

Packing Models for High-Pressure Polymeric Phases of C₆₀

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Packing models of three polymeric phases of C₆₀ obtained through pressure–temperature treatments have been reconsidered through a lattice energy minimization method using atom–atom potentials. Orthorhombic phase O', previously assigned *Immm* symmetry, is best described by space group *Pmnn*. Whereas the *Immm* model contains one orientation of the polymeric chains, the *Pmnn* model presents two orientations related by a glide plane. For the tetragonal phase, two packing patterns of polymeric tetragonal layers are possible: one with *Immm* symmetry represents a pseudotetragonal packing of translationally identical adjacent layers; the second packing pattern, actually tetragonal (*P4₂/mmc*), consists of two layers related by a 4₂ screw axis and is ~ 4 kJ mol⁻¹ more stable. Concerning phase R, three packing modes of hexagonal layers are possible; the previously published structure of phase R corresponds to the least stable packing. Thus, the previous structural descriptions should be reexamined. © 1998 Academic Press

INTRODUCTION

The solid-state polymerization of C₆₀ at high pressure leads to a new class of fulleride compounds. By varying the pressure–temperature treatment, one may obtain crystalline polymers containing chains (1D) or layers (2D) (1–6). At very high pressure, in the 10-GPa range, an amorphous 3D polycondensed compound of C₆₀ is formed (7,8). High-pressure *p*–*T* phase diagrams of C₆₀ have been proposed (5, 6, 8). It appears that there are two 2D polymeric phases of C₆₀: the tetragonal (T) and the rhombohedral (R) ones (3). Both phases are stable at high pressure up to approximately 1073 K and at higher temperatures they transform into hard amorphous carbon (5, 9). A mechanism of the T and R phase formation from the high-pressure orthorhombic phase (hereafter called phase O) is described in (5). However, there is some disagreement about the structure of phase O,

which may be indexed either as orthorhombic or as rhombohedral (10).

Concerning the low-pressure region, it was shown that an orthorhombic phase (O') that may be viewed as different from O is formed at 1.5 GPa and 723 K (10, 11). It was suggested that O' may be an intermediary for the formation of the tetragonal modification.

The main weakness of these studies lies in the poor resolution of the experimental X-ray profiles, which is likely the origin of the remaining discrepancies. In this work new structural models of the orthorhombic, tetragonal, and rhombohedral phases are proposed using energy packing calculations to supplement the X-ray data.

CALCULATION METHOD

Intermolecular potentials involving both Lennard-Jones potentials and electrostatic parts due to the interactions of bond-centered partial charges (12) were used. This scheme was chosen because it was found (13) that it gives better results than those proposed by Cheng and Klein (14) and Burgos *et al.* (15) as to what concerns the secondary minimum corresponding to the double bond to the hexagon orientation inside the C₆₀ crystal. In particular, it reproduces the two orientations (double bond to pentagon and double bond to hexagon) as two separate energy minima, the hexagon-oriented packing energy being 2.5 kJ mol⁻¹ higher than the pentagon-oriented one (to be compared with 18 kJ mol⁻¹ as calculated using (15), whereas the experiment-derived value is 1 kJ mol⁻¹). Furthermore, the deviations of molecular orientations (1 and 8°, respectively) with respect to those that David *et al.* derived from experiments (16) are quite satisfactory.

Program PMC (17) was used for crystal lattice energy calculations. The geometry of the C₆₀ unit of the polymeric chain was taken as identical to that of the free molecule with ideal *I_h* symmetry assuming that geometrical changes due to polymerization are not significant for calculation purposes. The shorter bonding distance between adjacent C₆₀ units

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within the polymer chain is determined from the lattice parameter length along the chain, which was set to that obtained experimentally.

The packing of polymeric units was optimized with respect to the experimental structural parameters of the corresponding polymeric phases.

STRUCTURAL DESCRIPTION

Vector Relations between Phases O', T, and R and the Cubic Phases (C)

It appears that the volume per C₆₀ unit of each polymeric phase is close to that of the corresponding high-pressure cubic phase (hpc) formed at moderate temperatures (18) (Table 1). Thus, one may assume that these phases are related to a fcc lattice and may be considered as generated by deformation of the cubic Phase (C) not considering the C₆₀ molecular orientations. Therefore they may be described approximately as deformations (due to polymerization of the C₆₀ molecules in the <110> cubic directions) of C according to the following vector relationships:

