

Reaction of benzyne with [70]fullerene gives four monoadducts: formation of a triptycene homologue by 1,4-cycloaddition of a fullerene

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Mono-, di-, tri- and tetra-benzyne adducts have been isolated by column chromatography of the products of the reaction of benzyne with [70]fullerene. ¹H NMR spectroscopy shows the monoadduct to consist of four isomers, the [1,2]-, [5,6]-, [7,21]- and [7,23]-benzeno[70]fullerenes in yields of 42, 12, 12 and 34%, respectively. The 7,23-isomer has C₂ symmetry and is produced by novel equator-spanning 1,4-addition ([2 + 4] cycloaddition) and is a fullerene homologue of triptycene; molecular orbital calculations predict this 1,4-addition. Strain may also render unfavourable the [2 + 2] cycloaddition of benzyne, whereas the atypical Diels–Alder[2 + 4] cycloaddition may be facilitated by the lower electrophilicity of [70]fullerene, especially in the equatorial region. The addition patterns account for the previously observed ability of [70]fullerene to accommodate 10 benzyne addends.

Studies of [60]fullerene reactions have dominated fullerene chemistry owing to the greater availability of the starting material. However, reactions of [70]fullerene are more interesting from the regiochemical and mechanistic viewpoint because of the greater variety of products that may be produced from a single reaction. Thus whereas all addition sites in [60]fullerene are equivalent, there are many nonequivalent sites in [70]fullerene; moreover, two products may be obtained with some additions if the addend is unsymmetrical.

We reported recently that [70]fullerene added up to 10 benzyne molecules.¹ Six benzynes add to [60]fullerene^{2,3} which is readily understandable in terms of an octahedral disposition of the addends. However the multiple addition to [70]fullerene could not be explained on the basis of addition primarily across the 1,2-bonds† (this being dominant in other reactions of this molecule), since unacceptable steric interactions would result. In order to resolve this problem we have now isolated the monoadduct and find that four isomers are present (the first time this many have been observed with [70]fullerene), and show that the structures can account for the multiple addition previously observed.

Experimental

A solution of [70]fullerene (50 mg, 0.06 mmol) and isopentyl nitrite (21.1 mg, 0.18 mmol) in benzene (150 ml) was heated to reflux, and anthranilic acid (24.7 mg, 0.18 mmol) was added. The red solution turned brown immediately, and heating under reflux was continued for a further 1.5 h under nitrogen. The cooled dark solution was washed with aq. sodium hydrogen carbonate and water, and the solvent removed (vacuum) from the dried (Na₂SO₄) benzene layer to give a black residue. Column chromatography (70–230 mesh silica gel, cyclohexane) of the product gave, in sequence: C₇₀, 20 mg; C₇₀C₆H₄, yellow, 7 mg (21.4%); C₇₀(C₆H₄)₂, yellow, 4 mg (11.3%); C₇₀(C₆H₄)₃, green–yellow, 2 mg (5.2%); C₇₀(C₆H₄)₄, green–yellow, 1 mg (2.5%), the corresponding R_f values (TLC, silica gel, cyclohexane) being 0.65, 0.51, 0.33, 0.22 and 0.10. Yields are based on the quantity of [70]fullerene consumed. Acetone

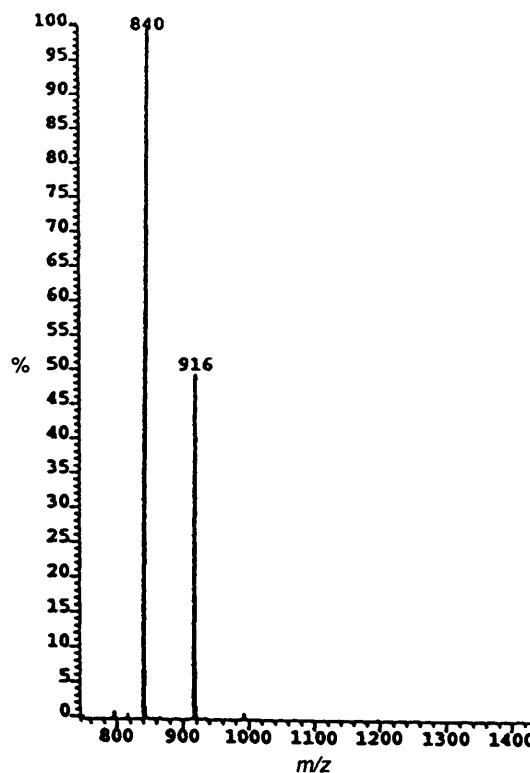


Fig. 1 EI mass spectrum for the monoadduct of benzyne and [70]fullerene

elution of the column produced traces of C₇₀(C₆H₄)₅ and oxides of all the fractions.

