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Communication

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One-Electron Oxidation of an Organic Molecule by B(C_6F_5)$_3$; Isolation and Structures of Stable Non-*para*-substituted Triarylamine Cation Radical and Bis(triarylamine) Dication Diradicaloid

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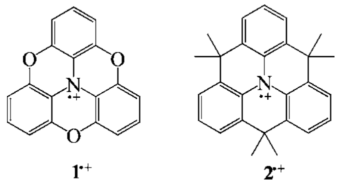
Supporting Information

ABSTRACT: The methylene-bridged triphenylamine **2** has been oxidized to planar radical cation **2**$^{\bullet+}$ by B(C_6F_5)$_3$ or Ag$^+$. Further reaction of **2**$^{\bullet+}$[Al(OR$_F$)$_4$]$^-$ and **2** with trace amounts of silver salt resulted in dication **3**$^{2+}$, providing a rare example of structurally characterized bis(triarylamine) "bipolarons". **3**$^{2+}$ can be directly prepared by the reaction of **3** with 2 equiv of Ag$^+$. X-ray structural analysis together with theoretical calculation shows that **3**$^{2+}$ has singlet diradical character and is analogous to Chichibabin's hydrocarbons.

Tris(pentafluorophenylborane), B(C_6F_5)$_3$, has important applications in preparation of weakly coordinating anions, synthetic organic transformations, and activation of olefin polymerization catalysts.[1] It is well known as a Lewis acid to form strong adducts with a number of Lewis bases through a dative bond.[2] More recently, the chemistry of frustrated Lewis pairs, in which B(C_6F_5)$_3$ acts as the archetypal Lewis acid and does not covalently bond to Lewis bases, has been extensively studied for applications in small-molecule activation and hydrogenation reactions.[3] However, B(C_6F_5)$_3$ acting as a one-electron oxidant was observed only during reactions with transition metal complexes, such as azazirconacyclobutene and molybdenum vinyl complexes, by Norton and Green and co-workers.[4] One-electron oxidation of an organic molecule by B(C_6F_5)$_3$ has not been reported.[5]

Materials based on triphenylamines and tetraphenylbenzidines have a wide range of applications in electrical conductivity, electroluminescence, organic light-emitting devices, polymer batteries, and photorefractive materials.[6] Bridged triphenylamines in which the three phenyl rings are locked by methylene or oxygen connectors are reported to have improved physical properties, and their planar radical cations are potential electromagnetic materials.[7] Triphenylamine radical cations without *para* substituents are generally unstable because of the large spin densities of the *para* positions.[8] The only stable but non-*para*-substituted example is the oxygen-bridged triphenylamine radical cation **1**$^{\bullet+}$ (Scheme 1), in which the radical is stabilized by partial spin delocalization on oxygen atoms.[7a] The methylene-bridged analogue **2**$^{\bullet+}$ was reported earlier but exsits only in solution with concentrated sulfuric acid or trifluoroacetic acid, and whether its structure is planar remains unknown.[9]

Scheme 1



In this paper we report the first example of one-electron oxidation of an organic molecule, **2**, by B(C_6F_5)$_3$. The formed stable triphenylamine radical cation **2**$^{\bullet+}$ is essentially identical to that obtained from the oxidation of **2** by silver salt Ag[Al(OR$_F$)$_4$] (OR$_F$ = OC(CF$_3$)$_3$).[10] Further reaction of **2**$^{\bullet+}$[Al(OR$_F$)$_4$]$^-$ and **2** with trace amounts of silver salt resulted in a bis(triphenylamine) dication with singlet diradical character. The current work is an extension of our recent efforts on stabilization of radical cations[11] by weakly coordinating anions.[12]

The reaction of **2** with freshly sublimed B(C_6F_5)$_3$ (molar ratio = 1:1) afforded a deep blue solution. The well-resolved electron paramagnetic resonance (EPR) spectrum (Figure 1a) of the reaction solution indicated the formation of radical cation **2**$^{\bullet+}$. The simulated EPR spectrum (Figure 1c) is in good agreement with the experimental EPR spectrum, revealing a pattern resulting from interactions of the radical with N and phenyl H atoms. The hyperfine coupling constants are similar to those for **2**$^{\bullet+}$ reported previously[9] and larger than those for **1**$^{\bullet+}$.[7a] There is no evidence for the formation of a boron-centered radical anion, which probably decomposes into various four-coordinate borates such as [ClB(C_6F_5)$_3$]$^-$ and [HB(C_6F_5)$_3$]$^-$.[13] Attempts to crystallize the salt of radical cation **2**$^{\bullet+}$ failed.

