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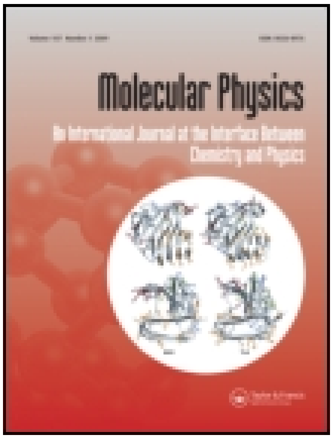

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ENDOR studies on X-irradiated single crystals of acridine and phenazine

V.P. Chacko [a], C.A. McDowell [a] & B.C. Singh [a]

[a] Department of Chemistry, University of British Columbia, 2075 Wesbrook Mall, Vancouver, B.C., Canada, V6T 1W5

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ENDOR studies on X-irradiated single crystals of acridine and phenazine

by V. P. CHACKO, C. A. McDOWELL and B. C. SINGH
Department of Chemistry, University of British Columbia,
2075 Wesbrook Mall, Vancouver, B.C., Canada, V6T 1W5.

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Stable radicals formed by room temperature *X*-irradiation of single crystals of acridine and phenazine have been identified and their structures determined by detailed ENDOR studies at 77 K. The E.S.R. spectra are of little assistance in the identification of these radicals. However, the high resolution of ENDOR has made it possible to study all the proton hyperfine interactions in detail. The radicals investigated in this study are formed as a result of the addition of atomic hydrogen to the nitrogen atom of the acridine and phenazine molecules. ENDOR lines of all the protons have been identified and analysed. Spin densities have been deduced from the proton hyperfine tensors. Although the unpaired electron is extensively delocalized throughout the molecule, there are large spin densities (0·475 and 0·584, respectively) on C_9 in acridine and the second nitrogen in phenazine. Excellent agreement has been obtained between the observed spin densities and those computed by INDO molecular orbital calculations. The design and construction of a simple rectangular ENDOR cavity operating in the TE_{101} mode is described.

1. INTRODUCTION

Electron spin resonance (E.S.R.) and electron nuclear double resonance (ENDOR) techniques have been extensively employed in the study of radicals produced by ionizing radiation in organic single crystals. A thorough knowledge of the spin density distribution and the geometrical structure of the radicals can be achieved only through the complete determination of the hyperfine interaction tensors for the different nuclei in the radicals under study. This is possible only by working with the oriented systems such as those having the radical species trapped in a single crystal. In general, radicals produced by ionizing radiation in aliphatic compounds yield well-resolved E.S.R. spectra, and hence they have been studied in detail. In aromatic systems, however, the unpaired electron is extensively delocalized and hence coupled to a large number of nuclei, a situation which generally yields inhomogeneously-broadened E.S.R. spectra. For these compounds in the solid state, the E.S.R. spectra appear very poorly resolved and thus generally yield little information [1].

The much better resolution of ENDOR spectroscopy makes it possible to study the hyperfine interactions of nuclei in such aromatic radicals in single crystals. Here we report the results of an ENDOR study of the predominant radicals produced by room temperature X-irradiation of single crystals of acridine and phenazine. No useful results could be obtained from the E.S.R. spectra because of very poor resolution as a result of the extensive delocalization of the unpaired electron. The hyperfine interaction tensors of all the protons in these radicals could be determined by the ENDOR technique. No ENDOR lines for the ^{14}N nucleus were observed in the present study. This did not, however, cause any difficulty in identifying the main paramagnetic species as being the N-hydroacridinyl and N-hydrophenazinyl radicals in acridine and phenazine, respectively.

2. EXPERIMENTAL

Single crystals of acridine were grown by slow evaporation of its saturated solution in ethanol at room temperature. Phenazine crystals were grown in a similar manner from propanone. Well-developed crystals of approximate dimensions 8 × 4 × 3 mm were easily obtained.

Five different crystalline modifications of acridine are known to exist [2]. In this study we have used acridine II, which is known to be the most stable modification. Acridine I is a hydrate; the other three modifications can be converted to acridine II by heating [2]. The crystal structure of acridine II has been determined by Phillips *et al.* [3]. The crystal is monoclinic with $a = 16{\cdot}292$, $b = 18{\cdot}831$, $c = 6{\cdot}072$ Å, $\beta = 95° \ 4'$, and space group $P2_1/a$. There are eight molecules in the unit cell, constituting four asymmetric units consisting of two molecules. The two molecules (hereafter designated by A and B) in each asymmetric unit exhibit significant and different departures from planarity, molecule A being more planar than molecule B. There are, however, no significant differences in bond lengths between the two molecules. The molecular structure of acridine is depicted in figure 1 (*a*), along with the numbering of the ring atoms.