The mass spectrum of fraction 2 (Fig. 1, EI conditions) shows that only the monoadduct is obtained; the [70]fullerene peak arises from the ring-opening retro cycloaddition. This fact was confirmed by HPLC using a 25 cm × 4.6 mm Cosmosil column (toluene eluent, 0.5 ml min⁻¹), which showed a complete absence of [70]fullerene, and only two peaks of retention times 13.7 min (11%) and 14.6 min (89%). Since the ¹H NMR spectrum showed that two of the isomers were present, each in 12% yield, we assume that one of these gives rise to the early peak, the other isomers co-eluting in the 14.6 min fraction.

† The 1,2, 5,6, 7,21, 7,23 and 20,21 bonds (I.U.P.A.C.) referred to throughout this text were numbered provisionally as 1,9, 7,8, 21,40, 21,42 and 23,24 in ref. 4.

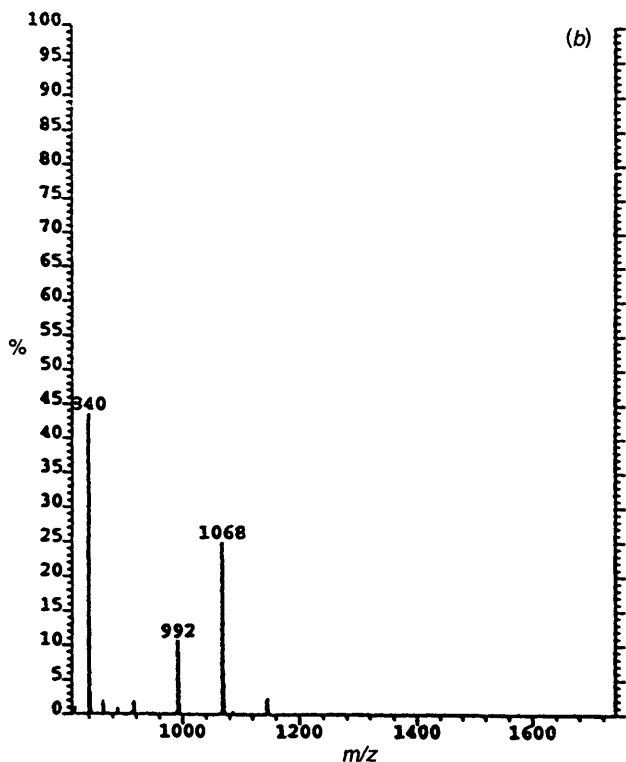
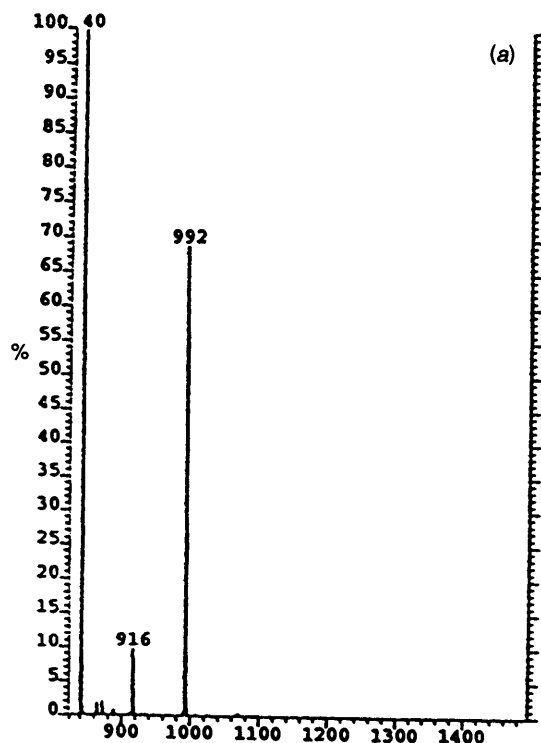


Fig. 2 EI mass spectra for the (a) di- and (b) tri-adducts of benzyne with [70]fullerene

The EI mass spectra of the di- and tri-adducts are shown in Fig. 2 and both show the presence of a lower adduct due to the retro reaction under these conditions. The di-adduct showed three peaks in HPLC analysis (conditions as above) with retention times of 9.5, 10.1 (main) and 11.1 min, suggesting that a mixture of isomers is present. The tri-adduct gave a peak centred at 8.0 min. The mass spectrum for the tetra-adduct (not shown) gave m/z 1144; again lower adducts were present due to the retro-reaction.

