One-electron Reduction of 2,1,3-Benzothiadiazole-4,7-dicarbonitrile in Aqueous Solutions

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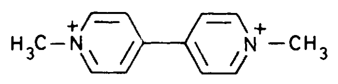
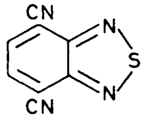
Some of the electrochemical properties of 2,1,3-benzothiadiazole-4,7-dicarbonitrile (BTDN) have been studied at various pH values by pulse radiolysis and cyclic voltammetry. The optical absorption spectrum of the one-electron-reduced species, BTDN$^{-\bullet}$, exhibits absorption maxima at 360, 460, and 500, 630, and 680 nm. The spectrum is independent of pH in the range 2.6—7.0, indicating a low pK_a for BTDN$^{-\bullet}$. This finding is supported by *ab initio* calculations on the anion radical species. The e.s.r. spectrum of BTDN$^{-\bullet}$ can be interpreted as arising from a radical with a^{H} 0.24, a^{NA} 0.39, and a^{NB} 0.08 mT (NA and NB are the ring and cyano nitrogen atoms, respectively). The one-electron reduction potential for the equilibrium BTDN + $e^{-} \rightleftharpoons$ BTDN$^{-\bullet}$ has been measured as -506 ± 10 and -490 ± 10 mV by cyclic voltammetry and pulse radiolysis, respectively. In the presence of O_2, BTDN$^{-\bullet}$, the natural lifetime of which is $\gg 10$ s at pH 7.0, decays with a rate constant of $(1.5 \pm 0.2) \times 10^{8}$ dm^3 mol^{-1} s^{-1}.

Artificial electron acceptors of the bipyridinium type have been used as electron carriers in a variety of photochemical and photoelectrochemical cells.[1,2] These molecules are doubly and single positively charged in the oxidised and reduced forms, respectively. Coulombic attraction between the reduced form of methylviologen (1,1′-dimethyl-4,4′-bipyridinium halide; MV^{2+}) and a negatively charged membrane has been found[3] to influence the electron-transport efficiency of this molecule. In fact, the replacement of MV^{2+} by zwitterionic bipyridyls, such as 1,1′-bis(carboxymethyl)-4,4′-bipyridyl and 1,1′-bis(sulphonatopropyl)-4,4′-bipyridyl, is reported[3] to increase the efficiency of hydrogen photoproduction by chloroplasts. Since these molecules become negatively charged on reduction, back reaction with the negatively charged thylakoid membrane is made less likely.



MV^{2+}



BTDN

During studies aimed at the design of neutral electron carriers with redox properties similar to those of the bipyridinium compounds, we have recently[4] reported the photochemical reduction of 2,1,3-benzothiadiazole-4,7-dicarbonitrile (BTDN) in the presence of micelles. The present study is concerned with the redox properties of this molecule in an aqueous medium, as determined by pulse radiolysis and cyclic voltammetry. We have also carried out *ab initio* calculations to examine the nature of the anion radical derived from BTDN.

Experimental

2,1,3-Benzothiadiazole-4,7-dicarbonitrile was provided by the Biological Sciences Research Centre, Shell Development Company, Modesto, California. For the pulse radiolysis measurements all solutions were prepared using triply distilled water, buffered at the appropriate pH and deoxygenated before use by passing either N_2 or N_2O through for about 30 min. The 4.3 MeV linear accelerator and the optical detection and data storage systems used in the pulse radiolysis study have been described previously.[5] Solutions contained in a quartz glass cell of 0.2 dm optical path length were irradiated at 294 K with electron pulses of 1.6 μs duration. Radiation doses were in the range 2—5 Gy, as determined using KSCN dosimetry.

In order to maintain a reducing system, solutions contained propan-2-ol (0.2 mol dm^{-3}), to convert $^{\bullet}OH$ radicals or $H^{\bullet}$ atoms into the reducing radical $(CH_3)_2\dot{C}OH$. Reaction (2)

$$^{\bullet}OH(H^{\bullet}) + (CH_3)_2CHOH \longrightarrow (CH_3)\dot{C}OH + H_2O(H_2) \quad (1)$$

$$(CH_3)_2\dot{C}OH + BTDN \longrightarrow (CH_3)_2C{=}O + BTDN^{-\bullet} + H^{+} \quad (2)$$

may then be utilised to produce the one-electron radical species. The rate constants for interaction of BTDN with e^{-}_{aq} and $(CH_3)_2\dot{C}OH$ were determined at 600 nm (from decay of e^{-}_{aq}) and 500 nm (formation of BTDN$^{-\bullet}$), respectively.

