

146. The Crystal Structure of $C_{70} \cdot 6(S_8)$ at 100 K

by Hans Beat Bürgi* and Paloth Venugopalan

Laboratorium für Kristallographie, Universität Bern, CH-3012 Bern

Dieter Schwarzenbach

Institut de Cristallographie, Université de Lausanne, BSP, CH-1015 Lausanne

and François Diederich and Carlo Thilgen

Laboratorium für organische Chemie, ETH-Zentrum, CH-8092 Zürich

(8.VI.93)

The crystal structure of $C_{70} \cdot 6(S_8)$ at 100 K shows C_{70} to be ordered and the S_8 molecules to be partially disordered. The symmetry of C_{70} is D_{5h} to within experimental accuracy.

Crystal structures of several phases containing unsubstituted C_{60} have been determined by single(or twinned)-crystal X-ray diffraction: the cubic low-temperature phase of C_{60} (at 110, 153, and 200 K) [1], the cubic room-temperature phase of C_{60} [2], several phases of C_{60} co-crystallized with organic molecule: $C_{60} \cdot 3(C_6H_6O_2)$ [3], $C_{60} \cdot 2(C_{10}H_8S_8)$ (at 150 K) [4], $C_{60} \cdot CS_2 \cdot (C_{20}H_{16}S_{16})$ [5], $C_{60} \cdot C_6H_6 \cdot CH_2I_2$ [6], and $C_{60} \cdot 4(C_6H_6)$ (at 173 [7] and 104 K [8]). In all of these structures, C_{60} is disordered or shows very large amplitudes of motion. Here, we describe a structure determination of the phase $C_{70} \cdot 6(S_8)$ at 100 K with ordered C_{70} molecules.

The results of a previous study of this compound at room temperature [9] were unsatisfactory for several reasons: 1) Some chemically *equivalent* C—C bond lengths, with e.s.d.'s quoted as 0.03 Å, differed by more than 0.2 Å which is chemically very unlikely. The differences between chemically *inequivalent* distances expected on the basis of quantum chemical calculations is only ~ 0.12 Å [10]. Hence, the experiment [9] cannot distinguish reliably between inequivalent C—C bonds. 2) If the refined distances of chemically equivalent bonds are averaged they agree well with theory [9] [10]. It has not been tested, however, whether a model consisting of C_{70} molecules with averaged bond lengths accounts for the diffraction data as well as the one which is not averaged. 3) The resolution of the diffraction data was limited to ~ 1 Å and the R values seemed rather high for an ordered structure ($R(|F|) = 6.5\%$, $wR(|F^2|) = 7.1\%$).

Thin platelets of $C_{70} \cdot 6(S_8)$ with well developed (100) faces were obtained, as described in [9], by slow evaporation of a CS_2 solution of C_{70} and S_8 in relative amounts of 1:6¹⁾.

¹⁾ *Crystal Data.* Dark platelets of $C_{70} \cdot 6(S_8)$, orthorhombic, space group $Amm2$ with $a = 37.953$, $b = 20.241$, $c = 10.226$ Å at 100 K, $Z = 4$, graphite monochromatized MoK_α radiation ($\lambda = 0.71069$ Å). Scan angle and counter aperture for the diffraction experiment were carefully chosen in order to minimize possible measurement errors resulting from partially overlapping reflection scans, the unit cell distance a being exceptionally long for a small molecule structure. Least-squares refinement of 4363 reflections with $F > 6\sigma(F)$, 409 parameters, $R = 3.73\%$, $wR = 3.82\%$ for the constrained and restrained model described in the text. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the *Cambridge Crystallographic Data Center*.

