# Isolation and Properties of Hydrocarbon Salts

Kunio Okamoto,* Toshikazu Kitagawa, Ken'ichi Takeuchi,* Koichi Komatsu,
Tomomi Kinoshita, Shuji Aonuma, Minoru Nagai, and Atsushi Miyabo

*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan*

*Received June 9, 1989*

Four solid hydrocarbon salts **2·1**, **3·1**, **4·1**, and **5·1** consisting of Kuhn's anion, tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion ($C_{67}H_{39}^-$, **1**) as a carbanion moiety, and tris[1-(5-isopropyl-3,8-dimethylazulenyl)]cyclopropenylium ($C_{48}H_{51}^+$, **2**), tricyclopropylcyclopropenylium ($C_{12}H_{15}^+$, **3**), 1-[(2,3-diphenylcycloprop-2-enylidene)methyl]-2,3-diphenylcyclopropenylium ($C_{31}H_{21}^+$, **4**), or 1,3,5-tricyclopropyltropylium ($C_{16}H_{19}^+$, **5**) as a carbocation moiety were prepared and their properties investigated. The salt formation was proved by satisfactory elemental analyses, IR spectra (KBr disk), and UV-vis (DMSO) spectra, the spectra consisting of those of the respective cations and Kuhn's anion superimposed. Essentially complete ionization of the hydrocarbon salts **2·1** and **3·1** in DMSO was also evidenced by electric conductivity measurements. In chloroform solutions, **2·1** and **4·1** are unstable and evaporation of the solvent gave covalent hydrocarbons whose structures were not wholly determined. Meanwhile, **3·1** is converted into a covalent hydrocarbon **3-1** in chloroform whose structure was determined by $^1$H NMR spectroscopy. Chilling of the chloroform solution of **3-1** or evaporation of the solvent, however, regenerates the original hydrocarbon salt **3·1**. Thus, **3-1** is the first covalent hydrocarbon that is existing only in solution. The hydrocarbon salt **5·1** also forms covalent hydrocarbon **5-1** in chloroform and regenerates **5·1** on immediate evaporation of the solvent; however, **5-1** gradually generates radicals **5**$^•$ and **1**$^•$. In THF **5·1** undergoes both coordination and single electron transfer, affording the ionic, radical, and covalent species coexisting in equilibria. This behavior provides the first example showing that the three types of elementary organic species (ions, radicals, and a covalent compound) coexist in equilibria. The occurrence of single electron transfer from **1** to **5** is attributed to the considerably greater electron affinity of **5** than **2**, **3**, and **4**.

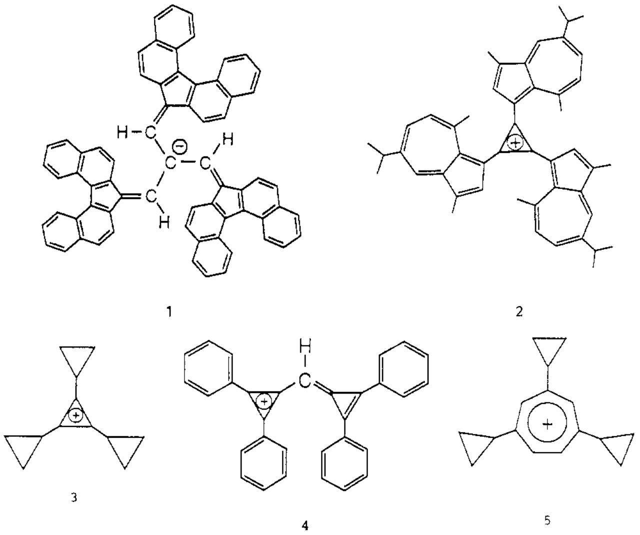
Over 20 years ago Le Goff and LaCount reported carbocation–carbanion salt formation by combining 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienide ion with cations such as tropylium and triphenylcyclopropenylium ions.[1] In the same year Matsumura and Seto also reported on such salt formation from tropylium tetrafluoroborate and potassium 1,2,4-tris(2,2-dicyanoethenyl)cyclopentadienide.[2]

In contrast with these organic salts containing some heteroatoms, oxygen or nitrogen, we recently reported the first example of an organic salt composed of only carbon and hydrogen, a *hydrocarbon* salt.[3] The salt $C_{48}H_{51}^+C_{67}H_{39}^-$ (**2·1**) was prepared by mixing the potassium salt of Kuhn's anion $C_{67}H_{39}^-$, tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion (**1**),[4] and the perchlorate salt of Agranat's cation $C_{48}H_{51}^+$, tris[1-(5-isopropyl-3,8-dimethylazulenyl)]cyclopropenylium ion (**2**),[5] in THF solution under argon (Chart I). We herein describe the details of isolation and properties of the hydrocarbon salt **2·1** and of three new hydrocarbon salts: $C_{12}H_{15}^+C_{67}H_{39}^-$ (**3·1**), $C_{31}H_{21}^+C_{67}H_{39}^-$ (**4·1**), and $C_{16}H_{19}^+C_{67}H_{39}^-$ (**5·1**), consisting of Kuhn's anion (**1**) as a carbanion moiety and tricyclopropylcyclopropenylium ($C_{12}H_{15}^+$, **3**),[6] 1-[(2,3-diphenylcycloprop-2-enylidene)methyl]-2,3-diphenylcyclopropenylium ($C_{31}H_{21}^+$, **4**),[7] and 1,3,5-tricyclopropyltropylium ($C_{16}H_{19}^+$, **5**)[8] ions, respectively, as carbocation moieties.

## Results and Discussion

### Isolation of Hydrocarbon Salts 2·1, 3·1, 4·1, and 5·1.

**Chart I**



1 2 3 4 5

Three years after Doering's discovery of the hygroscopic salt of tropylium bromide,[9] Vol'pin and his collaborators[10] reported that the tropylium ion (p$K_{R^+}$ 4.7)[9] gives a covalent compound with acetate ion (p$K_b$ 9.24) but not with isocyanate ion (p$K_b$ 10.1). This suggests that an anion with the p$K_b$ greater than 10.1 would give a salt with the tropylium ion. In the synthesis of the tricyclopropylcyclopropenylium ion (**3**) we found that it is much more stable in water (p$K_{R^+}$ ~10)[6a] than the tropylium ion and that a transition from covalent compound formation to no reaction in water is observed in the reaction of **3** with the nucleophiles with the p$K_b$ value between 4.79 ($CN^-$) and 6.85 (*p*-nitrophenoxide ion).[6a] Consequently, it was expected that Kuhn's anion (**1**), which has a p$K_b$ value (8.1)[4] greater than that of the *p*-nitrophenoxide ion, would give a stable salt when combined with carbocations with the p$K_{R^+}$ values close to 9 or 10. We selected as the candidate

---

(1) Le Goff, E.; LaCount, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1354.

(2) Matsumura, S.; Seto, S. *Chem. Pharm. Bull. (Tokyo)* **1963**, *11*, 126.

(3) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173.

(4) Kuhn, R.; Rewicki, D. *Angew. Chem.* **1967**, *79*, 648.

(5) Agranat, I.; Aharon-Shalom, E. *J. Org. Chem.* **1976**, *41*, 2379.

(6) (a) Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett.* **1980**, *21*, 947. (b) Moss, R. A.; Munjal, R. *Tetrahedron Lett.* **1980**, *21*, 1221. (c) Moss, R. A.; Shen, S.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J.; Munjal, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 134.

