

# Polymer chain packing analysis using molecular modeling

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*This article describes the methodology used in applying molecular modeling to investigate the chain packing of polymers. Models for polyethylene and trans-polyacetylene were developed in order to study the cell packing energy as a function of the chain setting angles. This approach was found to yield chain setting angle values that corresponded to those determined experimentally by other authors. The limitations of the method are also discussed.*

**Keywords:** structure, molecular modeling, polyethylene, trans-polyacetylene, chain packing, setting angle, cell parameters

## INTRODUCTION

The polymorphic nature of many polymers makes their structural analysis difficult, and very often insufficient reflections are observed from neutron or X-ray diffraction data of polymers to adequately define a crystal structure.<sup>1</sup> In these cases, molecular modeling can be a useful tool for obtaining supplementary information on the chain packing.

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To illustrate the use of molecular modeling as an aid in structural analysis, Chem-X was used to gain some insight into the structural variations possible on changing the geometric cell parameters ( $a$ ,  $b$ , and the setting angle,  $\Phi$ ) for a number of symmetrically packed chains. (Chem-X is a commercial molecular modeling package distributed by Chemical Design, Oxford, England.) Two examples of similar crystal packing were examined: polyethylene, which has a non-conjugated polymeric backbone, and polyacetylene, which has a conjugated backbone. Both polymers have the plane group projection  $p\bar{g}g$  along the chain axis with two chains in the unit cell.

The models considered were limited to straight chain segments and chain fold variations were not considered. The following parameters were investigated for each of the models:

- (1) The chain setting angle  $\Phi$  of chains packed along the  $c$ -axis for cell dimensions cited in literature.
- (2) The optimum cell lengths  $a$  and  $b$  for the lowest-energy packed structure determined by varying both  $a$  and  $b$  and the setting angle  $\Phi$ .

In both cases the resulting unit cell parameters were compared with those cited in literature.

This article describes the methodology used in molecular modeling applied to chain packing, and will hopefully enlighten those who are new to the field. A description on how to build the basic chain unit, how to apply space

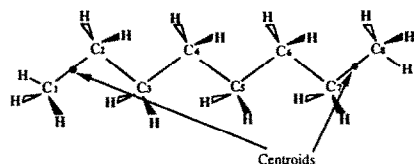
group operators, and how to monitor a physical parameter is also included.

## SETTING UP THE CALCULATIONS

### Building the Basic Chain Unit

First, the question of the length of the basic polymer chain unit should be addressed. Since theoretical and experimental investigations have shown that restricted  $\pi$ -delocalization systems can be adequately modeled using oligomers,<sup>2</sup> all of the models in this investigation were restricted to 8-carbon chains. Furthermore, the bond angles and bond lengths were set to values cited in literature. It should be noted that there are variations in the cell parameters cited in the literature which can be attributed to the fact that many polymers can exist in various polymorphic forms. For the polyethylene in this work the bond lengths were C—C = 1.53 Å, C—C—C = 112°, and cell lengths:  $a$  = 7.40,  $b$  = 4.93,  $c$  = 2.354.<sup>3</sup> For the polyacetylene model: C=C = 1.36 Å, C—C = 1.45 Å, C—H = 1.08 Å, C—C=C = 122°.<sup>4,5</sup> The cell parameters ( $a$  = 4.18,  $b$  = 7.34,  $c$  = 2.455) cited by Kahlert et al.<sup>5</sup> have been used for the calculations in this study since these parameters have been obtained on a particularly well crystallized, highly oriented sample. These parameters were maintained constant throughout the analyses since the overall packing is not sensitive to small changes in the geometry of the molecules.<sup>6,7</sup>

Having assembled the octamers they were then packed in three-dimensional (3D) space along the cell *c*-axis by inserting two centroids in the carbon backbone (one centroid between C1 and C2 and another between C7 and C8 as shown below):



In CHEM-X it is necessary to bind one of these centroids to a carbon atom to permit rotation of the octamer around this centroid. The basic chain unit was then manipulated so that its centroid axis is superimposed on the cell position (0, 0, 0) when viewed along the *c*-axis, as in Figure 1.

