Conformation preference and related intramolecular noncovalent interaction of selected short chain chlorinated paraffins

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Short chain chlorinated paraffins (SCCPs) are not only research focus of environmental issues but also interesting model molecules for organic chemistry which exhibit diverse conformation preference and intramolecular noncovalent interactions (NCIs). A systematic study was conducted to reveal the conformation preference and the related intramolecular NCIs in two C₁₀-isomers of SCCPs, 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane. The overall conformation profile was determined on the basis of relative energies calculated at the MP2/6-311++G(d,p) level with the geometries optimized by B3LYP/6-311++G(d,p) method. Then, quantum theory of atoms in molecules (QTAIM) has been adopted to identify the NCIs in the selected conformers of the model molecules at both B3LYP/6-311++G(d,p) and M06-2X/aug-cc-pvdz level. Different chlorine substitution modes result in varied conformation preference. No obvious *gauche* effect can be observed for the SCCPs with chlorination on adjacent carbon atoms. The most stable conformer of 5,5,6,6-tetrachlorodecane (tTt) has its three dihedral angles in the T configuration, and there is no intramolecular NCIs found in this molecule. On the contrary, the chlorination on interval carbon atoms favors the adoption of *gauche* configuration for the H–C–C–Cl axis. Not only intramolecular H···Cl contacts but also H···H interactions have been identified as driving forces to compensate the instability from steric crowding of the *gauche* configuration. The gggg and g'g'g'g' conformers are the most popular ones, while the populations of tggg and tg'g'g' conformer are second to those of the gggg and g'g'g'g' conformers. Meanwhile, the M06-2X method with large basis sets is preferred for identification of subtle intramolecular NCIs in large molecules like SCCPs.

short chain chlorinated paraffins, intramolecular noncovalent interactions, conformation preference, chlorination substitution mode

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1 Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated *n*-alkanes with carbon chain lengths from 10 to 30 carbon atoms and the chlorine content of 30%–70% by mass [1,2]. According to their chain length, CPs can be classified into 3 groups: short-chain CPs (SCCPs, C₁₀–C₁₃),

medium-chain CPs (MCCPs, C₁₄–C₁₇), and long-chain CPs (LCCPs, C₁₈–C₃₀). SCCPs are high production volume chemicals with total annual production estimate ranging from 7.5 to 11.3 kt in the region of the United Nations Economic Commission for Europe in 2007 [3,4] and have attracted considerable attention due to their long-range transport capacity, persistency in the environment, and adverse effect on environmental organisms and human health [5–7]. Moreover, the volatility of SCCPs is similar with that of chlorinated pesticides such as hexachlorocyclohexane

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and toxaphene according to the vapor pressures and Henry's law constants. Therefore, SCCPs in the aqueous phase and soil can volatilize after exposure to the air and thus support the long-range atmospheric transport of the chemicals. In fact, occurrence of short- and medium-chain chlorinated paraffins in the atmosphere of Fildes Peninsula of Antarctic was reported in 2014 [8–10]. Use of SCCPs has been restricted in Europe under Europe Commission Directive 76/769/EEC, and recently, the U.S. Environmental Protection Agency also intends to initiate action under Section 6 of the Toxic Substances Control Act to ban or restrict the manufacture, import, processing or distribution in commerce, export and use of SCCPs [11]. However, the necessary understanding in the environmental risk and health hazard of SCCPs is far from enough. The risk draft profile on SCCPs is still under review although SCCPs have already been nominated for inclusion in the Stockholm Convention in 2007. The inherent complexity of mixtures and the insufficient knowledge about the basic physical-chemical characteristics of SCCPs contribute to such dilemma [4]. Such drives Bogdal *et al.* [12] to calculate a series of physicochemical properties for short- and medium-chain chlorinated paraffins. Most recently, Chen's study [13] indicated that the reaction of SCCPs with OH radical in the atmosphere may depend on the prevailing conformations of SCCPs molecules. Nevertheless, there is no work reported for the conformational properties of SCCPs and related non-covalent interactions (NCIs) compared with the extensive studies on those of *n*-alkanes, while such information is important because NCIs play a fundamental role in determining and maintaining the three-dimensional structure of both SCCPs themselves and the SCCPs-macromolecule complexes [14]. Besides, the understanding of intramolecular NCIs in SCCPs and its resulting conformation preference helps to interpret the steric effect of SCCPs-relevant chemical reactions and gain insight into its interaction with target biomolecules.

Alkanes can exist in a great variety of conformations, including energy minimum (staggered) and energy maximum (eclipsed) conformers, due to C–C bond rotation. Generally, the lower energy *trans* (t) conformations of *n*-alkanes are divided from the higher energy *gauche* (g+ or g–) conformations by the t-g barrier. Chlorine substitution of hydrogen in alkanes may dramatically alter the molecular stereochemistry of *n*-alkane and even result in the different chemical reactivity [15,16]. Unlike the corresponding *n*-alkanes, selected alkyl halides prefer *gauche* conformations to *anti* structures [17]. According to the data of electron diffraction spectroscopy and microwave spectroscopy, the *gauche* conformer is favored for both 1-propyl chloride (CH₃CH₂CH₂Cl) and 1-propyl fluoride (CH₃CH₂CH₂F) [18,19], though slightly. The so-called *gauche* effect finds its origin in the nonconventional hydrogen bonds between halogen and hydrogen atom. The proportion of the *gauche* conformers increases with the electronegativity of halogen, and the

distance between halogen and one of the hydrogens in the interacting CH₂ or CH₃ is shorter than the sum of the van der Waals radii [17]. Moreover, in addition to weak hydrogen bonds with controversial features, other types of intramolecular NCIs may also appear in halogenated alkanes to maintain the specific conformations. Various calculation results show that intramolecular H–H bonds can be formed in highly branched alkanes and yield a stabilizing contribution to their increased stabilities in comparison with linear or less branched isomers [20]. Most recently, an attractive intramolecular halogen-halogen bonding interaction has been reported to assist in stabilizing the molecules of perhalogenated ethanes. The characteristics of such kind of NCIs cannot be explained by the σ -hole concept advanced for halogen bonds. Instead, the newly found halogen-halogen bonding appears to be an unusually strong van der Waals interaction, and the strength of the interaction is even comparable to that of hydrogen bonds when one of the halogens involved is chlorine [21]. Quantum chemical calculation is a useful tool to help to identify conformation preference of halogenated alkanes. The theory of "atoms in molecules" (AIM) has been used to characterize noncovalent interactions like such hydrogen bonding interactions and allows a hydrogen bond distinguished from a van der Waals interaction [22,23]. Monteiro and Firme's work [20] showed that the hydrogen-hydrogen bonds in alkane complexes play a role in their stabilities and their boiling points by using density functional theory (DFT), *ab initio*, quantum theory of atoms in molecules (QTAIM), and electron localization function (ELF). Johansson and Swart's study [21] showed that non-covalent halogen-halogen interaction in the perhalogenated ethanes is real and attractive with appreciable strength, when one of the halogens involved is chlorine. The study indicated that the chlorine atom has an overlooked, reasonably strong intramolecular bonding interaction between halogen atoms, which is rather different from other halogen bond. In fact, the relevance between NCIs and the preferred conformations for halogenated chemicals is a universal topic and its exploration helps to interpret the steric effect of the related reactions. Moreover, many persistent organic pollutants contain halogen atoms such as Cl, Br and F, while less attention has been paid on the existence of NCIs and their influence on the environmental transformation of halogenated persistent organic pollutants. Clearly, both insight into the prevailing intramolecular noncovalent interactions and the understanding of resulting conformation preference is not available for multiple halogenated alkanes, which represent one typical template of chemical structures. In comparison with simple model molecules studied before, such as mono-halogenated and perhalogenated alkanes, SCCPs exhibit more conformation possibility and diverse NCIs. Not only intramolecular H...Cl contacts but also H...H and Cl...Cl interactions may occur in SCCPs. More features can be obtained for elucidating the prevailing conformations of SCCPs.

