(MeOH) $\lambda_{max}$ ($\epsilon$) 227 (112 200), 265 (6760), 275 (8910), 297 (4900) nm; $^1$H NMR ($CDCl_3$) $\delta$ 2.40 (3 H, s, Me), 2.52 (3 H, s, Me), 4.77 (2 H, d, $J$ = 4 Hz, H-5′), 5.04 (1 H, m, H-4′), 6.07–6.30 (2 H, m, H-2′, H-3′), 6.46 (1 H, d, $J$ = 3 Hz, H-1′), 7.14–8.64 (20 H, m, aromatic H); MS $m/z$ 600.2151 ($M^+$, calcd $C_{38}H_{32}O_7$, 600.2121).

**2,3-Dimethyl-1-(β-D-ribofuranosyl)naphthalene (6a).** A solution of **5a** (0.100 g, 0.16 mmol) and sodium methoxide (45 mg, 0.8 mmol) in THF–MeOH (1:3 v/v, 2 mL) was stirred for 20 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent, and the solvent was evaporated in vacuo to give **6a** (38 mg, 80%) as a foam: UV (MeOH) $\lambda_{max}$ ($\epsilon$) 234 (64 600, sh), 238 (74 100), 274 (3550), 285 (5370), 295 (6030), 304 (4470 sh), 331 (490 sh) nm; $^1$H NMR ($CD_3OD$) $\delta$ 2.45, 2.52 (3 H, 2s, 2 x Me), 3.92 (3 H, m, H-4′, H-5′), 4.30 (1 H, m, H-3′), 4.45 (1 H, t, H-2′), 5.58 (1 H, d, $J$ = 7 Hz, H-1′), 7.31 (1 H, d, $J$ = 6 Hz, naphthalene H), 7.34 (1 H, d, $J$ = 6 Hz, naphthalene H), 7.59 (1 H, s, H-4), 7.69 (1 H, dd, $J$ = 6 Hz, $J$ = 3 Hz, naphthalene H), 8.35 (1 H, dd, $J$ = 6 Hz, $J$ = 3 Hz, naphthalene H); MS $m/z$ 288.1317 ($M^+$, calcd $C_{17}H_{20}O_4$, 288.1359).

**Reaction of 1,5-Dimethoxynaphthalene with 1.** A solution of **1** (1.00 g, 2 mmol) and 1,5-dimethoxynaphthalene (0.530 g, 2.8 mmol) in a 0.5 M solution of stannic chloride in benzene (10 mL) was stirred for 4 h at room temperature. The solution was diluted with AcOEt (15 mL), washed with 10% acetic acid (3 × 10 mL) and water, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by column chromatography on silica gel (120 g) with benzene as eluent and the solvent was evaporated in vacuo to give a solid. Recrystallization from AcOEt–MeOH gave 4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,5-dimethoxynaphthalene (**7a**) (0.620 g, 50%) as colorless needles: mp 169–171 °C; $[\alpha]^{20}_D$ +14.4° ($c$ 0.52, $CHCl_3$); IR ($CHCl_3$) 1720 (CO), 1120 cm$^{-1}$; UV (MeOH) $\lambda_{max}$ ($\epsilon$) 228 (109 600), 275 (7760), 285 (10 200), 300 (12 000), 310 (8710), 317 (9330), 330 (8130) nm; $^1$H NMR ($CDCl_3$) $\delta$ 3.64 (3 H, s, OMe), 3.94 (3 H, s, OMe), 4.61–4.94 (3 H, m, H-4′, H-5′), 5.72 (1 H, dd, $J$ = 8 Hz, $J$ = 4 Hz, H-3′), 5.96 (1 H, d, $J$ = 4 Hz, H-2′), 6.53 (1 H, s, H-1′), 6.59 (1 H, d, $J$ = 8 Hz, H-2), 6.82 (1 H, dd, $J$ = 10 Hz, $J$ = 1 Hz, H-6), 7.15–8.19 (18 H, m, aromatic H); MS $m/z$ 632 ($M^+$), 510. Anal. Calcd for $C_{38}H_{32}O_9\cdot{}^1/_8H_2O$: C, 71.89; H, 5.04. Found: C, 71.63; H, 5.16.

