solution in the same manner as the first water extracts gave an additional 0.023 g of **31**. Also obtained was 0.014 g of a compound identified as dimethyl 1,2-benzenedisulfonate by comparison with an authentic sample of this diester prepared as described below.

Preparation of Dimethyl 1,2-Benzenedisulfonate. 1,2-Benzenedisulfonic acid[18] (0.076 g, 0.32 mmol) in 10 ml of dry ether was treated with an excess of ethereal diazomethane at 0 °C. Evaporation of the solvent gave dimethyl 1,2-benzenedisulfonate: 0.082 g (97%); mp 67–69 °C after recrystallization from benzene/hexane; IR (KBr) 1365 (s), 1265 (s), 1190 (s), and 990 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 8.6–7.7 (m, 4 H), 3.93 (s, 6 H). Anal. Calcd for $C_8H_{10}O_6S_2$: C, 36.08; H, 3.79; S, 24.08. Found: C, 36.26 H, 3.85; S, 23.90.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. 1, 21691-14-5; *cis*-**2**, 86411-00-9; **6**, 86411-01-0; **8**, 86411-02-1; **9**, 86411-03-2; **11a**, 86411-05-4; **11b**, 86411-06-5; **12**, 86411-07-6; **13**, 86411-08-7; **14**, 86421-55-8; **15**, 86411-09-8; **26a** (isomer 1), 86411-10-1; **26a** (isomer 2), 86411-11-2; **26b** (isomer 1), 86411-12-3; **26b** (isomer 2), 86411-13-4; **30**, 47221-29-4; **31**, 86411-14-5; **36**, 86411-15-6; 1,2-benzenedisulfonyl chloride, 6461-76-3; morpholine, 110-91-8; benzenesulfenyl chloride, 931-59-9; hydrazine, 302-01-2; 2-(methylsulfonyl)phenyl disulfide, 86411-16-7; 2-methyl-2-propanethiol, 75-66-1; tetra-*n*-butylammonium hydroxide, 2052-49-5; sodium sulfite, 7757-83-7; methanol, 67-56-1; ethanol, 64-17-5; 1,2-benzenedisulfonic acid, 31375-00-5.

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[18] Buzbee, L. R. *J. Org. Chem.* **1966**, *31*, 8289.

Synthesis of Several New Electron-Acceptor Molecules and Their Electrochemical and EPR Properties

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Received August 16, 1982

A series of new organic electron acceptors was synthesized and electrochemical and EPR investigations were carried out. 1,2,5,6-Tetracyanoacenaphthylene exhibits a reversible one-electron reduction wave at +0.09 V. Other compounds of this series also reduce very easily. A small difference between the first two reduction waves was noted for 1,2-dibromo-5,6-dinitroacenaphthylene. The radical anions of these acceptors were studied by EPR. The first persistent radical anions of aryl bromides are reported here. It was also seen that the ^{14}N hyperfine splitting constants for the peri-nitro compounds were unusually small in comparison to other aromatic nitro compounds.

Introduction

The synthesis and study of low-dimensional highly conducting organic and organometallic materials continue to be an area of great interest. Regarding organic charge-transfer salts, the majority of these studies involve tetracyanoquinodimethane (TCNQ) or similar electron sinks that contain the dicyanomethylene function as an integral part of the electrophore. We have been interested in synthesizing new electron acceptors that do not contain dicyanomethylene units in the molecule. In this manuscript, we describe the synthesis of several potential electron acceptors for charge-transfer salts. We also report the redox properties of these molecules as well as the EPR of the corresponding radical anions.

Results and Discussion

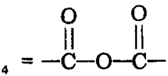
The first class of new electrophores investigated was the 1,2-dicyanoethylene functionality. It retains the well-known electron-withdrawing power of the two cyano groups present in the dicyanomethylene moiety. A very close relative of this moiety is the 1,2-ethylenedicarboxylic cyclic anhydride group. It too is planar with excellent electron-withdrawing substituents and is itself derived synthetically from the corresponding 1,2-dicyanoethylene group. We also examined a series of electrophores having electron-withdrawing substituents in the peri positions of condensed aromatic compounds.