In this study, two C_{10} -isomers of SCCPs, 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane, were selected as model molecules to favor the formation of different kinds of NCIs possibly identified in SCCPs, such as potential NCIs between chlorine and hydrogen attached to different carbons. An exhaustive conformational analysis of the two model molecules was implemented by using well cost-efficiency theoretical methods to provide a structural basis for subsequent NCIs study. Then QTAIM was adopted to reveal the underlying NCIs dominating the conformation preference [24]. The influence of different intramolecular NCIs on the conformation preference was also elaborated.

2 Methods

The conformation preference is explored to provide a starting point for the subsequent NCIs research. As for the two model SCCPs, there are at least two distinct kinds of staggered conformers, *gauche* and *trans* rotamers. The backbone arrangement for the model molecules is mainly defined by two dihedral angles involving chlorine substitution, $\phi(H-C-C-Cl)$ for both molecules, $\phi(Cl-C-C-Cl)$ only for 5,5,6,6-tetrachlorodecane (Table 1). Letters t(T), g(G) and g'(G') stand for *trans* isomer with torsion angle of $180^\circ \pm 30^\circ$, *+gauche* one with that of $60^\circ \pm 30^\circ$, and *-gauche* one with that of $-60^\circ \pm 30^\circ$, respectively. The corresponding capital letters represent the situation of heavy atoms in the backbone structure [25]. We check the possibilities of three conformations (t/T, g/G and g'/G') for each relevant torsion angle for the 2 molecules. When the other C-C related dihedral angles remain their *trans* conformations, the theoretical numbers of possible conformations for 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane are $3^3=27$ and $3^4=81$, separately. Meanwhile, molecular symmetry reduces the number of unique conformers to 18 for 5,5,6,6-tetrachlorodecane.

Concerning the size of two model SCCPs molecules and the number of possible minima on the potential energy surface we need check, the consideration of cost-efficiency becomes a crucial issue [26]. Therefore, the density functional theory (DFT) method combining the hybrid exchange-correlation functional Becke-3-Lee-Yang-Parr (B3LYP) with the 6-311++G(d,p) basis set was used for geometric optimization since it has been proved to yield good and consistent results in large molecules containing halogen atoms at a moderate computational cost [27,28]. Tight optimization criterion was used in all calculations. Then the harmonic vibrational frequency calculation was carried out at the same level of theory to characterize the nature of each stationary point. In order to obtain more reliable energy data, the single-point energy calculation was obtained using the Moller-Plesset second-order perturbation (MP2) method with the 6-311++G(d,p) basis set since systematic errors have been found in computing the energies for large alkane molecules by B3LYP and other popular

DFT functional [29,30]. The thermochemistry properties of all distinct conformations are the sum of single-point energy at MP2/6-311++G(d,p) level and thermodynamic correction at B3LYP/6-311++G(d,p) level at 298.15 K. The Boltzmann populations at 298.15 K were calculated based on relative Gibbs free energy. All calculations were performed using Gaussian 09 program package [31] and the calculations on the model molecules are in ideal gaseous state at 298.15, the same way when analyzing the reaction between SCCPs and hydroxyl radical [13,32].

The dispersed chlorination mode of alkanes decides that the dihedral angle $\phi(H-C-C-Cl)$ receives the preference over $\phi(Cl-C-C-Cl)$ in hexa- and heptachloro- decanes, the predominant isomers in commercial SCCPs [9,33]. Therefore, the potential energy profiles for intramolecular rotation of the dihedral angles $\phi(H-C-C-Cl)$ were calculated at the B3LYP/6-311++G(d,p) level to shed more light on the influence of different intramolecular NCIs on the conformations of the two molecules. The H-C-C-Cl dihedral angles were switched every 10° to obtain one starting geometry. For each point, the studied H-C-C-Cl dihedral angle was then kept fixed, whereas all the other internal coordinates were optimized from its starting structure. The barriers to the intramolecular rotation of the dihedral angle $\phi(H-C-C-Cl)$ in 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane were calculated at the same level and are presented in Figure 1.

Moreover, the NCIs formed in the selected dominant conformer of the two model molecules were decoded using Bader's theory with the B3LYP/6-311++G(d,p) method [22]. QTAIM was applied with the use of the AIM2000 program [34,35] to analyze bond critical points (BCPs) in terms of electron densities and related Laplacians. Molecular graphs with bond paths and BCPs are illustrated in Figure 2. In addition, the intramolecular NCIs are more subtle and thus difficult to explore their nature when being compared with the widely studied intermolecular ones. Therefore, M06-2X was also utilized for geometric optimization and subsequent QTAIM study with aug-cc-pvdz basis set for intramolecular NCIs exploration, which is proved to be adequate for long range interactions such as van der Waals interactions and can handle the large molecule with conformational flexibility [36–38]. Dessent *et al.* [39] have successfully used M06-2X for calculating the conformationally flexible anionic clusters with dispersion and ionic hydrogen-bonding interactions. Moreover, M06-2X was even utilized to explore the molecular recognition of imidacloprid with *Aplysia californica* AChBP as well as the NCIs in the system [40].

3 Results and discussion

3.1 Conformation preference of two model SCCPs

Table 1 presents the values of the calculated relative energy

Figure 1 Potential energy profiles for intramolecular rotation of the *n*-butyl fragments in 5,5,6,6-tetrachlorodecane around the dihedral angle $\phi_1(\text{H}_{19}-\text{C}_4-\text{C}_5-\text{Cl}_{20})$ (a), and 4,4,6,6-tetrachlorodecane around the dihedral angle $\phi_1(\text{H}_{17}-\text{C}_3-\text{C}_4-\text{Cl}_{19})$ (b) as well as the chloro-propane in 4,4,6,6-tetrachlorodecane around the dihedral angle $\phi_2(\text{Cl}_{19}-\text{C}_4-\text{C}_5-\text{H}_{20})$ (c). For each point, the studied dihedral angles are kept fixed, whereas all the other internal coordinates are optimized at the B3LYP/6-311++G(d,p) level of theory. The obtained minima are shown by the corresponding conformer codes in bold letters and Newman projections.

