SYNTHESIS AND ELECTROREDUCTION OF 2-[(8-HYDROXYQUINOLINE-5-YL)AZO]BENZO[*c*]CINNOLINE IN DMSO–H_2O (1:1) MEDIUM

Funda ÖZTÜRK[a1,*], Zehra DURMUŞ[a2], Öznur Ölmez UÇKAN[a3,b], Emine KILIÇ[a4] and Esma KILIÇ[a5]

[a] *Department of Chemistry, Faculty of Science, Ankara University, Ankara 06100, Turkey; e-mail: [1] fozanozturk@yahoo.com, [2] zdurmus@science.ankara.edu.tr, [3] oznurolmez@hotmail.com, [4] kilic@science.ankara.edu.tr, [5] ekilic@science.ankara.edu.tr*

[b] *Department of Chemistry, Faculty of Arts and Science, Giresun University, Giresun, Turkey*

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2-[(8-Hydroxyquinoline-5-yl)azo]benzo[*c*]cinnoline (HQAB) was prepared and characterized by elemental analysis, MS, FTIR and ^{1}H NMR techniques. The electrochemical reduction of HQAB has been investigated by cyclic voltammetry, chronoamperometry and controlled potential electrolysis at mercury pool electrode in the pH range 3.5–9.4. The number of electrons transferred in the electrode reaction, diffusion coefficients and standart rate constants were calculated. In acidic medium, cyclic voltammograms display four cathodic peaks, with the total exchange of 6 e^- and 6 H^+. By contrast, the reverse scan displays two anodic peaks. Constant potential electrolysis at –1.0 V and TLC analysis of the product reveals that the reduction of azo group (in the bridge) in HQAB does not stop at the hydrazo stage but goes further through the cleavage of –NH–NH– linkage to give amino compounds as the final products. The voltammograms recorded in basic medium exhibit two cathodic peaks corresponding to 4 e^-, 4 H^+ and two reverse anodic peaks, and thus the reduction stopped at hydrazo stage. A tentative mechanism for the reduction has been suggested.

Keywords: Azobenzo[*c*]cinnoline; Synthesis; Voltammetry; Electroreduction; Electrode reaction mechanism; HMDE; Azo compounds; Electrochemistry; Electron transfer.

Azo dyes are perhaps, among the most extensively studied classes of organic compounds both from theoretical and practical viewpoints. The major reason for this is that their widespread use as chromophoric and metallochromic reagents[1–3], colorants[4–8], non-linear optic materials[9–12], photosensitizers[13–15] and metal sensors[16–18]. An azo dye bearing the 8-hydroxyquinoline and benzo[*c*]cinnoline moieties would be expected to display, apart from the general characteristics of the azodyes, behaviors reminiscent to both compounds. Azo dyes attached to 8-hydroxyquinoline

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have already been reported to have antibacterial activities[19] and also suggested to be potential reagents for the trace analysis of some metals[20]. It would, of course, be desirable to incorporate some useful properties of benzo[*c*]cinnoline and its derivatives directing their use as dyes[21], fiber intermediates[22], charge-generating agents in electrophographic photoreceptors[23] and electrochromic polymers[24] into an azo dye. Such an attempt could also impart to the azo dye, some other characteristics of the benzo[*c*]cinnoline moiety as mutagenicity[25] and herbicidial/pesticidal activity[26]. On the other hand, exploring the electrochemical behavior of such an azo dye could be of value. For example, it is well known that bacterial cleavage of azo compounds is a reductive process[27]. Elucidation of the electrochemical process at the electrode surface could help in proposing mechanisms for the biochemical behavior of azo dyes[28]. As a contribution to the existing electrochemical studies on the electrochemistry of azo dyes and benzo[*c*]cinnoline derivatives[27,29–33], we synthesized the title compound 2-[(8-hydroxyquinoline-5-yl)azo]benzo[*c*]cinnoline (HQAB) (Fig. 1), and studied its electrochemical behavior on hanging mercury drop electrode (HMDE) in DMSO–H_2O (1:1 v/v) mixture. Adsorption characteristics, electrode reaction mechanisms and the kinetics of the reduction of this compound were investigated using cyclic voltammetry (CV), controlled potential electrolysis (CPE) and thin layer chromatography (TLC). To elucidate the electrode reaction mechanism of HQAB, electrochemical behavior of azobenzene (AZB) and benzo[*c*]cinnoline (BCC) were also investigated under identical conditions.

