J. Org. Chem. 1991, 56, 1569–1573

evaporated in vacuo. The residue was purified by radial chromatography, eluting with 10% $MeOH/CH_2Cl_2$ to yield 46 mg (44%) of product: $[\alpha]_D$ −125° (c 0.2, $CHCl_3$) (lit. −128).[23]

Reduction of Egenine and Corytensine. To a solution of the phthalide isoquinoline hemiacetal in ethanol was added 1 molar equiv of $NaBH_4$. The reaction mixture was stirred overnight at room temperature. After removal of the solvent in vacuo, saturated ammonium chloride was added, and the mixture was extracted with three portions of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by radial chromatography, eluting with 10% $MeOH/CH_2Cl_2$.

Bicucullinediol (17e) was obtained in 73% yield (8 mg) from 11 mg of **2**: $[\alpha]_D$ +16.3° (c, 0.4, $CHCl_3$) (lit. −17° for the [S-(R*,S*)] isomer).[18]

Adlumidinediol (17t) was obtained in 74% yield (14 mg) from 19 mg of **4**: $[\alpha]_D$ +25° (c 0.3, $CHCl_3$) (lit. −24° for the [S-(R*,R*)] isomer).[18]

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Supplementary Material Available: NMR spectra for compounds **2**, **4–6**, and **12–16** (18 pages). Ordering information is given on any current masthead page.

Synthesis and Electrochemical Properties of Benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones and Their *N*,*N*′-Dicyano Quinone Diimine Derivatives

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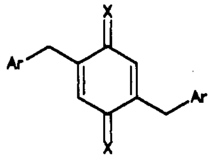
The reaction of 2,3-dichloro-1,4-naphthoquinone (1) and catechols 2 in pyridine affords a series of substituted benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones 3. The latter compounds are transformed to the corresponding *N*,*N*′-dicyano quinone diimines 4, by treating them with *N*,*N*′-bis(trimethylsilyl)carbodiimide. The electrochemical studies of compounds of the type 3 and 4 in DMF and CH_2Cl_2, respectively, by means of cyclic voltammetry are reported. The experimental reduction potentials provide information on electron–electron repulsion in the dianionic states of 3 and 4, and hence on their potential use as acceptor components in charge-transfer complexes and organic conductors.

Introduction

The attainment of electrical conductivity in organic materials composed of electron-donor–acceptor (EDA) complexes depends upon fulfilling some well-defined criteria.[1] One of these is the requirement of a partial degree of the transfer of charge (ρ) from donor to acceptor. In principle, ρ may be "tuned" via suitable substitution to vary the electron affinity of the acceptor and/or ionization potential of the donor. The propensity of any donor–acceptor pair to form a variety of stoichiometric complexes considerably reduces the chemist's control over predetermination of ρ. To a large extent stoichiometric control may be achieved by preparing single molecular entities, in which both donor and acceptor units are *chemically linked* by electronically noninteracting or weakly interacting linkages.

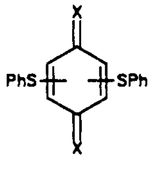
In accord with this strategy we have reported on compounds that contain two donors (D) linked to an acceptor (A) as in I or II,[1-3] or two acceptors linked to one donor, as in III.[4a] Attempts to synthesize planar CH_2-bridged D_2A molecules lead to new tetracyanopentacenquinodimethane acceptors (TCPQ).[4b]



I

X = O, N–CN, $C(CN)_2$

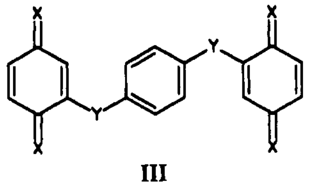
Ar = C_6H_5, p-$MeOC_6H_4$, β-Naphthyl



II

X = O, N–CN

(2,6–and 2,5–isomers)



III

(X = O, N–CN; Y = CH_2, S)

In spite of the rather surprising tendency for many of these compounds to form the segregated stacks necessary

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(1) Becker, J. Y.; Bernstein, J.; Bittner, S.; Levi, N.; Shaik, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 4469.

