# Notes

## Single-Crystal X-ray Structure of $C_{60}\cdot 6SbPh_3$. A Well-Ordered Structure of $C_{60}$ and a New Fullerene Solvent

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### Introduction

Benzene, toluene, and other aromatic solvents are recognized for their superior ability to dissolve $C_{60}$ and the higher fullerenes.[1] Crystallization of fullerene derivatives from these solvents has generally been the favored method of producing crystalline samples for X-ray crystal structure determination; however, the crystallization of unsubstituted $C_{60}$ from these solvents has not, to date, yielded ordered structures. We wish to report that dissolution of $C_{60}$ in liquid triphenylantimony (mp 52−55 °C) followed by slow cooling at room temperature produces a decolorized solution and well-formed dark red rhombohedrons which can be separated from colorless crystals of $SbPh_3$. Determination of the structure by single crystal X-ray diffraction of the dark red material revealed an ordered structure of formula $C_{60}\cdot 6SbPh_3$.

Crystals of pure $C_{60}$ are known to be plagued by twinning and by orientational disorder.[2] As a result, the determination of accurate geometrical features has been problematic to date. This is also the case for $C_{60}$ crystals containing benzene,[3] pentane,[4] hexane,[5] cyclohexane,[6] and benzene/$CH_2I_2$.[7] Co-crystallization of fullerenes with sulfur to give $C_{60}\cdot CS_2\cdot C_{20}H_{16}S_{16}$,[8] $C_{60}S_8CS_2$,[9] $C_{60}S_{16}$,[10] $C_{60}S_{16}\cdot 0.5C_6H_5Cl$,[11] and $C_{70}\cdot 6(S_8)$[12] has yielded ordered crystals of $C_{70}$, but not of $C_{60}$. Molecules such as ferrocene[13] and 1,4-hydroquinone[14] have demonstrated that the ability to form weak intermolecular interactions can produce more ordered phases.

**Table 1.** Crystal Data

| | | | |
|---|---|---|---|
| formula | $C_{168}H_{90}Sb_6$ | $\mu$(Mo Kα), mm$^{-1}$ | 1.446 |
| fw | 2839.06 | transm coeff | 0.67−0.76 |
| *a*, Å | 29.833(5) | $\varrho_{calc}$, g cm$^{-3}$ | 1.635 |
| *c*, Å | 11.224(3) | *T*, K | 130(2) |
| *V*, Å | 8651(3) | R1[a] | 0.0624 |
| space group | $R\bar{3}$ | wR2[a] | 0.0840 |
| Z | 3 | | |

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 28.2336P]$ where $P = (F_o^2 + 2F_c^2)/3$.

The ability of phenyl rings to lock $C_{60}$ into place is attractively demonstrated in the structure of $(\eta^2\text{-}C_{60})Ir(CO)Cl(C_6H_5CH_2OC_6H_4CH_2P(C_6H_5)_2$, which places $C_{60}$ balls into phenyl "cups".[15] Similar interactions between fullerenes and aromatic molecules are a striking feature of nearly every crystal structure with these consituents. Therefore, it was our hope that the trigonal pyramidal organometallic compound triphenylstibine would be a good solvent for the $C_{60}$ molecule. Since attachment at antimony is not expected to take place, van der Waals forces between the electrons delocalized on the phenyl rings should predominate over the interaction of the lone pair of electrons on antimony with $C_{60}$.

### Experimental Section

**Crystallization.** Well-formed, dark red rhombohedrons of $C_{60}\cdot 6SbPh_3$ were obtained by slow crystallization of $C_{60}$ from triphenylstibine at room temperature without addition of any other solvent. This is accomplished by heating $SbPh_3$ above its melting point (52−55 °C) in laboratory glassware that has been boiled in 1:1 $HNO_3/H_2O$, washed with redistilled water several times, and dried and adding to it solid $C_{60}$ (2.4 mg of $C_{60}$ /3 g of $SbPh_3$). Left undisturbed, $SbPh_3$ does not crystallize for several days at room temperature. If solidification occurs, the solution can usually be remelted and left to cool. Finally, dark red single crystals of $C_{60}\cdot 6SbPh_3$ can be separated from colorless crystals of $SbPh_3$. The solubility of $C_{60}$ in triphenylstibine is quite high (2.3 mg/mL), approaching that of aromatic solvents such as toluene.

