

Formation of Ground State Triplet Diradicals from Annulated Rosarin Derivatives by Triprotonation

Shunichi Fukuzumi,^{*,†,‡,§} Kei Ohkubo,^{†,‡} Masatoshi Ishida,^{||} Christian Preihs,[⊥] Bo Chen,[#] Weston Thatcher Borden,^{*,#} Dongho Kim,^{*,||} and Jonathan L. Sessler^{*,||,⊥}

[†]Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA and SENTAN, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan

[‡]Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea

[§]Faculty of Science and Engineering, ALCA, SENTAN, Japan Science and Technology Agency (JST), Meijo University, Nagoya, Aichi 468-0073, Japan

^{||}Department of Chemistry, Yonsei University, Seoul 120-749, Korea

[⊥]Department of Chemistry, The University of Texas, Austin, Texas 78712-1224, United States

[#]Department of Chemistry and the Center for Advanced, Scientific Computing and Modeling, University of North Texas, 1155 Union Circle, #305070, Denton, Texas 76203-5070, United States

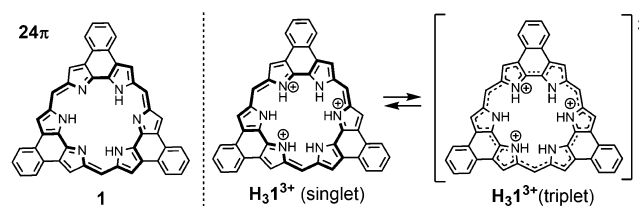
S Supporting Information

ABSTRACT: Annulated rosarins, β,β' -bridged hexaphyrin(1.0.1.0.1.0) derivatives **1**–**3**, are formally 24π -electron antiaromatic species. At low temperature, rosarins **2** and **3** are readily triprotonated in the presence of trifluoroacetic acid in dichloromethane to produce ground state triplet diradicals, as inferred from electron paramagnetic resonance (EPR) spectral studies. From an analysis of the fine structure in the EPR spectrum of triprotonated rosarin $\text{H}_3\mathbf{1}^{3+}$, a distance of 3.6 Å between the two unpaired electrons was estimated. The temperature dependence of the singlet–triplet equilibrium was determined by means of an EPR titration. Support for these experimental findings came from calculations carried out at the (U)B3LYP/6-31G* level, which served to predict a very low-lying triplet state for the triprotonated form of a simplified model system **1**.

Expanded porphyrins are a set of heteroannulenes with π -electron peripheries that are more extensive than their better studied tetrapyrrolic porphyrin congeners.¹ Expanded porphyrins with $[4n]$ annulene character are of particular interest in that they allow predictions about antiaromaticity to be tested experimentally within the context of systems with large π -electron frameworks.

One such prediction is that, although annulated rosarin model **1** is a closed shell species, triprotonation of **1**, should stabilize the lowest triplet state and quite possibly make it the ground state of $\text{H}_3\mathbf{1}^{3+}$ (Scheme 1).² This prediction comes from the results of (U)B3LYP/6-31G* calculations (Figure S1 and Tables S1 and S2 in the Supporting Information, SI). These calculations reveal that in **1** the triplet is 13.4 kcal mol⁻¹ higher in energy than the lowest closed-shell singlet state at C_{3h} geometries. However, in $\text{H}_3\mathbf{1}^{3+}$ the triplet is calculated to be only 1.0 kcal mol⁻¹ higher than the lowest closed-shell singlet state at D_{3h} geometries and just 0.5 kcal mol⁻¹ higher at the lower energy C_2 geometries.

Scheme 1. Structure of Model System **1** and Schematic Representations of Limiting Singlet and Triplet Forms of Its Triprotonated Derivative



The reason why the calculations predict a very low-lying triplet state in $\text{H}_3\mathbf{1}^{3+}$ can be readily understood, based on the depictions, shown in Figure 1, of the two π molecular orbitals (MOs) that are singly occupied in the triplet state. The a_2'' π MO of $\text{H}_3\mathbf{1}^{3+}$ is closely related to the lowest unoccupied (LU)MO of singlet **1**. Both of these MOs have density at all six nitrogen atoms. In contrast, the a_1'' MO of $\text{H}_3\mathbf{1}^{3+}$ and the highest occupied (HO)MO of singlet **1** both have nodes at the nitrogen atoms.

