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Modelling of Aniline-Vermiculite and Tetramethylammonium-Vermiculite; Test of Force Fields

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Abstract Molecular mechanics simulations in Cerius[2] have been used for modelling vermiculite intercalated with tetramethylammonium and aniline cations. The published structure data obtained for these intercalated structures from X-ray single crystal diffraction have been used to test the force fields and modelling strategy for organo-clays. The strategy of modelling was based on the nonbond host-guest interactions and on rigid silicate layers and rigid guest species. The rigidity of silicate layers requires that the cell parameters a, b and γ are kept fixed during the energy minimisation. The energy term was set up using the nonbond interaction terms only and the Crystal Packer module in Cerius[2] has been used for the energy minimisation. In Crystal Packer the rigid units, i.e. the silicate layers and guest species can be translated and rotated during energy minimisation and the cell parameters c, α, and β have been varied. Three sets of Van der Waals (VDW) parameters available in Crystal Packer: Tripos, Universal and Dreiding have been used in present molecular simulations. A*b initio* MP2 calculations were performed to justify the application of the force field. The best agreement of molecular mechanics simulations with both: experimental and *ab initio* data was obtained with the Tripos VDW parameters for both intercalates. The results of modelling are in good agreement with the experimental data as to the cell parameters and the interlayer packing. The cell parameters reported by Vahedi-Faridi and Guggenheim (1997) for tetramethylammonium-vermiculite are: c = 13.616 Å, α = 90°, β = 97.68° ; from the present modelling we obtained: c = 13.609 Å, α = 90.19°, β = 97.56°. Tetramethylammonium-cations are arranged in one layer in the interlayer space. One C-C edge of NC_4 tetrahedra is perpendicular to the silicate layers. The deep immersion of the methyl groups into the ditrigonal cavities suggested by Vahedi-Faridi and Guggenheim was not confirmed by modelling. Slade and Stone (1984) presented the measured cell parameters for aniline vermiculite: c = 14.89 Å, α = 90°, β = 97°; present result is: c = 14.81 Å, α = 90.72°, β = 96.70° for partially exchanged vermiculite and c = 14.84 Å, α = 90.53°, β = 97.17° for fully exchanged vermiculite. The aniline cations are positioned over the ditrigonal cavities alternating in their anchoring to lower and upper silicate layer. The C-N bonds are perpendicular to layers.

Keywords Vermiculite, Intercalate, Aniline, Tetramethylammonium, Molecular mechanics

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Introduction

Organo-clays intercalated with organic cations are attracting increasing attention because of their possible applicability in many different fields. They are potentially useful as sorbents, catalysts, molecular sieves, ion conductors etc. Recently a new application has emerged: organo-clays can be used as a matrix for the immobilisation of photoactive organic species in their interlayer space. The construction of ordered molecular assemblies in the interlayer space is a way of producing new photofunctional supramolecular systems [1 - 3].

Knowledge of the structure is crucial for the understanding of the physical and chemical properties of intercalated clays. It is evident that the interlayer structure is especially important in the case of selective sorbents, but the characteristics of photoprocesses are also very sensitive to the environment, in which the photoactive species are adsorbed. That means that structure investigation plays a key role in the development of new materials based on intercalated clays. However, the structure analysis of intercalated clays based on the conventional diffraction analysis is extremely difficult, especially in the case of smectites, see [4,5]. Samples are usually available in powder form only and the powder diffraction pattern is efected by disorder in interlayer structure and disorder in layer stacking. In addition, there is also a strong preferred orientation, which can obstruct the diffraction analysis of structure. In such a case molecular simulations represent a very powerful complementary tool to diffraction methods in structure analysis of intercalates.

In order to obtain reliable results from molecular modelling of difficult unknown structures, it is important to test the modelling strategy and force field parameters using published structure data, obtained from single crystal diffraction for similar or related structures. For this purpose we have choosen two examples of known structures:

• tetramethylammonium-vermiculite (TMA-vermiculite); this structure has been solved by A. Vahedi-Faridi and S. Guggenheim [6] using single crystal diffraction data.

• aniline-vermiculite structure, solved by P.G. Slade and P.A.Stone [7,19] from single crystal diffraction data.

Modelling of these two intercalated structures has been carried out in the Cerius[2] modelling environment, using molecular mechanics simulations in Crystal Packer module. Three different sets of Van der Waals parameters (VDW) in Crystal Packer: from Tripos [8], Universal [9] and Dreiding force field [10] have been tested and the results of modelling are compared with experimental data. The agreement of calculated and measured structure parameters was good for both intercalates.

Special attention was paid to the anchoring of methyl groups to silicate layers. The interaction energy between the tetramethylammonium cations and the silicate layer was investigated depending on their mutual distance. Two different approaches have been utilised: (1) molecular mechanics calculations with different force fields, and (2) quantum chemistry *ab initio* method based on MP2 correlation energy. Comparison of *ab initio* data with the results of molecular mechanics calculations were used to test the VDW parameters from three different force fields: Tripos, Universal and Dreiding.

