

Molecular Mechanics Studies of Montmorillonite Intercalated with Tetramethylammonium and Trimethylphenylammonium

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Abstract The intercalation of organoammonium cations into smectite structure is the important step in the technology of non-linear optical materials. In this study we investigated the structure of montmorillonite (MMT), intercalated with two organoammonium cations: tetramethylammonium (TMA) and trimethylphenylammonium (TMPA) using molecular mechanics simulations. The studies were focused to following aspects: arrangement of organoammonium cations in the interlayer, their positions and orientation with respect to silicate layers and their anchoring to the layers. The calculated (basal) d-spacings for MMT with TMA 14.29 Å and 15.36 Å for MMT with TMPA are in good agreement with X-ray diffraction data.

Keywords Intercalation, Montmorillonite, Tetramethylammonium, Trimethylphenylammonium

Introduction

The smectite group of layered clay minerals consisting of negatively charged silicate layers and readily exchangeable interlayer cations represents a very important class of host structures for intercalation. Weiss and Lagaly [1] have studied organically modified clays prepared by intercalation of different smectites and vermiculite with (n)alkylammonium molecules. Jaynes and Boyd [2] and Polubesova et al. [3] described the intercalation of montmorillonite with TMPA. This intercalated compound is perspective for sorption of aromatic hydrocarbons from water environment. Nowadays

smectite-organic intercalation compounds attract increasing attention as a perspective non-linear optical materials, exhibiting many remarkable photophysical and photochemical properties [4]. After the replacement of interlayer metal cations by organoammonium cations, the interlayer space

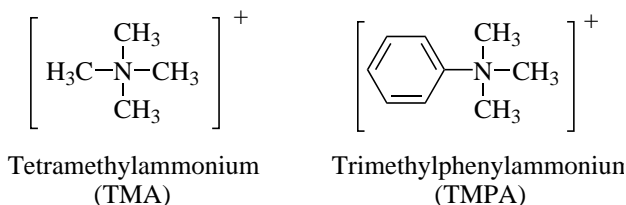
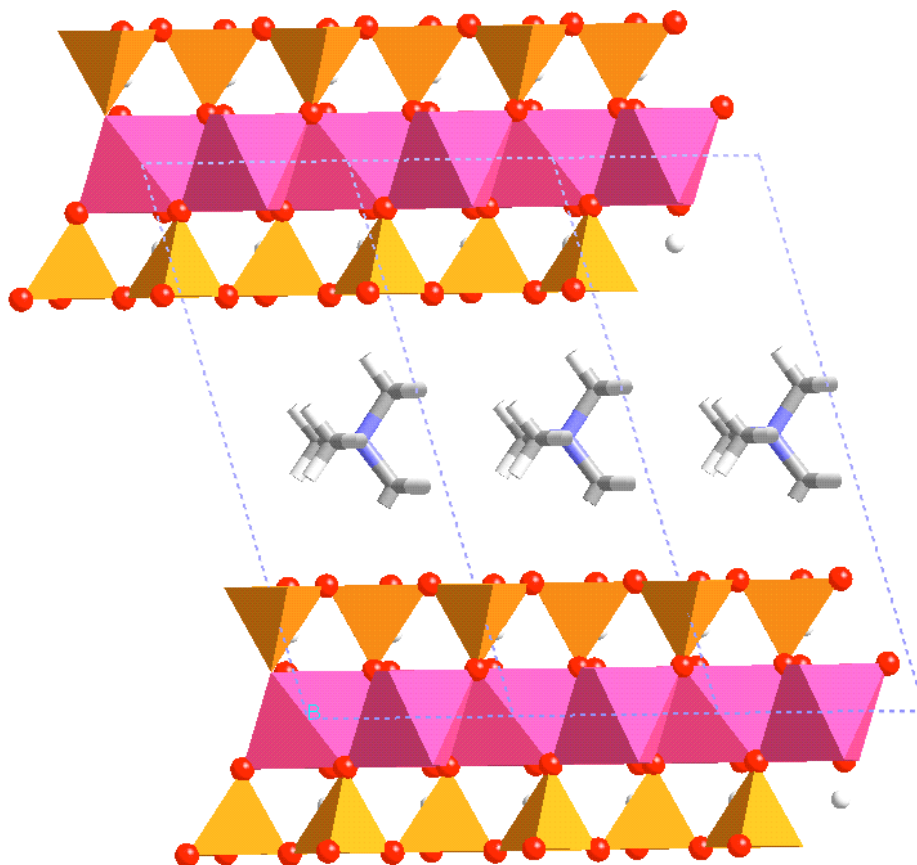


