# Electrochemical Properties of 1-Oxa-6,6a$\lambda^4$-dithia-2,5-diazapentalene Derivatives

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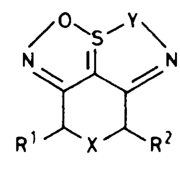
The electrochemical properties of a number of 1-oxa-6,6a$\lambda^4$-dithia-2,5-diazapentalenes have been studied by cyclic voltammetry and e.s.r. spectroscopy. In general, these compounds have half-peak reduction potentials in the range −380 to −540 mV (*vs.* Ag–AgCl). The reduction of these heterapentalenes leads to the formation of stable anion radicals, the e.s.r. spectra of which have been characterised.

In a recent publication,[1] we described the synthesis and the electrochemical properties of a number of heterapentalenes of type (I). These compounds were found to be excellent electron acceptors with half-peak reduction potentials ($E_{p/2}$) in the range −500 to −700 mV (*vs.* Ag–AgCl). In this paper, we report the electrochemical properties of a series of related compounds of type (II). In particular, we have examined the influence of molecular structure on the reduction potentials of these two types of heterapentalenes and on the e.s.r. spectra of their respective anion radicals. For convenience, we shall refer to the type (I) and type (II) compounds as the 'OSO' and 'OSS' systems, respectively.



(I) Y = O
(II) Y = S

## Results and Discussion

The oxadithiadiazapentalenes used were prepared essentially by the procedure outlined in reference 1, except that in our previous investigation we treated sulphur dichloride with the dioxime of cyclohexane-1,2,3-trienone to give the 'OSO' compound, whereas here the reaction of the same dioxime with sulphur monochloride gives the 'OSS' compound as the major product.[2] M.p.s and elemental analyses are given in Table 1.

The electrochemical properties of these heterapentalenes were evaluated by cyclic voltammetry on a carbon paste working electrode. Half-peak reduction potentials were measured in deoxygenated methanol–pH 7 buffer (3:1 by volume) at a scan rate of 150 mV s$^{-1}$ and are reported in Table 2, relative to Ag–AgCl. Under these conditions, all redox reactions were electrochemically reversible. Half-peak reduction potentials ($E_{p/2}$) vary between −480 and −540 mV for the cyclohexane derivatives (X = CR$^1$R$^2$) except for the dimethyl derivative (**10**) with $E_{p/2}$ −623 mV. The replacement of the methylene group in the cyclohexane ring (X = CH$_2$) by a hetero group [compounds (**7**)—(**9**)] increases the ability to accept an electron; this is most probably due to an inductive effect.

Figure 1 shows a comparison of the cyclic voltammograms of (**7**) with that of the corresponding 'OSO' compound from reference 1 under the same conditions. The half-peak reduction potentials of the 'OSS' compounds are about 200 mV more positive than those of the analogous 'OSO' derivatives. Thus, the lowest unoccupied molecular orbital (LUMO) for the 'OSO' system is about 0.2 eV (about 19 kJ mol$^{-1}$) higher in energy than that of the 'OSS' system. Hence, the replacement of an oxygen atom [Y = O; type (I)] by a sulphur atom [Y = S; type (II)] produces a more stable anion radical. Although CNDO/2 calculations have shown [3] that, in general, divalent sulphur has a greater ability than oxygen to take excess of charge into the *sp* valence shell, the appreciable difference in the stability of the two anion radicals may also be due to destabilisation by oxygen, rather than to stabilisation by sulphur. This last effect is consistent both with the $\sigma^+$ values for the $\alpha$-carbon in thiophene and furan from electrophilic reactivity studies,[4] and with the $\sigma^+$ values for CH$_3$O and CH$_3$S substituents from equilibrium p$K_a$ measurements on substituted benzoic acids.[5] Thus, the greater positive resonance effect of the oxygen in the 'OSO' system could make it accept an electron at a more negative potential than in the 'OSS' system. Supporting these observations is the fact that the wavelength of the first excited singlet state for the 'OSS' system ($\lambda$ 451 nm, $\varepsilon$ 8 040 dm$^3$ mol$^{-1}$ cm$^{-1}$) is red-shifted

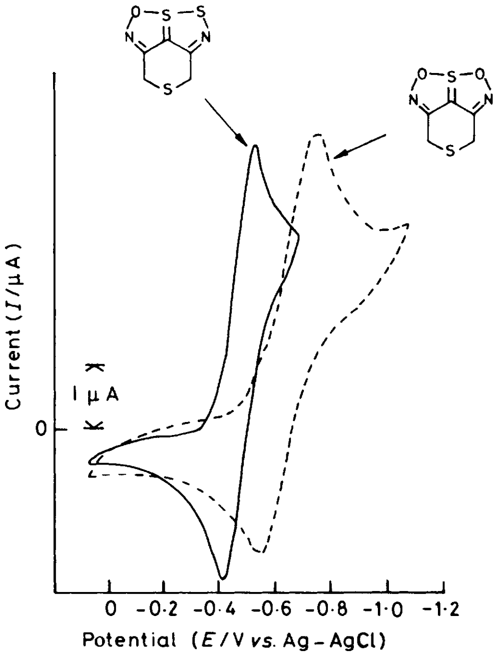
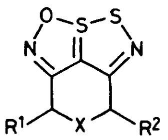