Further elution with benzene gave a solid, which was recrystallized from MeOH to give 4-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)-1,5-dimethoxynaphthalene (**7b**) (0.130 g, 11%) as colorless needles: mp 129–130 °C; $[\alpha]^{20}_D$ −67.8° ($c$ 0.5, $CHCl_3$); IR (KBr) 1720 (CO), 1265 cm$^{-1}$; UV (MeOH) $\lambda_{max}$ ($\epsilon$) 228 (131 800), 275 (8710), 285 (10 700), 300 (13 800), 310 (9330), 317 (10 700), 330 (8710) nm; $^1$H NMR ($CDCl_3$) $\delta$ 3.89 (3 H, s, OMe), 3.98 (3 H, s, OMe), 4.61–4.93 (3 H, m, H-4′, H-5′), 5.98 (1 H, dd, $J$ = 6 Hz, $J$ = 5 Hz, H-3′), 6.31 (1 H, t, $J$ = 4 Hz, H-2′), 6.73 (1 H, d, $J$ = 4 Hz, H-1′), 6.75 (1 H, d, $J$ = 8 Hz, H-2), 6.87 (1 H, d, $J$ = 8 Hz, H-6), 7.15–8.15 (18 H, m, aromatic H); MS $m/z$ 632 ($M^+$), 510. Anal. Calcd for $C_{38}H_{32}O_9$: C, 72.14; H, 5.10. Found: C, 72.14; H, 4.98.

**1,5-Dimethoxy-4-(β-D-ribofuranosyl)naphthalene (8a).** A solution of **7a** (1.00 g, 1.58 mmol) and sodium methoxide (0.341 g, 6.3 mmol) in MeOH–THF (1:2 v/v, 24 mL) was stirred for 20 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. Water (2 mL) was added to the residue and the resulting precipitate was collected by filtration, which was recrystallized from DMF–$H_2O$ to give **8a** (0.458 g, 90%) as colorless needles: IR (KBr) 3350 (OH), 1600 cm$^{-1}$; UV (MeOH) $\lambda_{max}$ ($\epsilon$) 226 (61 660), 288 (7940, sh), 299 (10 470), 317 (8320), 331 (6920) nm; $^1$H NMR (DMSO-$d_6$–$D_2O$) $\delta$ 3.80–4.13 (5 H, m, H-2′, H-3′, H-4′, H-5′), 3.94 (6 H, s, 2 × Me), 5.91 (1 H, s, H-1′), 6.92 (1 H, d, $J$ = 8 Hz, naphthalene H), 7.01 (1 H, d, $J$ = 8 Hz, naphthalene H), 7.42 (1 H, t, $J$ = 8 Hz, H-7), 7.78 (1 H, d, $J$ = 8 Hz, naphthalene H), 7.92 (1 H, d, $J$ = 8 Hz, naphthalene H); MS $m/z$ 320 ($M^+$), 217 (naphthalene + 30). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.49; H, 6.38.

**1,5-Dimethoxy-4-(α-D-ribofuranosyl)naphthalene (8b).** A solution of **7b** (90 mg, 0.14 mol) and sodium methoxide (32 mg, 0.59 mmol) in MeOH–THF (1:3 v/v, 4 mL) was stirred for 24 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. Water (2 mL) was added to the residue and the resulting precipitate was collected by filtration, which was recrystallized from DMF–ether to give **8b** (31 mg, 68%) as colorless needles: mp 172–173 °C; IR (KBr) 3400 (OH), 2935 cm$^{-1}$; UV (MeOH) $\lambda_{max}$ ($\epsilon$) 226 (49 000), 288 (6020, sh), 299 (8510), 317 (7080), 331 (5890) nm; $^1$H NMR (DMSO-$d_6$–$D_2O$) $\delta$ 3.56–4.32 (5 H, m, H-2′, H-3′, H-4′, H-5′), 3.93 (3 H, s, OMe), 3.95 (3 H, s, OMe), 6.05 (1 H, d, $J$ = 3 Hz, H-1′), 6.96 (1 H, d, $J$ = 8 Hz, aromatic H), 7.37 (1 H, t, $J$ = 8 Hz, aromatic H), 7.67 (1 H, s, $J$ = 8 Hz, aromatic H), 7.78 (1 H, d, $J$ = 8 Hz, aromatic H); MS $m/z$ 320.1213 ($M^+$, calcd $C_{17}H_{20}O_6$, 320.1258).

