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Benzyne Adds Across a Closed 5–6 Ring Fusion in C₇₀: Evidence for Bond Delocalization in Fullerenes

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Abstract: Addition of benzyne to C₇₀ results in four isomeric monoadducts (compounds **1a–d**) in a 42:35:13:10 ratio as determined by ¹H NMR. These compounds were separated by repeated passes through HPLC columns. The major isomer (**1a**) resulted from addition to the highly pyramidalized C1–C2 bond as shown by ¹³C NMR and UV/vis spectroscopy. The structure of the C1–C2 adduct (**1a**) was confirmed by X-ray crystallography. The second isomer (**1b**) was assigned as an adduct to the C5–C6 bond on the basis of ¹³C NMR and UV/vis spectroscopy. Compound **1c** exhibited a ¹³C spectrum consistent with an adduct to the C7 and C8 positions. The presence of sp³ ¹³C NMR resonances proved that the C7–C8 bond is still intact, making this the first identification of direct addition to a 5–6 ring fusion in a fullerene, and the first example of an adduct to a 5–6 ring fusion where the ring fusion bond remains intact. The fourth isomer (**1d**) displayed spectral data consistent with a compound with C₁ symmetry and is assigned as an adduct to the C7–C21 bond.

A great deal has been learned about the reactivity of the fullerenes in the short period since they became available in bulk quantities. The characteristic pyramidalization of sp² carbons of fullerenes results in high reactivity.¹ One of the most general patterns of reactivity is that fullerene chemistry is largely the chemistry of addition reactions.^{2,3} The structure of C₆₀ is usually drawn as a complex [5]radialene (Figure 1), with the double bonds positioned between six-membered rings (at “6–6 ring fusions”), and this is consistent with measured bond lengths⁴ and with the reactivity⁵ of C₆₀ toward nucleophilic addition,^{6–11} toward reduction,¹² and in a host of cycloadditions.¹³ Herein we report the addition of benzyne across the C7–C8 carbon–carbon bond in C₇₀, the first example of direct addition across a closed 5–6 ring fusion in a fullerene.¹⁴

The chemistry of C₇₀ is more complicated than the chemistry of C₆₀ due to lower symmetry and to differences in reactivity

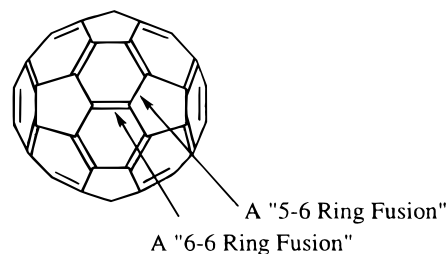


Figure 1. The 6–6 and 5–6 ring fusions in C₆₀.

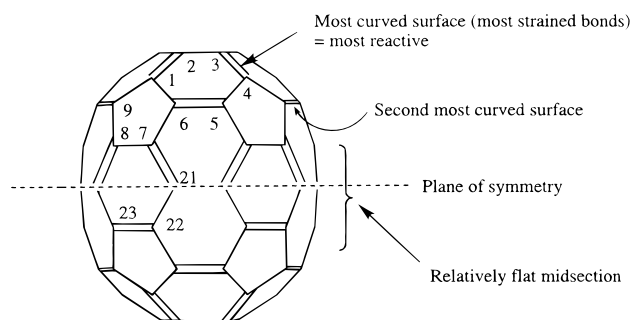


Figure 2. The structure and (partial) numbering of C₇₀. Numbering from Godly and Taylor.¹⁵

between the various double bonds. There are four different types of double bonds in C₇₀ in the valence-bond picture of C₇₀ shown in Figure 2. Drawing double bonds in the manner traditional for fullerenes leads to double bonds localized in a set of five-membered rings (e.g. the C22–C23 bond in Figure 2). The most pyramidalized carbons make up a set of reactive double bonds at the poles (e.g. C1–C2 in Figure 2). Pyramidalization and reactivity decrease for bonds closer to the relatively flat equator.

(14) An earlier report of 5–6 closed adducts was found to be in error. For details, see: Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289–2290.

- (1) Haddon, R. C. *Science* **1993**, 261, 1545–1550.
- (2) Hirsch, A. *Synthesis* **1995**, 895–913.
- (3) *Tetrahedron Symp. Print* 60, 1996; Smith, A. B., III, Ed.
- (4) David, W. I. F.; Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, 353, 147–149.
- (5) *The Chemistry of Fullerenes*; Taylor, R., Ed.; World Scientific: River Edge, NJ, 1995.
- (6) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, 114, 9697–9699.
- (7) Balch, A. L.; Cullison, B.; Fawcett, W. R.; Ginwalla, A. S.; Olmstead, M. M.; Winkler, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2287–2288.
- (8) Keshavarz-K., M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, 117, 11371–11372.
- (9) Kusakawa, T.; Ando, W. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1315–1317.
- (10) Wang, G.-W.; Shu, L.-H.; Wu, H.-M.; Lao, X.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1071–1072.
- (11) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023–2024.
- (12) (a) Bergosh, R. G.; Meier, M. S.; Laske Cooke, J. A.; Spielmann, H. P.; Weedon, B. R. *J. Org. Chem.* **1997**, 62, 7667–7672; (b) For an extensive review of reduced fullerenes, see: Gol'dshleger, N. F.; Moravshii, A. P. *Russ. Chem. Rev.* **1997**, 66, 323–342.
- (13) Meier, M. S. In ref 5, pp 174–194.

