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New Electron Acceptors: Synthesis, Electrochemistry, and Radical Anions of *N*,7,7-Tricyanoquinomethanimines and X-ray Crystal Structures of the Trimethyl and Tetramethyl Derivatives

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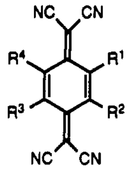
The reaction of a range of quinones **3** with malononitrile in the presence of titanium tetrachloride/pyridine yields dicyanoquinomethides **4**, which on reaction with *N*,*N*′-bis(trimethylsilyl)carbodiimide are converted into the corresponding *N*,7,7-tricyanoquinomethanimines **6**. The solution electrochemical redox properties of compounds **6** have been studied by cyclic voltammetry; they are strong acceptors which readily form radical anions and dianions. The radical anions of *N*,7,7-tricyanoquinodimethanimine **6a** and the tetra-, tri- and dimethyl derivatives **6c**, **6d**, and **6e**, respectively, have been studied by ESR and ENDOR spectroscopy. X-ray crystal structure analysis reveals that trimethyl derivative **6d** is planar, whereas the tetramethyl derivative **6c** is strongly deformed with the ring existing in a boat conformation, similar to that found previously for tetrasubstituted TCNQ derivatives.

Since the initial reports that the radical anion of tetracyano-*p*-quinodimethane (TCNQ) (**1a**) formed semiconducting salts[1] and organic metals,[2] derivatives and analogues of this electron acceptor have attracted much attention.[3] *N*,*N*′-Dicyano-*p*-quinodiimine (DCNQI) derivatives **2** are a new family of acceptors discovered by Hünig and co-workers.[4] They form charge-transfer complexes and radical anion salts which display remarkably high electrical conductivity. For example, the copper salt of 2,5-dimethyl-*N*,*N*′-dicyano-*p*-quinodiimine (1:2 stoichiometry)[4b] has a conductivity value at 3.5 K of $\sigma = 5 \times 10^5$ S cm^{-1}.



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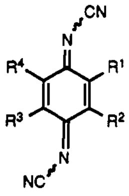

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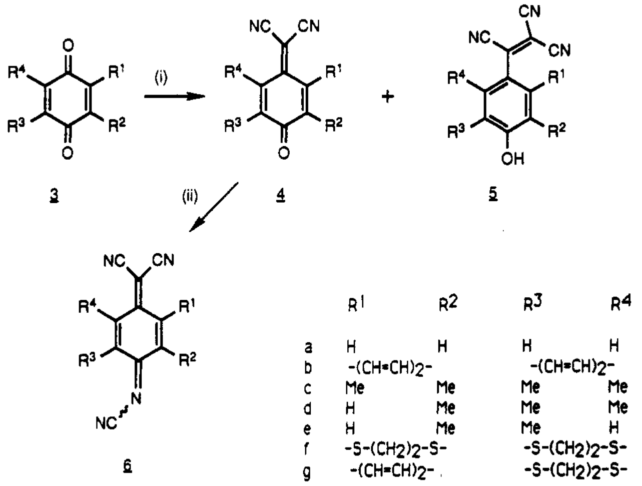
The synthesis of acceptors **2** is readily achieved by cyanoimination of the appropriate quinones with *N*,*N*′-bis(trimethylsilyl)carbodiimide.[4a] The synthesis of TCNQ derivatives directly from the quinone and malononitrile in the presence of titanium tetrachloride and pyridine (Lehnert's reagent)[5] was first reported by Aumüller and Hünig for the anthraquinodimethane system **1b**.[6] This method has subsequently been used for other TCNQ derivatives most of which are tetrasubstituted.[7] For example, Cowan et al. showed that tetramethyltetracyano-*p*-quinodimethane (**1c**) could be obtained from duroquinone by this method in ca. 55% yield.[7b]

We now report our studies on the dicyanomethylation and cyanoimination of a range of quinones. Some of the reactions described herein follow a different course from that reported by other workers. We have prepared *N*,7,7-tricyanoquinomethanimines **6a–g** which can be considered as hybrids of the TCNQ **1** and DCNQI **2** systems,[8] studied their solution electrochemistry by cyclic voltammetry, characterized four radical anions by ESR and

Scheme I[a]



	R1	R2	R3	R4
a	H	H	H	H
b	-(CH=CH)2-		-(CH=CH)2-	
c	Me	Me	Me	Me
d	H	Me	Me	Me
e	H	Me	Me	H
f	-S-(CH2)2-S-		-S-(CH2)2-S-	
g	-(CH=CH)2-		-S-(CH2)2-S-	

[a] Key: (i) $CH_2(CN)_2$, pyridine, $TiCl_4$, dichloromethane; (ii) $Me_3SiNCNSiMe_3$, $TiCl_4$, dichloromethane.

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ENDOR spectroscopy, and obtained X-ray crystal structures of derivatives **6c** and **6d**.

Results and Discussion

Synthetic Studies. In our laboratory, when the reaction of duroquinone **3c** with malononitrile and Lehnert's reagent was performed on 1–3 mmol of quinone, under a variety of conditions (see Experimental Section) including those described by Cowan et al.,[7b] no tetramethyltetracyano-*p*-quinodimethane (**1c**) was obtained. Instead, the mono(dicyanomethylated) product **4c** was isolated (maximum yield 26%) along with the phenolic product **5c** (15–30% yield). We have found that TCNQ derivative **1c** is obtained (15% yield) under Cowan's conditions[7b] *only when the reaction is carried out on a larger scale* (i.e., ≥1.0 g, 6 mmol, of duroquinone **3c**). On this scale, highly exothermic reaction occurred upon addition of the titanium tetrachloride to the reaction mixture, and no quinomethide **4c** was obtained.

