Supramolecular Arrangement of C_{60} and Phenol into a Square Packing Arrangement of π-π Interacting and Hydrogen-Bonded Rods in $C_{60}\cdot 5C_6H_5OH$

Martin Schulz-Dobrick,[a] Martin Panthöfer,[a] and Martin Jansen*[a]

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The supramolecular adduct $C_{60}\cdot 5C_6H_5OH$ was obtained as single crystals by the slow hydrolysis of a solution of C_{60} in triphenylphosphite. The crystal structure was determined with atomic resolution by single-crystal X-ray diffraction [triclinic, space group $P\bar{1}$, a = 1003.52(14) pm, b = 1011.71(14) pm, c = 1264.17(17) pm, α = 88.566(2) °, β = 84.026(2) °, γ = 83.485(2) °, V = 1.2681(3) nm^3, Z = 1]. The overall structure can be described as a distorted square packing pattern of hydrogen-bonded and π-π interacting rods, $^1_\infty[C_{60}(C_6H_5OH)_4]$. The fullerene molecules are fully ordered and the C–C bond lengths exhibit remarkably small variations within the 6:6 and 6:5 subsets. The results are discussed in the context of an analysis of reliable crystal structure data for several different fullerene co-crystal compounds.

Introduction

Fullerenes are promising candidates for the generation of novel materials due to their electron acceptor capabilities, and the interesting electronic and magnetic properties of chemically reduced fullerene species, e.g. A_3C_{60} (A = alkaline metal[1]), $[Cr(C_7H_8)_2]C_{60}$,[2] TDAE-C_{60},[3] and the ability of fullerenes to form adducts with π-donors. A variety of supramolecular π-donor-fullerene arrangements have been crystallographically characterized, including donors like porphyrins[4,5], calixarenes,[6] tetrachalcogenefulvalenes[7] and various aromatic donors.[8,9] In order to provide a sufficiently strong interaction, the donor molecules should be able to complement the spherical shape of the fullerene species. This may be realized by large molecules exhibiting an intrinsic concave or even bowl-like shape, as well as by the supramolecular organization of small donor molecules into a network that gives rise to spherical voids of the appropriate size. The latter case was observed in the crystal structure of $C_{60}\cdot 3HOC_6H_4OH$,[10] where the hydroquinone molecules form a hydrogen-bonded network in which the fullerenes are encapsulated by bowl-shaped moieties. The primary motivation behind these efforts has been to study the electronic and structural response of the fullerenes to the supramolecular interactions. However, in many cases crystal structure analysis has been hampered by severe orientational and librational disorder of the fullerene sub-structure.

In this work, we present the synthesis and structural characterization of a supramolecular adduct of C_{60} and phenol, where the hydrogen-bonded arrangement of the phenol molecules is strong, yet at the same time flexible enough to give rise to strong π-π interactions and a full ordering of the C_{60} molecules, thus enabling an extraordinary accurate determination of the molecular structure of the fullerene moieties (Figure 1).

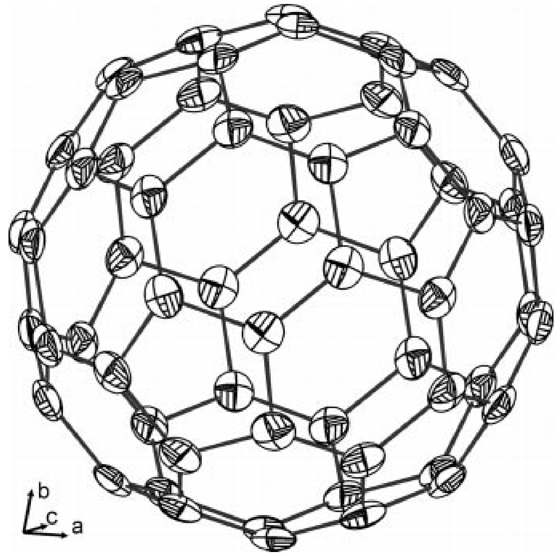

Figure 1. Molecular structure of the fullerene C_{60} moiety (probability density function corresponds to the 50% probability level).

