Is C_{119} a Spirane and the First Fullerene to Contain a Four-membered Ring?

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The newly discovered C_{119}, C_{129}, and C_{139} probably have spirane structures with a four-membered ring in one of the cages; diradicals, stable fullerenol radicals or fullerene diols are feasible though less probable alternatives.

Recently, McElvany *et al.* detected by mass spectrometry the extraordinary species C_{119}, C_{129}, and C_{139} in soot extracts obtained from various sources and produced by the arc-discharge process. The molecular masses of these species suggested that they are produced by combinations of the [60]- and [70]-fullerene cages, with concomitant loss of a carbon atom, and that they are fullerenes. They can be produced by reacting fullerenes with ozone.[1]

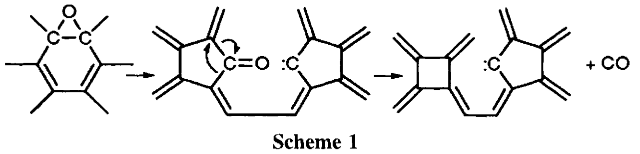
The structures of these species is at first sight baffling, especially in view of expectation by now that fullerenes will only be nC_2 structures. McElvany *et al.* tentatively suggested a coupled structure in which removal of a carbon from one cage would leave three bonds (it is actually four) which would join at the 1-, 3-, and 5-sites of a hexagon in a second cage (this though needs six bonds). Coalescence of two cages may be ruled out because of both the enormous energy needed for the complex bond reorganisation, and the fact that ozone would readily attack the severely-disrupted structures involved, leading to the substantial formation of oxidative degradation products. (An early report of fullerene coalescence[2] appears to be due to 2 + 2 cycloaddition.[3])

We now propose the probable structures of these species which takes account of the importance of ozone in their formation, is compatible with known chemistry, satisfies the normal carbon valencies, and preserves the preferred locations of the bonds of high π-bond order. The following mechanism uses reaction of [60]fullerene with itself as the example, but is equally applicable to the involvement of [70]fullerene.

Reaction of [60]fullerene with ozone leads to epoxide formation, and if prolonged, to gradual cage degradation.[4,5] Since one carbon atom is lost in the formation of the odd-carbon species, a reasonable mechanism is as shown in Scheme 1. Here bond reorganisation in the epoxide leads first to a ketocarbene, with subsequent carbon monoxide loss leading to formation of a four-membered ring. Epoxides are known to give ketones upon heating,[6] and carbonyl compounds can give carbenes by CO extrusion.[7] The carbene produced attacks a high-order bond of an adjacent [60]fullerene molecule (there is now ample evidence for carbene attack on fullerenes[8]), to give the product shown in Fig. 1, which is a spirane (spirofullerene); the stepwise sequence of events may of course be concerted. Because the carbene is trapped by another fullerene molecule, further cage degradation at the weakened cage site is inhibited, especially by steric hindrance. The product C_{119} has a plane of symmetry, and Fig. 2 shows the section of the two fullerene molecules involved in the bonding, and the location of the high-order bonds. In the fullerene that has been opened, the numbering[9] of the undegraded cage is retained so that it can be seen that C-2 has been eliminated. A very recent report[10] that C_{59} is detected in the mass spectrum of $C_{60}O$ provides strong support for our conjecture.

Although one cage has a four-membered ring, this is not unreasonable, because the structure of the relevant portion of the ring is that of biphenylene which is quite stable. Moreover, the bond fixation is the same as that found in biphenylene. Should the bond between C-3 and C-12 not be formed, the product will be a diradical. It is also conceivable, though rather less likely, that the bond from C-1 to C-1′ is not formed, hydroxy groups arising from the presence of ozone and adventitious hydrogen, being attached to one or both of the carbons. This would then give either a fullerenol radical (which could be stable) or a fullerene diol, respectively. However, fullerenols only show the parent hydrocarbon during mass spectrometry,[11] so the hydroxy groups would not be detectable.

One opened cage may of course attack another opened one to give a low concentration of a species C_{118}, indistinguishable (by mass spectrometry) from the single cage fullerene of the same mass; a peak at m/z 1417 (correct for C_{118} after allowing for the ^{13}C isotope effect) was evident in the work of McElvany *et al.*[1] There is no reason why three cages would not so combine, and although the concentrations would be low, it



Scheme 1

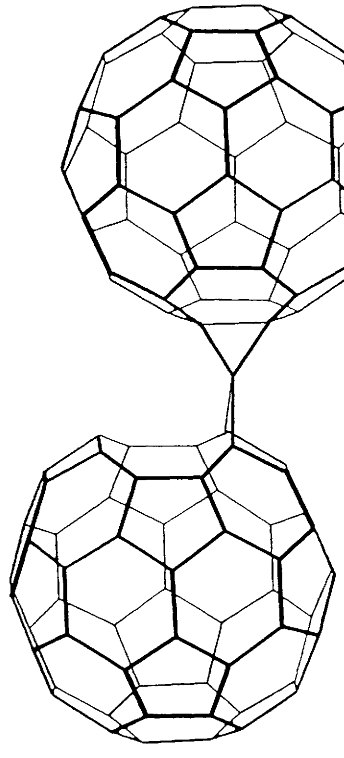


Fig. 1 Proposed structure for C_{119}

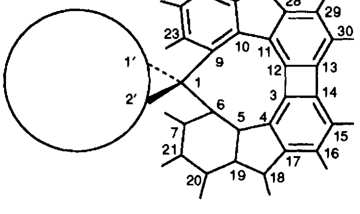


Fig. 2 Section of the 59-carbon cage, showing the bonding, enlarged opening, biphenylene moiety and carbon numbering

would seem reasonable to search for a peak corresponding to C_{178} in ozone-treated [60]fullerene.

For the cage combinations involving [70]fullerene, two predictions can be made, based on existing knowledge of its reactivity. Carbene addition is likely to take place at the double bond exocyclic to a pentagonal cap. The second cage should also be opened at the same site, but because strain is greatest at the polar caps of [70]fullerene,[12] it is reasonable to assume that the pentagon that collapses to a four-membered ring will be one of the two sets of five equivalent pentagons. Thus, using the provisional numbering system given in ref. 9, C-6 should be eliminated. Reaction of [70]fullerene with itself can lead to two possible isomers: in one of the 'hole' in one cage faces a cap pentagon, whilst in the other it faces one of the other pentagons.

Structural characterisation of these products will be a formidable task. The ^{13}C NMR spectrum for C_{119} of the proposed structure should yield three lines (intensity ratio 2 : 1) in the sp^3 region and sixty lines, 56 (× 2) and 4 (× 1) in the sp^2 region. Circumstantial evidence could be provided by the appearance in ozone treated soot extract of reasonances well downfield from the usual[13] fullerene region, due to the highly strained bridgehead carbons C-3, C-12, C-13, and C-14 of the biphenylene moiety (and the corresponding positions in C_{129} and C_{139}).

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