Modelling strategy

The host-guest interactions in phyllosilicates, intercalated with organic and anorganic cations are of a non-bonded nature. This generally accepted opinion is based on the character of the intercalation reaction (an ion exchange) and confirmed by vibrational spectroscopic measurements [11]. This is also the basic assumption in the modelling strategy. The rigidity of silicate layers during intercalation has been found to be a reasonable approximation for modelling in previous work [11-14]. The assumption of rigid layers is supported by vibrational spectroscopy and by diffraction measurements (see for example the comparison of cell parametrs *a, b* for Llano vermiculite natural [15] and Llano vermiculite intercalated with different organic species [6,7,16]). Assuming rigid layers and rigid guest cations, we can use the Crystal Packer module in the Cerius[2] modelling environment, which leads to significant reduction of CPU time for the calculations.

Crystal Packer is a computational module that estimates the total sublimation energy and packing of molecular crystals. Energy calculations in Crystal Packer only take into account the non-bond terms, i.e. van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (H-B), internal rotations and hydrostatic pressure. The asymmetric unit of the crystal structure is divided into fragment-based rigid units. Non-bond (VDW, COUL, H-B) ener-
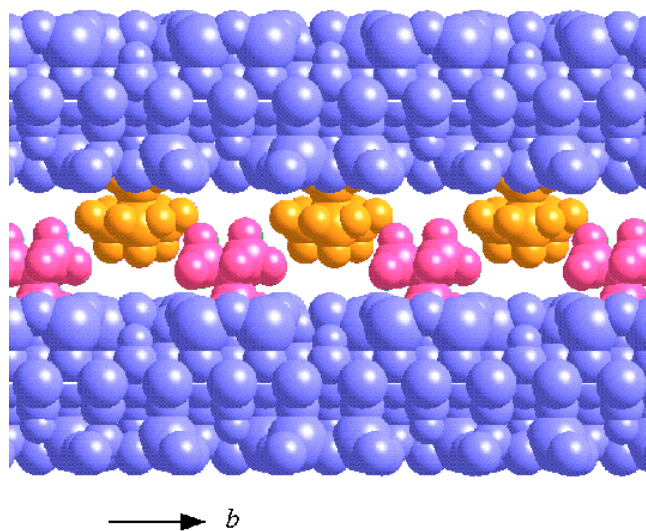

Figure 1 *Crystal packing in the interlayer space of TMA-vermiculite according to the model suggested by Vahedi-Faridi and Guggenheim [6]*

gies are calculated between the rigid units. During the energy minimisation, the rigid units can be translated and rotated and the unit cell parameters varied.

The hydrogen-bond term was a CHARMm-like angle-dependent potential with Dreiding parameters. The Ewald summation method is used to calculate the Coulombic energy in a crystal structure [17]. The Ewald sum constant was 0.5 Å^{-1}. The minimum charge taken into the Ewald sum was 0.00001e. All atom pairs with separations less than 10 Å were included in the real-space part of the Ewald sum and all reciprocal-lattice vectors with lengths less than 0.5 Å^{-1} were included in the reciprocal part of the Ewald summation. Charges in the crystal are calculated in Cerius^2 using the QEq-method (Charge equilibrium approach). This method is described in details in the original work [18]. For VDW we used the well known Lennard-Jones functional form, with the arithmetical radius combination rule. A non-bond cut-off distance for the VDW interactions was 7.0 Å. There are three force fields available in Crystal Packer for VDW parameters:Tripos [8], Universal [9] and Dreiding [10]. All three sets of VDW parameters have been used in our calculations and the results calculated with different VDW parameters were compared with the experimental results. As the Dreiding force field does not include the VDW parameters for Fe/Mg-atoms, we used the Dreiding VDW parameters combined with Universal VDW parameters for Fe and Mg.

The Tripos force field is fully described in [8], where the authors present the test of all force field parameters for bond and nonbond terms, comparing the calculated molecular geometries with the X-ray molecular structures for 76 diverse organic crystal structures in Cambridge Structural database.
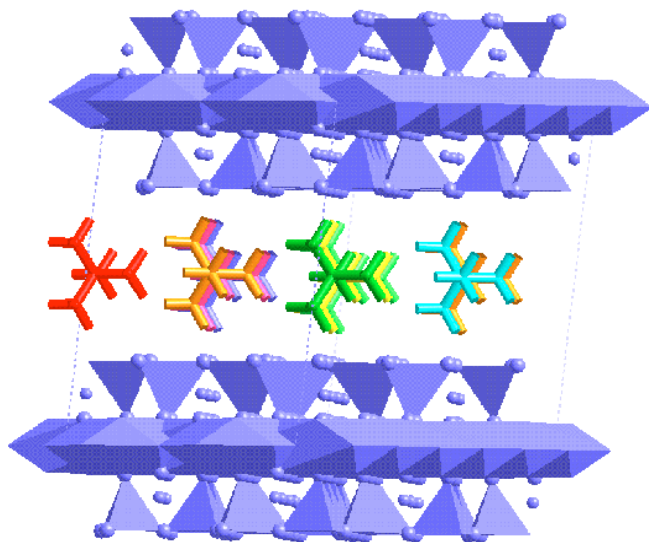
The Tripos force field test in [8] was focused to the distortions of the overal-shape of molecules i.e. the bond distances, angles, torsions and the authors have found that the results were superior when the electrostatic term was not used. However no tests have been performed to compare the calculated and experimental crystal packing using only the non-bond interactions. The main aim in the present work is the crystal packing in the interlayer space of intercalates. This crystal packing is dominated by the non-bond interactions. Therefore, in the present modelling we used the Tripos VDW parameters in an energy term including also Coulombic interactions, in spite of the conclusion in [8] that the best fit of molecular shape was achieved by omitting the electrostatic term.