Results and Discussion

The supramolecular adduct $C_{60}\cdot 5C_6H_5OH$ was obtained as red, plate-shaped crystals by the slow hydrolysis (with

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[a] Max Planck Institute for Solid State Research,
Heisenbergstraße 1, 70569 Stuttgart, Germany
Fax: +49-711-689-1502
E-mail: M.Jansen@fkf.mpg.de

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water vapor) of a solution of C_{60} in triphenylphosphite and the in-situ generation of phenol, which acts as a co-crystallization agent as well as a precipitation agent. This method (in-situ formation of the precipitation agent) has not been employed in the synthesis of fullerene co-crystals before. The majority of fullerene co-crystals, as reported in the literature, were obtained from solutions containing both the fullerene and the co-crystallization agent, either by the slow evaporation of the solvent or by vapor diffusion methods. It is particularly advantageous for precipitation to occur from a homogeneous solution by the slow chemical evolution of the co-crystallization agent, as in case of $C_{60}{\cdot}5C_6H_5OH$, as this allows crystal growth to proceed under low and almost constant super-saturation conditions, leading to well grown crystals of an appropriate size.

$C_{60}{\cdot}5C_6H_5OH$ crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. The fullerene C_{60} molecule is located on a centre of symmetry (Wyckoff position 1*f,* ½ 0 ½). Despite the low crystallographic symmetry, the symmetry of the molecular structure of the C_{60} molecule is very close to I_h [rms = 0.48 pm^2, module molsym, Platon[11]]. While the C_{60} and two of the phenol molecules are fully ordered, orientational disorder is observed for the third phenol molecule, which is also located on a centre of symmetry (1*e,* ½ ½ 0). A TLS analysis of the ordered part of the molecular structure converges at convincing reliability factors (R_1 = 0.043, Platon) and points toward a slight rigid body librational motion of the fullerene molecule [$(\lambda/°)^2$ = (7.68, 7.04, 4.49)]. Corrections to the C–C bond lengths due to librational shortening ($\langle\Delta d$ = 0.28 pm$\rangle$) are of the same order of magnitude as the corresponding estimated standard deviations and were regarded negligible.

As a general feature, the intramolecular C–C bond lengths of the C_{60} molecule separate into a set of short 6:6 bonds and a set of long 6:5 bonds, exhibiting a remarkably sharp distribution, as measured by the total span ($d_{\mathrm{max.}} - d_{\mathrm{min.}}$) and the standard deviation within each set (see Table 1 and the discussion below).

Each fullerene molecule is coordinated to four phenol molecules (see part a in Figure 2). The centre-to-centre distances are 660.5 pm (C_{60}–Phenol-0, 2×) and 673.8 pm (C_{60}–Phenol-1, 2×). The phenol molecules coordinate to different structural moieties, i.e. Phenol-0 to a hexagon [C(10), C(11), C(22), C(23), C(24), C(30)] and Phenol-1 to a pentagon [C(14), C(15), C(16), C(28), C(29)] with the closest phenol carbon to hexagon- and pentagon-plane approaches being 311(1) pm and 325(1) pm, respectively. The phenol and C_{60} rings have a virtual co-planar orientation [∠(Phenol-0 ···Hexagon) = 13.63(5) °, ∠(Phenol-1···Pentagon) = 8.95(5) °]. These distance values are shorter than the interlayer separation in graphite [d = 335.6(4) pm[12]], and lie in the range typically found in fullerene to arene π-π-interacting species (300 pm – 350 pm). Thus, π-π complex units, $[C_{60}(C_6H_5OH)_4]$, are present, and may be regarded as the basic building unit of this structure.

