

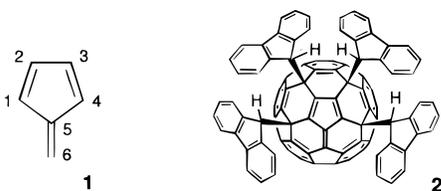
Synthesis, X-ray Structure, and Properties of the First Tetrakisadduct of Fullerene C₆₀ Having a Fulvene-Type π -System on the Spherical Surface

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Received May 6, 1997

Fulvene (**1**) is a polarized cross-conjugated π -system, which reacts with nucleophiles selectively at the exocyclic sp² carbon to generate a cyclopentadienide ion.¹ Intermediate formation of the fulvene structure on the surface of fullerene C₆₀ has been postulated in the recently reported reactions which produce C₆₀ derivatives having multiple organic addends with a remarkably high positional selectivity.^{2–4} However, there has been no report



of the direct observation or isolation of the C₆₀ derivative with a fulvene structure on its spherical surface. Here, we report the synthesis, X-ray structure, and properties of the first such example, i.e., the tetrakis(9-fluorenyl) derivative **2**.

The reaction of C₆₀ with an excess amount of potassium fluorenyl (3 equiv) in the presence of neutral fluorene (2 equiv) in THF for 72 h under argon (*but without rigorous exclusion of air*) afforded a black suspension, from which tetrakis(9-fluorenyl)adduct **2** was isolated as a black powder in 40% yield by preparative HPLC. All of the C₆₀ starting material was consumed, and the rest of the product was a mixture of insoluble materials, presumably the dimeric derivatives,⁵ and several inseparable C₆₀ derivatives having more than five fluorenyl groups, as indicated by MS spectroscopy.

Black single crystals of **2**·(toluene)₃ were obtained by the slow diffusion of toluene into a benzene solution of **2**. An X-ray structural analysis was conducted to give the results shown in Figure 1.⁶ As is clearly seen, the four sp² carbons (C-1–4)⁷ of the fulvene structure are isolated from the outer-rim π -conjugated system by four sp³ carbons each bearing a fluorenyl group. The lengths of the 6–6 and 5–6 bonds between the sp² carbons on the C₆₀ cage, except for the fulvenyl carbons, are 1.39 ±

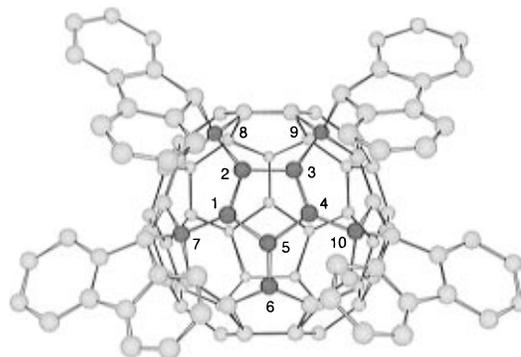


Figure 1. Molecular structure of **2** determined by X-ray crystallography. Toluene molecules and hydrogen atoms are omitted for clarity. The fulvenyl carbons and sp³ carbons on the C₆₀ cage are darkened for comprehensibility. Selected bond lengths (Å): C1–C2, 1.376(7); C2–C3, 1.488(8); C3–C4, 1.373(7); C4–C5, 1.464(8); C1–C5, 1.457(8); C5–C6, 1.350(8); C1–C7, 1.513(8); C2–C8, 1.494(8); C3–C9, 1.502(7), C4–C10, 1.512(7).