For ENDOR work in acridine we have chosen the reference coordinate system a^*, b, c ($a^* = b \times c$). The crystallographic axes were located prior to irradiation by means of X-ray diffraction measurements. The four molecules of each type are magnetically equivalent along the b-axis and in the ac-plane; in any other direction there are two distinct sites. Thus in a general direction four magnetically distinct sites are expected (two of each type A and B).

The crystal structure of phenazine near 80 K was determined by Hirshfield and Schmidt [4]. The crystal is monoclinic with $a = 12{\cdot}967$, $b = 4{\cdot}981$, $c = 7{\cdot}056$ Å, $\beta = 109{\cdot}0°$, space group $P2_1/a$, and $Z = 2$. The two molecules in the unit cell are magnetically equivalent along the b-axis and in the ac-plane; in all other orientations they are distinct. The crystallographic axes were located by external morphology and by identifying the crystal planes with the help of a two-circle optical goniometer. ENDOR measurements were carried out in the reference coordinate system a, b, c^* ($c^* = a \times b$). The molecular structure of phenazine is shown in figure 1 (*b*).

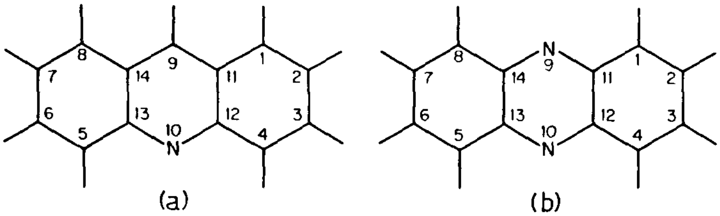

Figure 1. Molecular structure and numbering of the ring atoms of (*a*) acridine and (*b*) phenazine.

The crystals were X-irradiated at room temperature using a Machlett type OEG-60 X-ray tube operating at 40 kV, 20 mA. The optimum concentration of the radicals was obtained after the crystals were irradiated for about 80 hours. The irradiated crystals can be stored indefinitely in closed vials at room temperature without any significant decrease in the radical concentration.

ENDOR measurements were made at 77 K with our X-band superheterodyne spectrometer which is essentially the same as that described previously [5]. A TE_{101} rectangular cavity was modified in the following way for this ENDOR work. Two vertical columns of five straight gold plated brass posts of 0·5 mm diameter traverse (in the x-direction) the cavity, piercing the two end-walls. The posts are insulated from the end-walls by Araldite. They are connected by thin copper wires outside the cavity to form a single loop. One end of the loop is connected to the output of an ENI 3100L r.f. amplifier; the other end is soldered to the cavity to complete the r.f. circuit. In this design both the microwave magnetic field, H_1, and r.f. field H_2 are vertical, allowing the magnet to be rotated in the horizontal plane for studies of the anisotropy of the ENDOR spectra. The posts are everywhere perpendicular to the microwave electric field, which is in the y-direction, and have only a minor effect on the Q of the cavity. No net flux due to the microwave H_1 threads the loop; therefore, the loop does not harm the cavity Q. The spacing between the two columns (5 mm in our case) is determined by the sample size. The width of the cavity can be increased to accommodate larger spacing between the two columns. The cavity frequency for the TE_{101} mode is unaffected by the increased width. The space outside the rectangular cross section solenoid of posts, but inside the cavity, provides the return path for r.f. field lines. A similar construction of an ENDOR cavity operating in the TE_{201} mode has been reported by Castner and Doyle [6].

The crystal was mounted on a perspex wedge and fixed on to the side wall of the cavity using silicone grease, between the two columns of posts. Spectra were recorded at intervals of 2° (5° for phenazine) as the magnet was rotated about each of the reference axes. The most serious uncertainty in the ENDOR data is the absolute orientation of the crystal in the magnetic field. However, the reproducibility of the data with different crystals and the double check provided by the site-splittings present in the monoclinic crystallographic system indicate that ±1° is a reasonable estimate of this error. The uncertainties included with the results are based on statistics derived from the least-squares-fit [7] of the data to the spin hamiltonian given in equation (1).

