Electron Spin Resonance Spectra and Electronic Structure of Nitrophenoxatellurin Anion-radicals

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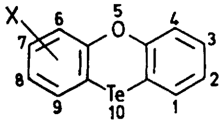
The e.s.r. spectra of mono- and di-nitrophenoxatellurin anion-radicals in different solvents are reported and interpreted in terms of solvent-induced line-width alternation. The perturbation effects of the nitro-group, oxygen, and tellurium are outlined by comparison with mono- and di-nitrodiphenyl ether anion-radicals. MO Calculations account well for the e.s.r. behaviour of these compounds.

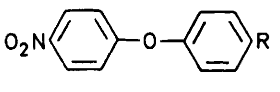
THE donor character of phenoxatellurin shown by its charge-transfer complexes with different acceptors [1-3] is well known and is only slightly modified by ring substitution with fluorine, chlorine, or methyl.[2] However, nitro-substitution of the benzene rings may seriously alter the character of the parent heterocycle, as was first pointed out by Hillebrand and her co-workers for a related compound, phenothiazine,[4] enabling the formation of anion-radical species.

This is also the case for phenoxatellurin, and this paper reports the e.s.r. spectra of the anion-radicals obtained by chemical and electrochemical reduction of 2-nitro- (1) and 2,8-dinitro-phenoxatellurin (2).



(1) X = 2-NO_2

(2) X = 2,8-$(NO_2)_2$



(3) R = H

(4) R = NO_2

As these are the first radicals obtained from a tellurium-containing anthracene-like heterocycle, the e.s.r. study of their spin distribution provides interesting information about the effects of the tellurium atom in competition with that of oxygen and the nitro-groups on the electronic structure.

The anion-radicals from 4-nitro- (3) and 4,4'-dinitrodiphenyl ether (4) [5] are also included in this study for comparison, and because they may be formed under certain conditions by detelluration of (1) and (2).[6]

RESULTS AND DISCUSSION

The e.s.r. spectrum obtained from (1) by electrolytic reduction in dimethyl sulphoxide (DMSO) is presented in Figure 1. Its analysis is straightforward; the hyperfine splitting (h.f.s.) constants are contained in Table 1. Chemical reduction of (1) in dimethylformamide (DMF) yields the spectrum in Figure 2, which was easily interpreted in terms of two radical species with slightly different *g* values. One is the 2-nitrophenoxatellurin anion-radical, with the h.f.s. constants and *g*-value shown in Table 1. The second radical (asterisked lines) was identified as the anion-radical from (3), as its pattern and *g* value were identical to those obtained by reduction of (3) in DMF (Table 1).

The detelluration process observed by e.s.r. when potassium is used as reducing agent is probably due to the formation of potassium hydroxide on contact with traces of water in the solvent; heating with KOH is a known method of detelluration for this heterocycle.[6]

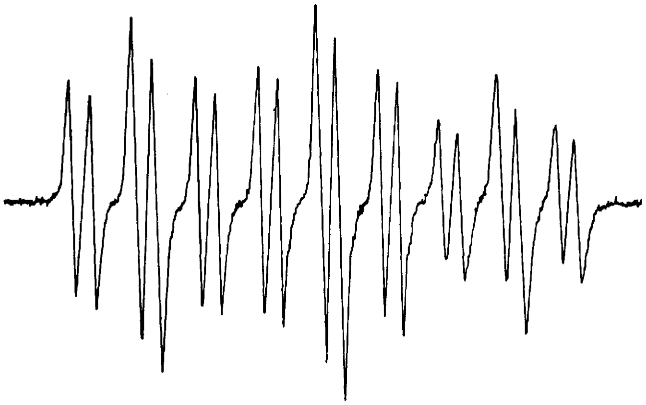


FIGURE 1 E.s.r. spectrum of the electrochemically generated 2-nitrophenoxatellurin anion-radical in DMSO

