



Partial physicochemical properties and relative stability of polyhydroxylated dibenzofurans: Theoretical and experimental study

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ABSTRACT

Polyhydroxylated dibenzofuran (PHODF) is an important degradation product of polychlorinated dibenzofuran (PCDF). Four types of hydrogen bonds (the one between a hydroxyl and the oxygen atom in the matrix, between hydroxyls at *ortho* positions, between the oxygen atom of hydroxyl at position 1 and the hydrogen atom of the matrix at position 9, and between hydroxyls at positions 1 and 9) exist in PHODFs. The energies of the hydrogen bonds were ascertained by comparing the two configurational isomers as approximately 8–11 kJ mol⁻¹, 16–21 kJ mol⁻¹, 5–8 kJ mol⁻¹ and 23–25 kJ mol⁻¹, respectively. An experiment was designed to verify the bond energies, and the entrance geometry on main paths was studied by AIM 2000 program. The most stable in each group of configurational isomers was ascertained on the basis of evaluating the effect of hydrogen bonds. Their thermodynamic properties (standard state entropy S° , standard enthalpy $\Delta_f H^\circ$ and standard Gibbs energy of formation $\Delta_f G^\circ$) were calculated from the combination of density functional theory (DFT) at B3LYP/6-311G** level and isodesmic reactions. Octanol/water partition coefficients ($\log K_{ow}$) were calculated on line with molinspiration methodology based on group contributions. The number and position of hydroxyl substitution (N_{PHOS}) can be a good indicator of these properties for all stable PHODF congeners. The configurations most likely to form are those with a hydrogen bond (Type IV). How intramolecular hydrogen bond influences ionization was also investigated and the first-order ionization constant for each stable conformation was obtained with the self-consistent reaction field (SCRF) method.

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1. Introduction

The persistent organic pollutants (POPs) such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), are released into the environment during the combustion of materials such as fossil fuels and hydrocarbons [1]. They have been studied extensively owing to the high toxicity [2,3]. PCDFs have been measured at various sites around the globe [4–7]. It is well documented that PCDFs have adverse biological effects and high toxicities, and consequently are important targets of source reduction. Under atmospheric conditions, PCDFs react with OH^{*}, NO₃^{*}, and O₃. But the reaction rates of PCDFs with NO₃^{*} and O₃ are so slow that the reaction with OH^{*} is the primary pathway. So in the environment, polyhydroxylated dibenzofuran (PHODF) is an important degradation product of PCDF [8]. Manuela Gesell [9] found that in the soil, the biotransformation of the filamentous fungus *Paecilomyces lilacinus* can make the dibenzofuran (DF) hydroxylated. Under atmospheric conditions, the degradation of DF

is initiated by HO^{*} addition [8]. In addition, during DF degradation by *Sphingomonas* sp. strain HH69, PHODF is detected as a product [10].

There is little research concerning the environment-related properties of PHODF. This work focuses on the thermodynamic data, hydrophobicity and first-order ionization constant, which are all closely related to the generation, degradation and potential environmental risk of chemicals [11–13]. The structure and carbon atomic numbering of DF are illustrated in Fig. 1.

In PHODFs, hydrogen bonds can form. The hydroxyl orientation will affect the strength of hydrogen bond and the configurational stability. There is little practical method for calculating the intramolecular hydrogen bond energy, so computational approaches are of particular importance. Various computational methods for estimating intramolecular hydrogen bond energy were proposed despite none of them were exact [14–16]. To the best of our knowledge, the most frequently adopted methods are as follows [17]: *cis/trans* analysis, isodesmic reactions, local potential energy density, conformational analysis, and empirical energy-geometry correlations. In this study, molecules were fully optimized with DFT method which has been widely used in various fields [18–21]. And thus thermodynamic properties (standard state entropy S° ,

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absolute enthalpy H° and Gibbs free energies G° were obtained. The standard enthalpies of formation ($\Delta_f H^\circ$) and the standard Gibbs energies of formation ($\Delta_f G^\circ$) were also obtained by designing isodesmic reactions. The energy of intramolecular hydrogen bond was obtained by the comparison of $\Delta_f G^\circ$. An experiment was designed to verify the calculation. The octanol/water partition coefficients ($\log K_{ow}$) values of the stable conformers were calculated based on group contribution method. Then correlations of $\log K_{ow}$, $\Delta_f H^\circ$ and $\Delta_f G^\circ$ with the number and position of hydroxyls substitution (N_{PHOS}) were discussed. According to the relative magnitude of their $\Delta_f G^\circ$, the relative stability order of PHODF congeners was theoretically proposed. As ionization is also an important property of chemicals and the focus of many researches [22,23], the influence of hydrogen bond on ionization was also explored and first-order ionization constant (pK_{a1}) of each congener was obtained. It is hoped that this work could contribute to the knowledge of relationship between intramolecular hydrogen bond and environment-related properties about hydroxylated chemicals.