(7) Komatsu, K.; Masumoto, K.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1977**, 232. See also ref 24.

(8) Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257.

(9) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.

(10) Vol'pin, M. E.; Akhrem, I. S.; Kursanov, D. M. *Khim. Nauka Prom.* **1957**, *2*, 656; *Chem. Abstr.* **1958**, *52*, 4294h.

0022-3263/90/1955-0996$02.50/0

**Table I. Some Physical Properties of Hydrocarbon Salts Prepared from Kuhn's Carbanion**

| countercation ($pK_R$+) | mol form | crystalline form and color | dec point,[a] °C | | combustion test[b] | anal. obsd (calcd) | | UV–vis (DMSO) $\lambda_{max}$, nm (log $\epsilon$) |
|---|---|---|---|---|---|---|---|---|
| | | | in air | in vacuo | | C | H | |
| **2** (>10) | $C_{115}H_{90}$ | greenish black needles | 218[c] | 238[c] | no ash | 93.71<br>(93.84) | 6.12[d]<br>(6.16) | 303 (5.08), 336 (4.92),[e] 350 (4.88), 483 (4.72),[e] 696 (5.17) |
| **3** (~10) | $C_{79}H_{54}$ | dark green powder | 150 | 170 | no ash | 94.40<br>(94.57) | 5.58<br>(5.43) | 303 (4.94),[f] 353 (4.78),[f] 696 (5.18) |
| **4** (8.9) | $C_{98}H_{60}$ | dark green powder | ~160 | ~200 | no ash | 95.31<br>(95.11) | 4.73<br>(4.89) | 304 (5.01),[f] 353 (5.03),[f] 696 (5.18) |
| **5** (8.7) | $C_{83}H_{58}$ | dark green powder | ~145 | ~145 | no ash | 94.37<br>(94.46) | 5.24[g]<br>(5.54) | 302 (5.01),[f] 351 (4.88),[f] 696 (5.17) |

[a] Not liquified; color changed to gray or orange. [b] Burned on a spatula. [c] Changed to greenish black liquid. [d] Cl = 0.00. [e] Absorption of the cation. [f] Overlapped by absorption of the cation. [g] F = 0.00.

cations **2** ($pK_{R^+}$ in 50:50 $H_2O$–MeCN >10),[5] **3** ($pK_{R^+}$ ~10),[6] **4** ($pK_{R^+}$ 8.9),[7] and **5** ($pK_{R^+}$, 8.7).[8]

Arnett and his collaborators recently presented empirical linear relations between the heats of cation–anion coordination reactions and the difference of the $pK_{R^+}$ of the carbocation and the $pK_a$ of the carbanion precursor.[11] From their equations it is anticipated that the cation–anion with null heat of reaction should have the value of ca. 10 for ($pK_{R^+} - pK_a$). This might be used as an index of feasibility for the salt formation, although the above-mentioned combinations of the anion **1** and the cations **2**–**5** give the values of 2.8–4.1 for the parameter ($pK_{R^+} - pK_a$).

The deep green solution of Kuhn's anion (**1**) was prepared by mixing potassium *tert*-butoxide and Kuhn's hydrocarbon[4] ($C_{67}H_{40}$) in THF. Since Kuhn's anion is sensitive to light and oxygen, the preparation was conducted under argon in the dark. The carbocation salts $\mathbf{2}\cdot ClO_4^-$, $\mathbf{3}\cdot BF_4^-$, $\mathbf{4}\cdot BF_4^-$, and $\mathbf{5}\cdot BF_4^-$ were dissolved respectively in THF, 50:50 THF-MeCN, 50:50 THF-MeCN, and MeCN.

The cation solutions were mixed with equivalent amounts of the THF solution of $K^+\cdot\mathbf{1}$ under argon in the dark. The $\mathbf{2}\cdot ClO_4^-$ solution instantly gave black precipitates of mixed $KClO_4$ and **2·1**. The salt **2·1** was isolated by recrystallization from DMSO as greenish black needles in a yield of 61%.

The solutions of tetrafluoroborates of the cations **3**, **4**, and **5** gave homogeneous green solutions when mixed with a THF solution of $K^+\cdot\mathbf{1}$. Evaporation of the solvents in vacuo or addition of pentane gave mixtures of organic products (hydrocarbon salts) and potassium tetrafluoroborate as green precipitates. Extraction of the organic products with chloroform (for **3·1**) or THF (for **4·1** and **5·1**) followed by evaporation of the solvent gave rise to the hydrocarbon salts containing small amounts of potassium tetrafluoroborate. The slightly impure hydrocarbon salts were further purified by reprecipitation from their THF solutions by adding acetonitrile (for **3·1**) or pentane (for **4·1** and **5·1**) to give analytically pure **3·1**, **4·1**, and **5·1** in overall yields of 60, 55, and 45%, respectively. Their molecular formula, crystalline forms, color, and the results of combustion tests and elemental analyses are summarized in Table I. All the hydrocarbon salts are stable for more than a year at 10 °C in the dark.

Besides satisfactory elemental analyses, proofs for the salt structures rest on their IR spectra (KBr disk) and UV-vis (DMSO) spectra. These spectra consist of those of the respective cations **2**, **3**, **4**, and **5** and Kuhn's anion (**1**) superimposed. Selected $\lambda_{max}$ values are shown in Table I. The observed UV-vis spectrum of **2·1** is shown as a representative in Figure 1 along with those of **2** and **1**. The IR spectra of **2·1**, **3·1**, **4·1**, and **5·1** are presented in Figure 2.

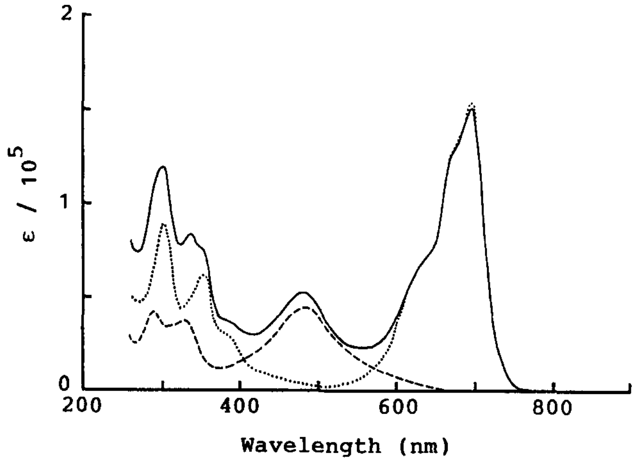


**Figure 1.** UV–vis spectrum of hydrocarbon salt **2·1** in DMSO: solid line, observed; dotted line, **1**; broken line, **2**.

**Electric Conductivity of DMSO Solutions of Hydrocarbon Salts 2·1 and 3·1.** The essentially complete ionization of the aforementioned hydrocarbon salts in DMSO has been demonstrated by quantitative generation of carbanion **1** and carbocations **2**, **4**, and **5** as determined by UV–vis spectra. Another piece of evidence may be provided by electric conductivity in solution. In particular, carbocation **3** has intrinsically no absorptions at a wavelength longer than 220 nm in the UV–vis region; therefore, there remained an ambiguity that **3** might have decomposed in DMSO in the presence of **1**. If the limiting equivalent conductance of **3·1** is equal to the sum of those of **3** and **1**, we can safely conclude that the ions stay in solution without significant deterioration. It also appears of interest to investigate whether the hydrocarbon salts behave as strong electrolytes or weak ones. In this work **2·1** and **3·1** were selected as candidates.

