

Synthesis, Characterization, and Electrochemistry of Some Acridine-1,8-dione Dyes

N. Srividya,[†] P. Ramamurthy,^{*,†} P. Shanmugasundaram,[‡] and V. T. Ramakrishnan^{*,‡}

Departments of Inorganic Chemistry and Organic Chemistry, School of Chemistry, University of Madras, Madras 600 025, India

Received January 3, 1996[⊙]

The synthesis, characterization, and electrochemical behavior of some acridinedione derivatives are reported. Cyclic voltammetric studies show that all the dyes undergo irreversible oxidation irrespective of the substitution on the nitrogen. The product formed on oxidation is the aromatic derivative in the case of N-H compounds and the acridinium salt in the case of the N-substituted compounds, which have been isolated and characterized. Formation of an intermediate carbon-centered radical is observed as evidenced by ESR spin-trapping experiments. A mechanistic scheme for the electrochemical oxidation is proposed. On carrying out reduction after oxidation, different products are formed depending on the substitution on the nitrogen. There is no reduction of the oxidized product in the case of N-H compounds, and compounds with substitution on nitrogen undergo reduction consistent with the observation in *N*-alkylpyridinium salts.

Introduction

Studies on the electrochemical characteristics of laser dyes are very few. Han made a brief study of fluorescent molecules which could be used as laser dyes.¹ The electrochemistry of some selected coumarin, rhodamine, and oxazine types of laser dyes were studied by Bard and Park.² Dye lasers with an electrochemical control of radiation parameters have been shown to have achieved stimulated emission in a broader spectral region.³ The spectral interval of dye laser tuning without changing the dye solution was possible by electrochemical methods⁴ showing that the electrochemical phenomena could be successfully used for improving the dye laser tuning. Detailed investigations involving a comparison of the redox potentials to the spectral characteristics have been studied in cyanine and thiocyanine dyes.⁵ In this paper we report the synthesis and electrochemical characteristics of acridine-1,8-dione dyes (AD). These dyes have been shown to have very high lasing efficiencies^{6,7} and are also interesting in view of the electrochemical behavior of heterocyclic compounds. They have been used as electron donors and electron acceptors^{8–10} and in the photoinitiated polymerization¹¹ of acrylates and methacrylates. They are also interesting because of the similarity in the properties with those of 1,4-dihydropyridines, which have similarities in structure to the biologi-

cally important compounds such as NADH and NADPH. The electrochemical oxidations of dihydropyridines, NADH, and related compounds have also received greater attention. Blaedel and Haas¹² studied the electrochemical oxidation of some NADH and structurally similar compounds. Other investigators have concentrated on the electrochemical oxidation of NADH, NADPH, and related compounds in aqueous and nonaqueous solutions and at different pH.^{13–15} The effect of substitution on the oxidation of 1,4-dihydropyridines was studied by Skala et al.¹⁶ The first unambiguous evidence for the formation of the electrolytically generated cation radical of 1,4-dihydropyridine in acetonitrile was demonstrated by Klima et al.¹⁷ The mechanistic aspects of the electrochemical oxidation of 1,4-dihydropyridines and NADH and its analogs have been studied in aqueous media at glassy carbon, pyrolytic graphite, and platinum electrodes.¹⁸ Different electrochemical techniques such as DC voltammetry, cyclic voltammetry, and coulometry were used by Abou-Elenien et al.¹⁹ to investigate the oxidation and reduction properties of different dihydropyridine and pyridine derivatives. Pragst et al.²⁰ studied the anodic dehydrogenation of 1,4 dihydropyridine by electrogenerated chemiluminescence. Ludvik et al.²¹ studied the influence of substituents on the oxidation potentials and proposed a suitable mechanism for the oxidation of 1,4-dihydropyridines. Klima et al.²² used the spin-trapping method for the identification of radical

[†] Department of Inorganic Chemistry.

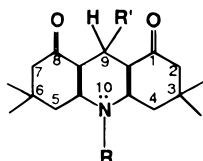
[‡] Department of Organic Chemistry.

[⊙] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

- (1) Han, M. V. *Compt. Rend.* **1971**, *273B*, 777.
- (2) Park, S. M.; Bard, A. J. *J. Electroanal. Chem.* **1977**, *77*, 137.
- (3) Tomin, V. I.; Nemkovich, N. A.; Rubinov, A. N. *Kvantovaya Elektron.* **1978**, *5*, 986.
- (4) Rubinov, A. N.; Tomin, V. I. *Spectrosc. Lett.* **1978**, *11*, 951.
- (5) Jamil, A.; Astin, K. B. *Dyes Pigm.* **1988**, *9*, 217.
- (6) Prabakar, K. J.; Ramakrishnan, V. T.; Sastikumar, D.; Selladurai, S.; Masilamani, V. *Ind. J. Pure Appl. Phys.* **1991**, *29*, 382.
- (7) Shanmugasundaram, P.; Murugan, P.; Ramakrishnan, V. T.; Srividya, N.; Ramamurthy, P. *Heteroat. Chem.* **1996**, *7*, 17.
- (8) Timpe, H. J.; Ulrich, S.; Ali, S. *J. Photochem. Photobiol. A: Chem.* **1991**, *61*, 77.
- (9) Timpe, H. J.; Ulrich, S.; Fouassier, J. P. *J. Photochem. Photobiol. A: Chem.* **1993**, *73*, 139.
- (10) Ulrich, S.; Timpe, H. J.; Fouassier, J. P.; Morlet-Savary, F. *J. Photochem. Photobiol. A: Chem.* **1993**, *74*, 165.
- (11) Timpe, H. J.; Ulrich, S.; Decker, C.; Fouassier, J. P. *Macromolecules* **1993**, *26*, 4560.

