Low temperature structural model of hcp solid C$_{70}$

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We report intermolecular potential energy calculation for solid C$_{70}$ and determine the optimum static orientations of molecules at low temperature which are consistent with the monoclinic structural model proposed by us in an earlier report [Solid State Commun., 105, 247 (1997)]. This model indicates that the C$_5$-axis of the molecule is tilted by an angle $\sim 18^\circ$ from the monoclinic b-axis in contrast with the molecular orientation proposed by Verheijen et al. [J. Chem. Phys., 166, 287 (1992)] where the C$_5$-axis is parallel to the monoclinic b-axis. In this calculation we have incorporated the effective bond charge Coulomb potential together with the Lennard-Jones potential between the molecule at the origin of the monoclinic unit cell and its six nearest neighbours, three above and three below. The minimum energy configuration for the molecular orientations turns out to be at $\theta = 18^\circ$, $\phi = 8^\circ$ and $\psi = 5^\circ$ where $\theta$, $\phi$ and $\psi$ define the molecular orientations.

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The orientational ordering transformation in solid C$_{60}$ is well understood. Potential energy calculations using only the Lennard-Jones potential derive the low temperature structure of solid C$_{60}$ to be orthorhombic in sharp contradiction with the experimentally observed simple cubic structure. Lu et al. could successfully derive the simple cubic structure for the low temperature phase of solid C$_{60}$ by adding a Coulomb potential term to the Lennard-Jones potential. This Coulomb interaction between neighbouring molecules arises from the effective charges at the single bonds and the double bonds of the molecules in the ordered phase at low temperature. In the case of solid C$_{70}$, the elongated molecular shape causes much greater diversity in the structural phase transformation sequence as well as in the orientational ordering of molecules. One of the first experimental studies of structural phase transformation, on cooling, in solid C$_{70}$ is by Verheijen et al. and they reported the following sequence of phase transformations

fcc $\rightleftharpoons$ rh $\leftrightarrow$ hcp-I ($c/a \approx 1.63$) $\leftrightarrow$ hcp-II ($c/a \approx 1.82$) $\vDash$ monoclinic

where the fcc is the high temperature phase and the monoclinic is the low temperature phase. The lattice parameters reported for the monoclinic unit cell are, $a = 19.96$ Å, $b = 18.51$ Å and $c = 105$ Å, $\beta = 120^\circ$ with space group $P112_1/m$. They proposed a structural model for this monoclinic structure in which the orientation of the long axis (C$_5$) of the static molecules is parallel to the monoclinic b-axis (i.e., the original hcp c-axis). Subsequently, they have also carried out the potential energy calculation using the atom-atom Lennard-Jones potential and the corresponding result was in agreement with their model. Later, Que et al. pointed out that the unique angle $\beta$ for a monoclinic structure with space group $P112_1/m$ cannot be $120^\circ$, but should be less than $120^\circ$ which is not consistent with the molecular orientations proposed by Verheijen et al. They have carried out a detailed group theoretical analysis of librations in solid C$_{70}$ and proposed an orthorhombic structure for which the two space groups $Pbmm$ or $Pnma$ have the same Raman modes. Nelissen et al. have carried out a harmonic lattice dynamical calculation using the Lennard-Jones potential which proposed that the structure of solid C$_{70}$ should be monoclinic at low temperature with space group $P2_1/m$. This structure requires two independent angles which they defined as $\phi_1$ and $\phi_2$ and pointed out that for their structure $\phi_1 + \phi_2$ should be $36^\circ$. Later, Agterberg et al. have pointed out that the calculation of Nelissen et al. can also admit of an orthorhombic structure with space group $Pbnm$. In another detailed study using the anisotropic interaction potential between two C$_{70}$ molecules in terms of Cayley-Klein parameters, they have confirmed that the structure could be orthorhombic with space group $Pbca$ or $Pnma$. The experimental results of van Smaalen et al. also conclude in favour of an orthorhombic structure with space group $Pbnm$ of the solid C$_{70}$ at low temperature. It is to be noted that this structure has resulted by a two step transformation from the ideal b.c.p. phase at high temperature. Oh et al. have reported detailed potential energy calculations using Girifalco-Lennard-Jones potential for different molecular orientations depicting various possible structures of the solid and the corresponding lattice parameters. They have compared their results with experimental reports by others. They reported two possible transformation sequences on cooling, viz.,

