Structure and stability of some C_{60} isomers

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We have investigated the stability of the ideal C_{60} molecule and of some isomers using a molecular-dynamics quenching technique. The atomic forces used for the quench algorithm are obtained from a minimal-orbital *sp*-basis tight-binding calculation with local charge neutrality placed on each site. The isomers are derived from the ideal structure by introducing one or more tiling faults. As expected, the most favorable structure is found to be the ideal C_{60} molecule. The introduction of one tiling fault leads to a change in the cohesive energy of about 0.02 eV per atom (1.3 eV per molecule) and the corresponding value for the introduction of two faults, whether isolated or coupled, is found to be about twice this value. These changes are extremely small in comparison with the absolute value of the cohesive energy, with the fault energy equal to about one-fifth of the cohesive energy per atom of ideal C_{60} (calculated to be 6.94 eV). In addition, we find that an isomer containing a seven-membered ring has a fault energy of about 2.7 eV. We conclude that the existence of these isomers is probable on energetic grounds although the considerable deformation and consequent stress in the isomer containing a seven-membered ring leads us to suggest that it would not be observed experimentally.

I. INTRODUCTION

About six years ago two groups of workers[1,2] independently suggested the existence of a remarkable spherical molecule composed of sixty carbon atoms. This C_{60} structure is unique in that it consists of a spherical ball of sixty carbon atoms, with each carbon atom having the same environment. The stress is thus evenly distributed among the atoms. As the coordination of each atom is three, the angles between the bonds are close to one hundred and twenty degrees, and in the absence of dangling bonds, the bonding is expected to be close to that in the graphite structure, and consequently exceptionally stable. Though not yet confirmed beyond doubt, the theoretical and experimental studies which followed the first proposals all point to its existence. We cite but a small sample of these experimental,[3–11] and theoretical,[2,12–18] studies.

Soon after the initial studies it was suggested that the observed samples of sixty atom molecules contained a range of structurally similar isomers.[19] The ideal molecule would be the most energetically stable though lying close in energy to the others. These other isomers would share most of the stabilizing characteristics of the ideal C_{60} molecule, that is, threefold coordination, the close to one hundred and twenty degree bond angles, and the absence of dangling bonds. These isomers can be thought of as the ideal C_{60} molecule with one or more faults in the atomic arrangement.[19] Their existence was given extra credibility by Stone and Wales[19] who noted that transitions from one isomer to the other are thermally forbidden, thus once formed the isomers are likely to persist rather than relax into the lower lying ideal C_{60} geometry. However these isomers are too computationally demanding for investigation by current *state-of-the art ab initio* methods, for which the upper limit at the time of writing is perhaps represented by the remarkable calculations of Fowler, Lazzeretti, and Zanisi[14] on the ideal C_{60} molecule with fixed bond lengths. These isomers are accessible to semiempirical methods.

In this paper we present a molecular dynamics tight-binding (MDTB) study of some of these isomers. The stability, the bond lengths, and the binding energies of three isomers are investigated by relaxing the atomic positions in the ideal isomer structures until all of the atomic forces are zero. We thus find three local energy minima for the sixty carbon-atom molecules. The same procedure is repeated for the ideal C_{60} molecule to provide a point of reference, and a check with previously published data.

The tight-binding calculations are based on the formulation due to Harrison,[20] with a set of parameters recently optimized[21] using a novel fitting technique.[22,23] The technique allows the fitting of a large number of bulk properties so as to ensure a high degree of transferability and has been extensively tested for silicon, on bulk and cluster properties,[22,23] and on liquid silicon and bulk point defects.[24] For silicon the tests showed that tight binding, though inherently less accurate than *ab initio* methods, can produce results which compare favorably with the latter if care is taken to ensure transferability. For carbon the properties fitted included the experimental values for the diamond lattice constant and bulk modulus, the experimental lattice constant for graphite to within a few tenths of an Å, reproduction of the principal features in the energy volume curves for five bulk lattices, and the reproduction of the diamond and graphite band structures up to the Fermi level.

