doi:10.1246/cl.2010.356

Electronic Communication in the Formation of a Quartet Molecule 2,6,10-Tris[bis(*p*-methoxyphenyl)aminium]triphenylene

Takeshi Ibe, Shu Kaiho, Kenichi Oyaizu, and Hiroyuki Nishide*
Department of Applied Chemistry, Waseda University, Tokyo 169-8555

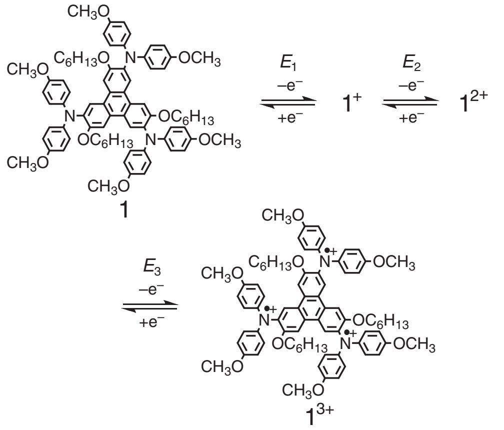
(Received January 5, 2010; CL-100004; E-mail: nishide@waseda.jp)

A quartet triradical molecule, 2,6,10-tris[bis(*p*-methoxyphenyl)aminium]triphenylene, was characterized by the electronic interaction among the three aminium sites based on the fused-aromatic, triphenylene-linked, and non-Kekulé connectivity, which lead to the stable high-spin triradical formation.

Triarylaminium-based and π-conjugated polyradicals have been synthesized in a fashion by satisfying the non-Kekulé, but non-disjoint connectivity of the radical unpaired electrons on their aromatic skeleton in order to investigate them as high-spin organic molecules or as a promising candidate for magnetically-responsive organic materials.[1] Typical examples of such molecules are 1,3,5-tris(diphenylaminium)benzene,[2] 1,3,5-tris[bis(methoxyphenyl)aminium]benzene,[3] and Wurster's blue-based triaminiums.[4] In these triradical molecules, the arylaminiums often produced radicals with sufficient chemical stability, and the significantly delocalized spin density of the arylaminium radicals could allow for a strong exchange interaction to align the radical spins. However, quantitative or defect-free generation of the aminium cationic radicals from the corresponding polyamine derivatives has not been achieved, because electrostatic repulsions among the formed radical cations on the connecting skeleton suppressed the subsequent radical cation formation, especially on the third radical formation.

On the other hand, arylaminium triradicals have been extended to hyperbranched and dendritic polyradical analogs by molecular design of non-Kekulé, but non-disjoint aromatic structures realizing very high-spin organic molecules.[5] The radical generation defect was crucial to forming the target arylaminium polyradicals, because the formation of polycationic structures were significantly suppressed by a strong electrostatic repulsion among the densely populated aminium cations. We recently synthesized 2,6,10-tris[bis(*p*-methoxyphenyl)aminium]-3,7,11-trihexyloxytriphenylene ($\mathbf{1}^{3+}$) to allow planarized conjugation and appropriate distance among amine sites, and succeeded in forming robust chemical stability and quartet state even above room temperature.[6]

In this paper we report for the first time intramolecular electronic communication of the spins in fused aromatic non-Kekulé triaminium formation as the stepwise oxidation of **1** (Scheme 1). Analysis of such radical–radical communication could be important for extending triaminiums toward defect-free and very high-spin poly(aminium radical) molecules. An effective electronic communication among the aminium radical sites through the triphenylene skeleton was described by the electrochemical and structural analyses of **1**.



Scheme 1. Stepwise oxidation of 2,6,10-tris[bis(*p*-methoxyphenyl)amino]-3,7,11-trihexyloxytriphenylene (**1**) to form its trication radical, 2,6,10-tris[bis(*p*-methoxyphenylaminium)-3,7,11-trihexyloxytriphenylene ($\mathbf{1}^{3+}$).