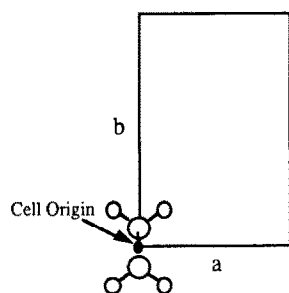


Figure 1. *ab*-projection of the polyethylene model oligomer after its centroid axis is positioned along the *c*-axis of the unit cell. The other molecules of the cell can be inserted by specifying individual symmetry operators.

## Inserting Other Chains—The Space Group

A packed cell is obtained by applying crystallographic space group symmetry operators to the basic chain unit. It is not necessary to generate atoms in the *c*-direction since the chains have been built to a predefined length.

The space group of polyethylene is known to be orthorhombic Pnam (see Table 1). In this work we examine both Pnam and a similar packing, Pbnm. In the case of polyacetylene, the dimerized chain has an alternating carbon bond length<sup>8</sup> which lowers the space group to monoclinic symmetry.<sup>9</sup> The  $P2_1/a(2_1//b)$  and  $P2_1/b(2_1//a)$  space groups have the double bonds on neighboring chains in-phase as shown in Figure 2. Although the chain pack-

ing is generally accepted as being pseudo-orthorhombic with a space group  $P2_1/a$  or  $P2_1/n$  with  $\beta$  varying by approximately  $1^\circ$  from a right angle (see Table 2), it was assumed to be a true orthorhombic structure for the purpose of the present calculations, i.e.,  $\beta = 90^\circ$ . The monoclinic spacegroup descriptors  $P2_1/a$  or  $P2_1/b$  are used throughout the text for clarity even when  $\beta = 90^\circ$ .

In order to have a molecule at each corner of the packed cell and one in the center as in the case of a two-dimensional (2D) plane group *pgg* the following symmetry operators were applied to the original chain at (*x*, *y*, *z*), resulting in the  $P2_1/b$  packing:

$$(x + 1, y, z; \quad x, y + 1, z; \quad x + 1, \\ y + 1, z; \quad \bar{x} + 1/2, y + 1/2, z)$$

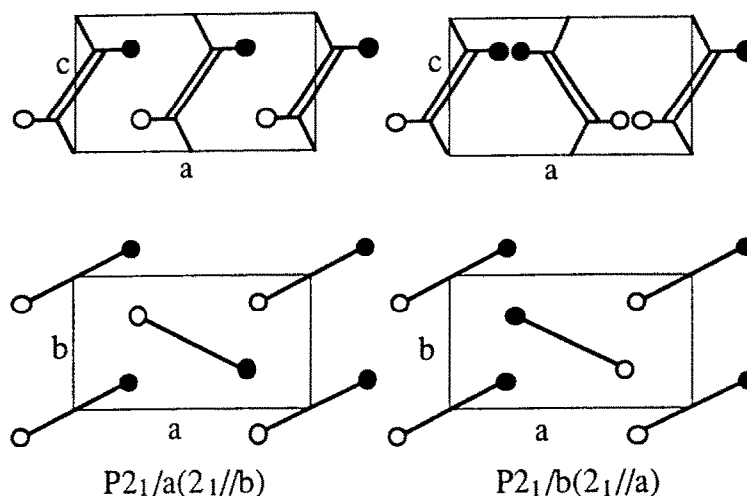


Figure 2. *ab*-projection of some possible trans-polyacetylene crystallographic unit cells demonstrating the difference between  $P2_1/a$  and  $P2_1/b$  space groups.

Table 1. Some experimentally determined unit cell parameters for polyethylene. The *ac*-projection has been included for comparative purposes. Calculated values have been given for comparison.