2. Computational and experimental method

In the study, the isomers with one to eight HO– are symbolized as mono-HODF, di-HODF, tri-HODF, tetra-HODF, penta-DF, hexa-HODF, hepta-HODF and octa-HODF, respectively. The name of a molecule depends on the position and orientation of the hydroxyls. The orientation where the hydroxyl faces the oxygen

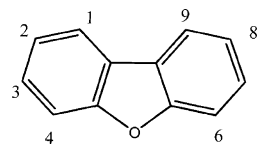
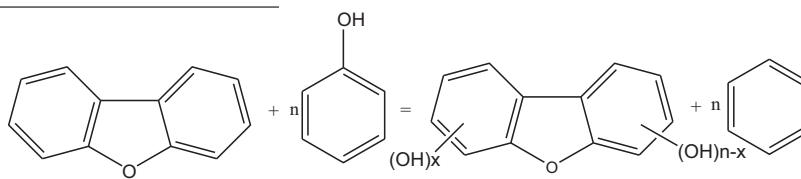


Fig. 1. Molecular structure and atomic number of DF.

positions 1 or 9 is defined as N_1 , the number of HO– at positions 2 or 8 is defined as N_2 , the number of HO– at positions 3 or 7 is defined as N_3 , the number of HO– at positions 4 or 6 is defined as N_4 , and the pair number of HO– at positions 1,9 is defined as $N_{1,9}$. The pair number of *ortho*, *meta* and *para* positions of HO– on one benzene ring is symbolized as N_o , N_m and N_p , respectively. For example, as for OHODF, N_1 – N_4 are all 2, $N_{1,9}$ is 1, and N_o , N_m and N_p are 6, 4, 2, respectively, which are shown in Fig. 2. The parameters mentioned above are defined as a general designation N_{PHOS} [24].

The theoretical calculations on PHODF were performed by DFT method using Gaussian 09 program on 6-311G** basis set. Each molecule was limited as planar during the optimization process. There are no negative frequencies in the calculation result of vibration analysis. All the calculations were scaled by 0.967 so that known systematic errors in calculated frequencies might be eliminated. Thermodynamic parameters, including S° , H° and G° , were obtained directly from Gaussian 09 output files.

The following isodesmic reaction was designed to calculate the $\Delta_f H^\circ$ and $\Delta_f G^\circ$ of PHODF [25].

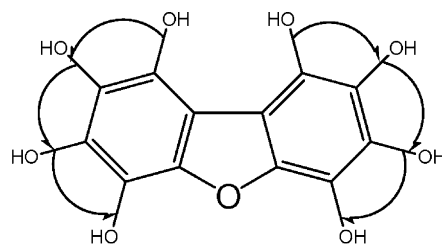


(1)

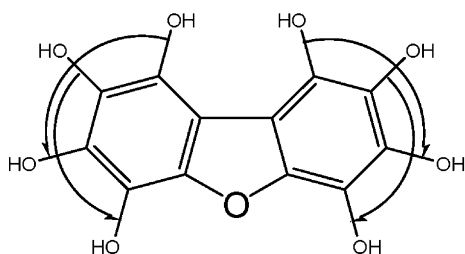
Eqs. (2) and (3) could be obtained.

$$\Delta_f H^\circ = [H^\circ(\text{PHODF}) + nH^\circ(\text{benzene})] - [H^\circ(\text{DF}) + nH^\circ(\text{phenol})] \quad (2)$$

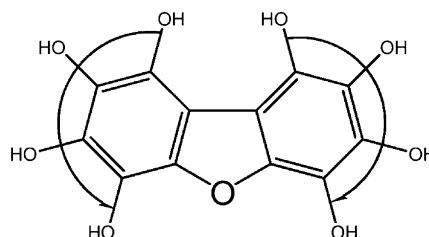
in the matrix was defined as positive, named as 1-, 2-, 3-, 4-, 6-, 7-, 8-, 9-, respectively. Conversely the orientation where the hydroxyl faces away from the oxygen in the matrix as negative, named as 1'-, 2'-, 3'-, 4'-, 6'-, 7'-, 8'-, 9'-, respectively. The number of HO– at



$$N_o = 6$$



$$N_m = 4$$



$$N_p = 2$$

Fig. 2. N_o , N_m , N_p of OHODF.

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