Synthesis and Structure of a Carbon Compound Bearing a Sterically Rigid 1,8-Dioxythioxanthylium (or Thioxanthene) Skeleton

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In order to obtain a pentacoordinate hypervalent carbon compound with two strong apical bonds, a new compound bearing the novel skeleton **4** was synthesized by the two-electron oxidation of **9** followed by deprotonation. The X-ray diffraction data and the NMR spectra showed that the structure of **4** is not pentacoordinate, but tetracoordinate.

Recently, we reported the synthesis of a pentacoordinate hypervalent[1] carbon compound (10-C-5) bearing a rigid 1,8-dimethoxyanthracene ligand **1**[2] and flexible pincer-type ligand **2** (Chart 1).[3] The two apical C–O bond lengths of **1** (2.43(1), 2.45(1) Å) and **2** (e.g., $Ar^1 = p\text{-}MeC_6H_4$, $Ar^2 = p\text{-}ClC_6H_4$: 2.671(4), 2.682(4) Å) were shorter than the sum of the van der Waals radius of C–O (3.25 Å),[4] and the attractive interaction between the central carbon atom and the two apical oxygen atoms was determined by the AIM analysis[5] and accurate X-ray analysis.[6]

Because, the C–O distances of these compounds were much longer than that of a covalent bond (1.43 Å), it was considered that the C–O attractive interaction was not very strong. To synthesize a pentacoordinate hypervalent carbon, which has stronger C–O apical bonds, we synthesized a compound bearing a 1,8-dioxyanthracene ligand **3** (Chart 2).[2b,7] However, the X-ray structural analysis of **3** showed that the central carbon atom of **3** was tetracoordinate and the oxygen anion was coordinated with the counter cation, K^+([18]crown-6).

Since the interaction of $O^- \cdots K^+$([18]crown-6) may inhibit the coordination of the oxygen anion to the central carbon, we designed compound **4** which has the two resonance structures (**4A** and **4B**) as shown in Figure 1. Resonance structure **4B** has an oxygen anionic donor and thioxanthylium skeleton. Since the compound is neutral (or zwitterionic) and does not have a counter ion, we expected the existence of attractive interaction between the oxygen donor and the central carbon atom to afford pentacoordinate structure **4C**. We now report the synthesis and structure of **4**.

The synthesis of **4** is illustrated in Scheme 1. The reaction of 1,8-dimethoxythioxanthone (**5**)[8] with *i*-PrMgCl afforded the corresponding alcohol, which was treated with *p*-toluenesulfonic acid to afford olefin **6**. The two-electron oxidation[9] of **6** by 2 equiv of $(2,4\text{-}Br_2C_6H_3)_3N^{\bullet+}SbCl_6^-$ or 3 equiv of $SbCl_5$ afforded monocation **7**, that should be produced via dication intermediate **8** (unfortunately, dication **8** could not be observed). Since the reaction of **7** with BBr_3 did not proceed, the demethylation of **6** was carried out using excess amounts of BBr_3 to give **9**. The two-electron oxidation of **9** by $SbCl_5$ afforded thioxanthyl-

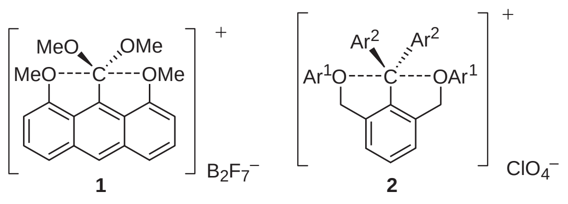


Chart 1.

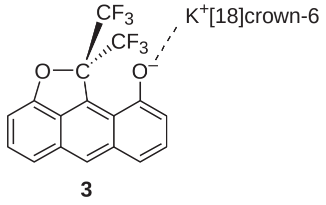


Chart 2.

