Potential energy surface and orientational disorder in solid fullerene C_{60}

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The polymorphism and molecular disorder in crystalline C_{60} have been studied by modelling the optimum packing of fullerene molecules by the atom-atomic potential method. The study includes the calculation of minima and saddle points of the potential energy surface with sorting out of the most common space symmetry groups. Two models of intermolecular potential for C_{60} have been checked, one of which assumes effective charges at the centers of C—C bonds. It has been found that the calculated barrier of reorientations is much lower in the case where the concerted character of rotations of different molecules is taken into account. The model of orientational disorder in the face-centered cubic phase is suggested, which is based on consideration of symmetrically arranged equivalent minima separated by low potential barriers.

Key words: fullerene C_{60}, molecular packing, potential energy calculation, orientational disorder, polymorphism.

Fullerene C_{60} is crystallized under the usual conditions in the face-centered cubic (FCC) lattice (space group *Fm*3*m*, $Z = 4$), in which molecules are orientationally disordered.[1—5] The polymorphous transformation occurs[1,6,7] at low temperature (260 K) to form an ordered structure with a simple cubic cell and *Pa*3 symmetry, $Z = 4$. While coordinates of atoms of the low-temperature form are determined with high reliability,[7] the mechanism of the orientational disorder in the FCC form remains unclear. X-ray experiments give the pattern averaged in time and space, which has been interpreted in terms of models both with completely[4] and partially[5] free rotations of molecules. On the other hand, the NMR data[2,3] and the molecular dynamics calculations[8] suggest that there are strong correlations in reorientational motion of molecules, which are characterized by the term "rotation diffusion".

The viewpoint on the mechanism of the orientational disorder in the FCC phase of fullerene C_{60} based on the results of the energy calculation of the optimum packing of molecules by the atom-atomic potential method is presented in this work.

It has been found in the previous studies that considering only van der Waals interactions between molecules results[9] in packing with an orthorhombic cell and the *Cmca* symmetry, which is not observed in fact in experiment. The situation has drastically been improved[10] by adding the Coulomb interaction of charged centers placed at the middles of C—C bonds: the positive charge q at the electron-deficient single bond and the negative charge $-2q$ at the electron-excessive double bond. Starting from some q value, the model reproduces the *Pa*3 form, which corresponds to the deepest potential energy minimum. This model is accepted as grounds in this work.

The peculiarity of our approach compared to previous studies is in the fact that we intend not only to determine the deepest energy minimum, but also to gain a notion of the potential energy surface (PES) as a whole, especially in the region, which is responsible for polymorphous transformations,[11] disorder, and other interesting phenomena observed experimentally. For this purpose, we consider saddle points of the PES between the deepest minima[12] and, mainly, take into account the PES symmetry, which depends on such factors as the space group, the symmetry group of a molecule,[13,14] and the permutation symmetry.[15]

Computational procedure

Coordinates of atoms of the C_{60} molecule for calculating the potential energy were obtained assuming the ideal symmetry I_h ($m\bar{5}m$) on the basis of the lengths of the double and single bonds, which are equal to 1.39 and 1.45 Å, respectively, according to averaged X-ray data.[8] To describe van der Waals

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interactions of the carbon atom, the 6—12-type potential (see Ref. 16) with the parameters $r_{\min} = 3.7$ Å (the equilibrium distance) and $\varepsilon = -0.0722$ kcal mol^{-1} (the depth of the potential well) were used. According to the intermolecular interaction model,[10] charges $q = 0.25$ e were placed in the centers of single bonds and charges $2q = -0.5$ e were placed in the centers of double bonds.

The search of the global minimum was performed for four most common space groups with the centrosymmetric arrangement of molecules: $P2_1/c$, $P\bar{1}$, *Pbca,* and $C2/c$ (see Ref. 17).

Packings found were checked for the positive determinancy of the matrix of second derivatives in the minimum point, *i.e.*, an additional calculation was performed in the *P*1 group with independently varied degrees of freedom of all molecules, which form an elementary cell. In the maximum variant, a system of four independent molecules was considered, to each of which six degrees of freedom (three translational and three rotational) were imparted. Subtracting three translations corresponding to shifting the system as a whole and taking into account six parameters of the unit cell, the total number of variables is equal to 27 in this case. A similar procedure has been used previously for studying the global PES of benzene.[18,19]

