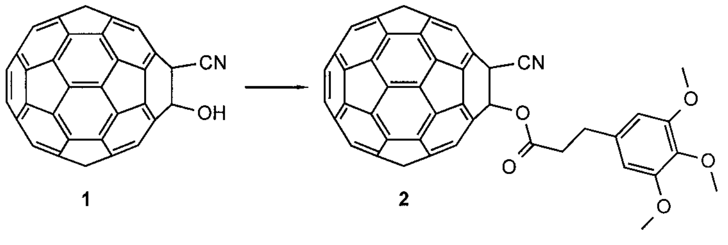
Determination of the Electron Density Distribution in the Bonds of a Fullerene Derivative by High-Resolution X-Ray Structure Analysis[**]

Hermann Irngartinger,* Anton Weber, and Thomas Oeser

Since the discovery of the synthesis of fullerenes on a macroscopic scale in 1990,[1] their derivatization, especially that of C_{60}, has led to a multitude of compounds with interesting properties. Theoretical considerations of the bonding showed[2] that of the 12500 possible resonance structures of C_{60} the lowest energy is found in the one in which all double bonds are located at the contact of two six-membered rings ([6,6] bonds). Therefore no double bonds occur in five-membered rings (as [5,6] bonds) which would contribute to an increase in strain. The question of the degree of electron delocalization and therefore the degree of aromaticity of C_{60} has been discussed controversially.[3–6] The more than 160 X-ray structure investigations of fullerenes[7] and their derivatives that have been published so far gave experimental insights into the nature of the bonds. These data confirm the results of spectroscopic studies and of calculations, according to which the [6,6] bonds are significantly shorter than the [5,6] bonds in [60]fullerenes.[8] Thus we were able to solve the structure of isoxazolo[60]fullerenes, which were synthesized by the addition of nitrile oxides to C_{60}.[9, 10] In the anthryl derivative[9] the average[11] bond lengths of the [6,6] and [5,6] bonds are 1.391(9) and 1.452(9) Å, respectively. As C_{60} is a highly strained, polycyclic ring system,[3] bent bonds are to be expected. We have now determined the distribution of electron density in the bonds of a fullerene derivative for the first time by high-resolution X-ray structure determination of the difference density.

The compound we have examined is a product of an isoxazolo[60]fullerene whose dihydroisoxazole ring was opened, as we reported,[12] which led to the fullerenol **1**. Its reaction with 3-(3,4,5-trimethoxyphenyl)propionic acid gave the novel 1,2-dihydro[60]fullerene derivative **2** (Scheme 1), which crystallizes from toluene as a 1:1 clathrate in the space group $P\bar{1}$ (Figure 1). The average lengths of the [6,6] and [5,6] bonds (excluding the bonds to the site of addition) are 1.395(8) and 1.452(8) Å, respectively, and the mean esd value (σ) for the 90 bonds of the fullerene is 0.002 Å. In order to make it easier to follow the discussion of the results, the numbering of the atoms mentioned is given in Figure 2. The distance between C1–C2 at the addition site (1.611(2) Å) is significantly larger than in the isoxazolo[60]fullerenes [1.584(5) Å,[9] 1.576(3) Å,[10] 1.564(4) Å,[10] 1.580(4) Å[13]]. Evidently, the short repulsive 1,4 contact C61···O1 [2.609(3) Å] of the eclipsed substituents is responsible for the bond lengthening. In the 1-fluorenyl-1,2-dihydro[60]fullerene[14] the C1–C2 bond is much shorter (1.570(6) Å) since the 2-position is unsubstituted.



1 2

Scheme 1. Esterification of 3-(3,4,5-trimethoxyphenyl)propionic acid with fullerenol **1** (see Experimental Section).

