

Isolation and characterisation of C_s -symmetry $C_{60}Me_5O_2OH$, the first methylated fullerene; a bis-epoxide with two oxygens in a pentagonal ring

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Received (in Cambridge, UK) 21st March 2000, Accepted 11th May 2000

From the reaction between [60]fullerene and MeLi, we have isolated $C_{60}Me_5O_2OH$, which has been characterised by both 1H and ^{13}C NMR spectroscopy and by single-crystal X-ray analysis; uniquely, both epoxide groups bridge 5 : 6-bonds in the same pentagon.

The significance of epoxyfullerenes has yet to be fully recognised. They may be formed by: (i) partial hydrolysis of a halogenofullerene to a *cis* halohydroxy derivative, followed by adjacent elimination of hydrogen halide, giving for example, the abundance of epoxides amongst the products of fullerene fluorination;¹ (ii) ozonolysis;² (iii) epoxidation of the fullerene with a peracid;³ (iv) direct reaction with oxygen, either in the arc-discharge reactors used for fullerene production,⁴ or on standing⁵ (this can be photochemically accelerated).⁶ The extent to which cage addends moderate the latter process is not yet known, but it is probable that all fullerene derivatives undergo this oxidation to some extent.

The formation of the only bis-epoxy fullerenes characterised previously, $C_{60}O_2$, involves addition of oxygen across the 1,2- and 3,4-bonds in a given hexagon;⁷ this motif is also believed to be present in $C_{60}O_3$.⁸ In the heterocycle $C_{60}Ph_4(C_6H_4)O_2$, we conjectured that one oxygen is present as an epoxide bridging a 5 : 6-bond in the central pentagon.⁹

There are few reports of the methylation of fullerenes. Olah and coworkers detected the addition of up to 24 methyl groups (with $C_{60}Me_6$ and $C_{60}Me_8$ being prominent) from the reaction of [60]fullerene with Li–MeI.¹⁰ Both 1,2- and 1,4- Me_2C_{60} have been obtained by electrochemical reduction,¹¹ and we have described preliminary results on the formation of $C_{60}Me_n$ ($n = 4, 6, 8$) and $C_{70}Me_n$ ($n = 2, 4, 6, 8, 10$).¹² Polyhydroxyfullerenes have been investigated extensively,¹³ but, to date, only one monohydroxyfullerene ($C_{70}Ph_9OH$) has been characterised.¹⁴

We now report the isolation and full characterisation of the first methylated fullerene, (and methylated fullerene) and the first bis-epoxide with both oxygens bridging a 5 : 6-bond. The structure was characterised by NMR spectroscopy, the interpretation of the latter being shown to be correct by single crystal X-ray crystallography.

An xs. of MeLi solution (4 ml of 1.0 M solution in THF–cumene, 110 : 90) was stirred under N_2 with $C_{60}Cl_6$ (100 mg),¹⁵ at room temp. The orange solution turned brown–black immediately and stirring was continued overnight. Normal work-up followed by column chromatography (70–230 mesh silica gel), gave a major fraction (9 : 1 cyclohexane–toluene elution) and then a minor fraction (1 : 1 cyclohexane–toluene elution). This latter was purified further by HPLC using a 10 mm \times 25 cm Cosmosil ‘Buckyrep’ column at a solvent flow rate of 4.7 ml min^{-1} to give $C_{60}Me_5O_2OH$, which eluted after 4.8 (toluene) or 8.8 min (1 : 1 toluene–heptane), and crystallised as ruby-red hexagonal plates.

The EI mass spectrum (Fig. 1) shows a peak due to the parent ion at 844 amu; notably, the C_{58} fragmentation ion peak at 696 amu is 40% of the intensity of the 720 amu peak. This is much higher than is found in the EI mass spectrum of C_{60} and arises because of the more facile loss of 2 CO molecules, which we have noted previously in the mass spectra of phenylated

epoxides of [60]fullerene, where the intensity of the 696 amu peak was 30% of that of the 720 amu peak.¹⁶ When the epoxide functions straddle 5 : 6-bonds, CO elimination creates a 7/5-membered ring combination, stabilised by the presence of sp^3 carbons bearing the addends.¹⁶

The IR spectrum (KBr) shows bands at 3520 (broad), 2971, 2924, 2857, 1438, 1384, 1099, 1074, 1047, 1037, 1016, 941, 665, 658, 572, 553, 535 and 513 cm^{-1} .

