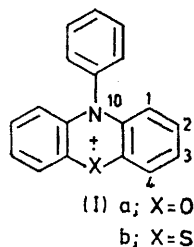


Heterocyclic Free Radicals. Part V.¹ An Electron Spin Resonance Investigation of the Cation-radicals of 10-Phenylphenoxazine and 10-Phenylphenothiazine

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Isotropic e.s.r. spectra of the stable cation-radicals of 10-phenylphenoxazine and 10-phenylphenothiazine are described; hyperfine splittings are assigned on the basis of MO calculations and experiments on selectively deuteriated derivatives. For both radicals, good agreement is obtained between calculated and experimental splittings when it is assumed that the plane of the phenyl ring in the 10-position is twisted *ca.* 70° from the plane of the remainder of the radical.

We have previously presented¹ spectroscopic evidence for some reactions of phenothiazine and its oxidised derivatives and we have reported^{2,3} the e.s.r. spectra and MO calculations for the cation-radicals, nitroxide radicals, and neutral radicals from phenoselenazine, phenothiazine, and phenoxazine. Our investigations have now been extended to the preparation and characterisation (from their e.s.r. spectra) of the cation-radicals of 10-phenylphenoxazine (Ia) and 10-phenylphenothiazine (Ib). Of particular interest has been the



comparison between the experimental e.s.r. splittings and values calculated using an MO method; it has been our aim not only to evaluate the electronic effects of the heteroatoms and the phenyl ring on the unpaired electron distribution in these radicals but also to probe the steric consequences of arylation at nitrogen. Interest has

¹ Part IV, P. Hanson and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 264.

² M. F. Chiu and B. C. Gilbert, *J.C.S. Perkin II*, 1973, 258.

³ M. F. Chiu, B. C. Gilbert, and P. Hanson, *J. Chem. Soc. (B)*, 1970, 1700.

⁴ L. Lunazzi, A. Mangini, G. Placucci, and C. Vincenzi, *J.C.S. Perkin I*, 1972, 2418.

recently centred on the restricted rotation of aryl rings attached to sterically hindered radicals (*e.g.* 9-phenyl-xanthenyl and its sulphur- and selenium-containing analogues,⁴ radical-ions from phenyl- and naphthyl-substituted anthracenes,⁵ triarylmethyl radicals,⁶ and some hindered nitroxides⁷) and magnetic resonance techniques, coupled with MO calculations, have provided estimates for angles of twist between the plane of the phenyl substituents and the plane containing the bonds at the radical centre.

The well-resolved e.s.r. spectra of the stable radicals (I) and their deuteriated derivatives have enabled us to make detailed conclusions about the structures of these species, with emphasis on spin-density distributions and approximate angles of twist for the phenyl rings.

EXPERIMENTAL

All e.s.r. spectra were obtained at ambient temperature on a Varian E3 spectrometer. Hyperfine splittings were determined by comparison with that for *p*-benzosemiquinone in aqueous ethanol⁸ and were verified by computer simulation using a FORTRAN IV program in which Lorentzian line-shape was assumed. FORTRAN IV programs for performing the Hückel and McLachlan⁹ MO calculations were kindly made available by Dr. D. R.

⁵ (a) L. S. Marcoux, A. Lomax, and A. J. Bard, *J. Amer. Chem. Soc.*, 1970, **92**, 243; (b) G. R. Underwood, D. Jurkowitz, and S. C. Dickerman, *J. Phys. Chem.*, 1970, **74**, 544.

⁶ W. J. Van der Hart, *Mol. Phys.*, 1970, **19**, 75.

⁷ A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

⁸ M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 1350.

⁹ A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

Burnham. MO Calculations and spectrum simulations were carried out on an Elliot 4130 computer at the University of York.

Cation-radicals were prepared by the oxidation of the parent heterocycles both with aluminium trichloride-nitromethane¹⁰ and with thallium(III) acetate sesquihydrate (Emanuel) in nitromethane containing a trace of acetic acid. Essentially similar spectra were obtained with both oxidants. Nitromethane was dried by distillation from calcium hydride and was stored over A-4 molecular sieve (Fisons); all solutions were deoxygenated with a stream of nitrogen both before and during mixing and were transferred to an e.s.r. flat cell under nitrogen. Under these conditions, solutions of stable free radicals were obtained.