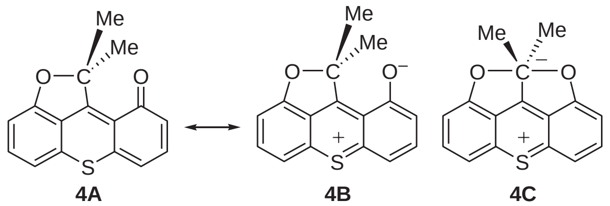
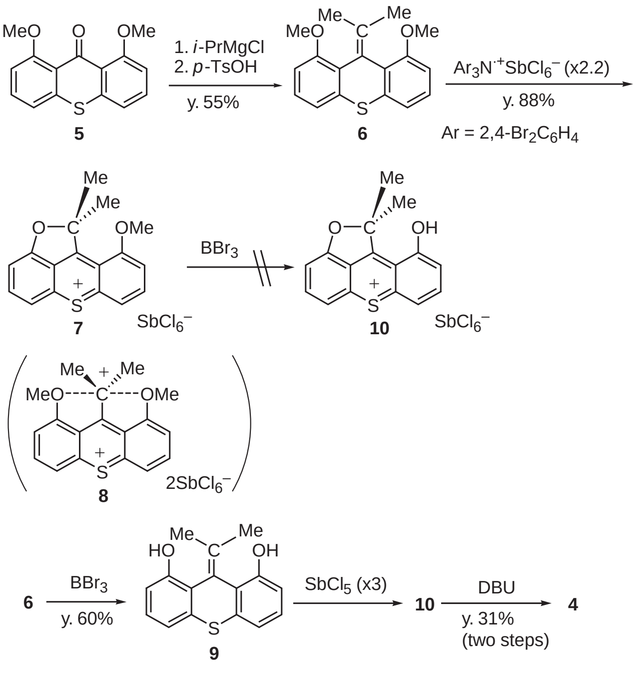


Figure 1.



Scheme 1.

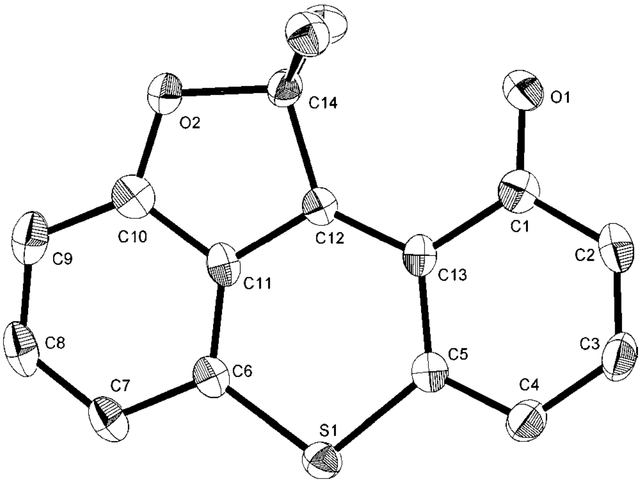


Figure 2. X-ray structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond length (Å): O1–C14 = 2.967(7), O2–C14 = 1.494(6), O1–C1 = 1.261(3), O2–C10 = 1.350(4), C1–C2 = 1.431(3), C1–C13 = 1.480(3), C2–C3 = 1.356(4), C3–C4 = 1.420(3), C4–C5 = 1.367(3), C5–C13 = 1.458(3), C6–C7 = 1.397(3), C6–C11 = 1.407(3), C7–C8 = 1.397(4), C8–C9 = 1.388(4), C9–C10 = 1.394(3), C10–C11 = 1.408(3), C5–S1 = 1.754(2), C6–S1 = 1.733(2).

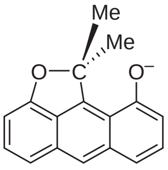


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Chart 3.

ium salt **10**.[10] The deprotonation of **10** using DBU afforded **4** as a dark green solid.[11]

Compound **4** was stable to atmospheric moisture and could be purified by silica-gel chromatography. Single crystals of **4** suitable for an X-ray analysis were obtained by recrystallization from CH_2Cl_2 and hexane as dark green plates, and the X-ray structure of **4**[12] is shown in Figure 2.