The paper is laid out as follows: the isomers of C_{60} and the notation used are described in Sec. II; the MDTB model is described in Sec. III; the results of the calculations are presented in Sec. IV; and conclusions are drawn in Sec. V.

II. THE C_{60} ISOMER MODEL

To describe the isomers we use the notation of Stone and Wales[19] whereby each isomer is considered as the ideal C_{60} molecule with one or more faults in the atomic arrangement. The creation of a Stone and Wales fault is shown schematically in Fig. 1 which represents a fragment of the ideal C_{60} molecule. The fault requires that the two atoms marked A and B are moved to the positions marked α and β. For this single fault the rearrangement can be thought of as interchanging a pair of pentagonal tiles with a pair of hexagonal tiles, although this picture is less useful for more complicated isomers in which the number of pentagonal and hexagonal tiles is not preserved. The visualization of the isomers is simplified by numbering the twelve pentagonal tiles of C_{60}, as shown in Fig. 2. Although we only show the front *surface* of the molecule, the notation is identical to that used by Stone and Wales[19] who show all of the pentagons. Thus a simple fault introduced into the molecule will produce a (1,2) isomer, if the rotated atoms originally lay in pentagons 1 and 2.

Using the above notation, the isomers we study are the following: the (1,2) isomer, which contains a single fault preserving the number of pentagonal and hexagonal tiles, and which is expected to be the lowest lying of the isomers; the (1,2)(7,8) isomer which contains two faults lying on opposing faces and which also preserves the number of pentagons and hexagons; and the (1,2)(2,3) isomer, in which the two faults give rise to a seven-sided tile.

III. THE MDTB MODEL

A more general overview of tight binding, and of related techniques, can be found in the review article by Finnis *et al.*[25] The total cohesive energy of a molecule is given by the sum of the energy deriving from the formation of chemical bonds, the energy change associated with the change in the orbital occupations relative to the atomic values, and the nonorthogonality, electrostatic, and exchange-correlation contributions:
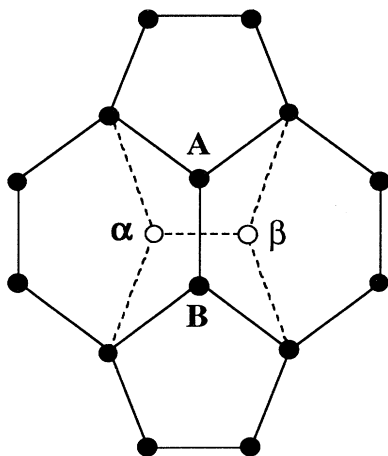

FIG. 1. Schematic illustration of a single fault in the ideal C_{60} structure. The relaxation of the surrounding atoms when atoms A and B move to α and β is not shown.
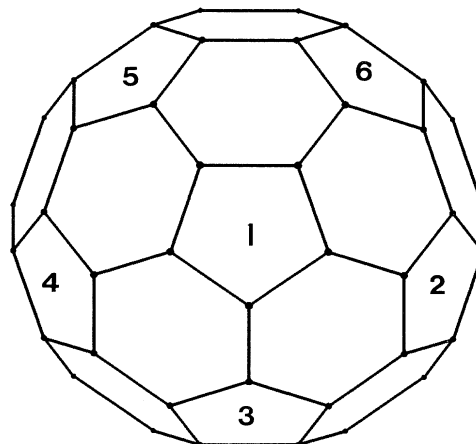

FIG. 2. The ideal C_{60} structure. Only those atoms lying on the front surface are shown. Each pentagon is numbered for purposes of identification.

$$E_{\text{coh}} = E_{\text{bond}} + E_{\text{prom}} + E_{\text{rep}} \ . \tag{1}$$

