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Chlorination pattern effect on thermodynamic parameters and environmental degradability for C₁₀-SCCPs: Quantum chemical calculation based on virtual combinational library

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ABSTRACT

Short-chain chlorinated paraffins (SCCPs) are still controversial candidates for inclusion in the Stockholm Convention. The inherent mixture nature of SCCPs makes it rather difficult to explore their environmental behaviors. A virtual molecule library of 42,720 C₁₀-SCCP congeners covering the full structure spectrum was constructed. We explored the structural effects on the thermodynamic parameters and environmental degradability of C₁₀-SCCPs through semi-empirical quantum chemical calculations. The thermodynamic properties were acquired using the AM1 method, and frontier molecular orbital analysis was carried out to obtain the E_{HOMO} , E_{LUMO} and $E_{\text{LUMO}}-E_{\text{HOMO}}$ for degradability exploration at the same level. The influence of the chlorination degree (N_{Cl}) on the relative stability and environmental degradation was elucidated. A novel structural descriptor, μ , was proposed to measure the dispersion of the chlorine atoms within a molecule. There were significant correlations between thermodynamic values and N_{Cl} , while the reported N_{Cl} -dependent pollution profile of C₁₀-SCCPs in environmental samples was basically consistent with the predicted order of formation stability of C₁₀-SCCP congeners. In addition, isomers with large μ showed higher relative stability than those with small μ . This could be further verified by the relationship between μ and the reactivity of nucleophilic substitution and $\cdot\text{OH}$ attack respectively. The C₁₀-SCCP congeners with less Cl substitution and lower dispersion degree are susceptible to environmental degradation via nucleophilic substitution and hydroxyl radical attack, while direct photolysis of C₁₀-SCCP congeners cannot readily occur due to the large $E_{\text{LUMO}}-E_{\text{HOMO}}$ values. The chlorination effect and the conclusions were further checked with appropriate density functional theory (DFT) calculations.

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Introduction

Chlorinated paraffins (CPs) are chlorinated derivatives of *n*-alkanes, which comprise thousands of complex isomers and congeners. The commercial CP products are typical mixtures and can be classified into 3 categories, short-chain

CPs (C₁₀–C₁₃), medium-chain CPs (C₁₄–C₁₇), and long-chain CPs (C₁₈–C₃₀), based on their chain length. Generally, short-chain chlorinated paraffins (SCCPs) refer to those with carbon chain lengths of 10 to 13 and chlorine numbers of 1 to 13 (SCCPs, C_yCl_xH_{22-x}, $x = 1-13$, $y = 10-13$) (Chénier, 2007). Due to their high chemical and thermal stability, CPs have been widely

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used in various industrial applications such as high temperature lubricants, flame retardants, and plasticizers in leather, rubbers, or sealants (Muir et al., 2000; Tomy et al., 1998). SCCPs are high production volume chemicals and their release to the ambient environment may occur through any process in their life cycle such as production, storage, transportation, industrial use and carry-off from manufactured products (Feo et al., 2009; Gao et al., 2012; Sverko et al., 2012; Zeng et al., 2011a, 2012a). Specifically, the annual CP production in China rapidly increased from a few thousand tonnes in 1990 to 600 kilotonne in 2007 (Fiedler, 2010), and SCCPs were detected in urban soils of Shanghai, terrestrial bird species inhabiting South China and some dietary products collected in China (Cao et al., 2015; Luo et al., 2015; Wang et al., 2014). In recent decades, more attention has been paid to SCCPs due to their potential capacity of long-range transport, persistence in the environment, bioaccumulation and toxicity to organisms (Cooley et al., 2001; Ma et al., 2014; Reth et al., 2006; Wania, 2003). However, the inherent mixture nature of SCCPs makes it rather difficult to explore the environmental behavior of individual SCCPs (Sverko et al., 2012; Wang et al., 2013a). The environmental exposure and toxicological data available for SCCPs is still too limited for the Convention's Persistent Organic Pollutant Review Committee to reach a decision, and SCCPs are still controversial candidates for inclusion in the Stockholm Convention. Accordingly in view of their persistence, concerns have been raised about the thermodynamic properties and environment degradability of SCCPs.

Sijm and Sinnige (1995) reported the experimental value of octanol–water partition coefficient for the commercial mixture Cereclor 60 L, while the effects of chain length, chlorination degree and structure on the octanol–water partition coefficients of selected polychlorinated *n*-alkanes have been analyzed (Bettina et al., 2011). The relationship between other basic properties such as vapor pressures and Henry's law constants with carbon chain length and chlorination degree was also proposed based on limited data for SCCPs (Drouillard et al., 1998). Moreover, estimated values from theoretical calculations were also introduced for limited congeners (Gawor and Wania, 2013; Glüge et al., 2013; Wang et al., 2012). EPI Suite™ and SPARC chemical prediction programs were used to calculate the subcooled-liquid vapor pressures and octanol–air partition coefficients for selected SCCP congeners with chlorine content of 50%–70% (Wang et al., 2012), while calculations of other physicochemical properties such as subcooled-liquid solubility in water and octanol, subcooled-liquid vapor pressure, Henry's law constant for water and octanol, and octanol–water partition coefficient were carried out for limited SCCP and MCCP congeners by adopting three tools, COSMOtherm, SPARC, and EPI Suite™ (Glüge et al., 2013). In addition, chemical fate models and the chemical partitioning space were coupled with quantitative structure–property relationships to investigate the potential of complex SCCP mixtures for long range transport and bioaccumulation (Gawor and Wania, 2013). Most recently, the gaseous reaction of ten SCCP molecules with hydroxyl radical was studied via quantum chemical calculations (Li et al., 2014; Liu et al., 2015). Previous attempts at estimating the physicochemical properties of SCCPs seemed to accord with the measured data with a few exceptions, while significant differences could be found between the absolute values obtained from different programs. Large

uncertainties and potential discrepancies between model predictions and experimental data can still be expected since SCCPs have not been included into the training set of the prevailing models. More importantly, the SCCP congeners discussed in the reported works cannot represent all the structural features of the whole SCCP data set. The virtual combinatorial chemistry technique, originating from efforts to efficiently synthesize libraries of diverse compounds, helps to shed light on the issue and thus provides a powerful approach to generate an *in silico* molecular structure library of SCCPs (Cho et al., 1998; Zhou, 2008). In fact, this method has developed rapidly and could generate thousands or even millions of chemical structures within a short time through correctly defined chemical reactions based on combinatorial theory and computational simulation (Freceer et al., 2009; Lokwani et al., 2015).

In this article, a strategy of obtaining overall thermodynamic data by semi-empirical methods with subsequent quantitative structure–property relationship (QSPR) investigation and appropriate quantum chemical calculation of high precision was adopted to elucidate the chlorination pattern effect on thermodynamic parameters and environmental degradability for C₁₀-SCCPs. Specifically, the virtual combinatorial chemistry technique was used to construct a molecule library of C₁₀-SCCPs to cover all of the possible structure spectrum. A comprehensive thermodynamic analysis of thousands of obtained structures was implemented using a high cost-efficiency semi-empirical method, AM1, to provide a theoretical pattern of thermodynamic properties for the C₁₀-congeners. The influence of the chlorination degree on the thermodynamic properties was elucidated, and the number of chlorine atoms (*N*_{Cl}) was adopted to present the dependency of related parameters on the chlorination degree as well as elaborate the reported patterns of C₁₀-congeners detected in different environmental media. Subsequently, a novel structural descriptor, μ , was proposed to characterize the dispersion tendency of the chlorine atoms in the SCCP molecules. The relationship between the new index and the thermodynamic parameters of C₁₀-SCCPs was then extracted to reveal the effect of chlorine dispersion on the isomers' stability. Moreover, the feasibility of direct and indirect photolysis as well as the potential reactivity in other environmental degradation processes of the C₁₀-congeners was also explored by frontier molecular orbital analysis coupled with calculation of the potential energy surface. Finally, the density functional theory (DFT) method was utilized for verification of the obtained rule since it takes the electron correlations into consideration and requires relatively few computational resources in comparison with other high level quantum chemical calculation methods (Chandra and Uchimaru, 2000). To our knowledge, the present work is the first study on the application of virtual combinatorial chemistry and a cost-efficient quantum chemical calculation scenario in understanding the environmental degradation of SCCPs.

