Sodium Borohydride Reduction of 1b. To a magnetically stirred suspension of 14.00 g (42.0 mmol) of **1b** in 220 mL of absolute EtOH were added 1.62 g (42.8 mmol) of $NaBH_4$ and 35 mL of absolute EtOH at room temperature. After 2.5 h, the suspension was diluted with 700 mL of water, stirred for 15 min, and cooled at 0 °C for 1.5 h. The white powder was collected, washed with water, and recrystallized from acetone–MeOH to give 6.12 g of the δ-lactone **7**, mp 234–235.5 °C. The mp was undepressed upon admixture with **7** prepared by hydrolysis of the imino ester **6**. Anal. Calcd for $C_{20}H_{17}NO_2$ (mol wt 303.4): C, 79.18; H, 5.65; N, 4.62. Found: C, 79.28; H, 5.66; N, 4.52.

The solid obtained by concentration of the mother liquor was recrystallized from acetone–MeOH to give an additional 675 mg of **7** with mp 235–236.5 °C; total yield, 54%.

The foam obtained by evaporation of the main mother liquor was chromatographed in two parts on silica gel. Elution with CH_2Cl_2 and 10% MeOH–CH_2Cl_2 gave a total of 4.51 g (32%) of methyl 1-cyano-*trans*-2(e),6(a)-diphenyl-4(e)-hydroxycyclohexane-1(e)-carboxylate (**8b**) as a colorless glass: IR 3600, 3460, 2241, 1738 (sh at 1750) cm^{-1}; ^{1}H NMR δ 1.97–2.67 (m, 4 H), 3.22 (s, 3 H), 3.55–3.95 (m, 2 H), 4.52 (m, $W \cong 40$, 1 H), 7.32 (s, 10 H). Anal. Calcd for $C_{21}H_{21}NO_3$ (mol wt 335.4): C, 75.20; H, 6.31; N, 4.18. Found: C, 75.42; H, 6.52; N, 3.99.

Methyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4-acetoxycyclohexane-1(e)-carboxylate (9b). A solution of 707 mg (2.11 mmol) of **9a** in 6 mL of pyridine and 1.5 mL of acetic anhydride was allowed to stand at room temperature for 17 h. Crushed ice and 6 mL of concentrated HCl were added with stirring. The resulting white powder was collected, washed with water, and recrystallized from 50% EtOH to give 555 mg (70%) of the acetate **9b** as tiny white crystals: mp 122.5–124 °C; IR 2244, 1735 cm^{-1}; ^{1}H NMR δ ~2.07 (s, 3 H), 2.0–2.67 (m, 4 H), 3.23 (s, 3 H), 3.60–3.97 (m, 2 H), 5.53 (m, $W \cong 38$, 1 H), 7.33 (s, 10 H).

When recrystallized again from EtOH–water, **9b** showed mp 142–143 °C. When another sample of the lower melting form of **9b** was recrystallized similarly but with seeding by the 143 °C material, the precipitate had mp 142–143 °C. Seeding of a solution of the higher melting polymorph gave **9b** with mp 123 °C in part and then 143–144 °C. Anal. Calcd for $C_{23}H_{23}NO_4$ (mol wt 377.4): C, 73.19; H, 6.14; N, 3.71. Found: C, 73.34; H, 6.15; N, 3.71.

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Registry No. (±)-**1a**, 111904-71-3; (±)-**1b**, 63087-40-1; **2a**, 111904-72-4; (±)-**3a**, 111904-73-5; (±)-**3b**, 111904-74-6; (±)-**4**, 111904-75-7; (±)-**5**, 62940-83-4; (±)-(*E*)-**6**, 111904-76-8; (±)-(*Z*)-**6**, 111957-24-5; (±)-**7**, 111904-77-9; (±)-**8a**, 111904-78-0; (±)-**8b**, 111904-80-4; (±)-**9a**, 111904-79-1; (±)-**9b**, 111904-81-5; PhCh=CHCOCH=Ph, 538-58-9; EtO_2CCH_2CN, 105-56-6.

