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Synthesis and Identification of a Trimethylenemethane Derivative π-Extended with Three Pyridinyl Radicals

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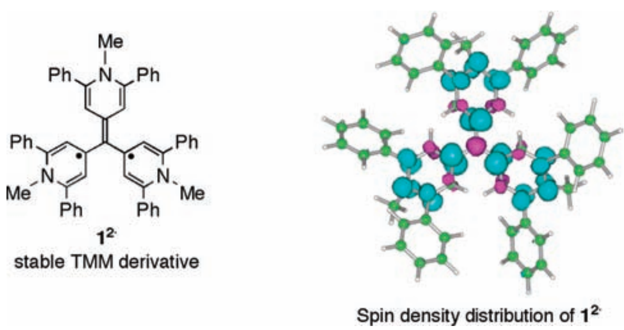
ABSTRACT



A trimethylenemethane (TMM) derivative $1^{2\cdot}$, in which the parent TMM is π-extended by the symmetric insertion of three pyridine rings into the C−C bonds of TMM, has been synthesized by the alkali metal reduction of the isolated corresponding dication. Although the frozen-glass X-band cw-ESR spectrum of $1^{2\cdot}$ gave unresolved fine structures due to the small ZFS parameters, pulsed ESR two-dimensional electron spin transient nutation (2D-ESTN) spectroscopy unambiguously can afford to identify diradical $1^{2\cdot}$ as a triplet species.

Trimethylenemethane (TMM) is the simplest non-Kekulé hydrocarbon[1] and has attracted much attention in variuos fields of chemistry and materials science, such as theoretical chemistry,[2] reactive intermediate,[3] organic synthesis,[4] and molecular magnetism.[5] Since the first detection of TMM by Dowd,[6] a number of TMM derivatives have been studied.[7] A drawback to the studies of TMM derivatives is that the

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parent TMMs can survive only at cryogenic temperature. Thus, a synthetic challenge relevant to TMM derivatives is to chemically stabilize this fascinating π-electron system. To our knowledge, there are only a few examples of stable ground-state triplet TMM derivatives. Yang's diradical, as shown in Figure 1, is such a TMM derivative and has been thoroughly investigated. Its ESR spectrum, magnetic susceptibility, and X-ray crystallographic analysis were reported.[8] Iwamura and Matsuda reported a TMM-based bis(nitroxide) diradical (see Figure 1) whose Mn^{II} complex exhibited the phase transition to a molecule-based bulk magnet at 5 K.[9] Among intriguing stable TMM-based diradicals, more recently, Rajca and co-workers reported a remarkably stable hydrocarbon diradical based on the TMM framework (see Figure 1).[10] The quest for new stable TMM derivatives can afford to contribute to the further development of TMM-based open shell chemistry. We have designed a new TMM diradical **1**$^{2\cdot}$ (see Figure 1), in which TMM is π-extended symmetrically with three pyridinyl radical moieties. Since the 2,4,6-triphenylpyridinyl radical is fairly stable[11] and the unpaired electron spins of pyridinyl radicals are delocalized over the sizable pyridinyl ring, **1**$^{2\cdot}$ is expected to be a stable TMM-based diradical with strong intramolecular ferromagnetic coupling.[12] Here we report the synthesis and direct identification of diradical **1**$^{2\cdot}$ by pulsed ESR-based two-dimensional electron spin transient nutation (2D-ESTN) spectroscopy.[13]

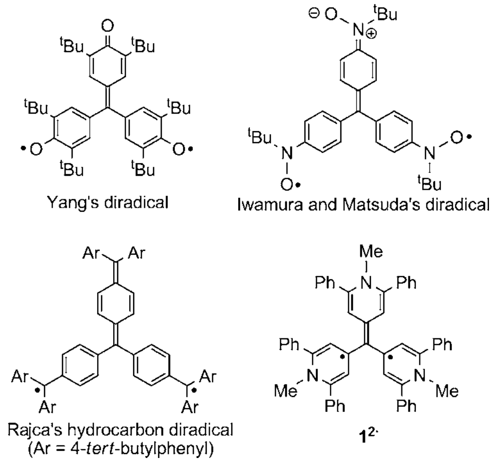
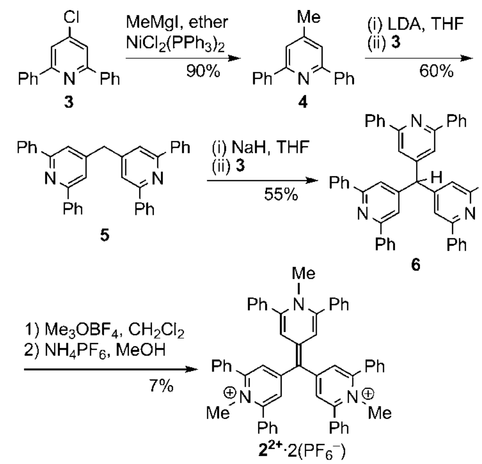


Figure 1. Stable TMM-based diradicals.