1. Computational methods

The virtual library of C₁₀-SCCPs was generated from a set of *n*-decane core scaffolds having 22 attachment points, and each was replaced by a chlorine substituent group through the halogenation reaction of *n*-alkanes, resulting in a total of

104,976 compounds using the Legion module in the SYBYL-X 1.2 software package from Tripos, Inc. Co. (SYBYL-X, version 1.2; Tripos International: St. Louis, MO, 2010). A brief flow chart is shown in Appendix A Fig. S1. After removing the reduplicative compounds from the library by the Ligand Structure Preparation function and deleting *n*-decane and the structures with a C₁₀Cl_{14–22} feature, a structural database of 42,720 C₁₀-SCCP congeners without enantiomers was then constructed. Prior to the subsequent calculation procedure, geometry optimizations of C₁₀-SCCP molecules were conducted with the standard Tripos Force Field and conjugate-gradient minimization with an energy change convergence criterion of 0.005 kcal/mol. Atomic charges were computed using the Gasteiger–Hückel charge. Then the optimized geometry was taken as the input structure for the subsequent quantum chemical calculation.

The structure-based rule for the thermodynamic properties and environmental degradability of SCCPs is in many respects much more important than the specific values of the corresponding feature. Clearly, the chlorination pattern, such as chlorination degree and dispersion tendency, plays a key role in the structure-activity relationship of SCCPs. In view of the number of C₁₀-congeners, semi-empirical methods of quantum mechanics were chosen to further optimize the geometries and acquire the overall profile of the molecules since the consideration of cost-efficiency changes from important to crucial when the size of a virtual library dramatically increases. In order to find an acceptable method to obtain the influence of the chlorination pattern on the thermodynamic parameters and related environmental degradability of C₁₀-SCCPs, we have compared three widely used semi-empirical methods, AM1, PM3 and PM6, for their performance in the calculation of the heats of formation ($\Delta_f H^\theta$) for typical chlorinated alkanes at 298.15 K. Four CPs including *n*-C₅H₁₁Cl, *n*-C₆H₁₃Cl, *n*-C₈H₁₇Cl and *n*-C₁₂H₂₅Cl were template molecules. The calculated and experimental values of $\Delta_f H^\theta$ are listed in Table 1, from which one can see that the discrepancies between the calculated values from AM1 and experimental ones are all less than 5.00 kJ/mol. The arithmetic means of absolute deviations between the experimental values and the calculated data are 3.0, 45.0 and 17.8 kJ/mol for AM1, PM3 and PM6, individually. Here the AM1 technique obviously outperformed the others, and was employed for geometry optimization and energy calculations for all C₁₀-congeners with the Gaussian 09 program package (Frisch et al., 2009). The computation was converged upon a true energy minimum, which was supported by the absence of imaginary frequencies.

Table 1 – Comparison between experimental and calculated $\Delta_f H^\theta$ values of 4 model molecules.

$\Delta_f H^\theta$ (kJ/mol)	<i>n</i> -C ₅ H ₁₁ Cl	<i>n</i> -C ₆ H ₁₃ Cl	<i>n</i> -C ₈ H ₁₇ Cl	<i>n</i> -C ₁₂ H ₂₅ Cl
Experiment	–174.9 ^a	–204.3 ^a	–238.9 ^a	–321.1 ^a
AM1	–179.3	–199.3	–240.9	–321.8
D-value ^b	4.4	–5.0	2.0	0.7
PM3	–133.8	–153.8	–195.3	–276.2
D-value ^b	–41.1	–50.5	–43.6	–44.9
PM6	–161.1	–180.9	–222.5	–303.4
D-value ^b	–13.8	–23.3	–16.4	–17.7

^a Data obtained from: John A. D, 1998.

^b The absolute derivation between experimental and calculated values of $\Delta_f H^\theta$.

In this study, the molecular thermodynamic properties (entropy (S^θ), heat capacity at constant volume (C_v^θ), enthalpy (H^θ), Gibbs free energy (G^θ), Gibbs energy of formation ($\Delta_f G^\theta$) and enthalpy of formation ($\Delta_f H^\theta$) were in the ideal gas state at 298.15 K and 101.325 kPa. The standard molar heat capacity at constant volume (C_v^θ), standard state entropy (S^θ), as well as the absolute enthalpy (H^θ) and Gibbs free energy (G^θ), were obtained directly from the calculations (Gaussian's output file). Moreover, the isodesmic reaction illustrated in Eq. (1) has been designed to calculate the standard enthalpy of formation ($\Delta_f H^\theta$) and standard Gibbs energy of formation ($\Delta_f G^\theta$) of the molecules because no relevant experimental data is available. A similar isodesmic reaction was used to calculate the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of C₈H₁₈, and obtained results consistent with the corresponding experimental data (Pollack et al., 2005). Therefore, comparatively accurate thermodynamic estimates are expected for C₁₀-SCCPs. The standard enthalpy change of the reaction ($\Delta_r H^\theta$) is equal to the sum of the standard enthalpies of the products minus the sum of the standard enthalpies of reactants, while the sum of the standard enthalpies of formation ($\Delta_f H^\theta$) of the products minus that of the reactants also yields $\Delta_r H^\theta$. Thus, we can get $\Delta_f H^\theta$ of C₁₀-SCCPs from Eq. (2). The calculation of the $\Delta_f G^\theta$ values of C₁₀-SCCPs can also be accomplished in the same way from Eq. (3). The experimental values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for decane, trichloromethane, and tetrachloromethane are listed in Table 2, while the calculated values of H^θ and G^θ for the same compounds are also provided. Since *n*-decane is liquid at room temperature, the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for decane in the ideal gas state were calculated based on the state change reaction as Eq. (4). $\Delta_r G^\theta$ of the reaction is equal to $\Delta_f G^\theta$ of gaseous decane minus that of liquid decane. The estimated $\Delta_f G^\theta$ of gaseous decane was then obtained through Eq. (5). In addition, frontier molecular orbital analysis was carried out to acquire the energies of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}).

$$\Delta_f H^\theta_{\text{SCCPs}} = H^\theta_{\text{SCCPs}} + H^\theta_{\text{trichloromethane}} - H^\theta_{\text{decane}} - H^\theta_{\text{tetrachloromethane}} - \Delta_f H^\theta_{\text{trichloromethane}} + \Delta_f H^\theta_{\text{decane}} + \Delta_f H^\theta_{\text{tetrachloromethane}} \quad (2)$$

$$\Delta_f G^\theta_{\text{SCCPs}} = G^\theta_{\text{SCCPs}} + G^\theta_{\text{trichloromethane}} - G^\theta_{\text{decane}} - G^\theta_{\text{tetrachloromethane}} - \Delta_f G^\theta_{\text{trichloromethane}} + \Delta_f G^\theta_{\text{decane}} + \Delta_f G^\theta_{\text{tetrachloromethane}} \quad (3)$$

Table 2 – Experimental and calculated data of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for *n*-C₁₀H₂₂, CCl₄, and CHCl₃.

Compound	$\Delta_f H^\theta$ (kJ/mol)	$\Delta_f G^\theta$ (kJ/mol)	H^θ (hartree)	G^θ (hartree)
<i>n</i> -C ₁₀ H ₂₂	–249.7 ^a	32.9 ^c	0.204111 ^d	0.145804 ^d
CCl ₄	–95.7 ^a	–53.6 ^a	–0.028093 ^d	–0.062715 ^d
CHCl ₃	–102.7 ^a	–70.4 ^b	–0.021336 ^d	–0.054556 ^d

^a Data obtained from: John, 1998.

^b Data retrieved from: Kotz and Treichel, 2006.

^c Data predicted from Eqs. (4) and (5).