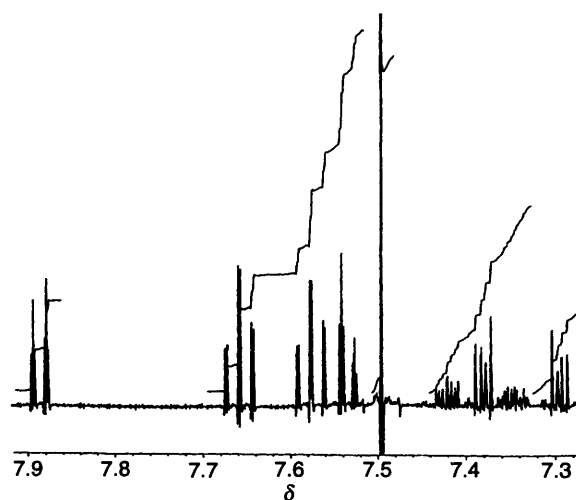


Fig. 3 ^1H NMR spectrum for the monoadduct of benzyne and [70]fullerene

Results

^1H NMR analysis

The ^1H NMR spectrum of the monoadduct (Fig. 3) revealed the presence of four isomers in relative yields of 42, 34, 12 and 12%. The monoadduct of benzyne with [60]fullerene was reported² to give an AA'BB' pattern, δ 8.02 and 7.780 [J_{AB} 7.6, $J_{AB'}$ 1.2, $J_{BB'}$ 6.7, $J_{AA'}$ 0.8 Hz (CD_2Cl_2)]. [The chemical shifts are solvent dependent: we find (CS_2) δ 7.60 and 7.36.] The coupling constants for our [70]fullerene monoadducts (below) are similar. (Note that the [60]fullerene monoadduct data appear to have been misreported, and this was confirmed by recalculation of these data: J_{AB} should read $J_{BB'}$ and $J_{AB'}$ should read $J_{AA'}$. Hoke *et al.* also detected a product giving the same pattern but centred at δ 7.618 and 7.470 and considered that it might be due to another monoadduct.² However, this chemical shift difference is almost exactly that (0.147 ppm) produced by biphenylene, a normal byproduct of benzyne reactions.)

[1,2]Benzeno[70]fullerene. This isomer [Fig. 4(a)] comprises 42% of the monoadduct and has four non-equivalent aryl hydrogens, giving an ABCD pattern with double triplet resonances centred at δ 7.888, 7.662, 7.578 and 7.538. The benzyne addend in this isomer is nearest to the cap pentagon, which is the most electron-deficient region in [70]fullerene as shown by the position of the resonances for the cage carbons.⁴ Consequently, the resonances for this isomer are the furthest downfield. The most downfield peak is attributed to the α -hydrogen (H_A) which lies over the most electron-deficient cap pentagon, the most upfield one being the α -hydrogen (H_D) over the other pentagon. Likewise the β -hydrogen (H_B) is the one nearest to the cap pentagon, and it also follows that since the β -hydrogens are further from the cage than the α -hydrogens, the separation between their resonances is smaller. Fig. 5(a) shows the observed spectrum together with that simulated using the following coupling constants: J_{AD} 1.1, J_{BC} 7.8, J_{AC} 0.94, J_{BD} 0.89, J_{AB} 7.6 and J_{CD} 7.45 Hz.

[7,21]Benzeno[70]fullerene. This (chiral) isomer [Fig. 4(b)] comprises 12% of the monoadduct and also has four non-equivalent aryl hydrogens, giving a complex ABCD pattern with resonances centred at δ 7.431, 7.415, 7.356 and 7.345. Here one α -hydrogen (H_A) lies over an electron-deficient pentagon whilst the other (H_D) lies over a relatively electron-rich hexagon, but since the benzyne addend is located nearer to the most electron-rich centre of the molecule,⁵ the resonances are overall considerably further upfield than for the 1,2-isomer, and the separation between them is much smaller. Fig. 5(b) shows the observed spectrum (note that there are four main peaks present due to the 5,6-isomer) and that simulated using the