- (12) Blaedel, W. J.; Haas, R. G. *Anal. Chem.* **1970**, *42*, 918.
- (13) McNamara, F. T.; Nieft, J. W.; Ambrose, J. F.; Huyser, E. S. *J. Org. Chem.* **1977**, *42*, 988.
- (14) Leduc, P.; Thevnot, D. *Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 543.
- (15) Braun, R. D.; Santhanam, K. S. V.; Elving, P. J. *J. Am. Chem. Soc.* **1975**, *97*, 2591.
- (16) Skala, V.; Volke, J.; Ohnaka, V.; Kuthan, J. *Collect. Czech. Chem. Commun.* **1977**, *42*, 292.
- (17) Klima, J.; Kurfurst, A.; Kuthan, J.; Volke, J. *Tetrahedron Lett.* **1977**, *31*, 2725.
- (18) Moiroux, J.; Elving, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 21.
- (19) Abou-Elenien; Reiser, J.; Ismail, N.; Wallenfalls, K. *Z. Naturforsch.* **1980**, *36B*, 386.
- (20) Pragst, F.; Kaltfofen, B.; Volke, J.; Kuthan, J. *J. Electroanal. Chem.* **1981**, *119*, 301.
- (21) Ludvik, J.; Klima, J.; Volke, J.; Kurfurst, A.; Kuthan, J. *J. Electroanal. Chem.* **1982**, *138*, 131.
- (22) Klima, J.; Ludvik, J.; Volke, J.; Krikava, M.; Skala, V.; Kuthan, J. *J. Electroanal. Chem.* **1984**, *161*, 205.

intermediates formed on electrochemical oxidation of 1,4-dihydropyridines. The electrochemical study was carried out using acridinediones because a knowledge of the electrochemical redox potentials is important in the process of ascertaining laser dye stability and reactivity and could give an insight into the feasibility of other reactions using these compounds. The products obtained on electrolysis have been isolated and characterized. The chemical oxidation does not yield a single desired product in the case of N-substituted compounds, whereas the electrochemical oxidation yields a single product of the type III. Therefore a synthetic pathway by the electrochemical method to yield I, II, and III is reported.



1. R=H ; R'=H
2. R=H ; R'=CH₃
3. R=H ; R'=C₆H₅
4. R=CH₃ ; R'=H
5. R=CH₃ ; R'=CH₃
6. R=CH₃ ; R'=C₆H₅
7. R=C₆H₅ ; R'=H
8. R=C₆H₅ ; R'=CH₃

Results and Discussion

Synthesis of Acridinediones 1–8. The condensation of ethyl acetoacetate with aliphatic aldehydes and ammonia to yield dihydropyridines was known as early as 1882.²³ The formation of the enamino moiety by such a condensation has led to the formation of the acridinedione dyes. The dyes chosen for the study have been previously reported as a class of laser dyes.^{6,7,24} Although their syntheses have already been reported, the present method is able to afford considerable yields of the product and also it does not give a mixture of products to complicate the separation process. The condensation of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with aldehyde furnished the tetraketone, which on reaction with amine or ammonia under suitable conditions yields the acridinedione. The condensation reactions, in general, were carried out under reflux conditions in acetic acid with or without methanol. The 10-unsubstituted acridinediones were synthesized by the reaction of the tetraketone with aqueous ammonia or ammonium acetate in acetic acid.

The ¹H NMR spectra of the acridinediones in general show the characteristic signals. The methyl groups present in the 3 and 6 positions due to 12 protons appear as a singlet around δ 0.9–1.0. The protons at the 2 and 7 positions and at the 4 and 5 positions appear around δ 2.3–2.5 as singlets in general. The acridinediones **3** and **6** show the C₂ and C₇ methylene protons as an AB quartet possibly due to the phenyl substituent at the 9 position. For compound **5**, an AB quartet is seen at δ 2.2–2.7 which is probably due to C₂/C₇ methylene protons. This splitting may be due to the effect of the 9-methyl

Table 1. Electrochemical Data^a

compd	E_{pa} (V) vs Ag/AgCl (air-equil)	E_{pa} (V) vs Ag/AgCl (argon-sat)
1	1.16, 0.97	1.17, 0.93
2	1.18	1.33, 1.16
3	1.25	1.26
4	0.91	1.03, 0.93
5	1.05	1.16
6	1.19	1.24
7	1.17, 1.01	1.18, 1.06
8	1.18	1.19

^a Recorded at a scan rate of 200 mV/s.

substituent which might assume a *cis* geometry with the N-methyl substituent. The 9 and 10 substituents of 9-methyl-10-(4-methylphenyl)acridinedione have been found to have the *cis* geometry as confirmed by X-ray crystallographic studies.²⁵ The signal due to the *gem*-dimethyl group is seen as a singlet in general, which however is distinguished as two singlets in the case of compounds **3**, **5**, and **6**, which must be due to a 9-phenyl or methyl substituent. This is analogous to the effect of 2-methylphenyl or 2-chlorophenyl substituent on the nitrogen of the acridinedione system which makes the C₄ (and C₅) methylene protons exhibit geminal coupling.²⁴ The C₉ methylene appears as a singlet at δ 3.1 in general whereas in the case of 9-phenyl compounds **3** and **6** the C₉ proton is seen at δ 4.85 and 5.2, respectively.

