Disorder in a Crystalline Form of Buckminsterfullerene: $C_{60}{\cdot}4C_6H_6$

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Refinement of the X-ray crystal structure of $C_{60}{\cdot}4C_6H_6$ shows that the position of the C_{60} molecules can be resolved into two orientations with relative populations of 55/45.

Solid-state phenomena involving crystalline C_{60} have attracted considerable interest.[1–9] Recent studies have reported on the X-ray crystal structures of C_{60} itself[3,4,6] and of two solvated forms; $C_{60}{\cdot}C_6H_6{\cdot}CH_2I_2$[10] and $C_{60}{\cdot}4C_6H_6$.[11] Here, we describe our independently obtained results on $C_{60}{\cdot}4C_6H_6$, which add to our appreciation of the complexity of this solvate.

Crystals of $C_{60}{\cdot}4C_6H_6$ were obtained by slow evaporation of a benzene solution of C_{60} that was layered over aqueous hydrogen chloride.† This peculiar procedure was developed during studies of the reactivity of organometallic C_{60} derivatives with hydrogen chloride. Nevertheless, in terms of cell dimensions, composition and gross structure, this corresponds to the material described previously.[11] The overall structure, which is shown in Fig. 1, has large channels that contain the benzene molecules. These lie between the columns of C_{60} molecules.

Significantly, we find that the C_{60} molecules are disordered between two sites. Our refinement proceeded after an initial solution was obtained by direct methods using 20 000 random phases. The solution with the best figure of merit was then refined by tangent expansion, and nearly all 60 carbon atoms of an entire C_{60} molecule along with carbons of four benzene molecules were located. One of these solvent molecules was disordered. At this stage, interatomic distances within the C_{60} portion were restrained to 1.389(5) and 1.446(5) Å. These bond distances were selected from values for the refinement of disordered C_{60}.[6] After refinement of this model, difference maps indicated fragments of another C_{60} molecule. Fig. 2 shows a particularly revealing view of this disorder. In Fig. 2, the framework for the major component is outlined in black while difference electron density is shown for the plane containing the uppermost pentagon. Difference peaks for a hexagon are clearly present. Through the use of difference data of this sort, we identified a second complete orientation of the C_{60} molecule. Upon location of the entire second molecule, distances in both orientations were fixed. The site occupancies were allowed to refine and converged to 0.55/0.45 for the two orientations of the molecule. Further refinements of the molecules as rigid groups led to final $R = 0.098$, $R_w =$

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† *Crystal data*: Dark-red blocks of $C_{60}{\cdot}4C_6H_6$ crystallized in the triclinic space group $P\bar{1}$ with $a = 9.938(2)$, $b = 15.031(3)$, $c = 17.425(4)$ Å, $\alpha = 65.38(2)$, $\beta = 88.31(2)$, $\gamma = 74.83(2)^\circ$ at 104 K with $Z = 2$ using Cu-Kα ($\lambda = 1.54178$ (Å) Ni-filtered radiation. Refinement of 2774 reflections with $F > 4.0\sigma(F)$ and 195 parameters yielded a final $R = 0.098$, $R_w = 0.089$ for the model described in the text. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

