

Synthesis of a Hydrocarbon Salt Having a Fullerene Framework

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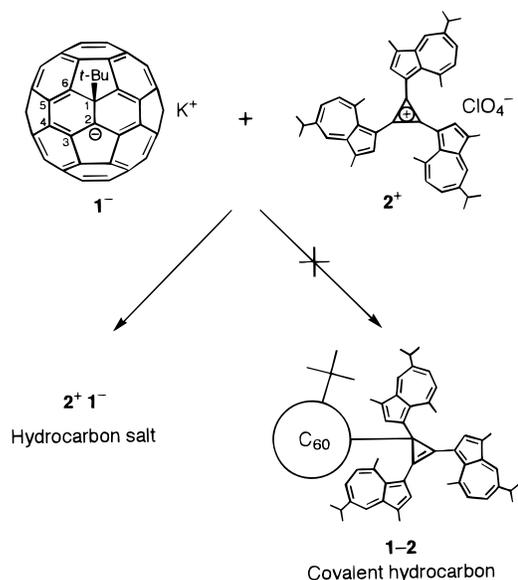
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Hydrocarbons generally consist of molecules that are entirely covalent in nature. Recently, however, we have demonstrated the existence of an unusual class of hydrocarbons, i.e., hydrocarbon salts, which are ionic solids and consist solely of carbon and hydrogen. We reported¹ the synthesis and characterization of the first example of such salts by combining a hydrocarbon containing an extensive planar π -conjugated system with a substituted cyclopropenylm or tropylium ion. As is shown by the facile formation of C_{60}^{n-} ($n = 1-6$)² and substituted fulleride ions (RC_{60}^-),^{2a,c,3-6} the fullerene skeleton, which has a spherical π -conjugated system, represents another important framework for the construction of highly stable anionic species. The unusually low basicities of C_{60}^{*-} , $C_{60}(CN)^-$, and $t\text{-Bu}C_{60}^-$ (pK_a of conjugate acids, 3.4–9,^{4c,d} 2.5,^{4b} and 5.7,⁵ respectively) and the isolation of the lithium salt of $t\text{-Bu}C_{60}^-$ (1^-) prompted us to synthesize a new hydrocarbon salt containing a fullerene framework. We report the isolation of a hydrocarbon salt consisting of 1^- and tris[1-(5-isopropyl-3,8-dimethylazulenyl)]-cyclopropenylm ion (2^+). In cation 2^+ , first synthesized by Agranat,⁷ the three guaiazulenyl groups effectively raise the thermodynamic stability of the cation and increase steric congestion around the positive charge, as well.

Spectroscopic studies showed that C_{60}^{*-} , $C_{60}(CN)^-$, and 1^- can coexist with 2^+ in solution.⁸ In addition, the molar conductivity (Λ) of DMSO solutions containing K^+1^- and $2^+ClO_4^-$ of equal concentrations (c) showed a linear $\Lambda-c^{1/2}$

relationship, indicating that 2^+1^- is a strong electrolyte in DMSO. Normally both carbocations and carbanions are so reactive that they cannot coexist because of coordination to form a carbon–carbon covalent bond. The stable existence of C_{60}^{*-} , $C_{60}(CN)^-$, or 1^- in the presence of 2^+ appears to be due principally to the extremely high thermodynamic stabilities of both cationic and anionic species. However, Arnett's empirical equation,⁹ which correlates the heat of coordination of a carbocation and a carbanion with their pK_R^+ and pK_{HA} values, predicts that the coordination of 1^- with 2^+ is energetically favorable by 7.5 kcal/mol.¹⁰ Therefore, the observed persistence of these ions in solution can be attributed also to the high degree of steric repulsion, especially that between the guaiazulenyl groups and the *tert*-butyl group.¹¹

For the isolation of a hydrocarbon salt, 2^+1^- , a reddish-brown colored solution of $2^+ClO_4^-$ in THF was added to a dark green THF solution of 1 equiv of K^+1^- under argon at room temperature, followed by reprecipitation by dilution with CH_3CN . The precipitated hydrocarbon was separated from the soluble $KClO_4$ by centrifugation and vacuum-dried to give a dark reddish-brown powder (41%).



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(1) (a) Okamoto, K.; Takeuchi, K.; Kitagawa, T. *Adv. Phys. Org. Chem.* **1995**, *30*, 173. (b) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J. Org. Chem.* **1990**, *55*, 996. (c) Komatsu, K.; Akamatsu, H.; Aonuma, S.; Jinbu, Y.; Maekawa, N.; Takeuchi, K. *Tetrahedron* **1991**, *47*, 6951. (d) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Miyabo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 923. (e) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173.