Scheme I

1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = Br$
5, $R_1 = R_2 = Br$
10, $R_1 = R_2 = CN$
15, $R_1 = R_2 = NO_2$

3, $R_3 = R_4 = R_6 = Br$; $R_5 = H$
4, $R_3 = R_4 = R_6 = CN$; $R_5 = H$
6, $R_3 = R_4 = R_5 = R_6 = Br$
7, $R_3 = R_4 = R_5 = R_6 = CN$

8, $R_3 = R_4 = Br$; $R_5 = R_6 = CN$
9, $R_3 = R_4 = R_6 = Br$; $R_5 = CN$
11, $R_3 = CN$; $R_4 = R_5 = R_6 = H$
12, $R_3 = R_4 = CN$; $R_5 = R_6 = H$



13, $R_3,R_4 = \overset{\displaystyle O}{\overset{\|}{\text{—C}}}\text{—O—}\overset{\displaystyle O}{\overset{\|}{\text{C}}}\text{—}$; $R_5 = R_6 = H$
14, $R_3 = R_4 = CO_2CH_3$; $R_5 = R_6 = H$
16, $R_3 = R_4 = Br$; $R_5 = R_6 = NO_2$
17, $R_3 = R_4 = CN$; $R_5 = R_6 = NO_2$
18, $R_3 = CN$; $R_4 = Br$; $R_5 = R_6 = H$
19, $R_3 = R_4 = R_5 = R_6 = H$

The synthesis of these molecules represents rather straightforward chemistry starting from acenaphthene (**1**) and is summarized in Scheme I. Acenaphthene (**1**) was converted into **5** by published procedures.[1,2] Compound **5** was then treated with 4 mol of NBS which after 1.5 h reflux yielded **6** in 70% yield. When **6** was heated in *N*-methyl-2-pyrrolidinone with CuCN at 160 °C for 1.5 h, **7** was obtained in low yield. This reaction is very sensitive to temperature and length of heating. If the temperature

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[1] Ross, S. D.; Finkelstein, M.; Peterson, R. C. *J. Am. Chem. Soc.* **1958**, *80*, 4327–4330.

[2] Constantine, P. R.; Deady, L. W.; Topsom, R. D. *J. Org. Chem.* **1969**, *34*, 1113–1115.

0022-3263/83/1948-2949$01.50/0

Table I. Electrochemical Results

compd[a]	$E_{1/2}$, V,[b] 1st wave	$E_{1/2}$, V,[b] 2nd wave	$\Delta E_{1/2}$, mV[f]
acenaphthylene series			
acenaphthylene	−1.567	−2.262[c]	708
1-cyano-	−1.040	−1.834[c,d]	794
1,2-dicyano-	−0.494	−1.515	1021
1,2,5-tricyano-	−0.127	−0.982	855
1,2,5,6-tetracyano-	+0.092	−0.613	705
1,2-dicarboxylic anhydride	−0.403	−1.316	913
1,2-dibromo-5,6-dicyano-	−0.432	−1.082	650
1,2-dibromo-5,6-dinitro-	−0.272	−0.616	344
acenaphthene series			
5,6-dinitroacenaphthene[e]	−1.007	−1.522	517
5,6-dicyanoacenaphthene	−1.516	−2.255[c,d]	739

[a] All compounds are approximately 1 mM in DMF–0.1 M TBAP unless otherwise specified. All experiments are on the DME. [b] Potentials vs. Ag/AgCl, saturated NaCl (aq).[9] [c] Chemically irreversible by cyclic voltammetry. [d] Current height is approximately one-half of first wave height; perhaps it is not a true diffusion process. [e] 1 mM in acetonitrile–0.1 M TBAP. [f] $\Delta E_{1/2}$ is the difference between the first and second reduction waves.

goes much above 160 °C, and if the reaction is heated for more than 1.5 h, little or no product is found. If, instead, the reaction vessel is heated up to only 118 °C, stirred for only 15 min at this temperature, and then worked up, two new products, **8** and **9**, are found. The structure of **9** was determined by converting **5** into **10** by standard methods.[3,4] Compound **10** was then converted into **9** by refluxing with NBS. It is interesting to note that the bromine atoms in the 5,6-positions of acenaphthylene are much more readily replaced by cyanide ion than the bromine atoms of the 1,2-positions. Compound **9** is the initial product of the reaction and is slowly converted into **8**, and is thus assigned the structure 1,2,5-tribromo-6-cyanoacenaphthylene. Compound **3** was readily prepared by refluxing **2** with 4 mol of NBS. Compound **3** was readily converted into the tricyano derivative by reaction with CuCN in *N*-methyl-2-pyrrolidinone. Compounds **11**, **12**, **13**, **14**, and **18** have been previously reported.[3] Compound **16** was easily prepared from the already reported **15** by refluxing with excess NBS. However, a variety of reaction conditions and several attempts failed in converting **16** into **17**.

The reduction potentials (Table I) of these acceptors reveal something about their relative π acidities and EA values.[5-7] As expected, the ease of reduction increases with addition of electron-withdrawing groups.[8] The tetracyano compound, **7**, is the easiest compound to reduce in this study. Like TCNQ, its reduction potential (+0.092 V) is on the positive side of 0.0 V[9] and indicates it is nearly as easy to reduce as TCNQ.[10] The cyclic anhydride, **13**, reduces approximately 1.1 V positive of acenaphthylene and is roughly 100 mV more easily reduced than its close relative, 1,2-dicyanoacenaphthylene. This trend has been observed before[11] but was not discussed. This result means that the cyclic anhydride is a better electron-withdrawing group than the dicyanoethylene electrophore and is a significant result in designing acceptor molecules. The 1,2-bis(carbomethoxy) derivative, **14**, is also much easier to reduce than acenaphthylene.