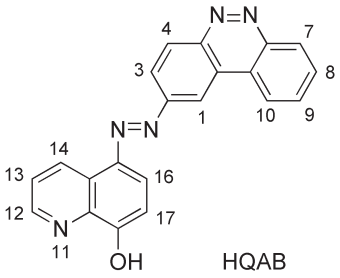


FIG. 1
The structure of HQAB

EXPERIMENTAL

Materials

All chemicals were of analytical grade and were obtained from Merck, except phosphoric acid which was purchased from Pancreac. Britton–Robinson buffer (BR) solutions (pH 2.0–11.0) were prepared from boric (Riedel), acetic (Merck) and phosphoric acids (Riedel) and adjusted to the desired pH with 0.20 M sodium hydroxide (Merck). Stock solutions of HQAB, AZB and BCC (1.0×10^{-3} M) were prepared in BR buffers. Standard solutions were prepared by appropriate dilution of the stock solutions over the range of desired concentrations with the same buffer. All solutions were prepared with doubly-distilled and deionized water. TLC comparison of the reduction products of HQAB and that of 2-aminobenzo-[*c*]cinnoline were made on silica gel 60 F_{254} (Merck) TLC plates with EtOH (Merck) and CH_2Cl_2–AcOEt–EtOH (5:1:0.5) (Merck) mixture as eluents.

Apparatus

CV and CPE studies were carried out on a CH-instrument electrochemical analyzer. A three electrode cell system incorporating HMDE as working electrode (BAS MF-9058), platinum wire auxiliary electrode (BAS MW-1034) and an Ag|AgCl reference electrode (BAS MF-2052 RE-5B) was used in all experiments. The deionized water was supplied from Human Power I^+, Ultra Pure Water System. All pH measurements were made on Thermo Orion Model 720A pH ion meter with an Orion combined glass pH electrode (912600) calibrated with pH 4.13 and 8.20 stock buffer solutions before measurements. AZB, BCC and HQAB were studied in the pH range of 3.5–9.4, the lower limit being the pH of the 1:1 mixture of DMSO–H_2O and the upper limit, the highest possible pH without any precipitation. No pH correction was made to take into account the fact that the medium used is a mixture of DMSO–H_2O (1:1). The absolute value of pH is not critical anyway because the order of the experimental pH readings would be the same as that of absolute pH values. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H and H,H-COSY NMR spectra (δ, ppm; *J*, Hz) were run on a Bruker DPX FT-NMR (400 MHz) spectrometer in DMSO-d_6 solvent using $SiMe_4$ as an internal standard. IR spectra (ν, cm^{-1}) were recorded on a Mattson 1000 FTIR spectrometer in KBr disc; microanalysis was carried out by The Scientific and Technological Research Council of Turkey (TUBITAK). Electron impact mass spectra (EIMS) were obtained on the PLATFORM II LC-MS spectrometer.

Electrolysis

Coulometric studies on HQAB, AZB and BCC were carried out on a BAS 100W/B instrument (Bioanalytical Systems, Inc., Indiana, USA). The three-electrode system for the CPE consisted of a mercury pool (55.4 cm^2) as working electrode, Ag|AgCl reference electrode (BAS MF-2052 RE-5B) and a coiled platinum wire auxiliary electrode (BAS MW-1033). The constant potentials were chosen to be about 100 mV more negative than the cathodic reduction peak potentials. Oxygen was removed with high purity argon. The solution was mixed with a magnetic stirrer.

Synthesis of 2-[(8-Hydroxyquinoline-5-yl)azo]benzo[*c*]cinnoline (HQAB)