Equivalent conductances for **1**, **2**, and **3** at infinite dilution at 25.0 °C were first determined by measuring $\Lambda_0$'s of $\mathbf{1}\cdot H^+$, $\mathbf{2}\cdot ClO_4^-$, and $\mathbf{3}\cdot ClO_4^-$ and then subtracting reported $\Lambda_0$ values for $H^+$ (14.6)[12] and $ClO_4^-$ (24.52).[13] Determination of $\Lambda_0$ for $H^+$ by using picric acid in this laboratory afforded an identical value with the reported one. Satisfactory Onsager's plots ($\Lambda$ vs $c^{1/2}$) for $\mathbf{1}\cdot H^+$, $\mathbf{2}\cdot ClO_4^-$, and $\mathbf{3}\cdot ClO_4^-$ were obtained, giving $\Lambda_0^{\pm}$ values of 19.9, 30.2, and

---

(11) (a) Arnett, E. M.; Chawla, B.; Molter, K.; Amarnath, K.; Healy, M. *J. Am. Chem. Soc.* **1985**, *107*, 5288. (b) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels* **1987**, *1*, 17.

(12) The $\Lambda_0$ value for $H^+$ (14.6) was obtained by subtracting $\Lambda_0$ for $Cl^-$ (24.12) (ref 13) from $\Lambda_0$ for HCl (38.7) (ref 14), both in DMSO at 25.0 °C.

(13) Gopal, R.; Shanker Jha, J. *J. Phys. Chem.* **1974**, *78*, 2405.

(14) Bolzan, J. A.; Arvia, A. J. *Electrochim. Acta* **1970**, *15*, 39.

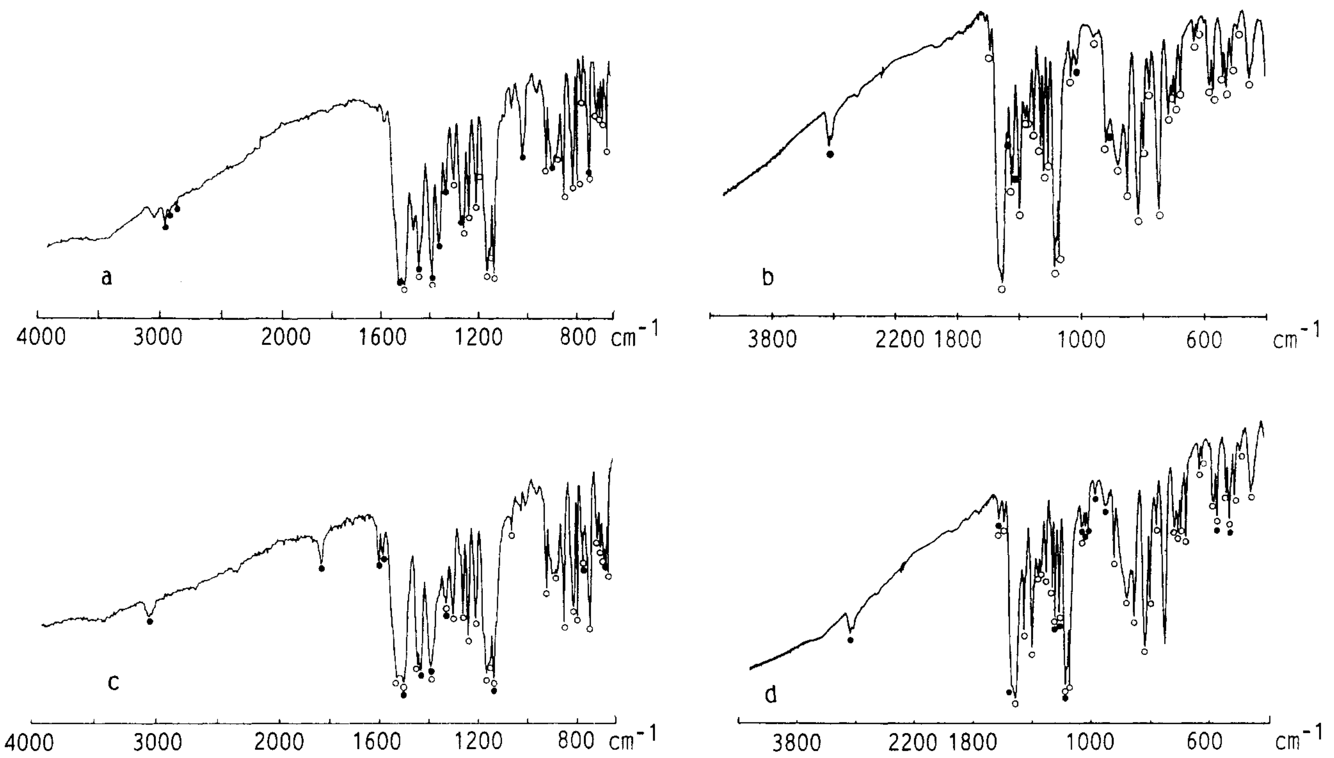


**Figure 2.** IR spectra (KBr disk) of hydrocarbon salts: closed circle, absorptions of cation; open circle, absorptions of 1: (a) 2·1; (b) 3·1; (c) 4·1; (d) 5·1.

36.5, respectively. From these values, $\Lambda_0(1)$, $\Lambda_0(2)$, and $\Lambda_0(3)$ were determined as 5.3, 5.7, and 12.0, respectively. These values afforded predicted $\Lambda_0$ values of 10.9 and 17.3 for 2·1 and 3·1, respectively. Conductance data for 2·1 and 3·1 followed Onsager's equation, indicating that they are strong electrolytes in DMSO, and gave $\Lambda_0^{\pm}$ values of 10.9 and 18.2 at 25.0 °C, respectively. Good agreements of the directly determined limiting equivalent conductances with the predicted ones indicate that the component ions exist in DMSO without significant deterioration under argon. It was also shown that 2·1 and 3·1 are dissociated to more than 99% in DMSO over a concentration range $10^{-4}$–$10^{-5}$ M.

**Behaviors of the Hydrocarbon Salts in Chloroform.** The four hydrocarbon salts are generally unstable in chloroform. However, as far as an early stage after dissolution is concerned, their behaviors can be classified into two categories: (a) 2·1 and 4·1 afford a brown solution, which on immediate evaporation gives a reddish solid that generates 1 only partly (<10%) when dissolved in DMSO, and (b) 3·1 and 5·1 afford a brown solution, which on immediate evaporation regenerates the original greenish salt almost quantitatively. In both categories, the formation of brown solutions suggests that covalent hydrocarbons are formed in chloroform. However, the fact that 2·1 and 4·1, when dissolved first in chloroform and recovered, no longer regenerate 1 in DMSO indicates that the reddish solids essentially consist of difficulty ionizing covalent hydrocarbons whose cationic moiety may be different from the original structure. The behaviors of 3·1 and 5·1 in various solvents are described in the following sections.