Cyclic voltammetry studies were carried out on a 3×10^{-4} mol dm^{-3} solution of BTDN in a deaerated phosphate buffer (0.2 mol dm^{-3}; pH 7.0) solution at 298 K. The cyclic voltammogram of this solution (Figure 3) was obtained using a CV-1A controlled-potential polarograph (Bioanalytical Systems Inc.) attached to an electrochemical cell, which consisted of a stationary carbon paste working electrode, a standard calomel electrode, and a platinum counter electrode. A voltage sweep rate of 500 mV s^{-1} was used, scanning through the potential range of +0.1 to −1.1 V.

E.s.r. spectra were recorded with a Brüker ER200D-SRC spectrometer. BTDN (10^{-3} mol dm^{-3}) was reduced electrochemically at a platinum wire cathode in methanol containing Bu_4NClO_4 (0.1 mol dm^{-3}) as carrier electrolyte. *Ab initio* calculations on the electronic structure of the radical anions derived from BTDN and 1,4-dicyanobenzene were performed by using a STO-3G basis set, with the computer program[6] Gaussian 80. For this purpose the Vax 11-780 computer at Shell Research, Sittingbourne, was used.

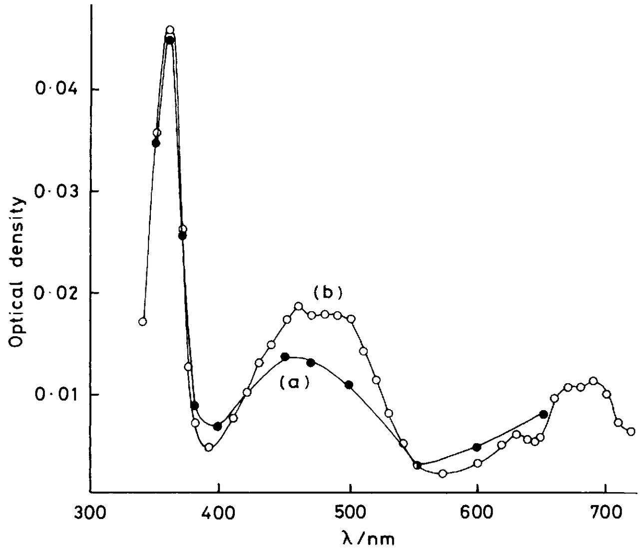


Figure 1. Transient absorption spectra from a 10^{-4} mol dm^3 solution of BTDN (oxygen-free) 20 μs after 1.6 μs pulse: (a) 0.2 mol dm^{-3} propan-2-ol, pH 6.5 buffer, 3.07 Gy per pulse, N_2; (b) 0.2 mol dm^{-3} propan-2-ol, pH 1.2 aqueous solution, 3.07 Gy per pulse, N_2O

