Molecular Modeling of Interlayer Catalytic Sites for Aniline Polymerization in a Zirconium Mixed Phosphonate Phosphate

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Theoretical modeling of a mixed zirconium 3-carboxypropylphosphonate phosphate system, $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$, is reported both for a series of stoichiometric compounds and for an aniline-intercalated system. Modeling of the interlayer spacing variation of selected stoichiometries of the host series predicts linear behavior for the intermediate compositions ($0.5 \leq x \leq 1.5$) accompanied by a significant contraction at the terminal stoichiometries ($x = 0.0$ and 2.0). Our results demonstrate that such behavior is a general feature of layered zirconium phosphonates whose pendant groups possess conformational degrees of freedom. For the host−guest series, the results have provided insight into the energetically stable orientations of the aniline molecule within the interlayer. It was found that the most probable geometry was one in which the aniline C_2 axis is in a tilted orientation with respect to the zirconium planes for the host systems studied. However, at slightly higher energy, molecular modeling predicts aniline to be in an orientation corresponding to the C_2 axis being parallel to the zirconium planes, which would be favorable for the formation of polyaniline within the interlayer. These results are interpreted in the context of experimental findings published earlier.

Introduction

Conducting polymers in general and polyaniline (PANI) in particular have attracted a significant amount of interest due to their interesting optical and electrical properties.[1] In an effort to discover new materials incorporating conducting polymers, several groups have recently synthesized or attempted to synthesize polyaniline within various layered, inorganic host lattices, such as MoS_2,[2] MoO_3,[3] layered metal phosphates (titanium,[4] zirconium,[4,5] and uranyl[4,6]), and a zirconium mixed phosphonate phosphate.[7]

The study of the zirconium phosphonate phosphate−polyaniline system by Rosenthal and co-workers[7] was the motivation behind the work to be described in this paper. Specifically, these researchers synthesized a zirconium 3-carboxypropylphosphonate phosphate (a butyric acid pendant moiety) with the stoichiometry $Zr(O_3P(CH_2)_3COOH)_{0.75}(O_3POH)_{1.25}$, into which aniline was intercalated and subsequently polymerized to a nonconducting form of polyaniline, $Zr(O_3P(CH_2)_3COOH)_{0.75}(O_3POH)_{1.25}$·PANI, within the interlayer of the mixed compound. It was concluded that the polyaniline that formed within the interlayer of this compound consisted of fairly short range oligomers. It was speculated that this was due to a predominance of intercalated anilines in a canted arrangement with respect to the zirconium planes and therefore not in favorable orientations for continuous long-range polymerization.

The present study attempts to theoretically model five compounds in the stoichiometric series of the host compound, $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$, and the aniline intercalate of two configurational substructures of the $x = 1.0$ compound, $Zr(O_3P(CH_2)_3COOH)_{1.0}(O_3POH)_{1.0}$·PANI, using molecular mechanics calculations. The above compound was used to model the aniline intercalation because of the difficulty in directly modeling the $x = 0.75$ stoichiometry of the polyaniline inclusion compound synthesized and studied by Rosenthal and co-workers, $Zr(O_3P(CH_2)_3COOH)_{0.75}(O_3POH)_{1.25}$·PANI. At $x = 0.75$, the stoichiometric ratio of butyric acid pendant group to phosphate moiety is 3:5. In our modeling environment (details below), we initiate the energy minimizations with four attachment sites per unit cell, which cannot support such a 3:5 ratio. As a reasonable approximation, a 1:1 stoichiometric ratio was deemed representative of the actual compound.

Calculational Details

Molecular mechanics calculations were performed using the Cerius/2 modeling environment,[8] using its universal force field,

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Table 1. Molecular-Mechanics-Calculated *d*-Spacing Values and Appropriate Unit Cell Parameters for the Minimum-Energy Structures of $Zr(butyr)_x(hydr)_{2-x}$

compound	butyr:hydr	d_{calc} (Å)	α (deg)	β (deg)	γ (deg)	*c* (Å)
$Zr(butyr)_2$	4:0	15.5	89.5	102.6	89.9	15.8
$Zr(butyr)_{1.5}(hydr)_{0.5}$	3:1	15.4	90.1	102.8	89.9	15.7
$Zr(butyr)_{1.0}(hydr)_{1.0}$	2:2a	13.7	100.2	111.3	89.5	14.9
$Zr(butyr)_{1.0}(hydr)_{1.0}$	2:2b	12.6	89.3	115.7	90.7	14.0
$Zr(butyr)_{0.5}(hydr)_{1.5}$	1:3	12.5	89.3	116.0	92.5	13.9
$Zr(hydr)_2$	0:4	6.8	97.5	114.1	87.8	7.5