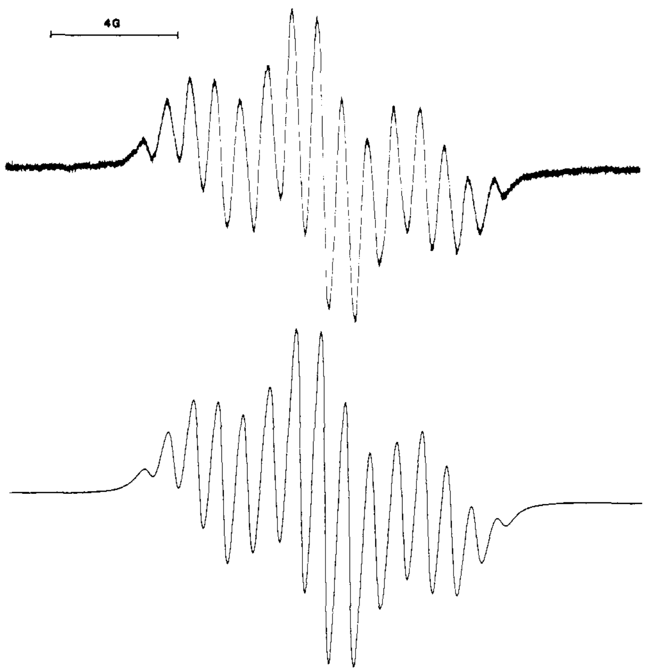

Figure 1. EPR spectrum of **8**. Upper: experimental. Lower: simulated with a = 3.23 G (2 H), a = 0.77 G (2 H), a = 0.77 G (2 N), Lorentzian line width = 460 mG.

The reductive electrochemistry of **15**, 5,6-dinitroacenaphthene, has been previously examined[12] under aqueous conditions. This study of **15** in nonaqueous solvents demonstrates how the presence of the two nitro groups changes the reduction of acenaphthene from a two-electron irreversible process to a one-electron reversible reduction. Furthermore, the reduction potential is shifted positive by well over 1 V. The extra delocalization available in the acenaphthylene ring system compared to the acenaphthene ring system makes **16** even more easily reduced.

Radical anions of the acceptors studied here are generally quite persistent. Of special note are the bromo compounds of this series of acceptors. It is well-known that bromine atoms are readily reductively cleaved from alkyl and aryl bromides. Nevertheless, compounds **8**, **16**, and **18** exhibited very reversible cyclic voltammograms. In addition, the radical anions of both **8** and **16** were produced in bulk and studied. To our knowledge, this is the only report of very stable radical anions of aryl bromides. The EPR results of all the stable radical anions are summarized in Table II.[23] Characteristic of the EPR spectra of both bromine-containing radical anions is the very large line width (see Figure 1). This is most likely the result of the large nuclear quadrupole moments of the ^{79}Br and ^{81}Br isotopes, each of which possesses a $^3/_2$ spin.[13,14] Moreover, the EPR results suggest that the cyclic anhydride electrophore is a better electron sink than the dicyanoethylene group.

The compounds with nitro groups in the 5,6-positions exhibit a rather unusual feature in the EPR spectra. The

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(3) Herold, D. A.; Rieke, R. D. *J. Org. Chem.* **1979**, *44*, 1359–1361.

(4) Newman, M. S.; Boden, H. *J. Org. Chem.* **1961**, *26*, 2525.

(5) Lyons, L. E. *Nature (London)* **1950**, *166*, 193.

(6) Maccoll, A. *Nature (London)* **1949**, *163*, 178–179.

(7) Hoijtink, G. J. *Recl. Trav. Chim. Pays-Bas* **1955**, *74*, 1525–1539 and references therein.

(8) Rieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683–693.

(9) The Ag/AgCl saturated NaCl (aq) reference is about 40 mV anodic of the SCE.

(10) Acker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 6408–6409.

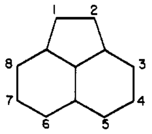
(11) Peover, M. E. *Trans. Faraday Soc.* **1962**, *58*, 2370–2374.

(12) LoPresti, G. M.; Huang, S.; Reidlinger, A. A. *J. Electrochem. Soc.* **1968**, *115*, 1135–1138. Bernard, D.; Mugnier, Y.; Tainturier, G.; Laviron, E. *Bull. Soc. Chim. Fr.* **1975**, 2364–2366.

