Single Crystal X-Ray Structure of Benzene-solvated C_{60}

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The crystal structure of benzene-solvated C_{60} shows ordered molecules of C_{60} in an approximately hexagonal close-packed arrangement separated by benzene molecules.

The recent breakthrough in the bulk production and purification of C_{60}[1,2] has confirmed[1–3] the original proposal concerning the truncated icosohedral structure of this species.[4] However, since the molecule rotates very rapidly in the lattice (10^{10} s^{-1}),[5] bond length determination by X-ray methods has proved difficult. Nevertheless, successful single crystal analyses have been completed for C_{60} complexed with $[OsO_4]$,[6] $[IrCOCl(PPh_3)_2]$,[7] $[Pt(PPh_3)_2]$[8] and $[\{Pt(PEt_3)_2\}_6]$,[9] and for derivatives of C_{60} containing six and eight[10] as well as twenty-four[11] bromine atoms in which rotation is necessarily restricted. These techniques will prove more difficult for higher fullerenes, which possess lower symmetry and are thus capable of forming a wide range of compounds that may be troublesome to separate. Measurement of ^{13}C–^{13}C dipolar coupling using ^{13}C-enriched free C_{60} provided an estimate of bond lengths[12] and a neutron diffraction study of C_{60}[13] yielded accurate information, but the latter method has its drawbacks because of the large amount (1 g) of material required. More recently, C_{60} bond lengths have also been measured by gas-phase electron diffraction[14] and comparable data have

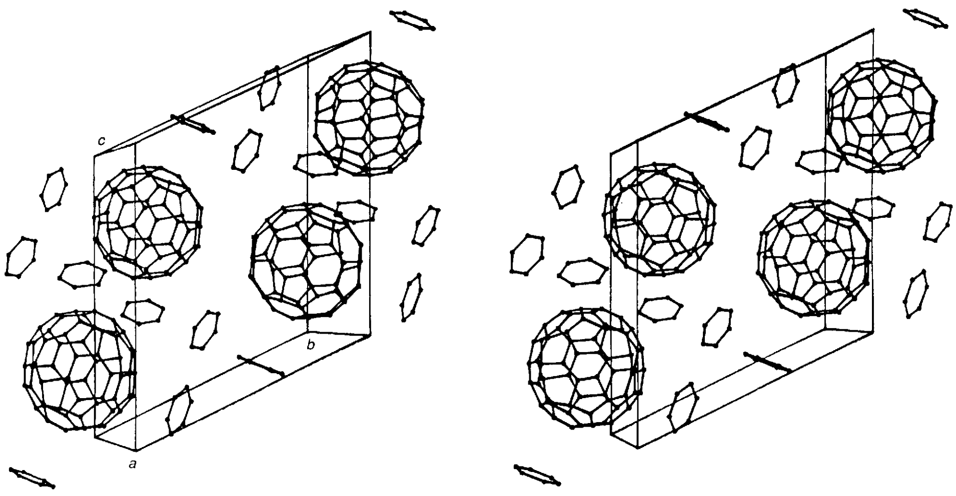

Fig. 1 Stereopair showing the crystal packing for $C_{60}{\cdot}4C_6H_6$

been obtained from an X-ray study of a twinned crystal.[15] The authors[15] drew attention to the unlikelihood of obtaining more reliable information unless twinning could be eliminated, perhaps by growing crystals below the phase transition (249 K) or by co-crystallising C_{60} with solvent. We have now succeeded in isolating and completing a single crystal diffraction study of a C_{60} benzene solvate.†