A. Electrochemical Studies. All the dyes chosen in the present study undergo irreversible oxidation. The oxidation potentials obtained for compounds **1–8** are given in Table 1. Solutions of the dyes in acetonitrile (1 mM) were chosen for the cyclic voltammetric studies. Substitution in the 9 position causes the oxidation peak to shift to a more positive potential, indicating a decrease in the ease of oxidation. Such a behavior has been attributed to steric factors based on the observation made by Stradins et al.²⁶ in the case of 1,4-dihydropyridines. Similar arguments can be extended to the acridinediones because the potentials for compounds **1–3** and **4–6** are shifted to positive potential as the substituent in the 9 position is varied from H to methyl to phenyl. Substitution on the heterocyclic nitrogen by a methyl group causes the peak to shift to less positive potentials. The electron-releasing substituent on the heterocyclic nitrogen favors oxidation as seen by the lower oxidation potential of **4** as compared to **1** and **7**.

There is a difference in the shape of the cyclic voltammograms when oxidation is carried out in air-equilibrated and argon-saturated conditions. In the case of compounds **1** and **7**, two well-defined peaks are obtained in both air-equilibrated and argon-saturated conditions. Methyl substitution on the nitrogen or in the 9 position (compounds **2** and **4**) shows two peaks in argon-saturated conditions but a single peak under air-equilibrated conditions. In the case of other compounds, either two peaks which are not very distinct or broad cyclic voltammograms are obtained in an argon atmosphere, but a sharp single peak is obtained in air-equilibrated conditions. Also the peaks are shifted to a more positive potential in argon-saturated conditions, thereby showing that the oxidation is favored by the presence of oxygen. Compounds containing two hydrogens in the 9 position

(23) Hantzsch, A. *Justus Liebigs Ann. Chem.* **1882**, 215, 1.

(24) Shanmugasundaram, P.; Prabakar, K. J.; Ramakrishnan, V. T. *J. Heterocycl. Chem.* **1993**, 30, 1003.

(25) Sivaraman, J.; Subramanian, K.; Velmurugan, D.; Subramanian, E.; Ramakrishnan, V. T. *Acta Crystallogr.* **1994**, C50, 2011.

(26) Stradins, Ya. P.; Dabur, G. Ya.; Bejlis, Yu. I.; Uldrikis, Ya. R.; Krotokova, A. F. *Khim. Geterosykl. Soedin* **1972**, 84.

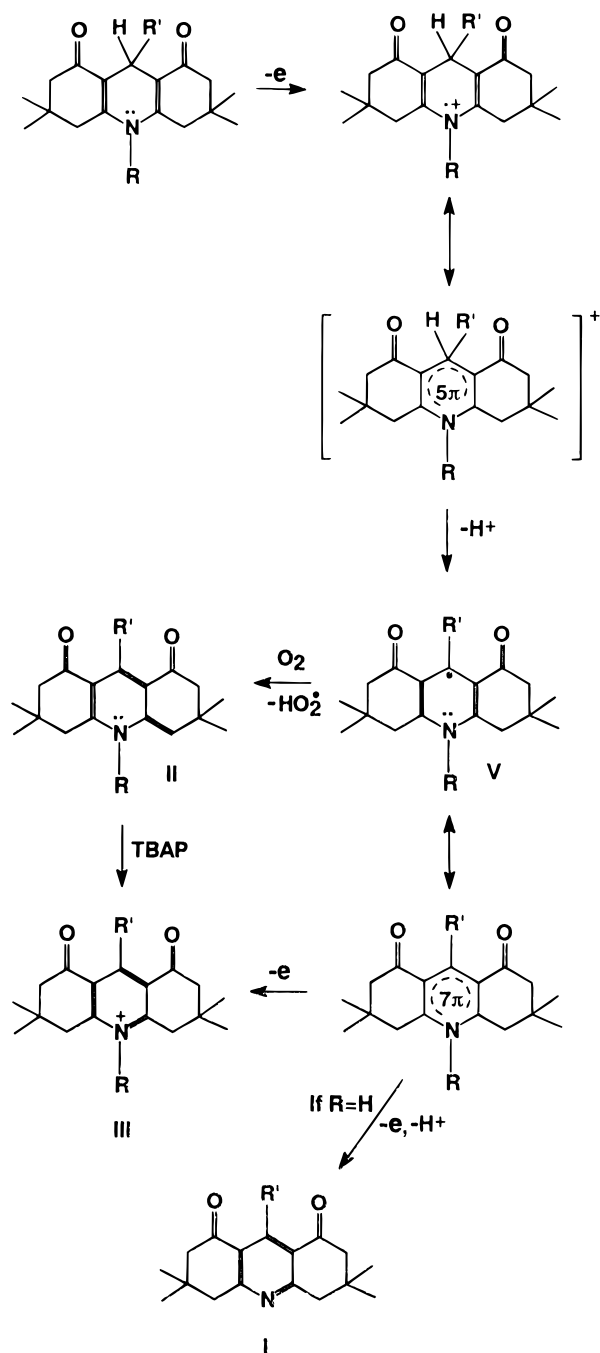
(1, 4, and 7) show two peaks in air-equilibrated and argon-saturated conditions. The first peak at the less positive potential can be attributed to the oxidation of the starting material. The first electron loss is followed by the proton loss. The second peak can be assigned to the subsequent loss of the second electron. The formation of the second peak is influenced by the presence of the methyl or phenyl substituents in the 9 position. The observation of two peaks for compounds 4 and 2 in argon-saturated conditions shows that the electron-releasing methyl group influences the rate of the second electron loss. In the case of compounds 1, 4, and 7, after the first electron and proton loss, the presence of the second hydrogen in the 9 position could facilitate the reaction of the radical with oxygen to yield HO_2^\cdot . This pathway is not favored in the case of other compounds because of the presence of the substituents in the 9 position (refer to Scheme 1). This may be the reason for the observation of broad cyclic voltammograms in argon-saturated conditions in those compounds which have an alkyl or aryl substitution in the 9 position.

