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Nanocrystalline Domains of a Monoclinic Modification of Benzene Stabilized in a Crystalline Matrix of C_{60}[1]

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The crystal structure of $C_{60}\cdot 4C_6H_6$ at 104 K has been refined to $R(|F|) = 0.070$, $wR(|F|) = 0.032$. The C_{60} molecules are arranged in infinite stacks which form a regular, honeycomb-like arrangement, whose voids (channels) are filled by benzene molecules. Contrary to earlier assertions, the C_{60} molecules form a defective and distorted cubic closest packing in which one C_{60} out of three is replaced by eight benzene molecules. The positions and orientations of the benzene molecules in each channel suggest a hitherto unobserved monoclinic packing of benzene molecules. The crystal structure may be considered as a macroscopically ordered nanocomposite of fullerene and benzene domains. Some of the properties of the benzene domains are typical of the nanocrystalline state of matter.

Introduction

Nanometer-sized crystalline domains and composites are of some interest in materials science because their properties often differ from those of the bulk materials. The crystal structure of $C_{60}\cdot 4C_6H_6$ may be looked at as a nanocomposite of C_6H_6 and C_{60} domains, as explained in the Discussion. The structure thus offers a rare opportunity to study phenomena connected with nanocrystallinity at atomic resolution.

When fullerenes are crystallized from organic solvents, the resulting crystal structures invariably incorporate solvent molecules.[2–10] This behavior contrasts with that of most molecular compounds.[11] It is therefore of some interest to analyze the molecular packing of such solvates and to compare it with those of the pristine, solvent-free fullerenes and with the structure of the pure solvent.

The molecular positions in $C_{60}\cdot 4C_6H_6$ at 173 K were first reported by Meidine et al.[2] Assuming the C_{60} molecules to be orientationally ordered, the structure was refined to $R = 0.101$, $wR = 0.123$; resulting average bond lengths were 1.32(9) Å for 6,6 bonds and 1.48(13) Å for 5,6 bonds (a *n,m* bond fuses an *n*-gon and an *m*-gon). Some displacement tensors were nonpositive definite. In a second study at 104 K, Balch et al.[3] found a 2-fold orientational disorder of C_{60}. Restraining the 6,6 and 5,6 distances to 1.389(5) and 1.446(5) Å and including only reflections with $|F| > 4\sigma(F)$, the data were refined to $R = 0.098$, $wR = 0.089$. Here we report (1) the results of further refinement of the 104 K data[3] to $R(F) = 0.070$, $wR(F) = 0.032$, $wR(|F|^2) = 0.060$, again including reflections with $|F| > 4\sigma(F)$; (2) a description of the orientational disorder of C_{60}; (3) a packing analysis of the C_{60} molecules with results differing from those given previously[2] and (4) a packing analysis of the benzene molecules, revealing edge-to-face packing in herringbone layers similar to that found in orthorhombic benzene[12–14] and in the high-pressure, monoclinic modification,[15,16] but with different layer stacking. The various benzene modifications are compared and conclusions are drawn concerning the recognition of benzene molecules by benzene molecules and by host molecules containing phenyl rings.

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(1) This paper is dedicated to the memory of Prof. M. C. Etter and is intended to pay tribute to Peggy's interests in and original contributions to the study of crystal architecture.

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Table 1. Refinement Results of $C_{60}\cdot 4C_6H_6$ at 104 K

	pop.	dist, Å		U_{eq}
C_{60} (C101–C160)	0.531(1)	1.378(3)[a]	1.456(3)[b]	0.0263–0.0438
C_{60} (C201–C260)	0.469	1.384(3)[a]	1.451(3)[b]	0.0259–0.0490
average		1.381[a]	1.454[b]	
C_6H_6 (C11–C16)	0.577(8)	1.386[c]		0.0261–0.0421(23)
C_6H_6 (C21–C26)	0.423	1.386[c]		0.0145–0.0433(30)
C_6H_6 (C31–C36)	1	1.384(3)	1.394(3)	0.0268–0.0352(27)
C_6H_6 (C51–C56)	1	1.381(5)	1.387(5)	0.0316–0.0432(30)
C_6H_6 (C71–C76)	1	1.382(4)	1.387(4)	0.0302–0.0380(28)
average		1.386(5)[d]		

[a] 6,6 bond. [b] 5,6 bond. [c] Fixed. [d] Mean and esd of sample.