First attempts to obtain C_{60} crystals suitable for diffraction, by evaporation from a benzene solution, were unsuccessful and resulted in thin needles which, on close inspection, proved to consist of layers of thin overlapping plates reminiscent of earlier work.[1] Very slow evaporation (7–10 days) produced better crystals but the diffraction patterns were unsatisfactory. However, when a benzene solution (10 cm^{-3}) of C_{60} (11.4 mg) was heated to *ca.* 50 °C and then allowed to evaporate slowly, black crystalline prisms of $C_{60}{\cdot}4C_6H_6$ formed: IR (KBr) ν/cm^{-1} C_{60} 527s, 576m, 1183m and 1429m (*cf.* ref 16); C_6H_6 673w. The origin of the difference may arise from the presence of minute particles of C_{60}, invisible to the naked eye, which act as nuclei for crystallisation; when these are dissolved the crystallisation process is retarded. (The presence of particles in apparently homogenous solutions creates problems, for example, in kinetic studies of hydrogen exchange in ^3H-labelled aromatics of low solubility.[17])

The C_{60} molecule has no imposed crystallographic symmetry. It shows no orientational disorder, but the thermal vibration ellipsoids show large amplitudes parallel, and very small amplitudes perpendicular, to the surface of the molecule. Six of the atoms have non-positive definitive U_{ij} values, which reflect the fact that the *actual* electron density distribution exhibits a shape that is poorly represented by an ellipsoid. The molecule shows no distortion from a sphere with the distance of individual atoms from the centroid of the molecule averaging 3.50(3) Å. The average bond length for the inter-pentagon bonds = 1.32(9) Å; intra-pentagon bonds = 1.48(13) Å.

The whole can be visualised in terms of a hexagonal close-packed arrangement of C_{60} molecules with the hexagonal axis along *a* (Fig. 1). The C_{60} spheres within a close-packed layer are then moved well apart and the benzene molecules are inserted, and the close-packed layers moved towards each other along the *a* axis until adjacent molecules (along the *a* axis) touch. The benzene rings A, C and D lie parallel to the C_{60} molecular surface. The distances from the centre of the benzene rings to the centre of C_{60} are 6.77, 6.74 and 6.81 Å respectively. Subtracting the radius of C_{60} (3.50 Å) gives the corresponding distances between the benzene rings and the C_{60} surface: 3.27, 3.24 and 3.31 Å. In each case, the benzene ring lies over an inter-pentagon bond of the C_{60} molecule, with A over the centre of a bond [Fig. 2(*c*)], D over one end of the bond [Fig. 2(*b*)] and C half-way between the centre and the end of a bond [Fig. 2(*d*)]. The other benzene ring, B, is not associated in this way with a C_{60} molecule and appears to fill an interstice between the other molecules.

In addition to its contacts with its associated three benzene rings, a given C_{60} molecule also has contacts with other C_{60} molecules. The centre-to-centre distances are 9.96 Å for adjacent molecules along the *a* axis [Fig. 3(*a*)], 10.04 Å for molecules related by an inversion centre at 0, 0.5, 0.5 [Fig. 3(*b*)]; 10.01 for molecules related by an inversion centre at 0.5, 0, 0.5 [Fig. 3(*c*)] and 10.28 for molecules related by an inversion centre at 0.5, 0.5, 0.5 [Fig. 3(*d*)]. The contact between molecules along the *a* axis is between hexagonal faces on both molecules and the contact between molecules, related by the inversion centre at 0.5, 0, 0.5, is similar, but the other two contacts are less specific.

It is interesting to compare the results obtained here with the relative orientational preferences shown in pure C_{60} as

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† *Crystal data* for $C_{84}H_{24}$, M = 1033.1, triclinic, space group $P\bar{1}$ (No. 2), a = 9.961(3), b = 15.072(7), c = 17.502(5), Å, α = 65.26(3), β = 88.36(2), γ = 74.94(3)°, U = 2294.9 Å^3, Z = 2, D_c = 1.50 g cm^{-3}, $F(000)$ = 1056. Monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 0.8 cm^{-1}, T = 173 K. A prism crystal of cross-section *ca.* 0.4 × 0.4 mm was transferred directly from the mother liquor to an inert oil. A 0.4 mm section was cut from this prism and mounted on a glass fibre on an Enraf-Nonius CAD4 diffractometer fitted with a low-temperature attachment set at 173 K. Cell dimensions were calculated from the setting angles for 25 reflections with $11 < \theta < 12°$. Intensities were measured for 6373 unique reflections with $2 < \theta < 23°$ and corrected for Lorentz and plarisation effects. In the refinement, 3290 reflections were used with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$. No crystal decay occurred during the data collection.