fcc $\rightleftharpoons$ ortho(I, II) $\rightleftharpoons$ rh $\leftrightarrow$ hcp I $\vDash$ mono

or, fcc $\rightleftharpoons$ hcp II $\leftrightarrow$ hcp (III, IV) $\vDash$ mono

where the fcc is the high temperature phase and the monoclinic is the low temperature phase. Here hcp I - IV correspond to the $c/a$ ratios of the unit cells which are 1.84, 1.61, 1.50 and 1.53 respectively. The ortho I and II correspond to the lattice parameters, $a = 16.2$ Å, $b = c = 14.0$ Å and $a = 16.0$ Å, $b = 14.4$ Å, $c = 14.8$ Å respectively. The monoclinic structures in both cases are the same and correspond to the C$_5$-axis of orientation being parallel to the b-axis of the unit cell. This
Their result indicates a two step transformation, \( \text{viz.} \) potential in a phase transformation study of fcc solid C, potential together with the bond charge Coulomb potential structure to be hcp with \( c/a \approx 1.77 \), instead of a monoclinic structure. The molecular orientations in their model, however, parallel to the unit cell c-axis. Sprik et al. have carried out constant pressure molecular dynamics calculations incorporating Lennard-Jones potential together with the bond charge Coulomb potential in a phase transformation study of fcc solid C\textsubscript{70}. Their result indicates a two step transformation, \( \text{viz.} \) fcc \( \rightarrow \) hcp \( \rightarrow \) monoclinic which is in excellent agreement with the experimental results reported by Christides et al.\textsuperscript{13}

We had proposed a structural model, consistent with the lattice parameters for the monoclinic structure measured from our x-ray diffractogram (XRD) at 100 K, wherein the molecular C\textsubscript{5} axis has a tilt of about 18\(^\circ\) from the monoclinic b\textsubscript{m}-axis. Our recent experimental studies on the kinetics of phase transformation in hcp solid C\textsubscript{70} show that, except for very slow cooling rates, a two step transformation invariably results. Such a two-step transformation may be similar to that reported by Verheijen et al.\textsuperscript{70} The low temperature monoclinic structures and the C\textsubscript{70} molecular orientations reported by these authors must, therefore, correspond to some local potential energy minima of the system raised above the global minimum by misorientation stresses.

In this paper, we report the results of the potential energy calculation pertaining to the monoclinic structure obtained by us from our 100 K XRD. Since the cooling rate was very slow (typically, 0.0033 K/min.) the monoclinic structure determined from our experiment is expected to be close to the equilibrium structure at low temperature. In this calculation, we have considered the interactions between the seven molecules, one at the origin (0,0,0) of the monoclinic unit cell and the remaining six at the six nearest neighbour positions, three above and three below the basal plane. The orientation of the molecules has been defined using the angles, \( \theta, \phi \) and \( \psi \), as explained later. The final orientation of the molecules, as obtained by locating the minimum of the potential energy has \( \theta = 18^\circ \), \( \phi = 8^\circ \) and \( \psi = 5^\circ \).

