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The stable radical cation of thiophene annelated with bicyclo[2.2.2]octene and its reaction with triplet oxygen to give a protonated cation of 2-butene-1,4-dione derivative

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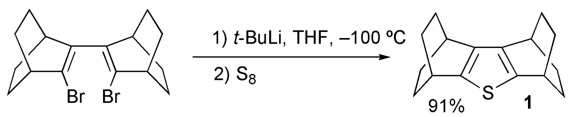
The first isolable salt of the thiophene radical cation was prepared from the derivative annelated with two bicyclo[2.2.2]octene units, and its reaction with triplet oxygen was found to give a novel cation of a proton-chelating 2-butene-1,4-dione derivative with remarkable stability.

The radical cation of thiophene derivatives is a key intermediate in the oxidative polymerization for the synthesis of polythiophenes that are receiving considerable attention as materials for electronic devices.[1] There has also been much recent interest in the radical cations of oligothiophenes, which are being studied as models for conducting polythiophenes to elucidate the mechanism of charge transport.[2] However, experimental studies on the radical cation of the thiophene monomer are quite limited due to the intrinsic instability of this radical cation. For example, the cyclic voltammetry of alkyl-substituted thiophene derivatives, such as tetramethylthiophene and perhydrodibenzo[*b*,*d*]thiophene, exhibits irreversible oxidation waves, indicating that the simple alkyl substitution is not sufficient for stabilizing the thiophene radical cation.[3] As the thiophene radical cations persistent in solution, 3-alkoxy-2,5-bis(alkylthio)thiophene radical cations have been prepared in 1,1,1,3,3,3-hexafluoropropan-2-ol,[4] but their half-lives were only a few hours or less.[5] On the other hand, we previously found that annelation with rigid bicyclic σ-frameworks, such as bicyclo[2.2.2]octene, is quite effective in stabilizing the radical cation of cyclic π-conjugated systems.[6] Here we report the synthesis and properties of a highly stabilized thiophene radical cation annelated with this bicyclic unit. In particular, we found a reaction of the thiophene radical cation with triplet oxygen that yielded a novel derivative of a proton-chelating 2-butene-1,4-dione cation.

The thiophene derivative **1**† was synthesized as colorless crystals by the reaction of the dilithiated dimer of bicyclooctene with sulfur in 91% yield as shown in Scheme 1. Cyclic voltammetry of **1** in CH_2Cl_2 at rt with 0.1 M Bu_4NClO_4 as a supporting electrolyte showed a well-defined reversible oxidation wave at $E_{1/2}$ = +0.79 V *vs* Fc/Fc^+, indicating that the radical cation of $\mathbf{1}^{\bullet+}$ is stable under these conditions. This is in sharp contrast to the irreversible oxidation waves observed for peralkylated thiophene derivatives.[3] The chemical one-electron oxidation of **1** with 1.5 equivalents of either $SbCl_5$ or SbF_5 in CH_2Cl_2 under argon at rt gave a yellow solution, which showed a five-line ESR signal (hyperfine coupling constant a_H = 0.346 mT, g = 2.00215) as shown in Fig. 1a. The results of theoretical calculations (B3LYP/6-31G*) on $\mathbf{1}^{\bullet+}$ (Fig. 1b) indicated that the spin is mostly localized on the 2,5-positions (C_α) and this spin is conveyed to the corresponding four equivalent *anti*-protons ($H_{anti\text{-}\alpha}$) of the ethano bridge through the bonding with a W-like arrangement. Thus the calculated a_H value for these four hydrogens was 0.323 mT, in good agreement with the observed value. On the other hand, the positive Mulliken charge was found to be mainly localized on the sulfur atom (+0.38). These results correspond well to the resonance structures shown in Fig. 1c. In fact, the comparison of the geometries of $\mathbf{1}^{\bullet+}$ and **1** optimized at the B3LYP/6-31G* level showed an elongation of the bond length of C_α–C_β (1.426 Å (neutral: 1.372 Å)) and a shortening of C_β–$C_{\beta'}$ (1.385 Å (neutral: 1.428 Å)) in $\mathbf{1}^{\bullet+}$.



Scheme 1

The electronic absorption spectrum of $\mathbf{1}^{\bullet+}$ in CH_2Cl_2 showed two maximum absorptions at 350 and 271 nm, which were assigned to the HOMO→SOMO and SOMO→LUMO transitions, respectively.

