

Low-Temperature Synchrotron Radiation Study of a Twinned Disordered Crystal of Bis(4,4'-bromophenyl)-61,61-diyl Methano Fullerene C₆₀

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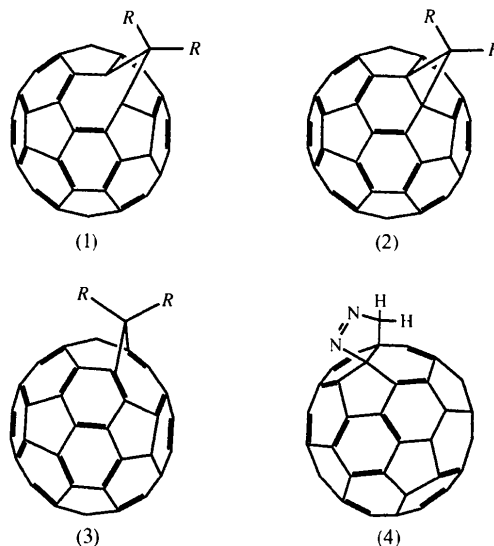
Abstract

Synchrotron radiation diffraction measurements at 100 (5) K have been carried out on bis(4,4'-bromophenyl)-61,61-diyl methano fullerene C₆₀ using area detector technology. In order to obtain a satisfactory description of the data it is necessary to introduce both a twinning model of the crystal and a disorder model consisting of two different isomers of the title compound. The study provides the first solid-state characterization of a 6–5 isomer of a methano fullerene. For the 6–6 isomer the geometry is in good agreement with recent literature on methano fullerenes. Unfortunately, the present study cannot resolve the bond lengths in the transannular region. The fact that the structure can be solved from diffraction data measured on a minute poorly scattering crystal shows that the low-temperature single-crystal synchrotron radiation technique is an indispensable tool in chemical crystallography.

1. Introduction

The reactions of C₆₀ with organic diazo compounds constitute a versatile approach to fullerene derivatization (Suzuki *et al.*, 1991; Wudl, 1992; Taylor & Walton, 1993; Diederich *et al.*, 1994). At first it was suggested that all diazomethane adducts contained the ring-opened structure (1), but later this assignment was revised to the closed 6–6 structure (2) on the basis of NMR structural analysis and energy minimization calculations (Prato *et al.*, 1993). Compounds of the open 6–5 structure (3) are known and in the case of R = H, it is the major isomer found upon thermolysis of the adduct (4) (Smith *et al.*, 1993).

In the past few years several solid-state structures of methano fullerenes have been solved: (a) 3,4-dimethoxyphenylphenyl methano fullerene (Osterodt *et al.*, 1994), (b) diethylmethano fullerene (Paulus & Bingel, 1995), (c) 61,61-bis(trimethylsilylbutadiynyl)-1,2-dihydro-1,2-methano fullerene (Anderson *et al.*, 1994) and (d) bis(4-methoxyphenyl)methano fullerene (Tezuka *et al.*, 1996). All these structures are of the



closed 6–6 form with transannular distances of 1.614 (7) (a), 1.606 (4) (b), 1.574 (3) (c) and 1.635 (4) Å (d). Recently evidence for open 6–6 bonds has been presented in the case of higher addition products such as C₆₀(NCOOR)₂, where R = Et, Bu' (Schick *et al.*, 1996). Based on semi-empirical calculations and NMR evidence Diederich *et al.* (1994) suggested that the large substituent effect on the transannular bond seen for methano[10]annulenes is much decreased in the case of methano fullerenes. They concluded that all 6–6 compounds have the closed form and all 6–5 compounds the open form. In their calculations the energy difference between 6–6 bonds of 1.6 and 1.9 Å, respectively, was less than 40 kJ mol⁻¹. Raghavachari & Sosa (1993) carried out semi-empirical, *ab initio* and density functional calculations on the parent methano fullerene (R = R' = H), and found the 6–6 isomer to be of the closed form with about 25 kJ mol⁻¹ difference between 6–6 forms having 1.6 and 1.9 Å bond lengths, respectively. With regard to the relative stability of the 6–6 and the 6–5 isomers the theoretical calculations are inconclusive.