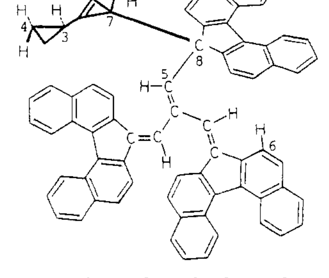


**Figure 3.** Structure of covalent hydrocarbon 3-1 existing in chloroform-*d*.

**Table II. $^1$H and $^{13}$C NMR Spectral Data for Covalent Hydrocarbon 3-1 Existing in Chloroform-*d***

| | δ ($CDCl_3$) |
|---|---|
| $^1$H NMR[a] | −0.46 (2 H, dddd, $H_2$(trans))<br>−0.33 (2 H, dddd, $H_2$(cis))<br>0.43 (1 H, tt, $J$ = 5.2, 8.4 Hz, $H_1$)<br>0.50 (2 H, dddd, $J$ = 4.2, 4.8, 8.2, 8.7 Hz, $H_4$(trans))<br>0.57 (2 H, dddd, $J$ = 4.2, 4.8, 8.2, 8.7 Hz, $H_4$(trans))<br>0.87 (4 H, dddd, $J$ = 4.2, 8.7, 8.7, 11.7 Hz, $H_4$(cis))<br>1.69 (2 H, tt, $J$ = 4.9, 8.2 Hz, $H_3$)<br>6.47 (1 H, br s, $H_5$)<br>6.55 (1 H, d, $J$ = 8.5 Hz, $H_6$)<br>7.05–8.70 (37 H, m, aromatic-H and =CH—) |
| $^{13}$C NMR[b] | 3.3 (t, $C_2$), 7.1 (d, $C_3$), 9.2 (t, $C_4$), 13.4 (d, $C_1$), 40.7 (s, $C_7$), 64.6 (s, $C_8$), 117.7–149.8 (others) |

[a] 400 MHz; the signal of chloroform (δ 7.26) was taken as internal standard. [b] 25 MHz.

**Behavior of 3·1 in Various Solvents.** Dissolution of 3·1 in chloroform gave a brown solution. When the solution was kept for a few hours at ca. 20 °C under argon and the solvents were evaporated in vacuo, a greenish solid was obtained. The solid quantitatively regenerated 1 when dissolved in DMSO. Thus both the cationic and the anionic moieties were not deteriorated in chloroform. Essentially no deterioration was observed even after a month at −10 °C. The greenish hydrocarbon salt was also precipitated by cooling the chloroform solution at −78 °C. The most characteristic feature is that the covalent hydrocarbon 3-1 exists only in solution.

**Table III. Thermodynamic Data for Coordination of 3 with 1 (3-1 $\rightleftarrows$ 3 + 1) in Various Solvents at 25 °C**

| solvent | dielect. const at 25 °C | initl concn, $10^5$ M | 1, $10^5$ M | $1^{\bullet}$, $10^6$ M | $K_{het}$ | ionic strength | $\gamma\pm^2$ | $K°_{het}$[a] | $\Delta G°_{het}$, kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3CN$ | 35.94 | 5.03 | 4.36 | 0 | $2.82 \times 10^{-4}$ | $5.61 \times 10^{-5}$ | 0.951 | $2.68 \times 10^{-4}$ | 4.87 |
| | | 5.28 | 4.60 | 0 | $3.08 \times 10^{-4}$ | $5.92 \times 10^{-5}$ | 0.950 | $2.92 \times 10^{-4}$ | 4.82 |
| EDC | 10.37 | 6.28 | 3.74 | 4.83 | $8.70 \times 10^{-5}$ | $3.39 \times 10^{-5}$ | 0.728 | $6.33 \times 10^{-5}$ | 5.73 |
| | | 5.53 | 3.27 | 6.31 | $9.32 \times 10^{-5}$ | $3.13 \times 10^{-5}$ | 0.737 | $6.87 \times 10^{-5}$ | 5.68 |
| $CH_2Cl_2$ | 8.93 | 6.08 | 1.68 | 9.12 | $1.92 \times 10^{-5}$ | $1.97 \times 10^{-5}$ | 0.732 | $1.41 \times 10^{-5}$ | 6.62 |
| | | 6.03 | 1.63 | 5.97 | $1.31 \times 10^{-5}$ | $1.69 \times 10^{-5}$ | 0.749 | $9.81 \times 10^{-6}$ | 6.83 |
| THF | 7.58 | 5.08 | 2.10 | 2.29 | $1.98 \times 10^{-5}$ | $2.65 \times 10^{-5}$ | 0.685 | $1.36 \times 10^{-5}$ | 6.64 |
| | | 5.53 | 2.26 | 2.27 | $2.04 \times 10^{-5}$ | $2.83 \times 10^{-5}$ | 0.677 | $1.38 \times 10^{-5}$ | 6.63 |

[a] $K°_{het} = K_{het} \times \gamma\pm^2$.

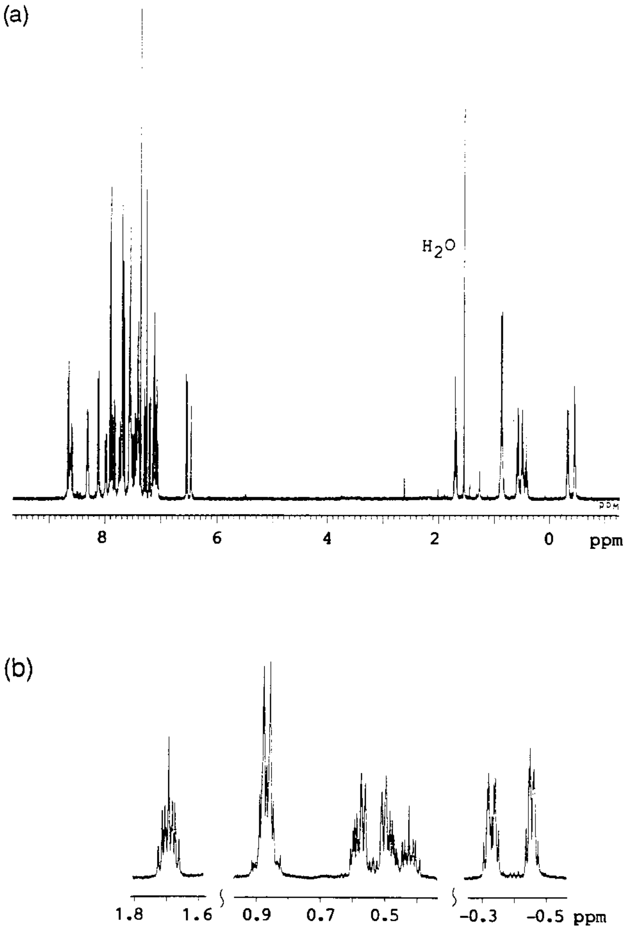


**Figure 4.** $^1H$ NMR spectrum (400 MHz) of covalent hydrocarbon 3-1 ($10^{-3}$ M) existing in chloroform-*d*: (a) full spectrum, (b) expanded spectrum showing cyclopropyl hydrogens.

