

TABLE II<sup>a</sup>  
 UV, CD, AND ORD DATA FOR (3*S*,6*S*)(+)-*trans*-3,6-DIMETHYL-1,2-DITHIANE (IaP)  
 AND (3*R*,6*R*)(-)-*trans*-3,6-DIMETHYL-1,2-DITHIANE (IaM)

		IaP <sup>b</sup> (ethanol)	IaM (ethanol)	IaM (isooctane)	(2 <i>S</i> ,5 <i>S</i> )-2,5-Hexane-dithiol <sup>b</sup> (ethanol)
UV	$\lambda_1$ m $\mu$ ( $\epsilon$ )	285 (243)		284 (233)	224 sh (275)
	$\lambda_2$	241 (158)		242 (174)	
CD	$\lambda_1$ m $\mu$	285	286	286	
	$[\theta]$ , deg	+9050 (+10,800) <sup>c</sup>	-11,000	-12,100	
	$\lambda_2$ m $\mu$	243	243	243	
	$[\theta]$ , deg	-13,100 (-15,600) <sup>c</sup>	+15,700	+17,800	
ORD <sup>d</sup>	$\lambda$ m $\mu$ $[\phi]$	310; +5,590 (+6,650) <sup>c</sup>	310; -6,740	310; -6,640	238; +1,310
	$\lambda$ m $\mu$ $[\phi]$	260; -8,890 (-10,600) <sup>c</sup>	260; +12,100	262; +12,300	208; -324
	$\lambda$ m $\mu$ $[\phi]$	228; +20,400 (+24,300) <sup>c</sup>	227; -25,300	222; -31,200	

<sup>a</sup> Measurements were made at 28° in 95% ethanol and in isooctane on a Cary 60 spectropolarimeter. <sup>b</sup> Approximately 84% optically pure. <sup>c</sup> Calculated for 100% optically pure material, assuming IaP to be 84% optically pure. <sup>d</sup> The maxima or minima are given in parentheses.

(3*R*,6*R*)(-)-*trans*-3,6-Dimethyl-1,2-dithiane (IaM).—The combined mother liquors from the brucine resolution were concentrated and acidified with dilute hydrochloric acid. The solid bis(hydrogen phthalate) ester (51.5 g, mp 184–186°) which precipitated was recovered by filtration. When this material was saponified as described above, 14.6 g of 2,5-hexanediol,  $[\alpha]_{25}^{20} +1.0^\circ$  (*c* 10.32, CHCl<sub>3</sub>), was recovered.

The filtrate from the isolation of the bis(hydrogen phthalate) ester was extracted three times with ether. Evaporation of the combined extracts yielded additional bis(hydrogen phthalate) ester as a thick oil which did not solidify. This material was saponified in the usual way. Distillation of the glycol yielded 9.09 g of 2,5-hexanediol: bp 119–120.5° (15 mm);  $[\alpha]_{25}^{20} +14.0^\circ$  (*c* 7.93, ethanol) and +21.2° (*c* 9.74, CHCl<sub>3</sub>).

This diol was converted into the di-*p*-toluenesulfonate as described above. By crystallization from acetone-petroleum ether (bp 60–68°), 11.0 g of the di-*p*-toluenesulfonate, mp 85–95°, was obtained. This material was crystallized to constant melting point (100–101°, yield 5.17 g) and constant rotation,  $[\alpha]_{25}^{20} 6.8^\circ$  (*c* 0.776, ethanol), by three additional crystallizations from acetone-petroleum ether (bp 60–68°).

Anal. Calcd for C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub>: C, 56.31; H, 6.14. Found: C, 56.46; H, 6.18.

