

Spin–spin interaction in a highly stable neutral diradical: σ -bonded dimer of trioxotriangulene

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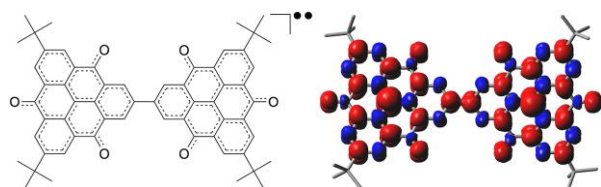
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Abstract

A σ -bonded dimer of 4,8,10-trioxotriangulene (TOT) was newly synthesized and its electronic spin structure was characterized. The neutral diradical had a singlet ground state due to the strong antiferromagnetic interaction through the σ -bond. The strong intramolecular interaction within the σ -dimer caused a near-infrared photoabsorption of around 700–1,000 nm, which is close to that of the π -stacked dimer of TOT monoradical.

Keywords: electron spin resonance, neutral diradicals, trioxotriangulenes.

Graphical Abstract



A dimer of 4,8,10-trioxotriangulene (TOT) neutral radical linked through the direct C–C σ -bond was synthesized. The electronic spin of the TOT skeletons delocalized over the whole molecular skeleton and the dimer showed strong intramolecular electronic and magnetic interactions. The DFT calculation and ESR measurement suggested the singlet ground state of the dimer with a strong antiferromagnetic interaction.

Organic open-shell molecules have attracted much attention in recent years as potential functional materials with various applications¹ such as molecular spintronics,² organic magnets,³ organic batteries,⁴ molecular-spin quantum information technology,⁵ etc. Organic radical oligomers and polymers having multiple electronic spins are attractive molecular systems whose electronic states can be manipulated by controlling their intramolecular spin–spin interactions.⁶ However, the high reactivity and synthetic difficulty of open-shell molecules have always remained challenges to obtaining these exotic phenomena and functions. A number of stable organic radicals, such as nitroxide, phenoxide, triphenylmethyl-types, etc., have been synthesized over the years.¹ However, in many of these organic radicals, the electronic spins are localized at specific positions in the molecules and, in most cases, intramolecular spin–spin exchange interactions of these radical oligomers and polymers are extremely weak. This is related to the small electronic spin density at the linking site (usually the periphery of the molecule) and the long distance between the radical centers. On the other hand, in the cases of radical oligomers of neutral π -radicals such as phenalenyl,⁷ dithiazolyl,⁸ and Blatter radicals,⁹ the electronic spin delocalizes throughout the entire molecular skeleton, including the linking site, and their radical oligomers, linked via direct

σ -bonds or π -linkers, can exhibit strong spin–spin interaction due to the π -connections.

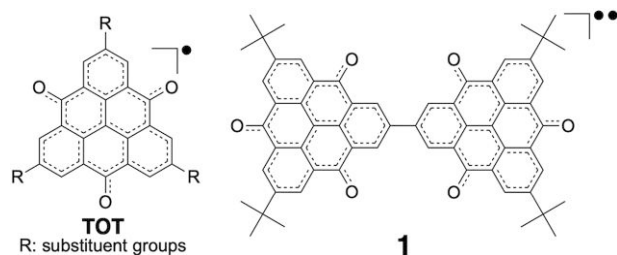
Recently, we developed a stable neutral π -radical, 4,8,10-trioxotriangulene (TOT, Scheme 1), using the topological design of the delocalized electronic spin structure.¹⁰ One of the most peculiar features of the TOT neutral radical is the high air and thermal stability even in the absence of steric protection effects and TOT can be fabricated into thin and thick films using a vapor deposition method.¹¹ The stability of the TOT neutral radical is maintained even when various chemical modifications are made around the molecular skeleton.¹² Furthermore, TOT neutral radicals exhibit strong intermolecular singly occupied molecular orbital (SOMO)–SOMO interactions based on two-electron-multicenter bonding,¹³ which derives interesting physical properties such as high electrical conductivity.^{10,14} Recently, we successfully realized a TOT neutral radical dimer with a triplet ground state ($J/k_B \sim +3.5$ K) in which 2 TOT skeletons are linked via an *m*-phenylene spacer.¹⁵ In addition, a recent theoretical study by Bredas and coworkers suggested that a 2D π -conjugated covalent organic framework composed of TOT neutral radicals possesses a high potential for exhibiting intriguing electrical/magnetic properties.¹⁶