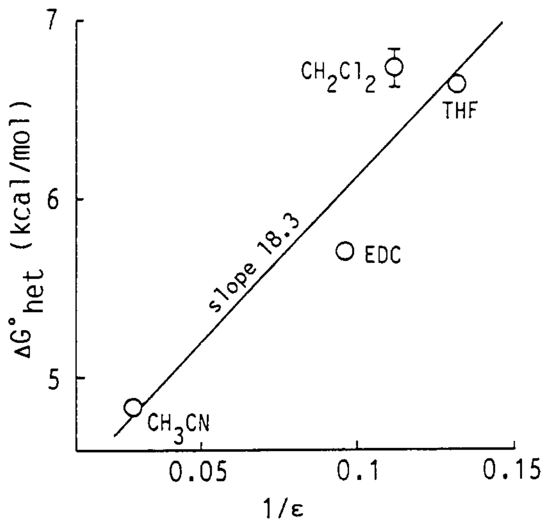


**Figure 5.** Born plot for coordination of 3 with 1 (3-1 $\rightleftarrows$ 3 + 1) in various solvents at 25 °C.

The structure of the covalent hydrocarbon 3-1 existing in chloroform-*d* was determined as shown in Figure 3 by the 400-MHz $^1H$ NMR spectrum. The $^1H$ NMR spectrum and the data are given in Figure 4 and Table II, respectively. The highly symmetric pattern exhibited by the cyclopropyl hydrogens and the singlet signal at $\delta$ 6.47 (H-7) amounting to unity suggests that the cyclopropyl group is attached at C-8 of one of the dibenzofluorenylidene moieties (see Figure 3). The doublet signal at $\delta$ 6.55 was assigned to the highly shielded aromatic hydrogen (H-6; Figure 3). The other signals due to aromatic hydrogen were too complex to analyze. The assignments of the cyclopropyl hydrogens were based on spin–spin decoupled spectra. Although the coupling constants of the signals at $\delta$ 0.43 (H-1), 0.50 and 0.57 (H-4 (trans)), 0.87 (H-4 (cis)), and 1.69 (H-3) could be determined, complete analysis of the signals at $\delta$ −0.46 (H-2 (trans)) and −0.33 (H-2 (cis)) was only partly successful. The $^{13}C$ NMR spectrum of 3-1 in chloroform-*d* could also be measured. The signals were assigned as given in Table II by taking their intensities and multiplicities into account.

The reason for nonexistence of the covalent hydrocarbon 3-1 in the solid state has not wholly been clarified. Most probably, great congestion in any hypothetical solid state of the hydrocarbon 3-1 may be relieved in the salt form, the latter form being stabilized by the lattice energy. Such conversion may be seen, in some sense, as a mechanochemical phenomenon at the molecular level.

The behavior of 3·1 was further examined in solvents other than DMSO and chloroform. In benzene and carbon tetrachloride the salt is completely converted to the covalent form 3-1. In acetonitrile the two forms coexist in clean equilibrium. On the other hand, in acetone, 1,2-dichloroethane, dichloromethane, and THF, 3–15% of radical $1^{\bullet}$ was detected at $\lambda_{max}$ 545–551 nm (see Experimental Section) even in vacuo in the dark, the amount depending on the period after mixing. For calculations of equilibrium constants for ionization, the combined concentrations of $1^{\bullet}$ and 1 were used as the total concentrations of 1. Following Arnett,[15] thermodynamic equilibrium constants, $K°_{het}$ (molarity), were calculated by using the Debye–Hückel limiting law equation and converted to the standard free energies of heterolysis. The results are summarized in Table III. A Born plot showed the increase of ionization with increasing dielectric constants (Figure 5).

**Behavior of 5·1 in Various Solvents.** Among the carbocations successfully employed for preparation of the hydrocarbon salts, the cation 5 is the least stable as judged

---

[15] Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.* 1984, *106*, 6726.

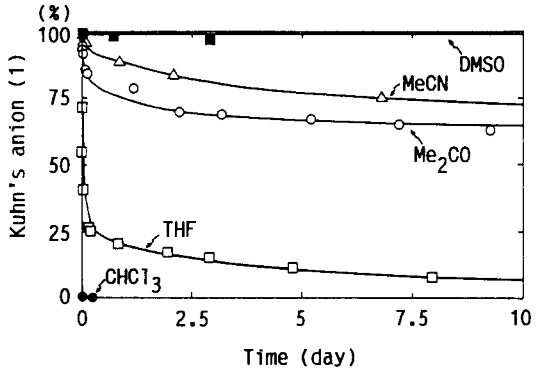


**Figure 6.** Change in concentration of anion **1** determined by the visible spectrum for the reaction of **1** (1 × 10$^{-4}$ M) and **5** (1 × 10$^{-4}$ M) in various solvents at 25 °C.

from its $pK_{R^+}$ value (vide supra). In accord with this, the salt **5·1** demonstrated characteristic behavior different from that of the other salts upon changing the solvent.[16] As has been briefly mentioned above, the salt **5·1** immediately afforded an orange-brown solution when dissolved in chloroform. This solution exhibited a visible spectrum quite similar to that of Kuhn's hydrocarbon $C_{67}H_{40}$ (**1**-H), and therefore the main component is supposed to be the covalent compound **5-1**. Formation of this covalent compound was confirmed by regeneration of **1** in the visible spectrum (in 80%) upon dilution of the freshly prepared chloroform solution with 10 volumes of DMSO. Also the compound **5-1** dissociated to the salt **5·1** upon reprecipitation in pentane or simply by evaporation under vacuum, as has been observed in the case of compound **3-1**.

However, **5-1** is markedly different from **3-1** in its stability. Whereas **3-1** was shown to be stable enough in a vacuum-sealed tube to give a well-defined $^1$H NMR spectrum, the $^1$H NMR spectrum of **5-1** was considerably broadened due to the rapidly developing radical species $\mathbf{1}^\bullet$. When a chloroform solution of **5-1** was allowed to stand for longer than 1 min under vacuum, the visible spectrum clearly indicated generation of the radical $\mathbf{1}^\bullet$ ($\lambda_{max}$ 546 nm), which finally amounted to 93% after 6 h at ca. 20 °C. This fact suggests that the single bond in the covalent compound **5-1** homolytically dissociates quite readily in chloroform.

When the salt **5·1** was dissolved, or the anion **1** was mixed with an equivalent amount of the cation **5**, in solvents with different polarity, the visible spectrum indicated that **1** was rapidly consumed by the reaction with **5** and reached the apparent equilibria as shown in Figure 6. Clearly the rate of initial cation–anion reaction increased as the solvent polarity decreased.

The characteristic behavior of the salt **5·1** is most evident in THF, which has been commonly used throughout our systematic study of cation–anion reactions. Thus, as shown in Figure 7, the anion **1** is rapidly consumed by the reaction with **5** ($t_{1/2}$ ca. 3 min when [**1**] = [**5**] = 1 × 10$^{-4}$ M), which is accompanied by the concomitant formation of the radical $\mathbf{1}^\bullet$. Yet the reaction does not reach the completion and some amounts of ionic species remain unchanged in apparent equilibrium with other species. The difference between the amounts of consumed anion **1** and of produced $\mathbf{1}^\bullet$ is due to the covalent compound **5-1**, since the corresponding amount of **1** was regenerated by 10-fold dilution of the reaction mixture with DMSO. The occurrence of a single-electron-transfer process was confirmed not only by spectral means but also by isolating the dimer of 1,3,5-tricyclopropylcycloheptatrienyl radical (**5-5**)[17] in 20% yield from the reaction mixture after 48 h at room temperature.

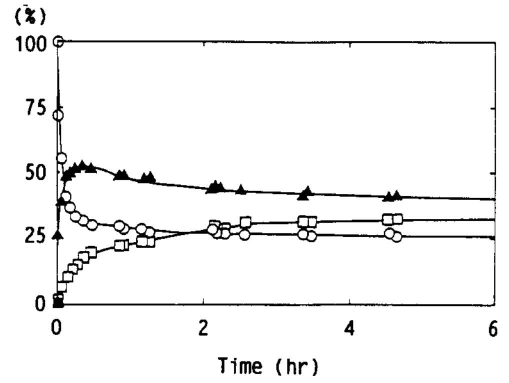
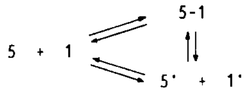


**Figure 7.** Change in concentration of anion **1** (○), radical $\mathbf{1}^\bullet$ (□), and covalent compound **5-1** (▲), as estimated from the visible spectrum for the reaction mixture of **1** (1 × 10$^{-4}$ M) and **5** (1 × 10$^{-4}$ M) in THF at 20 °C.