3. Results and discussion

3.1. *The spin hamiltonian*

The spin hamiltonian for a radical in the magnetic field, B, can be expressed as

$$\mathscr{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} - \sum_n (g^{(n)} \mu_N \mathbf{B} \cdot \mathbf{I}^{(n)} - \mathbf{S} \cdot \mathbf{A}^{(n)} \cdot \mathbf{I}^{(n)}), \tag{1}$$

where $\mathbf{g}$ is the electron $\mathbf{g}$-tensor, $\mathbf{S}$ is the unpaired electron spin operator and $\mathbf{A}^{(n)}$ is the hyperfine coupling tensor of the nth nucleus; the summation includes all nuclei of spin $I^{(n)}$ and magnetic moment $g^{(n)}\mu_N I^{(n)}$, coupled to the unpaired electron. For the ENDOR transitions nuclear couplings can be treated independently of each other, except in some cases of very strong nuclear–nuclear coupling

[8]. Assuming an isotropic **g**-tensor, the observed proton ENDOR frequencies can be expressed by $\nu_\pm = |\nu_0 \pm A/2|$ for small hyperfine interactions (i.e. $A/2 < \nu_0$), or $\nu_\pm = |A/2 \pm \nu_0|$ for large hyperfine interactions (i.e. $A/2 > \nu_0$), where ν_0 is the N.M.R. frequency of the free nucleus. No ENDOR lines due to the hyperfine coupling of the unpaired electron with the nitrogen atom were observed in our study. All the observed lines arise from interactions with the protons. Only those lines appearing at the higher frequency side of ν_0 were used in the analysis.

3.2. *Experimental results*

In X-irradiated single crystals of acridine, for an arbitrary orientation of the magnetic field there were many closely spaced ENDOR lines in the frequency region 15–22 MHz and a maximum of four lines in the region 22–38 MHz; above 38 MHz no lines were observed. For calculations and graphical presentation ν_0 was set equal to 13·875 MHz and the observed transition frequencies were corrected accordingly. The E.S.R. and ENDOR spectra of an X-irradiated acridine single crystal for the magnetic field parallel to the *b*-axis are shown in figure 2. Not shown in this figure are the high frequency ENDOR lines arising from the hyperfine coupling due to $C_{(9)} - H$ proton in the radicals under investigation. The doublet splitting in the E.S.R. spectrum in this orientation is approximately 42 MHz, in very good agreement with the more accurate values of 41·54 MHz and 43·47 MHz, obtained for the two radicals (*vide infra*) from ENDOR measurements. As is evident from figure 2 (*b*) the spectral density in the low frequency region (15–22 MHz) is very high on account of the large number of protons with nearly equal spin densities. The spectrum is further complicated by the existence of two sets of chemically and electronically similar but crystallographically non-related molecules in the unit cell (cf. § 2).

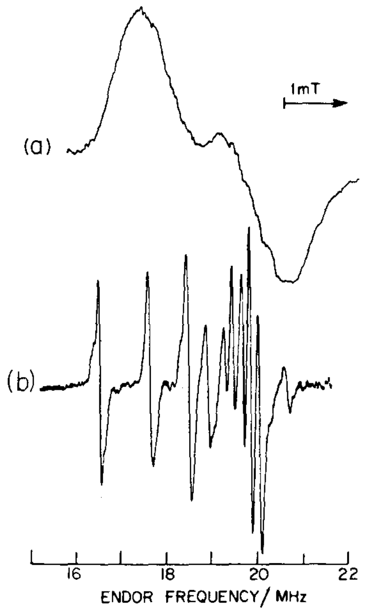

Figure 2. (*a*) First derivative X-band E.S.R. spectrum at room temperature and (*b*) ENDOR spectrum at 77 K of an X-irradiated single crystal of acridine II for the magnetic field parallel to the *b*-axis.