(ΔE_0) corrected with the zero-point vibrational energy at 0 K, relative enthalpy (ΔH), relative Gibbs free energy (ΔG) at 298.15 K and the dihedral angles (ϕ_1 , ϕ_2 , ϕ_3 and ϕ_4) of the distinct conformers of the two model molecules. The distinct conformers are listed in a descending order of equilibrium Boltzmann population based on relative Gibbs free energy. Geometry optimization of the 18 starting conformations of 5,5,6,6-tetrachlorodecane results in 17 distinct conformers. The possibility of the conformer g'Gg' is excluded due to the intense steric hindrance. Three distinct conformers of 5,5,6,6-tetrachlorodecane, tTt, tGt and g'Tt, are listed in Figure 2. Although the dihedral angle Cl-C-C-Cl could adopt either *gauche* or *trans* orientation, certain configuration is favored. The conformers in *gauche* configuration around ϕ_2 are less abundant, all together representing 11.76% of the conformational composition at 298.15 K. Especially, the most stable conformer has this

dihedral angle in the T configuration, comprising 80.73% of the gas phase conformational equilibrium mixture of 5,5,6,6-tetrachlorodecane. The energy difference between *trans* and *gauche* Cl-C-C-Cl configuration is about 1.516 kcal/mol (1 cal=4.1868 J) by comparing ΔE_0 values of the most stable conformer tTt with that of tGt or tG't. Both repulsion effect of C-Cl...Cl-C interaction and steric hindrance of alkyl groups may contribute to the higher stability of the *trans*-Cl-C-C-Cl axis over the *gauche* configuration. The minimum distance of 3.281 Å for two chlorine atoms of different carbons in the tTt conformer is larger than that of 3.240 Å for the tGt conformer. However, the possible formation of intramolecular hydrogen bond helps to compensate such geometric instability since the distance between H₁₈ and H₂₄ in the tGt conformer (2.097 Å) is significantly shorter than the sum of its individual van der Waals radius (2.400 Å). Besides, the molecular symmetry leads to the

Table 1 Dihedral angles, relative thermodynamic properties and equilibrium Boltzmann populations for the distinct conformers of 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane at 298.15 K

Conformer No.	Label	Dihedral angles (°) ^{a)}				ΔE_0 (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	Pops. (%) ^{b)}
		ϕ_1	ϕ_2	ϕ_3	ϕ_4				
5,5,6,6-Tetrachlorodecane									
C ₁	tTt	178.7	−180.0	−178.7	−	0.000	0.000	0.000	80.73
C ₃	tGt	175.5	60.7	177.6	−	1.516	1.631	1.480	5.16
C ₂	tG't	−177.6	−60.7	−175.5	−	1.516	1.631	1.480	5.16
C ₄	g'Tt	−59.2	−174.6	−175.7	−	1.660	1.943	1.584	3.05
C ₅	gTt	57.7	173.6	178.3	−	1.660	1.943	1.584	3.05
C ₆	gTg	55.7	168.4	56.8	−	2.141	2.820	1.957	0.69
C ₇	g'Tg'	−56.8	−168.4	−55.7	−	2.141	2.820	1.958	0.69
C ₈	g'G't	−59.5	−55.7	−174.8	−	2.581	2.979	2.464	0.53
C ₉	gGt	57.2	55.8	176.4	−	2.581	2.979	2.464	0.53
C ₁₀	gG't	57.8	−67.4	179.7	−	3.611	3.729	3.540	0.15
C ₁₁	g'Gt	−59.7	67.0	−177.3	−	3.611	3.729	3.540	0.15
C ₁₂	gGg	59.4	52.0	60.8	−	4.021	4.685	3.850	0.03
C ₁₃	g'G'g'	−60.8	−52.0	−59.4	−	4.021	4.685	3.850	0.03
C ₁₄	g'Tg	−64.1	−180.0	64.1	−	4.749	5.061	4.645	0.02
C ₁₅	g'G'g	−58.7	−59.2	66.6	−	5.375	5.495	5.270	0.01
C ₁₆	g'Gg	−66.6	59.3	58.7	−	5.375	5.495	5.270	0.01
C ₁₇	gG'g	80.0	−58.0	83.2	−	8.671	9.366	8.490	0.00
4,4,6,6-Tetrachlorodecane									
C ₁	gggg	58.3	63.7	64.4	58.4	0.000	0.000	0.000	13.24
C ₂	g'g'g'g'	−58.5	−64.4	−63.7	−58.2	0.000	0.000	0.000	13.24
C ₃	tggg	177.9	55.3	56.4	63.9	0.538	0.241	0.606	8.81
C ₄	tg'g'g'	−175.4	−55.5	−56.9	−63.7	0.538	0.241	0.606	8.81
C ₅	tggg	−179.9	49.8	49.0	177.5	0.643	0.376	0.768	7.02
C ₆	tg'g't	−177.3	−49.1	−49.7	179.6	0.643	0.376	0.768	7.02
C ₇	gggt	64.1	56.0	54.6	176.0	0.711	0.391	0.784	6.84
C ₈	g'g'g't	−64.3	−55.5	−54.4	−178.5	0.711	0.391	0.784	6.84
C ₉	tgtg	−178.9	43.8	166.7	57.2	1.306	1.142	1.421	1.93
C ₁₀	tg'tg'	−178.5	−43.2	−160.3	−58.1	1.306	1.142	1.421	1.93
C ₁₁	gtgt	57.4	160.4	43.0	179.1	1.387	1.205	1.508	1.73
C ₁₂	g'tg't	−56.5	−166.8	−43.7	178.1	1.387	1.205	1.508	1.73
C ₁₃	tgtg'	−178.3	43.9	166.6	−61.1	1.624	1.290	1.776	1.50
C ₁₄	tg'tg	−179.0	−43.3	−160.4	60.1	1.624	1.290	1.776	1.50
C ₁₅	ttgt	−176.1	−166.7	−43.7	178.0	1.647	1.359	1.800	1.33
C ₁₆	ttgt	179.4	160.0	42.9	179.3	1.647	1.359	1.800	1.33
C ₁₇	gtg't	60.8	−167.4	−44.1	178.8	1.746	1.416	1.899	1.21
C ₁₈	g'tgt	−59.7	161.2	43.4	178.5	1.746	1.416	1.899	1.21
C ₁₉	tg'tt	−179.0	−42.9	−160.3	−179.6	1.741	1.452	1.894	1.14
C ₂₀	tggt	−178.4	43.7	166.9	176.2	1.741	1.452	1.894	1.14
C ₂₁	g'tg'g'	−57.3	−168.0	−49.1	−69.2	1.890	1.672	1.953	0.79
C ₂₂	gtgg	57.6	161.2	48.2	68.8	1.890	1.672	1.953	0.79
C ₂₃	ttg'g'	−179.1	172.7	−58.0	−61.3	2.100	1.745	2.194	0.70
C ₂₄	ttgg	−177.9	178.8	58.3	61.2	2.100	1.745	2.194	0.70
C ₂₅	ggtg	68.9	49.5	169.1	57.3	2.038	1.818	2.096	0.61
C ₂₆	g'g'tg'	−69.2	−48.4	−162.3	−57.2	2.038	1.818	2.096	0.61
C ₂₇	g'tgg	−57.3	−178.9	59.1	60.0	2.329	1.832	2.401	0.60
C ₂₈	gtg'g'	57.2	166.5	−61.3	−58.2	2.329	1.832	2.401	0.60
C ₂₉	ggtg'	56.7	62.6	−163.7	−56.8	2.430	1.866	2.504	0.57
C ₃₀	g'g'tg	−56.3	−63.6	171.7	56.0	2.430	1.866	2.504	0.57
C ₃₁	g'g'tt	−57.9	−62.3	174.9	177.0	2.869	1.899	2.982	0.54
C ₃₂	tggtg'	178.6	40.1	−69.4	−56.1	2.138	1.974	2.225	0.47
C ₃₃	tg'gg	−177.0	−40.1	71.0	55.3	2.138	1.974	2.225	0.47
C ₃₄	ggtt	69.3	49.2	169.2	176.8	2.409	2.016	2.508	0.44