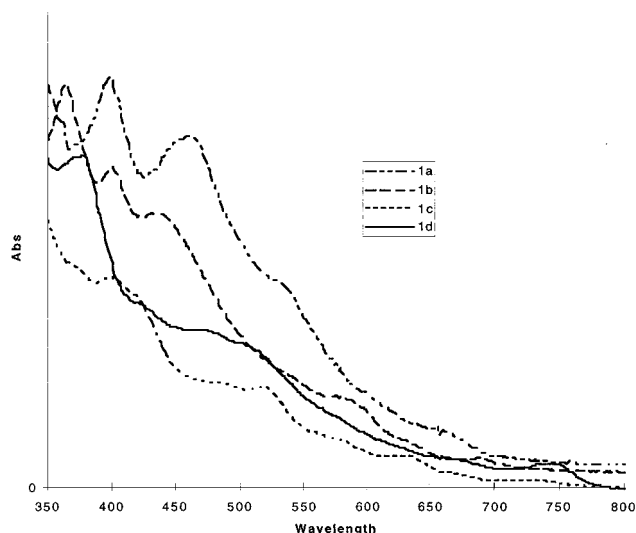


Figure 3. Absorption spectra of **1a–1d**. Figure 4.

The cycloaddition of benzyne to C_{70} has been reported to produce four isomers of monoadduct, although these were not characterized as purified compounds.¹⁶ We treated a solution of C_{70} and 2 equiv of anthranilic acid in benzene with 2 equiv of isoamyl nitrite, producing a mixture of products.^{16,17} The ensemble of monoadduct isomers, present in a 42:35:13:10 ratio as determined by 1H NMR, was separated from the crude reaction mixture by GPC¹⁸ and obtained in a combined yield of 34%. The individual isomers were purified by HPLC with use of, in separate steps, Regis “Buckyclutcher” and Cosmosil “Buckyprep” columns. The absorption spectra of these four isomeric monoadducts (**1a–d**) are shown in Figure 1.

The major isomer exhibits a ^{13}C NMR spectrum that consists of a total of 42 lines comprising 10 single-intensity resonances (2 sp^2 resonances and 2 sp^3 resonances from the fullerene, plus 6 sp^2 resonances from the benzene ring) and 31 sp^2 resonances of double intensity and one of quadruple intensity (2 overlapping double intensity resonances). These data are consistent with **1a**, resulting from addition to the C1–C2 bond. Under ideal conditions, **1a** should produce a spectrum consisting of 8 single intensity sp^2 resonances, 33 double intensity sp^2 resonances, and 2 single intensity sp^3 resonances. The absorption spectrum (Figure 3) is also consistent with a C1–C2 adduct.^{19–22} The C1–C2 double bond, involving two of the most pyramidal carbons in the molecule,^{1,23} is the most reactive site in C_{70} .^{19–35}

The structure of [1,2]benzeno[70]fullerene (**1a**) was determined by X-ray crystallography. Single crystals grown from

carbon disulfide/toluene included one toluene molecule in the crystal lattice. The structure was complicated by a positional disorder in which the benzyne moiety lies on a pseudomirror plane, and two positions of the C_{70} portion of the molecule are related by the pseudomirror. Site occupancies for the two positions refined to 60.97% and 39.03%. Because of limited data, only the coordinates of the benzyne addend and the six C_{70} atoms closest to it were allowed to vary, with the equivalent bond lengths constrained to be equal with a standard deviation of 0.03 Å. The remainder of the C_{70} cage and the molecule of toluene of crystallization were treated as rigid groups with idealized geometries. A plot of $C_{70}C_6H_4$ •toluene is shown in Figure 4. Essential crystal data and experimental details are given in Table 1, and selected bond distances and angles are given in Table 2. Full crystallographic tables are included in the Supporting Information.

The connectivity of the structure is firmly established by this structure determination. Bonding in the benzyne addend is quite delocalized, with C–C distances of about 1.38(2) Å. Fusion to C_{70} causes some angular distortions, with C–C–C angles in the benzyne ring ranging from 113(2)° to 124(1)°. The linking cyclobutene ring is strongly distorted, with C–C–C angles exo to the benzyne ring being about 10° larger than those exo to C_{70} . The C_{70} bond to which the benzyne is fused, C01–C02, is extremely stretched with a bond length of 1.66(2) Å. The

(15) Godly, E. W.; Taylor, R. *Pure Appl. Chem.* **1997**, *69*, 1411–1434.

(16) Taylor has pointed out that several different isomers of C_{70} adducts should display the same number of carbon resonances, and thereby casting doubt on some published structural assignments: Darwish, A. D.; Avent, A. G.; Taylor, R.; M., W. D. R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2079–2084.