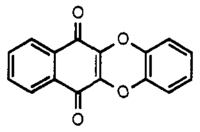
A range of quinones **3a–3g** yielded mono(dicyanomethylated) products **4a–4g** (typically 25–40% yield) along with the corresponding phenolic products **5a–5g** (mass spectroscopy, NMR and IR evidence). The latter products, with the exception of derivative **5e**, were not purified. Even when reactions of quinones **3d** and **3e** were conducted on a ≥6 mmol scale there was no evidence for the formation of TCNQ derivatives **1d** or **1e**! 2,3-Dimethylquinone and chloranil gave complex product mixtures which could not be purified. Proton NMR data clearly established that for unsymmetrical quinones **3d** and **3e** it was the less hindered ketone group which had reacted. (The X-ray crystal structure of product **6d**, discussed below, provided additional confirmation of this.) Our results with unsubstituted *p*-benzoquinone **3a** and with anthraquinone **3b** differ from those reported previously for these quinones which yielded TCNQ derivatives **1a**[7b] and **1b**,[6,7a] respectively. Attempts to obtain TCNQ derivatives **1a**, **1c**, and **1d** by sequential dicyanomethylation, using purified quinomethides **4**/malononitrile/$TiCl_4$/pyridine, failed; reaction yielded phenols **5a**, **5c**, and **5d**, respectively, as the only identifiable products (30–50% yield) in each case.

The unwelcome phenolic products **5** clearly arise by 1,6-addition of malononitrile to the quinomethide system **4** followed by 1,2-elimination of hydrogen cyanide. Such reactions are known to occur in the absence of Lehnert's reagent,[9] but in its presence, TCNQ formation (i.e., 1,2-addition) is usually the major, or sole, pathway.[6,7] However, Cowan et al.[7b] obtained phenol derivative **5c** alongside TCNQ derivative **1c**, and other workers have recently reported that several derivatives of the tetracyclic quinone system **7** could not be converted into TCNQ derivatives using Lehnert's reagent: quinomethides and phenolic products analogous to **4** and **5** were obtained.[10] It was suggested that for system **7**, the heterocyclic oxygen atoms might deactivate the carbonyl group of the intermediate quinomethide to attack by malononitrile anion.[10] However, while such an electronic effect may operate in compounds **3f** and **3g**, it clearly cannot explain our results with quinones **3a–3e**. We tentatively postulate that our results may be explained by steric crowding in the quinomethides **4**. The only TCNQ derivative we have obtained from the series of quinones **3a–3g** is tetramethyltetracyano-*p*-quinodimethane (**1c**). The intermediate **4c** in this reaction will be more sterically strained than the other quinomethides **4**, with the possible exception of **4b** (which is known from X-ray analysis to be nonplanar[11]). Compound **4c** probably, therefore, adopts a very distorted conformation (akin to the structure of compound **6c**, reported below) making the oxygen atom of the carbonyl group more accessible to complexation by $TiCl_4$. However, we have no explanation for why we do not obtain TCNQ derivative **1b** from anthraquinone **3b** under the conditions described by other workers for **3b**,[6,7a] and for substituted anthraquinones.[7e,g,h]

Quinomethides **4a–4g** reacted with bis(trimethylsilyl)carbodiimide in the presence of $TiCl_4$ to afford the title acceptors **6a–6g** typically in 65–80% yield. Almost concurrent with our initial report of this reaction,[8] Japanese workers also described compounds **6a** and **6b** prepared by this route.[12] They claimed that compound **6a** partially oligomerized after 24 h in polar solvents (THF, MeCN, acetone). In our hands, however, compound **6a** is stable for several days in acetonitrile solution at room temperature, without exclusion of air, from which it can be recovered unchanged in quantitative yield.

The ^1H NMR spectrum of dimethyl derivative **6e** is of interest. At 20 °C, two broad singlets are observed due to flipping of the cyano group attached to nitrogen. However, on cooling to 0 °C, the spectrum is strikingly different: each of the broad singlets is resolved into two singlets, demonstrating that the two conformations of the cyanoimine group are now frozen out to give compound **6e** as two isomers in ca. 1:1 ratio.

When quinones **3f** and **3g** were reacted with bis(trimethylsilyl)carbodiimide, the major products were the new DCNQI derivatives **2f** and **2g**, respectively; compound **8** was obtained as a minor product.



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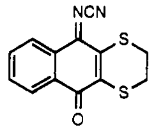

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Before discussing the electrochemistry of the new acceptors **6a–6g**, brief mention will be made of two alternative (unsuccessful) approaches to the unknown compound 2,6-dimethyltetracyano-*p*-quinodimethane (**1e**). The first is based on the synthesis of **1c**[13] and other TCNQ derivatives.[14] 4-Iodo-2,6-dimethylanilinium hydrochloride (**9**) was converted into 1,4-diiodo-2,6-dimethylbenzene (**10**); attempted substitution of both iodine atoms of **10** with malononitrile anion in HMPA in the presence of copper(I) iodide[13,14] gave only the monosubstituted product **11**. Reaction of the diazonium salt derived from **9** with malononitrile anion yielded hydrazone derivative **12** in low yield (Scheme II). This approach to **1e** was, therefore, abandoned. The second route we investigated is the classical synthesis of the TCNQ system from a cyclo-

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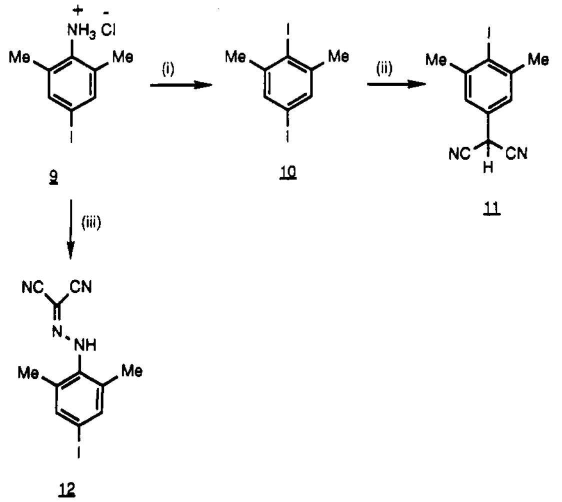
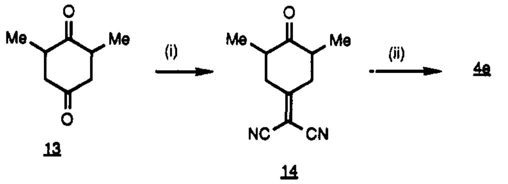
Scheme II[a]



[a] Key: (i) $NaNO_2$, KI, water; (ii) $CH_2(CN)_2$, NaH, HMPA, CuI; (iii) $NaNO_2$, $CH_2(CN)_2$, water.