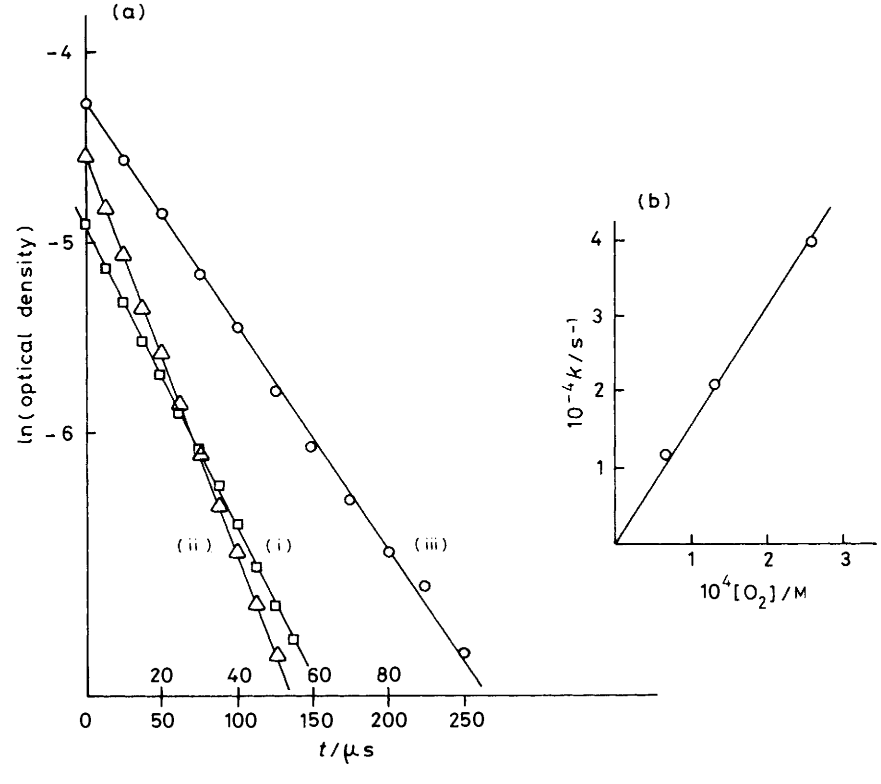


Figure 2. Kinetics of the reaction of oxygen with BTDN$^{-\bullet}$ at neutral pH: (a) first-order kinetics at oxygen concentration of (upper time scale) (i) 2.6 × 10^{-4}M; (lower time scale) (ii) 1.3 × 10^{-4}M, (iii) 7.5 × 10^{-5}M; (b) dependence of first-order rate constants on oxygen concentration

Results and Discussion

The optical absorption spectrum of the reduced species derived from BTDN at a pH of 6.5 is shown in Figure 1 (BTDN itself does not absorb at wavelengths above 350 nm). This optical spectrum, obtained 20 μs after irradiation with a 1.6 μs electron pulse, exhibits absorption maxima at about 360, 460, 500, 630, and 680 nm. The spectral characteristics are independent of pH in the range 2.6—7.0. However, a reduction in absorption intensity (at 460 and 500 nm) (Figure 1) is observed at pH values approaching unity, suggesting that the pK_a for the prototropic equilibrium (3) is low, probably ≤1. The rate constants for

$$\mathrm{BTDN}^{-\bullet} + \mathrm{H}^+ \rightleftharpoons \mathrm{BTDNH}^\bullet \qquad (3)$$

interaction of BTDN with e^-_{aq} and $(CH_3)_2\dot{C}OH$ were determined as 1.8×10^{10} and 3.1×10^9 dm^3 mol^{-1} s^{-1}, respectively. Table 1 gives the decay kinetics of the one-electron-reduced species, which disappears in a second-order manner, *via* reactions of the type (4)—(6).

$$\mathrm{BTDN}^{-\bullet} + \mathrm{BTDN}^{-\bullet} \longrightarrow \text{products} \qquad (4)$$

$$\mathrm{BTDN}^{-\bullet} + \mathrm{BTDNH}^\bullet \longrightarrow \text{products} \qquad (5)$$

$$\mathrm{BTDNH}^\bullet + \mathrm{BTDNH}^\bullet \longrightarrow \text{products} \qquad (6)$$

At pH values around neutral, the anion radical is long-lived; electrostatic repulsion makes the rate of the disproportionation reaction (4) insignificant. At lower pH the contribution of the protonated electron increases so that as the pH is decreased the main reactions responsible for the reduction of the lifetime of the one-electron-reduced species are (5) and (6); these observations are analogous to those on the lifetime of superoxide at different pH values.[7]

The absorption spectrum of BTDN$^{-\bullet}$ has characteristics similar to that observed[8,9] in the one-electron reduction of 1,4-dicyanobenzene (DCNB). In Table 2 the spectral characteristics of the two anion radicals BTDN$^{-\bullet}$ and DCNB$^{-\bullet}$ are compared. The shift in absorption near 350 nm to higher wavelength for

Table 1. Decay kinetics of the one-electron-reduced species from BTDN, determined by pulse radiolysis at 500 nm

pH	k/ε^a (cm s^{-1})
1.2	3.8×10^5
2.7	1.6×10^5
3.7	6.0×10^4
4.7	6.8×10^3
6.5—7.0	Long-lived (> 10 s)

[a] Extinction coefficient of radical at 500 nm.