10-Phenylphenoxazine, 10-phenylphenothiazine, and the deuteriated derivatives employed were prepared by the Ullmann reaction between either phenoxazine¹¹ or phenothiazine¹² (both Emanuel) and either iodobenzene or the appropriately deuteriated iodobenzene. Pentadeuterioiodobenzene, prepared from the Grignard reagent of C₆D₅Br (Ciba-Geigy) by adding excess of iodine¹³ was used to prepare 10-(pentadeuteriophenyl)phenoxazine and the corresponding phenothiazine. [4-²H]Iodobenzene was obtained from [4-²H]bromobenzene which itself was prepared¹⁴ from 1,4-dibromobenzene *via* a Grignard reaction followed by hydrolysis with deuterium oxide (99.9%; Koch-Light); this compound was then used to prepare 10-(4-deuteriophenyl)phenothiazine. [2,4,6-²H₃]Iodobenzene was prepared by Sandmeyer reaction from the corresponding deuteriated aniline which had been labelled by isotope exchange (three sealed-tube equilibrations at 100°) between aniline hydrobromide and deuterium oxide;¹⁵ 10-(2,4,6-trideuteriophenyl)phenothiazine was prepared as above. The crude products were purified with an alumina column by elution with 40:60 light petroleum-diethyl ether mixtures, followed by recrystallisation (twice) from ethanol. 10-Phenylphenoxazine and its deuteriated derivative (pale green crystals) had m.p. 138–139° (lit.,¹¹ 138–139°) and 10-phenylphenothiazine and its deuteriated derivatives (colourless crystals) had m.p. 94–95° (lit.,¹² 94.5°). The deuteriated compounds gave satisfactory C and N analyses; as estimated from their mass spectra, the extent of deuteration was *ca.* 100% for 10-(pentadeuteriophenyl)-phenoxazine and -phenothiazine and 90% for 10-(4-deuteriophenyl)phenothiazine. Owing to extensive loss of deuterium from the molecular ion, mass spectrometric determination of the extent of deuteration of 10-(2,4,6-trideuteriophenyl)phenothiazine was unreliable. By n.m.r. we estimate the sample to be at least 85% trideuteriated.

RESULTS AND DISCUSSION

(i) *E.s.r. Spectra.*—All the radicals were prepared as stable dilute solutions and showed well-resolved hyperfine splittings (ΔH typically *ca.* 20 μ T). The large number of lines observed for the parent cation-radicals (Ia and b) suggests that in addition to splittings from

¹⁰ W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, 1966, **88**, 2862.

¹¹ H. Gilman and L. O. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 3485.

¹² H. Gilman, P. R. Van Ess, and D. A. Shirley, *J. Amer. Chem. Soc.*, 1944, **66**, 1216.

the hydrogen atoms in the heteroaromatic moieties there are also observable splittings from hydrogen atoms in the 10-phenyl ring. As expected on this basis, the overall width and the complexity of the spectra were reduced for the deuteriated counterparts.

Figure 1 shows the spectrum from the cation-radical of 10-phenylphenoxazine and Figure 2 shows the corresponding spectrum from the 10-(pentadeuteriophenyl)phenoxazine cation-radical. Good agreement with experiment was obtained by spectrum simulation employing the splittings given in Table I (the basis for

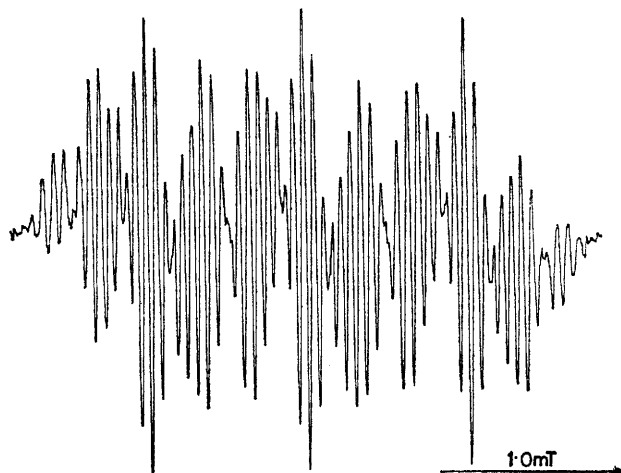


FIGURE 1 E.s.r. spectrum of the cation-radical of 10-phenylphenoxazine

the assignments, other than the indication provided by the deuteration experiment, is discussed in the next section).