The crystal structure is composed of close packed C_{70} ellipsoids extending in the b, c mirrorplanes at $x = 0$ and $1/2$ which are sandwiched by layers of S_8 molecules [9]. Part of the structure is shown in Fig. 1. The two C_{70} layers at $x = 0, 1/2$ are crystallographically independent but related by the *noncrystallographic symmetry* operation $1/2 - x, -y, -z$. Contrary to the original analysis [9], it was found that the two S_8 molecules which occupy the a, c mirror plane are disordered over two orientations with population coefficients 0.80(1) and 0.20. For clarity, in Fig. 1 only the major orientation is shown on the left hand side, while the minor orientation is shown on the right hand side of C_{70} . In the sandwich at $1/2 - x, -y, -z$, the populations of the two orientations are reversed. Two of the S-atoms of each of the S_8 molecules located in general position are also disordered. The positions of the ordered S-atoms deviate only slightly from the noncrystallographic symmetry.

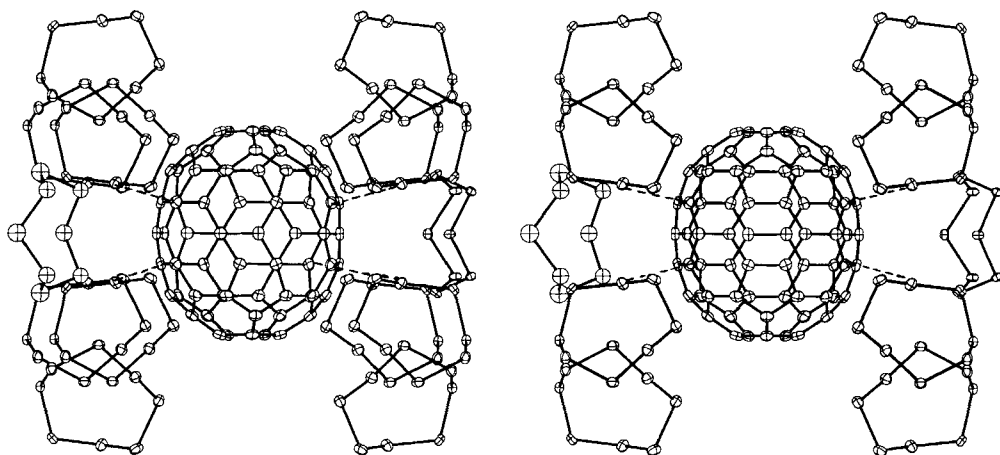


Fig. 1. One molecule of C_{70} surrounded by 14 molecules of S_8 which are in direct contact with it. The projection is down the c axis, a is horizontal, and b vertical. The crystallographic symmetry of this part of the structure is C_{2v} with the twofold axis perpendicular to the plane of projection of the picture on the left. For clarity, only the S_8 molecule with population 0.80(2) is shown on the left hand side of C_{70} ; only the one with population 0.20 is shown on the right hand side of C_{70} . The dotted lines show the short intermolecular $C \cdots S$ contacts.

With the improved accuracy and resolution of the low-temperature data, the spread of chemically equivalent C–C distances is considerably reduced. However, a conventional refinement of the structure with two crystallographically independent C_{70} molecules results in deviations from mean distances ranging between 0.015 and 0.062 Å. This spread is larger than may be expected from the quality of the data. Closer analysis indicated this to be due to the noncrystallographic symmetry which introduces correlations between related parameters in the least-squares refinement and prevents an accurate determination of the coordinates of the two crystallographically independent C_{70} molecules. To avoid this difficulty, the coordinates and displacement parameters of C_{70} were constrained in the final refinement cycles to the noncrystallographic symmetry. In addition, the bonded and nonbonded distances of C_{70} were restrained to obey D_{5h} molecular symmetry. The weights of the restraints were chosen as $w = (0.001)^{-2}$. The coordinates

of the disordered S-atoms but not their displacement parameters were also constrained to the noncrystallographic symmetry. The R values resulting from this refinement differ insignificantly from those obtained without constraints and restraints (3.56 vs. 3.73%), but the number of refined parameters is reduced from 611 to 409! This indicates that the constrained model explains the data as well as a conventional, unrestrained one, without suffering, however, from chemically unreasonable distance differences.