The structure of our C\textsubscript{70} sample at room temperature is ideal hcp\textsuperscript{70} and the XRD pattern of this structure has been analysed in detail in an earlier work\textsuperscript{70}. The hcp lattice constants are, \( a_h = b_h = 10.53 \)\( \AA \), \( c_h = 17.26 \)\( \AA \) and \( \gamma_h = 120^\circ \). The 100 K pattern fits well to a monoclinic structure with lattice parameters, \( a_m = 10.99 \)\( \AA \), \( b_m = 16.16 \)\( \AA \), \( c_m = 9.85 \)\( \AA \) and \( \beta_m = 107.75^\circ \) and space group \( P2_1/m \). It is clear that the following correspondence of lattice parameters is appropriate in going from the hcp to the monoclinic: \( c_h \) shrinks and forms \( b_m \), \( b_h \) increases and forms \( a_m \), and \( a_h \) shrinks to form \( c_m \). This correspondence is shown in Fig.1. The hexagonal angle \( \gamma_h \) can be seen to reduce to the monoclinic unique angle \( \beta_m \) by a shear along the direction shown by the arrows in Fig.1(b). It can be seen that the above correspondence indicates a tilt of the C\textsubscript{5}-axis of C\textsubscript{70} molecules by an angle of approximately 18\(^\circ\) from the b\textsubscript{m}-axis of the monoclinic unit cell (see Fig. 1(b)).

In this calculation we have used the Lennard-Jones potential together with the bond charge Coulomb potential. Following Lu et al.\textsuperscript{71} in the ordered state of the solid there is less charge density distribution around the C-C single bonds (long bonds) compared to that around the C-C double bonds (short bonds). Such a charge density difference on the surface of the molecule leads to short range intermolecular Coulomb interaction which decays as \( 1/R^2 \) at long distances in the case of C\textsubscript{70}. In this calculation we have used the same notation for the interaction sites as was done by Sprik et al.\textsuperscript{70} in their calculation for the fcc solid C\textsubscript{70}. The Lennard-Jones centres are taken to be the carbon atoms sites (C sites: \( \sigma_{CC} = 3.4 \)\( \AA \)) as well as the mid-points of the electron-rich C-C double bonds (D sites: \( \sigma_{DD} = 3.6 \)\( \AA \), whereas \( \sigma_{CD} = 3.5 \)\( \AA \)) and the magnitude of the interaction has been taken as, \( \epsilon = 2.964 \) meV\textsuperscript{70}.

The effective charge around the single bonds are assumed to be localised around the C sites. Though in C\textsubscript{70} molecules, there are five types of C sites, for the sake of simplicity all C sites can be treated to be of the same type as in the case of C\textsubscript{60}. If a C site carries an effective charge \( q_C \), the corresponding value at the D sites will be \( q_D = -2q_C \). The values of these effective charges are fractions of the electronic charge, e.g., \( q_C = 0.175e \) and \( q_D = -0.35e \). The bonds around the equatorial region of the molecule have a length intermediate between the length of a single bond and a double bond and, therefore, are termed as intermediate bonds (or, I bonds). For these bonds, \( \sigma_I = 3.5 \)\( \AA \) and \( q_I = 0.5q_D \). Since the polar cap of the molecule consists of both long bonds and short bonds, the Coulomb interaction is stronger at the two opposite poles of a molecule in the ordered phase. Therefore the bond charge interaction between two molecules in adjacent planes is dominated by the polar caps and can be termed "polar cap" interaction. The coordinates of the 70 carbon atoms in the molecule were generated from data available in published literature\textsuperscript{70}. The total interaction potential between any two C\textsubscript{70} molecules is given by
\[ V_{12} = \sum_{i,j} 4\varepsilon \left( \frac{\sigma_{xx}}{|r_{1i} - r_{2j}|} \right)^{12} - \left( \frac{\sigma_{xx}}{|r_{1i} - r_{2j}|} \right)^{6} + \sum_{m,n} \left( \frac{q_m q_n}{|b_{1im} - b_{2jn}|} \right) \]

where the subscript \( x \) indicates interaction sites, e.g., C, D, or I, and \( r_{1i,j} \) are the coordinates of the atoms, \( b_{1im}, b_{2jn} \) coordinates of bond centres and \( q_m, q_n \) are effective bond charges (e.g., \( q_C, q_D \) and \( q_I \)).