Figure 1 Chemical formulas of TMA and TMPA

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Figure 2 MMT intercalated with TMA, view along the y axis. Calculations were done for one unit cell (two rigid units - MMT layer and the TMA molecule)



in smectites is greatly modified to become strongly organophilic. Besides the organophilic behavior, the organoammonium cations provide micropores in the interlayer space and consequently the TMA-intercalated smectites are very often used as the host matrix for intercalation of polar organic molecules - to create ordered molecular assemblies with desirable photophysical, resp. photochemical properties [5,6,7].

Experimental basis

Montmorillonite from Ivančice (Czech Republic) was used for the experimental work. The original sample, containing less than 5% quartz, was ground in an agate mortar and the fraction with grain size less than 5 μm was prepared by sedimentation. The content of quartz in the fine fraction was less than 3%. A saturated sodium form of montmorillonite (Na-MMT) was prepared from this fraction by shaking with 1 mol/l NaCl solution. Following multiple saturation treatments, the sample was washed with deionized water and air dried.

The following crystallochemical formula was calculated (using the program VZORCE [8]) for fully saturated Na-montmorillonite from the bulk chemical analyses:

$(\text{Na}_{0.81}\text{K}_{0.03}\text{Ca}_{0.01})_{0.85}(\text{Al}_{2.65}\text{Mg}_{0.76}\text{Fe}^{3+}_{0.50}\text{Ti}_{0.04})_{3.95}\text{Si}_{8.02}\text{O}_{20}(\text{OH})_4$
 Na-montmorillonite was used as the starting material for intercalation by the following organic cations: trimethylphenylammonium (TMPA) and tetramethylammonium (TMA). Intercalated montmorillonites were prepared by a conventional ion exchange method using aqueous solutions of appropriate organoammonium chlorides. The amounts of added organoammonium salts were equal to amounts sufficient for reaching an equilibrium in fully saturated organo-montmorillonite systems. After the ion exchange, the products were washed with deionized water repeatedly until a negative chloride test was obtained. Products were air dried. [9,10]

The X-ray powder diffractograms were measured on the INEL powder diffractometer with the PSD 120 position sensitive detector (conditions: reflection mode, rotating sample holder, $\text{CuK}\alpha$ radiation, mixture of silicon and Ag-behenate as calibration standard for PSD). The profile fitting was done by Difpatan program [11]. The estimated basal spacing was $d=14.31\text{\AA}$ for MMT with TMA and $d=15.36\text{\AA}$ for MMT with TMPA.