The e.s.r. spectra of 2,8-dinitrophenoxatellurin obtained by electrolytic reduction in DMSO and acetonitrile are presented in Figure 3. Both spectra have a dominant triplet aspect, but in the DMSO spectrum (Figure 3a) two extra lines (asterisked) are apparent in the middle of the triplet; the spectrum recorded using high modulation amplitude settings, according to Bernal and Fraenkel's method [7] for identifying the nitrogen broadened components, clearly reveals the presence of the two $M_N \pm 1$ lines. Instead of the expected 1 : 2 : 3 : 2 : 1 splitting for two equivalent nitrogen atoms, the low-field nitrogen lines are, at room temperature, in a 1 : 0.440- : 1.140 intensity ratio. Raising the temperature to *ca.* 40° when the radical decays, the intensity of the median components is increased, pointing to a strong alternating line-width effect at room temperature. Therefore the spectrum in Figure 3a was interpreted as due to the interaction of two equivalent nitrogen atoms; further

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[1] B. Hetnarski and A. Grabowska, *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1969, XVII, 333.

[2] A. Gioaba, V. Em. Sahini, and E. Volanschi, *Rev. Roumaine Chim.*, 1970, **15**, 309.

[3] C. E. Heller, R. A. Zingaro, and E. A. Meyers, *Canad. J. Chem.*, 1974, **52**, 3814.

[4] M. Hillebrand and M. Răileanu, *Rev. Roumaine Chim.*, 1974, **19**, 1227.

[5] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 778.

[6] H. D. K. Drew and R. W. Thomason, *J. Chem. Soc.*, 1927, 116.

[7] J. Bernal and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1964, **86**, 1671.

splittings are due to four equivalent protons and a set of two equivalent protons (Table 1).

Alternating line-width effects commonly occur in the e.s.r. spectra of nitro-derivatives, when they are produced by chemical reduction, as a result of ion-pair formation.[8] However, for electrochemical reduction in highly polar solvents like DMSO, ion-pairs are not likely to be formed; therefore, the alternating line-width observed seems to be solvation induced, as in the case of *m*-dinitrobenzene and related compounds.[9-11]

TABLE 1

Experimental [a] and calculated [b] h.f.s. constants (mT), line-widths (mT), and *g* factors

Parent compound	Solvent method of reduction	a_N^2	a_N^8	a_H^1	a_H^3	a_H^4	a_H^6	a_H^7	a_H^9	Linewidth	*g*
(1)	Electrolytic, DMF	0.997		0.367	0.345	0.109				0.030	
	K, DMF	1.125		0.372	0.343	0.112				0.015	2.005 1
	Electrolytic, DMSO	1.051		0.350	0.350	0.117				0.044	
	Calc.	1.001		0.368	0.361	0.127	0.004	0.003	0.003		
(2)	CH_3CN	0.521	0.521	0.172	0.172	0.060	0.060	0.172	0.172	0.030	
	DMSO	0.495	0.495	0.180	0.180	0.060	0.060	0.180	0.180	0.022	2.005 5
	Calc. A [c]	0.469	0.469	0.179	0.176	0.058	0.058	0.179	0.176		
	Calc. B [c]	0.759	0.080	0.398	0.391	0.132	0.004	0.020	0.020		
		a_N^4	$a_N^{4'}$	$a_H^{3,5}$	$a_H^{2,6}$	$a_H^{2',6'}$	$a_H^{3'5'}$				
(3)	K, DMF	1.132		0.345	0.111					0.015	
	CH_3CN	1.034		0.365	0.119					0.045	2.004 8
	Calc.	0.986		0.359	0.126	0.002	0.001				
(4)	CH_3CN [d]	0.997		0.341	0.111					0.045	2.004 8
	Calc. A [c]	0.467	0.467	0.177	0.059	0.059	0.177				

[a] Estimated error ±0.002 mT. [b] Parameters from Table 2. [c] Models A and B (see text). [d] H.f.s. from ref. 5.

