Single-component CT Crystals Based on 1,4-Benzoquinone Derivatives and TEMPO Radical

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Four kinds of TEMPO-substituted 1,4-benzoquinone derivatives were found to afford single-component CT crystals formed by the interactions between a benzoquinone ring and one or two TEMPO groups of the neighboring molecules.

CT complexes are generally formed by two component systems normally composed of a donor and an acceptor by an intermolecular interaction.[1] Although a number of such molecules are known that have both donor and acceptor unit in a single molecule, examples of single-component CT complexes exhibiting remarkable functionality are still limited[2] probably because of the difficulty of controlling the donating and accepting ability and/or steric effects detrimental to forming a CT complex with sufficient CT interaction. To our knowledge, there is so far no example of a single-component CT complex based on stable radicals, even though several CT complexes involving stable radicals have been reported, consisting of two or more components.[3]

During our studies toward the development of organic multifunctional spin systems,[4] we prepared several benzoquinone derivatives carrying 4-amino-TEMPO radical to form CT complexes with TTF and its derivative.[5] Furthermore, it was clarified that 4-amino-TEMPO derivatives act themselves as donors to afford intermolecular CT complexes with some acceptors.[6]

We wish to report in this paper the preparation of several 1,4-benzoquinone derivatives with 4-oxy-TEMPO radical **1**–**3** (Chart 1) and serendipitous formations of the first examples of single-component CT crystals based on a stable radical together with their structures and magnetic properties.

The reaction of chloranil or bromanil with 4-hydroxy-TEMPO in the presence of potassium carbonate in DMF gave after separation by column chromatography on SiO_2 and recrystallization 2-(4-oxy-TEMPO)-3,5,6-trihalo-1,4-bezoquinone **1a** or **1b** as the major products (**1a**: 48%, **1b**: 65%). Noteworthy was the black color of the recrystallized crystals of **1a** and **1b** from the pale yellow pentane–*n*-hexane (1:1) solution, indicating occurrence of charge transfer within the molecules. Further examination of other eluants revealed the formation of bis-TEMPO-substituted benzoquinones **2** and **3** as the minor products (each <10%), which could be purified by recrystallization and elucidated by X-ray analyses. Again black crystals were obtained in the cases of **2a** and **2b**, while orange crystals were grown in the cases of **3a** and **3b**, suggesting occurrence of CT in the former crystals but not in the latter.

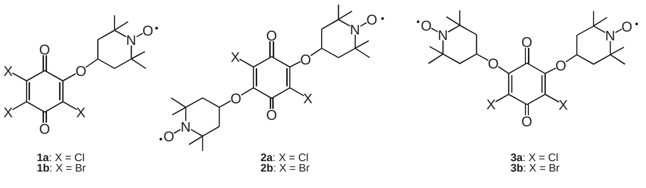

Chart 1.

Table 1. CV data of benzoquinone derivatives[a]

Compound	E_1^{RED}	E_2^{RED}	E_1^{OX}
1a	−0.26	−0.92	0.72
1b	−0.27	−0.92	0.72
2a	−0.40	−0.91	0.75
2b	−0.39	−0.96	0.74
3a	−0.37	−0.96	0.73
3b	−0.39	−0.92	0.75
Chloranil	−0.13	−0.84	
Bromanil	−0.12	−0.79	
TEMPO			0.70

[a] V vs. SCE, 0.1 M *n*-Bu_4NClO_4 in CH_3CN.

The reduction and oxidation potentials of each benzoquinone derivative were estimated by cyclic voltammetry and the data are summarized in Table 1.

It is apparent from the data that **1a** and **1b** are weaker acceptors compared to choranil or bromanil and still weaker acceptors are **2** and **3**. There is no significant difference between the redox data of chloro-series and bromo-series and between **2** and **3**. On the contrary, the colors of the crystals of **2** and **3** are different in spite of the similarity of their redox data and that implies the difference of their crystal structures.

The X-ray analyses of **1a** and **1b** indicate that they have similar molecular/crystal structures.[7] The TEMPO groups of **1a** and **1b** are largely distorted from the corresponding benzoquinone π-planes and a couple of benzoquinone rings face each other with the plane-to-plane distance of 3.61 Å in **1a** and 3.64 Å in **1b**, respectively (Figure 1). The most remarkable features of their crystal structures are the very close proximities of oxygen atoms of the radical moieties to the benzoquinone rings in **1a** and **1b** (2.79 Å in **1a** and 2.83 Å in **1b**), suggesting the occurrence of charge transfer between them and reflecting the black colors of their crystals (vide supra).