The hydroxyl groups of the phenol molecules are connected via almost linear, medium strength hydrogen bonds (d[O(100)-H(100)···O(110)] = 273.9(2) pm, ∠ = 174(2) °). Remarkably, these hydrogen-bonds do not appear between phenol molecules of the same complex unit, $[C_{60}(C_6H_5OH)_4]$, but in a pair wise manner with the phenol molecules of the neighboring complex units along the [100] and [$\bar{1}$00] directions. The Hydrogen-bonds between the complex units are the strongest intermolecular interactions present in this structure. The π-π complex units are connected via hydrogen-bonds to give ${}^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ rods along [100] (see part b of Figure 2). The overall structure is a distorted square packing of rods[13] in (100) plane. The remaining phenol molecules (Phenol-2) fill voids within the packing, which are located at a centre of symmetry.

Two symmetry equivalent Phenol-0 molecules, belonging to two different ${}^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ rods along the [011] diagonal

Table 1. Data for selected, reliable crystal structure analyses of C_{60} co-crystals, spans, statistical mean values, and standard deviations for the 6:6 and 6:5 sets of C–C bond lengths, and the results of thermal motion analyses of the structure models.

Compound	C_{60}·triphenyl-benzene· C_6H_5Cl	$C_{60}{\cdot}Ag(OEP){\cdot}C_6H_6$	$C_{60}{\cdot}Ni(OEP){\cdot}C_6H_6$	C_{60}·TMPDA	$C_{60}{\cdot}Pt(OEP){\cdot}C_6H_6$	$C_{60}{\cdot}5\,C_6H_5OH$
CCDC number	195338	168839	182460	213452	198536	267147
Reference	[8]	[21]	[22]	[23]	[24]	this work
$\langle d_{6:6}\rangle$ /pm	138.94(41)	139.12(42)	139.04(36)	138.81(43)	138.73(40)	138.74(28)
$d_{6:6}$: min., max.; Δ /pm	138.3, 140.0; 1.7	138.1, 140.0; 1.9	138.2, 139.8; 1.6	138.0, 139.7; 1.7	137.9, 139.6; 1.7	138.3, 139.5; 1.2
$\langle d_{6:6}\rangle$ /pm	144.70(54)	145.03(56)	145.18(33)	144.72(44)	145.09(41)	144.83(25)
$d_{5:6}$: min., max.; Δ /pm	143.6, 145.6; 2.0	143.7, 146.3; 2.6	144.3, 145.9; 1.6	143.7, 145.4; 1.7	144.0, 146.1; 2.1	144.3, 145.3; 1.0
Temperature /K	110	83	92	90	90	100
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Position of C_{60}	1*e* ($\bar{1}$)	general	general	2*a* ($\bar{1}$)	general	1*f* ($\bar{1}$)
Parameters	507	1018	1026	328	1018	478
Restraints	0	0	0	0	0	0
No. of refl. (all)	14107	14049	44245	17750	43336	10841
No. of refl. (unique)	9328	14040	19789	4512	19865	5623
No. of refl. ($I > 2\sigma$)	6297	12595	16575	2396	18705	3584
R_{int}	0.037	0.030	0.022	0.092	0.019	0.028
wR_2	0.272	0.130	0.107	0.158	0.054	0.108
TLS R_1	0.055	0.091	0.030	0.072	0.035	0.043
TLS $\lambda_1/\lambda_2/\lambda_3$ /(°)^2	6.69/5.08/3.90	8.44/5.65/4.76	7.82/5.76/4.11	5.75/4.34/3.81	9.37/6.08/4.98	7.68/7.04/4.49