(13) Fox, W. M.; Water, W. A. *J. Chem. Soc.* **1965**, 4628–4632.

(14) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498–3503.

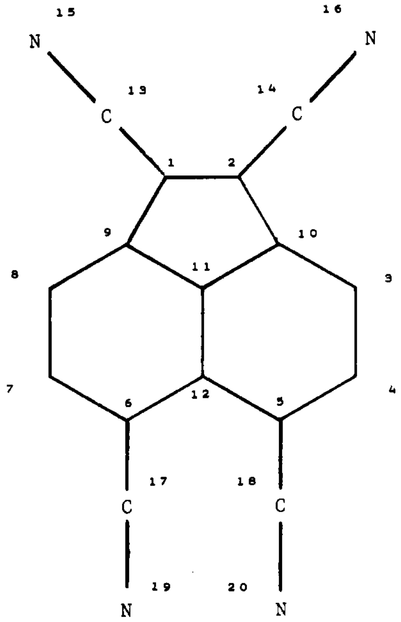
Table II. EPR Results



compd	1,2	3,8	4,7	5,6	N
		acenaphthylene series			
1,2-dicarboxylic anhydride		4.18	1.24	4.51	
1,2-dicyanoacenaphthylene		5.20	1.29	1.29	0.92
1,2,5,6-tetracyanoacenaphthylene		4.17	0.29		0.67
1,2-dibromo-5,6-dicyanoacenaphthylene		3.24	0.77		0.77
1,2-dibromo-5,6-dinitroacenaphthylene		1.89	1.89		0.28
		acenaphthene series			
5,6-dicyanoacenaphthene	9.39	1.10	2.33		0.49

(The columns 1,2 through N are headed "hyperfine splitting constants".)

^{14}N hfsc of the nitro groups are very small. Ordinarily, aromatic nitro groups have large hfsc values. Many times they are in excess of 5 G.[15,16] Clearly, these peri-nitro groups have some features which make them quite different. While the fraction of odd electron density must be high in the two nitro groups (the proton hfsc are very small), the small ^{14}N hfcs most likely results from a cancellation of positive and negative terms found in the hfcs equation.[16] Molecular orbital calculations at the Hückel and ω levels were carried out on a number of compounds to help assign hfsc to the proper nuclei. A number of parameters were adjusted in the calculations so as to find the best correlation to a plot of $E_{1/2}$ vs. LUMO coefficient.[7,24] For the sake of convenience, calculations for this series were limited to acenaphthylene and the cyano-substituted acenaphthylenes **19**, **11**, **12**, **4**, and **7**. The assumptions giving the best correlation of the $E_{1/2}$ vs. LUMO energy plots are listed in Figure 2.



Best

$\alpha_N = \alpha_C + 1.0\beta_0$
$\beta_{1,2} = 1.18\beta_0$
$\beta_{1,9} = 0.9\beta_0$
$\beta_{1,13} = 0.9\beta_0$
$\beta_{6,17} = 0.7\beta_0$
$\beta_{13,15} = 2.0\beta_0$

Other

$\beta_{1,2} = 1.0\beta_0$
$\beta_{1,9} = 1.0\beta_0$
$\beta_{1,13} = 0.7\beta_0$
$\beta_{6,17} = 0.9\beta_0$

Figure 2. Best assumptions for Hückel calculations.

Summary

A series of acenaphthylene and acenaphthene compounds were synthesized and investigated by electrochemical methods and by EPR. The primary aim was to search for new potential electrophores. Among those groups studied were the 1,2-dicyanoethylene, 1,2-ethylenedicarboxylic cyclic anhydride, peri-cyano, and peri-nitro moieties.

Polarographic and voltammetric measurements found that 1,2,5,6-tetracyanoacenaphthylene was reduced extremely easily; the reduction potential was positive of 0.0 V.[9] The cyclic anhydride has a reduction potential 100 mV positive of the 1,2-dicyano compound, but both are much easier to reduce than acenaphthylene. Cyano groups in the 5 and 6 positions also facilitate reduction, as do nitro groups in those positions. A rather small difference between the first and second reduction potentials of **16** was noted.

Coulometric studies showed that the reduction process for each of these compounds involves one electron. The resulting radical anions are very persistent and were studied by EPR. The first radical anions of aromatic bromides were produced in **8** and **16**. The line widths of the EPR spectra were shown not to be due to exchange broadening, but more likely to be due to the presence of the two bromine atoms. The cyclic anhydride appears to be a better electron sink than the 1,2-dicyanoethylene moiety by comparing the hfsc of the two compounds **12** and **13**. The peri-cyano groups appear to be roughly as good as 1,2-dicyanoethylene groups in capturing spin density, as can been seen from the EPR of **7**. Compounds with 5,6-dinitro substitution exhibit uncharacteristically small ^{14}N hfsc. The origin of this observation is unclear but may arise from small spin density on the nitro groups (which is felt to be unreasonable), near cancellation of all the terms in the Rieger and Fraenkel[16] expression due to solvent or interaction effects, or perhaps from through-space polarization due to the close proximity of the nitro groups.