Analysis of the spectra indicates that the hydrogen atoms in the heteroaromatic rings have four separate hyperfine splittings (0.303, 0.142, 0.063, and 0.056 mT) and that there are approximately equal splittings (0.050 mT) from four hydrogen atoms (evidently *ortho* and *meta*) in the 10-phenyl ring. Spectrum simulation on this basis, rather than with a splitting of 0.050 mT from only *two* protons in the 10-phenyl ring in (Ia), gave optimum agreement, although the outside lines of the spectrum could not be unambiguously located. Evidence that the *meta*-protons (at least) have a 0.050 mT is also implied by the modification of the spectra observed for *meta*-substituted derivatives [*e.g.* 10-(3-chlorophenyl)- and 10-(3-methoxyphenyl)-phenoxazine cation-radicals] for which a splitting of this magnitude has clearly been removed. There is also an indication in an expanded spectrum of the cation-radical (Ia) of an extra splitting (*ca.* 0.015 mT, too small to be detectable in the spectrum in Figure 1) from a single hydrogen (evidently the *para*-proton in the phenyl ring).

¹³ M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances,' Prentice-Hall, New York, 1954, p. 1332.

¹⁴ G. Fraenkel, D. G. Adams, and R. R. Dean, *J. Phys. Chem.*, 1968, **72**, 944.

¹⁵ R. I. Akawie, J. M. Scarborough, and J. G. Burr, *J. Org. Chem.*, 1959, **24**, 946.

The analysis and simulation of the spectra from the cation-radical (Ib) and its derivatives follows the pattern established for the phenoxazine counterparts. In the

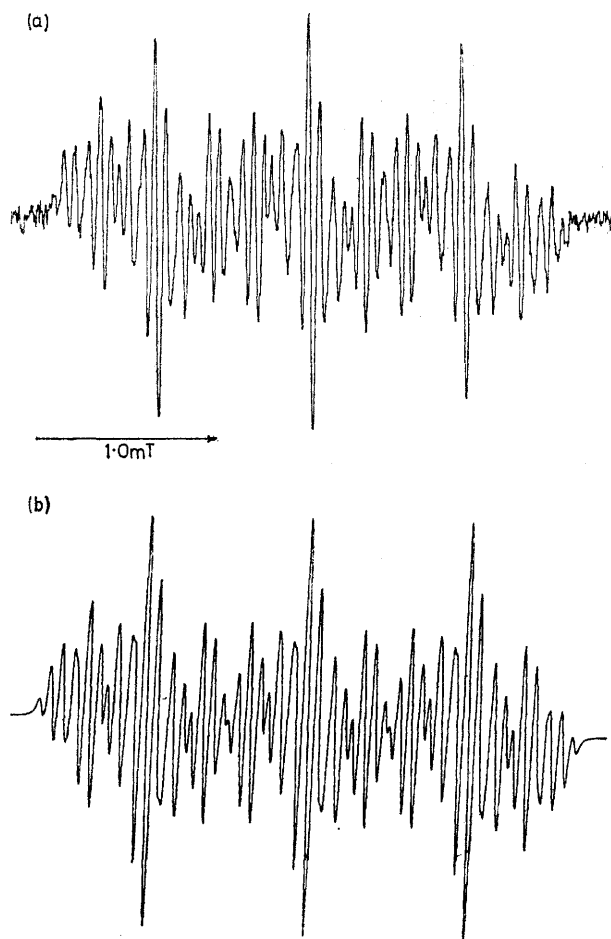


FIGURE 2 E.S.R. spectrum of the cation-radical of 10-(penta-deuteriophenyl)phenoxazine: (a) observed, (b) simulated using the splittings given in Table 1 and a linewidth of 0.025 mT

radical from the parent compound there are splittings of 0.215 (2H), 0.090 (4H), 0.033 (2H), 0.022 (4H), and 0.012 (1H) mT; results for the deuteriated derivatives

the spectrum from the 10-(penta-deuteriophenyl) derivative shows splittings from hydrogen atoms in the heteroaromatic ring of 0.215 (2H) and 0.090 (4H); the line width of the spectrum from this radical is such (0.045 mT) that the remaining splitting of 0.022 mT could not be resolved.

