Studies on Nitroaromatic Compounds. Part V.[1] The Electron Spin Resonance Spectra of Some Symmetrically Substituted Polynitroacenaphthenes

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The e.s.r. spectra of the radical anions of 3,8-dinitroacenaphthene and 3,5,6,8-tetranitroacenaphthene have been recorded at −40°. Proton and nitrogen hyperfine coupling constants have been assigned, where possible, on the basis of McLachlan MO calculations, and the spectra have been simulated using the values for the experimental coupling constants.

THERE are many examples where observed e.s.r. spectra of radical anions differ from theoretical spectra predicted on the basis of the usual isotropic hyperfine interaction between the unpaired electron and the magnetically active nuclei in the system. Modulation of the hyperfine coupling constants by migration of the counter ion between sites within the ion pair [2] or strong solvation of the radical anion [3,4] can lead to differences between the experimental and the predicted spectra, these differences being manifested by anomalous line broadening and line intensities in the experimental spectra. These anomalous effects have been observed in the e.s.r. spectra of the radical anions of a number of nitroaromatic

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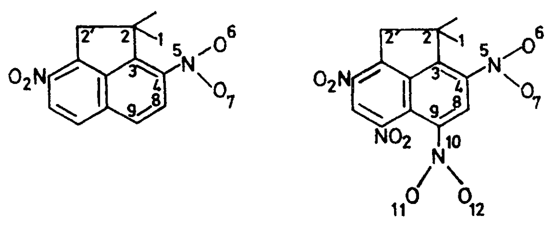
compounds.[2-14] The studies on nitroaromatic compounds have been restricted to nitrobenzenoid and nitronaphthalenic systems and in order to extend the range of investigations we have prepared the radical anions of 3,8-dinitroacenaphthene (I) and 3,5,6,8-tetranitroacenaphthene (II) and recorded their e.s.r. spectra.

RESULTS AND DISCUSSION



(I) (II)

SCHEME

The numbering system used for the description of the radical anions (I) and (II) is given in the Scheme. The spin densities at the nuclear sites in the radical anions (Table 1) were calculated using the McLachlan approximate configuration interaction method,[15] the calculations being performed on the basis that hyperconjugation between the methylene protons and the electron system accounted for the electron–nuclear interaction at the methylene protons.[16-18] The values used in the calculations for the parameters h_x and k_{x-y} in the Coulombic integral $\alpha_x = \alpha + h_x\beta$ and the resonance integral $\beta_{xy} = k_{x-y}\beta$ respectively are given in Table 2. The theoretical proton coupling constants, a, listed in Table 1, were obtained from the calculated spin densities, ρ, using the McConnell equation (1) [19] where for the methylene protons and aromatic ring protons values of 254 [18]

$$a = Q\rho \qquad (1)$$

and 23·7 Oe [20] were chosen respectively for the Q term.

TABLE 1

Spin densities and coupling constants for polynitroacenaphthene radical anions

Radical anion	Position [a]	McLachlan spin densities	Proton coupling constants (Oe) Theor.[b]	Proton coupling constants (Oe) Expt.	Nitrogen coupling constants (Oe) Theor.[c]	Nitrogen coupling constants (Oe) Expt.
(I)	1(H)	0·0014	0·36	0·25		
	8(H)	0·0042	0·10	2·16, 2·81 [d]		
	9(H)	0·1212	2·87	2·16, 2·81 [d]		
	5(N)	0·0088			0·27	0·25
	6,7(O)	0·0160				
(II)	1(H)	0·0013	0·33	0·32		
	8(H)	0·0921	2·18	2·74		
	5(N)	0·0020			0·49	0·42, 0·44 [d]
	6,7(O)	−0·0041				
	10(N)	0·0075			0·36	0·42, 0·44 [d]
	11,12(O)	0·0154				

[a] Numbering system refers to the structures shown in the Scheme. Calculated from equation (1). [c] Calculated from equation (2). [d] Cannot be unambiguously assigned.