For phases O' and T:

$$\begin{aligned}\mathbf{a}_{O,T} &= \frac{1}{2}\mathbf{a}_C + \frac{1}{2}\mathbf{b}_C \\ \mathbf{b}_{O,T} &= \frac{1}{2}\mathbf{a}_C - \frac{1}{2}\mathbf{b}_C \\ \mathbf{c}_{O,T} &= \mathbf{c}_C.\end{aligned}$$

For phase R:

$$\begin{aligned}\mathbf{a}_R &= \frac{1}{2}\mathbf{a}_C - \frac{1}{2}\mathbf{b}_C \\ \mathbf{b}_R &= \frac{1}{2}\mathbf{b}_C - \frac{1}{2}\mathbf{c}_C \\ \mathbf{c}_R &= \mathbf{a}_C + \mathbf{b}_C + \mathbf{c}_C,\end{aligned}$$

where \mathbf{a}_i , \mathbf{b}_i , and \mathbf{c}_i are unit cell vectors for phases $i = O', T, R$, and C.

When molecular orientations within the simple cubic phase are not taken into account, these relationships will lead to symmetries *Immm* for phases O' and T and *R-3m* for phase R. These are the symmetries which were used to generate the structural models of the high-pressure polymeric phases (3, 10).

TABLE 1
Cell Parameters of High-Pressure Phases of C₆₀

Phase	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³ ·mol ⁻¹)	(<i>a</i>) _{hpc} (Å)
O'	9.098	9.831	14.72	658	13.8
T	9.088		14.97	618	13.5
R	9.204		24.61	602	13.4

Note. The last column gives the parameter of a fcc phase with $Z = 4$ which would have the same volume per molecule as the polymeric phase of the first column.

Structure of Phase O'

From X-ray powder diffraction experiments, it was found (10) that a possible space group for O' is *Immm* with $Z = 2$, but an accurate assignment was not possible because of the limited number of Bragg peaks. In group *Immm*, all chains have the same orientations with two possibilities: the four-membered rings formed through [2 + 2] cycloaddition may be either in plane (010) or in the perpendicular (001) plane. In (19), these two cases are defined as $\mu = 0^\circ$ and $\mu = 90^\circ$, respectively, with μ being the angle between the 2-fold axis of the polymeric chain with unit cell *b* axis. If μ is not equal to 0 or 90° and the very improbable case of two independent chains is discarded, the space group for the ordered structure is *Pmnn* (nonstandard setting of *Pnmm*, No. 58).

The numerical characteristics of the calculated packings are recorded in Table 2, from which it follows that the optimal packing with $\mu = 29^\circ$ is about 8–18 kJ mol⁻¹ lower in energy than that with $\mu = 0$ or 90°. The optimal values (*b*, *c*, and *E*) calculated with the relaxed cell parameters ($\mu = 29^\circ$) are close to those obtained with nonrelaxed parameters ($\mu = 31^\circ$). Note that no energy minimum was found for the chain packing with $\mu = 45^\circ$, which characterizes the AC₆₀ (*A* = K, Rb) orthorhombic compounds (20).

On the other hand, calculations with $\mu = 90^\circ$ and 0° lead to considerable differences for parameters *b* and *c* and a loss in the packing energy. The latter is, to a large extent, due to considerable changes in Coulombic energy *E_C*, which turns out to be positive in the case of both *Immm* configurations.

Thus, according to our calculations, the chain packing with $\mu = 29\text{--}31^\circ$ is the most probable for the orthorhombic phase containing 1D polymerized chains of C₆₀. The *Pmnn* structure contains two molecular orientations defining two polymeric chains related by symmetry elements (Fig. 1A).

TABLE 2
Calculated Energies for Different Packings of Orthorhombic Phase O'

Parameter	Packing			
	I	II	III	IV
<i>E</i> (kJ mol ⁻¹)	-170	-164	-152	-162
<i>E_C</i> (kJ mol ⁻¹)	-6	-5	11	3
<i>a</i> (Å)	9.098*	9.086*	9.098*	9.098*
<i>b</i> (Å)	9.69	9.810*	10.13	10.16
<i>c</i> (Å)	14.38	14.730*	13.85	13.83
μ (deg)	29	31	90*	0*

Note. Structures I and II correspond to symmetry *Pmnn*, III and IV to *Immm*. *E* is the overall packing energy and *E_C* is the Coulombic contribution. *a*, *b*, and *c* are the lattice parameters and μ represents the rotation angle of the chains as defined in the text. The asterisk means that the corresponding parameters were kept fixed during the minimization process.