Here, a neutral diradical, in which 2 TOT skeletons are directly linked via a C–C σ -bond (1, Scheme 1), is the most

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Scheme 1. Chemical structures in text. R indicates the substituent groups.

fundamental molecule of TOT-based radical oligomers and polymers, and provides essential information about the intramolecular spin–spin interactions. In this study, we have newly synthesized a neutral diradical **1** and elucidated its electronic spin properties. Here, the periphery of the molecular skeleton was substituted with 4 *tert*-butyl groups to acquire the solubility of the diradical species in common organic solvents. It should be noted that diradical **1** may exhibit interesting electronic phenomena in the solid state that were demonstrated in the phenalenyl-type singlet biradicals^{7d,7e} due to the cooperation of spin–spin interactions within as well as outside of the molecule. The investigation of neutral radical dimers/oligomers composed of TOT would lead to the exploration of new electronic properties and functions based on the cooperation of intra/intermolecular spin–spin interactions.

To elucidate the electronic spin structure and spin–spin interaction via the σ -bond within diradical **1**, we performed density functional theory (DFT) calculations for both singlet and triplet states. However, the electronic spin structure of **1** calculated for the singlet state showed a behavior that was different from that suggested by the experimental results described below (Supplementary Fig. S1). Therefore, the result calculated for the triplet state was used in the following discussion of the electronic spin properties of **1** (Fig. 1). In the optimized structure, 2 TOT skeletons were twisted by $\theta = 35.2^\circ$ due to the steric repulsion between adjacent hydrogen atoms. The electronic spin-density distribution on 2 TOT skeletons of **1** was quite similar and the electronic spin structure was symmetrical. As for one TOT skeleton, the electronic spin density of the central carbon atom (C^c in Fig. 1) was the largest and those of the β -carbon atoms (C^4 and C^5) were larger than those of the α -carbon atoms (C^1 – C^3). These characteristics are the same as those of the TOT monomer. The distance between the central carbon atoms (C^c) of the largest electron spin density within **1** was around 10 Å. Both carbon atoms at the linking site (C^4) possess positive spins and that suggests that a bonding interaction is formed between 2 TOT skeletons. The exchange interaction between 2 radical spins within **1** was calculated, using the Broken symmetry method,¹⁷ to be $J/k_B = -475$ K, suggesting a strong intramolecular anti-ferromagnetic interaction. In the TOT monomer, the electronic spins at all 6 α -carbons are the same; however, in diradical **1**, those of the α -carbons near the linking site were smaller than those of the others (C^1 : -0.056 vs C^2 and C^3 -0.074 , Supplementary Table S1). This difference is considered to have been caused by the effect of anti-ferromagnetic interaction between 2 TOT skeletons. The effect of twist angles θ between 2 TOT skeletons within **1** was investigated (Supplementary Table S1). The anti-ferromagnetic interaction between the 2 TOT skeletons was strongest in the completely flat shape

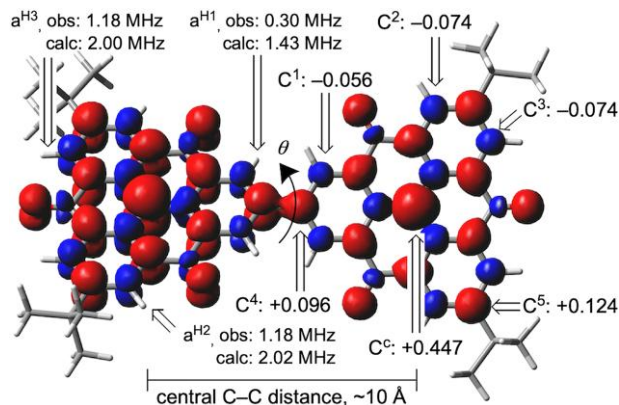
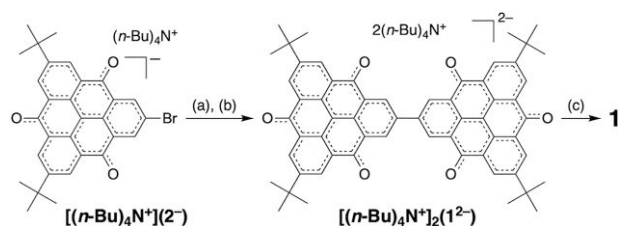


Fig. 1. Calculated spin-density distributions of **1** with the triplet state calculated at the UB3LYP/6-31G(d, p) level in the optimized structure. The red and blue colors denote positive and negative spin densities, respectively. The numerical values represented by C and a^H are electronic spin densities of the carbon atoms and hyperfine coupling constants of the hydrogen atoms (observed and calculated), respectively. The values of symmetrically equivalent atoms are averaged.