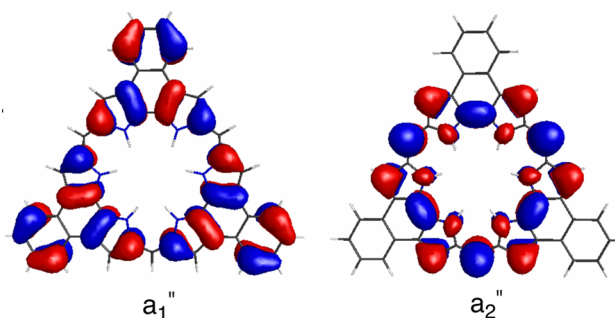


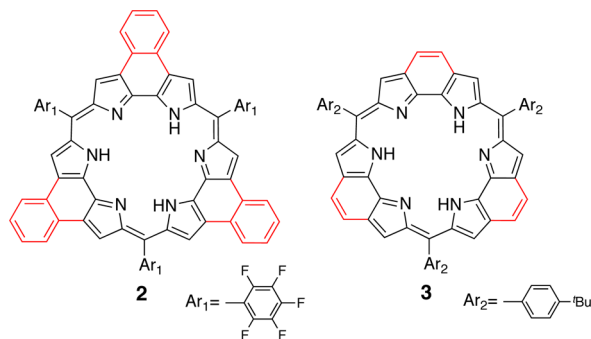
Figure 1. MOs a_1'' and a_2'' of D_{3h} symmetry, which are singly occupied in the lowest energy triplet state of $\text{H}_3\mathbf{1}^{3+}$.

Received: May 22, 2015

Published: July 23, 2015

Adding protons to the unprotonated nitrogens of **1** has the effect of increasing the electronegativity of these nitrogen atoms, thus stabilizing the a_2'' MO, relative to the a_1'' MO, in H_31^{3+} . For example, based on the calculated ionization energies (*IEs*) in the triplet state of **1**, the a_2'' -like MO is found to be higher in energy than the a_1'' -like MO by 12.8 kcal mol⁻¹ in **1**. However, based on the calculated *IEs* in the triplet state of H_31^{3+} , triple protonation of **1** is predicted to result in the a_2'' MO being only 2.1 kcal mol⁻¹ higher in energy than the a_1'' MO in H_31^{3+} .³

Inspection of Figure 1 also shows that the a_1'' and a_2'' MOs of H_31^{3+} have atoms in common. These MOs are nondisjoint;⁴ thus, if they were also exactly degenerate in energy, Hund's rule would apply.⁵ The ground state should then be the triplet. Consequently, the prediction, based on the UB3LYP total energies, that the triplet should either be the ground state of H_31^{3+} or very close to it seems qualitatively reasonable.⁶



Herein, we report the results of experiments on annulated rosarin **2**,⁷ the tris-perfluorophenyl derivative of **1**. Triprotonation of **2** to form H_32^{3+} results in a change in the spin of the ground state and the nearly quantitative formation of a triplet diradical, as evidenced by the low temperature electron paramagnetic resonance (EPR) spectrum of H_32^{3+} .^{8–10} We also carried out experiments on a new β,β' -vinylene-bridged rosarin (**3**). The synthesis and characterization of **3** is provided in the SI.

When HCl was used to protonate **2**, reduction of trication H_32^{3+} by Cl⁻ occurred spontaneously to produce the one-electron reduced species H_32^{2+} .⁷ The resulting radical gives rise to a characteristic EPR spectrum with a *g* value of 2.003 at 77 K. This spectrum proved largely invariant over the range from 77 K to room temperature.