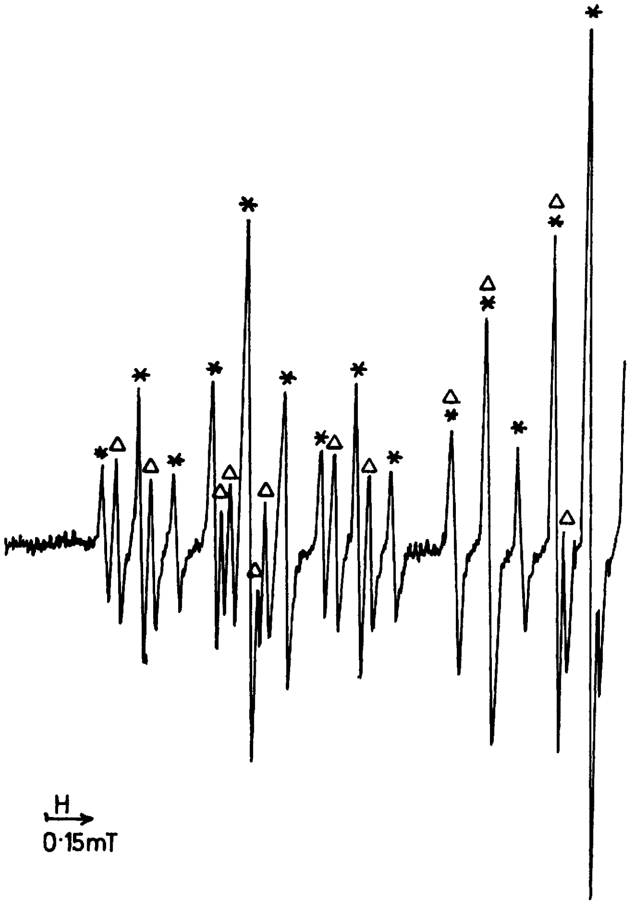

FIGURE 2 Low-field half of the e.s.r. spectrum obtained from 2-nitrophenoxatellurin on treatment with K in DMF: Δ, lines of anion-radical (1); *, lines of anion-radical (3)

The e.s.r. pattern observed in this solvent is entirely consistent with a spectrum undergoing exchange between two asymmetric conformers, at a rate which is of the same order of magnitude as $|\gamma_e| \times |\Delta a_N|$, where γ_e is the electron magnetogyric ratio (Table 3). Relaxation matrix theory [12,13] can be used for a simple two-site model to estimate the mean life-time of the interchanging asymmetric conformers. If the splittings of the two nitrogen atoms are correlated ' out-of-phase ', the line width for the *k* component is given by equation (1)

$$[T_2^K(M)]^{-1} = j_{aa}^{(o)}(m_a - m_b)^2 + T_{2,0}^{-1} \quad (1)$$

where $j_{aa}^{(o)}$ is the spectral density, m_a and m_b are the magnetic quantum numbers of the two nitrogen atoms, $M = m_a + m_b$, and $T_{2,0}^{-1}$ is the line-width contribution from the other mechanisms. Experimentally $[T_2^K]^{-1}$ was estimated from relationship (2) where δ_i is given by

$$[T_2^K]^{-1} = \sqrt{\tfrac{3}{2}}|\gamma_e|\delta_i \quad (2)$$

equation (3). In this equation A_i, D_i, and A_r, D_r are the

$$\delta_i = [(D_i/A_i)(A_r/D_r)]^{\frac{1}{2}}\delta_r \quad (3)$$

peak-to-peak amplitude and the degeneracy of the *i*th, and, respectively, a reference line, and δ_r is the full width of the reference line. As reference, the $\tilde{M}_N$[*] = −2 ($\tilde{M}_H = 0$) line was chosen and the $j_{aa}^{(o)}$ value was cal-

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[*] $\tilde{M}_N$ Is the spectral index number as defined by Fraenkel.[12]

[8] M. C. R. Symons, *J. Phys. Chem.*, 1967, **71**, 172.

