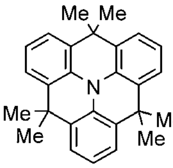
Heterocyclic Chemistry

2,2′:6′,2″:6″,6-Trioxytriphenylamine: Synthesis and Properties of the Radical Cation and Neutral Species**

*Masato Kuratsu, Masatoshi Kozaki, and Keiji Okada**

A planar stable triphenylamine radical cation is a fascinating π-electron system that is potentially applicable to electronic and magnetic materials. Hellwinkel and co-workers synthesized an interesting compound **1**,[1] from which the radical cation **1**$^{\bullet+}$ was generated in concentrated sulfuric acid[1a] or by oxidation with lead tetraacetate in trifluoroacetic acid.[1c] The triphenylamine framework of **1**$^{\bullet+}$ is most likely planar. The dimethylmethylene bridges contribute to its stabilization; however, they disrupt the CT-type intermolecular interaction that is crucial for the construction of electronic and magnetic materials. To overcome this disadvantage and to improve stability, we designed a synthetic route to the new oxygen-bridged analogue **2**.[2,3] Quite recently, Livant and co-workers described a product fraction showing a molecular ion of m/z = 287 in the thermolysis of tris(2,6-dimethoxyphenyl)amine. They assumed the structure **2** for the MS peak. However, the compound showed no NMR spectroscopic signal.[4] Herein, we report the preparation, structures, and properties of the neutral **2** and the radical cation **2**$^{\bullet+}$.



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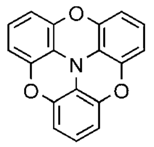

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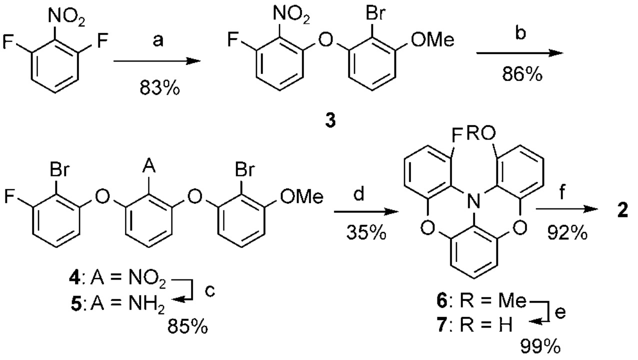
The synthesis of **2** is outlined in Scheme 1. Sequential aromatic nucleophilic substitution reactions of 2,6-difluoronitrobenzene with 2-bromo-3-methoxyphenolate and then with 2-bromo-3-fluorophenolate gave **4** (71 % yield in two steps). The reduction of **4** proceeded selectively in the presence of p-bromophenol (10 equiv) to avoid a competing reduction of aromatic bromide. Intramolecular cyclization of **5** was performed under Pd^0-mediated cross-coupling reaction conditions[5] to afford **6** in 35 % yield. Treatment of **6** with BBr$_3$ gave **7** in good yield. Intramolecular nucleophilic substitution of **7** in DMF with K$_2$CO$_3$ as a base proceeded efficiently under remarkably mild conditions to give the desired compound **2** in good yield. Compound **2** had a reversible oxidation wave at +0.59 V versus SCE in DMF (SCE = saturated calomel electrode). The chemical oxidation of **2** was performed by using tris(p-bromophenyl)aminium hexafluorophosphate as an oxidant in methylene chloride. The salt **2**$^{\bullet+}\cdot$PF$_6^-$ can be recrystallized from acetonitrile/diethyl ether.



Scheme 1. Reaction conditions: a) 2-bromo-3-methoxyphenol, NaH/DMSO, 130 °C; b) 2-bromo-3-fluorophenol, NaH/DMSO, 130 °C; c) hydrazine hydrate, Pd/C, p-bromophenol/ethanol, reflux; d) NaOtBu, [Pd(dba)$_2$], P(tBu)$_3$/toluene, reflux; e) BBr$_3$/CH$_2$Cl$_2$, −78 °C→room temperature; f) K$_2$CO$_3$/DMF, room temperature. dba = *trans,trans*-dibenzylideneacetone.

Figure 1 shows the molecular structures determined by X-ray crystallographic analysis of **2** and **2**$^{\bullet+}$.[6] The neutral compound **2** has a shallow bowl structure, whereas the radical cation **2**$^{\bullet+}$ has a planar structure. The C–N bond lengths become shorter and the C-N-C bond angles approach 120° in the radical cation **2**$^{\bullet+}$. The bond-length difference is in qualitative accordance with the HOMO shape of **2**; that is, the C–N and C–O bonds have an antibonding nature in the HOMO.