The 2,5-hexanediol di-*p*-toluenesulfonate was converted into the dithiane (IaM) (1.13 g) in the manner described for the dextrorotatory isomer. Purification of this material with preparative vpc gave the (3*R*,6*R*)(-)-*trans*-3,6-dimethyl-1,2-dithiane (IaM): mp 26–30°;  $[\alpha]_{25}^{20} -276^\circ$  (*c* 0.0718, ethanol), -269° (*c* 0.0201, isooctane); ORD (*c* 0.0718, ethanol) 28°,  $[\phi]_{600} -394^\circ$ ,  $[\phi]_{310} -6740^\circ$ ,  $[\phi]_{237} 0.0^\circ$ ,  $[\phi]_{260} +12,100^\circ$ ,  $[\phi]_{246} 0.0^\circ$ ,  $[\phi]_{227} -25,300^\circ$ ,  $[\phi]_{220} -22,700^\circ$ , (*c* 0.0201, isooctane) 28°,  $[\phi]_{600} -384^\circ$ ,  $[\phi]_{310} -6640^\circ$ ,  $[\phi]_{237} 0.0^\circ$ ,  $[\phi]_{262} +12,300^\circ$ ,  $[\phi]_{246} 0.0^\circ$ ,  $[\phi]_{222} -31,200^\circ$ ,  $[\phi]_{220} -30,600^\circ$ .

*cis*-3,6-Dimethyl-1,2-dithiane (II) was prepared using a similar sequence of reactions to those above and starting with the low melting 2,5-hexanediol bis(hydrogen phthalate). In this sequence, the 2,5-hexanediol di-*p*-toluenesulfonate, mp 112–115°, was purified by crystallization from acetone-petroleum ether, then from acetone-MeOH. The nmr spectrum of the *cis*-3,6-dimethyl-1,2-dithiane was identical with that previously reported.<sup>6</sup> Vpc indicated that the compound was pure.

The nmr spectra of I and II were run at -60 ± 5.0° and +90 ± 1.0° on a Varian A-60 spectrometer at 50-Hz sweep width. The spectra were calibrated using two side bands of TMS, generated with a Hewlett-Packard function generator, No. 3300A. Frequency was monitored with a Hewlett-Packard electronic counter, No. 3734A. The spectra were determined in triplicate on 20% (wt/v) solutions of I and II in 95% CDCl<sub>3</sub>-5% TMS. At 90°, so much of the TMS evaporated into the free space in the nmr tube that adequate reference bands were not obtainable. The tubes were opened and an additional 10% (v/v) TMS was added to them. The data, so obtained, should be accurate to ±0.07 Hz.

(2*S*,5*S*)-2,5-Hexanedithiol,  $[\alpha]_{25}^{20} +54.1^\circ$  (*c* 0.0594, 95% ethanol), was prepared by the reduction of the (+)-*trans*-3,6-dimethyl-1,2-dithiane with lithium aluminum hydride in tetrahydrofuran.<sup>12</sup> The dithiol should be ca. 84% optically pure:

(12) R. C. Arnold, A. P. Lien, and R. M. Alm, *J. Amer. Chem. Soc.*, **72**, 731 (1950).

ORD (*c* 0.0594, 95% ethanol) 28°,  $[\phi]_{600} +89^\circ$ ,  $[\phi]_{238} +1310^\circ$ ,  $[\phi]_{214} 0.0^\circ$ ,  $[\phi]_{208} -324^\circ$ , (*c* 0.0762, isooctane), 28°,  $[\phi]_{600} +83^\circ$ ,  $[\phi]_{243} +1320^\circ$ ,  $[\phi]_{221} 0.0^\circ$ .

Registry No.—IaM, 17299-08-0; IaP, 17299-01-3; *dl*-2,5-hexanediol bis(hydrogen phthalate), 17299-02-4; *meso*-2,5-hexanediol bis(hydrogen phthalate), 17299-03-5; 2,5-hexanediol, 17299-07-9; 2,5-hexanediol di-*p*-toluenesulfonate, 17299-04-6; II, 17299-05-7; (2*S*,5*S*)-2,5-hexanedithiol, 17299-06-8.

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### Charge-Transfer Properties and Electrochemistry of Quinones with Donor Substituents<sup>1a</sup>

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Whereas charge-transfer (CT) complexes have been investigated extensively, seldom have both donor and acceptor roles been ascribed to a single compound. The theory underlying these complexes intimates that a compound may display dual behavior provided that there is a good balance between its ionization potential and its electron affinity. We have already described the dual CT abilities of a series of nitro-*p*-terphenyls.<sup>2</sup> We have now extended our studies to the *p*-benzoquinone series in the hope of uncovering donor abilities to complement their well known CT acceptor properties. Consequently, we found that 2,5-diethoxy-*p*-benzoquinone (DEQ) and 2,5-bis-*N*-methylamino-*p*-benzoquinone (BAQ) can function as CT donors as well as playing traditional electron acceptor roles. As a corollary, these quinones also undergo electrochemical oxidation. Although the electrochemical reduction

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(2) R. L. Hansen, *J. Phys. Chem.*, **70**, 1646 (1966).

of quinones has become a pedagogical classic, their oxidation has not been reported.

