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Crystal Structure of Buckminsterfullerene (C_{60}) Incorporated by a U-Shaped Twin Donor

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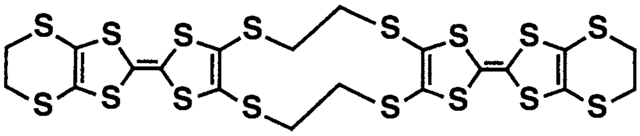
Buckminsterfullerene (C_{60}) was found to form single crystals of an inclusion complex with a double ethylene-bridged donor, a CT absorption band being observed in its UV spectrum. Crystal structure of the complex is characterized by two one-dimensional arrays of C_{60}'s with van der Waals contacts.

Charge transfer complexes are the basis of organic conductors. Recently we have synthesized novel twin donors in which two BEDT-TTF moieties are jointed by single or double bridges of alkyl group(s).[1)] Among them, a double ethylene-bridged donor (**1**) was found to form ClO_4 salts to exhibit metallic conductivity. A prominent structural feature of the twin donor **1** is that an inter-planar angle between two donor units varies by conformation of a thia-crown ring which combines donor units: two donor units are almost parallel, taking a U-shape conformation in neutral crystals, while the angle is ca. 90 degrees in the ClO_4 salts. The twin donor **1** may, therefore, have a possibility to include negative ions or acceptors in a flexible cavity created by donor planes.



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Buckminsterfullerene (C_{60})[2)] is a weak acceptor,[3)] and it forms superconducting complexes[4)] by doping with alkali metals or an organic molecular ferromagnetic complex with a strong donor, TDAE.[5)] Judging from a diameter (7.1 Å) of C_{60},[6)] twin donor seems to be an appropriate host for C_{60} and to have a chance to afford single crystals of an inclusion and/or charge transfer complex with C_{60}.

Slow evaporation of a carbon disulfide solution of donor **1** and an equimolar C_{60} gave single crystals (reddish black plates) with a composition of $\mathbf{1}\cdot C_{60}\cdot CS_2$. An X-ray crystallographic analysis[7)] at room temperature reveals that C_{60} is indeed included in the cavity. A volume of the cavity is larger than that in neutral crystals of **1** in order to fit the size of the guest molecule. Free rotational motions of C_{60} in the solid state is considerably suppressed in the complex, although large thermal ellipsoids are recognized in an equatorial region, suggesting that C_{60} librates and/or is disordered around an axis through the centers of two hexagonal faces (Fig. 1).[8)]

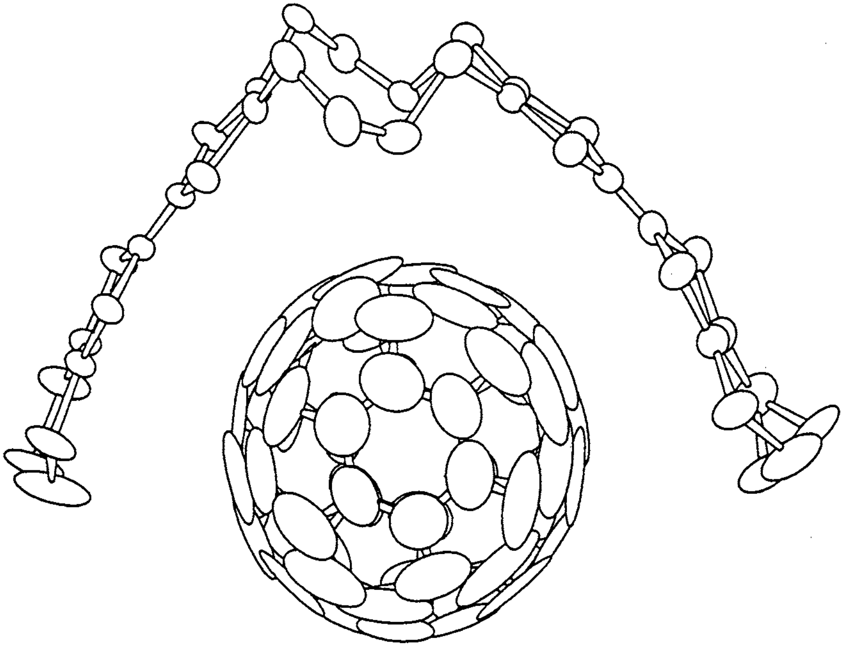

Fig. 1. ORTEP drawing of C_{60} surrounded by the twin donor **1** viewed along the three-fold axis of C_{60}.

The reason for quenching of rotational motions may be derived from charge transfer and/or van der Waals interaction between the twin donor and C_{60}. UV spectroscopic measurement of the complex in a KBr pellet shows a distinct absorption (λ_{max} = 750 nm) assignable to a CT band (Fig. 2). The degree of charge transfer, however, should not be so large, suggested by a convex units structure of the donor as usually observed in neutral species of the TTF family.