**Figure 1.** Cyclic voltammogram of (7) and the corresponding 'OSO' compound, in methanol–water (3:1 v/v); scan rate 150 mV s$^{-1}$

**Table 1.** Physical data



| | X | R$^1$ | R$^2$ | M.p. (°C) (solvent †) | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | C | H | N |
| **(1)*** | $CH_2$ | H | H | 158—160 (C) | 38.2 | 3.2 | 14.6 | 38.6 | 3.2 | 14.8 |
| **(2)** | CHMe | H | H | 137 (C) | 42.3 | 4.0 | 13.6 | 42.0 | 4.0 | 14.0 |
| **(3)*** | $CMe_2$ | H | H | 98 (C) | 44.7 | 4.5 | 12.8 | 44.9 | 4.7 | 13.1 |
| **(4)** | CHPh | H | H | 169 (B or E) | 54.2 | 3.6 | 10.6 | 55.0 | 3.8 | 10.7 |
| **(5)** | CH(2-furyl) | H | H | 107 (E) | 47.4 | 3.3 | 11.1 | 47.6 | 3.2 | 11.1 |
| **(6)** | CH(2-thienyl) | H | H | 150 (E) | 44.7 | 3.0 | 10.3 | 44.8 | 3.0 | 10.4 |
| **(7)** | S | H | H | 141 (C) | 29.4 | 1.9 | 13.7 | 29.4 | 2.0 | 13.7 |
| **(8)** | SO | H | H | 175 (M) | 27.4 | 1.8 | 12.6 | 27.3 | 1.8 | 12.7 |
| **(9)** | $SO_2$ | H | H | 185 (M) | 26.0 | 1.7 | 11.5 | 25.4 | 1.7 | 11.9 |
| **(10)** | $CH_2$ | Me | Me | 114 (C or E) | 44.6 | 4.9 | 12.7 | 44.9 | 4.7 | 13.1 |
| **(11)** | CHPh | Ph | H | 165 (C) | 63.9 | 4.1 | 8.2 | 63.9 | 4.1 | 8.3 |
| **(12)** | CHPh | H | Ph | 193 (C) | 63.6 | 4.0 | 8.1 | 63.9 | 4.1 | 8.3 |
| **(13)** | $CMe_2$ | Ph | H | 122 (E) | 57.1 | 4.7 | 9.5 | 57.9 | 4.8 | 9.7 |
| **(14)** | $CMe_2$ | H | Ph | 158(M) | 56.6 | 4.6 | 9.3 | 57.9 | 4.8 | 9.7 |
| **(15)** ‡ | $CMe_2$ | H | 2-pyridyl | 120—122 (M) | 54.2 | 4.6 | 14.5 | 53.6 | 4.5 | 14.4 |

* M.p.s reported[2] for compounds (**1**) and (**3**) are 164 and 97 °C, respectively. † B = benzene, M = methanol, E = ethanol, C = cyclohexane. ‡ Compound (**15**) is a mixture of isomers.

