*J. Org. Chem.* **1991**, *56*, 3737-3739 **3737**

The relationships between $\beta$ and $V_{min}$ for the molecules in Tables I-IV are shown in Figures 1-4, respectively. They are best described as exponential, with correlation coefficients between 0.94 and 0.98.

### Summary and Conclusion

We have shown that there exist good correlations between the solvatochromic hydrogen bond acceptor parameter $\beta$ and $V_{min}$ for four series of oxygen and/or nitrogen-containing molecules. Our results confirm that the calculated electrostatic potential, which refers to the gas-phase molecule, can be quantitatively related to its ability in solution to accept a proton in a solute to solvent hydrogen bond. The fact that different families of compounds must be treated separately indicates of course that other factors are important as well.

**Acknowledgment.** We thank Mrs. Pat Lane for computational assistance. We greatly appreciate the support of this work by the Office of Naval Research through contract No. N00014-85-K-0217.

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## Synthesis and Properties of 6-(Hydroxymethyl)-9,9,10,10-tetracyanonaphthoquinodimethane

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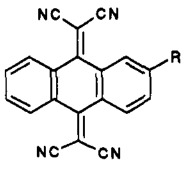
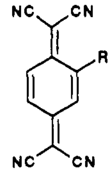
Our interest in alcohol-functionalized tetracyanoquinodimethanes (TCNQs) was the result of an ongoing research program that required them for the preparation of D-$\sigma$-A materials. The latter are extended molecules comprised of electron-donor and -acceptor moieties bridged together by a nonconjugated chain of C/N/O atoms (the $\sigma$ bridge). Similar structures have been proposed for their possible anisotropic electrical conductivity when properly organized between electrodes ($M_1|D\text{-}\sigma\text{-}A|M_2$) in an electronic device. Thus, they should allow facile unidirectional electron flow from the cathode, $M_2$, to the acceptor moiety, from the acceptor to the donor through the $\sigma$ bridge via electron tunneling, and then from the donor moiety to the anode, $M_1$. According to a recent report,[1,2] one of our D-$\sigma$-A molecules[3] exhibited asymmetric current-voltage characteristics when it was tested in a metal/Langmuir-Blodgett monolayer/metal device.

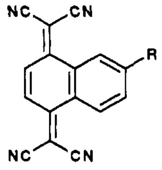
In earlier papers, we have described the syntheses of the electron acceptors, 2-(hydroxymethyl)-11,11,12,12-tetracyanoanthraquinodimethane[4] (HMTCANQ, 1) and 2-(2′-hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane[5] (HETCNQ, 3). We now report the synthesis of a third alcohol-functionalized tetracyanoquinodimethane, 6-(hydroxymethyl)-9,9,10,10-tetracyanonaphthoquinodimethane (HMTCNAQ, 11) from commerically available starting materials. A Diels-Alder reaction between *p*-benzoquinone and isoprene afforded 6-methyl-1,4-naphthoquinone (8) in 71% yield. This was brominated, and the product 9 was hydrolyzed to 6-(hydroxymethyl)-1,4-naphthoquinone (10).[6] Treatment of the latter with malononitrile, pyridine, and titanium tetrachloride produced the hydroxyl-functionalized tetracyanonaphthoquinodimethane 11 in 29% overall yield. $\beta$-Alanine was not essential in this Knoevenagel condensation as it was in the preparation of the (hydroxymethyl)tetracyanoanthraquinodimethane (1).[4] Also, protection of the alcohol function was not required, as first thought. A crystal structure of 11 was determined, and the results were compared to those of the parent compound (with no hydroxymethyl substituent, 6).[7] The greatest difference was in the dihedral angle between the planes defined by the two rings: 26.4° for the parent structure 6 and 10.5° in 11. Thus, 11 was a flatter molecule than either its parent or the tetracyanoanthraquinodimethane 1, which had a dihedral angle of 37.3° between the two least-squares outer six-membered rings.[8] This