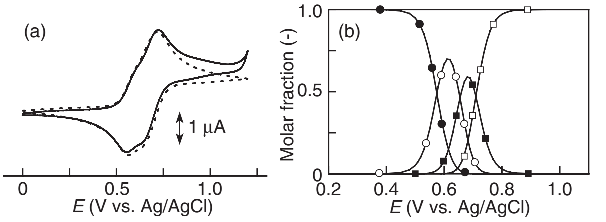


Figure 1. Cyclic voltammogram (solid curve) in a 0.33 mM CH_2Cl_2 solution of 1 with 0.1 M $(C_4H_9)_4NBF_4$ at 50 mV s^{-1} scan rate and the corresponding simulated voltammogram (dashed curve) (a). Molar fraction profile of **1** (●), $\mathbf{1}^+$ (○), $\mathbf{1}^{2+}$ (■), and $\mathbf{1}^{3+}$ (□) equilibrated at each potential vs. Ag/AgCl (b).

The electrochemical study of **1** revealed a stepwise three-electron redox reaction to form $\mathbf{1}^{3+}$. A cyclic voltammogram of **1** at a 50 mV s^{-1} scan rate was repeatedly recorded (Figure 1a) for more than 100 times in the potential range of 0–1.2 V at room temperature, and its oxidation and reduction currents in the redox wave almost coincided with each other. A coulometric analysis at the constant potential of 0.9 V[6] showed the three-electron oxidation of **1**. To determine the redox potentials for the three-electron redox of **1**, the voltammogram was simulated by fitting to the experimental voltammogram with the three redox potentials of E_1, E_2, and E_3 (0.575, 0.655, and 0.710 V, respectively), which corresponded to the equilibrium constant K_1 of 22.5 and K_2 of 8.51 assuming the diffusion coefficients for species **1**, $\mathbf{1}^+$, $\mathbf{1}^{2+}$, and $\mathbf{1}^{3+}$ to be equal. The equilibrium constants, K_1 and K_2, were defined by the following reactions: $\mathbf{1} + \mathbf{1}^{2+} \rightleftharpoons 2(\mathbf{1}^+)$ with $K_1 = [\mathbf{1}^+]^2[\mathbf{1}]^{-1}[\mathbf{1}^{2+}]^{-1} = \exp[(nFR^{-1}T^{-1})(E_2 - E_1)]$ and $\mathbf{1}^+ + \mathbf{1}^{3+} \rightleftharpoons 2(\mathbf{1}^{2+})$ with $K_2 = [\mathbf{1}^{2+}]^2[\mathbf{1}^+]^{-1}[\mathbf{1}^{3+}]^{-1} = \exp[(nFR^{-1}T^{-1})(E_3 - E_2)]$, respectively, where n, F, R, and T are the number of transferred electrons, Faraday's constant, the gas constant, and temperature, respectively. The order of $E_1 < E_2 < E_3$ suggested that the second and third oxidations suffered an electrostatic repulsion from the formed cationic radical(s). However, the potential shift was significantly lower than those reported for the redoxes of a di(arylamine) connected through the *m*-phenylene skeleton, 1,3-bis[bis(*p*-methoxyphenyl)amino]-4,6-dimethylbenzene ($E_1 =$

0.395 and $E_2 = 0.556$ mV vs. Ag/Ag$^+$)[7] and a tri(arylamine) connected through 1,3,5-benzene, 1,3,5-tris[bis(p-methoxyphenyl)amino]benzene ($E_1 = 0.67$, $E_2 = 0.87$, and $E_3 = 0.98$ V vs. SCE).[3b] Based on Nernstian electron-transfer approximations,[8] the equilibrium constants, K_1 and K_2, gave the molar fractions of the starting triamine **1**, the formed cationic radical $\mathbf{1}^+$, dicationic diradical $\mathbf{1}^{2+}$, and tricationic triradical $\mathbf{1}^{3+}$ at each potential (Figure 1b). The molar fraction profile revealed the three one-electron stepwise oxidation processes accompanied by the disproportionation of $\mathbf{1}^+$ and $\mathbf{1}^{2+}$, and the desired potential for the oxidizing agent to form $\mathbf{1}^{3+}$ of >0.9 V.