Initial models for both structures have been built using the published structure data [6,7]. According to the procedure recommended by authors of Cerius^2, the first minimisation has been carried out using external pressure, to find the minimum. Then the pressure was released and new minimisation started. In general, this procedure can be repeated in combination with the systematic translations or rotations of guest species in the initial model. The optimum value of high extrernal pressure must be estimated by trials for every individual intercalating species.

Modelling of tetramethylammonium-vermiculite

The initial model of tetramethylammonium-vermiculite (TMA-vermiculite) was built according to structure data published by by A. Vahedi-Faridi and S. Guggenheim [6]: space group *C2/m* with the cell parameters $a = 5.353$ Å, $b = 9.273$Å, $c = 13.616$ Å and $\beta = 97.68°$. The host structure was vermiculite from Santa Olalla, Spain, exchanged with Na$^+$. The structural formula of silicate layer was: $(Si_{5.48},Al_{2.52})(Mg_{5.05}Ti_{0.03},Mn_{0.01}Fe^{III}_{0.58}Al_{0.28})O_{20}(OH)_4$. In order to create a supercell of a reasonable size for modelling, we had to simplify the structure formula of one unit cell to the form: $(Si_{5.5},Al_{2.5})(Mg_{5.5}Fe^{III}_{0.25}Al_{0.25})O_{20}(OH)_4$ with the layer charge (-2).

The supercell *2a* x *2b* x *1c* was created with the supercell parameters:

$A = 2a = 10.706$ Å, B = 2b = 18.545 Å, C = c = 13.616 Å and $\beta = 97.68°$ and with supercell formula: $(Si_{22}Al_{10})(Mg_{22}Fe^{III}Al)O_{80}(OH)_{16}$. To compensate the layer charge -8 in this supercell, eight singly charged TMA cations $[N(CH_3)_4]^+$ were placed into the supercell and arranged according to model suggested by Vahedi-Faridi and Guggenheim (VF-G model) [6]. A view of this structure is shown in Figure 1. TMA cations in this model are in two partially overlapping layers in the interlayer space. The tetrahedral apex of each TMA cation is fixed to a silicate ring centre. One face of the NC$_4$ tetrahedra is parallel to the silicate layers. The VDW radius has been used in a ball display of individual atoms in Figure 1, to visualise how deeply the methyl groups are keyed into the silicate rings in this VF-G model [6].

Figure 2 *Calculated arrangement of TMA cations in the interlayer space of vermiculite as a result of the present modelling. Projection into a plane close to 110*

Table 1 *Experimental cell parameters for TMA-vermiculite, compared with the calculated values for different VDW force field parameters. Experimental values were obtained from* *X-ray single crystal diffraction data [6] (VF-G model). The cell parameters a=5.353 Å, b=9.273Å and γ=90° were fixed during energy minimisation*

Structure parameters for TMA-vermiculite				
	c (Å)	α (°)	β (°)	d (Å)
experiment	13.616	90.00	97.68	13.494
VDW-Tripos	13.609	90.19	97.56	13.490
VDW-Universal	13.848	90.16	97.44	13.731
VDW-Dreiding	14.009	90.18	97.34	13.894

For the energy minimisation, nine rigid units have been assigned to this initial model: eight TMA cations and a silicate layer. The energy term consists of non-bond interactions between rigid units. The rigidity of the silicate layers during intercalation requires the following constraints for energy minimisation: the cell parameters *a*, *b* and γ must be fixed. The first minimisation of this initial model without external pressure led to an unrealistic *c*- parameter and basal spacing, higher than 16 Å. We therefore used an external pressure of 50 kbar in the first minimisation. Afterwards the pressure was removed and a new minimisation was started. All three sets of VDW parameters available in Cerius[2] - Crystal Packer i.e Tripos, Universal and Dreiding have been used in present modelling. The best agreement of the calcu-

Figure 3 *Arrangement of TMA cations in the interlayer space and illustration of layer stacking in projection into* ab *plane. Dark blue polyhedra display the tetrahedral sheet of lower silicate layer, light blue cylinders illustrate the tetrahedral sheet of upper silicate layer*

lated structure parameters with the experimental X-ray diffraction data was obtained with the Tripos VDW parameters. These results are presented in Table 1 and compared with experiment. The total sublimation energy per one supercell $E_S = 1016$ kcal consists of the electrostatic contribution $E_S = 964.8$ kcal and VDW contribution $E_{VDW} = 51.2$ kcal.

