Adsorption of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) on a soil organic matter. A DFT M05 computational study

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Abstract

Adsorption of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) by soil organic matter considering the Leonardite Humic Acid (LHA) model at the M05/tzvp level of Density Functional Theory (DFT) applying cluster approximation has been investigated. Different orientations of CL-20 toward LHA surface were examined. It was found that deprotonation of LHA is required to obtain stable complexes with CL-20. Hydrogen bonds between CL-20 and deprotonated LHA were analyzed applying the atoms in molecules (AIM) theory. An attachment or removal of an electron with respect to the complex does not have significant effect on mutual orientation of the adsorbent in complexes. It was shown that adsorbed CL-20 does not undergo redox transformation and, therefore, adsorption on soil organic matter may be responsible for decrease of the degradation rate of CL-20 in soil.

Keywords: Leonardite Humic Acid; adsorption; AIM method; redox potential; CL-20.

1. Introduction

The polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), produced on a large scale at the industrial level chemicals, was found to be toxic to soil invertebrates and some aquatic organisms (Kuperman et al., 2006; Robidoux et al., 2004), thereby necessitating its removal from contaminated environments. Various nitrocompounds may cause environmental contamination through manufacturing, training, storage, application, and recycling. Degradation of CL-20 by environmental agents, including microorganisms and enzymes derived from microorganisms, light, iron, and alkaline soil and water leads to similar end products. They include ammonia, carbon dioxide, formate, glyoxal, nitrate and nitrite, nitrogen, and nitrous oxide indicating that CL-20 is generally unstable and readily mineralizes in the environment (Balakrishnan et al., 2004a; Balakrishnan et al., 2004b; Bhushan et al., 2004; Hawari et al., 2004; Hawari et al., 2006; Kuperman et al., 2006; Monteil-Rivera et al., 2009;). One-electron transfer process was found to be the initial step for many methods of the nitrocompound decay in the environment (Balakrishnan et al., 2004b; Bhushan et al., 2004; Hawari et al., 2006; Monteil-Rivera et al., 2009). For instance, CL-20 can be efficiently decomposed within a few hours in the presence of zerovalent iron in water in the absence of oxygen (Balakrishnan et al., 2004b). Ability of neither Fe^0 in anhydrous conditions nor Fe^{2+} ions in aqueous solution to degrade CL-20 indicates that surface-bound Fe^{2+} may be responsible for its degradation. The resulting CL-20 radical-anion is expected to undergo spontaneous decomposition starting from denitration process (Bhushan et al., 2004).

The release of CL-20 to surface water largely depends on its solubility while the mobility in soil depends also on sorption to organic matter, clays, or other substances in the soil. An understanding of sorption mechanisms is therefore essential for the accurate prediction of the fate and impact of CL-20 in soils and groundwater. Experimentally it was found that CL-20 has low water solubility at room temperature (3.16 mg/L) and its sorption depends on composition and characteristics of the soil (e.g., pH, clay and organic matter content, moisture, porosity) (Balakrishnan et al., 2004a; Hawari et al., 2006). CL-20 has a low tendency to adsorb on the mineral phases such as silica, ferric oxide, montmorillonite, kaolinite, and illite with sorption constants (K_d^S) of 0-0.62 L/kg (Hawari et al., 2006). The higher values of sorption constant ($K_d^S=311$ L/kg) obtained in soils with higher organic content suggest that soil organic matters may play a determining role in CL-20 sorption.⁷ In addition, as compared to the degradation in water medium, presorption of CL-20 on soil leads to decrease in efficiency of abiotic as well as biotic degradation (Balakrishnan et al., 2004a; Hawari et al., 2006).

To get more detailed insight in sorption process, we studied structures of adsorbed complexes formed by CL-20 and soil organic matter, taken here as the Leonardite Humic Acid (LHA) model monomer limited to 31 carbon atoms with formula $C_{31}H_{24}O_{12}$ (Niederer and Goss, 2007). This model, contained three carboxyl groups, one phenolic group and quinone structure that are important constituents in humic substances, was shown to be very promising tool for the prediction of sorption in soil organic matter (Niederer and Goss, 2007; Nuerla et al., 2013). It should be noted that both neutral LHA as well as its deprotonated forms were used due to spectroscopic evidence for existence of both protonated/deprotonated forms of humic acids under natural pH conditions (Fang et al., 2015). Recently, we have shown that environment significantly affects the redox properties of nitrocompounds such as trinitrotoluene, 2,4-dinitrotoluene, 2,4-dinitroanisole and 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (Sviateenko et al., 2015). Therefore, we have also compared the reduction and oxidation abilities of CL-20 in the hydrated and adsorbed states.