The present paper reports a low-temperature structural investigation of a twinned crystal containing both 6–6 and 6–5 isomers using synchrotron radiation in

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combination with imaging plate technology. Preliminary results of a conventional X-ray structure determination on the same crystal specimen were given earlier (Wudl, 1992), but in that study a model without twinning and disorder could not be refined to acceptable R values. It is the use of area detector technology in combination with intense synchrotron radiation that has revealed the much more complex nature of the crystal structure. A number of attempts to interpret less extensive data sets measured on smaller crystal specimens from the same batch of crystals has been unsuccessful.

2. Experimental

The crystal used in the measurements was obtained from the diazo compound (Wudl, 1992). Purification of the compound has later been achieved in solution, but no crystals of the pure isomer were isolated (Wudl, 1995). The data were measured at the National Synchrotron Light Source at the SUNY beamline X3A1, which is a fixed wavelength beamline equipped with an Huber four-circle diffractometer. The synchrotron beam is monochromated with a Si(111) bent crystal providing a wavelength of 0.643 (1) Å. Cooling to approximately 100 (5) K was achieved with a Displex helium refrigerator fitted with an *anti*-scattering device for imaging plate measurements (Darovsky *et al.*, 1994). The intensities were indexed and integrated with the *IPMS* and *HIPPO* programs, which employ the seed-skewness integration method (Bolotovskiy *et al.*, 1995). The mosaicity of the crystal (0.25°) was estimated from ω scans of selected reflections using a scintillation counter. The data were absorption corrected using the program *ABSORB* (DeTitta, 1982). Subsequently, the data were scaled and equivalent reflections were averaged in Laue group $2/m$ using the program *SORTAV* (Blessing, 1989). The space group was determined from systematic absences. Earlier difficulties with the structure could not be attributed to the wrong choice of space group as, for instance, the $h0l$, $l = \text{odd}$ reflections have significant intensity, thereby ruling out the more common space group $P2_1/c$ in place of $P2_1/m$. Owing to the uncertainty in the thickness of the very plate-like crystal, the absorption correction was optimized with regard to the internal agreement factor by slightly varying the crystal dimensions. In Table 1 crystallographic data and experimental conditions for the present study are given.

2.1. Structure solution and refinements

Structure solution was attempted with direct methods using the program *SIR92* (Altomare *et al.*, 1994), but only the Br atom could be located. When examining the structure factor list it became apparent that reflections with h even and l odd were systematically absent. This can be explained by a twinning model in which the b^* and c^* axes of the monoclinic crystals are common to

Table 1. *Experimental details*

Crystal data	
Chemical formula	C ₇₃ H ₆ Br ₂
Chemical formula weight	1044.68
Cell setting	Monoclinic
Space group	$P2_1/m$
a (Å)	9.863 (2)
b (Å)	17.36 (1)
c (Å)	11.19 (5)
β (°)	102.44 (1)
V (Å ³)	1871
Z	2
D_x (Mg m ⁻³)	1.117
Radiation type	Synchrotron
Wavelength (Å)	0.643 (1)
No. of reflections for cell parameters	14
θ range (°)	5–12
μ (mm ⁻¹)	2.202
Temperature (K)	100 (2)
Crystal form	Elongated hexagonal plates
Crystal size (mm)	\pm (001) 0.008, \pm (010) 0.06 \pm (100) 0.06, \pm (110) 0.02
Crystal color	Red–brown
Data collection	
Diffractometer	Huber four-circle
Data collection method	φ rotation
Area detector	Fuji image plates (20 × 25 cm), BA2000 off-line scanner, 0.1 × 0.1 mm pixel resolution, 10 ⁴ dynamic range
Crystal-to-detector distance (mm)	13.6
Orientation matrix	Scintillation detector, setting angles of low-order reflections
Range of data	8° oscillation, 2° overlap between plates, 182° total rotation
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.58
Absorption correction	ω scans
T_{\max}	0.83
T_{\min}	0.68
No. of measured reflections	3903
No. of independent reflections	1390
No. of observed reflections	1980
Criterion for observed reflections	$3\sigma(I)$
R_{int}	0.042
θ_{\max} (°)	21.9
Range of h, k, l	$-11 \rightarrow h \rightarrow 11$ $-17 \rightarrow k \rightarrow 17$ $-24 \rightarrow l \rightarrow 24$