In order to confirm the identity of **2**$^{\bullet+}$ and study its molecular structure, reaction of **2** with Ag[Al(OR$_F$)$_4$] in CH$_2$Cl$_2$ was carried out. Upon one-electron oxidation, **2** was converted to blue radical cation **2**$^{\bullet+}$ in high yield. Its EPR spectrum (Figure 1b) is essentially identical to that of the reaction solution of B(C_6F_5)$_3$ with **2** (Figure 1a). Radical cation

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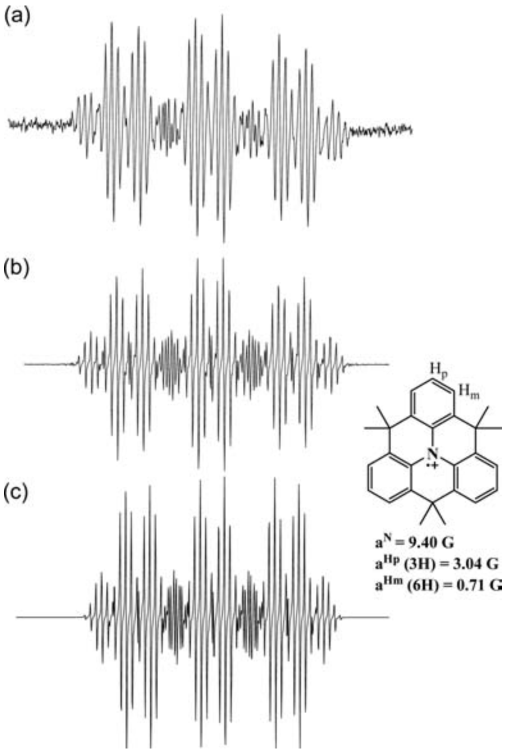


Figure 1. (a) EPR spectrum of the reaction solution of B(C_6F_5)$_3$ + **2** in CH_2Cl_2. (b) EPR spectrum of the reaction solution of Ag[Al(OC(CF$_3$)$_3$)$_4$] + **2** in CH_2Cl_2. (c) Simulated EPR spectrum of **2**$^{\bullet+}$.

2$^{\bullet+}$ has absorptions in the visible region around 600 nm (Figure S1, Supporting Information), slightly shifted to the purple compared to those of **1**$^{\bullet+}$.[7a] Crystals suitable for X-ray crystallographic studies were obtained by cooling the solution of **2**$^{\bullet+}$[Al(OR$_F$)$_4$]$^-$,[14] and the structure of **2**$^{\bullet+}$ is illustrated as stereoviews in Figure 2. It is a monomeric radical cation. The sum of the C−N−C bond angles is 360.0(3)°, and the NC$_3$ fragment is coplanar to three phenyl rings, indicating a planar structure of **2**$^{\bullet+}$, in contrast to the shallow bowl structure of neutral molecule **2**.[15] No obvious bond length changes between neutral **2** and radical cation **2**$^{\bullet+}$ are observed.

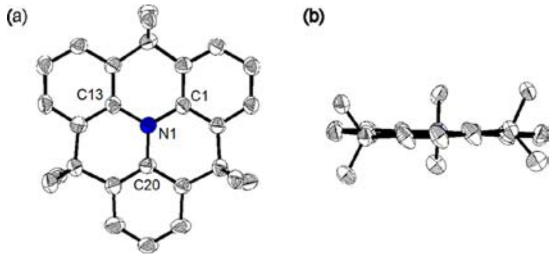


Figure 2. 50% ellipsoid drawings of **2**$^{\bullet+}$. H atoms are not shown. Selected bond lengths (Å) and angles (deg): N1−C1 1.419(4), N1−C13 1.438(4), N1−C20 1.440(4); C1−N1−C13 120.2(3), C1−N1−C20 120.7(3), C13−N1−C20 119.1(3).