The C_{70} molecule possesses crystallographic C_{2v} symmetry (see *Fig. 1*, stereopicture on the left): The C–C distances of C_{70} at 100 K are given in the *Table* (for atomic numbering, cf. *Fig. 2*). In the five-membered rings at the poles of C_{70} and in the adjacent six-membered rings they are nearly the same as those in C_{60} [1] at 110 K. The C–C bonds in the six-membered rings straddling the equator of C_{70} are all of similar length, in contrast to those of the six-membered rings near the poles and in C_{60} . The longest C–C bonds belong to the equator and are those which have no analogous counterparts in C_{60} [9] [10]. The distances reported here are compatible with, but more accurate by an order of magnitude than comparable distances in C_{70} -Ir complexes [11]. The five- and six-membered rings are nearly planar, except for the six-membered rings straddling the equator of C_{70} which show a boat conformation. The deviation of atom CY(17) from the plane of the four coplanar atoms CY(12) is 0.143(4) Å (*Fig. 2*).

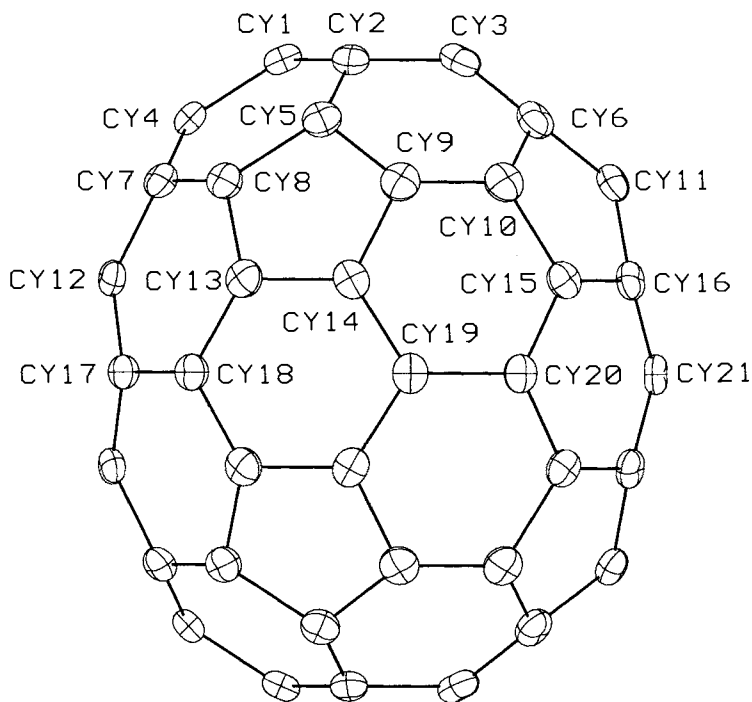


Fig. 2. Atomic numbering and scaled anisotropic r.m.s. displacement parameters in C_{70} ($1.54 U^{1/2}$). The top (labelled) and bottom half (unlabelled) of the molecule are related by a crystallographic mirror plane, as are the front and back halves. Note that the six-membered rings straddling the equator show a non-planar boat conformation (e.g. CY(12), CY(17)).

Table. C–C Distances [\AA] of C_{70} at 100 K, at Room Temperature, from ab initio Calculations and of C_{60} at 110 K

CY(1)–CY(2)	1.453(3)	1.458(6)	1.451	1.450(3)
CY(1)–CY(4)	1.387(4)	1.380(4)	1.375	1.387(3)
CY(4)–CY(7)	1.445(3)	1.459(5)	1.446	1.450(3)
CY(7)–CY(8)	1.378(3)	1.370(4)	1.361	1.387(3)
CY(7)–CY(12)	1.447(2)	1.460(4)	1.457	1.450(3)
CY(12)–CY(12)	1.426(3)	1.430(4)	1.415	1.450(3)
CY(12)–CY(17)	1.414(2)	1.407(7)	1.407	1.387(3)
CY(17)–CY(18)	1.462(4)	1.476(5)	1.475	–

a) This work; refinement restrained to D_{5h} symmetry (e.s.d. from structure factor least-squares).

b) From [9], averages of chemically equivalent bonds (e.s.d. of mean).

c) From [10].

d) From [1].