Experimental Section

The 104 K X-ray data measured by Balch et al.[3] were refined using the following variables and restraints[17] (supplementary material; see paragraph at end of paper): (1) C–C–C angle restraints to ensure icosahedral molecular symmetry of C_{60}: five-membered rings were restrained to be regular and planar by fixing five angles of 108° and five angles of 36°. Hexagons were restrained to be planar and semiregular with alternating long and short C–C bonds by fixing six angles of 120° and six angles of 60°. This leaves only two variables determining the geometry of C_{60}, namely, the 5,6 and 6,6 bond lengths; (2) the C–C–C and C–C–H angles of benzene were restrained to 120°, the C–H distance to 1.084 Å; (3) in the disordered benzene molecule (C11–C16, C21–C26) the C–C distances were fixed to 1.386 Å; (4) the atoms of C_{60} and of the ordered benzene molecules were refined with anisotropic displacement parameters (ADPs); the atoms of the disordered benzene were assigned individual isotropic displacement parameters; (5) ADPs of the atoms of C_{60} were restrained to rigid-body librations and translations by numerous rigid-bond conditions;[18] (6) the sums of the population parameters of disordered molecules (C_{60}, one benzene) were constrained to $P_1 + P_2 = 1$. The number of restraint equations, their weights and the largest weighted deviations ($|\Delta\sqrt{w}|$) upon completion of the refinement were respectively 42, 10^6 Å^{-2}, 0.3 for the distances, 840, 2500 deg^{-2}, 1.2 for the angles, and 900, 10^8 Å^{-4}, 0.3 for the rigid bonds.

During the last cycles of the refinement, the ADPs of the C_{60} molecules were kept fixed at the values attained in previous cycles since they were strongly correlated among themselves and with other parameters. The weighted root-mean-square deviations after the last cycle are 0.14 for the 1782 restraints and 1.52 for the 2957 Bragg intensities with $|F| > 4\sigma(|F|)$. The final combined goodness-of-fit value is 1.296. Geometrical calculations are based on the space group and cell constants reported earlier:[3] $P\bar{1}$, a = 9.938 (2), , b = 15.031 (3), c = 17.425 (4) Å, α = 65.38 (2), β = 88.31 (2), γ = 74.83 (2)°. Results are summarized in Table 1.

Results

Molecular Geometries. Bond distances in C_{60} obtained for the two orientations are very close and compare well with the most accurate values presently available from X-ray diffraction data of pristine C_{60}: 1.387(3), 1.450(3) Å (at 110 K)[19] and 1.372(6), 1.453(6) (at room temperature, corrected for libration).[20] Neutron diffraction,[21] gas-phase electron diffraction,[22] NMR,[23] and ab initio calculations[24] tend to show a somewhat longer 6,6 bond of 1.400–1.405 Å. The latter techniques provide internuclear distances, whereas X-ray measurements at limited resolution yield distances between the centers of gravity of nonspherical, atomic electron density distributions which may differ up to a few hundreds of an angstrom from internuclear distances.[25] The six independent distances refined for the benzene molecules are also close. Overall, the R values, the goodness-of-fit quantities, and the chemical consistency of geometric parameters show that the assumptions of icosahedral symmetry for C_{60} and of planar trigonal symmetry for C_6H_6 are compatible with the experimental diffraction data.

