26. The X-Ray Crystal Structures of a 1,9- and a 7,8-*Diels-Alder* Monoadduct of C_{70}

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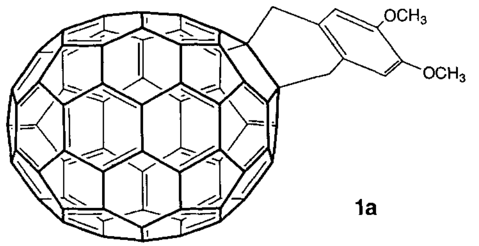
Accurate low-temperature X-ray crystal structures of the isomeric *Diels-Alder* monoadducts of C_{70} **1a**, bridged at the [6,6] bond between C(1) and C(9), and **1b**, bridged at the [6,6] bond between C(7) and C(8), have been determined. The latter structure is the first one solved for a 7,8-C_{70} monoadduct. The C_1-symmetrical **1a** and C_s-symmetrical **1b** co-crystallize with CS_2 molecules in the space groups $P2_1/c$ and $Pnma$, respectively, and the distances between bridgehead atoms are 1.603(3) and 1.584(3) Å. The degree of pyramidalization of atoms involved in [6,6] bonds near the 'unsubstituted' pole and near the equator of the fullerene was estimated; it is shown for the unsubstituted pole region that atoms corresponding to C(1) and C(9) are slightly more pyramidal than those corresponding to C(7) and C(8), in agreement with *ab initio* calculations obtained for the C_{70} spheroid. Some aspects of the crystal packings are discussed.

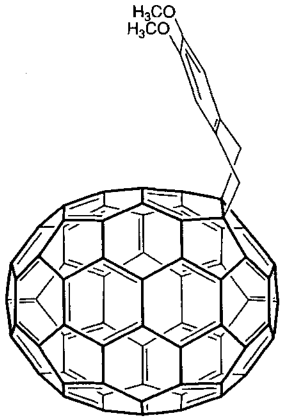
1. Introduction. – In contrast to *Diels-Alder* additions to I_h-C_{60} [1] those to higher fullerenes with lower molecular symmetry can lead to multiple isomeric monoadducts bridged at [6,6] bonds, *i.e.*, at the junctions between two six-membered rings. The addition of an intermediately formed *ortho*-quinodimethane to the higher fullerene D_{5h}-C_{70} was recently investigated [2], and three out of four possible [6,6] monoadducts of C_{70} (**1a–c**) were isolated and characterized. Adduct formation occurred preferentially at bonds located close to the poles of the spheroid, where the local curvature is highest [2–4]. Derivative **1a** is bridged at the C(1)–C(9) bond and was the most abundant product formed, followed by **1b** which is bridged at the C(7)–C(8) bond. Isomer **1c**, with a bridge at the C(22)–C(23) bond near the flatter equator, was produced in much lower yield than the two other isomers. A similar *Diels-Alder* adduct (**2**) of C_{60} had been previously prepared independently by two groups [1d] [5].

The experimental results for C_{70} confirmed that the regioselectivity for additions to higher fullerenes correlates with the degree of pyramidalization of the fullerene atoms as had been proposed in *ab initio* calculations by *Haddon* [6], and shown by *Hawkins* and coworkers [3c] [7] for the osmylation of higher fullerenes. They are also in agreement with a qualitative model in which the pyramidalization and thus the enhanced reactivity of C-atoms in [6,6] bonds was correlated with the number of pentagons adjacent to this bond [2].

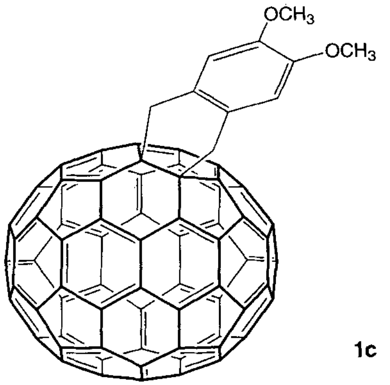
The molecular geometry of C_{70} has been estimated by various experimental and theoretical methods. X-Ray diffraction and electron-diffraction analyses have been published for crystals containing unsubstituted C_{70} structures [8] and for two C_{70} derivatives [3a, b]. In addition, a powder neutron diffraction study of pure C_{70} was reported [9]. Most of these analyses were restricted to average D_{5h} geometries, because the experimental data did not allow a more detailed interpretation. Accurate determination of individual



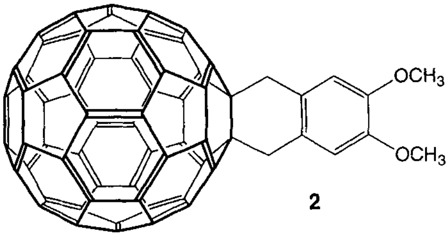
1a



1b



1c



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atomic positions, however, is a prerequisite for a characterization of subtle local distortions on a fullerene surface, as was shown recently in an X-ray analysis of a [6,6]-methano-bridged C_{60} fullerene [10]. In this structure, the shortest [6,6]-bond lengths are those which were experimentally found to show the highest reactivity towards nucleophiles [11].