The structure of the presumed intermediate, H_32^{3+} , could not be characterized in detail, due to the technical difficulties associated with preparing this species in solution. In fact, in initial studies, it proved difficult to protonate fully the inner nitrogen atoms of the structurally restricted rosarin **2** with organic acids, presumably as the result of crowding within the cavity of the trication. Therefore, we have explored trifluoroacetic acid (TFA), as a strong, redox-resistant acid that might aid in the stabilization of the hitherto poorly characterized tricationic species, H_32^{3+} . As can be seen from an inspection of Figure 2, addition of up to 1000 mol equiv of TFA to rosarin **2** gives rise to clear spectral shifts in the UV-vis spectrum,¹¹ which are clearly different from those obtained using HCl (Figures S4–5 in the SI).

The EPR spectrum of **2** recorded in the presence of three equiv of TFA in CH₂Cl₂ at extremely low temperature revealed features ascribable to the formation of a triplet diradical (Figure S6 in the SI). However, the resolution in the spectrum was less than desired, possibly reflecting the relatively long distance between the two electrons and their spins in the π -extended rosarin platform that comprises **2** (*vide infra*). In contrast, and as

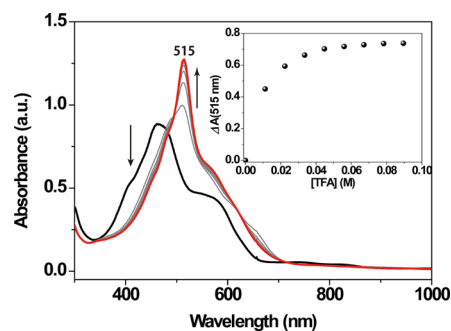


Figure 2. Absorption spectral changes observed upon the addition of TFA (up to 1.0×10^{-2} M) to **2** (1.0×10^{-5} M) in CH₂Cl₂ at 25 °C.

shown in Figure 3a and Figure S7, at 4 K the triply protonated form of the derivative, H_33^{3+} gives rise to a characteristic triplet

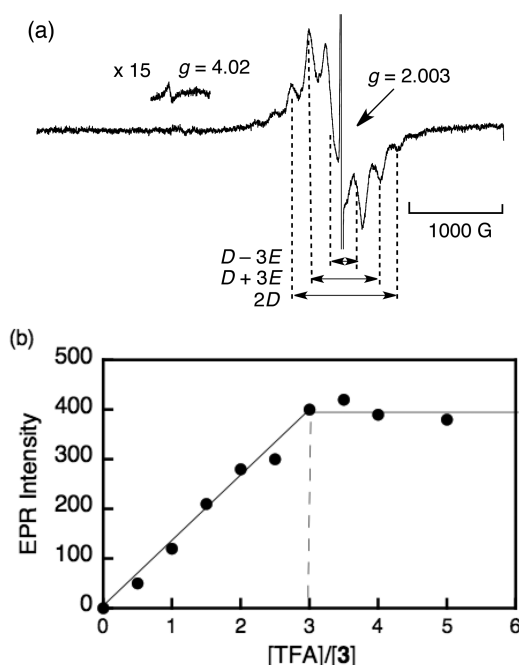


Figure 3. (a) EPR spectrum of a CH₂Cl₂ solution of **3** (1.0×10^{-4} M) in the presence of TFA (3.0×10^{-4} M) measured at 4 K. (b) Plot of EPR intensity of a CH₂Cl₂ solution of **3** in the presence of TFA measured at 4 K vs concentration of TFA.

EPR spectrum with features that are ascribable to zero-field splitting. The EPR parameters of H_33^{3+} were determined to be $g = 2.003$, $D = 577$ G, and $E = 63$ G. The EPR signal intensity increased with increasing concentration of TFA up to three equivalents, to reach a constant value as shown in Figure 3b. This is taken as evidence that rosarin **3** accepts up to three protons to produce H_33^{3+} , just as is observed in the case of the original phenylene-bridged system **2** (Figure S8 in SI).