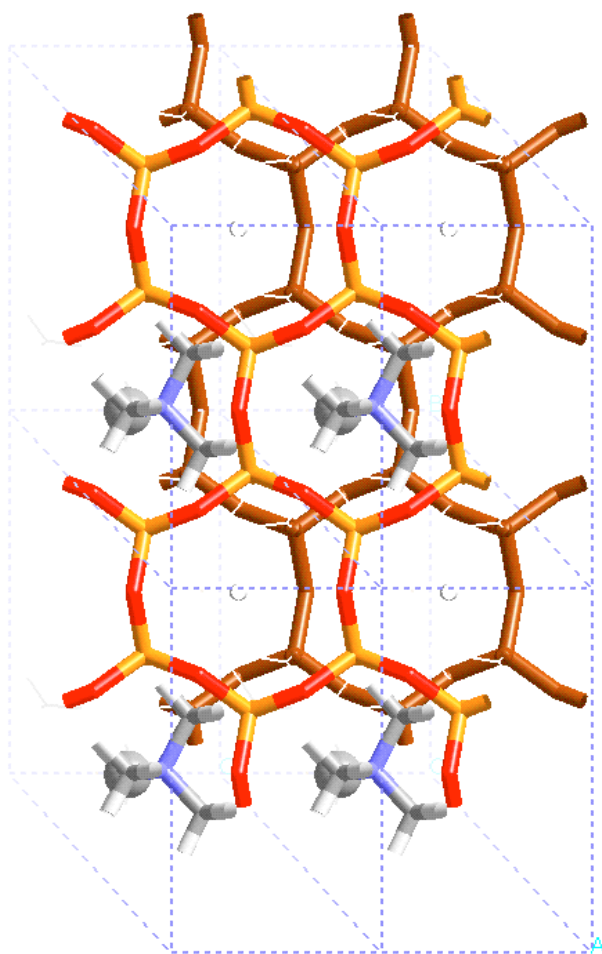


Figure 3 MMT intercalated with TMA, view along the z axis. Calculations were done for one unit cell (two rigid units - MMT layer and the TMA molecule). -Si-O- rings of two successive MMT layers. Upper layer is red/yellow and lower is brown. The carbon atoms from the methyl groups attracted to them are balls

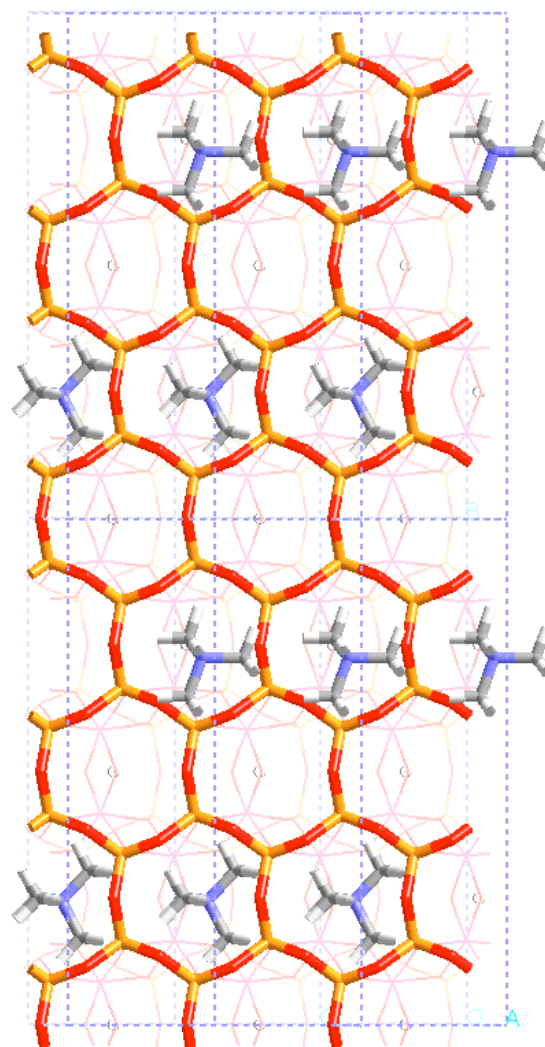


Figure 4 MMT intercalated with TMA, view along the z axis. Calculation were done for two unit cells (three rigid units - MMT layer and two TMA molecules). One can see that mutual orientation of the TMA molecules is different than in Figure 3 due to their rotation along the z axis

Strategy of modeling

Molecular modeling was based on and compared with the available experimental data from X-ray powder diffraction. The montmorillonite structures, especially the intercalated ones, are very disordered (disorder in layer stacking and intercalant distribution) and the information content of the powder diffractogram is usually limited to the d-value estimated from the (001) line which is the most intensive one. Also in these cases (MMT intercalated with TMA and MMT intercalated with TMPA) the results coming from the mod-

eling were compared with the d-spacing determined from the (001) line.

