Energy calculations of the crystal structure of the low temperature phase (II) of polytetrafluoroethylene

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Energy analysis is used to determine the low energy crystal structure for polytetrafluoroethylene molecules in the 13/6 and 54/25 conformations. The structure for the 54/25 conformation contains an ordered repeating pattern of a left- and right-handed pair of molecules in a unit cell having projected parameters, a', b', and γ', of 9.60 Å, 5.62 Å, and 91.4 degrees, respectively. These results, the relative orientations of the molecules, and the relative translations of the molecules are in good agreement with results obtained in a concurrent and independent analysis of diffraction data. Energies calculated for rotational and translational displacements in various modes suggest that a range of structures and a fairly large amount of disorder may be present, also in agreement with experiment.

INTRODUCTION

Although excellent diffraction patterns, remarkable in their detail, have been available for more than twenty years[1,2] for the low temperature phase (II) of polytetrafluoroethylene (PTFE), neither the correct unit cell nor the specific molecular packing of this polymer had been determined. It was known that the structure corresponds to nearly metrically hexagonal packing of the cylindrical molecules, and that the molecular conformation is approximately represented by a helix with 13 CF_2 groups per six turns. A recent article[3] showed that the $13/6 = 2.1666$ conformation is an approximation to the true conformation which is slightly untwisted to approximately $54/25 = 2.1600$ or $473/219 = 2.1598$ and which may well be incommensurable. These conformations are nearly identical in torsion angle and appearance, but offer somewhat different crystallographic constraints on the molecular packing.

Concurrently with the structure determination based on diffraction analysis reported in the preceding article[4], we began an investigation into the possible modes of packing using energy analysis. Such a dual approach offers a number of advantages over the use of a single technique. First, trial structures uncovered by one analysis can be examined by the other. Second, multiple structures found to be nearly equivalent by one analysis can be evaluated and perhaps weighted by examination by the other. Third, a common structure emerging independently from the two analyses could be anticipated to have greater reliability. Fourth, when independent methods are used to determine the structure, there is less likelihood that a better structure would go undetected.

While similar concurrent diffraction and energy analyses have been undertaken previously[5], the case at hand represents, to our knowledge, the first attempt to predict the molecular packing of such a low symmetry

structure. The problem is further complicated by the absence of a knowledge of the unit cell, or at least of a reasonable guess at a starting model for the unit cell.

COMPUTATIONAL METHOD

The energy calculations were performed using a program described previously[6]. The energy parameters given in *Table 1* were derived from fluoro polymer crystal structure data. Starting with the hydrocarbon parameters found by Williams (Set I)[7], the C—F, H—F, and F—F non-bonded interaction parameters were adjusted until they reproduced (within 3%) the observed unit cell parameters for several fluorine-containing crystalline polymers. The procedure used and the results of other tests of these energy function parameters will be presented elsewhere[8]. It can be noted that calculations undertaken with other previously published parameters[9,10] yielded results that were qualitatively similar to those obtained by using the parameters in *Table 1*.

All principle calculations were performed using one full turn of the PTFE molecule rigidly fixed into either the 13/6 or, in the latter stages of structure refinement, the 54/25 helical conformation. The molecules were generated from the three sets of cylindrical atomic coordinates given in *Table 2*, using a 1.30 Å translation/CF_2 unit and rotational advance angles of 166.1538 and 166.6667 deg/CF_2 unit for the 13/6 and 54/25 conformations, respectively. *Figure 1a* shows a schematic representation of the positions of the carbon atoms projected onto a plane perpendicular to the helix axis of a left-handed molecule. In this and all subsequent diagrams, the radially drawn lines extend from the axis toward the first carbon atom of the molecular segment (the one in the plane of the paper). Of course, both left- and right-handed molecules are possible. The right-handed molecule, shown schematically in *Figure 1b*, was generated by reflection through a mirror plane perpendicular to the y axis of the Cartesian coordinate

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Table 1 Potential functions for non-bonded interaction[a]

Interaction	a [(kcal mol^{-1}) Å^6]	b [kcal mol^{-1})]	c [Å^{-1}]	r_{min} [Å]	E_{min} [kcal mol^{-1}]
C---C[b]	−586.0	86910	3.60	3.85	−0.097
C---H[b]	−112.0	7880	3.67	3.25	−0.043
H---H[b]	−33.5	2923	3.74	3.20	−0.013
F---F	−267.8	19006	3.60	3.45	−0.082
F---C	−365.5	38765	3.60	3.69	−0.079
F---H	−34.5	3346	3.67	3.50	−0.010

[a] Parameters for the equation $E(r) = ar^{-6} + b \exp(-cr)$
[b] From Set I of Ref. 6

Table 2 Cylindrical atomic coordinates[a]

Atom	r [Å]	ϕ [degrees]	z [Å]
C	0.428	0	0
F_1	1.647	−43.10	−0.076
F_2	1.647	+43.10	+0.076

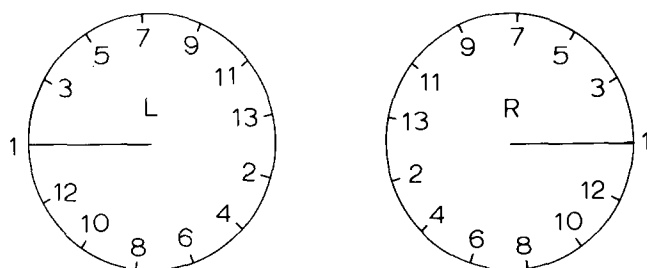[a] See text for helix generation parameters