**Scheme I**



These results illustrate that the cation **5** and the anion **1** exist in equilibria with the corresponding covalent as well as the radical species as formulated in Scheme I: thus, the three types of elementary organic species (ions, radicals, and a covalent compound) are now shown to be able to coexist in solution.[18] In this context Arnett and co-workers reported a system in which a carbocation (4,4′-bis(dimethylamino)triphenylmethylium ion) and a carbanion (4,4′,4″-trinitrotriphenylmethide ion) are in equilibrium with their corresponding radicals by way of a single-electron-transfer process.[19] The occurrence of single-electron transfer, which was not observed in the combination of **1** with the other cations **2**–**4**, is attributed to the greater electron affinity of **5** (the reduction potential −0.86 V vs Ag/Ag$^+$ in MeCN)[8] as compared with the cations **2** (−1.42 V), **3** (−2.20 V),[20] and **4** (−1.48 V).[20] The presence of three cyclopropyl groups on the tropylium ring should also be assisting the single-electron-transfer process, since it would bring about considerable steric congestion in the covalent hydrocarbon and some stabilization of the trisubstituted cycloheptatrienyl radical due to possible $\sigma$-conjugation between the cyclopropyl groups and the $\pi$-system.[21]

## Experimental Section

Melting and boiling points are uncorrected. IR spectra were taken on a Nicolet 20DXB FT IR spectrometer. UV–vis spectra were taken on a Hitachi 200-10 spectrometer. $^1$H NMR spectra

---

(16) Preliminary results have been reported as a communication: Komatsu, K.; Aonuma, S.; Takeuchi, K.; Okamoto, K. *J. Org. Chem.* **1989**, *54*, 2038.

(17) The same dimer was obtained by one-electron reduction of **5** with zinc powder in acetonitrile.

(18) The ESR experiment demonstrated that the dimer **5-5**, when heated to 170 °C in *m*-xylene, cleanly dissociates into the radical $\mathbf{5}^\bullet$. The dissociation constant at room temperature is estimated to be nearly 10$^{-18}$ M from the similar treatment of the data as in our previous study: Okamoto, K.; Komatsu, K.; Kinoshita, T.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1901. However, the whole system is supposed to be in equilibria, since the concentration of the stable radical $\mathbf{1}^\bullet$ is overwhelmingly high, thus, compensating the low concentration of $\mathbf{5}^\bullet$.

(19) Arnett, E. M.; Molter, K. E.; Marchot, E. C.; Donovan, W. H.; Smith, P. *J. Am. Chem. Soc.* **1987**, *109*, 3788.

(20) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011.

(21) Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoeller, J., Jr.; Gordon, R. D.; Hyde, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 6666.

were recorded on a JEOL GX-400 (400 MHz), a Nicolet NP-300NB (300 MHz), or a JEOL FX-90 (90 MHz) spectrometer. $^{13}C$ NMR spectra were recorded on a JEOL FX-100 (25 MHz) spectrometer. The conductivity was measured with a Toa Electronics Ltd. Model CM-6A equipped with a conductivity cell CG-2001PL (cell constant 0.0990). Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. A Sartorius 4503MP6 microbalance was used for precise weighing.

Dimethyl sulfoxide (DMSO) was stored at least for 2 weeks over molecular sieves, distilled under vacuum from alumina, and then doubly distilled under vacuum from calcium hydride ($CaH_2$) immediately before use. All other distillations were carried out under nitrogen or under argon. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride prior to use. Acetonitrile (MeCN) was distilled twice from phosphorous pentoxide ($P_2O_5$) and then from $CaH_2$ before use. Acetone was distilled from calcium sulfate. Chloroform was washed successively with sulfuric acid, 10% aqueous NaOH, and water, dried over potassium carbonate, and then distilled from $P_2O_5$. Carbon tetrachloride and dichloromethane were distilled from $P_2O_5$. Pentane was distilled from freshly cut sodium metal.

The carbocation salts $\mathbf{2}\cdot ClO_4^-$,[5] $\mathbf{3}\cdot BF_4^-$,[6] $\mathbf{4}\cdot BF_4^-$,[7] and $\mathbf{5}\cdot BF_4^-$[8] were prepared according to the literature.

**Preparation of Kuhn's Hydrocarbon (1-H).** The hydrocarbon 1-H was prepared by following the literature[4] with some modification as described below. A 2.83 M solution of NaOMe in MeOH (2.5 mL, 7.08 mmol) was added dropwise to a magnetically stirred mixture of dibenzo[*c,g*]fluorene[22] (1.63 g, 6.13 mmol) and 1-(dimethylamino)-2,2-bis[(dimethylimmonio)-methyl]ethene diperchlorate ($(Me_2N^+{=}CH)_2C{=}CHNMe_2\cdot 2ClO_4^-$)[23] (1.18 g, 3.08 mmol) in dry pyridine (4.8 mL) under argon. After being stirred at room temperature for 45 min, the black mixture was evaporated under vacuum (0.01 Torr). The residual solid was washed with MeOH (7 × 20 mL) and then recrystallized from benzene (85 mL) to give 1,1-bis(7*H*-dibenzo[*c,g*]-fluorenylidenemethyl)-2-(dimethylamino)ethene as dark red crystals (1.48 g, 77.6%): mp 274–276 °C (lit.[4] mp 265–270 °C); $^1H$ NMR ($CDCl_3$; 90 MHz) $\delta$ 9.00–7.20 (m, 27 H, aromatic-H and =CH—), 3.35 (s, 6 H, $CH_3$).

A THF solution of lithium dibenzo[*c,g*]fluorenide, which had been prepared by adding 1.76 M BuLi/hexane (1.25 mL, 2.20 mmol) to an ice-cooled solution of dibenzo[*c,g*]fluorene (0.567 g, 2.03 mmol) in THF (8 mL), was added to a stirred suspension of 1,1-bis(7*H*-dibenzo[*c,g*]fluorenylidenemethyl)-2-(dimethylamino)ethene (1.26 g, 2.03 mmol) in THF (10 mL) under argon. The mixture was refluxed for 1 h, during which period the color of the reaction mixture turned from dark brown to deep green. Pre-deoxygenated 2 N HCl (70 mL) was added to the dark green mixture with stirring. The resulting dark red suspension was extracted with benzene (3 × 100 mL). The benzene solution was washed with 10% NaCl, dried over $MgSO_4$, and evaporated to give a dark red-orange solid, which was then chromatographed over $SiO_2$. An orange solid eluted by hexane–$CHCl_3$ (2:1 v/v) was dissolved in $CH_2Cl_2$ (5 mL) and reprecipitated in pentane (100 mL) to give 1-(7*H*-dibenzo[*c,g*]fluoren-7-yl)-2,2-bis(7*H*-dibenzo-[*c,g*]fluorenylidenemethyl)ethene (1-H) as an orange powder (0.908 g; 53.0%): mp 217–225 °C dec (lit.[4] mp 210–215 °C dec); $^1H$ NMR ($CDCl_3$; 300 MHz) $\delta$ 8.66–7.19 (m, 38 H, aromatic-H and =CH—), 6.38 (dt, 1 H, $J$ = 10.5 Hz, $J$ = 1.4 Hz, =CH—), 5.41 (d, 1 H, $J$ = 10.5 Hz, >CH—); $^{13}C$ NMR ($CDCl_3$; 22.5 MHz) $\delta$ 144.1–118.0 (>35 peaks), 51.0 (d).

