but decomposes to unidentified products in a secondary reaction.

Radical Anions of Triptycene Bis- and Tris(quinones)[1]

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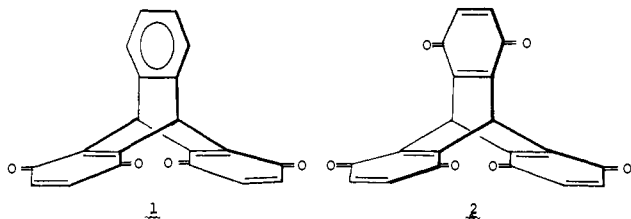*Myodaiji, Okazaki 444, Japan*

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The formation of radical ions upon reduction of **1** and **2** has been investigated in MeCN and Me_2SO solutions by ESR spectroscopy. We were interested in ascertaining if both radical mono-

and trianions could be detected and if their unpaired electrons are delocalized over all quinone rings, since the first reduction potential of **1** is reported to be considerably lower than the reduction potential of triptycene monoquinone.[2] We were surprised to observe, in addition to **1⁻·** and **1³⁻·**, an intermediate paramagnetic reduction product with a well-resolved ESR spectrum which appears to be the diradical (·**1²⁻·**), while for **2** at least three discrete paramagnetic radical anions can be detected by ESR spectroscopy.

Radical Monoanion of 1. Electrolytic reduction at Hg or Pt of **1** in MeCN or Me_2SO gave initially the 1:4:6:4:1 pentet of Figure 1a ($a^H = 1.10$ G, $g = 2.00506$ in Me_2SO). Occasionally a further hyperfine splitting of $\simeq 0.05$ G by two hydrogens was observed. This species does not have the electron delocalized over both rings, because cooling the MeCN solution resulted in selective line broadening of the second and fourth peaks. At −55 °C these peaks were essentially unobservable, and a ~1:4:1 triplet of sharp lines was observed (warming to 25 °C restored the 1:4:6:4:1 pentet). The hydrogen atoms of the bis(quinone) rings of **1⁻·** are time averaged by electron migration for which an energy barrier of $\Delta H^\ddagger = 6.2$ kcal/mol ($\Delta S^\ddagger = -7$ eu) was calculated from the selective line broadening observed between −50 and 0 °C. Dilution of solutions giving spectrum **1a** by 200-fold did not affect the line widths or intensities of the 1:4:6:4:1 pentet. The pentet was not immediately destroyed by exposure to oxygen.

Diradical Dianion of 1. Continued electrolysis of **1** in Me_2SO ($Bu_4N^+ClO_4^-$) at a Hg pool or Pt electrode resulted in the appearance of a 1:2:1 triplet, which was not time averaged with the pentet of **1⁻·**. After a sufficiently long period of electroreduction, the pentet disappeared completely to give the spectrum as shown
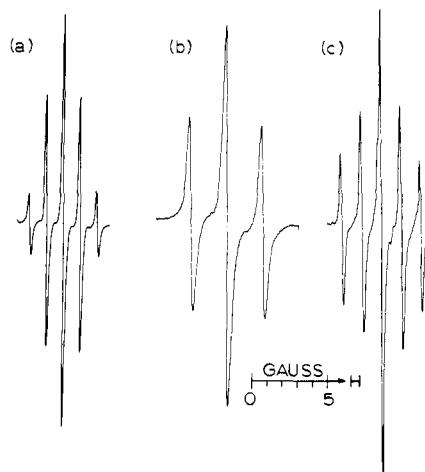
(1) Electron Transfer Processes. 26. This work was supported in part by Grant CHE-7823866 from the National Science Foundation.
(2) Iwamura, H.; Makino, K. *J. Chem. Soc., Chem. Commun.* **1978**, 720.

Figure 1. Radical anions derived from triptycene bis(quinone) in MeCN at 25 °C. (a) **1⁻·**, (b) ·**1²⁻·**, and (c) **1³⁻·** containing a trace of ·**1²⁻·** (shoulders on center and high-field peak).