Figure 1 Schematic representation of the positions of the carbon atoms projected onto a plane perpendicular to the molecular axis for a left-handed molecule (L) and a right-handed molecule (R) in the 13/6 conformation. The zero degree setting angle is horizontal and to the left for the left-handed molecule and to the right for the right-handed one. Positive angular displacements are defined to be counterclockwise. The radial lines point to the first carbon atom which is defined as the one in the plane
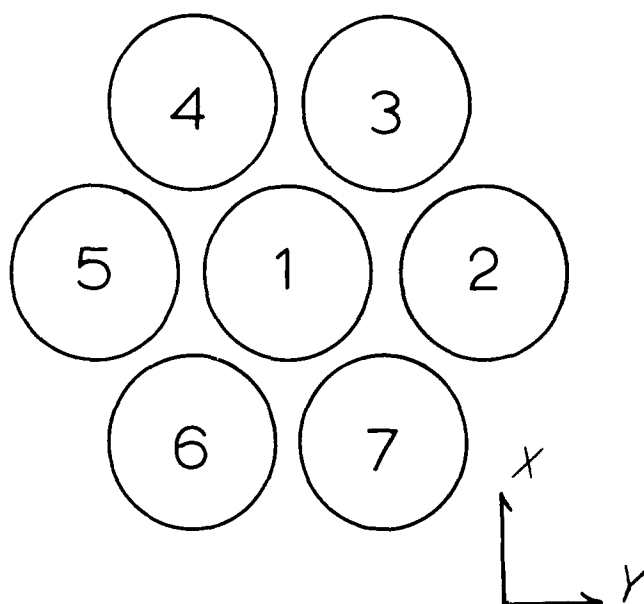

Figure 2 Illustration of the numbering system and the relative positions of the molecules used in the calculations. The molecules are normal to the page

system used throughout the analysis. The setting angles for each molecule were defined relative to the orientations shown in Figure 1—i.e., horizontal to the left for left-handed molecules, and horizontal to the right for right-handed ones. In both cases, positive rotations were defined as counterclockwise.

The numbering system and the relative positions of the molecules used in the calculation are shown in Figure 2. The grid dimensions, X and Y, (orthogonal) were fixed at 9.786 Å and 5.65 Å, respectively, for the exploration of various packing modes. These values for the separation of molecules 3 and 7 and 1 and 2 make all nearest neighbour molecules equidistant (hexagonal packing of cylinders) and were chosen to be slightly larger than the separation which yielded the minimum energy value for a pair of molecules. Thus, no specific set of molecular orientations (namely, those setting angles used to determine the minimum energy cell dimensions) would be inordinately favoured during the subsequent analysis. In the later refinement, the dimensions were adjusted to minimize the packing energy.

Once promising structures had been identified, final refinements of the setting angles and grid dimensions were carried out using a search technique. The variables were

adjusted by the required increments until the energy minimum was located. The minimum increments used were 1 degree and 0.01 Å for the setting angles and grid dimensions, respectively. All refinements were performed using one full turn of the helix at each of the seven numbered positions in Figure 2. Each energy calculated for the seven chain cluster totalled over 35000 individual interactions for the 54/25 conformation and required approximately 3.6 s on an Amdalh* 460/V8 computer.

MOLECULAR PACKING

Calculations for two molecules

There was no information on which to base a reasonable starting point for packing the molecules into a cluster of chains, such as that shown in Figure 2. Therefore, it was necessary to determine how pairs of molecules might orient with respect to one another. The energies relative for a pair of left-handed 13/6 molecules at positions 1 and 2 (Figure 2) are shown in Figure 3. The values were calculated at 27.69 degree intervals of the setting angles, θ_1 and θ_2. This interval, 360/13, referred to as a 'notch', was chosen for several

reasons. First, if any two $-CF_2-$ units in adjacent molecules are to be crystallographically equivalent, the orientations of the molecules must be related by an integer multiple of this notch which brings the projected positions of the $-CF_2-$ units into coincidence. Second, the increment is large enough to render the energy calculations manageable. Third, the increment is small enough to show the general features of the energy surface and to indicate the presence of any major energy minima (or maxima) that may be present. It was found that using angular increments of 30 degrees did not distort the general character of the energy surface. Further, a scan at 6 degree intervals showed that the energy surface was generally smooth and did not contain troublesome features such as very narrow, deep minima that might be overlooked using the notch. Similar results were obtained using two turns of the 13/6 molecule, indicating that end effects are small and the single-turn results approximate those for longer segments.

The most striking aspect of *Figure 3* is the remarkable lack of variation in the energy over virtually the entire surface, the total spread being only 2.5 kcal mol^{-1}. The only marked feature is the presence of the low energy band running along the diagonal, indicating that two like-handed molecules prefer to be oriented at setting angles within one notch of each other—i.e., $\theta_2 = \theta_1 + n \cdot 27.69$, where $n = -1, 0,$ or $+1$. Further, as long as this relation was preserved, the actual value of the setting angle had only a minor effect. The slight variations with angle amount to about 3% differences in the calculated energies within the diagonal band.

Figure 4 shows the relative energies calculated for molecules of opposite hand at positions 1 and 2. In this case, molecule 1 was left-handed and molecule 2 was right-handed. The character of this surface is quite
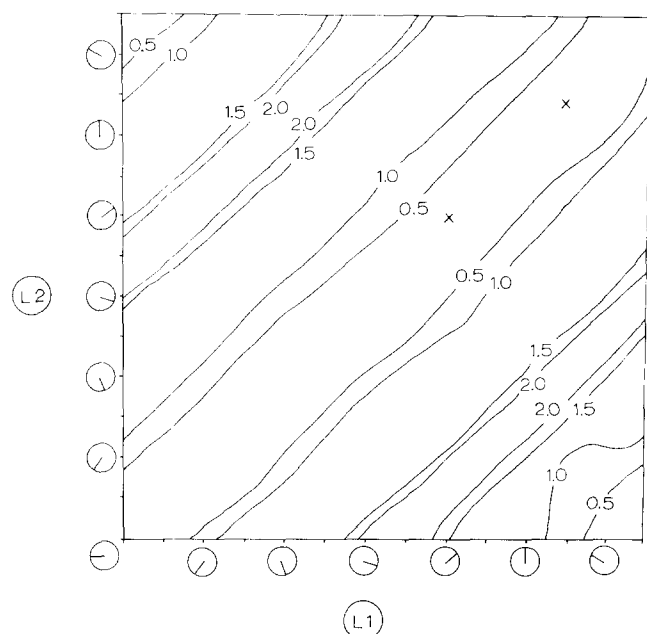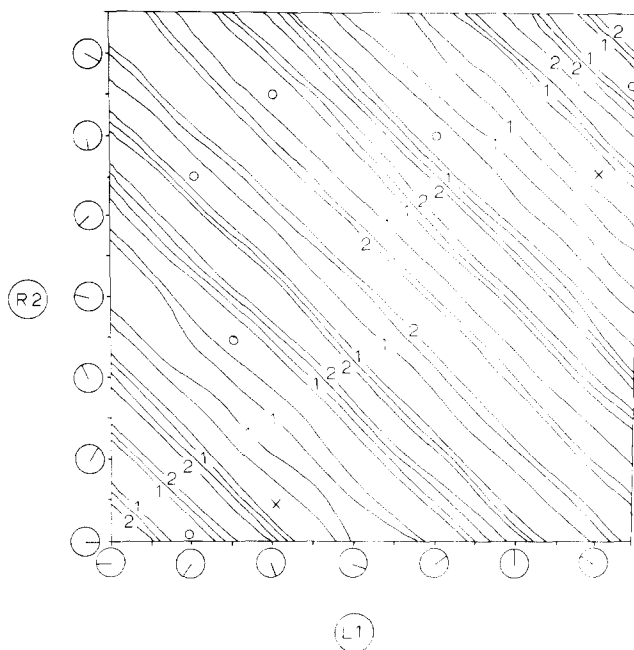

