A New Structure for Crystalline Natural Rubber

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ABSTRACT: Natural rubber becomes crystalline when stretched or when cooled, yet the structure of this ordered form has never been satisfactorily determined. We have used film-recorded fiber X-ray diffraction data from oriented unvulcanized natural rubber, combined with linked-atom-least-squares molecular modeling and refinement, to provide what we believe is a better structure for crystalline natural rubber than any proposed before. Having tested other plausible alternatives, our final crystal structure is orthorhombic with $P2_12_12_1$ symmetry. The molecular (and crystal) asymmetric unit is a di-isoprene in which the two isoprene residues have distinctive, not symmetrically related conformations. A significantly better fit with the Bragg diffraction pattern is obtained if it is assumed that sheets of rubber molecules can replace one another at random in the crystal structure. This structural feature also explains the non-Bragg layer line streaks that are a prominent feature of rubber diffraction patterns that hitherto have been largely ignored.

Introduction

Natural rubber, *cis*-polyisoprene, from the tropical tree *Hevea brasiliensis*, is still used to provide about one-quarter of rubber-based products sold worldwide, and this may increase in the future because the remainder, coming from synthetic rubber manufactured from petroleum products, is not renewable. Rubber exists as a viscoelastic, apparently amorphous solid at room temperature but becomes polycrystalline on cooling and provides an X-ray diffraction pattern of the crystalline powder type. Crystallinity can also be induced at ordinary temperatures by stretching rubber specimens and maintaining the tension. In this case, the microcrystals become uniaxially oriented in the direction of tension and provide X-ray patterns of the crystalline fibre kind. There have been many attempts to determine the molecular structure and packing in this system. The most intensive early analysis, undertaken by Bunn,[1] was much criticized by Nyburg,[2] whose own conclusions were in turn questioned by Natta and Corradini[3] without total resolution of the issues. Arnott and Wonacott[4] hoped that rubber would prove an easy target for structural analysis when they introduced the linked-atom-least-squares (LALS) approach to fiber diffraction analysis.[5] As it turned out, discrimination among the competing structures for rubber proved too challenging for LALS in the embryonic stages of its development, and their rubber project was suspended in favor of other more pressing investigations of polynucleotides and polypeptides. The present analysis essentially is a completion of this early project that exploits a more sophisticated version of LALS and many decades of experience in its use.

The difficulty with rubber was and is that all the plausible molecular models for rubber consist of more-or-less flat polyolefin chains that are very similar to one another at the resolution (2 Å) of the available diffraction data. These data, relative to the number of atoms in the di-isoprene unit of structure, which consists of 10 carbons and 16 hydrogens (Figure 1), are also few in number: about 45 rising to 90 if one includes the not unimportant below-threshold reflections in the same field. LALS makes atomic positions dependent on fixed bond lengths (always) and fixed bond angles (usually) and has as variables only a small number of conformation angles and other gross molecular parameters such as position and orientation in the crystal unit cell. Because these fewer variables are subject to further constraints such as polymer chain connectivity, the number of degrees of freedom for a low-resolution fiber structure becomes more appropriate for confrontation with the available X-ray data. The LALS analytical strategy was always right for crystalline rubber, but the multiple structural options for rubber made it an inappropriate test bed for the development of LALS, which only reached its mature stage a decade later.[6] An important factor in the mature use of LALS was its linkage with strong measures of significance when the optimum versions of competing structures needed to be compared[7,8] and especially when the number of parameters was different. Now that LALS has accumulated decades of successful applications to controversial fiber structures, it has become possible to complete the rubber project using the original data with the expectation that our results would provide a launchpad for further analyses using synchrotron-derived data that would test the accuracy of our conclusions and provide more precise models. In the event, three analyses[9−11] using synchrotron-derived data had been conducted without knowledge of our work and had reached conflicting conclusions that we believe our modeling had already resolved or at least had provided better interim solutions.

Experimental Section

The X-ray data of Arnott and Wonacott[4] were obtained at room temperature from a stretched specimen of natural (unvulcanized) rubber using Ni-filtered Cu Kα radiation with an Elliott toroidal focusing X-ray camera.[12] A conical film holder[13] with a pack of two films was used to cover the range of intensities. The reciprocal lattice coordinates of the reflections were calculated from film measurements using an instrument with a no-parallax setting arrangement. The intensities were measured using a Joyce−Loebl recording microdensitometer.

The diffraction pattern was indexed on the basis of a rectangular cell ($a = 12.58(6)$ Å, $b = 8.98(5)$ Å, $c = 8.20(5)$ Å, and fixed $\alpha = \beta = \gamma = 90°$). These dimensions are similar but not identical to Bunn's cell that had β ($= 92°$) as an additional variable. Like Nyburg, we observed no intensity that required us to fit the diffraction spot positions with four variables rather than the more

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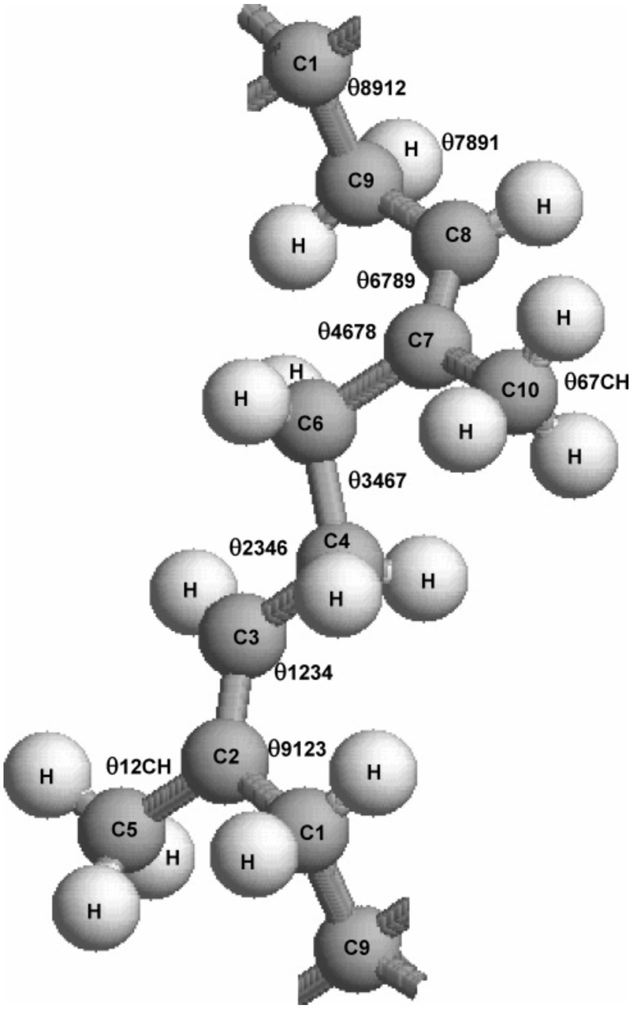

Figure 1. Di-isoprene unit of structure in crystalline rubber with the atomic numbering system used in the tables of coordinates. In addition to the conformation angles shown as *θpqrs*, the other molecular variables were three Eulerian angles, orienting the di-isoprene with respect to the unit cell axes, and a molecular radius. We are well aware that this description has more variables than there are degrees of freedom when the di-isoprene residue is part of a repetitious chain molecule with a known repeat length and an axis parallel to the fiber axis. Nevertheless, it seems to us desirable to make every conformation angle of the molecular asymmetric unit an explicit variable, and to segregate the molecular positioning and orienting variables from the conformations. Once allowance is made for connectivity and other constraints and the redundancy among the explicit variables is removed, the net number of degrees of freedom in these molecular structures is generally 6 fewer than the number of variables and 11 fewer when the two isoprene units are symmetrically related.

parsimonious three. In our dataset, there are 43 above-threshold reflections whose intensities can be measured, but in the same field of observation, there are a further 48 possible reflections with intensities that are below threshold (Table 1). Nyburg's replacement structure had a rectangular cell ($\beta = 90°$) but was intended to have the same monoclinic space group as Bunn's. Unwittingly the structural features adopted by Nyburg were those of orthorhombic space group *Pbac*, as was pointed out by Natta and Corradini[3].