in Figure 1b ($a^H = 2.45$ (Me_2SO), 2.40 (MeCN) G) with a g value equal to that of **1⁻·**. The triplet of Figure 1b would be consistent with a diradical structure if $J \ll a_H$ (i.e., no correlation between the electrons).[3,4] Time averaging of the two rings in the diradical state by a concerted migration of the two electrons would be highly improbable, and up to 100 °C the spectrum was a sharp 1:2:1 triplet with lines not appreciably broader than for **1⁻·**. Exchange of the two electrons by way of the dianion in which both electrons are in the same quinone ring does not occur rapidly. Frozen Me_2SO solutions of the species responsible for the 1:2:1 triplet still gave the 1:2:1 hyperfine splitting, and no $\Delta m = 2$ transition could be observed. The species responsible for the 1:2:1 triplet was observed in the presence or absence of excess base, the presence or absence of K^+, and was not converted to another species by dilution. The diradical reacted with an excess of the bis(quinone) to regenerate **1⁻·** but was stable to molecular oxygen. The biradical was more easily observed at very low free quinone concentrations. Thus electrolysis in Me_2SO-H_2O (80:20), $MeCN-H_2O$ (85:15), $MeCN-MeOH$, or $MeCN-Et_3N$ mixtures either gave rise to spectrum 1b as the initial species or greatly shortened the period required for the complete conversion of **1⁻·** to ·**1²⁻·**.[5]

In MeCN or Me_2SO **1** was reduced by KI in the presence of Hg or in MeCN by KI in the presence of [2.2.2]cryptand to give **1⁻·**. The cryptand had no effect upon the spectra but only served to make KI a better reducing agent (without the cryptand and in the absence of Hg, the formation of radical anions from **1** and KI was not observed). As the amount of KI in the presence of Hg was increased, the initial pentet (Figure 1a) was slowly converted to the triplet (Figure 1b). Another reducing agent, potassium *tert*-butoxide, had the same effect in MeCN or Me_2SO.[6] Traces of *tert*-butoxide gave the 1:4:6:4:1 pentet, while larger amounts yielded the 1:2:1 triplet.

Radical Trianion of 1. More extensive electrolytic or chemical reduction of **1** led to a species with a lower g value than **1⁻·** or ·**1²⁻·**. Continued electrolytic reduction at high voltages in Me_2SO or MeCN (Hg pool, $Bu_4N^+ClO_4^-$) produced a new pentet in addition to the composite spectra of Figure 1a and 1b. There was

(3) The value of a^H for triptycene monoquinone radical anion is the same as for ·**1²⁻·**.
(4) The 1:2:1 pattern of ESR lines results because for the case where the singlet–triplet diradical energy separation (J) is zero (or $\ll a_H$), there are only three $\Delta M_S = 1$ energy transitions between the $T_\pm$ states and the T_0 and singlet diradical states when each electron undergoes hyperfine splitting by two equivalent hydrogen atoms. See, for example: Lemaire, H.; Levy, B.; Rassat, A. *Colloq. Int. C. N. R. S.*, **1966**, *No. 164*, 401. Lemaire, H. *J. Chim. Phys.* **1967**, *64*, 559. Brière, R.; Dupeyre, R.-M.; Lemaire, H.; Morat, C.; Rassat, A.; Rey, P. *Bull. Soc. Chim. Fr.* **1965**, 3290.
(5) Presumably due to a reduced quinone concentration as a result of the formation of addition products.
(6) Russell, G. A.; Blankespoor, R. L. *Tetrahedron Lett.* **1971** 4573.

no exchange with $1^{-\cdot}$ or $\cdot1^{2-\cdot}$ since the high-field lines of the new pentet were clearly resolved from the high-field lines of the spectra of Figure 1a and 1b. Finally the spectrum of $1^{-\cdot}$ and $\cdot1^{2-\cdot}$ disappeared completely to yield the pentet of Figure 1c ($a^H = 1.26$ G in MeCN, $a^H = 1.30$ G in Me$_2$SO, $g = 2.00495$ in Me$_2$SO) which we assign to $1^{3-\cdot}$. Occasionally an additional partially resolved triplet or pentet splitting of ~0.05 G was observed. Upon standing, the pentent of Figure 1c slowly reverted to the high-g pentet and/or triplet, which upon further electroreduction regenerated the spectra of Figure 1c. Addition of 1 converted the spectrum of Figure 1c to the spectra of Figure 1a and/or 1b. Treatment of solutions giving the spectrum of Figure 1c with oxygen immediately converted the spectrum to a doublet of doublets ($a^H = 2.00, 2.35$ G; $g = 2.0050$), which we believe is a semiquinone radical di- to trianion in which one ring has been substituted by OH or OR.