Here, we report the accurate low-temperature structures of **1a** and **1b** obtained from ordered single crystals of good optical quality. The X-ray structure of **1b** is the first one solved for a 7,8-C_{70} monoadduct. In addition to the usual molecular geometries, the degree of pyramidalization of several types of atoms has been determined; the experimental values agree qualitatively with those obtained from theoretical calculations [12]. Moreover, some aspects of the crystal packings are discussed.

2. Experimental. – The X-ray measurements were made on an *Enraf-Nonius CAD4* diffractometer equipped with graphite monochromator (CuK_α radiation, λ = 1.5418 Å) and an *Enraf-Nonius* gas-stream low-temp. device.

Black, plate-like single crystals of **1a** and **1b** were obtained by slow evaporation of a CS_2 soln. Isomer **1a** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of **1a** and two CS_2 molecules (one of which is disordered) in the asymmetric unit. Isomer **1b** crystallizes in the orthorhombic space group *Pnma*, with one half molecule of **1b** and two half CS_2 molecules in the asymmetric unit; **1b** has a mirror plane which coincides with the crystallographic mirror plane at $y = 1/4$. One CS_2 molecule lies on an inversion center, the other is statistically disordered, with one S-atom lying on the mirror plane (see *Fig. 7*). We first produced single crystals of **1b** by diffusion of CH_2Cl_2 into a tetrachloroethane soln. The space group was also *Pnma*, and the cell parameters were nearly the same as those listed for **1b** (see *Table 1*); the asymmetric unit contained one half molecule of **1b** and two

Table 1. *Experimental Details of the X-Ray Diffraction Measurements for the 1,9- and 7,8-*Diels-Alder *Adducts of* C_{70}

Data set	**1a**	**1b**
Empirical formula	$C_{80}H_{12}O_2 \cdot 2\,CS_2$	$1/2\,C_{80}H_{12}O_2 \cdot CS_2$
Temp. of data collection [K]	193	100
Crystal dimensions [mm]	~ 0.25 × 0.25 × 0.25	~ 0.30 × 0.25 × 0.25
Space group	$P2_1/c$	*Pnma*
Cell dimensions a [Å]	17.550(2)	21.358(4)
b [Å]	14.912(2)	16.042(3)
c [Å]	19.442(4)	13.179(3)
β [°]	115.94(2)	
Formula weight	1157.2	578.6
D_c [g/cm^3]	1.68	1.70
$\sin\theta/\lambda$ [Å^{-1}]	0.626	0.626
Scan mode	ω/θ	ω/θ
No. of symmetry equivalent orientations measured	1	2
No. of measured reflections	10311	10121
$R_{int} = (\Sigma_H \Sigma_N \lvert I_{H,i} - \langle I_H \rangle \rvert)/\Sigma_H N \langle I_H \rangle$		0.027
No. of unique reflections	9803	4801
No. of observed reflections ($I > 3\sigma(I)$)	7065	4100
No. of variables in final least-square analysis	832	438
Type of refinement	F	F
Exponentially modified weight factor r [Å^2]	5.0	5.0
Extinction correction	isotropic	isotropic
$R(F)$	0.045	0.049
$R_w(F)$	0.055	0.054

half molecules of CH_2Cl_2. However, both solvent molecules were so disordered that the structural parameters of the C_{70} skeleton could not be determined with the desired accuracy.

The structures were solved by direct methods and refined by full-matrix least-squares analysis (*SHELXTL PLUS*), using an isotropic extinction correction and an exponentially modified weight factor [13] (heavy atoms anisotropic, H-atoms isotropic, whereby H-positions are based on stereochemical considerations). Additional experimental details are summarized in *Table 1*, and further details of the crystal structure analysis are available upon request from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB12 1EZ (UK), on quoting the full journal citation.