Into the solution of $\mathbf{1}^{\bullet+}SbCl_6^-$ in CH_2Cl_2, hexane was slowly diffused under argon so that yellow crystals were obtained in 84% yield after 8 days. A CH_2Cl_2 solution of this crystal displayed an ESR signal identical to that shown in Fig. 1a. The X-ray crystallography conducted on this crystal indicated that it included the thiophene moiety and hexachloroantimonate ion in a 1 : 1 molar ratio,‡ which was also supported by the result of elemental analysis (calcd for $C_{16}H_{20}Cl_6SSb$: C, 33.20; H, 3.48; found: C, 32.62; H, 3.54%). However, an unambiguous structure of the thiophene radical cation could not be obtained due to the disorder in the thiophene moiety. An attempt using SbF_6^- as a counter anion did not give a better result.

It is known that radical cations of olefins react with triplet oxygen to give products similar to those produced by the reaction of olefins with singlet oxygen.[7] Although a reaction of 2,5-dimethylthiophene with singlet oxygen to yield *cis*-3-hexene-2,5-dione and 5-sulfinyl-3-hexen-2-one has been reported,[8] to the best of our knowledge there has been no unambiguous example of the reaction of the thiophene radical cation with triplet oxygen. We therefore conducted a reaction of the persistent radical cation $\mathbf{1}^{\bullet+}$ with triplet oxygen (Scheme 2). The ESR measurements showed that the radical cation $\mathbf{1}^{\bullet+}$ generated by $SbCl_5$ or SbF_5 was consumed by reaction with oxygen in CH_2Cl_2 within 30 min. Into the solution, hexane was slowly diffused over 5 days to give pale yellow single crystals.

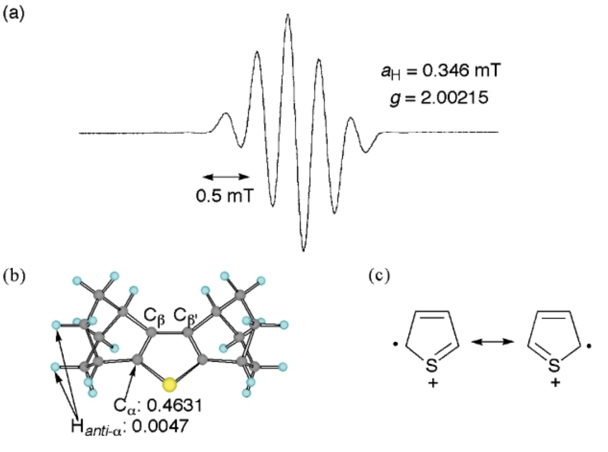


Fig. 1 (a) ESR spectrum of $\mathbf{1}^{\bullet+}$ in CH_2Cl_2 at rt. (b) The calculated structure and spin density of $\mathbf{1}^{\bullet+}$ at the B3LYP/6-31G* level. (c) Resonance structures of thiophene radical cation.

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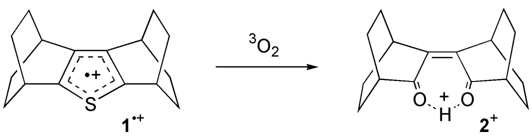
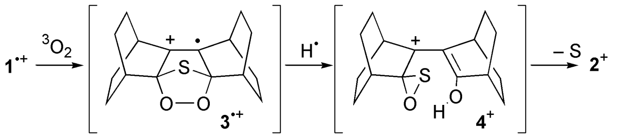


Scheme 2



Scheme 3

The X-ray crystallography revealed that this product was the novel cation salt **2**$^+$SbCl$_6^-$ or **2**$^+$SbF$_6^-$§ formed in 54% or 55% yield, respectively; these salts were remarkably stable so that no decomposition was observed upon standing under air for several days. The 2-butene-1,4-dione structure of **2**$^+$SbF$_6^-$ is clearly demonstrated by the bond lengths of O1–C1 (1.243(3) Å), C1–C2 (1.489(4) Å) and C2–C3 (1.355(4) Å), as shown in Fig. 2.

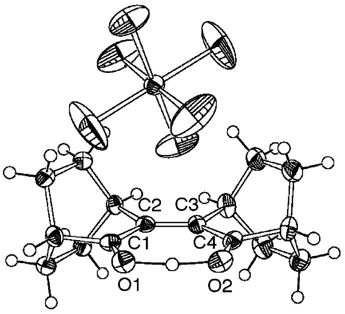


Fig. 2 ORTEP view of **2**$^+$SbF$_6^-$(50% probability). Selected bond length (Å): O1–C1 1.243(3), C1–C2 1.489(4), C2–C3 1.355(4), C3–C4 1.480(4), C4–O2 1.252(3).