Reference	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\Phi$ (degrees)	Space group	<i>ac</i> -projection	Method <sup>c</sup>
Kawaguchi <sup>24</sup>	7.41	4.93	2.54	46°–48°	Pnam	parallel	ED
Dorset <sup>16</sup>	7.48	4.97	2.55	46.7 <sup>a</sup>	Pnam	parallel	ED
Phillips <sup>17</sup>	7.38	4.90	2.55	48	—	—	XRD
Wunderlich <sup>18</sup>	7.418	4.946	2.546	45	Pnam	parallel	XRD
Bunn <sup>3</sup>	7.40	4.93	2.354	41.2	Pnam	parallel	XRD
CHEM-X <sup>b</sup>	<i>b</i>	<i>b</i>	<i>b</i>	48	Pnam	parallel	Calculated
	<i>b</i>	<i>b</i>	<i>b</i>	36	Pbnm	antiparallel	Calculated

<sup>a</sup>Value obtained after minimization of the crystallographic *R*-factor

<sup>b</sup>The *a*, *b*, and *c* values were fixed to the values cited by Bunn et al.<sup>2</sup>: *a* = 7.40, *b* = 4.93, *c* = 2.354. The setting angle was then calculated using these values.

<sup>c</sup>ED = Electron diffraction. XRD = X-ray diffraction.

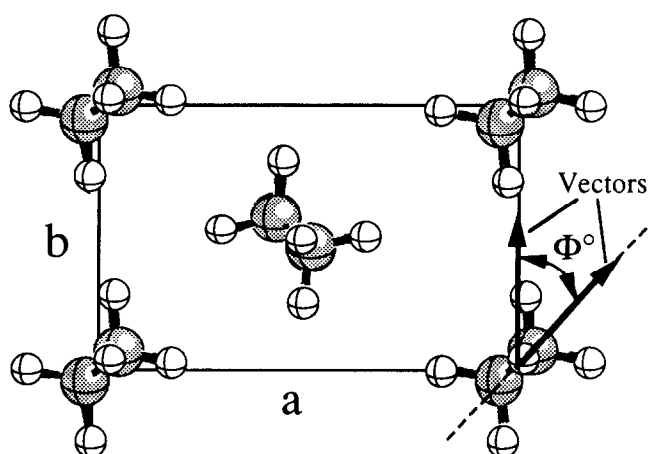
**Table 2. Summary of some cell parameters for trans-polyacetylene experimentally determined by different authors.**

Reference	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta^\circ$	$\Phi$ (010) <sup>a</sup>	Space group considered	Space Group	<i>ac</i> - projection	Method
Perego <sup>19</sup>	4.09	7.38	2.457	—	51	P2 <sub>1</sub> / <i>a</i> , P2 <sub>1</sub> / <i>n</i> Pnam	Pnam	parallel	XRD
Fincher <sup>20</sup>	4.25	7.32	2.46	91.4	55	P2 <sub>1</sub> / <i>a</i> , P2 <sub>1</sub> / <i>n</i>	P2 <sub>1</sub> / <i>n</i>	antiparallel	XRD
Shimamura <sup>22</sup>	4.24	7.32	2.46	—	24	P2 <sub>1</sub> / <i>a</i>	P2 <sub>1</sub> / <i>a</i>	parallel	ED
Sokolowski <sup>23</sup>	4.24	7.26	—	—	55	Pgg	Pgg	parallel	XRD/ED
Baughman <sup>13</sup>	4.08	7.41	2.46	91.3	51	P2 <sub>1</sub> / <i>a</i>	P2 <sub>1</sub> / <i>a</i>	parallel	XRD
Kahlert <sup>5</sup>	4.18	7.34	2.455	90.5	57	P2 <sub>1</sub> / <i>a</i> , P2 <sub>1</sub> / <i>b</i> P2 <sub>1</sub> / <i>n</i>	P2 <sub>1</sub> / <i>a</i>	parallel	XRD
CHEM-X <sup>b</sup>	<i>b</i>	<i>b</i>	<i>b</i>	90	54	P2 <sub>1</sub> / <i>a</i>	P2 <sub>1</sub> / <i>a</i>	parallel	Calculated
	<i>b</i>	<i>b</i>	<i>b</i>	90	52	P2 <sub>1</sub> / <i>b</i>	P2 <sub>1</sub> / <i>b</i>	antiparallel	Calculated

<sup>a</sup>The setting angle is the angle between the plane of the chain and (010)

<sup>b</sup>The *a*, *b*, and *c* parameters were fixed to the values cited by Kahlert et al.<sup>5</sup>: *a* = 4.18 Å, *b* = 7.34 Å, and *c* = 2.455 Å. The setting angle was then calculated using these values.