Preparation of Nitronium Tetrafluoroborate Free of Nitrosonium Ions

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In the course of our studies[1] on aromatic nitrations with nitronium tetrafluoroborate (NO_2BF_4), we were unable to obtain this salt with purities greater than about 80% from commercial sources.[2] The major impurity was found to be nitrosonium tetrafluoroborate ($NOBF_4$). During the course of their nitration studies, Yoshida and Ridd[3] found that commercial sources of NO_2PF_6 contained considerable amounts of $NOPF_6$ as an impurity. They described a method to separate $NOPF_6$ from NO_2PF_6 on the basis of solubility differences, but this technique is not readily applicable to the purification of NO_2BF_4. Although Olah et al.[4] have reported on the preparation of pure NO_2BF_4 by treating NO_2F with BF_3, we could not locate a commercial source of NO_2F; its preparation is quite elaborate.[5] Kuhn[6] reported two methods for the preparation of NO_2^+ salts, one from nitric acid, and the other from alkyl nitrate esters. The latter method reportedly gives a pure product.

It was suspected that the commercial samples of NO_2BF_4 were prepared by the method of Olah and Kuhn[7] where 95% red fuming nitric acid, anhydrous HF, and anhydrous BF_3 are combined in CH_2Cl_2 (eq 1). The source then of

$$HNO_3 + HF + 2BF_3 \rightarrow NO_2BF_4 + H_2O{\cdot}BF_3 \qquad (1)$$

the large amounts of $NOBF_4$ in these samples probably arises in part from the large amounts of dissolved nitrous oxides in the nitric acid[8] (eq 2). Utilizing nitric acid that

$$N_2O_4(N_2O_3) + BF_3 + HF \xrightarrow{HNO_3} NOBF_4 + NO_2BF_4 + H_2O{\cdot}BF_3 \qquad (2)$$

is free of nitrous oxides should provide NO_2BF_4 free of $NOBF_4$. Indeed, when purified anhydrous nitric acid was used in the preparation, the product was better than 95% NO_2BF_4, and no $NOBF_4$ could be detected in the sample (vide infra).

The determination of the nitronium ion and nitrosonium ion content in samples of NO_2BF_4 is not a trivial matter. An adaptation of the method of Yoshida and Ridd[3] was found suitable for determining NO_2^+ content. The method employs nitrating a twofold excess of 4-nitrotoluene directly in an NMR tube (CD_3CN) with a weighed amount of the NO_2BF_4 to be analyzed. Integration of the methyl signals of the formed 2,4-dinitrotoluene and unreacted 4-nitrotoluene gives the amount of NO_2^+ in the sample. It is known from previous work that this nitration reaction is quantitative with NO_2BF_4. Performing this reaction directly in the NMR tube reduces the limits of error in the analysis since workup and isolation are eliminated. Under these conditions, 4-nitrotoluene is inert with $NOBF_4$.

The determination of NO^+ in the presence of NO_2^+ is much less straightforward. This can be determined qualitatively by both Raman and infrared spectroscopy. Raman spectra of solid samples of NO_2BF_4 with small amounts of $NOBF_4$ showed only the symmetrical stretching frequency of NO_2^+ at 1400 cm^{-1}. It was only when these samples were dissolved in a solvent (e.g. 96% or 100% H_2SO_4) that the symmetrical stretching frequency of NO^+ at 2325 cm^{-1} was seen. The presence of NO^+ in samples of NO_2BF_4 could also be readily detected by preparing the 1:1 complex with 18-crown-6 ether in CH_2Cl_2.

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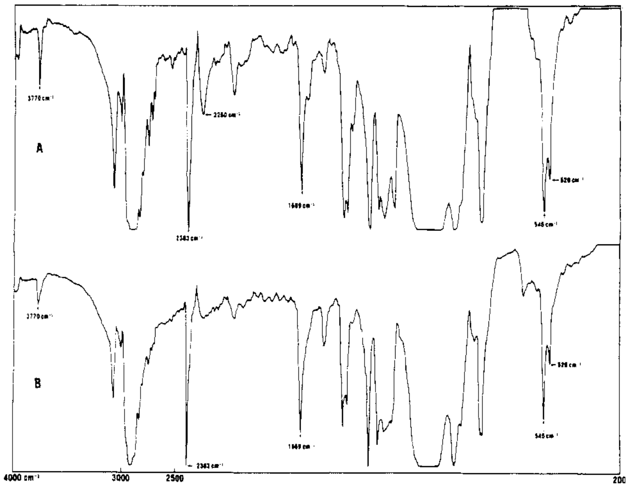

Figure 1. Transmittance infrared spectra of 18-crown-6 ether complexes of NO_2BF_4 in CH_2Cl_2. (a) Spectrum of the complex derived from commercially supplied NO_2BF_4 (sample 2) containing $NOBF_4$ as an impurity and (b) spectrum of the complex made from pure NO_2BF_4 (Experimental Section).