0.02 and 1.44 ± 0.02 Å, respectively, both of which are commonly observed values for derivatives of dihydro[60]-fullerenes.⁸ In contrast, a larger bond alternation is observed for the bonds within the fulvene framework. The average bond length for C1–C2 and C3–C4 is 1.375 Å while that of C1–C5 and C4–C5 is 1.461 Å. Particularly noteworthy is the bond length of the C5–C6 bond (1.350(8) Å), which is the shortest among the formal double bonds so far reported for C₆₀ derivatives.⁹ In contrast, the C2–C3 bond (1.488(8) Å) exhibits prominent elongation. This tendency for the bonds to alternate in length is quite similar to or slightly more pronounced than that observed in fulvene derivatives.¹⁰

Compound **2** possesses the typical reactivity of a fulvene π -system toward nucleophiles.¹ As shown in Scheme 1, **2** reacted with 1-octynyllithium¹¹ in THF and with sodium cyanide^{8c} in DMF/1,2-dichlorobenzene (ODCB) within 20 min to give pentakisadducts **3a**¹² and **3b**¹² in 63 and 68% isolated yields as single products after the reaction was quenched with CF₃CO₂H.

The multiaddition of potassium fluorenyl to C₆₀ did not proceed at all under high vacuum (<10^{−4} Torr). This reaction presumably involves a nucleophilic addition, a one-electron oxidation of the first-formed anion by a trace amount of air, and then a second nucleophilic addition, as has previously been proposed for the reaction with lithium fluorenyl to give a bis-(9-fluorenyl) derivative.⁵ In the present study employing

(8) For example, see: (a) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919–4920. (b) Nuber, B.; Hampel, F.; Hirsch, A. *Chem. Commun.* **1996**, 1799–1800. (c) Ishida, T.; Shinozuka, K.; Nogami, T.; Sasaki, S.; Iyoda, M. *Chem. Lett.* **1995**, 317–318. (d) Osterodt, J.; Nieger, M.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1607–1608. (e) Keshavartz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371–11372 and references cited therein.

(9) The only exceptions are the bonds reported for the C₆₀ derivatives with larger number of addends. For C₆₀Br₆ and C₆₀Br₈, see: Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1992**, *357*, 479–481. For C₆₀Br₂₄, see: Tebbe, F. N.; Harlow, R. L.; Chase, D. B.; Thorn, D. L.; Campbell, G. C.; Calabrese, J. C.; Herron, N.; Young, R. J.; Wasserman, E. *Science* **1992**, *256*, 822–825.

(10) In 6,6-dimethylfulvene, for example, the bond lengths of C1–C2 and C5–C6 are 1.346 and 1.343 Å, while those of C1–C5 and C2–C3 are 1.439 and 1.435 Å, respectively: Norman, N.; Post, B. *Acta Crystallogr.* **1961**, *14*, 503–507. For other examples, see: (a) Wingert, L. M.; Staley, S. W. *Acta Crystallogr.* **1992**, *B48*, 782–789. (b) Fronczek, F. R.; Cronan, J. M., Jr.; McLaughlin, M. L. *Acta Crystallogr.* **1990**, *C46*, 922–924 and references cited therein.

(11) For the reaction of C₆₀ with 1-octynyllithium, see: Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077–5090.

(12) Compounds **3a** and **3b** are orange powders. For the structural data, see the Supporting Information. The reaction of **2** with potassium fluorenyl gave pentakisadduct **5** in 68% yield.

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(1) Zeller, K.-P. Pentafulvene In *Methoden der Organischen Chemie (Houben-Weyl)*, Band V/2c; Müller, E., Ed.; Georg Thieme: Stuttgart, Germany, 1985; pp 504–684.

(2) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850–12851.

(3) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023–2024.

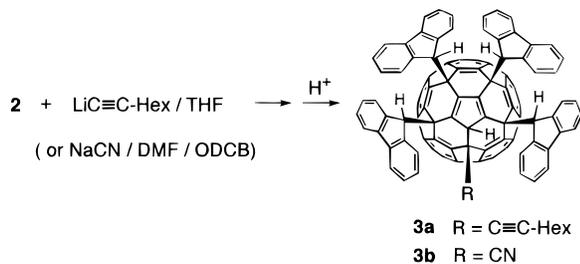
(4) For an example of the reaction starting with C₆₀Cl₆, see: Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 457–461.