Figure 2 shows the the best minimised model (Tripos). As one can see TMA cations are arranged in one layer. One C-C edge of the NC_4 tetrahedra is perpendicular to the layers. The ordering and orientation of cations in the interlayer is visualised in Figure 3, in a view perpendicular to the layers. The tetrahedral sheet adjacent to TMA in lower silicate layer is dark blue (display style: polyhedra). The adjacent tetrahedral sheet in upper layer is light blue (dispay style: cylinders). Figure 3 also shows clearly the mutual positions of two successive silicate layers, with the ditrigonal cavities opposite each other. This regular layer stacking is in agreement with the experimental diffraction data presented in [6] (VF-G model), where the perfect 3-dimensional periodicity has also been reported for TMA-vermiculite.

The CH_3 groups in our model are not so deeply keyed into the ditrigonal cavities, as suggested by Vahedi-Faridi and Guggenheim (VF-G model) [6] (see Figure 1). This is the main difference between these two models. In fact all the force fields strongly rejected this deep immersion of the methyl group into the silicate layer. The nitrogen atoms in our model are positioned just in the middle of the interlayer space. In fact, the positions of nitrogen atoms in VF-G model correspond to the positions of carbons in C-C edge, perpendicular to layers in our model. The z/c atomic coordinate for N in VF-G model is ~ 0.39. The z/c atomic coordinate for C in our model is ~ 0.41. Our model leads to the maximum interlayer electron density in the middle of the interlayer space, as well as the VF-G model. Taking into account the difficulties in the interpretation of smeared experimental electron density maps in the interlayer space, we can conclude that our model of interlayer packing agrees with the main features of the experiment.

Figure 4 shows the crystal packing in the interlayer in our calculated model, where the atoms are displayed using their VDW radii. Figure 4a illustrates the positions of methyl groups with respect to silicate layers (projection in the *bc* plane), Figure 4b shows the density of TMA cations in projection into the *ab* plane.
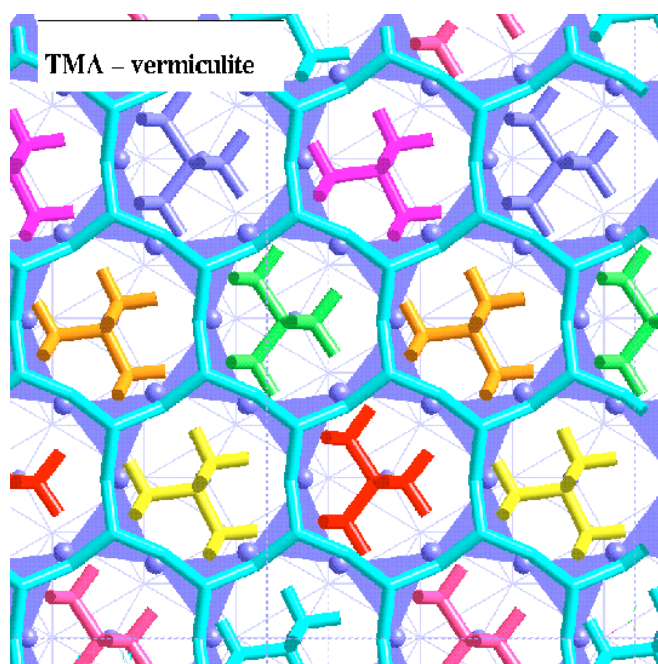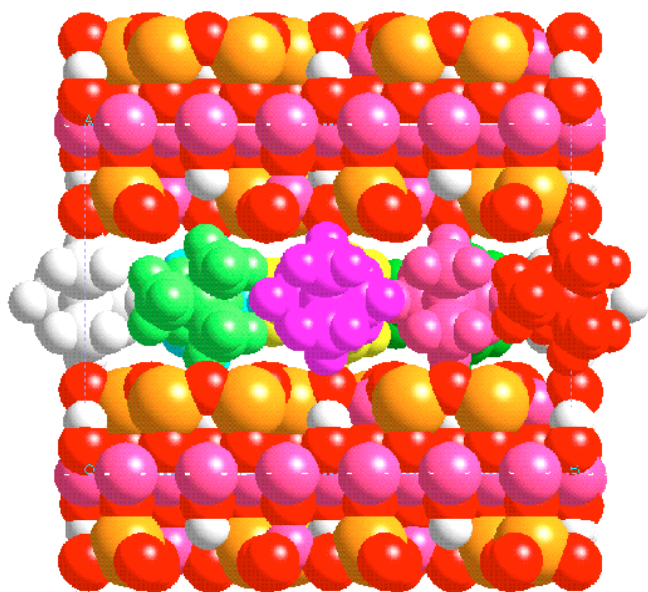
Figure 4a *The calculated crystal packing density in TMA-vermiculite illustrated using VDW radii of atoms: side view along the* a *axis*
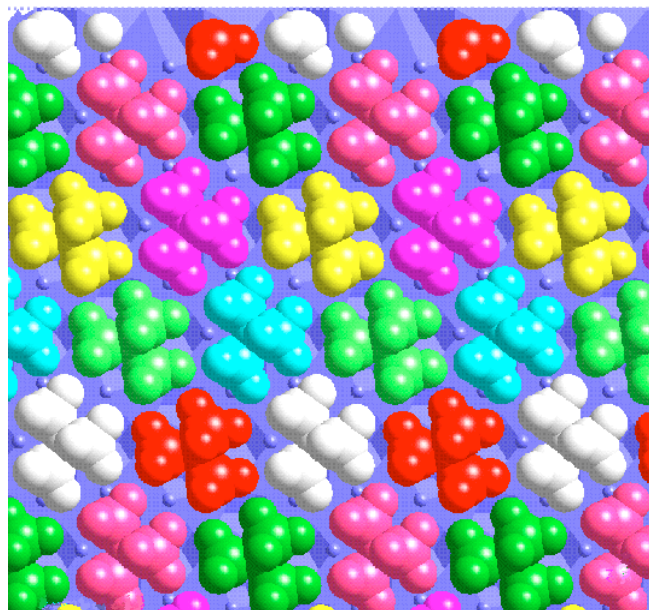