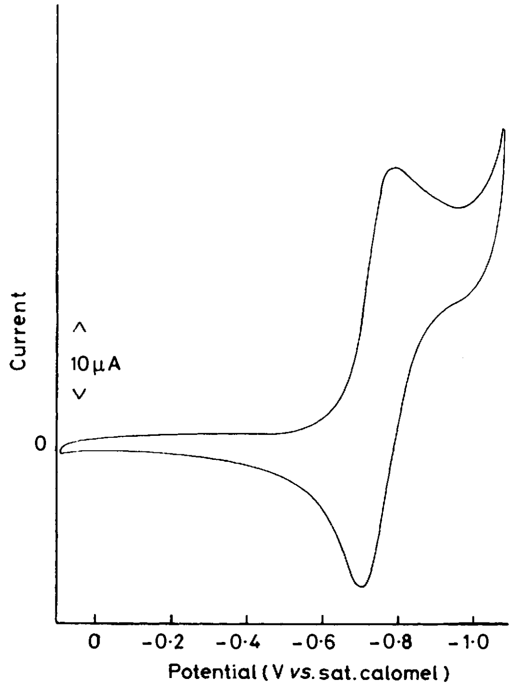


Figure 3. Cyclic voltammogram of a 3×10^{-4} mol dm^{-3} solution of BTDN in deaerated phosphate buffer (0.2 mol dm^{-3}; pH 7.0); scan rate 500 mV s^{-1}

$BTDN^{-\bullet}$ can probably be attributed to the extended π system.

The stability of $BTDN^{-\bullet}$ at neutral pH allowed the determination of the one-electron reduction potential (E^1_7) of BTDN, employing methylviologen (MV^{2+}) as the standard (E^1_7 = -447 mV).[10] The difference in reduction potentials (ΔE) of the reactants in the electron-transfer equilibrium (7) is related to the equilibrium constant K by the expression (8), where n = 1 and F is the Faraday constant.

$$BTDN^{-\bullet} + MV^{2+} \overset{K}{\rightleftharpoons} BTDN + MV^{+\bullet} \qquad (7)$$

$$\Delta E = E^1_7([BTDN]/\{BTDN^{-\bullet}\}) - E^1_7([MV^{2+}]/[MV^{+\bullet}]) \simeq RT\ln K/F \qquad (8)$$

By monitoring the absorption of $MV^{+\bullet}$ at 600 nm in solutions containing various concentration ratios of MV^{2+} and BTDN, the equilibrium constant K was measured as 5.4, from which $E^1_7([BTDN]/[BTDN^{-\bullet}])$ was determined as -490 ± 10 mV. This value is in very good agreement with that obtained from cyclic voltammetry measurements (see later).

Table 2. Spectral characteristics of the anion radicals derived from DCNB and BTDN

Species	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
$DCNB^{-\bullet}$	345^a	3.4×10^4
	400^a	4.0×10^3
	430^a	7.0×10^3
	525^b	5.8×10^3
	600^b	2.3×10^3
	640^b	2.5×10^3
$BTDN^{-\bullet}$	360	1.3×10^4
	460	4.9×10^3
	500	4.6×10^3
	630	1.6×10^3
	680	3.0×10^3

[a] From ref. 8. [b] From ref. 9.

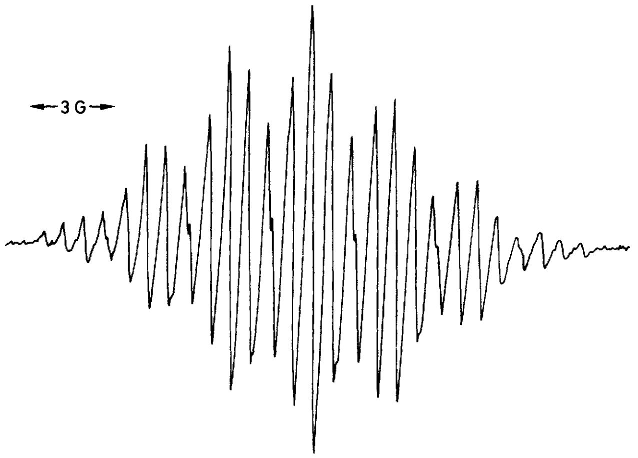


Figure 4. E.s.r. spectrum of $BTDN^{-\bullet}$

The rate constant for interaction of $BTDN^{-\bullet}$ with O_2 was determined as $(1.5 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1} from the dependence of the first-order of decay of $BTDN^{-\bullet}$, as monitored at 475 nm, on O_2 concentration (Figure 2). This value is of the same order of magnitude as that determined for the interaction of oxygen with other anion radicals or with bipyridinium cation radicals.[10] The reaction of oxygen with BTDN most probably results in the formation of superoxide and regeneration of the substrate [reaction (9)], as would be predicted on the basis of the large difference in the redox potentials of BTDN and O_2 (E^1_7 -155 mV).[11]