**X-ray Crystallography.** Crystal data are summarized in Table 1. A rhombohedron of dimensions 0.22 × 0.24 × 0.24 mm$^3$ was selected and mounted in the cold stream of a Siemens R3m/V diffractometer equipped with a locally-modified Enraf-Nonius universal low-temperature apparatus. Data were collected using Mo Kα radiation ($\lambda$ = 0.710 73 Å) to a maximum $2\theta$ of 55°. A total of 4771 reflections were collected, of which 4412 were unique ($R_{int}$ = 0.031). Only random fluctuations of less than 0.8% in the intensities of two check reflections were observed during the course of data collection. The structure

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**Table 2.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $C_{60}$·$SbPh_3$

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Sb | 4497.70(11) | 3577.63(11) | 760.0(3) | 27.41(9) |
| C(1) | 5723(2) | 3697(2) | 3857(4) | 30.7(10) |
| C(2) | 5439(2) | 3242(2) | 3119(4) | 30.9(10) |
| C(3) | 5308(2) | 2758(2) | 3548(4) | 31.2(10) |
| C(4) | 5447(2) | 2702(2) | 4765(4) | 31.9(10) |
| C(5) | 5715(2) | 3139(2) | 5476(4) | 30.9(10) |
| C(6) | 5853(2) | 3644(2) | 5010(4) | 33.0(10) |
| C(7) | 6362(2) | 4009(2) | 5469(4) | 30.5(10) |
| C(8) | 6538(2) | 3727(2) | 6218(4) | 30.5(10) |
| C(9) | 6136(2) | 3188(2) | 6224(4) | 31.5(10) |
| C(10) | 5586(2) | 2299(2) | 4760(4) | 31.1(10) |
| C(11) | 4944(2) | 4163(2) | 2062(3) | 26.0(9) |
| C(12) | 4784(2) | 4070(2) | 3254(4) | 33.8(10) |
| C(13) | 5055(2) | 4438(2) | 4123(4) | 39.6(10) |
| C(14) | 5492(2) | 4893(2) | 3827(4) | 36.2(11) |
| C(15) | 5658(2) | 4992(2) | 2662(4) | 34.2(10) |
| C(16) | 5382(2) | 4626(2) | 1782(4) | 28.9(9) |
| C(17) | 3976(2) | 3854(2) | 350(4) | 28.0(9) |
| C(18) | 3554(2) | 3558(2) | −386(4) | 38.7(11) |
| C(19) | 3220(2) | 3732(2) | −705(5) | 47.9(13) |
| C(20) | 3295(2) | 4198(2) | −286(4) | 40.8(12) |
| C(21) | 3708(2) | 4497(2) | 452(4) | 35.9(10) |
| C(22) | 4046(2) | 4323(2) | 764(4) | 30.5(9) |
| C(23) | 5003(2) | 3949(2) | −729(3) | 25.5(9) |
| C(24) | 4964(2) | 4309(2) | −1438(4) | 28.1(9) |
| C(25) | 5293(2) | 4529(2) | −2418(4) | 30.5(9) |
| C(26) | 5656(2) | 4390(2) | −2684(4) | 32.6(10) |
| C(27) | 5697(2) | 4033(2) | −1973(4) | 35.9(10) |
| C(28) | 5374(2) | 3816(2) | 1009(4) | 30.9(9) |

[a] U(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

was solved in the space group $R\bar{3}$ (No. 148) by direct methods and refined using SHELXL-93[16] software. An absorption correction (XABS2[17] ) was applied. All non-hydrogen atoms were refined with anisotropic thermal ellipsoids. Full-matrix, least-squares refinement (based on $F^2$) of 262 parameters using all reflections converged to final R1 = 0.062, wR2 = 0.082 (agreement factors based on 3382 reflections for which $F_o > 4\sigma(F_o)$ are 0.044 and 0.074, respectively). The final difference map contained minimum and maximum peaks of −0.430 e and 0.470 e $Å^{-3}$, respectively. Positional parameters are reported in Table 2.

## Results and Discussion

**Structure of $C_{60}$·$6SbPh_3$.** The $C_{60}$ molecule has $\bar{3}$ point symmetry. The asymmetric unit contains 10 carbons of the $C_{60}$ and a complete molecule of $SbPh_3$. The uniformity of the thermal ellipsoids for the structure (Figure 1) is in contrast to the flattened or elongated ellipoids seen in disordered structures of $C_{60}$. Average values and average deviations for the two types of C−C bonds are 1.383(4) and 1.453(5) Å. The lack of any perturbation to the $C_{60}$ sphere yields a remarkably consistent set of radii from the center of inversion to each carbon position. The average radius (average deviation in parentheses) is 3.537(3) Å.