Cyclic voltammograms were recorded at various scan rates, and plots of $i_{pa}/\nu^{1/2}$ vs scan rate give an indication of the probable mechanism of oxidation. This plot shows that $i_{pa}/\nu^{1/2}$ is independent of scan rate and there is a shift of the peak to less positive potential with decreasing scan rate. This gives an indication of a possible irreversible chemical reaction following charge transfer.

In order to understand the mechanism of oxidation in greater detail and to determine the number of electrons involved in the oxidation process, coulometric studies were carried out. Solutions containing accurately weighed amount of the dyes with tetrabutylammonium perchlorate (TBAP) were subjected to electrolysis at a constant potential, slightly beyond the potential of the desired oxidation. The working and counter platinum electrodes were separated by a sinter in order to avoid mixing of solutions. Coulometric studies in argon-saturated acetonitrile show the involvement of two electrons in the oxidation process.

In order to isolate the product formed on electrolysis, both N-H and N-methyl compounds were subjected to electrolysis for 12 h at a potential of +1.3 V vs Ag/AgCl. The reaction was followed by TLC from time to time. The electrolysis was carried out in a cell similar to that used in Coulometric studies, but the amount of substance used was in larger quantities. Compounds 1 and 4 were chosen as representative compounds for the product isolation. In the case of compound 1, the acetonitrile solution after electrolysis was evaporated under reduced pressure in order to remove the solvent. The resulting solid mixture was extracted with chloroform and was chromatographed over a column of silica gel and eluted with chloroform. Colorless crystals were filtered out. The absorption spectrum of the isolated product I was compared with the spectrum of the authentic sample obtained on chemical oxidation of the starting material with MnO_2 . In the case of compound 4 the separation of the product was not possible in a single step because the final product obtained was a salt and separation of the desired product from TBAP was difficult. The product obtained on electrochemical oxidation along with the excess perchlorate was concentrated by rotary evaporation under reduced pressure. To this mixture was added a concentrated solution of KOH, and the color of the product changed to red from yellow. The product formed also contained TBAP which is insoluble in ether. Extraction

Scheme 1

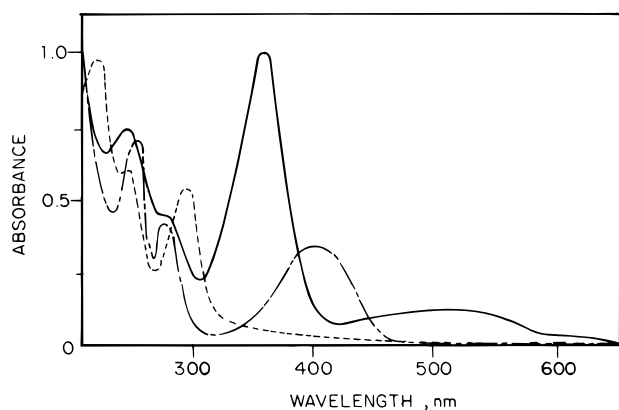


of the red product with ether and concentration of the ether layer gave dark red crystals of compound II, which was characterized by NMR and HRMS. The NMR spectrum clearly reveals that the product formed is due to a net loss of two hydrogen atoms as compared to the starting material. Acidification of a methanolic solution of II by perchloric acid turns the solution yellow and precipitates the final product III. Compounds II and III exist in an acid-base equilibrium and are reversibly converted from one form into another by the addition of a base or acid. In fact the product obtained after acidification with perchloric acid is the same as the product obtained on electrolysis, which is further confirmed by comparing their absorption spectra which have a characteristic maximum at 292 nm. Figure 1 gives the absorption spectra of compounds 4, II, and III.

The results of the UV-vis, NMR, IR, and mass spectra obtained are tabulated in Table 2. The NMR spectrum

Table 2. Spectral Data for the Products Separated after Electrolysis

compd	UV-vis (nm)	¹ H NMR data (δ, ppm)	IR (cm ⁻¹)	mass (<i>m/e</i>)	analytical data					
					calcd			found		
					C	H	N	C	H	N
I	220	1.12 (s, 12H)	1640	271	75.24	7.80	5.16	75.18	7.74	5.13
	250	2.50 (s, 4H)	1580	215						
	292	3.05 (s, 4H)		256						
		8.76 (s, 1H)								
II	520	1.10 (s, 12H)	1657	285	75.44	8.12	4.90	69.19	7.77	4.66
	356	2.25 (s, 2H)	1705							
	244	2.35 (s, 2H)								
	212	2.50 (s, 2H)								
		3.14 (s, 3H)								
		4.31 (s, 1H)								
III	350	1.16 (s, 12H)	1710	385	56.03	6.26	3.63	56.16	6.26	3.33
	292	2.69 (s, 2H)	1600							
	250	3.35 (s, 2H)								
	220	4.15 (s, 3H)								
		9.17 (s, 1H)								

**Figure 1.** Absorption spectra of compound **4** (---) and the products **II** (—) and **III** (- · -) formed on electrolysis.

of product **I** clearly indicates the presence of the aromatic proton at δ 8.7, corresponding to the proton at position 9, which is not present in the NMR spectrum of the starting material. In the case of product **III** the peak corresponding to the aromatic proton is shifted more downfield because of the positive charge on the heterocyclic nitrogen. The IR and mass spectral data are also incorporated in Table 2.

