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Dynamic equilibrium between dissociation and regeneration of the C–C bond in trispiro-conjoined cyclopropane compound

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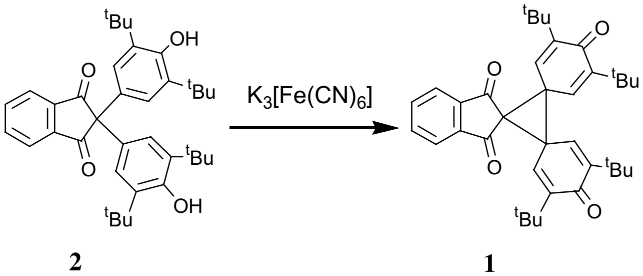
Abstract—The oxidation of 2,2-di(3,5-di-*t*-butyl-4-hydroxyphenyl)indan-1,3-dione by potassium hexacyanoferrate(III) afforded a trispiro-conjoined cyclopropane compound due to the bond formation between the ipso-carbons. Its cyclopropane ring was found to exist in solution in dynamic equilibrium with biradical species by the dissociation of the C–C bond, which is as long as 1.595 Å as revealed by X-ray crystal analysis.

The preparation and magnetic characterization of new persistent biradicals have been a rapidly growing area of research for the understanding of the basic strategy for the design of molecule-based magnets.[1] π-Systems containing two stable phenoxyl radicals such as Yang's biradical have been the subject of such research.[2] In the course of our study of the magnetic properties of bis(phenoxyl)radical compounds, we have been interested in compound **3** containing two stable phenoxyl radicals held together as closely as possible, and we intended to prepare it by oxidizing the precursor phenol compound **2**. However, contrary to our presumption, trispiro-conjoined cyclopropane **1** was obtained. The oxidation of compounds in which two phenol moieties are connected by a common carbon atom, in certain cases, gives rise to mono- or dispiro-conjoined compounds.[3] However, the formation of trispiro-conjoined compounds is rarely encountered in the oxidation of such compounds.[4] Furthermore, we found a novel dynamic behavior of ring opening and closing occurring in the cyclopropane ring of **1**. Herein, we report the fundamental structural characterization of **1**.

Cyclopropane compound **1** was derived from **2**, which was prepared by refluxing ninhydrin and 2,6-di-*t*-butylphenol in acetic acid.[5] The reaction of **2** with aqueous alkaline $K_3[Fe(CN)_6]$ in ether afforded insoluble solids, which were crystallized from dichloromethane to give **1** in 61% yield (see Scheme 1).[6] The structure of **1** was established by X-ray crystal analysis.[7]



2 **1**

Scheme 1.

A single crystal suitable for X-ray studies was obtained by slow evaporation of solvent from a dichloromethane solution containing **1**. The image obtained by the X-ray analysis shows the inclusion of solvent molecules in a 1:2 ratio. The crystal structure unequivocally demonstrates that **1** possesses a cyclopropane ring, two cyclohexadienone rings and an indan-1,3-dione moiety (Fig. 1). On the other hand, the ^{1}H and ^{13}C NMR spectra at room temperature are not consistent with such structure.

Only at low temperatures, such as −50 °C, either the ^{1}H or ^{13}C NMR spectrum was observed to be in accord with the structure of **1**, as disclosed by the X-ray analysis. In ^{1}H NMR at room temperature, the four equivalent

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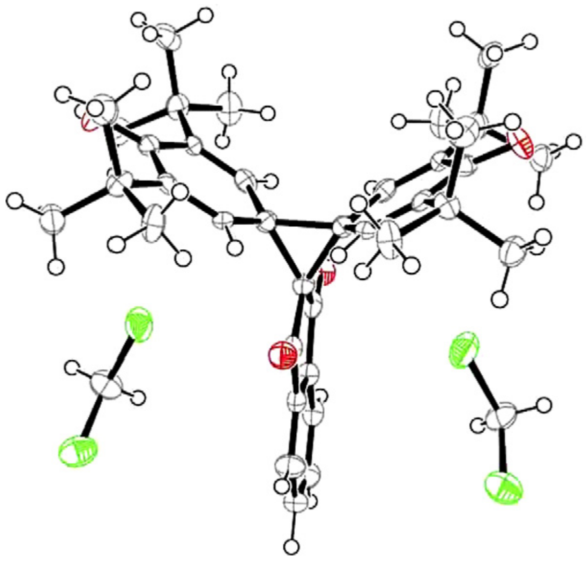


