

Evolution of the pseudo-1,3-dipolar cycloaddition chemistry of SNSMF₆ (M = As, Sb) leading to 2,5-dihydroxybenzo-1,3,2-dithiazolylium and 2,7-dicarbonylnaphtha-1,3,2-dithiazolylium salts and their corresponding radicals†

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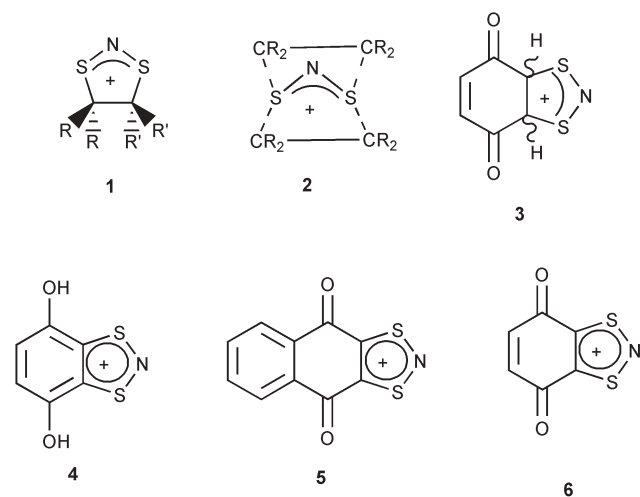
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We report the unprecedented formation of a benzo-fused 1,3,2-dithiazolylium [AsF₆⁻] salt by a one step, quantitative, cycloaddition of SNSAsF₆ with 1,4-benzoquinone. In contrast, the reaction of SNSbF₆ with 1,4-naphthaquinone results in 2,7-dicarbonylnaphtha-1,3,2-dithiazolylium [SbF₆⁻]. Both were reduced to the corresponding 7π radicals.

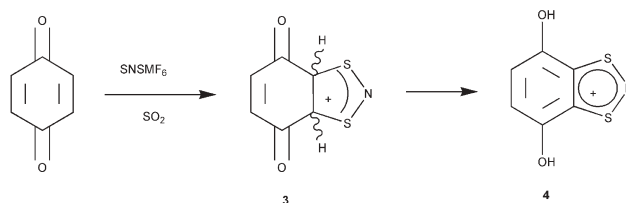
Our pursuit of cyclic thiazyl-based π-radicals has been facilitated by the general, and versatile symmetry-allowed cycloaddition of SNSMF₆ (M = As, Sb) with numerous unsaturated bonds.¹ This pseudo-1,3-dipolar cycloaddition provides a powerful synthetic tool for accessing a variety of mono- and bi-functional 6π heterocyclic 1,3,2-dithiazolylium cations from acetylene derivatives that can be readily reduced to 7π 1,3,2-dithiazoyl radicals.² In the case of olefins, two products are obtained.^{2e,3} The 1,3,2-dithiazolidine-like cations **1** are formed quantitatively in the presence of excess SNS⁺ at elevated temperatures, whereas the norbornene-like, 1,4-dithia-7-azabicyclo[2.2.1]heptane **2** derivatives are produced with an excess of olefin at room temperature.



Reaction of SNS⁺ with benzene results in electrophilic substitution (*cf.* NO₂⁺).⁴ However, in an analogous manner to olefins, the reaction with the 2,3-ethylenic bond of 1,4-benzoquinone

(IP = 10.11 eV)⁵ yields the cycloadduct **3**. Subsequent aromatization to the thermodynamically more stable aromatic derivative proceeded as anticipated by analogy with nitrile ylides⁶ and diazomethane derivatives⁷ according to Scheme 1. This is a novel and general route to benzo-fused 1,3,2-dithiazolylium derivatives using readily available starting materials. These, in turn, can be manipulated to prepare radicals with desirable physical and magnetic properties. It also permits the presence of the reactive OH substituent, not previously accessible by alternative routes, to be incorporated into these compounds. The available methods for preparing ring-annellated 1,3,2-dithiazolys are limited⁸ in that they are generally restricted by the accessibility of the appropriate *ortho* dithiols.⁹

