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Convenient Preparation and Properties of 2,5-Dichloro- and 2,5-Dibromo-3,6-Dicyano-1,4-Benzoquinone (CDDQ and CBDQ): DDQ Analogs with Centrosymmetry

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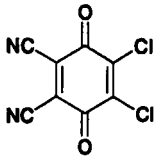
The synthetic procedure of DDQ analogs with centrosymmetry, 2,5-dichloro-, and 2,5-dibromo-3,6-dicyano-1,4-benzoquinone (CDDQ and CBDQ) was improved. These compounds showed strong electron acceptor properties like DDQ and gave semiconducting charge-transfer complexes with TTF derivatives. Crystal structures of CDDQ and perylene-CDDQ were also reported.

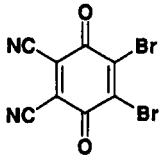
Keywords: Quinone, acceptor, charge-transfer complex, crystal structure, semiconductor.

INTRODUCTION

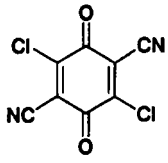
The solid state properties of molecular materials are related to the symmetry and spatial arrangement of the component molecules. The systematic study of such a correlation by using the isomeric molecules is important to understand the basic solid state properties and to obtain new materials. A strong electron, proton, and hydride acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), has been widely used in chemistry and solid state physics.[1,2] This acceptor molecule belongs to C_{2v}. A position isomer, 2,5-dichloro-3,6-dicyano-1,4-benzoquinone,[3,4] that is centrosymmetric DDQ (**1**, CDDQ), possesses C_{2h} molecular symmetry. Although CDDQ is a known compound, the solid state properties and structures have not been reported. This paper reports the improved synthetic procedures with reproducibility of CDDQ which is applicable to the preparation of the bromine analog, 2,5-dibromo-3,6-dicyano-1,4-benzoquinone (**2**, CBDQ). Furthermore, the preliminary results on the preparation and properties of their charge-transfer (CT) complexes are described.



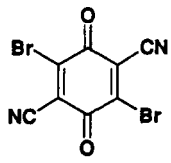
DDQ



DBDQ



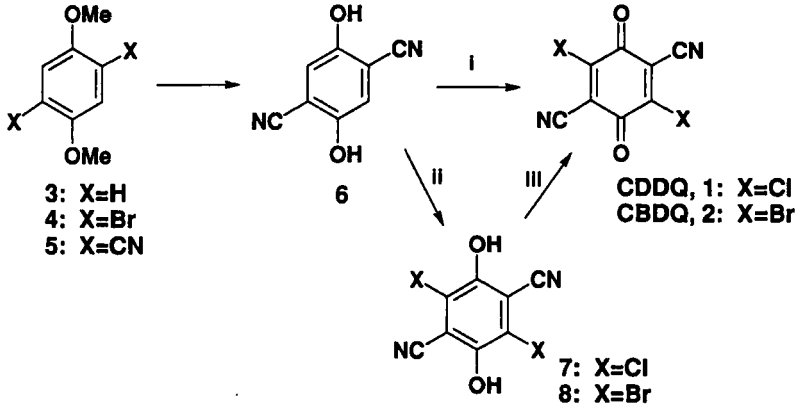
1, CDDQ



2, CBDQ

SYNTHESIS

The synthesis of **1** and **2** was first reported by Wallenfels and his co-workers.[3] Later, Neidlein and Leidholdt improved the synthesis of **1** into only a four steps-procedure from 1,4-dimethoxybenzene (**3**).[4] One of the final steps is chlorination and subsequent oxidation of 2,5-dicyanohydroquinone (**6**) with chlorine gas in HOAc containing water[5] at room temperature (Scheme 1). Another procedure for the conversion of **6** to **1** is to use antimony pentachloride. However, we obtained the hydroquinone **7** instead of **1**. Thus, compound **6** was treated with 5 equiv of antimony pentachloride in CH_2Cl_2 at room temperature for 2–3 days. The reaction product precipitated was washed with CH_2Cl_2 two or three times and dried under reduced pressure to give dichloro-substituted hydroquinone **7**[3] in 63% yield. Further purification, if necessary, could be done by dissolving in NaOH solution, filtration, and acidification. We treated the resulting hydroquinone **7** with NO_2 in CCl_4 to give **1**[6] in 70% yield.