Figure 1. X-ray structure of **1**. The crystal is solvated by CH_2Cl_2.

protons on the cyclohexadienone ring of **1** appeared as a remarkably broad signal at 7.83 ppm, which became broader at higher temperatures but sharper at lower temperatures (Fig. 2). The ^{13}C NMR at room temperature displayed five distinguishable signals, whereas that at 50 °C showed only three signals (Fig. 3). Eleven signals were observed at −50 °C including characteristic signals for cyclopropane and carbonyl carbons at 52.74 and 54.20 ppm, and at 184.58 and 194.07 ppm, respectively. In all the above measurements, the NMR signals show a reversible change depending on temperature.

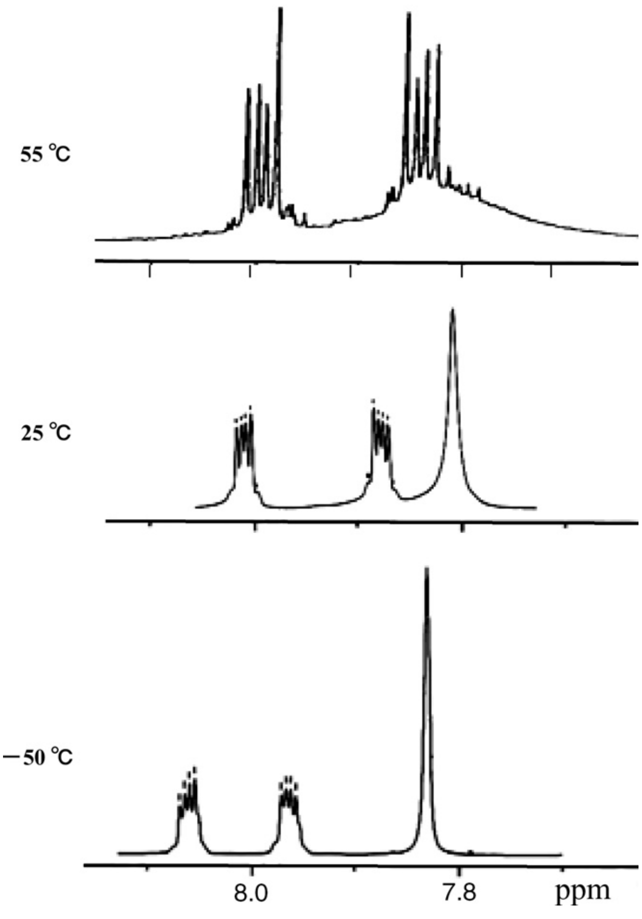


Figure 2. Temperature-dependent ^{1}H NMR spectra of **1** recorded in $CDCl_3$ solvent.