Scheme III[a]



[a] Key: (i) $CH_2(CN)_2$, β-alanine, water; (ii) Br_2, acetonitrile.

hexanedione derivative[15] that has yielded 2,5-dimethyl-[16] and 2,3-dimethyltetracyano-*p*-quinodimethane.[17] When 2,6-dimethylcyclohexanedione (**13**) was heated with malononitrile and β-alanine in aqueous solution,[15] only the less hindered ketone group reacted, giving product **14** (84% yield), which on oxidation with bromine in pyridine[15] provided an alternative synthesis of compound **4e**.

Electrochemical Studies. The electrochemical redox properties of the new acceptors **6a–g** were studied by cyclic voltammetry, and the data are collated in Table I, along with representative examples from the TCNQ **1** family. It is well-known that TCNQ and DCNQI derivatives that carry the same substituents have very similar acceptor strengths.[4d] Predictably, therefore, the acceptor strength of the parent *N*,7,7-tricyanoquinomethanimine derivative **6a** is very close to that of TCNQ (**1a**) and DCNQI (**2a**). The first reduction wave (i.e., formation of the radical anion) is reversible for all the compounds **6a–6g**. The second reduction wave to the dianion is reversible only for compounds **6a**, **6c**, **6f**, and **6g**; it is irreversible for compounds **6d** and **6e** and, surprisingly, it is not observed at all for compound **6b**. This result was reproduced on samples of **6b** from two different preparations.

There is a predictable lowering of the electron affinity with successive methyl substitution into system **6**, and anthraquinone derivative **6b** is by far the weakest acceptor (most negative reduction potential) within the series **6a–6g**. Compound **6b** is anomalous: only one single-electron wave is observed. A second reduction to the dianion was not observed, which contrasts with the results obtained by Iwatsuki et al.[12] for compound **6b** and with data for the TCNQ and DCNQI analogues **1b** and **2b**, respectively (Table I). However, we note that different workers have reported quite different data for compound **1b** even in the same solvent.[19,20]

Table I. Cyclic Voltammetric Data[a]

compd	solvent	$E^1_{1/2}$/V	$E^2_{1/2}$/V	ΔE/V
6a[b]	MeCN	+0.16	–0.42	0.58
6b[c]	CH_2Cl_2	–0.43	not observed	
6c	MeCN	–0.03	–0.23	0.20
6d	MeCN	+0.07	–0.41	0.48
6e	MeCN	+0.11	–0.43	0.54
6f	CH_2Cl_2	+0.28	–0.13	0.41
6g	CH_2Cl_2	+0.17	–0.22	0.39
1a[d]	CH_2Cl_2	+0.11	–0.31	0.42
1c[e]	CH_2Cl_2	–0.25 (2e)		0.00

[a] This work; versus Ag/AgCl. [b] Cf. +0.17, –0.44 in CH_2Cl_2, ref 12. [c] Cf. –0.43, –0.63 in CH_2Cl_2, ref 12. [d] Cf. +0.18, –0.37 vs SCE, ref 18. [e] Cf. –0.40 (2e) in MeCN, ref 7b.

From the reduction potentials of compounds **6** it is clear that sulfur substitution onto the ring increases the acceptor ability, such that tetrathio derivative **6f** is the strongest acceptor in the series and compound **2g** is among the strongest DCNQI acceptors known.[4,10] This is in accord with the known acceptor properties of sulfur atoms attached to double bonds [cf. electron-donor molecules of the tetrathiafulvalene (TTF) tribe, for which the donor ability is reduced upon thioalkyl substitution[21]].

The value of ΔE is sensitive to the amount of intramolecular coulombic repulsion resulting from addition of two electrons to an acceptor. The more planar is the dianion, the higher will be the coulombic repulsion. Within series **6** this value is markedly reduced for tetramethyl compound **6c** (ΔE = 0.20 V) in comparison with the other derivatives (ΔE = 0.39–0.61 V). (Japanese workers report ΔE = 0.20 V for anthraquinone derivative **6b**.[12]) This behavior for **6c** is intermediate between that for tetramethyltetracyano-*p*-quinodimethane (**1c**, ΔE = 0.00 V)[19] and tetramethyl-*N*,*N*′-dicyano-*p*-quinodiimine (**2c**, ΔE = 0.44 V).[4d] This is explained on steric grounds. Tetramethyltetracyano-*p*-quinodimethane (**1c**) has a severely distorted ring skeleton as revealed by a single-crystal X-ray structure.[13] Other tetrasubstituted TCNQ derivatives (e.g., derivative **1b**,[22] substituted analogues of **1b**,[7d,7g] and tetracyanobianthraquinodimethane[23]) are also substantially nonplanar, while, in contrast to this, tetrasubstituted DCNQI derivatives, e.g., **2b**, are essentially planar.[22] This is because the =N(CN) groups, being smaller than the $=C(CN)_2$

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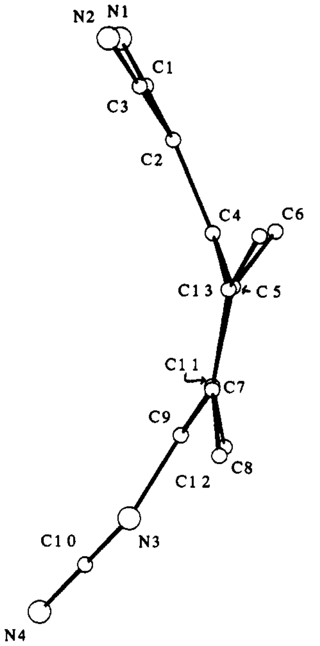

Figure 1. X-ray crystal structure of compound **6c**.

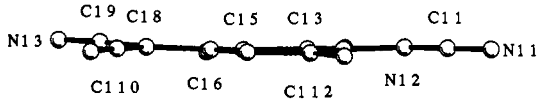

Figure 2. X-ray crystal structure of compound **6d** viewed perpendicular to the best plane of the ring.

groups, can bend within the molecular plane of the DCNQI system, while the latter groups are forced out of the plane, thus distorting the tetrasubstituted TCNQ ring into a boat conformation.