Studies on the formation of charge-transfer salts with these electron acceptors will be reported in the future.

Experimental Section

Electrochemistry. All electrochemical experiments were performed using a PAR Model 173 potentiostat/galvanostat equipped with *iR* compensation in conjunction with a PAR Model

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[15] For example: Ward, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 1296–1300. Geske, D. H.; Maki, A. H. *Ibid.* **1960**, *82*, 2671–2676. Russell, G. A.; Janzen, E. G. *Ibid.* **1962**, *84*, 4153–4154; Piette, L. H.; Ludwig, P.; Adams, R. N. *Ibid.* **1962**, *84*, 4212–4215.

[16] Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1963**, *39*, 609–629.

175 universal programmer and Model 179 digital coulometer. This system uses a conventional three-electrode configuration.

The cell used for polarography and voltammetry has been previously described.[17] The working electrodes of this cell include the dropping mercury electrode (DME), the platinum disk electrode, and the hanging mercury drop electrode (HMDE). The platinum disk electrode as an area of 0.83 ± 0.05 mm^2. The DME was of a standard type. The HMDE was purchased from Metrohm and had a micrometer device for expelling mercury drops of reproducible size. The drop size generally used in these experiments was 1.38 ± 0.05 mm^2.

The auxiliary electrode was a platinum screen buffered from the bulk solution by a fritted glass bridge assembly to minimize contamination by products formed there. The reference electrode was Ag/AgCl, saturated NaCl(aq) which is likewise buffered from the bulk solution by a fritted glass bridge assembly to keep water from entering the bulk solution. Buffer solutions always contained the same solvent and supporting electrolyte as the test solutions. All potentials given in this work are given vs. the Ag/AgCl reference. This reference electrode is +0.042 V from the saturated calomel electrode.

Dimethylformamide (DMF) was purified by pouring DMF (1.6 L) into a 2-L round-bottom flask with CaH_2 and refluxed at aspirator vacuum, approximately 15 torr, for 1 h in the distillation apparatus with a 12-in. Vigreux column between the flask and the distilling head. The DMF was then vacuum distilled at this reduced pressure, boiling at 57 °C, and was stored over 4 Å molecular sieves in the dark. Acetonitrile (AN) was purified for electrochemical use by distilling it from anhydrous Na_2CO_3 and $KMnO_4$ under nitrogen or argon and then passing it down a column of activated alumina. The AN so purified was stored over 4-Å molecular sieves. Supporting electrolytes used were tetraethylammonium perchlorate (TEAP) and tetra-*n*-butylammonium perchlorate (TBAP). Both were purchased from Eastman Chemicals and used without further purification except for drying for 1 h at 70 °C under vacuum. The inert atmosphere used was prepurified grade argon which was further purified by passing over heated copper catalyst, phosphorus pentoxide, and finally solid KOH to remove oxygen, water, and residual acidic gases, respectively.

Experiments were performed at ambient temperature, (23 ± 2 °C).

EPR. Electron paramagnetic resonance (EPR) spectroscopy was performed by generating the radical anions electrochemically in the EPR cavity.

Tetrahydrofuran (THF) used in the EPR experiments was freshly distilled for each experiment from NaK alloy from a permanent still and syringed out under inert atmospheric conditions.

Synthesis. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Ultraviolet and visible spectra were obtained from a Hewlett-Packard Model 8450-A spectrophotometer. The NMR data were recorded on either a Varian A-60 spectrometer or a Varian EM-390. The EPR spectra were taken on a Bruker Model ER 200 D spectrometer. All mass spectroscopy was performed as service work by the Midwest Regional Center for Mass Spectroscopy. All melting points were taken on a Hoover Unimelt apparatus or Electrothermal melting point apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

5-Bromoacenaphthene (2). The method of Ross, Finkelstein, and Petersen[1] was used to prepare 5-bromoacenaphthene. Recrystallization from 95% ethanol yielded 5-bromoacenaphthene, mp 54–54.5 °C. The reported melting point[1] was 51–52 °C.