<sup>c</sup>ED: Electron diffraction. XRD: X-ray diffraction.



**Figure 3.** *ab*-projection of the Pnam polyethylene model after packing with symmetry operators (*x*, *y*, *z*; *x* + 1, *y*, *z*; *x*, *y* + 1, *z*; *x* + 1, *y* + 1, *z*;  $\bar{x}$  + 1/2, *y* + 1/2, *z*). The chain setting angle  $\Phi$  measured with respect to the (010) plane is also shown.

The original basic chain unit is at (*x*, *y*, *z*). The effective difference between P2<sub>1</sub>/*a* and P2<sub>1</sub>/*b* space groups is that the central chain is rotated by 180°. In the case of P2<sub>1</sub>/*b* packing, the  $\bar{x}$  + 1/2, *y* + 1/2, *z* operator contains an inversion in the *x*-axis which results in the central chain unit being antiparallel to the others when projected onto the *ac*-plane. The effect of substituting (*x* + 1/2,  $\bar{y}$  + 1/2, *z*) for ( $\bar{x}$  + 1/2, *y* + 1/2, *z*) results in a 180° rotation of the center chain, giving the corresponding P2<sub>1</sub>/*a* space group packing with the central chain being parallel to the others when projected onto the *ac*-plane.

Effectively, the same operators can

be used to obtain the packed polyethylene cell: the set (*x*, *y*, *z*; *x* + 1, *y*, *z*; *x*, *y* + 1, *z*; *x* + 1, *y* + 1, *z*;  $\bar{x}$  + 1/2, *y* + 1/2, *z*) gives the Pbnm packing whereas (*x*, *y*, *z*; *x* + 1, *y*, *z*; *x*, *y* + 1, *z*; *x* + 1, *y* + 1, *z*;  $\bar{x}$  + 1/2, *y* + 1/2, *z*; *x* + 1/2,  $\bar{y}$  + 1/2, *z*) gives the Pnam packing.

### Energy Calculation

The van der Waal's (VDW) calculation algorithm was used throughout this work to calculate the total energy of the packed cells.<sup>10</sup> In order to reduce computational time, geometry optimization was disabled so that the chains retained their initial geometry during rotation.

### Monitoring the Chain Setting Angle

During the conformational analysis the energy of the packed cell was calculated as a function of the chain setting angle  $\Phi$ . In order to accomplish this, two vectors were defined with their origins in the plane of the carbon backbone: a reference stationary or home vector and a dynamic vector which rotated with the molecule. Both vectors were assigned (0, 1, 0) directions with respect to the crystallographic unit cell. The angle between these two vectors was then monitored during the analysis. Since the *c*-axis symmetry is C<sub>2</sub> the rotation around this axis during the search was limited to the range 0° ≤  $\Phi$  ≤ 90°.<sup>11</sup>

**Minimum energy value** During the conformational searches the chain setting angle was incremented in steps of 1°; the optimum chain setting angle values quoted throughout this work correspond to the minimum energy values output by the modeling program.

### Selecting the Number of Basic Chain Units

Trial calculations based on models containing from 5 to 60 chains did not reveal a significant difference in the minima positions for the setting angle optimization nor the crystallographic unit cell length optimization. The smaller packed cell was therefore em-

played throughout this work since it required less CPU time.

## Interaction Distance

The energy function contains an interaction term dependent on the distance between atom pairs whose separation is between a minimum and maximum value. The lower cutoff value relates to the repulsive energy component whereas the upper cutoff value applies to the polarization energy and the electrostatic terms. Figure 4 illustrates the effect of the energy as a function of the maximum distance of interaction. It can be seen that the energy function levels off when interactions up to 15 Å are taken into account: this was therefore the cutoff value used in these cal-

culations. As the number of cells in the calculation were increased it was necessary to increase the upper cutoff limit accordingly.

## Partial Charge Calculation

The partial charges present on the packed structure were calculated using the Gasteiger charge calculation method.<sup>12</sup> This is an empirical method based on orbital electronegativities and is an iterative process which takes into account charges on atoms other than nearest neighbors.

