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A Triphenylamine with Two Phenoxy Radicals Having Unusual Bonding Patterns and a Closed-Shell Electronic State**

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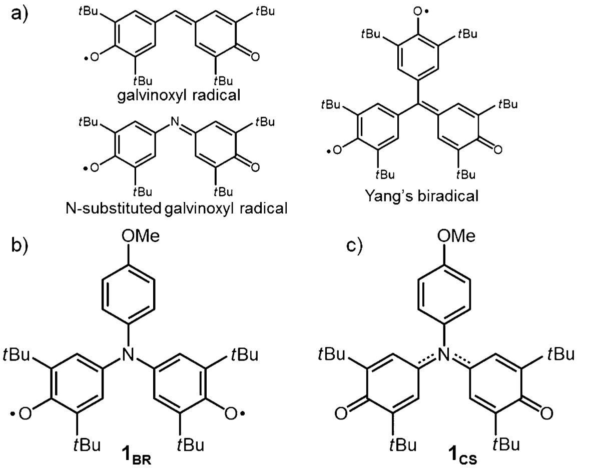
***Abstract:** Reported herein is the structure and the electronic properties of a novel triphenylamine derivative having two phenoxy radicals appended to the amino nitrogen atom. X-ray single crystal analysis and the magnetic resonance measurements demonstrates the unexpected closed-shell electronic structure, even at room temperature, of the molecule and two unusual C–N bonds with multiple-bond character. The theoretical calculations support the experimentally determined molecular geometry with the closed-shell electronic structure, and predicted a small HOMO–LUMO gap originating from the nonbonding character of the HOMO. The optical and electrochemical measurements show that the molecule has a remarkably small HOMO–LUMO gap compared with its triphenylamine precursor.*



Scheme 1. a) Structures of the galvinoxyl radical. Structures of **1** drawn as a biradical (b) and a closed-shell form (c).

The galvinoxyl radical is one of the most popular stable organic radicals (Scheme 1 a).[1] This molecule possesses two 2,6-di-*tert*-butylphenoxy radical moieties directly connected to a central methine carbon atom. One of the radical spins of the two 2,6-di-*tert*-butylphenoxy radicals is coupled to the unpaired *p* electron of the methine carbon atom to form a quinoid structure, and as a result, galvinoxyl acts as a monoradical having an unpaired spin delocalized over whole of the conjugated skeleton. The analogue of the galvinoxyl radical wherein the methine carbon atom is replaced by an imine nitrogen atom has been also reported to be a monoradical because of its isoelectronic structure to that of galvinoxyl (Scheme 1 a).[2] Yang et al. have reported another galvinoxyl derivative called Yang's biradical, which has one more 2,6-di-*tert*-butylphenoxy radical on the methine carbon atom instead of the hydrogen atom (Scheme 1 a).[3] In this case, one of the radical spins of the three phenoxy radicals is consumed to make a covalent bond with the unpaired *p* electron of the methine carbon atom, and therefore this molecule becomes a biradical. Following these results, we were curious as to how the radicals of the two phenoxy radicals would interact with each other if the central carbon atom of the galvinoxyl radical was substituted by an amino nitrogen atom and not by an imine nitrogen atom[4] In such a molecule, it is impossible to write a classical Kekulé structure for its closed-shell structure, but the strong spin–spin interaction between two radical spins through π conjugation is expected. To answer this question, we prepared a novel compound with two 2,6-di-*tert*-butylphenoxy radicals in a triphenylamine structure (**1**). Through this work, we found that **1** is not a biradical such as $\mathbf{1_{BR}}$ (Scheme 1 b) but an unexpected closed-shell molecule such as $\mathbf{1_{CS}}$ (Scheme 1 c) having two unique C–N bonds with multiple-bond character in the C-N-C moiety. Herein, we describe the details of the structure and the electronic properties of **1**.

The precursor of **1**, having two OH groups, was synthesized with the palladium-catalyzed amination reaction between *p*-anisidine and MOM-protected 2,6-di-*tert*-butyl-4-

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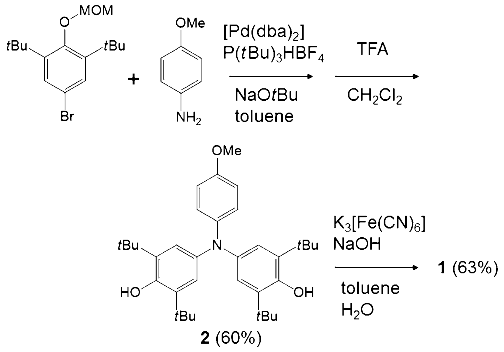
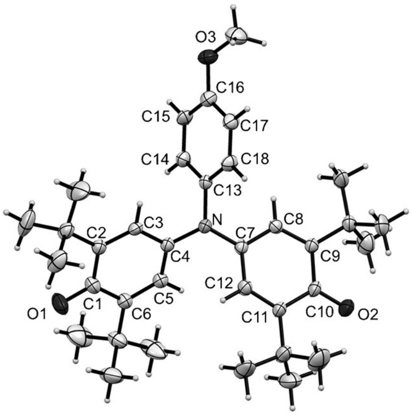