(To be continued on the next page)

(Continued)

Conformer No.	label	Dihedral angles (°) ^{a)}				ΔE_0 (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	Pops. (%) ^{b)}
		ϕ_1	ϕ_2	ϕ_3	ϕ_4				
4,4,6,6-Tetrachlorodecane									
C ₃₅	ggg't	56.3	69.0	-40.7	-178.5	2.239	2.038	2.333	0.42
C ₃₆	g'g'gt	-55.4	-70.6	40.7	176.9	2.239	2.038	2.333	0.42
C ₃₇	tgg't	179.7	42.4	-72.3	178.3	3.297	2.919	3.449	0.10
C ₃₈	tg'gt	-178.2	-42.1	74.4	179.0	3.297	2.919	3.449	0.10
C ₃₉	tg'g'g	-178.7	-50.3	-50.7	77.4	3.016	3.002	3.120	0.08
C ₄₀	tggg'	-178.3	51.4	50.3	-78.1	3.016	3.002	3.120	0.08
C ₄₁	gggg'	65.3	53.9	51.5	-79.6	2.923	3.125	2.961	0.07
C ₄₂	g'g'g'g	-66.1	-53.4	-52.1	79.1	2.924	3.125	2.961	0.07
C ₄₃	gg'g'g'	79.6	-51.1	-53.6	-65.4	3.027	3.210	3.061	0.06
C ₄₄	g'ggg	-79.1	51.9	52.7	66.3	3.027	3.210	3.061	0.06
C ₄₅	gg'g't	77.3	-49.6	-50.6	177.7	3.359	3.336	3.454	0.05
C ₄₆	g'ggt	-76.6	50.7	50.0	179.3	3.359	3.336	3.454	0.05
C ₄₇	ggg'g'	67.2	44.4	-75.9	-62.6	3.494	3.649	3.528	0.03
C ₄₈	g'g'gg	-66.3	-44.1	78.4	62.0	3.494	3.650	3.528	0.03
C ₄₉	g'ttg'	-56.4	-163.9	-156.9	-58.0	3.648	3.531	3.737	0.03
C ₅₀	tttg'	-176.1	-163.8	-156.9	-57.8	3.778	3.555	3.900	0.03
C ₅₁	g'ttg	-56.6	-164.0	-156.0	60.7	3.890	3.586	4.021	0.03
C ₅₂	gttg'	62.6	-163.3	-156.9	-58.0	3.936	3.639	4.067	0.03
C ₅₃	tttg	-175.9	-164.1	-156.3	60.2	4.095	3.689	4.257	0.03
C ₅₄	gtgg'	58.2	164.0	46.3	-75.0	3.804	3.876	3.892	0.02
C ₅₅	g'tg'g	-57.2	-171.9	-47.1	75.1	3.804	3.876	3.892	0.02
C ₅₆	ttg'g	-177.1	-173.3	-46.8	73.9	3.802	3.766	3.923	0.02
C ₅₇	ttgg'	-180.1	164.3	45.7	-74.5	3.802	3.766	3.923	0.02
C ₅₈	g'ttt	-56.6	-163.6	-156.6	-179.9	3.942	3.731	4.062	0.02
C ₅₉	g'tgg'	-58.2	165.9	46.1	-76.0	3.994	3.929	4.117	0.02
C ₆₀	gtg'g	59.8	-173.8	-47.1	75.1	3.994	3.929	4.117	0.02
C ₆₁	tttt	-176.1	-163.7	-156.3	-179.8	4.198	3.866	4.355	0.02
C ₆₂	gttg	62.4	-163.5	-156.8	60.9	4.302	3.784	4.479	0.02
C ₆₃	gttt	62.4	-162.7	-157.0	-179.8	4.313	3.903	4.478	0.02
C ₆₄	gg'tg'	75.6	-46.3	-164.1	-58.1	3.992	4.056	4.077	0.01
C ₆₅	g'gtg	-74.9	47.2	172.2	56.5	3.992	4.056	4.077	0.01
C ₆₆	gg'tt	74.9	-45.9	-164.2	179.4	4.178	4.170	4.285	0.01
C ₆₇	g'gtt	-74.2	46.9	172.5	176.7	4.178	4.170	4.285	0.01
C ₆₈	gg'tg	75.5	-45.8	-165.4	58.5	4.181	4.151	4.285	0.01
C ₆₉	g'gtg'	-75.1	47.4	172.9	-59.8	4.181	4.151	4.285	0.01
C ₇₀	g'ggg'	-76.9	54.6	53.8	-77.4	7.690	7.819	7.801	0.00
C ₇₁	gg'g'g	78.3	-54.1	-54.9	77.2	7.690	7.819	7.801	0.00

a) For 5,5,6,6-tetrachlorodecane, ϕ_1 , ϕ_2 and ϕ_3 are the dihedral angles of H₁₉-C₄-C₅-Cl₂₀, Cl₂₀-C₅-C₆-Cl₂₃, and Cl₂₃-C₆-C₇-H₂₄, respectively. For 4,4,6,6-tetrachlorodecane, ϕ_1 , ϕ_2 , ϕ_3 and ϕ_4 are the dihedral angles of H₁₇-C₃-C₄-Cl₁₉, Cl₁₉-C₄-C₅-H₂₀, H₂₀-C₅-C₆-Cl₂₂, and Cl₂₂-C₆-C₇-H₂₄, separately; b)

Boltzmann populations (%) are calculated by the formula $\text{Pops}_i(\%) = \frac{N_i}{N} = \frac{e^{-\Delta G_i/RT}}{\sum_{i=1}^M e^{-\Delta G_i/RT}}$, in which N_i is the number of molecules in conformation i , N is the

total number of molecules in the system at 298.15 K, M is the total number of conformations, and ΔG_i is the relative Gibbs free energy of the molecule in conformation i .

identical chemical environments of the two dihedral angles in 5,5,6,6-tetrachlorodecane, ϕ_1 and ϕ_3 . The energy difference between tTt and g'Tt or gTt conformer is about 1.660 kcal/mol. Clearly, the *gauche* configuration of Cl-C-C-H and H-C-C-Cl benefits from the absence of repulsion effect of C-Cl...Cl-C interaction, but the steric effect of the alkyl groups in the gTt and g'Tt conformations introduces certain energy barrier. In addition, the formation of intramolecular NCIs also contributes to stabilizing the *gauche* conformers.