Table 1. Measured Structure Amplitudes, *F*(obs)[a]

		F(obs)				
RR(Å^{-1})	*h k*	*l*				
		0	1	2	3	4
	0 0	M	N	N	N	N
0.0795	1 0	0	<*T*	<*T*	<*T*	<*T*
0.1114	0 1	0	<*T*	199	<*T*	<*T*
0.1369	1 1	<*T*	234	261	<*T*	<*T*
0.1590	2 0	1074	1160	612	158	205
0.1941	2 1	<*T*	219	124	<*T*	<*T*
0.2228	0 2	<*T*	<*T*	381	<*T*	<*T*
0.2366	1 2	2398	1117	204	244	<*T*
0.2385	3 0					
0.2632	3 1	182	527	446	143	115
0.2737	2 2					
0.3180	4 0	610	201	259	<*T*	<*T*
0.3264	3 2					
0.3342	0 3	<*T*	149	434	279	162
0.3369	4 1					
0.3435	1 3					
0.3701	2 3	<*T*	409	210		
0.3883	4 2	<*T*	<*T*	<*T*		
0.3975	5 0					
0.4106	3 3	<*T*	<*T*	629		
0.4128	5 1					
0.4456	0 4	628	<*T*	357		
0.4526	1 4					
0.4556	5 2					
0.4613	4 3	<*T*	201	428		
0.4731	2 4	<*T*	296	<*T*		
0.4769	6 0					
0.4898	6 1	<*T*	<*T*	<*T*		
0.5054	3 4	<*T*	<*T*	323		
0.5193	5 3	<*T*	<*T*	182		
0.5264	6 2					
0.5474	4 4	<*T*	<*T*	<*T*		
0.5570	0 5,7 0					
0.5626	1 5	<*T*	260	265		
0.5675	7 1					
0.5792	2 5	<*T*	<*T*	277		
0.5824	6 3					
0.5971	5 4	<*T*	279	<*T*		
0.5994	7 2					
0.6059	3 5					
0.6359	8 0	364	302			
0.6414	4 5					
0.6456	8 1					
0.6491	7 3					

[a] The values of RR(Å^{-1}) are the reciprocal space cylindrical polar radii for the *hkl* reflections. N indicates reflections inaccessible in this experiment. The amplitudes of below-threshold reflections are shown as <*T*.

Space Group Assignment

Every candidate crystal structure has to be able to provide calculated X-ray intensities in close correspondence with those that can be measured explicitly. In addition, accounting for the absent reflections is just as important a requirement. One way of doing this is to choose a space group with symmetry elements that result in appropriate classes of reflections having zero intensity. This is not generally appropriate for diffraction data from fibers, where the number of reflections in any class is relatively low and the observational thresholds so high that it would be unsafe to assume that a below-threshold reflection is likely to be systematically absent (i.e., with zero intensity due to the lattice). It is expressly inappropriate in the case of crystalline rubber, where the assumption that most of the absent reflections have zero intensities rather than values below a particular threshold immediately imposes constraints on the crystal and molecular models that should be considered. Bunn was a victim of this inappropriate approach. Having been led into the monoclinic system by accepting $\beta = 92°$ rather than 90°, he used the absence of $h0l$, $0k0$, and $h00$ reflections when h or k were odd to assign $P2_1/a$ as the space group and thereby condemned his crystal structures for rubber to have 2-fold screw axes, glide planes, and centers of symmetry. Nyburg followed Bunn and accepted his monoclinic space group, albeit with $\beta = 90°$, but then devised a statistical crystal structure using the crystal glide planes to create this. Because each of his molecules also had internal glide planes, he unwittingly[3] produced an orthorhombic structure *Pbac* for which there would be a great

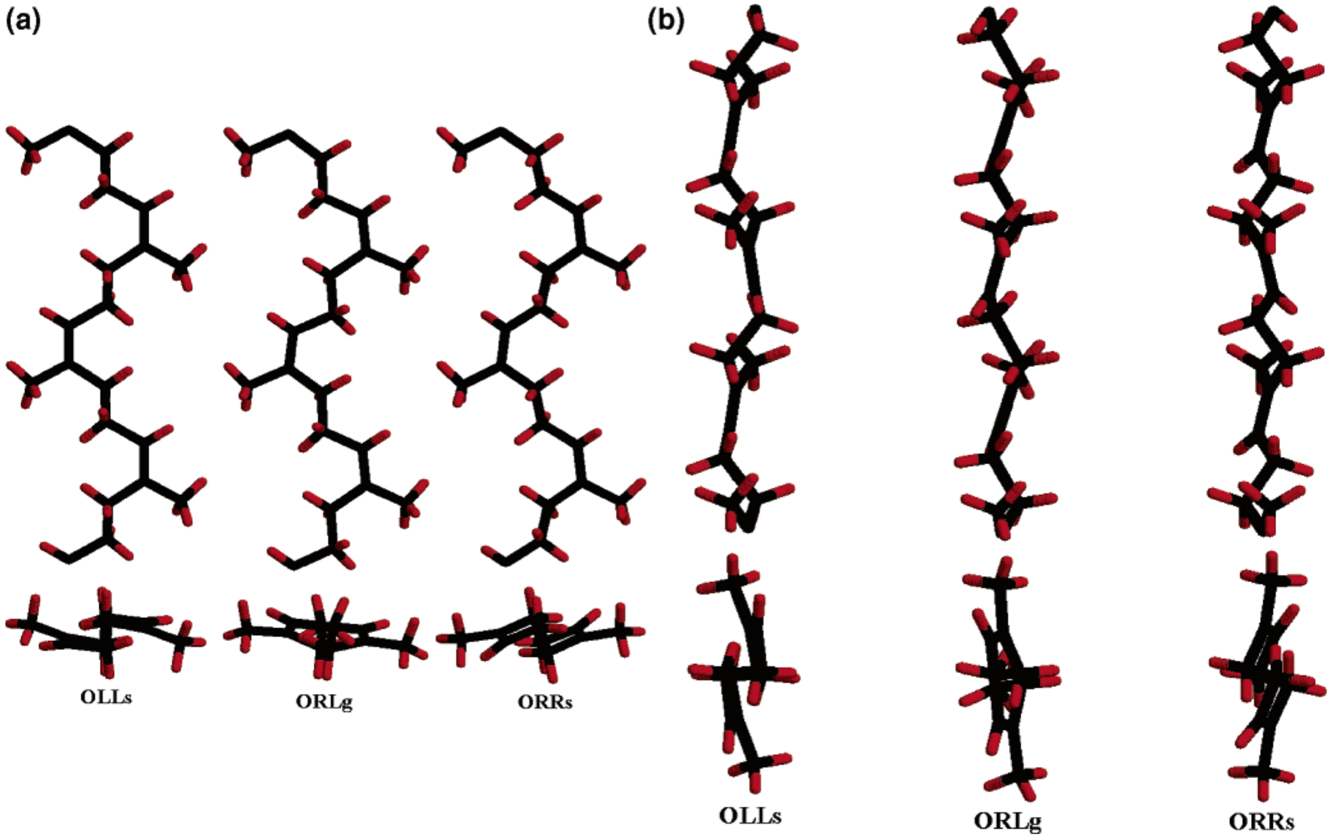

Figure 2. (a) Two successive isoprene residues from symmetric models for the molecular ribbons of rubber seen face on (above) and axially (below): in LLs and RRs, alternate residues are related by 2_1 screw axes, but the conformation angles in the latter are all negative and in the former all positive; in RLg alternate isoprene residues are related by a glide plane so that their corresponding conformations are precisely the negatives of each other. (b) The same molecular segments as in (a) but viewed edge on (above) and axially (below). These diagrams indicate how subtle are the differences among competing rubber models and therefore how meticulous the X-ray analyses have to be.

swathe of systematically absent (i.e., zero intensity) reflections: 0*kl*, *h*0*l*, *hk*0, *h*00, 0*k*0, 00*l* would be absent for *k*, *l*, *h*, *h*, *k*, *l* odd, respectively. In fact, some of these reflections are unambiguously and intensely present (e.g., 022), but inexplicably do not appear in Nyburg's list of observations. The lessons to be learned are clear: if a space group is pre-assigned, then the constraints it imposes on the crystal packing and internal molecular structure should be understood explicitly; reciprocally, when constraints are added to a structure, it should be understood that they may lead to a revision of the space group. In practice, it is better to adopt a space group from the options available that imposes the fewest constraints on the structures being explored and to exchange this for a more demanding alternative when the initial refinements indicate that this should be done.