Nitrosonium tetrafluoroborate forms a deep yellow charge-transfer complex with this crown ether (λ_{max} 300 nm, CH_2Cl_2), while the NO_2^+ complex is colorless. The infrared spectrum of a mixture of NO_2^+ and NO^+ crown ether complexes shows a strong band at 2383 cm^{-1} for NO_2^+ and a band at 2250 cm^{-1} for NO^+ (see Figure 1). The amount of NO^+ in samples of solid NO_2BF_4 was quantitatively determined by the potassium permanganate titrimetric[9] method for nitrite ion in the presence of nitrate ion on carefully hydrolyzed samples (see the Experimental Section).

Subjecting samples of NO_2BF_4 prepared from purified anhydrous nitric acid to the above analyses showed that this material contained over 95% NO_2BF_4 with no detectable amount of NO^+ present. Solutions of the 18-crown-6 ether complex with this salt in CH_2Cl_2 were colorless. Also, an infrared spectrum of this solution showed no band at 2250 cm^{-1}. Thus, the modified preparation procedure appears to give NO_2BF_4 of high purity.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 241 spectrometer. Dichloromethane (B&A) was purified by passage through alumina, activity super I, under N_2.

Purification and Preparation of Anhydrous HNO_3. To 400 mL of yellow 90% nitric acid (J. T. Baker; 604 g, 9.58 mol) was added a total of 4.0 g of urea in small portions at room temperature, waiting until gas evolution ceased before the next addition.[10] After the nitric acid turned colorless, it was cooled to 0 °C in an ice bath. This was then added to an equal volume of ice-cold 96% H_2SO_4 with cooling. Ammonium nitrate (1.0 g) was added, and the mixture was distilled [24 °C at 2.26 kPa (17 mmHg)]. The anhydrous nitric acid was collected in a dry ice cooled trap as a colorless solid (mp −42 °C). This material was stored as a liquid in a glass bottle at −17 °C until used. No coloration occurred after 5 years when stored at this temperature.

Nitronium Tetrafluoroborate. The procedure of Olah and Kuhn[7] was followed with anhydrous HNO_3 in place of 95% red fuming nitric acid.

Into a 500-mL polyethylene screw-top Erlenmeyer flask with a N_2 inlet, BF_3 inlet, and a drying tube exit was placed a Teflon-coated magnetic stirring bar. Into a smaller polyethylene Erlenmeyer flask was condensed 25 mL (25 g, 1.25 mol) of anhydrous HF at dry ice temperature. This was poured into the large flask along with 350 mL of dry CH_2Cl_2 and 42 mL (64 g, 1.02 mol) of anhydrous nitric acid. The mixture was cooled to dry ice temperature, and BF_3 was slowly passed in with vigorous stirring. After 1.5 h, 63 g of BF_3 was passed into the mixture, after which white fumes appeared at the exit tube. The solution was warmed to 0 °C (ice water) and an additional 100 g of BF_3 was added. A considerable amount of solid precipitated during the course of the BF_3 addition so the contents of the flask were swirled by hand occasionally (a mechanical stirrer with a polyolefin stirrer may be desired).

The precipitate and solution were transferred under N_2 to a 600-mL filter funnel equipped with a medium glass frit filter. The solid was suction filtered and washed with 300 mL of CH_2Cl_2 and sucked dry under N_2. The solid was transferred to a vacuum flask in a glove bag under N_2 and then dried at 70 °C under vacuum for 2 h to give a free-flowing white salt in 65% yield (85.9 g isolated).

Analysis of this product by the NMR method showed it to be greater than 95% NO_2BF_4. An infrared spectrum of the 18-crown-6 ether complex in CH_2Cl_2 showed no band at 2260 cm^{-1}, indicating essentially no $NOBF_4$. A solution of the salt complexed with 18-crown-6 ether (1:1) in CH_2Cl_2 was colorless, giving a visual indication that the NO^+ content was very low.

Quantitative Analysis of Commercial Samples of NO_2BF_4 for NO^+ and NO_2^+ Content. 1. NMR Method for NO_2^+. A slight modification of the method of Yoshida and Ridd[3] was used. This method determines the amount of NO_2^+ in the sample of NO_2BF_4 to be analyzed by determining the yield of 2,4-dinitrotoluene obtained by nitrating *p*-nitrotoluene.

