Synthesis, Structure, and Electron-Donating Ability of 2,2′:6′,2″-Dioxatriphenylamine and Its Sulfur Analogue

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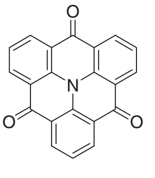
2,2′:6′,2″-Dioxa- and dithia-triphenylamines **4a** and **4b** were prepared. Both compounds had a C_2-like structure. The sulfur compound **4b** had a more twisted structure than **4a**; the dihedral angle between two edge phenyl rings was 43° for **4a**, and 62° for **4b**. The oxygen compound **4a** had a reversible oxidation wave at +0.81 V vs SCE, whereas **4b** had an irreversible peak at +1.14 V.

Some *p*-substituted triphenylamine radical cations are stable species in a propeller-like structure in solid state.[1] However, the unsubstituted triphenylamine shows an irreversible oxidation peak at +0.98 V vs SCE in its cyclic voltammogram,[2] indicating that the radical cation has much poorer stability. Flattening the structure into a planar form would increase the stability and lower the oxidation potential of triphenylamine. Hellwinkel and Melan prepared interesting compounds, **1** and **2**;[3a,b] the latter underwent smooth oxidation to give well-resolvable EPR spectrum of the radical cation.[3c] They also described tri(heteroatom)-bridged triphenylamines **3a**, **3b** as interesting unknown species of this class.[3a] Although these compounds have also been referred to in a patent,[4] the synthetic routes have not so far been reported. The related trioxatriphenylphosphine was recently prepared and shown to be a bowl-type structure exhibiting a pyroelectric property by Krebs and co-workers.[5]



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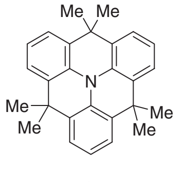

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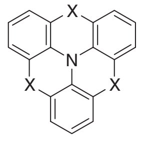
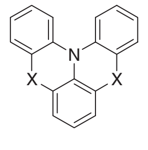
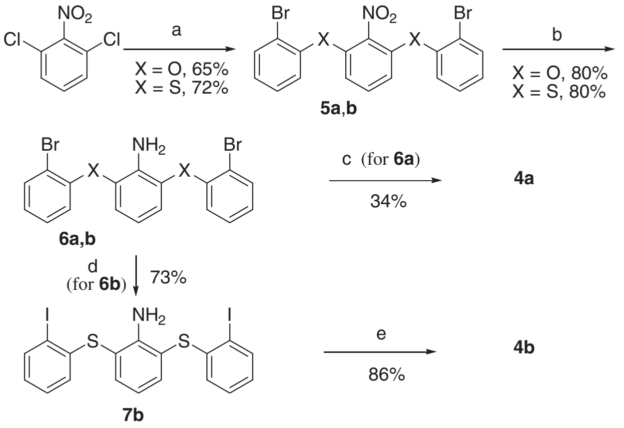


3, a: X = O, b: X = S



4, a: X = O, b: X = S

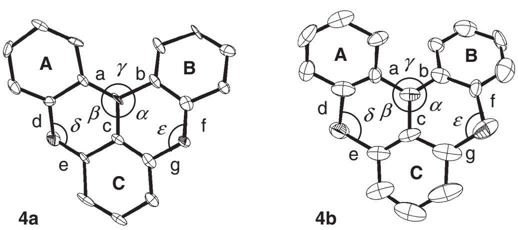
In the course of our study to develop new electronic and magnetic materials,[6] we have been interested in planar triphenylamine radical cations $\mathbf{3}^{\bullet+}$ as spin-building blocks of magnetic materials. In order to develop a general synthetic path for these compounds and also to obtain insight into their electron-donating ability, we have investigated the lesser bridged triphenylamines, 2,2′:6′,2″-dioxatriphenylamine **4a** and its sulfur analogue **4b**. In this paper, we report the synthesis, structure, and oxidation potential of **4a**, **4b**.



Scheme 1. (a) *o*-Bromophenol or *o*-bromothiophenol, NaH/DMSO, heat. (b) $H_2NNH_2 \cdot H_2O$, Pd/C, *p*-bromophenol/EtOH, reflux. (c) NaO*t*-Bu, Pd(dba)$_2$, P(*t*-Bu)$_3$/toluene, reflux. (d) KI–Cu/HMPA, 160 °C. (e) K_2CO_3–Cu/*o*-dichlorobenzene, reflux.