It was, therefore, of particular interest to establish by single-crystal X-ray analysis the conformation of a tetrasubstituted derivative of the new series of acceptors **6**. For this purpose the tetramethyl derivative **6c** was readily obtained in single-crystal form; the X-ray structure of trimethyl derivative **6d** has also been obtained.

X-ray Crystal Structures of Compounds 6c and 6d. The X-ray crystal structure of tetramethyl derivative **6c** is shown in Figure 1. The ring is strongly distorted into a boat conformation. Three planes were defined as follows: plane 1 by atoms C(4), C(5), and C(13); plane 2 by atoms C(7), C(9), and C(11); plane 3 by atoms C(5), C(7), and C(11). The angle between plane 1 and plane 3 is 29.81°, while that between plane 2 and plane 3 is 21.83°. Thus, there is greater deformation about the bulkier $=C(CN)_2$ group than about the =NCN group. This structure is reminiscent of that of tetramethyltetracyano-*p*-quinodimethane (**1c**), for which the corresponding interplanar angles are 30.2 and 28.1°.[13] In contrast to this, trimethyl derivative **6d** is essentially planar (Figure 2).

ESR/ENDOR Studies of the Radical Anions of 6a, 6c, 6d, and 6e. Reduction of *N*,7,7-tricyanoquinomethanimine (**6a**) and its tetra-, tri-, and dimethyl derivatives, **6c**, **6d**, and **6e**, respectively, to the corresponding radical anions, **6a**$^{\bullet-}$, **6c**$^{\bullet-}$, **6d**$^{\bullet-}$, and **6e**$^{\bullet-}$, was carried out by potassium in 1,2-dimethoxyethane (DME). Care had to be taken not to push the reaction too far, in order to minimize formation of the dianions **6a**$^{2-}$, **6c**$^{2-}$, **6d**$^{2-}$, and **6e**$^{2-}$. Such a precaution was particularly necessary for **6c** which has the first and the second reduction potentials close to each other (Table I). The ESR spectra were recorded in the range 213–273 K. Varying the temperature had only a slight effect on the ^{14}N- and proton-coupling constants, a_N and a_H, but it greatly affected the linewidths, lw. As has been observed for the radical anions of DCNQI **2** and its derivatives,[31] there is a large contribution to lw from the hyperfine anisotropy of the ^{14}N nucleus in the exocyclic position. This contribution is usually described by the equation[32,33a] $lw = A + BM_I + CM_I^2$ where $M_I = +1, 0, -1$ is the ^{14}N-spin quantum number. On raising the temperature, the terms BM_I and CM_I^2 decreased, but A increased, so that the resolution of the ESR spectra remained rather poor throughout the whole temperature range. The analysis of the hyperfine pattern was, therefore, not a simple task, moreover because the symmetry of the *N*,7,7-tricyanoquinomethanimine system **6** is lower than that of the corresponding compounds in the TCNQ **1**[34] and DCNQI **2**[31] series. The coupling constants a_H were determined by the ENDOR technique[35] which, however, could not be applied to a_N because of the unfavorable frequency range (1–7 MHz) in which the pertinent signals are due to occur. General-TRIPLE-resonance experiments[35] proved to be conclusive only for **6a**$^{\bullet-}$ and **6c**$^{\bullet-}$. In these two radical anions, all the protons are either directly attached to ring carbon atoms (**6a**$^{\bullet-}$) or located in the methyl substituents (**6c**$^{\bullet-}$). Theory[33b] requires a negative sign for the former (α-protons) and a positive one for the latter (β-protons), in accord with the TRIPLE-resonance experiments which confirmed that the a_H values for each of the two radical anions have the same sign.

Table II. Proton- and ^{14}N-Coupling Constants a_H and a_N, in mT, and g-Factors for 6a$^{\bullet-}$ and 6c$^{\bullet-}$–6e$^{\bullet-}$

	a_H[a]	a_N	g[b]
6a$^{\bullet-}$	0.167 (3 H)	0.395[c] (1 N)	2.0032
	0.136 (1 H)	0.110[c] (3 N)	
6c$^{\bullet-}$	0.176 (3 H)	0.35 ± 0.04[d] (1 N)	2.0032
	0.156 (3 H)	0.11 ± 0.02[d] (3 N)	
	0.067 (3 H)		
	0.035 (3 H)		
6d$^{\bullet-}$	0.142 (1 H)	0.35 ± 0.04[d] (1 N)	2.0032
	0.124 (6 H)	0.11 ± 0.02[d] (3 N)	
	0.090 (3 H)		
6e$^{\bullet-}$	0.154 (2 H)	0.315[c] (1 N)	2.0032
	0.129 (3 H)	0.130[c] (1 N)	
	0.108 (3 H)	0.105[c] (2 N)	

[a] Values from ENDOR; experimental error: ±0.002 mT. [b] Experimental error: ± 0.0001. [c] Experimental error: ±0.005 mT. [d] Within this range, slightly different values give closely similar computer simulations of the ESR spectra.

The ESR and proton-ENDOR spectra are exemplified in Figure 3 by those of the parent radical anion **6a**$^{\bullet-}$. The two pairs of ENDOR signals placed symmetrically about ν_H = 14.56 MHz, the frequency of the free proton,[35] are associated with the coupling constants a_H of 0.136 ± 0.002 and 0.167 ± 0.002 mT, attributed to one and three protons, respectively. This assignment has been verified by computer simulation of the ESR spectrum (Figure 3) from which the coupling constants a_N of 0.395 ± 0.005 and 0.110 ± 0.005 mT for one and three ^{14}N nuclei, respectively, were also derived.