Unlike the chlorination on adjacent carbon atoms in 5,5,6,6-tetrachlorodecane, that of 4,4,6,6-tetrachlorodecane

occurs on interval carbon atoms. Geometry optimization of the possible 4,4,6,6-tetrachlorodecane conformers results in 71 unique conformers, much more than 17 conformers of 5,5,6,6-tetrachlorodecane due to one more dihedral angle and loss of molecular symmetry. The possibility of "sterically forbidden" conformers, including g'gg'g', gg'gg', g'g'gg', tg'gg', ggg'g, g'gg'g, tgg'g, gg'gg, g'gg't, gg'gt, are excluded due to geometric limitation. Totally different from the equilibrium conformational pattern for 5,5,6,6-tetrachlorodecane, there is no dominant conformation for 4,4,6,6-tetrachlorodecane. Four distinct conformers of 4,4,6,6-tetrachlorodecane, gggg, tggg, tggt and gggt, are

illustrated in Figure 2. Moreover, *gauche* effect is observed in the molecule, and the gggg and g'g'g'g' conformers are the most popular ones with about 13.24% of the equilibrium Boltzmann population, respectively. The reason is that the crucial dihedral angles of the two molecules are different. There is only one kind of dihedral angles for 4,4,6,6-tetrachlorodecane, Cl–C–C–H between chlorinated alkane part and alkyl tail. The chlorine atoms stand a good chance to form weak hydrogen bond with certain hydrogen atoms in the molecule. Consequently, the *gauche* conformer was somehow favored, especially for the dihedral angles ϕ_2 or ϕ_3 . Besides, the repulsion effect of chlorine atoms on interval carbon was rather lower than that on adjacent carbons. Longer distance between chlorine atoms in *gauche* orientation enables the minimization of the steric crowding of chlorine atoms. The 8 most stable conformers all have the dihedral angles ϕ_2 and ϕ_3 in the G configuration. Only 25.61% conformers adopt *anti* configuration for ϕ_2 or ϕ_3 . The energy difference between gggg and ggtg or gtgg conformer is larger than 1.890 kcal/mol, which indicates the existence of attractive intramolecular NCIs such as hydrogen bonds between H and Cl may compensate the instability from steric crowding of chlorine atoms in the molecule. As a result, the minimum distance of 3.295 Å between chlorines in the gtgg conformer is much shorter than that of 4.247 Å in the gggg conformer. On the contrary, there is only about

0.538–0.711 kcal/mol energy difference between gggg and gggt or tggg conformer. The absence of chlorine-chlorine repulsion helps to stabilize the *trans* orientation for ϕ_1 or ϕ_4 , and 67.82% of the equilibrium conformational mixture prefer the T configuration to G configuration for the dihedral angles ϕ_1 and ϕ_4 . The contribution of attractive NCIs, such as weak hydrogen bonds and van der Waals interactions, to the configuration stability of the G configuration for the dihedral angles ϕ_1 and ϕ_4 is limited.

3.2 The potential energy profiles for intramolecular rotation of the dihedral angle ϕ (H–C–C–Cl)

Considering the dihedral angle ϕ (H–C–C–Cl) receives the preference over ϕ (Cl–C–C–Cl) in SCCPs due to its dispersed chlorination modes [9,33], the potential energy profiles for intramolecular rotation of the dihedral angles ϕ (H–C–C–Cl) for 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane have been calculated with ϕ (H–C–C–Cl) initially assigned the value 0°, respectively, to shed more light on the conformation preference of the two molecules (Figure 1). The H–C–C–Cl dihedral angles are switched every 10° to obtain one starting geometry. For each point, the H–C–C–Cl dihedral angles are then kept fixed, whereas all the other internal coordinates are optimized from its starting structure. The barriers to the internal rotation of the

Figure 2 Molecular topography of the selected conformers obtained from the QTAIM study at the M06-2X/aug-cc-pvtz level: tTt (a), tGt (b), g'Tt (c) of 5,5,6,6-tetrachlorodecane, while gggg (d), tggg (e), tggt (f), gggt (g) of 4,4,6,6-tetrachlorodecane. Red circles represent BCPs while yellow ones indicate the existence of RCPs (color online).

dihedral angle $\phi(\text{H}-\text{C}-\text{C}-\text{Cl})$ in 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane are presented in Figure 1.

Owing to the mirror symmetry of the molecule 5,5,6,6-tetrachlorodecane, the profile beyond 180° is just the mirror image of that between 0° and 180° . Only three first-order saddle points, tTt, gTt and g'Tt, can be found during the rotation of $\phi_1(\text{H}_{19}-\text{C}_4-\text{C}_5-\text{Cl}_{20})$. The lower energy *trans* (t) conformation is divided from the higher energy *gauche* (g and g') conformations by the t-g barriers, while direct transition between the *gauche* states requires traversing the *cis* barrier. The saddle points corresponding to the reaction coordinates are symbolized in bold letters. The calculated barriers do not exceed 2.496 kcal/mol in the direction of the expected conformational relaxation, that is, converging to the global energy minimum. The detection of imaginary frequency in the vibrational analysis of the conformations at the local energy maxima also confirms their instability. The C_4-C_5 bond length of the conformation at $\phi_1(\text{H}_{19}-\text{C}_4-\text{C}_5-\text{Cl}_{20})=120^\circ$ is 1.557 Å, longer than that of tTt (1.532 Å) and g'Tt (1.539 Å), which may be partly contributed by the steric effect of alkyl group. On the contrary, the barrier for the conformation transition from lower to high energy minima, identical to the *cis* barrier here, is 4.387 kcal/mol, about 1.8 times higher than that of expected conformational relaxation. Such means the geometry rearrangement helps to trap the molecule in its low energy conformer. Naturally, at least one eclipsed structure can be found in the conformations at the local energy maxima along with *cis*-H-C-C-Cl. For the transition states, when the dihedral angle $\text{H}_{19}-\text{C}_4-\text{C}_5-\text{Cl}_{20}$ is 120° , the chlorine atom and the propyl group are at eclipsed position. However, stronger steric repulsion can be observed when the $\text{H}_{19}-\text{C}_4-\text{C}_5-\text{Cl}_{20}$ dihedral angle reaches 0° because the propyl group and chlorinated pentyl group occur in the eclipsed structure.

Differently, $\phi_1(\text{H}_{17}-\text{C}_3-\text{C}_4-\text{Cl}_{19})$ in 4,4,6,6-tetrachlorodecane presents a relatively high t-g barrier. The calculated t-g barrier already exceeds 6.348 kcal/mol even though there is only small difference in relative electronic energy (0.139 kcal/mol) between the gggg and tggg conformer. Apparently, the interval chlorination can disable the rotation from *anti* to *gauche* configuration. Therefore, the tggg conformer can account for 8.81% of the equilibrium Boltzmann population as shown in Table 1. In addition, the gtgg conformer is not stable because the *anti* to *gauche* conversion crosses a barrier of ca. 2.019 kcal/mol while the barrier of ca. 4.094 kcal/mol is needed for the reversed process. Moreover, the direct *gauche*-*gauche* barrier is as high as 9.473 kcal/mol. The difficulty in the rotation of $\phi_2(\text{Cl}_{19}-\text{C}_4-\text{C}_5-\text{H}_{20})$ can be attributed to the steric effect as partly symbolized in the gtgg and tttt conformer. Additionally, similar to that of 5,5,6,6-tetrachlorodecane, unfavorable geometry such as the eclipsed structures with *cis*-H-C-C-Cl also attributes to the instability of the conformation at the local energy maxima. Specifically, when the value of

either dihedral angles, $\phi_1(\text{H}_{17}-\text{C}_3-\text{C}_4-\text{Cl}_{19})$ and $\phi_2(\text{Cl}_{19}-\text{C}_4-\text{C}_5-\text{H}_{20})$, reaches 0° , the intensive steric repulsion comes from the two eclipsed alkyl groups. Further rotation from *gauche* to *trans* configuration encounters the energetically less favored conformation with the eclipsed pair of hydrogen/chlorine and alkyl group. In fact, experimental data from molecules of similar structure verified such conformation preference. The infrared spectroscopic analysis of 1,2-dichloroethane provides an excellent example for the stable conformation determined by chlorination on adjacent carbon atoms. No *gauche* effect was observed and the *trans* rotamer is more stable in the gas phase due to steric repulsion between chlorine atoms [41]. Besides, recent photoelectron spectroscopy study supported the *gauche* rotamer as prevailing conformation of *n*-propyl fluoride [42], typical halogenated alkanes in which there is no halogenation on the adjacent carbon and the halogen atom is close to the hydrogen atom or a alkyl group.

