

Adsorption of 1,3,5-Trinitrobenzene on the Siloxane Sites of Clay Minerals: Ab Initio Calculations of Molecular Models

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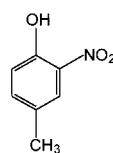
The interaction of 1,3,5-trinitrobenzene (TNB) with the basal siloxane surface of clay minerals is studied by ab initio computations of molecular models at the SCF, DFT (B3LYP), and MP2 levels of theory. A series of progressively increasing basis sets is used from the 6-31G up to the 6-311+G(d) set of atomic orbitals. Two molecular models are considered which correspond to the coplanar orientation of TNB with respect to the siloxane layer at the SiO₄ tetrahedra and the hexagonal ring. The calculations show that the basis set superposition error (BSSE) corrected DFT binding energy (E_b) of TNB at these surface sites is well approximated by the Coulombic contribution to this energy (CE_b). (CE_b is evaluated by the DFT calculations of TNB in the electric field of these sites mimicked via the electrostatic potential derived charges). This result rules out the earlier proposed hypothesis of the electron donor–acceptor mechanism of the adsorption. The smallest molecular model, the TNB at the SiO₄ tetrahedra, is computed using both the DFT and MP2 approximations. Three positions of TNB relative to this site are examined which can be obtained from each other by the rotation of TNB around the perpendicular to the surface crossing the center of the TNB ring. For this model the DFT method underestimates E_b compared to the MP2 method by a factor of ~ 3 . We infer from this result that the main contribution to the stabilization of TNB at the siloxane sites is given by the dispersion interaction which is included by the MP2 calculations. The averaged difference in MP2 E_b between the considered positions of TNB at the SiO₄ tetrahedra is small (7 kJ/mol) in comparison with the averaged MP2 E_b (38 kJ/mol). This result suggests that the interaction of TNB with the basal siloxane surface is substantially nonspecific in nature, the energetically optimal arrangement of TNB with respect to the surface being governed by the balance between favorable dispersion and electrostatic forces, and repulsive exchange forces.

Introduction

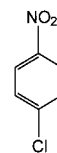
Nitroaromatic compounds (NACs) are widely used as pesticides, herbicides, solvents, explosives, and intermediates in the synthesis of dyes.^{1–3} Many of these compounds and their transformation products are ubiquitous environmental pollutants of significant toxicological concern.^{4,5} The development of efficient technologies which can expedite the remediation of NAC contaminants has recently raised considerable public attention.^{6,7} Experimental studies have shown^{3,5,7–9} that the key factor affecting the bioavailability and biodegradability of NACs in subsurface environments is their sorption onto natural clay minerals. Therefore the fundamental chemistry controlling this interaction should be understood for choosing the best strategy to follow in the management of the contaminated soils and sediments.

Systematic experimental studies by Haderlein and co-workers^{3,7,8} propose a novel molecular mechanism for the adsorption of NACs on clays under natural conditions. Unlike the common assumption of the predominant role of exchangeable cations and their water ligands in the adsorption,^{10–13} for the first time great importance was attached to the NAC interaction with the siloxane sites of clays. These authors concluded that this interaction should dominate the adsorption in the presence of

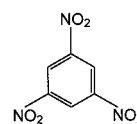
water when the hydration shells of exchangeable cations strongly decrease their accessibility for NACs. The strongest bonding to the siloxane sites was found for planar NACs with several electron-withdrawing substituents, as 4-methyl-2-nitrophenol, 4-chloronitrobenzene, and 1,3,5-trinitrobenzene (TNB). The in-



4-methyl-2-nitrophenol



4-chloronitrobenzene



1,3,5-trinitrobenzene

teraction was postulated to be electron donor–acceptor in nature: NACs (electron acceptors) interact by the electron-deficient π -system toward the oxygen atoms of the siloxane surface (electron donors). The found effect of water on the adsorptional behavior of clays suggests^{7,8} that previous experimental results on the interaction of NACs with clays in organic solvents (cf., for example, refs 10–13) are inapplicable to the sorption under natural conditions.