Table II lists the g-factors and the a_H and a_N values for all four radical anions **6a**$^{\bullet-}$, **6c**$^{\bullet-}$, **6d**$^{\bullet-}$, and **6e**$^{\bullet-}$. Assign-

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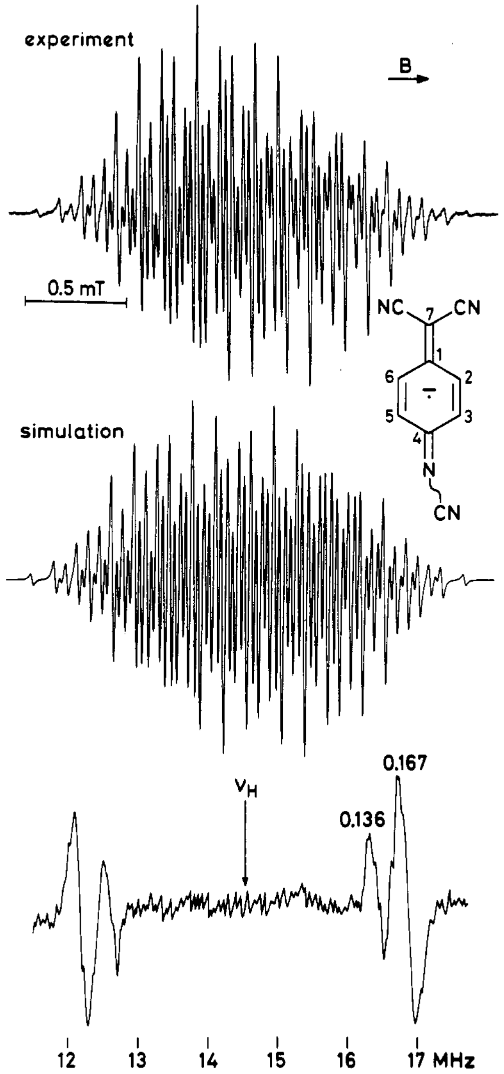

Figure 3. ESR (top and center) and proton-ENDOR spectra of **6a**$^{\bullet-}$. Solvent, DME; counterion, K$^+$; temperature, 243 K. The computer simulation made use of the coupling constants given in the text and Tables II and III: line shape, Lorentzian; line-width, 0.025 mT.

ments of the coupling constants a_N are straightforward by the use of MO calculations[36] and by analogy with the ^{14}N-hyperfine data for **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$ and their derivatives.[31,34] The larger a_N value (0.3–0.4 mT) undoubtedly belongs to the single ^{14}N nucleus in the exocyclic position, while the smaller one (0.10–0.13 mT) stems from the ^{14}N nuclei in the three cyano substituents. MO calculations[36] predict a positive sign for all ^{14}N-coupling constants; in the case of the larger a_N value, this sign is consistent with the lines being broader at the high field of the ESR spectrum than at the low field.[32,33a] Distinction between the ^{14}N nuclei in individual cyano substituents was difficult because of the similar coupling constants a_N and the insufficient resolution of the ESR spectra. Assignments of the coupling constants a_H were also problematic. Although, in contrast to a_N, the a_H values could exactly be determined from the positions of the ENDOR signals, this method suffered from the following handicaps: (i) Except for **6c**$^{\bullet-}$, there were less signals observed than sets of equivalent protons. Thus, some pairs of signals must represent more than one such set. (ii) As TRIPLE-resonance experiments were not conclusive for **6d**$^{\bullet-}$ and **6e**$^{\bullet-}$, it was not possible to distinguish the signals of β-protons from those of α-protons by the opposite signs of their coupling constants a_H. (iii) Because all a_H values fell in the relatively narrow range (0.09–0.18 mT), MO calculations[36] were not a proper guide for their assignments. Those made in Table II should, thus, in some cases, be regarded as tentative.

Table III. Comparison of Proton- and ^{14}N-Coupling Constants, a_H and a_N, in mT, for 1a$^{\bullet-}$, 6a$^{\bullet-}$, and 2a$^{\bullet-}$

	a_H		a_N
1a$^{\bullet-a}$	0.142 (4 H)	0.142	0.099 (4 N)
6a$^{\bullet-}$	0.167 (3 H)	0.159^b	0.395 (1 N)
	0.136 (1 H)		0.110 (3 N)
2a$^{\bullet-c}$	0.201 (2 H)	0.182^b	0.442 (2 N)
	0.163 (2 H)		0.121 (2 N)

[a] Reference 34. [b] Average value. [c] Reference 31.

For the parent radical anion **6a**$^{\bullet-}$, it is reasonable to assume that the protons ortho to the C(CN)$_2$ group (positions 2 and 6; Figure 3) have the same coupling constant, a_H, which is also shared by the one proton ortho to the NCN group (positions 3 and 5). Comparison of the a_H and a_N values for **6a**$^{\bullet-}$ with the analogous hyperfine data for **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$ (Table III) complies with the structure of the new system **6** being intermediate between that of TCNQ and DCNQI.

Experimental Section

General details of instrumentation have recently been reported.[24] Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver–silver chloride reference electrode. Measurements were made with a BAS 100 electrochemical analyzer and were current resistance compensated. The cell contained a solution of acceptor (ca. 1 × 10^{-5} mol dm^{-3}) with oven-dried (120 °C) tetrabutylammonium perchlorate (0.01 mol dm^{-3}) as supporting electrolyte in dry acetonitrile (ca. 10 mL); all solutions were purged with argon and retained under the inert atmosphere while the CV data were recorded.

Radical Anions. The preparation of the radical anions from the neutral compounds by reduction with potassium in DME was performed by a standard vacuum technique. In a modified procedure,[38] a direct contact of the compound with the metallic mirror was avoided and an "over-reduction" to the dianion was diminished. The ESR spectra were taken on a Varian-E9-instrument, while a Bruker-ESP-300-system served for ENDOR and TRIPLE-resonance studies.

Quinones **3a–3c** and **3e** were commercial materials; quinones **3d**,[25] **3f**,[26] and **3g**[27] were prepared by the literature routes. Pyridine (Aldrich HPLC grade) was stored over activated molecular sieves; dichloromethane was distilled from phosphorus pentoxide; acetonitrile was distilled from calcium hydride. For column chromatography, Merck silica gel (70–230 mesh) was employed.

