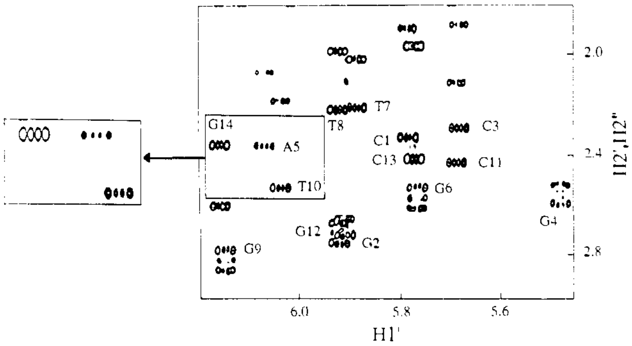

Figure 1. (H1')-(H2'-H2'') cross peak region of the phase sensitive ω_1-decoupled COSY spectrum of the oligonucleotide d(C-G-C-G-A-G-T-T-G-T-C-G-C-G) recorded on a Bruker AM 500 FT-NMR spectrometer. Four hundred t_1 increments were used in TPPI[14] (time proportional phase incrementation) fashion, with 2048 data points (t_2) for each t_1 value. The value of Δ which corresponds to $t_1^{\max}$ here was 56 ms. The data were zero-filled to 8192 along t_2 and 2048 along t_1, prior to window multiplication by sine bell shifted by $\pi/4$ and subsequent Fourier transformation. A separate one-dimensional spectrum was used to obtain the phase constants for phase correction to pure absorption (cross peak) along the ω_2 axis of the 2D spectrum. After the 2D transform, phase correction was applied along ω_1 (taking a cross section from the spectrum) to obtain pure absorptive phases. Digital resolution along ω_2 is 0.87 Hz/point, and along ω_1, 3.48 Hz/point. Experimental time was 14 h. Only the H1'-H2'' cross peaks are labeled in the figure. Side panel shows illustrative simulations of the multiplet patterns of the H1'-H2'' cross peaks of G14, A5, and T10 units.

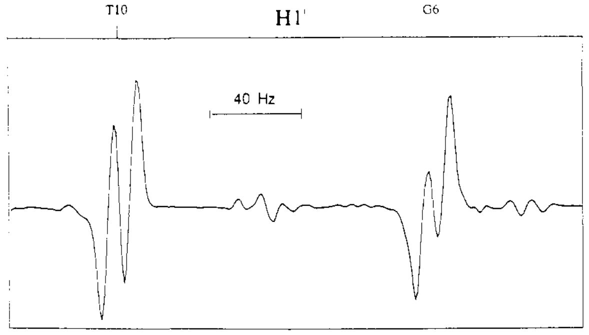

Figure 2. A horizontal cross section through the spectrum in Figure 1 showing the H1' multiplets of T10 and G6 nucleotide units.

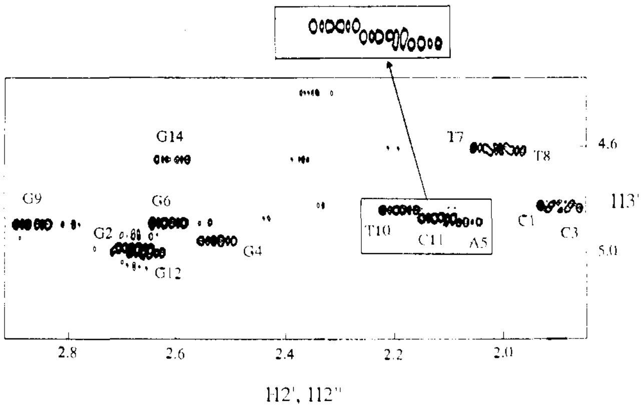

Figure 3. (H2'-H2'')-(H3') cross peak region of the same ω_1-decoupled COSY spectrum as in Figure 1. All the cross peaks are seen except for C13 which was bleached out by irradiation. On the top illustrative simulations of H2'-H3' cross peaks of T10, C11, and A5 units are shown.