Thus, methylene chloride solutions of DEQ and BAQ containing typical donors such as N,N-dimethyl-*p*-toluidine (DMT) and benzidine or acceptors like 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and tetracyanoethylene displayed extra absorption bands attributed to intermolecular complexes. For example, CT band maxima of DEQ complexes with DMT and DDQ appeared at 470 and 440 m $\mu$ , respectively. The BAQ-DMT complex displayed the long wavelength tail of a CT band (max  $\leq$  400 m $\mu$ ), while the interaction of BAQ with DDQ gave a CT max at 683 m $\mu$  and a second band at higher energy. For comparison, the benzoquinone-DMT complex showed a maximum at 526 m $\mu$  but no evidence for CT donor behavior was observed.

Only the complexes of DEQ were studied quantitatively owing to the low solubility of BAQ. The spectroscopic technique employed previously<sup>2</sup> showed the DEQ-DMT complex to be of 1:1 stoichiometry with  $K = 0.14 \pm 0.01$  l./mol at 25°,  $\epsilon_{470} = 430 \pm 30$  l./mol cm, and  $\Delta H = -1.9 \pm 0.2$  kcal/mol (typical numbers for a weak  $\pi$ - $\pi$  complex). Initial spectroscopic measurements on the DEQ-DDQ system suggested other than 1:1 interaction and a polarographic method was used to examine the system quantitatively.<sup>3</sup> Analysis of the data indicated both 1:1 and 2:1 complexes with DDQ in excess in the latter case. At 4° the formation constants were 1.3 l./mol and 0.2 l.<sup>2</sup>/mol<sup>2</sup>, respectively. Solutions of DEQ showed no evidence for the presence of an intermolecular self-complex such as was observed with the nitroterphenyls.<sup>4</sup> We had hoped that the  $b_g$  symmetry predicted for both the highest filled and lowest vacant molecular orbitals of DEQ and BAQ would favor self-complexing.

Novel quinone-quinone complexes containing DDQ with either DEQ or BAQ were readily isolated. Both solids were of 2:1 stoichiometry. While the DDQ was in excess in its complex with DEQ, the ratio was just inverted in the DDQ-BAQ complex. Both solids displayed epr signals although neither was completely paramagnetic. The spin concentration was some 550 times higher for the DDQ-BAQ complex with a Curie law temperature dependence. The epr signal disappeared abruptly upon heating the complex above 123° where a change in the color and crystallinity of the solid also occurred.

The acceptor properties of the quinones are related to their lowest unoccupied  $\pi$  levels but they could behave as either  $n$  or  $\pi$  donors as the oxygen and nitrogen atoms carry unshared electron pairs. The dual CT abilities of DEQ and BAQ afford unique opportunities to relate the energies of intermolecular CT bands to the absorption spectra of the quinones themselves, thereby providing information about the energy levels involved. This was outlined and applied in a previous paper with satisfying results.<sup>2</sup>

The long wavelength absorption bands of simple 2,5-disubstituted quinones have been attributed to  $\pi \rightarrow \pi^*$  transitions, their intensities reflecting configuration interaction.<sup>5</sup> If these same  $\pi$  levels of

DEQ or BAQ are those involved in complexing with DMT and DDQ, the energy of the quinone's long wavelength band should approximately equal the sum of the energies of the CT bands of its DMT and DDQ complexes minus the energy of the DMT-DDQ CT band.<sup>6</sup> On this basis we calculate 580 m $\mu$  for the DEQ-DMT CT band and 640 m $\mu$ , for the DEQ-DDQ band. These results are in gross disagreement with experiment since these band maxima actually appear below 400 m $\mu$  and at about 440 m $\mu$ , respectively. The disparity amounts to about 20 kcal/mol which seems too large to attribute to the approximations used. It is unlikely, however, that the carbonyl oxygen atoms of either quinone or the ethereal oxygen atoms of DEQ are sites of localized donor activity. We conclude that for the DEQ-DDQ complex at least the observed CT absorption is due to  $\pi$ - $\pi$  interaction.<sup>7</sup> The difference between the calculated and observed energies reflects configuration interaction which decreases the energy of DEQ's long wavelength band but is not involved in determining the energies of intermolecular CT bands.