Optimized Procedure for the Preparation of Quinomethides 4a–4g. To a stirring solution of quinone **3a–3g** (2.7 mmol), malononitrile (0.44 g, 6.75 mmol), and dry pyridine (1.06 g, 13.5 mmol) dissolved in dry dichloromethane (25 mL) under dry nitrogen was added a solution of titanium tetrachloride (1.28 g, 6.75 mmol) dissolved in dichloromethane (25 mL) at 0–5 °C. The reaction mixture was stirred at 20 °C for 15 h and washed with water and the organic phase separated and dried (MgSO$_4$). Column chromatography on silica eluting with dichloromethane yielded compounds **4a–4g**.

Compound 4a: 39%, mp 144–146 °C; δ_H (CDCl$_3$) 7.90 (2 H, d), 6.80 (2 H, d). Anal. Calcd for C$_9$H$_4$N$_2$O: C, 69.2; H, 2.6; N, 17.9. Found: C, 69.0; H, 2.4; N, 17.7.

Compound 4b: 27%, mp 250 °C dec; δ_H (CDCl$_3$) 7.80 (2 H, s), 2.23 (6 H, s). Anal. Calcd for C$_{17}$H$_8$N$_2$O: C, 79.6; H, 3.1; N, 10.9. Found: C, 79.9; H, 3.1; N, 10.6.

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(36) Calculations by the Hückel–McLachlan[37] method using conventional heteroatom parameters.[33c]

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Compound 4c: 26%, mp 124–128 °C; δ_H ($CDCl_3$) 2.44 (6 H, s), 2.02 (6 H, s). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.5; H, 5.7; N, 13.2. Found: C, 73.0; H, 5.7; N, 12.7.

Compound 4d: 43%, mp 102–106 °C; δ_H ($CDCl_3$) 7.46 (1 H, s), 2.52 (3 H, s), 2.12 (6 H, s). Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1. Found: C, 72.4; H, 4.8; N, 14.0.

Compound 4e: 28%, mp 134–138 °C; δ_H ($CDCl_3$) 7.26 (2 H, s), 2.06 (6 H, s). Anal. Calcd for $C_{11}H_8N_2O$: C, 71.7; H, 4.3; N, 15.2. Found: C, 71.8; H, 4.3; N, 15.5.

Compound 4f: 34%, mp 212–214 °C. Anal. Calcd for $C_{13}H_8S_4N_2O$: C, 46.4; H, 2.4; N, 8.3. Found: C, 46.2; H, 2.1; N, 8.1.

Compound 4g: 44%, mp 240–242 °C (after fractional sublimation at 220 °C, 0.05 mBar). Anal. Calcd for $C_{15}H_8N_2S_2O$: C, 60.8; H, 2.7; N, 9.5. Found: C, 60.6; H, 2.7; N, 9.5.

Compounds **4f** and **4g** were too insoluble for NMR spectra to be obtained.

A second component which eluted from the column was identified as phenol derivative **5a–5g** (crude yields 20–40%) by mass spectroscopy, IR, and NMR data. 2,6-Dimethyl-4-(tricyanoethenyl)phenol (**5e**) was purified by recrystallization from dichloromethane/hexane (ca. 1:1 v/v): orange solid, mp 174–176 °C; δ_H ($CDCl_3$) 7.80 (2 H, s), 2.33 (6 H, s). Anal. Calcd for $C_{13}H_9N_3O$: C, 70.0; H, 4.0; N, 18.8. Found: C, 70.3; H, 4.0; N, 18.8.

The reactions of quinones **3b–3e** followed the same course as that described above under the following conditions: (a) when $TiCl_4$ was distilled immediately before use, (b) when commercial $TiCl_4/CH_2Cl_2$ solution was used, (c) when the order of addition of reagents was changed, viz. when either pyridine or malononitrile was added last to solutions of the other reagents, (d) when molar ratios and conditions detailed by other workers for TCNQ synthesis were employed.[6,7]

Tetramethyltetracyano-*p*-quinodimethane (1c). To a solution of duroquinone (2.0 g, 12 mmol) in dichloromethane (40 mL) was added titanium tetrachloride (3.4 mL, 30 mmol) and the mixture stirred at 20 °C for 0.5 h. A solution of pyridine (4.8 mL, 60 mmol) and malononitrile (2.0 g, 30 mmol) in dichloromethane (15 mL) was added dropwise over 5 min. The mixture was stirred at 20 °C for 4 h and then poured onto water. The organic layer was separated, washed with sodium hydroxide, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica column eluting with dichloromethane to yield compound **1c** (0.47 g, 15%) as an orange solid: mp 239–241 °C (lit.[7b] mp 240–242 °C dec); δ_H ($CDCl_3$) 2.38 (s). Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.9; H, 4.6; N, 21.5. Found: C, 73.7; H, 4.5; N, 21.4.

***N,N'*-Dicyanoquinone Imines 2f and 2g. General Procedure.** To a solution of quinone **2g** (200 mg, 0.8 mmol) in dichloromethane (40 mL) was added titanium tetrachloride (0.44 mL, 4 mmol) and bis(trimethylsilyl)carbodiimide[28] (0.75 mL, 4 mmol). The mixture was stirred at 25 °C for 24 h and then poured onto water. The aqueous layer was separated, dried ($MgSO_4$), evaporated, and chromatographed on a silica column and eluted with dichloromethane to yield compound **8** as a black solid (100 mg, 46%): mp 172–174 °C; δ_H ($CDCl_3$) 8.90 (1 H, m), 8.10 (1 H, m), 7.70–7.67 (2 H, t), 3.27 (4 H, m). Anal. Calcd for $C_{13}H_8N_2S_2O$: C, 57.3; H, 3.0; N, 10.3. Found: C, 57.1; H, 2.7; N, 10.1. Continued elution yielded compound **2g** as a black solid (161 mg, 68%): mp 180–182 °C dec; δ_H ($CDCl_3$) 7.77–7.73 (4 H, m) and 3.28 (4 H, s). Anal. Calcd for $C_{14}H_8N_4S_2$: C, 56.7; H, 2.7; N, 18.9. Found: C, 56.5; H, 2.8; N, 18.3.