**Generation of Kuhn's Anion (1).** Except for the purpose of preparation of hydrocarbon salts, generation and spectral observation of the anion 1 were conducted in a vacuum-sealed tube equipped with a quartz cell. As has been reported by Kuhn and Rewicki,[4] the anion 1 was quantitatively generated when the hydrocarbon 1-H was dissolved in DMSO; UV–vis $\lambda_{max}$ (log $\epsilon$) 696 (5.18), 672 sh (5.11), 638 sh (4.86), 390 sh (4.44), 352 (4.79), 304 (4.95), 294 sh nm (4.89) (lit.[4] $\lambda_{max}$ 697 nm (5.15)). The anion 1 was also generated from 1-H and *t*-BuOK in THF under vacuum: UV–vis $\lambda_{max}$ (log $\epsilon$) 692 (5.18), 672 sh (5.13), 633 sh (4.79), 389 sh (4.34), 354 (4.69), 302 (4.85), 292 nm (4.83). Precautions were taken to protect the anion solution from the visible light, since the radical $1^\bullet$ was found to be readily formed by photoinduced electron transfer occurring even by room light.

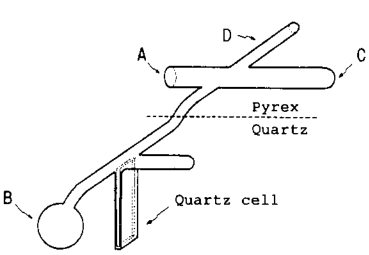


**Figure 8.** Quartz cell used for the measurements of UV–vis spectra under vacuum: cell path 1 mm.

**Generation of Kuhn's Radical ($1^\bullet$).** Into a deep green solution of the anion 1 generated in DMSO under vacuum, there was transferred an excessive amount (7 equiv) of iodine by sublimation. After sealing the tube, the solution was mixed to give a deep red solution of $1^\bullet$; UV–vis $\lambda_{max}$ (log $\epsilon$) 509 sh (4.49), 551 nm (4.90) (lit.[4] $\lambda_{max}$ (benzene) 545 nm).

**Hydrocarbon Salt 2·1.** To the hydrocarbon 1-H (0.0887 g, 0.105 mmol) was added a 0.033 M solution of *t*-BuOK in THF (3.0 mL, 0.099 mmol) with stirring under argon. After stirring for 5 min, a solution of $2\cdot ClO_4^-$ (0.065 g, 0.090 mmol) in THF (6.0 mL) was added to the resulting deep green solution to cause the formation of black precipitates. After stirring for additional 5 min, the precipitates were collected under nitrogen stream, sealed with degassed (three freeze–pump–thaw cycles) DMSO (4.8 mL) in an ampule under vacuum, and dissolved by heating at 120 °C for 5 min. The ampule was let stand undisturbed at room temperature in the dark for 10 h. The crystals that separated were collected by filtration under nitrogen and dried under vacuum to give 2·1 as greenish black needles (0.081 g; 61%).

**Hydrocarbon Salt 3·1.** A solution of $3\cdot BF_4^-$ (0.0205 g, 0.0833 mmol) in THF–MeCN (8:1 v/v) (7.2 mL) was added under nitrogen to a stirred solution of $K^+\cdot 1$ prepared from 1-H (0.0630 g, 0.0746 mmol) and *t*-BuOK (0.781 mmol) in THF (4.8 mL). The dark green mixture was stirred for 5 min in the dark and then the solvent removed by evaporation. The residue was taken up in $CHCl_3$ (5 mL) and filtered by means of a membrane filter (0.45 $\mu$m). The brown-colored filtrate was evaporated, leaving a dark green solid, which was redissolved in THF (1.5 mL) to give a green solution. The solution was added to MeCN (10 mL) with rapid stirring to cause the formation of green precipitates, which were collected by centrifugation, washed with MeCN (2 × 2 mL) under nitrogen, and dried under vacuum to give 3·1 as a dark green powder (0.0441 g; 60%).

**Hydrocarbon Salt 4·1.** A solution of $4\cdot BF_4^-$ (0.0435 g, 0.0906 mmol) in THF–MeCN (5:1 v/v) (10 mL) was added under nitrogen to a stirred solution of $K^+\cdot 1$ prepared from 1-H (0.0765 g, 0.0905 mmol) and *t*-BuOK (0.0904 mmol) in THF (5.2 mL). After stirring for 2 min in the dark, pentane (75 mL) was added to cause formation of dark green precipitates, which were collected by filtration under argon. To the precipitates was added THF (3.5 mL), and the mixture was centrifuged for 2 min. The supernatant solution was filtered by a membrane filter (0.45 $\mu$m) and the filtrate directly dropped into pentane (75 mL) with stirring under argon to cause the formation of dark green precipitates, which were filtered and dried under vacuum to give 4·1 as a dark green powder (0.0612 g; 54.6%).

**Hydrocarbon Salt 5·1.** A solution of $5\cdot BF_4^-$ (0.0255 g, 0.0856 mmol) in MeCN (1.0 mL) was added under argon to a stirred solution of $K^+\cdot 1$ prepared from 1-H (0.0730 g, 0.0848 mmol) and *t*-BuOK (0.0803 mmol) in THF (1.1 mL). After being stirred for 3 min in the dark, the mixture was carefully evaporated to dryness and then taken up in THF (1 mL), applying agitation in an ultrasonic bath for ca. 10 s under argon. The dark green mixture was filtered by a membrane filter (0.45 $\mu$m) and the filtrate directly dropped into pentane (7 mL) with stirring to cause formation of dark green precipitates, which were collected by filtration, washed with MeCN (2 mL), benzene–pentane (1:4 v/v), and pentane (15 mL), and dried under vacuum to give 5·1 as a dark green powder (0.0405 g; 45.3%).

**Measurements of UV–Vis Spectra of Hydrocarbon Salts under Vacuum.** For UV–vis measurements was employed a

---

[22] Martin, R. H. *J. Chem. Soc.* **1941**, 679.

[23] Jutz, C.; Amschler, H. *Chem. Ber.* **1964**, *97*, 3331.