Figure 4 Relative energy for a left-handed molecule at position 1 and a right-handed molecule at position 2 of *Figure 2*. Both molecules are in the 13/6 conformation. The quantities are as defined in *Figure 3*. The circles mark minima which have energies slightly greater than those marked by the crosses. Curves of equal energy are 0.5 kcal mol^{-1} apart. For simplicity, the curves corresponding to energies greater than 2 kcal mol^{-1} are not shown

different from that for like-handed chains. The energy range is now about 5 kcal mol^{-1}, with the low energies being lower and the high energies being higher. The optimum packing for opposite handed chains gave an energy of about -8.8 kcal mol^{-1}, compared to -8.4 kcal mol^{-1} for chains of the same hand*. The single diagonal band of *Figure 3* has now been replaced by a series of low energy bands in the opposite diagonal direction. Because the spacing of the bands appears to vary, this surface cannot be described so simply as could the like-handed map by a simple notch relationship. Instead, the low energy regions give the appearance one might expect from intermeshed screws of opposite hand, the best meshing being accomplished when the screws have a coordinated motion, but in opposite directions.

The effect of translations parallel to the helix axis were also investigated. For pairs of molecules with either the same or opposite hand, and for various relative orientations, the lowest energies were usually obtained when the $-CF_2-$ units on the two molecules were at the same levels. The largest deviations from the coplanar arrangements of the $-CF_2-$ units amounted to 0.2 c ($c = 1.3$ Å) for molecules of opposite hand, and 0.1 c for molecules of the same hand. The actual values giving the minimum energy varied slightly with the orientation of the molecules.

Figure 3 Relative energy for a pair of left-handed molecules in the 13/6 conformation and located at positions 1 and 2 of *Figure 2*. The radial lines in the figures along the axes indicate the setting angle of the carbon atom in the plane of the paper. The markings on the axes indicate 27.69 degree increments. The curves mark the points of equal energy and the numbers give the energy in kcal mol^{-1} with respect to the minima marked by the crosses. For simplification, the 2.5 kcal mol^{-1} curves are not shown

* While the differences in energies presented are significant, the individual energies have a more limited significance. They are given so that some assessment of the energy differences may be made. An energy difference of 0.5 kcal mol^{-1} out of 8 might be taken as more significant than a 0.5 kcal mol^{-1} difference out of 200. The errors inherent in energy calculations are very difficult to assess, there being no experimental error as such. Putting the same variables into the model will repeatedly give an identical energy.

Calculations for three and four molecules

It was necessary to investigate the extent to which the relationship of a pair of molecules might be altered by additional surrounding molecules. Using a cluster consisting of molecules at positions 1, 2, and 3 in *Figure 1* with various combinations of left- and right-handed molecules yielded the result that the -1, 0, 1 notch relationship between molecules of the same hand consistently gave the lowest energies. This relationship was a dominating factor in that it was maintained at the expense of the relationship between opposite handed molecules. The latter departed from the optimum found above for a pair of opposite-handed molecules (*Figure 4*). The energy spans became larger and the topographical features became better defined, suggesting that the tendencies might be reinforced with the addition of further molecules.

Four-molecule clusters were examined. Energies were calculated for molecules located at positions 1, 2, 3, and 4, at 1, 3, 4, and 5, at 1, 4, 5, and 6, and at 1, 5, 6, and 7 with all having the same hand. (Note that the symmetry of the molecules is not equal to that of the crystal.) Since the energies shown in *Figure 3* are fairly uniform along the diagonal, only a small (3 notch) range was examined for the orientation of each molecule. Again it was found that the lowest energies occurred when the -1, 0, 1 notch relationship was satisfied for every pair independently of the relative positions—that is, the relationship was followed for pairs of molecules located at positions 1 and 2, 1 and 3, 1 and 4, etc. It should be noted that the same was true when the X grid dimension was reduced to 9.7 Å.

Since the one notch correlation again appeared for clusters of four molecules of the same hand, and since it had also dominated in clusters of three molecules of mixed hand, it was decided to make further calculations more manageable by imposing this $-1,0,1$ notch restriction on same-handed molecules in larger clusters for the 13/6 conformation. In a crystal containing molecules of opposite hand, at least half of the interactions must be for like-handed pairs. Thus, the computational savings achieved by applying this restriction were substantial. Since no similar predominate relation had emerged for the interactions between opposite-handed molecules, no analogous restrictions were imposed on those pairs, and all thirteen possible orientations had to be considered for each molecule. It would, thus, have been a formidable task to proceed to larger clusters using the same mode of computation. A further simplification was needed.

Calculations for seven and more molecules

Since the calculations were being performed using 360/13 notches exclusively, the energies being calculated were, to a good approximation, simply recalculations of energies for molecules in the same relative orientations. In fact, the calculations could be viewed as primarily taking the energies from *Figures 3* and *4* (or similar ones) and summing them in the various combinations found within a given cluster. Further, it was clear that full exploitation of this fact, while involving the initial generation of a full set of pairwise energies, would allow the very rapid screening of a huge number of packing arrangements. Effectively, the generation of the model and the computation of thousands of atomic interactions could be replaced by fairly simple bookkeeping and indexing to the appropriate orientations in the proper energy table*.