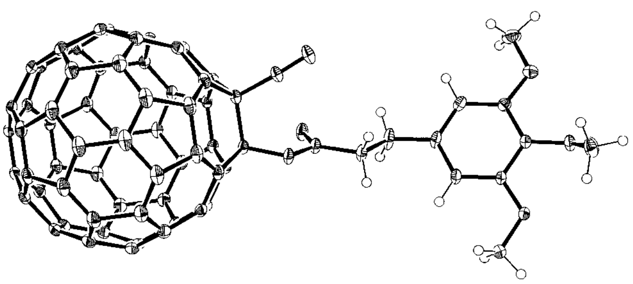


Figure 1. Molecular structure of **2** in the crystal.

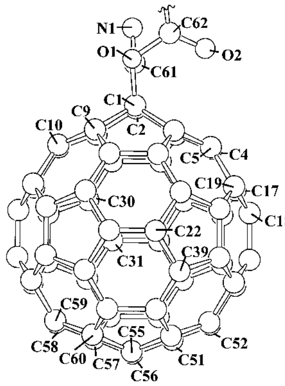


Figure 2. Numbering of the atoms in the fullerene skeleton relevant to the discussion.

A possible attractive interaction between nucleophilic O1 and electrophilic C61, on the other hand, seems to play a minor role because owing to the torsion angle C2-C1-O1-C62 of −72.1(2)° the lone electron pairs at O1 do not show a favorable orientation towards the C61 of the cyanide group. Furthermore, the nucleophilicity is smaller than that of an ether oxygen atom which, for example, in 8-methoxy-1-naphthonitrile causes a deviation from the linear arrangement of the cyanide group of 6.2° for an O···C distance of 2.594(4) Å.[15] In our case, however, an attractive interaction results with the carbonyl oxygen atom O2, to which the distance is slightly larger [2.919(3) Å], but still is significantly smaller than the van der Waals distance. The carbonyl group is twisted towards the cyanide group [C2-C1-O1-C62 −72.1(2)°, C1-O1-C62-O2 −2.6(3)°]. As a consequence the latter deviates from linearity by 3.7° [C2-C61-N1 176.3(2)°], and N1 bends away from O2 [C1-C2-C61-N1 −155(3)°]. A similar arrangement was found in 8-nitro-1-naphthonitrile.[15]

The determination of difference density resulted in significant differences in the distribution of electron density for the [6,6] and [5,6] bonds. Below the planes of the six-membered rings (0.4 Å towards the center of the fullerene skeleton) the

---

[*] Prof. Dr. H. Irngartinger, Dipl.-Chem. A. Weber, Dr. T. Oeser
Organisch-chemisches Institut der Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: (+49) 6221-544205
e-mail: e56@ix.urz.uni-heidelberg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft. We thank Prof. P. Hofmann and Dr. F. Rominger, Heidelberg, for the opportunity to record the X-ray data and Mrs. U. C. Wiesinger for the preparation of the crystal.

mean maximum electron density in the [6,6] bonds is significantly higher (0.19(4) e Å^{-3}) than in the [5,6] bonds (0.10(5) e Å^{-3}), in the planes of the six-membered rings the differences are at the limits of significance (0.45(7) versus 0.37(7) e Å^{-3}), and above the planes of the six-membered rings (0.4 Å) the bonding types do not differ [6,6/5,6: 0.22(4)/0.22(5) e Å^{-3}]. The average values were determined by means of cross sections through the planes of all six-membered rings with the exception of the two rings at the addition site. In Figures 3a and 3b this is illustrated for one six-membered ring. Overall, the maxima in the [6,6] bonds are higher than those in the [5,6] bonds in agreement with the bond character. From the above-mentioned values it also follows that in the [5,6] bonds the mean maximum electron densities are greater outside the fullerene skeleton than within, but not in the [6,6] bonds. The differences can evidently be ascribed to bent bonds. In the planes of the five-membered rings the bonds show a tendency to bend away from the five-membered ring; however, the mean distance of the maxima of electron density from the bond axes are at the limits of significance at 0.05(5) Å. Figure 3c shows this for one five-membered ring. No bends are observable in the [6,6] bonds (Figure 3a).

