before performing a NOE experiment, a HMBCGP NMR experiment was performed to determine which of the three methyl signals arises from the methyl adjacent to the tetrabromophenyl ring. This experiment showed (Fig. 3) that the methyl signals at 1.62 and 1.7 ppm had identical correlations, as expected for geminal methyl groups, and were different from the methyl signal at 1.92 ppm. This identifies the signal at 1.92 ppm as deriving from the methyl group attached to the same carbon as the tetrabromophenyl group. The NOE experiment was done by irradiating the aromatic signal at 7.92 ppm, and this confirmed that only one methyl signal at 1.92 ppm was in close proximity to it. This reveals that OBIND has structure **1** (Fig. 2b). Structure **2** would not be expected to give a correlation between the aromatic proton and the methyl group during an NOE experiment.

3.2 X-ray structure determination

An x-ray structure determination was completed to confirm the conclusion based on the NMR data that OBIND had structure **1**. Crystals suitable for x-ray structure determination were grown from toluene. The results clearly indicate that OBIND has structure **1**, (3*R/S*)-1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane, and not **2** (see Figure 4). Further details on the x-ray structure determination can be found elsewhere.⁵

3.3 GC/MS

Analysis of **1** by GC/MS under normal GC conditions showed no thermal degradation. The mass spectrum showed a strong MI signal with the base peak resulting from $[\text{MI}-\text{CH}_3]^+$ (Fig 5a). OBIND elutes before BDE-209 and decabromodiphenylethane (DBDPE) on a DB-5 column (Fig. 5b). This information should be helpful for analytical scientists attempting to identify OBIND as one of the unknown signals in an analysis.

It should be noted that OBIND has a chiral carbon and therefore exists as a pair of enantiomers. Therefore, separation of the enantiomers on a chiral column should be possible.

SUMMARY

NMR experiments and an x-ray structure determination identified OBIND as having structure **1**, (3*R/S*)-1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane.

OBIND elutes before BDE209 and DBDPE. Its thermal stability permits easy analysis by GC/MS.

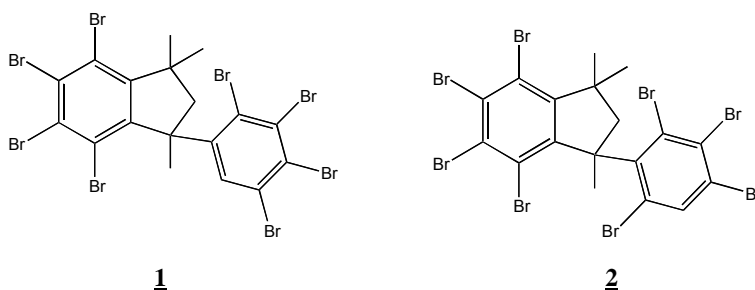


Figure 1. Possible structures for Octabromotrimethylphenylindane (OBIND)

REFERENCES

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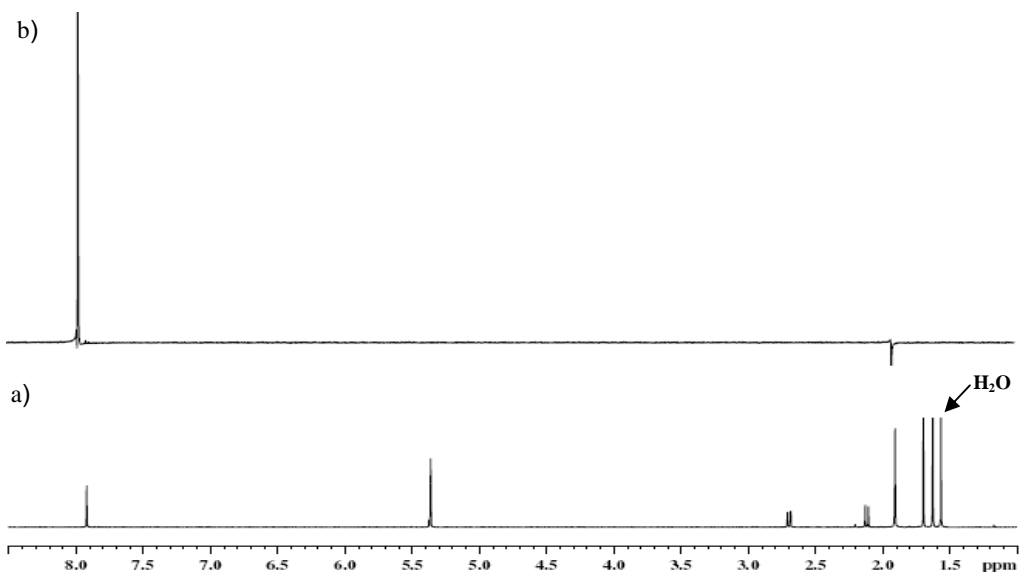


Figure 2. a) The ^1H NMR spectrum of **1** and b) NOE NMR experiment performed by irradiating the aromatic signal at 7.95 ppm.

