



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Molecular structure and vibrational spectra of 2,2',4,4',6-pentabromodiphenyl ether (BDE 100)

Katarzyna Chruszcz-Lipska<sup>a,\*</sup>, Bartosz Trzewik<sup>b</sup>, Bogumiła Winid<sup>a</sup><sup>a</sup> AGH University of Science and Technology, Faculty of Drilling, Oil and Gas, ul. Adama Mickiewicza 30, 30-059 Kraków, Poland<sup>b</sup> Jagiellonian University, Faculty of Chemistry, ul. Romana Ingardena 3, 30-060 Kraków, Poland

### ARTICLE INFO

#### Article history:

Received 18 March 2016

Received in revised form 19 March 2017

Accepted 20 March 2017

Available online 21 March 2017

#### Keywords:

2,2',4,4',6-Pentabromodiphenyl ether

BDE 100

IR spectroscopy

Raman spectroscopy

DFT calculations

### ABSTRACT

In this work, FT-IR ATR and Raman (laser line 532 nm) spectra of 2,2',4,4',6-pentabromodiphenyl ether (BDE 100) have been recorded in the range of 4000–650 and 4000–100 cm<sup>-1</sup>, respectively. A combined experimental and theoretical approach (DFT/B3LYP/6-311++ and aug-cc-pVDZ) was used to study molecular structure of BDE 100. Optimization of geometry in the gas phase at these levels of theory indicated that the BDE 100 has skew conformation. The detailed assignment of IR and Raman bands of BDE 100 was done on the basis of calculated results for the most stable conformer. The scaled theoretical frequencies are in good agreement with the experimental ones.

Both experimental and theoretical IR and Raman spectra of BDE 100, one of the members of the family of flame retardants, are presented here for the first time.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

(Poly)brominated diphenyl ethers (PBDEs) have from 1 to 10 atoms of hydrogen in aromatic rings substituted by bromine atoms. There are 209 potential PBDE congeners, including 3 monoBDEs. They feature high ignition temperatures and that is why they are widely used as inhibitors of combustion, also referred to as bromine flame retardants (BFRs). PBDEs are retained in polymers through physical interactions rather than chemical bonds, hence they are categorised as additive antipyrenes. PBDEs get easily released to the environment and their stability is related to the stage of bromine substitution: lighter PBDEs tend to be more stable. Transformations of PBDEs congeners are mostly activated by natural physical or chemical factors and certain products of such transformations have proven to be even more toxic. Debromination leads to either partially debrominated PBDEs or polybrominated dibenzofurans, (poly)brominated phenols and (poly)bromobenzenes. On account of their physicochemical properties, PBDEs are transported over long distances and, when released, they get easily dispersed in the environment. Like other poorly degradable persistent organic pollutants, PBDEs tend to bio-accumulate via the food chain of living organisms.

PBDEs have been manufactured since 1965 [1] and have served as additives to chemically hardened plastics for making household and office equipment (telephones, copying machines, electric and electronic devices, computers, TV sets, household goods, domestic appliances).

They also have found use in manufacturing of polyurethane foam used in various sectors of industry. Three dominant commercially available mixtures of these compounds are: penta-, octa-, and deca- blends of congeners. Commercially available penta-BDE is a component of flexible polyurethane foam, epoxy and phenol resins and textiles. In the early 21st century, the world production of penta-PBDE would approach 7500 tons [2]. Technical penta-BDE consists of BDE 47, BDE 99, and BDE 100, with lesser contributions from BDE 153, BDE 154, and BDE 85. BDE 100 makes up between 8 and 13% of the technical penta-BDE. Even though production of penta-BDEs was abandoned in the USA and in the EU in 2004, its main congeners are still to be detected in humans and the wildlife worldwide.

Concentrations of BDE 100 in biosolids in the US range from 75.3 to 229 ppb and estimated loads are: 910–1150 kg·a<sup>-1</sup> to biosolids, 457–688 kg·a<sup>-1</sup> to land applications, and 183–229 kg·a<sup>-1</sup> to incineration plants, and 255–194 kg·a<sup>-1</sup> to landfills [3]. PBDEs occurrence in the environment has become a growing concern because of their toxicity and endocrine disruptive effects. Research work has been undertaken to investigate the mechanisms of those processes. Results obtained by Zhang et al. [4] showed that BDE 100 may disrupt the endocrine system through interfering with some hormonal signalling pathways [4]. Testing done on rat livers revealed that BDE 100 was responsible for mitochondria damage. The study conducted by Pereira et al., who investigated rat liver mitochondria was focused on cytotoxicity induced by BDE 100 [5].