on selected stoichiometries in the $Zr(O_3P(CH_2)_3COOH)_x(O_3POH)_{2-x}$ series, hereafter referred to as $Zr(butyr)_x(hydr)_{2-x}$ (x = 0.0, 0.5, 1.0, 1.5, and 2.0) to better understand the structures of the host compounds prior to intercalation and to model the *d*-spacing variation with changes in composition for this series. The universal force field provided with Cerius/2 was used, and charge equilibration was performed on all structures.

The basic unit cell for all models consists of two zirconium atoms and four phosphonate sites and has been described in detail previously.[9−11] For each stoichiometry, a model was built using the appropriate number of butyric acid and hydroxyl groups. Calculations were performed to attempt to find the global minimum-energy structure, which was achieved by initiating the calculations from a range of different *c*-axis starting distances (both larger and smaller than those of the ultimate structures) and varying the initial relative conformations of the functional groups. For each minimized model, the X-ray diffraction pattern was simulated and the *d* spacing was calculated.

For the modeling of the aniline intercalates, calculations were carried out to seek the global minimum in the same manner as described above, but in addition, the orientations of the aniline molecules within the interlayer was varied. For simplicity, only a single aniline molecule was modeled per unit cell of the host compounds since the experimental stoichiometry for the aniline intercalate was not reported.[7] As was done for the host compounds, the X-ray diffraction pattern was simulated and the *d* spacing was calculated for each minimized model.

Results and Discussion

Host Systems. The calculated *d*-spacing values and the appropriate unit-cell parameters of the minimum-energy structures for each stoichiometry of the series are listed in Table 1. As examples, models of the minimum-energy structures of both the bis compound, $Zr(butyr)_{2.0}$, and a mixed, stoichiometric compound, $Zr(butyr)_{0.5}(hydr)_{1.5}$, are displayed in Figures 1 and 2, respectively.

For $Zr(butyr)_2$, the calculated *d*-spacing value of 15.5 Å was found to be slightly larger than the experimentally determined *d*-spacing value of 14.8 Å,[12,13] a trend that has also been observed in the modeling of a zirconium mixed phosphonate containing *p*-aminobenzyl and methyl pendant groups,[10,11] while the calculated *d* spacing of (hydrated) α-zirconium phosphate (6.8 Å) was found to be slightly lower than the experimental value of 7.6 Å.[14] It should be noted that there is some variability in the unit cell α and β angles (Table 1), which would not be expected to occur in the real systems and that will give rise to small deviations from the true *d* spacings. The largest contribution to the observed differences are attributed to inaccuracies in the force field used in this study and work is currently in progress to correct the systematic deviations.

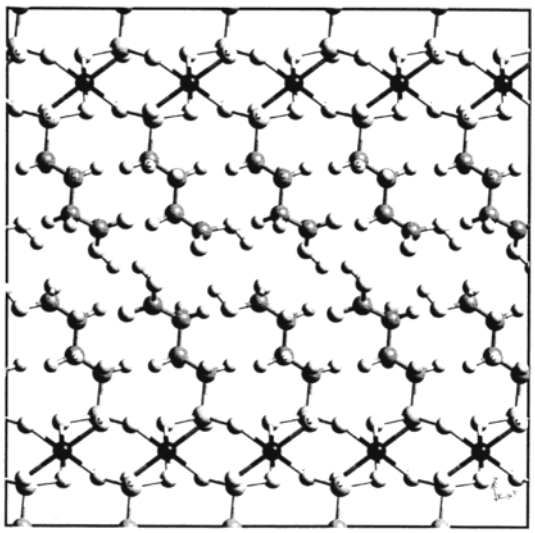

Figure 1. Molecular-mechanics-generated, energy-minimized structure of the bis compound $Zr(butyr)_2$ viewed along the [010] direction (*b* axis).