The used software for modeling was the Cerius² modeling environment, namely the module Crystal Packer (CP). CP is based on Dreiding II forcefield [12] and takes into account the non-bond interaction only: the van der Waals interaction (VDW), Coulombic interaction (COUL), hydrogen bonds (HB), energy of subrotations of the rigid units and hydrostatic pressure. The non-bond interaction is calculated between the rigid units, which can be rotated and translated during the minimization and internal subrotations in the rigid units can be defined.

Figure 5 MMT intercalated with TMA, clustering of the TMA molecules

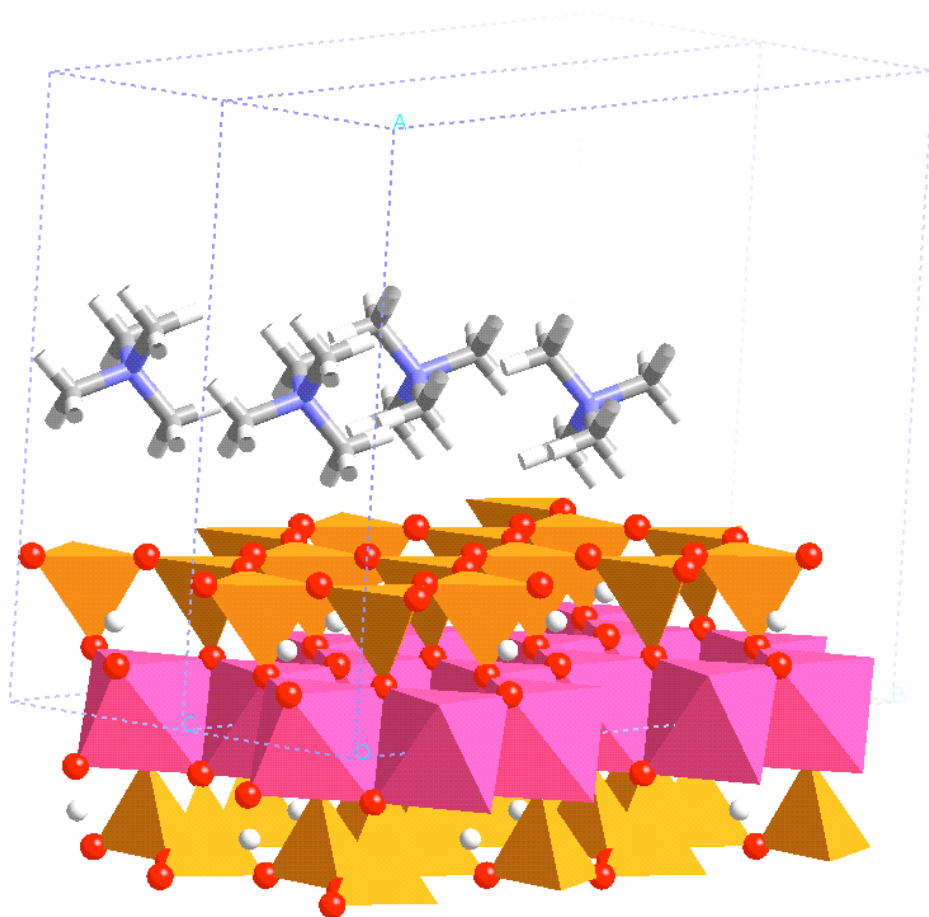
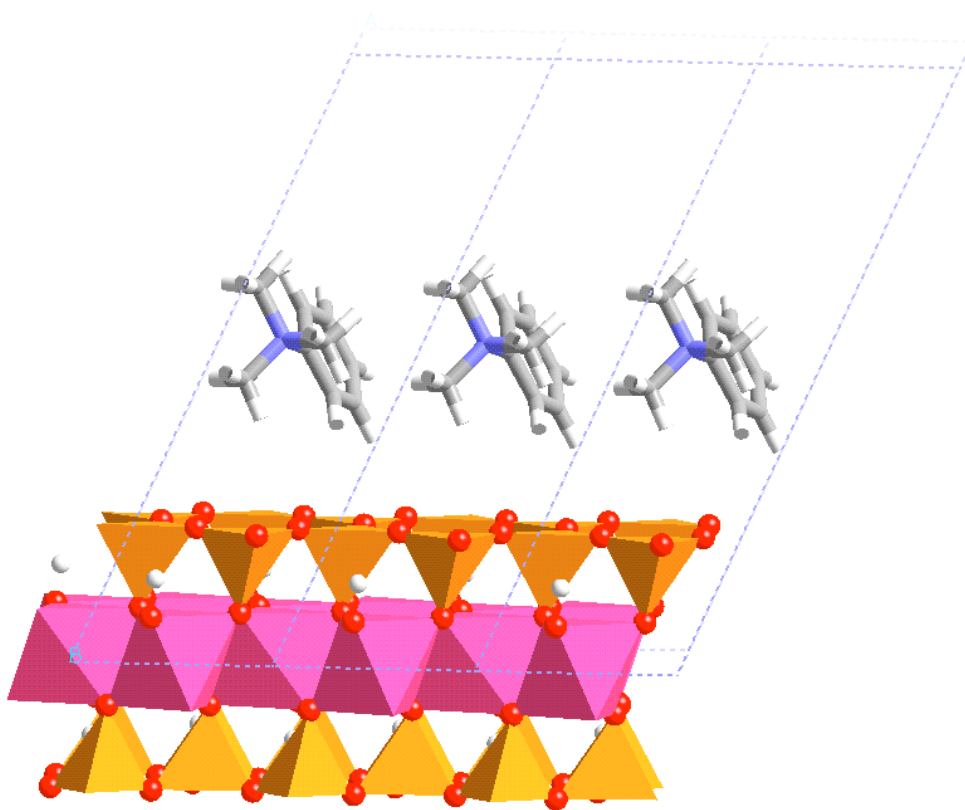