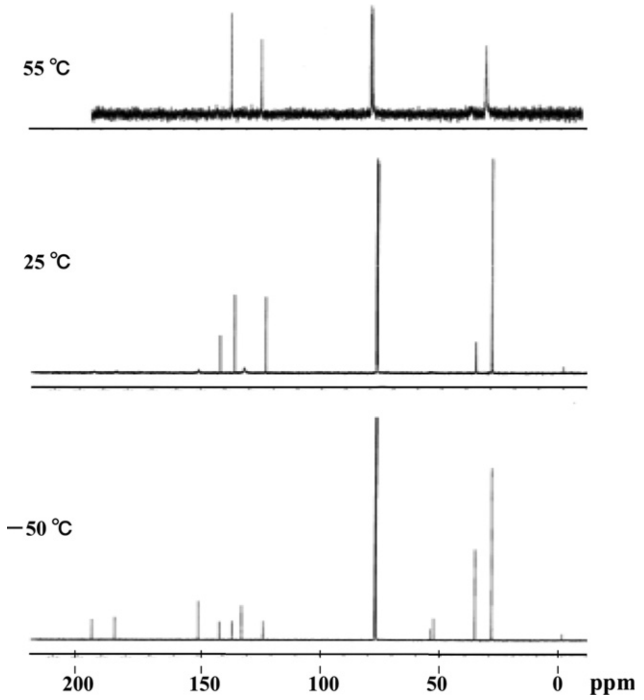
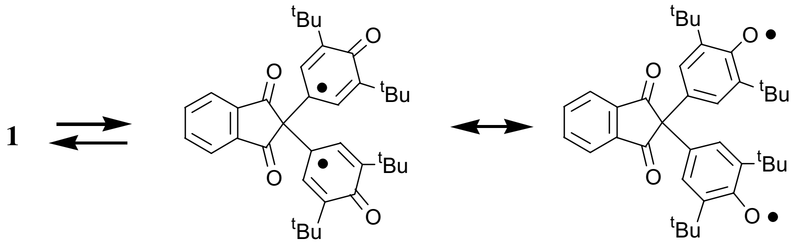


Figure 3. Temperature dependent ^{13}C NMR spectra of **1** recorded in $CDCl_3$ solvent.

These observations, that is, the broadening of the signals at high temperatures and the sharpening of the signals at low temperatures are readily interpreted in terms of the intervention of radical species, which enhance spin-lattice relaxation, further indicating that the population of radical species is high at high temperatures. Bis(phenoxyl)radical **3** should be an intermediate for the formation of **1** by the oxidation of **2** and could also be incorporated as a counterpart for the dynamic equilibrium of **1** (see Scheme 2). The ^{1}H-signal at 7.83 ppm that disappeared at 50 °C is assigned to the protons on the cyclohexadienone moiety that have a high spin density in equilibrium with **3**. On the other hand, the signals due to the indan moiety are intact during the change in temperature, which can be explained in terms of the low spin density at this position.

The involvement of radical species was supported also by the occurrence of an ESR signal for a toluene solution of **1** and a decrease in its intensity with decreasing temperature. The 1:2:1 three-line signal ($a = 0.18$ mT) implies that an unpaired electron is coupled with two protons in the two cyclohexadienone ring of **3**.

When a solid sample of **1** was heated up to 180 °C, the solid changed from pale yellow to orange and on cooling to room temperature reverted to pale yellow. On heating, an ESR signal appeared as a simple broad singlet



3

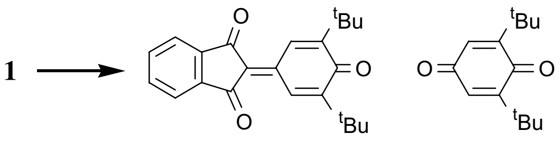
Scheme 2.

on the solid sample and its intensity increased with increasing temperature up to 170 °C.[8] These observations are in line with the event in solution. Thus, the C–C bond in **1** thermally undergoes homolytic bond dissociation also in the solid state, but the biradical produced in the solid state is persistent and gradually regenerates the cyclopropane ring with decreasing temperature. It is conceivable that, in a crystalline environment, dynamic movement is suppressed and a rather static equilibrium is achieved.

Small amounts of decomposition products were detected in the recovered solids. Thus, the solid-state thermochromism described above was not highly efficient. Above 190 °C, the solid sample decomposed and the ESR signal faded. The decomposition of **1** proceeded slowly in chloroform solution to afford **4** and **5** in 48% and 39% yields, respectively, along with **2** in 11% yield on standing for two weeks[9] (see Scheme 3).