**1,5-Dimethoxy-4-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)naphthalene (9a).** A solution of **8a** (50 mg, 0.15 mmol) and absolute *p*-toluenesulfonic acid (20 mg, 0.11 mmol) in DMF–acetone (1:2 v/v, 6 mL) was stirred for 3 days at room temperature. The solution was neutralized with $Ag_2O$ (52 mg), the resulting precipitate was filtered off, and the filtrate was evaporated in vacuo. The residue was recrystallized from MeOH–$H_2O$ to give **9a** (33 mg, 59%) as colorless needles: mp 164–165 °C; MS $m/z$ 360 ($M^+$), 216. Anal. Calcd for $C_{20}H_{24}O_6\cdot{}^1/_5H_2O$: C, 65.99; H, 6.75. Found: C, 66.14; H, 6.80.

**Acknowledgment.** We thank Drs. J. Quada and W. Lytollis for useful discussions and suggestions.

**Registry No.** 1, 6974-32-9; **2a**, 133009-56-0; **2b**, 133009-64-0; **3a**, 133009-57-1; **3b**, 133009-65-1; **4a**, 133009-58-2; **4b**, 133009-66-2; **5a**, 133009-59-3; **5b**, 133009-67-3; **6a**, 133009-60-6; **7a**, 133009-61-7; **7b**, 133009-68-4; **8a**, 133009-62-8; **8b**, 133009-69-5; **9a**, 133009-63-9; 1-methylnaphthalene, 90-12-0; 2,3-dimethylnaphthalene, 581-40-8; 1,5-dimethoxynaphthalene, 10075-63-5.

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# Correlations between the Solvent Hydrogen Bond Acceptor Parameter β and the Calculated Molecular Electrostatic Potential

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## Introduction

In the course of an extended effort to separate, identify, and quantify various types of solvent effects,[1-5] it was found that a number of experimentally measurable solution properties (e.g., rate constants, equilibrium constants, and IR, NMR, ESR, and UV/vis absorption maxima and intensities) can be expressed as linear combinations of several "solvatochromic parameters".[5] This approach has now been used to characterize a large number of systems, including supercritical solutions.[6-8] One of the solvatochromic parameters, designated as $\beta$, has been interpreted as providing a measure of a solvent's ability to accept a proton in solute to solvent hydrogen bond.[5]

In this paper, we demonstrate that the calculated molecular electrostatic potentials within several different families of solvents, treated separately, correlate well with the corresponding $\beta$ values. This further confirms the physical validity of $\beta$ and provides a practical means for predicting its magnitudes.

The molecular electrostatic potential $V(r)$ has emerged over the past two decades as an effective analytical tool for interpreting and predicting the reactive behavior of molecules.[9-13] It is a real physical property, which expresses the net electrical effect of the nuclei and electrons

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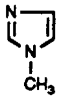
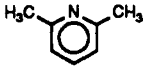
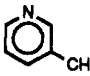
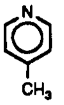
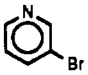
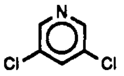
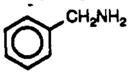
**Table I. Hydrogen Bond Acceptor Parameters $\beta^a$ and Calculated Electrostatic Potential Minima, $V_{min}$(N), for Some Nitrogen-Containing Heterocycles**

| molecule | hydrogen bond acceptor parameter $\beta$ | $V_{min}$(N) (kcal/mol) |
|---|---|---|
|  | 0.87 | -97.3 |
|  | 0.82 | -102.3 |
|  | 0.76 | -93.5 |
|  | 0.72 | -93.4 |
|  | 0.68 | -92.6 |
|  | 0.67 | -93.1 |
|  | 0.64 | -91.0 |
|  | 0.51 | -84.9 |
|  | 0.48 | -82.2 |
|  | 0.42 | -72.1 |

$^a$The hydrogen bond acceptor parameters $\beta$ are taken from ref 5.

