First X-Ray Structural Determination of Fullerene [2+2] Cycloadduct

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X-Ray crystallographic analysis of a 1:1 adduct of C_{60} and 4,5-dimethoxybenzyne exhibited a benzocyclobutene structure given by [2+2] cycloaddition reaction at a 6,6-ring junction. A fullerene C(sp^3)-C(sp^3) bond length is 1.645(8) Å. Relatively short intermolecular C···C, C···O, and C···S distances were found, where sulfur atoms belong to CS_2 molecules enclosed.

Benzyne has a great tendency to react with polycyclic aromatic compounds by [2+4] cycloaddition, as typically seen in preparation of triptycenes.[1] However, cycloaddition reactions of C_{60} favorably occur at 1,2-positions (6,6-ring junctions).[2] Polymeric fullerene chains have been proposed to be obtained by [2+2] cycloaddition in solid films or alkali metal salts.[3] Our[4] and other groups[5] reported the reaction of benzyne with C_{60}, and very recently Kroto *et al.* reported that with C_{70}.[6] We report here the structure of an adduct of C_{60} with a benzyne determined by means of X-ray crystallographic analysis. The adduct was found to have a four-membered ring, and the structure seems to be rather strained.

The 1:1 cycloadduct (**1**) of 4,5-dimethoxybenzyne and C_{60} was obtained in 15% yield according to the method previously reported.[4] The ^{1}H and ^{13}C NMR measurements[7] suggest that **1** has the same structure as $C_{60}(C_6H_4)$ except for two additional methoxy groups. The crystals were obtained as black prisms by slow evaporation of the solvent from a CS_2 solution of **1**. The X-ray diffraction data of a single crystal (*ca.* 0.1x0.1x0.2 mm^3) were collected on a Rigaku AFC-7R diffractometer with a graphite-monochromated Cu $K\alpha$ radiation.[8]

The crystallographic analysis revealed that the crystal contained an equimolar amount of CS_2 to **1**. Figure 1 shows the molecular structure of **1** with partial atomic numbering. Several geometrical parameters are listed in Table 1. The dimethoxybenzene moiety stands straight upon the C_{60} skeleton at a 6,6-ring junction. A crystallographic mirror plane bisects the molecule of **1** perpendicularly to the benzene ring added. However, the C_s structure of **1** can be almost regarded to be C_{2v} when the conformation of the methyl groups is ignored. The benzocyclobutene moiety and the methoxy carbon and oxygen atoms are almost coplanar with a maximum atomic deviation of 0.019 Å from the least-squares plane.

The bond length of C(5)-C(5*) is 1.645(8) Å, which is the longest in the corresponding bonds in the organic cycloadducts ever reported; 1.57 - 1.61 Å in methanofullerenes,[9] 1.58 Å in a 1,3-dipolar adduct of a nitrile oxide,[10] and 1.59 - 1.62 Å in Diels-Alder adducts.[11] The unusually long C-C bond is noticeable, compared with typical values for benzocyclobutenes (1.58 - 1.60 Å).[12] The sp^2 angle around C(3) and sp^3 angle around C(5) are enforced respectively to be 94.9(2)° for C(3*)-C(3)-C(5) and 85.1(2)° for C(3)-C(5)-C(5*). The long C(5)-C(5*) bond seems to arise from these bending deformations which are accommodated at the cost of increased bond length. The bond lengths of C(5)-C(6) and C(5)-C(9) are 1.50 Å, being in good agreement with sp^2-sp^3 bonds. The short C(6)-C(10) and C(9)-C(19) bonds (1.36 Å) and long C(10)-C(10*) and C(19)-C(19*) bonds (1.48 Å) are ascribable to "double" and "single" bonds respectively, and the bond alternation remains in the fullerene moiety of **1**; 6,6- and 5,6-bond lengths in the sp^2-sp^2 framework are 1.38 and 1.45 Å respectively on the average.

Figure 2 shows the molecular arrangement of **1**·CS_2. The molecules of **1** were revealed to locate quasi-hexagonally in a layer parallel to the *ac* plane. The dimethoxybenzene moieties and the enclosed CS_2 molecules are arranged in clearance within a layer. The CS_2 molecules have slight contacts to fullerene carbons; the short intermolecular S···C distances (3.49 - 3.59 Å) near the sum of van der Waals radii (3.55 Å) were found among three surrounding molecules of **1**. The S···C

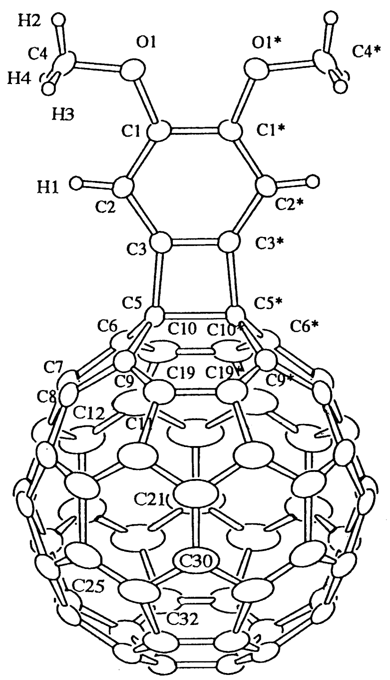

Figure 1. Molecular structure of **1** in the crystal of **1**·CS_2 with thermal ellipsoids at the 30% probability level.