The amount of spin was calculated by comparing the double integration of the EPR signal of the diradical species derived from **3** on full protonation with that of a known amount of a reference stable radical, 1,1-diphenyl-2-picrylhydrazyl radical (DPPH[•]) as shown in Figure S9 in SI. Normalized for concentration, the signal intensity of H_33^{3+} was approximately 180% that of DPPH[•] at 4 K. On this basis, we conclude that approximately 90% of H_33^{3+} exists as a ground state triplet (diradical) at 4 K.¹² From the zero-field splitting value ($D = 577$ G) shown in Figure 3a, the

distance r between the two electron spins in $\text{H}_3\text{3}^{3+}$ was estimated to be 3.6 Å using the relation, $D = 27800/r^3$.¹³ The r value is consistent with the resonance structures of the triplet state of $\text{H}_3\text{1}^{3+}$ shown in Figure 4 being significant contributors. However, it is to be appreciated that other limiting structures may also contribute to the overall depiction of $\text{H}_3\text{3}^{3+}$ in its triplet state.

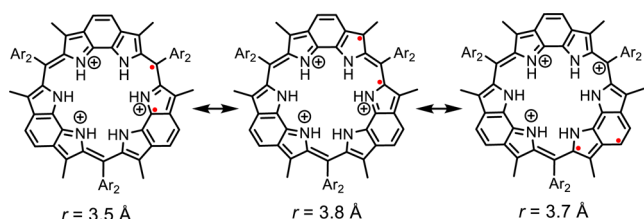


Figure 4. Proposed major contributing resonance structures for $\text{H}_3\text{3}^{3+}$.

From the triplet yield (90%) of $\text{H}_3\text{3}^{3+}$ at 4 K, the equilibrium constant (K) for the conversion from the singlet to triplet was determined to be 9, as calculated using the following equation:

$$\text{H}_3\text{3}^{3+} \underset{\text{singlet}}{\overset{K}{\rightleftharpoons}} [\text{H}_3\text{3}^{3+}]^2_{\text{triplet}}$$

The triplet yield decreased with increasing temperature as shown in Figure 5. From the temperature dependence of K derived from

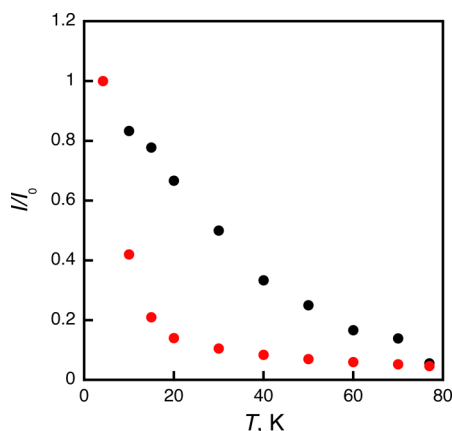


Figure 5. Plot of I/I_0 vs T for the singlet–triplet equilibrium of $\text{H}_3\text{3}^{3+}$ (black circles) and $\text{H}_3\text{2}^{3+}$ (red circles) produced by the triple protonation of **3** and **2**, respectively. [rosarin] = 1.0×10^{-4} M with three equiv of TFA. I , EPR intensity; I_0 , EPR intensity at 4 K.

the data (Figure S10 in SI), the ΔH and ΔS values were determined to be approximately 0.02 kcal mol⁻¹ and 0.2 cal mol⁻¹ K⁻¹, respectively. While the number of data points available for the derivation of these values was limited, the fact that the calculated ΔH and ΔS values were so low is fully consistent with the energy gap between the singlet and triplet states being very small. At 298 K, the triplet yield of $\text{H}_3\text{3}^{3+}$ produced by the reaction of **3** with three equiv of TFA is estimated to be 50%. Based on the above findings, we conclude that triprotonation of **3** produces a $4n$ π -electron species with a small energy gap associated with conversion from the singlet to triplet diradical state. Therefore, the triplet diradical electronic structure was expected to dominate under conditions of enforced full protonation. Such a finding is fully consistent with the theoretical calculations discussed above.

The reversibility of the protonation–deprotonation process was examined in the case of **2**. The addition of excess triethylamine (TEA) to a dichloromethane solution of trication $\text{H}_3\text{2}^{3+}$ gave rise to the original closed shell form of **2**, as inferred from a UV–vis spectral analysis (Figure S12).