**Table II. Hydrogen Bond Acceptor Parameters $\beta^a$ and Calculated Electrostatic Potential Minima, $V_{min}$(N), for Some Primary Amines**

| molecule | hydrogen bond acceptor parameter $\beta$ | $V_{min}$(N) (kcal/mol) |
|---|---|---|
| $CH_3CH_2CH_2CH_2NH_2$ | 0.72 | -105.3 |
|  | 0.63 | -101.8 |
|  | 0.60 | -103.4 |
| $CF_3CH_2NH_2$ | 0.37 | -92.2 |

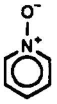
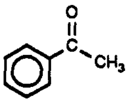
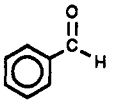
$^a$The hydrogen bond acceptor parameters $\beta$ are taken from ref 5.

**Table III. Hydrogen Bond Acceptor Parameters $\beta^a$ and Calculated Electrostatic Potential Minima, $V_{min}$(O), for Some Alkyl Ethers**

| molecule | hydrogen bond acceptor parameter $\beta$ | $V_{min}$(O) (kcal/mol) |
|---|---|---|
| $(CH_3)_2HCOCH(CH_3)_2$ | 0.49 | -70.7 |
| $H_3CH_2COCH_2CH_3$ | 0.47 | -65.1 |
| $H_3CH_2CH_2COCH_2CH_2CH_3$ | 0.46 | -65.7 |
| $H_3COCH_2CH_2OCH_3$ | 0.41 | -60.3 |

$^a$The hydrogen bond acceptor parameters $\beta$ are taken from ref 5.

**Table IV. Hydrogen Bond Acceptor Parameters $\beta^a$ and Calculated Electrostatic Potential Minima, $V_{min}$(O), for Some Molecules Containing Double-Bonded Oxygens**

| molecule | hydrogen bond acceptor parameter $\beta$ | $V_{min}$(O) (kcal/mol) |
|---|---|---|
| $O{=}P(CH_3)_3$ | 1.02 | -94.5 |
|  | 0.85 | -73.4 |
| $(H_3C)_2NC({=}O)N(CH_3)_2$ | 0.80 | -68.0 |
| $O{=}S(CH_3)_2$ | 0.76 | -69.5 |
| $(CH_3)_2NC({=}O)CH_3$ | 0.76 | -65.2 |
| $(CH_3)_2NC({=}O)H$ | 0.69 | -60.5 |
|  | 0.49 | -56.4 |
| $H_3CC({=}O)CH_3$ | 0.48 | -52.9 |
| $(CH_3)_2NC({=}O)CF_3$ | 0.46 | -48.2 |
|  | 0.44 | -53.5 |
| $H_3CC({=}O)OCH_3$ | 0.42 | -46.6 |
| $CH_3CH_2C({=}O)H$ | 0.40 | -54.0 |
| $HC({=}O)OCH_3$ | 0.37 | -52.5 |
| $ClH_2CC({=}O)CH_2Cl$ | 0.34 | -45.0 |
| $H_3CC({=}O)CCl_3$ | 0.14 | -13.0 |

$^a$The hydrogen bond acceptor parameters $\beta$ are taken from ref 5.

of a molecule at any point in space $r$, and is expressed rigorously by eq 1. $Z_A$ is the charge on nucleus A, located

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')\,dr'}{|r' - r|} \qquad (1)$$

at $R_A$; $\rho(r)$ is the electronic density function of the molecule, which we obtain from an ab initio self-consistent field molecular orbital (SCF-MO) wave function. An electrophile approaching a molecule will tend to go to those regions in which the electrostatic potential has its most negative values (the local minima, $V_{min}$), where the effects of the electrons are dominant. $V(r)$ can be determined experimentally by diffraction methods as well as computationally.[11]

In studies of hydrogen bonding interactions, the electrostatic potential has been used successfully as an indicator of sites and directionality of the hydrogen bonds.[10,14]

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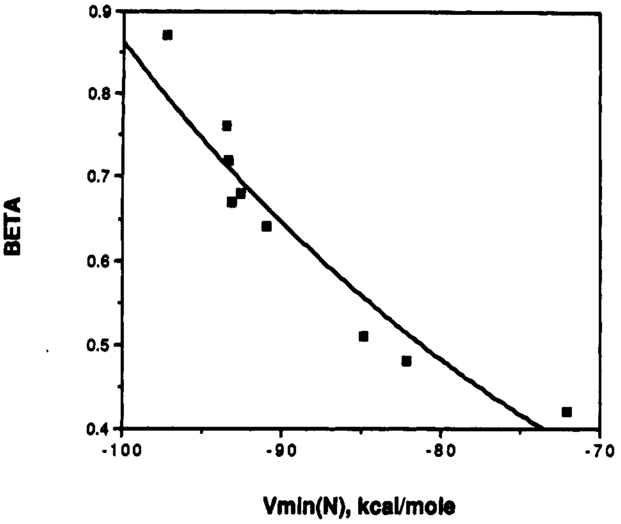

**Figure 1.** Correlation between $V_{min}(N)$ and $\beta$ for the group of azines listed in Table I. The correlation coefficient is 0.96.