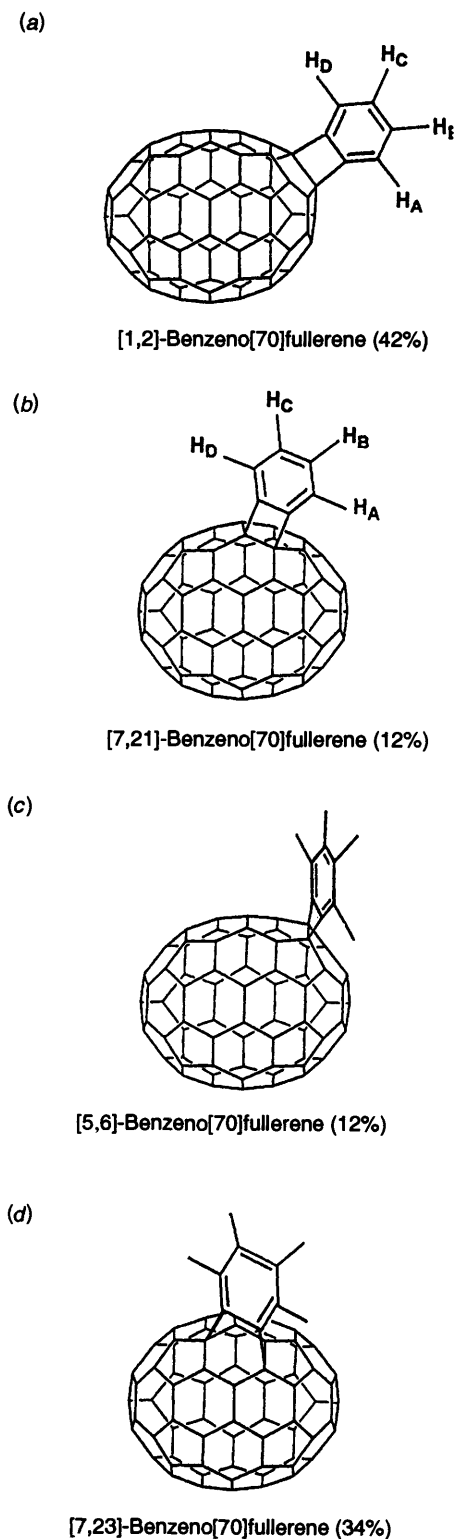


Fig. 4 (a) [1,2]Benzeno-1,2-dihydro[70]fullerene; (b) [7,21]benzeno-7,21-dihydro[70]fullerene; (c) [5,6]benzeno-5,6-dihydro[70]fullerene; (d) [7,23]benzeno-7,23-dihydro[70]fullerene

coupling constants: J_{AD} 1.0, J_{BC} 7.8, J_{AC} 0.92, J_{BD} 0.96, J_{AB} 7.6 and J_{CD} 7.6 Hz, which are almost the same as required for the 1,2-isomer. Compared to the 1,2-isomer, the peaks for the β -hydrogens are slightly more downfield relative to those for the α -hydrogens, due probably to the differential electronic effects of the adjacent polygons as noted above.

[5,6]Benzeno[70]fullerene. This isomer [Fig. 4(c)] comprises 12% of the monoadduct, and has C_s symmetry, the plane of symmetry being perpendicular to that of the aromatic ring.

Thus there are two pairs of equivalent hydrogens, and an AA'BB' pattern results as shown in Fig. 5(c), δ 7.382 and 7.297. Fig. 5(c) also shows the spectrum simulated with the coupling constants: J_{AB} 7.6, $J_{BB'}$ 7.9, $J_{AB'}$ 0.95 and $J_{AA'}$ 1.0 Hz.

[7,23]Benzeno[70]fullerene. This isomer (also chiral) is produced in 34% relative yield and gives two coincident peaks at δ 7.496 in CS_2 . However, addition of dichloromethane (CD_2Cl_2 - $CS_2 = 2:1$) resolved this peak into an AA'BB' pattern, at δ 7.507 and 7.495 (J_{AB} 7.5, $J_{BB'}$ 9.2, $J_{AB'}$ 0.97 and $J_{AA'}$ 1.02 Hz). The spectrum, and that simulated using these parameters, is shown in Fig. 5(d). This pattern is consistent (see also discussion) with the C_2 symmetric structure [Fig. 4(d)] a fullerene homologue of triptycene. The coincidence of the chemical shifts for the α - and β -aryl hydrogens may be attributable to the unusual location of the α -hydrogens. Whereas in the other three isomers these lie over the centre of a polygon, in the 7,23-isomer they lie directly over a C-C bond.