Polarographic oxidation and reduction potentials have been related to CT donor and acceptor abilities, respectively.<sup>8,9</sup> For example, the half-wave reduction potentials -0.46, -0.74, and -1.17 V for benzoquinone, DEQ, and BAQ at their first waves in acetonitrile, together with the benzoquinone-DMT CT max at 526 m $\mu$ , suggests 470 and 400 m $\mu$  for the DEQ-DMT and BAQ-DMT CT maxima, respectively. Although the electrochemistry of quinones in aprotic solvents is becoming well known<sup>10</sup> neither DEQ nor BAQ seem to have been studied. The epr spectra of their semiquinone anions prepared by electrolytic reduction are described below. The diethoxysemiquinone anion has been generated before using alkali.<sup>11</sup> The present hfsc are somewhat different. Few amino-semiquinone anion epr spectra have been reported.

As a consequence of their CT donor abilities we felt that the quinones might be capable of electrochemical oxidation. This expectation was realized as illustrated in Figure 1 which shows a cyclic polarogram of DEQ obtained at a stationary platinum electrode. In addition to the two reversible reduction waves, a clearly resolved oxidation wave with a peak at 2.32 V appears. The absence of a reverse wave at scan rates as high as 400 mV/sec indicates that the oxidation is chemically irreversible. In accord with its enhanced CT donor abilities the first oxidation peak for BAQ occurred at 1.33 V and a second at 2.1 V. These waves were also irreversible. By contrast, benzoquinone did not display an oxidation peak to 2.85 V, the solvent limit. The electrochemical oxidations were not investigated extensively enough to identify the products formed. Quantitative oxidation of DEQ required 2.5-3.0 electrons/molecule, destroyed the quinone chromophore, and produced at least two products, one of which was

(6) The CT maximum appeared at 900 m $\mu$ . See Experimental Section.

(7) The preliminary results of an X-ray study of the crystal structure of the 2:1 DDQ-DEQ complex were presented by B. T. Gorres and G. E. Gurr at the Winter Meeting of the American Crystallographic Association at Tucson, Ariz., Feb 1968. The results are consistent with  $\pi$ - $\pi$  interaction.

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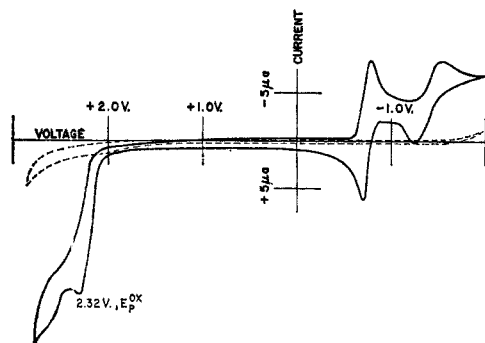


Figure 1.—Cyclic polarogram of 12.5 mM DEQ in acetonitrile with 0.1 M tetrabutylammonium perchlorate (scan rate 40 mV/sec). The dashed line is the residual current.

an acid. Electrode coating problems prevented meaningful study of the oxidation of BAQ at its first wave. Quantitative oxidation at the second wave required 4.0 electrons/molecule and also produced an acid among the products. The electrochemical oxidation of aromatic amines<sup>12</sup> and aliphatic amides<sup>13</sup> in aprotic solvents produces strong acid *via* initial cation-radical formation followed by coupling with elimination of a proton or proton abstraction from the solvent.

#### Experimental Section

DEQ<sup>14</sup> and BAQ<sup>15</sup> were prepared as described in the literature and purified by column chromatography and vacuum sublimation. The long wavelength absorption maxima of DEQ and BAQ in methylene chloride appeared at 372  $\mu$  ( $\epsilon$  3.13  $\times$  10<sup>3</sup>) and 478  $\mu$  ( $\epsilon$  2.44  $\times$  10<sup>3</sup>), respectively. DDQ and benzidine were sublimed. The preparation and purification of the other materials have been described.<sup>2,9</sup>

The quinone-quinone complexes were obtained by concentration and cooling of equimolar mixtures of DDQ with either DEQ or BAQ in methylene chloride causing the solid complexes to precipitate. The DEQ complex was obtained as brilliant orange plates, mp 193–194°.