For the synthesis of heteroatom-bridged triarylamines, we considered a stepwise route using a linear intermediate **6** as a key intermediate (Scheme 1). Aromatic nucleophilic substitution reaction of 2,6-dichloronitrobenzene with *o*-bromophenol (5 equiv.) or *o*-bromothiophenol (2 equiv.) using dimsyl anion as a base gave **5a** (65%, 130 °C for 1 day) or **5b** (72%, 90 °C for 2 h). The reduction of **5a**, **5b** was carried out by heating with hydrazine monohydrate (30 equiv.) in ethanol in the presence of *p*-bromophenol (10 equiv.) and a Pd/C catalyst for 2 h, giving **6a**, **6b** in good yields. The presence of *p*-bromophenol was essential to avoid a competing reduction of aromatic bromide. Intramolecular cyclization of **6a** was achieved using Pd(0)-mediated cross-coupling reaction conditions [NaO*t*-Bu–Pd(dba)$_2$–P(*t*-Bu)$_3$ in toluene, reflux 2 h],[7] affording the desired **4a**[8] in 34% yield. Application of similar conditions to **6b** produced **4b** in less than 3% yield. Then, halogen exchange (Br to I) was examined (KI–CuI in HMPA, 160 °C for 16 h), giving crude iodide **7b** (73% yield). The cross-coupling reaction of **7b** under the above conditions or the Ullmann reaction conditions (K_2CO_3–Cu in *o*-dichlorobenzene, reflux 5 h) gave **4b**[8] in good yields.

The structures of these compounds were determined by X-ray structure analysis.[9] Figure 1 shows the ORTEP drawings of these compounds (left for **4a**, right for **4b**). Both compounds were in a pseudo-C_2-like structure. Two similar but independent structures were found in a unit cell for **4b**. One of them is shown in the figure. The selected bond lengths and angles around the heteroatoms are shown in the caption of Figure 1. The C–O, C–S, and C–N bond lengths were in the region of 1.36–1.42 Å for C–O, 1.69–1.82 Å for C–S, 1.33–1.47 Å for C–N bonds. Because of the longer C–S bond compared to the C–O bond, the dihedral angle between two edge phenyl rings was larger in the



4a **4b**

Figure 1. Molecular structures of **4a** and **4b** drawn at 50% ellipsoid level; hydrogen atoms are eliminated for clarity. Selected bond lengths (Å), angles (°), and dihedral angles (°) between phenyl planes, **A**, **B**, and **C**. For **4a** measured at 123 K: a: 1.333(6), b: 1.472(6), c: 1.406(4), d: 1.401(6), e: 1.373(6), f: 1.364(6), g: 1.420(6), $\alpha = 114.6(5)$, $\beta = 118.1(5)$, $\gamma = 127.1(2)$, $\delta = 117.3(4)$, $\varepsilon = 113.5(4)$, $\mathbf{A/B} = 43.0$, $\mathbf{A/C} = 25.5$, $\mathbf{B/C} = 24.7$. For two independent molecules of **4b** measured at 298 K: a: 1.459(10), 1.459(9), b: 1.363(10), 1.382(10), c: 1.452(8), 1.382(9), d: 1.793(8), 1.736(7), e: 1.737(8), 1.818(10), f: 1.762(9), 1.774(9), g: 1.685(11), 1.796(10), $\alpha = 120.3(7)$, 123.0(7), $\beta = 118.4(7)$, 116.8(6), $\gamma = 121.3(6)$, 119.9(6), $\delta = 99.1(4)$, 98.8(4), $\varepsilon = 98.1(4)$, 101.6(4), $\mathbf{A/B} = 62.3$, 62.4, $\mathbf{A/C} = 32.4$, 32.1, $\mathbf{B/C} = 36.0$, 36.9.

sulfur derivative **4b**; A/B = 43° for **4a**, and 62° for **4b**. As a result, the sulfur derivative **4b** is more twisted than the oxygen derivative **4a**. This is also supported by the small $C(sp^2)$–S–$C(sp^2)$ bond angles (98–102°) for **4b** compared to a general nonstrained diphenylsulfide structure (ca. 105°).[10]

