Photochemical Studies. XVI.¹ Second Moment Analysis of the Electron Spin Resonance Spectra of Radicals Formed by Ultraviolet Irradiation of 9-Phenylacridine and of Acridine

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The irradiation of 9-phenylacridine in methanol, ethanol, or ether leads to the formation of the 9-phenylacridinyl radical. In methanol- d_4 , the radical formed is the singly deuterated analog. The structure of these radicals, which exhibit a hyperfine structure in their e.s.r. spectra measured at 233 °K, is supported by simulation of the spectra using calculated spin densities. The agreement between the experimental and theoretical second moment values of the deuterated radical indicates that the parameters previously chosen for the calculation of the theoretical second moments of pyridinyl-type radicals derived from six-membered ring azaaromatics are suitable and that the second moment method can be used in studies of radicals of this type. We conclude that acridine irradiated in methanol- d_4 leads to the formation of the singly deuterated acridinyl radical.

L'irradiation de la phényl-9 acridine dans le méthanol, l'éthanol ou l'éther, a conduit à la formation du radical phényl-9 acridinyle. Dans le méthanol- d_4 , le radical formé est l'analogue comportant un seul deutérium. La structure de ces radicaux, dont les spectres r.p.e. montrent une structure hyperfine lorsqu'enregistrés à 233 °K, est en accord avec la reconstitution des spectres à partir des densités de spin calculées. L'accord entre les valeurs expérimentales et théoriques des seconds moments pour les radicaux deutériés montre que les paramètres choisis antérieurement pour le calcul des seconds moments théoriques des radicaux du type pyridinyle obtenus de cycles azaaromatiques à six membres sont cohérents et que la méthode des seconds moments peut être utilisée pour l'étude des radicaux de ce type. On conclut alors que l'acridine irradiée dans le méthanol- d_4 conduit à la formation du radical acridinyle comportant un seul deutérium. [Traduit par le journal]

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The second moment method (2) was employed in the characterization of radicals formed by u.v. irradiation of six-membered ring azaaromatics in protic solvents in several of our previous studies. The radicals formed from pyridine (3), quinoline (4), isoquinoline (4), quinoxaline (5), pyrazine (5), pyrimidine (6), phthalazine (7), and cinnoline (7) are stable only in glassy matrices and give no hyperfine splitting in their e.s.r. spectra. On the other hand, the irradiation of 9-phenylacridine in ether, methanol, methanol- d_4 , or ethanol leads to radicals stable at room temperature, with hyperfine splittings in the spectra. We have simulated the spectra of these radicals and have found that there is good agreement between the experimental second moment of the radical formed by u.v. irradiation of 9-phenylacridine in methanol- d_4 and its theoretical value calculated from the equation used previously for unstable radicals, with the same parameters (3–7).

The main goal of this paper is to show that, if cautiously used, the second moment method can be an efficient tool in studies of radicals derived from six-membered ring azaaromatic compounds. Zanker and Erhardt (8) have already studied the e.s.r. spectra formed by u.v. irradiation of 9-phenylacridine and of 9-phenylacridane



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¹For parts XIII, XIV, and XV of this series, see ref. 1 (*a*), (*b*), (*c*) respectively.



FIG. 1. Experimental (A) and simulated e.s.r. spectra (B) of 9-phenylacridinyl radical II.

in ethanol at 173 °K, but they did not prove the structure of the radicals formed.

The structure which we suggest for the radical derived from 9-phenylacridine is in complete agreement with the structures known from the many previous photochemical studies of the acridine system (for a review on acridine photochemistry, see ref. 9). The π -radicals in the case of 9-phenylacridine are I and II. All these radicals contain sp² hybridized N and C-9 atoms.

Results

U.v. irradiation of 9-phenylacridine in 0.2 M solution at 233 °K in methanol, ethanol, or ether gives rise to an e.s.r. spectrum containing eight bands with a total width of 23.45 G. When the

solvent is methanol- d_4 the spectrum (for the same concentration of 9-phenylacridine) has only seven bands. Its total width is 20.90 G.

If the temperature is lowered following the irradiation, the hyperfine structure disappears rapidly. When the sample becomes glassy, only one band is observed. The width of the band is larger when the solvent is methanol than when it is methanol- d_4 . Otherwise, both spectra are identical.

When 9-phenylacridine is irradiated at a lower concentration, the spectrum has a much more complex hyperfine structure which is a function of the concentration and of the temperature. Figures 1a and 2a show the e.s.r. spectra obtained by irradiation of 0.04 M solutions of

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FIG. 2. Experimental (A) and simulated e.s.r. spectra (B) of 9-phenyl-10-deuteroacridinyl radical IV.