(ii) *MO Calculations.*—We have carried out Hückel and McLachlan calculations for the cation-radicals (Ia and b) in an attempt to rationalise and assign the hydrogen splittings (and hence the unpaired electron

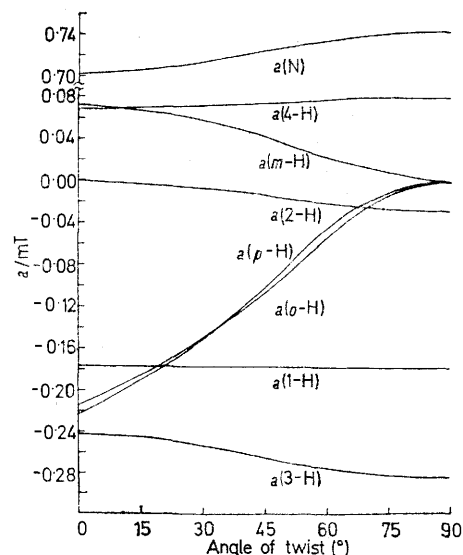


FIGURE 3 Results of Hückel-McLachlan MO calculations for the cation-radical of 10-phenylphenoxazine as a function of the angle of twist of the phenyl ring (for parameters, see text)

distributions), and, in particular to determine the electronic effect of the phenyl substituent by comparing these results with those previously obtained³ for the cation-radicals of phenoxazine and phenothiazine. We have employed parameters which proved suitable in the earlier calculations,³ namely h_N , 1.5, k_{CN} 1.0, h_O : 2.0, h_{CO} 0.8, h_S : 1.25, k_{OS} 0.57, and λ 1.2, and Q^H -2.7, Q^N 2.78 mT. We have also simulated the effect of twisting the 10-phenyl rings in (Ia and b) out of the plane

TABLE 1

Hyperfine splittings (mT) of the cation-radicals of 10-phenylphenoxazine, 10-phenylphenothiazine, and some deuteriated derivatives^{a, b}

Cation-radical	$a(N)$	$a(1-H)$	$a(2-H)$	$a(3-H)$	$a(4-H)$	$a(o-H)$	$a(m-H)$	$a(p-H)$
10-Phenylphenoxazine (Ia)	0.855	0.142	0.056	0.303	0.063	0.050	0.050	0.015
10-(Penta-deuteriophenyl)phenoxazine	0.855	0.142	0.056	0.303	0.063			
10-Phenylphenothiazine (Ib)	0.695	0.090	0.022	0.215	0.090	0.033	0.022	0.012
10-(Penta-deuteriophenyl)phenothiazine	0.695	0.090	<i>c</i>	0.215	0.090			
10-(2,4,6-Trideuteriophenyl)phenothiazine	0.695	0.090	0.022	0.215	0.090		0.022	
10-(4-Deuteriophenyl)phenothiazine	0.696	0.090	0.022	0.215	0.090	0.033	0.022	

^a ± 0.005 mT. ^b For assignments, see text. ^c Splitting not resolved; linewidth *ca.* 45 μ T.

clearly confirm that the splitting of 0.012 mT is from the *para*-hydrogen in the 10-phenyl ring and that the *ortho*-protons in this ring have $a(H)$ 0.033 mT. As expected,

of the remainder of the radical (itself assumed to be planar) by varying the value of β_{CN} for the bond joining the nitrogen atom (at position 10) to the phenyl ring:

we have taken $^{16} \beta(\theta) = \beta_0 \cos \theta$ where θ is the angle of twist.

The results for (Ia and b), calculated as a function of θ using the McLachlan modification (which gives much better overall agreement than the Hückel method, *cf.* ref. 3) are shown in Figures 3 and 4.

Inspection of the data for (Ia) indicates that good agreement is obtained between calculated and observed splittings for the heterocyclic hydrogens, which are not very sensitive to θ , over a range of twist angle, assuming that the assignments are as follows: $a(3\text{-H})$ 0.303,