What we and other investigators since Bunn have observed is a rectangular unit cell with four chains passing through it. It would be perverse not to start by assuming that these four chains might be identical and that the crystal symmetry might be orthorhombic. If orthorhombic, then the least-constraining set of consequent symmetry elements would be three mutually perpendicular 2-fold axes. These would define the positions of the three additional chains in the unit cell with respect to the generating chain, but would imply nothing about the relationship of the two isoprene units that comprise the molecular asymmetric unit within the generating chain. A staggered arrangement of chains in the *ab* plane (as shown later in Figure 4) has never been in dispute, whatever the space group assignment, and this implies that two of the 2-fold axes are screw axes and modestly requires that *h*00 and 0*k*0 are absent for *h* or *k* odd. Confirming also the absence of 00*l* (meridional) reflections with *l* odd has been a special concern of many investigators. Our assignment of $P2_12_12_1$ as the provisional space group (rather than $P2_12_12$) is, therefore, a very sensible place to start because it places the scattering material in uncontroversial positions and leaves the important question of the chain symmetry to be determined in the structure refinement.

Statistical Crystal Structures for Rubber. For all space groups mooted by us or by others, the four chains passing through each unit cell include two chains with one sense (up, say) and two that would have the opposite sense (down). Despite there being an equal number of chains of each sense in each unit cell, there is also the possibility that, in rubber "crystals", the chains are not so well segregated. Therefore, packing arrangements have to be considered where there is an equal probability of a chain of either sense being at each molecular site, leading to a "statistical" crystal structure. The diffraction patterns of statistical crystals show Bragg reflections just like an ordinary crystal, but the intensities of such reflections would derive from the Fourier transform of the "average" structure. In addition, the patterns would also show non-Bragg layer line streaks derived from the Fourier transform of the "difference" between the alternative structures.[14] In the case of rubber, this difference might not be large because "up" and "down" chains, even with different packing parameters, might look rather similar at low resolution, but it need not be negligible. In our rubber diffraction pattern, there are indeed weak streaks on the layer lines, so the possibility of statistical structures needs to be addressed, especially because the toroidally focused X-rays used in producing our X-ray diffraction data are quite monochromatic and the alternative conjecture that the streaks arise from contaminating "white" radiation can be ruled out. Streaking is clearest on the second layer line, where the diffraction pattern is free of the halo from uncrystallized rubber, and is also a very noticeable feature of the pattern published by Kanamaru et al.[11] that was obtained with monochromatic synchrotron radiation.

Discriminating between Different Models. The linked-atom-least-squares technology became tactically more sophisticated during the first decade of its use[6] and also has been modified continuously to exploit advances in computing technology. In its mature state, it has become a powerful tool for the purpose needed here. We need to supplement low-resolution (2 Å) X-ray data with high-resolution bond-length and angle data to sharpen the discrimination between alternative, rather similar, rubber models. The linked-atom molecular description does this in a number of ways, not least of which is the reduction in the number of degrees of freedom to at most 18 in the case of rubber, which is a number not discordant with the 91 X-ray observations and the dozens of close, nonbonded contacts that arise within the rubber molecules in each model unit cell. This concordance is important for the sensitivity and significance with which one can discriminate between competing structures that have each been optimized in a least-squares fashion. Hamilton[7,8] has dealt very thoroughly with the matter of hypothesis testing using the outcomes of least-squares refinements, and his approach is invoked frequently in those X-ray fiber analyses where competing models have to be considered. It is rarely the case in fiber diffraction analyses that there are experimentally derived phase angles to complement the amplitudes. Consequently, one has to resort to approximate phases calculated from possibly inaccurate models or rely exclusively on the diffraction amplitudes that are indeed experimentally derived. In controversial cases such as rubber, it is important to make the same fixed assumptions for each competing model, to optimize each model under the same regimen of constraints and restraints, and to ensure that any difference that discriminates between models is significant in the light of the number of degrees of freedom allowed. Thus Hamiltonian statistical analysis (or some well-understood equivalent) has to become a pervasive, routine, partner of multiple model optimizations that are intended to discriminate among competing structures and to lead, in favorable cases, to the authentification of one of them.

In the case of rubber we minimized:

$$\Omega = \mathbf{X} + \mathbf{C} + \mathbf{E} + \mathbf{L} = \sum \omega_m \Delta F_m^{\ 2} + \sum K_i \Delta c_i^{\ 2} + \sum \epsilon_j \Delta q_j^{\ 2} + \sum \lambda_h G_h$$

where **X** accounts for the sum of the squares of the differences between the observed and calculated X-ray amplitudes, **C** for the difference between chosen and actual values of tethered conformation angles, **E** for the differences between acceptable and calculated nonbonded distances for close contacts, and **L** for the Lagrangian constraints such as molecular connectivity or exact conformational relationships. When we had optimized each model, the final value of $\Omega^{1/2}$ became, theoretically, the appropriate statistic to compare different models. However, in practice, $\mathbf{X}^{1/2}$ may be a more demanding surrogate for $\Omega^{1/2}$, when $\mathbf{C} + \mathbf{E}$ are very similar for all competing structures, and because $\mathbf{L} = 0$ at the end of each refinement. Therefore, we have preferred to base our conclusions on $\mathbf{X}^{1/2}$, with one (noted) exception.

Molecular Structures and Crystal Packing. We decided to investigate first the alternative molecular conformations. The fiber axial spacing $c = 8.20$ Å implies that there are two isoprene units (Figure 1) in the crystallographic repeat. This repeat length is about 10% shorter than would be expected were the olefin chains to be completely extended with all their carbon atoms in one plane, and therefore, the isoprene units must be at least slightly buckled. This can occur in two ways, one with a right-handed twist (R, say), one with a left-handed twist (L, say). The space group absence of 00*l* reflections with *l* odd leaves open the question of whether the two isoprenes in the axial repeat are related by a 2_1 screw axis or a glide plane or neither symmetry element. There are three possibilities (Figure 2) for symmetric molecular conformations: RRs and LLs where the molecular chain has successive, identical, isoprenes of the R or L type related by a 2_1 screw axis (s), and RLg in which successive mirror-image isoprenes along the rubber chain are related by a glide plane (g) rather than a screw axis. Because there are no crystallographic requirements for these molecular symmetry elements to be perfect, it is necessary also to consider RR, LL, and RL models where alternate isoprenes are not exact symmetry mates. Thus there are at least six molecular models to be assessed.

We proceeded by constructing first the three molecular models with symmetrically related di-isoprene units (Figure 2) and optimizing with LALS the three corresponding orthorhombic (O) $P2_12_12_1$ crystal structures (ORRs, OLLs, ORLg). For these and later relaxed structures, we found it convenient to choose 20 variables: the 10 di-isoprene conformation angles (Figure 1), three Eulerian angles (to define the orientation of the molecular unit), a molecular radius, three Cartesian coor-

Table 2. Provenance of These Statistics Is Defined in the Text (a), Re-refinement of the best model, ORL (b), Final Set of Refinements of the Three Statistical Models (c)[a]

structure	⟨**C** + **E**⟩	⟨**X**⟩
	Part a	
OLLs	0.97	1.63
ORRs	0.90	1.63
ORLg	1.06	1.01
OLLt	1.01	1.56
ORRt	0.94	1.56
ORLt	1.04	0.99
ORL	0.37	1.07
	Part b	
ORLf	0.96	0.96
SRL12	0.96	1.07
SRL13	0.96	0.84
SRL14	0.96	1.51
	Part c	
SRL12f	1.02	1.35
SRL13f	1.00	1.00
SRL14f	0.93	1.74