both twin components, while two a^* axes point to opposite sides of the b^*c^* plane, see Fig. 1. Cell dimensions are such that reflections with $h = h' = \text{even}$ are common overlapping reflections, while reflections with $h = h' = \text{odd}$ belong to one of the two twin components. The correct cell therefore has a c^* axis twice as long as that of the cell originally calculated from the diffractometer setting angles. The twin ratio was determined from the intensities of the non-overlapping $h = \text{odd}$ reflections and used to 'detwin' the data set (Giacovazzo, 1992). With the detwinned data

Table 2. Refinement residuals

	N_{obs}	N_{par}	R_F	$R_{w,F}$	g.o.f.	Max. Δ/σ	Ave Δ/σ	Max./Min. residual peak ($e \text{ \AA}^{-3}$)	Weighting scheme
Single-isomer TLS model	1378	147	0.070	0.080	1.27	0.000	0.000	1.18, -0.72	$1/\sigma^2$
Single-isomer individual U 's	1378	343	0.042	0.043	0.75	0.003	0.000	0.69, -0.32	$1/\sigma^2$
Two-isomer TLS model, 6-6 open, 6-5 closed	1378	192	0.033	0.037	0.60	0.20	0.04	0.26, -0.26	$1/\sigma^2$
Two-isomer TLS model, 6-6 closed, 6-5 open	1378	192	0.033	0.037	0.60	0.45	0.03	0.26, -0.25	$1/\sigma^2$

set a straightforward structure solution was obtained with *SIR92* (Altomare *et al.*, 1994), see Fig. 2.

To refine the structure the TLS formalism (Schomaker & Trueblood, 1968) with rigid-body thermal motion parameters, T (translation), L (libration) and S (correlation), was used. At the same time refinement of the twin ratio was introduced using the original twinned data set in the refinements. The program *SDS94* (Petricek, 1994) was used for the refinement, in which only reflections with $I > 3\sigma(I)$ were included. The first structural model to be tested contained one 6-6 isomer and employed 147 parameters, which were refined against 1378 observations. At this point 12 reflections had been removed because they had $F_{\text{obs}} \gg F_{\text{calc}}$ due to integration errors. The molecule in this model corresponds to a 6-6 isomer with the transannular bond in the mirror plane. A one-isomer model was refined both with TLS parameters and with individual anisotropic displacement parameters. The results are given in Table 2. The R values for the one-isomer model were not unreasonable, but several features of the refined models were unsatisfactory. In the C₆₀ moiety a number of bond lengths had unrealistic values and the spread among supposedly equivalent bonds was too large ($\sim 0.4 \text{ \AA}$). Furthermore, in both models many atoms in the C₆₀ moiety had too large thermal motion parameters ($\sim 0.15 \text{ \AA}^2$) compared with values normally obtained at 100 K. In subsequent refinements a second 6-5 isomer was added to the model. Only the C₆₀ moiety of a 6-5 isomer was added, whereas the substituent atoms were assumed to superimpose for

both species. Based on Fourier maps the 6-5 isomer was placed with the bond in the mirror plane, even though the 6-5 bond is not in a mirror plane of the molecule. In Fig. 3 the central transannular regions of the two isomers are shown.