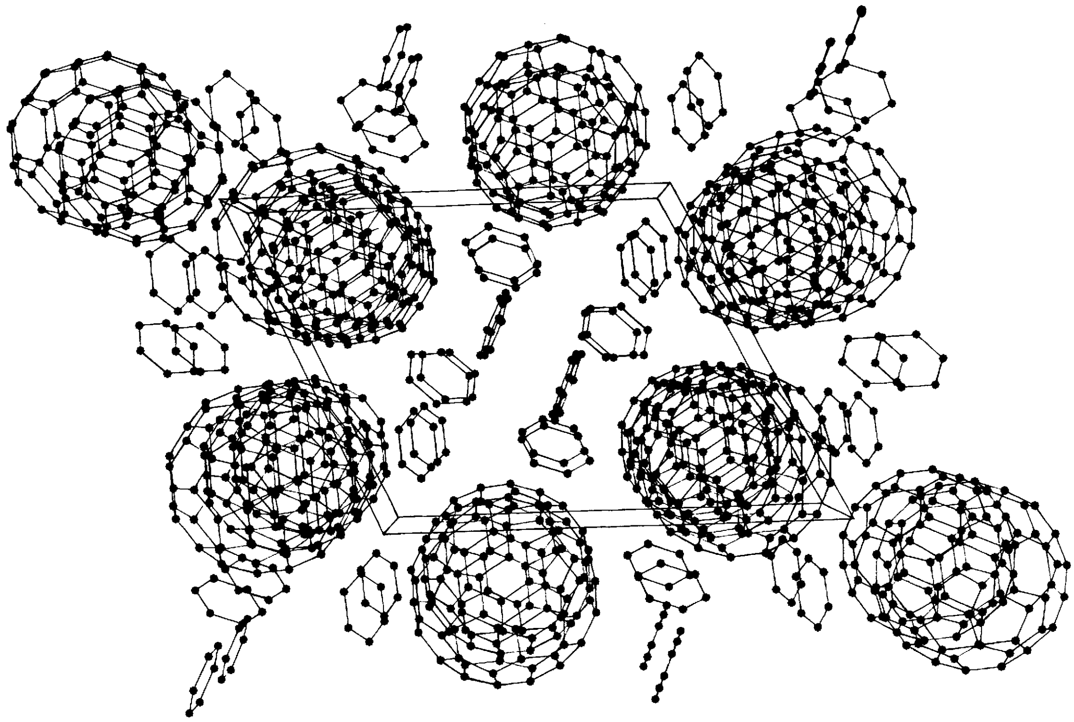

Fig. 1 A view of $C_{60}·4C_6H_6$ down the crystallographic *a* axis

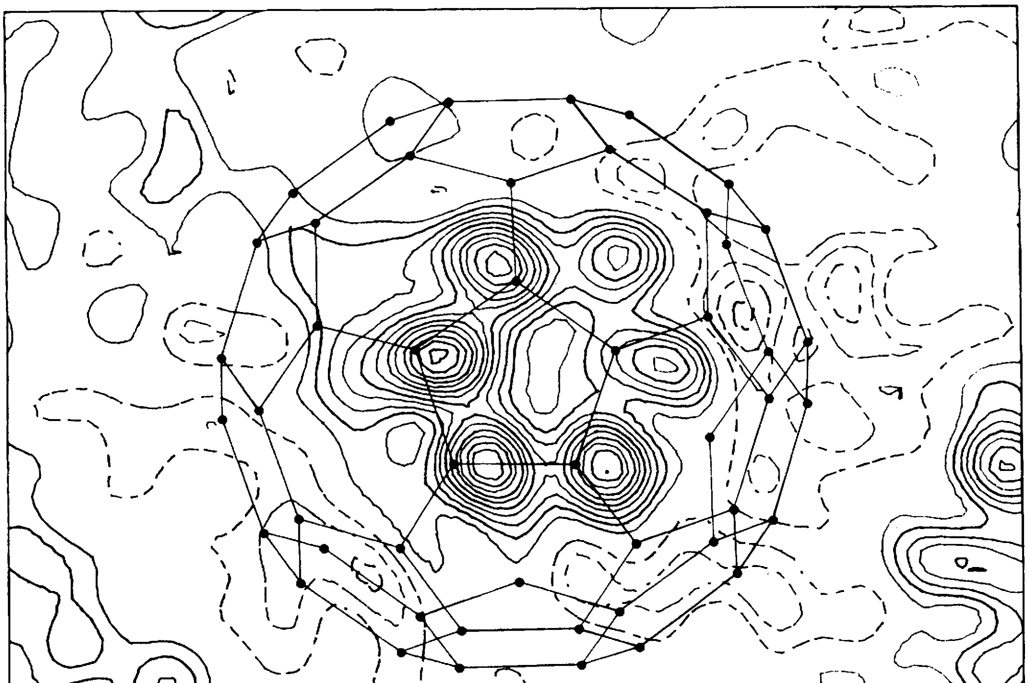

Fig. 2 A difference electron-density map superimposed upon a drawing of the upper hemisphere of the major form of the C_{60} molecule (shown as black lines). The difference map was calculated after refinement of a model consisting of an entire C_{60} molecule, but with the carbons of the C_{60} at 55% occupancy, three ordered and one disordered benzene molecule. The highest contour represents 2.7 e Å^{-3}.

0.089. Although similar disorder has been resolved in pure crystalline C_{60}, the two C_{60} molecules in $C_{60}·4C_6H_6$ are not related to one another in any simple way as they are in crystalline C_{60}.[6] The relative orientations of the C_{60} molecules in $C_{60}·4C_6H_6$ are shown in Fig. 3. The structure of the complete major form is presented as solid lines, while the upper hemisphere of the minor form is represented by open lines.