There was similarly obtained from quinone **3f** (150 mg, 0.53 mmol) compound **2f** (111 mg, 62%): black solid, mp >320 °C; δ_H ($CDCl_3$) 3.18 (s). Anal. Calcd for $C_{12}H_8N_4S_4$: C, 42.8; H, 2.4; N, 16.7. Found: C, 41.9; H, 2.1; N, 16.6.

***N*,7,7-Tricyanoquinomethanimines 6a–6g. General Procedure.** A solution of quinomethide **4** (2.3 mmol) dissolved in dichloromethane (20 mL) was cooled to 0–5 °C; freshly-distilled titanium tetrachloride (547 mg, 2.9 mmol) was added to give an orange precipitate. After 0.5 h at 0–5 °C, bis(trimethylsilyl)carbodiimide (534 mg, 2.9 mmol) was added rapidly and the mixture stirred at 20 °C for 40 h. Dichloromethane was then added until all the precipitate had dissolved. Water was added and the organic layer separated, dried ($MgSO_4$), evaporated, and chromatographed on a silica column with dichloromethane as eluent to furnish product **6a–6g**.

Compound 6a: 43%, mp 176–178 °C dec; δ_H ($CDCl_3$) 7.68 (d, 2 H), 7.49 (1 H, d), 7.16 (1 H, d). Anal. Calcd for $C_{10}H_4N_4$: C, 66.7; H, 2.2; N, 3.1. Found: C, 66.4; H, 2.2; N, 30.9.

Compound 6b: 38%, mp 242 °C dec; δ_H ($CDCl_3$) 8.90 (1 H, br m), 8.32–8.29 (3 H, m), 7.82–7.80 (4 H, m). Anal. Calcd for $C_{18}H_8N_4$: C, 77.1; H, 2.9; N, 20.0. Found: C, 77.3; H, 2.5; N, 19.9.

Compound 6c: 87%, mp 192 °C dec; δ_H ($CDCl_3$) 2.40 (6 H, br s), 2.21 (6 H, br s). Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1; N, 23.7. Found: C, 71.2; H, 5.1; N, 23.8.

Compound 6d: 88%, mp 136 °C dec; δ_H ($CDCl_3$) 7.45 (1 H, s), 2.58 (6 H, s), 2.33 (3 H, s). Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.2; H, 4.5; N, 25.2. Found: C, 70.6; H, 4.4; N, 25.3.

Compound 6e: 78%, mp 260 °C dec; δ_H ($CDCl_3$) 7.37 (2 H, br s), 2.50 (6 H, br s). Anal. Calcd for $C_{12}H_8N_4$: C, 69.2; H, 3.8; N, 26.9. Found: C, 69.3; H, 3.7; N, 26.9.

Compound 6f: 62%, mp >320 °C. Anal. Calcd for $C_{14}H_8N_4S_4$: C, 46.7; H, 2.2; N, 15.5. Found: C, 46.5; H, 2.1; N, 15.3.

Compound 6g: 68%, mp 258–260 °C, after preparative TLC (silica, eluent dichloromethane). Anal. Calcd for $C_{16}H_8N_4S_2$: C, 60.0; H, 2.5; N, 17.5. Found: C, 59.6; H, 2.3; N, 17.2.

Compounds **6f** and **6g** were too insoluble for NMR spectra to be obtained.

1,4-Diiodo-2,6-dimethylbenzene (10). Crude 4-iodo-2,6-dimethylaniline hydrochloride[29] (1.0 g) was dissolved in water (15 mL) and cooled to 0 °C. A solution of sodium nitrite (220 mg, 3.2 mmol) dissolved in water (1.5 mL) was added dropwise to the mixture which was stirred at 0–5 °C for 0.5 h. Potassium iodide (3.5 g, 21 mmol) dissolved in water (8 mL) was added over 10 min, and the solution was stirred at 0–5 °C for a further 1 h. After heating at reflux for 30 min, the mixture was cooled and extracted with dichloromethane. The organic layer was separated, dried ($MgSO_4$), evaporated and chromatographed on a silica column, eluting with hexane, to yield compound **10** (0.308 g) (10% yield based on 2,6-dimethylaniline), a white solid: mp 61–64 °C; δ_H ($CDCl_3$) 7.23 (2 H, s) and 2.20 (6 H, s). Anal. Calcd for $C_8H_8I_2$: C, 26.8; H, 2.2. Found: C, 26.5; H, 2.2.

2-Iodo-5-(dicyanomethyl)-1,3-dimethylbenzene (11). To HMPA (1 mL) and sodium hydride (0.160 g, 4 mmol) was added a solution of malononitrile (238 mg, 3.6 mmol) dissolved in HMPA (2.5 mL). After the solution was stirred at 20 °C for 0.25 h compound **10** (324 mg, 0.9 mmol) dissolved in HMPA (1 mL) was added, followed by copper iodide (689 mg, 3.6 mmol), and the mixture was gradually heated to 120 °C and maintained at this temperature for 3 h. The black mixture was quenched with dilute hydrochloric acid, the organic phase extracted with ether, and the extract washed with aqueous sodium sulfite to remove any free iodine. The solvent was evaporated to leave a brown residue. Silica column chromatography, with dichloromethane eluent, gave unchanged diiodide **10** (85 mg), followed by compound **11** (38 mg, 14%) as a white solid: mp 89–91 °C (from chloroform); δ_H ($CDCl_3$) 7.06 (2 H, s), 4.80 (1 H, s) and 2.46 (6 H, s). Anal. Calcd for $C_{11}H_9N_2I$: C, 44.6; H, 3.0; N, 9.5. Found: C, 44.6; H, 2.9; N, 9.7.

Phenylhydrazone Derivative 12. Crude amine hydrochloride salt **9** (500 mg) was diazotized as described above for the synthesis of compound **10**. Malononitrile (115 mg, 5.2 mmol) was added, and the mixture was stirred at 20 °C for 15 h and then extracted with chloroform. The organic phase was separated, dried ($MgSO_4$), evaporated, and chromatographed on a silica column eluting with hexane to yield compound **12** (150 mg, 11% based on 2,6-dimethylaniline): yellow solid, mp 140–143 °C (from water); δ_H ($CDCl_3$) 9.39 (1 H, br s, NH), 7.27 (2 H, s) and 2.29 (6 H, s). Anal. Calcd for $C_{11}H_9N_4I$: C, 40.7; H, 2.8; N, 17.3. Found: C, 40.9; H, 2.6; N, 17.5.