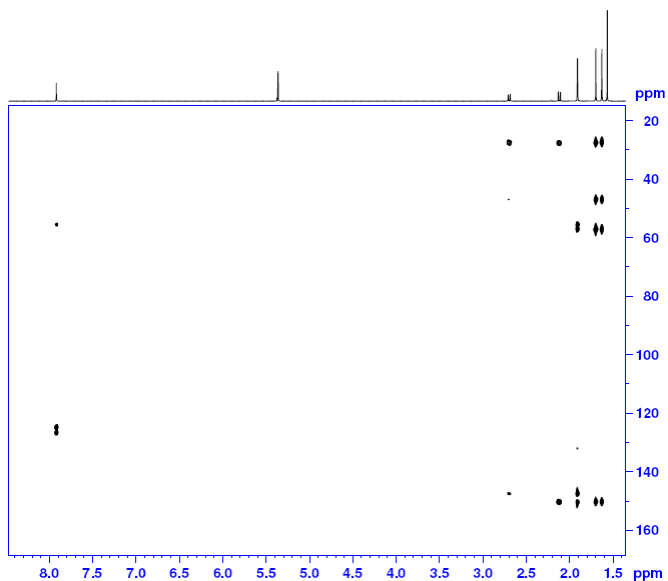


Figure 3. The HMBCGP NMR experiment for **1**.

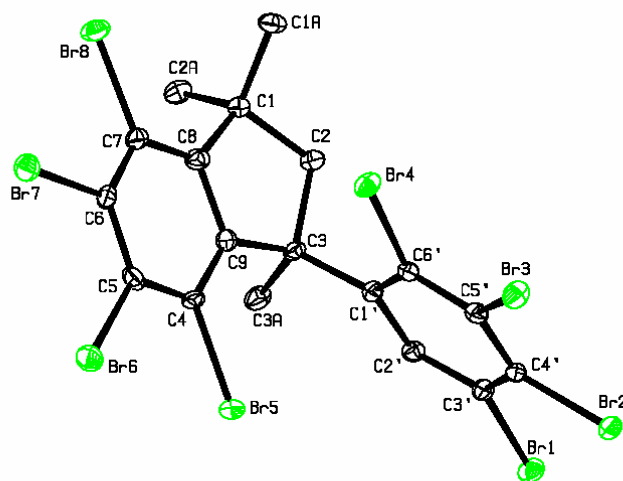


Figure 4. The molecular structure of 1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane (**1**). Displacement ellipsoids are at the 30% probability level.

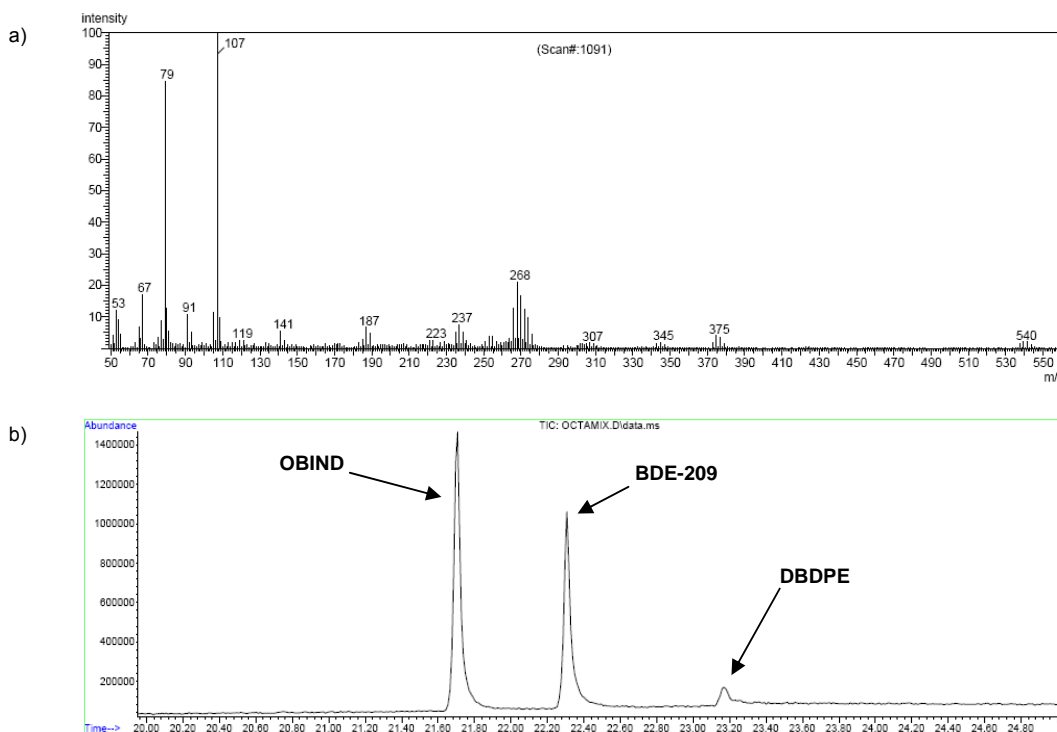


Figure 5. a) The mass spectrum of 1,1,3-trimethyl-4,5,6,7-tetrabromo-3-(2,3,4,5-tetrabromophenyl)indane (**1**) and b) the GC chromatogram of OBIND, BDE-209 and DBDPE (1:1:1 weight equivalent).