In the model refinement the two C₆₀ moieties were allowed separate TLS thermal parameters. The atoms in the major component 6-6 isomer were allowed free refinement of positional parameters, while the atoms of the minor 6-5 component were constrained to rigid-body motion. Only the positions of the crucial atoms in the transannular region were allowed to refine freely in the 6-5 isomer. The phenyl group atoms were refined with common TLS thermal parameters and individual positional parameters. The H atoms were kept fixed at calculated positions. The Br atom and the methano C atom were refined freely with anisotropic displacement parameters. Together with refinement on isotropic extinction [type I, Becker & Coppens (1974), Lorentzian distribution], two scale factors and population parameters for the C₆₀ groups, this model had 192 parameters. The two-isomer model results in a large

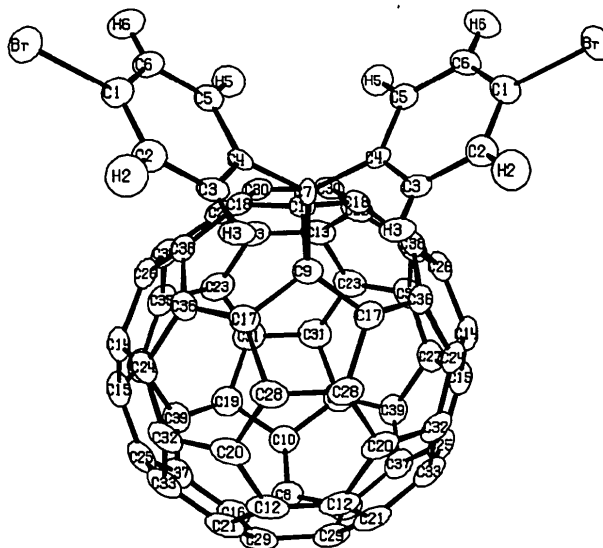


Fig. 2. ORTEP drawing (Johnson, 1976) of the major 6-6 isomer of bis(4,4'-bromophenyl)-61,61-diyl methano fullerene C₆₀ showing 50% ellipsoids and the atom numbering scheme.

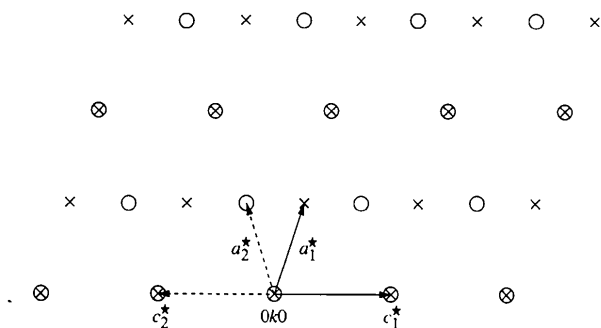


Fig. 1. Sketch of the twin lattices showing the common c^* axes and the different a^* axes.

improvement in the refinement residuals, which are listed in Table 2. Since especially the TLS parameters of the two C_{60} groups tend to oscillate in the least-squares procedure, the shifts were dampened. With the two-isomer model the anomalies observed for some of the 6-6 isomer C atoms in the single isomer model have disappeared and the bond lengths and angles in the C_{60} moiety away from the transannular region are in good

agreement with values found for other methano fullerenes. However the transannular distance is 2.01 (3) Å for the 6-6 isomer and 1.5 (2) Å for the 6-5 isomer. Compared with literature values for the 6-6 bond and theoretical predictions for the 6-5 bond, the two bonds have been interchanged. We therefore constrained the transannular 6-6 bond to be 1.600 Å, using the existing structural information summarized above, and refined the remainder of the parameters. This causes the 6-5 transannular atoms to move apart. In the final cycles it was possible to release the 6-6 bond and refine all parameters simultaneously. In the final model the 6-6 bond has opened up slightly to a distance of 1.76 (3) Å, while the 6-5 bond is 1.87 (14) Å. The minimum in χ^2 is extremely flat and the R values are basically unchanged compared with the model with interchanged transannular bonds. In both two-isomer models slightly nonpositive values are obtained for the L tensors of the phenyl group and of the minor C_{60} component, as well as for the T tensor of the latter. The final populations are 0.660 (8) for the major 6-6 isomer and 0.340 (8) for the minor 6-5 isomer, while the twin fractions are 0.2952 (5) and 0.7048 (5). Selected bond distances and bond angles are listed in Tables 3 and 4, respectively. A crystal packing diagram showing only the 6-6 isomer is shown in Fig. 4.†

