Reaction of [70]Fullerene with Benzyne

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Up to ten equivalents of benzyne can be added to [70]fullerene; the possible sites of addition are considered.

Much is now known concerning addition to [60]fullerene. A single entity X_2 generally adds across the 1,2-bond, provided steric hindrance between the two addends is not high.[1,2] Further addition of X_2 can in principle then take place at any of the remaining twenty-nine interpentagonal bonds within the molecule to give each of eight possible $C_{60}X_4$ isomers, as is found in hydrogenation.[3] If the addends are a little larger then all isomers except the 1,2,3,4-derivative may be obtained, as recently shown for $C(CO_2Et)_2$ groups.[4] If the addend is of the –X– type but very large (as in osmylation,[5] platinylation,[6] or iridylation[7]) the location of the diaddends is further restricted by steric constraints. In polyaddition, up to six interpentagonal bonds are usually involved, located octahedrally so that the addends are as far apart as possible, giving rise to a stable aromatic structure.[1,8] If steric hindrance within the addend X_2 is high, as in bromination[9] or alkylation,[10] a different addition pattern is obtained, the addends being located exo to a pentagonal ring.

For [70]fullerene, no comparable body of information exists. Of the two likely addition site, the 1,9-bond is more reactive than the 7,8-bond.[11–12] In principle, addition across the former and its equivalents gives five isomers (all are found in hydrogenation),[3] addition across the 1,9-bond and each of the equivalent 7,8-bonds gives six isomers (one found so far in hydrogenation),[3] and addition across the 7,8-bond and its equivalents should give five isomers. The only other report of diaddition concerns iridylation which, due to steric hindrance, takes place at the 1,9-bond and its equivalent at opposite ends of the molecule.[13]

As part of a programme investigating addition patterns of [70]fullerene we have examined the reaction with benzyne. [60]Fullerene reacts with 6 equiv. of benzyne[14] which may reasonably be assumed to have added at the octahedral positions. When a benzene solution of [70]fullerene (>99.5% purity, obtained by column chromatography[15] followed by HPLC using a preparative Regis 'buckyclutcher' column) was heated with a 45 molar xs. of 2-aminobenzoic acid and isoamyl nitrite for 90 min, up to 10 equiv. of benzyne added as shown by the mass spectrum of the product, Fig. 1 (Note that the ^{13}C isotope effect is responsible for the M + 1 peaks being dominant in the higher mass range. The peaks at 1527 and 1603 amu are too large by 2 amu, but this is attributed to the weak signals and lack of a satisfactory isotope pattern). As in the reaction with [60]fullerene, the mass spectrum also shows the presence of species containing one and two oxygen atoms. The HPLC trace of the product (Fig. 2, analytical cyano column, hexane eluent) indicates that various degrees of phenylenylation have occurred.

This result provides the first insight into the ability of [70]fullerene to accommodate a large number of addends. Determination of the addition sites will be a complex task, as is indicated by the fact that (i), there are twenty interpentagonal bonds in the molecule, ten at each end (long axis). If five benzynes add to each, then 210 structural isomers are theoretically possible even if one neglects the conformations of one half of the molecule relative to the other. (ii) If the benzynes add to the interpentagonal bonds in any other way, then another 61 isomers are possible (again neglecting conformations).
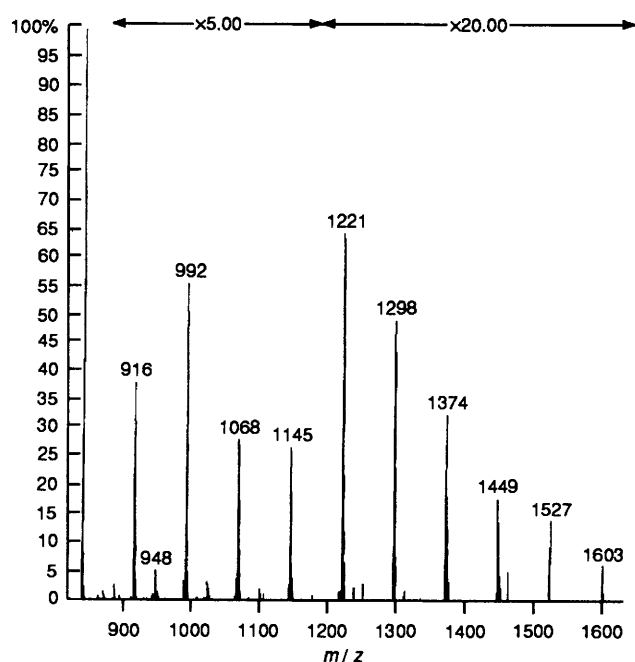

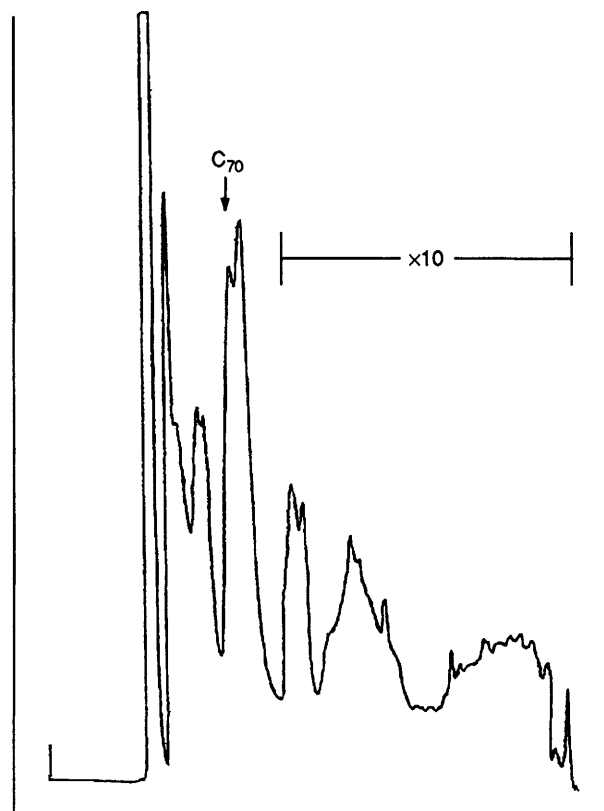Fig. 1 Mass spectrum of the product of reaction of [70]fullerene with benzyne