The empirical theory by Haderlein and co-workers^{3,7,8} is based on the assumption that the siloxane sites play an important role in the adsorption of NACs on clay minerals. As far as we know, no comprehensive quantum chemical analysis of this adsorption mechanism has been carried out. To further investigate this

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interaction, in the present study we perform SCF, DFT, and MP2 calculations of the adsorption of TNB on molecular models of these sites. Our choice of NAC was prompted by a recent investigation of TNB interaction with clays using a series of spectroscopic techniques.⁸ This experimental work further supported the hypothesis^{3,7} of the prevailing role of the siloxane sites in the adsorption.

Details of Calculations

The siloxane sites of clays were modeled within the molecular approach.¹⁴ Numerous quantum chemical studies (refs 14, 15, and references therein) have shown this approach to be adequate for describing adsorption on oxide surfaces. As is generally accepted for silica and silica-containing oxides,^{14,15} the “dangling” valences of the border oxygen atoms of the silicon–oxygen clusters were saturated with H atoms.

Calculations were performed with the GAUSSIAN-94 package¹⁶ using the 6-31G, 6-31G(d), 6-31+G(d), 6-311G(d), 6-311G(df,p), and 6-311+G(d) basis sets. For the geometry optimization the SCF and DFT methods were employed. The binding energies were computed at the DFT, DFT//SCF, and MP2//SCF levels. For the DFT calculations, the hybrid B3LYP functional¹⁷ is used which is a parametrized combination of the Becke’s exchange functional,¹⁸ the Lee, Yang, and Parr’s correlation functional,¹⁹ and the exact exchange. Corrections to the binding energies for the BSSE were estimated by the counterpoise method.²⁰ Electrostatic potential energy derived net charges (PED) were computed at the SCF level by means of the GAUSSIAN-94 POP=CHLPG option which utilizes the Breneman–Wiberg approximation.²¹

The geometry of TNB and its position with respect to the surface is fully optimized within the adopted symmetry constraints. The silicon–oxygen clusters mimicking the siloxane sites were constructed of SiO_4 tetrahedra with the Si–O bond length being equal to 1.61 Å, the average value for clay minerals.^{22,23} The H atoms modeling the interaction of the border O atoms with the Si atoms of the lattice lie on the corresponding “broken” O–Si bonds, the O–H bond length being equal to 0.95 Å. The effect of the interaction on the surface geometry was neglected, i.e., the geometry of the surface clusters were not optimized. This inclusion of the surface is in line with the usual methodology for molecular modeling of adsorption on oxides (refs 14, 15, 24–26 and references therein).

Results and Discussion

The siloxane surface of clays is composed of SiO_4 tetrahedra which share three corners each (the basal oxygens) with neighboring tetrahedra to form an hexagonal mesh pattern²⁷ (Figure 1). The fourth corner of each tetrahedra (the apical oxygen) is linked to a layer of the edge-sharing TO_6 octahedra (T normally is Mg, Al, or Fe) which causes the siloxane surface to be planar. For the majority of natural clays, a considerable amount of Si atoms in the siloxane layer (from 5 to 10%) is replaced by Al atoms^{8,27} with alkali exchangeable cations being added to compensate for the negative charge of the AlO_4 tetrahedra. The siloxane sites of these clays are represented by the relatively small “pure siloxane regions” of the basal surface composed of about 6–12 SiO_4 tetrahedra.⁸ These siloxane microplanes are surrounded by the exchangeable cations bonded to the neighboring AlO_4 tetrahedra. The adsorptional properties of these sites may be affected by many factors: the microplane size, the nature of exchangeable cations and their hydration shells, the nature of T atoms of the adjacent octahedral layer, the stacked layer when the adsorption takes place in the