† Lists of atomic parameters, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: BK0044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

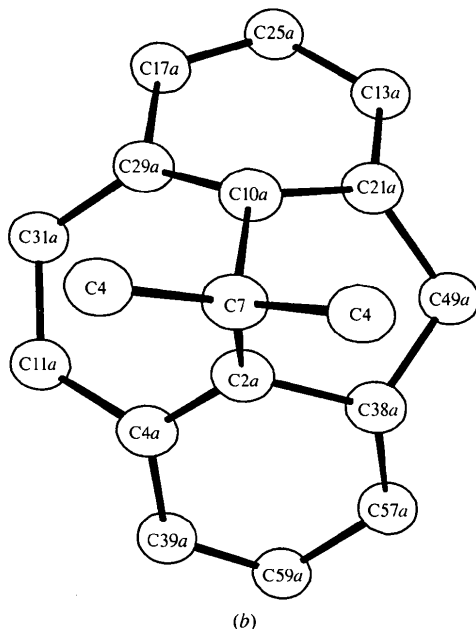
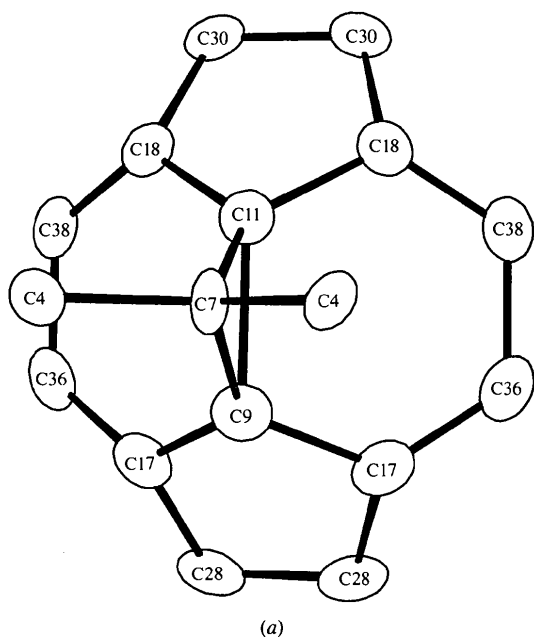


Fig. 3. ORTEP drawing (Johnson, 1976) of the central transannular regions, (a) is the 6-6 isomer and (b) the 6-5 isomer. In (b) the thermal parameters have been altered to arbitrary values for plotting due to slightly negative values on some of the atoms.

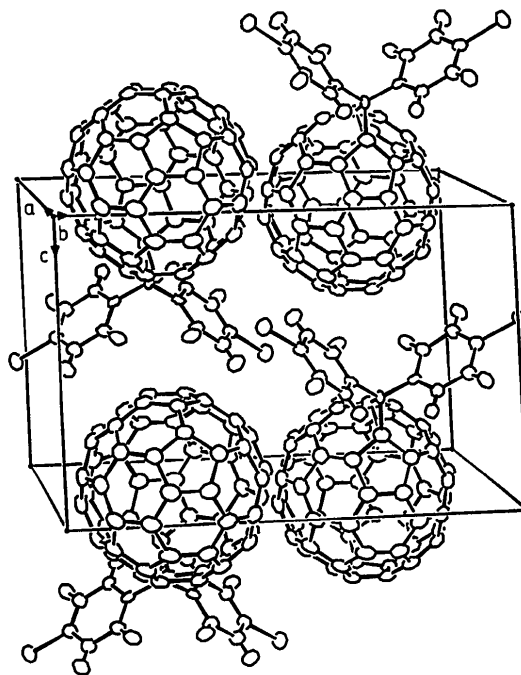


Fig. 4. Crystal packing diagram showing only the major 6-6 isomer of bis(4,4'-bromophenyl)-61,61-diyl methano fullerene C_{60} .

