Chemosphere 78 (2010) 950–957

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Isobutoxypentabromocyclododecanes (iBPBCDs): A new class of polybrominated compounds

Norbert V. Heeb [a,*], Heidi Graf [a,b], W. Bernd Schweizer [c], P. Lienemann [b]

[a] Swiss Federal Institute for Materials Science and Technology (Empa), Laboratory of Analytical Chemistry, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[b] Zurich University of Applied Sciences, Institute of Chemistry and Biological Chemistry, Reidbach, 8820 Wädenswil, Switzerland
[c] Swiss Federal Institute of Technology (ETH), Laboratory for Organic Chemistry, Hönggerberg, 8093 Zürich, Switzerland

ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 16 December 2009
Accepted 17 December 2009
Available online 18 January 2010

Keywords:
Brominated flame retardant
iBPBCDs
Crystal structure
Diastereomers
Enantiomers

ABSTRACT

Isobutoxypentabromocyclododecanes (iBPBCDs) represent a new class of polybrominated compounds found in several flame-proofed polystyrene materials and in a technical mixture of hexabromocyclododecanes (HBCDs). Of the 64 stereoisomers possible, we now have analytical evidence for 16 different stereoisomers. By reversed- and chiral-phase liquid chromatography we distinguished 8 diastereomeric pairs of enantiomers, named α-, β-, γ-, δ-, ε-, ξ-, η-, and θ-iBPBCDs in accordance with their chromatographic retention on a C_{18}-RP-column. Crystal structure analysis revealed the stereochemistry of the most prominent θ-iBPBCD stereoisomers, which were determined to be (1R)-1-iso-butoxy-(2R,5R,6S,9S,10R)-2,5,6,9,10-pentabromocyclododecane and its enantiomer. The eight iBPBCD diastereomers were also found in several expanded (EPS) and extruded polystyrene materials (XPS). Stereoisomer pattern varied to a large extent with δ-, η-, and θ-iBPBCDs dominating in EPS- and α-, β-, ε-, and ξ-isomers in XPS-materials. The substitution of a bromine atom with an alkoxy group is expected to result in more lipophilic compounds than the parent HBCD compounds. The chromatographic retention on the reversed-phase column supports this assumption. Therefore, we expect that certain iBPBCD stereoisomers may also have the potential to accumulate in biota like e.g. α-HBCDs. The presented spectroscopic and chromatographic data allow the identification of 16 different iBPBCD stereoisomers in plastic materials, environmental samples, and biota. With this, the occurrence, fate, and toxicological relevance of this new class of polybrominated compounds can now be studied in more detail.

1. Introduction

Plastic debris has turned out to be a major contaminant of many aquatic systems world wide (Derraik, 2002). Sands of sea shores contain substantial amounts of plastic particles of various sizes (Thompson et al., 2004). Plastic debris is often ingested by aquatic animals causing suffocation, entanglement, and starvation. Micrometer small plastic particles were found to translocate to inner organs of marine organism such as mussels, amphipods, and lugworms (Browne et al., 2007, 2008).

Polymer materials with comparably low densities can be transported along water ways. Sea currents are capable to transport plastic over long distances to remote areas. Certain areas of the northern Pacific are covered with substantial amounts of plastic debris due to circulating waters transporting plastic from North America's coasts and from Asian shores. Moore et al. (2001) found that in areas northeast of Hawaii near the center of the Pacific Subarctic gyre, the amounts of plastic often exceed those of plankton. About 1% of all the collected plastic pieces were found to be styrofoam particles of 0.3–5 mm size.

Plastic and its debris not only consists of polymeric material but also contains other compounds such as plasticizers, dyes, pigments, UV-stabilizers and flame retardants among other additives. Brominated flame retardants (BFRs) have become the most important polymer additive next to plasticizers (Alaee et al., 2003). Polystyrene, with a worldwide production of 10 Mio t y^{-1} (Wünsch, 2000), is a low density polymer suitable for long-range transport via water currents. It is mainly used as expanded (EPS, $\rho = 20$ kg m^{-3}) and extruded polystyrene (XPS, $\rho = 50$ kg m^{-3}). Both materials are available in flame-proofed forms. Hexabromocyclododecanes, with an estimated annual demand of >20 000 t y^{-1} in 2003, are the most important flame retardants for this application (BSEF, 2006). Increasing levels of HBCDs were found in Swiss lake sediments (Kohler et al., 2008). HBCDs can now be detected world wide in environmental samples (Sellström et al., 1998; de Wit, 2002; de Wit et al., 2006; Remberger et al., 2004; Marvin et al., 2006; Law et al., 2006), in wildlife (Law et al., 2003; Gerecke et al., 2003; Lindberg et al., 2004; Janak

* Corresponding author. Tel.: +41 44 823 4257; fax: +41 44 823 4041.
E-mail address: norbert.heeb@empa.ch (N.V. Heeb).
URL: http://www.empa.ch (N.V. Heeb).

0045-6535/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2009.12.045

et al., 2005; Sellström et al., 2003; Peck et al., 2008) and in humans (Covaci et al., 2006). Albeit the transport pathways for BFRs into the environment and biota are not clear yet, long-range transport of plastic particles might be an important pathway.

When isolating individual HBCD stereoisomers and elucidating their stereochemistry, we noticed that additional brominated compounds are present in technical HBCD mixtures. Herein we report analytical data of a new class of polybrominated compounds, which are found as constituents in several flame-proofed polystyrene samples and in technical HBCD mixtures. These new compounds are structurally related to HBCDs and are presumably emitted and distributed in the environment like HBCDs.