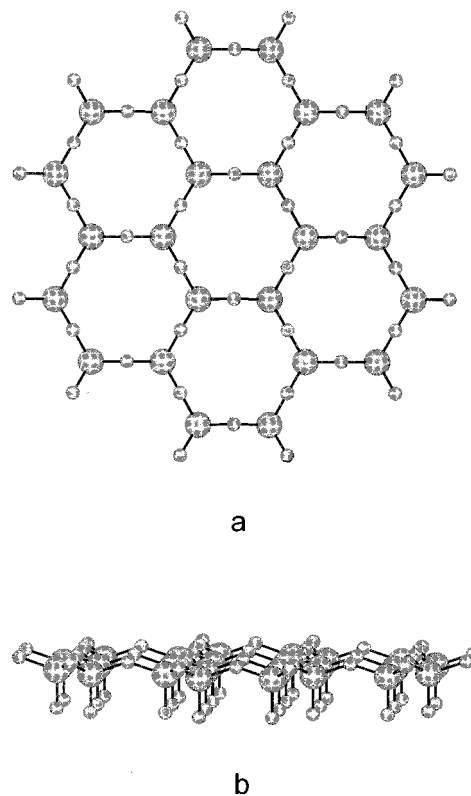


Figure 1. Top a and front b view of an idealized sheet of siloxane surface.

interlayer space, etc. However, the fact that NAC adsorption on clays with substantially different structures and compositions has been successfully rationalized in terms of an interaction with the same siloxane site^{3,7,8} implies that all of these factors are of secondary importance compared to the interaction with the “site” itself. Therefore in our quantum chemical study we consider the interaction of TNB with the siloxane sites. The effect of the above-mentioned factors can be taken into account when the interaction with these sites is understood in details.

An analysis of the diroic properties of IR bands of TNB on K^+ -hectorite by Haderlein and co-workers⁸ has verified their hypothesis^{3,7} of the coplanar orientation of TNB with respect to the surface for the adsorption of TNB on the siloxane sites. Figure 2 shows two molecular models (**1a** and **1b**) which we employed for the analysis of this adsorption. They correspond to the superimposition of TNB on the SiO_4 tetrahedra and the hexagonal ring of the surface (Figure 1), respectively.

In Table 1, for model **1a** we report the SCF, DFT//SCF, BSSE corrected DFT//SCF binding energies, and the SCF vertical distances (VD) between the siloxane surface and TNB. The difference between the related SCF and DFT//SCF binding energies is small, suggesting that the inclusion of electron correlation within the DFT approximation does not significantly affect E_b . The BSSE correction decreases the binding energy by a factor of ~ 2 , which implies that for an accurate description of the adsorption the BSSE is to be considered. The BSSE corrected binding energies computed with the basis sets augmented by polarization functions, namely the 6-31G(d), 6-311G(d), and 6-311G(df,p) basis sets, are smaller by ~ 7 kJ/mol than that calculated with the 6-31G basis set. As we will show below, the BSSE corrected DFT//SCF binding energy is dominated by electrostatics. Therefore we explain this result by a more accurate description of the electron distribution when including the polarization functions. The extension of the basis set from the 6-31G(d) to the 6-311(df,p) set of basis functions

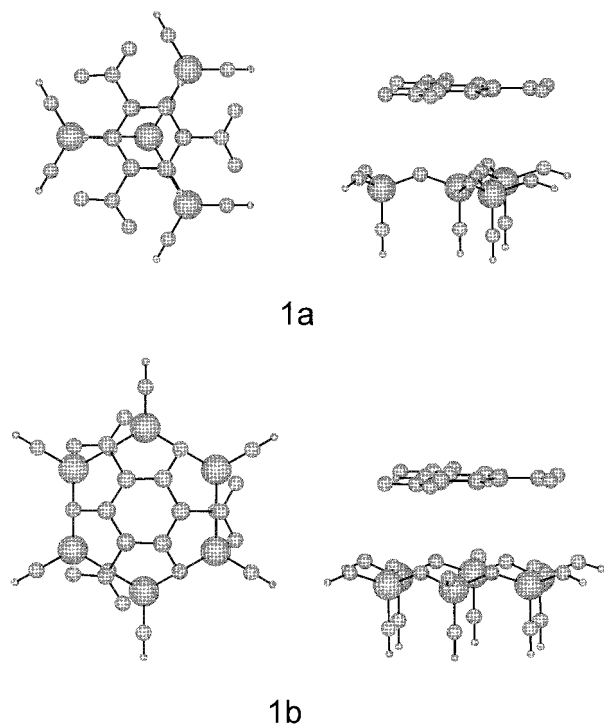


Figure 2. Molecular models of the TNB adsorption at the SiO_4 tetrahedra (**1a**) and the hexagonal ring (**1b**) of the siloxane surface. (left) Top and (right) front views.