(17) Darwish, A. D.; Abdul-Sada, A. K.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2133–2134.

(18) Meier, M. S.; Selegue, J. P. *J. Org. Chem.* **1992**, *57*, 1924–1926.

(19) Wilson, S. R.; Lu, Q. *J. Org. Chem.* **1995**, *60*, 6496–6498.

(20) Meier, M. S.; Poplawska, M.; Compton, A. L.; Shaw, J.; Selegue, J. P.; Guarr, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 7044–7048.

(21) Henderson, C. C.; Rohlfing, C. M.; Gillen, K. T.; Cahill, P. A. *Science* **1994**, *264*, 397–399.

(22) Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689–1706.

(23) Hawkins, J. M.; Meyer, A.; Solow, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7499–7500.

(24) Avent, A. G.; Darwish, A. D.; Heimbach, D. K.; Kroto, H. W.; Meidine, M. F.; Parsons, J. P.; Remars, C.; Roers, R.; Ohashi, O.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 15–22.

(25) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953–8955.

(26) Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1356–1358.

(27) Bellavia-Lund, C.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943–946.

(28) Gerst, M.; Beckhaus, H.-D.; Rüchardt, C.; Campbell, E. E. B.; Tellmann, R. *Tetrahedron Lett.* **1993**, *34*, 7729–7732.

(29) Seiler, P.; Herrmann, A.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 344–354.

(30) Wilson, S. R.; Wu, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10334–7.

(31) Wood, J. M.; Kahr, B.; Hoke, S. H. I.; Dejarne, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907–5908.

(32) Smith, A. B. I.; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492–5502.

(33) Wang, Y.; Schuster, D. I.; Wilson, S. R.; Welch, C. J. *J. Org. Chem.* **1996**, *61*, 5198–5199.

(34) Zhang, X.; Fan, A.; Foote, C. S. *J. Org. Chem.* **1996**, *61*, 5456–5461.

(35) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957–1959.

Table 1. Details of the Structure Determination of **1a**

formula	C ₇₆ H ₄ •C ₇ H ₈
crystal dims, mm	0.20 0.30 0.55
density (calcd)	1.634 g•cm ⁻³
temp	296(2) K
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.7107 Å)
space group	Pna2 ₁ (no. 33)
cell dims	
a	19.434(2) Å
b	13.628(1) Å
c	15.491(1) Å
α	90.00(0)°
β	90.00(0)°
γ	90.00(0)°
vol	4102.1(7) Å ³
Z	4
abs coeff μ	0.090 mm ⁻¹
2θ range	4–50°
decay	0.043% (linear correction)
total data collected	4041
unique data collected	3766
data with I > 2σ(I)	1376
no. of variables	138
restraints	7: 6 bond lengths and floating origin
R [on F; I > 2σ(I)]	0.089
wR [on F ² ; all data]	0.348
S	1.22
(Δ/σ) _{max}	0.009
Δ(ρ) _{max}	+0.48 e Å ⁻³
Δ(ρ) _{min}	–0.38 e Å ⁻³

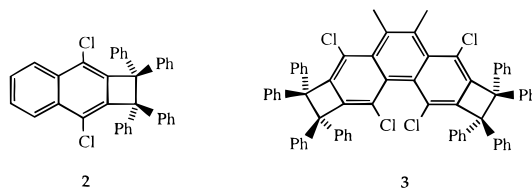
Table 2. Selected Bond Distances (Å) and Angles (deg) with ESDs for the Structure of [1,2]Benzeno[70]fullerene•Toluene

Distance			
C1'–C2'	1.38(2)	C01–C02	1.66(2)
C1'–C6'	1.38(2)	C01–C06	1.51(2)
C1'–C01	1.56(2)	C01–C09	1.50(2)
C2'–C3'	1.38(2)	C02–C03	1.52(2)
C2'–C02	1.56(2)	C02–C12	1.50(2)
C3'–C4'	1.40(2)		
C4'–C5'	1.38(2)		
C5'–C6'	1.38(2)		
Angle			
C6'–C1'–C2'	123.7(14)	C06–C01–C1'	125(2)
C6'–C1'–C01	140.4(14)	C1'–C01–C02	84.4(10)
C2'–C1'–C01	95.7(12)	C09–C01–C1'	116(2)
C3'–C2'–C1'	122.6(14)	C06–C01–C02	118.2(14)
C3'–C2'–C02	143(2)	C09–C01–C02	111(2)
C1'–C2'–C02	94.5(12)	C09–C01–C06	102.7(11)
C2'–C3'–C4'	113(2)	C2'–C02–C01	85.2(10)
C5'–C4'–C3'	124.2(14)	C03–C02–C2'	121(2)
C4'–C5'–C6'	122(2)	C12–C02–C2'	120(2)
C1'–C6'–C5'	115(2)	C03–C02–C01	111(2)
		C12–C02–C03	103.0(12)
		C12–C02–C01	117(2)

normal C(1)–C(2) bond length in C₇₀ is 1.387(4) Å.³⁶ The bonds from C01 and C02 to fullerene carbons C03, C06, C09, and C12, ranging from 1.50 to 1.52 Å, are longer than those bonds in C₇₀ itself, 1.453(3) and 1.445(3) Å. This is consistent with the sp³ character of carbons C01 and C02. The fullerene carbon atoms involved in the cycloaddition are displaced outward from their idealized positions in C₇₀.

