Sample 2 from above was found to contain 17% $NOBF_4$ as determined by this method.

Registry No. HNO_3, 7697-37-2; HF, 7664-39-3; BF_3, 7637-07-2; NO_2BF_4, 13826-86-3; NO_2^+, 14522-82-8; NO^+, 14452-93-8; NO_2BF_4·18-crown-6, 86959-82-2; $NOBF_4$·18-crown-6, 84868-78-0.

Electroactive Organic Materials. Preparation and Properties of 2-(2′-Hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane

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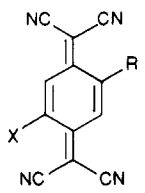
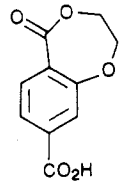
Much attention in recent years has been focused on organic materials with interesting electrical properties. Many conductive charge-transfer complexes between the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, **1**) and several organic electron donors have been prepared and reported as important examples of organic metals.



1: X, R = H
2: X = Br; R = OCH_2CH_2OH
3: X = H; R = OCH_2CH_2OH



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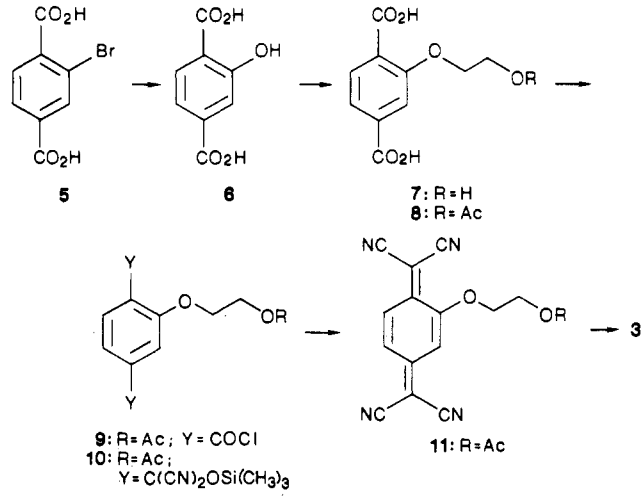
Our research program required a suitably functionalized TCNQ that could be covalently bonded to an organic donor to produce D-σ-A products,[1] which are generally flat compounds with an extended conformation comprised of three parts: electron donor (D) and acceptor (A) moieties at the ends bridged by a nonconjugated chain of C/N/O atoms (the σ bridge). Similar molecules have been proposed as candidates for prototype organic molecular rectifiers,[2] provided they can be oriented properly as M_1|D-σ-A|M_2 sandwiches between two metal electrodes, M_1 and M_2. Thus, they should allow electron flow only in one direction: from the cathode, M_2, to the acceptor terminus, from the acceptor to the donor through the σ bridge via electron tunneling, and then from the donor terminus to the anode, M_1. The advantage of this system over conventional electronic components is the extreme miniaturization possible when rectification is achieved at the molecular level.

Most D-σ-A products reported to date have been synthesized with 5-bromo-2-(2′-hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (BHTCNQ) (**2**) as the acceptor component. The addition of the hydroxyl group of acceptor **2** to the isocyanate moiety on a donor molecule produced D-σ-A products with carbamate σ bridges. The competitive formation of charge-transfer salts from the starting materials was not a problem. Unfortunately, very few functionalized TCNQ derivatives have been reported. Until now, BHTCNQ (**2**) was the only monohydroxy and monocyclic TCNQ described in the literature. It was prepared[3] by an eight-step synthesis from 2,5-dimethylphenol, which can be described as tedious, inefficient (<13% overall yield), and hazardous, since the highly toxic cyanogen chloride is required in a critical step.

We report here, for the first time, the relatively facile preparation of the desbromo derivative of **2**, 2-(2′-hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (HETCNQ, **3**), via a five-step synthesis from 2-bromoterephthalic acid (**5**, Scheme I) with an overall yield of 45%. The starting material was commercially available[4] and was almost quantitatively hydrolyzed to **6** by a published procedure.[5] Intermediate **6** was converted to **7** by a Williamson-type reaction, which produced a mixture of the two that could not be separated by recrystallization, column chromatography, or preparative thin-layer chromatography. However, complete separation and purification of **7** was achieved with centrifugal countercurrent chromatography.[6] The acetate ester of **7** (**8**) was then changed to the diacid chloride, **9**, which was treated with an excess of trimethylsilanecarbonitrile to produce a 1,4-bis[dicyano(trimethylsiloxy)methyl]benzene (**10**) by the recently published method of Yamaguchi and Hanafusa.[7] Treatment of **10** with phosphorus oxychloride removed the siloxy groups and acid hydrolysis cleaved the acetate ester to afford the target product, HETCNQ (**3**).