(5) Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061–7064.

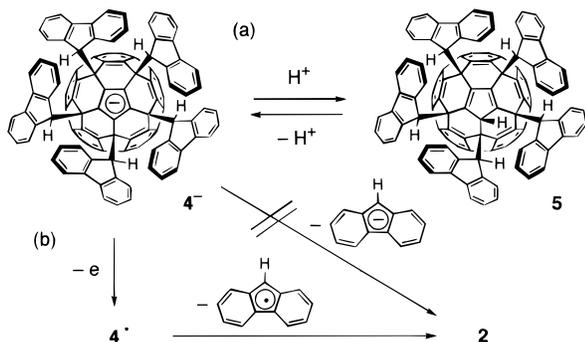
(6) Crystal data for **2**·(toluene)₃: monoclinic, P2₁/c, *a* = 16.762(6) Å, *b* = 18.341(4) Å, *c* = 27.198(4) Å, β = 107.69(2)°, *V* = 7966(3) Å³, *Z* = 4. Data were collected at −70 ± 1 °C on Rigaku AFC7R diffractometer with filtered Cu K α radiation to a maximum 2 θ = 110.2°, giving 10 436 unique reflections; the structure was solved by direct methods (SIR 92), yielding *R* = 0.061, *R_w* = 0.087 for 5680 independent reflections with *I* > 3 σ (*I*).

(7) For the purpose of comprehensibility, the numbering system of fulvene is used throughout the present paper.

Scheme 1



Scheme 2



potassium fluorenyl anion, the reaction should proceed further owing to the increased nucleophilicity of the carbanion. Actually, after a reaction time of 24 h, the pentakisadduct 4^- had already been produced as the major product, as shown by the isolation of cyclopentadiene **5** in 49% yield after protonation. We presume that **2** is formed irreversibly from 4^- during the following 48 h as shown in Scheme 2b; that is, the slow oxidation of 4^- by a trace amount of air proceeds to give the radical 4^\bullet , and the detachment of a fluorenyl group slowly occurs to give tetraakisadduct **2** as a major product with a total reaction time of 72 h. The possibility that the fluorenyl anion is detached from anion 4^- is ruled out because this anion was shown to be stable for at least 3 weeks under high vacuum. In support of the pathway proposed above, the oxidation of the reaction mixture with a reaction time of 24 h using iodine (1 equiv to the fluorenyl anion) also gave tetraakisadduct **2** as a single isolable product.

Compared with the recently reported C_{60} derivative which has five phenyl groups at the sp^3 carbons around the central cyclopentadienyl ring,^{2,13} pentakisadduct **5** is much more congested due to the bulky fluorenyl groups. As demonstrated by the MM2-optimized structure shown in Figure 2, the five fluorenyl groups are arrayed in a propeller-like arrangement in order to minimize the steric repulsion. The rotation of the fluorenyl group is sterically inhibited, as shown by the non-equivalence of all of the fluorenyl carbons. The C_1 symmetry in this molecule is also illustrated by the appearance of sets of five NMR signals (CDCl_3) for each of the fluorenyl's methine protons (δ_{H} 3.17, 3.06, 2.90, 2.79, 2.73) and tertiary carbons ($\delta_{^{13}\text{C}}$ 55.39, 54.80, 54.36, 53.50, 53.24), as well as of the quaternary carbons of the C_{60} moiety ($\delta_{^{13}\text{C}}$ 60.88, 60.75, 59.39, 58.89, 58.23).

Pentakisadduct **5** was readily converted into a dark red-brown solution of cyclopentadienide ion 4^- upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in $\text{DMSO}-d_6$ or with *t*-BuOK in $\text{THF}-d_8$. The C_5 symmetric structure of 4^- is demonstrated in the reduction in ^{13}C NMR signals (DBU/ $\text{DMSO}-d_6$) to one-fifth of those in **5**: the three groups of signals in **5** mentioned above converged into three signals at δ_{H} 3.16,

(13) Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463–1464.