B. Mechanism of Electrochemical Oxidation. As there was a difference in the shape of the cyclic voltammograms based on the differences in the substitution on the heterocyclic nitrogen and the products obtained on oxidation were different depending on the substitution on the nitrogen, the substituent on the nitrogen is expected to play a key role in the product formation. The presence of at least one hydrogen atom in the 9 position is extremely necessary for the completion of oxidation as in the case of 1,4-dihydropyridine.²⁰ Hence the mechanism of oxidation for the N-H and N-Me substituent follow different routes of oxidation after the initial loss of an electron. It is evident from the ESR spectra that the first proton loss is from the 9 position in all cases. This may be followed by loss of a second electron in the case of N-substituted compounds and an electron and proton loss in the case of N-H compounds in order to yield the final product as given in Scheme 1.

In all the compounds studied the first step of oxidation is the loss of an electron from the nitrogen to form the cation radical. This is followed by a rapid proton loss to produce a carbon-centered radical (V). Radical V under-

Table 3. Splitting Constants Obtained in the ESR Spectrum of the Spin-Trapped Adduct

compd	splitting constants	
	a_N , G	a_H , G
1	14.50	2.50
2	14.93	2.81
3	14.93	3.38
4	14.07	3.38
5	14.50	3.38
6	14.93	3.38
7	14.22	3.38
8	14.50	2.45

goes electrochemical oxidation to form a salt of type **III** in the case of N-substituted compounds. The radical V being reactive also undergoes subsequent oxidation in the presence of oxygen to form compounds of type **II**. Compounds of type **II** in the presence of TBAP, present under electrochemical conditions, form salts of type **III**. In the case of N-H compounds (**1**, **2**, and **3**), electrochemical oxidation of radical V is followed by a subsequent proton loss to yield a product of type **I**.

C. Identification of Radical Intermediates. In order to gather evidence for the mechanism of electrochemical oxidation and to establish that the oxidation proceeds by the formation of a radical, ESR experiments were carried out. Electrolysis in the presence of the spin trap *N-tert*-butyl- α -phenylnitron (PBN) yielded the spin adduct. The ESR spectra obtained after electrolysis of the dyes are given in Figure 2. The ESR spectrum shows the triplet due to the nitrogen and its splitting into a doublet due to the presence of the adjacent hydrogen. a_N values around 14 G and a_H splitting of 2–3 G have been obtained in the case of dihydropyridine spin adducts. There is no appreciable decrease in the a_H splitting as seen in the case of phenyl substitution in the 9 position as in the case of the dihydropyridines. The splitting constants for the spin adduct of about 14 G is consistent with that of a carbon-centered radical as reported for other compounds with the same spin trap.²⁷ The ESR data are collated in Table 3.

D. Reduction after Oxidation. The cathodic behavior of the anodic species formed is informative. The shapes of the cyclic voltammograms vary depending on the substituent in the heterocyclic nitrogen (Figure 3). A peak at about +1.0 V corresponds to oxidation in all the dyes and is assigned as peak A or A'. No dimeric

(27) Buettner, G. R. *Free Radical Biol. Med.* **1987**, 3, 259.

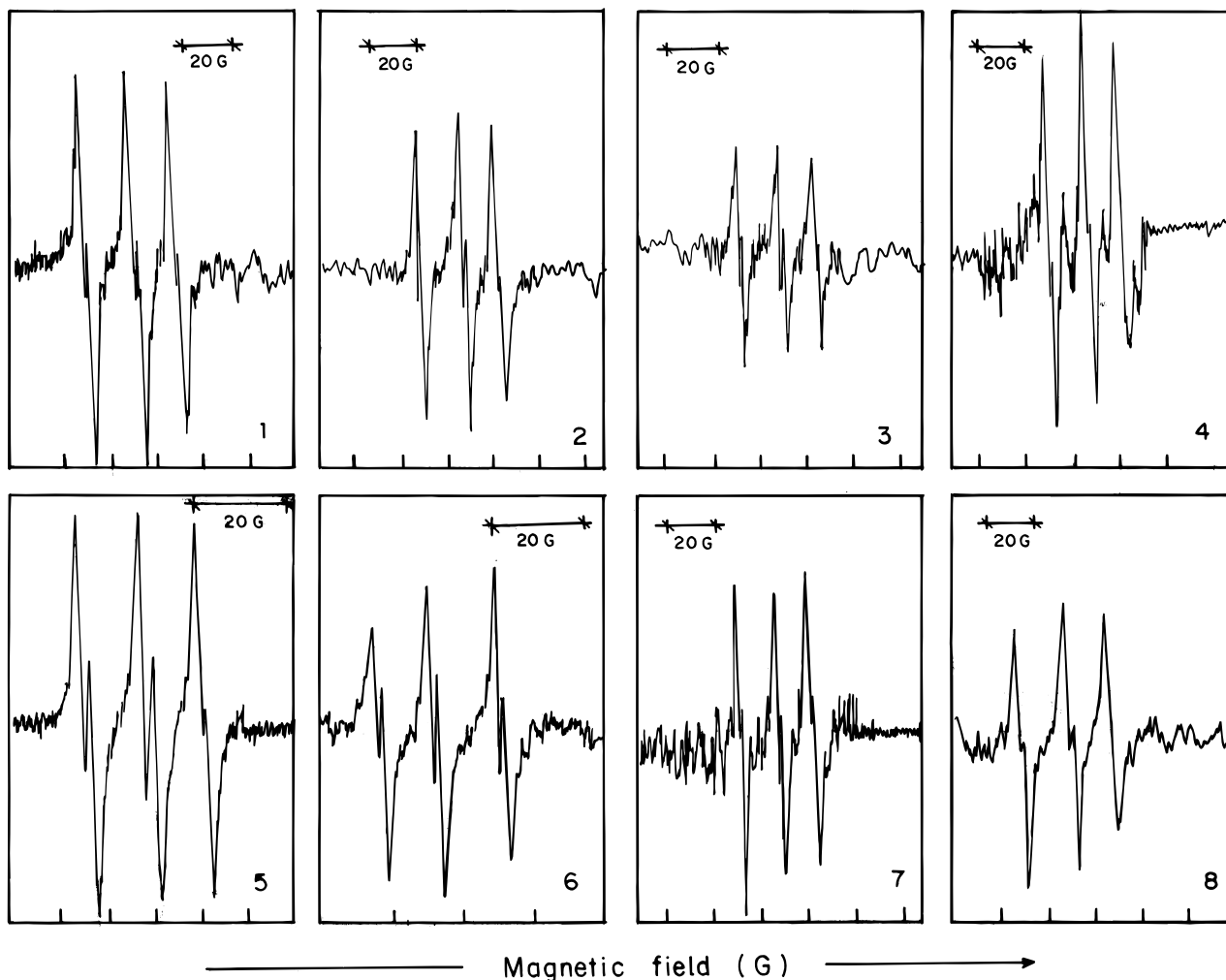
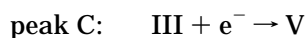
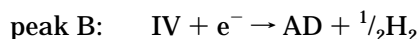
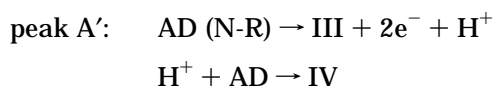