These data indicate a further level of complexity in the structure of $C_{60}·4C_6H_6$. The presence of two sites for the C_{60} molecules complicates the nature of the intermolecular interactions that may give rise to the degree of order seen in this solvate. Further analysis of all intermolecular interactions is in progress. It does appear, however, that the large thermal motion reported for some fullerene derivatives[10–12] may, upon further work, lead to resolution of these molecules into

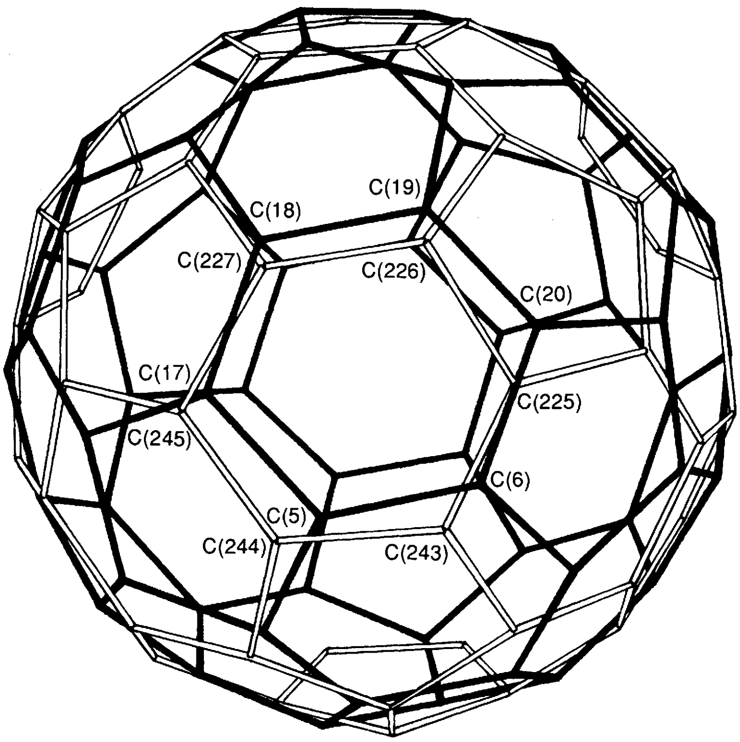

Fig. 3 A view of the C_{60} site showing the orientation of the minor (45% occupancy) form (represented as open lines) relative to the major (55% occupancy) form represented as solid lines. Only the upper half of the minor form is shown.

disordered forms as seen here and in ref. 6.‡ We anticipate that a large number of solvated, crystalline fullerenes await discovery and study.

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‡ *Note added in proof*: After reexamination of their data, the authors of refs. 10 and 11 have indeed resolved their structures to reveal this disorder.