[9] D. Jones and M. C. R. Symons, *Trans. Faraday Soc.*, 1971, **67**, 961.

[10] W. E. Griffith, C. J. W. Gutch, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc.* (*B*), 1968, 785.

[11] C. J. W. Gutch, W. A. Waters, and M. C. R. Symons, *J. Chem. Soc.* (*B*), 1970, 1261.

[12] G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139.

[13] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326.

culated from the difference between the widths of the $\tilde{M}_N = -1$ ($\tilde{M}_H = 0$) and $\tilde{M}_N = -2$ ($\tilde{M}_H = 0$) components. Using an averaged value from 12 scans, the correlation time was calculated from the relationship $j_{aa}^{(0)} = |\gamma_e|^2\tau_0 \langle(\delta a)^2\rangle$, and a value of 0.85×10^{-9} s was obtained. This value falls in the range of the mean life-times of other dinitro-derivatives which exhibit line-width alternation [14,15] in non-aqueous media.

Examining the acetonitrile spectrum in Figure 3b, it may be stated that the extent of line-width alternation is much enhanced, the $M_N = \pm1$ components being hardly observed. Slow interchange of the environments of the two nitro-groups is also reflected in the enhanced line-width alternation of the *ortho*-proton splittings (H-1, -3, -7, -9) on the $\tilde{M}_N = -2$ line, an intensity ratio of *ca.* 1 : 0.5 : 4 being observed for the low-field lines instead of the expected 1 : 4 : 6.

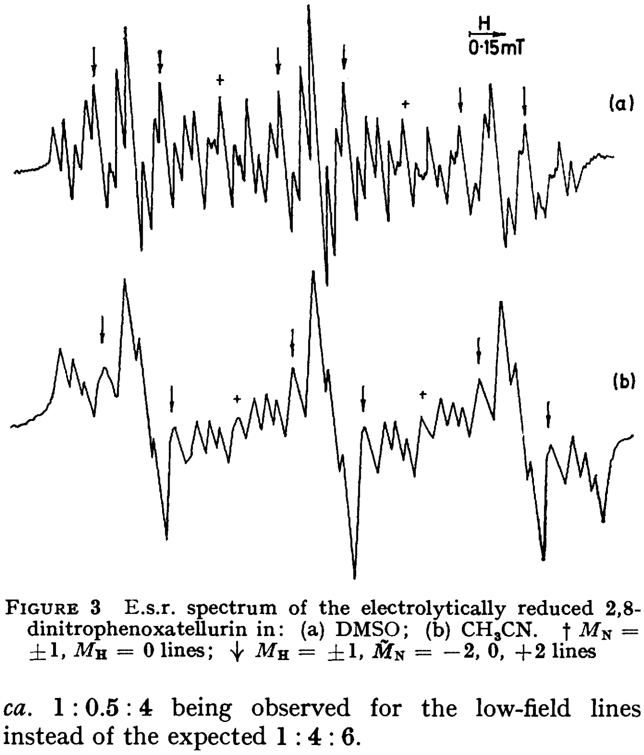


FIGURE 3 E.s.r. spectrum of the electrolytically reduced 2,8-dinitrophenoxatellurin in: (a) DMSO; (b) CH_3CN. † $M_N = \pm1$, $M_H = 0$ lines; ↓ $M_H = \pm1$, $\tilde{M}_N = -2, 0, +2$ lines

The *meta*-protons (H-4, -6) are also affected by this slow exchange, the intensity ratio of the smallest splitting being *ca.* 1 : 1.1 : 1 instead of the expected 1 : 2 : 1. The e.s.r. pattern observed in acetonitrile was therefore found to be consistent with an exchange rate between the asymmetric species the same order of magnitude as the proton splitting variation, that is 1.7 MHz ~ ν_{ex} <9.6 MHz.

If electrolysis in acetonitrile is performed at more negative potentials, or is prolonged for several hours, and especially when traces of water are present (added), a spectrum very similar to that of the anion-radical from (1) was obtained, revealing splittings from one ring only.

