Holey Fullerenes! A bis-Lactone Derivative of [70]Fullerene with an Eleven-atom Orifice

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$C_{70}Ph_8$ spontaneously oxidises in air to form a bis-lactone $C_{70}Ph_8O_4$, having an eleven-membered hole in the fullerene cage; the reaction is believed to proceed *via* insertion of oxygen into 5,6 bonds followed by oxidative cleavage of the adjacent double bond, a process which has a precedent in the spontaneous oxidation of vinyl ethers to esters.

Ever since fullerenes were first prepared, isolated and characterized,[1,2] related open-cage structures have been anticipated. A derivative of [60]fullerene having an eleven-membered hole in the cage has just been described,[3] as has another possessing two seven-membered holes.[4] We now report the *spontaneous* oxidative formation of a [70]fullerene derivative that possesses an eleven-membered hole.

Recently we described the preparation and characterisation of $C_{70}Cl_{10}$,[5] the structural assignment being supported both by calculations,[6] and by the formation of phenyl derivatives: in the presence of benzene–$FeCl_3$, it is possible to replace either 2, 4, 6, 8 or 10 chlorines by phenyl groups.[7] ^{13}C NMR and NOE analyses of the decaphenyl derivative confirm the $C_{70}Cl_{10}$ precursor structure. By heating [70]fullerene with benzene and iron(III) chloride under reflux for 15 min, followed by chromatographic separation (SiO_2, CCl_4), orange–red crystals of $C_{70}Ph_8$ (m/z 1457, EI conditions) can be isolated. ^1H NMR, ^{13}C NMR and NOE experiments show that $C_{70}Ph_8$ has C_s symmetry, has no two phenyl groups attached to adjacent carbon atoms of the cage, and that the two adjacent chlorine atoms in $C_{70}Cl_{10}$ are lost during the substitution of the remaining eight chlorines by phenyls; this is further confirmed by comparison with the ^1H and ^{13}C NMR data for $C_{70}Ph_{10}$.[7]

On allowing a CCl_4 solution of $C_{70}Ph_8$ to stand in air during 2 weeks, oxidation occurs readily to give, after separation from residual $C_{70}Ph_8$ by chromatography (SiO_2, toluene), hexagonal yellow plates (dichloromethane) of luminescent $C_{70}Ph_8O_4$ (Figs. 1, 2), in 45–*ca*. 100% yield (based on recovered $C_{70}Ph_8$); the FAB mass spectrum is shown in Fig. 3. The stuctural assignment is based on the ready loss of CO_2 from $C_{70}Ph_8O_4$ on heating (400 °C),[7] and is confirmed by both IR and NMR data below. The compound is a δ-lactone and is probably derived from $C_{70}Ph_8$ first by insertion of two oxygen atoms into σ bonds to give a bis(vinyl ether). The insertions could be into either 6,6- or 5,6-bonds [in this case C-49/C-50 and C-31/C-49 (and their

equivalents), respectively] neither of which processes has been observed previously in fullerene chemistry, though calculations predict that the latter should readily occur;[8] the symmetry, hole size, and lactone character are independent of the insertion site. Secondly, oxidative cleavage of the adjacent double bond takes place (the only one in a pentagon in $C_{70}Ph_8$) to produce two carbonyl groups. The drive for conjugation between the carbonyl groups and the adjacent oxygens, predicts that the oxygens should be pointing out of the cage, a result confirmed by molecular modelling. The structure has an *eleven-membered hole* in the cage. There is a precedent for this reaction in the facile atmospheric oxidation of vinyl ethers to esters, discovered independently by one of us and by a Russian group.[9,10]
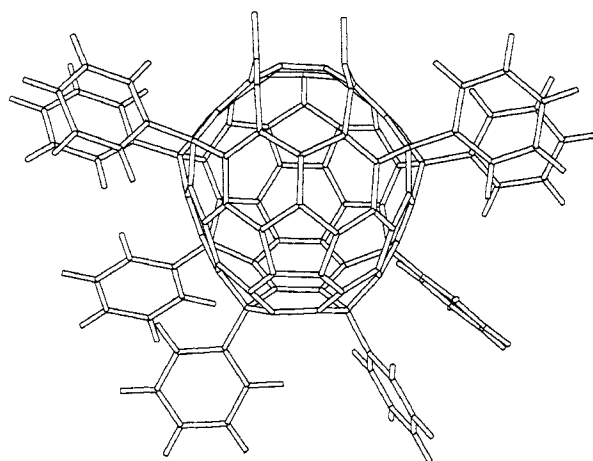

