The Cation-radical and the Neutral Radical from Phenothiazine[1]

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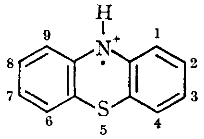
THE electron spin resonance spectrum of the phenothiazine cation-radical (I) has been studied by several workers[2–4] but has not yet been satisfactorily interpreted. We have prepared (I) as its perchlorate salt from phenothiazine, phenothiazine 5-oxide, and perchloric acid, by Billon's method,[5] and have observed its e.s.r. spectrum in acetonitrile; Figure 1a shows half the spectrum (from high field). The spectrum is analyzed as follows, the proton-assignments being consistent with MO calculations (below): $a^{N} = 6{\cdot}52$, $a^{N\text{-}H} = 7{\cdot}36$, $a_{1,9}{}^{H} = 1{\cdot}23$, $a_{2,8}{}^{H} = a_{4,6}{}^{H} = 0{\cdot}46$, and $a_{3,7}{}^{H} = 2{\cdot}58$ gauss ($g = 2{\cdot}0051$).

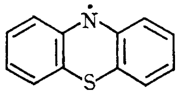
Figure 1b shows a simulated half-spectrum, computed using these hyperfine splitting constants and a Lorentzian line-shape, line-width at half-height = 0·60 gauss. The magnitude of the line-width precludes the observation of possible differences between the splitting constants of protons at positions 2 and 4.

Shine and Mach have recently reported the formation of a different paramagnetic species, which they believed to be the neutral radical (II), by the irradiation of phenothiazine in ethanol.[2] We have observed (II) as the initial product of the reaction of (I) in acetonitrile with an excess of water buffered at pH 7; the species decays by a second-order reaction whose nature and mechanism will be reported subsequently. Half the e.s.r. spectrum of (II) (from high field) is shown in Figure 2a and is analyzed, in conjunction with MO calculations, as follows: $a^{N} = 7{\cdot}06$, $a_{1,9}{}^{H} = 2{\cdot}68$, $a_{2,8}{}^{H} = 1{\cdot}00$, $a_{3,7}{}^{H} = 3{\cdot}64$, and $a_{4,6}{}^{H} = 0{\cdot}73$ gauss ($g = 2{\cdot}0053$). There is again close agreement with the simulated spectrum, Figure 2b, computed from these splittings and a line-width of 0·33 gauss.

Further evidence that the new species is the neutral radical (II) is that the same spectrum results when (I) is treated with triethylamine or with deuterium oxide; and that, whereas 3,7-dimethylphenothiazine cation-radical behaves similarly to (I) in giving a second free-radical analogous to (II) when treated with water, *N*-methylphenothiazine cation-radical does not.



(I)



(II)

Hückel MO calculations were carried out for both radicals. Following Longuet-Higgins[6] sulphur was treated as a pair of atoms, p, q. The parameters used were: $\alpha_{C} = \alpha_{0}$, $\beta_{C\text{-}C} = \beta_{0}$ for bonded carbons, zero otherwise; $\alpha_{p} = \alpha_{q} = \alpha_{0}$, $\beta_{pq} = \beta_{0}$, $\beta_{C\text{-}p} = \beta_{C\text{-}q} = 0{\cdot}8\beta_{0}$; $\beta_{C\text{-}N} = \beta_{0}$, and $\alpha_{N} = \alpha_{0} + f\beta_{0}$; f was taken as 1·0 for the cation-radical and as 0·75 for the neutral radical. The values of f were determined by numerical experiment, but are well within the accepted range for such parameters[7]; f is greater for the cation-radical than for the neutral radical, as would be expected.

The use of McConnell's method for assigning spin densities and with $|Q_{H}{}^{C\text{-}H}| = 22{\cdot}5$, $|Q_{H}{}^{N\text{-}H}| = 32{\cdot}0$, and $|Q_{N}| = 26{\cdot}5$ gauss[4] gave, for the cation-radical, $a^{N} = 6{\cdot}54$, $a^{N\text{-}H} = 7{\cdot}89$, $a_{1,9}{}^{H} = 1{\cdot}34$, $a_{2\text{-}8}{}^{H} = 0{\cdot}50$, $a_{3,7}{}^{H} = 1{\cdot}69$, and $a_{4,6}{}^{H} = 0{\cdot}20$, and,