For $1^{3-\cdot}$, the second and fourth peaks display selective line broadening at 25 °C. Cooling MeCN solutions yielded a ~1:4:1 triplet of sharp wing and center peaks at ~–20 °C, while heating caused the pentet to approach an intensity ratio of 1:4:6:4:1. From the line broadening, $\Delta H^{\ddagger}$ for electron jump was calculated to be 3.7 kcal/mol ($\Delta S^{\ddagger} = -24.3$ eu). The spectrum of Figure 1c was also produced by the reduction of 1 with Me$_3$COK in MeCN in the presence of [2.2.2]cryptand or 18-crown-6 ether. The cryptand or crown ether greatly increased the reducing ability of Me$_3$COK in MeCN, and in fact the addition of the cryptand of crown ether to Me$_3$COK solutions yielding the spectra of Figure 1a or 1b converted the spectra to that of Figure 1c.[7] Under these conditions the spectra often were a mixture of the three line pattern (high g) assigned to $\cdot1^{2-\cdot}$ and the low-g pentet of $1^{3-\cdot}$. Ion pairing did not appear to have any effect upon the observed spectra, since the low-g pentet was observed with either a deficiency or an excess of the cryptand or crown ether.[8]

The energy barrier for electron migration between the quinone rings is lower for $1^{3-\cdot}$ than for $1^{1-\cdot}$, but $\Delta S^{\ddagger}$ greatly favors the electron migration of $1\cdot^{-}$. This may be connected with more extensive solvation for $1^{3-\cdot}$ than for $1^{-\cdot}$. The normal Arrhenius behavior of both radical anions gives no evidence that electron tunneling is involved in the process which time averages the quinone rings.

Radical Anions of Triptycene Tris(quinone). Reduction of 2 at 25 °C in Me$_2$SO or MeCN at a Hg pool or Pt (Bu$_4$N$^+$ClO$_4^-$) also gave a number of discrete paramagnetic states, one of which is apparently the triradical trianion. The initially observed spectrum is a seven line pattern (in Me$_2$SO, $a^H = 0.66$ G (6 H), $g = 2.00507$) which is undoubtedly $2^{-\cdot}$. Reduction of 2 by KI in Me$_2$SO in the presence of Hg or by traces of Me$_3$COK in Me$_2$SO, MeCN, or DMF also yielded $2^{-\cdot}$. Selective line broadening was not observed at –90° C in DMF.

Reduction of 2 at higher potentials yielded a 1:2:1 triplet [$a^H = 2.60$ G (2 H)] which could also be observed by reaction with Me$_3$COK in Me$_2$SO. By analogy to the reduction products of 1, this ESR spectrum is assigned to the triradical trianion in which there is no exchange of the electrons.[4] There was no indication of a discrete species which could be identified as the diradical dianion, possibly because $\cdot2^{2-\cdot}$ has a heptet ESR spectrum indistinguishable from $2^{-\cdot}$.[7] The spectra asssigned to $2^{-\cdot}$ and $\cdot2^{3-\cdot}$ were not immediately destroyed upon exposure to oxygen.

At still higher reduction potentials at a Hg pool, a second heptet is produced [$\alpha^H = 0.68$ G (6 H)] which is not time averaged with

the triplet that precedes it. This species is quite reactive and cannot be observed in the absence of electrolysis. This heptet may be :$\mathbf{\dot{2}}^{4-\cdot}$ or :$\mathbf{\dot{2}}^{5-\cdot}$. In the triptycene tris(quinone) system intramolecular electron transfer between the quinone rings occurs more readily than for the bis(quinone), and the possibility of a completely delocalized system for $2^{-\cdot}$ and $2^{5-\cdot}$ exists.[9]

Triptycene tris(quinone) was synthesized in three steps from 1,4,5,8-tetraacetoxyanthracene[10] (3) and benzoquinone. The adduct 4 was prepated in 93% yield by refluxing 3 (18.7 g, 45.6 mmol) with benzoquinone (5.40 g, 50.2 mmol) in xylene (200 mL) for 20 h: mp 244–248 °C from 1,2-dichloroethane; ^{1}H NMR (CDCl$_3$) δ 6.95 (2 H), 6.85 (2 H), 6.45 (2 H), 5.1 (2 H), 3.15 (2 H), 2.45 (6 H), and 2.40 (6 H). Anal. Calcd for C$_{28}$H$_{22}$O$_{10}$: C, 64.9; H, 4.23. Found: C, 64.6; H, 4.63.