[a] (Part a) (**C** + **E**) sums the disagreement of a model with the restraints imposed upon it, including a measure of the shortness of nonbonded interatomic contacts below a certain limit. The number of the latter varies from model to model, and therefore, we show the mean value ⟨(**C** + **E**)⟩, the more relevant statistic. However, its values, 0.90−1.06, are relatively invariant (The interesting exception is the case of the best model when all constraints and restraints on the conformations of the two isoprene residues of the molecular asymmetric unit are finally removed.) when compared to the analogous X-ray statistic, ⟨**X**⟩, which has a much greater variability, 0.99−1.63, and is therefore a more discriminating measure of a model's acceptability. The total number of X-ray reflections in the field is 91, and therefore, **X** includes contributions from not only the 43 above-threshold reflections but also from the $N(\mathbf{X}) - 43$ reflections that have unduly large calculated values $F(\text{calc}) > T$, but observed values $F(\text{obs}) < T$. Using $\langle \mathbf{X} \rangle = X/N(X)$ rather than $X/91$ implies that the average reflections with calculated values $< T$ are assigned a ΔF that is not zero, but has the same average value as ΔF for the above threshold reflections. (Part b) A re-refinement of the best model, ORL, from Table 2a with rebalanced weights gave the model ORLf whose molecular conformation and weighting scheme were kept constant in an even-handed comparison with the various SRL statistical models, which showed SRL13 to be overwhelmingly superior. (Part c) A final set of refinements of the three statistical models with the weighting scheme rebalanced yet again, and with the molecular conformations allowed to be variable as well as the packing parameter, confirms the superiority of the best SRL13f structure.

Table 3. Cartesian Coordinates of the Di-isoprene Unit in the Best Nonstatistical Crystal Structure for Rubber, ORLf[a]

	ORLf		
atom	*X*	*Y*	*Z*
C7	3.11	1.59	12.84
C8	4.36	1.31	12.05
C9	4.39	0.82	10.81
HC9	5.27	0.67	10.35
C1	3.18	0.48	9.99
H1C1	2.41	0.27	10.59
H2C1	3.37	−0.33	9.42
C2	2.81	1.66	9.07
H1C2	3.62	1.96	8.57
H2C2	2.46	2.41	9.62
C3	1.76	1.23	8.09
C5	0.40	1.00	8.68
H1C5	0.42	1.18	9.67
H2C5	−0.27	1.61	8.25
H3C5	0.12	0.05	8.53
C4	1.96	1.06	6.78
H1C4	1.18	0.87	6.18
C6	3.29	1.12	6.09
H1C6	3.71	0.21	6.10
H2C6	3.89	1.76	6.57
C7	3.11	1.59	4.64
H1C7	2.92	2.57	4.62
H2C7	2.34	1.10	4.22
C8	4.36	1.31	3.85
C10	5.64	1.61	4.57
H1C10	5.61	2.55	4.93
H2C10	5.75	0.98	5.34
H3C10	6.41	1.52	3.95
C9	4.39	0.82	2.61

[a] The molecular origin is at $X = 3.2997$ Å, $Y = 1.5257$ Å, $Z = 6.7789$ Å in the $P2_12_12_1$ unit cell.

dinates, and an angle to define the position and orientation of the basic di-isoprene in the unit cell, a scale, and an overall temperature factor. We are well aware that this description has redundant variables, but it seems to us desirable to make every conformation angle of the molecular asymmetric unit an explicit variable and to segregate the molecular positioning variables and the diffraction scaling variables from one another as well as from the conformations. Once allowance is made for connectivity and other constraints and redundancy among the explicit variables, the net degrees of freedom in these crystal structures reduces to 14 generally and to 9 when the two isoprene units are symmetrically related. There are algorithms within LALS that conduct eigenvalue analysis of the normal matrixes followed by filtering to ensure that all redundancy of variables, witting or unwitting, is remedied before these matrixes are inverted. In effect, this means that LALS uses the correct number of degrees of freedom rather than the input number of variables.

In preliminary refinements of structure, we used only the 43 above-threshold reflections to establish preliminary shapes for the isoprene residues in rubber. We then moved on to refinements that took into account all 91 reflections in the experimentally accessible field All three systems provided calculated X-ray amplitudes in reasonable correspondence with those observed while being stereochemically reasonable. However, the differences in the LALS statistic **X** showed the ORLg model to be significantly superior[7,8] to the next best model (ORRs) at the 99.5% level (Table 2a).

Next, the symmetric models were relaxed in a restrained fashion by allowing the conformations in alternate isoprenes to vary independently while being tethered elastically to the final values for ORLg, ORRs, and OLLs, respectively. This tethering allowed us artificially to make a statistical comparison among the tethered ORLt, ORRt, and OLLt models, which then favored ORLt at the 99.5% level of significance. Without tethering, all models mutated to the same ORL model, which may be an even more significant indication of its superiority! We therefore felt able to abandon further consideration of molecular models with an approximate or exact 2_1 screw axis.

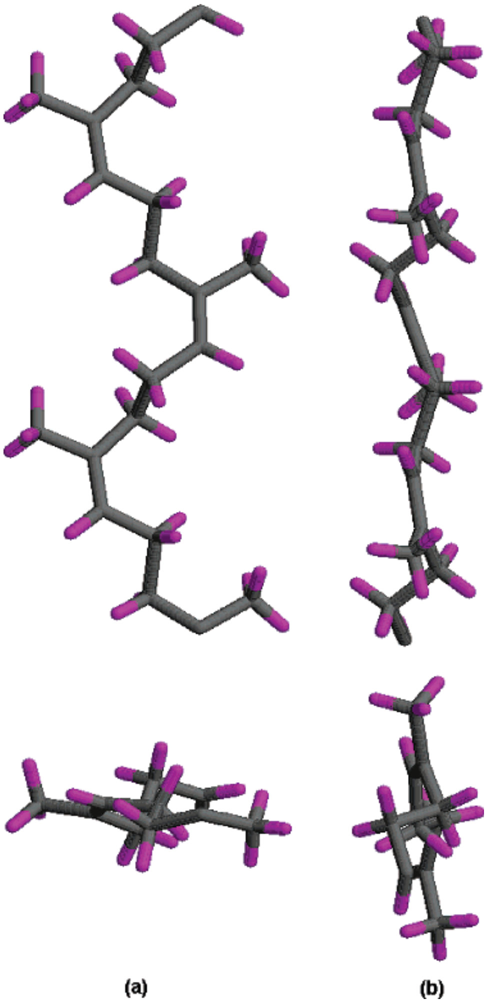

Figure 3. (a) Our best molecular model, RLf, which has a general similarity to RLg, but the conformations in alternate residues are no longer related by exact glide symmetry and differ by up to 28° from their values in RLg. The views are like those in Figure 2a. (b) View of RL from the same vantage point as the models in Figure 2b.

Removal of tethering from the conformation angles in the successful ORLt model, followed by a further LALS refinement, resulted in further changes in the conformation angles and a dramatic reduction in steric compression within the ORL molecule. Because of this, the relative weighting of the steric and X-ray terms was changed and a final (ORLf) refinement conducted. The coordinates of the resulting RLf molecular model are in Table 3 and its conformation angles in Table 7. Views of this RLf model are provided in Figure 3, and a projected view of it and its ORLf unit cell symmetry mates is shown in Figure 4a.