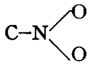
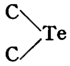
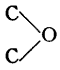
It is possible that in these conditions the long-lived asymmetric species could undergo further reduction, leading to the amino-nitro-derivative, as in the case of other polynitro-compounds.[16] Cyclic voltammetry studies are being undertaken to elucidate the further reduction mechanism of this compound in acetonitrile.

MO Calculations.—The MO calculations performed on these compounds were intended to account for two facts. Firstly to see if good agreement with the experimental splittings could be obtained. Secondly, to outline the influence of the heteroatoms on the spin distribution and to explain in terms of electronic structure why anion-radicals from (2) and (4) should be so sensitive to solvent perturbation, leading to long-lived asymmetric species.

The parameters and equations used in the calculation are contained in Table 2 and the computed h.f.s. are listed in Table 1. Examining the data in Table 1 the following may be stated. Good agreement is obtained for the mononitro-derivatives (1) and (3). The h.f.s. constants calculated for anion-radical (2), considering the nitro-groups as equivalent (model A), agree well with the average experimental splittings but do not reflect the strong line-width alternation experimentally observed as a consequence of the fluctuation between two conformers with asymmetric spin-distribution. As the extent of line-width alternation is proportional to the square of the instantaneous difference of the nitrogen splittings, $(a_N^2 - a_N^8)^2$, model A, which yields a symmetrical spin-distribution, ($a_N^2 = a_N^8$), is inadequate to describe the real state of anion-radical (2). Therefore asymmetric perturbation caused by the solvent was taken into account in terms of the reduced conjugation of one nitro-group with the ring, $k'_{CN} < k_{CN}$ (model B); the results reflect the electronic structure of the interchanging asymmetric conformers and the line-width alternation experimentally observed for both nitrogen atoms and ring protons. The h.f.s. constants of anion radical (4) are better accounted for by calculations involving a single nitro-group [*i.e.* those calculated for (3)], in agreement with the slow exchange rate reported for

TABLE 2

Parameter sets and equations used in the MO calculations

				Ref.
	$h_N = 2.20$	$k_{CN} = 1.20$		17
	$h_o = 1.40$	$k_{NO} = 1.67$		
	$h_{Te} = 1.00$	$k_{CTe} = 0.57$		2
	$h_o = 2.00$	$k_{CO} = 0.71$	(ring oxygen)	2
	$h_o = 1.50$	$k_{CO} = 0.50$	(bridge oxygen)	18

$a_N = Q_N^N\rho_N^\pi + 2\ Q_{ON}^N\rho_0^\pi$, with $Q_N^N = (9.90 \pm 1.02)$ mT, $Q_{ON}^N = -(3.58 \pm 0.59)$ mT. $a_H = Q_{CH}^H\rho_C^\pi$, with $Q_{CH}^H = |2.5|$mT.

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[14] R. D. Allendoerfer and P. H. Rieger, *J. Chem. Phys.*, 1967, **46**, 3410.

[15] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[16] R. D. Allendoerfer and P. H. Rieger, *J. Amer. Chem. Soc.*, 1966, **88**, 3711.

[17] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.

[18] L. I. Lagutskaia, *Teor. i eksp. Khim.*, 1966, **2**, 313.

this compound in acetonitrile.[5] The effect of the tellurium atom on the spin-distribution is very small in comparison with that of oxygen or the nitro-groups, as seen from the similarity of both calculated and experimental splittings for nitrophenoxatellurin and nitrodiphenyl ether anion-radicals. The dominant effect of the nitro-substituent is also apparent from the quasi-equivalence of the two *ortho*-positions in both mono- and di-nitrophenoxatellurin anion-radicals.