^d Data obtained from calculation at AM1 level.

$$\begin{aligned}\Delta_f G^\theta_{\text{gas-decane}} &= \Delta_r H^\theta - T \Delta_r S^\theta = (\Delta_f H^\theta_{\text{gas-decane}} - \Delta_f H^\theta_{\text{liquid-decane}}) \\ &\quad - 298.15 \times (S^\theta_{\text{gas-decane}} - S^\theta_{\text{liquid-decane}}) \\ &\quad + \Delta_f G^\theta_{\text{liquid-decane}}\end{aligned}\quad (5)$$

As mentioned above, both chlorination degree and dispersion tendency of chlorine atoms control the thermodynamic properties and stability of C_{10} -SCCPs. We can easily use N_{Cl} to describe the chlorination degree of a specific SCCP molecule, while there is no descriptor available to effectively denote the relative dispersion of chlorine atoms in a SCCP molecule. We then defined a structural descriptor, μ , as the standard deviation of the position codes of all chlorine atoms in a molecule to symbolize the chlorine dispersion degree in SCCPs (Eq. (6)). The position codes of chlorine atoms were assigned according to IUPAC nomenclature. Take 1,6-dichlorodecane as an example: the chlorination position codes for the 2 chlorine atoms are 1 and 6, respectively, and the calculated μ is 3.54. Finally, the validity of the general structure-based tendency obtained by AM1 calculation was checked by comparing it with limited experimental data or by first-principle calculations at higher level. A DFT method with the Becke-3-Lee-Yang-Parr (B3LYP) hybrid functional and the 6-311++G(d, p) basis set was adopted to verify the structure-based rule obtained though AM1 calculation since electron correlation is very important for the electronic structure and stability of chlorinated chemicals.

$$\mu = \sqrt{\frac{\sum (N_i - \bar{N})^2}{(N_{\text{Cl}} - 1)}} \quad (6)$$

where, N_i is chlorination position code based on carbon skeleton; $\bar{N}$ is the arithmetic mean of the chlorination position codes in a molecule.

The QSPR models were developed by multiple linear regression analysis, and a freely available R package from the Comprehensive R Archive Network (<http://CRAN.R-project.org>) was used to calculate the squared correlation coefficient of leave-one-out cross validation (Q^2_{LOO}) (Xie et al., 2014).

2. Results and discussion

2.1. Effect of chlorination degree on thermodynamic properties of C_{10} -SCCPs

The relationship between calculated thermodynamic properties and N_{Cl} of C_{10} -SCCP congeners is illustrated in Fig. 1. The values of C^θ_v varied from 0.209 to 0.394 kJ/(mol·K) and a significant linear correlation was found between C^θ_v and N_{Cl} , with a large adjusted squared regression coefficient R^2_{adj} (0.988) and a small root mean standard deviation ($\text{SD} = 3.42 \times 10^{-3}$). Similarly, a linear increase in S^θ values with N_{Cl} can also be observed for C_{10} -SCCP congeners with large R^2_{adj} (0.904). The maximum differences for the congeners with the same N_{Cl} are 0.022 and 0.105 kJ/(mol·K) for C^θ_v and S^θ , respectively. Clearly, the chlorination characteristics other than N_{Cl} exerted more influence on S^θ than C^θ_v . As for H^θ and G^θ , it seemed that the other chlorination feature became much more important, and negative linear correlations with N_{Cl} were obtained with relatively small R^2_{adj} of 0.600 and 0.672 respectively. Specifically,

the ranges of H^θ and G^θ were 93.297–490.044 and –149.919–329.954 kJ/mol, separately, while the maximum differences for the congeners of same N_{Cl} reached 266.848 and 293.639 kJ/mol, individually. Obviously, the chlorination characteristics other than N_{Cl} cannot be neglected in understanding the structural basis of H^θ and G^θ . The calculated values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ also presented large variances among different isomers. The maximum values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ were –228.359 and 109.235 kJ/mol for separately, while the minimum $\Delta_f H^\theta$ and $\Delta_f G^\theta$ values were only –398.925 and –75.834 kJ/mol for the isomers when $N_{\text{Cl}} = 7$. Being different from other thermodynamic parameters, both calculated $\Delta_f H^\theta$ and $\Delta_f G^\theta$ data exhibited a parabolic relationship with N_{Cl} , with the congeners possessing around 5–7 chlorine atoms locating around the vertex. The reason might be that the decrease of electronic energy was greater than the increase of nuclear repulsive energy when N_{Cl} increased from 5–7, whereas the nuclear repulsive energy overcame the electronic energy when N_{Cl} reached a certain value and continued to increase (Kollman, 1974). Moreover, in order to highlight the effect of chlorination degree, the arithmetic means of thermodynamic parameters with the same N_{Cl} were used to reduce the effect of isomerization. The best fitting models showed good linear correlations between N_{Cl} and C^θ_v , S^θ , $\bar{H}^\theta$ and $\bar{G}^\theta$ ($R^2_{\text{adj}} > 0.960$). When N_{Cl} increased by 1, the increases in the values of C^θ_v and S^θ were 1.42×10^{-2} and 2.15×10^{-2} kJ/(mol·K), individually. At the same time, the decreases of $\bar{H}^\theta$ and $\bar{G}^\theta$ were 26.67 and 33.07 kJ/mol, respectively. However, the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ had parabolic relationships with N_{Cl} ($R^2_{\text{adj}} > 0.990$). This indicates that the substituted chlorine atom number significantly affected the stability of the congeners. The lower stability of the C_{10} -SCCPs with high chlorination degree certainly results from repulsive force between the chlorine atoms.

Considering the limitation of the AM1 method, the $\Delta_f G^\theta$ values of 65 selected C_{10} -SCCPs (1-chlorodecane, 2-chlorodecane, 3-chlorodecane, 4-chlorodecane, 5-chlorodecane, 1,10-dichlorodecane, 1,8-dichlorodecane, 2,6-dichlorodecane, 2,4-dichlorodecane, 5,5-dichlorodecane, 1,5,10-trichlorodecane, 3,4,8-trichlorodecane, 1,2,8-trichlorodecane, 3,6,6-trichlorodecane, 5,5,6-trichlorodecane, 1,3,6,10-tetrachlorodecane, 4,4,7,7-tetrachlorodecane, 2,4,4,8-tetrachlorodecane, 1,1,3,8-tetrachlorodecane, 4,4,6,6-tetrachlorodecane, 1,2,5,8,10-pentachlorodecane, 2,3,4,6,8-pentachlorodecane, 1,1,4,7,8-pentachlorodecane, 2,4,4,6,6-pentachlorodecane, 4,4,5,6,6-pentachlorodecane, 2,3,4,6,7,8-hexachlorodecane, 1,1,4,7,10,10-hexachlorodecane, 3,3,5,5,6,7-hexachlorodecane, 4,4,5,5,6,6-hexachlorodecane, 1,1,1,4,5,9-hexachlorodecane, 1,1,3,5,8,10,10-heptachlorodecane, 3,3,4,5,6,7,7-heptachlorodecane, 1,1,2,2,3,3,8-heptachlorodecane, 1,4,4,5,5,9,10-heptachlorodecane, 4,4,5,5,6,6,7-heptachlorodecane, 1,1,2,4,5,8,10,10-octachlorodecane, 2,2,3,4,6,6,8,8-octachlorodecane, 3,4,4,5,6,7,7,8-octachlorodecane, 1,2,3,4,8,8,9,9-octachlorodecane, 4,4,5,5,6,6,7,7-octachlorodecane, 1,1,2,4,5,7,8,10,10-nonachlorodecane, 1,2,2,4,4,5,6,9,10-nonachlorodecane, 2,3,3,4,4,5,7,9,9-nonachlorodecane, 2,3,4,5,5,6,6,7,8-nonachlorodecane, 3,4,4,5,5,6,6,7,7-nonachlorodecane, 1,2,2,3,6,6,7,8,9,9-decachlorodecane, 1,1,2,3,4,5,6,9,10,10-decachlorodecane, 3,3,4,4,5,5,6,7,7,9-decachlorodecane, 3,3,4,4,5,5,6,6,7,7-decachlorodecane, 1,1,1,2,3,3,4,4,5,9-decachlorodecane, 1,1,2,3,4,5,6,7,9,10,10-undechlorodecane, 1,1,3,3,5,5,7,7,8,8,10-undechlorodecane, 2,2,3,3,4,4,5,6,7,7,8-undechlorodecane, 3,3,4,4,5,5,6,6,7,7,8-undechlorodecane, 1,1,1,2,2,3,3,4,4,7,9-undechlorodecane, 2,2,3,4,5,5,6,6,7,7,8,8-dodecachlorodecane, 3,

Fig. 1 – Relationship between thermodynamic properties and N_{Cl} : blue lines represent overall fitting models while dotted lines in purple represent the models of arithmetic means of thermodynamic parameters with the same N_{Cl} .