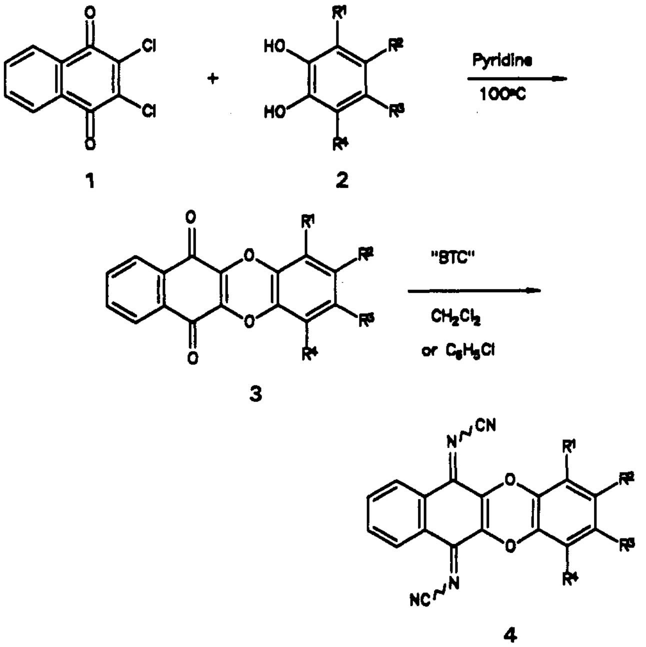
(2) (a) Becker, J. Y.; Bernstein, J.; Bittner, S.; Levi, N.; Shaik, S. S.; Zer-Zion, N. *J. Org. Chem.* **1988**, *53*, 1689. (b) Bittner, S.; Harlev, E. *Synthesis* **1989**, 868.

(3) Becker, J. Y.; Bernstein, J.; Bittner, S.; Harlev, E.; Sarma, J. A. R. P.; Shaik, S. S. *Nouv. J. Chem.* **1988**, *12*, 875; *Chem. Materials* **1988**, *1*, 412.

(4) (a) Becker, J. Y.; Bernstein, J.; Bittner, S.; Shaik, S. S. *Pure Appl. Chem.* **1990**, *62*, 467; *Syn. Metals* **1988**, *27*, B197. (b) Martin, N.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1522. Martin, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563.

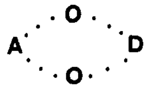
0022-3263/91/1956-1569$02.50/0

Scheme I



2–4	R¹	R²	R³	R⁴
a	H	H	H	H
b	H			H
c	OMe	H	H	H
d	H	Me	H	H
e	Me	H	H	H
f	H	*t*-Bu	H	H
g	*t*-Bu	H	*t*-Bu	H
h	H	OMe	OMe	H
i	H	NO$_2$	H	H
j	H	CN	H	H

for electrical conductivity of either the donors or the acceptors, most of them adopt conformations in which the donor and acceptor moieties are nearly orthogonal, thus preventing the simultaneous formation of segregated stacks of both donors and acceptors. To restrict this geometric degree of freedom, we have undertaken the syntheses of a series of rigid molecules, in which one donor is linked to one acceptor by two oxygen bridges, as shown schematically in IV.



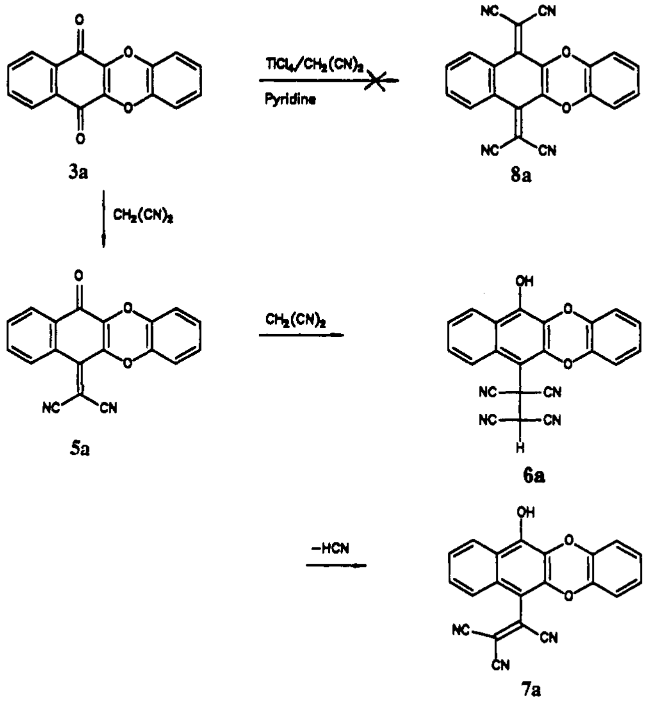
IV

We report here on the synthesis and electrochemical properties of the conformationally more restricted substituted quinones and their *N,N'*-dicyano quinone diimine derivatives, based on IV, in which an acceptor (naphthoquinone or naphthoquinonediimine) is attached to a donor (benzene ring with electron-donating or -withdrawing substituents) through two oxygen bridges.