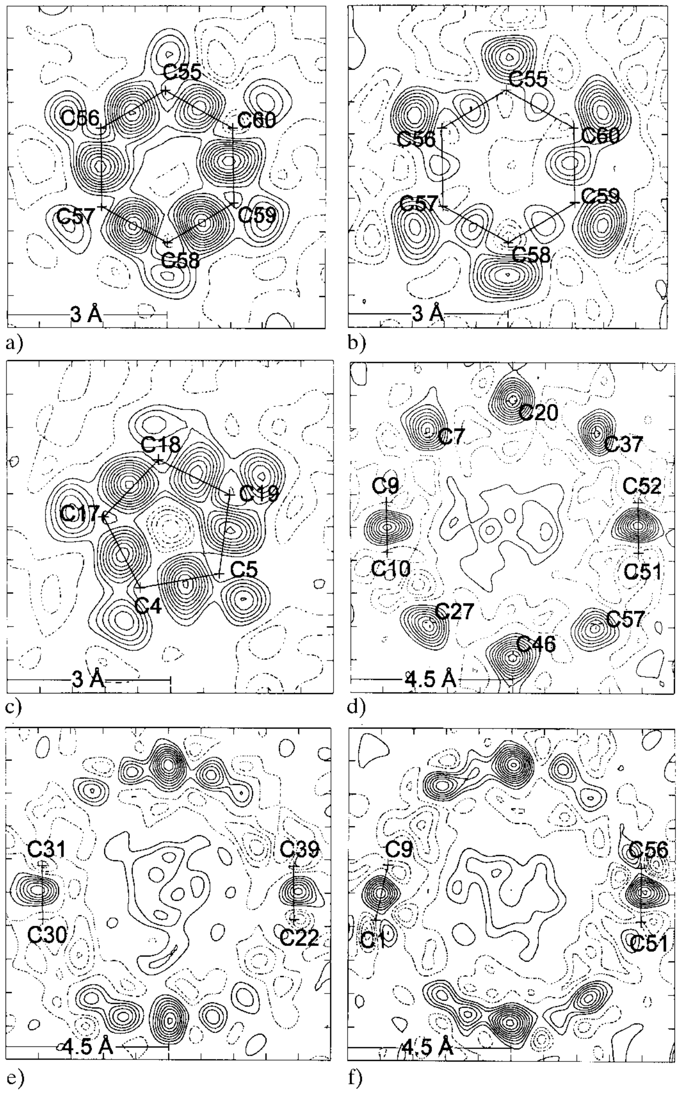


Figure 3. Difference density maps of **2**. The distance between contours is 0.05 e Å^{-3}, and solid lines correspond to positive and broken lines to negative electron densities. a) Cross section through the plane of a six-membered ring. [5,6] bonds: C55–C60, C56–C57, C58–C59; [6,6] bonds: C55–C56, C57–C58, C59–C60. b) Cross section through the same six-membered ring, 0.4 Å below the plane. c) Cross section through the plane of a five-membered ring. d) Cross section through the plane of two parallel [6,6] bonds. e) Cross section through the plane of two parallel [5,6] bonds. f) Cross section through the plane of two opposite [5,6] bonds, one of which is the C(sp^3)–C(sp^2) bond C1–C9 which originates at the addition site.

Figure 3d shows a section through two parallel [6,6] bonds (C9–C10, C51–C52) which divides the fullerene skeleton into two halves (mirror symmetric with respect to the skeleton). The atoms C7, C20, C37, C57, C46, and C27 lie above the projection plane, and [6,6] bonds (C20–C19 and C46–C47) and [5,6] bonds (C7–C6, C36–C37, C49–C57, and C27–C28) lead vertically downward from these atoms. The figure shows that the maximum electron densities in the [6,6] bonds lie on the interatomic axes. This is also confirmed by the average value for all [6,6] bonds. Corresponding sections are also possible for parallel [5,6] bonds; these, however, do not divide the fullerene skeleton with mirror symmetry. Figure 3e shows such a section through the bonds C30–C31 and C22–C39. In this case the maximum electron densities lie significantly outside the fullerene framework in both bonds. In the [5,6] bonds (except the four leading away from C1 and C2), the shift in the maxima of the electron densities from the bond axes outwards is on average 0.07(5) Å.