3,4,4,5,5,6,6,7,7,8,8-dodechlorodecane, 1,1,1,3,4,5,6,7,8,9,10,10-dodechlorodecane, 1,1,1,3,4,4,5,6,6,7,8,8-dodechlorodecane, 1,1,1,2,2,4,4,5,6,8,9,9-dodechlorodecane, 1,1,2,2,3,3,4,6,7,7,8,9,10-tridechlorodecane, 2,3,3,4,4,5,5,6,6,7,8,9,9-tridechlorodecane, 2,3,3,4,4,5,5,6,6,7,7,8,8-tridechlorodecane, 1,1,1,3,3,4,4,5,5,6,7,7,10-tridechlorodecane, 1,1,1,2,4,4,5,7,7,9,10,10,10-tridechlorodecane) were calculated at B3LYP/6-311++G(d, p). Fig. 2 illustrates the comparison between the calculated values from the two methods. Clearly, the DFT values of $\Delta_r G^0$ were smaller than those from AM1 calculation for corresponding SCCPs, which

means that AM1 underestimated the stability of SCCPs. Moreover, the differences between DFT and AM1 values became larger with increasing N_{Cl} . However, the thermodynamic property $\Delta_r G^0$ obtained from both AM1 and DFT techniques shared the same structure-based tendency. Statistical analysis showed that the N_{Cl} -effect model of the calculated $\Delta_r G^0$ from the DFT method also followed a parabolic function with minimum value at $N_{Cl} = 7$. Moreover, the two curves in Fig. 2 possessed quite similar features, so we may shift the parabola from DFT calculation horizontally and vertically to approach the other from AM1. If the

Fig. 2 – $\Delta_f G^\theta$ values obtained by the two calculation methods and the fitting models for arithmetic means of $\Delta_f G^\theta$ with the same N_{Cl} .

parabola of $\overline{\Delta_f G^\theta} = 2.37(N_{Cl}-6.74)^2 - 104.77$ is shifted 1.55 units left and 91.76 kJ/mol units up, the transformed equation would be $\Delta_f G^\theta = 2.37(N_{Cl}-6.74+1.55)^2 - 104.768 + 91.76$, rather similar to the AM1 model of $\Delta_f G^\theta = 1.52(N_{Cl}-5.19)^2 - 13.01$. Therefore, the change tendencies of $\Delta_f G^\theta$ are consistent with each other, although the absolute values of $\Delta_f G^\theta$ calculated using different methods are different. This confirms the validity of the structural-based characteristics of thermodynamic properties obtained by the semi-empirical method. In brief, the thermodynamic properties of C_{10} -SCCP congeners are sensitive to changes in chlorination degree, and calculated parameters other than $\Delta_f H^\theta$ and $\Delta_f G^\theta$ are linearly correlated with N_{Cl} . The rules for $\Delta_f H^\theta$ vs N_{Cl} and $\Delta_f G^\theta$ vs N_{Cl} are quadratic parabolas. Generally, the congeners with low free energy are more stable than those with higher free energy. Based on the magnitude of the relative free energy, with 100% defined as the lowest $\Delta_f G^\theta$ value of -75.834 kJ/mol, the relative stability for C_{10} -SCCPs was then theoretically determined and symbolized in terms of percentage $\Delta_f G^\theta_r$. Apparently, the most theoretically stable congeners are those with 5 to 9 substituted chlorine atoms, as found at high concentration in all environmental samples ever reported. In fact, the C_{10} -SCCP congeners with 5–10 substituted chlorine atoms appeared in most environmental samples. Considering the matrix interference and vulnerability of monitoring data to the mismatch between the SCCPs' patterns in the calibration standard and in the sample (Bogdal et al., 2015), the present N_{Cl} -dependent pollution profile of C_{10} -SCCPs is basically consistent with the predicted order of formation stability of C_{10} -SCCP congeners (Appendix A Fig. S2). Specifically, $C_{10}Cl_{6-8}$ congeners were the prevailing ones in water samples (Lu, 2013; Yuan et al., 2012; Zeng et al., 2011b, 2012a, 2012b), while those with 5–7 chlorine atoms were dominant in air samples (Chaemfa et al., 2014; Fridén et al., 2011; Li et al., 2012; Wang et al., 2012, 2013b, 2015). As for sediment and soil samples, the most abundant congeners possessed 5–10 chlorine atoms (Chen et al., 2011; Gao et al., 2012; Hüttig and Oehme, 2006; Iino et al., 2005; Iozza et al., 2008; Marvin et al., 2003; Štejnárova et al., 2005; Tomy et al., 1999; Wang et al., 2013b, 2013c; Zeng et al., 2011a, 2012c, 2013), quite similar to those in food, human milk and wildlife samples (Harada et al., 2011; Thomas et al., 2006; Zeng et al., 2011b). Regardless of the method limitation in

analyzing C_{10} -congeners with 1–4 chlorine atoms (Moore et al., 2004; Reth et al., 2005), the low stability of C_{10} -congeners with 1–4 and 12–13 chlorine atoms was verified by the experimental data, indicating the instability and higher biodegradability of C_{10} -congeners with low or high chlorination degree in the aerobic or aerobic environment, respectively (Allpress and Gowland, 1999; Chen et al., 2011; Fisk et al., 1998; Omori et al., 1987).

2.2. Effect of chlorination dispersion on thermodynamic properties of C_{10} -SCCPs

There are 30, 106, 324, 771, 1597, 2788, 4307, 5785, 6944, 7334, 6944, and 5785 isomers with 2 to 13 chlorine atoms in one C_{10} -SCCP molecule, individually. Chlorination dispersion tendency is another chlorination pattern feature controlling the properties of C_{10} -SCCPs. The novel descriptor μ was used here to explore the chlorination dispersion effect on the thermodynamic properties of C_{10} -SCCPs (Table 3). Naturally, the dominant control of C^θ_v under N_{Cl} resulted in low R^2_{adj} of less than 0.5 for its correlation with μ . However, a positive correlation with μ was found for standard molar entropy S^θ , while the negative linear correlations between μ and other thermodynamic properties including H^θ , G^θ , $\Delta_f H^\theta$ and $\Delta_f G^\theta$ were statistically significant, with $R^2_{adj} > 0.6$ for the isomers with N_{Cl} of 4 to 13, and the values of R^2_{adj} increased with increasing N_{Cl} . The relative position of Cl in the isomers highly influenced the above thermodynamic properties for C_{10} -SCCPs with N_{Cl} over 6. It has been widely accepted that C–H groups can act as weak hydrogen donors and that the hydrogen atom in halogenated ethane may act as a Lewis acid or proton donor (Guy, 2008; Thomas and Gautam, 1998). Moreover, halogen atoms have been generally considered as weak proton acceptors, and the recent study has demonstrated that chlorine atoms in perhalogenated ethane establish strong attractive intramolecular *van der Waals* interactions (Johansson and Swart, 2013). Therefore, higher chlorination degree leads to more diverse chlorine dispersion patterns related with different profiles of weak hydrogen bonds as intramolecular $H\cdots Cl$ contacts, as well as possible *van der Waals* interactions of $Cl\cdots Cl$ contacts. The C_{10} -SCCP isomers with more intramolecular attractive interactions are more stable than the others with less intramolecular stabilization factors. On the contrary, the steric repulsion among chlorine atoms, which counterbalances the above intramolecular stabilization interactions, also increases with N_{Cl} . Clearly, the larger N_{Cl} is, the higher the influence of chlorine dispersion pattern on the establishment of various intramolecular interactions becomes. Thus, the linear relationship between μ and $\Delta_f G^\theta$ or $\Delta_f G^\theta_r$ becomes much more statistically significant when N_{Cl} keeps increasing. Moreover, the relative Gibbs free energy of formation $\Delta_f G^\theta_r$ was employed to rank the relative stability of the isomers and obtained through deducting the lowest $\Delta_f G^\theta$ of the isomers with same N_{Cl} from their absolute $\Delta_f G^\theta$ values. Fig. 3 illustrates the linear relationship between the relative stability of isomers and μ . It is clear that the isomers with $\mu = 0$ exhibit lowest stability because of the enormous steric effect of chlorine atoms located on the same carbon atom. The isomers with $0 < \mu < 1$ having Cl on adjacent carbons are more stable than those with $\mu = 0$, while the isomers with $\mu > 1$ having Cl on more separated carbons present highest stability. Establishment of more intramolecular $H\cdots Cl$ attractive

Table 3 – The linear relationship between μ and thermodynamic properties as $Y = (a \pm SE_a) \mu + (b \pm SE_b)$.