The electron-donating ability was estimated using cyclic voltammetry.[11] The oxygen derivative **4a** showed a reversible oxidation peak at $E_{1/2} = +0.81$ V vs SCE in DMF. On the other hand, the sulfur derivative **4b** showed an irreversible peak at $E_p = +1.14$ V with a shoulder (+1.04 V), indicating instability of the radical cation. The oxidation potential of **4a** was lower than that of triphenylamine ($E_p = +1.07$ V under the identical conditions) but higher than that of 10-phenylphenoxazine **8** ($E_{1/2} = +0.75$ V). The peak potential of **4b** was higher than that of triphenylamine and 10-phenylphenothiazine **9** ($E_{1/2} = +0.77$ V). These results strongly suggest that the planarity in radical cation states is very important for the oxidation of these compounds. The radical cation species $\mathbf{4a}^{\bullet+}$, $\mathbf{4b}^{\bullet+}$ should not be planar and $\mathbf{4b}^{\bullet+}$ should be more twisted than $\mathbf{4a}^{\bullet+}$. This factor explains the higher oxidation potential of **4b**. The lower oxidation potential of **8**, compared to that of **4a**, can also be rationalized by the planar (twisted) phenoxazine radical cation framework in $\mathbf{8}^{\bullet+}$ ($\mathbf{4a}^{\bullet+}$).

The present study establishes a general synthetic route to heteroatom-bridged triphenylamines. The sulfur derivative **4b** turned out to be in a largely twisted structure giving a higher and irreversible oxidation peak. Preliminary calculations for the targets **3a** and **3b** using the present bond lengths and angles as initial parameters in the geometrical optimization suggests that the sulfur derivative **3b** is in a deep bowl-shape, whereas the oxygen derivative **3a** is in a shallow bowl-shape. Oxidation of **3a** would give rise to shrinkage (≈2%) of the C–N bonds,[6a] leading to a planar $\mathbf{3a}^{\bullet+}$. It seems that $\mathbf{3a}^{\bullet+}$ is an ideal spin building block for our purpose. Synthesis of **3a** and $\mathbf{3a}^{\bullet+}$ is under way.

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8 **4a**; colorless prisms, mp 165 °C, MS (FAB) m/z 273 (M^+), ^{1}H NMR (400 MHz, in DMSO-d_6): δ 6.64 (d, 2H, $J = 8.3$ Hz), 6.88 (t, 1H, $J = 8.3$ Hz), 6.96–7.08 (m, 6H), 7.37 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (100 MHz, in $CDCl_3$): δ 111.06, 114.60, 117.42, 120.92, 123.34, 123.54, 123.60, 129.09, 145.33, 146.98, Anal. Calcd. for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13; Found: C, 78.88, H, 3.98, N, 5.02. **4b**; pale yellow prisms, mp 202 °C, MS (FAB) m/z 305 (M^+), ^{1}H NMR (400 MHz, in $CDCl_3$): δ 6.93–6.98 (m, 1H), 6.98–7.02 (m, 2H), 7.04 (ddd, 2H, $J = 7.6$, 7.2, 1.4 Hz), 7.13 (ddd, 2H, $J = 8.1$, 7.2, 1.6 Hz), 7.18 (dd, 2H, $J = 8.1$, 1.4Hz), 7.21 (dd, 2H, $J = 7.6$, 1.6 Hz); ^{13}C NMR (100 MHz, in $CDCl_3$) δ 120.64, 124.67, 124.83, 125.65, 125.87, 127.08, 127.45, 127.92, 139.55, 142.64, Anal. Calcd. for $C_{18}H_{11}NS_2$: C, 70.79; H, 3.63; N, 4.59; Found: C, 70.62; H, 3.52; N, 4.51.

9 Crystallographic data for **4a**: a cololess prism, orthorhombic, space group $Pna2_1$ (#33), $a = 7.0441(9)$ Å, $b = 9.738(2)$ Å, $c = 17.841(3)$ Å, $V = 1223.8(3)$ Å^3, $Z = 4$, $T = 123$ K, $R_1(I > 2\sigma) = 0.050$, $R_w(I > 0\sigma) = 0.067$, Crystallographic data for **4b**, a pale yellow prism, orthorhombic, space group $P2_12_12_1$ (#19), $a = 8.231(2)$ Å, $b = 17.792(4)$ Å, $c = 19.180(3)$ Å, $V = 2808.7(1)$ Å^3, $Z = 8$, $T = 293$ K, $R_1(I > 2\sigma) = 0.069$, $R_w(I > 0\sigma) = 0.073$. CCDC 240403 and 240404, These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieing.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposite@ccdc.cam.ac.uk).

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