TABLE 3

Energy gaps, π-bond orders, and estimated exchange rates for the dinitro-anion-radicals

Parent	$\Delta E_{m+1,m+2}/\beta$	C–N π-Bond-order	ν_{ex}/s^{-1} CH$_3$CN	ν_{ex}/s^{-1} DMSO
(1)	0.047 6	0.429 7	$\sim 1.7 \times 10^6$	$\sim 2.7 \times 10^7$
(2)	0.031 0	0.426 8	1×10^6 [a]	3×10^6 [a]

[a] Values from ref. 5.

TABLE 4

AO Coefficients and spin-densities of the NO$_2$ group atoms in ψ_{m+1}, ψ_{m+2}, and $\psi_{M(1,2)}$

	2,8-Dinitrophenoxatellurin anion-radical						2-Nitrophenoxatellurin anion-radical		
	O	O	N	O	O	N	O	O	N
ψ_{m+1}	0.312 0	0.312 0	−0.335 9	−0.312 0	−0.312 0	0.335 9	0.441 4	0.441 4	−0.481 5
ψ_{m+2}	0.313 6	0.313 6	−0.346 6	0.313 6	0.313 6	−0.346 6			
$\psi_{M(1,2)}$	0.443 7	0.443 7	−0.484 0	0.001 1	0.001 1	−0.007 6			
$\rho^{\pi}_{\text{Hückel}}$	0.196 9	0.196 9	0.234 2	0.000 0	0.000 0	0.000 0	0.194 8	0.194 8	0.231 8
a_N/mT		0.910			0.000			0.900	

It was pointed out by Gutch *et al.*[11] that anion-radicals with a low-lying electronic excited state and a low *C–N* bond-order are very sensitive to solvent perturbation. Therefore the energy difference between the highest occupied and the lowest empty molecular orbital, $\Delta E_{m+1,m+2}$, and the C–N π-bond-order were calculated for the anion-radicals of (2) and (4) and are collected in Table 3, together with the estimated exchange rates. It may be seen that the presence of the tellurium atom does not increase the energy gap markedly, nor the C–N bond-order, producing only an increase of the exchange rate, more important for DMSO than for acetonitrile.

If we further consider the interaction between the nearly degenerate states ψ_{m+1} and ψ_{m+2}, two equivalent asymmetric structures ψ_m are obtained, in which one nitrogen splitting is almost equal to that of the mono-nitro-derivatives, while the other is zero. This is illustrated for the anion-radical of (2) by the data in Table 4.

In conclusion it may be stated that nitro-substitution in phenoxatellurin brings about major modifications. It confers acceptor character to the parent molecule, enabling the formation of anion-radials. The presence of the nitro-groups produces a strong solvent-dependent line-width alternation. The effect of the nitro-group is therefore dominant in comparison with that of tellurium for both energy levels and spin distribution.

EXPERIMENTAL

2-Nitrophenoxatellurin, m.p. 129°, 2,8-dinitrophenoxatellurin, 4-nitrodiphenyl ether, m.p. 60°, and 4,4′-dinitrodiphenyl ether, m.p. 142°, were prepared by literature methods.[5,19,20] The anion-radicals were prepared by electrolytic reduction, using an *in situ* technique previously described.[21] The solvents used were acetonitrile and DMSO, purified by literature methods.[22,23] As supporting electrolyte tetra-n-butylammonium perchlorate (0.1M). Solutions of *ca.* 10^{-3}M substrate were carefully outgassed before the reduction was performed.

E.s.r. spectra were recorded on a JES-3B spectrometer in the X-band frequency, and peroxyammonium disulphonate was used as standard (*g* 2.005 5). Spin-density calculations were carried out using the Hückel and McLachlan approximations on an IBM-360 computer at the Computing Centre of the University of Bucharest.

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[20] J. J. Randall, C. E. Lewis, and P. M. Slagan, *J. Org. Chem.*, 1962, **27**, 4098.

[21] E. Volanschi, C. Vlădescu, and C. Volanschi, *Rev. Roumaine Chim.*, 1974, **19**, 755.

[22] Th. Reddy, *Pure Appl. Chem.*, 1971, **25**, 459.

[23] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.