Reagents and conditions

i) HOAc-distilled H_2O, chlorine gas for 3 h, stirring 1.5 h, 36%; ii) for **7**: 5 equiv. $SbCl_5$, CH_2Cl_2, rt., 2-3 d, 63%, and for **8**: HOAc-H_2O, Br_2, 78%; iii) for both **1** and **2**: excess NO_2, CCl_4, 0 °C ~ rt., 1 h, 70% and 80%, respectively.

We successfully prepared CBDQ (**2**)[3] by a similar procedure using the same precursor **6**. Thus, the dicyanohydroquinone **6**, which contains strong electron-withdrawing cyano groups, was treated with an excessive amount of bromine in HOAc containing water to give the dibromohydroquinone **8**[3] in 78% yield. The hydroquinone **8** was converted to desired **2**[7] in 80% yield by treating with NO_2 in CCl_4. It is

recommended that all the operations for the purification of **1** and **2**, as well as storage, should be carried out under an inert atmosphere because these compounds are slightly sensitive to air and water.

PHYSICAL PROPERTIES AND DISCUSSION

Single crystals of CDDQ (**1**) suitable for X-ray crystal structure analysis[8] were obtained by two-time recrystallization from CH_2Cl_2 at 0 °C. The molecular structure with the atomic labeling scheme is shown in Figure 1. The molecular dimension showed a quinonoid geometry and was almost identical with that found in DDQ.[9] The chlorine atom, carbon atom of cyano group, and oxygen atom deviated 0.005, 0.040 and 0.028 Å from the mean plane, respectively. The planarity of CDDQ is higher than that of DDQ. The bond angle of O(1) – C(1) – C(2) in CDDQ (121.9°) was smaller than that in DDQ (123.1°), indicating a smaller steric repulsion between C = O group and Cl atom in CDDQ. The molecular packing is a typical herring-bone type (Fig. 2).

Reduction potentials of the quinones to the corresponding anion radical and dianion species together with selected known benzoquinone type acceptors were measured by cyclic voltammetry (Table 1). Both half-wave reduction potentials of CDDQ and CBDQ were slightly lower than those of DDQ and DBDQ.

In view of the electron-acceptor properties and molecular symmetry, both CDDQ and CBDQ are of interest as acceptors for organic conductors. They formed CT complexes with TTF type donors, whose electrical conductivities measured by standard two-probe or four-probe methods on compressed powder or crystal samples are summarized in Table 2 together with the activation energies (*Ea*, eV) and the CT transition energies ($h\nu_{CT}$). Interestingly, the resistivity (3 Ω cm) of ET-CDDQ is considerably lower than that (1.2×10^5 Ωcm) of ET-DDQ.[10] Single crystal growing for X-ray crystal analysis is now under investigation. We have also tried to

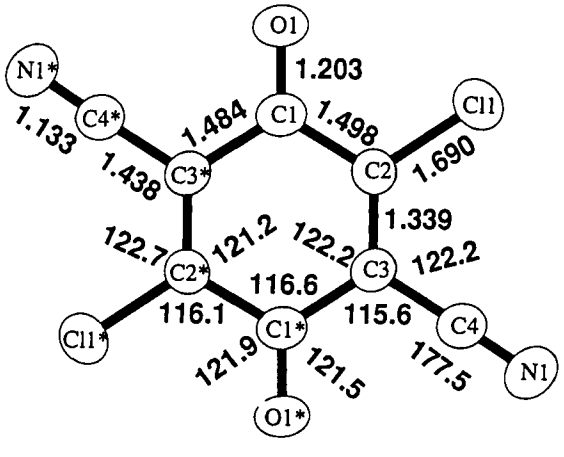


FIGURE 1 Bond lengths, angles, and numbering scheme of CDDQ.