3. Discussion of the Structures. – In a D_{5h}-C_{70} fullerene, there are five independent types of atom, giving rise to eight different types of bond (four [6,6] and four [6,5] bonds, respectively) and 11 distinct bond angles. The designation of bond types and angles used in this paper is given in *Fig. 1*. The numbering of the fullerene skeleton in *Figs. 2–5* refers to a paper by *Taylor* [14]. In *Fig. 5*, starred (*) and unstarred atoms of isomer **1b** are related by the mirror plane; the corresponding numbering used for **1a** is given in brackets. Estimated standard deviations (e.s.d.'s) from least-squares refinements are nearly the same in both structures; for bond lengths, they range from 0.002 Å to 0.004 Å, for bond angles from 0.1 to 0.3°. Standard deviations (s) of mean values (given in parentheses) are based on the equation $s = [\Sigma_m (x_m - \langle x \rangle)^2/(m-1)]^{1/2}$.

In solution, the cyclohexene ring of the *Diels-Alder* adducts can interconvert between two boat conformations. According to ^{1}H-NMR spectroscopic investigations, the average symmetry at 353 K is C_s for both adducts; on cooling to about 263 K, however, the symmetry of **1a** is reduced to C_1, whereas **1b** remains C_s-symmetrical [2]. The symmetry observed at low temperatures corresponds to that found in the crystal structures.

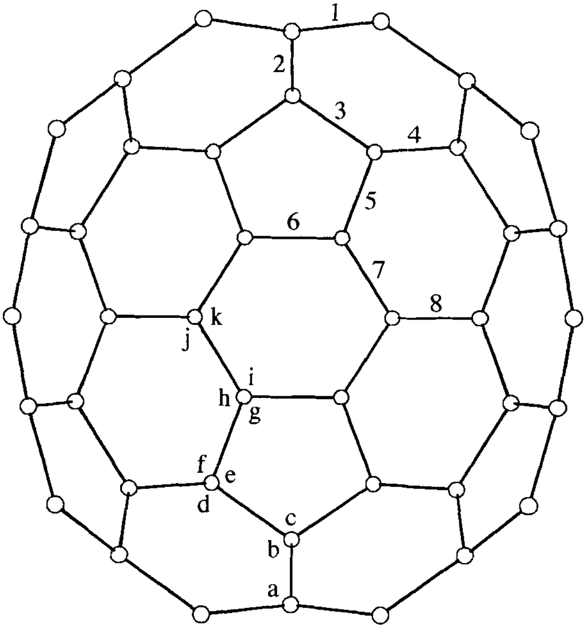

Fig. 1. *Symmetry-independent bonds and angles in a C_{70} molecule*

The molecular structures of **1a** and **1b** are shown in *Figs. 2* and *3*. Bond lengths for the two pyracylene sub-units, containing the bridgehead bonds are given in *Figs. 4* and *5*. Selected bond angles of these sub-units are given in *Table 2*.

The conformation of the tetrahydro-dimethoxynaphthalene moiety in **1a** and **1b**, as well as in the C_{60} adduct **2** [1d] is practically the same. In all three structures, the cyclohexene ring adopts a boat conformation, and the MeO groups are almost coplanar with the benzene rings. In **1a**, the angle between the mean planes of atoms C(1), C(9), C(71), C(76), and C(71), C(72), C(76), C(77) (see *Fig. 2*) is 127.0(3)°; the corresponding values in **1b** and in **2** are 127.4(3)° and 129.1(5)°, respectively.

The interatomic distance between the bridgehead atoms in **1a** and **1b** is 1.603 Å and 1.584 Å, respectively. The lengthening with respect to (mean) type 2 and type 4 [6,6] bonds (see *Table 3*) is 0.211 Å and 0.203 Å, respectively. The bridgehead–bridgehead bond lengths observed here agree within 0.012 Å with that obtained in **2** [1d].

The angle deformations at the bridgehead atoms are also very similar in the three derivatives. The angles in question range from 99.0° to 113.9° in **1a**, from 100.2° to 113.9° in **1b**, and from 99.5° to 114.4° in **2**, their (average) sums being 326.5°, 327.5°, and 327.4°, respectively. For comparison, the corresponding angle sum in a [6,6]-methano-bridged C_{60} fullerene [10] is *ca.* 10° larger.

The shortest [6,6] bonds in **1a** (see *Fig. 4*) are those on the edges of the bridged pyracylene sub-unit, as was also observed in the [6,6]-methano-bridged C_{60} structure [10]. The type-4 bonds C(7)–C(8) and C(10)–C(11), as well as the type-2 bonds C(5)–C(6) and C(2)–C(12), are *ca.* 0.02 Å shorter than the corresponding mean values given in