Figure 4b *The calculated crystal packing density in TMA-vermiculite illustrated using VDW radii of atoms: upper view along direction perpendicular to the layers*

The results of energy minimisation with Universal and Dreiding force fields showed the same arrangement of TMA cations in the interlayer space but worse agreement with the experimental cell parameters. The results obtained with all three force fields, are summarised in Table 1.

Modelling of aniline-vermiculite

The structure data presented by Slade and Stone [7,19] were used for building of the initial model of aniline-vermiculite: space group *C2/m* with the cell parameters $a = 5.33$ Å, $b = 9.268$Å, $c = 14.89$ Å and $\beta = 97°$. The host structure was Na-saturated Llano vermiculite from Llano County, Texas. The structural formula of the silicate layer was: $(Mg_{5.62}Al_{0.16}Fe^{III}_{0.13}Ti_{0.04}Mn_{0.01})(Si_{5.79}Al_{2.21})O_{20}(OH)_4$. In order to create a the supercell of reasonable size for modelling, we had to simplify the structure formula of one unit cell, taking into account not only the layer charge, but also the reported C and N content in the intercalate. There was a certain discrepancy between the layer charge and nitrogen and carbon content estimated in [7,19] (Slade and Stone 1983) leading to the conclusion that the Na-vermiculite was not fully exchanged with aniline. Taking into account this uncertainty in the cell content, we built two initial models:
- *Model-I:* The supercell *2a* x *1b* x *1c* with the simplified layer formula: $(Mg_{12})(Si_{14}Al_2)O_{40}(OH)_8$ carries the charge -2. This formula represents a reasonable approach to the partially exchanged vermiculite with only one aniline cation $[C_6H_5NH_3]^+$ in a single layer cell. To compensate the layer charge two aniline cations have been placed into this *2a* x *1b*

x *1c* supercell, thus three rigid units have been assigned to this model.
- *Model-II:* Two aniline cations have been placed into the single unit cell with the layer formula $(Mg_6)(Si_6Al_2)O_{20}(OH)_4$, carrying the charge -2 and corresponding to the fully exchanged vermiculite.

Results for Model-I, with one aniline cation in a single unit cell

This model represents a partially exchanged vermiculite. In this case the first minimisation without higher external pressure led to a reasonable result, illustrated in Figure 5. The aniline cations are positioned over the ditrigonal cavities in the silicate layers to which the C-N bonds are perpendicular. The aniline cations alternate in anchoring their terminal NH_3^+ groups to the lower and upper silicate layers. The three amine-hydrogen atoms of aniline are involved in hydrogen bonds to the surface oxygens in adjacent silicate layers. The best agreement with the experimental structure model (Slade and Stone model [7,19]) was obtained with the Tripos force field VDW parameters. A comparison of calculated cell parameters for aniline vermiculite with the experimental structure data of Slade and Stone [7,19] (Slade-Stone model) is presented in Table 2. The total sublimation energy per one supercell *2a* x *1b x 1c* for the best minimised model (VDW-Tripos) is $E_S = 467.4$ kcal. The VDW, Coulombic and HB contributions to the total sublimation energy are: $E_{VDW} = 23.3$ kcal, $E_{COUL} = 428.0$ kcal, $E_{HB} = 16.1$ kcal.