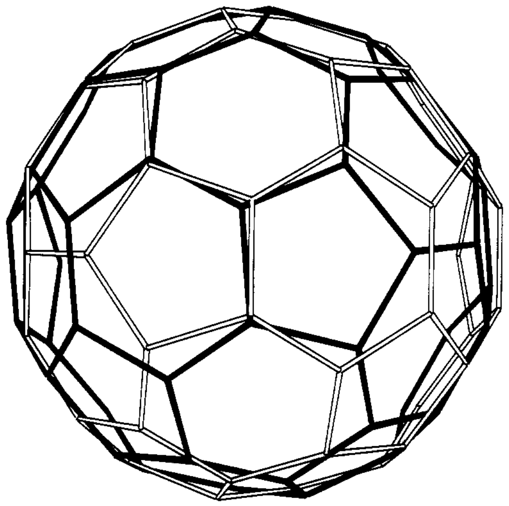

Figure 1. Orientational disorder of C_{60} in $C_{60}\cdot 4C_6H_6$. Only the upper halves of the molecules are shown. Solid lines correspond to the orientation with population 0.531(1), open lines to the orientation with population 0.469. Note the approximate, vertical mirror plane perpendicular to the plane of projection relating the large to the small atoms in both figures. The lower halves of the molecules superimpose in nearly the same way since lower and upper halves are related by a noncrystallographic molecular center of symmetry.

Orientational Disorder of C_{60}. The two orientations are related closely by a noncrystallographic mirror plane, defined by the equation $4.097x + 14.838y + 7.017z = 3.355$. Figure 1 shows that a six-membered ring and an adjacent 5,6 bond of one orientation almost coincide with corresponding fragments of the other orientation. This disorder is very similar to that found in the low-temperature, $Pa\bar{3}$ modification of C_{60}.[19,21]

Packing Analysis of $C_{60}\cdot 4C_6H_6$. The C_{60} molecules are stacked in columns along the unit-cell axis a; the individual stacks form a somewhat distorted honeycomb arrangement.[2] The channels formed by this arrangement are filled with C_6H_6. (See Figure 1 of ref 3.) The stacking of the C_{60}'s and the arrangement of C_6H_6 in the honeycomb channels are discussed separately below.

Packing of the C_{60} Molecules. In the first paper on $C_{60}\cdot 4C_6H_6$ it was stated that the packing "can be visualized in terms of a hexagonal close-packed arrangement of C_{60} molecules with the hexagonal axis along a".[2] Here we show

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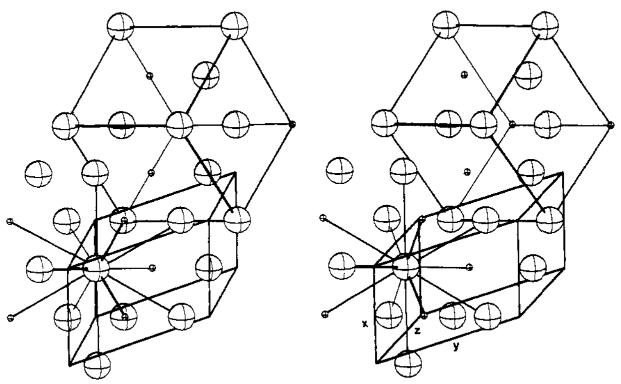

Figure 2. Stereoscopic drawing of the distribution of C_{60} molecules (large spheres) in and around a unit cell of $C_{60}{\cdot}4C_6H_6$ (axes are labeled *x,y,z*). The molecular centers are drawn at the idealized positions $\mp{}^1/_6,\pm{}^1/_6,\pm{}^1/_6$. Together with the centers of the unit cells at $^1/_2,{}^1/_2,{}^1/_2$ (small spheres) they form a pseudo-translation lattice which may be described by a distorted face-centered cubic unit cell (shown at the top). Correspondingly, there are 12 nearest neighbors to each C_{60} molecule (bottom left). Seven of them are C_{60} molecules. Close-packed layers of lattice points are approximately parallel to the plane of projection. Note the ...ABC... arrangement of close-packed layers typical of cubic close-packing.

that a description in terms of a distorted cubic close packing is more appropriate.