Table I. Measured ^{1}H-^{1}H Coupling Constants from the ω_1-Decoupled COSY Spectrum of d(C-G-C-G-A-G-T-T-G-T-C-G-C-G)

	J (H1'-H2'')	J (H1'-H2')	J (H2'-H3')	J (H2'-H2'')
C1	5.7	9.6		
C3	5.2	9.2		
C13	5.7	9.8		
A5	5.9	10.4	5.2	-14.0
T7	5.2	10.0	5.4	-14.0
T8	5.0	9.8	6.1	-14.0
T10	5.0	9.1	6.3	-14.0
C11	5.2	9.2	6.2	-14.0
G14	5.0	9.8	5.1	-14.0

Figure 3 shows the (H2', H2'')-H3' cross peak region of the same ω_1-decoupled COSY spectrum as in Figure 1. Each peak here has the H2' multiplicity with the arrangement of +, - signals as (+ - + + - - + -). These multiplet patterns have also been simulated (illustrated on the top of the figure) to obtain the H2'-H3' coupling constant in the units A5, T7, T8, T10, C11, and G14. C1 and C3 peaks overlap significantly and are not amenable to proper simulation. For the G2, G4, G6, G9, and G12 units, the H2'-H3' coupling constant could not be obtained accurately owing to strong coupling complications. The C13 peak has been bleached out by water irradiation. H2''-H3' cross peaks are extremely weak in every case, which must be attributed to the very small (1-1.5 Hz) value of the H2''-H3' coupling constant. These cross peaks are not seen in any of the J-correlated spectra of the oligonucleotide. The same conclusion holds good for the H3'-H4' coupling constant.

Thus it seems possible that most of the measurable coupling constants can be obtained from one ω_1-decoupled COSY spectrum, and the coupling constants measured in the present case are listed in Table I. The data can be analyzed for sugar geometries by following the functional dependence of the individual coupling constants on sugar geometries.[12,13] Suffice it to say that the data are consistent with sugar geometries in a narrow domain around C2'-endo conformation for all the measured nucleotide units.

Acknowledgment. The research was funded by NIH Grant GM34504. The NMR spectrometers were purchased from funds donated from the Robert Woods Johnson Jr. Trust and Matheson Trust toward setting up an NMR Center in the Basic Medical Sciences at Columbia University. We thank Ajay Kumar at the Tata Institute of Fundamental Research for his help in developing graphics software.

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(14) Redfield, A. G.; Kunz, S. D. *J. Magn. Reson.* **1975**, *19*, 250.

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p-Diphenoquinone Analogues Extended by Dihydrothiophenediylidene Insertion: A Novel Amphoteric Multistage Redox System

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Organic molecules having an enhanced amphoteric redox property,[1] namely, a small span of the oxidation and reduction potentials $E^{\text{sum}} = E^{\text{ox}} + (-E^{\text{red}})$ which is oxidized and reduced easily by a multistage electron transfer, have attracted much attention in recent years in relation to single-component molecular assemblies with electrical conductivity.[2] The most definitive example would be graphite exhibiting $E^{\text{sum}} = 0$. In order to build up a novel closed-shell system with an amphoteric multistage redox property, we designed extended quinones in which one or more dihydrothiophenediylidene moieties are inserted between the two

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(1) (a) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Sandman, D. J.; Richter, A. F. *J. Am. Chem. Soc.* **1979**, *101*, 7079. (c) Hagenbruch, B.; Hesse, K.; Hunig, S.; Klug, G. *Liebigs Ann. Chem.* **1981**, 256. (d) Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1982**, *104*, 1432. (e) Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136.

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Scheme I

1 : n = 1 2 : n = 2
3 : n = 3 4 : n = 4

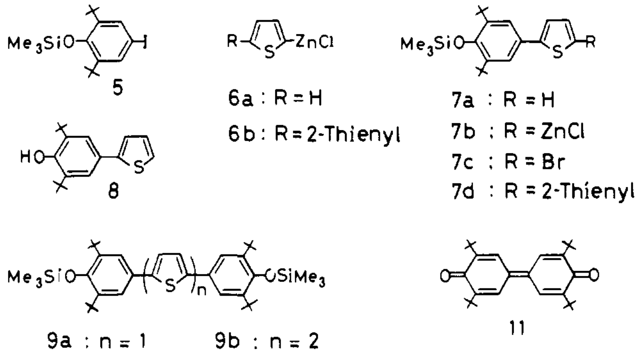
10a : n = 1 10b : n = 2
10c : n = 3 10d : n = 4

rings of diphenoquinone, that is 2,5-bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene and its oligodihydrothiophene analogues. In such a system, amphotericity can be enhanced by the conjugated sp^2 carbon chain and the heteroaromatic stabilization of the corresponding radical ions and divalent ions created through the redox processes. To this end, we have now synthesized *tert*-butyl-substituted quinones **1**, **2**, **3**, and **4**, proving that these quinones exhibit actually an amphoteric redox property and that **4** exhibits noticeably the smallest E_1^{sum} and E_2^{sum} values among the closed-shell organic compounds reported so far.