3.3 Noncovalent interactions in the model molecules

Specifically, the preferred conformers tTt, tGt and g'Tt were chosen for thorough investigation on the intramolecular noncovalent interaction occurring in 5,5,6,6-tetrachlorodecane, while elucidation of NCIs in the conformers gggg, tggg, tggt and gggt were conducted to verify the driving forces for configuration stabilization of 4,4,6,6-tetrachlorodecane. Considering the dispersion binding and method limitations, calculations of NCIs in the above selected conformers were performed using the QTAIM theory pioneered by Bader and collaborators at both B3LYP/6-311++G(d,p) and M06-2X/aug-cc-pvdz level. Table 2 lists the topological properties at all BCPs and ring critical points (RCPs) of the 7 conformers obtained by QTAIM method, and there is no $\text{Cl}\cdots\text{Cl}$ contact identified in the two models by the QTAIM calculation. The molecular graphs with bond paths and BCPs are illustrated in Figure 2.

As we expected, no NCIs was identified in the tTt (Figure 2(a)) conformer of 5,5,6,6-tetrachlorodecane, while there are two (3, -1) BCPs existing between H_{16} and Cl_{22} , and H_{25} and Cl_{21} in the g'Tt conformer of 5,5,6,6-tetrachlorodecane, separately, satisfying electron density and density Laplacian conditions for hydrogen bonding [23] (Figure 2(c)). The electron densities at the BCPs of $\text{H}_{16}\cdots\text{Cl}_{22}$ and $\text{H}_{25}\cdots\text{Cl}_{21}$ are 0.012 and 0.015 a.u. at the M06-2X level, individually, and all values lie within the range of 0.002–0.040 a.u. but below the medium level. The corresponding Laplacian of the electron density $\nabla^2\rho$ at the BCPs of $\text{H}_{16}\cdots\text{Cl}_{22}$ and $\text{H}_{25}\cdots\text{Cl}_{21}$ are 0.043 and 0.060 a.u. at the M06-2X level, separately, also indicating weak hydrogen bonds. Besides, the interpenetration between the corresponding hydrogen and chlorine is also confirmed since the distances for $\text{H}_{16}\cdots\text{Cl}_{22}$ (2.743 Å) and $\text{H}_{25}\cdots\text{Cl}_{21}$ (2.601 Å) are significantly shorter than the sum of the non-bonded radii of hydrogen and chlorine ($d_{\text{Cl}\cdots\text{H}} < r_{\text{H}}^0 + r_{\text{Cl}}^0 = 1.20 + 1.75 =$

Table 2 Topological parameters for the NCIs identified by QTAIM method at the B3LYP/6-311++G(d,p) and M06-2X/aug-cc-pvtz level

Molecule	Conformer	Interaction	Method	d^a (Å)	ρ^b (a.u.)	$\nabla^2\rho^c$	λ_1^d	λ_2^e	λ_3^f	ε^g	$d_{\text{BCP-RCP}}^h$ (Å)
5,5,6,6-Tetrachlorodecane	tTt	—	B3LYP(6-311++G(d,p))	—	—	—	—	—	—	—	—
		—	M06-2X(aug-cc-pvdz)	—	—	—	—	—	—	—	—
	tGt	$\text{H}_{18}\cdots\text{H}_{24}$	B3LYP(6-311++G(d,p))	2.097	0.012	0.042	−0.010	−0.006	0.059	0.617	0.347
			M06-2X(aug-cc-pvdz)	2.135	0.012	0.046	−0.010	−0.006	0.062	0.637	0.312
	g'Tt	$\text{H}_{16}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.746	0.011	0.040	−0.008	−0.006	0.054	0.410	0.722
			M06-2X(aug-cc-pvdz)	2.743	0.012	0.043	−0.009	−0.005	0.057	0.589	0.706
		$\text{H}_{25}\cdots\text{Cl}_{21}$	B3LYP(6-311++G(d,p))	2.601	0.014	0.055	−0.011	−0.005	0.071	1.321	0.209
			M06-2X(aug-cc-pvdz)	2.601	0.015	0.060	−0.012	−0.004	0.076	1.815	0.168
	gggg	$\text{H}_{15}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.952	0.007	0.023	−0.005	−0.003	0.032	0.482	0.425
			M06-2X(aug-cc-pvdz)	2.778	0.010	0.034	−0.008	−0.006	0.048	0.316	0.624
		$\text{H}_{16}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.706	0.011	0.038	−0.009	−0.008	0.055	0.228	0.742
			M06-2X(aug-cc-pvdz)	2.697	0.012	0.041	−0.009	−0.007	0.058	0.231	0.708
		$\text{H}_{24}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.706	0.011	0.038	−0.009	−0.008	0.055	0.229	0.742
			M06-2X(aug-cc-pvdz)	2.700	0.012	0.041	−0.009	−0.007	0.057	0.237	0.706
		$\text{H}_{27}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.952	0.007	0.023	−0.005	−0.003	0.032	0.474	0.429
			M06-2X(aug-cc-pvdz)	2.778	0.010	0.035	−0.008	−0.006	0.048	0.321	0.630
4,4,6,6-Tetrachlorodecane	tggg	$\text{H}_{17}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.707	0.011	0.040	−0.009	−0.007	0.056	0.333	0.721
			M06-2X(aug-cc-pvdz)	2.743	0.012	0.041	−0.008	−0.006	0.055	0.466	0.661
		$\text{H}_{17}\cdots\text{H}_{24}$	B3LYP(6-311++G(d,p))	2.856	—	—	—	—	—	—	—
			M06-2X(aug-cc-pvdz)	2.366	0.006	0.023	−0.003	−0.003	0.028	0.085	0.310
		$\text{H}_{24}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.784	0.010	0.034	−0.008	−0.006	0.047	0.272	0.677
			M06-2X(aug-cc-pvdz)	2.747	0.011	0.038	−0.008	−0.006	0.052	0.227	0.656
		$\text{H}_{27}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.858	0.008	0.027	−0.006	−0.005	0.039	0.286	0.603
			M06-2X(aug-cc-pvdz)	2.774	0.010	0.035	−0.008	−0.006	0.048	0.289	0.674
	tggt	$\text{H}_{17}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.821	0.010	0.035	−0.007	−0.004	0.046	0.561	0.614
			M06-2X(aug-cc-pvdz)	2.783	0.011	0.039	−0.007	−0.005	0.051	0.456	0.617
		$\text{H}_{17}\cdots\text{H}_{25}$	B3LYP(6-311++G(d,p))	2.424	0.006	0.018	−0.003	−0.002	0.023	0.166	0.294
			M06-2X(aug-cc-pvdz)	2.249	0.008	0.026	−0.005	−0.005	0.037	0.075	0.490
		$\text{H}_{25}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.819	0.010	0.035	−0.007	−0.004	0.046	0.557	0.614
			M06-2X(aug-cc-pvdz)	2.781	0.011	0.039	−0.007	−0.005	0.051	0.468	0.616
		$\text{H}_{15}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.853	0.008	0.028	−0.006	−0.005	0.039	0.283	0.608
			M06-2X(aug-cc-pvdz)	2.775	0.010	0.034	−0.008	−0.006	0.048	0.287	0.666
	gggt	$\text{H}_{16}\cdots\text{Cl}_{22}$	B3LYP(6-311++G(d,p))	2.786	0.010	0.034	−0.008	−0.006	0.047	0.272	0.674
			M06-2X(aug-cc-pvdz)	2.744	0.011	0.038	−0.008	−0.006	0.052	0.225	0.659
		$\text{H}_{16}\cdots\text{H}_{25}$	B3LYP(6-311++G(d,p))	2.838	—	—	—	—	—	—	—
			M06-2X(aug-cc-pvdz)	2.371	0.006	0.023	−0.003	−0.003	0.028	0.090	0.300
		$\text{H}_{25}\cdots\text{Cl}_{18}$	B3LYP(6-311++G(d,p))	2.712	0.011	0.040	−0.009	−0.007	0.056	0.345	0.717
			M06-2X(aug-cc-pvdz)	2.744	0.012	0.041	−0.008	−0.006	0.055	0.480	0.661