Figure 2. ESR spectrum of the spin-trapped adducts of acridinediones with PBN.

product has been isolated on oxidation which might form from the radical V, but the possibility of the formation of a dimer cannot be ruled out. On carrying out reduction after oxidation the compounds with substitution on nitrogen show two reduction peaks (B and C), one at about -0.5 V and the second cathodic peak at about -1.0 V. Only peak B is seen in compounds with N-H substituent at about -0.5 V. At the peak B the protonated acridinedione (IV), formed in the reaction between proton released due to the oxidation of AD and the unoxidized AD, gets reduced to the starting material and liberates hydrogen. The second cathodic peak C is attributed to reduction of the N-substituted acridinium ion (III).

The peaks obtained in cyclic voltammetry can be assigned as



Peak C, which is present for compounds 4–8, is not present in the case of compounds 1–3 because the

oxidation terminates at the aromatic product by loss of the second proton. There is no peak present on direct reduction of the starting materials in the potential range 0 to -1.5 V. This gives a clear indication that the reduction peaks are only due to the reduction of the oxidation products. The reduction of a compound of type III to form V is consistent with the fact that the N-alkylpyridinium ion forms a dimer on reduction.^{28–31}

Experimental Section

Preparation of 2,2'-Methylenebis(5,5'-dimethylcyclohexane-1,3-dione). A mixture of dimedone (2 mol) and the corresponding aldehyde (1 mol) was stirred at 40 – 45 °C for 10 min in aqueous methanol until the solution became cloudy and was allowed to stand overnight. The tetraketone (A = formaldehyde, B = acetaldehyde, C = benzaldehyde) was collected by filtration and dried. Yield: tetraketone A, 96%, mp 186 – 188 °C; tetraketone B, 93%, mp 136 – 138 °C; tetraketone C, 94%, mp 190 – 192 °C.

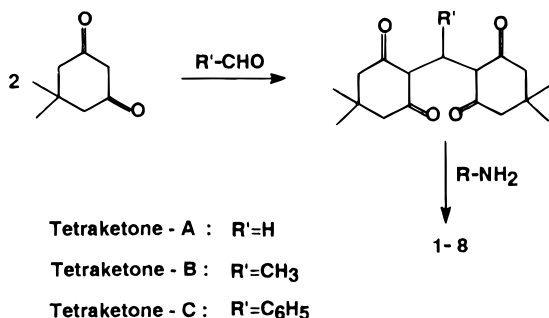
3,3,6,6-Tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (1). To the tetraketone A (2.92 g, 10 mmol) in methanol (10 mL) was added a 25% aqueous solution of ammonia (2 mL), and the solution was warmed on a steam

(28) Volke, J.; Naarova, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 3361.

(29) Naarova, M.; Volke, J. *Collect. Czech. Chem. Commun.* **1973**, *38*, 2671.

(30) Webber, A; Osteryoung, J. *J. Electrochem. Soc.* **1982**, *12*, 2732.

(31) Gaudiello, J. G.; Larkin, D.; Rawn, J. D.; Sosnowski, J. J.; Bancroft, E. E.; Blount, H. N. *J. Electroanal. Chem.* **1982**, *131*, 203.



bath for 4 h. A bright yellow solid separated out and was filtered, dried, and recrystallized from a chloroform–methanol mixture: yield 88%; mp 317–319 °C; ¹H NMR (CDCl₃) δ 1.1 (s, 12H, *gem*-dimethyl), 2.2 (s, 4H, =CCH₂), 2.3 (s, 4H, C(O)CH₂), 3.0 (s, 2H, =CCH₂C=), 8.0 (s, 1H, NH).

3,3,6,6,9-Pentamethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (2). The tetraketone **B** (1.53 g, 5 mmol) and ammonium acetate (0.42 g, 5.5 mmol) in acetic acid (10 mL) heated to reflux for 2 h furnished acridinedione **2**: yield 92%; mp 256–258 °C; IR (cm⁻¹) 3280 (NH), 1610 (C=O), 1595 (C=C); ¹H NMR (CDCl₃) δ 1.0 (d, 3H, =CCHCH₃), 1.1 (s, 12H, *gem*-dimethyl), 2.3 (s, 4H, =CCH₂), 2.4 (s, 4H, C(O)CH₂), 3.95–4.15 (q, 1H, =CCHC=), 8.45 (s, 1H, NH). Anal. Calcd for C₁₈H₂₅NO₂: C, 75.21; H, 8.78; N, 4.87. Found: C, 75.00; H, 8.42; N, 4.90.