The calculated charges on the C atoms owing to the slight polarization of the C—H bonds were  $-0.07e$  for trans-polyacetylene and  $-0.06e$  for polyethylene. These values correspond

to those calculated by other authors.<sup>13-15</sup>

## POLYETHYLENE

### Determination of the Optimum Chain Setting Angle $\Phi$

The chains were built and packed according to the parameters cited by Bunn.<sup>3</sup> The unit cell values for this calculation were:  $a = 7.40$  Å,  $b = 4.93$  Å, and  $c = 2.354$  Å. Both Pnam and Pbnm symmetries were studied and the VDW energy calculated as the chains were rotated. The energy as a function of  $\Phi$  for both types of chain packing is shown in Figure 6. A minimum VDW energy of  $-17.46$  kcal/mol occurs at  $\Phi = 48^\circ$  for the Pnam structure and a minimum VDW energy of  $-16.75$  kcal/mol at  $\Phi = 35^\circ$  for the Pbnm crystal structure.

Literature values for the cell parameters are summarized in Table 1. These results show that the Pnam structure is energetically more feasible than the Pbnm structure which is in agreement with the experimental data summarized in Table 1. The calculated setting angle of  $48^\circ$  is within the range of possible experimentally determined values.

### Determination of the Optimum Cell Lengths, $a$ and $b$

The energy of a packed polyethylene cell was calculated for a range of values of  $a$  and  $b$  between 3.7 Å and 7.6 Å. The cell was packed for each pair of values of  $a$  and  $b$ , and the energy was calculated as a function of the setting angle. The minimum energy was plotted as a function of  $a$  and  $b$  as shown in the contour plot in Figure 7. The minimum is located at  $a = 7.0$  Å and  $b = 4.9$  Å. These values are in agreement with those cited in literature for both polyethylene and paraffins.<sup>24</sup>

## trans-POLYACETYLENE

### Determination of the Optimum Chain Setting Angle $\Phi$

The trans-polyacetylene chains were built according to the bond lengths and angles cited by Kahlert et al.<sup>4,5</sup> The chains were subsequently packed in the unit cell having  $a = 4.18$  Å,  $b = 7.34$  Å, and  $c = 2.455$  Å. The energy of

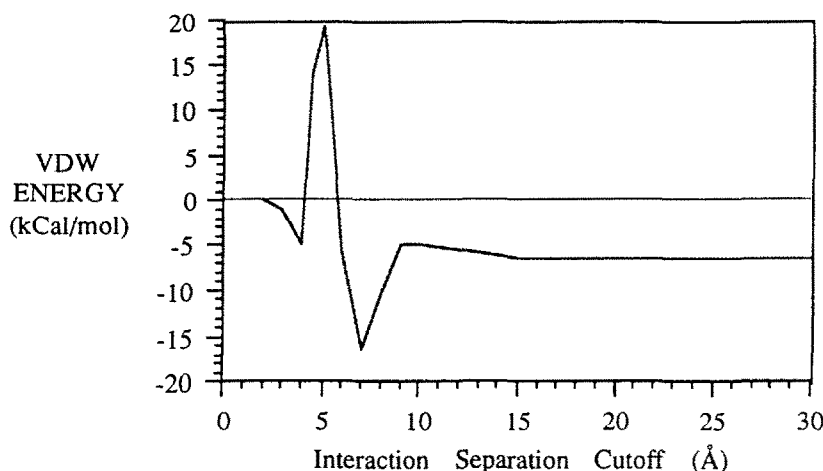


Figure 4. VDW energy as a function of the maximum cutoff distance for intermolecular interactions.