2. Methods

Geometry optimization for all species was performed using the Gaussian 09 program package (Frisch et al., 2009). The geometries of neutral, cation- and anion-radical species were optimized using the Density Functional Theory at the M05/tzvp level (Head-Gordon et al., 1988; Weigend and Ahlrichs, 2005). The present functional and basis set were chosen because of the results of our recent study where such level of theory was able to provide accuracy close to that obtained by experimental measurements (Sviateenko et al., 2011). Harmonic vibrational frequencies were calculated for all optimized structures to establish that a minimum was obtained. Adsorption energy was calculated as a difference between the total energy of the adsorbed complex and the energy of the LHA and CL-20

monomers within the complex geometry, corrected for basis set superposition error using the counterpoise method (Boys and Bernardi, 1970). Deformation energy of the deprotonated LHA ($E_{\text{def}}(\text{LHA})$) was computed as a difference in energies of the deprotonated LHA within the corresponding complex geometry and that of the separately optimized deprotonated LHA. Deformation energy of CL-20 ($E_{\text{def}}(\text{CL-20})$) was computed as a difference in energy of CL-20 within the complex geometry (adsorbed complex) and the energy of a fully optimized CL-20. The AutoDock Vina 4.0 was used to run the rigid docking simulations (Trott and Olson, 2010).

The topological analysis of the distribution function of the electron density $\rho(r)$ was carried out for the optimized geometry of the complexes in the framework of the Bader's *atoms in molecules* (AIM) theory (Bader, 1990) using the Multiwfn program (Lu and Chen, 2012).

The solvent effects for CL-20 and adsorbed CL-20-LHA complexes were assessed by single-point energy calculations using a PCM(Pauling) and SMD solvation models for ions, ion-radical and neutral molecule calculations, respectively (Cossi et al., 2002; Marenich et al., 2009; Sviatenko et al., 2011). Adiabatic electron affinities (E_A) and ionization potentials (I_p) were calculated as the total energy difference between charged species and neutral forms, corrected for zero point energy.

The Gibbs free energy of electron transfer for CL-20 under dissolution was calculated as follows:

$$\begin{aligned}\Delta G_{\text{red},\text{solv}}^0 &= \Delta G^0(R_{\text{solv}}^-) - \Delta G^0(O_{\text{solv}}) \\ \Delta G_{\text{ox},\text{solv}}^0 &= \Delta G^0(O_{\text{solv}}^+) - \Delta G^0(R_{\text{solv}})\end{aligned}\quad (1)$$

The values of reduction and oxidation potentials are expressed as

$$\begin{aligned}E_{\text{red}}^0 &= -\frac{\Delta G_{\text{red}}^0}{nF} + E_H \\ E_{\text{ox}}^0 &= \frac{\Delta G_{\text{ox}}^0}{nF} + E_H\end{aligned}\quad (2)$$

The absolute potential of the NHE reference electrode E_H is taken as -4.36 eV (Lewis et al., 2004).

3. Results and Discussion

3.1. Adsorbed complexes

There are several conformers of CL-20. Based on the reported MBPT(2)/6-311G(d,p) and B3LYP/6-31G+(d,p) calculated data the most stable one, which is β conformer, was chosen for the present study (Fig. S1, SI) (Kholod et al., 2007; Molt et al., 2012). MBPT(2)/6-311G(d,p) calculation showed that β conformer of CL-20 is 2.5 – 5.5 kcal/mol more stable than the other forms (Molt et al., 2012). Optimized neutral LHA and its deprotonated form are shown in Fig. S2 (SI). Preliminary structures of adsorbed CL-20-LHA complexes were obtained by performing molecular docking

calculations using AutoDock Vina 4.0 (Trott and Olson, 2010). Geometry of the obtained complexes was further optimized at M05/tzvp level. Complexes of CL-20 with neutral LHA were found to be unstable (data not shown), while anionic form of LHA readily binds CL-20. Optimization of several complexes with different orientation of CL-20 related to deprotonated LHA resulted in two stable clusters CL-20-LHA(a)³⁻, CL-20-LHA(b)³⁻, with adsorption energy of -32.81, and -26.04 kcal/mol, respectively (Fig. 1, Table 1).