Table 2 *Comparison of cell parameters for aniline-vermiculite. Experimental values were obtained from x-ray single crystal diffraction data [7,19] (Slade and Stone 1984). The calculated values have been obtained by modelling us-* *ing Cerius² Crystal Packer with the VDW parameters from different force fields for Model-I (partially exchanged vermiculite), Model-II (fully exchanged vermiculite)*

Structure parameters for Aniline-vermiculit		c (Å)	α (°)	β (°)	d (Å)
experiment		14.89	90.00	97.00	14.78
VDW-Tripos	*Model-I*	14.81	90.72	96.70	14.71
VDW-Tripos	*Model-II*	14.84	90.53	97.17	14.72
VDW-Universal	*Model-I*	15.04	90.25	97.19	14.92
VDW-Universal	*Model-II*	15.28	90.69	97.94	15.13
VDW-Dreiding	*Model-I*	15.16	90.34	97.11	15.04
VDW-Dreiding	*Model-II*	15.42	90.78	97.90	15.27

The arrangement of aniline cations in the interlayer space and the mutual positions of two successive silicate layers are illustrated in the Figure 6. (Green cations are anchored with their NH_3^+ group to upper layer and dark red to lower layer.) The ditrigonal cavities in adjacent silicate layers are positioned opposite to each other and this order in layer stacking is controlled by the well defined positions of the aniline cations. This regular layer stacking has been also confirmed by diffraction measurements, in the Slade-Stone model [7,19].

The average N-O distance (averaged over 6 oxygens surrounding the adjacent ditrigonal cavity) in our calculated model d_{N-O} is 3.01 Å; in the experimental Slade-Stone model model d_{N-O} = 3.03 Å. The results of energy minimisation with VDW parameters from the Universal and Dreiding force field led to the same arrangement of aniline cations, but to worse agreement with the experimental cell parameters and basal spacing, as shown in Table 2.
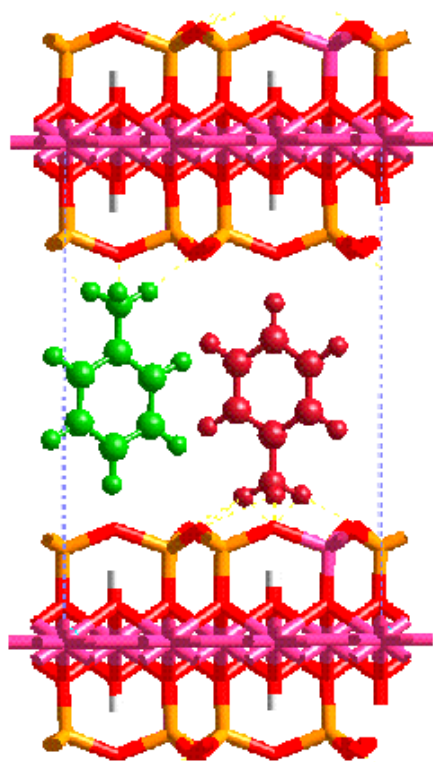

Figure 5 *Anilin-vermiculite Model-I: calculated positions of aniline cations in the interlayer space of vermiculite*
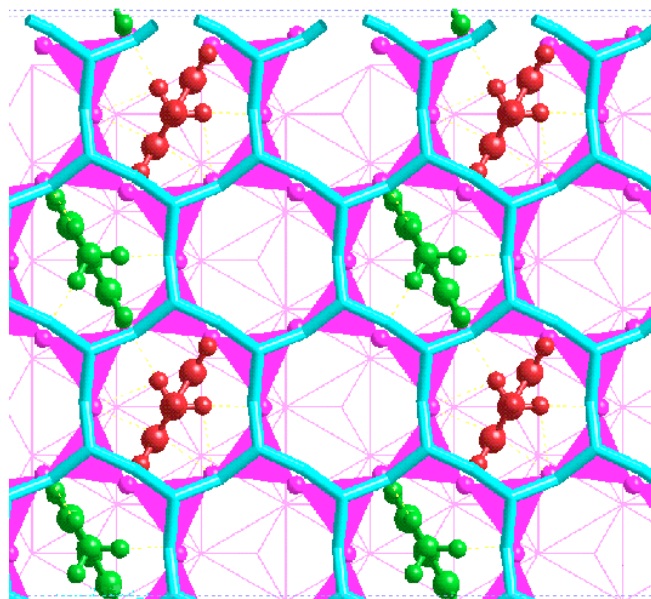

Figure 6 *Arrangement of aniline cations in the interlayer space of partially exchanged vermiculite (Model-I) . Projection into* ab *plane shows the mutual positions of two successive silicate layers. The purple polyhedra display the tetrahedral sheet of lower silicate layer, light blue cylinders illustrate the tetrahedral sheet of upper silicate layer. Green cations are anchored with their NH_3^+ group to upper silicate layer, the dark red cations to lower silicate layer*

Results for Model-II, with two aniline cation in single unit cell

This model corresponds to a fully exchanged vermiculite. An external pressure of 5kbar was found as optimum for the first minimisation. The second minimisation with normal pressure 0.001kbar led to the results summarised in Table 2. The same positions and orientations of the aniline cations with respect to the silicate layers, shown in Figure 5 was found in both models: *Model -I* and *Model-II*. This arrangement of aniline cations corresponds very well to the electron density map obtained from single crystal diffraction data, by Slade and Stone (1984) [7,19]. A view of interlayer packing and layer stacking in *Model-II* is shown in Figure 7. As in the previous models, one can see the regular layer-stacking with ditrigonal cavities positioned opposite to each other. Comparing Figures 6 and 7, one can see the same position and orientation of NH_3 groups with respect to the ditrigonal cavities.