2,6-Dimethyl-4-(dicyanomethylene)cyclohexanone (14). Diketone **13**[30] (2.04 g, 14.5 mmol), malononitrile (1.44 g, 22 mmol), and β-alanine (0.170 g, 1.9 mmol) were dissolved in water (22 mL) and heated at reflux for 1 h. On cooling, the aqueous mixture was extracted with chloroform, and the organic layer was separated, dried ($MgSO_4$), and evaporated to yield a viscous oil which was chromatographed on a silica column, eluent dichloromethane–toluene (2:1 v/v), to yield compound **14** (2.3 g, 84%): white solid, mp 56–58 °C; δ_H ($CDCl_3$) 3.26 (2 H, m), 2.63 (2 H, m), 2.46 (2 H, m), 1.10 (6 H, m). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.2; H, 6.4; N, 14.9. Found: C, 69.7; H, 6.3; N, 15.1.

Alternative Synthesis of Quinomethide 4e. A stirred solution of compound **14** (0.086 g, 0.46 mmol) and bromine (0.154

g, 0.96 mmol) in dry acetonitrile (5 mL) was cooled to 0–5 °C under nitrogen. Pyridine (0.145 mg, 1.84 mmol) was added slowly over 15 min. After stirring at 20 °C for 15 h the mixture was quenched with water and the aqueous solution extracted with chloroform. The organic layer was separated, dried ($MgSO_4$), and evaporated. Vacuum sublimation of the resulting brown solid (ca. 100 °C, 0.001 mBar Hg) yielded compound **4e** (50 mg, 59%) identical with the sample described above.

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Registry No. **1a**, 1518-16-7; **1b**, 70359-39-6; **1c**, 97218-71-8; **1d**, 138385-47-4; **1e**, 86317-43-3; **2f**, 130891-30-4; **2g**, 130891-33-7; **3a**, 106-51-4; **3b**, 84-65-1; **3c**, 527-17-3; **3d**, 935-92-2; **3e**, 527-61-7; **3f**, 105855-49-0; **3g**, 10251-80-6; **4a**, 83928-83-0; **4b**, 10395-02-5; **4c**, 123849-29-6; **4d**, 123849-28-5; **4e**, 95276-20-3; **4f**, 138385-48-5; **4g**, 130891-41-7; **5a**, 72971-39-2; **5b**, 138385-49-6; **5c**, 97218-72-9; **5d**, 138385-50-9; **5e**, 25751-81-9; **5f**, 138385-51-0; **5g**, 138385-52-1; **6a**, 116267-99-3; **6a** anion, 138385-53-2; **6b**, 116387-65-6; **6c**, 123849-27-4; **6c** anion, 138385-54-3; **6d**, 123849-26-3; **6d** anion, 138385-55-4; **6e**, 123849-25-2; **6e** anion, 138385-56-5; **6f**, 138385-57-6; **6g**, 138385-58-7; **8**, 130891-39-3; **9**, 138385-59-8; **10**, 4102-48-1; **11**, 138385-60-1; **12**, 138385-61-2; **13**, 14384-30-6; **14**, 138385-62-3; malononitrile, 109-77-3; *N,N′*-bis(trimethylsilyl)carbodiimide, 1000-70-0; potassium, 7440-09-7.

Supplementary Material Available: Mass and IR spectroscopic data for compounds **1c**, **4a–4g**, **10**, **11**, **12**, and **14**; mass IR and UV/vis spectroscopic data for compounds **2f**, **2g**, and **6a–6g**; variable-temperature NMR spectra of compound **6e**; complete listings of bond lengths, bond angles, and anisotropic temperature factors for compounds **6c** and **6d** (23 pages). Ordering information is given on any current masthead page.

New Vinylogous Tetrathiafulvalene π-Electron Donors with Peripheral Alkylseleno Substitution

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Efficient syntheses are described for five new vinylogous π-electron donors, viz. **5**, **6**, and **8–10**, which are related to bis(ethylenediseleno)tetrathiafulvalene (**3**): symmetrical and unsymmetrical systems, containing mixed alkylseleno and alkylthio groups, have been obtained. The solution electrochemical redox properties, studied by cyclic voltammetry, establish that these molecules undergo two, single-electron, oxidations at low potentials. The single-crystal X-ray structure of 4,5-bis(methylseleno)-4′,5′-bis(methylthio)-2,2′-ethanediylidene(1,3-dithiole) (**6**) is reported. Semiconducting complexes of the new donors with tetracyano-*p*-quinodimethane have been obtained.

Quasi-one-dimensional organic metals have been intensively studied since the discovery of high electrical conductivity in the charge-transfer complex of tetrathiafulvalene (TTF) (**1**) (Chart I) and tetracyano-*p*-quinodimethane (TCNQ).[1] The synthesis of new multichalcogen π-electron donors has remained at the forefront of research,[2] with a few systems, notably, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (**2**),[3] providing radical cation salts which are superconductors,[4] with T_c values as high as 11.6 K.[5]

The incorporation of conjugated spacers between the 1,3-dithiole ring of TTF has been a prominent theme in the design of new donors. For example, the parent TTF vinylogue **4** has been studied by Yoshida et al.,[6] and recently the BEDT-TTF vinylogue **7** has been synthesised independently by three groups.[7-9] Molecules **4** and **7** were reported to undergo multistage redox reactions with relatively low oxidation potentials; extending the conjugation in this manner stabilized the dication state, relative to TTF (**1**) and BEDT-TTF (**2**), by reducing the intramolecular Coulomb repulsion energy. Salts of extended donors may, therefore, show electronic and magnetic properties that are quite different from salts of donors **1** or **2**. We now describe the synthesis and solution redox behavior of new vinylogues **5**, **6**, and **8–10**, which are the first derivatives of system **4** that have selenium atoms attached to the

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