

First X-Ray Determination of Cyclopropane Structure in Methanofullerenes

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The X-ray crystal structure of [(3,4-dimethoxyphenyl)phenylmethano][60]fullerene **1** confirming firstly the cyclopropane structure for methanofullerenes is reported; one of two chloroform molecules (enclosed in the crystal lattice) forms a hydrogen bond pattern to both oxygen atoms of **1**.

Wudl and coworkers (1991) synthesized the first methano-bridged fullerenes¹ for which a 6–6 ring junction with a ten-membered methanoannulene structure was proposed, based on NMR, UV–VIS, CV, and comparison with a methano-[10]annulene. These new fullerene derivatives were named fulleroids (homofullerenes) to point out the difference from methanofullerenes with a cyclopropane (methanonaphthalene) structure. It became apparent that monoaddition of

diazomethanes to [60]fullerene leads to more than one isomer (Fig. 1). 6–6- and 5–6-ring-methano-bridged fullerenes were detected by ¹H and ¹³C NMR spectroscopy,^{2–5} but only in a few cases was the separation of these isomers successfully achieved.² Calculations were done in order to determine whether the isomers are homofullerenes with an open methanoannulene structure or methanofullerenes with a cyclopropane (*4a,4b*-methanonaphthalene) structure.^{2b,4} It became evident that, in good agreement with the observed spectroscopic data, but in contrast to the first assumptions¹ and reported crystal data,⁵ the 6–6-ring-bridged derivatives should be methanofullerenes and the 5–6-ring-bridged should be homofullerenes.

We now report the first X-ray crystal structure of a methanofullerene **1** confirming the cyclopropane structure for 6–6-ring-methano-bridged fullerenes.[†] The crystals were obtained as black prisms by slow evaporation from a chloroform–toluene solution of **1**.[‡] In good agreement with our previous calculations^{2b} and those of Diederich *et al.* with different methanofullerenes,^{4b} the bond length between the two decisive bridged C-atoms C(1) and C(2) is 161.4(7) pm, only 6 pm longer than the calculated value and 9 pm longer than in cyclopropane (152 pm) (Fig. 2). It is of the same order of magnitude as in Diels–Alder (159–162 pm)⁶ and [3 + 2]cycloaddition adducts (158 pm),⁷ and clearly proves the transannular bond between C(1) and C(2). The other bonds in the cyclopropane ring are 151.0(7) [C(1)–C(61)] and 151.5(7) pm [C(2)–C(61)] long. This indicates slight bond length and angle deformations of the three-membered ring (Table 1) from typical values for cyclopropanes.

