

Synthesis and Isolation of Stable Hypervalent Carbon Compound (10-C-5) Bearing a 1,8-Dimethoxyanthracene Ligand

Kin-ya Akiba,*† Makoto Yamashita,†
Yohsuke Yamamoto,† and Shigeru Nagase‡

Department of Chemistry, Graduate School of Science
Hiroshima University, 1-3-1 Kagamiyama
Higashi-Hiroshima 739-8526, Japan

Department of Chemistry, Graduate School of Science
Tokyo Metropolitan University, 1-1 Minami-osawa
Hachioji, Tokyo 192-0397, Japan

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The bimolecular nucleophilic substitution (S_N2) reaction at saturated carbon such as hydrolysis of methyl halides is one of the most important and the most popular reactions in organic chemistry.^{1,2} The mechanism of the reaction invoking inversion of configuration of the central carbon is one of the fundamental ideas of organic reactions and is described commonly in textbooks for undergraduate students.³ The structure of the transition state (TS) of S_N2 should be trigonal bipyramid (TBP) around the central carbon.⁴ Hence the bonding about the carbon involves, at least formally, expansion of the valence shell and is called hypervalent.⁵ Due to the fundamental importance of S_N2 , there have been a variety of efforts to stabilize the TS and even to prepare model compounds of TS; typical examples are by Hojo⁶ and Martin.^{7–10} They claimed that they observed symmetrical TBP structure for the model compounds in solution. However, the X-ray structure of dimethyl-1-fluorenylcarbenium hexachloroantimonate bearing two methylthio groups at the 9-position⁶ revealed that the two S–C⁺ distances were different and the compound should be regarded as a sulfonium structure,⁶ and X-ray analysis of the 9-anthracenylmethyl dication bearing phenylthio groups at 1 and 8 positions has not been reported.^{7–10} Theoretical calculations on S_N2 are also numerous and they conclude that hypervalent 10-C-5 species should be TBP and energy maximum.¹¹ On the other hand, recently reported exotic highly coordinate carbon species such as CH_5^+ ^{12,13} and CLi_6 ,¹⁴ CLi_6 ,¹⁵ and $(Ph_3PAu)_5C^+$ ¹⁶ are electron deficient carbocations and/or are stabilized by metal–metal cage interactions. Therefore, these compounds cannot be regarded as hypervalent 10-C-5 species for models of the S_N2 transition state. Here we report the synthesis and crystal structure

of 1,8-dimethoxy-9-dimethoxymethylanthracene monocation (**1**) as the first fully characterized hypervalent 10-C-5 compound.

Preparation of **1** is illustrated in Scheme 1. Commercially available 1,8-dihydroxyanthraquinone (**2**) was converted to **5** via methylation¹⁷ followed by reduction¹⁸ and trifluoromethane-sulfonation. Carbon monoxide insertion¹⁹ to **5** in methanol mediated by $Pd(PPh_3)_4$ gave **6** in 52% yield. **6** was treated with trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$) under CH_2Cl_2 reflux for 20 h, and after filtration of excess $Me_3O^+BF_4^-$ and removal of the solvent, **1** was obtained as a yellow-green solid. **1** is thermally stable but is sensitive to atmospheric moisture. ¹³C NMR chemical shift of the central carbon is found at δ 192.58 ppm, which is confirmed by independent preparation of **1** using carbon monoxide (¹³C 99%) in the process to convert **5** to **6**.

Crystals of **1** suitable for X-ray analysis were obtained by careful recrystallization from dry $CDCl_3$, and the X-ray structure is shown in Figure 1.²⁰ The counteranion is $B_2F_7^-$ unexpectedly but it is well separated from the cationic part. The structure clearly shows the symmetrical nature of the compound. The sum of the angles (C9–C19–O3, C9–C19–O4, and O3–C19–O4) around the central carbon is 360.0°, indicating that the carbon is planar with sp^2 hybridization. The angles around the oxygen atoms of the methoxy groups are 119.2(9)° (C1–O1–C15) and 120.3(9)° (C8–O2–C16), showing that both oxygen atoms have sp^2 hybridization. Since the carbon atoms of the methoxy groups at 1,8-positions are in the plane of the anthracene, one of the lone pairs of each oxygen atom should be directed toward the empty p-orbital of the central carbocation at the 9 position. Therefore, geometry around the central carbon atom is TBP, which is only slightly distorted. The two O–C distances are almost identical (2.43(1) and 2.45(1) Å), which is significantly longer than that of a covalent C–O bond (1.43 Å)²¹ but shorter than the sum of the van der Waals radius (3.25 Å).²¹