In summary, these NMR data (including those for [1,2]benzeno[60]fullerene), show *meta* (AB') and *para* (AA') coupling constants of 0.8–0.97 and 1.0–1.2 Hz, respectively. These values are consistent with the results of Cooper and Manatt, who showed that for unstrained aromatics the *meta* value was greater than the *para*, whereas for strained aromatics the reverse was true. The *meta* and *para*-values of 1.3 and 0.6 (9,10-dihydroanthracene), 0.80 and 1.00 (biphenylene) and 0.30 and 1.85 (benzocyclopropane) show the effect of increasing strain.⁶ Values of 1.2 and 0.6 for triptycene indicate lower strain, because on addition of benzyne to anthracene, the outer aryl rings of the latter fold back to relieve strain in the bridgehead sp^3 -hybridised carbons. This phenomenon is not possible in the analogous compound produced by addition of benzyne to [70]fullerene, and thus the coupling constants become almost equal.

¹³C NMR analysis

In the sp^3 region of the spectrum, four main peaks are present (intensities in parentheses) at δ_C 71.46 (2.93) and 69.90 (2.96) (C-1 and C-2 of the 1,2-isomer), 68.54 (2.07) (C-5 and C-6 of the 5,6 isomer) and 65.68 (4.62) (C-7 and C-23 of the 7,23-isomer). The intensities correspond almost exactly to the isomeric composition indicated by the ¹H NMR data. Peaks for the unsymmetrical 7,21-isomer were not resolvable from the background noise, due to their expected low intensities. The upfield location of the signals for the 7,23-isomer is consistent with the more upfield location of the d carbons in [70]fullerene itself,⁵ and provides further evidence for the correct assignment of this isomer.

In the sp^2 region of the spectrum, only the resonances for the two most abundant 1,2- and 7,23-isomers and the symmetrical 5,6-isomer should give signals sufficiently strong to be detectable in a realistic acquisition time. Peaks detected should thus be: 33 (2 C) + 2 (1 C) for the cage and 6 (1 C) for the aryl ring of the 1,2-isomer; 34 (2 C) for the cage and 3 (2 C) for the aryl ring of the 7,23-isomer; and 32 (2 C) + 4 (1 C) for the cage and 3 (2 C) for the aryl ring of the 5,6-isomer. The 4 (1 C) peaks for the 5,6-isomer will be of too low intensity to be distinguishable. Thus, taking into account the proportions of each isomer, the peak distributions and intensities should be ca. 70 (2 C), 8 (1 C), 35 (0.5 C), hence a total of 113 peaks. The number found (110, including three coincident) is in excellent agreement, the small discrepancy between the number of 2 C peaks predicted (70) compared with the number observed (72), being attributable to the difficulty in accurate integration of shoulder peaks: δ_C 148.66 (4 C); 148.05, 130.25 (both 3 C); 156.71, 154.52, 151.96, 151.61, 151.34, 150.91, 150.53, 150.30, 150.11, 150.02, 149.74, 149.54, 149.39, 149.34, 149.27, 149.09, 148.98, 148.93, 148.79, 148.21, 148.16, 148.12, 147.38, 147.36, 147.23, 147.10, 146.93, 146.76, 146.73, 146.27, 146.14, 146.08, 146.00, 145.88, 145.70, 145.57, 145.31, 144.93, 144.77, 144.63, 144.38, 144.12, 144.00, 143.66, 143.53, 143.43, 142.97, 142.90,