2-Aminobenzo[*c*]cinnoline (0.20 g, 1.0 mmol) was dissolved in diluted 3 M hydrochloric acid (10 ml) and was diazotized with a solution of $NaNO_2$ (0.80 g, 1.2 mmol) in H_2O (2.0 ml) at 0 °C. 8-Hydroxyquinoline (0.15 g, 1.0 mmol) dissolved in 2.0 M NaOH solution (10 ml) was added to the diazonium solution. The mixture was neutralized with sodium acetate. The precipitated product was filtered and recrystallized twice from pyridine, yielding 0.10 g (28%) of the pure HQAB (raw HQAB 0.24 g; 67%); m.p. 300 °C. EIMS (*m/z*, %): 351 (M, 100), 323 (M – 28), 195 (2-aminobenzo[*c*]cinnoline), 179 (BCC fragment), 167 (2-aminobenzo-[*c*]cinnoline – N_2), 160 (4-amino-8-hydroxyquinoline), 151 (biphenylene – H), 144 (8-hydroxyquinoline fragment), 116 (8-hydroxyquinoline fragment – CO). For $C_{21}H_{13}N_5O$ (351.37) calculated: 71.79% C, 3.73% H, 19.93% N; found: 71.39% C, 3.69% H, 19.52% N. FTIR (KBr): 3214 (O–H), 3067 (Ar–H), 1571, 1473, 1290, 1227 (C–O), 758. ^{1}H NMR (DMSO-d_6): 9.46 (d, *J* = 8.5, 1 H, H-14); 9.35 (bs, 1 H, H-1); 9.12 (d, *J* = 6.8, H-7); 9.00 (bs, 1 H, H-12); 8.83 (d, *J* = 8.58, H-4); 8.74 (d, *J* = 7.75, H-10); 8.57 (d, *J* = 8.6, 1 H, H-3); 8.22 (d, *J* = 8.88, H-16); 8.11 (m, 2 H, H-8 and H-9); 7.83 (m, 1 H, H-13); 7.24 (d, *J* = 8.9, 1 H, H-17).

Synthesis of 2-[(8-Acetoxyquinoline-5-yl)azo]benzo[*c*]cinnoline (AcQAB)

AcQAB was obtained by the reaction of HQAB (0.1 g, 0.28 mmol) with Ac_2O (1.09 g, 10 mmol) in pyridine (20 ml) at room temperature. After 1 h, the mixture was poured into cold water (0 °C). The precipitate was filtered, washed with cold water and dried in air. The crystallization from CH_2Cl_2 yielded 55 mg (50%) of AcQAB; m.p. 288 °C (decomp.). The compound was found to be readily hydrolysable in aqueous pyridine. EIMS (*m/z*, %): 390 (M – 3 H, 2.4), 350 (M – 43), 335 (M – 58), 197 (2-aminobenzo[*c*]cinnoline + 2 H), 180 (BCC), 167 (2-aminobenzo[*c*]cinnoline – N_2), 58 ($C_2H_2O_2$), 43 (CH_3CO, 100). FTIR (KBr): 3072 (Ar–H), 2930 (C–H), 1765 (C=O), 1499, 1374 (CH_3), 1297, 1194 (Ar–O–Ac), 768. ^{1}H NMR ($CDCl_3$): 9.43 (dd, 1 H, *J* = 8.56 and 1.49, H-14); 9.26 (d, 1 H, *J* = 1.75, H-1); 9.09 (dd, *J* = 4.09 and 1.42, H-12); 8.94 (d, 1 H, *J* = 8.82, H-4); 8.86 (dd, *J* = 7.17 and 2.27, H-7); 8.78 (dd, *J* = 7.15 and 2.03, H-10); 8.55 (dd, 1 H, *J* = 8.86 and 1.78, H-3); 8.15 (d, *J* = 8.30, H-16); 8.04 (m, 2 H, H-8 and H-9); 7.71 (dd, 1 H, *J* = 8.53 and 4.12, H-13); 7.65 (d, 1 H, *J* = 7.28, H-17); 2.60 (s, 3 H, CH_3CO).

RESULTS AND DISCUSSION

Characterization of HQAB

HQAB was synthesized by coupling reaction of diazotized 2-aminobenzo-[*c*]cinnoline with 8-hydroxyquinoline. The structure of HQAB is confirmed on the basis of mass, ^{1}H NMR, H,H-COSY (Fig. 2a) and FTIR spectra. The ^{1}H NMR spectrum of HQAB is fairly complex, owing to the splitting pattern of some protons and phenolic hydroxyl signal have been obscured, that might be caused due to its low solubility in DMSO-d_6 and intermolecular H-bonding interactions, to clarify the assignments of protons of HQAB, its

O-acetylated derivative (AcQAB) was prepared and characterized by mass, FTIR, ^{1}H NMR and H,H-COSY spectra (Fig. 2b) and used to elucidate the proton assignments of HQAB. The assignment of the aromatic proton sig-