a) For the distance between the two atoms involved in identified NCIs; b) for the electron density (a.u.) at the bond critical points; c) for the Laplacian of the electron density at the bond critical points; d–f) for the first, second and third eigenvalues of the Hessian Matrix; g) for the bond ellipticity; h) for the distance between the bond critical points and the corresponding ring critical points.

2.95 Å), which also supports the existence of intramolecular hydrogen bond interaction. In addition, the ellipticity ε of $\text{H}_{16}\cdots\text{Cl}_{22}$ BCP is 0.589 at the M06-2X level, obviously lower than that of $\text{H}_{25}\cdots\text{Cl}_{21}$ BCP, 1.815. The high ellipticity of $\text{H}_{25}\cdots\text{Cl}_{21}$ BCP stems from the close proximity (0.168 Å) of $\text{H}_{25}\cdots\text{Cl}_{21}$ BCP to the associated RCP in the interior of the five-membered ring defined by H_{25} – C_7 , C_7 – C_6 , C_6 – C_5 , C_5 – Cl_{21} , $\text{Cl}_{21}\cdots\text{H}_{25}$ paths, which reveals the instability of the $\text{H}_{25}\cdots\text{Cl}_{21}$ interaction.

In fact, the stabilization effect of intramolecular interactions from the two $\text{H}\cdots\text{Cl}$ pairs is really weak, and the structural torsion from the tGt configuration change causes significant steric crowding. As a result, only few conformers have the dihedral angles ϕ_1 and ϕ_3 in the G configuration. Differently, the rotation of the dihedral angle $\phi_2(\text{Cl}_{20}$ – C_5 – C_6 – $\text{Cl}_{23})$ from *anti*(tTt) to *gauche*(tGt) configuration leads to structural adjustment of C–C bonds. The bond length of

the single bond C_5 – C_6 is shortened by 0.15% from tTt to tGt, but the bond lengths of C_4 – C_5 and C_6 – C_7 elongate from 1.528 to 1.531 Å simultaneously at the M06-2X level. Such helps to build a $\text{H}_{18}\cdots\text{H}_{24}$ contact in the tGt conformer, the only NCI identified by the QTAIM calculation (Figure 2(b)). According to Popelier, $\text{H}\cdots\text{H}$ bonding can be characterized using the same criteria proposed for hydrogen bonds [23]. Apparently, the $\text{H}_{18}\cdots\text{H}_{24}$ interaction satisfies the first four topological criteria proposed for hydrogen bonds by Koch and Popelier (Table 2). The value of charge density of the BCP from the $\text{H}_{18}\cdots\text{H}_{24}$ contact is 0.012 a.u. at the M06-2X level, which is typical for weak hydrogen bonds and higher than that for weak van der Waals interactions. Such $\text{H}\cdots\text{H}$ contact is not a typical donor-acceptor interaction with charge-transfer potential since the two hydrogen atoms bearing identical charge are somehow chemically equivalent. The most recently reported study on the C_8H_{18} isomers

shows that the existence of intramolecular H $\cdots$ H bonds in highly branched alkanes plays a secondary role in their increased stabilities in comparison with linear or less branched isomers [20]. Hence the stability of the tGt conformer, higher than that of g'Tt, is expected due to the relatively strong attraction capacity of H₁₈ $\cdots$ H₂₄ contact with its obvious low ellipticity ε . The chlorine-chlorine repulsion, admittedly, is significant. In the tTt conformer of 5,5,6,6-tetrachlorodecane, the C–C bond length, at the M06-2X level, is 1.532 Å in average for the C–C bonds involving chlorine substitution, statistically significantly longer than that of decane, 1.526 Å. Thus, *anti* configuration is preferred not only for Cl–C–C–Cl but also H–C–C–Cl axis. However, the chlorination on interval carbon atoms favors the adoption of *gauche* configuration for the H–C–C–Cl axis. The average bond length of the C–C bonds with chlorine substitution in the gggg conformer of 4,4,6,6-tetrachlorodecane is 1.529 Å at the M06-2X level, shorter than that of the tTt conformation of 5,5,6,6-tetrachlorodecane. The QTAIM calculation at the M06-2X level reveals 4 H $\cdots$ Cl contacts, H₁₅ $\cdots$ Cl₂₂, H₁₆ $\cdots$ Cl₂₂, H₂₄ $\cdots$ Cl₁₈ and H₂₇ $\cdots$ Cl₁₈, possess consistent BCPs between its donor and acceptor atoms and fit with the first four topological criteria proposed for hydrogen bonds (Figure 2(d)). Table 2 shows that four H $\cdots$ Cl contacts all exhibit significant overlap of the van der Waals spheres and deliver hydrogen bonding feature with more favorable geometries than the H₂₅ $\cdots$ Cl₂₁ pair in the g'Tt conformer at the M06-2X level. The rotation of the dihedral angle ϕ_1 (H₁₇–C₃–C₄–Cl₁₉) from *gauche*(gggg) to *anti*(tggt) configuration cuts off the Cl₂₂ interactions with H₁₅ and H₁₆ and establishes the H₁₇ contacts with Cl₂₂ and H₂₄ instead (Figure 2(e)). The charge density at the BCP of the H₁₇ $\cdots$ H₂₄ pair (0.006 a.u.) is only half of that from the H₁₈ $\cdots$ H₂₄ contact in the tGt conformer of 5,5,6,6-tetrachlorodecane at the M06-2X level. Obviously, such H $\cdots$ H contact cannot introduce sufficient stability as H $\cdots$ Cl contact to the tggt conformer. Likewise, the rotation of the dihedral angle ϕ_4 (Cl₂₂–C₆–C₇–H₂₄) from *gauche*(gggg) to *anti*(gggt) configuration results in the similar change in NCI formation. The Cl₁₈ interaction with H₂₄ and H₂₇ sacrifices for the forming of two new NCIs, the H₁₆ $\cdots$ H₂₅ and H₂₅ $\cdots$ Cl₁₈ contact (Figure 2(g)). Moreover, the synchronous rotation of the dihedral angle ϕ_1 (H₁₇–C₃–C₄–Cl₁₉) and ϕ_4 (Cl₂₂–C₆–C₇–H₂₄) from *gauche*(gggg) to *anti*(tggt) configuration destroys all old NCIs in the gggg conformer and results in the formation of 3 new intramolecular NCIs at the M06-2X level, the H₁₇ $\cdots$ Cl₂₂, H₁₇ $\cdots$ H₂₅ and H₂₅ $\cdots$ Cl₁₈ (Figure 2(f)).