Based on their stronger retention on a reversed-phased column, iBPBCDs are possibly more lipophilic than HBCDs and might also have altered bioaccumulation potentials. The presented analytical methods allow a more specific search for these formerly unknown compounds. In a first approach, these compounds are expected to be found in those materials and environmental compartments where HBCDs already have been identified. More data on their occurrence, persistence, bioaccumulation potential, and toxicology are needed to assess environmental risks for this new class of compounds.

2. Materials and methods

2.1. Materials

Individual iBPBCD diastereomers were isolated from a low-melting, technical grade HBCD mixture (Saytex HP-900®, mp = 168–184 °C) by normal-phase liquid chromatography on silica 60 (Merck, Darmstadt, Germany) with mixtures of *n*-hexane (Merck) and dichloromethane (Merck). HPLC-grade methanol, acetonitrile (ROMIL, Cambridge, UK), and water (Merck) were used for reversed- and chiral-phase liquid chromatography. The examined plastic materials, two low-density EPS boards ($\rho = 19\ \mathrm{kg\ m^{-3}}$)

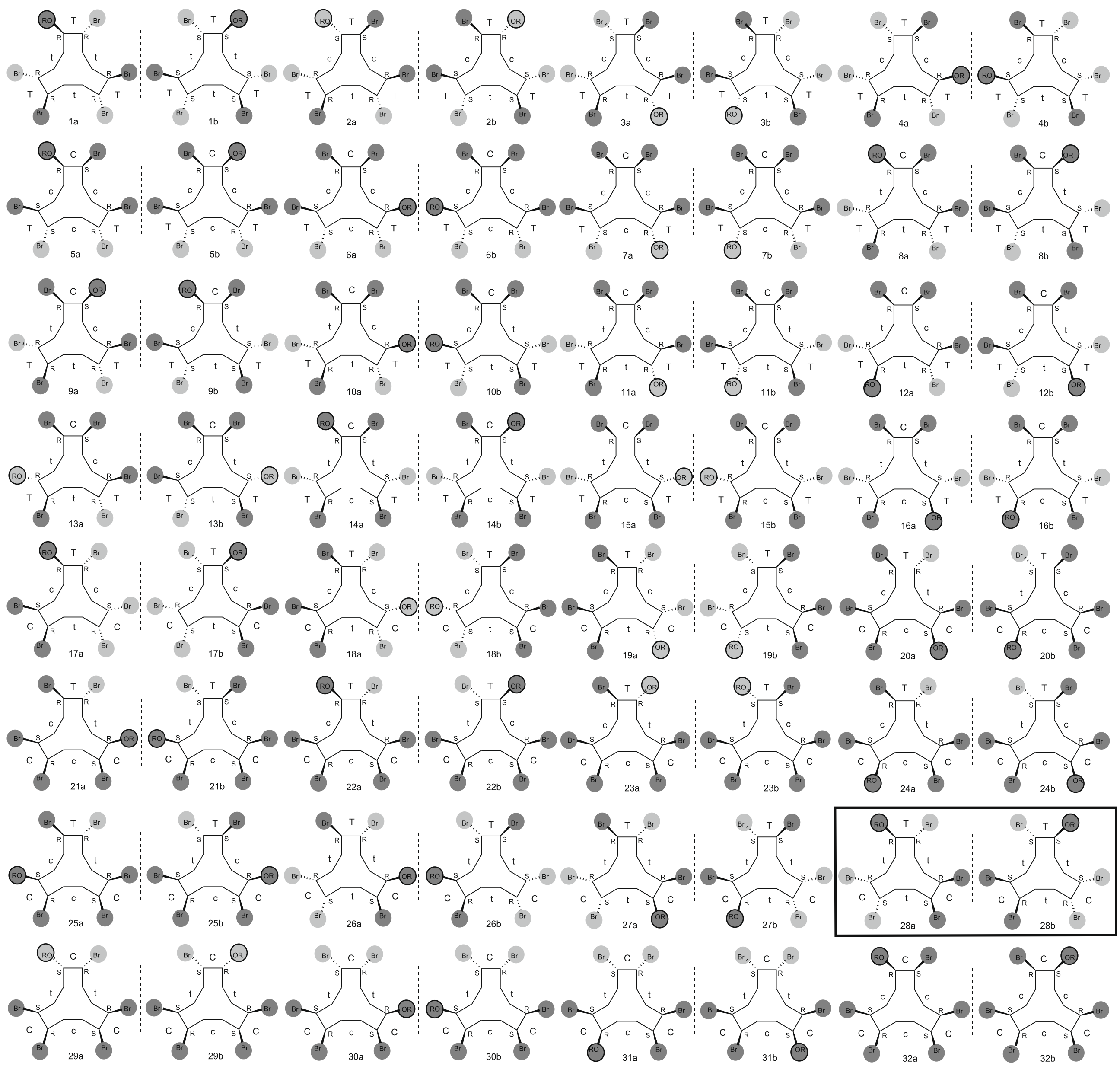

Fig. 1. Schematic representation of all 64 possible 1-iso-butoxy-2,5,6,9,10-pentabromocyclododecane stereoisomers. Mirror planes (dashed lines) separate enantiomers. Substituents above (dark gray) and below (light gray) the paper plane are distinguished. The structures of θ-iBPBCDs (framed) were assigned to compounds **28a/b** by XRD-analysis.