The centers of the two orientations of C_{60} are only 0.086 Å apart. More importantly, they are at distances of only 0.49 and 0.57 Å from $-{}^1/_6$, $^1/_6$, $^1/_6$. The second C_{60} in the unit cell is positioned near $^1/_6$, $-{}^1/_6$, $-{}^1/_6$. These two positions suggest a pseudo translation lattice generated by the vectors [100], [010], and $[-{}^1/_3,{}^1/_3,{}^1/_3]$ whose unit-cell volume is one-third of the observed volume. Two out of three pseudo-lattice points are occupied by C_{60} whereas the third point at $^1/_2,{}^1/_2,{}^1/_2$ is in the center of the channels (Figure 2). Of the 12 pseudo-lattice points closest to a C_{60} molecule, 7 are occupied by other C_{60} molecules. Corresponding center-to-center distances are 9.94 Å for the two neighbors related by translations [±100], 9.95 Å for pseudo-translation $\sim[{}^1/_3,-{}^1/_3,-{}^1/_3]$, 9.99 Å for $\sim[-{}^2/_3,{}^2/_3,-{}^1/_3]$, 10.07 Å for $\sim[{}^1/_3,-{}^1/_3,{}^2/_3]$, 10.34 Å for $\sim[{}^1/_3,{}^2/_3,-{}^1/_3]$, and 12.74 Å for $\sim[-{}^2/_3,-{}^1/_3,{}^2/_3]$ (major population, *non*idealized positions). An additional C_{60} is farther away, at 13.04 Å with pseudo-translation $\sim[-{}^2/_3,-{}^1/_3,-{}^1/_3]$. The 12 points closest to C_{60} form a distorted cuboctahedron, indicative of cubic closest packing. The corresponding face-centered unit cell, defined by the vectors $a(\mathrm{fcc}) = b - c$, $b(\mathrm{fcc}) = {}^4/_3a - {}^1/_3b - {}^1/_3c$ and $c(\mathrm{fcc}) = -{}^2/_3a - {}^1/_3b - {}^1/_3c$, is shown at the top right of Figure 2. Its lattice constants and angles are 17.64, 14.81, and 12.11 Å and 85.4°, 89.1°, and 105.8°. The corresponding cell volume is 2906 Å^3, about 5% larger than that of the cubic 14.05-Å cell of C_{60} at 110 K.

Packing of Benzene Molecules. A very interesting part of the crystal structure is the arrangement of the benzene molecules in the channels of the C_{60} honeycomb framework (Figure 3). The benzene substructure is built from centrosymmetric arrays of 2 × 4 benzene molecules whose midpoints are almost coplanar (Figure 3a). The same motif may be identified in the crystal structure of orthorhombic benzene[12-14] (Figure 3b). The molecules within the two-by-four motif show herringbone packing, their contacts being between the hydrogen atoms of one molecule and the π-electron cloud of its neighbors. In $C_{60}{\cdot}4C_6H_6$ the $(C_6H_6)_8$ motifs are repeated by translation (along *a*); in pure benzene successive motifs are related by glide planes parallel to the plane of the motif.