The four sp³–sp² bonds are, as expected, slightly elongated

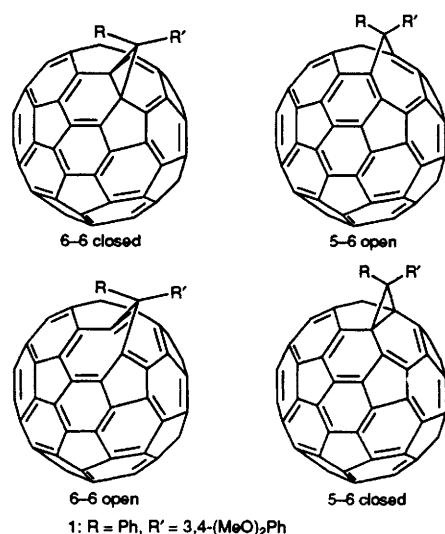


Fig. 1 Isomers of methano[60]fullerenes with 5–6 and 6–6 junction

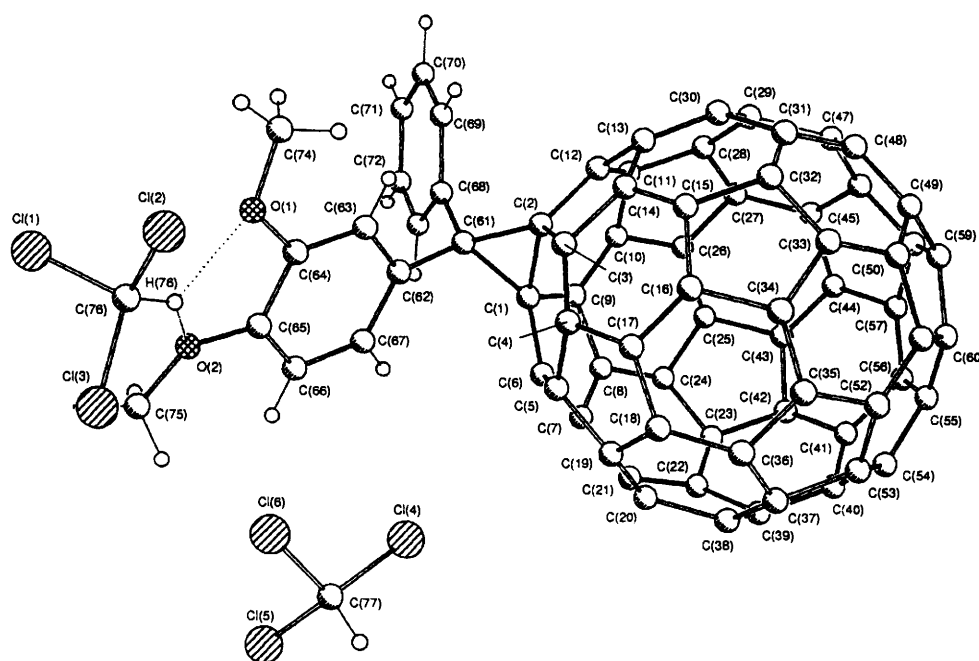


Fig. 2 X-Ray crystal structure of **1**·2CHCl₃

to 149 [C(1)–C(6), C(1)–C(9)] and 148 pm [C(2)–C(3), C(2)–C(12)]. The average bond lengths for the two other bond types in **1** are 144 (5–6-ring) and 139 pm (6–6-ring), being in good agreement with reported values for other [60]fullerene adducts.^{6,7} One of the enclosed chloroform molecules forms less common three-centre hydrogen bonds to the O-atoms of the methoxy groups of **1** (Fig. 2).

The two phenyl groups of **1** form a niche in which the neighbouring fullerene molecule is situated. The shortest distances between the two O-atoms and one of the C-atoms are 359 [O(1a)–C(25b)] and 346 pm [O(2a)–C(26b)] (Fig. 3). This is more than the van der Waals radii, and an intermolecular donor–acceptor interaction like in a Diels–Alder [60]fullerene adduct^{6c,d} is not observed. The distances between the 4,4'-C-atoms of the phenyl groups and the neighbouring fullerene are 328 [C(65a)–C(25b)] and 335 pm [C(71a)–

C(22b)], only slightly more than the van der Waals radii, pointing to an interaction (Fig. 3, 4).

Due to this interaction, the molecules form parallel planes of zigzag chains. The non-hydrogen-bonded chloroform molecules are situated in the space between these parallel planes. The closest distance between two fullerene C-atoms of related chains is 321 pm [C(52)–C(52)].[§] This is less than the van der Waals radii and an interaction in addition to stacking effects is probable.

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Table 1 Selected bond lengths and angles of **1**

d/pm		α°	
C(1)–C(2)	161.4(7)	C(61)–C(2)–C(1)	57.6(3)
C(1)–C(61)	151.0(7)	C(61)–C(1)–C(2)	57.9(3)
C(2)–C(61)	151.5(7)	C(1)–C(61)–C(2)	64.5(3)
H(76)–O(1)	240	C(62)–C(61)–C(68)	115.4(4)
H(76)–O(2)	234	O(2)–O(1)	65

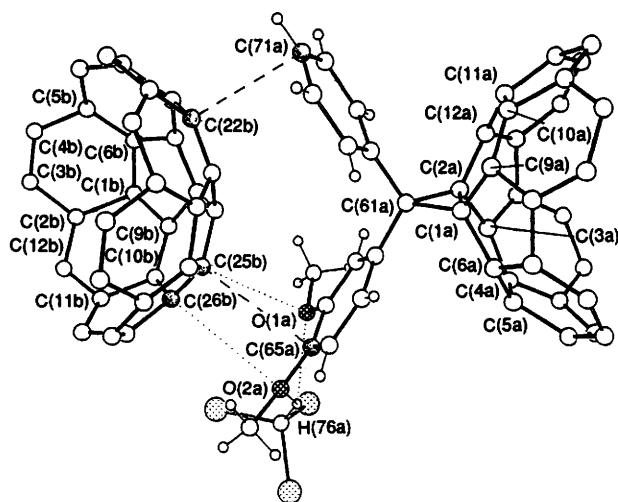


Fig. 3 Section from the crystal packing of **1**-2CHCl₃ indicating intermolecular contacts between two phenyl groups and the nearest neighbouring fullerene