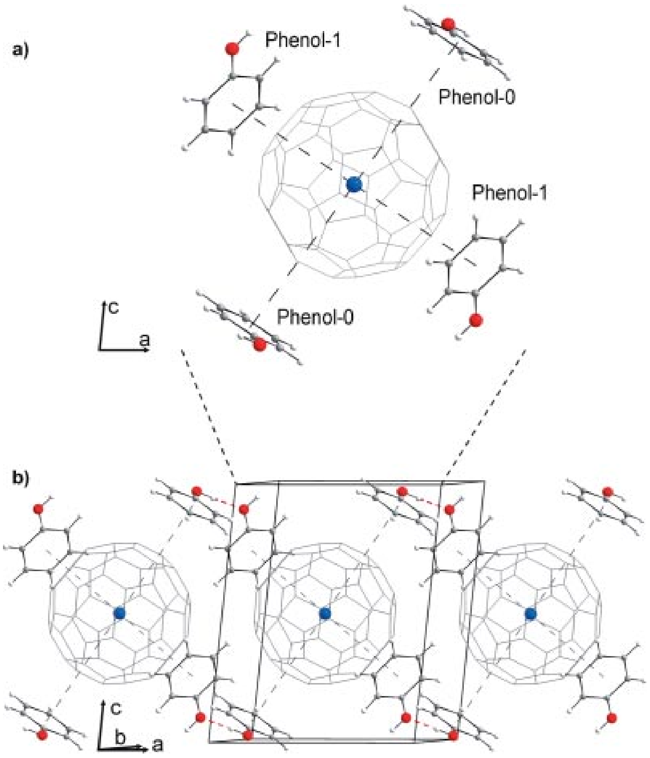

Figure 2. a) Coordination of C_{60} to four phenol molecules to give the supramolecular building unit $[C_{60}(C_6H_5OH)_4]$, and b) interconnection of these units via hydrogen bonds to give $^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ strands along [100]. Blue dots indicate the centers of gravity of the C_{60} molecules, and hydrogen bonds are emphasized in red.

of the square packing pattern, are found to be potential hydrogen-bond acceptors for different, but symmetry equivalent, orientations of the Phenol-2 molecules (d[O(120)···O(100)] = 275.9(3) pm, ∠ = 172(2) °). Thus, the orientational disorder of this particular phenol molecule is a consequence of the requirements of the supramolecular self assembly of the $^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ rods, and the comparably strong hydrogen-bond donor and acceptor capability of phenol.

The shortest intermolecular distances between fullerene molecules within this supramolecular arrangement, with d = 1003.5(1) pm, are observed along [100], i.e. the propagation direction of the $^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ rods, and are found to be significantly higher than those in pristine C_{60} (d = 992.8 pm[14]). While the fullerene-to-fullerene distances along [010] are only slightly higher [d = 1011.7(1) pm], the ones observed along [001] are significantly larger [d = 1264.2(2) pm]. This is due to the spatial requirements of the herring-bone like arrangement of the Phenol-0 and Phenol-1 molecules in the distorted square packing of the $^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ rods, and the occupation of the voids at symmetry site 1e by the orientationally disordered Phenol-2 molecules (Figure 3).

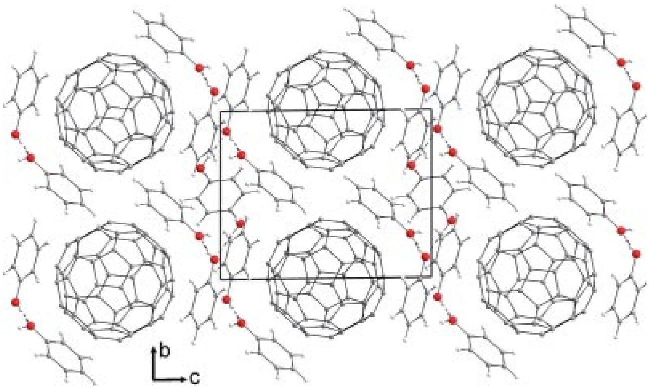

Figure 3. Distorted square packing of the $^{1}_{\infty}[C_{60}(C_6H_5OH)_4]$ strands in the (100) plane, the filling of the voids at 1e by further disordered phenol molecules is also shown.