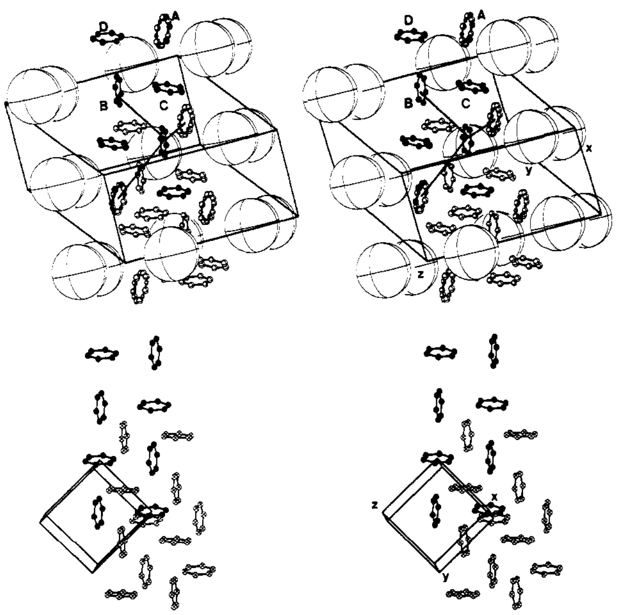

Figure 3. (a, top) Stereoscopic view of the channels formed by stacks of C_{60} molecules (large spheres) which contain eight benzene molecules per unit cell. In the first and second layer, one C_{60} has been omitted to give a free view on the arrangement of the benzene molecules. The latter may be described in terms of a centrosymmetric, two-by-four array of eight benzene molecules whose centers are almost coplanar (molecules in black). The crystallographically independent molecules are labeled A, B, C, and D. The pseudo-translation vectors describing the benzene-packing in the channels are given between centers of benzene molecules ($a(C_6H_6)$ to bottom left, $b(C_6H_6)$ to top right, $-c(C_6H_6)$ to top left, see text). (b, bottom) Stereoscopic view of a selected portion of the crystal packing in orthorhombic benzene. The centrosymmetric, two-by-four array of eight benzene molecules with coplanar centers (in black) has been selected to resemble as closely as possible the arrangement in (a).

The qualitative similarity of the benzene packings is confirmed by a quantitative comparison. For $C_{60}{\cdot}4C_6H_6$ approximate translation vectors in the plane motif of eight benzenes have been determined by a least-squares fit to the molecular centers (Table 2a, $a(C_6H_6)$, $c(C_6H_6)$). The root-mean-square deviation between observed and calculated centers is 0.35 Å. A third pseudo-translation vector relates successive $(C_6H_6)_8$ motifs in each channel (Table 2a, $b(C_6H_6)$). The lattice constants of this pseudomonoclinic cell and those of orthorhombic benzene at 104 K interpolated from Jeffrey[14] are reported in Table 2a, and comparison of the unit-cell volumes indicates that the packing of the benzene molecules is about 6(5)% less dense in $C_{60}{\cdot}4C_6H_6$ than in C_6H_6.

Figure 3a shows that the planes of molecules A, C, and D are related approximately by a glide operation with translational component $a(C_6H_6)/2$ or a 2-fold screw operation parallel to $c(C_6H_6)$. The plane of molecule B obeys these relationships somewhat less well. If we nevertheless assume them to hold, the positions of the benzene molecules in $C_{60}{\cdot}4C_6H_6$ are related by space group symmetry $P2_1/a$ (unique axis *c*). For a more quantitative discussion, the direction cosines of the normals to the benzene planes with respect to the $a(C_6H_6)$ and $c(C_6H_6)$ axes are compared to those with respect to *a*(ortho) and *c*(ortho) of orthorhombic benzene (Table 3a). Alternatively, the angles between the normals of the benzene molecules may be compared (Table 3b). The similarity

Table 2. Characteristics of Monoclinic and Orthorhombic Benzene Modifications

(a) Cell Constants[a]

	pseudo-monoclinic (104 K)			monoclinic (25 kbar)	
	primitive[b]	C centered[c]	orthorhombic (104 K)[d]	primitive[e]	C centered[f]
a, Å	7.47(14)	7.47	7.388	7.352	7.352
b, Å	5.48(16)	9.42	9.419	5.417	10.814
c, Å	7.23(14)	7.23	6.757	5.376	5.376
α, deg	92.7(3.0)	93.4	90	90	90
β, deg	90.3(2.2)	90.3	90	90	90
γ, deg	122.2(3.9)	80.1	90	110.0	70.3
V, Å^3	250(13)	500	470.2	201.2	402.2
Z	2	4	4	2	4

(b) Center-to-Center Distances (Å) between a Benzene Molecule (Taken at 0,0,0) and Its Nearest Neighbors

neighbor at	A[g]	B[g]	C[g]	D[g]	M[h]	O[i]	M[j]
$\pm^1/_2,0,\pm^1/_2$	5.45	4.93	4.93	5.45	5.18	5.006	4.554
					5.18	5.006	4.554
$\pm^1/_2,0,\mp^1/_2$	5.45	5.15	5.20	5.15	5.21	5.006	4.554
		5.20	5.45		5.21	5.006	4.554
$0,\pm^1/_2,\pm^1/_2$		5.55		5.55	5.77	5.796	6.038
					5.77	5.796	6.038
$0,\pm^1/_2,\mp^1/_2$	6.04	6.06	6.04	6.06	6.11	5.796	6.038
		6.29	6.29		6.11	5.796	6.038
$\pm^1/_2,\pm^1/_2,0$		5.85	6.85	6.85	6.49	5.985	7.493
					6.49	5.985	7.493
$\pm^1/_2,\mp^1/_2,0$	5.71	5.71	5.33	5.33	5.48	5.985	5.376
					5.48	5.985	5.376