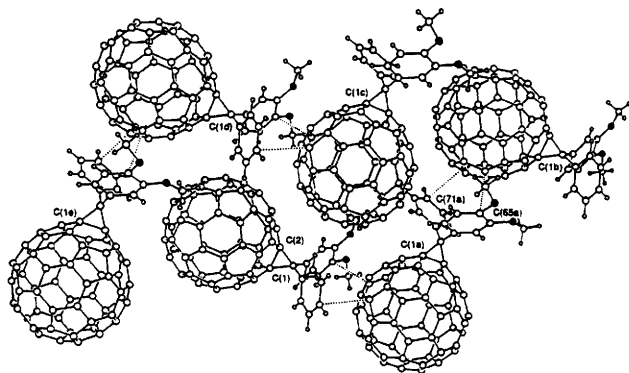


Fig. 4 Zigzag chains in the crystal packing of **1** (CHCl₃ omitted)

Footnotes

† Crystal data for **1**: C₇₅H₁₄O₂·2CHCl₃, *M* 1185.6, monoclinic, space group *P*2₁/*n* (no. 14), black crystals, dimensions 0.50 × 0.45 × 0.40 mm³, *a* = 10.796(1), *b* = 18.369(1), *c* = 24.007(1) Å, β = 101.69(1)°, *U* = 4662.1(5) Å³, *D*_c = 1.69 Mg m⁻³, *Z* = 4, μ(Cu-Kα) = 3.86 mm⁻¹, *T* = 293(2) K, 5852 symmetry independent reflections were used for the structure solution (direct methods) and refinement (full-matrix least squares on *F*², 768 parameters), non-hydrogen atoms were refined anisotropically, H atoms localised by difference electron density and refined using a 'riding' model. wR₂ 0.188 {*R*₁ 0.062 [*I* > 2σ(*I*)]}. An empirical absorption correction was applied (DIFABS).⁸ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

The numbering of the fullerene cage in crystallographic data does not agree with that in Figs. 2–4.

‡ Synthesis, NMR, and MS data of **1** are reported in ref. 2(b).

§ Generated by symmetry transformation $-x, -y, -z$.

References

- T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and Ö. Almarsson, *Science*, 1991, **254**, 1186.
- (a) A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens and R. C. King, *J. Am. Chem. Soc.*, 1993, **115**, 5829; (b) J. Osterodt, M. Nieger, P.-M. Windscheif and F. Vögtle, *Chem. Ber.*, 1993, **126**, 2331; (c) A. Skiebe and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1994, 335.
- T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7300, 7301; L. Isaacs, A. Wehrsig and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 1231; M. Prato, T. Suzuki, F. Wudl, V. Lucchini and M. Maggini, *J. Am. Chem. Soc.*, 1993, **115**, 7876; L. Isaacs, F. Diederich, *Helv. Chim. Acta.*, 1993, **76**, 2454.
- (a) M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 8479; (b) F. Diederich, L. Isaacs and D. Philp, *J. Chem. Soc., Perkin Trans. 2*, 1994, 391; cf. also R. Taylor, *Phil. Trans. R. Soc. Lond. A*, 1993, **343**, 87.
- F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.
- (a) Y. Rubin, S. Khan, D. I. Freedberg and C. Yeretjian, *J. Am. Chem. Soc.*, 1993, **115**, 344; (b) S. I. Khan, A. M. Oliver, M. N. Paddon-Row and Y. Rubin, *J. Am. Chem. Soc.*, 1993, **115**, 4919; (c) F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf and C. Thilgen, *Helv. Chim. Acta*, 1993, **76**, 2445; (d) P. Belik, A. Gügel, A. Kraus, J. Spickermann, V. Enkelmann, G. Frank and K. Müllen, *Adv. Mater.*, 1993, **5**, 854.
- H. Irmgartinger, C.-M. Köhler, U. Huber-Patz and W. Krätschmer, *Chem. Ber.*, 1994, **127**, 581.
- N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1993, **39**, 158.