Fig. 2 HPLC trace of the product of the reaction of [70]fullerene with benzyne

These possibilities may be reduced, as follows: (iii) It seems likely that addition will be symmetrical about the molecular equator so that we need consider only those isomers under (i). (iv) Models indicate that addition across all of the 1,9-bonds and equivalents produces a highly strained structure due to interactions of the *ortho* hydrogens of the benzyne moieties; structures containing this arrangement are reasonably ruled out. (v) The least strained structures will involve additions only across the 7,8-bonds and equivalents. However, assuming that no rearrangement occurs, this structure is also unlikely since the first benzyne should add at each end of the molecule across the 1,9-bond and its equivalent. (vi) For minimal steric hindrance, no pentagon should have more than two benzynes attached (exocyclic) to it. The remaining possible arrangements are as shown in Figs. 3a–d (considering one end of the molecule only). Given that some rings must have two benzynes attached, then the structures involving more of the most reactive bonds must be favoured, *i.e.* 3a–c. Of these we intuitively prefer 3a and 3b because they are the most symmetrical. If the product is also symmetrical about the

equator then either possibility will give one isomer, but three if it is not because of the five-fold symmetry.

Fig. 3 Possible locations (thick bonds, one end of the molecule detailed) for the addition of five benzyne molecules

References

1 R. Taylor, *Phil. Trans. Roy. Soc. Lond. A*, 1993, **343**, 87.

2 R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685.

3 A. G. Avent, A. D. Darwish, D. K. Heimbach, H. W. Kroto, M. F. Meidine, J. P. Parsons, C. Remars, R. Roers, O. Ohashi, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1994, 15.

4 A. Hirsch, I. Lamparth and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 437.

5 J. Hawkins, A. Meyer, T. A. Lewis, U. Bunz, R. Nunlist, G. E. Ball, T. W. Ebbeson and K. Tanigaki, *J. Am. Chem. Soc.*, 1992, **114**, 7954.

6 P. J. Fagan, J. C. Calabrese and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408.

7 A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1992, **114**, 10985.

8 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1667; P. D. Fowler, D. J. Collins and S. J. Austin, *J. Chem. Soc., Perkin Trans. 2*, 1993, 275.

9 P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, 479.

10 P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton and K. F. Preson, *Science*, 1991, **254**, 1183.

11 Contiguous numbering for [70]fullerene can be achieved (*cf.* R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1993, 813, in which the carbons of the pentagonal cap were labelled 1–5), by commencing numbering around a hexagon adjacent to the pentagonal cap. The 1,2-bond in then the most reactive one as in [60]fullerene; this revised numbering will be used in subsequent publications.

12 C. C. Henderson, C. M. Rohlfing, K. T. Gillen and P. A. Cahill, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 786; A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 5456; J. Hawkins, A. Meyer and M. A. Solow, *J. Am. Chem. Soc.*, 1993, **115**, 7499; A. Hirsch, T. Grösser, A. Skiebe and A. Sol, *Chem. Ber.*, 1993, **126**, 1061.

13 A. L. Balch, J. W. Lee and M. M. Olmstead, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1356.

14 S. H. Hoke, J. Molstad, D. Dilettato, M. J. Jay, B. Kahr and R. G. Cooks, *J. Org. Chem.*, 1992, **57**, 5069; M. Tsuda, T. Ishida, T. Nogami, S. Kurono and M. Ohashi, *Chem. Lett.*, 1992, 2333.

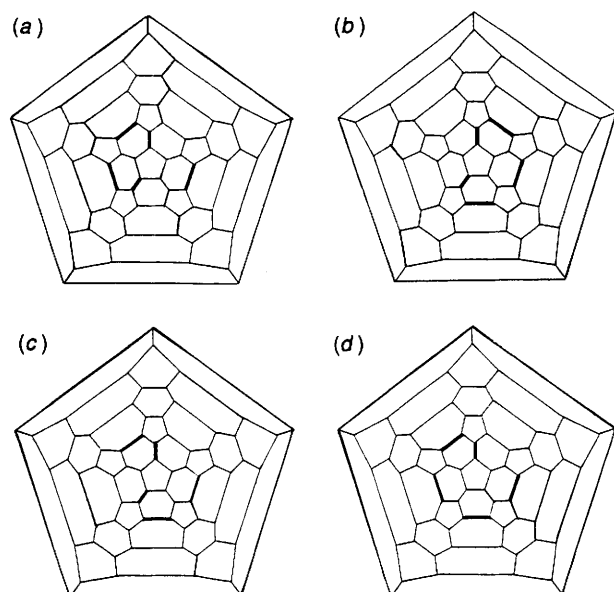15 A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1994, 15.