TABLE 1: SCF, DFT//SCF, and BSSE Corrected DFT//SCF Binding Energies E_b (kJ/mol), Vertical Distance between TNB and the Siloxane Surface VD (Å)

basis set	$E_b(\text{SCF})$	$E_b(\text{DFT})$	$E_b(\text{DFT})^a$	VD
6-31G	44	39	24	3.3
6-31G(d) ^b	29	27(28)	17(17)	3.5(3.3)
6-311G(d)	31	28	18	3.5
6-311G(df,p)	29	27	16	3.5

^a Corrected for BSSE. ^b B3LYP/6-31G(d) values in parentheses.

TABLE 2: BSSE Corrected DFT//SCF/6-31G(d) Binding Energy $E_b(\text{DFT})$ (kJ/mol), Contribution of Coulombic Interaction to the Binding Energy CE_b (kJ/mol), and the SCF/6-31G(d) Vertical Distance between TNB and the Siloxane Surface VD (Å)

model	$E_b(\text{DFT})$	CE_b^a	VD
1a	17	16	3.5
1b	15	18	3.4

^a Evaluated by DFT//SCF calculations of TNB in the electric field of the surface models.

marginally changes E_b . This conforms to the conclusion by Ugliengo and co-workers,²⁹ that the SCF method with a basis set of double- ζ polarization quality is quite adequate for reproducing molecular electrostatic potentials. Model **1a** was also calculated at the DFT/6-31G(d) level. A comparison of the DFT/6-31G(d) and DFT//SCF/6-31G(d) binding energies (Table 1) shows that the optimization of the geometry by the DFT method increases the binding effect by ~ 1 kJ/mol only. On the basis of these results, we suggest that the BSSE corrected DFT//SCF/6-31G(d) binding energy nearly corresponds to the best accuracy which can be achieved by the adopted DFT approximation for the studied models.

In Table 2 we report the BSSE corrected DFT//SCF/6-31G(d) E_b and the SCF VD for TNB at the hexagonal ring of the surface (model **1b**). For comparison the corresponding values for model **1a** are also presented. As Haderlein and co-workers

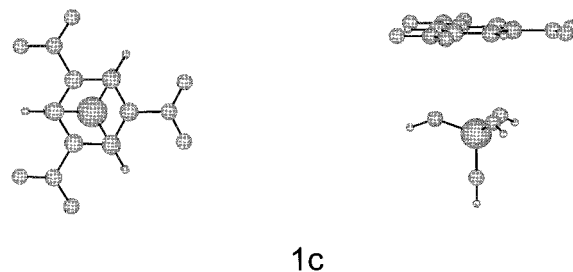


Figure 3. Molecular model (a reduced analogue of model **1a**) used for checking the difference in description the adsorption between the DFT and MP2 methods. (left) Top and (right) front views.

proposed,^{3,7,8} for NACs at the siloxane sites the binding effect is mainly provided by the electron donor–acceptor interaction between the π -system of the NACs (acceptor) and the oxygen atoms of the surface (donor). However, recent theoretical studies^{28–31} show that a significant contribution to the interaction of neutral molecules with non-d oxides is given by electrostatics. To discriminate between these two interactions for the studied adsorption, we computed the Coulombic energy of TNB at both the SiO_4 tetrahedra and the hexagonal ring. The calculations were carried out in the DFT approximation with the 6-31G(d) basis set by means of the GAUSSIAN-94 CHARGE option. The electric field produced by the surface models was simulated by the PED charges of these models centered on the related nuclei positions. The arrangement of TNB with respect to the point charges corresponded to the optimized SCF/6-31G(d) geometry of models **1a** and **1b**. The Coulombic binding energies turn out to be equal to the related BSSE corrected DFT//SCF E_b values ($E_b(\text{DFT})$) within a few kJ/mol (Table 2). Considering the known limitations in modeling molecular electric fields by point charges,^{28–30} one can regard this agreement between the DFT and Coulombic binding energies as very good. Therefore we can consider $E_b(\text{DFT})$ to represent the Coulombic contribution to the binding energy, or