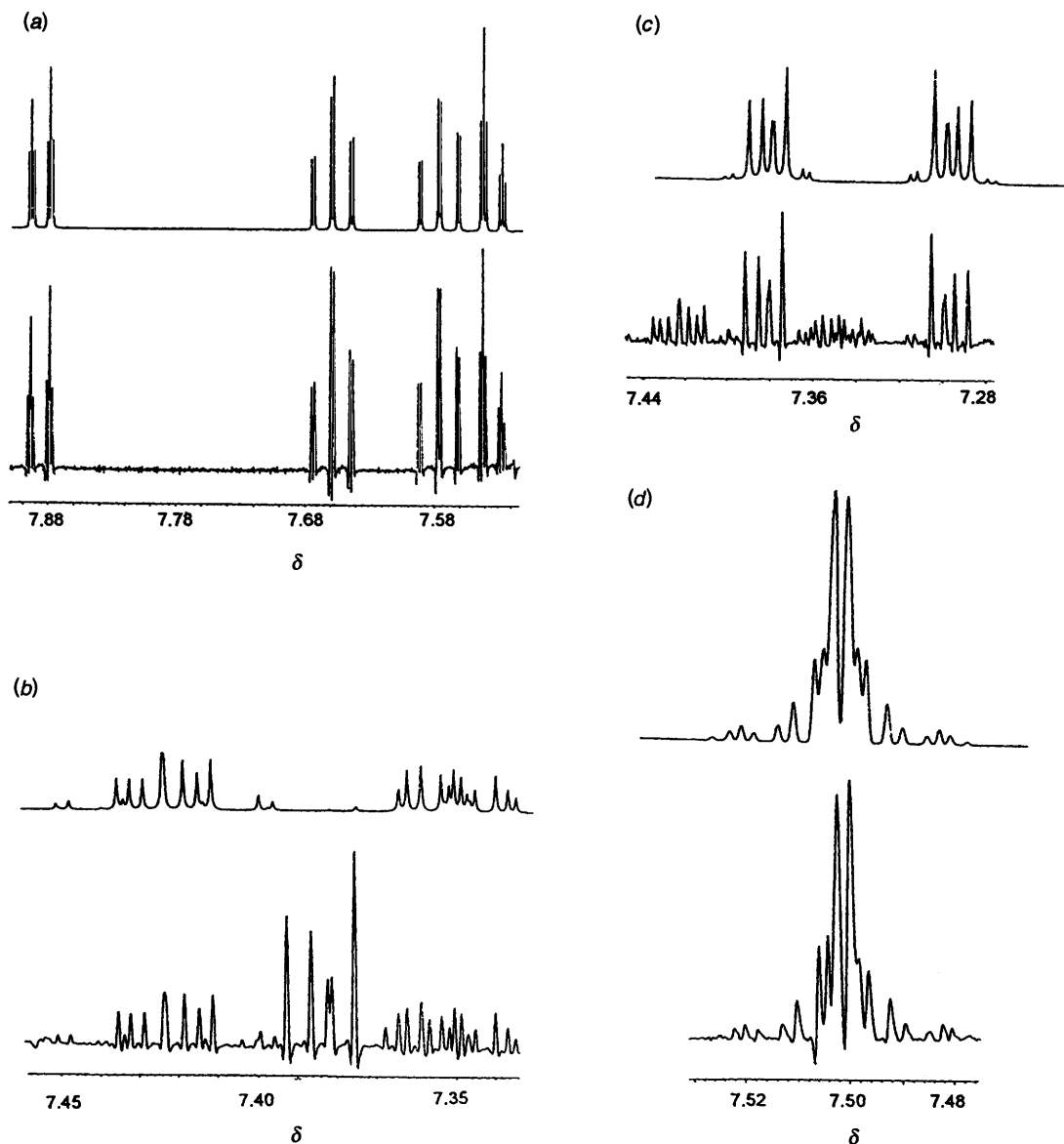


Fig. 5 ^1H NMR spectra (observed below and simulated above) for the (a) 1,2-, (b) 7,21-, (c) 5,6- and (d) 7,23-isomers, respectively