Results and Discussion

The class of planar substituted benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones **3** (Scheme I) is relatively unknown, with the exception of **3a**[5] and **3b**.[6] Compound **3a** was synthesized by the condensation of 2,3-dichloro-1,4-naphthoquinone (**1**) with catechol (**2a**) in the presence of *N,N*-diethylaniline.[5] We have now found that this condensation takes place smoothly and in better yields using pyridine as both base and solvent (100 °C, 5–6 h). The same reaction conditions can be extended to the substituted catechols **2b–j** to provide the class of materials **3** outlined in Scheme I.

Scheme II



We converted the quinones **3** into the corresponding dicyanoimines **4** by "cyanoimination" of the quinones[7] with *N,N'*-bis(trimethylsilyl)carbodiimide (BTC).[8]

Before presenting the electrochemical results, we report on the inapplicability of the Lehnert Reagent (TiCl$_4$/pyridine)[9] for the conversion of the 1,4-quinones[3] prepared here to the corresponding tetracyanoquinodimethane (TCNQ) derivatives.

It is known that 1,4-quinones can be efficiently transformed into the tetracyanoquinodimethanes (TCNQ)[10,11] by dicyanomethylation with malonodinitrile using the Lehnert reagent. Surprisingly however, the reaction of benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones **3** with Lehnert reagent proceeded according to Scheme II (demonstrated for **3a**) to generate the tricyano derivative **7**, instead of the expected TCNQ derivative **8**.

As exemplified in the case of **3a**, the initially formed quinomethid **5a** (supported by MS data) undergoes a 1,6-addition of malonodinitrile to give **6a**, which eliminates hydrogen cyanide forming **7a**. The 1,6-addition of malonodinitrile to the quinomethide **5a** is so rapid that malonodinitrile cannot react with the carbonyl function via a 1,2-addition reaction. Also, the carbonyl group may be less active in these compounds compared to other quinones due to the neighboring oxygen atoms. Compound **7a** was characterized by IR (OH, ~3350 cm^{-1}; CN 2205 cm^{-1}) and MS data (M$^+$ = 351, 100%).

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(5) Ullmann, F.; Ettisch, M. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 259.

(6) Buu-Hoi, Ng. Ph. *J. Chem. Soc.* **1952**, 489.

(7) Aumüller, A.; Hünig, S. *Angew. Chem.* **1984**, *96*, 437; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 447; *Liebigs Ann. Chem.* **1986**, 142 and 165.

(8) Birkofer, L.; Ritter, A.; Richter, P. *Tetrahedron Lett.* **1962**, 195.

(9) (a) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723. (b) Lehnert, W. *Synthesis* **1974**, 667.

(10) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618.

(11) Kobayashi, K.; Mazaki, Y. *J. Synth. Org. Chem.* (*Jpn.*) **1988**, *46*, 638.

Table I. Cyclic Voltammetry Data for 3a–j[a]

substrate[b]	E_{red}^1 (V)	E_{red}^2 (V)	$E_{red}^2 - E_{red}^1$ (V)	$E_{red}^2 + E_{red}^1$ (V)	$K_{dis} \times 10^{13}$ (at 20 °C)
3a	−0.51	−1.21	−0.70	−1.72	5.2
3b	−0.53	−1.15	−0.62	−1.68	130
3c	−0.46	−1.15	−0.69	−1.61	7.8
3d	−0.49	−1.19	−0.70	−1.68	5.2
3e	−0.51	−1.20	−0.69	−1.71	7.8
3f	−0.50	−1.18	−0.68	−1.68	11.7
3g	−0.49	−1.23	−0.74	−1.72	1.0
3i	−0.35	−1.06	−0.71	−1.41	3.5
3j	−0.41	−1.13	−0.72	−1.54	2.3
1,4-naphthoquinone[c]	−0.64	−1.40	−0.88	−2.11	650

[a] Substrate concentration: 1 mM in 0.1 N $(Bu)_4NClO_4$–DMF on GC working electrode vs Ag/AgCl. Scan rate: 100 mV/s between 0.0 and −1.8 V. [b] Compound **3h** is insoluble. [c] Potential values are taken from ref 19.