($\theta = 0^\circ$, $J/k_B = -700$ K), weakened as θ increased, and became negligible at $\theta = 90^\circ$. In addition, the electronic spin density of the α -carbon at the C1 site increased with increasing θ , and it became as large as the other ones at $\theta = 90^\circ$. This result indicates that the influence of through-bond interaction via the σ -bond is dominant in **1**, where direct bonding of delocalized electronic spins produces strong spin–spin coupling. It should be noted that, since the rotational barrier between 2 TOT skeletons in **1** is expected to be small, the effect of twist angle θ is thought to be approximately averaged. Similarly to “singlet diradicaloids” such as tschitschibabin hydrocarbons and indacenodiphenalene derivatives,¹⁸ **1** can also be drawn as a close-shell electronic structure. The natural orbital occupation number analysis¹⁹ indicated that the diradical contribution of **1** was 76% in the optimized structure, indicating that the diradical structure has a significant contribution (Supplementary Table S1). The diradical contribution increased when the twist angle increased (Supplementary Table S1), suggesting the importance of the through-bond spin–spin coupling.

The synthetic method of neutral diradical **1** is shown in Scheme 2. The homo-coupling reaction of the monobromo TOT derivative $[(n\text{-Bu})_4\text{N}^+](2^-)$ ¹⁵ using $\text{Ni}(\text{COD})_2/2$, 2'-bipyridine followed by the treatment with $(n\text{-Bu})_4\text{N}^+\text{OH}^-$ afforded the dianion salt $[(n\text{-Bu})_4\text{N}^+]_2(1^{2-})$. The oxidation of the dianion salt with an excess amount of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in a CH_2Cl_2 solution yielded diradical **1** and the purification was carried out using silica-gel column chromatography in air. Similarly to other TOT neutral radical monomers,¹⁰ diradical **1** can be treated under air in both solution and solid states, and was stable for 1 month in a CH_2Cl_2 solution (Supplementary Fig. S2).

The electrochemical behavior of **1** was studied using the differential pulse voltammetry (DPV) of $[(n\text{-Bu})_4\text{N}^+]_2(1^{2-})$ in a tetrahydrofuran (THF) solution (Fig. 2; see also Supplementary Fig. S3). The oxidation of dianion 1^{2-} to generate the neutral diradical **1** occurred at -0.36 vs Fc/Fc^+ , whereas the monomer 3^- (tri-*tert*-butylated TOT anion) showed one oxidation peak (E_1 , -0.46 V). The weak wave (-0.22 V) near the E_1 peak of 1^{2-} may suggest that the 2 TOT skeletons in 1^{2-} are individually oxidized due to the electrostatic interaction.¹⁵ Similarly, the reductions of 1^{2-} (E_2 and E_3) were also observed as double



Scheme 2. Synthesis of **1**. Reagents and conditions: (a) 2 equiv Ni(COD)₂, 2 equiv 2,2'-bipyridine, 300 wt% molecular sieves 4A, DMF, 50 °C; (b) excess (n-Bu)₄N⁺OH⁻, acetone, rt; (c) excess DDO, CH₂Cl₂, rt.