The outward bending of the [5,6] bonds also accounts for the fact that the electron density for this bond type is about twice as high 0.4 Å above the planes of the six-membered rings as it is 0.4 Å below them. Figure 3f shows another section through two [5,6] bonds. However, these are not parallel since the C1–C9 bond originates from the addition site. In contrast to the C(sp^2)–C(sp^2) bond C51–C56, this C(sp^3)–C(sp^2) bond is not bent as the ring strain is locally decreased at the addition site.

Experimental Section

2-Cyano-1,2-dihydro[60]fullerenyl 3-(3,4,5-trimethoxyphenyl)propionate **2**: 3-(3,4,5-Trimethoxyphenyl)propionic acid (6.2 mg, 2.6×10^{-5} mol), dicyclohexylcarbodiimide (5.4 mg, 2.6×10^{-5} mol) and 4-(dimethylamino)pyridine (0.3 mg, 2.6×10^{-6} mol) were added to a solution of the alcohol **1**[12] (10 mg, 1.3×10^{-5} mol) in toluene/acetonitrile (9/1; 50 mL) under nitrogen. The mixture was stirred at ambient temperature for 72 h and subsequently concentrated in vacuo. The product was isolated by column chromatography on silica gel with toluene/acetonitrile (9/1) ($R_f = 0.5$). Compound **2** (11.8 mg, 92 %) was obtained as a dark brown solid. Single crystals suitable for X-ray structure analysis were obtained by crystallization from toluene.

^{1}H NMR (300 MHz, $CDCl_3/CS_2$ 1/8): $\delta = 6.51$ (s, 2H, arom.), 3.81 (s, 6H, CH_3), 3.70 (s, 3H, CH_3), 3.26 (s, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1/8): $\delta = 172.49$ (CO), 153.09 (arom.), 148.13 (1C), 147.61 (1C), 146.41 (2C), 146.37 (4C), 146.04 (4C), 145.98 (2C), 145.78 (2C), 145.44 (2C), 145.24 (2C), 145.12 (2C), 145.08 (2C), 144.34 (2C), 144.29 (2C), 143.88 (2C), 143.71 (2C), 142.76 (2C), 142.54 (2C), 142.51 (2C), 142.07 (4C), 141.62 (2C), 141.27 (2C), 141.24 (2C), 140.72 (2C), 139.85 (2C), 139.46 (2C), 137.48 (2C), 136.26 (2C + arom.), 135.07 (arom.), 115.54 (CN), 105.58 (arom.), 59.92 (CH_3), 55.55 (CH_3), 36.61 (CH_2), 31.16 (CH_2) (because of the long relaxation time the signals for C1 and C2 could not be detected); FT-IR (KBr): $\tilde{\nu} = 2930$ (m, CH), 2331 (w), 2241 (w, CN), 1756 (m, CO), 1127 (s), 527 cm^{-1} (m, fullerene); UV/Vis ($CHCl_3$): λ_{max} (lgε) = 232 nm (5.10), 256 (5.22), 318 (4.79), 580 (3.09), 680 (2.60); MALDI-TOF-MS: m/z (%):

985.4 (18) [M^-, $C_{73}H_{15}NO_5$], 746.1 (100) [$C_{61}N^-$], 720.0 (7) [C_{60}^-]; HR-FAB-MS: m/z: 985.0950 [$C_{73}H_{15}NO_5^+$] calcd; 985.0942 found.