The formation of a phenolic product of this type has been observed earlier on the addition of malonodinitrile to 2,6-dialkyl-*p*-benzoquinone in the absence of catalyst,[12] as well as in the synthesis of tetramethyl-TCNQ via the $TiCl_4$-mediated Knoevenagel condensation.[13]

Electrochemical Studies

The electrochemical reduction of **3a–j** and **4a–j** was carried out by cyclic voltammetry in DMF and CH_2Cl_2, respectively. The corresponding dimethoxy derivatives **3h** and **4h** were insoluble, and therefore no data are available for them. All others, except **4e** and **4i**, exhibited two 1*e*-reversible reduction waves. Compounds **4e** and **4i** exhibited quasireversible behavior at both waves. For each compound studied, the first reduction wave corresponds to the formation of the corresponding anion-radical, and the second reduction wave to the dianion. Comparison of the first and second reduction potentials for **3a–j** shows that **3a–g** share similar values, while **3i** and **3j**, which contain electron-withdrawing substituents, are more easily reduced.

Disproportionation equilibrium constants (K_{dis}) can be determined from the difference in potentials for the first and second reversible waves [$\Delta E = E_{red}^2 - E_{red}^1 = (RT/nF) \ln K_{dis}$].[14]

$$2\ (\text{anion-radical}) \xrightleftharpoons{K_{dis}} (\text{dianion}) + \text{neutral molecule}$$

This constant is highly dependent on solvent and counterion, because the reversible waves are sensitive to solvation and ion pairing.[15,16] It has been found[17] that in polar solvents the equilibrium lies completely on the side of the anion-radical due to their high dissociation. Consequently, the low values of K_{dis} for the quinones **3**, shown in Table I, are not surprising, and the disproportionation is sufficiently slow to be detected directly by cyclic voltammetry.

The ΔE values also afford a measure of the electrostatic repulsion resulting from addition of $2e^-$ to a substrate. The compounds of type **3** give a similar value of ΔE ~0.7 V, indicating that there is no substituent effect on electron–electron repulsion. This result is perhaps not surprising since the substituents are to a large extent "insulated" from the quinone ring by oxygen bridges. It is noteworthy that both the first and second reduction potentials in the quinones are more positive in comparison with the corresponding potentials of 1,4-naphthoquinone (NQ) (last entry in Table I). Furthermore, the Coulombic repulsion in the former is smaller (~0.7 V) than in the latter (~0.9 V). These differences can be attributed to the inductive effect of the two oxygen bridges, which is absent of course, in the NQ. A consequence of the oxygen bridges being electron-withdrawing groups is a decrease in the first and second reduction potentials and increased delocalization of the negative charges in the dianionic species.

Table II. Cyclic Voltammetry Data for 4a–j[a]

substrate[b]	E_{red}^1 (V)	E_{red}^2 (V)	$E_{red}^2 - E_{red}^1$ (V)	$E_{red}^2 + E_{red}^1$ (V)	$K_{dis} \times 10^9$ (at 20 °C)
4a	+0.07	−0.44	−0.47	−0.41	5.7
4b	−0.03	−0.44	−0.47	−0.41	5.7
4c	−0.04	−0.42	−0.46	−0.38	8.5
4d	+0.02	−0.45	−0.47	−0.43	5.7
4e	+0.02	−0.45	−0.47	−0.43	5.7
4f	−0.03	−0.43	−0.40	−0.46	96
4g	+0.02	−0.43	−0.45	−0.41	13
4i	+0.17	−0.34	−0.51	−0.17	1.1
4j	+0.11	−0.38	−0.49	−0.27	2.5
DCNQ[c]	+0.05	−0.54	−0.59	−0.49	450

[a] Substrate concentration: 1 mM in 0.1 N $(Bu)_4NClO_4$–CH_2Cl_2 on GC working electrode vs Ag/AgCl. Scan rate: 100 mV/s between +1.0 and −1.0 V. [b] Compound **4h** is insoluble. [c] The synthesis of DCNQ (= *N,N′*-dicyano-1,4-naphthoquinonediimine) and the electrochemical measurements were carried out in Beer Sheva, Israel.