3,3,6,6-Tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione (3). The compound was prepared similar to **2** using tetraketone **C** **3**: yield 90%; mp 250–252 °C; IR (cm⁻¹) 1620 (C=O), 1575 (C=C); ¹H NMR δ 0.90 (s, 12H, *gem*-dimethyl), 1.9–2.3 (ABq, 4H, *J*_{gem} = 15 Hz), 2.4 (s, 4H), 4.85 (s, 1H), 7.0–7.2 (s, 5H), 9.2 (s, NH); mass spectrum *m/z* (relative intensity) 349 (M⁺) (98), 348 (100), 332 (18), 292 (18), 273 (72), 264 (35), 220 (14), 217 (18), 180 (20). Anal. Calcd for C₂₃H₂₇NO₂: C, 79.04; H, 7.78; N, 4.07. Found: C, 78.81; H, 7.81; N, 4.14.

3,3,6,6,10-Pentamethyl-3,4,6,7,9,10-hexahydro-1,8-(2H,5H)-acridinedione (4). To tetraketone **A** (1.46 g, 5 mmol) in acetic acid (15 mL) was added a 40% aqueous solution of methylamine (0.41 mL, 5.2 mmol), and the solution was heated under reflux conditions for 2 h. The reaction mixture was concentrated and poured into cold water (200 mL), and the solid obtained was filtered, dried, and recrystallized from a chloroform–methanol mixture: yield 81%; mp 226–28 °C; IR (cm⁻¹) 1615 (C=O), 1570 (C=C); ¹H NMR (CDCl₃) δ 1.1 (s, 12H, *gem*-dimethyl), 2.25 (s, 4H, =CCH₂), 2.45 (s, 4H, C(O)CH₂), 3.15 (s, 2H, =CCH₂C=), 3.3 (s, 3H, NCH₃); mass spectrum *m/z* (relative intensity) 287 (M⁺) (100), 286 (55), 272 (22), 271 (6). Anal. Calcd for C₁₈H₂₅NO₂: C, 75.22; H, 8.76; N, 4.87. Found: C, 75.40; H, 8.68; N, 5.03.

3,3,6,6,9,10-Hexamethyl-3,4,6,7,9,10-hexahydro-1,8-(2H,5H)-acridinedione (5). From tetraketone **B** (1.53 g, 5 mmol) and a 40% aqueous solution of methylamine (0.44 mL) on heating to reflux with acetic acid (2 h) the acridinedione **5** was obtained: yield 86%; mp 206–208 °C; IR (cm⁻¹) 1610 (C=O), 1570 (C=C); ¹H NMR (CDCl₃) δ 0.85 (d, 3H, =CCHCH₃), 1.15 (2s, 12H, *gem*-dimethyl), 2.2–2.7 (dd, *gem* coupling, 4H, C(O)CH₂), 2.3 (s, 4H, =CCH₂), 3.3 (s, 3H, NCH₃), 4.05–4.25 (q, 1H, =CCHC=). Anal. Calcd for C₁₉H₂₇NO₂: C, 75.70; H, 9.02; N, 4.64. Found: C, 75.52; H, 8.96; N, 4.41.

3,3,6,6,10-Pentamethyl-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (6). The compound was prepared similar to **4** using tetraketone **C**. **6**: yield 80%; mp 200–202 °C; IR (cm⁻¹) 1615 (C=O), 1570 (C=C); ¹H NMR (CDCl₃) δ 1.07–1.13 (s, 12H, *gem*-dimethyl), 2.3 (s, 4H, =CCH₂), 2.4–2.85 (ABq, 4H, C(O)CH₂), 3.2 (s, 3H, NCH₃), 5.2 (s, 1H, =CCHC=), 7.3–7.6 (m, 5H, Ar H); mass spectrum *m/z* (relative intensity) 363 (26) (M⁺), 286 (100), 273 (100), 217 (65). Anal. Calcd for C₂₄H₂₉NO₂: C, 79.3; H, 8.04; N, 3.85. Found: C, 78.0; H, 7.67; N, 3.85.

3,3,6,6-Tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (7). (a) Tetraketone **A** (2.92 g, 10 mmol) and aniline (1.0 g, 11 mmol) in ethanol with catalytic