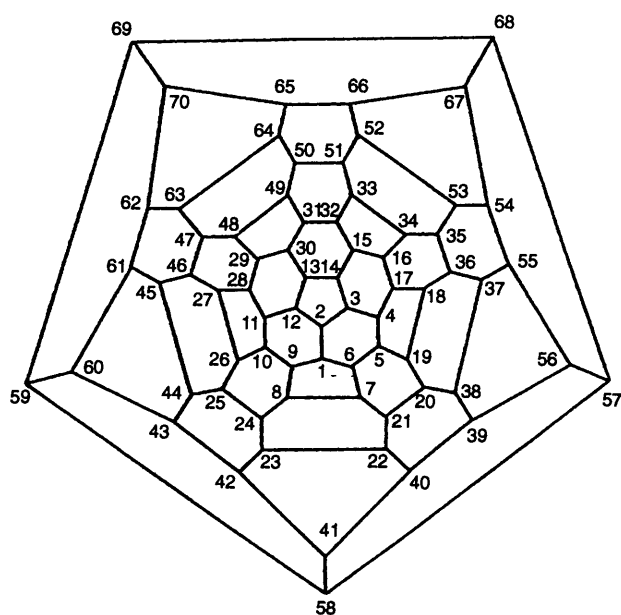


Fig. 6 Schlegel diagram for [70]fullerene showing numbering

142.40, 141.35, 140.97, 139.74, 134.30, 133.42, 132.23, 131.95, 131.88, 131.81, 131.58, 131.19, 131.11, 130.43, 130.15, 127.62, 123.39, 123.04, 122.96, 122.87 (all *ca.* 2 C); 153.85, 151.59, 151.26, 150.16, 149.91, 149.70, 149.46, 149.15, 149.10, 148.36, 148.15, 146.98, 146.89, 146.87, 146.48, 146.42, 146.38, 146.21, 146.17, 145.95, 145.80, 145.67, 145.63, 144.69, 144.49, 142.80, 141.73, 139.91, 139.37, 137.95, 132.76, 132.53, 131.87, 131.54, 129.43, 127.30 (all 0.5–1 C).

If the assignments of the 5,6- and 7,23-isomers was the wrong way around, 117 lines would be required, with 69 of 2 C intensity and 49 of *ca.* 0.5–1 C intensity, a significantly greater disagreement with the observed results.

Discussion

Our results show that four monoadduct isomers are produced, but before discussing this fact it is appropriate to consider both the theoretical predictions of the addition patterns and patterns obtained in other reactions.

Theoretical predictions of reactivity patterns

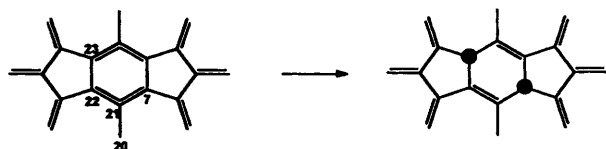
Calculations of [70]fullerene π -bond orders^{4,7} showed that the 5,6-bond (see Schlegel diagram, Fig. 6) should be the most reactive towards addition, followed by the 1,2-bond.

Table 1 Isomer yields in additions to [70]fullerene^a

Addend	Isomer yield (%)				Ref.
	1,2	5,6	7,21	7,23	
Ir(CO)Cl(PPh ₃) ₂	100				14
OsO ₄	68	22			15
HMe, HPh	100				16
H ₂ (diimide)	96	4			17
H ₂ (diborane)	67	33			9
1,2,3,4,5-pentamethylcyclopentadiene	mainly	detected			18
C(CO ₂ Et) ₂	100				19
Pyrazoline (→ CH ₂)	87	13			20
(MeO) ₂ -orthoquinodimethane	24	10	1.5		12
<i>N</i> -Methylidenemethylamine	46	41 ^b	13		13
Methylisoxazole	67	33 ^c			21
4-Methoxyphenylisoxazole	75	25 ^c			21
Benzyne	43	12	12	34	This work

^a An entry of 100% indicates that only this isomer was detected. Other entries scaled to total of 100%. ^b The ¹H NMR data is also consistent with this being the 7,23-isomer. ^c The ¹³C NMR data is also consistent with this being the 7,23 isomer.

Subsequent semi-empirical MNDO studies of the preferred sites of addition of H₂ to [70]fullerene⁸ confirmed these conclusions (at higher calculation levels the order is reversed),⁹ and showed also that 1,4-addition should take place in an equatorial six-membered ring, and diagonally across the equator at the 7,23-positions (see Fig. 6). Valence Bond theory provides us with an understanding of the reasons for this latter addition pattern. The generally accepted proposal that the double bonds in fullerenes are preferentially located exocyclic to pentagonal rings¹⁰ accounts for the addition chemistry observed. Applying this criterion to [70]fullerene produces the bond dispositions in the equatorial region (Scheme 1); there are three electrons in



Scheme 1 Bond dispositions in the equatorial region of [70]fullerene arising from locating double bonds exocyclic to pentagons; 1,4-addition restores normal valencies

each of the extended 'double' bonds within the central hexagon, and the valency problem can be relieved by 1,4-addition across the 7,23-positions as shown. It is significant therefore that this addition pattern has been observed recently in chlorination.¹¹

Both Valence Bond and MO methods predict also that addition across the 20,21-bond should fail because of the very low π -bond order (*cf.* refs. 12 and 13 in which it was assumed that such addition might occur). By contrast, some addition should be observed across the 7,21 bond, and this has been confirmed in these recent studies.^{12,13}

Additions found in other reactions of [70]fullerene

These are summarised in Table 1. It is evident that there are considerable differences in the isomer distributions between reactions; the exclusive 1,2-addition in some work originates probably from the analytical limitations.