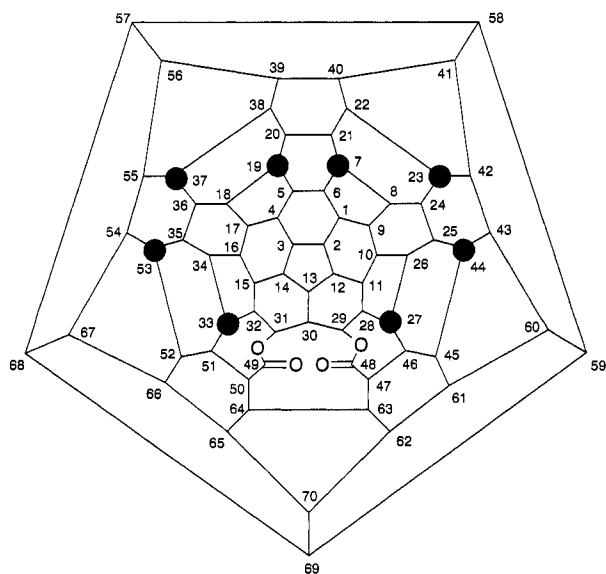**Fig. 2** Energy-minimised structure for $C_{70}Ph_8O_4$

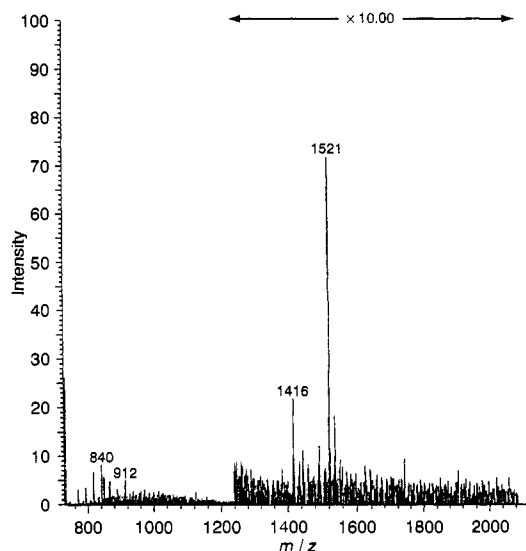**Fig. 1** Schlegel diagram for $C_{70}Ph_8O_4$

Fig. 3 FAB mass spectrum for $C_{70}Ph_8O_4$

The IR spectrum (KBr disc, Fig. 4) shows a strong band at 1785 cm^{-1}. Lactones exhibit bands between 1895 cm^{-1} (α-lactones) and 1750–1735 cm^{-1} (δ-lactones),[11] the increase in wavenumber with smaller ring size being associated with decreased flexibility, and to greater resonance between the oxygen lone pair and the carbonyl double bond. The reduced flexibility in the fullerene derivative should cause the band to shift to a slightly higher wavenumber compared to the usual δ-lactone value. On heating the KBr disc to 450 °C, the main band disappears as CO_2 moieties are lost, and this loss also occurs under EI mass spectrometry conditions, giving $C_{68}Ph_8$.[7]

The ^1H NMR Spectrum (not shown) displays four distinct pairs of phenyl groups as evident also in the spectrum of the $C_{70}Ph_8$ precursor,[7] confirming the C_s symmetry of each. The ^{13}C NMR Spectrum (Fig. 5) consists of four peaks (intensity 2) in the sp^3 region, and thirty-three peaks (intensities 29 × 2; 4 × 1) in the sp^2 region, as required for the proposed structure. The spectrum is however, unlike any other reported hitherto for a fullerene in that four peaks appear much further upfield, including one for the on-axis carbon (peak no. 32). The
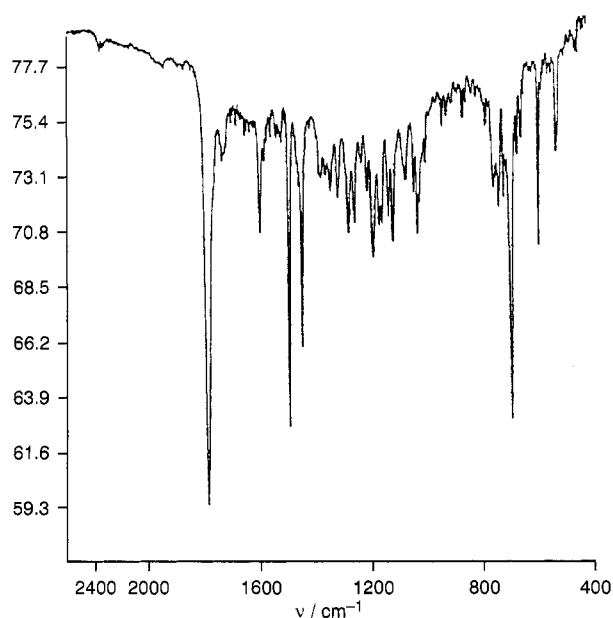
generally downfield locations of the sp^2 peaks for a fullerene has been attributed previously by us to strain.[2] However, for the bis-lactone, strain is greatly relieved in the eleven-atom hole region, and this is reflected in the location of the NMR peaks. It is notable that (excluding the carbonyl carbon, see below) there are seven carbons in the perimeter of the hole (C-29, C-30, C-31, C-47, C-50, C-63, C-64) leading to the expectation of an upfield location of the resonances (3 × 2; 1 × 1), exactly as observed. In particular we may assign with confidence the resonance at δ 125.78 to C-30. (Numbering of [70]fullerene was described previously,[5] the ten possible commencement points for numbering is reduced to six through symmetry; that selected gives the lowest locants for the phenyl addends.)