	N _{Cl}	b	SE _b	a	SE _a	R ² _{adj}	Min	Max	SD	F	p
C ⁰ _v	2	2.26E-01	4.39E-04	−6.52E-04	1.53E-04	0.37	0.220	0.228	1.51E-03	18	2.05E-04
	3	2.41E-01	4.37E-04	−1.18E-03	1.57E-04	0.35	0.233	0.242	1.97E-03	57	1.83E-11
	4	2.57E-01	3.62E-04	−1.84E-03	1.27E-04	0.39	0.246	0.259	2.23E-03	210	6.03E-37
	5	2.73E-01	2.99E-04	−2.44E-03	1.04E-04	0.42	0.259	0.273	2.33E-03	553	1.42E-92
	6	2.89E-01	2.54E-04	−3.08E-03	8.70E-05	0.44	0.273	0.289	2.46E-03	1252	6.81E-203
	7	3.05E-01	2.26E-04	−3.68E-03	7.63E-05	0.45	0.286	0.303	2.52E-03	2324	<6.81E-203
	8	3.21E-01	2.09E-04	−4.20E-03	6.96E-05	0.46	0.300	0.319	2.58E-03	3639	<6.81E-203
	9	3.36E-01	2.04E-04	−4.66E-03	6.74E-05	0.45	0.314	0.333	2.61E-03	4786	<6.81E-203
	10	3.52E-01	2.07E-04	−5.06E-03	6.78E-05	0.45	0.328	0.350	2.63E-03	5568	<6.81E-203
	11	3.68E-01	2.22E-04	−5.40E-03	7.22E-05	0.43	0.343	0.364	2.60E-03	5596	<6.81E-203
	12	3.84E-01	2.51E-04	−5.65E-03	8.09E-05	0.41	0.358	0.380	2.57E-03	4886	<6.81E-203
	13	3.99E-01	3.00E-04	−5.85E-03	9.62E-05	0.39	0.374	0.394	2.51E-03	3698	<6.81E-203
S ⁰	2	5.62E-01	1.19E-03	1.28E-03	4.13E-04	0.23	0.558	0.576	4.07E-03	10	0.00449
	3	5.82E-01	1.11E-03	2.72E-03	3.98E-04	0.30	0.579	0.604	5.00E-03	47	5.68E-10
	4	5.99E-01	9.34E-04	5.26E-03	3.28E-04	0.44	0.592	0.647	5.75E-03	258	5.21E-43
	5	6.14E-01	7.74E-04	7.92E-03	2.69E-04	0.53	0.612	0.665	6.04E-03	868	2.50E-128
	6	6.28E-01	6.48E-04	1.07E-02	2.22E-04	0.59	0.626	0.694	6.26E-03	2327	<2.50E-128
	7	6.41E-01	5.94E-04	1.37E-02	2.01E-04	0.63	0.645	0.711	6.63E-03	4683	<2.50E-128
	8	6.51E-01	5.73E-04	1.73E-02	1.91E-04	0.66	0.658	0.744	7.08E-03	8182	<2.50E-128
	9	6.59E-01	5.65E-04	2.10E-02	1.87E-04	0.69	0.673	0.762	7.24E-03	12,617	<2.50E-128
	10	6.66E-01	5.87E-04	2.50E-02	1.92E-04	0.71	0.686	0.779	7.44E-03	16,917	<2.50E-128
	11	6.71E-01	6.39E-04	2.91E-02	2.08E-04	0.73	0.702	0.798	7.49E-03	19,616	<2.50E-128
	12	6.75E-01	7.36E-04	3.35E-02	2.37E-04	0.74	0.714	0.819	7.55E-03	19,881	<2.50E-128
	13	6.78E-01	8.93E-04	3.77E-02	2.86E-04	0.75	0.733	0.836	7.46E-03	17,313	<2.50E-128
H ⁰	2	453.39	1.94	−4.36	0.68	0.58	421.834	464.028	6.67	41	5.76E-07
	3	426.31	1.96	−8.69	0.70	0.59	376.993	430.842	8.84	152	4.88E-8
	4	406.41	1.72	−14.23	0.60	0.63	332.609	416.764	10.57	558	2.97E-72
	5	392.16	1.53	−20.57	0.53	0.66	291.782	402.248	11.92	1507	2.39E-183
	6	383.84	1.41	−27.81	0.48	0.68	253.345	402.970	13.59	3339	<2.39E-183
	7	379.92	1.34	−35.44	0.45	0.69	213.285	383.851	14.90	6167	<2.39E-183
	8	381.19	1.31	−43.74	0.44	0.70	190.493	389.556	16.25	9942	<2.39E-183
	9	387.46	1.35	−52.70	0.45	0.71	166.023	371.036	17.30	13,968	<2.39E-183
	10	399.43	1.43	−62.51	0.47	0.72	147.839	378.545	18.18	17,712	<2.39E-183
	11	417.15	1.59	−73.18	0.52	0.73	122.558	359.812	18.64	20,058	<2.39E-183
	12	440.79	1.84	−84.74	0.59	0.75	100.982	367.830	18.91	20,338	<2.39E-183
	13	470.32	2.22	−97.16	0.71	0.76	93.297	346.471	18.60	18,564	<2.39E-183
G ⁰	2	286.07	2.23	−4.75	0.78	0.56	250.045	297.784	7.66	37	1.35E-06
	3	252.79	2.20	−9.50	0.79	0.58	198.199	257.947	9.92	145	2.09E-21
	4	227.85	1.90	−15.80	0.67	0.63	146.881	240.233	11.71	560	1.86E-72
	5	209.05	1.69	−22.94	0.59	0.67	98.808	219.943	13.16	1535	2.07E-185
	6	196.59	1.54	−31.00	0.53	0.68	52.394	212.576	14.87	3470	<2.07E-185
	7	188.95	1.45	−39.53	0.49	0.70	6.524	191.593	16.23	6467	<2.07E-185
	8	187.25	1.43	−48.90	0.48	0.71	−23.118	193.539	17.67	10,510	<2.07E-185
	9	190.96	1.46	−58.95	0.48	0.72	−52.728	170.329	18.75	14,879	<2.07E-185
	10	200.99	1.55	−69.96	0.51	0.73	−80.214	174.097	19.67	18,962	<2.07E-185
	11	217.11	1.72	−81.85	0.56	0.75	−111.269	150.709	20.11	21,546	<2.07E-185
	12	239.65	1.99	−94.70	0.64	0.76	−138.619	155.020	20.37	21,893	<2.07E-185
	13	268.26	2.39	−108.38	0.77	0.78	−149.919	126.867	20.00	19,976	<2.07E-185
$\Delta_f H^0$	2	−282.52	1.94	−4.35	0.68	0.58	−314.079	−271.884	6.67	41	5.77E-07
	3	−284.86	1.96	−8.69	0.70	0.59	−334.179	−280.330	8.84	153	4.11E-22
	4	−280.02	1.72	−14.23	0.60	0.63	−353.823	−269.667	10.57	558	2.93E-72
	5	−269.53	1.53	−20.57	0.53	0.66	369.909	−259.443	11.92	1507	2.37E-183
	6	−253.11	1.41	−27.81	0.48	0.68	−383.605	−233.981	13.59	3339	<2.37E-183
	7	−232.29	1.34	−35.44	0.45	0.69	−398.925	−228.359	14.90	6167	<2.37E-183
	8	−206.28	1.31	−43.74	0.44	0.70	−396.976	−197.913	16.25	9942	<2.37E-183
	9	−175.28	1.35	−52.70	0.45	0.71	−396.705	−191.693	17.30	13,968	<2.37E-183
	10	−138.56	1.43	−62.51	0.47	0.72	−390.149	−159.444	18.18	17,711	<2.37E-183
	11	−96.1	1.59	−73.18	0.52	0.73	−390.690	−153.436	18.64	20,058	<2.37E-183
	12	−47.74	1.84	−84.73	0.59	0.75	−387.525	−120.677	18.91	20,336	<2.37E-183
	13	6.56	2.22	−97.16	0.71	0.76	−370.470	−117.295	18.60	18,565	<2.37E-183
$\Delta_f G^0$	2	12.61	2.23	−4.75	0.78	0.56	−23.421	24.319	7.66	37	1.35E-06
	3	17.55	2.20	−9.50	0.79	0.58	−37.045	22.703	9.92	145	2.09E-21
	4	30.83	1.90	−15.8	0.67	0.63	−50.142	43.211	11.71	560	1.86E-72
	5	50.25	1.69	−22.94	0.59	0.67	−59.993	61.142	13.16	1535	2.07E-185
$\Delta_f G^0$	6	76.01	1.54	−31.00	0.53	0.68	−68.185	91.997	14.86	3470	<2.07E-185