Figure 6 MMT intercalated with TMPA, orientation of the TMPA molecules in the MMT interlayer



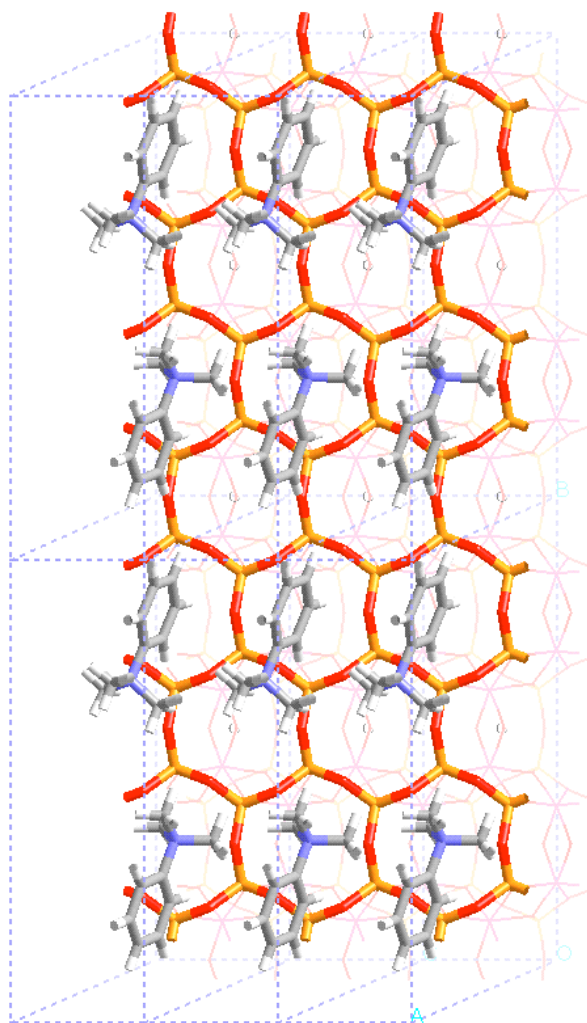


Figure 7a MMT intercalated with TMA, view along the *z* axis. The TMA molecules are placed regularly in the interlayer without any preferred orientation