The structure was solved using the SHELXS-86 direct method routines, revealing all atoms of the C_{60} molecule together with four molecules of benzene solvate (Fig. 1), and refined by full-matrix least-squares analysis using programs from the Enraf-Nonius MOLEN package. A difference map showed two possible orientations of the benzene molecule D [Fig. 2(*b*)] which refined to a 65 : 35 occupancy ratio. The carbon atoms of the C_{60} molecule were allowed anisotropic thermal parameters while the remaining carbon atoms (benzene) were left isotropic because of limited data. H atoms for the lower occupancy benzene site were omitted, while the rest were held fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. Refinement converged at R = 0.101, R_w = 0.123, s = 3.7, 661 variables, 3290 observed reflections, max. shift/esd = 0.5, final difference map +0.53, −0.13 e Å^{-3}.

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.

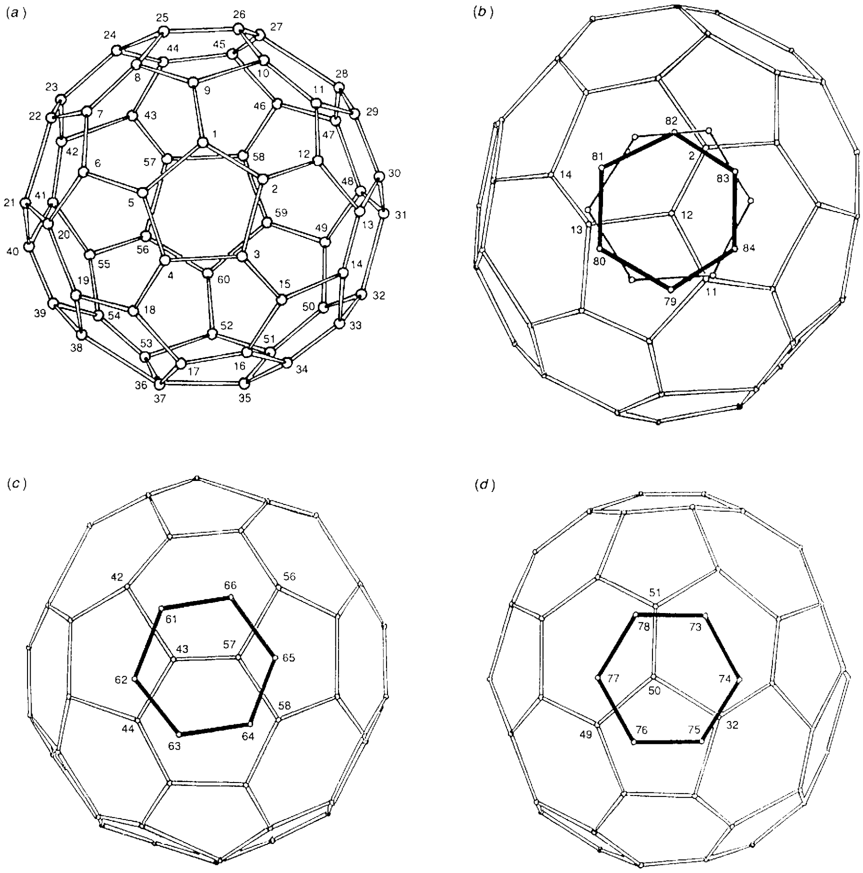

Fig. 2 Benzene ring positions relative to the C_{60} cage: (*a*) numbering system used for the cage; (*b*) location of ring D (thinner lines show alternative low occupancy site); (*c*) location of ring A; (*d*) location of ring B