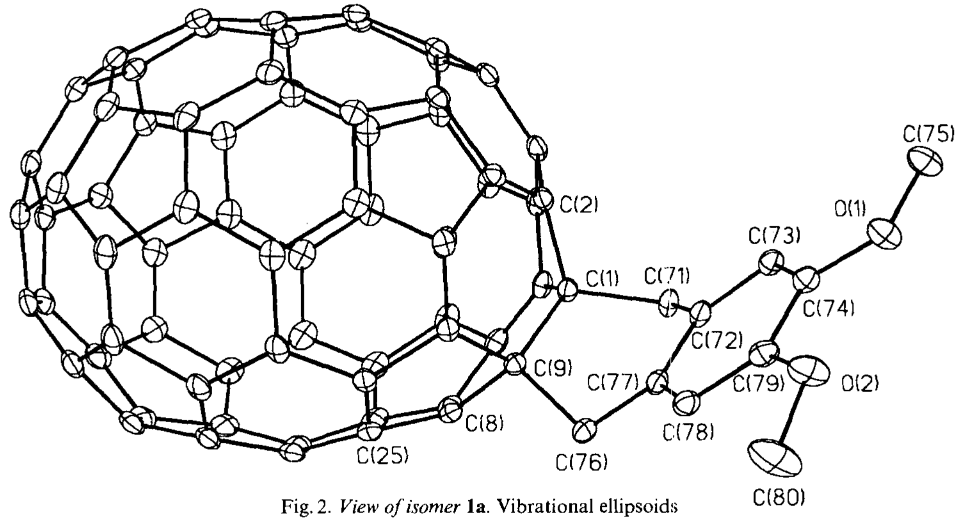

Fig. 2. *View of isomer* **1a**. Vibrational ellipsoids are shown at the 30% probability level.

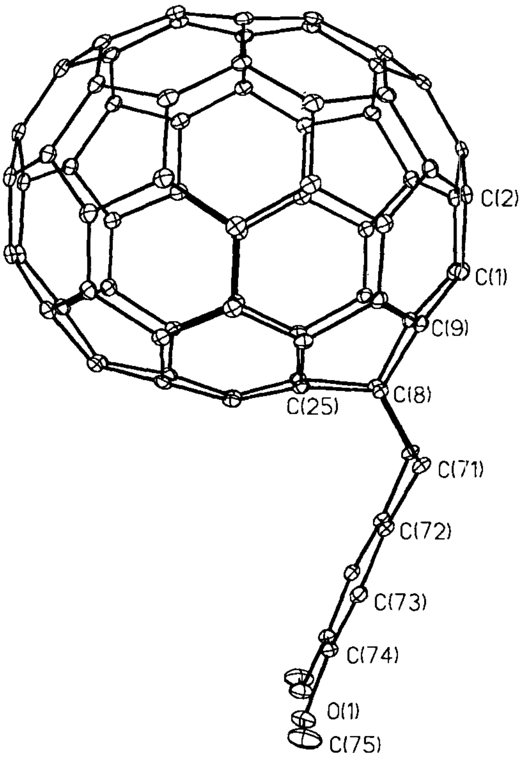

Fig. 3. *View of isomer* **1b**. Vibrational ellipsoids are shown at the 30% probability level.

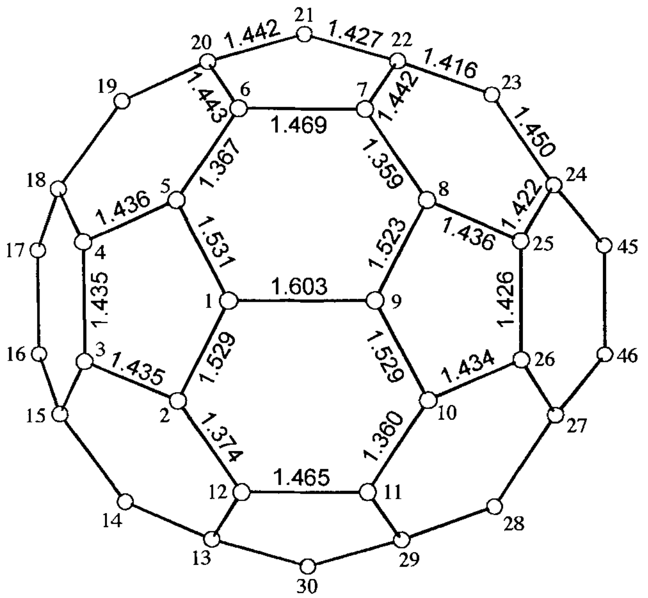

Fig. 4. *Bond lengths on the substituted pole of* **1a**. The corresponding bond angles are given in *Table 2*.