The sum of the first and second reduction potentials $E_{red}^2 + E_{red}^1$, reflects the total energy change involved in the conversion of the quinones **3** to their dianions, 3^{2-}. The smaller the sum the higher the aromatic stabilization of the dianions. Quinones **3a–j** exhibit similar values ranging from −1.4 to −1.7 V (Table I). These energy sum values are significantly smaller than that obtained for the corresponding NQ (−2.1 V). This observation may indicate that the aromatic character in 3^{2-} is stronger than in NQ^{2-}, presumably because of a more efficient charge delocalization due to the presence of the two bridging oxygens. This consequence is in good agreement with our former observation that the coulombic repulsion in the quinones studied is smaller than in NQ.

All the first and second reduction potentials for the *N,N′*-dicyano quinone diimines **4a–j** (Table II) are more positive than the corresponding ones for **3a–j**, indicating that as a group, the former ones are all better acceptors than the latter.

The K_{dis} values for **4a–j** are also small, although 3–4 orders of magnitude higher than those for their parent quinones. This phenomenon could stem from the fact that the potential measurements for them were carried out in a nonpolar solvent, CH_2Cl_2, compared with DMF for **3a–j**. A larger extent of disproportionation was found in e.g., ether solutions.[18]

The values (Table II) for the energy gap (ΔE ~0.5 V) and the energy sum (~−0.4 V) for compounds **4a–j** are

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[12] Rieker, A. *Chem. Ber.* **1970**, *103*, 656.

[13] Kini, A.; Mays, M.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1985**, 286.

[14] (a) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211. (b) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

[15] Zabolotny, E. R.; Garst, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 1645.

[16] Troll, T.; Baizer, M. M. *Electrochim. Acta* **1974**, *19*, 951.

[17] (a) Cserkegyi, A.; Chaudhuri, J.; Franta, E.; Jagur-Grodzinski, J.; Swarc, M. *J. Am. Chem. Soc.* **1967**, *89*, 7129. (b) Dietz, R.; Peover, M. E. *Discuss. Faraday Soc.* **1968**, 154.

[18] (a) Garst, J. F.; Pacifici, J. G.; Zabolonty, E. R. *J. Am. Chem. Soc.* **1966**, *88*, 3872. (b) Garst, J. F.; Cole, R. S. *J. Am. Chem. Soc.* **1962**, *84*, 4352. (c) Evans, A. G.; Tabner, B. J. *J. Chem. Soc.* **1963**, 4613. (d) Roberts, R. C.; Swarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5542.

[19] Breslow, R.; Murayama, D.; Drury, R. *J. Am. Chem. Soc.* **1974**, *96*, 249.

Table III. Spectral Data of Benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones 3

product	yield[a] (%)	mp (°C)	MS *m/z* (%)	IR (KBr) (ν, cm^{-1})	^{1}H NMR (CDCl$_3$/TMS) δ, *J* (Hz)
3a	69	286–288[b]	264 (M^+, 100)	1670, 1646, 1600	6.98 (s, 4 H), 7.62–7.84 (m, 2 H), 7.96–8.22 (m, 2 H)
3b	87	>320[c]	314 (M^+, 100)	1671, 1645, 1586, 1576	*d*
3c	57	274–275	294 (M^+, 100)	1661, 1610, 1597	3.90 (s, 3 H), 6.64 (d, 2 H, *J* = 8.9), 6.93 (t, 1 H, *J* = 8.4), 7.71–7.80 (m, 2 H), 8.07–8.16 (m, 2 H)
3d	49	297–298.5	278 (M^+, 100)	1673, 1649, 1597	2.25 (s, 3 H), 6.76 (d, 1 H, *J* = 8.2), 6.82 (s, 1 H), 6.89 (d, 1 H, *J* = 8.2), 7.67–7.80 (m, 2 H); 8.06–8.19 (m, 2 H)
3e	36	244–245	278 (M^+, 100)	1675, 1669, 1651, 1609, 1592	2.30 (s, 3 H), 6.75–6.87 (m, 3 H), 7.68–7.79 (m, 2 H), 8.06–8.17 (m, 2 H)
3f	49	188–190	320 (M^+, 50) 305 ($M^+ - CH_3$, 100)	1668, 1642, 1596	1.27 (s, 9 H), 6.93 (d, 1 H, ^3J = 8.4), 6.98 (dd, 1 H, ^3J = 8.4, ^4J = 2.1), 7.06 (d, 1 H, ^4J = 2.1), 7.69–7.79 (m, 2 H), 8.06–8.16 (m, 2 H)
3g	58	161–163.5	376 (M^+, 60) 361 ($M^+ - CH_3$, 100)	1674, 1664, 1651, 1593	1.27 (s, 9 H), 1.45 (s, 9 H), 6.95 (d, 1 H, *J* = 2.3), 6.99 (d, 1 H, *J* = 2.3), 7.69–7.77 (m, 2 H), 8.04–8.16 (m, 2 H)
3h	25	>310	324 (M^+, 100)	1671, 1651, 1603, 1593	3.83 (s, 6 H), 6.65 (s, 2 H), 7.70–7.80 (m, 2 H), 8.09–8.17 (m, 2 H)
3i	91	>320	309 (M^+, 100)	1663, 1621, 1603, 1592	*d*
3j	83	308–310.5	289 (M^+, 100)	1675, 1664, 1657, 1592	7.11 (d, 1 H, ^3J = 8.3), 7.29 (d, 1 H, ^4J = 1.9), 7.34 (dd, 1 H, ^3J = 8.3, ^4J = 1.9), 7.75–7.85 (m, 2 H), 8.09–8.19 (m, 2 H)