Into a dry 5-mm NMR tube was placed 58.7 mg (0.442 mmol) of the NO_2BF_4 to be analyzed in a glove bag under N_2. The NMR tube was fitted with a septum cap, and 300 μL of dry CD_3CN was added. To this was then added 121.2 mg (0.884 mmol, 2.0 equiv) of *p*-nitrotoluene as a solution in 200 μL of CD_3CN. The contents were mixed (slight exotherm), and the NMR spectrum was recorded. The methyl region signals were integrated. The percent of NO_2^+ in the sample of NO_2BF_4 is given by

$$2[(\text{integral of signal at } \delta\ 2.71\ (2,4\text{-dinitrotoluene})]/(\text{integral of signals at } \delta\ 2.71 \text{ and } 2.50\ (p\text{-nitrotoluene})]] \times 100\%$$

Three commercial samples of NO_2BF_4 from different sources were analyzed by this technique. Sample 1 was found to contain 57% of the theoretical amount of NO_2^+, sample 2 contained 80% NO_2^+, and sample 3 contained 71% NO_2^+. The sample prepared from anhydrous nitric acid free of nitrous oxides was found to contain 96% NO_2^+.

2. Potassium Permanganate Titrimetric Method for NO^+ in Samples of NO_2BF_4.[9] Samples of NO_2BF_4 containing NO^+ as an impurity were first carefully hydrolyzed in NaOH (at 0 °C, closed system) to give nitrate and nitrite ions, respectively:

$$NO_2BF_4 + 2NaOH \rightarrow NaNO_3 + NaBF_4 + H_2O$$

$$NOBF_4 + 2NaOH \rightarrow NaNO_2 + NaBF_4 + H_2O$$

The hydrolyzed samples were analyzed for nitrite by oxidation to nitrate with standardized $KMnO_4$. The amount of nitrite present (thus nitrosonium ion content) is given by the amount of $KMnO_4$ consumed according to the equation:

$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

A typical procedure follows: To 0.477 g (3.59 mmol) of a NO_2BF_4 sample to be analyzed in a stoppered 25-mL Erlenmeyer flask was slowly added 4 mL of 50% NaOH solution at 0 °C. After all had been hydrolyzed, this solution was added to 25 mL of 0.2002 N $KMnO_4$ acidified with 10 mL of 10 N H_2SO_4. This solution was warmed on a steam bath for 10 min. The warm solution was titrated just past the end point (clear solution) with standardized sodium oxalate (0.2000 N, 20.5 mL). This was back-titrated with standardized $KMnO_4$ until a faint pink color persisted (1.9 mL, 0.2002 N). The amount of NO^+ in the sample is given by total $KMnO_4$ less sodium oxalate, where 1 mL of 0.2 N $KMnO_4$ = 0.069 g of $NaNO_2$.

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[9] *Standard Methods of Chemical Analysis*, 6th ed.; Furman, N. H., Ed.; Van Nostrand: Princeton, New Jersey, 1962; p 746.

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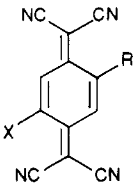
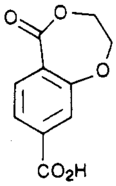
Much attention in recent years has been focused on organic materials with interesting electrical properties. Many conductive charge-transfer complexes between the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, 1) and several organic electron donors have been prepared and reported as important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

Scheme I

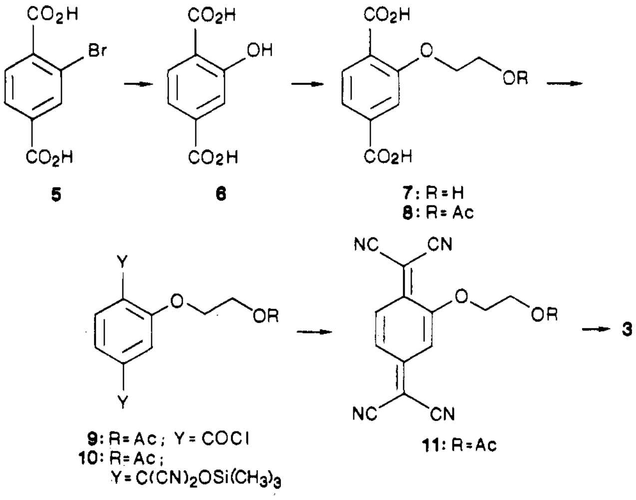

Table I. Half-Wave Reduction Potentials[a]

	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.

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).

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