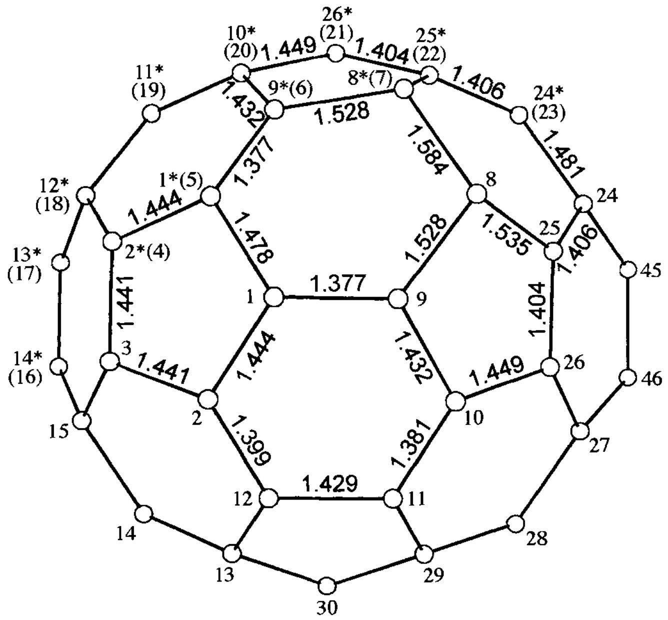

Fig. 5. *Bond lengths on the substituted pole of* **1b**. The corresponding bond angles are given in *Table 2*. Starred (*) and unstarred atoms are related by the mirror plane; the corresponding numbering used in *Fig. 4* is given in brackets.

Table 2. *Bond Angles* [°] *Obtained for the Substituted Pyracylene Moiety of* **1a** *and* **1b**

Angle [°]	**1a**	**1b**	Angle [°]	**1a**	**1b**
C(2)–C(1)–C(5)	99.0(1)	107.3(1)	C(1)–C(9)–C(8)	114.1(2)	125.5(2)
C(2)–C(1)–C(9)	113.6(2)	120.1(2)	C(1)–C(9)–C(10)	114.1(2)	119.1(2)
C(5)–C(1)–C(9)	113.9(2)	119.3(1)	C(8)–C(9)–C(10)	98.9(2)	109.3(2)
C(1)–C(2)–C(3)	110.6(2)	108.5(2)	C(9)–C(10)–C(11)	125.0(2)	121.8(2)
C(1)–C(2)–C(12)	124.5(2)	120.0(2)	C(9)–C(10)–C(26)	110.5(2)	108.4(2)
C(2)–C(3)–C(4)	108.0(2)	108.4(2)	C(10)–C(11)–C(12)	119.9(2)	119.3(2)
C(3)–C(4)–C(5)	108.2(2)	108.5(2)	C(2)–C(12)–C(11)	120.5(2)	119.7(2)
C(1)–C(5)–C(4)	110.4(2)	107.3(1)	C(6)–C(20)–C(21)	109.0(2)	108.4(2)
C(1)–C(5)–C(6)	124.2(2)	119.3(1)	C(20)–C(21)–C(22)	108.0(2)	108.6(2)
C(5)–C(6)–C(7)	120.5(2)	125.5(2)	C(7)–C(22)–C(21)	108.6(2)	110.1(2)
C(7)–C(6)–C(20)	106.5(2)	109.3(2)	C(7)–C(22)–C(23)	121.8(2)	125.7(2)
C(6)–C(7)–C(8)	120.1(2)	113.9(1)	C(22)–C(23)–C(24)	117.8(2)	118.1(1)
C(6)–C(7)–C(22)	107.9(2)	100.2(1)	C(23)–C(24)–C(25)	118.2(2)	118.1(1)
C(8)–C(7)–C(22)	120.7(3)	113.4(1)	C(8)–C(25)–C(24)	122.5(2)	125.7(2)
C(7)–C(8)–C(9)	124.9(2)	113.9(1)	C(8)–C(25)–C(26)	108.1(2)	110.1(2)
C(7)–C(8)–C(25)	118.6(2)	113.4(1)	C(10)–C(26)–C(25)	108.2(2)	108.6(2)
C(9)–C(8)–C(25)	110.6(2)	100.2(1)			

Table 3. In **1b**, the shortest [6,6] bond (1.377 Å) is the type-2 bond C(1)–C(9). The [6,5] bonds in **1a** and **1b**, connected to the bridgehead atoms, range from 1.523 Å to 1.535 Å.