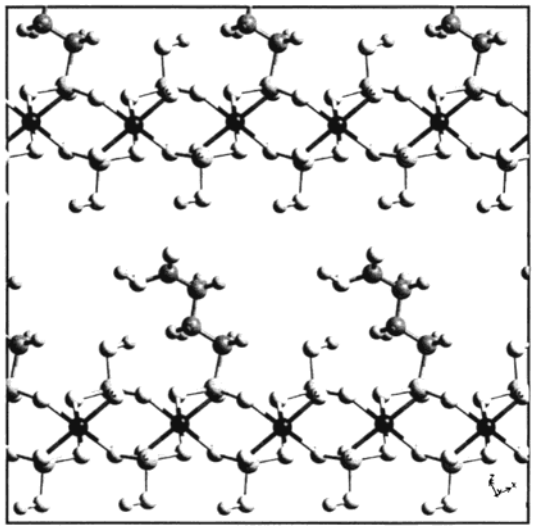

Figure 2. Molecular-mechanics-generated, energy-minimized structure of a mixed, stoichiometric compound, $Zr(butyr)_{0.5}(hydr)_{1.5}$, viewed along the [010] direction (*b* axis).

The variation of the calculated *d*-spacing values with stoichiometric parameter x for the series $Zr(butyr)_x(hydr)_{2-x}$ is displayed in Figure 3. For this series, the interlayer spacing was found to increase with increasing values of x and is in qualitative agreement with Vegard's law,[15] which predicts a linear change in lattice parameters with changing composition for an ideal, solid solution. For the intermediate stoichiometries (x = 0.5−1.5), the variation of calculated *d* spacing with composition is fairly linear but significant deviations from the mixed-compound line are calculated for the unmixed,

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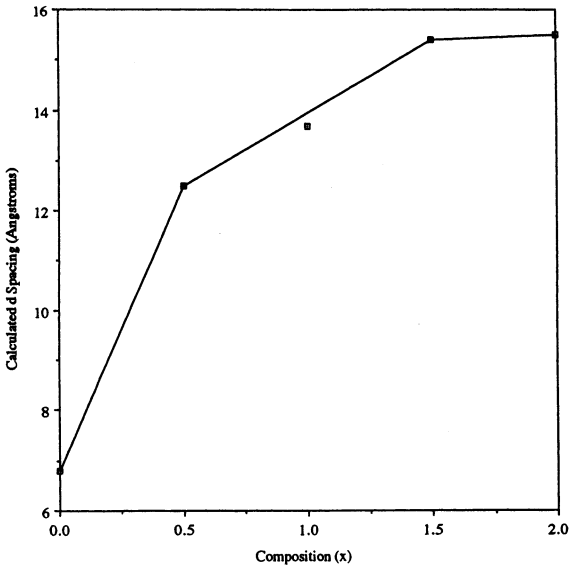

Figure 3. Variation in calculated *d* spacing as a function of the composition for the energy-minimized models of the series $Zr(butyr)_x(hydr)_{2-x}$.

bis(phosphonate) compounds at both ends of the stoichiometric range. This compression or compacting effect was also theoretically predicted and experimentally observed for the mixed *p*-aminobenzyl/methyl group series.[10,11] The compacting effect for the zirconium bis(phosphonates), as compared to the intermediate stoichiometries, can be understood in light of the fact that crystal packing forces act most effectively when only one type of molecule is involved. The predicted compacting is, however, uncharacteristically more severe for the modeling of α-zirconium phosphate ($x = 0.0$). For this system, it is reasonable to observe such a dramatic compacting effect since the hydroxyl groups can participate in hydrogen-bonding interactions, rather than only van der Waals interactions.

In the minimum-energy structure of $Zr(butyr)_2$ (Figure 1), the carbon chains of the butyric acid groups are in their fully extended, staggered conformation and rotation about the P−C bond is restricted due to the crowded nature of the interlayer region. As the small-group content is increased, the *d*-spacing values of $Zr(butyr)_x(hydr)_{2-x}$ are reduced compared to those of $Zr(butyr)_2$ for the following reason. In modeling of the conformations of the *p*-aminobenzyl pendant group in zirconium phosphonates,[10,11] it was found that the anchoring P−C bond is tilted by approximately 30° with respect to the zirconium layer, precisely the value found experimentally for the $P-C_{aromatic}$ bond in a prototypical compound, zirconium phenylphosphonate.[16] As can be seen clearly in Figure 2, the pendant-group attachment in the present series is also not normal to the zirconium plane. Thus, when a hydroxyl group is introduced into the unit cell, the increased freedom allows for rotation of the butyric acid chain on an imaginary cone about the P−C bond, toward the zirconium layer that the group is attached to (i.e., the butyric acid moiety "folds over"), resulting in reduced *d* spacing. This effect is amplified when additional hydroxyl groups are placed in the interlayer region, leading to the observed linearity of the stoichiometric behavior.