9-phenylacridine in methanol and in methanol- d_4 , respectively, at 233 °K.

The spectra obtained by irradiation of a 0.2 M solution of acridine in methanol or ether are very similar and are observed only at a temperature lower than 173 °K. The signal consists of a broad band with a very poorly resolved hyperfine structure which is different when methanol- d_4 is used as the solvent instead of methanol. It is larger in methanol than in methanol- d_4 .

Structure of the Radical Formed by U.V. Irradiation

From our earlier e.s.r. results (3-7) and from

the knowledge of acridine photochemistry (9), the observed signals can be identified as those of the π -radicals I and II in the case of 9-phenylacridine and of III and IV in the case of acridine. The C-9 and N atoms in these radicals are sp² hybridized. The identification is supported by simulation of the spectra having hyperfine structure and by comparison of the experimental and theoretical second moments. In both cases, calculated spin densities of the radicals were used.

Calculation of Spin Densities

The spin densities were calculated using the McLachlan method (10) as was done in our pre-

vious studies (4, 5). The parameters were taken in the usual form, *i.e.*

$$\alpha_{\rm N} = \alpha_{\rm C} + h\beta_{\rm C-C}$$

(where α_N is the Coulomb integral of the nitrogen, α_C is the Coulomb integral of an electron in the $2p_z$ atomic orbital of carbon and β_{C-C} is the resonance integral of a C—C bond in benzene)

$$\beta_{C-N} = k\beta_{C-C}$$

and

 β_{C-N} being the resonance integral of the C—N bond.

The numerical values of the coefficients h and k used in our study were: h = 0.9, k = 1, and $\lambda = 1.2$ where λ is the parameter of the interatomic exchange integral. Its value is that already used by Lunazzi *et al.* in the case of the quinoline and isoquinoline anion radicals (11).

In the case of 9-phenylacridine, the value of the resonance integral between C-9 and C-15 is certainly different from β_0 , being a function of the interatomic distance between C-9 and C-15 and of the angle θ between the planes of the phenyl substituent and of the acridine ring. According to Dewar (12), $\beta = \beta_0 \cos \theta$. Wheeler and co-workers (13) have found that the angle of the plane of the phenyl substituent and of the 9,10-diphenylanthracene anion radical and 61° for the corresponding cation radical. They assumed all the interatomic distances between adjacent carbons as equal. In our calculations we have chosen $\beta = 0.3 \beta_0$ which corresponds to $\theta \simeq 70^\circ$.

Table 1 shows the calculated spin densities for 9-phenylacridinyl radicals, I and II, whereas Table 2 gives the calculated spin densities for acridinyl radicals III and IV.

Simulation of the Spectra with Hyperfine Structure

Spectra obtained from 9-phenylacridine in the liquid phase have been simulated. A series of theoretical coupling constants were calculated from spin densities by varying the Q parameter until the simulated spectra matched the experimental spectrum. The values at which this occurs are: $Q_{C-H} = 25.0 \text{ G}$; $Q_N = 28.3 \text{ G}$; $Q_{N-H} = 31.8 \text{ G}$. These optimized values of Q_N and Q_{CH} are nearly equal to those which were used for the calculation of the theoretical second moment of quinoline (4), isoquinoline (4), and quinoxaline (5) ($Q_N = 28.0 \text{ and } Q_{CH} = 24.5 \text{ G}$). The value chosen for Q_{N-H} is also very similar to the value (32.0) used by Malrieu and Pullman for a sp²

Position	$h = 0.9; k = 1; \lambda = -1.2; \beta = 0.3$		
1	0.13770		
2	-0.01658		
3	0.08423		
4	0.03149		
5	0.03150		

TABLE 1.

9-Phenylacridinyl radical*

Spin densities calculated for

5	0.05150
6	0.08422
7	-0.01658
8	0.13770
9	0.42564
10(N)	0.11191
16	0.01049
17	-0.00349
18	0.01088
19	-0.00349
20	0.01050

*Width: experimental 23.95 G; theoretical 24.31 G.

TABLE 2. Acridinyl radical

Position	Spin densities calculated for $h = 0.9$; $k = 1$; $\lambda = -1.2$		
1	0.14312		
2	-0.01862		
3	0.08720		
4	0.03167		
5	0.03168		
6	0.08719		
7	-0.01862		
8	0.14311		
9	0.44065		
10(N)	0.11049		

hybridized nitrogen (14). Variation of width of the Lorentzian bands can be used to simulate the influence of temperature and of concentration upon the shape of the spectra of the radicals. Figures 1b and 2b contain the simulated spectra of radicals I and III for a 0.04 M solution and a temperature 233 °K. The band width in this case is 0.25 G. The coupling constant of deuterium has been neglected in the simulation of radical II. There is good agreement between the experimental and theoretical total width of the spectrum of radical I:23.45 and 24.31 G, respectively. The experimental total width of the spectrum of radical II is 20.90 G, the theoretical one 20.75 G. Assuming that $a_{N-D} = 0.15 a_{N-H}$, we deduce experimentally $a_{N-H} = 3.64$ G. The theoretical value is $a_{N-H} = 3.56$ G.