The average bond lengths and bond angles in **1a** and **1b** are listed in *Tables 3* and *4* and refer to the unsubstituted halves of the fullerene skeletons. *Table 3* shows that the mean bond lengths agree on the whole very well with those obtained for unsubstituted C_{70} compounds from X-ray and neutron-diffraction experiments, as well as with those obtained from theoretical calculations. Remarkable is the significant lengthening (to *ca.* 1.47 Å) of the [6,6] bond 8 at the equator, which strongly contrasts with the short [6,6] bonds near the poles. Likewise, the bond angles given in *Table 4*, and those based on *ab initio* calculations show good agreement. The excellent agreement among the X-ray diffraction results (**1a**, **1b**, and [8c]) may be somewhat misleading, since the individual refinements are based on low-order data. One can expect that refinements based on high-order data would lead to a slight expansion of the spheroids and thus to somewhat longer bond lengths (possibly up to 0.005 Å). Note that a correction for librational motion [15] would increase the bond lengths in **1a** and **1b** by *ca.* 0.002 and 0.001 Å, respectively.

The five- and six-membered rings at the unsubstituted poles are planar within 0.002 Å in both molecules. The rings at the bridged pyracylene unit show marked deviations from

Table 3. *Experimental and Calculated C· · · C Distances Obtained for the Different Types of Bond in* C_{70}. Values given for **1a** and **1b** refer to the unsubstituted halves of the C_{70} spheres.

Bond	**1a** This work	**1b** This work	C_{70} [8c]	C_{70} [9]	C_{70} [12a]	C_{70} [12b]	C_{70} [12c]
1	1.447(5)	1.449(6)	1.453(3)	1.459(4)	1.448	1.451	1.4608
2	1.393(4)	1.391(9)	1.387(4)	1.385(7)	1.393	1.375	1.3788
3	1.445(6)	1.450(4)	1.445(3)	1.449(6)	1.444	1.446	1.4553
4	1.378(3)	1.384(3)	1.378(3)	1.376(7)	1.386	1.361	1.3643
5	1.448(3)	1.447(6)	1.447(2)	1.46(1)	1.442	1.457	1.4702
6	1.428(3)	1.431(4)	1.426(3)	1.438(4)	1.434	1.415	1.4174
7	1.417(3)	1.415(9)	1.414(2)	1.417(6)	1.415	1.407	1.4136
8	1.460(7)	1.470(9)	1.462(4)	1.479(7)	1.467	1.475	1.4859

Table 4. *Experimental and Calculated Bond Angles in C_{70}.*
Values given for **1a** and **1b** refer to the unsubstituted halves of the C_{70} skeletons. Note that the mean bond angle in the central pentagons at the unsubstituted poles is 108.0(3)°.

Bond angles	**1a** This work	**1b** This work	C_{70} [12b]	C_{70} [12c]
a	119.7(3)	119.9(2)		119.59
b	120.2(2)	120.0(2)	120.3	120.34
c	107.2(1)	106.8(3)		106.79
d	120.1(2)	120.1(1)		120.07
e	108.3(2)	108.5(4)	108.4	108.38
f	119.9(2)	119.8(2)		120.04
g	108.1(2)	108.0(3)		108.22
h	121.2(2)	121.4(4)	121.4	121.24
i	121.3(2)	121.2(2)		121.57
j	118.8(2)	118.6(6)	118.5	118.53
k	116.2(3)	116.1(3)		115.78

planarity, as observed in other substituted fullerene structures. The five-membered rings containing the bridgehead atoms have practically identical envelope conformations, *i.e.*, the bridgehead atom is out-of-plane by *ca.* 0.3 Å with respect to the remaining four coplanar atoms. The six-membered rings containing the bridgehead atoms have a slight out-of-plane deformation towards a boat conformation. In **1a** (see *Fig. 4*), C(2) and C(10) deviate by *ca.* 0.13 Å from the four coplanar atoms C(1), C(9), C(11), C(12); the corresponding deviations of C(5) and C(8) in the opposite ring are practically identical. In **1b** (*Fig. 5*), the two six-membered rings containing the bridgehead atoms have slightly different shapes, *i.e.*, the corresponding deviations of C(25) and C(25*), and C(9) and C(9*), are *ca.* 0.2 and 0.14 Å, respectively. The six-membered rings in the equatorial region of the spheroids exhibit a similar boat-like conformation, as described in [3a] [8c]. In each hexagon, the two C-atoms lying on the equator deviate by *ca.* 0.14 Å, with respect to the remaining four coplanar atoms.

The addition at two different sites leads to slightly different spheroidal shapes. The distance between the centers of the opposite poles is 7.98 Å in **1a** and 7.92 Å in **1b**. The distances between the center of the spheroid and the individual C-atoms lying on the equator vary between 3.525 Å and 3.575 Å (mean 3.549 Å) in **1a**, and between 3.530 Å to 3.564 Å (mean 3.552 Å) in **1b**.