When two solutions (SO₂, 6.03 g) of sublimed 1,4-benzoquinone (0.23 g, 2.06 mmol) and SNSAsF₆ (0.64 g, 2.4 mmol) were mixed at ambient temperature they produced a dark green solution. The coupled ¹³C NMR spectrum (100.58 MHz; SO₂; -40 °C) displayed resonances centered at δ 140.7 (*J*_{CH} 176 Hz) and δ 74.6 (*J*_{CH} 156 Hz) assigned to ethylenic and bridge-head carbons of **3**, in Scheme 1, respectively. Furthermore, a singlet down-field at δ 186, typical of a carbonyl carbon, was also detected. After 6 h, new resonances emerged in the coupled ¹³C NMR (-40 °C) spectrum at δ 119.5 (*J*_{CH} 167 Hz) which we assigned to the aromatic C-H in **4**, and two singlets at δ 154.8 and δ 146.5 attributed to the C-S and C-O of **4** in Scheme 1. All of these assignments were made with the assistance of calculated isotropic ¹³C NMR tensors.‡§ The ¹³C NMR spectrum indicates a quantitative aromatization to the product **4** after 24 h, which was isolated in 96% recovered yield. Unequivocal evidence was also provided by the *in situ* ¹⁴N NMR (28.901 MHz; SO₂; -40 °C) which showed a broad resonance at δ 122.6 (*v*_{1/2} 1042 Hz) after 6 h, indicative of **3**,¹⁰ and after 24 h only one signal was observed δ -7.4 (*v*_{1/2} 540 Hz) assigned to **4**.^{10†} In the gas phase, **4** was calculated to be thermodynamically favoured over **3** by 171 kJ mol⁻¹.†



Scheme 1

† Electronic Supplementary Information (ESI) available: Elemental analysis and structure calculations. See <http://www.rsc.org/suppdata/cc/b4/b418137a/>

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Dark blue single crystals were grown by slow evaporation of the solvent over a temperature gradient of 5 °C (5–0 °C) and shown by X-ray crystallography[¶] to consist of discrete planar cations of **4** hydrogen bonded to a distorted octahedral AsF_6^- (Fig. 1). The C–O bond lengths are indicative of a C–O single bond, further supporting the formation of the hydroquinone ring system. The shortest hydrogen bond (~ 2.1 Å) is between the hydroxyl proton and the anion, which causes a lengthening of the As–F bond to which it makes closest contact. This suggests that strong hydrogen bonding is responsible for the stability of the potentially reactive substituent group. Notably there are no $\text{N}^{\sigma^-}-\text{H}^{\sigma^+}$ contacts. The introduction of the hydroxyl group on the aromatic ring does not have any significant impact on the intramolecular character of the benzo and dithiazolyl ring in comparison to the simple benzo-1,3,2-dithiazolylum $[\text{SO}_2\text{Cl}]^+$.^{11†}

The *in situ* reduction of **4** with NBu_4Cl and SbPh_3 in liquid SO_2 immediately changed the solution's colour from blue to turquoise and caused it to exhibit a strong and persistent EPR signal at 25 °C ($g = 2.0046$, 1 : 1 : 1 triplet due to the nitrogen hyperfine splitting, $a_N = 1.073$ mT).[†] We tentatively assign this to the corresponding 7π 1,3,2-dithiazolyl radical. Hyperfine coupling to the two apparently equivalent aromatic protons was not observed and emphasis on obtaining these splittings will be the focus of further studies.

The ionisation potential of 1,4-naphthaquinone (9.5 eV)⁵ is lower than that of 1,4-benzoquinone (10.11 eV)⁵ and therefore the cycloaddition reaction of SNSbF_6 (1.61 g, 5.1 mmol) with sublimed 1,4-naphthaquinone (1.49 g, 9.4 mmol) in liquid SO_2 (5.7 g) proceeded faster.^{1e} On stirring at ambient temperature for 15 min the solution turned brown. After stirring for 48 h the solvent was slowly evaporated, giving a bright yellow crystalline material that was mechanically separated from a brown solid.