Comparison of various force fields with *ab initio* data

Since some doubts appeared about the reliability of the empirical potential used for molecular modelling, some *ab initio* calculations were performed to justify the application of the chosen force field.
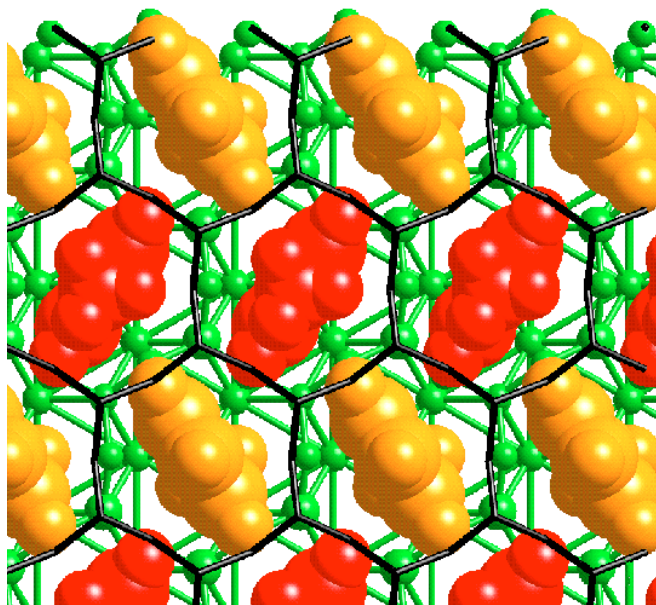

Figure 7 *Arrangement of aniline cations in the interlayer space of fully exchanged vermiculite (*Model-II*) . Projection into* ab *plane shows the mutual positions of two successive silicate layers. VDW radii of aniline atoms illustrate the packing density in the interlayer space. The green balls and sticks display the lower silicate layer, black cylinders illustrate the tetrahedral sheet of upper silicate layer*

The TMA cation was approximated by a small cluster – twelve-member ring based on the vermiculite structure. In order to keep the size of design system as small as possible free valences of the silicon and aluminium atoms of the ring were anchored with hydrogens. The orientation of TMA cation towards the cluster was chosen so that one of its C_3 axes was perpendicular to the plain of the ring, passing its centre (see Figure 8). The whole pseudomolecule was held as a neutral singlet state. Non-relaxed potential energy curves (with frozen both TMA and vermiculite cluster) are displayed in Figure 9. Discrete points from individual methods were fitted by Morse polynomial functions [20]. Quantum chemical *ab initio* results (Figure 9a) were obtained with the inclusion of correlation energy at the MP2 level. Pople's 6-31G* basis sets [21] were used for the H, C, N, and O atoms, Stuttgart's pseudopotentials were used for the description of Si and Al atoms [22]. Recommended basis sets for these two atoms were extended by d-polarisation functions (with exponents α_{Si}=0.45 and α_{Al}=0.32). For the anchored hydrogens only the minimal basis set STO-3G was used. Calculations were done with the program packet Gaussian 94 [23]. The dependence of the dissociation energy on the distance d(C-Si plane) is shown in Figure 9a.

The same cluster described above was used to investigate the dissociation energy in dependence on d(C-Si plane) using molecular mechanics with three sets of VDW parameters from: Tripos, Universal and Dreiding force field. The results are plotted in the Figure 9b. Comparing the equilibrium distance d(C-Si plane), denoted as x_O, one can see, that the best agreement with *ab initio* data was obtained for the Tripos VDW parameters. Moreover, this set of VDW parameters reproduce most accurately the experimentally found interlayer distances.
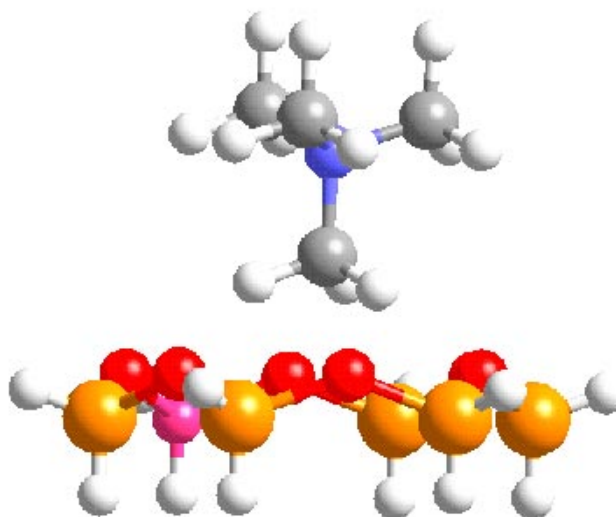