The structure of **2**$^{\bullet+}$ is well reproduced by density functional theory (DFT) calculation at the UB3LYP/6-31G* level.[16] The well-resolved solution EPR spectra are consistent with radical species that exhibit spin delocalization over the whole molecule. This is supported by the calculated spin density values (Figure 3). It is worth noting that, in contrast to those in the oxygen-bridged **1**$^{\bullet+}$,[7a] spin polarization leads to higher spin density on N and the *para*-C atoms in **2**$^{\bullet+}$, consistent with its larger hyperfine coupling constants.

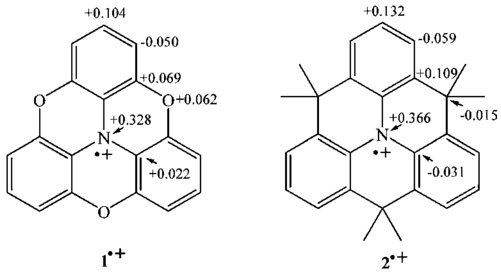
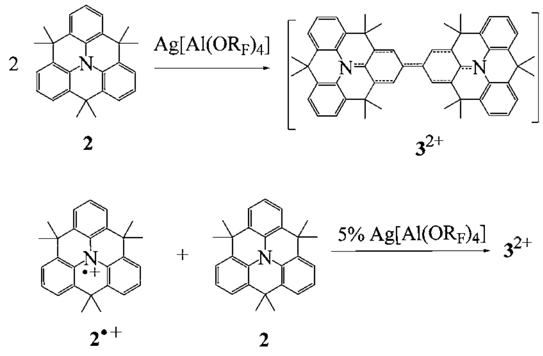


Figure 3. Calculated spin density values for **1**$^{\bullet+}$ [7a] and **2**$^{\bullet+}$ at the UB3LYP/6-31G* level.

Unexpectedly, the reaction of **2** with 0.5 equiv of Ag[Al(OR$_F$)$_4$] led to bis(triarylamine) dication **3**$^{2+}$ (Scheme 2). However, **2**$^{\bullet+}$ did not react directly with **2** (molar ratio **2**$^{\bullet+}$:**2** = 1:1), as revealed by the UV−vis spectrum, but they reacted upon addition of 5 mol % Ag[Al(OR$_F$)$_4$] and afforded the same product **3**$^{2+}$ in higher yield (Scheme 2).[17,18] Consequently and straightforwardly, **3**$^{2+}$ was obtained by direct oxidation of **3** with 2 equiv of Ag[Al(OR$_F$)$_4$]. Neutral **3** was prepared by the reaction of **2** with Cu(ClO$_4$)$_2$ followed by addition of K_2CO_3, similar to the synthesis of nonbridged tetraarylbenzidines.[8d,19]

Scheme 2



Cooling the solution of **3**$^{2+}$·2[Al(OR$_F$)$_4$]$^-$ afforded crystals suitable for X-ray crystallographic studies.[14] The curved structure of **3**$^{2+}$ (Figure 4) has C_i symmetry and shows planar geometries about the nitrogen centers, and the N−C(13,20) bond lengths to the peripheral aryl ring systems (1.445(5), 1.438(5) Å) are longer than those to the biphenyl moiety (N1−C1$_{(\text{biphenyl})}$ = 1.404(5) Å). The biphenyl moiety (C1−C4−C4′−C1′) is planar and rotated into a position closer to the NC$_3$ planes (interplanar angle = 12.6 (1)°). The bond length between the two triphenylamine moieties is C4−C4′ = 1.467(8) Å, which is slightly shorter than a typical biphenyl single bond (1.48 Å) but much longer than a typical double bond (1.34 Å), indicating that **3**$^{2+}$ may have diradical nature.