Table 3 (continued)

N_{Cl}	b	SE_b	a	SE_a	R^2_{adj}	Min	Max	SD	F	p
7	106.59	1.45	−39.53	0.49	0.70	−75.834	109.235	16.23	6467	<2.07E-185
8	143.12	1.43	−48.90	0.48	0.71	−67.254	149.402	17.67	10,510	<2.07E-185
9	185.04	1.46	−58.95	0.48	0.72	−58.643	164.414	18.75	14,879	<2.07E-185
10	233.3	1.55	−69.96	0.51	0.73	−47.908	206.403	19.67	18,962	<2.07E-185
11	287.63	1.72	−81.85	0.56	0.75	−40.741	221.23	20.11	21,546	<2.07E-185
12	348.4	1.99	−94.70	0.64	0.76	−29.869	263.769	20.37	21,893	<2.07E-185
13	415.23	2.39	−108.38	0.77	0.78	−2.948	273.837	20.00	19,976	<2.07E-185

interactions and less Cl⋯Cl repulsion contact in the isomers with large μ supports such findings (Grant Hill and Legon, 2015). The linear correlation between $\Delta_f G_R^\theta$ and μ is also verified by DFT calculation using 16 isomers with $N_{Cl} = 9$ (Appendix A Fig. S3). We then tried to obtain the quantitative structure–property

relationship (QSPR) model for $\Delta_f G^\theta$ with N_{Cl} and μ as two descriptors of chlorination pattern. Surprisingly, the obtained model of Eq. (7) has both large R^2 (0.764) and the squared correlation coefficient of leave-one-out cross validation ($Q^2_{LOO} = 0.764$), even when the effect of chlorination position is

Fig. 3 – Relationship between $\Delta_f G_R^\theta$ and μ .

excluded. Successful QSPR models can also be constructed for other thermodynamic properties using N_{Cl} and μ (Eqs. (8)–(12)).

$$\Delta_f G^\theta = (1.235 \pm 0.369)N_{Cl}^2 + (-8.128 \pm 0.369)N_{Cl} + (-60.148 \pm 0.225)\mu + (161.878 \pm 1.775) \quad (7)$$

$$n = 42, 720, SD = 22.95, R^2 = 0.764, F = 46, 131, p < 0.01,$$

$$Q^2_{LOO} = 0.764, RMSE = 22.95$$

$$C^\theta_V = (1.46 \times 10^{-2} \pm 5.99 \times 10^{-6})N_{Cl} + (-4.43 \times 10^{-3} \pm 2.58 \times 10^{-5})\mu + (2.04 \times 10^{-1} \pm 9.06 \times 10^{-5}) \quad (8)$$

$$n = 42, 720, SD = 2.63 \times 10^{-3}, R^2 = 0.992, F = 3, 020, 990, p < 0.01,$$

$$Q^2_{LOO} = 0.992, RMSE = 2.63 \times 10^{-3}$$

$$S^\theta = (1.86 \times 10^{-2} \pm 1.99 \times 10^{-5})N_{Cl} + (2.14 \times 10^{-2} \pm 8.59 \times 10^{-5})\mu + (4.89 \times 10^{-1} \pm 3.01 \times 10^{-4}) \quad (9)$$

$$n = 42, 720, SD = 8.75 \times 10^{-3}, R^2 = 0.960, F = 525, 660, p < 0.01,$$

$$Q^2_{LOO} = 0.960, RMSE = 8.75 \times 10^{-3}$$

$$H^\theta = (-17.50 \pm 5.01 \times 10^{-2})N_{Cl} + (-54.49 \pm 2.16 \times 10^{-1})\mu + (556.06 \pm 7.58 \times 10^{-1}) \quad (10)$$

$$n = 42, 720, SD = 22.00, R^2 = 0.839, F = 111, 476, p < 0.01,$$

$$Q^2_{LOO} = 0.839, RMSE = 22.00$$

$$G^\theta = (-23.06 \pm 5.46 \times 10^{-2})N_{Cl} + (-60.87 \pm 2.36 \times 10^{-1})\mu + (410.42 \pm 8.27 \times 10^{-1}) \quad (11)$$

$$n = 42, 720, SD = 24.01, R^2 = 0.872, F = 145, 590, p < 0.01,$$

$$Q^2_{LOO} = 0.872, RMSE = 24.01$$

$$\Delta_f H^\theta = (1.145 \pm 0.018)N_{Cl}^2 + (-14.346 \pm 0.338)N_{Cl} + (-53.826 \pm 0.206)\mu + (-135.392 \pm 1.625) \quad (12)$$

$$n = 42, 720, SD = 21.01, R^2 = 0.667, F = 28, 525, p < 0.01, Q^2_{LOO} = 0.667, RMSE = 21.01$$

2.3. Effect of chlorination pattern on environmental degradability of C_{10} -SCCPs

The calculated $\Delta_f G^\theta$ implies a significant chlorination pattern-effect for the relative stability of C_{10} -SCCPs. In fact, experimental studies have revealed the distinct degradability and diverse toxicity of the individual CPs (Damborský et al., 2001; Tomy and Fisk, 1998). The effect of chlorination pattern on the environmental degradability of C_{10} -SCCPs was further analyzed by evaluating its influence on direct photolysis, oxidation by hydroxyl radical as well as other transformation processes of C_{10} -SCCPs involving nucleophilic substitution reactions. Frontier molecular orbitals have been employed to depict the reactivity of pollutants extensively, among which the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play a fundamental role in the characterization of the nucleophilicity and electrophilicity of a molecule, respectively (Lee et al., 2003). In general, E_{HOMO} directly correlates with the susceptibility of a molecule toward the attack by electrophilic substances, while the nucleophilic substitution reactions easily occur for the molecules with low E_{LUMO} . In addition, the HOMO–LUMO gap, $E_{LUMO}-E_{HOMO}$, is also a stability indicator of a molecule. The larger the gap is, the greater the stability of the molecule becomes. Therefore, the relationships between the chlorination