Table 1. M05/tzvp calculated adsorption energies (ΔE_{ads}), deformation energies of the deprotonated LHA ($E_{\text{def.}}(\text{LHA})$) and adsorbed CL-20 ($E_{\text{def.}}(\text{CL-20})$) (kcal/mol).

Structure	ΔE_{ads}	$E_{\text{def.}}(\text{CL-20})$	$E_{\text{def.}}(\text{LHA})$
CL-20-LHA(a) ³⁻	-32.81	4.16	5.04
CL-20-LHA(b) ³⁻	-26.04	4.21	4.97

CL-20-LHA(a)³⁻ CL-20-LHA(b)³⁻ CL-20-LHA(a)^{4-•} CL-20-LHA(b)^{4-•} CL-20-LHA(a)^{2-•} CL-20-LHA(b)^{2-•}

Figure 1. The optimized structures of CL-20 adsorbed on a deprotonated LHA and intermolecular H-bonds.

Adsorption of CL-20 on deprotonated LHA occurs through the formation of ΘH^- -C bonds. These hydrogen bonds are formed between oxygen atoms of nitro-group of CL-20 molecule (proton acceptors) and aromatic hydrogen atoms of LHA, and between the oxygen atoms of the deprotonated carboxylic group and quinone moiety of LHA anion (proton acceptors) and hydrogens of CH group of CL-20 (Fig. 1). Calculated deformation energy is larger for deprotonated LHA than for CL-20 (Table 1). Structures of the complexes after ionization are shown in Fig.1. Ion-radicals CL-20-LHA(a)^{4•} and CL-20-LHA(b)^{4•} are formed after electron attaching, while electron detachment leads to ion-radicals CL-20-LHA(a)^{2•} and CL-20-LHA(b)^{2•}. Analysis of the data presented in Fig. 1 and Table 2 enable us to conclude that after losing or attaching an electron, there is no significant change in total orientation of nitrocompound and deprotonated LHA, though, ionization of the complexes leads to slight change in the hydrogen bond distances.

Table 2. M05/tzvp level calculated geometrical characteristics of adsorbate-adsorbent H-bonds including H...Y, X...Y distances (Å) and X-H...Y angles (degree) for CL-20-LHA(a) and CL-20-LHA(b) complexes.

Bond	Bond type	X...H	X...Y	XHY	X...H	X...Y	XHY	X...H	X...Y	XHY
		CL-20-LHA(a) ³⁻			CL-20-LHA(a) ^{4•}			CL-20-LHA(a) ^{2•}		
HB1	C11-H... ⁻ OOC	2.05	2.83	125.6	2.11	2.89	126.3	2.17	2.92	123.7
HB2	C3-H... ⁻ OOC	2.07	2.83	124.6	2.10	2.88	126.6	2.03	2.85	130.0
HB3	(N4N-)O...H-C _{Ar}	2.60	3.53	144.5	2.61	3.55	144.2	2.36	3.33	148.9
HB4	C5-H... O=C	2.45	3.04	112.4	2.17	2.87	120.1	2.48	3.03	110.1
HB5	C9-H... O=C	—	—	—	—	—	—	2.40	3.38	149.5
HB6	(N2N-)O...H-C _{Ar}	—	—	—	2.48	3.04	110.5	—	—	—
		CL-20-LHA(b) ³⁻			CL-20-LHA(b) ^{4•}			CL-20-LHA(b) ^{2•}		
HB1	(N12N-)O...H-C _{Ar}	—	—	—	2.60	3.54	143.7	2.42	3.37	145.2
HB2	(N8N-)O...H-C _{Ar}	2.57	3.50	143.3	2.61	3.46	134.9	2.38	3.38	153.9
HB3	C1-H... ⁻ OOC	2.09	2.89	128.0	2.32	3.06	123.1	2.24	3.02	126.1
HB4	C7-H... ⁻ OOC	1.99	2.86	133.0	1.97	2.89	139.3	2.03	2.92	135.9
HB5	(N6N-)O...H-C _{Ar}	2.54	3.40	135.1	2.56	3.45	137.8	2.50	3.36	135.2
HB6	C9-H... O=C	2.45	3.09	116.4	2.21	2.85	115.1	2.35	3.05	120.2
HB7	C5-H... O=C	—	—	—	2.45	2.98	109.0	—	—	—

To provide deeper insight into the nature of intermolecular interactions in complexes of CL-20 with deprotonated LHA, the analysis of their electron density was carried out (Table 3). The

topological analysis of the electron density shows the presence of intermolecular bond critical points (BCPs) between hydrogens of CH group and the closest oxygen of deprotonated carboxyl group ($\text{C}-\text{H}\cdots\text{OOC}$) or oxygen of quinone moiety ($\text{C}-\text{H}\cdots\text{O}=\text{C}$), and between oxygen of nitro-group and the closest aromatic hydrogens of LHA ($\text{NO}\cdots\text{H}-\text{C}_{\text{Ar}}$).