1,2,5-Tribromoacenaphthylene (3). The procedure used was taken from the thesis of David Herold.[18,22] 5-Bromoacenaphthene (4.0 g, 17.2 mmol), *N*-bromosuccinimide (12.25 g, 68.8 mmol), dibenzoyl peroxide (50 mg), and carbon tetrachloride (100 mL) under argon were refluxed for 1.5 h. The solution was cooled and filtered to remove succinimide and any excess *N*-bromosuccinimide. The collected solid was washed with warm carbon tetrachloride (100 mL) to remove any remaining product. The filtrate was washed twice with 10% aqueous sodium thiosulfate (500 mL), and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure, leaving 6.9 g of a dark orange solid. This solid was chromatographed on a 3 × 51 cm alumina column (Fisher, 80–200 mesh) slurry packed with hexane. The column was eluted with hexane (technical, distilled), and 250-mL fractions were collected. Fractions 9–17 gave 1,2,5-tribromoacenaphthylene (4.48 g). The compound was recrystallized from 95% ethanol to yield light orange crystals (3.63 g, 54%, mp 116.5–117 °C): IR (KBr) 1465, 1419, 1170, 1150, 1040, 825, 800, 753 cm^{-1}; high-resolution mass spectrum calcd 387.79232 and 389.79035, found 387.79233 and 389.78996.

1,2,5-Tricyanoacenaphthylene (4). The procedure used to prepare 1,2,5-tricyanoacenaphthylene was similar to the method used by Herold and Rieke[3] to prepare 1,2-dicyanoacenaphthylene. 1,2,5-Tribromoacenaphthylene (2.14 g, 5.50 mmol), cuprous cyanide (3.04 g, 34.0 mmol), and *N*-methyl-2-pyrrolidinone (20 mL) under argon were heated to 160 °C and then kept at 160 °C for 2.5 h. The dark brown solution was cooled, poured into a solution of sodium cyanide (4 g) in water (100 mL), shaken well, and extracted with benzene (4 × 100 mL). The water and benzene layers were filtered. The benzene layer was washed with 10% sodium cyanide solution (50 mL) and water (50 mL) and dried over anhydrous sodium sulfate. Removal of the benzene at reduced pressure gave 0.728 g of a brown solid, which was chromatographed on a 3 × 24 cm silica gel (Baker, 60–200 mesh) column slurry packed with benzene.

The column was eluted with benzene; 250-mL fractions were collected. Fractions 4–8 yielded 1,2,5-tricyanoacenaphthylene (204 mg), which was recrystallized from 95% ethanol to yield yellow-orange crystals of 4 (179 mg, 14%, mp 246.5–247 °C): IR (nujol) 2220 (C$\equiv$N), 1610, 1280, 1081, 810, 760; high-resolution mass spectrum, calcd 227.04833, found 227.04859.

5,6-Dibromoacenaphthene (5). The method of Constantine, Deady, and Topsom[2] was used to prepare 5,6-dibromoacenaphthene. 5,6-Dibromoacenaphthylene was recrystallized from methylene chloride; mp 172–172.5 °C (lit.[2] mp 165–168 °C).

1,2,5,6-Tetrabromoacenaphthylene (6). A mixture of 5,6-dibromoacenaphthene (2.46 g, 7.90 mmol), *N*-bromosuccinimide (5.76 g, 32 mmol), dibenzoyl peroxide (25 mg), and carbon tetrachloride (50 mL) was refluxed under argon for 1.5 h, during which time the solution turned dark red. The solution was cooled and filtered. A carbon tetrachloride extract (200 mL) of the collected solid was added to the first filtrate, which was washed with 10% aqueous sodium thiosulfate (600 mL), diluted with methylene chloride to dissolve the precipitate which formed, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was recrystallized from methylene chloride to give 2.58 g (70%) of fluffy orange crystals of 1,2,5,6-tetrabromoacenaphthylene: mp 255–255.5 °C (lit.[19] mp 255.5–256.5 °C); IR (nujol) 1560, 1195, 1150, 1098, 822 cm^{-1}; high-resolution mass spectrum, calcd 467.70160, found 467.70138.

1,2,5,6-Tetracyanoacenaphthylene (7). A mixture of 1,2,5,6-tetrabromoacenaphthylene (1.145 g, 2.45 mmol), cuprous cyanide (1.58 g, 17.64 mmol), and *N*-methyl-2-pyrrolidinone (35 mL) under argon was slowly heated to 160 °C, where it was maintained for 1.5 h. The dark solution was cooled slightly and then poured into a warm solution of sodium cyanide (34 g) in water (100 mL). The mixture was shaken thoroughly and extracted with methylene chloride (800 mL). The organic layer was filtered, washed with 250 mL of 10% sodium cyanide solution and then water, filtered, dried (Na_2SO_4), and evaporated under reduced pressure; the small amount of remaining *N*-methyl-2-pyrrolidinone was removed by vacuum distillation. The residue (0.185 g, 30%) was chromatographed on a 3 × 61 cm silica gel column (E. Merck, 70–230 mesh) slurry packed with methylene chloride.