[a] Definitions of a, b, c, α, β, and γ in footnotes b–f. [b] $a(C_6H_6) = -0.309(21)a - 0.149(15)b + 0.416(13)c$; $b(C_6H_6) = a - a(C_6H_6) - c(C_6H_6)$; $c(C_6H_6) = -0.459(21)a - 0.213(15)b - 0.143(13)c$. [c] $a'(C_6H_6) = a(C_6H_6)$; $b'(C_6H_6) = 2b(C_6H_6) + a(C_6H_6)$; $c'(C_6H_6) = c(C_6H_6)$. [d] a(ortho), b(ortho), c(ortho). [e] c(hp), b(hp), a(hp), γ(hp), β(hp), α(hp).[15] [f] a'(hp) = c(hp); b'(hp) = $2a$(hp) + c(hp); c'(hp) = b(hp). [g] Observed. [h] Idealized low density, monoclinic modification derived from $C_{60}{\cdot}4C_6H_6$. [i] Orthorhombic modification, 104 K. [j] High-pressure, monoclinic modification.

Table 3. Orientation of Benzene Molecules in $C_{60}{\cdot}4C_6H_6$ and C_6H_6

(a) Direction Cosines of Plane Normals with Respect to Axes Indicated[a]

	$C_{60}{\cdot}4C_6H_6$		C_6H_6[b]	
molecule	$a(C_6H_6)$	$c(C_6H_6)$	a(ortho)	c(ortho)
A	0.51	−0.79	0.68	−0.69
B	0.65	−0.69	0.68	−0.69
C	0.83	0.51	0.68	0.69
D	0.73	0.62	0.68	0.69
average[c]	0.68	0.65	0.68	0.69

(b) Angles (deg) between Plane Normals in $C_{60}{\cdot}4C_6H_6$ (Upper Triangular Matrix)[a] and C_6H_6 (Lower Triangular Matrix)[b]

	A	B	C	D
A		38.8	84.8	91.2
B	0		83.1	92.5
C	87.6	87.6		9.5
D	87.6	87.6	0	

[a] See also Table 3 of the supplementary material. [b] At 15 K.[14] [c] Of absolute values.

between the $(C_6H_6)_8$ motifs in the two crystal structures is apparent in both comparisons, as is the misorientation of molecule B in $C_{60}{\cdot}4C_6H_6$.

Discussion

The packing analysis shows that the positions of the constituent molecules of $C_{60}{\cdot}4C_6H_6$ can be described by two independent, interpenetrating approximate translation lattices. The lattice of the C_{60} molecules is distorted fcc, extends through the whole structure, and shows a regular arrangement of defects in the form of channels. The lattice of the benzene molecules is realized only locally within each channel of the C_{60}-lattice. This observation suggests a discussion of the crystal structure of $C_{60}{\cdot}4C_6H_6$ as a nanocomposite or in terms of an ordered array of nanocrystalline domains of a new, hitherto unobserved, monoclinic modification of benzene stabilized by a matrix of C_{60} molecules.