Numerical calculations were performed using a PMC program,[20,21] which makes it possible to calculate the lattice energy and its analytical first derivatives from formulas of accelerated convergence in the case of slowly converging sums containing r^{-6} and r^{-1} terms. An improved variant compared to that suggested previously[22] was used, which allows one to remove restrictions on parameters of atom-atomic potentials at r^{-6}. The "quasi-Newton" minimization was performed, using the VA09A procedure[23] and a special scheme for selecting intermolecular contacts, which removed a poor convergence to minimum due to the limited radius of the summation sphere.[21] (The latter was assumed to be equal to 9 Å, *i.e.,* 1 Å greater than the recommended radius[22] with the constant of accelerated divergence of 0.175 Å^{-1}.) No summation over the reciprocal space was performed in the minimization process.[22] However, in the case of the Coulomb energy, the contribution of the reciprocal lattice was once calculated in the minimum point, which was considered as a correction to the total energy for comparing different minima.

Comparison of structures and recognition of symmetry

In the course of global search, such a problem as different PES minima corresponding to the same crystalline structure is often met. To select unique solutions, we use a CRYCOM ("*Crystal Comparison*") program, which automatically compares structures specified by the corresponding sets of coordinates and lattice parameters.[24] The algorithm of the program is based on enumerating equivalent structural descriptions, in the course of which alternative methods for choosing a unit cell, an origin of coordinates, and an independent region allowable in terms of a given space group are taken into account. Permutations of independent molecules and molecular symmetry (which, speaking in general, may have an approximate character) are also considered. Equivalent descriptions of one structure are compared to those of another structure. Structures are considered to be similar, if at least one pair of descriptions, whose numerical parameters coincide within specified deviations, is found.

One of remarkable peculiarities of CRYCOM is in the fact that this program makes it possible to reveal *all* ways of structural correspondence if several. This ways of the possibility to use this method for recognition of the hidden symmetry (which is present implicitly in numerical values of parameters of unit cells and atomic coordinates) by comparing the structure with itself. This problem is very urgent, because the optimum structure can possess a higher symmetry compared to that accepted for the calculation.[25] In the case of C_{60}, the problem of computational comparison is especially important, because a very high symmetry is considered. For example, in the *P*1 group the number of equivalent combinations of Euler angles per one independent molecule is at least 2880: it is determined by the product of 24 variants of choice of the basis vectors of the unit cell and 120 operations of the symmetry of the C_{60} molecule.

Results and Discussion

The intermolecular potential model without bond-centered charges was tested as the first step. We have found by a procedure similar to that described previously[9] that the structure in the deepest minimum is characterized by the pseudo-tetragonal unit cell and *Cmca* symmetry (Table 1). It should be mentioned in addition that the minimum of the *Pa*3 phase has also been found in this calculation, although it is considerably less in energy than the main minimum.

Turning to the model with bond-centered charges dramatically changes the situation: the packing with *Pa*3 symmetry is realized as the deepest minimum in the calculation both in the *Pbca* group (which is a subgroup of *Pa*3) and the *P*1 group with four independent molecules. The calculated and observed structures very well coincide: angles of the molecular rotation around the third-order axis differ only by 1.5°.

In addition to the global minimum, the calculation has revealed several local minima, the deepest of which are listed in Table 1. They can be of interest as models of hypothetical polymorphous phases (which are possible, for example, at high pressures).

We tried to estimate the value of the potential barrier of molecular reorientations. Generally speaking, this requires the knowledge of the saddle point between symmetrically identical minima of the same phase (while saddle points between minima of different phases characterize barriers of polymorphous transformations[12]).

Different hypotheses about the character of molecular rotations can be advanced. Usually, one molecule is rotated with fixed positions of the other molecules. Barriers of such rotations are estimated[10] as 7 to 9 kcal mol^{-1}. This coincides with our estimate for this approach. How-

Table 1. Minima and saddle points of the PES of crystalline C_{60} calculated on the basis of two intermolecular interaction models