Despite the considerable effort made in determining reliable experimental values for the 6:6 and 6:5 bond lengths, reference data is still subject to review. For comparison, we have selected a set of reliable crystal structure analyses of fullerene co-crystals on the basis of the overall quality, span and standard deviation of the bond length distribution, and the results of thermal motion analyses in context of the TLS formalism.[15] The data presented in Table 1 and Figure 4 include the overall statistical mean values of the corresponding bond sets within the range of the individual statistical standard deviations. From consideration of the span, as well as the standard deviation, of the reported 6:6 and 6:5 sets of bond lengths, the structure data in this work have to be regarded as the most precise.

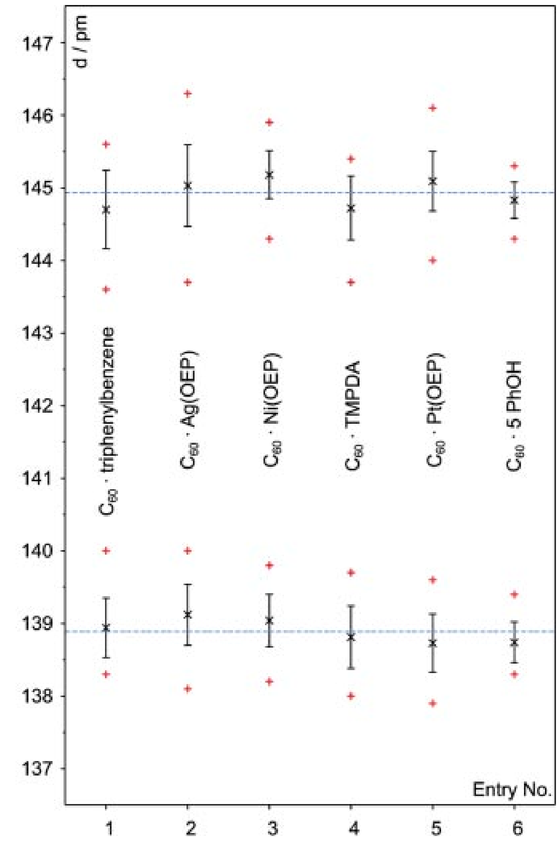

Figure 4. Spans (red), mean values and standard deviations (black) for the selected crystal structure data (Blue dashed lines correspond to the overall mean values of 138.9 pm and 144.9 pm; entry numbers correspond to the appearances of the compound in Table 1).

The kinds of interaction, e.g. pure π-π interactions, multipolar π interactions, and dipole–multipole interactions, and the strength of interaction differ between the various co-crystals. The strength of the overall interaction may be estimated by means of the mean square liberation amplitudes (λ_i, see Table 1). Surprisingly, the reported values do not differ significantly. There is no significant experimental evidence to indicate a change in the molecular structure of C_{60} upon alteration of the nature of a co-crystallization agent. Furthermore, the selected data are, despite the varying spans and standard-deviations, virtually identical and exhibit a significantly higher reliability than the data reported for pristine C_{60}.[14] The mean values are $\langle d_{6:6} \rangle$ = 138.9 pm and $\langle d_{6:5} \rangle$ = 144.9 pm.

Conclusions

Precipitation of $C_{60}·5C_6H_5OH$ from a homogeneous solution of C_{60} in triphenylphosphite yields single crystals of high quality. The combination of hydrogen-bonding and π-π interactions leads to a distorted square packing of $^1_\infty[C_{60}(C_6H_5OH)_4]$ strands, in which the fullerene molecules are fully ordered. The 6:6- and 6:5-bond lengths were determined to be 138.74(28) pm and 144.83(25) pm, respectively. A careful analysis of selected, reliable structure data for C_{60}-co-crystals hints to i) no significant influence of the co-crystallization agent, and ii) $\langle d_{6:6} \rangle$ = 138.9 pm and $\langle d_{6:5} \rangle$ = 144.9 pm for the 6:6 and 6:5 bond lengths, respectively.