Overlong C–C single bonds have been observed in related structures.³⁷ The longest reliably determined C–C bonds in nonfullerene structures are found in the benzocyclobutenes **2**

and **3**,^{38,39} with C(sp³)–C(sp³) bond lengths of 1.720(4) Å in **2** and 1.710(5) and 1.724(5) Å in **3**.



A search of the Cambridge Structural Database⁴⁰ reveals that in several fullerene cycloadducts, the 6,6-ring-fusion bond to which cycloaddition has occurred is very long. The structure of the [2+2] cycloadduct of C₆₀ and 4,5-dimethoxybenzynes shows a C–C length of 1.645(8) Å for this bond,⁴¹ and similar C–C bond lengths of 1.59 to 1.65 Å are seen in certain methanofullerenes^{42–46} and adducts of C₆₀ with piperazine,^{7,47} *o*-quinodimethanes,^{48–50} 1,3-cyclohexadiene,⁵¹ and a nitrile ylide.⁵² Similarly, two isomers of the cycloadduct of C₇₀ and 4,5-dimethoxy-*o*-quinodimethanes show long C(sp³)–C(sp³) bond lengths of 1.603(4) and 1.584(5) Å.²⁹ Thus, the C01–C02 bond in **1a** meets the criteria for being overly long, both as part of a benzocyclobutene like **2** and **3** and as a 6,6 ring fusion bond to which cycloaddition has occurred. Distortions at the site of cycloaddition are most likely due mainly to pyramidalization at C01 and C02. As these two carbon atoms move out from their normal positions, some bond stretching must occur. In **1a**, most of the strain is relieved by elongation of the C01–C02 bond.

The second major isomer (**1b**) exhibits spectral data consistent with another C_s product resulting from addition to the C5–C6 bond. The ¹³C NMR spectrum exhibits a total of 39 lines, composed of 34 double intensity sp² resonances, 3 single intensity sp² resonances, 1 triple intensity resonance (overlapping single and double intensity resonances), and one double intensity sp³ resonance. Ideally, structure **1b** would produce a ¹³C NMR spectrum consisting of 35 double intensity sp² resonances, 4 single intensity sp² resonances, and one double intensity sp³ resonance. The absorption spectrum of **1b** (Figure 3) resembles that of other compounds resulting from addition to the C5–C6 carbon–carbon bond.^{19–21} There are also numerous examples

(38) Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *Acta Crystallogr., Sect. C* **1996**, 52, 177.

(39) Toda, F.; Tanaka, K.; Sano, I.; Isozaki, T. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1757.

(40) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, 16, 146–153.

(41) Ishida, T.; Shinozuka, K.; Nogami, T.; Sasaki, S.; Iyoda, M. *Chem. Lett.* **1995**, 317–318.

(42) Osterodt, J.; Nieger, M.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1607–1608.

(43) Anderson, H. L.; Boudon, C.; Diederich, F.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1628–1632.

(44) Paulus, E. F.; Bingel, C. *Acta Crystallogr., Sect. C* **1995**, 51, 143.

(45) Lamparth, I.; Maichle-Mossmer, C.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1607–1609.

(46) Tezuka, Y.; Kawasaki, N.; Yajima, H.; Ishii, T.; Oyama, T.; Takeuchi, K.; Katayama, C. *Acta Crystallogr., Sect. C* **1996**, 52, 1008.

(47) Balch, A. L.; Ginwalla, A. S.; Olmstead, M. M.; Herbst-Immer, R. *Tetrahedron* **1996**, 553, 5021–5032.

(48) Diederich, F.; Jonas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thigen, C. *Helv. Chem. Acta* **1993**, 76, 2445.

(49) Belik, P.; Gugel, A.; Kraus, A.; Spickermann, J.; Enkelmann, V.; Frank, G.; Mullen, K. *Adv. Mater.* **1993**, 5, 854.

(50) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretizian, C. *J. Am. Chem. Soc.* **1993**, 115, 344–345.

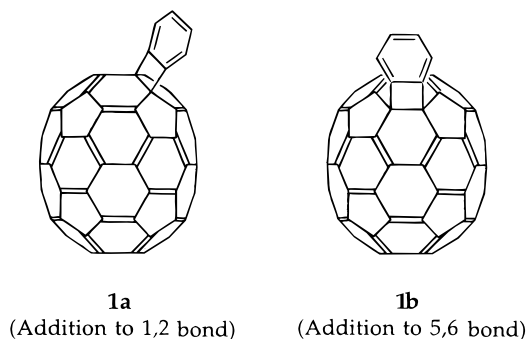
(51) Kräutler, B.; Müller, T.; Maynollo, J.; Gruber, K.; Kratky, C.; Ochsenbein, P.; Schwarzenbach, D.; Bürgi, H. B. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1204.