$$E_b(\text{DFT}) = \text{CE}_b \quad (1)$$

Since the DFT methods should cover the electron donor–acceptor interaction, our result implies that the role of this interaction in the studied adsorption is negligible. TNB represents the NACs with strongly electron-deficient π -system. For these compounds the electron donor–acceptor interaction should give the most weighty contribution to the binding effect.^{3,7,8} Therefore, our finding for TNB suggests that this interaction is unimportant for NACs at the siloxane sites of clay minerals in general.

To compare the DFT and MP2 levels of description of the adsorption, we performed DFT//SCF and MP2//SCF calculations of model **1c** (Figure 3) (a reduced analogue of model **1a**) with the 6-31G, 6-31G(d), 6-31+G, 6-31+G(d), 6-311G(d), and 6-311+G(d) basis sets. The $\text{Si}(\text{OH})_4$ moiety of model **1c** cannot be considered as an adequate model of the surface since it is unable to fully accommodate the adsorbed molecule. We use this model to only check the difference between the DFT and MP2 methods when including the electron correlation. Since model **1c** is small, we can compare these two approximations and examine the basis set effect on MP2//SCF E_b ($E_b(\text{MP2})$) with reasonable computational cost. The results of our calculations (Table 3) show that the DFT method systematically underestimates E_b compared to the MP2 method. A similar discrepancy between the DFT (B3LYP) and MP2 results has been found by Sponer and co-workers³² for the stacking interaction in nucleic acid base pairs. They explained this

TABLE 3: BSSE Corrected MP2/SCF Binding Energy E_b (MP2) (kJ/mol), Contributions of Coulombic and Dispersion Interactions to the Binding Energy CE_b and DE_b (kJ/mol), and the SCF Vertical Distance between TNB and Siloxane Surface VD (Å) for Model 1c

basis set	E_b (MP2)	CE_b^a	DE_b^b	VD
6-31G	28	26	2	3.2
6-31+G	33	25	8	3.2
6-31G(d)	25	20	5	3.3
6-31+G(d)	31	21	10	3.4
6-311G(d)	27	22	5	3.3
6-311+G(d)	31	22	9	3.3

^a $CE_b = E_b$ (DFT) (cf. 1). ^b $DE_b = E_b$ (MP2) - CE_b .

difference by the intermolecular correlation energy (dispersion energy) being not included at the DFT level. We suggest that this interpretation is valid also for the interaction in question. Like the overlap of plane nucleic acid bases, superimposition of TNB on the siloxane surface provides maximum overall closeness between the atoms of the interacting partners. Considering that the dispersion energy can be approximated by pair-additive London's potential, in both cases this mode of complexation results in a significant contribution of dispersion interaction to the binding effect. Therefore we conclude that the DFT approximation is inadequate to describe the E_b of TNB at the siloxane sites since it covers only the CE_b contribution to E_b (see above). To include the contribution of dispersion interaction (DE_b) to the binding energy, we will use the MP2 method, assuming

$$E_b(\text{MP2}) = CE_b + DE_b \quad (2)$$

For model **1c** the dependence of E_b (DFT) (CE_b) on the basis set is congruent with our previous analysis for model **1a** suggesting that a basis set of double- ζ polarization quality is sufficient for evaluating CE_b . As the charge distribution related to the basic electronic states is described by the valence-shell atomic orbitals, the effect of the diffuse basis functions on CE_b is insignificant (Table 3). At the same time the diffuse functions affect E_b (MP2) (Table 3). To be precise, these outershell basis functions strongly increase DE_b . As a perturbational treatment of dispersion interaction involves excited electronic states, the inclusion of these basis functions is indispensable for the MP2 calculations of the adsorption.