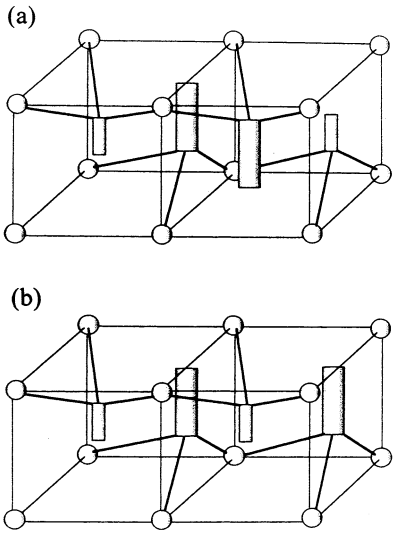

Figure 4. Schematic depictions of $Zr(butyr)_{1.0}(hydr)_{1.0}$ unit cells in which the oppositely placed large groups are (a) at closest approach distance, model **a**, and (b) at maximized separation from each other, model **b**. The large and small columns represent, respectively, the butyric acid and the hydroxyl groups.

The modeling of the $Zr(butyr)_{1.0}(hydr)_{1.0}$ compound presents a slight complication that was not present with the other stoichiometries, in that there are two possible ways in which to arrange the functional groups in their four unit-cell sites (excluding the arrangement in which the butyric acid and hydroxyl groups are segregated on opposite sides of the interlayer). As discussed previously,[10,11] the organic moieties can be arranged such that the butyric acid groups pointing into the interlayer region from opposite planes are near one another or such that the butyric acid groups are nearest a hydroxyl group (see Figure 4). These two different configurations are denoted as **a** and **b**, respectively. Calculations were performed for each of these orientations, and their lowest energy minima were found to be only on the order of 5% different in energy. However, it was found that the *d* spacings of the minimum-energy structures for these were different: 13.7 Å for **a** and 12.6 Å for **b**. The rationale for using the former value as a more realistic representation of the true *d* spacing has been discussed in detail previously,[10,11] but can be summarized as follows. In the **a** model, the butyric acid groups have as nearest neighbors another butyric acid group from the opposite layer, which "prop up" the layers to a larger interlayer distance. The butyric acid groups in the **b** model, however, are nearest to a hydroxyl group from the opposite layer, allowing for a closer approach of the pendant groups. The true structural representation of $Zr(butyr)_{1.0}(hydr)_{1.0}$ would most likely be a random sum of models **a** and **b**. For this scenario, the true *d* spacing for this compound would most likely be the higher value of 13.7 Å since there should be a sufficient number of butyric acid groups in the former arrangement.

The fact that configuration **a** is one in which bulky butyric acid groups are quite close to one another manifests itself in an additional structural parameter. As seen in Table 1, this compound exhibits a larger α angle value as compared to those of the other mixed-

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Table 2. Molecular-Mechanics-Calculated *d*-Spacing Values and Appropriate Unit Cell and Geometrical Parameters for the Structures of a-AN and b-AN

structure	d_{calc} (Å)	α (deg)	β (deg)	γ (deg)	∠ZrC$_2$[a] (deg)	∠ZrBz[b] (deg)	N··H$_p$[c] (Å)
tilted **a-AN**	17.1	106.3	107.3	90.3	39	52	5.7
tilted **b-AN**	17.0	93.6	110.0	87.4	36	37	6.1
parallel **a-AN**	16.8	106.1	109.1	91.8	15	29	3.8
parallel **b-AN**	17.1	92.3	111.6	89.2	14	29	3.6

[a] Approximate angle between the C_2 (para) axes of the aniline and the zirconium planes. [b] Approximate angle between the benzenoid rings and the zirconium planes. [c] Distance between the aniline nitrogen and the para-position hydrogen on the neighboring aniline ring.

stoichiometry compounds, including that of model **b**. Clearly, in compound **a**, the ensuing repulsive forces push the α angle out to a slightly larger value as compared to the others.