pattern and the calculated values of E_{LUMO} and $E_{LUMO}-E_{HOMO}$ of C_{10} -SCCPs were obtained using N_{Cl} and μ as pattern descriptors and listed in Eqs. (13)–(14). Obviously, both parameters exhibit linear correlation with μ and N_{Cl} , and the obtained models of Eqs. (13)–(14) had similar values for R^2 (0.605 and 0.623) and Q^2_{LOO} (0.605 and 0.623). Specifically, the minimum value of $E_{LUMO}-E_{HOMO}$ is 9.96 eV, and the direct photolysis is rather difficult for C_{10} -SCCP congeners due to the first law of photochemistry. According to the equation $E_{LUMO}-E_{HOMO} = h\nu = hc/\lambda$, only photons of $\lambda < 125$ nm can be absorbed by the C_{10} -SCCP molecules to accomplish electron transition from HOMO to LUMO. However, the minimum wavelength for sunlight near the earth surface is 295 nm (Harfoot et al., 2007). Therefore, the C_{10} -SCCP congeners cannot readily undergo direct photolysis in the near-surface air and aqueous environment. As for the C_{10} -SCCPs in the upper atmosphere, the congeners with more substituted chlorine atoms possess more susceptibility to photolysis since $E_{LUMO}-E_{HOMO}$ declines gradually with increasing N_{Cl} . Moreover, the dispersion trend of chlorine atoms is a favorable factor for the photo-stability of the C_{10} -SCCP isomers with the same N_{Cl} . Sixty-five C_{10} -SCCP congeners with $\mu = 0-6.364$ were calculated using the DFT method to verify the effect of the above structural feature on direct photolysis. Fig. 4 illustrates a significant correlation between the $E_{LUMO}-E_{HOMO}$ values obtained from AM1 and DFT calculation ($R^2 = 0.921, p < 0.01$), and smaller gaps were obtained by the DFT method than those from AM1 calculations. Nevertheless, C_{10} -SCCPs are also quite stable in the stratosphere under UV radiation (Smith et al., 2011) since the minimum value for $E_{LUMO}-E_{HOMO}$ and its corresponding wavelength found for the C_{10} -SCCP congeners at DFT level is 5.93 eV and 210 nm, from 1,2,3,3,4,4,5,5,6,6,7,7,8- $C_{10}H_9Cl_{13}$. The study of Friedman and Lombardo verified that CPs cannot absorb UV light (Fredricks and Tedder, 1960).

$$E_{LUMO} = (-0.106 \pm 4.160 \times 10^{-4})N_{Cl} + (0.053 \pm 0.002)\mu + (0.496 \pm 0.006) \quad (13)$$

$$n = 42, 720, SD = 1.830 \times 10^{-1}, R^2 = 0.605, F = 32, 733, p < 0.01,$$

$$Q^2_{LOO} = 0.605, RMSE = 1.830 \times 10^{-1}$$

$$E_{LUMO}-E_{HOMO} = (-0.116 \pm 4.570 \times 10^{-4})N_{Cl} + (0.235 \pm 0.002)\mu + (11.262 \pm 0.007) \quad (14)$$

$$n = 42, 720, SD = 2.010 \times 10^{-1}, R^2 = 0.623, F = 35, 340, p < 0.01,$$

$$Q^2_{LOO} = 0.623, RMSE = 2.010 \times 10^{-1}$$

$$E_{HOMO} = (1.880 \times 10^{-3} \pm 9.212 \times 10^{-5})N_{Cl}^2 + (-2.571 \times 10^{-2} \pm 1.75 \times 10^{-3})N_{Cl} + (-0.181 \pm 0.001)\mu + (-10.611 \pm 0.008) \quad (15)$$

$$n = 42, 720, SD = 1.090 \times 10^{-1}, R^2 = 0.408, F = 9830, p < 0.01,$$

$$Q^2_{LOO} = 0.408, RMSE = 1.090 \times 10^{-1}$$

Moreover, chlorinated alkanes are known to react with various nucleophilic reagents such as OH^- , H_2O and ROH . Not only is chemical hydrolysis of chlorinated alkanes a kind of nucleophilic substitution reaction, but many haloalkane dehalogenases also follow a similar pathway (Janssen, 2004). Eq. (13) shows that more substituted chlorine atoms in a C_{10} -SCCP molecule led to lower E_{LUMO} values and thus higher activity toward nucleophilic substitution. On the contrary, larger μ values implied lower nucleophilic substitution ability, although the

Fig. 4 – Significant correlation between the $E_{\text{LUMO}}-E_{\text{HOMO}}$ values obtained from AM1 and DFT calculation for 65 C_{10} -SCCP congeners (1-chlorodecane, 2-chlorodecane, 3-chlorodecane, 4-chlorodecane, 5-chlorodecane, 1,10-dichlorodecane, 1,8-dichlorodecane, 2,6-dichlorodecane, 2,4-dichlorodecane, 5,5-dichlorodecane, 1,5,10-trichlorodecane, 3,4,8-trichlorodecane, 1,2,8-trichlorodecane, 3,6,6-trichlorodecane, 5,5,6-trichlorodecane, 1,3,6,10-tetrachlorodecane, 4,4,7,7-tetrachlorodecane, 2,4,4,8-tetrachlorodecane, 1,1,3,8-tetrachlorodecane, 4,4,6,6-tetrachlorodecane, 1,2,5,8,10-pentachlorodecane, 2,3,4,6,8-pentachlorodecane, 1,1,4,7,8-pentachlorodecane, 2,4,4,6,6-pentachlorodecane, 4,4,5,6,6-pentachlorodecane, 2,3,4,6,7,8-hexachlorodecane, 1,1,4,7,10,10-hexachlorodecane, 3,3,5,5,6,7-hexachlorodecane, 4,4,5,5,6,6-hexachlorodecane, 1,1,1,4,5,9-hexachlorodecane, 1,1,3,5,8, 10,10-heptachlorodecane, 3,3,4,5,6,7,7-heptachlorodecane, 1,1,2,2,3,3,8-heptachlorodecane, 1,4,4,5,5,9, 10-heptachlorodecane, 4,4,5,5,6,6,7-heptachlorodecane, 1,1,2,4,5,8,10,10-octachlorodecane, 2,2,3,4,6,6, 8,8-octachlorodecane, 3,4,4,5,6,7,7,8-octachlorodecane, 1,2,3,4,8,8,9,9-octachlorodecane, 4,4,5,5,6,6, 7,7-octachlorodecane, 1,1,2,4,5,7,8,10,10-nonachlorodecane, 1,2,2,4,4,5,6,9,10-nonachlorodecane, 2,3,3,4,4,5,7, 9,9-nonachlorodecane, 2,3,4,5,5,6,6,7,8-nonachlorodecane, 3,4,4,5,5,6,6,7,7-nonachlorodecane, 1,2,2,3,6,6,7, 8,9,9-decachlorodecane, 1,1,2,3,4,5,6,9,10,10-decachlorodecane, 3,3,4,4,5,5,6,7,7,9-decachlorodecane, 3,3,4,4,5,5,6,6, 7,7-decachlorodecane, 1,1,1,2,3,3,4,4,5,9-decachlorodecane, 1,1,2,3,4,5,6,7,9,10,10-undechlorodecane, 1,1,3,3,5,5,7,7, 8,8,10-undechlorodecane, 2,2,3,3,4,4,5,6,7, 7,8-undechlorodecane, 3,3,4,4,5,5,6,6,7,7,8-undechlorodecane, 1,1,1,2,2,3,3,4,4,7,9-undechlorodecane, 2,2,3,4,4,5,5,6,6,7,7,8, 8-dodechlorodecane, 3,3,4,4,5,5,6,6,7,7,8,8-dodechlorodecane, 1,1,1,3,4,5,6,7,8,9,10,10-dodechlorodecane, 1,1,1,3,4,4,5,6,6,7,8,8-dodechlorodecane, 1,1,1,2,2,4,4,5,6,8, 9,9-dodechlorodecane, 1,1,2,2,3,3,4,6,7,7,8,9,10-tridechlorodecane, 2,3,3,4,4,5,5,6,6,7,8,9,9-tridechlorodecane, 2,3,3,4,4,5,5,6,6,7,7,8,8-tridechlorodecane, 1,1,1,3,3,4,4,5,5,6,7,7,10-tridechlorodecane, 1,1,1,2,4,4,5,5,7,7,9,10,10,10-tridechlorodecane).

addition of μ to the equation only resulted in limited improvement in the goodness-of-fit of the model. Furthermore, radical reaction is also an important transformation pathway for chlorinated alkanes. Both E_{HOMO} and E_{LUMO} are key indices for radical reactions (Pearson, 1986) and the calculated E_{HOMO} values present a negative linear correlation with μ and a poor parabolic relationship with N_{Cl} . This means that the C_{10} -SCCP congeners with less Cl substitution and lower dispersion degree are susceptible to environmental degradation via direct photolysis, nucleophilic substitution and radical reactions. The effect of chlorination pattern on the degradability is basically consistent with that on thermo-stability symbolized by $\Delta_f G_{\text{R}}^{\circ}$.