Our primary aim in this study has been to explore the possibility of a relationship between the hydrogen bond acceptor parameter $\beta$ and the magnitudes of the most negative potentials ($V_{min}$) associated with the hydrogen bond accepting heteroatoms oxygen and nitrogen. In this work, we present correlations between $\beta$ and $V_{min}$ for four series of oxygen and/or nitrogen-containing molecules: azines, primary amines, alkyl ethers, and molecules containing double-bonded oxygens.

## Methods and Procedure

Using the GAUSSIAN 88 systems of programs,[15] we have carried out ab initio SCF-MO geometry optimizations for all of the molecules listed in Tables I–IV (except pyridine *N*-oxide) at the STO-3G level, which is generally effective for this purpose.[16] (To obtain an N–O bond length in satisfactory agreement with that found experimentally for pyridine *N*-oxide,[17] a 6-31G* geometry was required.) Electrostatic potentials have been computed at the STO-5G level by use of the STO-3G (or 6-31G*) geometries. We have found the former basis set to be reliable for properties related to the electronic density function, such as $V(r)$.

## Results

In Tables I–IV are listed the hydrogen bond acceptor parameters $\beta^5$ and the most negative electrostatic potentials ($V_{min}(N)$ or $V_{min}(O)$) for groups of azines, primary amines, alkyl ethers and molecules containing double-bonded oxygens, respectively. Our choice of molecules was necessarily limited by the availability of $\beta$ values. Within each family of molecules, the general tendency is for the magnitude of $V_{min}$ to decrease with diminishing $\beta$.

In Table I, the tabulated $V_{min}(N)$ are in each instance associated with a ring nitrogen. Similarly, in Table IV, the $V_{min}(O)$ are consistently associated with the double-bonded (or zwitterionic) oxygens and not, for example in the case of the esters, with the single-bonded oxygens. It is noteworthy that the molecules in Table IV include the S=O, P=O, and *N*-oxide groups as well as a variety of acyl-containing systems, e.g., aldehydes, ketones, amides, esters, and ureas.

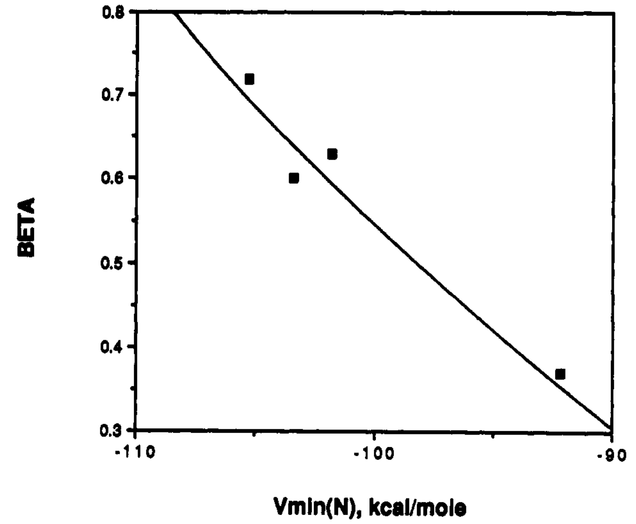

**Figure 2.** Correlation between $V_{min}(N)$ and $\beta$ for the group of primary amines listed in Table II. The correlation coefficient is 0.98.