Table 3. Topological parameters (electron density (ρ), Laplacian of electron density ($\nabla^2\rho$) and electron energy density (H)) for adsorbed CL-20-LHA complexes.

Bond	Bond type	ρ , $e\cdot\text{\AA}^{-3}$	$\nabla^2\rho$, $e\cdot\text{\AA}^{-5}$	H, au	Bond	Bond type	ρ , $e\cdot\text{\AA}^{-3}$	$\nabla^2\rho$, $e\cdot\text{\AA}^{-5}$	H, au
CL-20-LHA(a) ³⁻					CL-20-LHA(b) ³⁻				
HB1	C11-H $\cdots$ O	0.0221	0.0899	0.0025	HB2	(N8N-)O $\cdots$ H-C _{Ar}	0.0061	0.0257	0.0014
HB2	C3-H $\cdots$ O	0.0224	0.0877	0.0024	HB3	C1-H $\cdots$ $\cdots$ OOC	0.0189	0.0825	0.0029
HB3	(N4N-)O $\cdots$ H-C	0.0058	0.0243	0.0014	HB4	C7-H $\cdots$ $\cdots$ OOC	0.0254	0.0959	0.0018
HB4	C5-H $\cdots$ O	0.0091	0.0427	0.0022	HB5	(N6N-)O $\cdots$ H-C _{Ar}	0.0067	0.0291	0.0016
					HB6	C9-H $\cdots$ O=C	0.0088	0.0409	0.0022
CL-20-LHA(a) ^{4•}					CL-20-LHA(b) ^{4•}				
HB1	C11-H $\cdots$ O	0.0195	0.0795	0.0026	HB1	(N12N-)O $\cdots$ H-C _{Ar}	0.0057	0.0233	0.0013
HB2	C3-H $\cdots$ O	0.0212	0.0818	0.0024	HB2	(N8N-)O $\cdots$ H-C _{Ar}	0.0057	0.0246	0.0014
HB3	(N4N-)O $\cdots$ H-C	0.0056	0.0235	0.0013	HB3	C1-H $\cdots$ $\cdots$ OOC	0.0116	0.0524	0.0025
HB4	C5-H $\cdots$ O	0.0173	0.0737	0.0028	HB4	C7-H $\cdots$ $\cdots$ OOC	0.0265	0.0971	0.0015
HB6	(N2N-)O $\cdots$ H-C	0.0101	0.0425	0.0019	HB5	(N6N-)O $\cdots$ H-C _{Ar}	0.0065	0.0274	0.0015
					HB6	C9-H $\cdots$ O=C	0.0164	0.0709	0.0028
					HB7	C5-H $\cdots$ O=C	0.0106	0.0463	0.0021
CL-20-LHA(a) ^{2•}					CL-20-LHA(b) ^{2•}				
HB1	C11-H $\cdots$ O	0.0168	0.0718	0.0028	HB1	(N12N-)O $\cdots$ H-C _{Ar}	0.0082	0.0353	0.0020
HB2	C3-H $\cdots$ O	0.0235	0.0926	0.0023	HB2	(N8N-)O $\cdots$ H-C _{Ar}	0.0083	0.0373	0.0021
HB3	(N4N-)O $\cdots$ H-C	0.0089	0.0400	0.0022	HB3	C1-H $\cdots$ $\cdots$ OOC	0.0137	0.0603	0.0027
HB4	C5-H $\cdots$ O	0.0088	0.0419	0.0022	HB4	C7-H $\cdots$ $\cdots$ OOC	0.0231	0.0878	0.0022
HB5	C9-H $\cdots$ O	0.0083	0.0362	0.0020	HB5	(N6N-)O $\cdots$ H-C _{Ar}	0.0041	0.0154	0.0010
					HB6	C9-H $\cdots$ O=C	0.0106	0.0491	0.0025