Molecules of $C_{60}$ are stacked along the 3-fold axis parallel to *c* with a center-to-center distance equal to the length of the *c* axis, namely 11.224(3) Å. By crystallographic symmetry, the contact surfaces between $C_{60}$'s are eclipsed six-membered rings. The unique C···C distance is 4.742(6) Å, much longer than the shortest van der Waals diameter of 3.13 Å for pure $C_{60}$.[1e] Alternatively, the sphere-to-sphere separation can be calculated by subtracting the $C_{60}$ diameter of 7.074 Å from the center-to-center distance of 11.224 Å. This yields a value of 4.150 Å. The unprecedented long contact between $C_{60}$'s may be due to $\pi-\pi$ repulsion of the eclipsed hexagons; alternatively, it may arise from the presence of partially intervening atoms of the $SbPh_3$ groups.

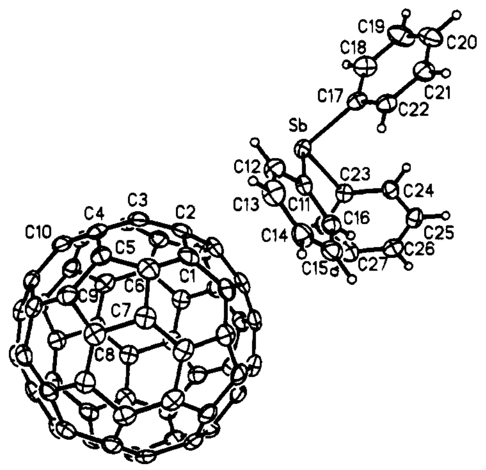

**Figure 1.** Thermal ellipsoids (50% probability level) and atom-numbering scheme.

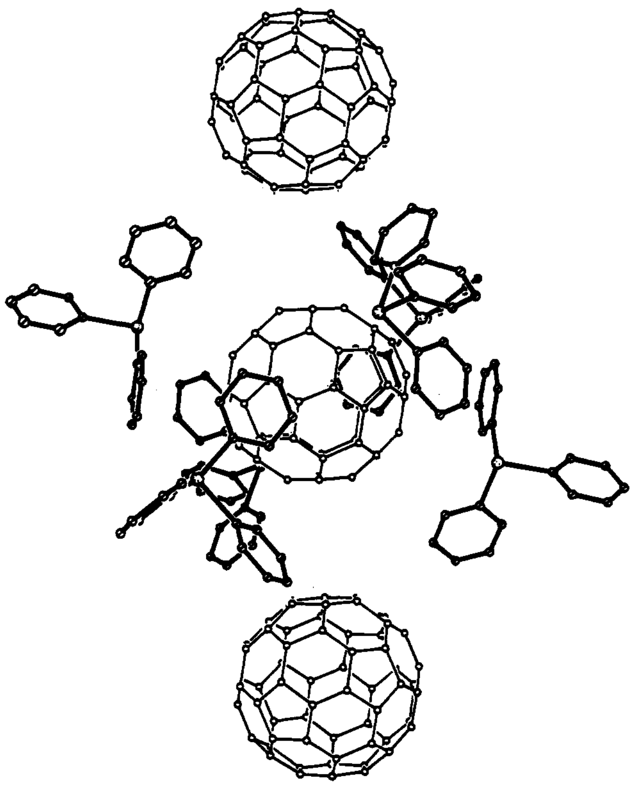

**Figure 2.** View perpendicular to *c* (*c* is in the plane of the paper pointing up) of the immediate surroundings of a $C_{60}$ molecule.

Figure 2 depicts how six molecules of $SbPh_3$ form the remaining set of close contacts to an individual $C_{60}$. Three of these are shared by the $C_{60}$ above and the other three are shared by the $C_{60}$ below, in keeping with the stoichiometry $C_{60}$·$6SbPh_3$. There are two predominant types. The first (Figure 3) appears to position the phenyl face over a 6:5 ring junction of $C_{60}$. This represents an electrostatic interaction between a region of partial negative charge in the center of a benzene or phenyl group and a region of partial positive charge on the $C_{60}$ surface. There

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(16) SHELXL-93: Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.