The diradical character of **3**$^{2+}$ is supported by theoretical calculation,[16] which shows a small singlet−triplet energy gap ($\Delta E_{\text{OS-T}}$ = −1.0 kcal/mol) and that the most stable electronic state is the open-shell singlet (OS) (Table 1). Comparison of the bond lengths and the differences in the averages of bonds C$_o$−C$_m$, C$_i$−C$_o$, and C$_m$−C$_p$ of the X-ray structure, optimized closed-shell singlet (CS), OS, and pure diradical triplet (T) structures (Table 1) suggests an intermediate diradical character in the singlet ground state of **3**$^{2+}$, as the values of the X-ray structure and the optimized OS are found to lie

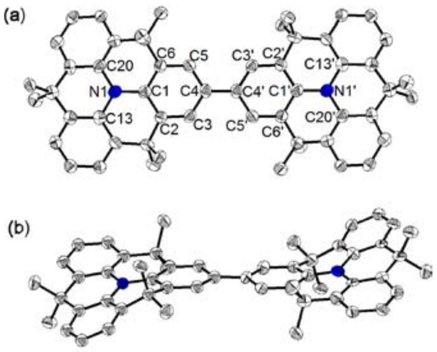


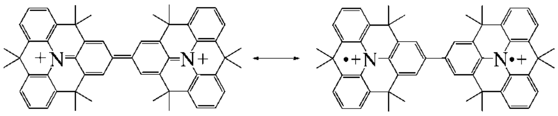
Figure 4. 50% ellipsoid drawings of 3^{2+}. H atoms are not shown. Selected bond lengths (Å) and angles (deg): N1−C1 1.404(5), N1−C13 1.445(5), N1−C20 1.438(5), C1−C2 1.427(6), C2−C3 1.373(6), C3−C4 1.410(6), C4−C5 1.422(6), C5−C6 1.388(6), C1−C6 1.430(6), C4−C4 1.467(8); C1−N1−C20 120.8(4), C1−N1−C13 119.5(4), C13−N1−C20 119.5(3), N1−C1−C2−C3 172.3(4).

between those for the optimized CS and diradical T. This species is thus best described as a resonance hybrid of quinoidal structure and diradical structure (Scheme 3). The diradical character (y) of 3^{2+}, estimated by the occupancy of the lowest unoccupied natural orbital at the UBHandHLYP/6-31G* level on the X-ray structure, is 0.77, which is higher than that (0.615) of the recently reported tetracation bis(acridine) dimer.[20]

The dication has an absorption in the visible region (λ = 841 nm, Figure 5a). Analysis of time-dependent DFT results indicates that this absorption is related to the HOMO−LUMO transition (Figures 5b and S4).[16] The small HOMO−LUMO gap and near-IR absorptions support the diradical character of 3^{2+}. In addition, the ^{1}H NMR spectrum is broad at room temperature but becomes sharper upon cooling (Figure S5), further indicating the singlet diradical nature of 3^{2+}.[20] However, the excited triplet species could not be observed in SQUID measurements, probably due to the small population as well as intrinsic measurement error.[20]

Singlet diradicals are not only important for understanding the nature of chemical bonds but also expected to have interesting physical properties and promising applications in materials science.[21] Singlet diradical aromatic hydrocarbons have attracted much attention, and their synthesis, structure, and electronic properties have been extensively studied in conjunction with theoretical calculations.[21,22] Among them, Chichibabin's hydrocarbon, the backbone of which is isoelectronic to that of 3^{2+}, has been of interest for decades.[23] Very recently, bis(acridine) tetracation was serendipitously obtained and shown to be a singlet diradicaloid with excellent two-photon absorptions.[20]