(52) Ramm, M.; Luger, P.; Averdung, J.; Mattay, J. *Acta Crystallogr., Sect. C* **1996**, 52, 2590–2594.

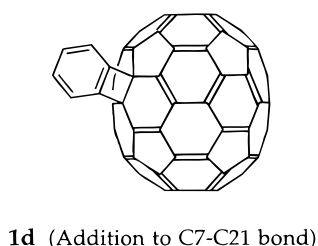
(36) Bürgi, H. B.; Venugopalan, P.; Schwarzenbach, D.; Diederich, F.; Thilgen, C. *Helv. Chim. Acta* **1993**, 76, 2155–2159.

(37) Kaupp, G.; Boy, J. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 48–49.

of addition to this bond,^{19–23,27,29} generally the second most reactive site after the C1–C2 carbon–carbon bond.

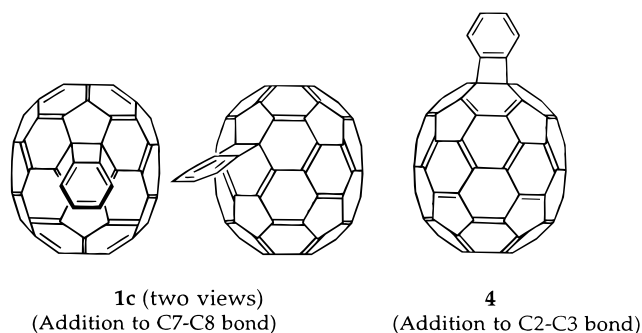


The third and fourth products (**1c** and **1d**) are obtained in smaller quantities: 13% and 10% of the monoadduct mixture, respectively. The ¹³C NMR spectrum of **1d** shows a complex spectrum of 74 lines, comprised of two single intensity sp³ resonances, 70 single intensity sp² resonances, and 2 double intensity sp² lines (overlapping single intensity resonances). These data are consistent with a product with only C₁ symmetry, resulting from addition to the C7–C21 bond.

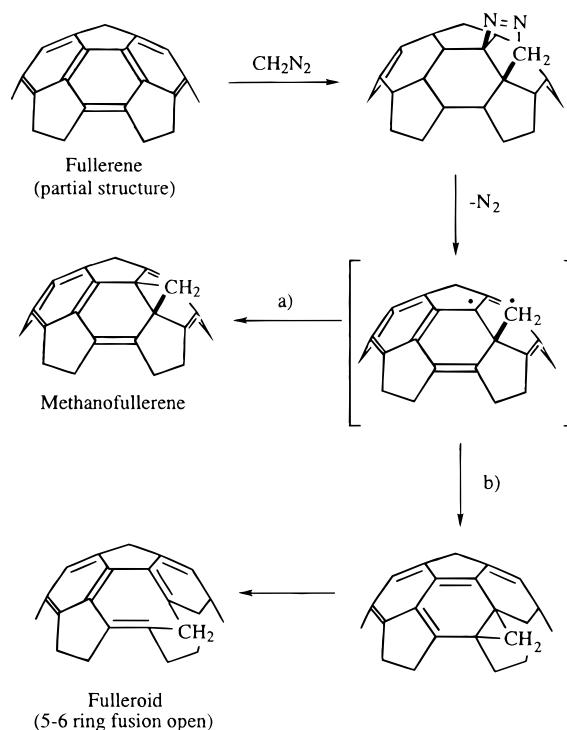


The ¹³C NMR spectrum of **1c**, however, exhibits a spectrum typical of products with C_s symmetry. The spectrum exhibits 38 lines, comprising 1 double intensity sp³ resonance, 3 single intensity sp² resonances, 1 triple intensity sp² resonance (overlapping single and double intensity resonances), 32 double intensity sp² resonances, and 1 quadruple intensity sp² resonance (overlapping double intensity resonances).

A structure with C₂ symmetry, resulting from a Diels–Alder reaction bridging C7 and C23, should produce a ¹³C NMR spectrum with only 38 double intensity resonances;¹⁶ the NMR data are not consistent with such a structure. The only other structures that would produce a single sp³ carbon resonance result from addition to the C5–C6, the C7–C8, and the C2–C3 carbon–carbon bonds, producing **1b**, **1c**, and **4**, respectively. Each of these structures has a plane of symmetry that bisects the sp³–sp³ bond. We feel that **4** is the least viable of the possibilities, in analogy with known fullerene chemistry.



Scheme 1



Inspection of **1c** reveals that the benzyne unit has added across the fusion of a five-membered ring and a six-membered ring (a 5–6 ring fusion). There are no other examples of direct addition to a 5–6 ring fusion in fullerene chemistry. Stepwise reactions that result in addition across 5–6 ring fusions have been observed in other fullerene systems, most notably in the formation of fulleroids and aza fulleroids.⁵³ The preparation of fulleroids and aza fulleroids involves initial addition to a double bond at a 6–6 ring fusion, followed by expulsion of N₂ and closure across the 5–6 ring fusion (Scheme 1, path b). A subsequent norcaradiene rearrangement results in cleavage of the ring fusion bond to produce an opening in the fullerene cage. Closure of the diradical intermediate across the 6–6 ring fusion results in a stable methanofullerene (Scheme 1, path a).