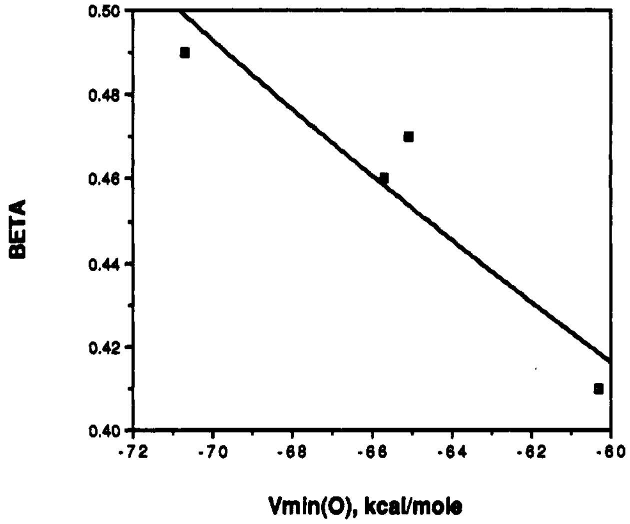

**Figure 3.** Correlation between $V_{min}(O)$ and $\beta$ for the group of alkyl ethers listed in Table III. The correlation coefficient is 0.94.

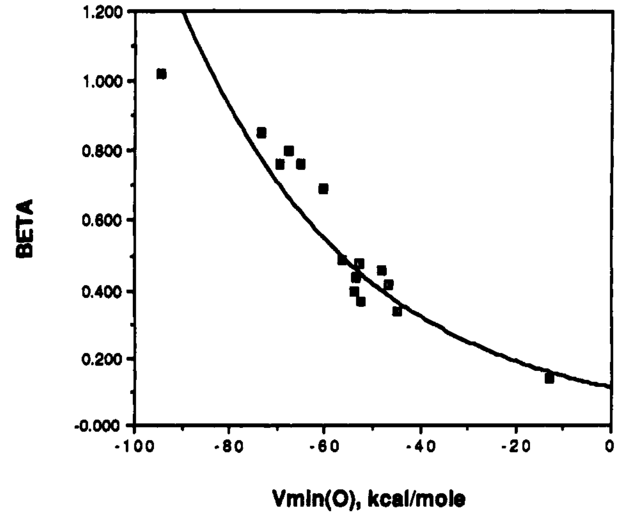

**Figure 4.** Correlation between $V_{min}(O)$ and $\beta$ for the group of molecules containing double-bonded oxygens listed in Table IV. The correlation coefficient is 0.95.

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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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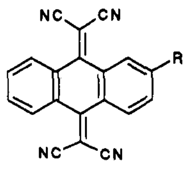
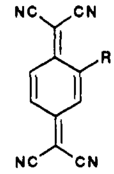
Our interest in alcohol-functionalized tetracyanoquinodimethanes (TCNQs) was the result of an ongoing research program that required them for the preparation of D-$\sigma$-A materials. The latter are extended molecules comprised of electron-donor and -acceptor moieties bridged together by a nonconjugated 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.

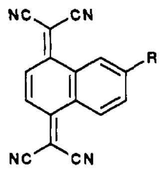
In earlier papers, we have described the syntheses of the electron acceptors, 2-(hydroxymethyl)-11,11,12,12-tetracyanoanthraquinodimethane[4] (HMTCANQ, 1) and 2-(2′-hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane[5] (HETCNQ, 3). We now report the synthesis of a third alcohol-functionalized tetracyanoquinodimethane, 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



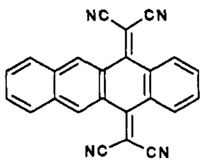
1: R = $CH_2OH$
2: R = H



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



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



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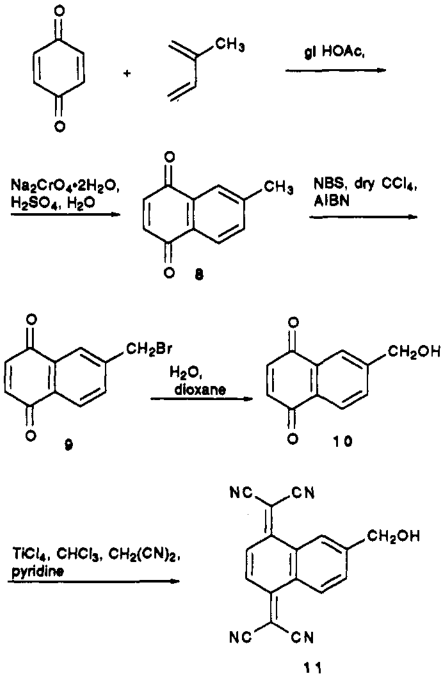

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