A series of benzoquinones has been most thoroughly investigated in electrochemistry,[3] but there has been no description in literature so far of one which exhibits an amphoteric property. This is also true for the extended quinones such as diphenoquinones, stilbenequinones, and others including bis(4-oxo-2,5-cyclohexadien-1-ylidene)ethene[4] and tetrakis(4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutane derivatives.[5] Thus **1–4** provide a new mode of an amphoteric redox system constructed from extended *p*-benzoquinonoid structures where the comprised chalcogen atom(s) may increase an intermolecular interaction in a solid state by the S····S contact.[6] In this paper we wish to report the synthesis and characteristic electrochemical properties of the novel quinones **1**, **2**, **3**, and **4**.

Thienylzinc chloride **6a**, obtainable by the reaction of thienyllithium with zinc chloride, reacted readily with **5**[7] in the presence of 5 mol % of $Pd(PPh_3)_4$ generated in situ by treating $Cl_2Pd(PPh_3)_2$ with *i*-Bu_2AlH,[8] to give a key precursor **7a** in 85% yield. Organozinc chloride **7b** prepared from lithiated **7a** and zinc chloride was allowed to react again with **5** to produce **9a** in 75% yield by the Pd-catalyzed cross-coupling. By the same cross-coupling reaction of **7b** with **7c** derived from the bromination of **7a**, **9b** was prepared in 86% yield. Two successive Pd-catalyzed cross-couplings were also successful to afford **9c** in 54% yield when 2 molar equiv of **7b** were treated with 2,5-dibromothiophene. Siloxyphenylbithienyl **7d**, obtained in 89% yield by cross-coupling reaction of bithienylzinc chloride with **5**, was first lithiated with LDA and then submitted to an oxidative homo-coupling reaction by treating with $CuCl_2$ to give **9d** in 39% yield. Desilylation of **9a–d** with 1 M HCl in THF yielded the respective hydroquinones **10a** (colorless needles; mp 91–93 °C), **10b** (orange needles; mp 279–282 °C), **10c** (yellow needles; mp 232–235 °C), and **10d** (orange needles; mp 255–260 °C). Two-phase oxidation of **10a–d** in benzene or dichloromethane with potassium ferricyanide dissolved in 0.1 M KOH solution afforded the corresponding quinones **1** (brilliant violet needles; mp 270–273 °C), **2** (deep green needles or gold plates; mp 268–269 °C), **3** (black violet needles; mp 183–187 °C), and **4** (black needles; mp 175–176 °C) in quantitative yields.[9] When **8** produced from the desilylation of **7a** was allowed to react with the basic potassium ferricyanide, quinone **2** was obtained quantitatively through an initial formation of **10b** by regioselective homo-coupling of **8** and subsequent oxidation. This is the first synthesis and isolation in solid state of ter-, quater-, quinque-, and sexiphenoquinone derivatives although the inner cyclohexadienediylidene(s) are replaced by dihydrothiophenediylidene moieties. Quinones **1**, **2**, **3**, and **4** were reduced quantitatively with $Na_2S_2O_4$ to **10a–d**, respectively.