The synthesis of dication **2**$^{2+}$, which is the precursor of the targeted diradical **1**$^{2\cdot}$, is illustrated in Scheme 1. Kumada−Tamao coupling of 2,6-diphenyl-4-chloropyridine (**3**)[14] with methylmagnesium iodide in the presence of nickel catalyst afforded the corresponding 4-methyl derivative **4**[15] in excellent yield. A tris(4-pyridyl)methane derivative **6** was obtained from **4** by iterative deprotonation−nucleophilic substitution of **3** by way of bis(4-pyridyl)methane derivative **5**.[16] Tri-*N*-methylation of **6** was accomplished with trimethyloxonium tetrafluoroborate to give dication **2**$^{2+}$. Since the BF_4 salt of **2**$^{2+}$ hardly crystallized, counterion exchange

Scheme 1. Synthesis of **2**$^{2+}$



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was carried out to obtain the PF_6 salt of $\mathbf{2}^{2+}$, which was obtained as dark red crystals with green luster.

A single crystal of $\mathbf{2}^{2+}\cdot 2(PF_6^-)$ for X-ray crystallographic analysis was obtained from a chloroform solution by the technique of slow vapor diffusion with hexane (Figure 2).[17]

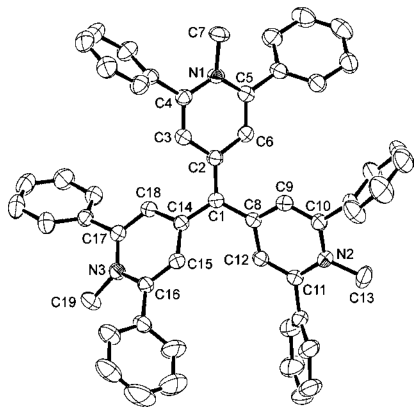

Figure 2. ORTEP drawing of $\mathbf{2}^{2+}$ (50% probability). Hydrogen atoms, PF_6^- ions, and $CHCl_3$ molecules are omitted for clarity.

A relatively large R_1 value is mainly due to the disorder of chloroform molecules, and the molecular structure of $\mathbf{2}^{2+}$ is well determined. Although $\mathbf{2}^{2+}$ does not take C_3 symmetry in the crystal, the structures of the three *N*-methylpyridinium moieties are similar. The valence bond plane of the central carbon atom is approximately planar (the sum of the bond angles around C1 is 359.9°). Three pyridinium rings form a propeller structure, and the dihedral angles between the pyridinium rings and the central C1−C2−C8−C14 plane are 47.0°, 23.7°, and 30.8°. Judging from the bond lengths, the contribution of the quinonoid structure is appreciable in all the pyridinium rings, indicating that two positive charges are delocalized over the three pyridinium rings. On the other hand, the dihedral angles between the phenyl groups and pyridinium rings are relatively large (in the range of 44.8°−79.1°). This may be due to the steric repulsion between the phenyl group and the adjacent methyl group on the nitrogen site. The repulsion causes the deformation of the pyridinium ring into a boat form. As a result, the methyl groups are deviated from the plane of the pyridinium ring.

To estimate the stability of diradical $\mathbf{1}^{2\cdot}$, the redox properties of $\mathbf{2}^{2+}\cdot 2(PF_6^-)$ were examined by cyclic voltammetry (Figure 3). Dication $\mathbf{2}^{2+}$ exhibited two reversible reduction waves (${}^{red}E_1 = -1.61$ V, ${}^{red}E_2 = -2.04$ V vs Fc/Fc$^+$) as well as one reversible oxidation wave (${}^{ox}E_1 = +0.40$ V).[18] Peak intensities observed in the CV and NPV (normal pulse voltammetry) measurements[19] revealed that the two reduction and oxidation waves involve two-electron and one-electron processes, respectively. Therefore, dication $\mathbf{2}^{2+}$ exhibits a multiredox system from tricationic monoradical to dianion with high reversibility. This suggests that diradical $\mathbf{1}^{2\cdot}$ is a fairly stable species although the overreduction yields the corresponding anion or dianion.