The first of these terms, the bond energy, E_{bond}, is formed from the local densities of states, $n_{i\alpha}(\varepsilon)$, and the diagonal elements of the Hamiltonian, $\varepsilon_{i\alpha}$, i being the site index and α the orbital index,

$$E_{\text{bond}} = \sum_{i\alpha} \int_{-\infty}^{\varepsilon_F} (\varepsilon - \varepsilon_{i\alpha}) n_{i\alpha}(\varepsilon) d\varepsilon \ . \tag{2}$$

The second term, the promotion energy E_{prom}, is formed from the set of $\varepsilon_{i\alpha}$'s and the changes in the orbital occupations, $\Delta n_{i\alpha}$ relative to the free atomic values,

$$E_{\text{prom}} = \sum_{i\alpha} \varepsilon_{i\alpha} \Delta n_{i\alpha} \ . \tag{3}$$

The local densities of states $n_{i\alpha}(\varepsilon)$, and hence the $\Delta n_{i\alpha}$'s, are found by occupying the energy levels from the solution of the tight-binding Schrödinger equation. The Hamiltonian matrix off-diagonal elements are constructed, in the usual way,[26] from the angle cosines for the interatomic vectors, and the hopping integrals for pure $ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$ bonding, each of which has a parametric form taken to vary as an inverse power of the interatomic separation multiplied by a decaying exponential function. The less important three center terms are ignored:

$$V_{ll'm}(r) = V_{ll'm}(r_0)(r_0/r)^{2.796}$$
$$\times \exp\{2.796[-(r/2.32)^{22} + (r_0/2.32)^{22}]\} \ . \tag{4}$$

The equilibrium neighbor separation in the diamond lattice, r_0, is equal to 1.55 Å. Local charge neutrality is enforced on each site, such that each atom has four (± 0.01) valence electrons, by adjusting the on-site energies by amounts proportional to the excess charge on the site. The constant of proportionality is about two-fifths of an electron volt per electron. This is done to provide a first approximation to self-consistency[25] and to ensure a

reasonable charge distribution.

Finally the nonorthogonality, electrostatic, and exchange-correlation contributions, collectively referred to as the repulsive energy E_{rep}, are approximated by a sum of pairwise interactions, $V_{rep}(r_{ij})$, in which r_{ij} denotes an interatomic separation,

$$E_{rep} = \sum_{i<j} V_{rep}(r_{ij}) \ . \tag{5}$$

Like the hopping integrals, the pair potential $V_{rep}(r_{ij})$ also varies, as an inverse power of the interatomic separation, multiplied by a decaying exponential function:

$$V_{rep}(r) = V_{rep}(r_0)(r_0/r)^{4.455}$$

$$\times \exp\{4.455[-(r/2.32)^{22}+(r_0/2.32)^{22}]\} \ . \tag{6}$$

The pair potential coefficient $V_{rep}(r_0)$, is equal to 10.92 eV.

The atomic forces are found by summing the contributions from each atom, each of which is given by the analytic derivative of the individual energy terms, Eqs. (2), (3), and (5), and can be evaluated given the previously calculated energy levels and states,

$$\mathbf{f}_i = \sum_j \delta E_{coh}/\delta \mathbf{r}_{ij} \ . \tag{7}$$

The relaxations are performed using a hybrid molecular-dynamics quench scheme in which the kinetic energy is slowly removed as the forces on the atoms in motion gradually approach zero. A starting geometry is input and then the atoms allowed to move according to the forces acting on them, and their velocities at a given moment. The velocity of an atom is approximated as the product of the discrete time interval (δt) and the vector displacement since the previous time step, $[\mathbf{r}(t)-\mathbf{r}(t-\delta t)]$. The molecular-dynamics algorithm which is due to Verlet[27] is written out explicitly in Eq. (8):

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + [\mathbf{r}(t)-\mathbf{r}(t-\delta t)] + \delta^2 t \mathbf{F}(t) \ . \tag{8}$$

The kinetic energy of the evolving system is gradually removed by inspecting, at each coordinate updating step, the values of the forces and the corresponding velocities.[28] If the x component of the force on atom i is positive, and the x component of the velocity is negative, the force is acting to slow the atom down. In this case we update the atoms x coordinate by adding on simply $\delta^2 t F_x(t)$, i.e., we have reduced the atoms' kinetic energy systematically. If the force has the same sign as the velocity component then we update the x coordinate as per the Verlet equation. This is repeated for the other two Cartesian coordinates, and for all atoms. In practice we find that this method is effective not only for optimizing geometries, as we are doing in this paper, but also for finding stable minimal energy geometries the form of which is not known beforehand.