It should be noted that the C–C bond for dissociation is significantly elongated as long as 1.595(8) Å in contrast to 1.564(9) Å of the other two bonds. We examined crystal data deposited in the Cambridge Structural Database (CSD) for the C–C bond lengths of compounds bearing a cyclopropane ring as a partial structure.[10] The distribution of the cyclopropane C–C bond lengths for 12,960 bonds in 2719 compounds are shown in Fig. 4. The C–C bond in **1** is obviously within 10% of the longest bond. The high reactivity of **1** to bond dissociation could be attributed, at least in part, to this long but weak C–C bond.

In summary, we have demonstrated the dynamic behavior of bond dissociation and regeneration in the trispiro-conjoined cyclopropane compound **1** in solution. In the solid state, such dynamic behavior was suppressed and reversible bond dissociation and recombination were thermally induced accompanied by color change. The X-ray crystal structure of **1** revealed a significantly elongated C–C bond.



4 **5**

Scheme 3.

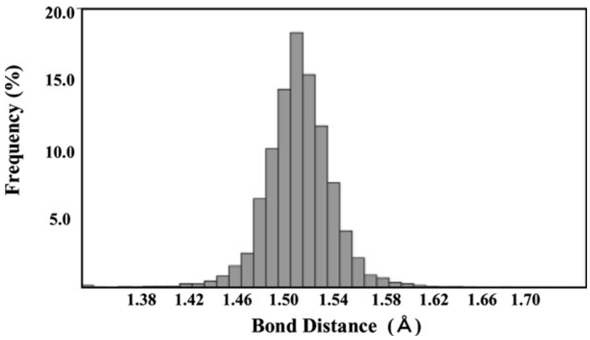


Figure 4. Histogram for the C–C bond distances in cyclopropane compounds.

Acknowledgments

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5. *Compound* **2**: Yellow crystals; mp 184–187 °C. ^{1}H NMR (CDCl$_3$, 500 MHz). δ 1.34 (36H, s), 5.18 (2H, s), 7.04 (4H, s), 7.87 (2H, symmetric m of AA′BB′), 8.07 (2H, m of AA′BB′), EI-MS (70 eV) *m*/*z*: 554. Anal. Calcd for $C_{37}H_{46}O_4$: C, 80.11; H, 8.36. Found: C, 80.09; H, 8.36.
6. *Compound* **1**: Yellow powder; mp 174.2–175.9 °C. ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.27 (36H, s), 7.81 (4H, br s), 7.88 (2H, m of AA′BB′), 8.02 (2H , m of AA′BB′). ^{13}C NMR (CDCl$_3$, 125 MHz, at −50 °C) δ 29.05, 35.79, 52.74, 54.20, 123.34, 132.26, 136.22, 141.43, 150.05, 184.58, 194.07 ppm. EI-MS (70 eV) *m*/*z*: 552. IR (KBr): $\nu_{C=O}$ 1705 cm^{-1}. Anal. Calcd for $C_{37}H_{44}O_4$: C, 80.40; H, 8.02. Found: C, 80.02; H, 7.98.
7. *Crystal data*: $C_{39}H_{48}O_4Cl_4$ orthorhombic, *Pbcm* (#57), $a = 9.692(3)$ Å, $b = 16.725(4)$ Å, $c = 23.261(7)$ Å, $V = 3770$ (1) Å^3 $Z = 4$, $R = 0.086$, $R_w = 0.158$, GOF = 1.052. Crystallographic data for the structural analysis of compound **1** has been deposited with the Cambridge Crystallographic Data Centre (CCDC 650916). These data can be obtained free of charge via, www.ccdc.cam.ac.uk/conts/retrieving.html.
8. At this temperature, the crystal is not a single crystal; guest molecules are lost to give opaque solids.
9. *Compound* **4**: Red crystals; mp 157–158 °C, ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.36 (18H, s), 7.83 (2H, m of AA′BB′), 7.98 (2H, m of AA′BB′), 8.83 (2H, s) ppm. EI-MS (70 eV) *m*/*z*: 348. Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.42; H, 6.96.
10. Data were retrieved for the crystals in which *R* is less than 7.5%.