The structures of the organic molecules TMA and TMA have been minimized in the module Minimizer using the forcefield Universal 1.01 [13, 14, 15]. The MMT layer has been built using the knowledge of the structure of the MMT [16, 17]. The MMT layer content per one unit cell has been assumed in the form: $\text{Si}_8\text{Al}_3\text{MgO}_{20}(\text{OH})_4$, i.e. one Al atom was substituted by the Mg atom which gives the layer charge -1 per unit cell. The initial model has been built from the MMT layer and organic molecules, each of them being an independent rigid unit (one unit cell contains one TMA, TMA resp. molecule, according to the charge neutrality of the whole system). The unit cell has the cell parameters: $a = 5.208 \text{ \AA}$, $b = 9.02 \text{ \AA}$, $\gamma = 90^\circ$, the cell parameters c , a , b have been the scope of interest. To get the rigid units to closer contact external pressure 50 kbar has been applied in the first steps of minimization. During the CP minimization the montmorillonite layer has been supposed to be rigid (based on the infra-

red spectroscopy and X-ray diffraction studies [18]) and only the unit cell parameters c , α , β have been variable. Before the minimization started the charges have been calculated by the Charge Equilibration method [19].

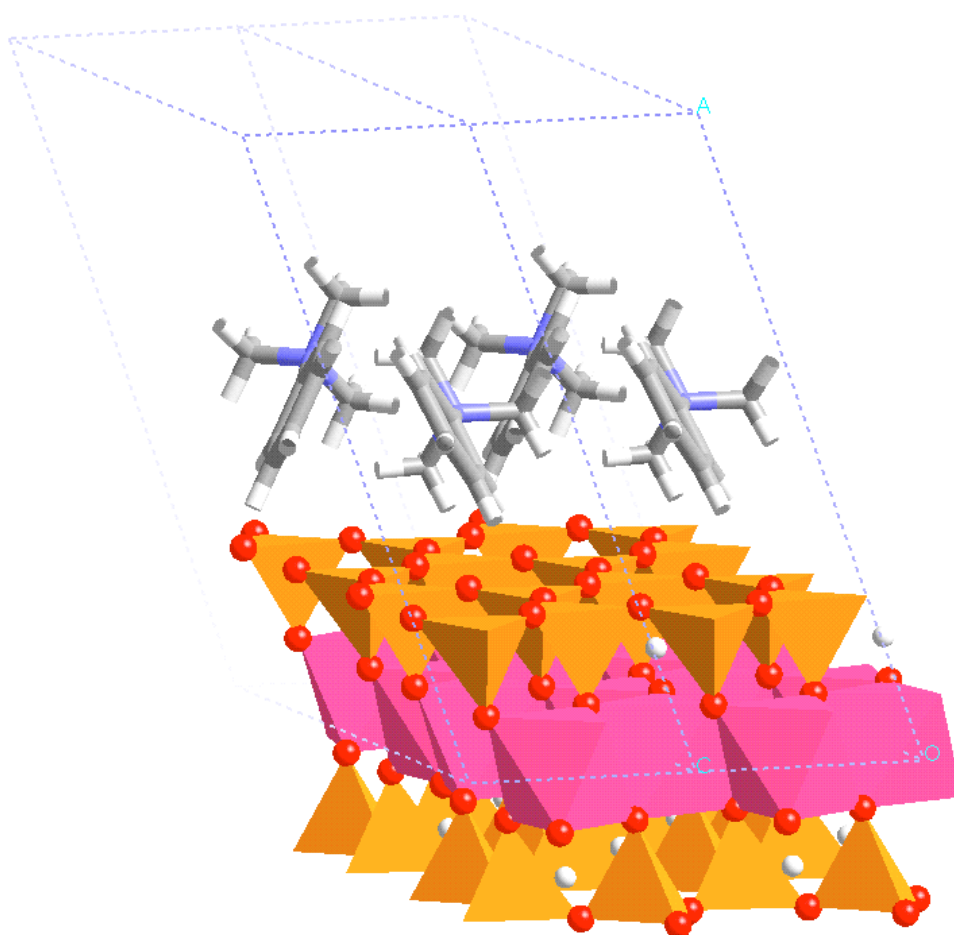
Results and discussion

Montmorillonite intercalated with tetramethylammonium

In the first step the concentration 1 TMA molecule per one MMT unit cell was considered (according to the total charge neutrality) and the TMA molecule and MMT layer have been two different rigid units. Several models have been calculated with different starting TMA positions and orientations in the interlayer. In all cases the minimization ended in a minimum with the *d*-spacing $d = (14.17 \pm 0.01) \text{ \AA}$. The TMA molecule (which has the form of a tetrahedron with the methyl groups in the vertices and the nitrogen atom in the center) was oriented with one edge parallel with the MMT layers and one edge perpendicular to the MMT layers (this means parallel with the *z*-axis), see Fig. 2. However, two methyl groups are in the middle of interlayer and the other two methyl groups are attracted to the -Si-O- rings of the upper and lower MMT layer. Two successive MMT layers may be shifted (see Fig. 3) and the magnitude and direction of the shift depends on the TMA molecule orientation in the interlayer (without influencing the *d*-value). Even a zero shift (a projection of the following layer) has been obtained from several minimizations. This irregularity in the layer stacking found by modeling has been confirmed by the so called *hk*-bands (characteristic for turbostratic structures) on experimental powder diffractograms. The distance $d_{\text{N-N}}$ between the TMA molecules (let us represent this distance by the distance of the central nitrogen atoms) in *a* and *b* directions is equal to the unit cell parameters ($d_{\text{N-N}} = 9.02 \text{ \AA}$ and $d_{\text{N-N}} = 5.208 \text{ \AA}$). The resulting crystal energies (for unit cell, 2 rigid units) for these models have been $E_{\text{tot}} = (-525 \pm 4) \text{ kcal/mol}$, namely $E_{\text{VDW}} = -30 \text{ kcal/mol}$ and $E_{\text{COUL}} = -495 \text{ kcal/mol}$.

Modeling the TMA-MMT structure in one unit cell does not provide the information about the mutual interaction of the TMA molecules in the interlayer. To study the guest-guest interactions, also the calculations with two unit cells have been performed. A unit supercell has been built from two unit cells and the structure was divided into three rigid units - MMT layer and two TMA molecules. During these calculations different starting positions (i.e. the $d_{\text{N-N}}$ has been changed) and orientations of the TMA molecules have been taken into account. The minimization ended with the *d*-spacing $d = (14.40 \pm 0.25) \text{ \AA}$. The *d*-value is a little bit higher than in the previous case and also the variance is higher. Mostly the position and orientation of TMA molecules in the interlayer is again the same (one edge is parallel with the MMT layers and one is perpendicular with the MMT layers) but in many cases the TMA molecules can be rotated along the *z* axis (see Fig. 4). Several minimizations also lead to the

Figure 7 b MMT intercalated with TMPA The TMPA molecules are place regularly in the interlayer without any preferred orientation (different phenyl ring deflection)