The column was eluted with methylene chloride and 250-mL fractions were collected. Fractions 17–27 yielded 0.057 g (9%) of 1,2,5,6-tetracyanoacenaphthylene; the compound was washed three times with very small amounts of methylene chloride to yield amber-colored needle-like crystals: mp above 360 °C; IR (nujol) 2220 (C$\equiv$N), 1442, 1278, 1195, 1095, 860 cm^{-1}; mass spectrum (70

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[17] Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Wileford, B. R.; Radonovich, L. J.; Eyring, M. *Organometallics* **1982**, *1*, 938–950.

[18] Herold, D. A., Masters Thesis, University of North Carolina, Chapel Hill, NC, 1972.

[19] Usachenko, V. G.; Petrenko, G. P. *Ukr. Khim. Zh.* (*Russ. Ed.*) **1975**, *41*, 663.

eV), m/e (relative intensity) 252 (100), 227 (27), 225 (22), 200 (8), 123 (4), 99 (7); high-resolution mass spectrum, calcd 252.0435, found 252.0434.

1,2-Dibromo-5,6-dicyanoacenaphthylene (8) and 1,2,5-Tribromo-6-cyanoacenaphthylene (9). 1,2,5,6-Tetrabromoacenaphthylene (1.809 g, 387 mmol), cuprous cyanide (2.77 g, 30.96 mmol), and *N*-methyl-2-pyrrolidinone (15 mL) under argon were stirred and heated to 118 °C over 30 min; the reaction was heated at 118 °C for 15 min. The reaction was worked up as for the preparation of 7.[20] The crude product was chromatographed on a 3 × 66 cm silica gel column (E. Merck, 70–230 mesh) with 10% methylene chloride/90% hexane as solvent; 250-mL fractions were collected. After four fractions the solvent was changed to 20% methylene chloride/80% hexane, after five more fractions the solvent was changed to 50% methylene chloride/50% hexane, and after fraction 30 the solvent was changed to 75% methylene chloride/25% hexane.

Fractions 13–25 yielded 0.536 g of 9 and fractions 34 and 35 yielded 0.282 g of 8. Fractions 34 and 35 were combined and recrystallized from methylene chloride to yield red crystals of 1,2-dibromo-5,6-dicyanoacenaphthylene (0.245 g, 18%): mp extensive softening 354–360 °C but not melted by 360 °C; IR (KBr) 2210 ($C\equiv N$), 1605, 1485, 1445, 1165, 848, 670, 500 cm^{-1}; high-resolution mass spectrum, calcd 359.8722, found 359.8722.

Fractions 13–25 were combined and recrystallized from methylene chloride to yield orange crystals of 1,2,5-tribromo-6-cyanoacenaphthylene (0.501 g, 31%): mp 319.5–323 °C; IR (nujol) 2209 ($C\equiv N$), 1480, 1415, 1202, 1160, 1140, 1050, 980, 825, 660 cm^{-1}; high-resolution mass spectrum, calcd 412.7872, found 412.7871.

1,2-Dibromo-5,6-dicyanoacenaphthylene (8). 5,6-Dicyanoacenaphthene (0.408 g, 2 mmol), *N*-bromosuccinimide (1.44 g, 8 mmol), dibenzoyl peroxide (11 mg), and carbon tetrachloride (25 mL) under argon were refluxed for 7 h. The carbon tetrachloride was removed under reduced pressure, leaving 1.77 g.

The crude mixture was chromatographed on a 4 × 43.5 cm silica gel column (E. Merck, 70–230 mesh) slurry packed with methylene chloride. The column was eluted with methylene chloride (250-mL fractions). Fractions 6 and 7 yielded 0.160 g of red crystals mixed in with light colored crystals of succinimide. Recrystallization from methylene chloride yielded 38 mg (5%) of 1,2-dibromo-5,6-dicyanoacenaphthylene: mp extensive softening 354–360 °C but not melted by 360 °C; IR (nujol) 2210 ($C\equiv N$), 1600, 1165, 670 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 362 (45), 360 (100), 358 (47).

5,6-Dicyanoacenaphthene (10). 5,6-Dibromoacenaphthene (2.35 g, 7.53 mmol), cuprous cyanide (2.43 g, 27.10 mmol), and *N*-methyl-2-pyrrolidinone (35 mL) under argon were slowly heated to 160 °C over 1 h and then heated at 160 °C for 40 min. The reaction was worked up the same as that for 7. The crude reaction material (1.37 g) was chromatographed on a 3 × 65 cm column of silica gel (E. Merck, silica gel 60, 70–230 mesh) slurry packed with methylene chloride. The column was eluted with methylene chloride; 250-mL fractions were taken. Fractions 11–19 yielded 1.00 g of 5,6-dicyanoacenaphthene, which was recrystallized from methylene chloride to give white crystals of 10 (0.83 g, 54%, mp 310–311 °C, charred before melting): IR (KBr) 2210 ($C\equiv N$), 1590, 1432, 843 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 204 (100), 203 (39), 202 (12), 149 (17), 85 (17), 71 (25), 57 (34); high-resolution mass spectrum, calcd 204.0685, found 204.0684.