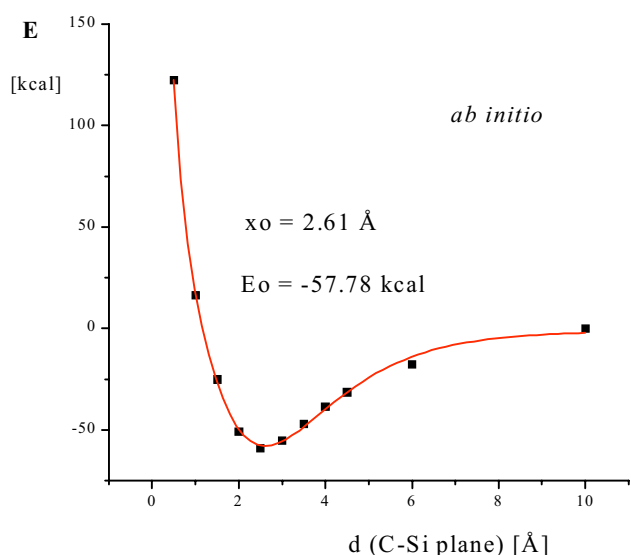**Figure 8** *Cluster used for* ab initio *calculations and the test of force fields*

Figure 9a *Dependence of the dissotiation energy on the distance d(C-Si plane) as a result of* ab initio *calculation. (d(C-Si plane) is the distance between carbon atom in methyl group and plane of Si- atoms in silicate layer*

Also some speculation that methyl groups of the TMA molecules can be immersed into the vermiculite rings was not confirmed taking into account the high potential barrier found in the calculations. The same conclusion can be reached for the NH_3 group in case of aniline cations.

Conclusions

Conclusions of present work can be summarised as follows:
• The best agreement between the calculated and experimental structure models was found for the VDW-Tripos parameters for both intercalates: TMA- and aniline-vermiculite.
• Molecular mechanics using VDW Tripos parameters exhibits the best agreement with the *ab initio* MP2 calculations
• The agreement in calculated and experimental structure models means the agreement in cell parameters and the agreement in the arrangement of guest species in the interlayer space. The apparent difference between the model proposed on the basis of diffraction data by Vahedi-Faridi and Guggenheim [6] and the present calculated model for TMA-vermiculite comes from the difficulties in interpretation of smeared electron density map in the interlayer region.
• The present results have shown, that the strategy of modelling for intercalated clays using molecular mechanics simulations, based on the nonbond host-guest interactions, rigid silicate layers and rigid guest species leads to good agreement with the experimental data in the case of organo-clays.
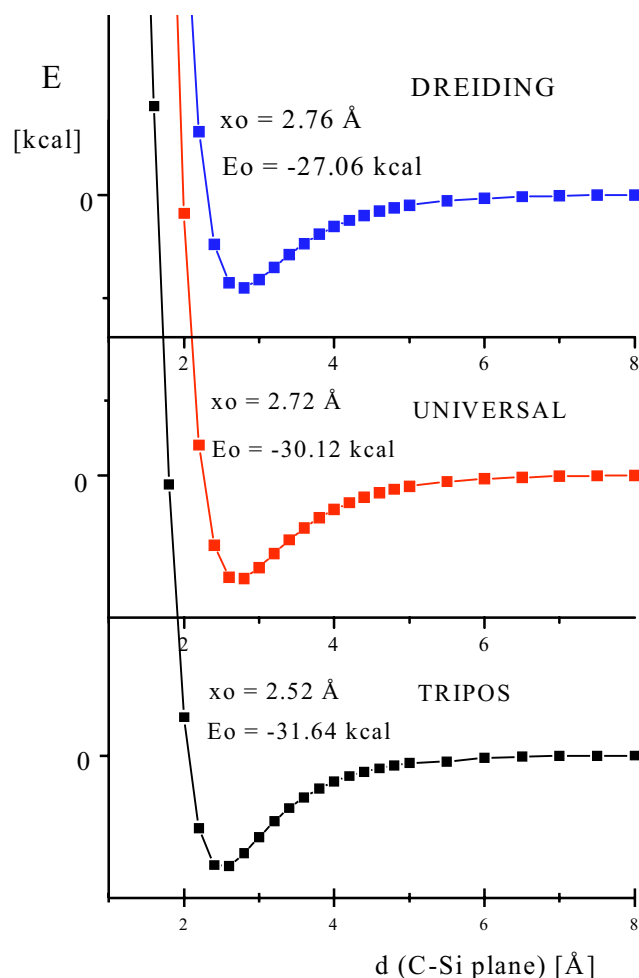
Figure 9b *Dependences of the dissotiation energy on the distance d(C-Si plane) as a result of molecular mechanics calculation, using electrostatic term and three sets of VDW parameters from : Tripos Universal and Dreiding force field*

This strategy can be used successfully in combination with X-ray diffraction for the structure analysis of partially disordered phyllosilicates intercalated with organic guests and occurring in powder form only. This modelling is also very helpful in the interpretation of smeared experimental electron density maps in the interlayer space of organo-clays with 3D ordered structures.

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