X-ray crystallography[¶] showed the yellow crystals to be 2,7-dicarbonyl naphtho-1,3,2-dithiazolylum **5** as its SbF_6^- salt. The intramolecular bond distances and angles for **5** SbF_6^- were as expected (Fig. 2). There is weak hydrogen bonding between SbF_6^- and the aromatic protons, but in contrast to **4**, there are cation–anion $\text{S}^{\sigma^+}-\text{F}^{\sigma^-}$ contacts. Separation of **5** SbF_6^- from the

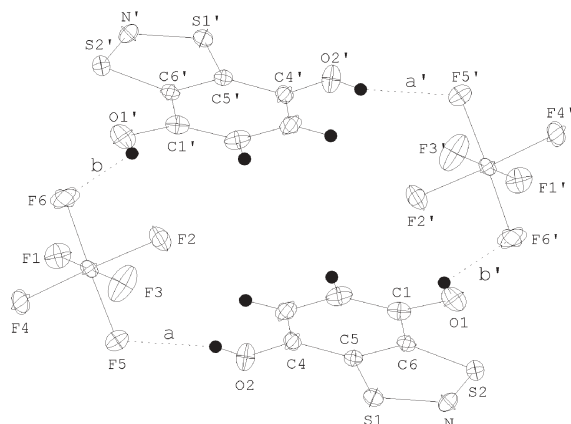


Fig. 1 Hydrogen bonding between the cation **4** and the $[\text{AsF}_6^-]$. Selected bond lengths (Å): $a = 2.12(4)$, $b = 2.35(4)$, As–F1 = 1.701(2), As–F2 = 1.719(2), As–F3 = 1.712(2), As–F4 = 1.693(2), As–F5 = 1.731(2), As–F6 = 1.708(2), S1–N = 1.597(2), S2–N = 1.600(3), S1–C5 = 1.707(2), S2–C6 = 1.702(2), C1–O1 = 1.355(3), C4–O2 = 1.360(3).

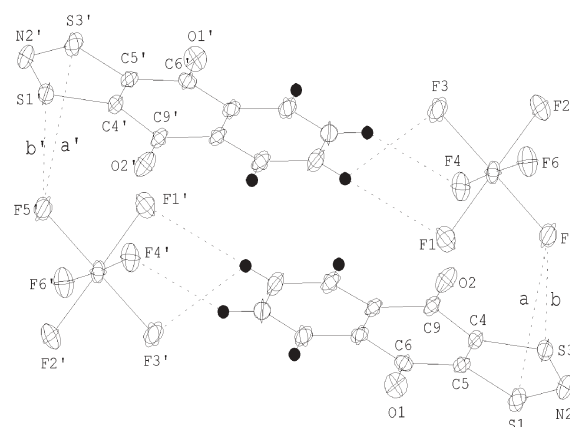


Fig. 2 Contacts between the cation **5** and the $[\text{SbF}_6^-]$. Selected bond lengths (Å): $a = 3.414(4)$, $b = 3.269(5)$, Sb–F1 = 1.876(3), Sb–F2 = 1.870(3), Sb–F3 = 1.857(3), Sb–F4 = 1.867(3), Sb–F5 = 1.874(3), Sb–F6 = 1.875(3), S1–N2 = 1.595(4), S2–N2 = 1.157(4), S1–C5 = 1.692(4), S3–C4 = 1.697(4), C6–O1 = 1.209(6), C9–O2 = 1.211(9).

complex brown reaction mixture with a $\text{SO}_2/\text{CH}_2\text{Cl}_2$ combination (1 : 10) allowed its isolation (0.385 g, 17%). The IR (**4** and **5**) and Raman (**5**) spectra were also obtained and are consistent with the proposed products.^{¶†} Low yields have also been reported in analogous reactions of 1,4-naphthaquinone with nitrile ylides, which also gave complex reaction mixtures.^{6,7}

The reduction of **5** (0.06 g, 0.13 mmol) by the *in situ* reaction with one equivalent NBu_4Cl (0.04 g, 0.144 mmol) and a large excess of $\text{Na}_2\text{S}_2\text{O}_4$ in SO_2 led to the corresponding 7π 1,3,2-dithiazolyl radical (Fig. 3).¹²

The quinoidal form of **5** is readily reducible in solution to the corresponding 7π radical and the lack of possible exchange by the thermodynamically stable, but kinetically labile proton of the hydroxyl substituent is circumvented.