Therefore, the necessary energies were generated in the same manner as those shown in *Figures 3* and *4*. Because the notch increments do not coincide with the geometrical arrangement of the chains around the central molecule, separate energies had to be calculated for interactions between 1 and 2, 1 and 3, and 1 and 4. By interchanging indices, the same energies could be used for interactions between chains 1 and 5, 1 and 6, and 1 and 7. Separate values had to be obtained for left–left, left–right, and right–right combinations at each of these positions. (Because of the lack of 2-fold symmetry about the molecular axis and because of the way the rotational origins were chosen, the energies for like-handed pairs of molecules were different for left- and right-handed cases, the energies being sampled at orientations that were offset by 1/2 notch.)

It was found that the lower energies for a seven-chain cluster of molecules all having the same hand were somewhat lower than -97.0 kcal mol^{-1}. To eliminate consideration of arrangements that had relatively high energies, a -97.0 kcal mol^{-1} cut-off was used. When clusters containing molecules of opposite hand were computed, a cut off limit of -99.5 kcal mol^{-1} was found to be satisfactory. (Recall that the lowest energy for pairs of opposite hand was lower than that for like-handed pairs.) Since the ultimate goal was to arrive at the best mode for packing the molecules into a crystal, the clusters meeting the cut-off requirements had to extend in space. That is, the cluster had to be such that the next surrounding layer of molecules could be added in a comparably favourable fashion. Therefore, energetically acceptable modes of adding the next layer were sought.

Except when all molecules had the same hand, it was assumed that the overall crystal would have equal numbers of left- and right-handed molecules. For the seven molecule clusters, this suggested that rows of molecules (e.g., 1, 3, and 6) would be of the same hand, while the adjacent rows would be of opposite hand (2 and 7, and 4 and 5, for example). Thus, a typical computation would be for three opposite-handed molecules (1, 2, 5) that could assume any of the thirteen notch orientations, and four other molecules which could have any of the three $-1,0,1$ notch orientations, giving almost 180 000 possible clusters. For those meeting the initial cut-off criteria, generally fewer than fifty, an additional surrounding layer of twelve molecules was sought using the same methodology as for the interior cluster.

The specific choice of positions to designate as a row should not, in principle, affect the results. However, the notch relationship does not allow for alignment of a given molecule's 0 degree setting angle along each of the three rows. Thus, the choice of the rows does affect the results. Accordingly, like-handed rows of molecules 6–1–3, 5–1–2, and 4–1–7 were all computed. Further, the small cluster size could lead to some edge effects which differ when either left- or right-handed molecules constitute the central row. Both of these possibilities were explored.

One additional class of computations was done for clusters having molecules of the same hand. The $-1,0,1$ notch relationship was maintained within a row, but was relaxed between rows. This afforded the same scope to the calculation as for mixed-hand clusters. In no case were

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* Approximately 180 000 different seven chain clusters could be examined in about 5 s, a time about 10^{-5} of that for the direct computation.
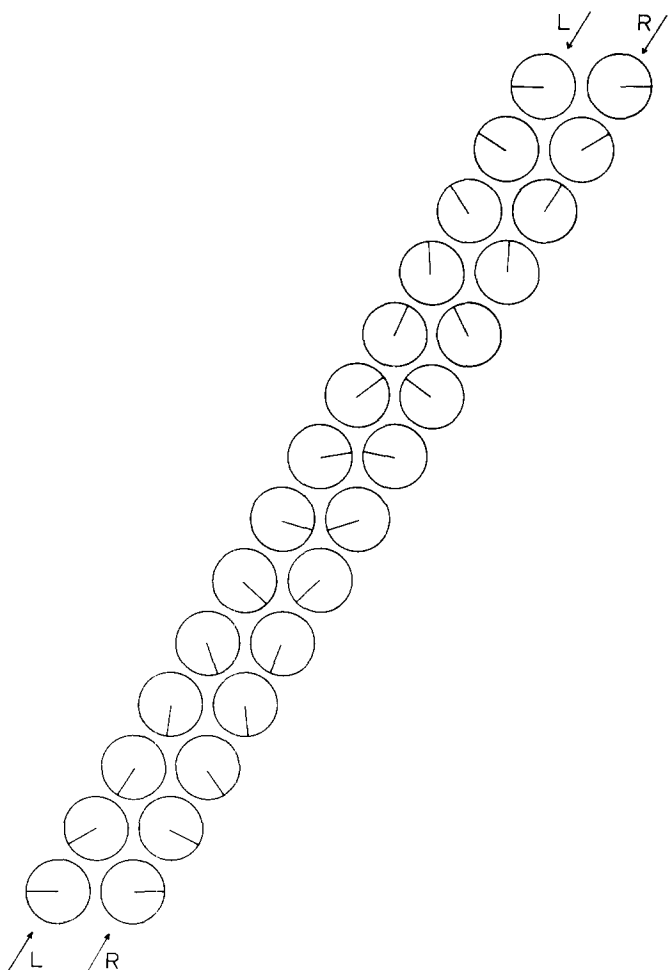
Figure 5 Illustration of the relative change of setting angle for successive molecules in rows of right- and left-handed molecules in the low energy structures for the 13/6 conformation. Left-handed molecules are indicated by L and right-handed by R. The radial lines indicate the setting angle of the carbon atom in the plane of the paper. The lowest energy relationships between the rows are given in *Figure 6*

molecule with an equivalent setting angle has this same environment (except for interchanging left- and right-handed molecules) when the array is viewed 'upside down'.

To ascertain that there were no other packing modes of a similar nature, all possible arrangements of such ascending/descending row pairs, as in *Figure 5*, were computed. It was found that the three arrangements already presented in *Figure 6* are indeed the lowest energy structures.