Theoretical studies^{33–37} show that for aromatic compounds, the MP2 method with large basis sets exaggerates DE_b by 15–30% compared to the CCSD(T) method. This implies that higher order contributions to the intermolecular correlation energy are repulsive. Presently, the computation of the involved models at the CCSD(T) level with an extended basis set is beyond the capabilities of the most of modern computational facilities. However, ab initio calculations^{37–41} have shown that due to a compensation of errors, the MP2 calculations with medium-sized, diffuse-polarization basis sets provide reasonable values of DE_b . Therefore, as a reasonable compromise between accuracy and cost of computation, in the following analysis we use the MP2 method with the 6-31+G(d) basis set. Considering the amount of available computer memory only model **1a** is calculated.

In Table 4 we present the E_b (MP2), CE_b , and DE_b energies for models **1a**, **1a**(30°) and **1a**(60°). Models **1a**(30°) and **1a**(60°) are obtained from model **1a** by rotating the TNB molecule around the symmetry axis for 30° and 60°, respectively. The averaged E_b (MP2) (38 kJ/mol) is in good agreement with the experimental data ($\Delta H_{\text{ads}} \approx -40$ kJ/mol^{3,8}). A comparison of CE_b and DE_b shows that the stabilization of TNB at the siloxane

TABLE 4: BSSE Corrected MP2/SCF/6-31+G(d) Binding Energy E_b (MP2) (kJ/mol), Contributions of Coulombic and Dispersion Interactions to the Binding Energy CE_b and DE_b (kJ/mol), and the SCF/6-31G(d) Vertical Distance between TNB and Siloxane Surface VD (Å)

model	E_b (MP2)	CE_b^a	DE_b^b	VD
1a	39	15	24	3.4
1a (30°)	42	15	27	3.4
1a (60°)	32	10	22	3.7

^a $CE_b = E_b$ (DFT) (cf. 1). ^b $DE_b = E_b$ (MP2) - CE_b .

sites is mainly provided by dispersion interaction. The averaged difference in E_b (MP2) between models **1a**, **1a**(30°), and **1a**(60°) is small (7 kJ/mol) compared to the averaged E_b (MP2) (38 kJ/mol). This result suggests that for the coplanar orientation of TNB with respect to the basal plane the difference in energy between various positions of TNB at the surface is small; this conforms to the nonspecific character of dispersion interaction in general. This also explains the high mobility of TNB adsorbed on the clay minerals as revealed by NMR experimental studies.⁸

The vertical distances between the adsorbed TNB and basal surface (Table 4) approximately correspond to the sum of the van der Waals radii of the C and O atoms (~ 3.2 Å). This is the minimum VD allowed by the exchange repulsion between the outer-shell electrons of the aromatic π -system of TNB and the oxygen atoms of the basal layer. Therefore we conclude that the optimal arrangement of TNB with respect to the siloxane surface is governed by the balance between favorable dispersion and electrostatic forces, and repulsive exchange forces.

Conclusion

To summarize, our ab initio calculations of TNB at the siloxane sites of clays suggests that the complexation of NACs with these sites is mainly governed by dispersion interaction. The estimated binding energy is in good agreement with the experimental adsorption enthalpy of ~ -40 kJ/mol. As far as we know, such a strong dispersion interaction of a neutral molecule with siloxane sites has never been described in the literature. The large contribution of dispersion interaction to the binding effect is accounted for by the planar structure of both the NACs and the siloxane surface. Due to the pair-additive character of the attractive dispersion interaction between the atoms of two interacting partners, the superimposition of plane NACs on the siloxane layer results in a strong stabilization effect. Considering that dispersion interaction is short-range in nature, this explains the stronger binding of planar NACs compared to those with branched alkyl substituents;^{3,7} the nonplanarity hinders the maximum closeness of the molecules to the surface. Our findings imply that the previous interpretations of the adsorption in terms of the electron donor–acceptor interaction between the electron-deficient π -system of NACs and the siloxane oxygens^{3,7,8} should be reconsidered.

The predominant role of the short-range dispersion interaction in the adsorption justifies the use of small molecular models of the siloxane surface in our study.

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