Scheme I



5 **6** **7**: R = H; **8**: R = Ac
9: R = Ac; Y = COCl
10: R = Ac; Y = $C(CN)_2OSi(CH_3)_3$
11: R = Ac

Table I. Half-Wave Reduction Potentials[a]

	TCNQ (1)[b]	BHTCNQ (2)	HETCNQ (3)[c]
$E_{1/2}^1$	0.190	0.305	0.107
$E_{1/2}^2$	−0.350	−0.170	−0.398

[a] In volts vs SCE as determined by cyclic voltammetry at a Pt-button electrode in acetonitrile with n-$Bu_4N{\cdot}ClO_4$, n-$Bu_4N{\cdot}PF_6$, or n-$Bu_4N{\cdot}BF_4$ (0.1 M). [b] Data from ref 10. [c] 1.514×10^{-3} M.

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The crystal structure of 2-(2′-acetoxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (AETCNQ, 11) has been determined by X-ray diffraction, and the results will be published elsewhere.[8]

The cyclic voltammogram of **3**, obtained by Prof. Charles L. Hussey of the Department of Chemistry at The University of Mississippi, showed the usual two one-electron reduction waves characteristic of TCNQ-type electron acceptors. According to the half-wave reduction potentials (Table I), product **3** was a slightly poorer acceptor when compared with TCNQ (**1**) or the bromo derivative **2**.

Experimental Section

Melting points were run on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab 3 instrument. E. Merck silica gel (9385) was used in column chromatography. Cyclic voltammagrams were obtained by using an Amel Model 551 potentiostat programmed by a PARC 175 universal programmer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2-Hydroxyterephthalic Acid (6). The procedure given here was essentially that reported by Field and Engelhardt.[5] 2-Bromoterephthalic acid[4] (50.0 g, 0.204 mol) and 16.4 g (0.408 mol) of NaOH were dissolved in 940 mL of water. After the addition of 36.8 g (0.448 mol) of NaOAc, 0.26 g of Cu power, and a few drops of phenolphthalein, the aqueous mixture was stirred and heated to the reflux temperature. Aqueous KOH (5%) was added occasionally in order to keep the reaction mixture alkaline. Completion of the reaction was indicated by TLC after 3 days. After cooling, the mixture was filtered, and the filtrate was acidified with 1.2 N HCl. The white crystals were collected by filtration and then dried in a vacuum oven to afford 36.7 g (99%) of **6**: mp 315–319 °C (lit.[5] mp 320–322 °C). This product exhibits a blue fluorescence during irradiation with UV light.

2-(2′-Hydroxyethoxy)terephthalic Acid (7). 2-Chloroethanol (2.2 mL, 2.66 g, 33.0 mmol), was added in one portion to a stirred solution of 2.2 g (55.0 mmol) of NaOH, 2.0 g (10.98 mmol) of **6**, and 15 mL of water. The resultant mixture was stirred at room temperature for 2 days. The reaction mixture was then filtered, and the filtrate was acidified with 1.2 N HCl. The white precipitate was collected by filtration and dried (≅2.9 g). According to silica gel TLC (EtOAc–HOAc, 97:3), the white solid was a mixture of product, **7**, and starting material, **6**. Silica gel normal and reversed-phase column chromatography, preparative thin-layer chromatography, and recrystallization failed to separate this mixture. However, it was completely separated into its components with countercurrent chromatography[6] on an Ito Coil Planet centrifuge[9] [the solvent system was chloroform–MeOH–water (37:37:26); the upper phase was the mobile phase; the multilayer coiled column was 1.6-mm i.d., 130 m long, and 330-mL capacity; the flow rate was 180 mL/h at 800 rpm; the sample sizes for two runs were 1.5 and 1.42 g]. The product (**7**) was obtained as white crystals from acetone–hexane and weighed 1.88 g (76%): mp 223–224 °C; IR (KBr) 3550, 2650, 2550, 1695, 1245, 760 cm^{-1}. Anal. Calcd for $(C_{10}H_{10}O_6)_4 \cdot H_2O$: C, 52.05; H, 4.59. Found: C, 52.30; H, 4.41.