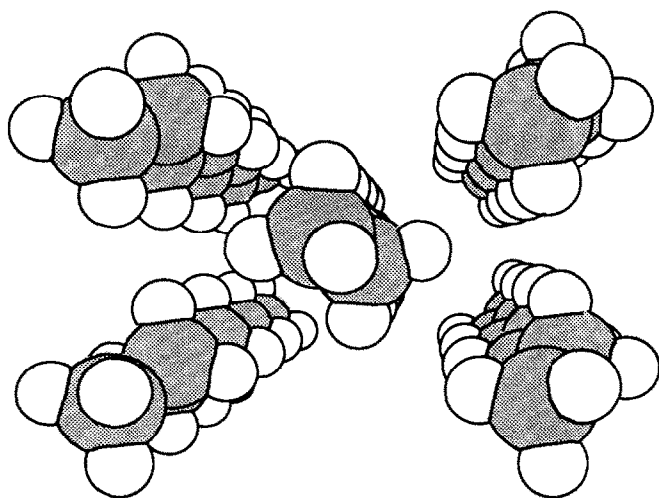


Figure 5. Perspective view of the Pnam packed polyethylene model looking along the c-axis.

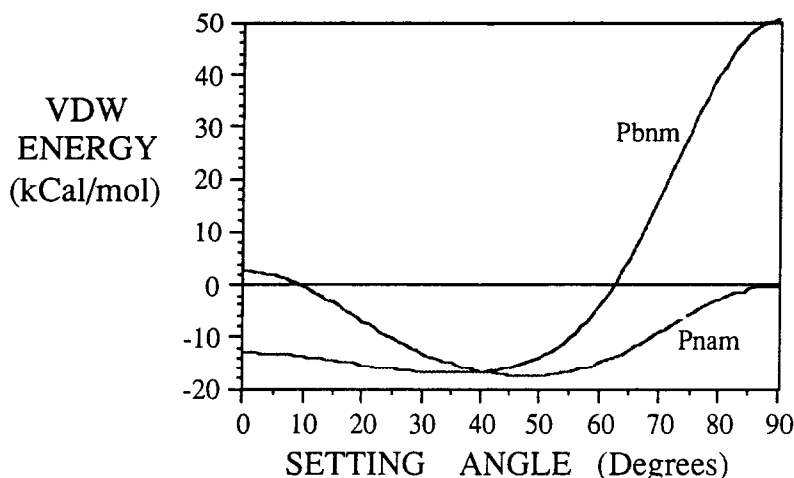


Figure 6. Total energy of the packed polyethylene cell as a function of the setting angle  $\Phi$  for both Pnam and Pbnm geometries. The cell parameters used were  $a = 7.40 \text{ \AA}$ ,  $b = 4.93 \text{ \AA}$ , and  $c = 2.354 \text{ \AA}$ .<sup>3</sup>

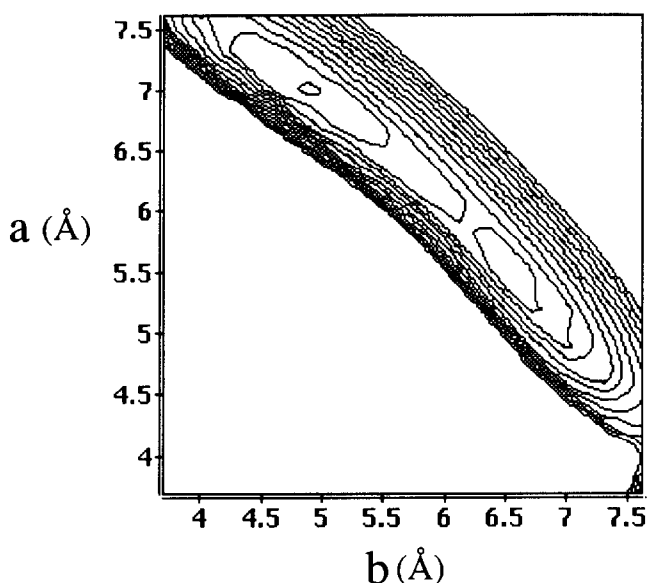


Figure 7. Contour plot of energy as a function of the unit cell parameters,  $a$  and  $b$  for a packed polyethylene cell. The smallest circle represents the lowest energy. Each contour is  $0.26 \text{ kcal/mol}$ .

both  $P2_1/a$  and  $P2_1/b$  symmetries were studied. Figure 9 shows the energies of both  $P2_1/a$  and  $P2_1/b$  packed cells as a function of the chain setting angle.