Table 1. Selected bond lengths (Å) and angles (degree)

C(2)-C(3)	1.390(6)	C(1)-C(2)-C(3)	115.0(4)
C(3)-C(3*)	1.385(9)	C(2)-C(3)-C(3*)	123.2(3)
C(3)-C(5)	1.533(5)	C(3*)-C(3)-C(5)	94.9(2)
C(5)-C(5*)	1.645(8)	C(3)-C(5)-C(5*)	85.1(2)
C(5)-C(9)	1.502(6)	C(5*)-C(5)-C(9)	114.2(2)
C(9)-C(19)	1.357(6)	C(6)-C(5)-C(9)	102.2(4)
C(19)-C(19*)	1.477(10)	C(5)-C(9)-C(19)	124.0(4)

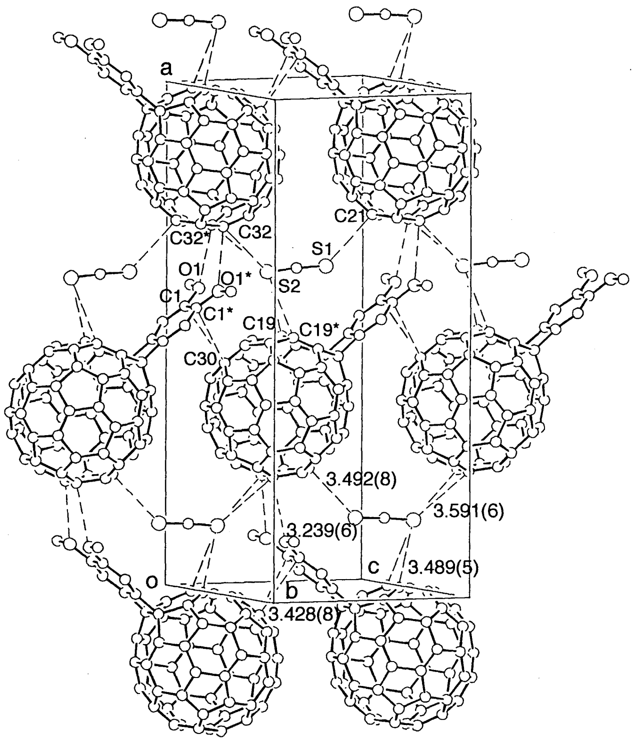

Figure 2. Molecular arrangement of **1** · CS_2 in a layer parallel to the *ac* plane. Selected intermolecular atomic distances are shown (in Å) with broken lines. Hydrogen atoms are omitted.

interaction seems to be responsible for high solubility of C_{60} in CS_2. Relatively short intermolecular O···C distance (3.24 Å) is found along the *a* axis in a zigzag manner. Similar interactions have been found in Diels-Alder adducts[11c] and a complex of C_{60} with macrocyclic cyclotriveratrylene[13] in which the C···O distances were reported to be 3.06 - 3.34 Å. The electron-rich benzene locates to face with the fullerene skeleton of **1** related by a translation along the *c* axis. The shortest C···C distance between the benzene and fullerene skeleton is 3.43 Å which is close to the sum of van der Waals radii. These C···O and C···C distances may be interpreted in terms of weak intermolecular donor-acceptor interaction.

The methyl groups do not contact in a layer, but locate near neighboring fullerene skeletons belonging to a *b*/2 upper or lower layer. The shortest distances between the methyl groups and fullerene carbons are 3.38 Å for C(4)···C(7) and 2.88 Å for H(2)···C(7).[14a] The shortest C···C distance between the neighboring fullerene skeletons of **1** is 3.26 Å for C(12)···C(25).[14b] This distance is shorter than the inter-layer distance of graphite (3.35 Å).

In conclusion, the addition of benzyne to C_{60} was clarified unequivocally to lead a [2+2] cycloadduct which is consistent with the structure proposed by the chemical shifts and molecular symmetry found in ^{13}C NMR measurements.[5,7] The present work provides an example showing a contrast between the reactivities of C_{60} and polycyclic aromatic compounds.

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7 ^1H NMR (1:3 acetone-d_6/CS_2, 500 MHz) δ 4.07 (s, 6H), 7.61 (s, 2H). ^{13}C NMR (125 MHz) δ 56.42 (2C, methyl), 77.91 (2C, fullerene sp^3), 107.87 (2C, methine), 139.17 (4C), 140.50 (4C), 140.88 (2C), 142.30 (4C), 142.41 (4C), 142.92 (4C), 143.01 (2C), 143.03 (4C), 144.67 (4C), 145.35 (2C), 145.43 (8C), 146.11 (4C), 146.14 (4C), 146.52 (4C), 146.86 (2C), 152.74 (2C), 155.78 (4C). The carbon abundances were determined by the relative signal integrals.

8 Crystal data for **1**·CS_2: $C_{69}H_8O_2S_2$, *M* 932.94, orthorhombic, *P*nma, $a = 24.795(2)$, $b = 14.076(2)$, $c = 10.298(1)$ Å, $V = 3594.1(6)$ Å^3, $Z = 4$, $D_{calc} = 1.724$ g cm^{-3}, μ(Cu $K\alpha$) = 18.65 cm^{-1}, $R = 0.058$, $R_w = 0.046$, 3053 unique reflections, 2070 reflections ($I > 3\sigma(I)$) for the structure solution (direct methods) and refinement (full-matrix least-squares).

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14 a) Generated by symmetry operations: 1-*x*, -*y*, -*z*; b) 1/2-*x*, -*y*, 1/2+*z*.