The C_{70} molecule is surrounded by six other C_{70} molecules in the b, c plane and by 14 S_8 molecules. The two mirror-symmetric disordered S_8 molecules make different types of contacts with C_{70} ; for the one to the right of C_{70} in *Fig. 1* (minor orientation) two S-atoms related by mirror symmetry point towards the centers of two six-membered C-rings next to the equator of C_{70} . For the one to the left of C_{70} in *Fig. 1* (major orientation), a single S-atom on the mirror plane points towards the center of a six-membered ring on the equator. The closest $C \cdots S$ distance is 3.128 \AA and is found to an S_8 molecule in general position (CY(13) \cdots SY(1)). This value is short compared to the sum of *van der Waals* radii ($1.70 + 1.85 = 3.55 \text{\AA}$) [12]. The $C \cdots S-S$ angle is 160.8° and the $S \cdots C-C$ angles are $95.9, 98.8,$ and 105.6° . This indicates that the C-atom involved is nucleophilic, the S-atom electrophilic, in contrast to general expectations based on the redox properties of C_{60} and C_{70} . In any case, $S \cdots C$ contacts with this geometry are often considerably shorter than would be expected from atomic radii [13]. The short contact does not affect the S–S distances in the S_8 rings. An effect on SSS angles and on the details of ring conformation is neither evident nor can it be ruled out completely. Short intermolecular contacts are also found in C_{60} at 110 K [1] and at room temperature [2], the shortest $C \cdots C$ distances are $\sim 3.15 \text{\AA}$, $\sim 0.2 \text{\AA}$ shorter than in graphite. The ability to form short nonbonded contacts may well be connected to the pyramidality of the C-atoms and may even be a general feature of fullerene crystal structures.

We gratefully acknowledge support by the *Swiss National Science Foundation*.

REFERENCES

- [1] H. B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y. Lu, M. M. Kappes, J. A. Ibers, *Angew. Chem.* **1992**, *104*, 667; *ibid. Int. Ed.* **1992**, *31*, 640.
- [2] H. B. Bürgi, R. Restori, D. Schwarzenbach, *Acta Crystallogr., Sect. B* **1993**, in press; P. C. Chow, X. Jiang, G. Reiter, P. Wochner, S. C. Moss, J. D. Axe, J. C. Hanson, R. K. McMullan, R. L. Meng, C. W. Chu, *Phys. Rev. Lett.* **1992**, *69*, 2943.
- [3] O. Ermer, *Helv. Chim. Acta* **1991**, *74*, 1339.
- [4] A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, H. Shinohara, *J. Chem. Soc., Chem. Commun.* **1992**, 1472.
- [5] A. Izuoka, T. Tachikawa, T. Sugawara, Y. Saito, H. Shinohara, *Chem. Lett.* **1992**, 1049.

- [6] U. Geiser, S. K. Kumar, B. M. Savall, S. S. Harried, K. D. Carlson, P. R. Mobley, H. H. Wang, J. M. Williams, R. E. Botto, W. Liang, H.-M. Whangbo, *Chem. Mater.* **1992**, *4*, 1077.
- [7] M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1992**, 1534.
- [8] A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *J. Chem. Soc., Chem. Commun.* **1993**, 56.
- [9] G. Roth, P. Adelmann, *J. Phys. I Fr.* **1992**, *2*, 1541.
- [10] G. E. Scuseria, *Chem. Phys. Lett.* **1991**, *180*, 451.
- [11] A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, S. R. Parkin, *J. Am. Chem. Soc.* **1991**, *113*, 8953; A. L. Balch, J. W. Lee, M. M. Olmstead, *Angew. Chem.* **1992**, *104*, 1400; *ibid. Int. Ed.* **1992**, *31*, 1356.
- [12] L. Pauling, 'The Nature of the Chemical Bond', 3rd edn., Cornell University Press, 1960.
- [13] R. E. Rosenfield, R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860.