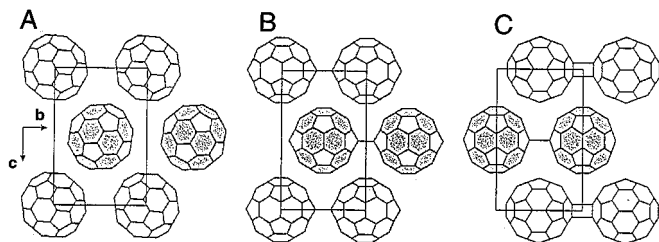


FIG. 1. Structure of phase O' as compared with that of phase T: (A) $Pmnn$ packing ($\mu = 29^\circ$) for orthorhombic phase O'; (B) $Immm$ packing for tetragonal phase T; (C) $P4_2/mmc$ packing for tetragonal phase T. Mass centers at $x = 0.0$ (white) and $x = 0.5$ (gray).

The X-ray diffraction pattern simulated with $\mu = 29^\circ$ is very similar to that obtained with $\mu = 90^\circ$ of phase O' (10). It shows that the strongest reflections correspond to hkl with $h + k + l = 2n$ (I condition) but the reflections with $h + k + l \neq 2n$ are probably too weak to be observable in our X-ray diffraction patterns.

Recently, Moret *et al.* (19) succeeded in synthesizing a single crystal of O' and investigating it by X-ray single-crystal analysis. They tested two models: one with $\mu = 45^\circ$ taken from the KC_{60} $Pmnn$ phase (20), and the second with $\mu = 29^\circ$ as taken from the present study. However, using a semiquantitative approach to calculate the intensities, they could not decide which of the two models is to be preferred.

Structure of Phase T

The orthorhombic $Immm$ setting of phase T was first proposed in (3). It contains 2D four-coordinated layers perpendicular to direction [001], each layer being made of C_{60} molecules in the same orientation (Fig. 1B). However, the packing energy calculations show that packing $Immm$ has an energy higher by about 4 kJ mol^{-1} than another one of (true tetragonal) $P4_2/mmc$ symmetry (Table 3). The latter

TABLE 3
Calculated Energies (E), Densities (d), and Unit Cell Parameters (a , c) for Different Structural Models of Tetragonal Phase T and Rhombohedral Phase R

Structural model	a (Å)	c (Å)	d (g cm^{-3})	E (kJ mol^{-1})
Tetragonal phase T				
$P4_2/mmc$	9.09	14.74	1.97	-160
$Immm$	9.09	14.78	1.96	-156
Rhombohedral phase $R-3m$				
I	9.17	25.11	1.96	-186
II	9.17	24.34	2.02	-206
III	9.17	49.00	2.01	-213

Note. Parameter a was kept fixed during the calculations. Models I, II, and III for phase R refer to Fig. 2.

model contains successive layers stacked on one another along [001] via a 4_2 screw axis, i.e., neighboring layers are related by a rotation of 90° (Fig. 1C).

The X-ray diffraction pattern simulated with the $P4_2/mmc$ model shows that the strongest reflections correspond to hkl with $h + k + l = 2n$, but the $h + k + l \neq 2n$ reflections are probably too weak to be observable in a real powder X-ray diffraction pattern.

Structure of Phase R

A structural model of phase R has been proposed by Nuñez-Regueiro *et al.* (3). It consists of layers of chemically bonded C_{60} molecules formed as a result of a $[2 + 2]$ cycloaddition reaction. The layers of perfectly hexagonal ($P6/mmm$) symmetry are stacked on one another due to weak van der Waals forces, so that the model as a whole looks very similar to that of graphite, with the quasi-spherical C_{60} unit playing the role of an atom.

However, even when the three molecular mass center positions in the unit cell remain unchanged, different orientations of the C_{60} units with respect to the crystal axes lead to different structural models. We chose orientations related to each other through a 60° rotation of the C_{60} unit around the crystallographic 3-fold axis. At the same time, the overall crystal structural difference between these two models can be equally described as due to different positions of the three layers composing the unit cell, namely, $0,0,0$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; and $\frac{1}{3},\frac{2}{3},\frac{2}{3}$ (Fig. 2, model I, after Nuñez-Regueiro *et al.*) on the one hand and $0,0,0$; $\frac{1}{3},\frac{2}{3},\frac{1}{3}$; and $\frac{2}{3},\frac{1}{3},\frac{2}{3}$ on the other hand, whereas the C_{60} orientations are the same (Fig. 2, model II) The latter can also be seen as an ...ABCABC... sequence of layers instead of ...ACBACB..., where A, B, and C stand for C_{60} center positions $0,0$; $\frac{2}{3},\frac{1}{3}$; and $\frac{1}{3},\frac{2}{3}$ within the layer, respectively.