High-resolution X-ray structure analysis with low-temperature data:[16] $C_{73}H_{15}NO_5 \cdot C_7H_8$, $M_r = 985.86$, dark brown crystal 0.44 × 0.22 × 0.12 mm, triclinic, space group $P\bar{1}$, $a = 10.0417(2)$, $b = 14.5831(4)$, $c = 16.8772(4)$ Å, $\alpha = 68.277(1)$, $\beta = 75.985(1)$, $\gamma = 84.583(1)^\circ$, $V = 2227.59(9)$ Å^3, $Z = 2$, $T = 123(2)$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.607\ kg\,dm^{-3}$, $F(000) = 1100$, $\mu = 0.1\ mm^{-1}$, an empirical absorption correction was carried out, Bruker SMART diffractometer, ω and φ scan, $\theta_{max.} = 50.6^\circ$, $-21 \leq h \leq 20$, $-30 \leq k \leq 30$, $-32 \leq l \leq 36$, 43 s measuring time per frame; of 119878 measured reflections, 44299 were independent and 22618 were observed. The structure was solved by direct methods (SHELXS-97).[17] Refinement (F^2 after the LSQ method with SHELXL-97[18]) and calculation of the difference density in the following order: a) With the reflections from $\theta = 5-28^\circ$, 10592 independent, 8791 observed [$I > 2\sigma(I)$], 867 variables. Isotropic refinement of the hydrogen atoms and anisotropic refinement of the heavy atoms, $R = 0.046$, $wR = 0.11$, $R_{int.} = 0.03$, GOF = 1.07. b) High-angle refinement with the reflections from $\theta = 28-50.6^\circ$, 33719 independent, 13839 observed [$I > 2\sigma(I)$], 775 variables. Anisotropic refinement of the heavy atoms, parameters of the hydrogen atoms were adopted from (a), $R = 0.105$, $wR = 0.154$. The Hirshfeld rigid bond test[19] resulted in a mean deviation of 6.3×10^{-4} Å^2 for the 90 bonds of the fullerene skeleton. An R value of 0.028 was obtained for the fullerene skeleton by applying a T,L,S analysis according to Schomaker and Trueblood.[20] c) With the reflections from $\theta = 5-50.6^\circ$, 44299 independent, 22618 observed [$I > 2\sigma(I)$]. Refinement of the scale factor, $R = 0.081$, $wR = 0.175$. d) Calculation of the structural factors (F_{calcd}) for $\theta = 5-28^\circ$ [$I > 5\sigma(I)$] with the structure model from (b) and the scale factor from (c).

Figure 1 was generated with the program ORTEP3.[21] The difference density sections in Figure 3 were calculated with the program WinGX-98.[22] The rigid bond test and the T,L,S analysis were carried out with the program PLATON.[23]

Received: October 21, 1998 [Z12552IE]
German version: *Angew. Chem.* **1999**, *111*, 1356–1358

Keywords: difference electron density distribution · fullerenes · structure elucidation · X-ray scattering

---

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 345–358.

[2] D. J. Klein, T. G. Schmalz, G. E. Hite, W. A. Seitz, *J. Am. Chem. Soc.* **1986**, *108*, 1301–1302.

[3] R. C. Haddon, *Science* **1993**, *261*, 1545–1550.

[4] M. Prato, T. Suzuki, F. Wudl, V. Lucchini, M. Maggini, *J. Am. Chem. Soc.* **1993**, *115*, 7876–7877.

[5] A. Hirsch, *Synthesis* **1995**, 895–913.

[6] M. Krygowski, M. Cyrañski, *Tetrahedron* **1996**, *52*, 1713–1722.

[7] Researched with the Cambridge Structural Database, CD-ROM version 5.16.

[8] A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**, p. 25.

[9] H. Irngartinger, C. M. Köhler, U. Huber-Patz, W. Krätschmer, *Chem. Ber.* **1994**, *127*, 581–584.

[10] H. Irngartinger, A. Weber, T. Escher, *Liebigs Ann.* **1996**, 1845–1850.

[11] For average values, the mean square deviation is given in parentheses, for single values the esd value (σ) is bracketed.