Antiferromagenetic interactions obeying the Curie–Weiss law are observed in the spins of **1a** and **1b** with the Weiss temperature of −0.41 K for **1a** and −1.87 K for **1b**, respectively.[8] As no close contact is observed in their crystal structures other than those described above, the antiferromagnetic interactions observed are probably due to those between the spin centers mediated by a couple of benzoquinone rings.

Again, similar molecular/crystal structures are apparent between 2,5-disubstituted derivatives **2a** and **2b** as shown in Figure 2. In this case, the benzoquinone ring of a molecule is being put between two TEMPO groups of two neighboring molecules with a short distance of 2.90 Å for **2a** and 2.89 Å for **2b**, respectively, resulting in the occurrence of charge transfer between the donor and acceptor groups.

The magnetic data of these compounds obey a singlet–triplet

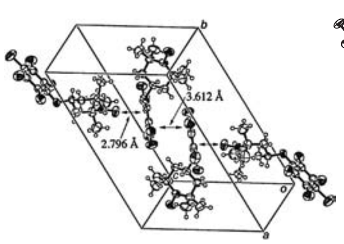

Figure 1. Crystal structures of **1a** (left) and **1b** (right). Four molecules are depicted in each structure. The arrows indicate short intermolecular contacts.

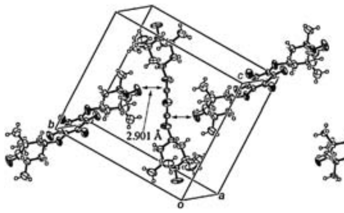

Figure 2. Crystal structures of **2a** (left) and **2b** (right). Three molecules are depicted in each structure. The arrows indicate short intermolecular contacts.

model and almost the same weak antiferromagnetic interactions with $J = -2.9\,\mathrm{K}$ for **2a** and $J = -3.0\,\mathrm{K}$ for **2b** are estimated from the data possibly by intermolecular spin–spin interactions.[9] Although the magnetic data cannot be well understood yet by considering the structural motifs, singlet formation is apparently operating through a benzoquinone ring at cryogenic temperature for each crystal.

Contrary to the previous crystals, no close contact is seen between TEMPO and benzoquinone groups in the crystals of **3a** and **3b**, while somewhat short distances are observed between the oxygen atoms of a TEMPO group in a molecule and that of a neighboring molecule (4.28 Å for **3a** and 4.37 Å for **3b**) and between the oxygen atom of another TEMPO group of the molecule and the carbon atom of a methyl group of another neighboring molecule (3.31 Å for **3a** and 3.35 Å for **3b**) as shown in Figure 3. The orange colors of the crystals suggest no occurrence of charge transfer interactions in the crystals in these cases.

Whereas the intermolecular magnetic interactions of **3a** are antiferromagnetic, ferromagnetic interactions are observed in the spins of **3b**. The difference of the magnetic interactions is supposed to reflect the difference of the distances between the spins described above. The shorter O–O distance found in **3a** compared to that of **3b** may result in the predominance of antiferromagnetic interactions in **3a**, while ferromagnetic interactions due to spin polarization through the hydrogen bonds may comparatively contribute to the ferromagnetic interactions observed between the spins of **3b**.

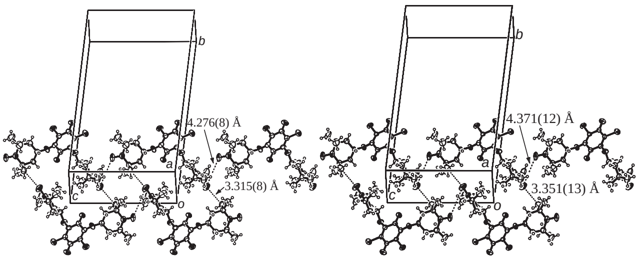

Figure 3. Crystal structures of **3a** (left) and **3b** (right). Five molecules are depicted in each structure. The broken lines indicate short intermolecular contacts.

In summary, several single-component CT crystals based on TEMPO-substituted 1,4-benzoquinone derivatives were found to form by the interactions between a benzoquinone ring and one or two TEMPO groups of the neighboring molecules, giving the first examples of single-component CT complexes involving a stable radical.

References and Notes

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7 Crystal data of **1**–**3** reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

8 Magnetic data of **1**–**3** are electronically available as Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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