For C_{60}, the interactions in the crystal are much more anisotropic than for C_{70}. The interactions within the plane have $R_e = 9.92 - 10.06 \text{Å} (10.00 \text{ average})$ and $D_e = 8.23 - 8.79 \text{ kcal mol}^{-1} (8.47 \text{ average})$, whereas those out-of-plane have $R_e = 10.83 - 10.96 \text{Å} (10.91 \text{ average})$ and $D_e = 6.75 - 7.18 \text{ kcal mol}^{-1} (6.90 \text{ average})$. This can be compared with the optimal dipole interactions of $R_e = 9.94 \text{Å}$ and $D_e = 8.97 \text{ kcal mol}^{-1}$.

After submission of this manuscript, ref. 15 reported heats of sublimation of $\Delta H_{\text{sub}} = 40.1 \pm 1.3 \text{ kcal mol}^{-1}$ for C_{60} and $\Delta H_{\text{sub}} = 43.0 \pm 2.2 \text{ kcal mol}^{-1}$ for C_{70}. Our calculations lead to a cohesive energy of 43.9 kcal mol$^{-1}$ for C_{60} and 49.5 kcal mol$^{-1}$ for C_{70}. Correcting for zero-point energy and temperature dependence of the specific heat capacity $C_v$, entropy $S$ and $H$ for both the crystal and free molecule, we calculate $\Delta H_{\text{crys}} = 40.9 \text{ kcal mol}^{-1}$ for C_{60} and $\Delta H_{\text{crys}} = 46.4 \text{ kcal mol}^{-1}$ for C_{70}, in excellent agreement with experiment.

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occurs for two hexagonal faces in contact (the same orientation, but with the centres shifted by 0.92 Å towards one edge). The equilibrium bond distance is $R_e = 9.84$ Å (centre to centre) and the bond energy is $D_e = 7.30$ kcal mol$^{-1}$. This leads to a separation of the faces of 3.27 Å and a closest atom–atom distance of 3.36 Å. The least favourable orientation leads to an energy of 6.10 kcal mol$^{-1}$, about 1 kcal mol$^{-1}$ smaller than the best.

For the $C_{70}$ dimer, the optimal interaction is with the long axes parallel. The waist of the monomer involves both concave and convex graphite-like regions, and the best interaction of the dimer ($D_e = 8.97$ kcal mol$^{-1}$, $R_e = 9.94$ Å) has a convex side matched with a concave side. Here the worst orientation leads to an energy of 6.09 kcal mol$^{-1}$, about 3 kcal mol$^{-1}$ worse than the best.

Because of non-crystallographic symmetries (fivefold axes), it is not possible for these fullerenes to retain the optimal dimer orientation in the closest-packed structures. The symmetry of the fullerene does, however, affect the packing. To understand why $C_{60}$ prefers f.c.c. whereas $C_{70}$ prefers h.c.p., consider a closest-packed layer B and the optimized closest-packed layer A on top as in Fig. 1. The fullerenes orientate so as to optimize interactions, on average, both within and between layers. For $C_{60}$ (symmetry $I_h$) this leads to hexagonal faces almost in contact (see molecules a and b in Fig. 1a). The inversion symmetry of $C_{60}$ implies that the optimal interaction of the molecule b in layer B with molecules of layer C is to have each c molecule on the opposite side of the optimal b–a interaction. Thus we expect $C_{60}$ to prefer ABCABC (f.c.c.) packing, as in Fig. 1a.

For $C_{60}$ (symmetry $D_{5h}$), optimal packing in a closest-packed plane is achieved with the long (fivefold) axis perpendicular to the plane (see Fig. 1b), with the horizontal reflection $σ_h$ in the plane. In this case the optimal interaction of molecules b and c is on the same side as the optimal b–a interaction. Thus the best packing is for layers C and A to be the same, leading to ABABAB (h.c.p.) packing for $C_{70}$, as in Fig. 1b.