IV. RESULTS AND DISCUSSION

Not surprisingly the quench on the ideal unfaulted geometry shows that C_{60} is highly stable, with a cohesive energy per atom of 6.94 eV. The corresponding values, calculated using the same parameters, for graphite and diamond are 7.06 and 7.03 eV per atom.[21] C_{60} is thus predicted to be energetically extremely stable. For the bond lengths we find values of 1.48 Å for a pentagon side and 1.43 Å for all other bonds. This is consistent with the values found in semiempirical Austin model 1 and modified neglect of differential overlap (MNDO) calculations which are about 1.47 and 1.40 Å.[16,17] Nevertheless these smaller values are probably closer to the actual values, given that the tight-binding model is known to overestimate the graphite lattice constant by a similar amount. For the energy levels, the order and the degeneracies are in agreement with previous calculations. For the highest-occupied-molecular-orbital–lowest-unoccupied-molecular-orbital (HOMO-LUMO) energy gap the calculations give a value of 1.7 eV, compared with the value typically found of 7.5 eV. This discrepancy is consistent with the model's description of the band structure of graphite, which though good at energies below the Fermi level, is rather poor at higher energies. Thus it is unreasonable to expect a good value for the highest-occupied-molecular-orbital–lowest-unoccupied-molecular-orbital (HOMO-LUMO) energy gap. For the bonding we find a large s to p promotion almost equal to one electron per atom, corresponding to approximately single occupancy of each of the sp basis orbitals, corresponding to strong p bonding in agreement with previous calculations.

For the (1,2) isomer, the quench also leads to a highly stable structure having a cohesive energy per atom extremely close to the ideal value of 6.92 eV, the total energy change, or (1,2) fault energy, being about 1.3 eV. This structure, illustrated in Fig. 3, is distorted from the perfect sphere, with changes in the bond lengths seen up to three nearest-neighbor hops away from one of the two
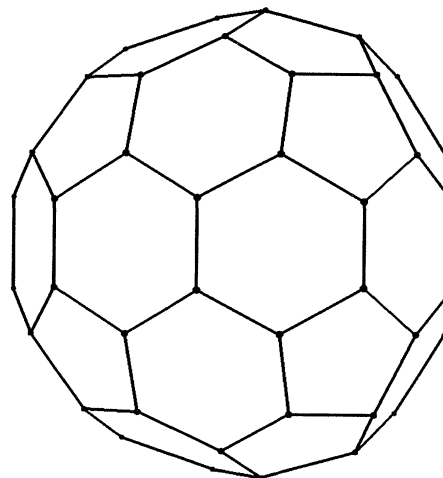

FIG. 3. The output from a quench on a (1,2) isomer. Only the front atoms are shown. The number of hexagons and pentagons has been preserved.
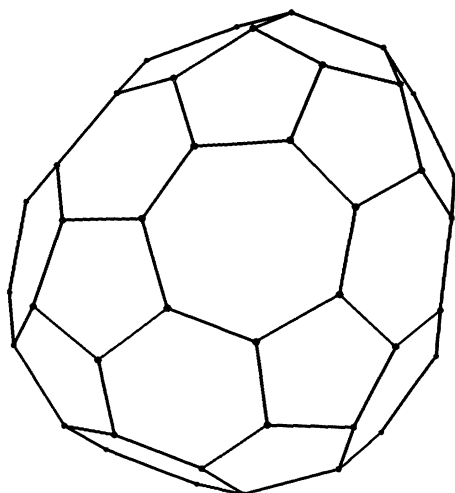
FIG. 4. The output from a quench on a (1,2)(2,3) isomer. The faults introduce a seven-sided polygon into the tiling, and a considerable distortion of the originally spherical structure.