A level of industrialisation, population figures, and social and economic status are major determinants of human exposure to PBDEs. BDE 100 belongs to the most commonly detected congeners in

\* Corresponding author.

E-mail address: [lipska@agh.edu.pl](mailto:lipska@agh.edu.pl) (K. Chruszcz-Lipska).

environmental samples. However, its detected concentrations are usually lower than of other congeners: BDE 209, BDE 47, and BDE 99.

Determinable amounts of BDE 100 have also been detected in plants [6,7] and fish tissues [8–10]. In humans BDE 100 has been found in serum [11–14], in adipose tissue, in breast milk [11,12,15] and in liver [16]. In the environment BDE 100 has been detected in polluted waters (landfill leachate, sewage water) [8,17,18], in surface water [7,18–21] and in precipitation water [22–24]. Major receptors of man-made organic pollutants include soils and bottom sediments in rivers and water reservoirs. BDE 100 is detectable in water sediments [19,25–30] and in soils [6,7,31–34]. Studies of atmospheric air condition in urban areas, including those distant from the emission sources, revealed the presence of BDE 100 in the gaseous phase and in particulate matter [17,18,20,24,26,31,32,35–45]. Attempts were made to estimate the BDE 100 content in bulk atmospheric deposition [26,46–49]. Concentration levels several orders of magnitude higher than in outdoor air were registered in dust from closed rooms [42,50–56], showing it to be a hazard factor as well. Environmental occurrences of BDE 100 in the biotic and the abiotic components of the environment are summarized in Table I SI.

Gas chromatography-mass spectrometry (GC–MS) operating in a negative chemical ionization (NCI) or in an electrical ionization (EI) modes are analytical techniques widely used for determining the concentration of PBDEs in samples of various origins. Moreover, according to the literature, the presence of PBDEs in samples can be analyzed with success by other methods like: X-ray fluorescence [58] or scanning electron microscopy with energy dispersive X-ray spectroscopy [59].

In spite of many proven methods, the laboratories are seeking other straightforward and inexpensive analytical techniques of detection of PBDEs in various samples. One of them can be vibrational spectroscopy, which offers a molecular-level identification of polybrominated flame retardants in the environmental matrices and consumer items as well [57,60–66]. In a past few years it has been shown that IR spectroscopy can be a method for easy checking the presence or absence of decabromodiphenyl ether (BDE 209) in a resin [64]. Raman microscopy is a tool suitable for recognize of PBDEs as components of diverse heterogeneous samples with a micrometer scale spatial resolution [63, 65]. Also, a portable dispersive Raman system can be used to recognize and quantify a level of concentration of PBDEs in various polymers by rapid measurements (lasting 10–20 s) with no special sample preparation [62]. Moreover, surface-enhanced Raman spectroscopy (SERS) technique provides promising results of PBDEs detection in water solutions [60,61]. Jiang et al. showed that quantitative detection of BDE 15 based on SERS technique in real sea water is possible in the range of 250–5000  $\mu\text{g}\cdot\text{dm}^{-3}$  with a detection limit equal to 120  $\mu\text{g}\cdot\text{dm}^{-3}$  [60].

The literature data concerning the application of vibrational spectroscopy to detection of PBDEs in various environmental samples by using portable instruments designed for field application are relatively new. Chemical identification of this method involves qualitative/quantitative spectral matching of an unknown spectrum with the reference spectrum from a spectral library. Thus, creation of a well-documented spectral library for commonly used PBDEs is essential for their identification in a broad range of samples. However, the number of congeners for which experimental IR and Raman spectra have been published so far is limited. To our knowledge, only the experimental IR and Raman spectra of 4,4'-dibromodiphenyl ether (BDE 15) [60,67–69], 2,2',4,4'-tetrabromodiphenyl ether (BDE 47) [61,70] and decabromodiphenyl ether (BDE 209) [57,62–64] are presented in literature. Also, Raman spectra of commercial penta-, octa- and hexa-BDE samples are measured [57,62].

