Polychlorinated Terphenyls (PCTs): Backbone Angle of ortho and nonortho Chlorination

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Abstract

Polychorinated Terphenyls is considered as one of persistent organic pollutants (POPs) and have been banned in the use mostly in United State and Europe countries. A study of the ortho chlorination toward backbone angle has been done in order to obtain the information of –C-C- angle of between aromatic groups of terphenyls. Five hexachlorinated terphenyl standards have been deployed for the purpose. Firstly, five terphenyl standards of 2,2",3,3",5,5"-hexachlorinated-meta-, 2',3,3",5,5',5"-hexachlorinated-para-, 2',3,3",4,4",5'-hexachlorinated-para-, 2,2”,3,3”,5,5”-hexachlorinaated-para-, 3,3´,3”,5,5´,5”-hexachlorinated-para- have been measured by GC-FTIR. From the data obtained, IR spectra of each standard were then compared to the theoretical calculation with Gaussian Program. The result showed that IR spectra of all five standard congeners were fit to the each spectra of the theoretical calculation. Based on the theoretical IR spectra obtained, furthermore, backbone angle of each five standards were able to be obtained related to the position of the chlorination pattern of the backbone. The angle between aromatics groups because of ortho chlorination or without ortho chlorination was clearly different. The ortho chlorination contributed to angle resulted in the lowest structure energy level around 51°-58°. Without ortho chlorination, the angle is around 36°.

INTRODUCTION

Some approaches have been made to analysis of PCTs in the enviroment. The method that is used untill now is not adequate to be used for determination of PCTs congeners in some matrix. Lack of accuracy and precision ist the most consideration of the need of good method to be used as standard method in the PCT quantitation. A requirement that is urgently need for the new method is capability of the new method to analysis spesific congener of the thousands PCTs of total PCTs that have been produced worldwide untill around 60 000 tons.

The application patterns of PCT were similar to those of PCB due to similar chemical and physical properties of both substance groups (de Boer, 2000). From the former application fields, disposal sites like landfills as well as from combustion processes (new formation) PCT are emitted into the environment as low volatile, persistent, and bioaccumulating substances. In spite of comparably limited knowledge about this substance group, its environmental and toxicological relevance should not be neglected. The main reason for this lack of knowledge is that the 8557 possible PCT

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congeners (Remberg et al., 1998) could not be handled sufficiently by common gas chromatographic techniques so far. Furthermore, with a few exceptions, single reference substances are not available, which are necessary for the development of suitable analytical methods. In consequence, published data on the occurrence of PCT should be dealt with utmost care, due to strongly varying analytical procedures and calculation methods used (Gallagher et al., 1993; Wester et al., 1996; Fernandez et al.,1998).

Synthesis of particular PCT congeners as standards for analytical investigations were done by Chittim et al. (1977) that are about 22 PCT congeners. Than, the next approach in the synthesis of PCT was successfully started (Bahadir et al., 2003; Hopf et al., 2007) based on the SUZUKI-coupling (Miyaura et al.,1981; Lehmler and Robertson, 2001). Within the work, introduced here, the number of single PCT congeners was extended.

A new method based on the measurement of GC-FTIR are able to be used for the solution of the analysis of PCT congeners by collecting of some synthesized PCTs and measuring some quantities of sample to be injected into GC-FTIR. The pattern of the spectra are able to be fitted with the Gaussian Program. In this study, the influence of the ortho substitution of chlor atom towards backbone angle of PCTs is aimed to be investigated.

METHOD

Two different groups of PCTs with ortho substitution of 2,2",3,3",5,5"-hexachlorinated-meta-, 2',3,3",5,5',5"-hexachlorinated-para-, 2',3,3",4,4",5'-hexachlorinated-para-, 2,2”,3,3”,5,5”- hexachlorinated-para-terphenyl and without ortho substitution of 3,3´,3”,5,5´,5”-hexachlorinated-para-terphenyl have been dilluted into dichlormethane and than injected with GC-FTIR. The IR measurement of congeners was done in the gas phase after pass trough GC coloumn. The spectra resulted is than fitted with the Gaussian Program that was done in the istitute of organic chemistry, TU-Braunschweig. The influence of the ortho substitution is than investigated by comparing backbone angle of the fitted PCTs.