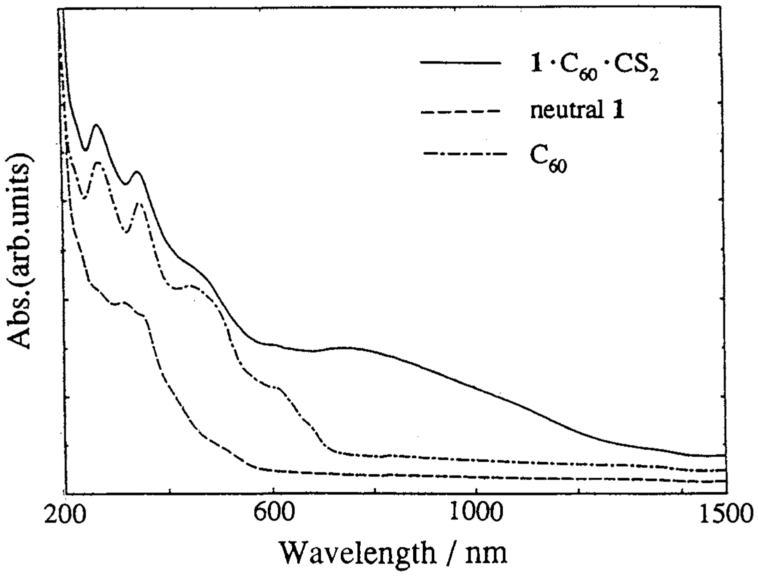

Fig. 2. UV spectra of **1**·C_{60}·CS_2 together with those of neutral **1** and C_{60}.

The crystal structure is characterized by two arrays of one-dimensional arrangement of C_{60} along the *c* axis showing the presence of van der Waals contacts each other: intermolecular distances between C_{60}'s along the chain and those between chains are 10.1 Å and 10.0 Å, respectively (Fig. 3). It is to be noticed that complexation with the twin donor arranges C_{60} in one-dimensional chains, otherwise the spherical molecule are likely to be packed in a three dimensional manner. Although the complex does not show an electrical conductivity, doping with alkali metals on this complex may exhibit intriguing physical properties.$^{9)}$

At any rate the X-ray structural result on C_{60} without chemical modifications was obtained by taking advantage of the newly developed twin donor **1** which is capable of including large spherical molecules. This method seems to be powerful in determining molecular structures of larger fullerenes$^{10)}$ or endohedral metal fullurenes (dopy balls)$^{11)}$ by an X-ray diffraction method.

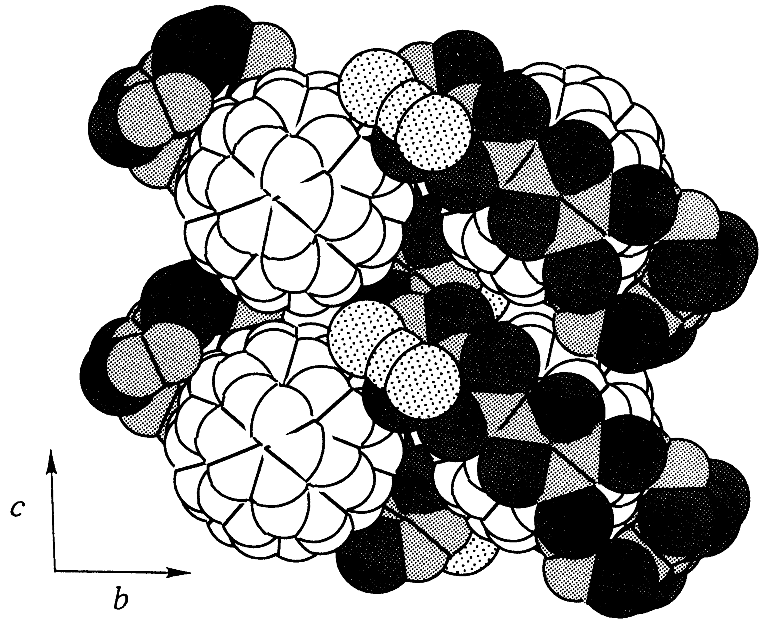

Fig. 3. Crystal packing of the complex viewed along the *a* axis. CS_2 molecules are shown by dotted balls.

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7) $[C_{20}S_{16}H_{16}\cdot C_{60}\cdot CS_2]$: *Triclinic, space group* $P\bar{1}$, a = 13.875(5), b = 23.081(9), c = 10.116(3) Å, α = 95.43(3)°, β = 106.76(2)°, γ = 74.85(3)°, V = 2994(2) Å^3, Z = 2, All atoms except hydrogen were located and all positions were refined. All located atoms anisotropic thermal parameters, R = 7.3%; 902 parameters, 7332 independent reflections. The bond distances and angles of C_{60} can not be determined precisely at the present stage because of the presence of librational motions and/or disorder. The X-ray diffraction experiment at low temperature is in progress under these laboratories.

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