The theoretical nitrogen coupling constants, a_N, given in Table 1, were obtained from the calculated spin densities using equation (2) [21] where ρ_N and ρ_O are the

$$a_N = \pm 99\rho_N{}^{\pi} \mp 71\cdot6\,\rho_O{}^{\pi} \qquad (2)$$

spin densities at the nitrogen nucleus and at the neighbouring oxygen nucleus respectively.

The e.s.r. spectrum of radical anion (I) is shown in Figure 1(a) and that for radical anion (II) in Figure 2(a). The experimental coupling constants derived from these spectra are listed in Table 1. There is no apparent linewidth alternation in the spectra under the experimental conditions used and the spectra could be simulated satisfactorily using the experimental coupling constants and integer ratios for the predicted line intensities [Figures 1(b) and 2(b)].

The spectrum of radical anion (I) can be analysed in terms of electron–nuclear spin interaction involving four equivalent protons, two equivalent nitrogens, and two pairs of equivalent protons. The basic pattern in the spectrum is that of a triplet of triplets and this, taken in conjunction with the values for the calculated coupling constants, indicates that the major splittings arise from interaction with the two pairs of aromatic ring protons.

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The experimental values for the coupling constants of these protons are similar (2·16 and 2·81 Oe) and it is not possible to use the calculated values to assign the couplings to specific protons. In view of the similarity between the experimental values it is surprising that there is such a large difference between the calculated values for positions 8(H) and 9(H) (Table 1). The presence of the nitro-groups obviously has a marked effect since the experimental coupling constants for the positions corresponding to 8(H) and 9(H) in the radical anion of acenaphthene are notably different and there is good agreement between the experimental and theoretical values.[18] The molecular orbital parameters used for the nitro-group determine the agreement between the experimental and calculated coupling constants, and in the present work some sixty calculations were performed with gradual variation of the parameters until the best fit was obtained with those parameters quoted in Table 2. It did not prove possible to find a set of parameters which gave similar values for the coupling constants at positions 8(H) and 9(H) and at the same time gave reasonable agreement between the experimental and calculated coupling constants for the other magnetically active sites in radical anions (I) and (II).

TABLE 2

MO Parameters used in calculations

Position [a]	h_x	Bond [a]	k_{x-y}
1(H)	−0·40	1–2(C–H)	3·0
2(C)	−0·35	2–3(C–C)	0·2
3(C)	−0·0,[b] −0·35 [c]	2–2′(C–C)	0·8
		4–5(C–N)	1·8
5,10(N)	2·2	5–6,7(N–O)	2·4
6,7,11,12(O)	1·2	9–10(C–N)	1·2
		10–11,12(N–O)	2·4

[a] Numbering system refers to the structures shown in the Scheme. [b] Value used for radical anion (I). [c] Value used for radical anion (II).

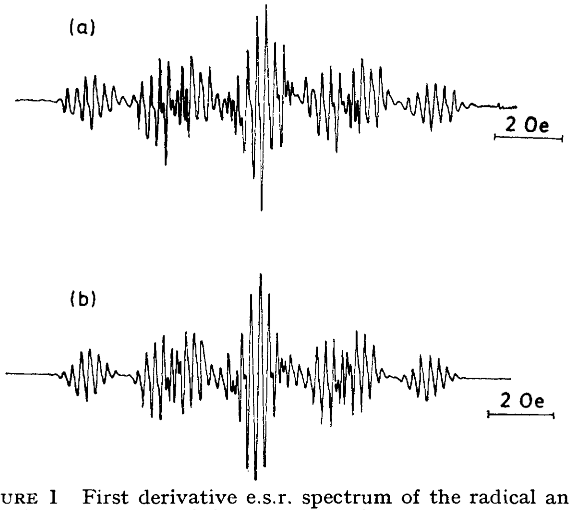

FIGURE 1 First derivative e.s.r. spectrum of the radical anion of 3,8-dinitroacenaphthene at −40 °C; (a) experimentally observed; (b) simulated

The experimental coupling constants for interaction at the nitrogen nuclei and at the bridge protons in radical anion (I) have the same value and the agreement with the calculated values is reasonable. The coupling constant for the bridge protons in radical anion (I) is much lower than the corresponding value for the radical anion of acenaphthene (7·53 Oe),[18] presumably because of the electron-withdrawing properties of the *ortho*-substituted nitro-groups in radical anion (I).