Interestingly, the quinodal form of **6** is not observed with a two-fold excess of 1,4-benzoquinone with respect to SNSMF_6 ($M = \text{As}, \text{Sb}$) according to Scheme 1. Instead, an inclusion lattice containing 1,4-benzoquinone is obtained, as shown by X-ray crystallography.¹³ The formation of zwitterionic compounds upon removal of the labile protons of **4** and related species, may also lead to new interesting compounds.¹⁴

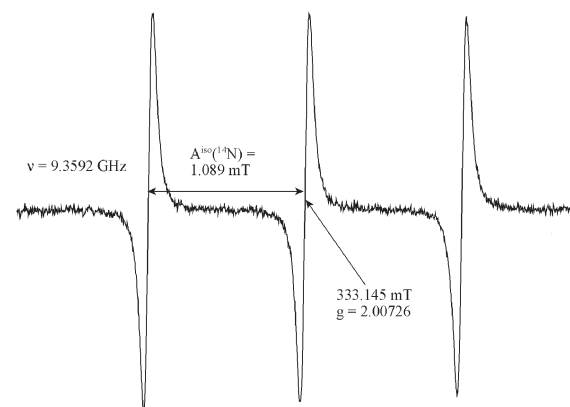


Fig. 3 EPR spectra of **5•** in dilute solution (SO_2) at room temperature ($g = 2.0073$, 1 : 1 : 1 triplet $a_N = 1.089$ mT).

The three potential states of the quinoidal template (quinoidal–semiquinone–dianion) and the two oxidation states of the dithiazolyl core provide the basis for the preparation of a new class of radicals with unique electronic and magnetic properties.

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Notes and references

‡ Calculated and observed NMR ^{13}C chemical shifts for **3** and **4** are within ± 5 ppm.†

§ All calculations were carried out at the B3LYP/6-311++G** level of theory.

¶ *Crystal data*: X-ray data were collected at 198 K on a Bruker AXS P4/SMART 1000 diffractometer with a graphite monochromator ($\lambda = 0.71073$ Å) using ω and ϕ scans. The structures were solved by direct methods and refined by full matrix least-squares analysis on F^2 . Compound **[4][AsF₆]**: $\text{C}_6\text{H}_4\text{NO}_2\text{S}_2\text{AsF}_6$, $M = 375.14$, monoclinic, $P2_1/c$, with $a = 6.3985(3)$, $b = 20.4261(9)$, $c = 8.8399(4)$ Å, $\beta = 109.599(1)^\circ$, $V = 1088.41(9)$ Å³, $Z = 4$, $D_c = 2.124$ g cm⁻³, $\mu = 3.582$ mm⁻¹. 179 parameters were refined using 2409 independent reflections to give $R1 = 0.0265$ and $wR2 = 0.0735$. Hydrogen atoms were found and refined isotropically. Compound **[5][SbF₆]**: $\text{C}_{10}\text{H}_4\text{NO}_2\text{S}_2\text{SbF}_6$, $M = 470.01$, monoclinic, $P2_1/n$, with $a = 7.3986(3)$, $b = 17.885(5)$, $c = 10.435(3)$ Å, $\beta = 90.144(4)^\circ$, $V = 1380.8(6)$ Å³, $Z = 4$, $D_c = 2.261$ g cm⁻³, $\mu = 2.374$ mm⁻¹. 199 parameters were refined using 2299 independent reflections to give $R1 = 0.0390$ and $wR2 = 0.103$. Hydrogen atoms were included in calculated positions and refined using a riding model. CCDC 257723 and 257724. See <http://www.rsc.org/suppdata/cc/b4/b418137a/> for crystallographic data files in .CIF format.

|| **4**: $\nu_{\text{max}}/\text{cm}^{-1}$ (Nujol mull on CsI plates) 3481vs, 1586s, 1285s, 1236m, 1136w, 963w, 891m, 835m, 773m, 697s (AsF₆⁻), 602w, 564w, 451w, 393s (AsF₆⁻); A satisfactory chemical analysis for **4** was obtained.† **5**: $\nu_{\text{max}}/\text{cm}^{-1}$ (Nujol mull on CsI plates) 1685s, 1584s, 1329m, 1265s, 1169m, 1102m, 1031vw, 986vw, 961vw, 915vw, 850m, 832w, 798m, 763m, 656s (SbF₆⁻), 574m, 473w, 426w, 407w, 381vw, 363w, 289s (SbF₆⁻). Raman of **5** (res. 2 cm⁻¹, 1000 scans) 3087w, 1678s, 1584m, 1481w, 1330vw, 1315vw, 1171w, 1102s, 1032s, 916w, 763w, 644w, 573w, 473w, 281w.†

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