Both curves are similar in shape with minima occurring in the same region. The energy difference between the structures is quite small, with  $\Delta E = 0.76 \text{ kcal/mol}$ . The minimum energy conformation corresponds to a  $\Phi$  value of  $52^\circ$  for the  $P2_1/b$  structure ( $E = -15.48 \text{ kcal/mol}$ ) and  $54^\circ$  for the

$P2_1/a$  structure ( $E = -14.72 \text{ kcal/mol}$ ). Both these setting angle values are in agreement with those generally cited in the literature (Table 2). It should be noted, however, that a much smaller setting angle of  $24^\circ$  has been reported by Shimamura<sup>22</sup> from an electron diffraction analysis. Such variations in literature values can be attributed to the polymorphic nature of this type of polymer and to variations in the method of synthesis.

## Determination of the Optimum Unit Cell Lengths, $a$ and $b$

The optimum crystallographic values of  $a = 4.9 \text{ \AA}$  and  $b = 5.2 \text{ \AA}$  calculated for the  $P2_1/a$  model did not correspond with the generally accepted literature values (Table 2). Furthermore, the chain setting angle  $\Phi$  is  $90^\circ$  for this conformation, in contrast to a generally accepted value of  $\approx 55^\circ$ . This discrepancy has been mainly attributed to neglect of  $\pi$ -bond interactions in the calculation function.

The contour plot of  $E$  as a function of  $a$  and  $b$  is shown in Figure 10.

## DISCUSSION

These investigations have shown that the CHEM-X package is a useful molecular modeling tool for obtaining information on the chain packing of polymeric structures. This study revealed that the unit cell parameters determined using a model with a large number of chains (60) did not differ significantly to those obtained using a limited 5-chain unit cell model. It has proven very useful in estimating the chain setting angle for both polyethylene and *trans*-polyacetylene when the cell parameters  $a$  and  $b$  were known (from diffraction analysis). In the former case, the Pnam structure yielded a setting angle of  $48^\circ$  for the input cell parameter set:  $a = 7.40 \text{ \AA}$ ,  $b = 4.93 \text{ \AA}$ , and  $c = 2.354 \text{ \AA}$ , which is in close agreement with literature values for both polyethylene and paraffins.<sup>24</sup> Likewise for transpolyacetylene, the optimum chain setting angle was determined as  $54^\circ$  for the  $P2_1/a$  structure ( $a = 4.18 \text{ \AA}$ ,  $b = 7.34 \text{ \AA}$ , and  $c = 2.455 \text{ \AA}$ ) in close agreement with literature values. The  $P2_1/b$  structure indicated a slightly lower total energy for a setting angle of  $52^\circ$ , indicating that variations in the packing are possible.

The program has proven less useful when applied to a more general type of chain packing analysis where the cell parameters are unknown. An analysis of the energy variations for different combinations of  $a$  and  $b$  revealed a shallow troughlike curve for both polymers. The optimum values determined in the case of polyethylene ( $a = 7.0 \text{ \AA}$  and  $b = 4.9 \text{ \AA}$ ) were in agreement with literature values. On the contrary, the optimum cell parameters determined

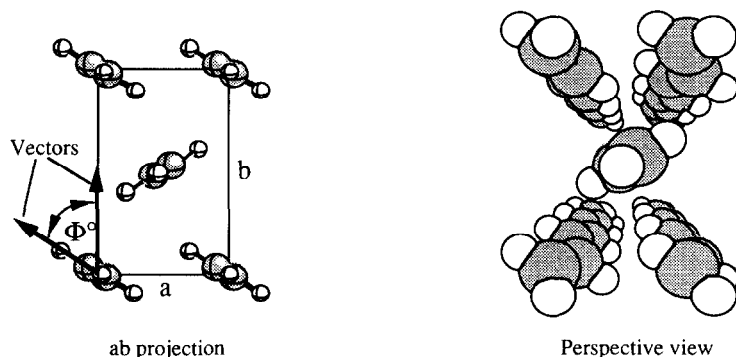


Figure 8. The packed unit cell for the  $P2_1/b$  trans-polyacetylene model showing the ab-projection and corresponding perspective view.