To elucidate the property and the degree of interaction between the central carbon atom and the two oxygen atoms in **1**, several compounds were synthesized and were structurally characterized for comparison.²² The side views of crystal structures of 1,8,9-tribromo- (**7**), 1,8-dimethoxy-9-trifluoromethanesulfonyloxy- (**5**), and 1,8-dimethoxy-9-cyanoanthracene (**8**) are shown in Figure 2 together with **1**. In the structure of tribromo derivative **7**, the three

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(20) Data were collected at 200 K on a MacScience DIP2030 imaging plate equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell parameters were determined by autoindexing several images in each data set separately with the program DENZO. For each data set, rotation images were collected in 6° increments with a total rotation of 180° about ϕ . Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares. Final $R = 0.105$ ($R_w = 0.163$) for 1356 observed reflections (290 parameters) with $I > 3\sigma(I)$. Crystal data for **1**: monoclinic system, space group $P2_1/c$ (no. 14), $a = 10.9810(2) \text{ \AA}$, $b = 14.7010(4) \text{ \AA}$, $c = 13.4300(3) \text{ \AA}$, $\beta = 107.81(2)^\circ$, $V = 2064.2(8) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.503 \text{ g cm}^{-3}$. Details of the X-ray structure determination are available; see Supporting Information. The programs DENZO and SCALEPACK are available from Mac Science Co. Z. Otwinowski, University of Texas, Southwestern Medical Center. The program teXsan is available from Rigaku Co.

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(22) Crystal data for **5**: triclinic system, space group $P\bar{1}$ (no. 2), $a = 8.5460(6) \text{ \AA}$, $b = 9.4300(8) \text{ \AA}$, $c = 11.1650(7) \text{ \AA}$, $\alpha = 73.016(4)^\circ$, $\beta = 82.571(5)^\circ$, $\gamma = 81.014(4)^\circ$, $V = 846.6(1) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.52 \text{ g cm}^{-3}$. $R = 0.0510$ ($I > 3\sigma(I)$), $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. Crystal data for **7**: monoclinic system, space group $P2_1/c$ (no. 14), $a = 10.1530(5) \text{ \AA}$, $b = 7.2480(2) \text{ \AA}$, $c = 17.3580(9) \text{ \AA}$, $\beta = 106.064(2)^\circ$, $V = 1227.48(9) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 2.25 \text{ g cm}^{-3}$. $R = 0.0397$ ($I > 3\sigma(I)$), $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. Crystal data for **8**: tetragonal system, space group $I4_1/a$ (no. 88), $a = b = 25.057(3) \text{ \AA}$, $c = 8.3710(5) \text{ \AA}$, $V = 5255.8(7) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calc}} = 1.33 \text{ g cm}^{-3}$. $R = 0.0645$ ($I > 3\sigma(I)$), $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$.

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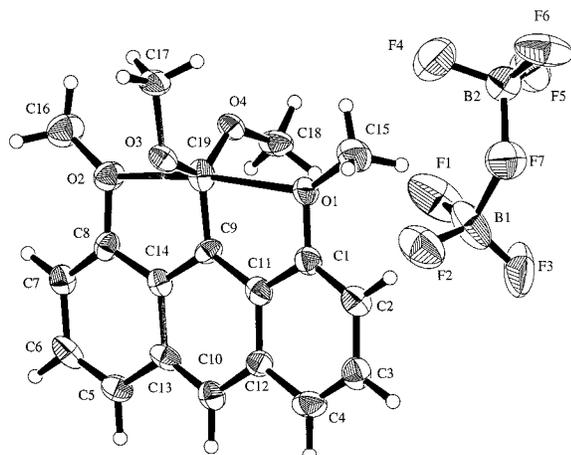
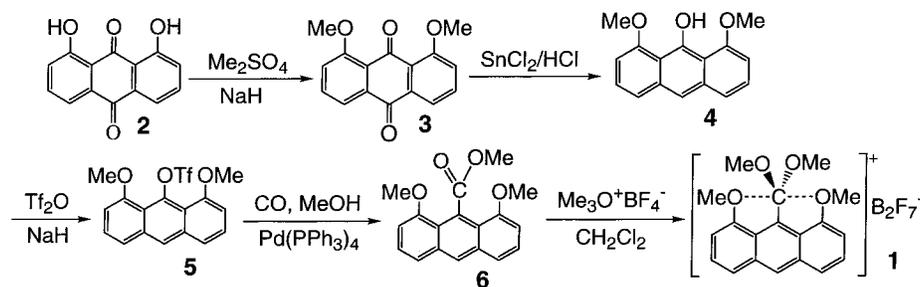
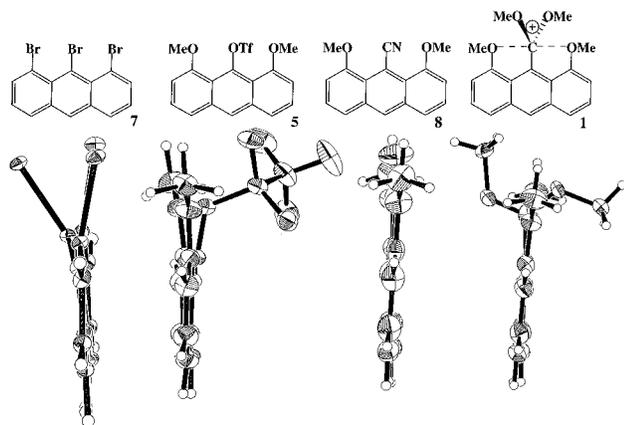
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Scheme 1