TMA molecules clusters which can be seen in the Fig. 5. The TMA molecules are closer to each other and they have two edges parallel with the MMT layers. In these cases the d_{N-N} distances decreased from previous 9.02 Å to 5.5-7.0 Å and the higher values of the d-spacing have been obtained. The resulting crystal energies (for a double cell, 3 rigid units) have been $E_{tot}=(-874\pm 10)$ kcal/mol, namely $E_{VDW}=-50$ kcal/mol and $E_{COUL}=-824$ kcal/mol. The same energy was obtained for the models with the distance $d_{N-N}=5.5-7.0$ Å and for the models with $d_{N-N}=9.02$ Å when a double cell was taken into account. The similar energy values indicate that all structures (ordered TMA, rotated TMA molecules, TMA clusters) are possible and can be present at the same time and the variety in the d-spacing broadens the diffraction lines. The average d-value for all calculated models is 14.29 Å which corresponds very good with the measured d-value 14.31 Å.

Montmorillonite intercalated with trimethylphenylammonium

The strategy of modeling was the same as in the previous case. First only one unit cell of TMPA-MMT was considered which lead to the d-spacing $d = (15.32\pm 0.16)$ Å. The struc-

ture can be seen in the Fig. 6. The plane of the phenyl ring is nearly parallel with the z axis (perpendicular to the MMT layers) and the methyl groups are oriented as in the case of TMA. Two methyl groups nearby the upper and lower -Si-O-rings (with the parallel edge of the TMA tetrahedron) and the last methyl group is in the middle of the interlayer. TMPA is a bigger molecule than the TMA molecule and interacts with two neighboring -Si-O- rings (Fig. 7a). The successive MMT layers can be also shifted as in the case of MMT with TMA. The crystal energies for one unit cell (two rigid units) have been $E_{tot}=(-524\pm 5)$ kcal/mol, namely $E_{VDW}=-33$ kcal/mol and $E_{COUL}=-491$ kcal/mol. Several attempts have been done when in the starting model the phenyl ring plane was parallel with the MMT layers but in all cases even these starting conditions lead to the described model.

To get the information about the mutual interactions of TMPA molecules in the interlayer, the minimization was done with two unit cells (3 rigid units - MMT layer and 2 TMPA molecules). The idea was to find some way of clustering (like in the case of TMA) or to find out any rules for the orientation of the neighbors. As a result it is possible to say that there is not any preferred orientation for the molecules and the TMPA molecules can neighbor with phenyl rings both, ammonium groups both or ammonium groups and phenyl ring. Even the deflection of the phenyl ring plane from the

plane perpendicular to the MMT layers can in both ways - clockwise or counter-clockwise (see Fig. 7a, b). The TMPA molecules are placed regularly in the MMT interlayer without any significant clustering. The minimizations ended with the d-value $d = (15.40 \pm 0.11) \text{ \AA}$. The calculated crystal energies (for two unit cells, 3 rigid units) have been: $E_{\text{tot}} = (-843 \pm 2) \text{ kcal/mol}$, namely $E_{\text{VDW}} = -61 \text{ kcal/mol}$ and $E_{\text{COUL}} = -782 \text{ kcal/mol}$. The same energy was obtained for the previous models when a double cell was taken into account. The similar energy values indicate that the described models are equivalent and can exist at the same time and the variety in d-spacing will again affect the width of the diffraction line. The average d-spacing for all the calculated TMPA - MMT models is 15.36 \AA which is the same value as the value measured by X-ray diffraction.

Conclusion

Cerius² modeling software was used for structural studies of MMT intercalated with TMA and TMPA. Arrangement of organoammonium cations in the interlayer, their positions and mutual orientation and orientation with respect to silicate layers has been investigated. In both cases the calculated d-value corresponds very good with the diffraction measurements. In the case of TMPA the molecules can be placed almost regularly in the interlayer without clustering (Fig. 7a). In the case of TMA the molecules are smaller and the variety in their mutual orientation and clustering might be higher. The arrangement of TMA molecules in the interlayer of MMT is also different than that of vermiculite [20]. Besides of the positions and orientations of the TMA and TMPA molecules in the MMT interlayer, also the irregular layer stacking has been found which can be confirmed by the character of the powder diffractograms.

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