(2) (a) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327. (b) Wu, M.; Wei, X.; Qi, L.; Xu, Z. *Tetrahedron Lett.* **1996**, *37*, 7409. (c) Chen, J.; Cai, R.-F.; Huang, Z.-E.; Wu, H.-M.; Jiang, S.-K.; Shao, Q.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1553. (d) Subramanian, R.; Boulas, P.; Vijayashree, M. N.; D'Souza, F.; Jones, M. T.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1847. (e) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

(3) Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077.

(4) (a) Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J. F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925. (b) Keshavarz-K., M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371. (c) Niyazymbetov, M. E.; Evans, D. H.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093. (d) Cliffl, D. E.; Bard, A. J. *J. Phys. Chem.* **1994**, *98*, 8140.

(5) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.

(6) (a) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061. (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766.

(7) Agranat, I.; Shalom, E. A. *J. Org. Chem.* **1976**, *41*, 2379.

The salt structure of this solid was confirmed by IR spectroscopy (Figure 1). The absorption spectrum of the obtained solid, measured using a KBr disk, was superimposable with the sum of the spectra of 2^+ and 1^- , indicating that the solid is a salt 2^+1^- rather than a covalent compound $2-1$.^{12,13} In addition, the absence of solvent molecules, THF and CH_3CN , was indicated by the spectrum, which showed no absorption peaks corresponding to those molecules.

(8) The sodium salt of C_{60}^{*-} was prepared by reducing C_{60} with sodium naphthalene. $K^+C_{60}(CN)^-$ and K^+1^- were prepared by treating $C_{60}(CN)H^{4b}$ and $t\text{-Bu}C_{60}H$,^{5,6} respectively, with $t\text{-BuOK}$. Details are described in the Supporting Information.

(9) For tertiary carbocations, $-\Delta H_{\text{coord}} = 8.895 - 0.648(pK_R^+) + 1.294(pK_{HA})$: (a) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, Jr., L. G. *Energy Fuels* **1987**, *1*, 17. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

(10) Agranat reported that the pK_R^+ value of 2^+ is greater than 10 in 50% aqueous acetonitrile by potentiometric titration (ref 7). We determined the pK_R^+ value by spectrophotometrical titration of a glycine-buffered solution of $2^+ClO_4^-$ in 50% aqueous acetonitrile with aqueous NaOH. Although hydrolysis of 2^+ was not reversible, rapid measurement gave a titration curve corresponding to a pK_R^+ of 13.6 ± 0.1 .

(11) Addition of an electrophile to 1^- usually occurs at positions C-2 and C-4, since both the negative charge and the HOMO electrons are mostly located in the vicinity of the *tert*-butyl group: Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *Tetrahedron* **1997**, *53*, 9965. Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, *60*, 1490. See also refs 2a,c and 3–6.

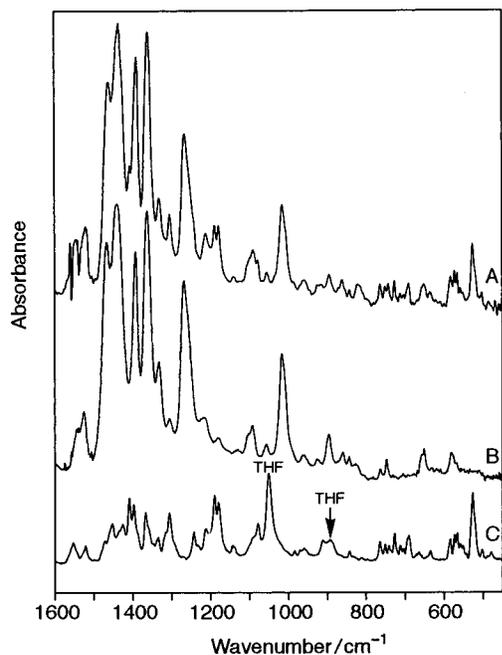


Figure 1. Infrared absorption spectra measured using KBr disks under an atmosphere of argon: (A) 2^+1^- , (B) 2^+Cl^- , (C) $K^+1^- \cdot (THF)_x$.

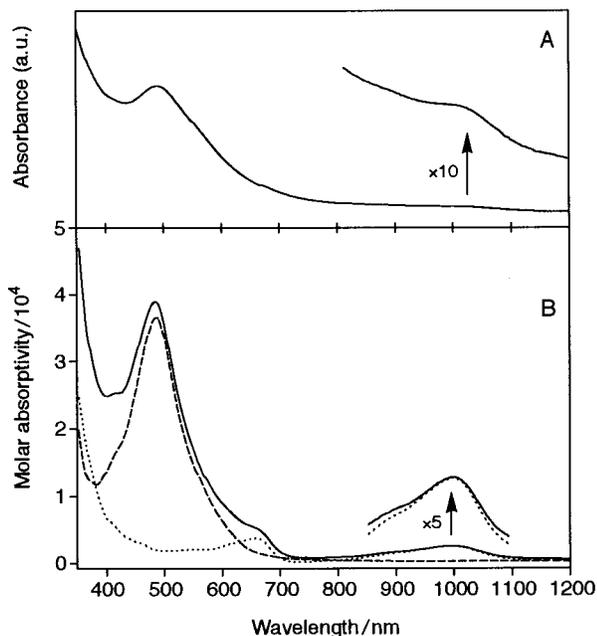


Figure 2. Visible/near-IR absorption spectra: (A) 2^+1^- , KBr disk; (B) DMSO-THF (4:1 v/v) solutions; (—) 2^+1^- ; (---) $2^+ClO_4^-$; (···) K^+1^- .