A domain of benzene molecules has dimensions of about 1 nm in two directions and is infinite only in the third direction. It is crystalline in that it can be described, approximately, in terms of a crystallographic space group and is bounded by faces with the well-defined Miller indices (100), (011), and (21$\bar{1}$) relative to $a(C_6H_6)$, $b(C_6H_6)$, and $c(C_6H_6)$. It shows some properties which are considered typical of nanocrystals.[26,27] First, there is a change of symmetry from orthorhombic in the bulk to monoclinic. Second, the nanocrystal density is somewhat lower than that of bulk crystals. Third, all benzene molecules are on the surface of the nanodomains resulting in deviations from the regularity expected for infinite crystals by ~0.3 Å on average. Finally, the orientational mobility of the benzene molecules depends on the number of nearest-neighbor molecules: molecule A has only four C_6H_6 neighbors and is disordered over two orientations, whereas molecules B, C, and D with eight, seven, and six neighbors respectively, are orientationally ordered. It is unlikely that the C_{60} environment is responsible for this difference since molecules A and B both orient their π-planes in a similar way to a neighboring C_{60}. The distances from the midpoints of A and B to the respective C_{60} centers are 6.77 and 6.76 Å; the angles between the normals to the planes of A and B and the $C_{60}{\cdots}C_6H_6$ center-to-center vectors are 3.3° and 4.9°.

In all benzene modifications—the monoclinic one derived from $C_{60}{\cdot}4C_6H_6$, the orthorhombic and the high-pressure monoclinic ones—each benzene molecule is surrounded by 12 nearest neighbors in a more or less cuboctahedral arrangement. To compare their packings, it is convenient to use analogous unit cells for all of them (Table 2a; $C2_1/a$, unique axis c for both pseudomonoclinic $C_{60}{\cdot}4C_6H_6$ and high-pressure C_6H_6). In all three structures, the 12 nearest neighbours of a benzene at 0,0,0 are then at $0,\pm^1/_2,\pm^1/_2$, $0,\pm^1/_2,\mp^1/_2$, $\pm^1/_2,\pm^1/_2,0$, $\pm^1/_2,\mp^1/_2,0$, $\pm^1/_2,0,\pm^1/_2$, and $\pm^1/_2,0,\mp^1/_2$.

The constant feature in all three packings is the edge-to-face contact mediated by crystallographic glide planes with roughly constant glide components $a/2$ but different distances $c/4$ of the benzene molecules from the glide planes (Table 2a). The resulting planar motifs are stacked in different ways along b. The quantity $b/2{\cdot}\sin\gamma$, measuring the stacking distance, is 4.64, 4.71, and 5.09 Å for the pseudo-monoclinic, orthorhombic, and high-pressure phases, respectively. Thus the edge-to-face interactions become stronger with increasing density, while the stacking distance increases. The same conclusion follows from the center-to-center distances listed in Table 3b. Edge-to-face distances are smallest in all three modifications (4.5–5.2 Å; to molecules at $\pm^1/_2,0,\pm^1/_2$ and $\pm^1/_2,0,\mp^1/_2$). Their

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(26) For a review on nanocrystalline solids, see: Gleiter, H. *J. Appl. Crystallogr.* **1991**, *24*, 79.

(27) For a review on nanocrystalline, atomic and molecular clusters in the gas phase, see: Bartell, L. S. *Chem. Rev.* **1986**, *86*, 491.

decrease parallels that in c. The distances to molecules at $0,\pm^1/_2,\pm^1/_2$ and $0,\pm^1/_2,\mp^1/_2$ are larger but fairly constant (5.8–6.1 Å), those to molecules at $\pm^1/_2,\pm^1/_2,0$ and $\pm^1/_2,\mp^1/_2,0$ show the largest variations (5.4–7.5 Å).

The various ways of packing benzene molecules are of some interest in connection with a recent analysis[28] of the geometries of host–guest complexes between different cyclophanes and benzene. There it was shown that self-recognition of molecules in their crystal structures, i.e., molecular packing, provides a guide for the design and synthesis of hosts that are specific receptors for the molecule in question. From our results it would seem that hosts specific to benzene guests must provide the possibility of optimal edge-to-face interactions, whereas details of the disposition of additional phenyl rings in the host are probably less important.

Supplementary Material Available: **T** and **L** tensors for C_{60} molecules, shortest contact distances between C_{60} and C_6H_6, atomic positional and displacement parameters, list of restraints used in refinement, centers of benzene molecules and normals to their planes (15 pages). Ordering information is given on any current masthead page.

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[28] Klebe, G.; Diederich, F. *Philos. Trans. R. Soc. London* **1993**, *345*, 37.