atoms originally moved. The pentagon sides vary from 1.44 to 1.51 Å, a change of ±0.03 Å. All other bonds vary from 1.39 to 1.49 Å, a change of about ±0.04 Å. A better way to look at the bond-length changes is to divide up the bonds into single and double, and to insist that the bonds far from the faulted region are unchanged. This leads to one consistent arrangement for which the double bonds are generally shorter than the single bonds as would be expected. Thus single bonds vary from 1.45 to 1.51 Å, a change of ±0.03 Å, and double bonds from 1.39 to 1.44 Å, a change of $^{+0.01}_{-0.04}$ Å. The average s to p promotion is almost identical to the previous value of 0.79 electrons, and thus not significant. Unlike the ideal C_{60} molecule the sites in the (1,2) isomer are not all identical, and consequently we see some variation in the value from site to site, the variation being of the order of 0.01 electrons. The energy levels are seen to be singly degenerate and with smaller interlevel energy gaps than the ideal molecule as expected.

As expected the (1,2)(7,8) isomer is comparable to the (1,2) isomer in that the two faults behave as if the one does not affect the other, the bond deformations in the region of each fault being identical to those seen for the single fault in the (1,2) isomer. Correspondingly, the (1,2)(7,8) fault energy is equal to twice the (1,2) fault energy, the average s to p promotion is equal to 0.79 electrons, and the bond lengths around the faults are comparable to those seen around the single fault in the (1,2) isomer. There are no degeneracies seen in the energy levels though some are very close together.

Perhaps rather surprisingly, the (1,2)(2,3) isomer

behaves in many ways like the (1,2)(7,8) isomer, in that its fault energy is extremely close at 2.7 eV, i.e., an increase of only 0.1 eV over the (1,2)(7,8) fault energy, and the average s to p promotion is equal to 0.78 electrons, i.e., almost identical to the previous three values. Structurally though, this isomer is markedly distorted from ideal C_{60}. For the bond lengths the sides of pentagons vary between 1.44 and 1.51 Å, a change of about ±0.03 Å, the seven-sided polygon sides between 1.41 and 1.51 Å, and the remaining bonds between 1.42 and 1.46 Å. The molecule is consequently severely distorted from the spherical form as seen in Fig. 4 with no clear separation between single and double bonds. For the energy levels we again see no degeneracies, and a HOMO-LUMO gap of 0.9 eV. Although as already stated the model does not reproduce the absolute values of HOMO-LUMO energy gaps, the reduction is consistent with other predictions.

V. CONCLUSIONS

In summary we have performed molecular-dynamics quenches, within a tight-binding framework, to find the energies of three simple isomers of the ideal C_{60} molecule, and the associated bond lengths, and s to p promotions. We find, as have many previous studies, that the ideal molecule is stable, and that it lies extremely close in energy to the graphite and diamond lattice structures, although we find it to be considerably closer than most theoretical studies. We find that the cohesive energy per atom for each of the isomers is very close to that for the ideal. This is probably because the weakening of bonds by the inclusion of a fault is very much localized to the neighboring bonds. Thus dividing the total energy change, which is not so small, by the number of atoms, which is large, produces a small number. A more realistic quantity is the fault energy, defined as the energy difference between the ideal C_{60} molecule and the faulted molecule, or isomer. We find an energy of approximately 1.3 eV per fault introduced. An interesting result of our calculations is that we find an isomer with a seven-sided polygon to be comparable in energy to one containing just five- and six-sided polygons. However, the distortion of the bond lengths and the bond angles (see Fig. 4) is so severe that we suggest that this isomer is unlikely to be observed experimentally.

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