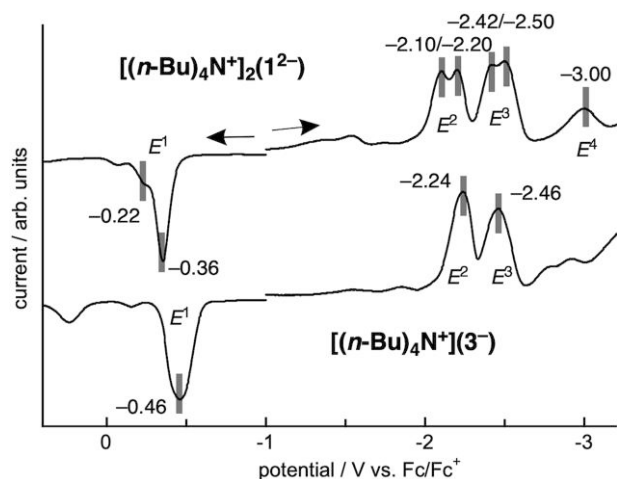


Fig. 2. Differential pulse voltammetry (DPV) of **1** and **3** in THF solution. The results were calibrated with a ferrocene/ferrocenium couple (Fc/Fc⁺). Corresponding dianion and monoanion salts, [(n-Bu)₄N⁺]₂(1²⁻) and (n-Bu)₄N⁺3⁻, respectively, were used for the measurement.

waves at almost the same potentials as the monoanion 3⁻. This result indicates that the electrostatic interaction between the 2 TOT skeletons is effective also in the anionic states.

To elucidate the electronic spin structure of **1**, we carried out electronic spin resonance (ESR) measurement in a degassed toluene solution (1.0×10^{-5} M) (Fig. 3a). The ESR spectrum at 293 K showed a broad signal with hyperfine structures owing to the contributions from small hyperfine splitting. The observed g -value was 2.0030, which was similar to that of **3** ($g = 2.0042$).²⁰ The ESR spectrum is well reproduced by the 3 kinds of hyperfine couplings (Fig. 3a). Considering the molecular symmetry, the observed hyperfine couplings of the protons (a^H) were assigned with the help of DFT calculations (Fig. 1) and are summarized in Supplementary Table S1. The a^H values of 1.18 MHz are assignable to α -protons in the TOT skeleton (a^H2 and a^H3 in Fig. 1) and were approximately half the corresponding values of monomer **3** (2.46 MHz).²⁰ This observation suggests that the intramolecular exchange interaction between the 2 TOT units in **1** is significantly larger than the hyperfine coupling of protons, and that 2 unpaired electrons extensively delocalize on the whole π -electronic system of **1**, as shown in Fig. 1. The a^H1 value of the α -proton neighboring the linking site, at 0.30 MHz, was significantly smaller than those of the others. This result showed good agreement with the DFT calculation in which the electronic spin density at the C1 site was small and is experimental evidence of the strong antiferromagnetic interaction through the σ -bond (Fig. 1).

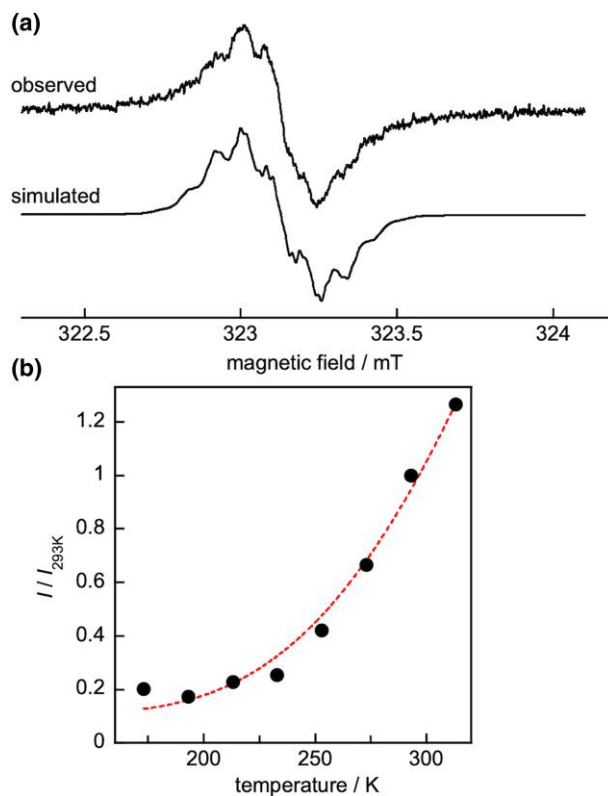


Fig. 3. a) Observed and simulated ESR spectra of **1** in toluene at 293 K. b) Temperature dependence of the ESR intensity of **1** in toluene. Plots denote the experimental values normalized at 293 K.