2-(2′-Acetoxyethoxy)terephthalic Acid (8). A mixture of 440 mg (1.95 mmol) of **7**, 1.0 mL (1.08 g, 10.6 mmol) of Ac_2O, a few drops of pyridine, and 5.0 mL of dry $CHCl_3$ was heated to the reflux temperature for 2 h. The reaction mixture was distilled at reduced pressure in order to remove all volatile materials. The residue sometimes required chromatography on a silica gel column with EtOAc–HOAc (96:4) or MeOH (100) as the eluant. The crystalline product (**8**) weighed 483 mg (92%) and could be recrystallized from EtOAc–acetone: mp 219–220 °C; IR (KBr) 2650, 2550, 1745, 1690, 1250, 760 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_7$: C, 53.73; H, 4.51. Found: C, 53.73; H, 4.41.

In some runs, a faster moving product, **4**, was obtained in minor amounts from the silica gel column. It crystallized as colorless needles from EtOAc: mp 263–265 °C; IR (KBr) 2620, 1720, 1705, 1660, 1230, 740 cm^{-1}. Anal. Calcd for $C_{10}H_8O_5$: C, 57.70; H, 3.87. Found: C,57.63; H, 3.82.

2-(2′-Acetoxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (11). One mL of $SOCl_2$ (1.64 g, 13.8 mmol) was added to a stirred solution of 0.399 g (1.49 mmol) of **8** in 10 mL of dry benzene. The resultant solution was heated to the reflux temperature for 2 h, after which the solvent and unreacted $SOCl_2$ were removed by distillation under reduced pressure. The residual viscous brown oil (the diacid chloride, **9**) was treated first with 1.0 mL of pyridine and then with 3.0 mL (2.23 g, 22.5 mmol) of trimethylsilanecarbonitrile, and this was stirred and heated to the reflux temperature under Ar for 5 h. The volatile material was removed by reduced pressure distillation, and the semisolid residue (**10**) was stored in a desiccator for 16 h. The latter was then treated with 1.3 mL (2.14 g, 13.9 mmol) of $POCl_3$ and 1.5 mL of dry pyridine, and this reaction mixture was stirred under Ar at room temperature for 20 min. The above was added to about 50 mL of EtOAc and 200 mL of ice water, the resultant mixture was shaken, and the phases were separated. The organic phase was washed with 50 mL of water and dried over anhydrous $MgSO_4$. The filtrate was distilled under reduced pressure, and the semisolid residue weighed 530 mg. Purification by silica gel column chromatography (EtOAc–hexane, 68:32) afforded 0.43 g (95%) of red crystals of **11**. These could be recrystallized from EtOAc–hexane: mp 156–158 °C; IR (KBr) 2210, 1725, 1220, 835 cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_4O_3$: C, 62.74; H, 3.29; N, 18.29. Found: C, 62.55; H, 3.14; N, 18.38.

2-(2′-Hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane, HETCNQ (3). A solution of 50 mg (0.16 mmol) of **11**, 5.0 mL of CH_3CN, and 1.5 mL of 1.2 N HCl was stirred at 60 °C for 23 h. The reaction solution was poured into ≅10 mL of EtOAc, and the organic layer was washed with ≅5 mL of water. After drying, the EtOAc solution was distilled under reduced pressure, and the residue was chromatographed on silica gel (EtOAc–hexane, 30:70) to afford 31 mg (69%) of red crystals (**3**), which could be recrystallized from EtOAc: mp 173.0–174.5 °C de; IR (KBr) 3500–3300, 2230, 1605, 1550, 1530, 1240, 860, 825 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 63.64; H, 3.05; N, 21.20. Found: C, 63.50; H, 2.80; N, 21.15. The cyclic voltammogram of **3** showed two one-electron reduction waves, and the half-wave reduction potentials are given in Table I.

Acknowledgment is made of support by the National Science Foundation, Solid State Chemistry (Grant DMR 84-17563). We also acknowledge the assistance of Prof. C. L. Hussey for the cyclic voltammogram of **3**.

Registry No. **3**, 111822-79-8; **5**, 586-35-6; **6**, 636-94-2; **7**, 111822-80-1; **8**, 111822-81-2; **9**, 111822-82-3; **10**, 111847-84-8; **11**, 111822-83-4; $Cl(CH_2)_2OH$, 107-07-3; $(H_3C)_3SiCN$, 7677-24-9.

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An Efficient Electrophile-Initiated Homoconjugate Addition of Acetate to Cyclopropyl Ketones

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The homoconjugate addition of nucleophiles to cyclopropanes activated by a carbonyl substituent is a potentially powerful method for achieving 1,4-difunctionalization. A number of important strategies for effecting 1,5-additions of nucleophilic species to electron-deficient cyclopropanes have been reported,[1] and several cyclopropane

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