In conclusion, the annulated rosarins **2** and **3** are triprotonated upon exposure to three or more equivalents of strong protic acids to produce $\text{H}_3\text{2}^{3+}$ and $\text{H}_3\text{3}^{3+}$, respectively. The triprotonated rosarins are found to exist primarily as triplet diradical species at 4 K. The energy difference between the singlet and triplet state is very small (0.02 kcal mol⁻¹). To the best of our knowledge, this is the first time the acid-induced formation of triplet diradical species has been reported. The present systems also represent a rare example of an antiaromatic species whose electronic configuration may be readily modified by application of an external chemical stimulus. The present work thus highlights a new approach to controlling the fundamental properties of highly conjugated systems.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05309.

Experimental details, computational methods, structures and MO pictures of **1**, H1^+ , and $\text{H}_3\text{1}^{3+}$ (Figure S1), relative energies of the electronic states of **1**, H1^+ , and $\text{H}_3\text{1}^{3+}$ (Table S1), ionization energies of SOMOs of triplet states of **1**, H1^+ , and $\text{H}_3\text{1}^{3+}$ (Table S2), relative energies of the electronic states of **4** (Table S3), geometries and absolute energies of calculated structures (Table S4), and TD-DFT excitation energies (Table S5) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*fukuzumi@chem.eng.osaka-u.ac.jp

*sessler@cm.utexas.edu

*dongho@yonsei.ac.kr

*weston.borden@unt.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid (Nos. 26620154 and 26288037 to K.O.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, the U.S. National Science Foundation (grant CHE-1402004 to J.L.S.), the Robert A. Welch Foundation (grant F-1018 to J.L.S. and B0027 to W.T.B.), and NRF/MEST of Korea through the WCU (R31-2008-000-10010-0 and R32-2010-000-10217-0) and GRL (2010-00353) Programs.

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(3) Our (U)B3LYP calculations also reveal that in the C_{2v} isomer of the monoprotonated species, H_11^+ , the triplet is $8.7 \text{ kcal mol}^{-1}$ higher than the lowest closed-shell singlet state, and the *IE* of the a_2'' -like MO (b_1 in C_{2v} symmetry) is $8.0 \text{ kcal mol}^{-1}$ lower than that of the a_1'' -like MO (a_2 in C_{2v} symmetry). The B3LYP values of ΔE_{ST} and of ΔIE (HOMO – LUMO) in **1**, H_11^+ , and H_31^{3+} make it appear that each proton that is added to **1** decreases both ΔE_{ST} and ΔIE by ca. 4 kcal mol^{-1} .

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(6) In test calculations, carried out using a model molecule **4** for H_31^{3+} where the nitrogen atoms are replaced by CH_2 moieties and the benzene rings are omitted, different predictions about whether the triplet is actually the ground state of H_31^{3+} were obtained by different types of calculations. Unfortunately, the size of **1** and its protonated derivatives makes it impossible to perform calculations at high enough levels of theory to make the computational results definitive. However, we have recently found that, in another molecule where this was the case, a Hund's rule argument, based on the very similar *IE*s of the MOs that are singly occupied in the triplet state, correctly predicts that the triplet is, in fact, the ground state. See (a) Zhou, X.; Hrovat, D. A.; Borden, W. T. *J. Phys. Chem. A* **2010**, *114*, 3683. (b) Guo, J.-C.; Hou, G.-L.; Li, S. D.; Wang, X.-B. *J. Phys. Chem. Lett.* **2012**, *3*, 304. (c) Bao, X.; Hrovat, D. A.; Borden, W. T.; Wang, X. B. *J. Am. Chem. Soc.* **2013**, *135*, 4291.

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(11) TD-DFT calculations at the UB3LYP/6-31G(d) level predict no change in the UV spectrum on formation of singlet H_31^{3+} from **1** but a small red shift on formation of triplet H_31^{3+} . Therefore, the experimental observation of a small red shift upon formation of H_32^{3+} is consistent with a triplet ground state for this trication. Addition of base reverses these spectral changes, as noted in the main text.

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