*Anal.* Calcd for C<sub>26</sub>H<sub>12</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>8</sub> (2:1 DDQ-DEQ): C, 48.0; H, 1.9; N, 8.6. Found: C, 47.8; H, 1.9; N, 8.5.

The BAQ complex was a black crystalline solid which turned brick red abruptly and irreversibly at 123° and melted with decomposition at about 200°.

*Anal.* Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>6</sub>N<sub>6</sub>Cl<sub>2</sub>O<sub>6</sub> (2:1 BAQ-DDQ): C, 51.5; H, 3.6; N, 15.0. Found: C, 51.6; H, 3.7; N, 15.0.

The procedures used for the spectroscopic study of CT complexes and treatment of the data have been described.<sup>2</sup> A special technique was required to observe the DMT-DDQ complex because it had a half-life of only a few seconds. Briefly, the CT absorption band which had a maximum at 900  $\pm$  20  $\mu$  was reconstructed from data obtained at several wavelengths. A hypodermic syringe was used to rapidly add a DMT solution to the DDQ solution in an absorption cell in the spectrophotometer. The spectrophotometer recorded the rapid increase and decay of the absorbance at a fixed wavelength as a function of time.

Polarographic measurements were made on deoxygenated solutions containing 1–15 mM quinone together with 0.1–0.5 M tetrabutylammonium perchlorate in methylene chloride or acetonitrile. Polarograms were obtained at both dropping mercury and stationary platinum electrodes *vs.* an aqueous sce. Three-electrode electronics was employed. Quantitative reductions were done at a mercury pool; the oxidations were done at a rotating platinum mesh anode. The *i/t* curves were recorded and intergrated with a planimeter. The semiquinone anion-radicals generated for epr spectra were the final products from

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quantitative reductions of the quinones at their first waves. Aliquots were transferred under nitrogen to a flat quartz cell and spectra were recorded with equipment described earlier.<sup>16</sup> In the case of diethoxysemiquinone anion the epr spectrum at  $g = 2.0050$  was analyzed in terms of two-proton hfsc;  $a_H = 0.89 \pm 0.01$  G for the methylene protons of the ethoxy groups and  $0.76 \pm 0.01$  G for the ring protons. The spectrum of the bis-N-methylaminosemiquinone at  $g = 2.0042$  contained 91 resolved lines and was fitted with a septet,  $a_H = 2.27 \pm 0.04$  G, due to splitting by the protons of the methyl groups; a pentet,  $a_N = 2.03 \pm 0.06$  G arising from the nitrogen nuclei; and two sets of unassigned triplets,  $a_H = 1.36 \pm 0.04$  G and  $0.91 \pm 0.04$  G due to the amino and ring protons. The solids were examined in evacuated quartz tubes. A Varian temperature control unit was employed.

**Registry No.**—DEQ complex, 17299-14-8; BAQ complex, 17299-15-9.

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### Chromyl Chloride Oxidations. I. Preparation of Carbonyl Compounds from Alkenes

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Recently several reports have described the preparation of aldehydes and ketones from alkenes.<sup>2</sup> We wish to report a simple, convenient, and one-step, high yield synthesis of aliphatic carbonyl compounds *via* the chromyl chloride oxidation of readily accessible alkenes. The formation of aldehydes and ketones in good yields is unique since the chromyl chloride oxidation of alkenes has been reported to give a mixture of products in low yields.<sup>3–5</sup> This procedure differs from previous methods primarily in the reductive hydrolysis step. In some of the past reports,<sup>3,5</sup> the alkene-chromyl chloride adduct was isolated and reductive hydrolysis was carried out on the adduct, while in other reports,<sup>4,6</sup> the entire reaction mixture was subjected to reductive hydrolysis with sulfur dioxide. We have found that zinc dust is a more effective reducing agent than sulfur dioxide.<sup>7–11</sup> Also, it appears that sul-

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(7) During hydrolysis, chromium(IV), -(V), and -(VI) are produced. It appears that zinc dust is more effective than sulfur dioxide in reducing the chromium species to chromium(III), since it is known that chromium(VI) cleaves alkenes to carbonyl compounds<sup>8,9</sup> and that chromium(IV) and -(V) are more powerful oxidizing agents than chromium(VI).<sup>10,11</sup>

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