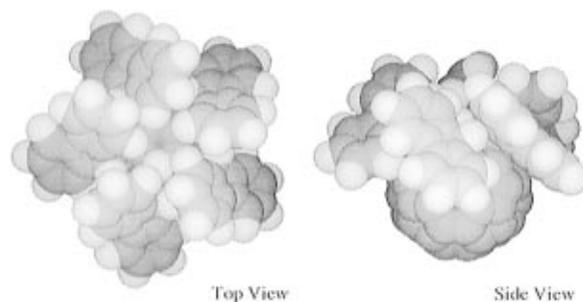


Figure 2. Space-filling representation of the MM2-optimized structure of **5**.

$\delta_{^{13}\text{C}}$ 55.86, and $\delta_{^{13}\text{C}}$ 60.39, respectively. The propeller-like molecular structure is retained, as indicated by the appearance of eight signals for the CH carbons on the fluorenyl groups.¹⁴ The singlet at δ 128.06 in the off-resonance spectrum is assigned to the cyclopentadienide ring carbon.

Upon cyclic voltammetry of the potassium salt of anion 4^- in benzonitrile, a reversible oxidation wave was observed at $E_{1/2} -0.54$ V vs the ferrocene/ferrocenium (Fc/Fc^+) couple,¹⁵ indicating the formation of a stable cyclopentadienyl radical. This redox potential is less negative than that observed for the pentaphenylcyclopentadienide ion (6^- , $E_{1/2} -0.63$ V vs Fc/Fc^+ in acetonitrile),¹⁶ implying that anion 4^- is more stable and more resistant to oxidation than 6^- . This stability of anion 4^- can be ascribed to the electron-deficient character of the C_{60} cage, as has been indicated by the strong acidity of a proton directly attached to C_{60} .¹⁷ Such stability appears to cancel out the unfavorable π -conjugation caused by the outward-tilted geometry of the 2p orbitals on the cyclopentadienide ring of 4^- .

In summary, we have demonstrated that a spacious π -conjugated carbanion such as the fluorenyl anion can add to C_{60} with a high level of positional selectivity when the reaction is carried out in the presence of a trace amount of oxygen, to afford novel C_{60} derivative **2** having a fulvene π -electronic system. Adduct **2** was found to be formed by detachment of a fluorenyl group from the anion of pentakisadduct 4^- upon very slow oxidation. Pentakisadduct **5** as well as 4^- appears to have five fluorenyl groups arranged in a chiral propeller-like array, and the optical resolution of **5** is now under investigation.

Acknowledgment. We thank the Japan Society for the Promotion of Science (RFTF97R11601) for support of the present study. We are also grateful to Professor Takeaki Miyamoto for his kind encouragement.

Supporting Information Available: Experimental details for the preparation of **2**, **3**, 4^- , and **5**, ^1H and ^{13}C NMR spectra for **2**, **3**, 4^- , and **5**, UV-vis spectra for **2**, **3**, and **5**, analytical data for **2** and **5**, cyclic voltammograms of 4^- , and details of the structure determination of $2\cdot(\text{toluene})_3$ (45 pages). See any current masthead page for ordering and Internet access instructions.

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(14) The appearance of 14 signals including 10 signals for sp^2 carbons in the C_{60} cage and four signals for quaternary carbons in fluorenyl groups is also in agreement with the C_5 symmetry.

(15) Another reversible redox wave was observed at $E_{1/2} -1.78$ V, corresponding to the formation of the dianion.

(16) Converted from the data obtained with reference to Ag/Ag^+ : Komatsu, K.; Fujiura, R.; Okamoto, K. *Chem. Lett.* **1988**, 265–268.

(17) (a) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697–9699. (b) Niyazymbetov, M. E.; Evans, D. H.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093–13098.