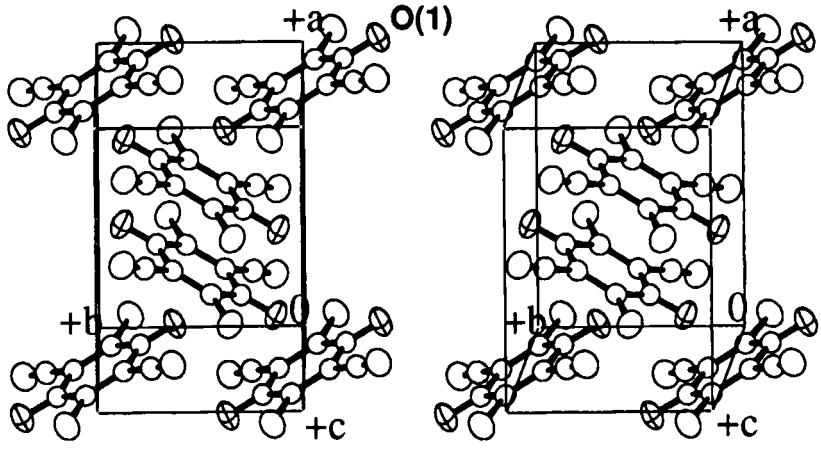


FIGURE 2 Stereoview of crystal structure of CDDQ.

TABLE 1

Cyclic voltammetry data[a]

Acceptor	E_1red	E_2red	ΔE
CDDQ	+0.55	−0.36	0.91
CBDQ	+0.53	−0.31	0.84
DDQ	+0.59	−0.30	0.89
DBDQ	+0.58	−0.29	0.87

[a] Experiment conditions: electrolyte Bu_4NClO_4 0.1 mol dm^{-3} in PhCN, under argon, rt., V *vs* saturated calomel electrode, (SCE). Pt electrode, scan rate 50 mV s^{-1}.
All values are irreversible.

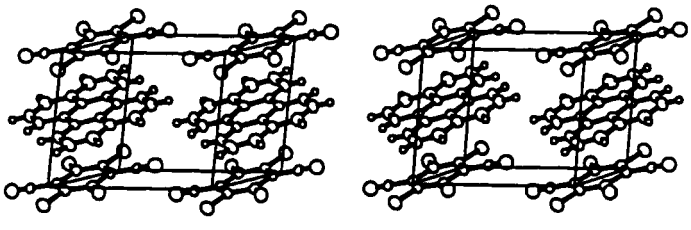


FIGURE 3 Stereoview of crystal structure of CDDQ-perylene.

prepare CT complexes with condensed polycyclic aromatics such as perylene and pyrene. X-ray crystallographic analysis of perylene-CDDQ showed an alternated uniform stacking of the donor and acceptor along the *c* axis (Fig. 3).[8] No significant differences between bond lengths and angles of the molecules in CDDQ crystal and in perylene-CDDQ crystal were found. A similar molecular packing mode was reported

TABLE 2

Selected physical properties of the CT complexes of CDDQ and CBDQ with TTF type donors[a]

CT complex	D:A[b]	$h\nu_{CT}$[c]/cm^{-1}	ρ_{RT}[d]/Ωcm	Ea/eV
TTF-**1**	1:1	4850	6.1×10^5 (2p)	0.24
TTF-**2**	–	4700	1.5×10^3 (2p)	0.01
ET-**1**[e]	2:1	4200	3.0 (4s)	0.11
ET-**2**	2:1	4700	2.7×10^5 (2p)	0.08
TMTTF-**1**[e]	2:1	4150	4.0×10^2 (4s)	0.12
TMTTF-**2**[e]	2:1	4280	5.7×10 (4s)	0.06
DBTTF-**1**	1:1	4650	2.5×10^3 (2p)	0.15
DBTTF-**2**	3:1	4900	4.0×10^6 (2p)	0.29
OMTTF-**1**[e]	3:2	11750	1.4×10^4 (2s)	–
TTT-**1**	3:2	7600	4.1×10^3 (2p)	0.13