The C7–C8 bond in **1c** does not open, as shown by the presence of an sp³ carbon NMR resonance and by the fact that the absorption spectrum of **1c** is significantly different from the spectrum of C₇₀. Fulleroids exhibit spectra that are similar to their parent fullerene (C₆₀ or C₇₀) rather than to methanofullerenes.³²

In the valence-bond picture of C₇₀ (Figure 2), double bonds must be localized in five-membered rings. However, the C22–C23 “double bond” is equivalent by symmetry to the C7–C8 “single bond”. It is not possible to draw a valence bond picture of C₇₀ that makes these two bonds appear equivalent and still maintain the [5]radialene pattern of bonds. Addition to the C7–C8 bond, resulting in **1c**, is addition to a 5–6 ring fusion, an addition mode that has not been identified in a fullerene before.

Addition across a 5–6 ring fusion in C₆₀ introduces strained double bonds into five-membered rings. However, addition to the C7–C8 bond in C₇₀ results in a structure with four double bonds formally positioned within five-membered rings, rather than the five double bonds formally localized in five-membered rings in C₇₀ itself. It is clear that the C7–C8 bond, a 5–6 ring

(53) Prato, M.; Wudl, F. In ref 5, pp 151–173.

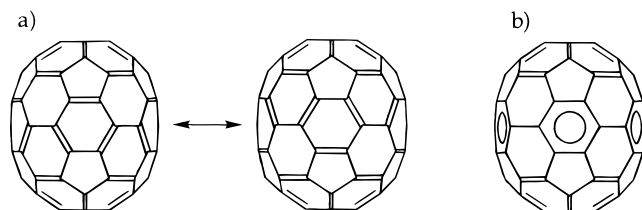


Figure 5. (a) Two resonance forms of C_{70} . (b) The resonance hybrid.

fusion, has significant double bond character. To represent C_{70} , two resonance structures are required, and the delocalized structure is also appropriate (Figure 5).

This is entirely equivalent to the situation in benzene, which is conventionally represented in terms of resonance hybrids of Kekulé structures, or with the central circle denoting a delocalized structure. The only qualification that must be raised is the possibility of a symmetry-breaking second-order Jahn–Teller distortion. It is known that the higher $[4n+2]$ annulenes eventually become unstable to such a distortion as the energy gap is progressively reduced. C_{70} is strongly colored so there is at least the possibility of symmetry breaking in this extended electronic structure.

In fact this possibility was investigated within Hückel MO theory some time ago by diagonalizing the bond–bond polarizability matrix⁵⁴ of some of the lower capsulenes.^{55,56} These species were generated from C_{60} in the same manner as C_{70} is obtained—by inserting a belt of 10 carbon atoms between the hemispheres. This procedure leads to capped arm-chair [5,5] single-walled carbon nanotubes. The following energy gaps (ΔE , β) and largest eigenvalue of the bond–bond polarizability matrix (λ_{\max} , β^{-1}) were reported: C_{60} ($\Delta E = 0.757$, $\lambda_{\max} = 0.893$), C_{70} ($\Delta E = 0.529$, $\lambda_{\max} = 0.909$), C_{80} ($\Delta E = 0.073$, $\lambda_{\max} = 0.913$), C_{90} ($\Delta E = 0.499$, $\lambda_{\max} = 0.938$), C_{100} ($\Delta E = 0.350$, $\lambda_{\max} = 0.942$). The invariance seen in the λ_{\max} values is all the more remarkable in the face of the large variations in the energy gap ΔE . It is generally agreed that $\lambda_{\text{critical}} > 1.8$ is required for the onset of bond alternation (distortion to a single Kekulé structure).⁵⁴ This behavior finds its analogy in the extended nanotubes which are also stable to symmetry-breaking distortions such as charge-density wave formation.

We examined the nature of the maximum eigenvalues for C_{60} and C_{70} . C_{60} has triply degenerate λ_{\max} values, while C_{70} has a nondegenerate maximum eigenvalue. The eigenvectors of the bond–bond polarizability matrix give the nature of the preferred distortion. We find that the unique eigenvector in the case of C_{70} has its largest coefficients at the central benzene rings. Thus, if there were to be a distortion it would have its largest effect on the bond lengths of these benzenes. The symmetry of this eigenvector is the same as that of the Kekulé structures which would become preferred over the delocalized structure if there were a distortion. The low values of λ_{\max} for all of these capsulenes support the view that the fullerenes are best considered as extremely strained but aromatic (delocalized) molecules.¹ Apart from the many other pieces of evidence in favor of this view, it is now apparent that the fullerenes fit within the Binsch⁵⁴ definition of aromatic character: “A conjugated π -electron system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation.”