The adduct 4 (0.55 g, 1.06 mmol) was hydrolyzed and rearranged to 1,4,5,8,13,16-hexahydroxytriptycene (5) by treatment with KOH (0.5 g) in 10 mL of water and 10 mL of acetonitrile (25 °C, 2 h) under nitrogen. Acidification with dilute H$_2$SO$_4$ gave 5 (0.29 g, 65%). A sample for analysis was precipitated from Me$_2$SO with benzene. Anal. Calcd for C$_{20}$H$_{14}$O$_6$·4H$_2$O: C, 56.8; H, 5.2. Found: C, 56.5; H, 5.3; ^{1}H NMR (Me$_2$SO-d_6) δ 6.2 (2 H) and 6.1 (6 H).

The hexaacetyl derivative of 5, recrystallized from acetic acid, melted at 340 °C. Anal. Calcd for C$_{32}$H$_{26}$O$_{12}$: C, 63.8; H, 4.35. Found: C, 63.7; H, 4.42. IR (KBr) 1770, 1490, 1370, 1200, 1170, 1060, and 900 cm^{-1}.

The tris(hydroquinone) (5) (10.0 g, 28.5 mmol) was stirred with Na$_2$Cr$_2$O$_7$·2H$_2$O (8.52 g, 28.5 mmol) in 1 L of acetic acid at 25 °C for 1 h. On dilution with 1 L of water, 2 (8.8 g, 90%) precipitated (mp >330 °C) from 1,2-dichloroethane. ^{1}H NMR (Me$_2$SO-d_6) δ 6.1 (6 H), and 5.7 (2 H); UV (CH$_2$Cl$_2$) λ_{max} (ϵ) 242 (3444) and 342 nm (78). Anal. Calcd for C$_{20}$H$_8$O$_6$: C, 69.8; H, 2.34. Found: C, 69.4; H, 2.60.

(9) The rate of triplet exiton transfer in triptycene is $>10^{10}$ s^{-1} at 77 K. At 20 K the triplet exiton in tribenzotriptycene is localized mainly in one naphthtalene ring (de Groot, M. S.; Van der Walls, J. M. *Mol. Phys.* **1963**, 545).
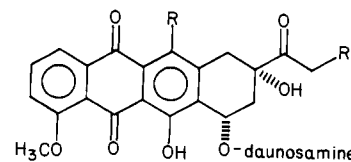
(10) Brockmann, H.; Budd, G. *Chem. Ber.* **1953**, *86*, 432.

Anthracyclines and Related Substances. 3. Regiospecific Total Synthesis of 11-Deoxydaunomycinone

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The antitumor drugs adriamycin[1] (1a) and daunomycin[2] (1b) have enjoyed widespread use in the treatment of neoplastic conditions due to their relatively broad spectrum of antitumor activity.[3]

1a, R = R' = OH
b, R = OH; R' = H
2a, R = H; R' = OH
b, R = R' = H

(1) (a) F. Arcamone, G. Franceschi, and S. Penco, *Tetrahedron Lett.*, 1007 (1969); (b) A. DiMarco, M. Gaetani, and B. Scarpinato, *Cancer Chemother. Rep.*, **53**, 33 (1969).

(2) (a) F. Arcamone, G. Cassinelli, G. Fantini, A. Grein, P. Orezzi, C. Pol, and C. Spalla, *Biotechnol. Bioeng.*, **11**, 1101 (1969); (b) F. Arcamone, G. Franceschi, P. Orezzi, G. Cassinelli, W. Barbiere, and R. Mondelli, *J. Am. Chem. Soc.*, **86**, 5334 (1964).

(7) Treatment of the monohydroquinone derivative of 1 with KOCMe$_3$ in Me$_2$SO initially forms a mixture of $1^{3-\cdot}$ and $\cdot1^{2-\cdot}$ with the percentage of $\cdot1^{2-\cdot}$ increasing with the amount of base employed. Addition of [2.2.2]-cryptand to these solutions results in an excellent spectrum of $1^{3-\cdot}$ containing only a trace of $\cdot1^{2-\cdot}$. In solution the monohydroquinone is known to disproportionate to 1 and the bis(hydroquinone).[2]

(8) Addition of *tert*-butyl alcohol or water to solutions of $1^{3-\cdot}$ generated by KOCMe$_3$/[2.2.2]cryptand increases the proportion of $\cdot1^{2-\cdot}$ present and with sufficient water will convert the spectrum completely to $\cdot1^{2-\cdot}$. There is no evidence of time averaging between the two species as would be expected if they were protonated and deprotonated forms of the same reduction state. The effect of proton donors apparently involves the equilibrium, $21^{3-\cdot} \rightleftharpoons \cdot1^{2-\cdot} + 1^{4-\cdot}$, which is shifted to the right by preferential protonation of $1^{4-\cdot}$.