The 1H NMR spectrum shows peaks at δ_H 3.88 (1 H, s, OH), 1.99 (3 H, s, Me_A), 1.86 (6 H, s, Me_C), 1.75 (6 H, s, Me_B). The peaks were identified by NOE couplings of 2.4, 2.5 and 0.6% between OH and Me_A , Me_B , and Me_C , respectively, and of 0.9 and 0.3% between Me_A and Me_B . Saturation transfer to water confirmed the presence of an OH group; the NOE couplings between OH and *all three* methyls confirmed that OH must be present in the central pentagon.

The ^{13}C NMR spectrum shows 24 2 C and 2 1 C peaks for the cage sp^2 -carbons at δ_C (all 2 C except where indicated) 151.56, 148.79, 148.72, 148.69, 148.68, 148.59, 148.49 (1 C), 148.45, 148.44, 148.03, 147.99, 147.90, 147.87, 147.57 (1 C), 147.12, 145.13, 144.39, 144.03, 144.01, 143.97, 143.72, 143.38 (4 C), 143.30, 143.25, 143.08; the half-intensity on-symmetry plane peaks appear in the usual 147–149 ppm range. The sp^3 -carbons appear at δ_C 86.60 (2 C, COC), 75.11 (1 C, COH), 72.35 (2 C, COC), 53.12 (1 C, C_1Me), 47.21 (2 C, $C_{15,30}Me$), 46.49 (2 C, $C_{4,11}Me$), 27.38 (1 C, Me_A), 24.88 (2 C, Me_C), 24.20 (2 C, Me_B).

The compound thus has C_s symmetry and was deduced to have the two epoxide functions in the central pentagon, since the only other reasonable locations would be across the 16,17- and 28,29-positions (Fig. 2). However, little difference in the

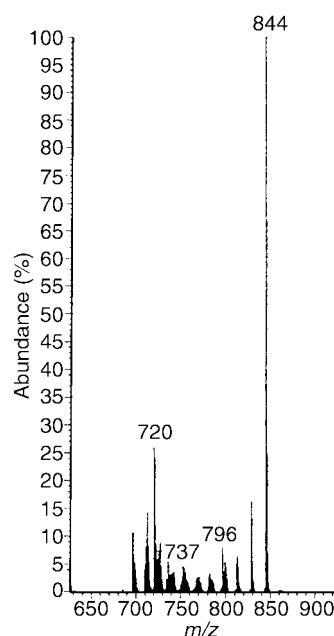


Fig. 1 EI mass spectrum (70 eV) for $C_{60}Me_5O_2OH$.

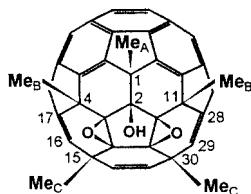


Fig. 2 Structure of symmetrical $C_{60}Me_5O_2OH$, showing numbering.

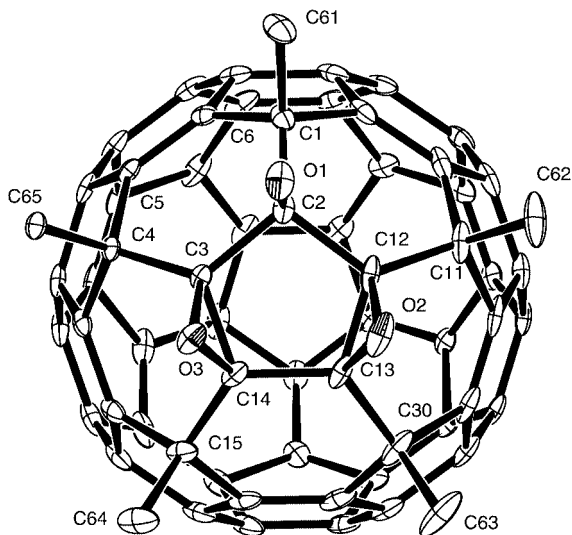


Fig. 3 X-Ray structure of $C_{60}Me_5O_2OH$.

chemical shifts for carbons C-17 and C-28, compared with C-16 and C-29 would then be expected, whereas an experimental difference of 14 ppm is found. This is consistent with two of the epoxide carbons being adjacent to that bearing the OH group (Fig. 2). The structure was confirmed by X-ray crystallography (Fig. 3).[†]

The structure is thus unique in having two epoxide functions straddling 5 : 6-bonds in the central pentagon. The addend locations in $C_{60}X_6$ structures requires placing two double bonds in the central pentagon, thereby increasing the strain; this can be partially relieved by addition across these bonds. The C–C bonds bridged by the epoxide function are short, at 1.48 Å, whereas all other cage C–C bonds in the central pentagon area and the cage–Me bonds, have an average bond length of 1.55 ± 0.02 Å. The C–O–C bond angles are 61.5° , and some repulsion between the epoxides and the OH group is manifest in the C-3–O-3 bond (1.459 Å), which is longer than the O-3–C-14 bond (1.437 Å).