Chart I



5

6a : R = H
6b : R = 2-Thienyl

7a : R = H
7b : R = ZnCl
7c : R = Br
7d : R = 2-Thienyl

8

9a : n = 1 9b : n = 2
9c : n = 3 9d : n = 4

11

The cyclic voltammogram of **1** exhibited two reversible one-electron reduction and one reversible oxidation waves of equal height showing the formation of both the stable radical anion and the radical cation as well as the dianion of **1**. Quinones **2**, **3**, and **4** showed one reversible two-electron reduction wave and two reversible one-electron oxidation waves in cyclic voltammograms, while the second oxidation step of **2** is quasi-reversible. The reduction wave was divided into two one-electron steps according to the Myers–Shain method.[10] The radical anions and radical cations generated from **1** and **2** were proved to be very stable species by their ESR spectral investigation.[11] The electrochemical data of **1–4** are summarized in Table I along with those of **11**. The first reduction potential (E_1^{red}) of **1** appears in a more positive region than **11**. Moreover, the E_1^{red} increases in the order of **1** < **2** < **3** < **4**, and the first oxidation potential (E_1^{ox}) does so in the reverse order. The same trend is observed for the second potentials, E_2^{red} and E_2^{ox}. Consequently, the E_1^{sum} and E_2^{sum} become smaller in the order of **1** > **2** > **3** > **4**. Compounds **1–4** are thus characterized as a new type of quinones exhibiting a high amphoteric redox behavior. The E_1^{sum} of **1** is comparable to that of 1,2-bis(phenalen-1-ylidene)ethane (1.51 V),[2d] and the E_1^{sum} of **3** is slightly less than those of pentaleno[1,2,3-*cd*:4,5,6-*c′d′*]diphenalene (0.99 V)[2e,12] and cyclobuta[*b*]quinoxaline-1,2-dione (0.91 V).[13] Indeed, quinone **4** exhibits the smallest E_1^{sum} (0.75 V) and the smallest E_2^{sum} (1.15 V) among the closed-shell organic compounds previously reported. The high electron-donating ability of **1–4** can be accounted for by the conjugative effect of the 3p electrons on the sulfur atom(s) stabilizing effectively the corresponding radical cations $[1–4]^{\bullet+}$ and dications $[2–4]^{2+}$ and for the aromatic and heteroaromatic stabilization of the constituent rings created through the amphoteric redox processes (Scheme II).

In CNDO/2 calculations,[14] the LUMO (−1.15 eV) and HOMO (−9.33 eV) of **1′** (where the *tert*-butyl groups of **1** are replaced by H's) lie at a lower level by 0.15 eV and at a higher level by 0.97 eV, respectively, than the corresponding MO's of diphenoquinone; this results in a pronounced decrease of HOMO–LUMO energy split, which is in accord with the amphoteric behavior of **1**. Another insight into the decreasing order of the HOMO–LUMO gap (**1** > **2** > **3** > **4**) and increasing order of amphotericity

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(4) Benham, J. L.; West, R. *J. Am. Chem. Soc.* **1980**, *102*, 5054.

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(6) (a) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaad, K. *J. Phys. Lett.* **1980**, *41*, 95. (b) Saito, G.; Enoki, T.; Toriumi, K.; Inokuchi, H. *Solid State Commun.* **1982**, *42*, 557.

(7) Compound **5** (colorless needles; mp 127–130 °C) was prepared from 2,6-di-*tert*-butyl-4-iodophenol (Ley, K.; Muller, E.; Mayer, R.; Scheffler, K. *Chem. Ber.* **1958**, *91*, 2670) on treatment with 1 equiv of *n*-butyllithium and then with trimethylsilyl chloride at −78 °C in THF.

(8) For cross-coupling reactions catalyzed by Pd(0), see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

(9) Satisfactory elemental analyses and spectral data were obtained for all new compounds.

(10) Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980.

(11) The details of the ESR spectral properties of the radical anions and radical cations of the quinones **1–4** will be reported in a separate paper.

(12) The 0.99 V is the smallest of the values for hydrocarbons reported so far.

(13) Hunig, S.; Putter, H. *Chem. Ber.* **1979**, *110*, 2524. The 0.91 V was the smallest of the values for non-hydrocarbons reported before this work.

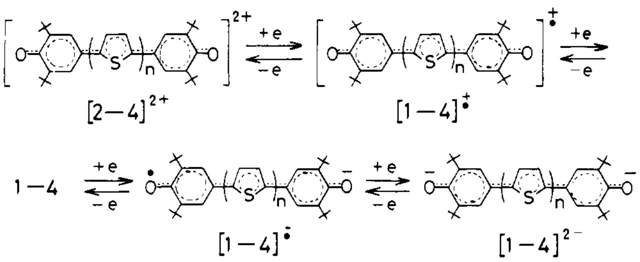
(14) The HOMO and LUMO of **1** belong to symmetry species b_1 and a_2, exhibiting large bonding and antibonding 2pπAO's on the intercyclic bonds, respectively.

Table I. Oxidation and Reduction Potentials, Their Numerical Sums, and the Longest Wavelength Absorption Maximum of Quinones **1**, **2**, **3**, **4** Compared with a Reference Compound, Tetra-*tert*-butyldiphenoquinone (**11**)

	electrochemical properties[a]						absorptn max[b]
quinone	E_2^{ox}	E_1^{ox}	E_1^{red}	E_2^{red}	E_1^{sum}	E_2^{sum}	λ nm (log ε)
11			-0.52	-0.89			420 (4.85)
1		+1.20	-0.46	-0.60	1.65	1.81	558 (4.90)
2	+1.44	+0.91	-0.31	-0.39	1.22	1.83	678 (4.50)
3	+1.07	+0.63	-0.26	-0.30	0.89	1.37	785 (4.77)
4	+0.89	+0.55	-0.20	-0.26	0.75	1.15	830 (4.45)

[a] Obtained by cyclic voltammetry vs SCE with 0.1 M Et_4NClO_4 at room temperature (scan rate, 50 mV/s; solvent, **1**, **11** in MeCN, **2** in CH_2Cl_2; **3**, **4** in EtCN); E^{ox} and E^{red} values were calculated by averaging the anodic and cathodic peak potentials: $E = E_p^a + E_p^c)/2$. [b] In MeCN.