Another aspect of the electronic delocalization of the aminium radicals through the triphenylene-skeleton could be discussed from the viewpoint of a mixed-valence species. The equilibrium constants, K_1 and K_2, described above correspond to the comproportionation constants[9] for the cationic radical site(s) with the remaining neutral amine site(s) ($\mathbf{1}^+$ and $\mathbf{1}^{2+}$). The K_1 and K_2 values were estimated to be 23 and 9 which were significantly larger than the statistical value[9b] of 4; the aminium cationic radicals $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ could be categorized as a Robin–Day class II cation. The triphenylene-skeleton allowed the electronic interaction among the aminium radical and the neutral amine sites. The shoulder absorption in the near-IR region at 6450 cm^{-1} (1550 nm) that appeared for the **1** solution under the given potential of 0.70 V was ascribed to an intervalence transfer band or a charge transfer from the neutral amine to the aminium cationic radical (See Supporting Information).[10] The 2,6,10-substituted triphenylene skeleton acted as an effective π-conjugation coupler to yield a relatively strong electronic interaction among the radical sites, although the distance between them was not short.

The molecular structure of **1** was determined by the X-ray crystallographic analysis of a single crystal of $\mathbf{1}\cdot CH_3CN$ (Figure 2).[11] The planarized polycyclic fused-aromatic structure of the triphenylene was determined. The molecule displayed a propeller-like geometry in each triarylamine moiety; the dihedral angles between two aryl planes were 65.2, 71.8, and 84.9°, which were almost in the same range as typical triarylamines (e.g., the crystallographic data for the tri-p-tolylamine: 58.9, 76.0, and 79.4°),[12] in spite of the sterically hindered hexyloxy groups at the ortho positions of the amino groups. The atomic arrangement around the nitrogen atom also offered some information about the π-conjugated structure via the triphenylene. For example, the significant absence of nitrogen displacement from the C3–C7–C14 plane (only 0.047 Å) suggested the sp^2 character of these nitrogen atoms. These results supported the molecular design using the planarized triphenylene skeleton without fatal twist of the triarylamine core that leads to the effective electronic communication among the radical sites and results in the high-spin poly(cationic radical) state.

A theoretical calculation was performed based on a density functional method (DFT) at the UB3LYP/6-31G* level with Gaussian 03. The parent compounds of **1**, $\mathbf{1}^+$, $\mathbf{1}^{2+}$, and $\mathbf{1}^{3+}$ without hexyl and methyl substituents were modeled and geometrically optimized by imposing a propeller-conformation on the triphenylamine moieties (similar to the crystal structure) as the initial structure. The computed heat of formation revealed a thermodynamically stable high-spin state for $\mathbf{1}^{2+}$ and $\mathbf{1}^{3+}$; the computed singlet–triplet energy gap, $\Delta E_{S\text{–}T}$ or $2J$ (J: the magnetic exchange coupling constant), for $\mathbf{1}^{2+}$ was calculated to be 4.30 kcal mol^{-1}, supporting the strong ferromagnetic interaction among the aminium radical spins through the triphenylene skeleton even above room temperature.[6] A large spin density was even distributed on the triphenylene in the tricationic state (See Supporting Information).[10] These results also could support the fact that the triphenylene-linker realized the formation of $\mathbf{1}^{3+}$ with delocalized spins.

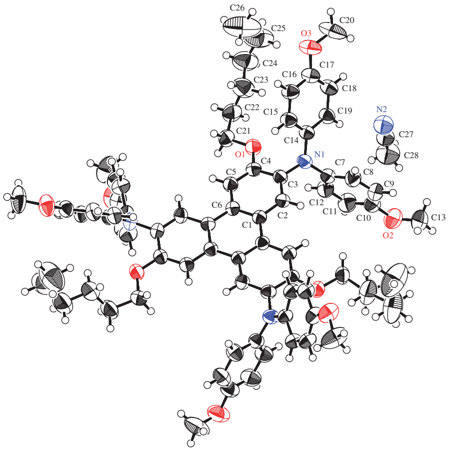


Figure 2. ORTEP diagram of $\mathbf{1}\cdot CH_3CN$.