[12] H. Irngartinger, A. Weber, *Tetrahedron Lett.* **1997**, *38*, 2075–2076.

[13] V. N. Drozd, V. N. Knyazev, F. M. Stoyanovich, F. M. Dolgushin, A. I. Yanovsky, *Russ. Chem. Bull.* **1997**, *46*, 113–121.

[14] Y. Murata, K. Komatsu, T. S. M. Wan, *Tetrahedron Lett.* **1996**, *37*, 7061–7064.

[15] G. Procter, D. Britton, J. D. Dunitz, *Helv. Chim. Acta* **1981**, *64*, 471–477.

[16] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104120. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. Code +(44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

[17] G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1997**.

[18] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.

[19] F. L. Hirshfeld, *Acta Crystallogr. Sect. A* **1976**, *32*, 239–244.

[20] V. Schomaker, K. N. Trueblood, *Acta Crystallogr. Sect. B* **1968**, *24*, 63–76.

[21] L. J. Farrugia, ORTEP3 for Windows, University of Glasgow, Scotland, **1998**.

[22] L. J. Farrugia, WinGX-98, University of Glasgow, Scotland, **1998**.

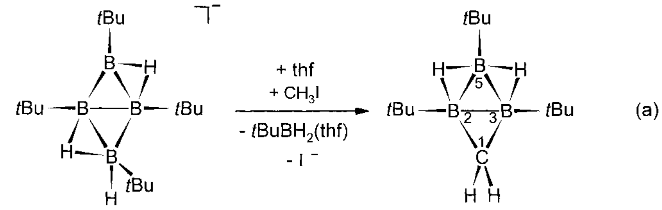
[23] A. L. Spek, PLATON, University of Utrecht, The Netherlands, **1998**.

2,3,5-Tri-*tert*-butyl-1-carba-*nido*-tetraborane**

Andreas Neu, Krzysztof Radacki, and Peter Paetzold*

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

In the series of isoelectronic *nido* clusters B_4H_8, CB_3H_7, and NB_3H_6, the *tert*-butyl derivatives $B_4H_4tBu_4$[1] and $NB_3H_2tBu_4$[2] are well known. We report here on a derivative, $CB_3H_4tBu_3$, of the missing link. It is formed by the reaction of iodomethane and the *nido*-tetraborane $[B_4H_3tBu_4]^-$[1] in thf in 90% yield [Eq. (a); the numbering of the skeletal atoms follows the IUPAC *nido* cluster rules that attribute the number 4 to the missing atom of the corresponding trigonal-bipyramidal *closo* cluster]. Traces of $B_4H_2tBu_4$[3] and $B_4H_4tBu_4$[1] cannot be removed from the product.



The structure of the product follows from the NMR spectra. C_s symmetry is concluded from the equivalence of the tBu(2) and tBu(3) groups and of the bridging protons. The coupling between the methylene protons in *exo*/*endo* position ($^2J = 13$ Hz) and between these and the bridging protons ($^3J(\mu/endo) = {}^3J(\mu/exo) = 6$ Hz) are found at the expected values. Homonuclear 2D couplings are observed between B(2)/B(3) and B(5) and between the methylene protons. All of the five ^{1}H NMR chemical shifts give heteronuclear 2D cross peaks: the μ-H atoms are coupled to both kinds of B atoms, the methylene-H atoms are related to the methylene-C atom, and the methyl-H atoms display 2D hetcor coupling not only with each neighboring C atom, but also with the more remote C

---

[*] Prof. Dr. P. Paetzold, Dr. A. Neu
Institut für Anorganische Chemie der Technische Hochschule
D-52056 Aachen (Germany)
Fax: (+49)241-8888-288
E-mail: peter.paetzold@ac.rwth-aachen.de
M. Sci. K. Radacki
Politechnika Gdańska
Department of Chemistry
G. Narutowicza 11/12, PL-80952 Gdańsk (Poland)

[**] This work was supported by the Deutsche Forschungsgemeinschaft.