The present results shed some light on another interesting aspect of fullerene chemistry. Measurements of the magnetic

susceptibility of C_{70} ^{57,58} and the ^3He chemical shift in $^3\text{He}@C_{70}$ ^{59,60} show that there is a larger ring current magnetic susceptibility associated with this fullerene than all of the other neutral fullerenes examined to date. It is possible that the presence of Kekulé resonance hybrids is associated with this property. It will be of interest to see if other fullerenes can be isolated which require a consideration of multiple resonance hybrids in specifying their electronic structure.

Conclusions

Addition of benzyne to C_{70} produces four adducts, one of which results from addition to the C7–C8 bond, a 5–6 ring fusion. Crystal structure data³⁶ and calculations⁶¹ both suggest that the C7–C8 bond and the C7–C21 bond in C_{70} are of comparable lengths (bond orders), so the equatorial six-membered rings are benzenoid, unlike all other six-membered rings in C_{60} and C_{70} . The valence-bond drawing of C_{70} (Figure 2) has a serious shortcoming in that it implies that the C7–C8 bond is a single bond and that the C22–C23 bond is a double bond. Symmetry and reactivity argue that the hybrid shown in Figure 5 is a much more accurate portrayal of the structure of C_{70} . Pyramidalization of these aromatic rings results in higher reactivity than seen in planar benzenoid hydrocarbons.

Experimental Section

A mixture of C_{70} (101.0 mg, 0.12 mmol) and anthranilic acid (32.9 mg, 0.24 mmol) in 300 mL of benzene was heated to reflux under argon, then isoamyl nitrite (32.3 μL , 0.24 mmol) was added via syringe. After being stirred under reflux for 2 h, the reaction mixture was concentrated, filtered (0.2 μm), and separated by gel permeation chromatography (GPC) on a bank of four preparative GPC columns (JordiGel, 2–500 Å Waters Ultrastagel, 1–100 Å Waters Ultrastagel) with use of toluene (5 mL/min) as the mobile phase to afford 37.4 mg (34%) of four isomers of monoadduct $C_{70}\text{C}_6\text{H}_4$, along with 48.2 mg (48%) of recovered C_{70} . The monoadduct consists of four isomers according to ^1H NMR (42:35:13:10). The mixture of monoadducts was chromatographed on a 20 mm \times 250 mm Buckyclutcher Prep I column with 1:1 hexane–toluene (15 mL/min) as eluent to give [1,2]-benzeno[70]fullerene (**1a**) and a band composed of the remaining three isomers (**1b–d**). Compounds **1b–1d** were separated by chromatography on a 10 mm \times 250 mm Cosmosil Buckyprep column with 1:1 hexane–toluene (5 mL/min) as the mobile phase. The 7,8 isomer (**1c**) was obtained in nearly pure form after one pass, but the 5,6 (**1b**) and 7,21 (**1d**) isomers required several passes for satisfactory purity.

[1,2]Benzeno[70]fullerene (1a). ^{13}C NMR (CS_2 , 10% acetone- d_6 , $\text{Cr}(\text{acac})_3$ added, relative integrals given in parentheses) 157.00 (2), 154.85 (2), 152.26 (2), 151.87 (1), 151.62 (2), 151.19 (2), 150.81 (2), 150.58 (2), 150.40 (2), 150.30 (2), 150.02 (2), 149.63 (2), 149.22 (2), 148.95 (4), 148.41 (1), 147.67 (2), 147.65 (2), 147.52 (2), 147.17 (1), 147.14 (1), 147.02 (2), 146.29 (2), 146.17 (2), 144.45 (2), 143.95 (2), 143.81 (2), 143.72 (2), 143.19 (2), 142.68 (20), 141.27 (2), 140.02 (2), 134.59 (2), 133.70 (2), 131.87 (2), 131.47 (2), 131.40 (2), 130.87 (1), 130.59 (1), 123.72 (1), 123.36 (1), 71.80 (1), 70.23 (1).

(a) X-ray Structural Determination of 1a. Crystals of [1,2]-benzeno[70]fullerene•toluene were grown at room temperature from a carbon disulfide/toluene solution. A single crystal was mounted on a glass fiber and coated with epoxy resin. Crystal data and experimental

(57) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbagh, G.; Kortan, A. R.; Muller, A. J.; Mujica, A. M.; Rosseinsky, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature* **1991**, *350*, 46–47.

(58) Ruoff, R. S.; Beach, D.; Cuomo, J.; McGuire, T.; Whetten, R. L.; Diederich, F. *J. Phys. Chem.* **1991**, *95*, 3457–3459.

(59) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256–258.

(60) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Billups, W. E.; Gesenberg, C.; Gonzales, A.; Luo, W.; Haddon, R. C.; Diederich, F.; Herrmann, A. *J. Am. Chem. Soc.* **1995**, *117*, 9305–9308.

(61) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *180*, 451–456.

(54) Binsch, G.; Tamir, I. *J. Am. Chem. Soc.* **1969**, *91*, 2450–2455.

(55) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459–464.