Scheme 2. Synthesis of **1**. dba = dibenzylideneacetone, MOM = methoxymethyl.

bromophenol, with subsequent removal of the MOM groups (Scheme 2). This precursor **2** was oxidized with potassium ferricyanide in toluene combined with an aqueous sodium hydroxide solution. Just after the reaction started, the reaction solution turned deep-blue. After workup and purification by silica gel chromatography, we obtained the product **1** as a red-purple solid with metallic luster. This compound was stable enough to be handled under ambient air, moisture, and light exposure. To our surprise, this compound exhibited no ESR signals but showed sharp NMR signals at room temperature, thus indicating the singlet electronic state.[5]

The structure of **1** was confirmed by the single-crystal X-ray analysis as shown in Figure 1, thus suggesting that both phenoxy groups are quinoidal structures with remarkable bond length alternation.[6] This structural deformation clearly indicates that **1** is not a singlet biradical but a closed-shell molecule.[7] The sum of the three bond angles around the central nitrogen atom is 359.96°, thus showing that C4, C7, C13 and the nitrogen atom are in the same plane. It is noteworthy that the lengths of the C4–N and C7–N bonds were the same, and significantly shorter (1.383 Å) than the usual C–N single bond, such as C13–N (1.441 Å), thus indicating that the C4–N and C7–N bonds have multiple-bond character. The smaller torsion angles around these two C–N bonds, compared to that around C13–N, also suggest the existence of a multiple-bond character for these bonds.



Selected bond lengths	
O1-C1	1.244 Å
C1-C2	1.462 Å
C2-C3	1.356 Å
C3-C4	1.415 Å
C4-N	1.383 Å
C7-N	1.383 Å
C7-C8	1.417 Å
C8-C9	1.354 Å
C9-C10	1.463 Å
C10-O2	1.234 Å
C13-N	1.441 Å
C13-C14	1.377 Å
C14-C15	1.375 Å
C15-C16	1.379 Å
C16-O3	1.370 Å
Selected dihedral angles	
C5-C4-N-C7	31.04°
C8-C7-N-C13	22.27°
C14-C13-N-C4	53.66°

Figure 1. X-ray structure of **1**. Thermal ellipsoids are set at 50% probability.

The multiple-bond character of the two C–N bonds was also seen in the NMR spectra. The ^{1}H and ^{13}C signals of the *tert*-butyl groups and the aromatic protons of the 2,6-di-*tert*-butylphenoxy groups were split into two peaks at 298 K, thus suggesting that the rotations of the two phenoxy groups were much slower than the NMR timescale at this temperature (Figure 2 and see Figures S3–S7 in the Supporting Information). We observed the temperature dependence of the chemical shifts of the *tert*-butyl protons in [D$_{10}$]*p*-xylene. As the temperature increased from 298 K, these two peaks became broader and coalesced at 358 K. From this coalescence temperature, the rotation barrier of these C–N bonds were estimated to be about 73 kJ mol^{-1},[8] and this value is comparable with that of the typical amide C–N bond, which also has multiple-bond character.[9] After cooling from 388 K to 298 K, the initial spectrum was recovered, thus suggesting the high thermal stability of **1** (see Figure S8 in the Supporting Information).

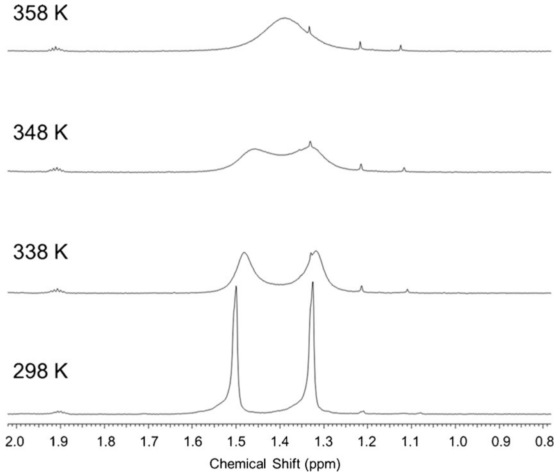
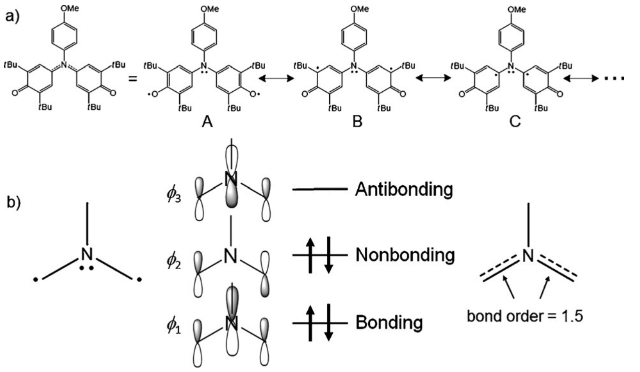