It should be noted that the lowest energy model of Zr(butyr)$_{0.5}$(hydr)$_{1.5}$ is predicted to have a *d*-spacing value of 12.5 Å, which is essentially equivalent to that calculated for the **b** model of Zr(butyr)$_{1.0}$(hydr)$_{1.0}$ (12.6 Å). This is understandable and internally consistent since for both models the butyric acid groups are nearest hydroxyl groups from the opposite layer. This result is in agreement with the equivalency of *d* spacings predicted for the corresponding structures in the mixed *p*-aminobenzyl/methyl group series.[10,11]

As would be expected, the final compound in the series, with only hydroxyl groups in the interlayer, α-zirconium phosphate, was found to have the lowest *d*-spacing value, 6.8 Å. The severe reduction in conformational degrees of freedom for this pendant group results in extremely efficient crystal packing. Also, as mentioned earlier, these pendant groups can participate in increased hydrogen-bonding interactions as compared to the other compounds in the series; this would be expected to bring the layers closer to one another. It is therefore not surprising that the Vegard's law deviation is most pronounced for this compound.

The similarities between the results of the calculated variation in *d* spacing with the compositional parameter *x* for the present system, Zr(butyr)$_x$(hydr)$_{2-x}$, and those for the mixed *p*-aminobenzyl/methyl group series discussed in refs 10 and 11, implies that this is a general result for zirconium phosph(on)ate systems in which the organic functional groups possess rotational degrees of freedom.

Intercalation Systems. In the modeling of the intercalation of aniline within interlayers of the host compounds, two systems were investigated: the **a** and **b** forms of aniline-intercalated Zr(butyr)$_{1.0}$(hydr)$_{1.0}$, hereafter referred to as **a-AN** and **b-AN**, respectively. It was found that a multitude of local minimum-energy structures emerged, but in the forthcoming discussion, generally only the lowest minimum-energy structure ("global" minimum) and local minimum-energy structures relevant to the formation of polyaniline within the interlayer will be described.

For both aniline intercalates, **a-AN** and **b-AN**, the global minimum-energy structures were observed to be ones in which the aniline C_2 axes (para-axes) are in the "tilted" orientation with respect to the zirconium planes. The calculated parameters of these structures are given in Table 2. It was found that the tilt angle of the C_2 axes of the aniline groups with respect to the zirconium planes were similar for the two types, at 36° and at 39° for **b-AN** and **a-AN**, respectively. (Concomitantly, the benzenoid ring planes are situated at 37° and 52° with respect to the zirconium planes.) The distance between one aniline nitrogen and the hydrogen in the para position of an adjacent aniline was found to range from 5.7 to 6.1 Å for the two systems. An example of this tilted aniline arrangement is shown in Figure 5 for the **a-AN** system.

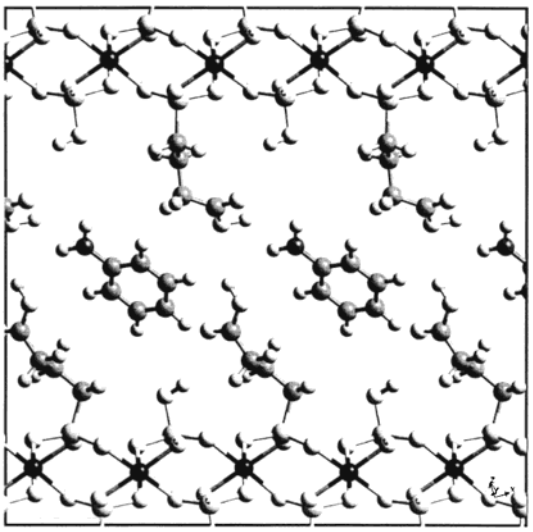

Figure 5. Lowest energy-minimized structure of Zr(butyr)$_{1.0}$(hydr)$_{1.0}$, model **a**, with aniline in the tilted orientation, and viewed along the [010] direction (*b* axis).

The *d* spacings were calculated to be 17.1 and 17.0 Å for these lowest energy structures of **a-AN** and **b-AN**, respectively. It was experimentally found by Rosenthal and co-workers that the *d* spacing of Zr(butyr)$_{0.75}$(hydr)$_{1.25}$ increased from 10.3 to 14.5 Å ($\Delta = 4.2$ Å) upon intercalation of aniline within the interlayer of the solid.[7] Comparing the calculated *d*-spacing values of these aniline intercalate structures to those of the corresponding host compounds (Table 1), increases of 4.0 and 4.4 Å for **a-AN** and **b-AN**, respectively, were observed, a close match to the experimental values.

As mentioned earlier, the calculations produced many local minima for the **a-AN** and **b-AN** systems whose structures and energies were very close in energy to their global minima. This suggests that the aniline intercalate exists as an ensemble of low-energy structures, rather than possessing a unique global minimum energy. Among such near-global minimum-energy structures, we found for both **a-AN** and **b-AN** systems cases in which the aniline C_2 axis is arranged in a "parallel" orientation with respect to the zirconium planes (and to one another) and whose energies were only 5% and 3% higher, respectively, than those of the tilted structures.