Exploring Statistical Crystal Structures. We generated three plausible statistical models by merging our best ORLf model with an identical $P2_12_12_1$ structure shifted in the *ab* plane: (i) so that molecule 1 in Figure 4a would share its site with a translated molecule 2 to form SRL12, (ii) so that molecule 1 in Figure 4a would share its site with a translated molecule 3 to form SRL13, and (iii) so that molecule 1 in Figure 4a would share its site with a translated molecule 4 to form SRL14. Thus

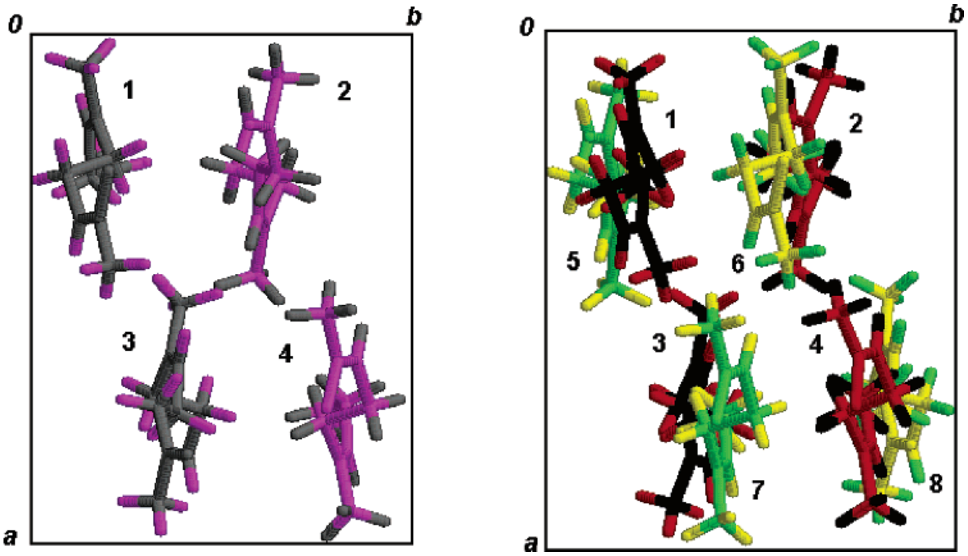

Figure 4. (a) $P2_12_12_1$ unit cell of the nonstatistical crystal model of rubber viewed down the *c*-axis. Of the four chains, two are up-pointing (1 and 3) and two down-pointing (2 and 4). (b) The $P2_12_12_1$ unit cell of the statistical crystal model of rubber viewed down the *c*-axis. Eight chains are shown, two up-pointing (1 and 3) and two down-pointing (2 and 4) as in the nonstatistical crystal structure, but in this case, there is an equal probability of there being a molecule of the opposite sense in each molecular site; 5, 6, 7, 8 with 1, 2, 3, 4, respectively. The positions of atoms in the 1,5 pair in the statistical structure cluster around $x = a/4$, $y = b/8$ as do those of molecule 1 in the nonstatistical structure. Clearly, the scattering material is more broadly distributed in the statistical structure, and consequently, the calculated temperature factor for the SRLf structures is noticeably smaller ($B \sim 4$ rather than 10) than in the ORLf statistical structure, where the larger temperature factor apparently is an inadequate attempt to produce with one variable what is achieved more significantly with the statistical model.

SRL12 and SRL13 would both contain up- and down-pointing chains at each site, but with different displacements in the *c*-axis direction, while SRL14 would have parallel chains with different displacements in the *c*-axis direction at each site. The conformations were kept fixed at the RLf values, while three Cartesian positional coordinates and an orientation were refined for the generating molecules of the two $P2_12_12_1$ structures independently. A scale and temperature factor were also refined, giving each statistical model $4 + 4 + 2 = 10$ variables and, in this case, the same number of degrees of freedom. Models with parallel displaced chains, like SRL14, were dramatically inferior to the best ORLf model with $\langle X \rangle$ rising from 0.96 to 1.51 (Table 2b). The two models with antiparallel chains were superior to SRL14: in the refined versions of SRL12 and SRL13, $\langle X \rangle$ is 1.07 and 0.84, respectively, making the latter the best model that we have found and at the highest level of significance.

For completeness, we returned to rejected models such as ORRt and OLLt and tested whether they could be rescued by creating statistical versions. We found they could not be rescued. Finally, we rebalanced the steric and X-ray weights and completed LALS refinements of the SRL models in which refinements of the molecular conformations were also allowed as well as the packing variables. The conformations changed little and superiority of SRL13f over SRL14f and SRL12f was confirmed (Table 2c).

The Nature of Our Best Model for Rubber. It is rarely possible to put fiber structures derived from X-ray diffraction data beyond cavil. The paucity of data, their low resolving power, and the absence of experimentally derived phase angles make this inevitable. However, oriented "crystalline" rubber is a fiber, and no other kind of data are available. Our best model is just that, the best of the models we have so far tested by an objective process of comparing structures refined in exactly the same fashion. We have imposed the same fixed, standard bond lengths and angles on all our candidate structures and for each have minimized steric compression while obtaining the best fit with the X-ray amplitudes. Even so, we have obtained a good fit in traditional terms for our best model ($R = 0.18$).

Table 4. Cartesian Coordinates of the Di-isoprene Unit in One Component of the Best Statistical Crystal Structure for Rubber, SRL13f[a]

	SRL13f		
atom	*X*	*Y*	*Z*
C7	3.21	1.65	12.78
C8	4.51	1.57	12.04
C9	4.65	1.10	10.79
HC9	5.57	1.02	10.39
C1	3.53	0.68	9.89
H1C1	2.78	0.31	10.45
H2C1	3.84	−0.03	9.26
C2	3.02	1.89	9.09
H1C2	3.78	2.30	8.58
H2C2	2.63	2.57	9.71
C3	1.97	1.44	8.11
C5	0.61	1.21	8.71
H1C5	0.70	0.96	9.68
H2C5	0.06	2.04	8.64
H3C5	0.15	0.46	8.23
C4	2.16	1.26	6.80
H1C4	1.40	0.96	6.22
C6	3.47	1.46	6.09
H1C6	4.05	0.66	6.23
H2C6	3.93	2.27	6.45
C7	3.21	1.65	4.58
H1C7	2.80	2.54	4.42
H2C7	2.60	0.93	4.25
C8	4.51	1.57	3.84
C10	5.71	2.06	4.59
H1C10	5.49	2.92	5.05
H2C10	5.98	1.38	5.28
H3C10	6.47	2.21	3.96
C9	4.65	1.10	2.59

[a] For the up-pointing chain, the molecular origin is at $X_1 = 3.5098$ Å, $Y_1 = 1.7188$ Å, $Z_1 = 6.8003$ Å. The coordinates of the other component can be obtained by changing the origin to $X_2 = 3.1928$ Å, $Y_2 = 0.9366$ Å, $Z_2 = 2.8388$ Å.

Our structure is more satisfactory than Bunn's[1] in its stereochemical orthodoxy and gives a much better fit with the X-ray data. It is also more parsimonious in requiring only one type of molecular structure. This follows from our choice of space group $P2_12_12_1$ rather than Bunn's $P2_1/a$, which would

Table 5. Calculated Structure Factors for ORLf with the Values for Below-Threshold Reflections Shown in Italics

F(calc)(ORLf)						
RR	*h k*	*l*				
		0	1	2	3	4
	0 0	M	N	N	N	N
0.0795	1 0	0	84	64	25	28
0.1114	0 1	0	*112*	*141*	*176*	*179*
0.1369	1 1	*217*	68	405	*303*	*252*
0.1590	2 0	1009	983	508	17	66
0.1941	2 1	*3*	388	67	*213*	*98*
0.2228	0 2	*244*	*50*	521	*110*	*72*
0.2366	1 2	2395	1162	155	152	233
0.2385	3 0					
0.2632	3 1	200	413	412	293	120
0.2737	2 2					
0.3180	4 0	466	266	362	*223*	*74*
0.3264	3 2					
0.3342	0 3	*238*	310	641	257	191
0.3369	4 1					
0.3435	1 3					
0.3701	2 3	84	242	153		
0.3883	4 2	*121*	*31*	*207*		
0.3975	5 0					
0.4106	3 3	*148*	*275*	*587*		
0.4128	5 1					
0.4456	0 4	*627*	*303*	*397*		
0.4526	1 4					
0.4556	5 2					
0.4613	4 3	200	124	304		
0.4731	2 4	*63*	*384*	*159*		
0.4769	6 0					
0.4898	6 1	*13*	*192*	*233*		
0.5054	3 4	*83*	*121*	*92*		
0.5193	5 3	*68*	*110*	*209*		
0.5264	6 2					
0.5474	4 4	*136*	*78*	*175*		
0.5570	0 5,7 0					
0.5626	1 5	*153*	200	*113*		
0.5675	7 1					
0.5792	2 5	*71*	*156*	*215*		
0.5824	6 3					
0.5971	5 4	*131*	208	*138*		
0.5994	7 2					
0.6059	3 5					
0.6359	8 0	148	229			
0.6414	4 5					
0.6456	8 1					
0.6491	7 3					