Scheme 3



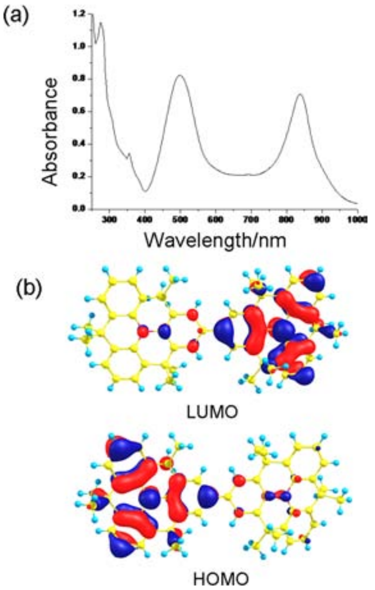
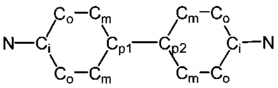


Figure 5. (a) UV−vis absorptions of 3^{2+} in CH_2Cl_2. (b) Frontier orbitals (α) of 3^{2+} calculated on its crystal structure at the UB3LYP/6-31G* level.

In summary, we have shown that the methylene-bridged triphenylamine **2** is oxidized to radical cation $\mathbf{2}^{\bullet+}$ by $B(C_6F_5)_3$ or Ag^+, the identity and stability of which have been unequivocally confirmed by EPR, UV−vis spectroscopy, and single-crystal X-ray diffraction. This work provides the first example of one-electron oxidation of an organic molecule by $B(C_6F_5)_3$, which can be viewed as a linkage between Lewis acid−base adducts and frustrated Lewis pairs. $\mathbf{2}^{\bullet+}$ is a rare (the second) example of the stable triphenylamine radical cation without *para*-substitution. The reaction of radical $\mathbf{2}^{\bullet+}$ and **2** with trace amounts of Ag^+ leads to the formation of dication 3^{2+}, a rare example of structurally characterized bis(triarylamine) "bipolarons",[24] which play important roles in many conducting polymers.[25] Moreover, X-ray structural analysis and theoretical calculation indicate that 3^{2+} has

Table 1. Selected Experimental and Calculated Bond Lengths for 3^{2+} and Calculated Relative Energy for 3^{2+}



	$\Delta E_{X\text{-}OS}$[a] (kcal/mol)	N−C_i (Å)	C_{p1}−C_{p2} (Å)	avg C_i−C_o and C_m−C_p (Å)	avg C_o−C_m (Å)	bond length difference[b] (Å)
X-ray structure[c]	–	1.404(5)	1.467(8)	1.422(6)	1.380(6)	0.042
closed-shell singlet (CS)[c,d]	4.9	1.378	1.441	1.428	1.375	0.053
open-shell singlet (OS)[c,e]	0	1.412	1.472	1.413	1.388	0.025
triplet (T)[c,e]	1.0	1.423	1.482	1.409	1.392	0.017

[a] Energy relative to the OS state. X = CS, OS, or T. [b] Difference between the average of all C_i−C_o and C_m−C_p bond lengths and the average of C_o−C_m bond lengths. [c] Bond lengths are the average of corresponding bonds of the biphenyl moiety. [d] Calculated at the B3LYP/6-31G* level. [e] Calculated at the UB3LYP/6-31G* level.

diradical character and is analogous to Chichibabin's hydrocarbons.[23]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data in CIF format, UV−vis and VT ^{1}H NMR spectra, theoretical calculations, and complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) X-ray data for $\mathbf{2}^{\bullet+}[Al(OR_F)_4]^-$ and $\mathbf{3}^{2+}{\cdot}2[Al(OR_F)_4]^-$ are listed in Table S1. CCDC files 946858−946859 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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(17) A tentative mechanism for the formation of the dication is proposed (Figure S3). Most probably, radical $\mathbf{2}^{\bullet+}$ slowly σ-dimerizes to dication $[\mathbf{3}\text{-}2H]^{2+}$. The loss of two protons affords a neutral benzidine **3**, which is then oxidized to dication $\mathbf{3}^{2+}$. Such a reaction path way via radical−radical coupling is supported by variable-temperature UV−vis absorption spectra of $\mathbf{2}^{\bullet+}$ (Figure S1). We thank one reviewer for comments on this issue.

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