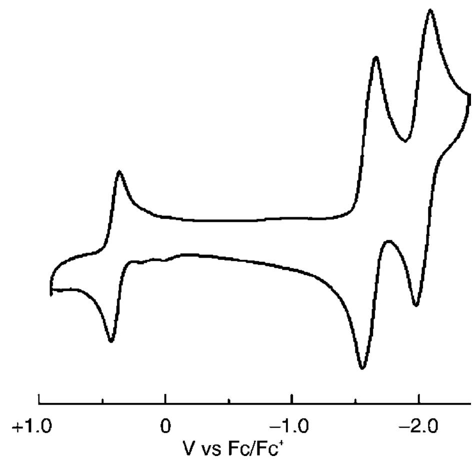

Figure 3. Cyclic voltammogram of $\mathbf{2}^{2+}\cdot 2(PF_6^-)$ in acetonitrile.

Alkali metal reduction of $\mathbf{2}^{2+}\cdot 2(PF_6^-)$ was performed with 3% Na−Hg in the mixture of degassed acetonitrile-2-methyltetrahydrofuran (2-MTHF). The reduction was monitored by UV−vis-NIR spectroscopy (Figure 4a). The absorption peak at 540 nm due to $\mathbf{2}^{2+}$ slightly decreased in intensity by reduction, and a new broadband appeared in the range of 700−1000 nm. This broad absorption is ascribable

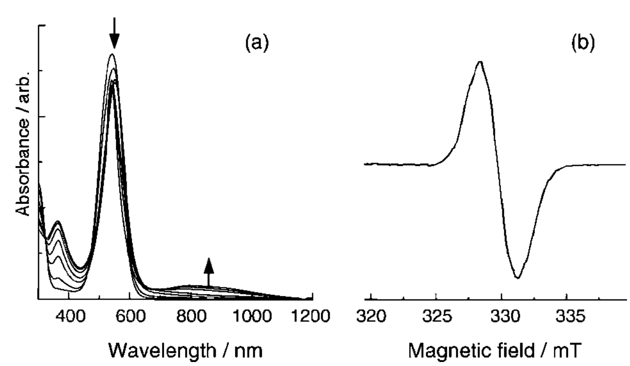

Figure 4. (a) UV−vis−NIR spectral change upon the reduction of $\mathbf{2}^{2+}\cdot 2(PF_6^-)$ with 3% Na−Hg. (b) X-band ESR spectrum of diradical $\mathbf{1}^{2\cdot}$ in CH_3CN−MTHF at 77 K.

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(17) Crystallographic data for $\mathbf{2}^{2+}\cdot 2(PF_6^-)\cdot 1.3CHCl_3$: $C_{56.3}H_{46.3}Cl_{3.9}F_{12}N_3P_2$, $FW = 1193.10$, monoclinic, space group $P2_1/a$ (no. 14), $a = 17.276(5)$, $b = 17.432(5)$, $c = 18.466(5)$ Å, $\beta = 91.919(13)°$, $V = 5558(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.426$ g·cm^{-3}, $T = 200$ K, of the 49 171 reflections which were collected, 12 553 were unique ($R_{int} = 0.037$) used in refinement. $R1 = 0.098$ (8475 data, $I > 2\sigma(I)$), $wR2 = 0.342$ (all data), GOF = 1.305.

to the formation of diradical **1**$^{2\cdot}$, noting that Yang's biradical also exhibits the weak absorption ($\lambda_{max} = 810$ nm)[8f] in a similar range. The spectrum of **1**$^{2\cdot}$ remained unchanged under the inert atmosphere at room temperature, suggesting the high stability of **1**$^{2\cdot}$. This absorption band due to **1**$^{2\cdot}$ disappeared by further reduction, probably due to formation of the corresponding dianion species. When the intensity of the absorption in 700−1000 nm became maximized, we measured X-band cw-ESR spectra at 77 K in the same acetonitrile-2-MTHF glass (Figure 4b). As expected from the extended nature of the π-electron network of **1**$^{2\cdot}$ and the geometrical symmetry of its molecular structure, only a broad signal with shoulder wings corresponding to canonical peaks due to the fine-structure D tensor was observed, suggesting the existence of triplet species in addition to doublet species such as radical cation or radical anion species. The signal region of the ESR spectrum covers about 10 mT, and the estimated zero-field parameter, D-value ($|D| = 0.002$ cm^{-1}), is comparable to those of reported TMM derivative diradicals.[7b,8i,9a,10] Apparently, the signals of diradical **1**$^{2\cdot}$ were masked by the doublet species. The fine-structure forbidden transitions due to $\Delta M_s = \pm 2$ were too weak to be detected, being consistent with the calculated transition intensities.