Figure 2. Variable-temperature ^{1}H NMR spectra of *t*Bu protons of **1** in [D$_{10}$]*p*-xylene.



Scheme 3. a) Selected canonical resonance structures of **1**. b) Hückel calculations for an isodistant azomethine ylide as a model of the central C-N-C moiety of **1**.

In Scheme 3a, three selected canonical forms of **1**, A–C, are shown. The actual ground electronic state of **1** is described by a linear combination of all the possible canonical forms, and among them, form C seemed to have a largest contribution judging from the X-ray structure. Form C possesses radicals on the two carbon atoms connected to the nitrogen atom, and is similar to the diradical structure of azomethine ylides.[10] Therefore, it might be meaningful to look closely into this central C-N-C moiety for a better understanding of the unique C–N bonds of **1**. By carrying out the Hückel calculation for an isodistant azomethine ylide, the three MOs were obtained as shown in Scheme 3b. In common with the case of the allyl radical, the frontier MO with the nonbonding character (ϕ_2) appeared between the bonding MO (ϕ_1) with no nodes and the antibonding MO with two nodes (ϕ_3). In the case of the allyl radical, there exist three electrons: the bonding ϕ_1 orbital is doubly occupied and the nonbonding ϕ_2 is singly occupied. In the case shown in Scheme 3b, the bonding ϕ_1 orbital is doubly occupied, thus leading to a multiple-bond character (bond order of 1.5) for the two C–N bonds, whereas the remaining two electrons occupied by the nonbonding ϕ_2 do not contribute to those C–N bonds. Accordingly, the present compound **1** can be considered as a structural analogue of the isodistant azomethine ylide. In fact, the frontier MOs of **1** by the DFT calculations had some characteristic similarities with the isodistant azomethine ylide. More interestingly, the orbital patterns of the HOMO and the LUMO of **1**, calculated at RB3LYP/6-31G(d) level, clearly possess the nonbonding and antibonding character around the central nitrogen atom, coincided with the ϕ_2 and ϕ_3 orbital, respectively, in Scheme 3b (Figure 3). Thus, the HOMO–LUMO gap was estimated to be a lower value of 1.68 eV to reflect the nonbonding character of the HOMO. Yamaguchi et al. have reported the very similar bonding situation in the theoretical investigation of the ring-opened form of aziridine, which is an unstable intermediate,[11] and **1** is thought to be a rare example of molecules with such bonding patterns and sufficient stability to be isolated.

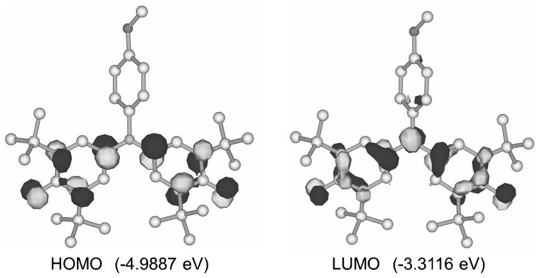


Figure 3. Kohn–Sham HOMO and LUMO of **1**. Data calculated at the RB3LYP/6-31G(d) level of theory.

The UV/Vis-NIR absorption spectra of **1** and its precursor **2** in a CH_2Cl_2 solution were dramatically different. As shown in Figure 4, **1** had a strong absorption with a peak top at 1.80 eV (688 nm with $f = 0.526$, evaluated from the numerical accumulation of the spectrum in the range of 9500–18000 cm^{-1}), which could be attributed to the HOMO–LUMO and (HO-2)MO–LUMO transitions according to the TD-DFT calculation at the RB3LYP/6-31G(d) level of theory (see the Supporting Information). The extremely large f of over 0.5 is reproduced by the TD-DFT calculation ($f > 0.45$), and supported by the overlapped Kohn–Sham HOMO and LUMO represented in Figure 3. The optical HOMO–LUMO gap of **1** was estimated to be about 1.4 eV from the low-energy tail of this band. This value was in good agreement with the electrochemical HOMO–LUMO gap of 1.41 eV, which was obtained from the cyclic voltammetry and the differential pulse voltammetry of **1** in CH_2Cl_2 (see Figures S12–S14 in the Supporting Information). These results indicate that the electronic properties of **1** were completely changed from that of usual triphenylamine compounds having large HOMO–LUMO gap (typically about 4 eV) reflecting the peculiar bonding structure of **1**.