Theoretical calculations, complementary to the experiment can facilitate understanding of molecular properties of investigated compounds. Theoretical study of the vibrational spectra would be of help in understanding conformational and physicochemical properties of a studied molecule and can help in prediction of molecular properties of its analogues. Thus, the DFT/B3LYP method has been previously

successfully applied in the cases of other polybrominated diphenyl ethers, for calculation of: geometrical and/or vibrational properties [60,61,67,68,70,71–73],  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts [73], solvent effects [68], atomic charges [71], dipole moments [71,72], prediction of oxidative degradation pathways [74], and prediction reaction profile of the reductive debromination [75,76].

In the present work, a combined experimental and theoretical (DFT/B3LYP/aug-CC-pVDZ) approach was used to study the molecular structure of 2,2',4,4',6-pentabromodiphenyl ether (BDE 100). According to our knowledge, both experimental and theoretical IR and Raman spectra of BDE 100 are presented here for the first time.

## 2. Experimental Methods

### 2.1. Synthesis of 2,2',4,4',6-Pentabromodiphenyl ether (BDE 100)

#### 2.1.1. 2,2',4,4'-Tetrabromodiphenyliodonium Halides (1a–c)

2,2',4,4'-Tetrabromodiphenyliodonium chloride **1a** and iodide **1c** were obtained according to the method by Marsh, Stenutz, and Bergman [77] (Fig. 1). Similarly we prepared the bromide **1b**, not reported previously. We started from half the original amount of the substrates and the intermediate hydrosulphate salt solution was divided into three equal parts, from which **1a**, **1b**, and **1c** were obtained, respectively. We noticed that the Authors probably made calculation mistakes when reporting their yields: they should have been 69% for **1a** (numbered as **3** [77]) and 67% for **1c** (numbered as **38** [77]).

#### 2.1.2. 2,2',4,4'-Tetrabromodiphenyliodonium Chloride (1a)

White powder, yield 2.51 g (45%), mp. 158.5–161.5 °C (dec.) (Lit. mp. 167–168 °C (dec.) [77], 164–165 °C [78]).

#### 2.1.3. 2,2',4,4'-Tetrabromodiphenyliodonium Bromide (1b)

White powder, yield 2.91 g (49%), mp. 151.0–155.0 °C (dec.).

#### 2.1.4. 2,2',4,4'-Tetrabromodiphenyliodonium Iodide (1c)

Light yellow powder, yield 3.92 g (61%), mp. 108.0 °C (rapid dec.) (Lit. mp. 115–120 °C [77]) exit.

#### 2.1.5. 2,2',4,4',6-Pentabromodiphenyl Ether (BDE 100) (2)

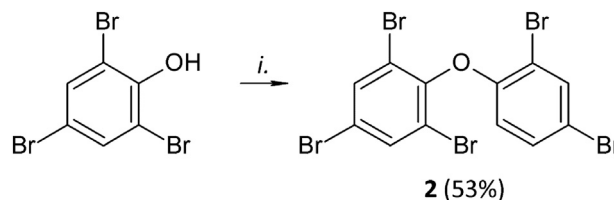
2,2',4,4',6-Pentabromodiphenyl ether **2** was synthesized according to Marsh et al. [78], but instead of using chloride **1a** we used iodide **1c**, which increased the yield of **2** from 36% to 53%.

White powder, yield 0.75 g (53%), mp. 97.0–98.0 °C (Lit [78]).

### 2.2. Spectroscopic Measurements

The FT-IR ATR spectrum of **2** (BDE 100) in the solid state was recorded at room temperature using a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an iD5 ATR adapter. The spectrum was measured with 32 scans, in a range of 4000–650  $\text{cm}^{-1}$ , with a spectral resolution of 1  $\text{cm}^{-1}$ .

The Raman spectrum of **2** (BDE 100) in the solid state was collected using a Thermo Scientific DXR™ Raman microscope with a 532 nm excitation laser. The instrument was operated using the Thermo Scientific



**Fig. 1.** The synthetic route to the title 2,2',4,4',6-pentabromodiphenyl ether **2** (BDE 100). Reagents and conditions: *i.* 1. NaOH, H<sub>2</sub>O; 2. 2,2',4,4'-tetrabromodiphenyliodonium iodide **1c**, reflux.

Download English Version:

<https://daneshyari.com/en/article/5139804>

Download Persian Version:

<https://daneshyari.com/article/5139804>

[Daneshyari.com](https://daneshyari.com)