(17) Program XABS2 calculates 24 coefficients from a least-squares fit of $1/A$ vs $\sin^2(\theta)$ to a cubic equation in $\sin^2(\theta)$ by minimization of $F_o^2$ and $F_c^2$ differences: S. Parkin, Department of Chemistry, University of California, Davis, 1993.

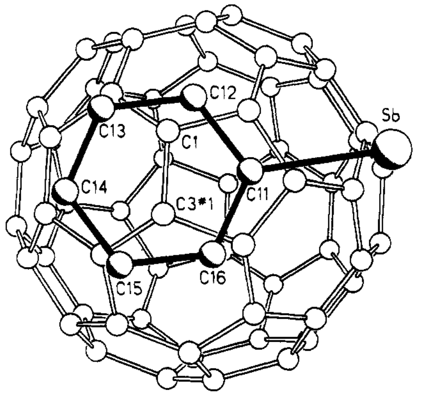

**Figure 3.** View down the plane of a phenyl ring facing the $C_{60}$ molecule.

are six equivalent contacts of this type per $C_{60}$; the distance between the center of the 6:5 bond (C1−C3#1) and the centroid of the face is 3.441(6) Å. There is a comparable distance between the center of the 6:5 bond and the center of a phenyl bond (C11−C16) of 3.451(6) Å. A second type of weak attraction (Figure 4) places a hydrogen atom close to the centroid (X) of a hexagonal $C_{60}$ ring. In this structure there are six per $C_{60}$ with X−H distances (C-H of 0.95 Å assumed) of 2.80 Å and X···H−C angles of 139°. The shortest contact between a $C_{60}$ carbon and Sb is 3.933 Å, greater than the sum of the van der Waals radii (1.91 Å for Sb, ca. 1.57 Å for C of $C_{60}$). The angle of approach of the $SbPh_3$ yields C($C_{60}$)···Sb−C(phenyl) angles of 166.6, 84.1, and 70.7° instead of the usual tetrahedral angles when $SbPh_3$ acts as a donor in transition metal complexes.

Molecular packing of the $SbPh_3$ portion mimics part, but not all, of that seen in the crystal structure of pure $SbPh_3$.[18] A motif that places inversion-related pairs of $SbPh_3$ with all six phenyls in close proximity is common to both structures. In the present case, this yields three sets of H-to-phenyl face interactions with 3.06, 3.28, and 3.07 Å H···X contacts and X···H−C angles of 142, 133, and 137°, respectively.

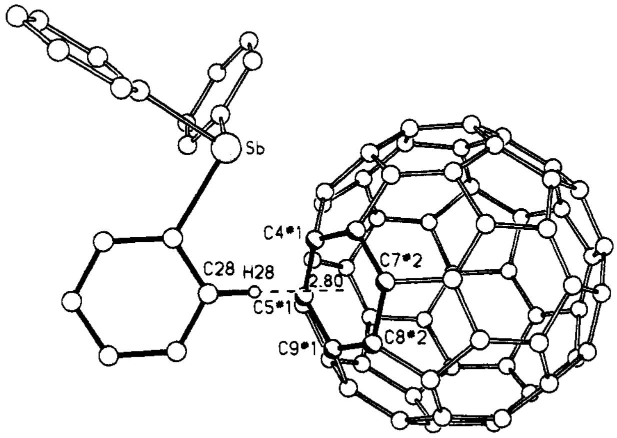

**Figure 4.** View of the edge-to-face interaction between a phenyl ring and the $C_{60}$ molecule.

In comparison to other, rotationally disordered, structures of uncomplexed $C_{60}$, this structures exhibits the lowest number (2) of $C_{60}$−$C_{60}$ neighbors and a correspondingly high number of intermolecular phenyl contacts (12). We believe that this solid state solvation gives rise to the orientational order of the $C_{60}$ molecule. Such an effect was predicted[2d] but not fully realized until now.

We are continuing to explore the utility of this crystallization method. Low-melting, low-symmetry phenylated materials show promise as solvents for the fullerenes, both for their potential in broadening the range of reactants for fullerene chemistry and as cocrystallizing agents that help prevent rotational disorder.

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**Supplementary Material Available:** Tables giving additional details of the crystal structure determination, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and a stereoview of the packing (8 pages).

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