Table 6. Calculated Structure Factors for SRL13f with the Values for Below-Threshold Reflections Shown in Italics

F(calc)(SRL13f)						
RR	*h k*	*l*				
		0	1	2	3	4
	0 0	M	N	N	N	N
0.0795	1 0	0	95	98	3	72
0.1114	0 1	0	*74*	*137*	*40*	*163*
0.1369	1 1	*201*	*239*	*124*	*96*	*53*
0.1590	2 0	1130	1088	535	65	153
0.1941	2 1	294	216	129	78	46
0.2228	0 2	*214*	*127*	*459*	*156*	*90*
0.2366	1 2	2424	1188	177	232	208
0.2385	3 0					
0.2632	3 1	269	375	335	183	178
0.2737	2 2					
0.3180	4 0	468	338	331	*216*	*51*
0.3264	3 2					
0.3342	0 3	153	265	344	266	265
0.3369	4 1					
0.3435	1 3					
0.3701	2 3	73	313	241		
0.3883	4 2	*117*	*70*	*331*		
0.3975	5 0					
0.4106	3 3	*267*	*120*	*391*		
0.4128	5 1					
0.4456	0 4	483	*217*	229		
0.4526	1 4					
0.4556	5 2					
0.4613	4 3	*228*	164	326		
0.4731	2 4	*56*	367	*195*		
0.4769	6 0					
0.4898	6 1	*21*	*45*	*128*		
0.5054	3 4	*156*	*187*	129		
0.5193	5 3	*114*	*134*	285		
0.5264	6 2					
0.5474	4 4	*158*	*99*	*221*		
0.5570	0 5,7 0					
0.5626	1 5	*54*	329	344		
0.5675	7 1					
0.5792	2 5	*145*	*250*	292		
0.5824	6 3					
0.5971	5 4	*179*	341	*136*		
0.5994	7 2					
0.6059	3 5					
0.6359	8 0	242	314			
0.6414	4 5					
0.6456	8 1					
0.6491	7 3					

require there to be both RRs and LLs molecules in each unit cell if one assumes, as he did, that the molecules have 2_1 screw axes and the unit cell contains centers of symmetry.

Superficially, our model more resembles Nyburg's[2] in having "statistical" crystallinity and orthorhombic symmetry. A fundamental difference, however, is the less-constraining unit cell with no glide plane symmetries imposed within and between molecules. This allows us to have an RL and not an RLg molecular structure and different molecular packing. It cannot be emphasized too strongly that the inappropriateness of his symmetry choices should have been very evident because they predict zero intensity for prominent reflections, which have been observed as being very much present by other investigators, including ourselves. Nyburg's claim for a superior X-ray fit for his structure over Bunn's rests entirely on the inexplicable omission of many intense (*hk*2) reflections from his published list.

We have provided Tables (3 and 4) of Cartesian coordinates for the asymmetric units of our best ORL and SRL structures, the nonstatistical (ORLf) and statistical (SRL13f) models, and their calculated X-ray amplitudes (Tables 5 and 6), where it can be seen that all the below-threshold reflections are indeed small (cf. Table 1). The conformation angles for the di-isoprene units in these structures (Table 7a) are very similar to one another, but noticeably different from the set from the symmetric RLg structure. Nevertheless, the overall molecular shape remains ribbonlike (Figure 3a,b).

It is important to mention that our statistical structure, which requires the structure factors of the Bragg reflections to be calculated as if each molecular site might contain an up or a down molecule with equal probability, does not require that replacement of one by the other is utterly random. Complete randomness would lead to unacceptably short intermolecular contacts in some instances. To avoid these, it has to be postulated that it is sheets of molecules that replace one another at random, as illustrated in Figure 5. The consequences for the diffraction pattern are the same as for a statistical structure with random vicarious replacement of molecules, but the possibility of steric compression is avoided. A similar solution was offered by Natta and Corradini[3] to deal with one of the many difficulties of Nyburg's structure.

Revisiting the Space Group Symmetry. The question of whether the *lattice* symmetry of crystalline rubber is orthorhombic or monoclinic (i.e., whether β is 90° or 92°) is a matter

Table 7. (a) Values for the Conformation Angles (θ°) of Di-isoprene Units in ORLg, ORLf, and in SRL13f (a), Comparison of Unit Cell Dimensions in the present (RSA) and Other Analyses (b), Comparison of Bond Lengths in Different Structures (c), and Comparison of Bond Angles in Competing Structures (d)[a]

Part a

(θ°)	SRL13f	SRLg	T&K	ORLf	C(Ietc)	ORLg	Ketc	B(Ietc)
9123	148.6	118.8	115.0	138.3	116.0	133.2	122.5	112.5
1234	4.8	−4.9	(0)	−0.4	(0)	−3.1	−2.9	(0)
2346	89.0	119.1	115.0	95.7	85.6	133.1	129.3	113.2
3467	175.5	174.7	157.0	170.4	170.8	163.3	169.2	163.6
4678	−102.0	−118.8	−115.0	−109.1	−87.7	−133.2	−122.5	−112.5
6789	0.2	4.9	(0)	6.8	(0)	3.1	2.9	(0)
7891	−159.8	−119.1	−115.0	−151.3	−120.4	−133.1	−124.3	−113.2
8912	−168.6	−174.7	−157.0	−165.2	−169.6	−163.3	−169.2	−163.6
12CH	−27.2	23.2		−0.2		43.1		
67CH	−44.8	−23.2		−52.4		−43.1		

Part b

	RSA	T&K	Ketc	
a (Å)	12.58	12.41	12.60	12.45
b (Å)	8.98	8.81	8.85	8.87
c (Å)	8.20	8.23	8.27	8.29
β (deg)	90.0	93.1	91.9	90.0

Part c

l (Å)	SRL13f	SRLg	T&K	ORLf	C(Ietc)	O−RLg	Ketc	B(Ietc)
46=91	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54
12=67	1.50	1.50	1.53	1.50	1.50	1.50	1.51	1.50
78=23	1.34	1.34	1.34	1.34	1.34	1.34	1.32	1.34
89=34	1.50	1.50	1.53	1.50	1.50	1.50	1.51	1.50
710=25	1.50	1.50	(1.53)	1.50	1.50	1.50	1.50	1.50

Part d

τ (deg)	SRL13f	SRLg	T&K	ORLf	C(Ietc)	O−RLg	Ketc	B(Ietc)
467=912	110	110	109	110	108	110	114	109
678=123	125	125	129	125	137	125	122	127
789=234	125	125	121	125	137	125	127	127
891=346	110	110	111	110	108	110	113	109
6710=125	115	115	115	115	(111)	115	115	(116)
1078=523	120	120	116	120	(112)	120	123	(117)

[a] (Part a) Values for the conformation angles (θ°) of di-isoprene units in ORLg, ORLf, and in SRL13f (the best model from this analysis) compared with one another and also with some from recent publications by others. As part of this comparison, we include also the conformations in one of our rejected models (SRLg). The final results of T&K[9] may be compared with SRLg or ORLg; two models from Ietc[10] are also comparable C (Ietc) with ORLf and B (Ietc) with ORLg; the preferred model of Ketc[11] is also to be compared with ORLg. In analyses where the ethylenic conformations were fixed at zero, these are shown in parentheses. Only in our analysis were the methyl conformations varied to provide the best H⋯H contacts. (Part b) Comparison of unit cell dimensions in the present (RSA) and other analyses. Ietc[10] used the X-ray data of T&K[9] and have no independent X-ray observations. Ket**c**[11] used a monoclinic cell to produce their best $P2_1/a$ model and an orthorhombic cell to produce their rejected *Pbac* statistical model. (Part c) Comparison of bond lengths in different structures. (Part d) Comparison of bond angles in competing structures. In B and C (Ietc[10]), the bond angles were varied (or allowed to be different in different models). In T&K,[9] some bond angles were allowed to vary. In our analyses and those of Ketc,[11] bond angles were fixed.