$$O_2 + BTDN^{-\bullet} \rightleftharpoons O_2^{-\bullet} + BTDN \qquad (9)$$

The cyclic voltammogram of a 3×10^{-4} mol dm^{-3} solution of BTDN in neutral solution is shown in Figure 3. The electrochemical behaviour of this compound is typical[12] of a very fast reversible one-electron charge-transfer process. The cathodic and anodic peak currents are nearly of equal magnitude. From the separation of the anodic and cathodic peak potentials, the half-wave reduction potential $E_{\frac{1}{2}}$ was measured as -506 ± 10 mV, in excellent agreement with the thermodynamic reduction potential, measured by pulse radiolysis. This is not surprising as there is generally little difference between the diffusion coefficients of the oxidised and the reduced forms, D_R and D_O respectively [see equation (10)], and since $BTDN^{-\bullet}$ is very stable at pH 7 based on the pulse radiolysis results.

$$E_{\frac{1}{2}} = E^1_7 + \frac{RT}{nF}\ln\left(D_R/D_O\right)^{\frac{1}{2}} \qquad (10)$$

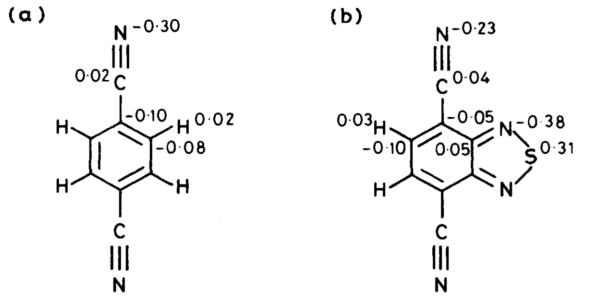


Figure 5. Residual electron densities determined for BTDN$^{-\bullet}$ and DCNB$^{-\bullet}$ from *ab initio* calculations

The e.s.r. spectrum of electronically generated BTDN$^{-\bullet}$ (Figure 4) can be interpreted as arising from a radical with hyperfine couplings to all magnetically active nuclei (a^{NA} 0.3, a^{NB} 0.08, and a^{H} 0.24 mT). This spectrum is almost identical with that obtained from BTDN$^{-\bullet}$ generated by photochemical electron transfer to BTDN from ethylenediaminetetra-acetic acid disodium salt in the presence of cetyltrimethylammonium bromide micelles.[4] In that case, however, the weakness of the e.s.r. spectrum made it impossible to observe the five other lines on each side of the spectrum and this led to an erroneous assignment of the coupling constants.

The hyperfine coupling to NB is less than that observed in DCNB$^{-\bullet}$ (0.10 mT); that to H is larger than that for DCNB$^{-\bullet}$ (1.5 mT).[13] This, together with the large hyperfine coupling to NA, suggests that the unpaired electron is delocalised throughout the π system.

Ab initio calculations on the electronic structures of BTDN$^{-\bullet}$ and DCNB$^{-\bullet}$ were carried out to evaluate the approximate distribution of charge on the anion radicals and hence deduce the most likely site of protonation. From the results (Figure 5) it appears that protonation of DCNB$^{-\bullet}$ should occur at the nitrogen atom of one of the cyano groups, in agreement with predictions made in ref. 8. This protonation would lead to unfavourable loss of charge resonance and hence result in a lowering of the pK_a for protonation of the anion radical.

In the case of BTDN$^{-\bullet}$, *ab initio* calculations seem to indicate that there are two possible sites for protonation; a proton could dwell either on the nitrogen atom of the cyano group or on one of the nitrogen atoms in the heterocyclic ring. Both types of protonation would lead to loss of conjugation in the extended π-system and therefore are expected to occur only under strongly acidic conditions; hence the long lifetime of BTDN$^{-\bullet}$ at neutral pH.

The redox properties of BTDN make it an interesting candidate for incorporation in an electron-transfer process. In fact we have already found that this molecule is an efficient electron acceptor from broken chloroplasts at concentrations as low as 10^{-6} mol dm^{-3} (unpublished results). This concentration is of the same order of magnitude as that obtained with MV^{2+} under the same conditions. Moreover, BTDN quenches[14] the emission of the excited state of [Ru(bipyridyl)]$^{2+}$ at a rate which is more than eight times that of MV^{2+}. At present, we are carrying out studies on the effect of micelles on the electrochemical behaviour of this molecule. Initial results clearly indicate that a change in environment can lead to an appreciable change both in the redox potential of this molecule and in the lifetime of the anion radical. This study has been useful in allowing us to design other neutral electron acceptors that are analogues of BTDN and that may be suitable for the photoproduction of hydrogen. Results will be reported at a later stage.

Acknowledgements

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