In addition, photooxidation mediated by active oxygen species such as hydroxyl radical ($\cdot\text{OH}$), ozone (O_3), and hydrogen peroxide (H_2O_2) may act as the dominant loss process for C_{10} -SCCPs. According to the “frontier electron theory” developed by Parr and Yang (1984), the greatest electron density in the frontier molecular orbitals of C_{10} -SCCP molecules favors the electron transfer from their HOMO or HOMO-1 to the LUMO of O_3 and H_2O_2 or the singly occupied molecular orbital (SOMO) of $\cdot\text{OH}$. The calculated E_{LUMO} of O_3 , H_2O_2 and the SOMO energy (E_{SOMO}) of $\cdot\text{OH}$ at AM1 level were -1.94 , 2.93 and -12.61 eV, respectively, in which the E_{LUMO} values of O_3 and H_2O_2 were much higher than the highest E_{HOMO} values (-10.71 eV) for C_{10} -SCCPs. The oxidation of C_{10} -SCCPs by O_3 or H_2O_2 in vacuum is nearly impossible. However, the reaction between C_{10} -SCCPs and $\cdot\text{OH}$ may occur in the environment, since E_{SOMO} is lower than -10.71 eV. The DFT calculation supported the supposition that oxidation of C_{10} -SCCPs can take place in the presence of $\cdot\text{OH}$ radical, as the calculated E_{LUMO} of O_3 , H_2O_2 and the SOMO energy (E_{SOMO}) of $\cdot\text{OH}$ at DFT level were -5.56 eV, -0.66 eV and -8.96 eV, respectively, while the DFT result for the maximum E_{HOMO} was -7.80 eV. The theoretical half-lives of C_{10} – C_{13} polychlorinated alkanes in the atmosphere, which ranged from 1.2 to 1.8 days, also verified our conclusion (Tomy et al., 1998). In addition, the negative linear correlations between the E_{HOMO} values and μ (Appendix A Fig. S4) imply that the isomers with low Cl dispersion are more vulnerable to attack by hydroxyl radical. According to Atkinson’s $\cdot\text{OH}$ reaction mechanism, chlorinated alkanes prefer H-abstraction pathways to $\cdot\text{OH}$ -addition ones, and the abstraction of Cl atoms exhibits a much higher energy barrier (E_{a}) than H atom abstraction for polychlorinated alkanes (Atkinson, 1985). We here selected two pentachlorodecane isomers, 1,3,6,9,10-pentachlorodecane ($\mu = 4.0$) and 5,5,6,7,7-pentachlorodecane ($\mu = 1.0$), to calculate their reaction pathways via H-abstraction mechanisms using M06 functional with the 6-311 + G(d,p) basis set. Different H reactive sites for 1,3,6,9,10-pentachlorodecane ($-\text{CH}_2\text{Cl}$, $-\text{CH}_2$, $-\text{CHCl}-$) and 5,5,6,7,7-pentachlorodecane ($-\text{CH}_3$, $-\text{CH}_2$, $-\text{CHCl}-$) were considered, and three channels of H-abstraction for the two molecules are shown in Fig. 5 with all the relevant molecular structures illustrated in Fig. 6. Obviously, both kinds of pentachlorodecanes easily incur H-abstraction by $\cdot\text{OH}$. The reaction is a spontaneous process due to its significant exothermicity (>18.7 kcal/mol) and the low energy barriers involved (≤ 3.6 kcal/mol), which is in accordance with a study on the OH-initiated chemical transformation of 1,2,4,6,8,10,11-heptachloroundecane in the atmosphere (Liu et al., 2015). The existence of a chlorine atom near the abstracted H, like those in $-\text{CH}_2$ (channels 2&5) and $-\text{CHCl}-$ (channels 3&6) groups, results

Fig. 5 – Different potential energy surfaces for the reaction of 1,3,6,9,10-pentachlorodecane (left) and 5,5,6,7,7-pentachlorodecane (right) with $\cdot\text{OH}$.

in a higher reaction barrier, which is in accordance with the chlorination dispersion effect on E_{HOMO} . The small R^2 of 0.408 for such effect indicates the importance of chlorination position in addition to N_{Cl} and μ shown in Eq. (15). In fact, the QSPR models for E_{LUMO} , $E_{\text{LUMO}}-E_{\text{HOMO}}$ and E_{HOMO} are obviously inferior to those of thermodynamic properties because the electronic structures and molecular orbital energies are sensitive to the absolute chlorination position of SCCPs. For instance, the $E_{\text{LUMO}}-E_{\text{HOMO}}$ values of 1-chlorodecane, 2-chlorodecane, 3-chlorodecane and 4-chlorodecane are 12.64, 12.52, 12.48 and 12.45 eV at the AM1 level, separately. Using chlorination degree and chlorine dispersion pattern alone cannot fully describe the key structural characteristics influencing E_{LUMO} , $E_{\text{LUMO}}-E_{\text{HOMO}}$ and E_{HOMO} . A similar substituent effect on the frontier molecular orbital energy was reported for pentacene and tetracene derivatives (Kaur et al., 2008; Shen et al., 2014). A recent theoretical study on 9 SCCPs also showed that the chlorine substitution position and steric effect have great influence on the reaction rates of the molecules with $\cdot\text{OH}$, and the conformations with the cis-H-C-C-Cl substructure facilitate the H-abstraction channels through forming six-membered ring transition states by hydrogen bonds of $\text{H}\cdots\text{O}$ or $\text{H}\cdots\text{Cl}$ contacts (Li et al., 2014). According to the calculated reaction barriers of channels 1 and 4 in this study, chlorination on the terminal carbon atoms significantly elevates the reaction barrier for H-abstraction. Moreover, chlorination occurring around the abstracted H in $-\text{CH}_2$ (channels 2&5) and $-\text{CHCl}-$ (channels 3&6) group causes higher activation free energy as well.

3. Conclusions

The inherent mixture nature of SCCPs makes it rather difficult to explore the environmental behavior of individual SCCPs, and the semi-empirical method coupled with DFT verification was adopted to extract the structural features of stability and degradability for the chemicals. A molecule library of 42,720 C_{10} -SCCP congeners covering the full structure spectrum was constructed using the virtual combinatorial chemistry technique. The values of thermodynamic properties such as C_p^θ , S^θ , H^θ , G^θ , $\Delta_f H^\theta$ and $\Delta_f G^\theta$ were calculated using the AM1 method, while frontier molecular orbital analysis was also carried out to obtain the E_{HOMO} , E_{LUMO} and $E_{\text{LUMO}}-E_{\text{HOMO}}$ for degradability

exploration. The influence of the chlorination degree (N_{Cl}) on the relative stability and various environmental degradation processes was elucidated. A novel structural descriptor, μ , was proposed to measure and characterize the dispersion tendency of the chlorine atoms in the SCCP molecules. There were significant correlations between thermodynamic values and N_{Cl} , while the reported N_{Cl} -dependent pollution profile of C_{10} -SCCPs was basically consistent with the predicted order of formation stability of C_{10} -SCCP congeners. In addition, chlorination dispersion plays an important role in the stability of C_{10} -SCCP isomers. Isomers with large μ showed relatively higher stability than those with small μ . This can be further verified by the relationship between μ and the activity toward direct photolysis, nucleophilic substitution and $\cdot\text{OH}$ attack, respectively characterized by $E_{\text{LUMO}}-E_{\text{HOMO}}$, E_{LUMO} and E_{HOMO} . Direct photolysis of C_{10} -SCCP congeners in both the troposphere and stratosphere under UV-Vis radiation cannot readily occur due to the large values for $E_{\text{LUMO}}-E_{\text{HOMO}}$. The C_{10} -SCCP congeners with less Cl substitution and lower dispersion degree are susceptible to environmental degradation via nucleophilic substitution and hydroxyl radical attack. The chlorination effect and the corresponding conclusion were checked with appropriate DFT calculations. The present work provides a successful example of the application of virtual combinatorial chemistry and a high cost-efficiency quantum chemical calculation strategy in understanding the environmental degradability for persistent organic pollutant candidates.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.10.013>.

Fig. 6 – Optimized structures of the reactants, transition states and products in the reaction of 1,3,6,9,10-pentachlorodecane (A), 5,5,6,7,7-pentachlorodecane (B) with $\cdot\text{OH}$.

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