Although the ^{13}C NMR spectrum exhibits exactly the required number of lines (with the correct intensities), initially we were expecting the resonance for the carbonyl carbon to be well downfield from those for the other sp^2 carbons. However, we note that, for example, the ^{13}C carbonyl resonance for the lactone $\overline{RCHCH_2O}C{=}O$, is moved upfield from δ 168.6 (R = H) to δ 154.7 (R = vinyl),[13] well within the range of resonances that we observe, for what is effectively a vinyl-substituted lactone.

A further notable feature is that whereas there is a good correlation between the chemical shifts of the cage sp^2 carbons and the *ipso* carbons of the phenyl rings in each of $C_{70}Ph_{10}$ and $C_{70}Ph_8$,[7] this is not so in $C_{70}Ph_8O_4$. We provisionally attribute this phenomenon to through-space interactions between the p orbitals on the carbonyl carbons and those of the *ipso* carbons of the nearest pair of phenyl groups, which further supports the proposed structure.

The results of $C_{70}Ph_8O_4$ degradation, which has major implications for fullerene science, will be described in a subsequent publication.

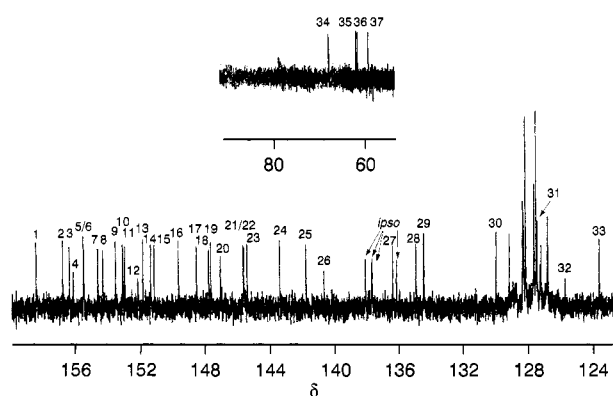**Fig. 4** IR spectrum for $C_{70}Ph_8O_4$; the lactone carbonyl peak is at 1785 cm^{-1}

Fig. 5 ^{13}C NMR spectrum for $C_{70}Ph_8O_4$, showing the exact number of lines and intensities required by the structure. Un-numbered peaks are due to the phenyl ring carbons, identified by proton-coupling.

References

1 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.

2 R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423.

3 J. C. Hummelen, M. Prato and F. Wudl, *J. Am. Chem. Soc.*, 1995, **117**, 7003.

4 T. Grösser, M. Prato, V. Lucchini, A. Hirsch and F. Wudl, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1345.

5 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1995, 683.

6 S. J. Austin, P. W. Fowler, J. P. B. Sandall, P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1027.

7 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, unpublished work.

8 K. Raghavachari, *Chem. Phys. Lett.*, 1992, **195**, 221; K. Raghavachari and C. Cosa, *Chem. Phys. Lett.*, 1993, **209**, 223.

9 R. Taylor, *J. Chem. Res.* (S), 1987, 178.

10 B. A. Trofimov, V. I. Lavrov, L. N. Parshina and Z. A. Akhmedzhanova, *J. Org. Chem. USSR*, 1983, 1751.

11 G. V. Boyd, *The Chemistry of Functional Groups, Supplement B: The Chemistry of Acid Derivatives*, ed. S. Patai, Wiley, New York, 1979, p. 495.

12 H.-O. Kalinowski, S. Berger and S. Braun, *^{13}C NMR Spectroscopy*, Wiley, New York, 1991, p. 371.

13 A. Cowell and J. K. Stille, *J. Am. Chem. Soc.*, 1980, **102**, 4193.