[a] Yields of isolated products not optimized. Elemental microanalyses were satisfactory. [b] 280 °C (ref 4). [c] >340 °C (ref 5). [d] Substance insoluble in most organic solvents.

Table IV. Reaction Conditions for the Formation of 4a–j[a]

product	mol ratio of: subs/TiCl$_4$/BTC	starting temp (°C) → elevated temp (°C)	solvent	reaction time (h) at elev temp
4a	1/5/6	20 → 40	CH_2Cl_2	24
4b	1/6/7	100	C_6H_5Cl	48
4c	1/3/3.5	20 → 40	CH_2Cl_2	24
4d	1/3/3.5	20 → 40	CH_2Cl_2	24
4e	1/5/6	20 → 40	CH_2Cl_2	48
4f	1/3/3.5	20 → 40	CH_2Cl_2	24
4g	1/3/3.5	20 → 40	CH_2Cl_2	5
4h	1/3/3.5	120	C_6H_5Cl	24
4i	1/3/3.5	120	C_6H_5Cl	24
4j	1/3/5	120	C_6H_5Cl	24

[a] All products are dark green in CH_2Cl_2 as well as in the solid state, except for **4b**, **4i**, and **4j**, which is dark red. The progress of the reaction was followed by TLC (CH_2Cl_2 as eluent) using a 1-mL aliquot which was shaken with water and dried over $MgSO_4$.

significantly lower than those obtained for the parent quinones, indicating that on the whole, the former ones possess smaller electrostatic repulsion and better charge delocalization than the latter, which might be expected due to the presence of the cyano groups on the imino nitrogens.

Compounds **4i** and **4j** and the parent quinones **3i** and **3j** exhibit slightly more positive first and second reduction potentials and smaller values for the energy sum when compared with the other derivatives in their corresponding series. Apparently, the cyano and nitro substituents present in these compounds cause the oxygen bridges to be better electron-withdrawers and therefore to further increase the aromatic stabilization of the corresponding dianions.

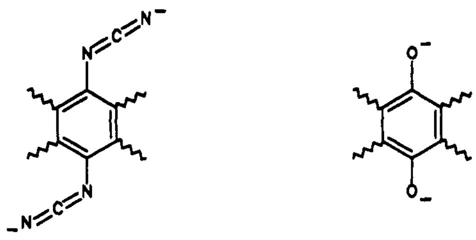
Comparison of the electrochemical results of **4a–j** with those obtained for *N*,*N*′-dicyano-1,4-naphthoquinone diimine (DCNQ), last entry in Table II, indicates that the differences in electrostatic repulsion and aromatic stabilization are not as big as those found between **3a–j** and NQ. This observation implies that the negative charges in type **4** compounds are mostly localized in the quinonediimine ring and that the charges are spatially remote from each other, compared with type **3** compounds, as is schematically represented by the two canonic forms, V and VI, in Scheme III.