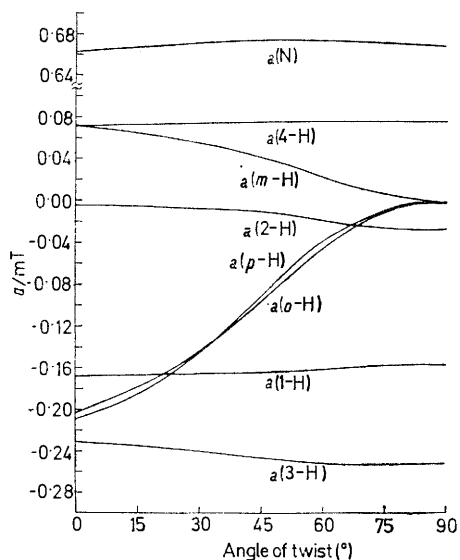


FIGURE 4 Results of Hückel-McLachlan MO calculations for the cation-radical of 10-phenylphenothiazine as a function of the angle of twist of the phenyl ring (for parameters, see text)

$a(1\text{-H})$ 0.142, $a(2\text{-H})$, $a(4\text{-H})$ 0.056, 0.063 mT. The last-mentioned pair of splittings are too close for their separate reliable attribution, and the assignment suggested by the calculations must remain tentative; we note that $a(4\text{-H})$ is predicted to be opposite in sign to the other hydrogen splittings.

Comparison of these results with the observed and calculated splittings³ for phenoxazine cation-radical itself reinforces these conclusions and indicates that the 10-phenyl substituent in (Ia) is responsible for some redistribution of spin density in the heterocyclic system.* Thus, the hydrogens at positions 1 and 3 in (Ia) have splittings (presumably negative) which are smaller in magnitude than those of the unsubstituted radical and which reflect smaller positive spin densities at the attached carbons. On the other hand, the splitting assigned to the C-2 hydrogens has increased slightly in magnitude, though this effect is not reflected in the calculations.

* The assignments of $a(2\text{-H})$ and $a(4\text{-H})$ for the phenoxazine cation-radical given in ref. 3 (Table 1) should be reversed (see Table 3).

¹⁶ A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

Inspection of the predicted and observed splittings for the phenyl ring protons in (Ia) strongly suggests that there is a considerable degree of twist in the radical: only when θ is $\geq ca. 70^\circ$ is $a(p\text{-H})$ predicted to be of the observed magnitude (and considerably smaller than the other aryl proton splittings). This behaviour is understandable in terms of the de-coupling of the phenyl ring's π -system from that of the remainder of the radical, so that spin density can no longer effectively be transmitted to the remote *para*-position. Analogous examples include the observation⁴ of low *para*-proton splittings for the twisted radical 9-phenylxanthenyl [$|a(o\text{-H})| > |a(m\text{-H})| \approx |a(p\text{-H})|$] and its sulphur- and selenium-containing counterparts [$|a(o\text{-H})| > |a(p\text{-H})| > |a(m\text{-H})|$] and similar patterns⁷ for some hindered phenyl nitroxides [$|a(o\text{-H})| \approx |a(m\text{-H})| > |a(p\text{-H})|$]; calculations,^{4,7} including those with the INDO method on the benzyl radical¹⁷ and on twisted nitroaromatic anion-radicals¹⁸ (see also Figures 3 and 4) give good general agreement with this type of limiting behaviour for $a(p\text{-H})$ as θ is increased.

It is perhaps surprising that the *ortho*- and *meta*-proton splittings are so much larger than the *para*-splitting in the 10-phenyl ring and that these are also greater than the values calculated here for $\theta > ca. 50^\circ$ (*cf.* angles of twist of *ca. 70^\circ* for the 9-phenylxanthenyl and related radicals). This probably implies that spin density is transferred to these protons not only through the π -orbitals of the 10-phenyl group but also, fairly effectively, through the σ -system (the Hückel-McLachlan calculations do not take this contribution into account). Further, as has been proposed^{4,19} for 9-phenylxanthenyl and its analogues, it may be possible that direct transfer of spin density to the *ortho*-protons from $p(\pi)$ -orbitals on nearby atoms in the heterocyclic ring can contribute to the splitting from these atoms. The latter contribution has been expressed as $a_H(\text{MHz}) = 1420.4 \sum_i \rho_i^\pi |\psi_i(\text{H})|^2$. Here ρ_i^π is the spin density on a particular atom of the heterocyclic ring and $|\psi_i(\text{H})|^2$ is the probability of finding the associated p -orbital electron at the nucleus of the *ortho*-hydrogen atom. For 9-phenylxanthenyl and its sulphur-containing analogue the calculated contributions to $a(o\text{-H})$ are dominated by the interaction of the spin density at C-10 and for $\theta ca. 70^\circ$ the estimated contributions from this source are +2.58 (0.09) and +1.91 MHz (0.07 mT), respectively. These are opposite in sign to the normal contributions produced by spin polarisation. The possible validity of this explanation for the magnitudes of $a(o\text{-H})$ in our examples is discussed later.