Since the shorter C–O bond length (C14–O2) is 1.494(6) Å and the longer C–O (C14–O1) distance is 2.967(7) Å, the central carbon atom should be regarded as tetracoordinate. The C–O distances are similar to those of **3** (1.470(5) and 2.991(5) Å, respectively).[2b,7] In addition, the AIM analysis of the calculated structure of **4**[13] did not show a bond path between C14 and O1 (the C–O distance is calculated to be 2.949 Å, which is consistent with the X-ray structure). Therefore, it was confirmed that the central carbon atom of **4** was tetracoordinate. Furthermore, the NMR spectra (^{1}H and ^{13}C) also showed the unsymmetrical structure of **4**, and the bond switching process could not be observed even at 110 °C (in toluene-d_8).

The bond lengths of O1–C1 (1.261(3) Å) and O2–C10 (1.350(4) Å) indicate that the effect of the resonance structure **4A** is significant. However, calculated Mulliken charge of **4** (O1 = −0.563, O2 = −0.537) indicates that some anionic charge is located at O1 and that the resonance structure **4B** plays some role (cf. the Mulliken charge of **11** (Chart 3) is −0.663 at O1, and −0.580 at O2, the calculation was carried out at the same level).

Therefore, the oxygen atom of O1 should have some donating ability, but the AIM analysis did not show the attractive interaction between C14 and O1 despite the shorter interatomic distance than the sum of the van der Waals radius. The results indicate that the synthesis of a pentacoordinate anionic hypervalent carbon with two strong apical bonds by the simply steric fixation is difficult.

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9 When 1 equiv. of the oxidant was used, the reaction afforded the mixture of **6** and **7**, which did not show the ESR signals. The results indicate this reaction proceeds by two-electron oxidation.
10 Also, **10** was obtained by treatment of **4** with excess amount of TfOH. In this reaction, dication (like **8**) was not observed in ^{1}H NMR analysis. Data for **10**•OTf− ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 6H), 7.31 (d, 1H, $^3J = 8$ Hz), 7.56 (d, 1H, $^3J = 8$ Hz), 7.73 (d, 1H, $^3J = 8$ Hz), 7.86 (d, 1H, $^3J = 8$ Hz), 8.08 (t, 1H, $^3J = 8$ Hz), 8.29 (t, 1H, $^3J = 8$ Hz).
11 Data for **4**: Mp 198–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 6H), 6.41 (d, 1H, $^3J = 9$ Hz), 6.55 (d, 1H, $^3J = 7$ Hz), 6.71 (d, 1H, $^3J = 8$ Hz), 6.91 (d, 1H, $^3J = 8$ Hz), 7.20 (dd, 1H, $^3J = 9$ Hz, $^3J = 7$ Hz), 7.51 (t, 1H, $^3J = 8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (CH_3), 99.5 (C), 106.2 (CH), 110.5 (CH), 114.4 (CH), 120.1 (C), 120.5 (C), 124.4 (CH), 135.9 (C), 137.5 (CH), 137.6 (CH), 138.3 (C), 164.7 (C), 168.7 (C), 183.0 (C). UV–vis (CH_2Cl_2) λ_{max} ($\log \varepsilon$): 272 (4.22), 337 (4.14), 448 (3.88), 615 (3.71).
12 Crystal data for **4**: $C_{16}H_{12}O_2S$, fw 268.32, orthorhombic, *Pbca* (No. 61), $a = 12.1950(3)$, $b = 13.6590(4)$, $c = 15.0020(3)$ Å, $V = 2498.91(11)$ Å^3, $Z = 8$, $D_{calcd} = 1.426$ g/cm^3, $R = 0.0586$ ($I > 2\sigma(I)$), $R_w = 0.1861$ (all data), GOF = 1.185 for 2972 reflections and 200 parameters. The data were collected at 173 K using a Mac Science DIP 2030 imaging plate equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). In the X-ray structure of **4**, O1, O2, and C14 are disordered and the proportion of the major structure is 81%. The structure of the remaining 19% is similar to the major one (O1′–C14′ = 2.96(3) Å, O2′–C14′ = 1.48(3) Å) (CCDC-663067).
13 The structure was optimized by the density functional theory (DFT) at the B3PW91/6-31G(d) level[14] using the Gaussian 98 program.[15] The AIM analysis was carried out at the same level.
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