Using the above interaction potentials between the seven nearest neighbour molecules for the lattice parameters measured from our 100 K x-ray diffractogram, we optimise the molecular orientations with respect to the unit cell parameters by minimising the total energy. The molecular orientations are defined using the polar coordinates \( \theta \) and \( \phi \), where \( \theta \) is the polar angle, i.e., the angle between the \( b_{nm} \)-axis and the molecular long axis and \( \phi \) is the azimuthal angle. Further minimisation of the potential energy has been performed by varying the angle (\( \psi \)) which defines the body rotation (spin) of the molecules around their \( C_5 \)-axes of the six molecules above and below the basal plane relative to the molecule at the origin of the monoclinic unit cell.

We calculate the potential energy per cluster for each configuration of the seven molecules defined by the values of \( \theta \) between 0° and 90°, \( \phi \) between 0° and 180°, and \( \psi \) between 0° and 72°. In Fig.2, we show the variation of potential energy with respect to \( \theta, \phi \) and \( \psi \). Clearly, for \( \phi = 8^o \) and \( \psi = 5^o \) the potential energy is minimum at \( \theta = 18^o \). This result is consistent with the model we proposed for the molecular orientation in the monoclinic unit cell experimentally measured by us.

The minimum potential energy per cluster obtained for our model is -3.923 eV which is significantly lower than other calculations reported in literature. It is to be mentioned here that there are two other minima with respect to \( \theta \) at 54° and 88° (not shown in the figure). Though these three minima have energy values comparable to each other, the energy barriers between them are nearly 0.04 eV which is too large to spontaneously flip the molecule from one minimum to the other at low temperatures (100 K). These multiple minima indicate that the system may have degenerate states with respect to \( \theta \), or, that they may even correspond to different structures which can be obtained by applying some external driving force, e.g., pressure etc. The degeneracy may arise as a consequence of the repulsive interactions between the C-C bonds as indicated by Sprik et al. in their extended model. Since the present calculation is based on the static orientations of molecules (molecular static calculation) the study of the structural transformation or the change of molecular orientations with temperature cannot be carried out by this method. A detailed molecular dynamics calculation is needed for this purpose which is in progress. Nevertheless, we argue that the equilibrium low temperature structure will be consistent with the molecular \( C_5 \)-axis tilted away from the unit cell long axis, because of the polar cap interaction, as proposed in the present model and supported by the potential energy calculation, rather than being oriented parallel to it. We recall from the introductory section that the molecular dynamics calculation of Sprik et al. leads to two competing orientations for the molecules. A pictorial view of the optimised static orientation of the seven molecules for our monoclinic lattice parameters is shown in Fig.3. This picture is generated using a public domain software MOLDRAW.

In conclusion, our results of potential energy calculation using the Lennard - Jones potential together with the bond charge Coulomb potential support the structural model proposed by us in our earlier paper. The calculation shows that the minimum potential energy state appears with a tilt of the \( C_5 \)-axis of the molecule with respect to the monoclinic long axis (\( b_{nm} \)-axis) by an angle of 18°. Further minimisation of the interaction energy between the neighbouring molecules has been carried out using an angle \( \psi \) which defines the rotational configuration of the molecule around its own \( C_5 \)-axis. The molecular orientations obtained from our calculation have an implication of significant polar cap interaction between the nearest neighbour molecules in adjacent planes. The bond charge interaction is thus seen to play a key role in determining the equilibrium low temperature structure of solid \( C_{70} \). Our calculations show also that the structural model proposed by us corresponds to the most stable low temperature structure of solid \( C_{70} \) reported so far.

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FIG. 1. (a) High temperature hcp structural model; C\textsubscript{70} molecules are freely rotating mimicking spheres, (b) Monoclinic unit cell model proposed for the lattice parameters obtained from XRD pattern at 100 K (Ref. 10).

FIG. 2. Variation of the potential energy in eV/ cluster (a) with \( \theta \), (b) with \( \phi \), and (c) with \( \psi \).

FIG. 3. Final orientational configurations of the 7 molecules of the unit cell arising from the potential energy calculation; \( a_m \), \( b_m \), and \( c_m \) represent the monoclinic cell parameters.
Ideal h.c.p.

Monoclinic