These structures are termed parallel because it was found that the C_2 axes of the anilines are at an angle of only ≈14° with respect to the zirconium planes (accompanied by an orientation of the benzenoid ring planes at an angle of 29° with respect to the zirconium planes) for both **a-AN** and **b-AN**. This represents a considerable decrease as compared to the angles found for the tilted structures (36° and 39°). Also, the distance between the nitrogen of one aniline molecule and the

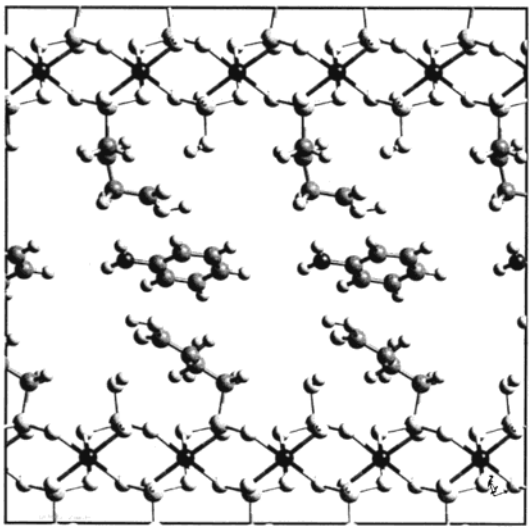

Figure 6. Local energy-minimum structure of $Zr(butyr)_{1.0}(hydr)_{1.0}$, model **a**, with aniline in the parallel orientation, and viewed along the [010] direction (*b* axis). The energy of this structure is 5% higher than that of the lowest energy structure shown in Figure 5.

para-position hydrogen on the adjacent aniline was found to be in the range of 3.6−3.8 Å, which is considerably decreased when compared to distances of 5.7 and 6.1 Å for the tilted models. An example of such a parallel structure is displayed in Figure 6 for the **a-AN** system; the calculated geometrical parameters of these structures are listed in Table 2. These results indicate that a mixed zirconium 3-carboxypropylphosphonate phosphate system can indeed provide catalytic sites for the polymerization of aniline, as was observed experimentally.

The *d* spacings for these parallel structures of **a-AN** and **b-AN** were calculated to be 16.8 and 17.1 Å, respectively. The *d*-spacing value of the parallel **a-AN** model is decreased by 0.3 Å as compared to the lowest minimum-energy tilted **a-AN** model and is as expected for anilines in this type of configuration. The *d*-spacing value of the parallel **b-AN** model is increased by 0.1 Å, however, as compared to that of the lowest minimum-energy tilted **b-AN** model. Since the difference in the unit-cell β angles of these two types of structures is fairly small ($\Delta = 1.6°$), this slight increase in *d* spacing is believed to be due to differences in the conformations of the carbon chains, with those of the parallel **b-AN** model possessing a slightly more extended arrangement than those of the chains in the tilted **b-AN** model.

Conclusions

For the zirconium 3-carboxypropylphosphonate phosphate host systems, we have obtained the stoichiometry-dependent interlayer spacing via a molecular mechanics modeling study. A pseudo-Vegard's law is seen to arise, identical in its qualitative behavior to what was seen experimentally and theoretically for two systems reported previously.[10] Again, the tuning of the interlayer spacing with large-to-small pendant group ratio is a direct result of conformational adjustments that the large group undergoes in order to occupy the space vacated by like groups. One can thus conclude that such behavior is a general feature of layered zirconium phosphonates whose pendant groups possess conformational degrees of freedom.

The results of the modeling of aniline within these systems suggest that the most probable arrangement of the anilines within the interlayer is that of a tilted orientation, but it is believed that a sizable population exists of aniline molecules that are in a parallel configuration with respect to the zirconium layer. It is these parallel orientations that are most favorable for the formation of polyaniline within the interlayer. The predicted presence of both tilted and parallel configurations of aniline within the interlayer is in agreement with, and supports the conclusion of, Rosenthal et al.[7] in that the polyaniline formed within the interlayer of their $Zr(butyr)_{0.75}(hydr)_{1.25}$ consisted of short-range oligomerization rather than longer chain formation. The presence of tilted anilines can then be thought of as aniline configurations that result in the polymerization termination steps.

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