Finally, the pyramidality has been estimated for the atom pairs involved in [6,6] bonds near the unsubstituted pole and near the equator. As mentioned in the introduction, the *Diels-Alder* addition to C_{70} takes place preferentially at the C(1)–C(9) (type 2) bond, although its π-bond order is considered to be somewhat smaller than that of a C(7)–C(8) (type 4) bond [14]. According to *Hawkins et al.* [3c], the regioselectivity observed for the osmylation of C_{70} can be correlated with the degree of local curvature (estimated *via* σ-π interorbital angles [6]) of an *ab initio* calculated C_{70} structure.

In this analysis, the pyramidality at a given atom is expressed by the difference between 360° and the sum (S) of the three bond angles at that atom (this approach has the advantage that the pyramidality does not depend on the bond lengths, as does, for example, the distance of the atom from the plane of its three bonded neighbors). The results, summarized in *Table 5*, show that the largest pyramidality occurs at atom pairs involved in C(1)–C(9) (type 2) bonds, their mean S values being 12.5° and 12.6° for **1a**

Table 5. *Estimates of the Mean Pyramidality of Atoms Involved in [6,6] Bonds Near the Unsubstituted Poles and Near the Equator in* **1a** *and* **1b**. $S = 360° -$ sum of bond angles.

Bond	Mean S values					
	1a			**1b**		
C(1)$\overset{2}{-}$C(9)	12.5(2)		12.6(3)	12.2(4)		13.1(2)
C(7)$\overset{4}{-}$C(8)		11.6(2)			11.6(2)	
C(22)$\overset{7}{-}$C(23)	9.4(2)		6.7(5)	9.3(4)		6.8(3)
C(23)$\overset{8}{-}$C(24)		6.7(5)			6.8(3)	

and **1b**, respectively, followed by the atoms involved in C(7)–C(8) bonds, which exhibit mean S values of 11.6°. The atoms near the equator are much less pyramidalized, as expected. Hence, the trend found here is similar to that derived in the calculations by *Hawkins et al.* [3c].

4. Crystal Packing. – In several crystal structures, short intermolecular contacts among fullerenes (or between fullerenes and co-crystallized solvent molecules) have been observed and interpreted mainly in terms of (weak) donor-acceptor interactions. Similar short-range interactions occur in the crystal structures of isomers **1a** and **1b** (since the (mean) atomic positions of the highly disordered CS_2 molecules were located from difference-density maps, short intermolecular distances involving these molecules are neglected here).

Fig. 6 shows a layer of **1a** and solvent molecules parallel to the (0 0 1) plane of the monoclinic unit cell. All molecules are in general positions; the ordered CS_2 molecules lie roughly parallel to b, the disordered ones roughly parallel to c. The calculated density of 1.68 g/cm^3 suggests that the packing is quite compact. Indeed, each fullerene molecule is involved in two short C···S contacts of *ca.* 3.4 Å, seven C···C contacts between 3.2 Å and 3.35 Å, and one C···O contact of 3.08 Å, between C(41) and a methoxy O-atom of a neighboring adduct (indicated in *Fig. 6*). A similar short C···O distance of 3.07 Å has been found for **2**, which co-crystallizes with benzene in the space group $P2_1/n$ [1d] [5].

Fig. 7 shows a layer of **1b** and solvent molecules parallel to the (1 0 0) plane of the orthorhombic unit cell. The mirror-symmetric fullerene molecules are located on crystallographic mirror planes, the ordered CS_2 molecules on inversion centers. The other CS_2 molecules (with one S-atom lying an a mirror plane) are statistically disordered. According to a recent attempt to frame a 'grammar of crystal packing' [16], the space group *Pnma* occurs almost exclusively, when the mirror planes are occupied by mirror-symmetric molecules, as in the present case.

The packing of isomer **1b**, based on its calculated density (1.70 g/cm^3), as well as on the analysis of intermolecular contacts is even more compact than that of **1a**. Each fullerene molecule is involved in 2 C···S contacts of *ca.* 3.5 Å and 10 C···C contacts between 3.06 Å and 3.35 Å. The shortest of these (roughly parallel to the diagonals of the (0 0 1) plane, see *Fig. 7*) occurs between C(10) and C(50). The second shortest C···C contact (3.12 Å) occurs between the atoms C(74) and C(74*) of the mirror-symmetric adduct and C(67) of a neighboring C_{70} sphere. The overall arrangement, indicated in *Fig. 7*, is a hexagonal