There are no definitive crystal structures published for $C_{60}$ or $C_{70}$. Kratschmer et al. concluded that the structure for $C_{60}$ is h.c.p., but their data did not really distinguish between h.c.p. and f.c.c. Stoddart quoted unpublished work by F. Diederich, indicating that f.c.c. is more stable for $C_{60}$. Indeed, Diederich (personal communication) observes only cubic crystal habits for $C_{60}$ and only hexagonal habits for $C_{70}$, as would be expected from our predictions (diffraction data from the crystals are not of sufficient quality for structural analysis). There are other, as yet unpublished, experimental studies supporting the f.c.c. structure for $C_{60}$ (for example, refs 4, 6). The predicted differences

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**FIG. 1** Top, calculated crystal structure of $C_{60}$ fullerene. Shown (in blue) is one of the four molecules of the f.c.c. unit cell, surrounded by its optimum 12 neighbours. Bottom, calculated crystal structure of $C_{70}$ fullerene. Shown (in blue) is one of the four molecules of the h.c.p. unit cell, surrounded by its optimum 12 neighbours.

**FIG. 2** Optimal f.c.c. structure: the f.c.c. unit cell of $C_{60}$ projected along the three axes: left, [100]; centre, [010]; right, [001]. The orthorhombic unit cell is shown with blue lines. Balls of different colour are in different planes.
occurs for two hexagonal faces in contact (the same orientation, but with the centres shifted by 0.92 A towards one edge). The equilibrium bond distance is R = 9.94 Å (center to center) and the bond energy is D_b = 15.79 kcal mol\(^{-1}\). This leads to a separation of the faces of 3.4 Å and a smallest atom-atom distance of 3.16 Å. The least favourable orientation leads to an energy of 6.10 kcal mol\(^{-1}\), about 1 kcal mol\(^{-1}\) smaller than the best.

For the C\(_6\)B\(_3\) dimers, the optimal interaction is with the long axes parallel. The waist of the monomer involves both concave and convex graphite-like regions, and the best interaction of the dimer (D\(_{2h}\) 4.89 kcal mol\(^{-1}\) \(R = 9.84 \AA\) ) has a convex side matched with a concave side. Here the worst orientation leads to an energy of 6.09 kcal mol\(^{-1}\) , about 3 kcal mol\(^{-1}\) worse than the best.

Because of non-crystallographic symmetries (fivefold axes), it is not possible for these fullerenes to retain the optimal orientation in the closest-packed structures. The symmetry of the fullerene does, however, affect the packing. To understand why CsB prefers f.c.c. whereas CsB prefers h.c.p., consider a closest-packed layer B and the optimized closest-packed layer A on top as in Fig. 1a. The inversion symmetry of CsB implies that the optimal interaction of the molecule B in layer B with molecules of layer C is to have each molecule on the opposite side of the optimal A-B interaction. Thus we expect CsB to prefer ABCABC (f.c.c.) packing, as in Fig. 1c.

For CsB (symmetry D\(_{3h}\)), optimal packing in a closest-packed plane is achieved with the long (fivefold) axis perpendicular to the plane (see Fig. 1b), with the horizontal reflection a\(_{1}\) in the plane. In this case the optimal interaction of molecules and is on the same side as the optimal A-B interaction. Thus the best packing is for layers C and A to be the same, leading to ABCABC (f.c.c.) packing (see Fig. 1c).

There are no definitive crystal structures published for CsB or CsB. Kratschmer et al. concluded that the structure for CsB is h.c.p., but their data did not really distinguish between h.c.p. and f.c.c. Stoddart quoted unpublished work by F. Diederich, indicating that the structure for CsB (indeed, Diederich personal communication) observes only cubic crystal habits for CsB and only hexagonal habits for CsB, as would be expected from considering the (diffusion data from the crystals are of sufficient quality for structural analysis). There are other, as yet unpublished, experiments that suggest a CsB structure for CsB (for example, refs 4, 6). The predicted differences in energy between h.c.p. and f.c.c. suggests that compression annealing might be used to obtain samples of fullerenes with higher crystallinity. The calculated densities for f.c.c. CsB = 1.74 g cm\(^{-3}\) and h.c.p. CsB = 1.67 g cm\(^{-3}\) at 300 K (from molecular dynamics) are in agreement with the observed density of 1.678 g cm\(^{-3}\) at room temperature.