The agreement between the theoretical and experimental results supports the postulated structure of radicals I and II and indicates that the parameters used in our previous calculations

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TABLE 3. Second moment (G^2)

Solvent	Radical II		Radical IV	
	Experimental	Theoretical	Experimental	Theoretical
Methanol	42		73	
Methanol- d_4	38	31	66	65
Ethanol	41		72	
Ether	45		72	

of spin densities and of coupling constants are consistent with the experimental data.

Second Moments of the Spectra with no

Hyperfine Structure

To test the validity of the second moment method, which experimental factors obliged us to use in earlier studies (4, 5), and the values of the parameters used in the calculations of the theoretical second moment, we have determined the experimental and theoretical second moment of the spectra obtained by irradiation of 9phenylacridine and acridine in a glassy matrix at 113 °K. The experimental second moments have been calculated as about g = 2.0023 for solutions in methanol, methanol- d_4 , and ether. The results are summarized in Table 3. Note that similar values are obtained for all hydrogenated solvents. When the solvent is methanol- d_4 , the second moment is smaller than in methanol, because the N-D coupling constant is lower than the N-H constant although this difference is rather small.

We have calculated the theoretical second moments of radicals II and IV, using the same equations as previously (4, 5). They are deduced from Vincow and Johnson's work (2): the second moment M_2 of radical II is

$$M_2 = M_{2\rm H} + M_{2\rm g} + \frac{\sigma^2}{4} + M_{2\rm N} + M_{2\rm ND}$$

 $M_{2\rm H} = \sum_{i} n_i \, 174 \, \rho_i^2$ contribution of the

 $M_{2N} = 914 \rho_N^2$ contribution of the nitrogen $M_{2ND} \simeq 0$

For the sum of $M_{2g} + (\sigma^2/4)$, M_{2g} being the contribution of the anisotropy of g and σ the width of the "monocristalline band", we took 10 G² as we did previously.

The theoretical value of the second moment calculated from the previous equations is 31 G^2 for radical II, 65 G^2 for radical IV. They agree with the experimental values: 38 and 66 G^2 ,

respectively. Using the second moment method on spectra with unresolved hyperfine structure we conclude that II is the radical formed by u.v. irradiation of 9-phenylacridine in methanol- d_4 and IV is the radical formed under the same conditions from acridine.

Conclusions

The results obtained by simulation of spectra and by calculation of the second moment of the spectra confirm our hypothesis concerning the structure of the radicals formed by u.v. irradiation of 9-phenylacridine in protic solvents.

Radicals I and II are the first to be described of the pyridinyl type, obtained by u.v. irradiation of azaaromatic compounds in a neutral protic solvent, which are stable at room temperature and have a hyperfine structure.

In previous work (3–7) we were unable to obtain radicals in phase other than the glassy one. The spectra so formed had no hyperfine structure and so we were forced to use the second moment method to characterize them and thus were obliged to choose many parameters empirically. The validity of the conclusions made from those calculations was not, therefore, certain.

In this study, we were able to identify a radical with a hyperfine structure and to prove its structure unambiguously by simulation of its spectra. This demonstrates that the parameters chosen for the calculations of the theoretical second moments of the radicals previously studied are reasonable and that the conclusions we made are correct. Thus we are now able to use the second moment method to characterize the structure of pyridinyl type radicals derived from six-membered ring azaaromatic compounds even if their spectra have no hyperfine structure. We conclude from the second moment results that the radical formed by u.v. irradiation of acridine in methanol- d_4 is IV and must be III in methanol and ether.

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Experimental

Products and Solvents

9-Phenylacridine was synthetized by Dr. L. Ivan according to the method of Bernthsen (15). The reaction product was washed with methanol, recrystallized four times from methanol, and dried. Fluka acridine was used without further purification.

Methanol used was Merck methanol for analysis; 100% ethanol and ether were commercial products redistilled four times. Ether was dried over sodium.

Methanol- d_4 was obtained from "Spectrometrie. spin et technique". Its purity was greater than 99%.

Samples and Irradiation

The experimental technique was the same as reported previously (4).

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