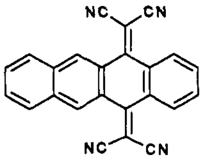
1: R = $CH_2OH$
2: R = H



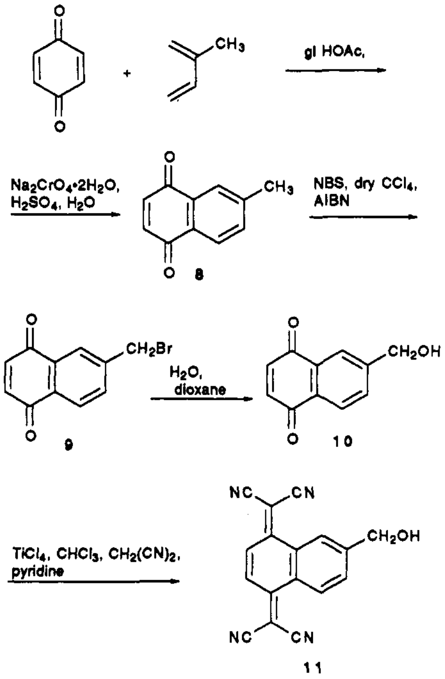
3: R = $O(CH_2)_2OH$
4: R = H



5: R = $CH_3$
6: R = H



7



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divergence from planarity was also confirmed by the relatively high IR stretching vibrations of the conjugated cyano groups that appeared at 2221 cm$^{-1}$ in the spectra of **11** and **5**. Complete crystallographic data of **11** will be published elsewhere.

Cyclic voltammetry of **11** revealed two successive reduction waves each with an associated oxidation wave similar to that seen for HETCNQ (**3**)[5] and TCNQ (**4**). The peak potential separations of these two pairs of waves suggested that both pairs originated from one-electron reversible processes. The peak current ratios for both pairs of waves were close to unity in the range of scan rates examined, 0.050–0.200 V s$^{-1}$, indicating that the products of these reactions, presumably the radical anion and dianion, respectively, were stable on the time scale of voltammetry. However, HMTCANQ (**1**) showed a single two-electron reduction wave, suggesting direct reduction to the dianion. A similar two-electron charge-transfer reaction has been found for the unsubstituted parent structure TCANQ[9] (**2**). This reaction is believed to arise from facile disproportionation of the radical anion produced during the first electron-transfer step.[10] Interestingly, benzotetracyanoanthraquinodimethane (**7**) and other tetra- and pentacyclic TCNQs[11] produce two successive one-electron reduction waves that are more similar to the CVs of the mono- and bicyclic derivatives than those of the tricyclic TCANQs **1** and **2**. UV data[11] suggested that **7** was as severely deformed from planarity as was **1** or **2**. The half-wave reduction potentials ($E_{1/2}$) of **11** and **5**, estimated from the average values of the cyclic voltammetric reduction and oxidation peak potentials of each pair of waves, were comparable with those of the unsubstituted tetracyanonaphthoquinodimethane (TCNAQ, **6**),[9] but were less than those of **3** (see Table I).

Attempts to prepare D-$\sigma$-A materials in which **11** was the acceptor moiety were not immediately successful. (Hydroxymethyl)tetracyanonaphthoquinodimethane did not form carbamate products with phenyl, 4-(dimethylamino)phenyl, or 1-pyrenyl isocyanates under conditions that were effective with either **1** or **3**. Apparently, **11** was not stable during these experiments, since none of it could be recovered from the reaction products.

## Experimental Section

All commercial starting materials were obtained from Aldrich Chemical Co. and were used without further purification. Melting points were run on a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Series 1600 FTIR and the NMR spectra on a Bruker AC300 instrument. E. Merck silica gel (9385) was used in column chromatography. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cyclic voltammograms were obtained by using an EG & G Princeton Applied Research Corp. (PARC) Model 173 potentiostat/galvanostat, which was equipped with a PARC Model 179 digital coulometer plug-in module. A PARC Model 175 universal programmer was used to provide triangular potential waveforms. Data were displayed on a Houston Instruments Model 100 X-Y recorder. Electronic resistance compensation was applied during all experiments. The working electrode was either a glassy carbon or a platinum disk sealed in glass. The reference electrode was a silver wire immersed in a 0.01 M solution of $AgNO_3$ in MeCN, containing the supporting electrolyte at the same concentration as the bulk solution. The reference electrode was isolated from the bulk solution with a porous Vycor plug. The supporting electrolyte, tetrabutylammonium hexafluorophosphate ($n$-$Bu_4N{\cdot}PF_6$), was prepared and purified according to standard procedures.

