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Electron spin resonance spectrum of imidazo *p*-benzoquinone anion: a possible case of proton jump

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Several free radicals containing the ¹⁴N nucleus have been studied in recent years [1-8] by E.S.R. with a view to correlating the observed nitrogen splitting constant (a_N) with the unpaired spin density (ρ_N^{π}) on the nitrogen atom, as calculated in MO theories. Relationships of the McConnell type, $a_{\rm N} = Q_{\rm N} \rho_{\rm N}^{\pi}$ where $Q_{\rm N}$ is the sigma-pi interaction parameter, and a modified relationship of the type $a_{\rm N} = Q_1 \rho_{\rm N}^{\pi} + Q_2 (\rho_{\rm adj.} + \rho_{\rm adj.})$ where the subscript adj. refers to the spin densities on the neighbouring carbon atoms, have been proposed. In the nitrogen containing quinones like imidazo p-benzoquinone the greater part of the charge is expected to be in the quinonoid ring with the nitrogen carrying smaller spin densities; therefore it would be of interest to see the extent to which the contribution to the splitting constant $(a_{\rm N})$ comes from the spin densities on the adjacent carbon atoms. We wish to report here our E.S.R. results on the imidazo p-benzoquinone anion radical. Earlier, it was proposed by Gronowitz and Hoffman [9] that in imidazole type molecules the proton attached to the nitrogen exchanges fast in solution between the two nitrogens and our results suggest the possibility of such an exchange.

The E.S.R. spectrum of the anion radical is shown in the figure. The free radical was produced electrolytically in degassed N,N-dimethylformamide (DMF) containing $(n-butyl)_4NClO_4$ as the supporting electrolyte by reducing at -0.7 v relative to a saturated calomel electrode corresponding to the first reduction wave in polarography. We have also carried out the generation of the free radical in the E.S.R. cell placed in the cavity by passing a current of 0.1 mA between two platinum electrodes. The spectrum was recorded with 100 Kc modulation with a spectrometer partially built in our laboratories [10]. The spectrum obtained by the two methods described above gave identical results.

The spectrum clearly shows three groups of lines which arise from two protons giving a 1 : 2 : 1 triplet; these are split further by interaction with two equivalent nitrogens and a proton and the spectrum is in agreement with the stick plot generated using the coupling constants given below. The major splitting, with a coupling constant $a_{\rm H} = 3.50$ G, is assigned to the protons in the 5 and 6 positions. The values of the other splitting constants are $a_{\rm N} = 0.94$ G and $a_{\rm H} = 0.37$ G. The smaller proton splitting constant appears to come from the proton attached to nitrogen, as HMO calculations show the carbon in the 2 position to have a node in the plane of the odd electron ($\rho_{\rm C}^{\pi} = 0$). The use of McLachlan's method ($\lambda = 1.2$) gives a very small negative spin density at this position which cannot account for





Figure 1. E.S.R. spectrum of the imidazo *p*-benzoquinone anion radical generated by electrolytic reduction in DMF.

the large coupling constant. The linewidth of the spectrum is typically ~ 80 mg. The nitrogen coupling constant in acetonitrile differed from that in DMF by about -90 mg.

The experimental coupling constants and the ρ^{π} values calculated by HMO theory are shown in the table. The HMO coulomb (α) and resonance integral (β)

Anion	Position	Experimental coupling constant (G)	HMO‡ spin density	Theoretical coupling constant (G)
	5, 6	$a_{\rm H}=3\cdot 50$	0.116	$3 \cdot 49 (Q_{\rm CH} = 30)$
5 9 2CH	1, 3	$a_{\rm N}=0.94$	0.030	$\begin{pmatrix} 0.75 & (Q_{\rm N} = 25) \\ 0.92 & \uparrow \end{pmatrix}$
	1 or 3	$a_{\rm H}=0.37$	0.030	_

 $\dagger a_{\rm N} = 19 \cdot 1 \rho_{\rm N}^{\pi} + 9 \cdot 1 \ (\rho_{\rm adj.} + \rho_{\rm adj.}'), Q$ values taken from reference [4].

 \downarrow Using $\alpha_0 = \alpha_C + 1 \cdot 4\beta_{C-C}$ and $\beta_{C-O} = 1 \cdot 18\beta_{C-C}$ and $\beta_{C-N} = \beta_{C-C}$ given in reference [14].

Observed hyperfine splitting constants and calculated spin densities for the imidazo *p*-benzoquinone anion radical.

parameters were adjusted to give the best fit with the experimental coupling constant for the ring protons involving $Q_{\rm CH}=30$ G. In the calculations the α values for nitrogen at positions 1 and 3 are assumed to be equal and we used $\alpha_{\rm N} = \alpha_{\rm C} + 1.3\beta_{\rm C-C}$. It should be pointed out that conventional formulae [11, 12] for the case when the nitrogen contributes two electrons to the pi network ($\alpha_{\rm N} = \alpha_{\rm C} + 1.5\beta_{\rm C-C}$, as in heterocyclic–NH) and when the nitrogen contributes only

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one electron to the pi system ($\alpha_N = \alpha_C + 0.5\beta_{C-C}$), give inequivalent spin densities at positions 5 and 6 and at 1 and 3. The inequivalency in the 5 and 6 positions amounts to 170 mG and is in complete disagreement with the experimental spectrum. Ionization of the hydrogen in the 1 position, if assumed, again gives two inequivalent nitrogens, as one of them carries a negative charge and hence a different α value. It is possible that the equivalency of the two nitrogens in the radical is caused by the fast exchange of the hydrogen at position 1. However, the absence of any alternating line width in the spectrum suggests that the exchange frequency is greater than 10⁹ Hz. This explanation derives further support from NMR studies carried out by Gronowitz and Hoffman [9] on imidazoles where the proton jumps between the two nitrogens to make them equivalent and to sharpen the -NH proton resonance signal. We intend to study the exchange phenomenon by deuterium substitution.

The results in the table indicate that the a_N cannot reproduce the ρ_N^{π} using the simple McConnell relationship with $Q_N = 25$. The modified Karplus and Fraenkel expression [13] gives better agreement with experimental results, and the contribution to a_N from the ρ^{π} on the neighbouring carbon atoms amounts to one-third of the total splitting.

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