The E.S.R. and ENDOR spectra of an X-irradiated phenazine single crystal for the magnetic field parallel to the *b*-axis are shown in figure 3. Although the E.S.R. spectrum in this orientation appears quite well-resolved, the resolution was very much poorer in most other orientations. No useful data could, therefore, be obtained from the analysis of the E.S.R. spectra. As can be seen from figure 3, the ENDOR spectra were, however, quite well-resolved. A maximum of 14 ENDOR lines could be observed in an arbitrary orientation, coalescing into seven when the magnetic field was oriented along the *b*-axis or in the *ac*-plane. Besides these strong lines, there were other weaker ENDOR lines associated with each of the strong lines. The nature and origin of these weaker lines will be discussed in § 3.3.2.

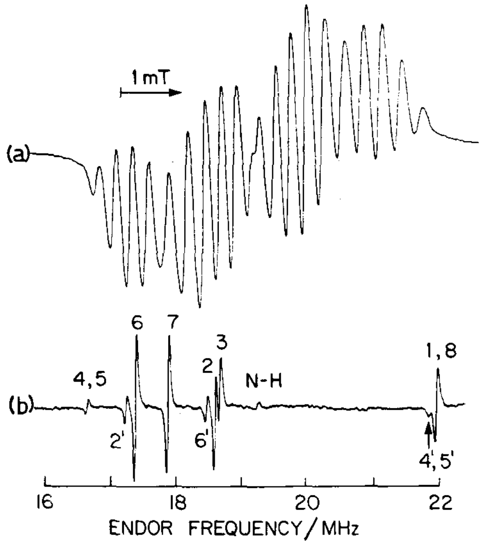

Figure 3. (*a*) First derivative X-band E.S.R. spectrum at room temperature and (*b*) ENDOR spectrum at 77 K of the N-hydrophenazinyl radical in an X-irradiated single crystal of phenazine for the magnetic field parallel to the *b*-axis. Assignment of the ENDOR lines is indicated. For detailed explanation of the lines with primed numbers, see the text.

The experimentally observed frequencies belonging to the same proton coupling were then fitted to the spin hamiltonian (1) with the least-squares-adjustment program LSF [7] using an IBM 370/168 computer. The E.S.R. spectrum in most orientations consists of an unresolved broad line. Therefore, the **g**-tensor could not be determined accurately. For convenience we used, therefore, the isotropic **g**-value of 2·0023 in place of the **g**-tensor. Approximately 120 data points were used to fit each tensor and the rms error was typically less than 20 kHz for acridine and 10 kHz for phenazine. The diagonalized forms of the hyperfine tensors thus calculated, along with their direction cosines, are presented in tables 1, 2 and 3.

3.3. *Assignment of the couplings and radical identification*

3.3.1. *N-hydroacridinyl radical*

The assignment of the hyperfine coupling tensors to specific protons is indicated in tables 1 and 2. At the outset we should note that these coupling tensors are typical of an aromatic π-radical. All hyperfine tensors have one principal axis in common, which is perpendicular to the molecular plane, as expected for a radical with the unpaired electron in a π-molecular orbital. We attempted to relate the directions of another component of the hyperfine tensors to various C–H bond directions in the undamaged crystal. Undoubtedly the largest coupling tensor is associated with $C_{(9)}$–H. However, because the unpaired electron is extensively delocalized over the entire molecule, the direct comparison of small coupling tensors with bond directions cannot yield unequivocal conclusions.

Four types of radicals are encountered in solid organic matter as a result of ionizing radiation, involving either removal or attachment of an electron, dissociation of covalently bonded atomic hydrogen, or association of atomic hydrogen on unsaturated positions of the non-radical molecules [9]. Of these the ionic radicals resulting from electron removal or attachment have been found to be stable only at low temperatures, and can, therefore, be ruled out in the present study. Of the remaining two possibilities, namely, the radicals produced either by the addition or removal of a hydrogen atom, only the former is relevant in this study because we observe more intramolecular proton couplings than can be accounted for

Table 1. Proton hyperfine interaction tensors for the N-hydroacridinyl radical in molecule *A* of X-irradiated single crystal of acridine II.