of precision and trivial in structural terms compared with the question of whether the unit cell contents are arranged with $P2_12_12_1$ or $P2_1/a$ symmetry. A lattice that is genuinely monoclinic cannot have unit cells with orthorhombic contents. The converse is not true. Therefore, we refined a crystal model (M-RLg) containing RLg molecules arranged with $P2_1/a$ symmetry in our $\beta = 90°$ cell and compared it with the corresponding $P2_12_12_1$ model (O-RLg). Using only the X statistic, M-RLg can be rejected with more significance than any other pairwise comparison we have made in this project. When we move on, as Nyburg did, to test statistical structures, there is a dramatic improvement and our best Nyburg-like, monoclinic, statistical structure (MS12RLg) is rejectable in comparison with our best orthorhombic model (OS13RLg) only at the 97.5% level using the X statistic, but at the 99.5% level using the comprehensive Ω statistic. (In this connection, it may be worth observing that none of the competing structures in the literature include H atoms as we have. Of course, these are relatively transparent to X-rays and from that point of view might be ignored, but they are responsible for the majority of the nonbonded interatomic interactions within the rubber molecules and should not be ignored in assessing the stereochemical plausibility of competing structures.)

Comparisons with Other Recent Structures. The precise experimental conditions for the various more recent analyses of crystalline rubber were different from ours and from one another, and therefore, it is not surprising that the unit cell dimensions obtained are not identical (Table 7b). An additional complication is that we chose a rectangular cell, while Takahashi and Kumano[9] (T&K) chose a monoclinic cell with $\beta = 93°$ (which had to be followed by Immirzi et al.[10] (Ietc) who were parasitic on the T&K data). Helpfully, the independent analysis by Kanamaru et al.[11] (Ketc) considered both shapes of cell, and their two results show what a modest difference results.

We, like all the other investigators, kept bond lengths fixed at similar but not identical values (compared in Table 7c). Although LALS permits refinement of bond angles in either a free or restrained fashion, we and Ketc kept them fixed at similar values. T&K, on the other hand, explicitly permitted some of their bond angles to be variable, without justifying either the variation or the specific selection, but apparently ended up with plausible values (Table 7d). By contrast Ietc implicitly allowed

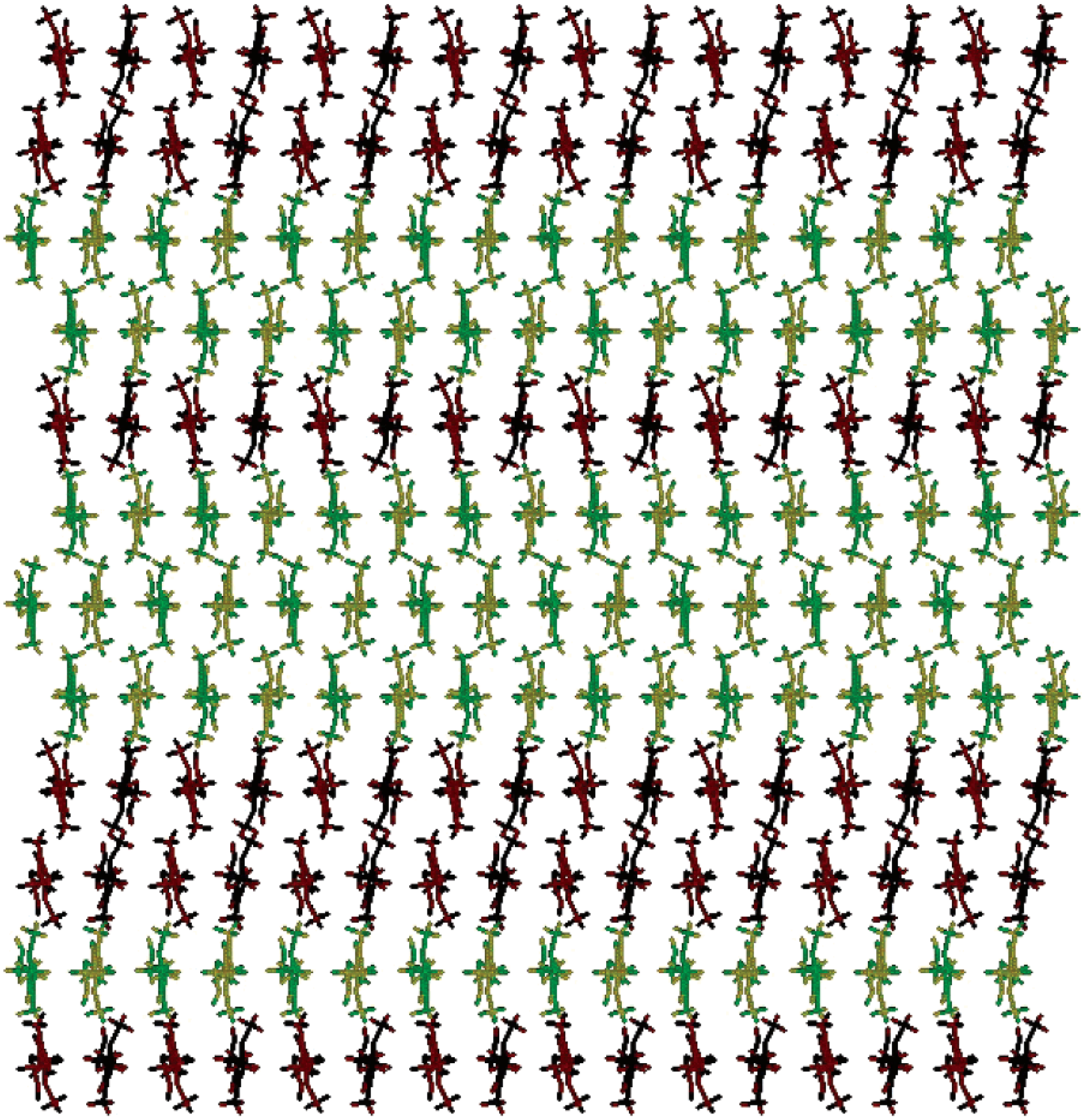

Figure 5. Sterically feasible model for the statistical model of crystalline rubber. In effect, this structure provides "up" and "down" molecules with equal probability at each molecular site as required by the Bragg diffraction pattern. In it, up-pointing molecules are not replaced by their down-pointing counterparts completely at random because this would result in overclose contacts. What has to happen is that rows of ...1212121212... or ...3434343434... molecules have to be replaced by rows of ...5656565656... or ...7878787878... molecules.

bond angles to vary, but in a fashion that resulted in some being equal ($\tau123 = \tau678 = \tau234 = \tau789$). They then allowed them to drift (in different models) to values (e.g., 131° and 137°) well above the expected upper limits for bond angles at ethylenic linkages. The accumulated effect of forcing equality as well as improbability on four bond angles in each molecular asymmetric unit, and the further requirement that the conformations at each ethylenic linkage should be precisely zero, must have a negative impact also on the values obtained for the conformation angles because, mathematically, bond angles are equivalent to rotations about bonds (albeit of zero length!). In the circumstances, the structural details of the models C and D of Ietc must be profoundly suspect, as must be these authors' subsequent rejection of a statistical crystal model that had components derived from the same flawed process.

We have treated all 10 conformation angles in the di-isoprene unit as variables. These included the rotations about the ethylenic linkages, which in our case and in that of Ketc, end up with magnitudes a few degrees away from zero rather than the precisely zero values imposed by T&K and Ietc. Uniquely, we included the rotations about the C−Me bonds, since we included the hydrogen atoms in our analyses, not because they have a large effect on the X-ray amplitudes, but because the main nonbonded intramolecular contacts involve hydrogens, and in the production of all our models, we ensured that we minimized intramolecular steric compression in concert with minimizing the discrepancy between the observed and calculated diffraction.