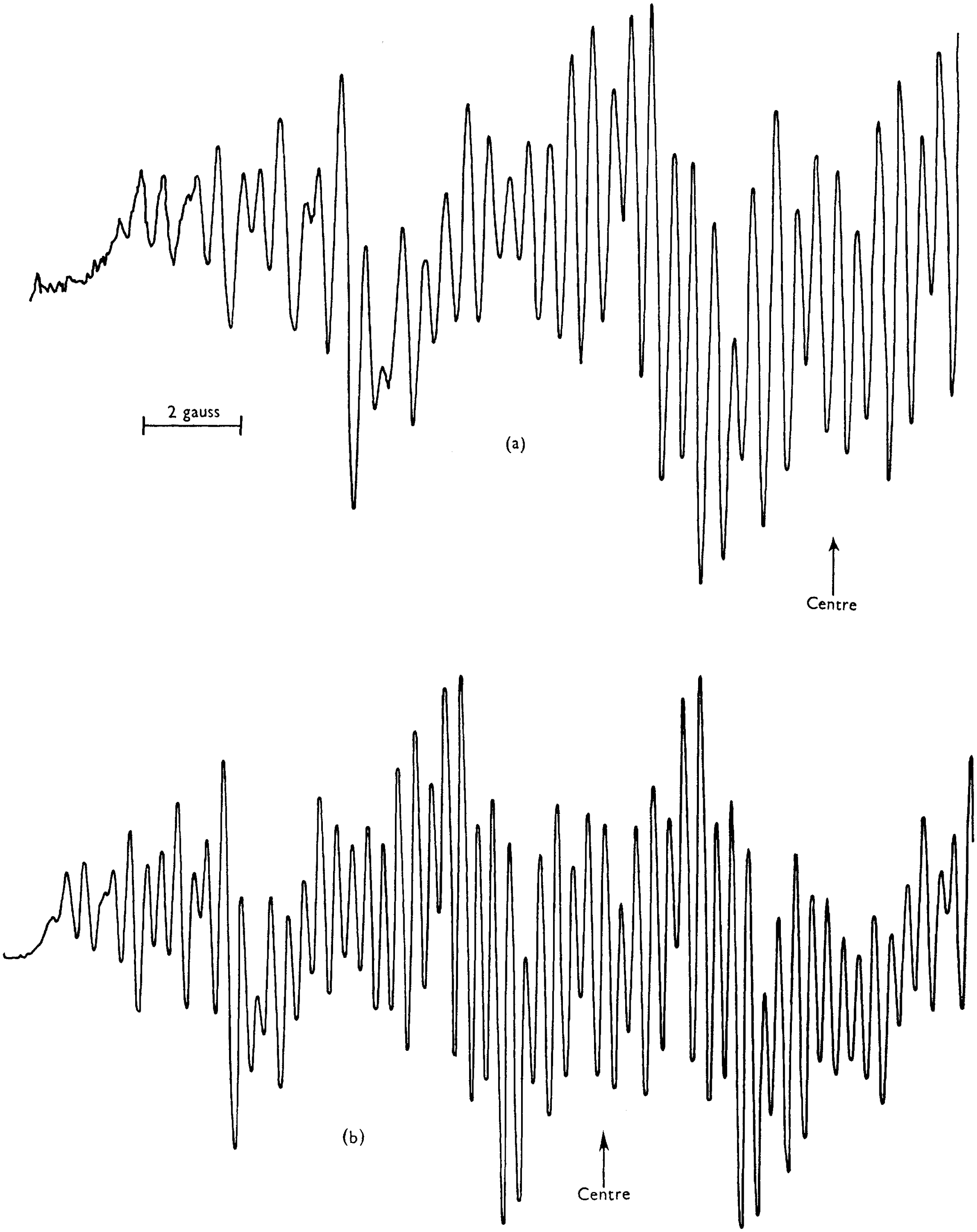


FIGURE 1: *E.s.r. spectrum of the phenothiazine cation-radical:* (a) *observed,* (b) *simulated.*

for the neutral radical, $a^{\mathrm{N}} = 7\cdot53$, $a_{1,9}{}^{\mathrm{H}} = 1\cdot55$, $a_{2,8}{}^{\mathrm{H}} = 0\cdot37$, $a_{3,7}{}^{\mathrm{H}} = 1\cdot77$, and $a_{4,6}{}^{\mathrm{H}} = 0\cdot19$ gauss.