To interpret and predict various properties for fullerene molecules and microcrystals, including vibrational spectroscopy\(^{25}\) and crystal structure analysis\(^{26}\), we developed a force-field\(^\dagger\) for sp\(^{2}\) carbon centers by fitting to experimental lattice constants and phonon frequencies for graphite. This force field uses Lennard-Jones 6-12 van der Waals interactions (Fig. 2b, c) for our simple graphite, with 12 nearest neighbours, and has the following parameters: a\(_0\) = 3.77Å, \(\sigma\) = 2.4Å, \(\varepsilon\) = 0.0662 MeV, \(k_B\) = 1.41 kcal mol\(^{-1}\), \(k_B\) = 720, \(k_B\) = 136 kcal mol\(^{-1}\), a core angle B (\(\alpha\) = 120, \(\varepsilon\) = 196.13 Å, \(k_B\) = 7.24, \(k_B\) = 68 kcal mol\(^{-1}\)) and a bond order (V = 21.28), where all distances and c\(_{1\varepsilon}\) and c\(_{2\varepsilon}\) are in Å, all angles in degrees, all energies in kcal mol\(^{-1}\), and all force constants in kcal mol\(^{-1}\) Å and radian units. For more details on the forms of these potentials see ref. 12. All calculations in this work were carried out using POLYGRAF (Polymer of Predictions for Graphite, Samovar, Caltech) or the program with additional vibrational analysis software written by N.K. Thomas and J.D. A.G. The calculations were carried out on Silicon Graphics 4D/380 and 4D/25 graphics workstations.

Using this force field and allowing four independent molecules per unit cell (permitting these molecules to reorientate with respect to each other), we calculated the optimal crystal structures for both simple types of closest packing, h.c.p. and f.c.c. We also considered bcc. packing (8 neighbours instead of 12), but this led to much higher energies. The force fields in these calculations used periodic boundary conditions with accuracy-bounded convergence. For Cs\(_6\), we used a length of 3 Å involving 4x4x4 = 64 unit cells. These calculations used periodic boundary conditions with accuracy-bounded convergence. For Cs\(_6\), we used a length of 3 Å involving 4x4x4 = 64 unit cells. For Cs\(_6\), we used a length of 3 Å involving 4x4x4 = 64 unit cells. We calculated the energy with respect to these 726 degrees of freedom to determine the most stable local potential. The optimisation structure for Cs\(_6\) is shown in Fig. 1a and Fig. 2c, where we have depicted the unit cell only. This structure is an orthorhombic distortion (space group Cmca) of Fm3m. Allowing rotations of the \(\varepsilon\) molecules per unit cell to be independent, we find that the optimisation structure has two equivalent pairs of molecules, as indicated in Figs 1a and 2c. We have found three other stable (and second and third derivatives positive) configurations at energies (per \(\varepsilon\)) of 0.31, 0.51 and 0.66 kcal mol\(^{-1}\) higher. The h.c.p. structure (also locally stable) is 0.90 kcal mol\(^{-1}\) higher in energy. From symmetry, one might expect f.c.c. Cs\(_6\) to orientate each molecule with the diagonal (threefold) axes parallel to the threefold axes of a cubic crystal (in this orientation, the twofold axes of Cs\(_6\) are along the cubic axes). Our calculations show, however, that this structure is not stable (leading to three negative eigenvalues of second-derivative matrix (hessian), corresponding to rotations of the Cs\(_6\)). We will refer to this as the 'ideal' f.c.c. structure. As shown in Table 1, the energy of the ideal f.c.c. structure is 4.9 kcal mol\(^{-1}\) higher than the experimental one. This is close to that for b.c.c. and five times as high as for h.c.p. The reason is that this packing does not allow contact between the hexagonal faces; instead, it leads to poor nearest-neighbour interactions.