**Table I. Cyclic Voltammetric Half-Wave Potentials (in Volts)**

| compd | $E_{1/2}$ (first wave) | | $E_{1/2}$ (second wave) |
|---|---|---|---|
| TCNQ (**4**)[a] | −0.09 | | −0.75 |
| TCNAQ (**6**)[a] | −0.26 | | −0.745 |
| TCANQ (**2**)[a] | | −0.71<br>(2e$^-$) | |
| HETCNQ (**3**)[b] | −0.184 | | −0.689 |
| HMTCANQ (**1**)[b] | | −0.624<br>(2e$^-$) | |
| TCNQ (**4**)[c] | −0.136 | | −0.693 |
| MeTCNAQ (**5**)[c] | −0.325 | | −0.702 |
| HMTCNAQ (**11**)[c] | −0.315 | | −0.781 |
| HETCNQ (**3**)[c] | −0.189 | | −0.690 |
| benzoTCANQ (**7**)[d] | −0.440 | | −0.930 |

[a] vs $Ag/AgNO_3$ (0.01 M), electrolyte $Bu_4N{\cdot}BF_4$, in BuCN, data taken from ref 9. [b] vs $Ag/AgNO_3$, potentials estimated from data obtained vs SCE, in MeCN, taken from refs 4 and 5. [c] vs $Ag/AgNO_3$ (0.01 M), electrolyte $n$-$Bu_4N{\cdot}PF36$ (0.1 M), in MeCN, this work. [d] vs SCE, in MeCN, data taken from ref 11.

**6-Methyl-1,4-naphthoquinone (8).** The literature procedure[6] for the preparation of **8** was modified slightly, which resulted in an increased yield. A mixture of 54 g (0.5 mol) of $p$-benzoquinone, 34 g (0.5 mol) of isoprene, and 300 mL of glacial HOAc was stored with occasional shaking in a stoppered flask for 3 days at rt. It was filtered, and the filtrate was warmed to 60 °C to remove any unreacted isoprene. The residue was stirred with a mechanical stirrer at 50 °C while a preheated solution of 200 g of $Na_2Cr O_4{\cdot}2H_2O$, 10 mL of concd $H_2SO_4$, and 125 mL of water was added. The temperature was carefully maintained at 50 °C for 30 min through the use of an ice–water bath and then at 65–68 °C for 45 min. The resultant solution was poured into 600 g of ice and 1 L of water, and this was stored overnight at rt. A solid separated and was collected by filtration and washed with water. It was dissolved in 200 mL of HOAc, and a solution of 10 g of $Na_2CrO_4$ in 10 mL of water was added with stirring. The solution was heated on a steam bath for 15–20 min. Water was added to the cloud point, a solid precipitated on standing, and the mixture was filtered. The product was recrystallized from HOAc to afford 61.05 g (71%) of **8**: mp 90–91 °C (lit.[6] mp 91 °C); IR (KBr) 1664, 1600, 1306, 1050, 822 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.5 (3 H, s, $CH_3$), 6.9 (2 H, s, quinone H), 7.5–8.0 (3 H, m, Ar H).

**6-(Bromomethyl)-1,4-naphthoquinone (9).** The following method gave a much greater yield of **9** compared to that reported in the literature.[6] NBS (13 g, 89.6 mmol) was added to a solution of 10 g (58 mmol) of **8** and 200 mL of dry $CCl_4$. The mixture was warmed, 2 g of AIBN was added, and the result was heated to the reflux temperature for 4 h. The solvent was removed, and the residue was chromatographed on a column of silica gel with acetone/hexane (20:80) to yield 14.53 g (94%) of **9**: mp 122–123 °C; IR (KBr) 1664, 1600, 1307, 839 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.55 (2 H, s, $CH_2$), 7.0 (2 H, s, quinone H), 7.75–8.0 (3 H, m, Ar H).