	Coupling MHz			Direction cosines‡		
Proton	Principal value†	Isotropic	Dipolar	*a**	*b*	*c*
1,8	+0·81	−7·21	+8·02	+0·372	∓0·067	+0·925
	−8·69		−1·48	−0·823	±0·437	+0·362
	−13·75		−6·54	−0·429	∓0·896	+0·107
2	+4·53	+10·00	−5·47	+0·144	±0·801	−0·580
	+9·70		−0·30	−0·813	±0·431	+0·393
	+15·77		+5·77	+0·566	±0·415	+0·713
3	−4·86	−10·48	+5·63	−0·591	∓0·672	−0·447
	−10·18		+0·30	−0·805	±0·448	+0·390
	−16·41		−5·93	+0·062	∓0·590	+0·805
4,5	+4·70	+9·20	−4·50	+0·274	∓0·274	+0·922
	+10·48		+1·28	−0·792	±0·479	+0·378
	+12·41		+3·21	+0·545	±0·834	+0·086
6	−4·71	−10·37	+5·65	−0·143	∓0·817	+0·559
	−10·10		+0·27	−0·801	±0·428	+0·419
	−16·29		−5·92	−0·581	∓0·388	−0·715
7	+4·55	+8·78	−4·23	+0·068	∓0·573	+0·817
	+9·48		+0·69	−0·828	±0·424	+0·367
	+12·31		+3·54	+0·556	±0·702	+0·446
9	−14·26	−30·20	+15·95	+0·353	∓0·104	+0·930
	−29·46		+0·74	−0·821	±0·442	+0·361
	−46·89		−16·69	−0·448	∓0·891	+0·070
10	−6·27	−10·81	+4·53	+0·306	±0·492	+0·815
	−8·72		+2·09	−0·920	±0·371	+0·121
	−17·43		−6·62	−0·243	∓0·778	−0·556

† Signs of the principal elements are assumed on the basis of INDO results. Uncertainty in the principal values is ±0·02 MHz except ±0·05 MHz for $H_{(9)}$.

‡ The two sign combinations chosen consistently relate one distinguishable crystal site to the other.

Table 2. Proton hyperfine interaction tensors for the N-hydroacridinyl radical in molecule *B* of X-irradiated single crystal of acridine II†.

	Coupling MHz			Direction cosines		
Proton	Principal value	Isotropic	Dipolar	*a**	*b*	*c*
1,8	+1·64	−7·65	+9·29	−0·297	±0·393	+0·870
	−9·75		−2·10	−0·853	±0·300	−0·427
	−14·84		−7·19	−0·429	∓0·869	+0·246
2	+4·50	+9·68	−5·18	+0·590	±0·669	−0·453
	+9·32		−0·36	−0·806	±0·449	−0·387
	+15·22		+5·54	−0·555	±0·592	+0·804
3	−4·66	−10·42	+5·76	−0·152	∓0·955	−0·255
	−10·25		+0·17	−0·892	±0·244	−0·380
	−16·35		−5·93	−0·426	∓0·170	+0·889
4,5	+4·56	+9·15	−4·59	−0·439	±0·096	+0·894
	+10·52		+1·37	−0·819	±0·452	−0·354
	+12·37		+3·22	−0·370	∓0·887	−0·277
6	−4·33	−9·89	+5·56	+0·540	±0·489	−0·685
	−9·69		+0·20	−0·841	±0·319	−0·436
	−15·64		−5·75	+0·005	±0·812	+0·584
7	+4·89	+9·32	−4·43	−0·323	∓0·119	+0·939
	+9·93		+0·61	−0·834	±0·505	−0·223
	+13·13		+3·81	+0·448	±0·855	+0·262
9	−13·85	−30·19	+16·35	−0·286	±0·392	+0·874
	−29·76		+0·44	−0·872	±0·272	−0·408
	−46·98		−16·79	−0·398	∓0·879	+0·264
10	−6·10	−10·73	+4·63	+0·280	±0·496	+0·822
	−8·67		+2·05	−0·930	±0·353	−0·104
	−17·41		−6·68	−0·238	∓0·793	+0·560

† See footnotes to table 1.

without an extra hydrogen added to the acridine molecule. Therefore, it can be concluded with reasonable certainty that the radical is formed as a result of the attachment of a hydrogen atom to one of the ring positions.

Now, if a hydrogen atom is attached to any of the carbon atoms (other than at positions 11–14) the resulting radical would have a methylene group with a large spin density on the adjacent carbon atom. These two protons of the methylene group (β-protons) should then have fairly large isotropic coupling. Moreover, if the hydrogen atom is added on any of the positions 1, 3, 6, 8 or 9, there would also be a large spin density in the π-orbital of the nitrogen atom, resulting in large anisotropic coupling with the ^{14}N nucleus. Although we cannot rule out that situation on the basis of our ENDOR results, because we have not observed any ENDOR lines due to nitrogen, still such a conclusion is possible on the basis of the E.S.R. results. In most orientations the E.S.R. spectrum is a structureless line with a maximum width of about 45–50 MHz. This certainly rules out the existence of a large coupling due to ^{14}N nucleus.