Experimental Section

Commercially available C_{60} (5 mg, 99.9%, MER Corporation, USA) was dissolved in triphenylphosphite (10 mL, >97% purity, Fluka). The violet solution was hydrolyzed slowly by exposure to water vapor under ambient conditions. During a period of ten days, the solution turned brown and then red, and plate-shaped crystals of $C_{60}·5\ C_6H_5OH$ had formed. The crystals could be stored without any sign of decomposition in the mother liquid at 35 °C, which was necessary to prevent the crystallization of the phenol. Upon separation from the mother liquid, the crystals turned black within hours, this color change was accompanied by total loss of crystallinity.

A crystal suitable for X-ray diffraction was transferred into inert oil, picked with a loop and cooled rapidly to 100 K. Intensity data were collected on a SMART-APEX CCD X-ray diffractometer (Bruker) at 100 K with graphite-monochromated Mo-K_α radiation. A total of 1800 frames were collected with an exposure time of 30 s/frame. The reflection intensities were integrated using the SAINT[16] subprogram in the SMART[17] software package. Intensities were corrected for absorption effects by the application of a semi-empirical method (SADABS[18]). A total of 10841 reflections were measured, 5623 of which were independent, and 3584 of which had intensities greater than 2σ. The crystal structure was solved by direct methods and subsequent Fourier syntheses (SHELXS[19]). All non-hydrogen atoms were refined anisotropically (SHELXL[19]). Hydrogen atoms were located from the residual electron density map and refined individually with isotropic thermal parameters fixed to 1.2 and 1.5 times that of the equivalent isotropic displacement parameter of the carbon or oxygen atom to which it is bound. The disordered hydrogen atom, H(121), was fixed using the HFIX command.

In order to elucidate the nature of the disorder of the phenol-2 molecule, the structure was also solved and refined in space group $P1$. Two oxygen atoms at the 1,4 positions of the phenol-2 molecule (in $P\bar{1}$) were located in the residual electron density maps, and refined to a occupancy of ½, i.e. refined as an orientationally disordered phenol molecule, but not as a hydroquinone molecule. The

Table 2. Crystal and refinement parameters for $C_{60}·5C_6H_5OH$.

Chemical moiety	$C_{60}·5C_6H_5OH$
Molecular formula	$C_{90}H_{30}O_5$
Molecular mass /g mol^{-1}	1191.14
Temperature /K	100(2)
Wavelength /pm	71.073
Crystal system, space group	triclinic, $P\bar{1}$
Cell parameters /pm, °	a = 1003.52(14), α = 88.566(2) b = 1011.71(14), β = 84.026(2) c = 1264.17(17), γ = 83.485(2)
Cell volume /nm^3	1.2681(3)
Z, density (calcd.) /Mg·m^{-3}	1, 1.560
Absorption coefficient /mm^{-1}	0.096
F(000)	610
Crystal size /mm	0.3 × 0.1 × 0.03
θ Range /°	2.03–28.42
Range (H)	$-12 \le h \le 12$ $-12 \le k \le 12$ $-16 \le l \le 16$
Reflections measured / unique / observed	10841 / 5623 / 3584
$R_{\text{int.}}$, R_σ	0.028, 0.056
Completeness to θ = 28.42°	88.1%
Absorption correction	empirical (SADABS[18])
Refinement method	full-matrix least-squares on F^2 (SHELXL[19])
Data / restraints / parameter	5623 / 0 / 478
$S(F^2)$	1.002
Residuals (obsd.)	R_1 = 0.043, wR_2 = 0.092
Residuals (all)	R_1 = 0.085, wR_2 = 0.108
$\Delta\rho_{\text{min.}}$, $\Delta\rho_{\text{max.}}$ /10^{-6} e pm^{-3}	–0.25(5), 0.24(5)

Table 3. Selected bond lengths [pm] and angles [°] for $C_{60}{\cdot}5C_6H_5OH$.