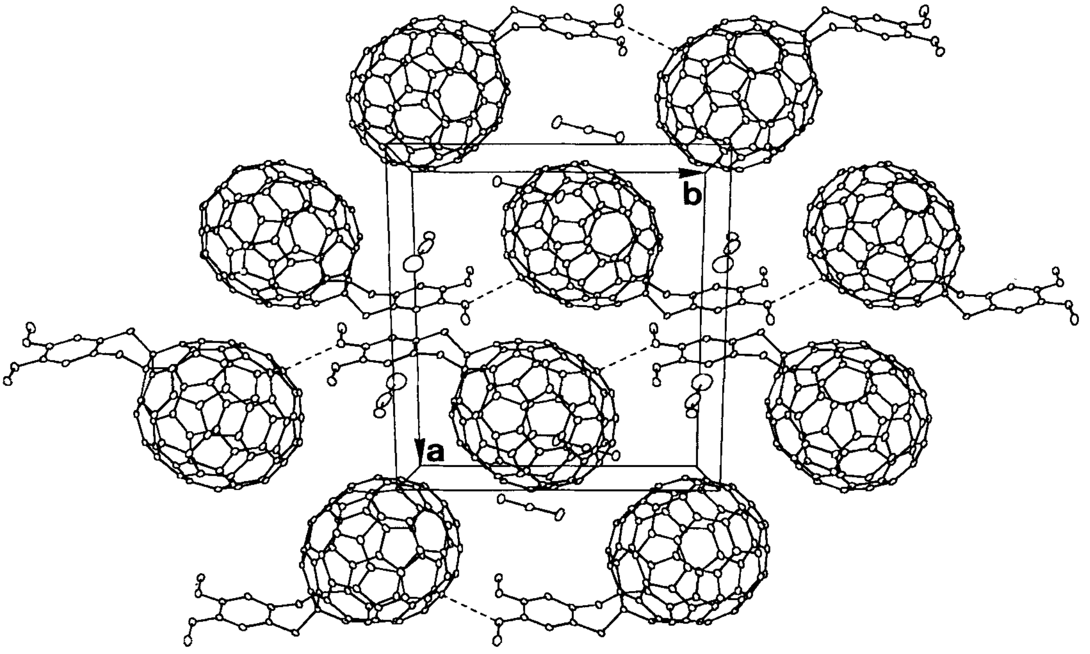

Fig. 6. *A layer of* **1a** *and* CS_2 *molecules, projected to the (0 0 1) plane, showing short C···O contacts*

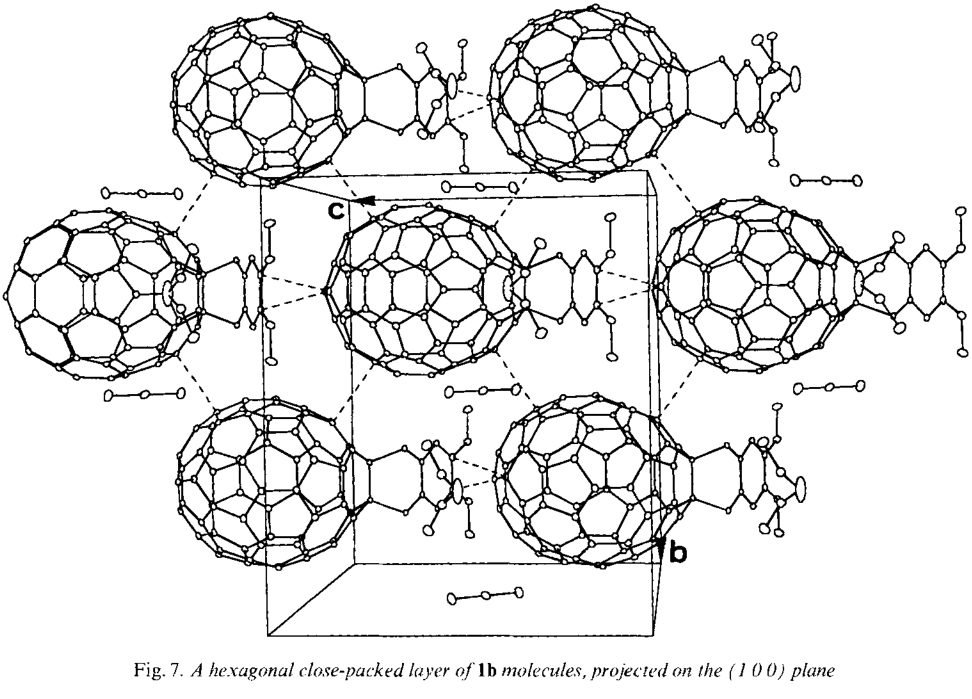

Fig. 7. *A hexagonal close-packed layer of* **1b** *molecules, projected on the (1 0 0) plane*

close-packed layer. The C···O distance between the methoxy O-atom and the C_{70} sphere is 3.2 Å, appreciably longer than in **1a** and the C_{60} derivative. Thus, the pattern of short-range interactions in the two crystal packings is appreciably different, in spite of the similarity of the two molecules.

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