5,6-Dinitroacenaphthene (15). The method of Sachs and Mosebach[21] was used to prepare 15: mp 219.5–222.5 °C (lit.[21] mp 220–224 °C).

1,2-Dibromo-5,6-dinitroacenaphthylene (16). 5,6-Dinitroacenaphthene (22.6 g, 93 mmol), *N*-bromosuccinimide (66.7 g, 375 mmol), and carbon tetrachloride (500 mL) under argon were brought to reflux, at which point several crystals of dibenzoyl peroxide were added.

Reflux was maintained for 6 days. The cooled dark red solution was washed with three portions (150 mL each) of aqueous concentrated sodium thiosulfate and then water. When any solids precipitated out, they were collected and saved for recrystallization. The red tar was washed with acetone, giving a red powder and a red solution. All red solids were recrystallized from toluene while all solutions were combined for chromatography on silica gel by eluting with benzene. The center-most portion of the red fraction gave quite pure compound which was also recrystallized from toluene. The yield was 5.0 g (12%); mp 283–284 °C; UV (THF) 231 (ϵ 2.9 × 10^4), 287 (ϵ 1.4 × 10^4), 346 (ϵ 1.4 × 10^4), 452 (ϵ 9.1 × 10^2) nm; IR (KBr) 3080 (w), 1530 (s), 1485 (m), 1445 (m), 1350 (s), 915 (m), 860 (m), 805 (m), 735 (m), cm^{-1}. Anal. Calcd for $C_{12}H_4Br_2N_2O_4$: C, 36.03; H, 1.01; Br, 39.96, N, 7.01. Found: C, 36.10; H, 1.01; Br, 40.17; N, 6.95.

Acknowledgment. We thank the National Science Foundation for support of this research by grant support to R.D.R. (Grant CHE78-06661). We also acknowledge a Du Pont Fellowship administered by the University of Nebraska Chemistry Department to S.N.M.

Registry No. 2, 7267-03-0; 3, 18105-07-2; 4, 86528-75-8; 5, 19190-91-1; 6, 56564-74-0; 7, 86528-76-9; 7 radical anion, 86528-83-8; 8, 86528-77-0; 8 radical anion, 86528-84-9; 9, 86528-78-1; 10, 86528-79-2; 10 radical anion, 86528-86-1; 11, 39653-72-0; 12, 69038-43-3; 12 radical anion, 86528-82-7; 13, 33239-23-5; 13 radical anion, 86528-81-6; 15, 4406-87-5; 16, 86528-80-5; 16 radical anion, 86528-85-0.

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(20) A solution of 34 g of sodium cyanide in 100 mL of water was later found to be more effective in breaking up the complex formed.

(21) Sachs, F.; Mosebach, G. *Chem. Ber.* 1911, *44*, 2852–2867.

(22) Trost, B. M.; Brittelli, D. R. *J. Org. Chem.* 1967, *32*, 2620–2621.

(23) For more details and simulated spectra see Ph.D. Thesis of Stuart N. Milligan, University of Nebraska—Lincoln, 1982.

(24) For more details on molecular orbital calculations see Ph.D. Thesis of Stuart N. Milligan, University of Nebraska—Lincoln, 1982.

Synthesis of Electron-Deficient Oxetanes. 3-Azidooxetane, 3-Nitrooxetane, and 3,3-Dinitrooxetane[1]

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Received January 10, 1983

A facile synthesis of 3-hydroxyoxetane is described and is based on the addition of acetic acid to epichlorohydrin, protection of the resulting primary alcohol as an acetal, basic acetate hydrolysis and ring closure, and removal of the protecting group. 3-Azidooxetane was prepared from 3-(tosyloxy)oxetane and sodium azide. Reduction of the azide with triphenylphosphine or hydrogen gave 3-aminooxetane, and oxidation of the amine with *m*-chloroperbenzoic acid gave 3-nitrooxetane. Oxidative nitration or reaction with tetranitromethane gave 3,3-dinitrooxetane. 3-Azidooxetane and 3,3-dinitrooxetane were polymerized with Lewis acids.

Recently we reported the synthesis of 3-fluoro-3-nitrooxetane by the base-catalyzed ring closure of the monotriflate derived from 2-fluoro-2-nitro-1,3-propanediol.[2] The "fluorine effect", or the destabilization of a nitronate

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