Fullerene C_{60}	6:6 bonds		
C13–C14	138.3(3)	C19–C20	138.8(3)
C3–C15	138.4(3)	C22–C30[a]	138.8(3)
C1–C9	138.5(3)	C25–C26	138.8(3)
C21–C29[a]	138.5(3)	C16–C17	138.9(3)
C27–C28	138.5(3)	C2–C12	139.1(3)
C10–C11	138.6(3)	C4–C18	139.1(3)
C23–C24	138.7(3)	C5–C6	139.5(3)
C7–C8	138.8(3)		
	6:5 bonds		
C17–C30	144.3(3)	C7–C27[a]	144.9(3)
C19–C23[a]	144.3(3)	C8–C9	144.9(3)
C26–C27	144.4(3)	C10–C22	144.9(3)
C28–C29	144.5(3)	C12–C13	144.9(3)
C2–C3	144.6(3)	C18–C19	144.9(3)
C11–C12	144.6(3)	C4–C5	145.0(3)
C15–C16	144.6(3)	C8–C21	145.0(3)
C16–C29	144.7(3)	C11–C24	145.0(3)
C20–C26[a]	144.7(3)	C14–C15	145.0(3)
C1–C5	144.8(3)	C24–C25	145.0(3)
C6–C7	144.8(3)	C3–C4	145.1(3)
C6–C20	144.8(3)	C14–C28	145.1(3)
C9–C10	144.8(3)	C17–C18	145.1(3)
C23–C30[a]	144.8(3)	C21–C22	145.2(3)
C1–C2	144.9(3)	C13–C25	145.3(3)
Phenol-0		Phenol-1	
O100–C101	136.7(2)	O110–C111	137.4(2)
O100–H100	94(3)	O110–H110	89(3)
C101–C102	138.4(3)	C111–C112	138.0(3)
C101–C106	138.5(3)	C111–C116	138.2(3)
C102–C103	138.3(3)	C112–C113	138.0(3)
C103–C104	138.5(3)	C113–C114	137.9(3)
C104–C105	138.3(3)	C114–C115	138.2(3)
C105–C106	138.6(3)	C115–C116	138.1(3)
Phenol-2			
C121–C122	138.2(3)	C123–C122[b]	138.7(3)
C121–C123	138.6(3)	C121–O120	132.6(4)
D–H···A	*d*(D–H)	*d*(D···A)	∠(DHA)
O100–H100···O110[c]	94(3)	273.9(2)	174(2)
O120–H120···O100[d]	91(4)	275.0(3)	172(4)

[a] Symmetry operators: $1-x, -y, 1-z$. [b] Symmetry operators: $1-x, 1-y, -z$. [c] Symmetry operators: $-x, -y, 1-z$. [d] Symmetry operators: $1-x, -y, -z$.

implementation of this disorder model, as well as the application of an inversion-twin law, enabled the refinement to converge to virtually the same residuals as the refinement of the structure model in space group $P\bar{1}$, but the model in $P1$suffered from strong pair wise correlation of positional and anisotropic displacement parameters for all the atoms, and exhibited esd values about four times higher for the C–C bond lengths than for the disordered structure model in $P\bar{1}$. Furthermore, no indications to the presence of a superstructure or modulation were observed. Thus, we conclude $C_{60}{\cdot}5C_6H_5OH$ crystallizes in space group $P\bar{1}$ with phenol-2 being orientationally disordered, due to the structural boundary conditions set by the supramolecular motif. Further details of the structure analysis and selected bond lengths are given in Table 2 and Table 3.

CCDC-267147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Raman spectra were recorded on individual single-crystals, which were protected by a thin layer of the mother liquid, with a microscope laser Raman system (Jobin–Yvon, LabRam) operating at an excitation wavelength of 784.7 nm at 20 mW. Bands corresponding exclusively to C_{60} were observed (270, 432, 492, 772, 1424, 1468 cm^{-1}). The deviations from the resonances of pristine C_{60}[20] are not larger than 3 cm^{-1}, which is expected for non-ionic molecular crystals.

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