Because of variable small edge effects, calculations for small clusters of molecules yielded energies which varied slightly with the orientation of the central molecule.
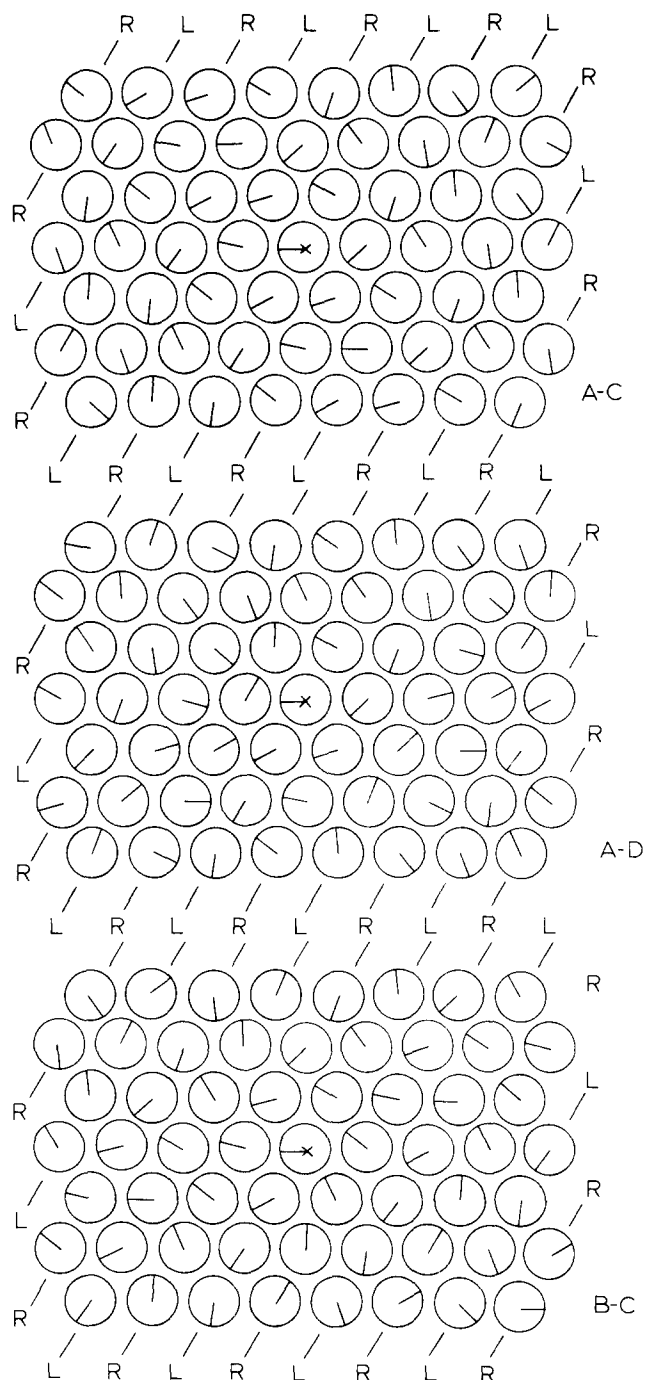
Figure 6 The three different low energy structures for molecules in the 13/6 conformation. The rows of left-handed molecules are indicated by L and right-handed by R. For comparison purposes, note that the central left-handed row which contains the molecule marked with a cross is identical in all three structures

acceptable clusters found which did not of themselves maintain the −1,0,1 notch relationship both between and within rows.

It was found that the great majority of energetically suitable and extendable structures were merely variations of three fundamental clusters. Those that did not fit the three modes were higher in energy.

The recurring structures are simply interrelated. In each, the like-handed rows were found to exhibit a monotonic progression of setting angle. Along a given row, the setting angles are given by $n(360/13)$ for $n = 1, 2, 3$ ... 13 in sequence. The adjacent rows (of opposite hand) were arranged in the same fasion, but progressing in the opposite direction, as shown in *Figure 5* where the radial lines indicate the setting angle. The different structures exhibited different lateral relationships between these rows. The arrangements are shown in *Figure 6*.

The relationships among the three structures are as follows. The two designated A–D and A–C have the same relative positions for the central row and the row to its right. Structures A–C and B–C have the same relative positions for the central row and the row to its left. These patterns (row to the left, row to the right) are reapplied to generate the entire array. This can be seen by noting that every left-handed molecule with a given setting angle has an identical environment. Further, every right-handed

Table 3 Energies for row-based packing modes for the 13/6 conformation

Packing mode	Energy[a] [kcal mol^{-1}]
A–C	–348.5
A–D	–349.0
B–C	–348.2

[a] Average calculated for a nineteen-chain cluster, centred about a molecule at each of the thirteen possible orientations

Therefore, the arrays in *Figure 6* were compared on the basis of total energy for a nineteen-molecule cluster, averaged over clusters having the central molecule at each setting angle. These average energies, given in *Table 3*, show the energy differences among the three arrays to be quite small, especially in light of the magnitude of the total energies. This result was also obtained if the edge effects were minimized by performing calculations for clusters with each molecule extended to three helix repeats.

It should be noted that the data in *Table 3* are for like-handed rows being taken as 6–1–3 etc. The results obtained when the 4–1–7 rows were like-handed were identical. When the like-handed rows were taken as 5–1–2, similar structures resulted, but the energies were considerably higher, with the best having an energy 4 kcal mol^{-1} higher than the worst 6–1–3 case. Therefore, only rows in the 6–1–3 direction are considered. Also, it should be noted that the energies for arrays of molecules having the same hand were 9–10 kcal mol^{-1} higher than those in *Table 3*, allowing the rejection of that type of structure.

Unit cell for the 13/6 molecule

The arrays in *Figure 6* can each be described by a two-molecule unit cell. Because the rotationally ascending and descending rows contain oppositely handed molecules and because positive rotation is counterclockwise for all molecules, the relative translation, parallel to the chain axis, between equivalent $-CF_2-$ units on successive molecules in the same row is the same (magnitude and direction) for all rows. Thus, as shown in *Figure 7*, the unit cells all have a two $-CF_2-$ unit z-component of the $\underline{b}$ cell dimension (shown as its projected length $\underline{b}'$) and differ only in the z-component of the $\underline{a}$ cell dimension (shown as its projected length $\underline{a}'$).