The observed splittings for (Ib) (see Table 1) are assigned on the basis of the deuteration experiments and the McLachlan MO calculations. The calculations suggest that $a(3\text{-H})$ is smaller for (Ib) than for (Ia), and

¹⁷ J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

¹⁸ B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1973, 2010.

¹⁹ L. Lunazzi, A. Mangini, G. Placucci, C. Vincenzi, and I. Degani, *Mol. Phys.*, 1970, **19**, 543.

we accordingly assign to these protons the splitting of 0.215 mT [*cf.* 0.303 mT for (Ib)]. On a similar basis, the protons at C-1 are assigned a splitting of 0.090 mT. The remaining splittings from the heterocyclic ring (0.090 and 0.022 mT) are tentatively assigned to the protons at C-4 and -2, respectively (calculated values 0.0767 and -0.0228 mT, respectively) though the former appears unusually large if the sign is indeed positive. The lower nitrogen splitting for (Ib) than for (Ia) is accounted for. The assignment of the splittings from the protons in the 10-phenyl ring, $|a(o-H)| > |a(m-H)| > |a(p-H)|$ (*i.e.* 0.033, 0.022, and 0.012 mT, respectively) is broadly in agreement with results for other twisted radicals. McLachlan calculations with *θ ca.* 70° successfully predict that $a(o-H)$ is greater than

observed splittings for the *para*-protons in the 10-phenyl rings is good: these splittings should be very sensitive to the extent of twisting and we believe that the Hückel-McLachlan approach is realistic for them. However, we would not expect this to be also true for *meta*- and, particularly, *ortho*-protons in the 10-phenyl rings, for which transmission of spin density through the π -orbitals would be expected to be augmented by contributions transmitted through the σ -orbitals at high angles of twist. We suggest that such a mechanism could lead to negative spin density at the *ortho*-protons and positive spin density at the *meta*-protons (*i.e.* the same signs as the contributions from spin density in the π -orbitals at the respective carbons). It is notable that INDO calculations (which take into account σ - and

TABLE 2

Calculated splittings (mT) for the cation-radicals of 10-phenylphenoxazine (Ia) and 10-phenylphenothiazine (Ib) assuming an angle of twist (θ) of 70°^a

Radical	$a(N)$	$a(1-H)$	$a(2-H)$	$a(3-H)$	$a(4-H)$	$a(o-H)$	$a(m-H)$	$a(p-H)$
(Ia)	0.7400	-0.1783	-0.0258	-0.2815	0.0789	-0.0222	0.0109	-0.0190
(Ib)	0.6730	-0.1588	-0.0228	-0.2526	0.0767	-0.0202	0.0114	-0.0157

^a For MO parameters (McLachlan method) and Q values, see text.

$a(p-H)$ and yield calculated splittings of the correct order of magnitude (0.020, 0.011, and 0.016, respectively) but the *ortho*- and *meta*-splittings are underestimated [*cf.* calculations for (Ia)].

Table 2 shows the calculated splittings for both (Ia and b) with the same angle of twist in the two cases (70°). Agreement is, on the whole, reasonable; a good account is apparently given of the effect on the heterocyclic proton splittings of the presence of the 10-phenyl ring and of substitution of S for O. [However, it must be remembered that the signs of the splittings given here are predicted, and not yet verified. This must await further experiments (*e.g.* the recording of the n.m.r. spectra⁷ of some suitably substituted derivatives).]

We note that the agreement between calculated and

π -electrons) on π -radicals in which considerable twisting has been allowed (benzyl,¹⁷ and nitroaromatic radical-anions¹⁸) indicate that for θ in the range 60–75° the predicted splittings are $|a(o-H)| \simeq |a(m-H)| > |a(p-H)|$ [$a(o-H)$ negative and $a(m-H)$ positive]. This is similar to the trends reported here; further, the calculated ratios $a(o-H) : a(p-H)$ *ca.* 2:1 are similar to those reported here. Although the signs of the splittings are not available, these results suggest that, at least for the radicals reported here, the enhanced *ortho*- and *meta*-splittings stem from through-bond σ -polarisation at high twist angles, rather than from direct overlap.

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