Another possibility is, of course, the attachment of a hydrogen atom to the nitrogen, resulting in a large spin density on the carbon atom at position 9. This possibility is indeed indicated by our experimental observations. The largest coupling we have measured has an isotropic component of 30·2 MHz. If the sign of the isotropic part is taken as negative, then the largest positive component of the dipolar coupling is in the direction of the $C_{(9)}$–H bond, the smallest component is perpendicular to the molecular plane. These characteristics are typical of an α-proton coupling in a π-radical [10]. The spin density in the π-orbital of the carbon atom at position 9 can then be calculated by the familiar McConnell relation [11]:

$$a_{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}} \rho_{\pi}, \qquad (2)$$

where a_{H} is the isotropic coupling, ρ_{π}, the spin density and $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ is the proportionality constant. Using a Q value of −63·5 MHz, we calculate a spin density of 0·475 at $C_{(9)}$.

To confirm that our radical identification is correct, INDO–MO calculations [12] were performed on several possible radical structures. Of the many radicals considered, only the one with the hydrogen atom added to the nitrogen yielded good agreement for the spin densities. Moreover, this radical has significantly lower total energy (INDO) as compared to all other structures considered. Thus we are fairly certain of the identity of the radical.

Table 3. Proton hyperfine interaction tensors for N-hydrophenazinyl radical in X-irradiated single crystal of phenazine.

		Coupling MHz		Direction cosines‡		
Proton	Principal value†	Isotropic	Dipolar	*a*	*b*	*c**
1,8	+2·64	−10·50	+13·14	+0·697	±0·249	−0·673
	−14·22		−3·72	−0·634	±0·652	−0·415
	−19·91		−9·41	−0·336	±0·716	−0·612
2	+3·38	+7·58	−4·20	−0·552	±0·003	+0·834
	+9·21		+1·63	−0·641	±0·639	−0·425
	+10·15		+2·57	−0·533	±0·769	−0·353
3	−4·01	−9·46	+5·45	−0·032	±0·483	+0·875
	−9·43		+0·03	−0·589	±0·698	−0·407
	−14·93		−5·47	−0·808	±0·529	+0·262
4,5	+2·42	+6·19	−3·77	+0·574	±0·643	−0·508
	+7·75		+1·56	−0·799	±0·576	−0·175
	+8·39		+2·20	−0·179	∓0·506	−0·844
6	−4·13	−9·62	+5·49	+0·700	±0·704	+0·121
	−9·58		+0·04	−0·603	±0·673	−0·428
	−15·15		−5·53	−0·383	±0·226	+0·896
7	+3·12	+7·20	−4·08	+0·782	±0·385	−0·490
	+8·83		+1·63	−0·583	±0·730	−0·357
	+9·64		+2·44	−0·220	±0·565	−0·796
10	−2·93	−8·50	+5·57	+0·286	±0·367	−0·885
	−9·79		−1·29	−0·799	±0·418	−0·432
	−12·79		−4·29	+0·529	±0·831	−0·174

† Signs of the principal elements are assumed on the basis of INDO results. Uncertainty in the principal values is ±0·01 MHz.

‡ The two sign combinations chosen consistently relate one distinguishable crystal site to the other.

After this work was completed Hiratsuka and co-workers reported polarized absorption and E.S.R. spectra of the N-hydroacridinyl radical (acridine C-radical in their parlance) produced by γ-irradiation of a stretched PVA film saturated with acridine [13]. They have identified the radical based on the agreement between the results of MO calculations and the optical absorption spectrum of the radical. In the X-irradiated single crystal of acridine we have observed optical absorption bands similar to those reported by them, confirming the nature of the radical.

The assignment of the remaining coupling tensors to the other protons is not as straightfoward. As can be verified from tables 1 and 2, all the couplings are of α-proton nature, with fairly small spin densities on the respective ring atoms. The assignment of these couplings has been accomplished on the basis of the direction cosines, the sign of the isotropic part, symmetry considerations and comparison with INDO results. The ENDOR lines assigned to the N–H proton have anomolously low intensity and large linewidth as compared to all other lines. This may be an indirect effect of the fast spin lattice relaxation of the ^{14}N nucleus.