In an attempt to obtain better agreement with experiment for the protons bonded to carbon, the methods proposed by Giacometti, Nordio, and Pavan[8] (GNP) and by Colpa and Bolton[9] (CB) were applied. (Both these methods allow for the effect on spin density of neighbouring atoms. It did not seem necessary to consider similar effects for nitrogen, for which the simple treatment was satisfactory, in accord with the experience of others.[10]) With the parameters used originally[8,9] the GNP and CB methods gave, respectively, for the cation-radical, $a_{1,9}{}^{\mathrm{H}} = 1\cdot95$, $1\cdot88$; $a_{2,8}{}^{\mathrm{H}} = 0\cdot74$, $0\cdot69$; $a_{3,7}{}^{\mathrm{H}} = 2\cdot47$, $2\cdot23$; $a_{4,6}{}^{\mathrm{H}} = 0\cdot30$, $0\cdot28$; and, for the neutral radical, $a_{1,9}{}^{\mathrm{H}} = 2\cdot24$, $2\cdot18$; $a_{2,8}{}^{\mathrm{H}} = 0\cdot54$, $0\cdot51$; $a_{3,7}{}^{\mathrm{H}} = 2\cdot55$, $2\cdot44$; $a_{4,6}{}^{\mathrm{H}} = 0\cdot27$, $0\cdot26$ gauss. Both these methods are an improvement on the simple McConnell treatment and there is little to choose between them (*cf.* Snyder and Amos[11]). However, neither method can yield simultaneously both the 1,9- and the 3,7-coupling constants and further refinements of the treatments of these radicals are required.

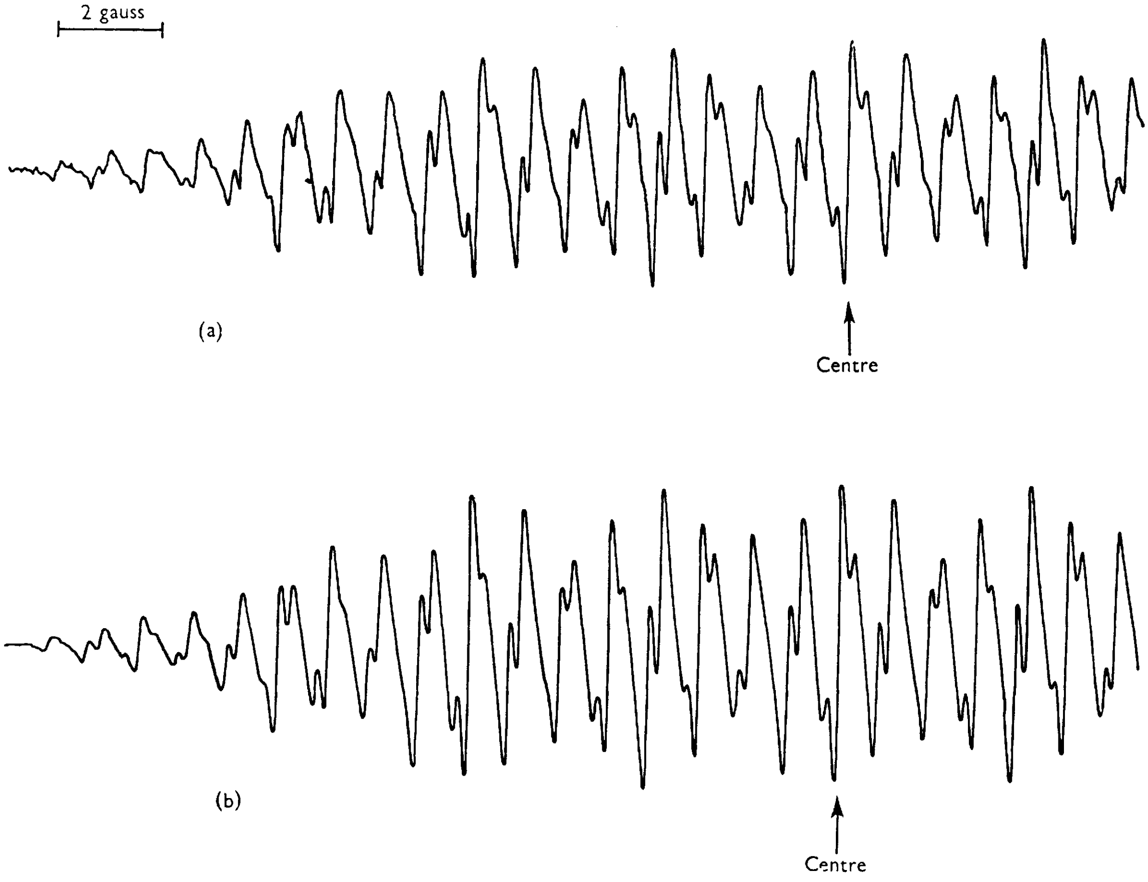


FIGURE 2: *E.s.r. spectrum of the phenothiazine neutral radical:* (a) *observed,* (b) *simulated.*

The e.s.r. spectra were determined on a Varian V-4502 spectrometer with a 12-in. magnet and 100-kc./sec. field modulation, and the simulated spectra were plotted by a Japan Electron Optics Laboratory JNM-RA-1 spectrum accumulator which was made available to us by the Inorganic

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