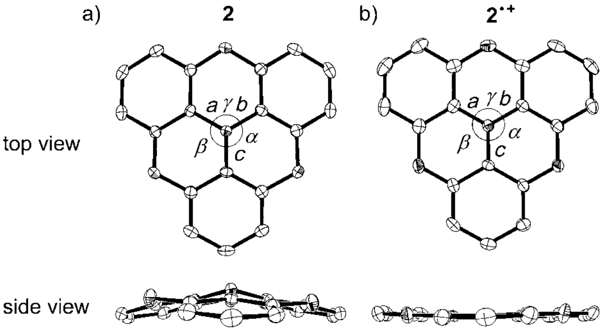


Figure 1. Molecular structures of **2** and **2**$^{\bullet+}$ drawn at 50 % ellipsoid level; hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°]. a) For **2** measured at 123 K: a = 1.408(2), b = 1.403(3), c = 1.412(3); α = 115.3(2), β = 115.6(2), γ = 115.7(2). b) For **2**$^{\bullet+}$ measured at 113 K: a = 1.376(3), b = 1.377(3), c = 1.378(3); α = 120.1(2), β = 119.9(2), γ = 120.0(2).

Triphenylamine radical cations without *para* substituents are generally unstable because of the large spin densities of

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[*] M. Kuratsu, Dr. M. Kozaki, Prof. K. Okada
Graduate School of Science, Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81) 6-6690-2709
E-mail: okadak@sci.osaka-cu.ac.jp

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the *para* positions.[7] For $\mathbf{2}^{\cdot+}$, neither dimerization tendency in the crystal structure nor oxygenation under aerated conditions in solution was observed. The spin delocalization in a whole molecule involving the oxygen atoms (phenoxazine radical cation structure) contributes to the stability of $\mathbf{2}^{\cdot+}$. The radical cation $\mathbf{2}^{\cdot+}$ exhibited a well-resolved EPR spectrum. The hyperfine coupling constants for $\mathbf{2}^{\cdot+}$ ($g = 2.0031$, $a_N = 0.90$, $a_{H_p} = 0.26$, and $a_{H_m} = 0.06$ mT) in butyronitrile at room temperature were slightly smaller than those for $\mathbf{1}^{\cdot+}$ ($g = 2.0027$, $a_N = 0.95$, $a_{H_p} = 0.30$, and $a_{H_m} = 0.07$ mT).[1c] The smaller spin density values for $\mathbf{2}^{\cdot+}$ are clearly related to the positive spin density of the oxygen atoms. The calculated spin-density map and values are shown in Figure 2.[8]

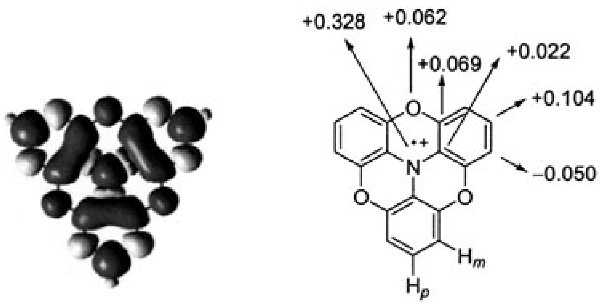

Figure 2. The spin-density map (black: positive spin, white: negative spin) and values (UB3LYP/6-31G*) for $\mathbf{2}^{\cdot+}$.

The radical cation $\mathbf{2}^{\cdot+}$ had broad absorptions in the visible region ($\lambda = 709$ and 785 nm, Figure 3). These absorptions can be related to the electronic transitions from the occupied MOs delocalized on the outer electron-rich trioxytris(1,3-phenylene) moieties to the delocalized unoccupied orbital involving the nitrogen cation. The theoretical calculation (TD-DFT/6-31G*) roughly reproduced this situation ($\lambda_{calcd} = 729$ nm as a degenerate transition with the main contribution ($\approx 90\,\%$) of HOMO-1(β), HOMO(β)→LUMO(β) (oscillator strength of 0.01 in both cases); Figure 4).[8,9] The observed absorptions with a rather broad slope in the region of 500–700 nm can be attributed to vibrational fine structure of the degenerate band. The peak separation of 1370 cm^{-1} is close to that observed for the 10-phenylphenoxazine radical cation (1270 cm^{-1}).

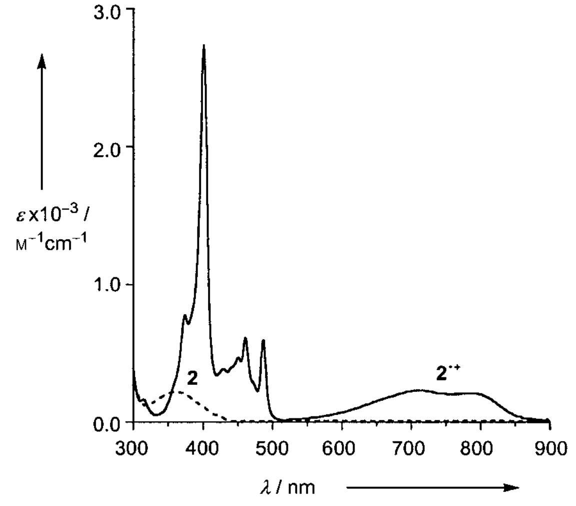

Figure 3. UV/Vis absorptions of **2** (-----) and $\mathbf{2}^{\cdot+}$ (——) in dichloromethane.