Table V. Spectral Data of *N*,*N*′-Dicyanobenzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinone Diimines 4

product	yield (%)[a]	mp (°C)	MS (*m/z*, %)[b]	IR (ν, cm^{-1})	^{1}H NMR (CDCl$_3$/TMS), δ ppm
4a	72	>300	312 (M^+, 100)	2164, 2150, 1630, 1602	8.33 (m, 2 H), 7.78 (dd, 2 H), 7.09 (s, 4 H)
4b	70	>300	362 (M^+, 100)	2167, 2154, 1616	*c*
4c	80	292	342 (M^+, 100)	2164, 2149, 1637, 1602, 1574	8.30 (m, 2 H), 7.77 (dd, 2 H), 6.99 (t, 1 H), 6.72 (d, 2 H), 3.96 (s, 3 H)
4d	86	>300	326 (M^+, 100)	2170, 1637, 1602, 1595	8.30 (m, 2 H), 7.77 (dd, 2 H), 7.0 (d, 1 H), 6.95 (s, 1 H), 6.84 (d, 1 H), 2.26 (s, 3 H)
4e	84	>300	326 (M^+, 100)	2164, 2152, 1637, 1602	8.31 (m, 2 H), 7.78 (dd, 2 H), 6.96 (s, 3 H), 2.43 (s, 3 H)
4f	95	265.5	368 (M^+, 52) (M^+ – 15, 100)	2171, 2150, 1630, 1602	8.32 (m, 2 H), 7.78 (dd, 2 H), 7.09 (s, 1 H), 7.05 (d, 1 H), 7.04 (s, 1 H), 1.29 (s, 9 H)
4g	96	188.5	424 (M^+, 100)	2168, 1630, 1602, 1568	8.91 (br s, 1 H), 8.35 (bs, 1 H), 7.8 (m, 2 H), 7.05 (d, 1 H), 6.98 (1 H), 1.45 (s, 9 H), 1.29 (s, 9 H)
4h	45	>300	369 (M^+, 100)	2164, 1609	*c*
4i	73	>300	357 (M^+, 17) 309 (100)	2164, 2151, 1606, 1567	*c*
4j	73	>300	334 (M^+, 100)	2242, 2171, 1630, 1602, 1588	8.33 (m, 2 H), 7.81 (d, 2 H), 7.42 (dd, 1 H), 7.41 (d, 1 H), 7.2 (1 H)

[a] Yields of isolated products (not optimized). [b] Satisfactory elemental analyses obtained. Mass spectroscopy measurements were carried out at 20 eV, except for **4a** and **4g** (at 70 eV). [c] Substance insoluble in most organic solvents.

Scheme III



V VI

The crystal structure of some of the newly made acceptors type **4**, their charge-transfer complexes with donors, as well as their copper salts, are currently under investigation. Recently we succeeded in preparing a copper salt of **4j**, in a ratio of 1:2. A 4-probe conductivity measurement on its pressed pellet yielded a value of $\sigma = \sim 1$ S/cm^{-1} at ambient temperature.

Experimental Section

Melting points were determined with a Gahlenkamp melting point apparatus and are uncorrected. The following instruments were used for spectroscopic analyses: Bruker IF S-48 (Fourier-Transformation IR spectrometer, KBr pellets), Bruker AC 250 (^{1}H NMR), Varian MAT 711 (mass spectrometer, 70 eV). The microelemental analyses C, H, N: Carlo Erba Elementar Analyser 1104 and 1106.

2,3-Dichloro-1,4-naphthoquinone (**1**), catechols **2a–g,i,j**, pyridine, and solvents are commercially available. 4,5-Dimethoxycatechol (**2h**) was prepared by the reduction of 4,5-dimethoxy-1,2-benzoquinone[20] with H_2 (ambient pressure) on 10% Pd/C as catalyst in methanol analogous to literature procedure:[21] yield 73%; colorless needles; mp 114–116 °C (toluene) (lit.[21] mp 111–112 °C); ^{1}H NMR (CD_3COCD_3) 3.69 (s, 6 H), 6.53 (s, 2 H), 7.37 (br s, 2 H); MS *m/z* 170 (M$^+$, 100). Anal. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.38; H, 6.05.

Quinones of type **3** were obtained in yields of 29–91% as colored crystalline materials (**3i,j**, orange; **3b**, orange-red; **3a,c–g**, red to dark red; **3h**, dark violet). Most products are at best only very slightly soluble in organic solvents; however, the solubility can be increased by introducing *tert*-butyl substituents, as was found in the cases of **3f** and **3g**. Yields, IR, ^{1}H NMR, and spectral data of **3a–j** are listed in Table III.