3.3.2. *N-hydrophenazinyl radical*

Based on structural and chemical similarities between acridine and phenazine, N-hydrophenazinyl radical should be the first choice to be considered in X-irradiated phenazine. If a hydrogen atom is attached at $N_{(10)}$, then the resulting radical would have a large spin density on the π-orbital of $N_{(9)}$. In the case of N-hydroacridinyl radical the large spin density ($\sim 0{\cdot}5$) on $C_{(9)}$ was verified by determination of the hyperfine tensor of $H_{(9)}$. A large π-spin density on $N_{(9)}$ would give rise to large anisotropic hyperfine coupling with the ^{14}N nucleus. However, on account of the poor resolution of the E.S.R. spectra, the ^{14}N coupling tensor could not be determined. The orientation dependence of the E.S.R. linewidth and spectral spread indicate the highly anisotropic nature of the coupling. Moreover, none of the proton hyperfine couplings observed in this radical was large enough to account for the E.S.R. spectral spread. These observations point to a large π-spin density on the nitrogen atom.

All the proton hyperfine tensors in this radical are typical of an aromatic π-radical, since they all have one principal axis in common, which is perpendicular to the molecular plane. For protons attached to carbon atoms expected to have positive spin densities, the directions of the largest positive component of the dipolar tensor are very nearly parallel to the C–H bond directions in the undamaged crystal. For other protons, deviations from the C–H bond directions were observed. All the hyperfine tensors could, however, be assigned to specific protons without much difficulty on the basis of the direction cosines, the sign of the isotropic part, symmetry considerations and comparison with the INDO results.

In figure 3 (*b*) the weaker lines with primed numbers do not belong to the same radical as the other lines. This was verified by selectively saturating different portions of the E.S.R. spectrum. In all orientations these lines were about five times weaker than the main lines. Although only three such weak lines are seen in figure 3 (*b*), all the main lines had such accompanying weaker lines, but they were clearly resolved only in some orientations. Analysis of these lines showed that they belong to a radical which is almost identical in structure and orientation to the N-hydrophenazinyl radical.

Because of the centre of inversion of the phenazine molecule, the two nitrogen atoms are completely equivalent in the undamaged crystal. Addition of hydrogen to either $N_{(9)}$ or $N_{(10)}$ should, therefore, yield radicals identical in all respects. ENDOR lines from the symmetry-related protons should, therefore, be indistinguishable for the two radicals. If there are some slight conformational differences between the two radicals because of constraints in the solid state, they would yield a different set of ENDOR lines for the corresponding protons. We propose, therefore, that these weaker lines belong to the same type of radical, but with the hydrogen atom added on $N_{(9)}$ resulting in a slight conformational change with respect to the radical formed by the addition of hydrogen to $N_{(10)}$.

It is difficult, however, to understand the intensity differences between these two sets of ENDOR lines. Since the structures of the two radicals are identical, the relaxation pathways in both the radicals must be similar, leading to similar ENDOR enhancements. The different intensities, therefore, indicate different concentrations of the two radicals in the crystal. As the two nitrogen atoms are completely equivalent in the undamaged crystal, it is hard to understand why the addition of a hydrogen atom to one of them is more favourable than to the other. Similar intensity differences were observed by Böhme and Wolf [14] in the α-hydronaphthyl radicals produced by X-irradiation of naphthalene single crystals. They ascribe the intensity difference to the different rates of formation of the two symmetry-related radicals.

3.4. *Spin densities*

Spin densities on the ring atoms were calculated from the isotropic coupling using McConnell relation (2) with $Q_{CH}{}^{H} = -63{\cdot}5$ MHz and $Q_{NH}{}^{H} = -78{\cdot}5$ MHz. These spin densities are tabulated in table 4, along with those obtained from the INDO calculations. The agreement can be deemed excellent considering the INDO approximations. The carbon atoms expected to have negative 2p spin densities have unusually large spin populations. This is especially true of the N-

Table 4. Spin densities on the ring atoms of the N-hydroacridinyl and phenazinyl radicals