The visible/near-IR absorption spectrum for a transparent KBr disk of 2^+1^- (Figure 2A) showed absorption maxima corresponding to 2^+ (485 nm) and 1^- (1020 nm). No charge-transfer band was observed up to 1400 nm, indicating that 2^+1^- can be classified as a charge-separated salt, rather than a charge-transfer complex.

The solid is stable under vacuum but is highly sensitive to air and reacts to give oxygen-containing compounds. Elemental analyses show that the carbon and hydrogen contents decrease rapidly on exposure to air, while the C%:H% ratio remains constant at the theoretical value of $C_{48}H_{51}^+ \cdot C_{64}H_9^-$.¹⁴

The salt 2^+1^- is slightly soluble ($\sim 10^{-5}$ M) in DMSO, to give a reddish-brown solutions. The visible/near-IR spectra of a solution in DMSO-THF (4:1 v/v) agreed with the sum of independently measured spectra of 1^- and 2^+ (Figure 2B),¹⁵ indicating that the ionization of the salt in polar media is essentially complete and that no carbon-carbon bonds are formed.

The salt is much more soluble ($> 10^{-2}$ M) in THF. Although the visible/near-IR and 1H NMR¹⁶ spectra showed quantitative ionization in THF, the ions are not stable in this solvent: signals corresponding to 1^- and 2^+ simultaneously disappeared with a half-life of 1.5 h at 25 °C. Dissolving 2^+1^- in less polar solvents such as toluene and carbon disulfide afforded brown solutions which exhibited no absorptions consistent with 1^- nor 2^+ , indicating immediate decomposition. NMR analysis showed the formation of a mixture of unidentified compounds.

In conclusion, we have successfully synthesized a new hydrocarbon salt using a fullerene-derived anion, 1^- , as a component. The present results demonstrate the utility of using the C_{60} skeleton for the synthesis of a new class of hydrocarbons and provide insight into the potential importance of fullerenes in hydrocarbon chemistry.

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Supporting Information Available: Time dependence of the 1H NMR spectrum of 2^+1^- in THF- d_8 , detailed synthetic procedure for 2^+1^- , experimental methods, and the results of the measurements of the visible/near-IR spectra of $2^+ \cdot C_{60}^{\cdot -}$ and $2^+ \cdot C_{60}(CN)^-$ in solution and electric conductivity measurements (9 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Another possible carbocation-carbanion reaction, a single-electron transfer from 1^- to 2^+ to produce a pair of radicals, is unlikely to occur, since the oxidation potential of 1^- (-0.33 V vs ferrocene/ferrocenium in DMSO, ref 5) is much more positive than the reduction potential of 2^+ (-1.51 V vs ferrocene/ferrocenium in DMSO).

(13) Powder X-ray diffraction (Cu K α radiation) showed no sharp lines, indicating that only a very low degree of order exists in the obtained solid.

(14) Elemental analysis. Calcd for $C_{112}H_{60}$: C, 95.70; H, 4.30. Found: C, 91.71; H, 4.12 (immediately after preparation); C, 87.91; H, 3.86 (after exposure to air for 30 min).

(15) While 2^+ is stable toward air and moisture, 1^- is highly sensitive to air. The visible/near-IR spectrum of 1^- was measured in a degassed solution of K^+1^- in DMSO, prepared from *t*-BuC $_{60}$ H with excess *t*-BuOK: λ_{max} at 995 (ϵ 2400) and 656 (ϵ 3650) nm. This anion showed no absorption maximum near 430 nm, which is characteristic of 1,2-disubstituted dihydrofullerenes. Samples of $K^+1^- \cdot (THF)_x$ for IR spectral measurements were obtained by evaporating and vacuum-drying a THF solution of K^+1^- .

(16) 1H NMR of 2^+1^- (THF- d_8 , 400 MHz): 8.49 (d, $J = 2.0$ Hz, 3H), 8.16 (s, 3H), 7.85 (dd, $J = 10.7, 2.0$ Hz, 3H), 7.52 (d, $J = 10.7$ Hz, 3H), 3.26 (septet, $J = 6.8$ Hz, 3H), 2.90 (s, 9H), 2.62 (s, 9H), 2.27 (s, 9H, 1^-), 1.41 (d, $J = 6.8$ Hz, 18H). The time dependence of the NMR spectrum is given in the Supporting Information.