The chemical shift values of ^{1}H and ^{13}C NMR signals of **2**$^+$ are shown in Table 1, and are in fairly good agreement with the calculated values for **2**$^+$ (GIAO/HF/6-31+G**//B3LYP/6-31G*). In particular, the ^{1}H NMR signal of the chelated proton was observed at such an extremely downfield shift as 21.15 ppm, indicating that the proton not only carries a full positive charge but is subjected to the strong deshielding effect of the two carbonyl groups. It should also be noted that the signals of the olefinic carbons are considerably shifted downfield, suggesting the delocalization of a considerable amount of positive charge to these carbons.¶

Table 1 ^{1}H and ^{13}C NMR chemical shifts for **2**$^+$

	δ_H			δ_C			
	CH	CH$_2$	H$^+$	C=O	C=C	CH	CH$_2$
Obs.^{a}	3.49 3.18	2.17^b 2.00 1.80	21.15	217.4	152.4	42.3 34.0	23.5 22.3
Calc. ^{c}	3.04 2.90	2.09^b 1.68 1.51	23.64	223.9	150.6	39.0 30.4	22.1 19.5

^{a} In CD$_2$Cl$_2$. ^{b} Two peaks are overlapped. ^{c} GIAO/HF/6-31+G**//B3LYP/6-31G*.

This reaction is most probably initiated by the addition of a triplet oxygen to the spin-localized α-carbons of the thiophene radical cation **1**$^{•+}$ to give the thioozonide radical cation **3**$^{•+}$. The O–O bond of **3**$^{•+}$ is then cleaved to give the cation of oxathiirane derivative **4**$^+$, from which the cation **2**$^+$ is formed with elimination of the sulfur atom (Scheme 3).[9]

The present result that the thiophene radical cation reacted readily with oxygen is in agreement with the previous finding that the oxidative polymerization of 3-alkylthiophenes gave the polythiophenes contaminated with oxygen incorporated as carbonyl groups when no attempts were made to eliminate air.[10]

In conclusion, we have succeeded in remarkable stabilization of the thiophene radical cation by annelation with rigid bicyclic frameworks to allow isolation of its salt. This radical cation was found to be sensitive to oxygen, which adds to the highly spin-localized α-carbons, and gave a novel cation of a proton-chelating 2-butene-1,4-dione derivative with noticeable stability.

Notes and references

† *Selected analytical data*: **1**: NMR (CDCl$_3$), δ_H 3.23 (m, 2H), 3.19 (m, 2H), 1.73 (m, 8H), 1.39 (m, 4H), 1.30 (m, 4H); δ_C 140.0, 134.3, 31.2, 29.5, 27.7, 27.1; mp 148.2–148.5 °C; HRMS *m/z* 244.1296 (M$^+$) (Calcd for C$_{16}$H$_{20}$S: 214.1286); Anal. Calcd for C$_{16}$H$_{20}$S: C, 78.63; H, 8.25. Found: C, 78.35; H, 8.29%.

‡ *Crystallographic data*: **1**$^+$SbCl$_6^-$: C$_{16}$H$_{20}$Cl$_6$SSb, FW = 578.83, monoclinic; space group *P*2(1)/*c*; a = 7.8754(8) Å, b = 25.639(3) Å, c = 10.9809(12) Å, β = 100.423(3)°, U = 2180.7(4) Å^3, Z = 4, D_c = 1.763 Mg m^{-3}.

§ *Crystallographic data*: **2**$^+$SbF$_6^-$: C$_{16}$H$_{21}$F$_6$O$_2$Sb, FW = 481.08, Orthorhombic; space group *P*2(1)2(1)2(1); a = 7.2353(5) Å, b = 14.7165(11) Å, c = 16.5155(13) Å, U = 1758.5(2) Å^3, Z = 4, D_c = 1.817 Mg m^{-3}. Intensity data were collected at 123 K on a Bruker SMART APEX diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 10209 reflections were measured and 3104 (R_{int} = 0.0277) were independent. The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares on F^2 (SHELXL-97). The chelated proton was restrained so that the two O–H distances become equal using the SADI instruction. All other hydrogen atoms were placed using AFIX instructions. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically and the refinement converged to R_1 = 0.0211, wR_2 = 0.0508 (I > 2 σ (I)), and GOF = 1.047. CCDC 180852. See http://www.rsc.org/suppdata/cc/b2/b201958b/ for crystallographic data in .cif or other format.

¶ The Mulliken charges (B3LYP/6-31G*) on the chelated proton, the carbonyl carbon, the olefinic carbon, and the carbonyl oxygen are +0.50, +0.44, +0.08 and −0.51, respectively.

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