**6-(Hydroxymethyl)-1,4-naphthoquinone (10).** The literature[6] procedure was followed exactly to afford a 75% yield of **10**: mp 80.0–81.5 °C (lit.[6] mp 81–82 °C); IR (KBr) 3467, 1663, 1599, 1308, 1143, 1062 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 4.82 (2 H, s, $CH_2$), 6.92 (2 H, s, quinone H), 7.58–8.1 (3 H, m, Ar H).

**6-Methyl-9,9,10,10-tetracyanonaphthoquinodimethane (5).** Titanium tetrachloride (0.4 mL, 0.66 g, 3.5 mmol) was added during a 30-min period to a stirred, ice-cold solution of 100 mg (0.6 mmol) of **8** in 15 mL of dry $CHCl_3$ under Ar. The cold reaction solution was stirred for an extra 30 min during which time a red color developed and a small amount of insoluble material was observed. A solution of 0.075 g (1.14 mmol) of freshly distilled malononitrile and 15 mL of dry $CHCl_3$ was added during a 10-min period, the result was stirred for 15 min, and then a solution of 0.5 mL (0.49 g, 6.2 mmol) of pyridine and 10 mL of dry $CHCl_3$ was added during 1.5 h. The ice cooling bath was removed, allowing the reaction mixture to warm to rt. It was stirred for 18 h and then poured into ~50 mL of cold water. The aqueous layer was extracted with 5 × 50 mL of $CHCl_3$, the organic extract

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was washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was column chromatographed with EtOAc/hexane (30:70), which yielded 121 mg of a bright yellow solid. Recrystallization from EtOAc/hexane afforded 101 mg (65%) of pure **5**: mp 211–212 °C; IR (KBr) 2221, 1604, 1329, 809 $cm^{-1}$; UV ($CH_3CN$) 209 (26 830), 283 (13 640), 386 (40 120) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 2.6 (3 H, s, $CH_3$), 7.65 (3 H, m, Ar H), 8.6–8.8 (2 H, m, quinodimethane H); CV half-wave reduction potentials are listed in Table I. Anal. Calcd for $C_{17}H_8N_4$: C, 76.11; H, 3.00; N, 20.88. Found: C, 76.09; H, 3.01; N, 21.06.

**6-(Hydroxymethyl)-9,9,10,10-tetracyanonaphthoquinodimethane (11).** The procedure presented previously for the preparation of **5** was used here with the following amounts of reagents and solutions: 0.9 mL (1.56 g, 8.2 mmol) of $TiCl_4$; 0.25 g (1.3 mmol) of **10** in 50 mL of $CHCl_3$; 0.19 g (2.9 mmol) of malononitrile in 25 mL of $CHCl_3$; and 1.25 mL (1.2 g, 15.5 mmol) of pyridine in 25 mL of $CHCl_3$. Column chromatography of the crude product using acetone/hexane (20:80) produced 237 mg of a bright yellow solid that was recrystallized from EtOAc/hexane to afford 215 mg (57%) of pure **11**: mp 190.5–191.5 °C; IR (KBr) 2221, 1606, 1524, 1051, 810 $cm^{-1}$; UV ($CH_3CN$) 213 (5834), 295 (4175), 385 (9764) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 4.95 (2 H, s, $CH_2$), 7.65–7.9 (3 H, m, Ar H), 8.8–8.95 (2 H, m, quinodimethane H); CV half-wave reduction potentials are listed in Table I. Anal. Calcd for $C_{17}H_8N_4O$: C, 71.83; H, 2.83; N, 19.71. Found: C, 71.44; H, 2.77; N, 19.77.

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# Phenylthiolation of Arylvinyl Bromides by Photolysis

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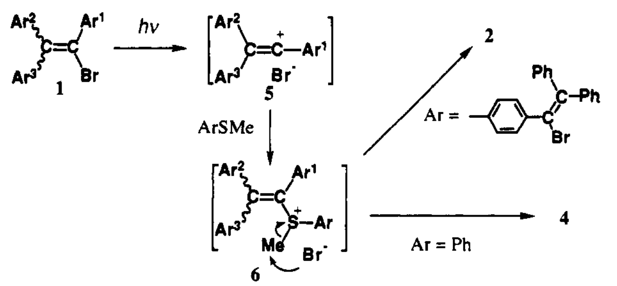
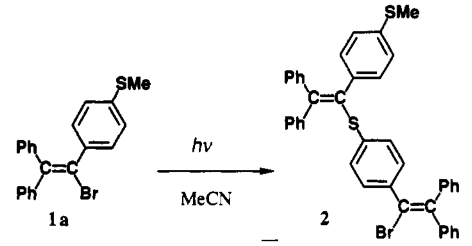
*Received November 12, 1990*