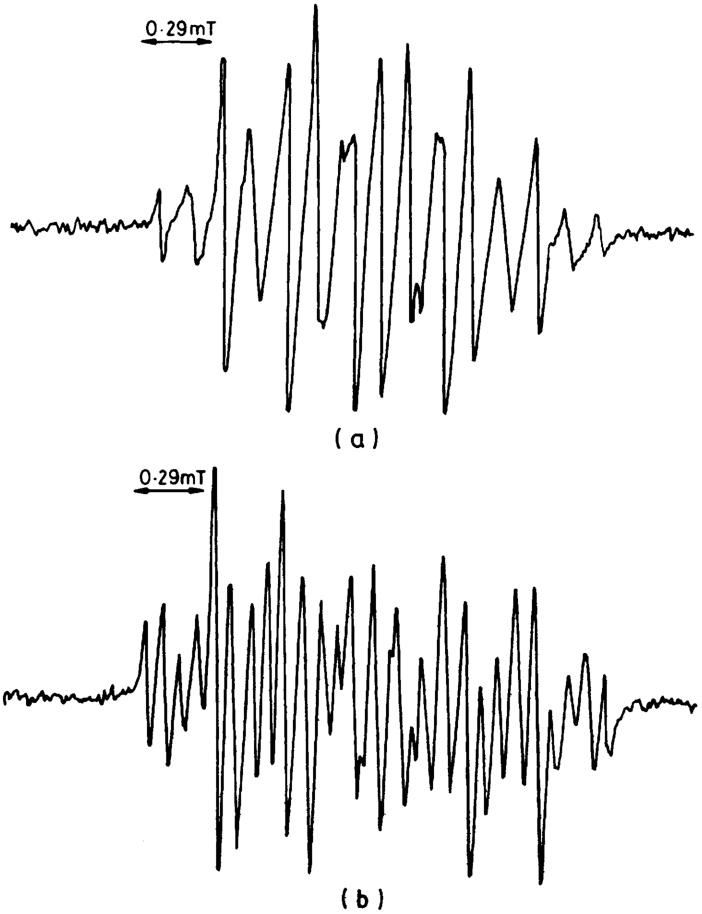


**Figure 2.** E.s.r. spectrum of (a) the anion radical derived from (**7**) and (b) that from (**3**) in methanol

**Table 2.** Half-peak reduction potentials ($E_{p/2}$ *vs.* Ag–AgCl)

| Compound | $-E_{p/2}$/mV ($\pm 10$ mV) | Compound | $-E_{p/2}$/mV ($\pm 10$ mV) |
|---|---|---|---|
| **(1)** | 523 | **(9)** | 383 |
| **(2)** | 533 | **(10)** | 623 |
| **(3)** | 543 | **(11)** | 513 |
| **(4)** | 513 | **(12)** | 503 |
| **(5)** | 523 | **(13)** | 493 |
| **(6)** | 513 | **(14)** | 483 |
| **(7)** | 473 | **(15)** | 523 |
| **(8)** | 423 | | |

from that of the corresponding 'OSO' system (λ 353 nm, ε 6 580 $dm^3\ mol^{-1}\ cm^{-1}$).

In order to measure e.s.r. spectra, anion radicals from the heterapentalenes **(3)** and **(7)** were generated by electrochemical reduction at a platinum electrode in solution (*ca.* $3 \times 10^{-3}$ mol $dm^{-3}$). The resulting e.s.r. spectra of $[(\mathbf{7})]^{-\bullet}$ and $[(\mathbf{3})]^{-\bullet}$ are shown in Figures 2(a) and 2(b), respectively. The hyperfine coupling constants are given in Table 3. In the case of both anion radicals, the higher $a_N$ coupling probably relates to nitrogen attached to sulphur in the heterapentalene ring system. The coupling constants for the hydrogen atoms are more difficult to assign. For $[(\mathbf{7})]^{-\bullet}$ the sulphur in the six-membered ring will probably invert rapidly so that the higher coupling to hydrogen is on the same side as that for the higher $a_N$ value. In the case of $[(\mathbf{3})]^{-\bullet}$ two possibilities can be envisaged: either the $CMe_2$ group is flipping quickly and the higher coupling to hydrogen is again on the same side as the higher $a_N$ constant; or, the same group is flipping slowly and the difference in $a_H$ between one side and the other is not resolved, so that the axial and equatorial protons have different values of $a_H$. We have tried to distinguish between these two possibilities using $^1H$ n.m.r. and the coalescence temperature method.[6,7]

The low-temperature (−110 °C) spectrum for the protons in the $CMe_2$ group consists of two sharp peaks from a clear AB system ($\delta_A$ 0.76, $\delta_B$ 1.38, $J_{AB}$ 210.69 Hz). These peaks coalesce at about −80 °C and appear as a single peak (δ 1.12) at temperatures above −70 °C. These changes are characteristic of a simple conformational interconversion ($A \rightleftharpoons B$). The free energy of activation at the coalescence temperature has been estimated to be around 36.5 kJ $mol^{-1}$. This small energy barrier can be compared with that of the boat/chair flipping process of cyclohexane[8] and cyclo-octane[9] (42.8 and 32.3 kJ $mol^{-1}$, respectively) and indicates that the conformational flipping, involving **(3)**, is not easily frozen. It can be concluded that although the time scale of the e.s.r. experiment is about a thousand times less than that of the n.m.r. experiment, the conformational equilibrium will be fast on the e.s.r. time scale at room temperature; hence the different couplings must be to the two different methylene groups.

**Table 3.** Hyperfine coupling constants (mT)

| Anion radical | $a_{N(1)}$ | $a_{N(2)}$ | $a_{H(1)}$ | $a_{H(2)}$ |
|---|---|---|---|---|
| $[(\mathbf{3})]^{-\bullet}$ | 0.31 | 0.40 | 0.08 | 0.24 |
| $[(\mathbf{7})]^{-\bullet}$ | 0.29 | 0.40 | 0.14 | 0.15 |

## Experimental

Cyclic voltammetry and e.s.r. studies were carried out under the conditions outlined in reference 1. Variable-temperature n.m.r. spectra were recorded with a Bruker WH360 spectrometer; compounds were dissolved in $CD_2Cl_2$ and tetramethylsilane was used as an internal standard. All solvents were of AnalaR grade.

The heterapentalenes in Table 1 were synthesized by the reactions of the corresponding 1,3-dioximes with sulphur monochloride. For example, sulphur monochloride (2.2 mol) was added dropwise with vigorous stirring to a suspension of the dioxime (1 mol) in dry THF (1 l) maintained at −65 to −78 °C, under nitrogen. After addition was complete, the mixture was stirred overnight as it warmed to ambient temperature, and then poured onto ice. The solution was filtered through glass wool to remove any sulphur, extracted with dichloromethane, washed with water, and dried. Chromatography on a silica column, using toluene, dichloromethane, or chloroform, separated the 'OSS' from the 'OSO' heterapentalene. Crystallisation from a suitable solvent (see Table 1) gave the pure 'OSS' heterapentalene.

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