Scheme II



(**1** < **2** < **3** < **4**) is given by the first excitation band in the electronic absorption spectra of these quinones, namely, the bands of **1**, **2**, **3**, and **4** show a bathochromic shift by 138, 258, 365, and 410 nm, respectively, from that of **11** in acetonitrile (Table I). The X-ray crystallographic analysis of these quinones and synthesis of other correlated systems exhibiting small E^{sum} values are in progress.

Acknowledgment. This work was supported by a Grant-in-aid from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: IR, UV-vis, MS, and ^1H NMR and ^{13}C NMR spectral data of **1-4**, **10a-d**, and **9a-d**, including elemental analysis (6 pages). Ordering information is given on any current masthead page.

High Diastereofacial Selectivity in the Additions of the Enolates of Aminocarbene Complexes to Chiral Aldehydes without the Assistance of a Lewis Acid

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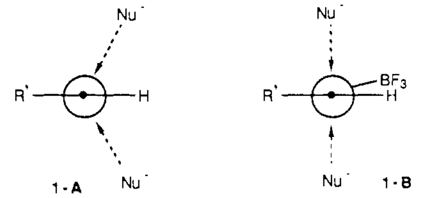
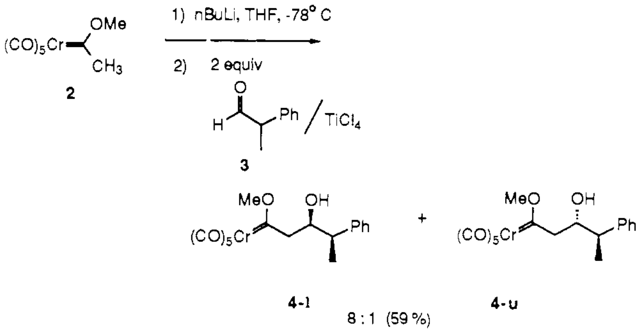
The diastereofacial additions of nonchiral enolates to chiral aldehydes can be quite selective, but in the case of α-unsubstituted enolates the facial selection is not significant enough to be practically useful.[1,2] The best solution involves the Lewis acid mediated addition of enolsilanes to chiral aldehydes.[3-6] Heathcock proposes that the Lewis acid complex **1-B** enhances facial selectivity by favoring approach of the nucleophile on a trajectory that brings it in greater proximity to the chiral substituent than in the case of the uncomplexed aldehyde (**1-A**).[3] This same kind of analysis has been successfully applied to the addition of nucleophiles to chiral ketones[6b] and chiral thionium ions.[6c]



In a previous report from our laboratory,[7] it was observed that the enolate of methoxyl stabilized carbene complex **2** would add to *dl*-2-phenylpropanal that had been pretreated with titanium tetrachloride to give the aldol adduct **4** as an 8:1 mixture of diastereomers (l:u).[8-11] The carbene complex **2** can serve as a synthon for methyl acetate since the products **4** can be oxidatively converted to their corresponding methyl esters, however, for the purposes of diastereoselection appeared not to be practical since the selectivity is only slightly better than is observed for methyl acetate.[3] One approach to the search for the greater expression of this asymmetric induction with the enolates of carbene complexes is to consider variations in the ancilliary substituent of the carbene carbon, and in this regard our attention was first turned to the (dimethylamino)carbene complex **5**.



The aldol reactions of aminocarbene complexes have not been previously reported, and very quickly it was found that there is a major difference between the aldol reactions of alkoxy- and aminocarbene complexes.[9] Whereas the enolates derived from

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(1) Heathcock, C. H. In *Asymmetric Synthesis*, Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Part B.

(2) (a) Flippin, L. A.; Onan, K. D. *Tetrahedron Lett.* **1985**, *26*, 973. (b) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353.

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(10) The diastereomers **4-l** and **4-u**, **10-l**, and **10-u**, and **13-l** and **13-u** each represent the structure as drawn and its enantioner.

(11) The descriptors l and u are used as defined in the following: Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

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