General Procedure for the Preparation of Benzo[*b*]naphtho[2,3-*e*][1,4]dioxin-6,11-quinones 3a–j. To a stirred solution of catechol **2** (0.03–0.05 mol) in pyridine (20–25 mL) at 100 °C was added 2,3-dichloro-1,4-naphthoquinone (**1**) (4.54 g, 0.02 mol) under N_2 atmosphere. The mixture was stirred at this temperature for 5–6 h and allowed to stay overnight at room temperature. The precipitate formed was filtered (if necessary the mixture can be diluted with MeOH) and washed with MeOH and Et_2O. The precipitate can also be refluxed in MeOH and filtered. The product was dried in vacuo. The compounds **3a,c–e,h–j** obtained by this way were analytically pure. Compound **3b** was purified by crystallization from pyridine, **3f** from pyridine/petroleum ether (bp 60–90 °C), and **3g** from EtOH (Table III).

General Procedure for the Synthesis of *N,N'*-Dicyano Quinone Diimines of Type 4a–j. The appropriate **3** (1 mmol) was dissolved in CH_2Cl_2 (~60 mL) under an inert atmosphere, after which $TiCl_4$ (3 mmol) was added dropwise, causing the mixture to turn dark. Then BTC (3.5 mmol) was added, and after being stirred for 4 h at ambient temperature the reaction mixture was warmed to 40 °C for 24 h. The solution was allowed to cool slowly to room temperature, followed by addition of CH_2Cl_2 (100 mL) and ice/water (100 mL), and shaken rapidly. The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated by evaporating most of the solvent. A dark green precipitate of the desired product was formed upon addition of petroleum ether (**4b**, **4i**, and **4j** afforded dark red color). The products could be recrystallized from CH_2Cl_2–petroleum ether mixture or chlorobenzene.

The reaction conditions for the formation of each individual product **4a–j** are described in Table IV and their yields and spectral properties in Table V.

Electrochemical Measurements. All cyclic voltammetric measurements were carried out in HPLC grade solvents (DMF and CH_2Cl_2, Biolab Co.), containing 0.1 M tetrabutylammonium perchlorate (Fluka Co.). About 1 mM of a substrate was used, employing a polished homemade glassy carbon (GC) disk as a working electrode, and Pt wire as a counter electrode. All potentials were determined under inert atmosphere, using a standard two-compartment cell made of a cylindrical glass sealed at one end. Commercially available (Bioanalytical Systems Co.) Ag/AgCl reference electrode was used. Voltammograms were generated by utilizing a PAR (Princeton Applied Research Co.) Model 173 Potentiostat, Par Model 175 Universal Programmer, and a Yokogawa XY-recorder, Type 3086.

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Registry No. 1, 117-80-6; **2a**, 120-80-9; **2b**, 92-44-4; **2c**, 934-00-9; **2d**, 452-86-8; **2e**, 488-17-5; **2f**, 98-29-3; **2g**, 1020-31-1; **2h**, 1664-27-3; **2i**, 3316-09-4; **2j**, 17345-61-8; **3a**, 118210-25-6; **3b**, 118210-26-7; **3c**, 131079-88-4; **3d**, 131079-89-5; **3e**, 131079-90-8; **3f**, 131079-91-9; **3g**, 131079-92-0; **3h**, 131079-93-1; **3i**, 131079-94-2; **3j**, 131079-95-3; **4a**, 131079-96-4; **4b**, 131079-97-5; **4c**, 131079-98-6; **4d**, 131079-99-7; **4e**, 131080-00-7; **4f**, 131080-01-8; **4g**, 131080-02-9; **4h**, 131080-03-0; **4i**, 131080-04-1; **4j**, 131080-05-2; **5a**, 131080-06-3; **7a**, 131080-07-4; *N,N*-bis(trimethylsilyl)carbodiimide, 1000-70-0; 4,5-dimethoxy-1,2-benzoquinone, 21086-65-7; malononitrile, 109-77-3.

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(20) Wanzlick, H.-W.; Jahnke, U. *Chem. Ber.* **1968**, *101*, 3744.

(21) Eltsov, A. V. *Zh. Obshch. Khim.* **1963**, *33*, 2006.