In the optimal f.c.c. structure, each Cs\(_6\) leads to eight good interactions (with hexagonal rings in contact as in the optimal f.c.c.) and four contacts that are energetically worse by 1 kcal mol\(^{-1}\). The average energy and the good distance for the four contacts are 7.11 kcal mol\(^{-1}\) and 9.83 Å (compared with 7.20 and 9.84 Å for the optimal f.c.c. structure). The distances for these good interactions are 6.12 kcal mol\(^{-1}\) and 10.06 Å. On the other hand, the ideal f.c.c. structure leads to 12 interactions that are nearest the worst possible (6.01 kcal mol\(^{-1}\) and 10.06 Å). This difference of 8.11 kcal mol\(^{-1}\) accounts for 4.4 kcal mol\(^{-1}\) of the 5.1 kcal mol\(^{-1}\) difference in energy. Interestingly, for f.c.c. Cs\(_6\) we find a f.c.c. unit cell with exactly this ideal structure of the Cs\(_6\) unit cell; here the electronic and van der Waals interactions between Cs\(_6\) and Cs\(_6\) dominate.

The optimal f.c.c. structure leads to a distorted orthorhombic crystal structure at 9 K, and the other low-lying structures with f.c.c. packing (at 0.3-0.7 kcal mol\(^{-1}\) ) also distort at low temperature. Molecular-dynamics calculations carried out for short periods (20 ps) show that at low temperature (100-200 K), the Cs\(_6\) molecules librate locally around the equilibrium and do not rotate. But near room temperature (300-400 K), the Cs\(_6\) molecules tunnel from one favoured orientation to another. Such orientational fluctuations lead to an average structure that is cubic (lattice parameter \(a = 14.13\) Å at 300 K) with orientational disorder (but not free rotation) among the Cs\(_6\) molecules. (Note that this cubic structure is not the ideal f.c.c. structure.) This suggests that we expect a phase transition to occur between the distorted orthorhombic form (at low temperature) and the cubic, orientationally disordered form (at room temperature). The first-order transition observed at 249 K might correspond to this transition.

The transition temperature could in principle be lower if the lattice parameter decrease as better quality crystals are produced.
For C\textsubscript{70} the interactions in the crystal are much more anisotropic than for C\textsubscript{60}. The interactions within the plane have \( R_s = 9.92 - 10.06 \text{ Å} \) (10.00 average) and \( D_s = 8.23 - 8.79 \text{ kcal mol}^{-1} \) (8.47 average), whereas those out-of-plane have \( R_s = 10.83 - 10.96 \text{ Å} \) (10.91 average) and \( D_s = 6.75 - 7.18 \text{ kcal mol}^{-1} \) (6.90 average). This can be compared with the optimal dimer interactions of \( R_s = 9.94 \text{ Å} \) and \( D_s = 8.97 \text{ kcal mol}^{-1} \).

After submission of this manuscript, ref. 15 reported heats of sublimation of \( \Delta H_{300K} = 40.1 \pm 1.3 \text{ kcal mol}^{-1} \) for C\textsubscript{60} and \( \Delta H_{300K} = 43.0 \pm 2.2 \text{ kcal mol}^{-1} \) for C\textsubscript{70}. Our calculations lead to a cohesive energy of 43.9 kcal mol\(^{-1}\) for C\textsubscript{60} and 49.5 kcal mol\(^{-1}\) for C\textsubscript{70}. Correcting for zero-point energy and temperature dependence of the specific heat capacity \( C_v \), entropy \( S \) and \( H \) for both the crystal and free molecule, we calculate \( \Delta H_{300K} = 40.9 \text{ kcal mol}^{-1} \) for C\textsubscript{60} and \( \Delta H_{300K} = 46.4 \text{ kcal mol}^{-1} \) for C\textsubscript{70}, in excellent agreement with experiment.

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