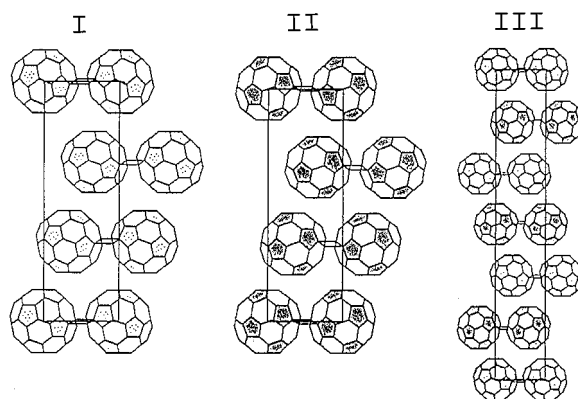


FIG. 2. Structures for phase R: (I) rhombohedral phase R according to Nuñez-Regueiro *et al.* (3); (II) phase R in which the C_{60} units have been rotated 60° around the 3-fold axis (this work); (III) phase R with a six-layer packing and multiplying parameter c by 2 (this work).

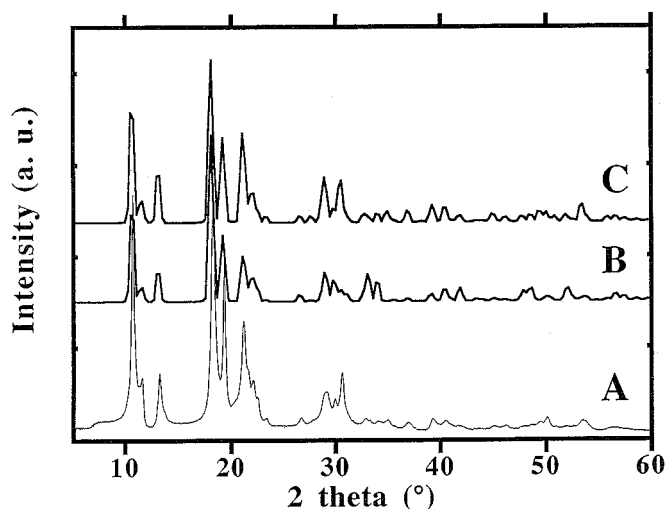


FIG. 3. X-ray diffraction profiles for rhombohedral phase R: (A) experimental (spectrum recorded with an INEL CPS 120 position-sensitive detector using CuK α_1 radiation); (B) calculated according to the model of Ref. 3; (C) calculated according to model II of the present work.

Other models could be suggested by considering combinations of the two C₆₀ orientations taken in different proportions. The most obvious of them assumes a six-layer packing (along the *c*-axis whose length would be multiplied by 2), with both C₆₀ orientations occurring in the stack in an alternating way (Fig. 2, model III).

Figure 3 shows calculated X-ray diffraction profiles for phase R corresponding to models I (B) and II (C) and the experimental profile (A). No clear conclusion can be deduced from the comparison.

To determine which of the three models is the most stable from the thermodynamic point of view, we calculated their optimal packing by minimizing the lattice energy with respect to the *c*-axis length (Table 3).

We found that the energies corresponding to the three models are significantly different, the six-layer model (III) being the most stable (unfortunately, model III would lead to some superstructure Bragg peaks, some of them lying at low 2θ values, which we could not observe). Note that the main part of the energy differences is due to electrostatic forces; if they had been neglected, II would have been the most stable structure, which could have been deduced by comparing the crystal densities. In either case, however, model I corresponds to the least stable packing.

CONCLUSION

To supplement the poorly resolved X-ray diffraction profiles of the three crystalline phases formed by pressure-temperature treatment of C₆₀, energy calculations have been performed using an atom-atom potential method which takes Coulombic interactions into account. They

have shown that (i) *Immm* packings of the orthorhombic and tetragonal phases appear to be less favored from the energy point of view than *Pmnn* or *P4₂/mmc* packings and (ii) the rhombohedral packing obtained by 60° rotation of the C₆₀ units around the crystallographic 3-fold axis is more stable than model I previously described (3).

Concerning phase O', the observation of Bragg spots with $h + k + l \neq 2n$ by Moret *et al.* (19), which confirms space group *Pmnn*, supports our calculations. In any case, these results suggest that previously proposed structures should be reexamined.

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