Figure 1. Crystal structure (30% thermal ellipsoids) of **1**.Figure 2. Crystal structures (30% thermal ellipsoids) of **5**, **7**, **8**, and **1**.

bromine atoms are placed out of plane of the anthracene skeleton to avoid large steric repulsion. Although the distortion from the plane of the skeleton is not at all significant, the three oxygen atoms in **5** are not placed in the plane because of repulsion. In the case of **8** and the cation **1**, the atoms attached to the 1,8,9-positions are almost in the plane of anthracene, indicating the interaction between the central carbon atom and the two oxygen atoms is not repulsive but attractive. The comparison of the distances between the atom at the 9-position of the anthracene and the atoms at the 1,8-positions (a and a') and the distances between the ipso carbons (b and b') is also worthy of note (Table 1). In the cases of **7** and **5** the averaged distances of a and a' (3.2698(6) Å in **7**, 2.572(2) Å in **5**) are longer than those of b and b' (2.566(6) Å in **7**, 2.550(3) Å in **5**), while in **8**, the averaged distance of a and a' (2.531(3) Å) is comparable with that of b and b' (2.540(5) Å). In contrast, in **1** the averaged distance of a and a' (2.44(1) Å) is clearly shorter than that of b and b' (2.51(2) Å). Therefore, it can be concluded that the interaction between the central carbon atom and the two oxygen atoms in **1** should be clearly attractive.

Table 1. Comparison of the Distances between the Atoms at the 1,8,9-Positions (a and a') with Those between the Ipso Carbons (b and b') of Anthracene Derivatives

compd	a	a'	b	b'
7 : X = Y = Br	3.2658(6)	3.2738(6)	2.564(6)	2.567(6)
5 : X = OTf, Y = OMe	2.572(2)	2.571(2)	2.554(3)	2.545(3)
8 : X = CN, Y = OMe	2.530(3)	2.531(3)	2.538(6)	2.542(4)
1 : X = C ⁺ (OMe) ₂ , Y = OMe	2.45(1)	2.43(1)	2.49(2)	2.52(2)

The geometry of **1** was fully optimized by hybrid nonlocal density functional theory (DFT) at the B3LYP/6-31G* level using the Gaussian 94 program.²³ The calculation indicates that the symmetrical C_s structure of **1** is the energy minimum. The two C—O distances are identical (2.480 Å), and are slightly longer than the experimental distances (2.44(1) Å). It should be noted that the bond paths are found between the central carbon atom and the two oxygen atoms, clearly showing that these atoms are bonded.²⁴ The bond is weak and ionic based on the small value of the electron density ($\rho(r)$) (0.022 e/ao³) and the small positive Laplacian value ($\nabla^2\rho(r)$) (0.078 e/ao⁵) at the bond critical points.²⁴ These values are consistent with those of axial C—H bonds in CH₅⁻ ($\rho(r)$: 0.067 e/ao³, $\nabla^2\rho(r)$: 0.009 e/ao⁵).²⁵ A large value (0.233) of the ellipticity of the O—C bond reflects the electron donation to the central carbocation from the two lone pairs of the oxygen atoms of the methoxy groups at 1,8-positions within the anthracene plane. In conclusion, the anthracene carbocation **1** is the first fully characterized pentacoordinate 10-C-5 compound for a model of the transition state of S_N2.

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Supporting Information Available: Preparation of **1** and tables of crystal data, structure solution and refinement, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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