PROPERTIES OF THE MAJOR COMMERCIAL PBDPO FLAME RETARDANT, DBDPO, IN COMPARISON TO PBB AND PCB

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Introduction

Various literature references reporting the environmental detection of certain polybrominated diphenyl oxides (PBDPO, PBDE) include statements that the PBDPO flame retardants have characteristics similar to the polychlorinated biphenyls (PCB) and polybrominated biphenyls (PBB).[1,2] Accompanying these statements is the assumption that all PBDPO, including decabromodiphenyl oxide (DBDPO), pose the same potential environmental risks as the PCB.

DBPDO is the major PBDPO flame retardant in commercial production and use. The assumption that DBPDO shares many similar characteristics with the PCB/PBB appears based on their chemical structures. Their structures do appear similar when viewed in one dimension (Fig 1). However, there are significant differences between the PCBs, PBBs and DBPDO. These differences affect their uses, potential for environmental release, toxicology and biological uptake. This paper will explore these differences.

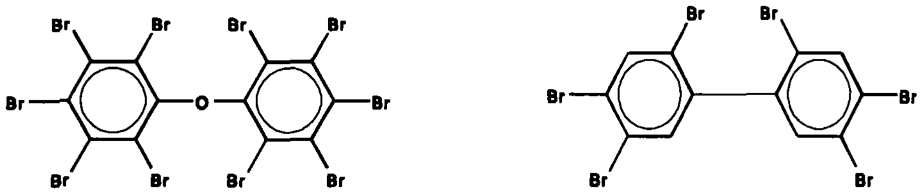

Figure 1. Chemical structure of DBDPO (left) and a representative PBB, hexabromobiphenyl (right).

Results and Discussion

Major differences exist between the PCB, PBB and DBDPO. The first difference is in their physical/chemical properties. The molecular weights and volumes of the PCBs, PBBs and DBDPO differ greatly due to the difference in atomic weight and volume of Cl (35) and Br (70). The molecular weight of hexachlorobiphenyl (HxCB), hexabromobiphenyl (HxBB), and DBDPO are 358, 622 and 959 g/m, respectively. Br atoms occupy a considerably larger volume than due Cl atoms. The distinctly different molecular geometries of DBDPO, HxBB, TCDD and TCDF are compared in TABLE 1.[3]

The common commercially important PCB products were liquids.[4] DBDPO, and the former commercial PBB products, are solids. The greater mobility of liquids combined with the large scale use of PCBs as functional fluids where leaks and spills could occur made the likelihood of their rapid, large scale loss to the environment much greater than that of DBDPO and PBB.[4] The common PCB products had much greater volatility than DBPDO or PBB. The vapor pressure of

DBDPO is 4.63 x 10-6 Pa @ 20°C.[5] DBPDO remains a solid at 306°C exerting a vapor pressure of only 5 mm Hg whereas Arochlor (A) 1242 (average of 3 Cl atoms/molecule) boils at 325-366°C. DBDPO should not volatilize significantly from plastics even on exposure to temperatures >250°C, because of its low mobility and vapor pressure.[4] In contrast, A1248 (average of 4 Cl atoms/molecule) volatilized from polyvinyl chloride at a rate of 19% in 24 hrs during exposure to 87°C.[4] The water solubilities of PCBs and DBPDO are also different: DBDPO<0.1 ug/L[5], A1260 (average of 6 Cl atoms/molecule) ~25 ug/L[4], and A1242 ~200 ug/L[4]. DBDPO is also far less soluble in organic solvents than PCB which are readily soluble in most common organic solvents.[4] In contrast, DBDPO's solubility is: acetone 0.05%, benzene 0.48%, methylene bromide 0.42%, and xylene 0.87%.[4]

TABLE 1. Comparison of the molecular geometries of several aromatic compounds.

Molecule	Box Size					
	Area	Volume	X	Y	Z	Box Volume
DBDPO	424.4	359.2	14.2	9.7	9.7	1339.1
2,2',4,4',5,5'-HxBB	366.0	270.8	13.8	11.9	8.4	991.1
2,3,7,8-TCDD	305.6	203.9	13.8	7.6	3.6	372.6
2,3,7,8-TCDF	261.49	197.3	13.7	7.7	3.6	378.9

Area = molecules surface area calculated using Van Der Waals dot surface.
Volume = represents molecular volume including the electronic cloud (Van Der Waals radii).
Box Volume = minimum box in which the molecule will fit (just touching the Van Der Waals radii.)

The above properties greatly influence the bioavailability, absorption and bioaccumulation of the PCB, PBB, and DBDPO in biotic systems. Pharmacokinetic studies show DBDPO has a half life in rats of less than 24 hours and that >99% of oral dose is excreted in the feces in 72 hrs.[6,7] In contrast, Pomerantz et al. estimated that < 10% of a HxBB dose would be excreted by rats.[8] A study directly comparing the bioconcentration of DBDPO, octabromobiphenyl (OctaBB) and tetrachlorobiphenyl (TetraCB) in fish showed that DBDPO and OctaBB were not absorbed by the fish, but that TetraCB bioconcentrated at least 50 times over the exposure level within 4 hours.[9] A six wk bioconcentration study and various environmental monitoring programs have also shown no bioaccumulation of DBDPO in fish.[10]

PCB and PBB effect levels in mammals are considerably lower than those of DBDPO and present a different toxicological profiles from DBDPO; properties which may be related to their molecular arrangement in space.[3] The structures of representative PCB, PBB and DBDPO appear similar when drawn in one dimension (Fig 1,2,3). However, there are substantial differences between these molecules when viewed in three dimensions. The toxicological properties of the toxic PCB and PBB isomers, like those of 2,3,7,8-substituted chlorinated dioxins and furans, are related to their ability to exist in a planar or near planar configuration (Fig 4). However, unlike the PCBs and the PBBs, DBPDO cannot adopt a coplanar conformation.