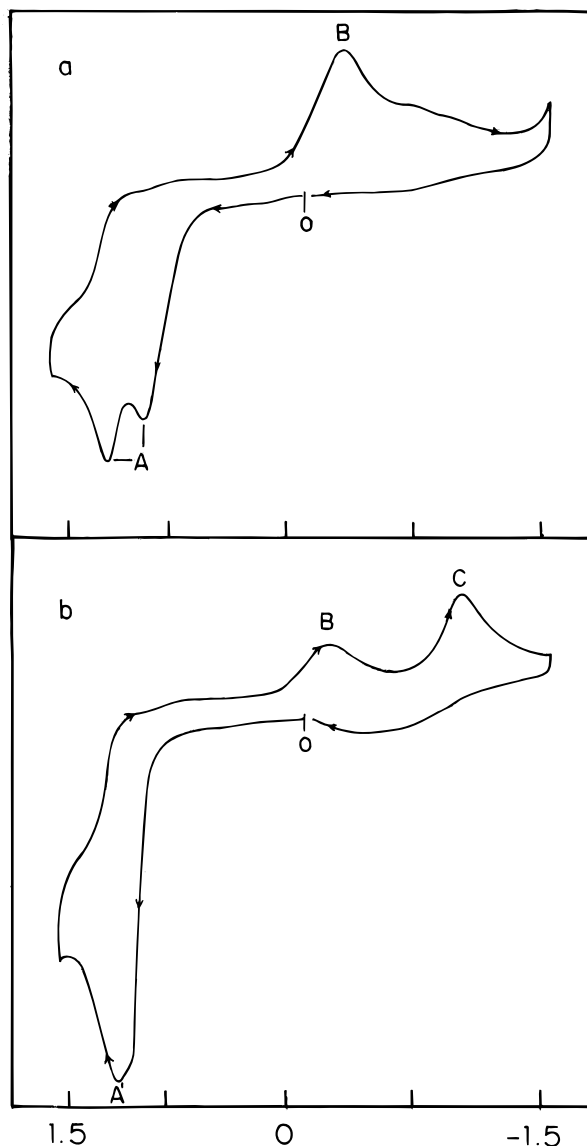


Figure 3. (Top) Cyclic voltammogram of compound **1** on oxidation followed by reduction, showing peaks A and B due to the formation of I and reduction of IV, respectively. (Bottom) Cyclic voltammogram of compound **4** oxidation followed by reduction, showing peaks A', B, and C due to the formation of III and reduction of IV and III, respectively.

amounts of P₂O₅ on stirring at room temperature for 12 h and concentrating the solvent under reduced pressure furnished the acridinedione **7**.

(b) To tetraketone **A** in acetic acid was added aniline and the solution was heated under reflux conditions for 4 h. The formation of the product was followed by TLC. Concentration and pouring the contents into ice-cold water yielded the acridinedione **7**: yield 86%; mp 262–264 °C; IR (cm⁻¹) 1620 (C=O), 1575 (C=C); ¹H NMR (CDCl₃) δ 0.90 (s, 12H, *gem*-dimethyl), 1.8 (s, 4H, =CCH₂), 2.25 (s, 4H, C(O)CH₂), 3.3 (s, 2H, =CCH₂C=), 7.3–7.7 (m, 5H, Ar H). Anal. Calcd for C₂₃H₂₇NO₂: C, 79.05; H, 7.79; N, 4.01. Found: C, 79.03; H, 7.72; N, 3.98.

3,3,6,6,9-Pentamethyl-10-phenyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (8). The compound was prepared similar to **7** using tetraketone **B**. **8**: yield 80%; mp 264–265 °C; IR (cm⁻¹) 1615 (C=O), 1570 (C=C); ¹H NMR (CDCl₃) δ 1.0 (d, 3H, =CCHCH₃), 1.1 (s, 12H, *gem*-dimethyl), 2.3 (s, 4H, =CCH₂), 2.4 (s, 4H, =C(O)CH₂), 3.9–4.1 (q, 1H, =CCHC=), 7.3–7.7 (m, 5H, Ar H); mass spectrum *m/z* (relative intensity) 363 (16.5) (M⁺), 286 (71), 273 (100), 217 (38), 203 (16.5). Anal. Calcd for C₂₄H₂₉NO₂: C, 79.3; H, 8.04; N, 3.85. Found: C, 78.8; H, 7.81; N, 4.04.

The preparations of some of the dyes chosen for the study have been reported previously by different methods.^{32,33}

Acetonitrile used for the study was HPLC grade obtained from Qualigens Fine Chemicals Ltd., India. Tetrabutylammonium bromide from Fluka was converted into its perchlorate with perchloric acid. The excess acid was washed with water, and the TBAP obtained was recrystallized twice from a 1:1 methanol-water mixture. The purity of the sample was ascertained by running a cyclic voltammogram with TBAP in acetonitrile. The spin trap *N-tert-butyl- α -phenylnitrone* obtained from Sigma Chemical Co. was used as received.

Cyclic voltammograms were recorded on a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat. A cyclic triangular wave of potential was produced by a PAR model 175 universal programmer and applied to the system through the potentiostat/galvanostat. The current output was monitored using a PAR model 176 current follower. The voltammograms were recorded using a Perkin Elmer Hitachi model 057 *x-y* recorder. Platinum was used as both the working and counter electrodes and Ag/AgCl was used as the reference electrode. The electrodes were cleaned after each experiment to remove the adsorbed impurities. All the experiments were

carried out at room temperature, and the solutions were purged with argon when necessary. The electrochemical cell has four necks for the working, counter, and reference electrodes and inlet and outlet for the gas, respectively. The absorption spectra were recorded using Hitachi-320 or HP-8452A diode array spectrophotometers. IR spectra were recorded on a Perkin-Elmer 258 spectrophotometer. ¹H NMR spectra were recorded on a Varian EM-390 spectrometer. Mass spectra were recorded on a HP 5985 GC/MS. Melting point measurements are uncorrected. ESR experiments were performed on a Bruker ER-200-D ESR spectrometer with a TE102 cavity. The electrochemical oxidations were performed with the spin trap added to the solution in a cell in which all three electrode compartments were kept separated using a sinter. The oxidized solution containing the spin trap was taken into the ESR cavity to record the ESR spectrum of the spin adduct formed.

Acknowledgment. N.S is thankful to CSIR for providing a fellowship. The authors are also thankful to the University Grants Commission for its sustained support through the COSIST program.

(32) Bakibaev, A. A.; Filimonov, V. D. *Zh. Org. Khim.* **1989**, 25, 1579.
(33) Greenhill, J. V. *J. Chem. Soc. (C)* **1971**, 2699.