Table 3. Selected bond lengths (Å)

a refers to atoms belonging to the minor 6-5 isomer.

6-5 isomer		6-6 isomer	
C2a—C10a	1.87 (14)	C9—C11	1.76 (3)
C2a—C7	1.47 (8)	C7—C9	1.48 (2)
C10a—C7	1.66 (9)	C7—C11	1.42 (2)
C2a—C9	0.29 (7)	C9—C17	1.46 (2)
C10a—C11	0.34 (11)	C11—C18	1.46 (2)

Table 4. Selected bond angles (°)

a refers to atoms belonging to the minor 6-5 isomer.

C17—C9—C17'	105 (2)	C7—C9—C11	51 (1)
C18—C11—C18'	103 (1)	C7—C11—C9	54 (1)
C11—C9—C17	109 (1)	C4—C7—C2a	116 (5)
C9—C11—C18	119 (1)	C4—C7—C10a	114 (6)
C4—C7—C9	115.3 (5)	C2a—C7—C10a	73 (5)
C4—C7—C11	117.9 (5)	C7—C2a—C10a	58 (4)
C9—C7—C11	75 (1)	C7—C10a—C2a	49 (4)

3. Discussion

Since the transannular region contains two sets of atoms close to each other, correlations between parameters result in rather large e.s.d.'s on the transannular distances. To better resolve the structural features in this region high-order data are needed, but even the very intense synchrotron beam in combination with low temperatures and a very sensitive detector did not give observable diffraction intensities beyond 0.58 \AA^{-1} . The present study presents the first solid-state characterization of a 6-5 methano fullerene. Unfortunately, the data do not allow unconstrained refinement of the structural parameters of the atoms belonging to the 6-5 isomer. Clearly it would be of interest to be able to isolate and characterize the pure isomers in order to better determine the features of methano fullerene structures. It seems that the question of the transannular bond length can only be put firmly to rest if crystals of the pure isomers can be made.

If we disregard the transannular bond the average distance for the double bonds in the 6-6 isomer is $1.381 (4) \text{ \AA}$ compared with 1.39 \AA for (*a*) (Osterodt *et al.*, 1994), $1.393 (5) \text{ \AA}$ for (*b*) (Paulus & Bingel, 1995) and $1.391 (5) \text{ \AA}$ for (*c*) (Anderson *et al.*, 1994). The standard deviation on this number is found from the scatter of the bond lengths and it is less than half the size of a typical least-squares error on the individual bonds. For the fullerene single bond the corresponding value is $1.444 (4) \text{ \AA}$ compared with 1.44 \AA in (*a*), $1.453 (4) \text{ \AA}$ in (*b*) and $1.449 (5) \text{ \AA}$ in (*c*). The bond angles are generally within 2° ($= 2 \text{ e.s.d.'s}$) of 120° in the six-membered rings and within 2° of 108° in the five-membered rings. The good agreement with other studies of methano fullerenes indicates that only the immediate surroundings of the carbene attachment are influenced by the derivatization. With regard to the

phenyl ring the geometry is in good agreement with typical distances listed in *International Tables for Crystallography* (1992, Vol. C).

4. Conclusions

The study shows the advantage of area-detector data collection in revealing twinning of the crystal which had hitherto left the structure unsolved. Furthermore, the large intensity of the synchrotron beam makes it possible to measure enough reflections from a poorly scattering crystal to allow use of a sophisticated crystallographic two-isomer model. Poorly scattering crystals of minute dimensions are often the only available crystals of fullerene derivatives. In such cases it is clear that synchrotron radiation is an indispensable tool in chemical crystallography.

The present diffraction study of bis(4,4'-bromophenyl)-61,61-diyl methano fullerene C₆₀ affords the first solid-state structural characterization of a 6-5 isomer of a methano fullerene. However, due to the complexity of the crystallographic model the bond lengths in the transannular region for both the 6-6 and the 6-5 isomer remain inaccurate. For the atoms away from the immediate surroundings of the carbene attachment the structural parameters are in good agreement with other studies of methano fullerenes.

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