A notable feature (and one which we have found recently with phenylated [84]fullerene as well) is that on strongly heating the KBr disc ($250^\circ C$) of $C_{60}Me_5O_2OH$, a very sharp peak appears at 2170 cm^{-1} after 3 h and grows in intensity with heating during the next 24 h. This is consistent with the presence of matrix-isolated C_5 ,¹⁷ and parallels earlier work in which

similar treatment of KBr discs of insoluble [84]fullerene residues, produced a sharp band at 2035 cm^{-1} attributed to matrix-isolated C_3 .¹⁸ We hope to investigate this aspect more fully at a later date.

We thank Kuwait University for a research grant (to H. A.-M.).

Notes and references

[†] Crystal data for $C_{65}H_{16}O_3$: $M_r = 844.8$, triclinic, $P\bar{1}$ (no. 2), $a = 14.6057(3)$, $b = 15.2988(4)$, $c = 15.6144(4)$ Å, $\alpha = 81.596(1)$, $\beta = 81.663(1)$, $\gamma = 83.954(2)^\circ$, $V = 3402.5(1)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.10\text{ mm}^{-1}$, $T = 173\text{ K}$, $R_f = 0.075$ for 9548 reflections with $I > 2\sigma(I)$, $wR_2 = 0.205$ for all 11 740 independent reflections. Two independent molecules were evident: one ordered, the other showing some disorder of the oxygen atoms around the pentagon. CCDC 186/1637. See <http://www.rsc.org/suppdata/cc/b0/b002254n/> for crystallographic data in .cif format.

- O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1845.
- D. Heymann and L. P. F. Chibante, *Rec. Trav. Chim.*, 1993, **112**, 531; 639; R. Malhotra, S. Kumar and A. Satyam, *J. Chem. Soc., Chem. Commun.*, 1994, 1339; J. P. Deng, C. Y. Mou and C. C. Han, *Fullerene Sci. Technol.*, 1997, **5**, 1033.
- A. L. Balch, D. A. Costa, B. C. Knoll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1995, **117**, 8926; M. P. Barrow, N. J. Tower, R. Taylor and T. Drewello, *Chem. Phys. Lett.*, 1998, **293**, 302; A. B. Smith, R. M. Strongin, L. Brard, G. T. Furst, J. H. Atkins, W. J. Romanov, M. Saunders, H. A. Jiménez-Vázquez, K. G. Owens and R. J. Goldschmidt, *J. Org. Chem.*, 1996, **61**, 1904.
- F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548; V. N. Bezmelnitsin, A. V. Eletsii, N. G. Schepetov, A. G. Avent and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 683.
- R. Taylor, M. P. Barrow and T. Drewello, *Chem. Commun.*, 1998, 2497.
- K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, J. P. McCaulay, D. R. Jones and R. T. Gallagher, *J. Am. Chem. Soc.*, 1992, **114**, 1103.
- A. L. Balch, D. A. Costa, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1995, **117**, 8926.
- T. Hamano, T. Mashino and M. Hiroba, *J. Chem. Soc., Chem. Commun.*, 1995, 1537.
- A. D. Darwish, A. G. Avent, H. W. Kroto, R. Taylor and D. R. M. Walton, *Chem Commun.*, 1997, 1579.
- J. W. Bausch, G. K. S. Prakash, G. A. Olah, D. S. Tse, D. C. Lorents, Y. K. Bae and R. Malhotra, *J. Am. Chem. Soc.*, 1991, **113**, 3205.
- C. Caron, D. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505.
- H. Al-Matar and R. Taylor, *Recent Adv. Chem. Phys. Fullerenes Relat. Mater.*, 1999, **7**, 163.
- L. Y. Chiang, in *The Chemistry of Fullerenes*, ed. R. Taylor, World Scientific, Singapore, 1995, ch. 5.
- P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *Chem. Commun.*, 1996, 1231.
- P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.
- A. D. Darwish, P. R. Birkett, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *Fullerene Sci. Technol.*, 1997, **5**, 705.
- J. Szezepanski and M. Vale, *J. Phys. Chem.*, 1991, **95**, 2792.
- R. Taylor, A. Pénicaud and N. J. Tower, *Chem. Phys. Lett.*, 1998, **295**, 481.