Energy* /kcal mol^{-1}	Symmetry	Z	Cell parameters						d /g cm^3
			a	b	c	α	β	γ	
			/Å			/deg			
I. Calculation without charges									
				Minima					
−42.72	*Cmca*	4	13.35	14.04	14.04	90.0	90.0	90.0	1.82
−39.98	*Pa*3	4	13.92	13.92	13.92	90.0	90.0	90.0	1.77
II. Calculation with charges at bonds									
				Minima					
−44.82 (−4.50)	*Pa*3	4	13.88	13.88	13.88	90.0	90.0	90.0	1.79
−43.14 (−3.44)	$P2_1/n$	2	13.80	9.92	9.80	90	91.3	90	1.78
−42.90 (−2.89)	$R\bar{3}$	1	9.74	9.74	9.74	61.2	61.2	61.2	1.79
−42.65 (−2.68)	*C*2/*c*	4	17.07	9.84	16.87	90	108.9	90	1.79
				Saddle points					
−41.92 (−3.03)	*Cmca*	4	14.24	13.92	13.66	90	90	90	1.77
−41.36 (−1.36)	*F*2/*m*	4	13.67	14.05	13.97	90	90	90	1.78
−39.78 (−2.37)	*Fm*3	4	14.01	14.01	14.01	90	90	90	1.74

* The Coulomb component of the energy is given in parentheses.

ever, it is easy to understand that the rotational barrier can be decreased due to the relaxation of surrounding molecules. For example, a mechanism can be suggested, in which molecules make *mutually dependent* turns. (A concerted rotation of gear-wheels in a gear box illustrates well this idea.) Rotating fullerene molecules in such a way that their mutual orientation obeys the *Pbca* group (unlike *Pa*3, this group does not restrict the three-dimensional rotation of a molecule), we have found the barriers of the order of 4 to 4.5 kcal mol^{-1}, depending on the choice of the molecular axis (we do not take into account the relaxation of parameters of the unit cell a, b, c in the course of rotation, which would decrease the barrier even more noticeably).

The correct procedure for searching the saddle point in the multidimensional space requires scanning along the essential variable from the first minimum to the second minimum with optimization over all variables except the essential variable.[12] We did not manage to perform it in full due to the large body of calculations. Therefore, we restrict our discussion to the following simplified consideration.

A three-dimensional rotation of a C_{60} molecule can be characterized by three Euler angles φ, θ, and ψ corresponding to rotations around three mutually perpendicular two-fold axes of symmetry. Let us count these angles from the state when molecular axes are perpendicular to Cartesian axes of the crystal. Due to the existence of equivalent descriptions caused by alternative methods for choosing crystallographic and molecular axes,[13,14] the following equivalent sets of Euler angles take place in addition to other sets in the case of the *Pa*3 form: φ,θ,ψ; $\varphi,-\theta,-\psi$; $-\varphi,\theta,-\psi$, and $-\varphi,-\theta,\psi$. This results in the existence of local extrema in the points: $\varphi,0,0$; $0,\theta,0$; $0,0,\psi$. Optimizing the packing in the *Pbca* group at $\theta = 0$ and $\psi = 0$, we have found the saddle point of the PES with the energy of −41.92 kcal mol^{-1} (see Table 1), which corresponds to the barrier of 2.9 kcal mol^{-1} relative to the minimum of the *Pa*3 form. This barrier corresponds to a complex motion, in which four molecules forming the unit cell make concerted turns around their axes, whose directions do not coincide. This concerted rotation results in the transition of the system to the equivalent minimum, which at the same time is related to the initial minimum by a reflection in the plane (100), (010), or (001) (although the *Pa*3 symmetry group does not contain mirror reflection planes!). Thus, it turns out that the structure is mapped to itself, but becomes oriented in space in a different way. If initial and mapped structures are superposed, the centers of molecules coincide and their mutual orientations differ by 30°. The result of this combination of mappings relative to all three planes can be imagined as some dynamically averaged structure with *Fm*3 symmetry, in which molecules make hindered rotations with amplitudes of 30° in three mutually perpendicular directions.

The model obtained (we will call it the dynamic model) can be compared to the static model with *Fm*3 symmetry (see Table 1), which is obtained by minimization of packing at fixed zero values of Euler angles (*i.e.*, when molecular axes are oriented parallel to axes of a crystal cell) and corresponds to the saddle point of the PES.

We can continue these reasoning, considering rotational motions of molecules, which lead the system to the equivalent minimum related to the initial minimum by the rotation of the system as a whole around the fourth-order axis or by mapping relative to one of diagonal directions. Finally, this results in *Fm*3*m* symmetry typical of the observed disordered phase of C_{60}. The analysis by CRYCOM shows that amplitudes of molecular reorientations are equal to 37° in this case. Unfortunately, we didn't manage to calculate the saddle point for estimation of the potential barrier value due to the large body of calculations, because PES scanning of four independent molecules in the space of Euler angles is needed in this case. However, one can assume on the basis of similarity of situations that this barrier is quite comparable to the estimate presented above for *Fm*3 symmetry.

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