These studies clearly indicated that the non-Kekulé triphenylene skeleton offered planarized conjugation and significant electronic interaction during the formation of $\mathbf{1}^{3+}$, which realized both a defect-free generation and delocalized spins of the triradical $\mathbf{1}^{3+}$. Such a quartet module could be a building block for very high-spin poly(aminium radical) molecules.

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 19105003), the Global COE program at Waseda University from MEXT, Japan. We thank Dr. M. Shiro for his assistance with the crystallography of $\mathbf{1}\cdot CH_3CN$.

References and Notes

1 a) T. Makarova, F. Palacio, *Carbon Based Magnetism*, Amsterdam, Elsevier, **2006**. b) K. Itoh, M. Kinoshita, *Molecular Magnetism: New Magnetic Materials*, Tokyo and Amsterdam, Kodansha and Gordon & Breach, **2000**.

2 K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi, M. Shiro, *J. Am. Chem. Soc.* **1992**, *114*, 5994.

3 a) S. Sasaki, M. Iyoda, *Chem. Lett.* **1995**, 1011. b) K. R. Stickley, S. C. Blackstock, *J. Am. Chem. Soc.* **1994**, *116*, 11576.

4 a) K. R. Stickley, T. D. Selby, S. C. Blackstock, *J. Org. Chem.* **1997**, *62*, 448. b) A. Ito, D. Sakamaki, H. Ino, A. Taniguchi, Y. Hirao, K. Tanaka, K. Kanemoto, T. Kato, *Eur. J. Org. Chem.* **2009**, 4441.

5 T. Michinobu, J. Inui, H. Nishide, *Org. Lett.* **2003**, *5*, 2165.

6 E. Fukuzaki, H. Nishide, *Org. Lett.* **2006**, *8*, 1835.

7 M. Yano, K. Sato, D. Shiomi, A. Ichimura, K. Abe, T. Takui, K. Itoh, *Tetrahedron Lett.* **1996**, *37*, 9207.

8 A. J. Bard, L. R. Faulkner, *Electrochemical Methods*: *Fundamentals and Applications*, 2nd ed., John Wiley & Sons, New York, **2001**.

9 a) W. Kaim, A. Klein, M. Glöckle, *Acc. Chem. Res.* **2000**, *33*, 755. b) D. E. Richardson, H. Taube, *Coord. Chem. Rev.* **1984**, *60*, 107.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

11 The single crystal of $\mathbf{1}\cdot CH_3CN$ was prepared from an acetonitrile/diethyl ether solution using the vapor diffusion technique. Crystallography: yellow plate from diethyl ether/acetonitrile, $0.40 \times 0.30 \times 0.20$ mm^3, formula: $C_{80}H_{90}N_4O_9$, $M_r = 1251.61$, trigonal, space group $P31c$, $T = 223$ K, $Z = 2$, $a = 16.7364(3)$, $b = 14.4499(3)$ Å, $V = 3505.25$ Å^3, $D_{calcd} = 1.186$ g cm^{-1}, $\lambda(\mathrm{Cu}\,K\alpha) = 1.54187$ Å, $F(000) = 1340$. 32480 reflections were recorded at a threshold intensity of $2\sigma(I)$. 2148 independent reflections were analyzed with 284 parameters using SHELX-97. For 2148 reflections with $I > 2\sigma(I)$ $R(I > 2\sigma) = 0.0516$, $wR(I > 2\sigma) = 0.1506$, goodness of fit on $F^2 = 1.084$.

12 S. L. Reynolds, R. P. Scaringe, *Cryst. Struct. Commun.* **1982**, *11*, 1129.