An X-Ray Crystallographic Analysis of a (BEDT-TTF)$_2$C$_{60}$ Charge-transfer Complex

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An X-ray crystallographic analysis of a (BEDT-TTF)$_2$C$_{60}$ CT complex reveals that C$_{60}$ molecules are sandwiched by BEDT-TTF and their librational motion is suppressed sufficiently at 150 K to show distinctive bond alternation.

Many physical properties of C$_{60}$ have been found[1] following the discovery of a large-scale preparation technique.[2] Recently, molecular ferromagnetism has been observed in the TDAE–C$_{60}$ charge-transfer (CT) complex [TDAE = tetrakis-(dimethylamino)ethylene].[3] Further preparation and characterization of CT complexes[4] will be of great significance for developing novel physical properties. Here, we report an X-ray crystallographic analysis of a C$_{60}$ complex with BEDT-TTF (ET) [bis(ethylenedithio)tetrathiafulvalene].

Single crystals (black needles) were obtained by slow evaporation of a carbon disulfide solution of C$_{60}$ and two equivalents of the ET. The crystals have a composition of (ET)$_2$C$_{60}$ without including CS$_2$. X-Ray crystallographic measurements on the single crystal were performed at 290 and 150 K; the X-ray crystal structure at 150 K is shown in Fig. 1.† The analysis reveals that a C$_{60}$ molecule is sandwiched

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† *Crystal data*: C$_{80}$H$_{16}$S$_{16}$, M = 1489.97, monoclinic, space group $C2/c$, a = 25.956(3), b = 21.889(3), c = 9.923(2) Å, β = 105.08(1)°, V = 5444(1) Å^3, Z = 4, D_c = 1.095 g cm^{-3}. Mo-Kα radiation (graphite monochromator, λ = 0.71069 Å), T = 150 K. Final conventional R factors: R = 5.8%, R_w = 6.2% for 3300 observed reflections [$F_o > 3\sigma(F)$] and 475 parameters.

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.

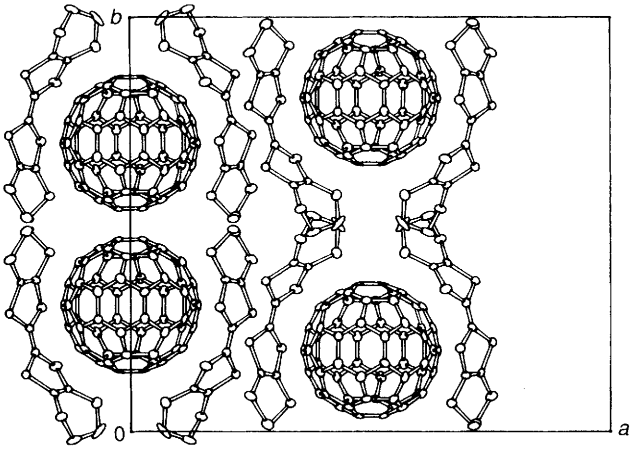

Fig. 1 Projection of $(ET)_2C_{60}$ crystal structure along the *c* axis. The 50% probability ellipsoids of thermal vibration are shown.

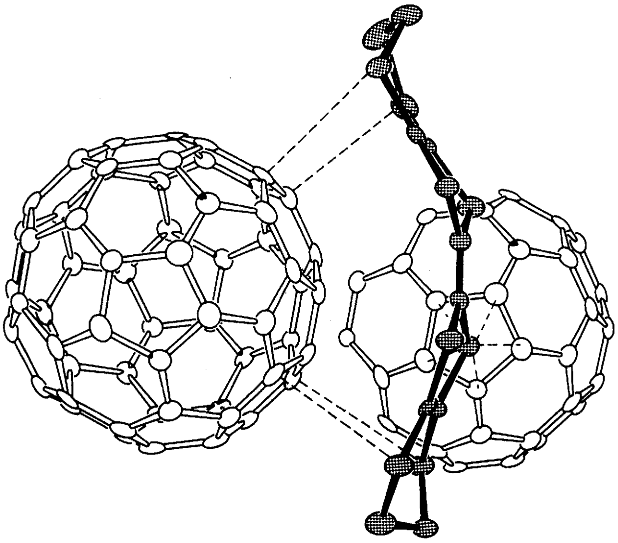

Fig. 2 Partial structure around an ET molecule: intermolecular $C(C_{60})\cdots S(ET)$ contacts are depicted by dotted lines

between a pair of largely concave ET molecules and that the rotational motion of C_{60} is quenched completely: all thermal parameters of carbon atoms could be analysed as isotropic at 150 K; while larger anisotropies of thermal parameters were observed at 290 K owing to librational motions around an axis along the direction of [1, 0, −1]. Solid-state ^{13}C NMR (CP-MAS) spectra of the complex, however, exhibit a sharp singlet at δ 143.8 due to C_{60} from room temp. to 190 K, suggesting that the C_{60} rotates isotropically even at 190 K.[5] The apparent inconsistency between X-ray and NMR experiments is also observed for the neat crystals of C_{60}. Its dynamic behaviour in the solid state, however, may be rationalized by assuming the existence of jumping rotational motions.[6]

The UV spectroscopic measurements of the complex (KBr pellet) show a distinct absorption (λ_{max} 750 nm) assignable to a CT band. While the ET molecule is planar in the CT complexes, it is more concave in this crystal than in the neutral state. The geometry of ET suggests that charge transfer occurs between an n-orbital on sulfur atoms of ET and a π*-orbital of C_{60}, by pyramidalizing sulfur atoms in the concave molecular structure. Besides intermolecular $C(C_{60})\cdots S(ET)$ contacts [3.540(7)–3.598(7) Å] between a pair of ETs and the incorporated C_{60}, there are even shorter contacts [3.446(6)–3.566(7) Å] between carbon atoms of the pentagonal ring and a sulfur atom of the neighbouring ET along the direction of the librational axis (Fig. 2). An attempt to crystallize a complex between C_{60} and TTF, which is a stronger donor than ET, resulted in crystallisation of each component separately in CS_2 solution. Therefore, efficient complexation by ET must be achieved not only because of the CT interaction but also because the flexible ET can surround the C_{60} molecule.

Bond lengths in C_{60} tend to alternate, although some of the altered bond lengths are indistinguishable within experimental error. The sixteen independent C–C bonds shared by two hexagonal rings are between 1.377(9)–1.402(9) Å; [average 1.389(7) Å]. The thirty independent C–C bonds shared by two pentagonal and hexagonal rings are between 1.436(9)–1.477(9) Å; [average 1.452(10) Å]. The average values are consistent with the results of a gas-phase electron diffraction experiment [1.398(10) and 1.455(6) Å][7] and of a recent X-ray analysis of C_{60} itself at 110 K [1.399(7) and 1.445(5) Å, respectively].[8] The contribution of the CT interaction to the bond lengths does not seem to be significant since the degree of charge transfer is estimated to be very small on the basis of the difference in the redox potentials (1.0 V) between ET and C_{60}.[9]

The C_{60} molecules interpenetrating between ET donors form a one-dimensional closest packing arrangement, with a regular triangle lattice framework along the *c* axis: the distances between centres of C_{60} molecules along the *c* axis and along the diagonal direction to the *c* axis are nearly the same [9.923(2) and 9.919(3) Å, respectively]. The closest intermolecular $C\cdots C$ distance between the C_{60}s is 3.296(10) Å, which is close to the van der Waals distance (3.35 Å) in graphite.

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