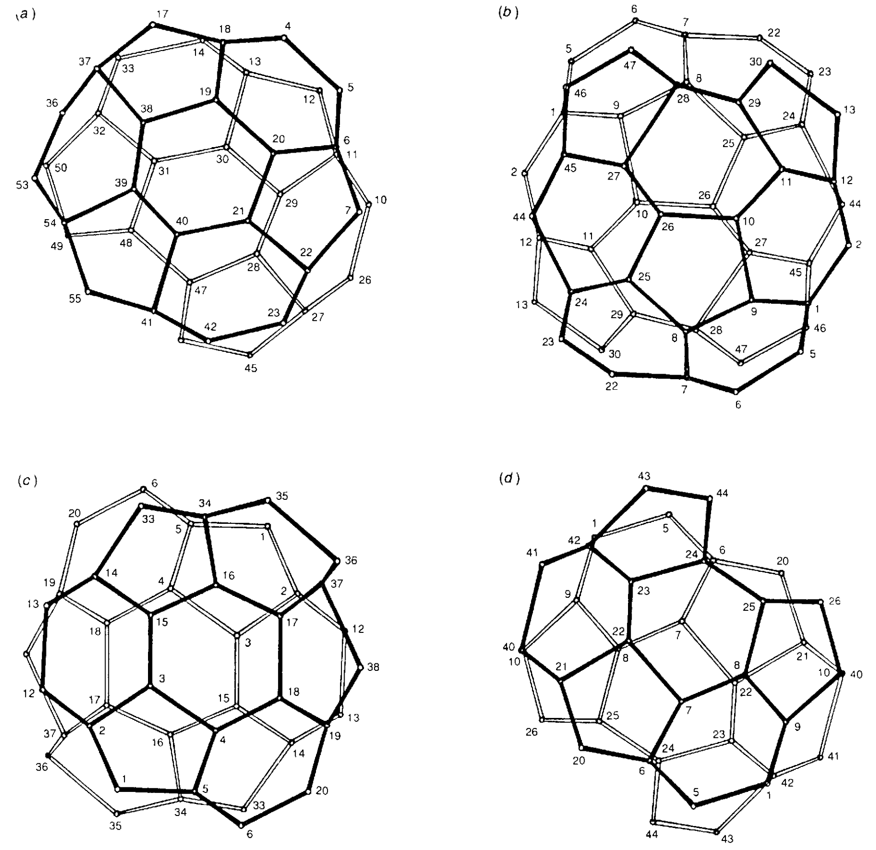

Fig. 3 Intercage relationships: (*a*) for adjacent molecules along the *a* axis; (*b*) at an inversion centre 0, 0.5, 0.5; (*c*) at an inversion centre 0.5, 0, 0.5; (*d*) at an inversion centre 0.5, 0.5, 0.5. For sake of clarity only those atoms close to the contact centre are shown.

observed by David *et al.*[13] using neutron diffraction. In the latter case it was found that the C_{60} molecule was jumping (or ratcheting) between configurations in which the electron-rich pentagon–pentagon bond [essentially a localised double bond (5=5)] preferentially lies more-or-less centrally over a pentagon (an electron deficient domain). Some 20% of the molecules adopt a second orientation in which the 5=5 bond lies more-or-less centrally over a hexagon. In the present study we find [Fig. 2(*b*)–(*d*)] that one benzene solvate molecule lies almost directly over the 5=5 bond similar to the low preference site in the pure material whereas two others adopt a somewhat shifted configuration [Fig. 2(*b*) and (*d*)].

In this exercise we have shown that it is indeed possible to obtain untwinned crystals of solvated fullerene-60 in which the molecules appear to be locked in position. This augurs well for structural analysis of high accuracy in future.

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Note added in proof: After submission of this communication, we were informed by Professor A. L. Balch of his results on this structure. We have reexamined our data using a constrained refinement, and confirm that the C_{60} molecule can be resolved into two orientations.

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