In the temperature-dependent ESR spectra of the toluene solution at 173–313 K, the signal intensity became smaller when the temperature was lowered (Figs. 3b and Supplementary S4). The result indicates that the electronic spins of 2 adjacent TOT skeletons are canceled out by the intramolecular antiferromagnetic interaction or by the aggregation through intermolecular π - π interaction. Here, it was not possible to separate the contributions of intra- and intermolecular interactions. In order to roughly evaluate the spin-spin interaction, we fitted the temperature dependence of the ESR signal intensity by simply using the singlet-triplet model,²¹ which suggested a strong antiferromagnetic interaction of $J/k_B < -900$ K (-0.94 kcal/mol, Fig. 3b). Since this fitting would include the influences of both intra- and intermolecular interactions, a simple comparison cannot be made, although the absolute value in **1** is dramatically larger than that of the m -phenylene dimer of our previous study, at $J/k_B \sim +3.5$ K.¹⁵ The $|J/k_B|$ of **1** was close or higher than those of directly linked nitroxide and trioxotriphenylamine dimers^{22,23} and the radical dimers linked through π -conjugation.²⁴

In the solution-state electronic spectra, **1** exhibited a low-energy absorption band of around 700–1,000 nm (Fig. 4). Similar absorption bands are also observed in TOT derivatives such as **3** ($\lambda_{\max} = 835$ nm) and are attributed to intermolecular transitions within π -dimers.²⁰ At a higher temperature, an absorption maximum was observed at around 800 nm and the intensity decreased with temperature lowering, and then an absorption at 880 nm became stronger at the lower temperature. The former band would relate to the intramolecular transition between 2 TOT skeletons and the latter can be identified as the intermolecular transitions in the π -dimer of **1**.²⁰

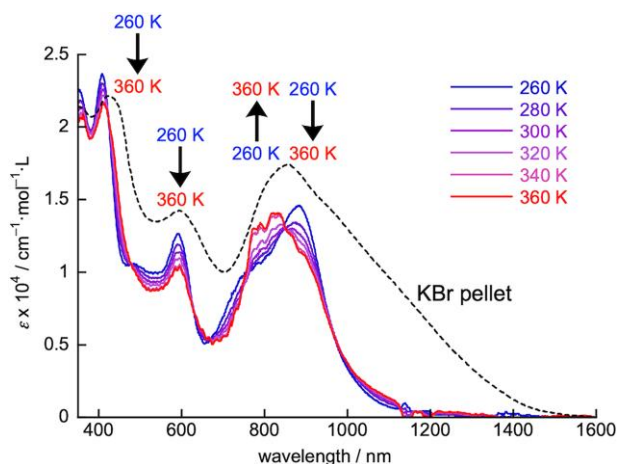


Fig. 4. Temperature-dependent electronic spectra of **1** in toluene (5.0×10^{-5} M) from 360 to 260 K. The dotted line shows the spectrum of **1** in the KBr pellet.

In the solid-state electronic spectrum (dotted line in Fig. 4), a tail of the low-energy absorption band extended to 1,500 nm. In our previous study, we elucidated that further π -stacking of the π -dimer of TOT neutral radicals causes a longer wavelength shift of the absorption band to the near-infrared region.²⁰ At present, the crystal structure of **1** has not been clarified; however, **1** may form larger π -stacking aggregates or a 1D chain in the solid state.

In conclusion, a neutral diradical **1**, in which 2 TOT skeletons are directly linked through a σ -bond, was synthesized and its electronic spin structure was investigated. The DFT calculation and ESR spectrum revealed the singlet ground state of **1** due to the through-bond intramolecular antiferromagnetic interaction between 2 delocalized electronic spins. In the solid-state and temperature-variable solution electronic spectra of **1**, a near-infrared photoabsorption was observed, suggesting the collaboration of intra- and intermolecular electronic interaction. The present study will provide a milestone for the exploration of new functionalities with the cooperation of intra- and intermolecular spin-spin interactions between neutral radical units with a highly spin-delocalized nature on whole molecular skeletons. Our current interest is aimed at the design and synthesis of π -extended TOT oligomers with various topologies, such as linear, two-sheet, or macrocyclic structures, and the investigation of their electronic functions.

Supplementary data

Supplementary material is available at *Chemistry Letters* online.

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Conflict of interest statement. None declared.

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