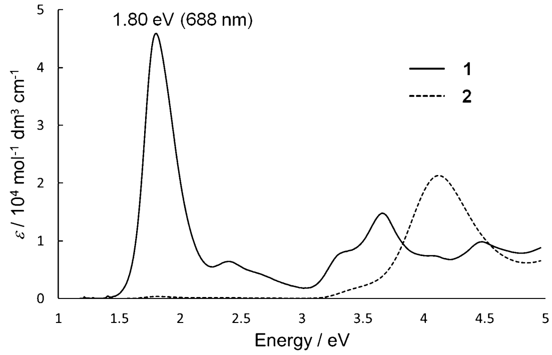


Figure 4. UV/Vis-NIR absorption spectra of **1** and **2** in CH_2Cl_2 at 298 K.

For further investigation of the bonding structure of **1**, we measured the Raman spectra of the powder samples of **1** and **2** (Figure 5).[12] For both **1** and **2**, the strongest peaks were the C=C stretching modes of the phenyl rings around 1600 cm^{-1}, and their frequencies were almost same (for **1**; 1601 cm^{-1}, for **2**; 1595 cm^{-1}) in spite of the apparent quinoidal deformation of **1**. The most remarkable difference was found in the peaks around 1300 cm^{-1} region, which could be assigned to the C–N stretching and the aromatic C–H bending modes.[13] For **2**, the peak was assigned to the peak at 1321 cm^{-1}. In contrast, for **1**, this peak was split into two peaks (1256 and 1294 cm^{-1}). According to the frequency analysis based on DFT calculations, the former is mainly attributed to the C–N stretching

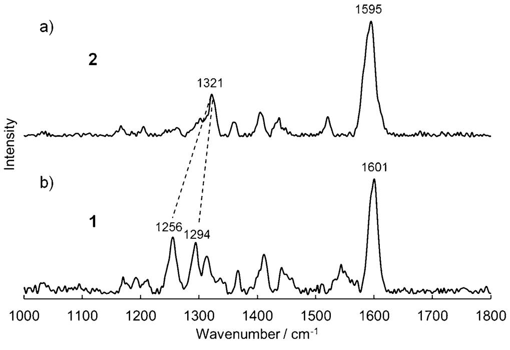


Figure 5. Raman spectra of solid samples of a) **2** and b) **1**.

between the central nitrogen atom and the anisyl group, and the latter to the cooperative stretching of three C–N bonds including two C–N bonds with multiple-bond character (see Figure S15 in the Supporting Information). The results imply the nonequivalence of the bond strengths of the C–N bonds in **1**.

In summary, we have prepared a novel triphenylamine derivative **1** bearing two phenoxy radicals connected through the central amino nitrogen atom. By using the X-ray single-crystal analysis and the magnetic resonance spectroscopy measurements, we experimentally determined that **1** possesses a closed-shell singlet electronic state even at 388 K. Both of the C–N bonds clearly have multiple-bond character. The DFT calculations of **1** indicated the small HOMO–LUMO gap originating from the nonbonding character of the HOMO. The molecular design proposed in this study could provide novel closed-shell π-conjugated compounds with unusual bond character and a low HOMO–LUMO gap, and further investigations into constructing such molecules is in progress.

Keywords: conjugation · density functional calculations · electronic structure · radicals · structure elucidation

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[5] At room temperature, the ESR for a solid powder sample of **1** was almost silent except for very weak signal (less than 0.5% of that of equimolar galvinoxyl radical) with a typical hyperfine structure of an N-centered monoradical, which could be attributable to the monoprotonated **1**. The somewhat broadened peaks in the ^{1}H NMR spectra of **1** was caused by a trace amount of this monoradical impurity. In addition, the DFT calculations based on the broken symmetry approach (BS-DFT) have been conducted for the open-shell singlet state of **1** by using UB3LYP functional. However, it was confirmed that the calculated results supported the closed-shell singlet electronic state for **1**. Moreover, the triplet energy was found to be higher than the closed-shell singlet energy by 31 kJ mol^{-1} (3700 K) at (U)B3LYP/6-31G*level. Such a large S-T gap suggests that the diradical character of **1** is too small to affect the NMR and ESR measurements.

[6] CCDC 1054708 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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