Much attention has been devoted to vinyl cations as reactive intermediates in organic reactions.[1] They have been generated mainly by solvolytic reactions so far. Our studies on photolysis of arylvinyl halides have revealed that photochemical reactions are useful for generation of vinyl cations and their reactions.[2] In the course of the investigation of the photochemical generation of vinyl cations and their behavior, it became desirable to learn the effect of the methylthio group (MeS) on the $\alpha$ aryl group. From the $\sigma^+$ value reported for MeS,[3] the methylthio group is expected to be highly stabilizing for the resulting arylvinyl cation and the behavior is similar to that of the oxygen analogue OMe.[4] However, photolysis of a [$p$-(methylthio)phenyl]vinyl bromide surprisingly resulted in the substitution by ArS. In this paper, we wish to report this novel substitution by ArS and the application to phenylthiolation of arylvinyl bromides using methyl phenyl sulfide.

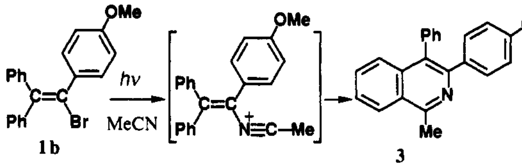
**Scheme I**



Photolysis of 1-bromo-1-[$p$-(methylthio)phenyl]-2,2-diphenylethene (**1a**) in acetonitrile gave pale yellow crystals, which are assigned as the aryl vinyl sulfide **2** on the basis of the spectral data (eq 1). This result is quite interesting because photolysis of the corresponding oxygen analogue 1-bromo-1-($p$-methoxyphenyl)-2,2-diphenylethene (**1b**) in acetonitrile affords isoquinoline **3** derived from the reaction with acetonitrile.[4] In connection with the photolysis of arylvinyl halides,[2] it is considered that the photogenerated arylvinyl cation is the key intermediate. Accordingly, the aryl vinyl sulfide **2** should be formed from the reaction of the photogenerated arylvinyl cation **5a** with the other starting vinyl bromide **1a**. This may be attributable to a relative high nucleophilicity of sulfur atom,[5] although the sulfur substituent also stabilizes the resulting cation.[3] If this explanation is correct, this type of the reaction can occur with other sulfur nucleophiles. The photolysis of arylvinyl bromides **1** with methyl phenyl sulfide was examined in order to confirm this.

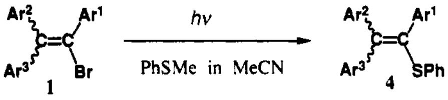


(1)



(2)

Photolysis of 1,2,2-triaryl-1-bromoethenes **1** in acetonitrile was conducted similarly in the presence of methyl phenyl sulfide (5 molar equiv). Crystalline PhSMe-incorporated products **4** were obtained in good to high yields (eq 3). These results indicate that the resulting arylvinyl cations **5** are effectively trapped by nucleophilic methyl phenyl sulfide and suggest that this method is applicable to phenylthiolation of arylvinyl bromides **1** by the photochemical method (Scheme I).



(3)

a: $Ar^1 = p\text{-}MeSC_6H_4$, $Ar^2 = Ar^3 = Ph$
b: $Ar^1 = p\text{-}MeOC_6H_4$, $Ar^2 = Ar^3 = Ph$
c: $Ar^1 = p\text{-}MeC_6H_4$, $Ar^2 = Ar^3 = Ph$
d: $Ar^1 = p\text{-}EtOC_6H_4$, $Ar^2 = Ar^3 = Ph$
e: $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$, $Ar^3 = Ph$

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[3] $\sigma_p^+$ for OMe, −0.788; $\sigma_p^+$ for SMe −0.604. See: Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

[4] Photolysis of arylvinyl bromides in acetonitrile gave isoquinoline derivatives derived from the Ritter-type reaction of arylvinyl cations with acetonitrile. See: Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1984**, 1351.