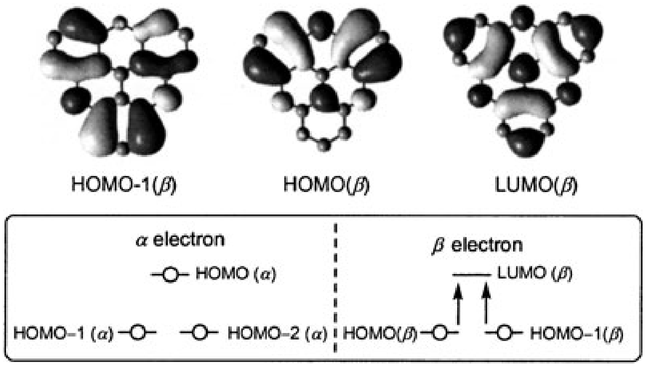

Figure 4. MOs and the energy diagram (UHF) of $\mathbf{2}^{\cdot+}$.

These studies clearly establish that 1) the neutral compound **2** is a good electron donor with a shallow bowl structure and 2) the radical cation $\mathbf{2}^{\cdot+}$ is a highly stable planar species. Moreover, the neutral compound **2** can form stable CT complexes with several electron acceptors, suggesting applicability to electronic and magnetic materials. We are particularly interested in forthcoming projects to follow up this work. The introduction of stable radicals at the *para* positions followed by the formation of CT complexes with electron acceptors would provide a magnetic CT-salt material.[10] Furthermore, the small geometrical change between the neutral and radical cation states may allow photostimulated phase transition to the photoconductive state $\mathbf{2}_2^{\cdot+}$.[11] The preparation of such materials is in progress.

Experimental Section

The synthesis of compounds **2**–**7** and the EPR spectrum for $\mathbf{2}^{\cdot+}$ with its simulation are described in the Supporting Information.

$\mathbf{2}^{\cdot+}\cdot PF_6^-$: Compound **2** (25.0 mg, 0.0870 mmol) was dissolved in dichloromethane (20 mL). A solution of tris(*p*-bromophenyl)aminium hexafluorophosphate (54.8 mg, 0.0874 mmol in CH_2Cl_2 (10 mL)) was added dropwise at room temperature with stirring in a glove box. After 30 min, the solvent was evaporated under vacuum and the crude product was recrystallized from acetonitrile/diethyl ether to give $\mathbf{2}^{\cdot+}$ as deep green plates (29.4 mg, 78 %); m.p. ≈ 278.0 °C (decomp). MS: *m*/*z* (%): FAB$^+$ (*m*-NBA) 287 (100) [$C_{18}H_9NO_3^+$], FAB$^-$ (*m*-NBA) 145 (100) [PF_6^-]. Elemental analysis calcd (%) for $\mathbf{2}^{\cdot+}\cdot PF_6^-$ ($C_{18}H_9F_6NO_3P$): C 50.02, H 2.10, N 3.24; found: C 50.12, H 2.00, N 3.21.

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[6] Crystallographic data for **2**: crystal size $0.40\times0.30\times0.20$ mm, monoclinic, space group $P2_1$ (#4), $a=10.0772(13)$ Å, $b=6.8136(6)$ Å, $c=10.0712(13)$ Å, $\beta=119.964(4)°$, $V=599.08(12)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.592\,\text{g}\,\text{cm}^{-3}$, $2\theta_{\text{max}}=55.0°$, Mo$_{\text{K}\alpha}$ radiation (0.71070 Å), $T=123$ K, $\mu=1.10\,\text{cm}^{-1}$, $T_{\text{min}}=0.977$, $T_{\text{max}}=0.989$, 4450 measured reflections, 1412 unique reflections, 1367 observed reflections ($I>-10\sigma$, all data), 208 parameters, $R_1(I>2\sigma)=0.035$, $R_w(I>2\sigma)=0.044$, GOF = 1.004; Crystallographic data for $\mathbf{2}^{\cdot+}\cdot\text{PF}_6^-$: crystal size $0.30\times0.20\times0.10$ mm, orthorhombic, space group *Pbca* (#61), $a=15.5415(10)$ Å, $b=13.4237(8)$ Å, $c=15.5653(10)$ Å, $V=3247.3(4)$ Å^3, $Z=8$, $\rho_{\text{calcd}}=1.768\,\text{g}\,\text{cm}^{-3}$, $2\theta_{\text{max}}=55.0°$, Mo$_{\text{K}\alpha}$ radiation (0.71070 Å), $T=113$ K, $\mu=2.58\,\text{cm}^{-1}$, $T_{\text{min}}=0.953$, $T_{\text{max}}=0.980$, 25720 measured reflections, 3708 unique reflections, 2763 observed reflections ($I>-10\sigma$, all data), 271 parameters, $R_1(I>2\sigma)=0.043$, $R_w(I>2\sigma)=0.047$, GOF = 1.030. CCDC 262144 (**2**) and CCDC 262145 ($\mathbf{2}^{\cdot+}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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