The calculated electron density properties of the complexes studied show that interactions between CL-20 and deprotonated LHA is characterized by low electron density ρ and positive Laplacian ($\nabla^2\rho>0$) (Table 3). These values indicate that $\text{C}-\text{H}\cdots\text{OOC}$, $\text{C}-\text{H}\cdots\text{O}=\text{C}$, and $\text{NO}\cdots\text{H}-\text{C}_{\text{Ar}}$

contacts may be classified as the closed-shell interactions in which electronic charge is concentrated towards nucleus and is depleted in the internuclear region (Espinosa et al., 1998; Tang1 et al., 2006). Positive electron energy density values ($H > 0$) indicate on noncovalent interactions. Calculated topological characteristic are similar to those reported for C-H $\cdots$ O hydrogen bonds (Espinosa et al., 1998; Koch and Popelier, 1995; Mata et al., 2010; Tang1 et al., 2006).

3.2. Redox properties

Attempt to calculate redox properties of CL-20 adsorbed on deprotonated LHA was not successful due to the fact that the unpaired electron was found to be localized on LHA (Fig. S3, SI). Moreover, attempts to force the unpaired electron to be located on CL-20 by using the guess=alter option of Gaussian 09 program were also not successful. Therefore, we speculate that CL-20 adsorbed by humic acids is expected to be resistant to redox transformations. This result is expected to be related to the experimental fact that degradationability of CL-20 in soil is decreased.^{6,7} However, desorption and dissolution in water keeps the ability of CL-20 to be reduced and oxidized as evident from the data presented in Table 4. Comparative analysis of the electron affinities, ionization energies, Gibbs free energies of reduction and oxidation, reduction and oxidation potentials shows that solvation significantly promotes redox transformation of CL-20 (Table 4).

Table 4. M05/tzvp and SMD/PCM(Pauling)/M05/tzvp//M05/tzvp levels calculated electron affinities, ionization energies, Gibbs free energies of reduction and oxidation, reduction and oxidation potentials of CL-20.

Structure	E_A , eV	ΔG_{red}^0 , eV	E_{red}^0 , eV	I_p , eV	ΔG_{ox}^0 , eV	E_{ox}^0 , eV
CL-20 (gas phase)	-1.60	-1.60	-2.92	9.30	9.30	4.78
CL-20 (aq. solution)	-3.95	-3.88	-0.48, (-0.39) ^a	4.94	4.99	0.63

^aExperimental data taken from ref. Uchimiya et al., 2010.

In addition, according to Pourbaix diagram of an iron/water system (Pourbaix, 1974) the Fe(II)/Fe(III) couple and metallic iron are not able to reduce CL-20 under natural conditions at neutral pH (Fig.S4, SI). Experimental evidence completely supports calculated data indicating that Fe⁰ and dissolved Fe²⁺ ions were not responsible for the degradation of CL-20 (Balakrishnan et al., 2004b). In alkaline conditions (pH>9) iron (II) hydroxide is capable of reducing CL-20, while mixed iron (II,III) oxide provides sufficient reducing potential for CL-20 at very high pH>11. Reduction of CL-20 under natural conditions may be performed, for instance, by surface-bound Fe²⁺ (Balakrishnan et al., 2004b). The CL-20 molecule also undergoes aerobic and anaerobic biotransformation mainly

by enzyme catalyzed one-electron reduction to form an anion-radical of CL-20 which eventually undergoes spontaneous denitration, ring-cleavage, and decomposition to end products (Hawari et al., 2006). Our calculations (Table 4) show that in case of absence of adsorption, (for example, in pure dissolved state), oxidation of CL-20 may be accomplished, for instance, by advanced oxidation processes that involves generation of strong oxidant species with oxidation potentials larger than 0.63 eV such as hydroxyl radical ($E_{ox}^0=2.80$ eV), atomic oxygen ($E_{ox}^0=2.42$ eV), etc. (Loures et al., 2013).

4. Conclusions

The present study sheds new light into the nature of binding of CL-20 with organic component of soil. Structures and energetics of adsorbed complexes of CL-20 on deprotonated LHA were modeled at M05/tzvp level. Calculations show formation of C-H $\cdots$ OOC, C-H $\cdots$ O=C, and NO $\cdots$ H-C_{Ar} hydrogen bonds between CL-20 and LHA anion. According to topological analysis of electron density these H-bonds may be classified as noncovalent closed-shell interactions. Inability of CL-20 to be reduced or oxidized in adsorbed state explains experimentally observed retardation of the onset of abiotic and biotic degradation and decrease of the degradation rate of CL-20 in soil. These findings will assist the assessment of environmental behavior and ecological risk of CL-20.

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