**Table IV. Electric Conductivities of 1•H, $2\bullet ClO_4^-$, $3\bullet ClO_4^-$, 2•1, and 3•1 in DMSO at 25.00 ± 0.05 °C**

| compd | concn, $10^4$ M | Λ, $mho{\cdot}cm^2{\cdot}mol^{-1}$ |
|---|---|---|
| 1·H | 0 | 19.9 |
| | 2.36 | 17.6 |
| | 4.67 | 16.6 |
| | 5.58 | 16.5 |
| | 6.37 | 16.1 |
| | 7.06 | 15.9 |
| | 7.67 | 15.7 |
| | 8.22 | 15.5 |
| | 8.70 | 15.6 |
| $2{\cdot}ClO_4^-$ | 0 | 30.2 |
| | 0.800 | 29.7 |
| | 1.53 | 29.8 |
| | 2.19 | 29.8 |
| | 2.80 | 29.7 |
| | 3.36 | 29.4 |
| | 3.87 | 29.3 |
| | 4.35 | 29.3 |
| | 4.80 | 29.3 |
| | 5.21 | 29.3 |
| | 5.59 | 29.4 |
| $3{\cdot}ClO_4^-$ | 0 | 36.5 |
| | 0.252 | 37.2 |
| | 0.692 | 35.3 |
| | 1.06 | 35.7 |
| | 1.38 | 36.1 |
| | 1.65 | 36.1 |
| | 1.88 | 36.2 |
| | 2.09 | 36.3 |
| | 2.27 | 36.3 |
| 2·1 | 0 | 10.9 |
| | 0.347 | 10.4 |
| | 0.950 | 9.65 |
| | 1.45 | 9.13 |
| | 1.89 | 9.30 |
| | 2.24 | 9.13 |
| | 2.56 | 8.96 |
| | 2.85 | 8.96 |
| | 3.09 | 8.87 |
| | 3.31 | 8.78 |
| | 3.51 | 8.70 |
| 3·1 | 0 | 18.2 |
| | 0.253 | 18.6 |
| | 0.693 | 16.8 |
| | 1.06 | 17.2 |
| | 1.38 | 17.4 |
| | 1.65 | 17.5 |
| | 1.89 | 17.5 |
| | 2.09 | 17.5 |
| | 2.28 | 17.4 |

quartz cell shown in Figure 8. The typical procedure is as follows. The sample (0.200–0.500 mg) was weighed by the use of a microbalance in a tared glass tube and placed in room C from the inlet A. After port A was sealed off, freshly distilled DMSO (2–5 mL) was placed in room B; the volume of DMSO was determined from its weight and density (1.096 at 25 °C). After degassing DMSO by repeating the freeze–pump–thaw cycle for 4 times, the tube was sealed under vacuum at position D, and the sample solution was prepared in the dark to be ready for the measurement. Measurements in other solvents were carried out in the same way except that the solvents were vacuum-distilled directly into room B.

In order to follow the carbocation–carbanion reaction spectrophotometrically under vacuum, the following procedures were taken. A known weight of a carbocation salt was placed in room C, while a known amount of the carbanion salt $K^+{\cdot}1$ was placed in room B by carefully evaporating a known volume of the THF solution of $K^+{\cdot}1$ under vacuum. After a given solvent was added to $K^+{\cdot}1$ by vacuum distillation, the tube was sealed and the UV–vis spectrum was taken to confirm the concentration of the anion 1. Then the solution was mixed with the carbocation in room C, and the spectral change was recorded as the function of time.

**Measurements of Electric Conductivity of 2·1 and 3·1 in DMSO.** Electric conductivity in DMSO was measured at 25.00 ± 0.05 °C in the range of $10^{-4}$ to $10^{-5}$ M. Since 1 is sensitive to oxygen and light, freshly degassed DMSO was used for the preparation of stock solutions ($10^{-3}$ to $10^{-4}$ M) of 1-H, 2·1, and 3·1. They were handled under argon in the dark during the measurements. A typical procedure is as follows. A portion (1.000 or 2.000 mL) of the stock solution which had been maintained at 25.0 °C in a kerosene constant temperature bath was added every 3 to 5 min to a cell tube containing 20.00 mL of DMSO. Specific conductance at each concentration, calculated by subtracting specific conductance of DMSO from the observed value, was converted to equivalent conductance (Λ). A plot of Λ against the square root of concentration (Onsager's plot) gave equivalent conductance at infinite dilution ($\Lambda_0$). The results of electric conductivity measurements for 1-H, $2{\cdot}ClO_4^-$, $3{\cdot}ClO_4^-$, 2·1, and 3·1 are summarized in Table IV.

**Reduction Potential of Cation 2.** Reduction potential of cation 2 was determined by means of cyclic voltammetry by the method and instruments previously reported.[24] The measurements were carried out with a scan rate of 0.1 V/s for the 1 mM cation solution in MeCN using tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. The reference electrode was Ag/0.01 M $AgNO_3$, and the potential was calibrated with $E_{1/2}$ of ferrocene added as an internal standard immediately after the measurement.

**Reductive Dimerization of Cation 5.** To a stirred solution of $5{\cdot}BF_4^-$ (0.0488 g, 0.614 mmol) in 10% HCl was added zinc powder (0.103 g, 1.58 mmol) under argon. After being stirred for 10 min, the mixture was extracted with ether and worked up in the usual way to give the dimer 5-5 as a colorless oil (0.0289 g; 83.4%): IR (neat) $\nu$ 3080, 3000, 2950, 1618, 1458, 1424, 1020, 895, 820 $cm^{-1}$; UV (EtOH) $\lambda_{max}$ 214 (log $\epsilon$ 4.45), 222 sh (4.44), 282 nm (3.84); $^1H$ NMR ($CCl_4$) $\delta$ 6.04 (br t, 2 H, =CH—), 5.71–5.50 (br m, 3 H, =CH—), 4.66 (br d, 1 H, =CH—), 2.97 (br m, 2 H, >CH—), 1.37 (br m, 6 H, >CH— (cyclopropyl)), 0.57 (br m, 24 H, $CH_2$ (cyclopropyl)).

**Isolation of Dimer 5-5 from Reaction of 5 with 1.** In a glass tube with a side arm containing $5{\cdot}BF_4^-$ (0.0270 g, 0.0906 mmol), there was placed a 0.0306 M solution of $K^+{\cdot}1$ in THF (3.0 mL, 0.0918 mmol). After degassing the solution, the tube was sealed under vacuum and the solution mixed with $5{\cdot}BF_4^-$. After magnetically stirring the mixture at 30 °C in the dark for 2 days, the tube was opened, the greenish ionic materials were removed by reprecipitation in pentane, and the covalent compounds were separated by MPLC. From the early fraction eluted with hexane was isolated 5-5 (0.0032 g; 20%), which was identified by spectral comparison with the authentic compound described above.

**Effects of Added DMSO upon Reaction of 5 with 1.** (a) A $6.99 \times 10^{-4}$ M MeCN solution of $5{\cdot}BF_4^-$ (0.995 mL, $6.96 \times 10^{-4}$ mmol) was mixed with a $6.96 \times 10^{-4}$ M THF solution of $K^+{\cdot}1$ (0.995 mL, $6.93 \times 10^{-4}$ mmol) under argon and the solvents were immediately evaporated. The resulting dark green solid was dissolved in $CHCl_3$ (1 mL) under argon to give a red solution. After 15 s the solution was diluted with DMSO (10 mL), affording a dark green solution, the UV–vis spectrum of which indicated the presence of 1 (80%) and $1^\bullet$ (8%).

(b) Similarly, $5{\cdot}BF_4^-$ ($2.77 \times 10^{-4}$ mmol) and $K^+{\cdot}1$ ($2.75 \times 10^{-4}$ mmol) were mixed in MeCN–THF (1:1 v/v) in the vacuum cell depicted in Figure 8 and the solvents immediately evaporated. To the mixture was added THF (2.00 mL) by vacuum distillation, and the reaction was allowed to proceed at about 25 °C under vacuum in the dark for 15 min. At this time the UV–vis spectrum showed that only 25% of the anion 1 and 17% of the radical $1^\bullet$ were present. Then the tube was opened under argon and DMSO (8.0 mL) was added. The UV–vis spectrum indicated that the amount of 1 increased to 74%.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Special Project Research (No. 62124035) and a Grant-in-Aid for Scientific Research on Priority Areas (No. 01648002) from the Ministry of Education, Science and Culture, Japan.

---

[24] Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* 1982, *55*, 2470.