In brief, the establishment of the intramolecular NCIs such as H $\cdots$ H and H $\cdots$ Cl contacts leads to the occurrence of *gauche* configuration for both H–C–C–Cl and Cl–C–C–Cl axis for SCCPs. Specifically, *n*-alkane prefer *anti* configuration because no strong NCIs can be constructed. The chlorination on adjacent carbon atoms results in the construction of the weak H₁₈ $\cdots$ H₂₄ contact for the Cl–C–C–Cl axis of the tGt conformer for 5,5,6,6-tetrachlorodecane, and

only one relatively strong H₁₆ $\cdots$ Cl₂₂ pair with small bond ellipticity presents in the g'Tt conformer for the H–C–C–Cl axis. Therefore, neither tGt nor the g'Tt conformer is found to be energetically more favorable than the tTt conformer. The chlorination on adjacent carbon atoms favors the adoption of *anti* configuration for both H–C–C–Cl and Cl–C–C–Cl axis in SCCPs. Differently, more and much stronger NCIs can be established in the SCCPs with the chlorination on interval carbon atoms. The formation of NCIs favors the adoption of *gauche* configuration for the H–C–C–Cl axis. For example, there are 4 strong H $\cdots$ Cl pairs with small bond ellipticity presents in the gggg conformer of 4,4,6,6-tetrachlorodecane, while the conformers tggt, tggt and gggt exhibit at least 2–3 strong H $\cdots$ Cl pairs with 1 H $\cdots$ H/H $\cdots$ Cl contact. Clearly, different chlorine substitution modes result in different NCIs construction and thus lead to varied conformation preference. Besides, the conformation preference caused by NCIs plays an important role in the reactivity of the pollutants. According to a new PCDD/Fs formation mechanism from 2-chlorophenol, the *syn* conformer of 2-chlorophenol is more stable than the *anti* one due to the establishment of the intramolecular hydrogen bond and is apt to act as the initial reaction conformation of the precursor [43]. Moreover, a recent study shows that the different conformations of SCCPs have considerable influence on the reaction barriers and pathways in the gaseous reaction of SCCPs with $\cdot$ OH. The conformations of SCCPs with *cis*-H–C–C–Cl substructural units were found to facilitate the H-abstraction by $\cdot$ OH due to the establishment of the six-membered ring transition states formed by hydrogen bonds either between H and O or between H and Cl atoms [13]. Interestingly, Figure 1 revealed that the eclipsed substructures with *cis*-H–C–C–Cl locate at the local energy maxima on the potential energy profiles for intramolecular rotation of the dihedral angles ϕ (H–C–C–Cl) for the selected SCCPs, and the formation of intramolecular NCIs in the prevailing configurations for H–C–C–Cl axis with the chlorination on interval carbon atoms results in higher *cis* barriers than those with chlorination on adjacent carbon atoms. Hence, it seems reasonable to expect different reaction barriers for the reactions between $\cdot$ OH and the SCCPs with different chlorination modes.

Concerning the performance of computational methods in discovering intramolecular NCIs, M06-2X/aug-cc-pvdz identifies more delicate intramolecular NCIs interactions, and provides more accurate predictions and gives better performance. Specifically, less intramolecular H $\cdots$ H contacts can be discovered by B3LYP/6-311++G(d,p) method for the two SCCPs molecules. The B3LYP method failed to find the H₁₇ $\cdots$ H₂₄ pair in the tggt conformer and the H₁₆ $\cdots$ H₂₅ pair in the gggt conformer of 4,4,6,6-tetrachlorodecane. It is not surprising because the DFT calculation accuracy mainly depends on the quality of the exchange-correlation functional while B3LYP cannot accurately describe medium-range exchange-correlation energy. B3LYP

is rather inferior to M06-2X in exploring NCIs, one of the adequate performer recommended by Truhlar [36]. Further comparison between the B3LYP and M06-2X results of QTAIM indicates the better performance of M06-2X method in dispersion binding. For example, the $H_{15}\cdots Cl_{22}$ and $H_{27}\cdots Cl_{18}$ pair identified by B3LYP method in the gggg conformer of 4,4,6,6-tetrachlorodecane exhibit less mutual penetration of the donor/acceptor atoms, and the $d_{Cl\cdots H}$ from M06-2X calculation is significantly shorter than the sum of the non-bonded radii of hydrogen and chlorine. Such also reflects in $H_{17}\cdots Cl_{22}$ and $H_{25}\cdots Cl_{18}$ pairs of tggt, $H_{16}\cdots Cl_{22}$ of g''Tt, separately. Obviously, M06-2X calculations with large basis sets are preferred for identification of intramolecular NCIs for SCCPs.

4 Conclusions

We have accomplished a systematic study to reveal the nature and role of the intramolecular NCIs in 5,5,6,6-tetrachlorodecane and 4,4,6,6-tetrachlorodecane, two C_{10} -isomers of SCCPs. First, the overall conformation preference was determined on the basis of relative energies calculated at the MP2/6-311++G(d,p) level with the geometries optimized by B3LYP/6-311++G(d,p) method. Then, QTAIM has been adopted to identify the NCIs in the selected conformers of the model molecules at both B3LYP/6-311++G(d,p) and M06-2X/aug-cc-pvdz level. Different chlorine substitution modes result in varied conformation preference since the chlorine-chlorine repulsion is admittedly significant. No significant *gauche* effect can be observed for the SCCPs with chlorination on adjacent carbon atoms, and the most stable conformer of 5,5,6,6-tetrachlorodecane (tTt) has its three dihedral angles in the T configuration, comprising 80.73% of the gas phase conformational equilibrium mixture. There is no intramolecular NCIs found in this molecule using both computation methods. On the contrary, the chlorination on interval carbon atoms favors the adoption of *gauche* configuration for the H-C-C-Cl axis. Longer distance between chlorine atoms in *gauche* orientation enables the minimization of the steric crowding of chlorine atoms. The chlorine atoms stand a good chance to form weak hydrogen bond with certain hydrogen atoms in 4,4,6,6-tetrachlorodecane. Not only intramolecular H $\cdots$ Cl contacts but also H $\cdots$ H interactions have been identified as driving forces to compensate the instability from steric crowding of the *gauche* configuration. The gggg and g'g'g'g' conformers are the most popular ones with about 13.24% of the equilibrium mixture, respectively. The population of tggt and tg'g'g' conformers are second only to the gggg and g'g'g'g' conformers. Meanwhile, the M06-2X method with large basis sets is preferred for identification of subtle intramolecular NCIs in large molecules like SCCPs. The calculation presents a thorough study leading to a better understanding of conformation selection determined by

intramolecular noncovalent interactions, which may be closely related to the reactivity of halogenated chemicals.

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Conflict of interest The authors declare that they have no conflict of interest.

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