It is useful to compare these packing arrangements with the results of the concurrent X-ray structure analysis[4]. The latter showed that the unit cell contains two molecules of opposite hand arranged in a manner analogous to those in *Figure 7*. Also, it showed that the helix is not 13/6, but is slightly untwisted to a 54/25 or more accurately a 473/219 helix and might well be incommensurable. The molecules of the same hand at the corners of the cell have a setting angle difference, $\Delta\theta_b$, along the $\underline{b}'$ direction of about 36 degrees and along $\underline{a}'$, $\Delta\theta_a$, of about 46 degrees. The 36 degree value is similar to the one-notch (27.7 degree) difference found along $\underline{b}'$ in the present analysis, and the 45 degree value is similar to that in structure B–C. However, as noted before, imposing crystallographic constraints on the 13/6 molecules requires that the differences between the setting angles of crystallographically equivalent molecules must be integral multiples of the 27.69 degree notch. Thus, the results for the 13/6 molecule cannot be crystallographically identical to the results obtained from

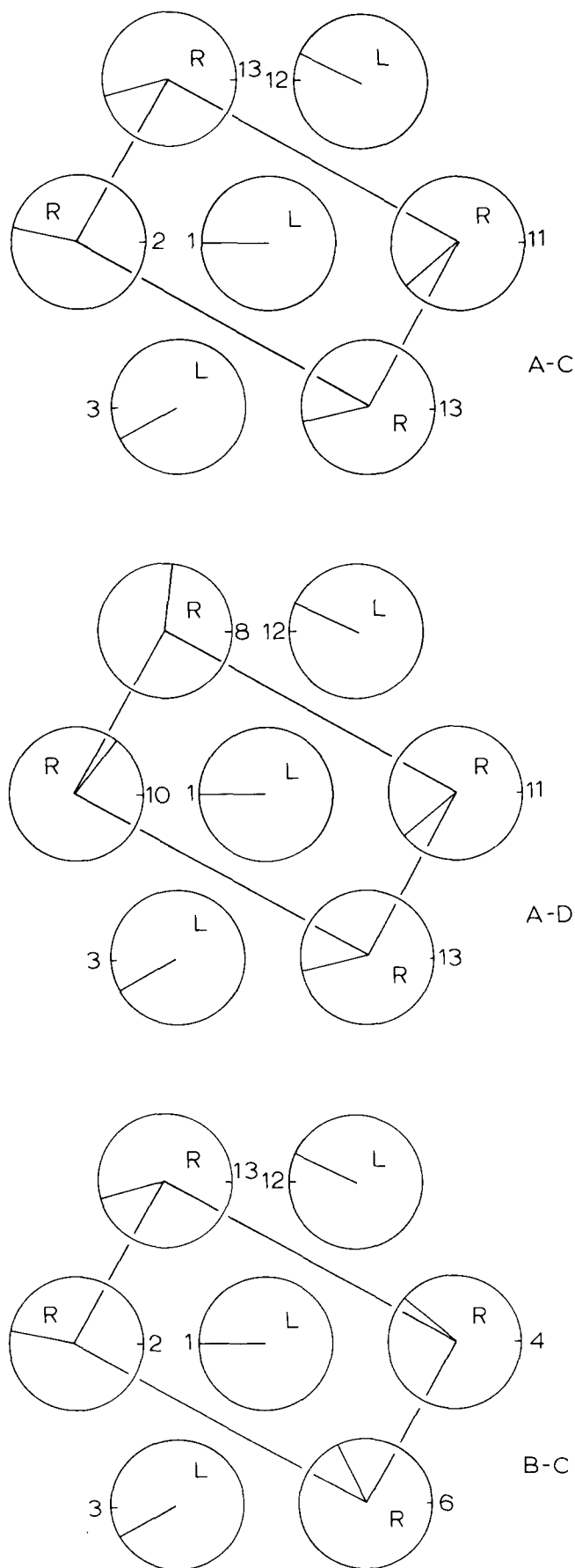*Figure 7* The three lower energy unit cells for molecules in the 13/6 conformation. The radial lines indicate the setting angle of the carbon atoms in the plane of the paper and the numbers are for the crystallographically equivalent carbon atoms on each molecule. The larger edge is the projected cell dimension $\underline{a}'$ and the shorter is $\underline{b}'$
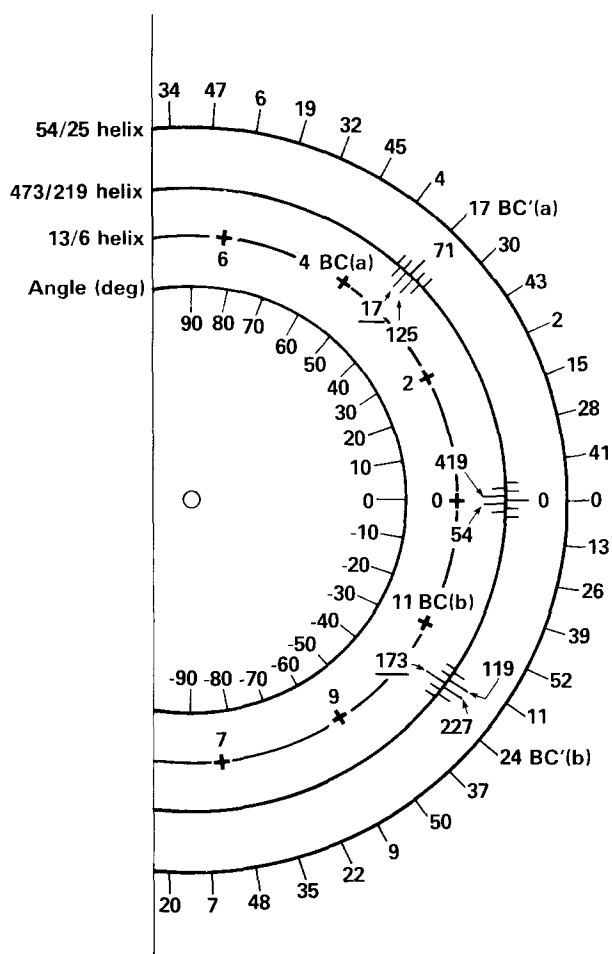
Figure 8 Schematic representation of the positions of the carbon atoms projected onto a plane perpendicular to the molecular axis for right-handed molecules in the 13/6, 54/25, and 473/219 conformations. The meaning of the marked carbon atoms is discussed in the text

the X-ray analysis. It was found, however, that removing the crystallographic constraints allowed the 13/6 molecules to pack in a mode with an energy about 2.5 kcal mol^{-1} lower than the energies given in *Table 3*. This suggested that if the calculations were extended to the 54/25 conformation for which the notch is only 6.67 = 360/54 degrees, the molecules might pack in a crystallographic mode which exhibited lower energy and corresponded more closely to the results from the X-ray analysis.