To confirm the existence of the targeted diradical **1**$^{2\cdot}$ in a straightforward manner, we measured pulse ESR-based X-band two-dimensional electron spin transient nutation (2D-ESTN) spectra of **1**$^{2\cdot}$. The 2D-ESTN spectroscopy as transition moment spectroscopy is a powerful method for the discrimination of spin multiplicity when the sample contains the chemical species of different spin multiplicity.[20]

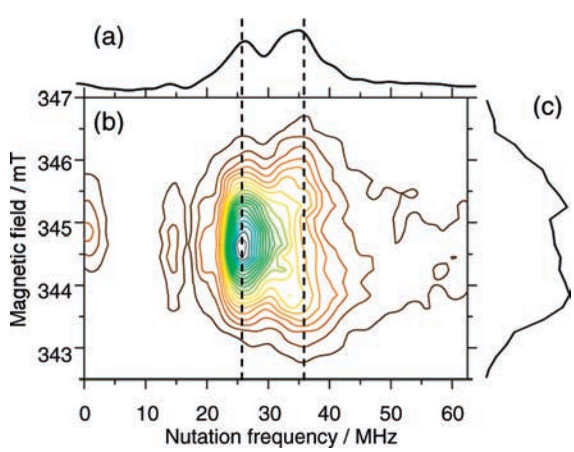

Figure 5. Slices and contour plot of the 2D-ESTN spectra of diradical **1**$^{2\cdot}$ ($T = 50$ K, $\nu_{MW} = 9.667854$ GHz). (a) Field slice of the 2D-ESTN spectra at 345.9 mT. (b) Contour plot. The broken lines at 25.2 and 35.5 MHz correspond to the doublet and triplet species, respectively. (c) Frequency slice of the 2D-ESTN spectra at 35.5 MHz.

Figure 5 shows the field-swept 2D-ESTN spectra of diradical **1**$^{2\cdot}$ observed at 50 K. Besides an intense nutation frequency peak at 25.2 MHz, nutation peaks corresponding to the canonical orientations are observed at 35.5 MHz. The latter peak at 35.5 MHz is unequivocally recognized from the field slice of the ESTN spectrum at 345.9 mT (Figure 5a). A ratio of the observed nutation frequencies, 35.5/25.2, corresponds to that of $\sqrt{2}/1$ expected for a triplet state from the equation of $\omega_n = [S(S + 1) - M_s(M_s - 1)]^{1/2}\omega_1$ in the weak limit of microwave excitation for $S = 1$, where ω_1 denotes the nutation frequency for $S = 1/2$.[19] Therefore, the nutation frequency peaks at 35.5 MHz are assignable to the XY canonical peaks of triplet-state diradical **1**^{2} in a straightforward manner. The contour plot illustrates that the triplet species is not a trace species but contributes a great deal to the field-swept ESTN spectra. It seems reasonable that the $|D|$ value of **1**$^{2\cdot}$ is comparable to that of Yang's diradical, by confirming that the observed nutation peaks at 35.5 MHz are ascribed to the canonical transitions from the triplet state in our ESTN experiments. Sophisticated quantum chemical calculations of zero-field splitting tensors for TMM and sizable TMM derivatives are underway.[21]

In summary, we have synthesized a novel TMM diradical **1**$^{2\cdot}$ as a stabilized TMM derivative. Diradical **1**$^{2\cdot}$ with three pyridinyl moieties is stable under an inert atmosphere at room temperature. The spin multiplicity of **1**$^{2\cdot}$ has unambiguously been identified as a triplet species by pulse ESR-based 2D-ESTN spectroscopy. The experimental D value of **1**$^{2\cdot}$ has been derived from the contour plot of the 2D-ESTN spectra and is comparable to that of Yang's diradical. This finding suggests that the spin distribution of **1**$^{2\cdot}$ is extended over the three pyridinyl moieties, being consistent with the molecular orbital calculation. The experimental determination of the ground state for diradical **1**$^{2\cdot}$, the isolation, and quantum chemical calculations of the zero-field splitting tensors for TMM and its sizable derivatives are in progress.

Acknowledgment. This work was supported by a Grant-in Aid for Scientific Research (No. 21750045) from the Japan Society for the Promotion of Science and the Global COE program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University.

Supporting Information Available: Experimental procedures and product characterization for all new compounds and the X-ray crystallographic data for compound **2**$^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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