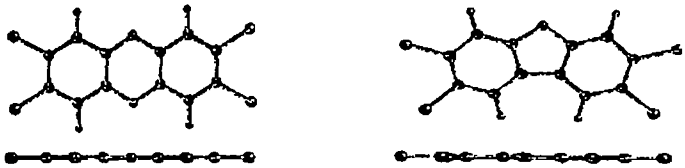

Figure 4. Chemical structures of a 2,3,7,8-substituted chlorodibenzo-p-dioxin (left) and a 2,3,7,8-substitued chlorodibenzofuran (right) shown in the typical one dimensional flat view (top) and more uncommon side view (bottom of each figure) showing the coplanarity.

The ether linkage in the diphenyl oxide molecule introduces a high barrier to rotation which prevents the two aromatic rings from assuming a planar configuration (Fig 5). The ether bridge also introduces a 120 degree bend in the alignment of the phenyl rings. PCB and PBB, having no oxygen link between the two aromatic rings, lack this bend (Fig 6).

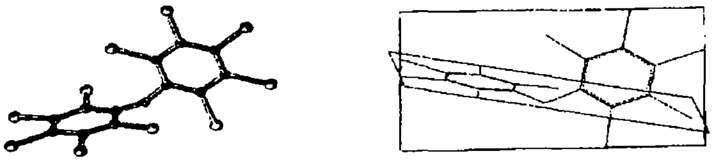

Figure 5. Two different representations of the orthogonal confirmation of DBDPO. Both images show DBPDOs aromatic rings are arranged in space at a 90 degree angles with a bend at the ether linkage.

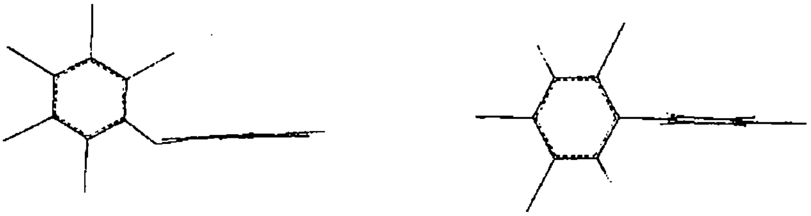

Figure 6. Comparison of the alignment of the two aromatic rings in DBDPO (left) and the polybrominatedbiphenyl, hexabromobiphenyl (right). Note the 120 degree bend in the alignment of the two aromatic rings in the DBPDO due to the presence of the oxygen bridge.

Also, the ortho positions of the PCB, PBB, and diphenyl oxide molecule must be nonhalogen-substituted to assume a coplanar configuration. Substitution in the ortho positions (2,2',6,6') of diphenyl oxide will force the aromatic rings orthogonal to one another; e.g., the phenyl rings will be forced 90 degrees to one another. DBDPO, fully substituted at all ring positions, exists with its two aromatic rings arranged in space at a 90® angle (Fig 5). Given that the toxicology of the PCB/PBB/dioxins are generally accepted to be receptor-mediated events, the lack of coplanarity and the orthogonal relationship of the diphenyl rings will not allow DBDPO to induce toxicity via that mechanism.

Another major difference between the PCBs, PBB and DBDPO is their use. PCB were used in applications with a high potential for environmental release, e.g. liquids in large volume transformers/capacitors and in paperless copies. As a result of their physical properties and uses, PCB residues were detected in many diverse locations around the world as early as the 1970s.[8] The production, distribution and use of the PBB were never as wide spread as the PCB, and PBB, unlike PCB, were not used in applications with significant potential for release to the environment. The main use of the HxBB commercial product was in thermoplastics used as housing for typewriters and business machine and in this use had little tendency to migrate from the thermoplastic.[8] In fact, PBB are of concern due to a single contamination incident occurring in the State of Michigan.[8] In 1973, a HxBB-based commercial product was accidentally mixed in animal feed and the feed was subsequently fed to a number of different farm animals.[8] PBB congeners in that commercial product ranged from tetra- to octabromobiphenyl.[11] Shortly after this accident, all PBB production in the U.S. was voluntarily discontinued. Re-initiation of manufacture requires approval of the U.S. Environmental Protection Agency. From the time U.S. PBB production was discontinued, the only PBB in commercial production was decabromobiphenyl (DecaBB) manufactured by one company at one location in France. That company has announced DecaBB production will cease in 2000.[12] The number of PCB congeners reaching the environment numbered nearly 100 different compounds. In contrast, the commercial PBB products consisted of a comparatively small number of congeners[8,11], and DBPDO exists as a single isomer.

As a result of these differences in properties and uses, the environmental release of PCB, PBB and DBDPO has been vastly different in magnitude. PCB were steadily released into the environment, in many countries, presumably over decades, and were found to be pervasive, worldwide contaminants as early as 1978.[8] PBB environmental release is essentially limited to one accident occurring in the US in 1973. DBDPO, the major PBDPO in commercial production and use, is not a widespread or diffuse environmental contaminant and its primary use in thermoplastics limits its environmental release and thus environmental exposure.[13] Further, major differences exist between the PCB, PBB and DBDPO in terms of toxicological effects and biological uptake. These differences show DBDPO is not comparable to PCB and PBB.

References

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