(56) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *131*, 165.

details are given in Table 1. The structure was solved with the SHELXL PC program package⁶² and refined with the program SHELXL93.⁶³ The coordinates of the 6 atoms of the fullerene closest to the substituent were allowed to vary, with the equivalent bond lengths constrained to be equal with a standard deviation of 0.03 Å. The remainder of the C₇₀ cage and the molecule of toluene of crystallization were treated as rigid groups with idealized geometries.³⁶ Isotropic displacement parameters were refined for the carbon atoms of **1a**. Hydrogen atoms were included in calculated positions with $U_H = 1.2U_{iso}$ for the attached carbon atom. Disorder was modeled at a late stage of the refinement by reflecting both [1,2]benzeno[70]fullerene and toluene molecules in the pseudomirror plane and treating the images as rigid groups. The site occupation factor for the second position refined to 39.03%. Figures showing the atom-numbering scheme, a unit cell and the pseudosymmetry, as well as tables of coordinates and *U* values for the refined atoms, all bond lengths and angles, hydrogen atom parameters, and observed and calculated structure-factor amplitudes are included in the Supporting Information.

[5,6]Benzeno[70]fullerene (1b). ¹³C NMR (CS₂, 10% acetone-*d*₆, Cr(acac)₃ added, relative integrals given in parentheses) 154.20 (1), 151.93 (2), 150.48 (1), 149.86 (2), 149.73 (2), 149.68 (2), 149.49 (1), 149.42 (2), 149.30 (2), 149.12 (2), 148.53 (2), 148.50 (2), 148.48 (2), 148.47 (2), 148.39 (2), 147.43 (2), 147.26 (3), 147.09 (2), 146.62 (2), 146.45 (2), 146.40 (2), 146.05 (2), 145.89 (2), 145.65 (2), 145.26 (2), 145.11 (2), 144.95 (2), 144.67 (2), 144.32 (2), 143.28 (2), 141.71 (2), 132.57 (2), 132.29 (2), 132.22 (2), 132.14 (2), 130.76 (2), 127.94 (2), 123.26 (2), 66.06 (2).

[7,8]Benzeno[70]fullerene (1c). ¹³C NMR (CS₂, 10% acetone-*d*₆, Cr(acac)₃ added, relative integrals given in parentheses) 153.87 (1), 153.57 (1), 151.56 (2), 150.23 (2), 149.99 (2), 149.78 (2), 149.44 (2), 148.67 (2), 148.54 (2), 148.47 (2), 147.28 (2), 146.79 (2), 146.71 (3), 146.54 (2), 146.48 (2), 146.40 (2), 146.32 (2), 146.30 (2), 146.10 (4), 145.99 (2), 145.95 (2), 145.00 (2), 144.78 (2), 143.13 (1), 143.11 (2), 142.02 (2), 140.30 (2), 140.24 (2), 139.84 (2), 138.25 (2), 133.07 (2), 132.85 (2), 132.21 (2), 130.71 (2), 129.79 (2), 127.74 (2), 123.36 (2), 68.92 (2).

(62) Sheldrick, G. M. *SHELXL PC*, Release 4.1; Siemens Analytical Instruments, Inc., 1990.

(63) Sheldrick, G. M. *SHELXL 93*. Program for the Refinement of Crystal Structures; University of Göttingen, 1993.

[7,21]Benzeno[70]fullerene (1d). ¹³C NMR (CS₂, 10% acetone-*d*₆, Cr(acac)₃ added, relative integrals given in parentheses) 155.66 (1), 152.50 (1), 152.12 (1), 151.36 (1), 151.22 (1), 150.58 (1), 150.56 (1), 150.40 (1), 150.29 (1), 150.09 (1), 150.05 (1), 149.90 (1), 149.79 (1), 149.39 (1), 149.26 (1), 149.22 (1), 149.13 (1), 148.92 (1), 148.85 (1), 148.64 (1), 148.52 (1), 148.43 (1), 148.40 (1), 148.38 (1), 148.24 (1), 147.63 (1), 147.48 (1), 147.46 (1), 147.43 (2), 147.25 (1), 147.21 (2), 147.17 (1), 147.16 (1), 147.03 (1), 146.92 (1), 146.88 (1), 146.64 (1), 146.54 (1), 146.45 (1), 146.33 (1), 146.03 (1), 146.00 (1), 145.89 (1), 145.52 (1), 145.11 (1), 144.98 (1), 144.92 (1), 144.89 (1), 144.80 (1), 144.58 (1), 144.29 (1), 144.04 (1), 144.01 (1), 143.09 (1), 142.33 (1), 141.67 (1), 139.60 (1), 139.36 (1), 138.78 (1), 133.89 (1), 133.74 (1), 133.31 (1), 133.15 (1), 133.14 (1), 132.35 (1), 131.06 (1), 130.73 (1), 130.61 (1), 130.54 (1), 128.41 (1), 123.11 (1), 121.99 (1), 67.47 (1), 54.53 (1).

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Supporting Information Available: ¹H NMR, ¹³C NMR, MALDI mass spectra, and crystallographic data for **1a** (tables of coordinates and *U* values for the refined atoms, all bond lengths and angles and hydrogen atom parameters, as well as figures showing the atom-numbering scheme, the unit cell, and the pseudosymmetry for the crystal structure) (27 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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