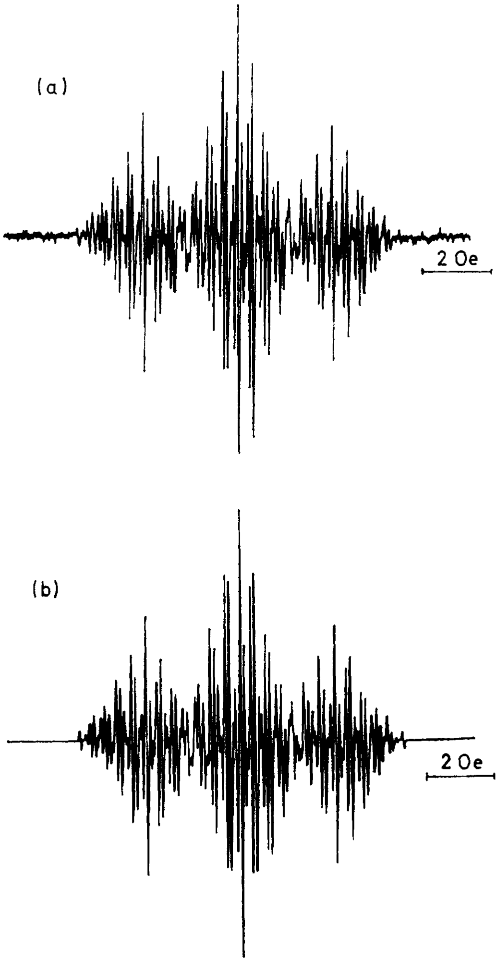

FIGURE 2 First derivative e.s.r. spectrum of the radical anion of 3,5,6,8-tetranitroacenaphthene at −40 °C: (a) experimentally observed; (b) simulated

The spectrum of radical anion (II) can be analysed in terms of splittings from two equivalent protons, two pairs of equivalent nitrogens, and four equivalent proton nuclei. There is good agreement between the values for the experimental and theoretical proton coupling constants and this allows the proton coupling constants to be assigned unambiguously to specific protons. Here, as for radical anion (I), the major splitting arises from interaction with the aromatic ring protons and the spectrum exhibits a basic triplet pattern. Although the values for the theoretical nitrogen coupling constants agree well with the experimental values the difference between the experimental values is too small to allow an unambiguous assignment to be made.

EXPERIMENTAL

3,8-Dinitroacenaphthene was prepared by a reported method.[22] 3,5,6,8-Tetranitroacenaphthene was prepared by the method of Vernon and Wilson [23] with the modification that recrystallisation was performed using nitromethane instead of benzene. 5,6-Dinitroacenaphthene was prepared by a literature method.[24] The synthesis of the unreported compound 4,7-dinitroacenaphthene was attempted but was not successful

The radical anions of 3,8-dinitroacenaphthene and 3,5,6,8-tetranitroacenaphthene were prepared by reduction with sodium.[25] Repeated attempts to prepare the radical anion of 5,6-dinitroacenaphthene by the same method were unsuccessful. The 1,2-dimethoxyethane which was used as solvent was dried over sodium, trap-to-trap distilled from alumina and sodium hydroxide pellets onto sodium and anthracene, and stored under vacuum.

The e.s.r. spectra of the radical anions were recorded at −40° on a Varian E-4 spectrometer. The experimental proton and nitrogen coupling constants derived from the spectra were checked by simulating the spectra using a computer program based on a Lorentzian line-shape function.

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