	N-hydroacridinyl radical			N-hydrophenazinyl radical	
	ρ_π(observed)				
Position	Molecule *A*	Molecule *B*	ρ_π(INDO)	ρ_π(observed)	ρ_π(INDO)
1,8	+0·114	+0·120	+0·144	+0·165	+0·152
2	−0·157	−0·152	−0·087	−0·119	−0·095
3	+0·165	+0·164	+0·142	+0·149	+0·146
4,5	−0·145	−0·144	−0·089	−0·097	−0·082
6	+0·163	+0·156	+0·161	+0·151	+0·146
7	−0·138	−0·147	−0·101	−0·113	−0·095
9	+0·475	+0·475	+0·473	—	+0·584
10	+0·138	+0·137	+0·208	+0·108	+0·171
11,14	—	—	−0·127	—	−0·127
12,13	—	—	+0·171	—	+0·129

hydroacridinyl radicals. A spin density of $-0{\cdot}107$ at one of the carbon atoms was reported for the α-hydronaphthyl radical [14].

3.5. *Direction cosines*

As mentioned earlier, for all radicals reported in this study, all tensors have an axis in common, indicating that the unpaired electrons in these radicals occupy molecular orbitals with π-symmetry. However, mention must be made of several significant deviations from collinearity of these common principal directions. First of all, the dipolar component of smallest magnitude for the N–H proton in all the radicals show a deviation of approximately 15°, indicating that the N–H bond may be bent with respect to the molecular plane. This is further confirmed by comparing the directions of the largest positive dipolar component, expected to be along the N–H bond direction, with those calculated from crystallographic data. Our results thus indicate that the hydrogen atom that is added onto the nitrogen, is out of the molecular plane by approximately 15°.

In the N-hydroacridinyl radical derived from molecule *A*, the common directions for all the C–H proton tensors are collinear within experimental uncertainties; however, significant deviations are present for molecule *B*. Notable deviations are observed for protons 2, 7 and 4, 5 (10°, 17° and 11°, respectively). These deviations are probably caused by the non-planarity of molecule *B* in the undamaged crystal.

In N-hydrophenazinyl radical significant deviation from collinearity is observed only for the tensor associated with protons 4 and 5. No relevant explanation for this deviation can be given, except that the ENDOR data for these two protons are less accurate because of very low signal intensity (cf. figure 3 (*b*)).

4. CONCLUSIONS

As can be verified from tables 1, 2 and 4, there are small differences in the corresponding values for the radicals produced from the two types of molecules *A* and *B* in acridine. Although these differences are hard to justify on a quantitative basis, they can be attributed to the slight differences in the structures of molecules *A* and *B*. The isotropic coupling of $C_{(9)}$–H is equal (within experimental error) in both the molecules. However, the dipolar parts of this coupling tensor are slightly different. This can arise from the fact that molecule *A* is more planar than *B*, and hence the contribution to the dipolar tensor from the spin densities on atoms at positions other than 9 would be different for the two molecules. Similar arguments would have to be invoked to justify the differences in the smaller couplings. The dipolar part of the tensors for all the protons were calculated analytically by the method of McConnell and Strathdee [15] for the two molecules separately. However, the accuracy of these calculations is not good enough to compare such small differences. Therefore, no further effort was made to explain them.

As expected, the spin density distribution in the N-hydrophenazinyl radical is quite similar to that found in the acridinyl radical. Although the spin density on $N_{(9)}$ in the phenazinyl radical was not experimentally determined, the INDO calculations indicate that it is slightly larger than on $C_{(9)}$ in the acridinyl radical (cf. table 4). This difference can probably be justified by the difference in the electronegativities of the two atoms. Accordingly, the spin densities on the other atoms in the two radicals are also slightly different.

Whereas there is little doubt about the identity and nature of the radicals discussed here, the mechanism of their formation cannot be ascertained from the present study. Most probably ionic species are produced as primary radicals as a result of the impact of X-rays. As these ionic radicals are unstable at room temperature, they undergo proton addition to form the radicals identified in this study. However, this can be verified only by low-temperature irradiation studies. There is little we can say about the source of the hydrogen atoms. They are probably extracted from other molecules. However, no hydrogen abstraction radicals are identified in the present work. In some orientations there were some weak ENDOR lines which did not belong to the hydrogen addition radicals. However, these lines could not be studied in detail because of their very poor intensity and overlap with other prominent lines. These weak lines most certainly belong to another radical the nature of which we cannot ascertain at present.

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