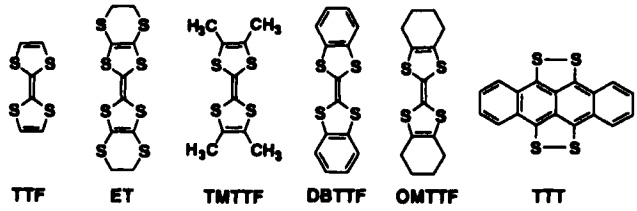
[a] Prepared by diffusion method for crystal samples and by mixing hot solutions of the components for the other samples.

[b] Determined by elemental analysis of the complexes.

[c] Measured on KBr disk.

[d] Measured by two-probe method on compressed powder (2p), two-probe method on single crystal (2s), and four-probe method on single crystal (4s).

[e] Crystal sample.



for perylene-chloranil[11a] and perylene-fluoranil,[11b] though the crystal structure of perylene-DDQ has not been reported yet.

Now, the centrosymmetric DDQ analogs, CDDQ and CBDQ, are easily available in a reproducible manner from the same precursor, 2,5-dicyano-1, 4-hydroquinone (**6**), and can be used for a variety of solid state chemistry.

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5. It is preferable to use distilled water to maintain the reproducibility of this reaction.
6. CDDQ: brilliant yellow crystals, m.p. 209 °C, IR (KBr) 2244 (w, C ≡ N), 1686 (st, C = O), 1578 (st, C = C), 1272, 1188 (m, C – C), and 797 (m, C – Cl) cm^{-1}; UV (KBr): λ_{max} 300 and 226 nm; ^{13}C NMR (C_6D_6): δ 169.2 (C = O), 149.3 (C – Cl), 120.5 (C – CN), and 109.4 (C ≡ N). MS: *m/z* (%) 226 (83.42), 227 (7.59), 228 (66.97), 229 (6.47), and 230 (15.89).
7. CBDQ: light yellow solid, m.p. 220 – 221 °C, IR (KBr) 2241 (w, C ≡ N), 1684 (st, C = O), 1569 (st, C = C), 1256, 1161 (m, C – C), and 750 (m, C – Br) cm^{-1}; UV (KBr): λ_{max} 236 and 244 nm; ^{13}C NMR (C_6D_6): δ 169.2 (C = O), 149.3 (C – Cl), 120.5 (C – CN), and 109.4 (C ≡ N). MS: *m/z* (%) 314 (37.9), 315 (4.3), 316 (71.9), 317 (7.3), 318 (37.9), and 319 (3.7).
8. Crystal Data for CDDQ: $C_8N_2O_2Cl_2$, *monoclinic*, space group = $P2_{1/n}$. $a = 8.298$ (3) Å, $b = 6.129$ (3) Å, $c = 8.881$ (2) Å, $\beta = 106.00(2)°$, $V = 434.2$ (3) Å^3, $Z = 2$, $R = 0.037$, $R_W = 0.032$. Crystal Data for perylene-CDDQ: $C_{28}H_{12}N_2O_2Cl_2$, triclinic, space group = $P\bar{1}$ $a = 8.376$ (2) Å, $b = 9.895$ (2) Å, $c = 7.160$ (3) Å, $\alpha = 109.54$ (2)°, $\beta = 94.52$ (2)°, $\delta = 69.12$ (2)°, $V = 522.0(3)$ Å^3, $Z = 1$, $R = 0.055$, $R_W = 0.040$. All calculations were performed by using the teXsan crystallographic software of Molecular Structure Corporation.
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