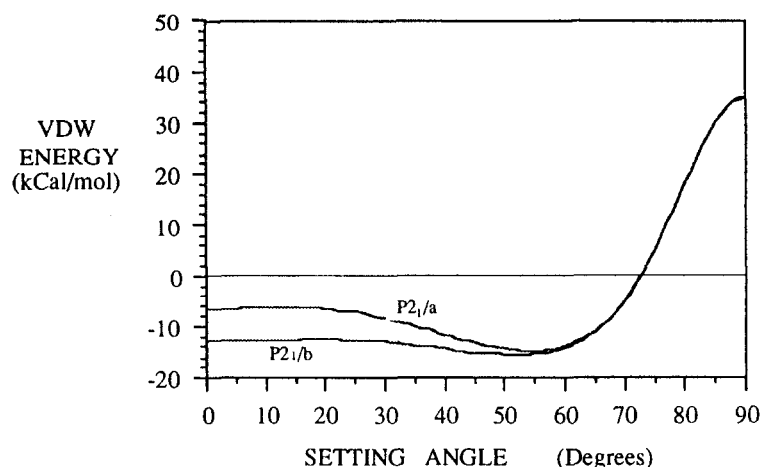


Figure 9. The total VDW energy of the packed trans-polyacetylene model cell as a function of the setting angle  $\Phi$ , for both  $P2_1/a$  and  $P2_1/b$  geometries. The minima are  $54^\circ$  for  $P2_1/a$  and  $52^\circ$  for  $P2_1/b$ .

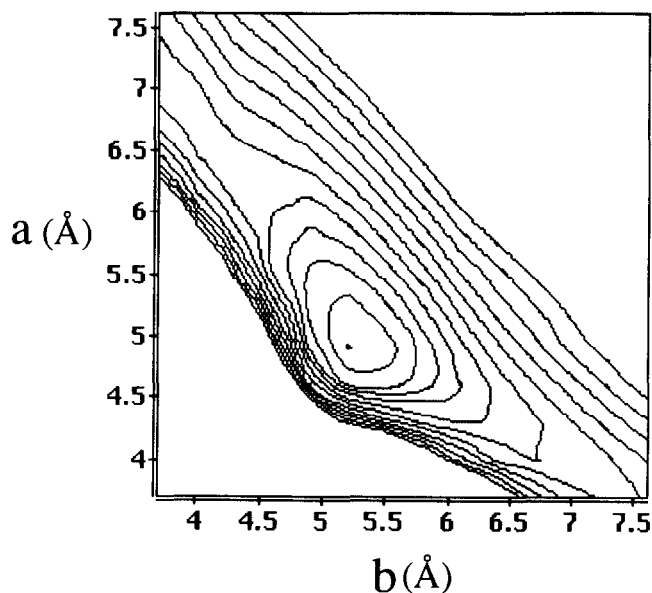


Figure 10. Contour plot of VDW Energy as a function of the unit cell parameters,  $a$  and  $b$  for trans-polyacetylene  $P2_1/a$  model. The smallest circle represents the lowest energy at  $-24.20$  kcal/mol. Each contour is  $1.45$  kcal/mol.

for trans-polyacetylene were  $a = 4.9$  Å and  $b = 5.2$  Å which differ significantly from reported values. This discrepancy has been mainly attributed to neglect of  $\pi$ -bond interactions in the energy calculation function. Discrepancies in the geometric cell parameters cited in literature can often be attributed to the polymorphic nature of many polymers which makes their structural analysis difficult. Furthermore, variations in the methods employed to synthesize the same polymers can incur chain packing variations. Care must be taken, therefore, when interpreting such molecular modeling calculations when applied to packing studies and the limitations of the method kept in mind.

## CONCLUSION

Molecular modeling has proven to be a useful tool in gaining some insight to molecular packing of polymeric chains especially when applied to determining the chain setting angle. A simple van der Waal's calculation algorithm has yielded setting angle values for both polyethylene and trans-polyacetylene models which are in agreement with experimentally determined literature values. The considerations to be taken into account when designing and building a packed chain model have been highlighted so that this simple approach can be adopted and applied to similar systems.

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