At this point, it is appropriate to compare those of our conclusions that involved symmetrically related isoprenes with the corresponding conclusions of the other investigators since, thereafter, there is a major divergence of view about both molecular symmetry and whether the crystallinity of rubber is merely statistical. Our conclusion that Bunn's 2_1 molecular model is inferior to Nyburg's glide plane model is now universally shared. It is appropriate therefore to compare (Table 7a) only our RLg model with the final models of T&K and Ketc and with the *B* model of Ietc, which shares the same symmetry. First, there is a remarkable concordance between our

RLg molecular model and that of Ketc despite all the small differences in the details of cell dimensions and the values of fixed bond lengths and angles: no corresponding conformation angle differs by more than 9° and the mean difference is only 3°. (It is worth noting at this point the implicit endorsement of our "old fashioned data". Ketc had no more above-threshold X-ray amplitudes than we had despite their cooled specimens, synchrotron light source, and imaging plate recording of diffraction, and they reached almost identical conclusions to us with models of the same symmetry.) The T&K values for their RLg model are almost as concordant. Those of Ietc are rather less so as would be expected from the wayward values they allowed their varied bond angles to assume.

Unfortunately, Ketc and T&K then concluded their analyses using symmetric molecular models to explore the question of statistical crystallinity and did not explore whether alternate isoprenes might have different conformations. It was doubly unfortunate that Ketc adhered to the oversymmetric *Pbac* model of Nyburg when exploring the possibility of statistical crystallinity. Inevitably, their statistical crystal model led to no significant improvement in the fit with the X-ray amplitudes. One just has to compare our ORLg and SRLg models to see how little impact there is on the molecular conformation by postulating statistical packing. Conversely, if one uses an inappropriate molecular structure to explore the issue of statistical packing, one cannot expect a useful result.

As we found, when the glide-plane symmetry between alternate isoprene residues is relaxed, there are interesting major changes. These are concentrated in the values of two conformation angles, θ2346 and θ7891. In our ORLg structure, these angles have similar magnitudes (120°) to one another and to those of the θ9123, θ4678 pair (Table 7a). This similarity vanishes in ORL, and the magnitudes of the first pair both fall about 25°, with those of the second pair rising by about the same amount. (An attenuated version of this effect can be seen between the D and C models of Ietc, but the sharpness of the changes appears to have been diluted by their earlier acceptance of poor values of bond angles.) Going on to develop statistical crystal models from ORL to OSRL in our case modestly augments this conformational divergence, but allows the new packing parameters to make a beneficent and quantitatively significant impact on the X-ray agreement for the Bragg-type X-ray data. In addition, there is now an explanation for the layer line streaks, which have been almost ignored in other analyses.

Concluding Discussion

We have presented details of two new structures for crystalline rubber, in both of which the molecules are poly(diisoprene) with no internal symmetry and the arrangement of the four molecules in each unit cell conforms to space group symmetry $P2_12_12_1$. One of the structures is only statistically crystalline and provides the significantly better set of calculated structure amplitudes as well as one possible explanation for the weak layer line streaks in the fiber diffraction patterns of crystalline rubber.

Our analysis has been based on the linked-atom-least-squares (LALS) approach, which allows sparse, low-resolution diffraction data to be augmented by uncontroversial high-resolution information such as bond lengths and angles. An important adjunct of LALS optimization is its use in determining whether one of several competing models is significantly superior to the others. This is vital in fiber diffraction analyses, where it is rarely possible to provide experimentally determined phase angles and almost never possible to obtain a large enough set of intensity data to support a claim that one structural solution is superior to all possible alternatives. Thus fiber diffractionists have to be content to present optimized structural models that have been shown to be statistically superior to specific alternatives (similarly optimized) and to be prepared for another round of arbitration with new competitors if and when they arise. This is the philosophy we have used in analyzing the structure of crystalline rubber, which has been a subject of controversy for at least 60 years. In this section, we summarize the issues that we felt should be addressed and the conclusions that we reached in each case.

First, there is the question of the *lattice* symmetry, orthorhombic or monoclinic. In the former case, the unit cell is a prism with base and sides all rectangles. In the latter case, only the sides are rectangles and the base (in this case defined by *a* and *c*) is a parallelogram with, in the case of rubber, an angle $\beta = 92°$. We observed 40 above-threshold Bragg reflections, all of which can be indexed on the basis of an orthorhombic lattice. If the unit cell variables are increased from three (*a*, *b*, *c*) to four (*a*, *b*, *c*, β), there is, unsurprisingly, a slightly better fit with the observed spacings, but not a significant one. The observation that prompted Bunn and others following him to resort to a monoclinic lattice is some very weak diffraction at $\xi = 0.3$ Å^{-1} on the second layer line, which he assumed was a Bragg reflection requiring a monoclinic lattice to accommodate it. We, on the other hand, interpret the very weak intensity as being part of the layer line streaking, which is observable on the second layer line and on the equator. What we have done, therefore, is to conduct our analyses on the basis of an orthorhombic *lattice* shape without assuming that the *space group* symmetry is necessarily orthorhombic also.

The second question concerns the space group symmetry. Bunn's (1942) choice of a monoclinic lattice and space group $P2_1/a$ has rarely been challenged. Nyberg (1956), for example, chose an orthorhombic *lattice*, but nevertheless chose the monoclinic $P2_1/a$ as the *space group* symmetry for his non-statistical and statistical models (but unwittingly constructed a packing arrangement for his statistical model that corresponded to the orthorhombic space group symmetry *Pbac*). Therefore, when considering monoclinic packing arrangements, we have confined our attention to space group $P2_1/a$ as the only model in contention.

If one wittingly chooses to proceed with an orthorhombic *space group*, then the minimal space group has to be $P2_t2_t2_t$ where $t = 1$ for a screw axis and blank for a simple rotation. Of the four possible space groups ($P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$), only the last places the four rubber molecules that pass through each unit cell in the same relative *x*, *y* positions that all investigators are agreed upon. $P2_12_12_1$ is also compatible with the observed absences. Of supreme importance in the context of rubber is that this space group also imposes no constraints on the symmetry of the rubber molecules themselves. Internal molecular symmetry is another controversial issue that surely requires that it be investigated without a prejudicial space group assignment. For all these reasons, we chose to explore systems with $P2_12_12_1$ packing symmetry. If an orthorhombic space group of more complex symmetry would be appropriate, then this should be evident from the refined values of the molecular conformations and packing variables.

To compare and contrast our analyses with those of the pioneers and their uncritical followers, we started by comparing systems in which the two isoprene residues in the molecular asymmetric unit were related either by a (2_1) screw axis or a glide plane (g). In this first LALS arbitration, the 2_1 possibility preferred by Bunn was eliminated. The next arbitration was to test the Nyberg $P2_1/a$ structures against their $P2_12_12_1$ analogues. (At this stage, the rubber molecules have glide plane symmetry relating successive isoprene residues, and the operation of the centers of symmetry or glide plane symmetry elements of space group $P2_1/a$ do not lead to an enantiomeric molecule.) The arbitration between nonstatistical $P2_1/a$ and $P2_12_12_1$ structures decisively eliminated the former. (When later we considered statistical structures, we checked that with these, too, the orthorhombic $P2_12_12_1$ version rather than the monoclinic $P2_1/a$ version was significantly superior.)

The third issue with the structure of crystalline rubber is whether the molecules indeed have internal symmetry, and this was resolved in favor of a molecular asymmetric unit of two isoprene units with no symmetry. In moving to a larger (two isoprene residues) molecular asymmetric unit, we obviously introduce extra degrees of freedom and thereby obtain improved agreement between observed and calculated quantities. This is the case also when statistical, i.e., disordered, models are adopted. The issue therefore is not the improvement but the significance of the improvement. This is why LALS optimization of each hypothesis followed by Hamilton tests of significance have been the crucial tactical ingredients of our analyses.

The fourth issue tested by LALS arbitration was whether a disordered crystal structure might provide a better solution than the straightforward orthorhombic structure proposed. Such a structure would be one possible explanation for the layer line streaks and would also have a substantial impact on the Bragg reflections. We present one statistical model that indeed provides a significantly better fit to the Bragg dataset. In keeping with the LALS philosophy, we cannot claim that this is the unique solution to the structure of crystalline rubber, but we do believe it is the one against which any newer models have to be able to compete convincingly.

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