Two factors should be considered in accounting for the isomer distributions: the strain present in [70]fullerene before reaction and the strain present in the intermediate leading to the product. With regard to the former, although calculations predict predominantly 5,6-addition, 1,2-addition is thought to dominate because of greater curvature across the 1,2-bond²² and hence greater relief of strain through addition. The widely differing results for hydrogenation (which are especially accurate because of the simplicity of the analysis) demonstrate the importance of the structure of the intermediate. Where

strain in the intermediate is an important factor, it is likely to be greater for 1,2-addition compared to 5,6-addition, and this may be the reason for the formation of larger proportions of the 5,6-isomer in some reactions. Note that the yields obtained in methylene addition do not argue against this concept, because the product-determining pyrazoline intermediate in this reaction²⁰ involves a five-membered ring rather than a three-membered one.

Strain effects may contribute to the benzyne results. 1,2-Addition creates considerable strain due to the formation of the four-membered ring, whereas addition across the 7,23-bond, (which corresponds to the well known addition of benzyne to anthracene to give triptycene) produces a somewhat less strained six-membered ring. However, another factor may be important here. Unlike the [2 + 2] cycloaddition, the [2 + 4] cycloaddition is thermally allowed, but in [60]fullerene the latter is unfavourable due to the high electrophilicity of the cage, and so far has not been observed. By contrast, [70]fullerene is less electrophilic, especially in the equatorial region, thereby facilitating this atypical Diels–Alder reaction.

Polyaddition of benzyne to [70]fullerene

The present study was stimulated by our observation that up to ten benzyne molecules could add to [70]fullerene, a result which is difficult to understand in terms of the belief that 1,2-addition dominates.¹ Steric interactions would prevent more than two such additions occurring at each cap, giving only four benzyne addends. The present results resolve the difficulty, because there are two major addition sites: four benzyne can add around the equator, and when this is done a double bond is introduced into a pentagon (equivalent to the 7,8-position) and so further addition can take place there. (This pattern is then the same as observed in addition of ten chlorines to [70]fullerene.⁹) Four benzyne can add to the caps as previously proposed; the fifth may then add across the least hindered 5,6-type bond giving the structure shown in Fig. 7. Notably this derivative has five benzenoid rings in which resonance should be more favourable due to the reduction of strain in the adjacent rings (which now have sp³ carbons in them). It will thus be more aromatic than [70]fullerene, and hence especially stable.

Photochemical addition of disilirane

Ando and co-workers reported that photochemical addition of disilirane, R₂SiCH₂SiR₂ (R = 1,3,5-trimethylphenyl) to [70]fullerene gave a product which they believed to arise from addition across the 20,21-bond.²³ This was based on the observation of 34 signals in the sp² region for the cage; all methyl groups in the pair of aryl rings attached to a given silicon were nonequivalent, as were the hydrogens in the methylene

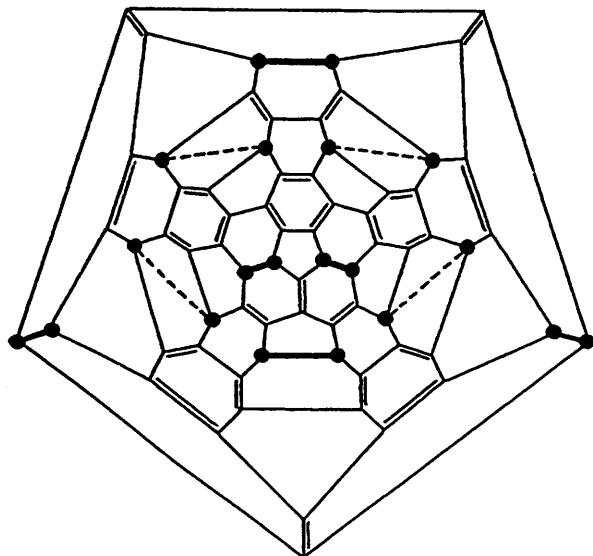


Fig. 7 Probable location of ten benzyne addends on [70] fullerene (bold lines show 1,2-addition, dotted lines show 1,4-addition); the five benzenoid rings created by these additions are evident

group. It was assumed that a twisted five-membered ring structure existed, in order to account for these difficulties. Our results suggest however that the addition occurred across the 7,23 bond. This structure would also require the 34 ^{13}C NMR signals observed, and account for all of the anomalies in the ^1H NMR spectrum.

Acknowledgements

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