Extension to 54/25 conformation

Figure 8 shows, for three different conformations, the crystallographically permissible relative setting angles for pairs of equivalent right-handed molecules, all with their 0th carbon atom at the same orientation (horizontal to the right). The inner circle is graduated in degrees for reference. The ' + ' marks at slightly larger radius show the setting angles for the carbon atoms of a 13/6 molecule. On the outer circle are marked the setting angles for a 54/25 molecule. The angle by which carbon 13 misses the right-horizontal position is indicative of the small amount of untwisting necessary to form the 54/25 conformation from a 13/6 conformation. The circle for the 473/219 conformation shows a few of the setting angles which are only 0.76 = 360/473 degrees apart. The angle by which carbon 54 of this conformation misses the right-horizontal position is indicative of the very small amount

of untwisting necessary to form the 473/219 conformation from the 54/25 conformation. There is very little difference among the conformations, and the major difference is just a relaxation of the angular constraints imposed by crystallography. The 13/6 positions are well separated, the 54/25 positions are separated by about a quarter as much, and the 473/219 imposes virtually no constraints.

Since the 162 atoms in one turn of the 54/25 molecule represent a much more manageable calculation than the 1419 in the 473/219 molecule, subsequent calculations were made with the former. Because the ends represent a much smaller proportion of the model than in the 13/6 case, end effects are smaller. Therefore, the calculations were made with one turn of the molecule. A seven-molecule cluster was used. The energy of each of the three packing modes described previously was minimized simultaneously with respect to $\Delta\theta_b$ and $\Delta\theta_a$, while holding the central molecule at a fixed orientation and the cell dimensions fixed at the values used previously. Then, because there is no crystallographic constraint between the central chain in the unit cell and those at the corners of the cell, the energy was minimized with respect to the actual setting angle values. This was accomplished by changing the setting angles of 1, 3, and 6 as a group, and the angles of 2, 4, 5, and 7 as a group to minimize the energy. In all cases the crystallographic constraints for the 54/25 molecule were maintained. These two constrained minimizations were repeated in sequence until the setting angles no longer changed. The grid dimensions, *X* and *Y*, were then adjusted to give the minimum energy, and the setting angle minimization was repeated. (*X* and *Y* were, however, maintained mutually perpendicular so that a', b', and γ' were not varied independently.) Any changes led to subsequent repetition of the grid dimension adjustment and so on. A similar process was then followed to minimize the energy with respect to small translations of the molecules parallel to their axes. Thereafter, the whole process was repeated until the molecular packing was optimized.

Unit cell for the 54/25 conformation

The results of these minimizations for three packing modes are shown in *Table 4*. Of the three, B C' is the lowest in energy and is in good agreement with the results of the diffraction analysis which are also given in the table. This agreement can be illustrated with the use of *Figures 8* and *9* and the data in *Table 4*. If a right-handed molecule in the lower left corner of the unit cell has an orientation defined at the 0 setting angle position, the equivalent molecule at the upper left corner (a distance b' away) will have the orientation denoted BC' (*b*) (*Figure 8*) with its 24th - CF_2 - unit in the same orientation as the 0th - CF_2 unit of the molecule at the origin. Similarly, for the molecule at the lower right (a distance a away), the 17th - CF_2 - unit [BC'(*a*)] will be the one equivalent to the 0th - CF_2 of the molecule at the origin. The carbon positions shown on the 473/219 circle are those orientations which give nearly the same good agreement to the X-ray results, and the underlined values are those giving the best agreement. Clearly, the orientations available to the 54/25 molecule are closer than those for the 13/6 molecule to the experimentally determined orientations. Certainly the former are close enough that it would be difficult to place much significance on the slight differences, especially considering the degree of disorder apparently present in the structure[4].

Table 4 Three packing modes for the 54/25 conformation

Packing mode	a'^a [Å]	b'^a [Å]	γ'^a [degrees]	$\Delta\theta_a$ [degrees]	$\Delta\theta_b$ [degrees]	Energy[b] [kcal mol^{-1}]
A–C'	9.61	5.64	91.6	40	33.33	−229.0
A–D'	9.63	5.62	91.1	140	33.33	−228.7
B–C'	9.60	5.62	91.4	−46.67	40	−230.8
Experimental[c]	9.649	5.648	90	−46.4	35.8	

[a] Projected unit cell parameters
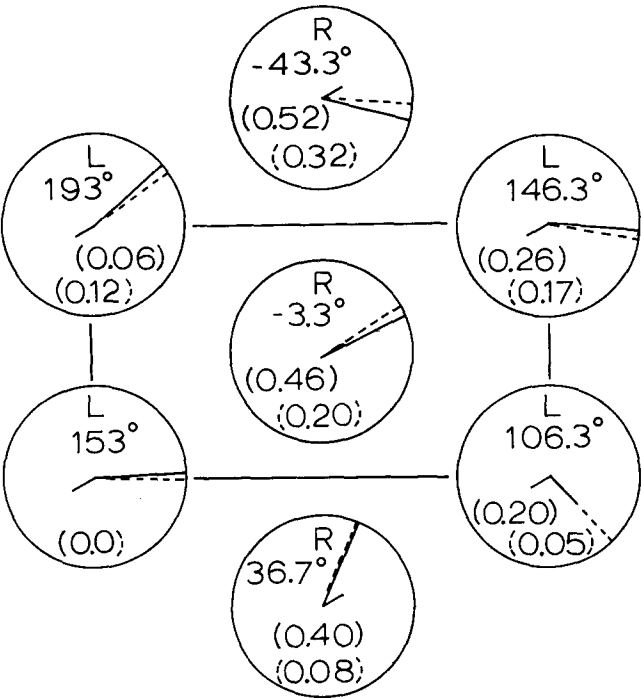[b] Calculated for a seven chain cluster
[c] From ref. 4