RESULT

The angle of backbone is investigated based on the rotation energy of C-C between aromatic groups of congeners. The lowest energy occured of the congeners is considered as stable form of the PCTs structure compared with others in which the backbone angle is assumed as structure having rigid bonds. After fitting the congeners of 2,2",3,3",5,5"-hexachlorinated-meta-, 2',3,3",5,5',5"-hexachlorinated-para-, 2',3,3",4,4",5'-hexachlorinated-para-, 2,2”,3,3”,5,5”- hexachlorinated-para-terphenyland3,3´,3”,5,5´,5”-hexachlorinated-para- terphenyl measured with GC-FTIR and calculated with the Gaussian Program, the form of substitution of chlor atoms in the backbone are able to be depicted on to 3D figure in the following:

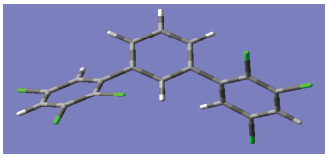


Fig 1. 2,2",3,3",5,5"-hexachlorinated-m-terphenyl

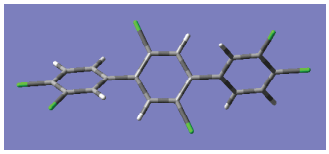


fig 2. 2',3,3",4,4",5'-hexachlorinated-p-terphenyl

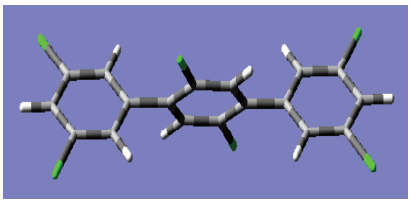


Fig 3. 2',3,3",5,5',5"-hexachlorinated-p-terphenyl

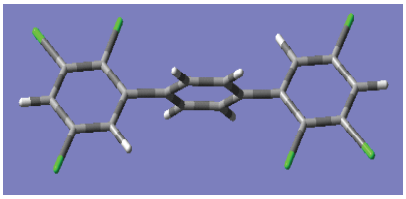


fig 4. 2,2",3,3",5,5"-hexachlorinated-p-terphenyl

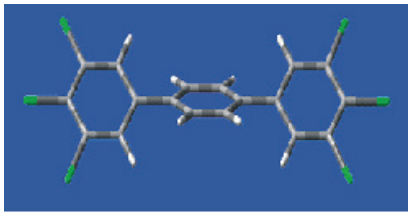
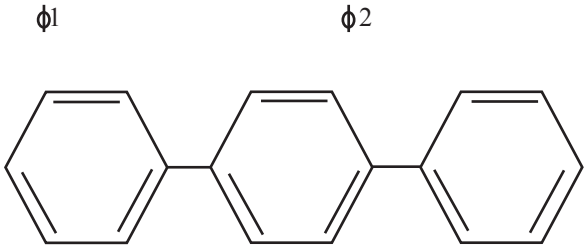


Fig 5. 3,3",4,4",5,5"-hexachlorinated-p-terphenyl

The backbone angle of the congeners after calculation with the program resulted angle variation beetween C-C group of the aromatics. The table of the angle backbone of the congeners showed that the ortho substitution of chlor atom on to PCT backbone contributed around 51°-58° angle between two aromatic groups. Without ortho substitution group, the backbone angle of the congeners resulted was around 36°. The detail angle of the backbone each measured congeners is listed in the following table.

Table 1. List of the angle backbone of the measured PCTS



Congeners	f 1	f 2
2,2",3,3",5,5"-Hexachlorinated-*m*-terphenyl	$\phi 1 = 55{,}68^\circ$	$\phi 2 = 59{,}27^\circ$
2',3,3",4,4",5'-Hexachlorinated-*p*-terphenyl	$\phi 1 = 51{,}62^\circ$	$\phi 2 = 54{,}69^\circ$
2',3,3",5,5',5"-Hexachlorinated-*p*-terphenyl	$\phi 1 = -52{,}99^\circ$	$\phi 2 = 55{,}78^\circ$
2,2",3,3",5,5"-Hexachlorinated-*p*-terphenyl	$\phi 1 = -58{,}42^\circ$	$\phi 2 = 55{,}03^\circ$
3,3",4,4",5,5"-Hexachlorinated-*p*-terphenyl	$\phi 1 = -36{,}95^\circ$	$\phi 2 = 36{,}95^\circ$

The non ortho substitution showed that having angle of around 36° is considered close to the planarity form of dioxine planarity. It means that the toxicology aspect of the structure must be also investigated as well as planar dioxine.

CONCLUSION

The ortho chlorination of the aromatic rings contributed angle backbone to around 51°-58°. Without ortho chlorination, the angle between aromatic groups is around 36°. Hence, the non ortho substition of PCTs has the potential toxicology risk as like as dioxine planar pollutant. Therefore, an analytical method for spesific determination of non ortho congener is urgently needed.

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