Figure 9 The lowest energy unit cell, BC', for molecules in the 54/25 conformation. The solid radial lines indicate the setting angle of the carbon atoms nearest to the plane of the paper and the numbers in brackets are translations (in Å) of the molecules perpendicular to and above the plane of the paper. The broken lines give the corresponding quantities obtained from the analysis of X-ray diffraction data. The short radial lines mark the zero-degree setting angle

The solid radial lines in *Figure 9* show the orientations for the molecules in the unit cell calculated to have the lowest energy, while the dotted lines indicate the values determined by X-ray analysis. The discrepancies are small. The change in setting angle along a' is about − 46 degrees in both cases. Along b', the energy analysis yields a setting angle change of + 40 degrees, while the X-ray analysis yields about + 36 degrees. (Note that the sign of the rotation with progression along a' and b' depends on whether left- or right-handed molecules are placed at the corner positions.) *Figure 9* places left-hand molecules at the corners, yielding − and + signs for $\Delta\theta_a$ and $\Delta\theta_b$, respectively. *Figure 8* is drawn for a right-handed molecule and, thus, has the signs reversed. The agreement between the orientations for the central (independent) molecule as derived from both methods is also good. The discrepancy is only a few degrees and can probably be ascribed to the differences in $\Delta\theta_b$, since the lowest energy orientation of the central molecule could be dependent on the orientations of neighbouring molecules to the extent necessary to yield the small discrepancy. The translations of the molecules parallel to their axes are close to the

Table 5 Excess energy[a] of other packing modes for the 54/25 conformation

$\Delta\theta_a$ (degrees)\ $\Delta\theta_b$ (degrees)	33.33	40
40	1.8	0.8
46.67	1.0	0
53.33	1.5	0.4

[a] In kcal mol^{-1} with respect to BC'

experimentally determined values (both sets are given in *Figure 9*). Finally, the values of a', b', and γ' given in *Table 4* are in close agreement with the experimental values.

While the small differences in the results obtained by the two analyses warrant comment, it is also important to bear in mind that good overall agreement has resulted. From markedly different starting points and with different approaches, the energy calculations and X-ray analyses converged to essentially a single structure.

Variations and disorders in the structure

Figure 8 suggests that a number of other structures might also approximate the structure found by analysis of the X-ray data. These result from various combinations of 33.33 and 40 degrees for $\Delta\theta_b$ with 40, 46.67 and 53.33 degree for $\Delta\theta_a$. They were analysed to yield the results in *Table 5* which shows the excess energy of the structures with respect to BC'. In view of the small values, a number of these could coexist with BC' and contribute some disorder to the crystal. For the 473/219 conformation with a smaller notch, an even larger number of structures can be expected to exist.

A related question is whether the low-energy structures are located in broad or sharp energy minima. That is, are the structures found for given values of $\Delta\theta_a$ and $\Delta\theta_b$ unique? To examine this, molecules number 1, 3, and 6 were rotated in one angular direction while molecules 2, 4, 5, and 7 were rotated by the same amount in the opposite direction. In this mode of rotation, the original structure repeats every 6.67 degrees, but different structures occur at intermediate angles. The results obtained with BC' as the starting structure show that the other structures have only slightly higher energies. Very likely, they coexist and disrupt the regularity of the crystal.

Uncoordinated rotations (and translations) of the molecules is a disorder suggested by the diffraction analysis. To investigate this possibility, the central molecule, number 1, was subjected to these disorders. The energy increased by about 0.5 kcal mol^{-1} for a rotation of 3 degrees and by slightly more than 2 kcal mol^{-1} at 6 degrees. Translation by about 0.07 Å increased the energy by 0.5 kcal mol^{-1} and by 0.13 Å increased it by 1.3 kcal mol^{-1}. Screw displacement of the molecule yielded only slightly different energy results with, for example, a

rotation of 3 degrees combined with a translation of 0.07 Å increasing the energy by 0.7 kcal mol^{-1}. Rotation by 6 degrees combined with a translation of 0.13 Å increased the energy by 2.1 kcal mol^{-1}. All these numbers were almost unchanged when the grid dimensions were increased to 5.55 and 9.86 Å. Coordinated displacement of pairs of molecules yielded similar results.

The results presented in the three preceding paragraphs are consistent with disorders existing in the crystal. The root-mean-square deviations of about 0.2 Å and 10 degrees suggested by analysis of the X-ray data cannot be ruled out.

CONCLUSIONS

Energy analysis has been used to determine the mode of packing molecules of polytetrafluoroethylene in the 13/6 and 54/25 conformations into a low-energy crystal structure. The structure given in *Figure 9* and *Table 4* for the 54/25 conformation agrees well with the results of analysis of diffraction data. It consists of two molecules of opposite hand in a unit cell having projected parameters, a', b', and γ', of 9.60 Å, 5.62 Å, and 91.4 degrees, respectively. The relative orientations of the molecules are in good agreement with the results of an analysis of the diffraction data. Energies calculated as a function of rotational and translational displacement in various modes suggest that a range of structures coexist and that a fairly large amount of disorder may be present, also in agreement with experiment. These results demonstrate the usefulness of energy analysis techniques and of the energy functions and parameters used. The analysis offers insight, not otherwise available, to the molecular origins of the various structural details observed.

REFERENCES

1   Bunn, C. W. and Howells, E. R., *Nature (London)*, 1954, **174**, 549
2   Clark, E. S. and Muus, L. T., *Z. Krist*, 1962, **117**, 119
3   Clark, E. S., Weeks, J. J. and Eby, R. K., *ACS Symposium Series*, 1980, **141**, 183
4   Weeks, J. J., Clark, E. S. and Eby, R. K., *Polymer* 1981, **22** (in press)
5   Farmer, B. L. and Lando, J. B. *J. Macromol. Sci.-Phys.* 1974, **B10**, 381 and 403
6   Farmer, B. L. *M. S. Thesis* (Case Institute of Technology, 1972). The basic program may be obtained from B. L. Farmer
7   Williams, D. E., *J. Chem. Phys.* 1967, **47**, 4680
8   B. L. Farmer (to be published)
9   Tonelli, A. E. *Macromolecules* 1976, **9**, 547
10 Liquori, A. M. and DeSantis, P., *J. Polym. Sci. C*, 1969, **16**, 4583