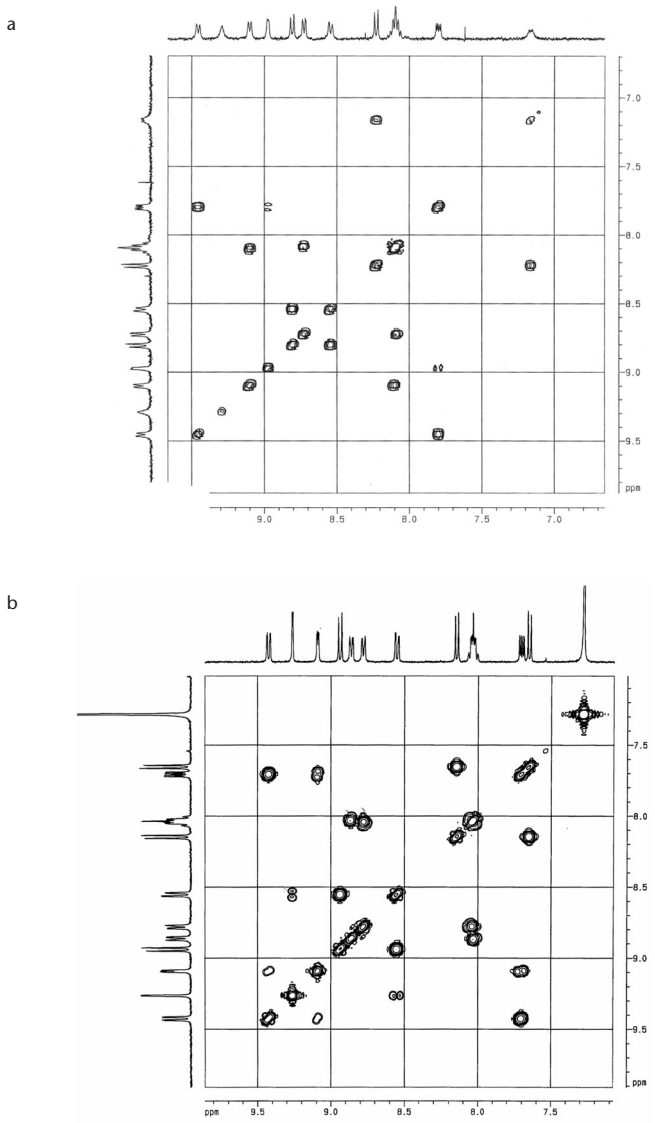


FIG. 2
H,H-COSY NMR spectra of HQAB (a) and AcQAB (b) (aromatic part)

nals have been accomplished using the H,H-COSY spectra of both HQAB and AcQAB spectrum. In the H,H-COSY spectrum of HQAB (Fig. 2a), the signals at 9.46, 9.00 and 7.83 ppm are assigned to H14, H12 and H13 because these signals show a H,H correlation. The signals at 9.35, 8.83 and 8.57 ppm are assigned to H1, H4 and H3, respectively. The signals at 9.12 and 8.74 ppm, and a multiplet for two protons at 8.11 ppm are assigned as H7 and H10, and H8 and H9, respectively. The signals appearing as doublets at 8.22 and 7.24 ppm belong to H16 and H17 protons, respectively. The signals attributed to H14, H1 and H7 are unshielded as expected; H14 and H1 are coplanar with the nitrogen of azo group and H7 is orto positioned to the azo group in the heterocyclic ring that become more electronegative due to the substituted azo group at the para position of the fused benzenoid ring. In the IR spectrum of HQAB, the main characteristics are the O–H stretching band at 3214 cm^{-1}, the C–O streching of the phenolic hydroxyl group at 1290 and 1227 cm^{-1}, and Ar–H, aromatic C=C and N=N streching peaks are found at 3067, 1571 and 1473 cm^{-1}, respectively.

Cyclic Voltammetric Studies

For HQAB, *cis/trans*-isomerism and azo/hydrazone tautomerism are both plausible. But, no strict evidence has been observed to indicate the existence of isomers or tautomers. The reduction potentials read for AZB and for the bridging azo group of the title compound are very close, which possibly indicates that hydrazone type tautomer is unlikely.

The electrochemical behavior of HQAB was investigated using HMDE in DMSO–H_2O (1:1) medium with BR buffer as a supporting electrolyte. CVs of the solution containing 2.0×10^{-5} M HQAB, AZB and BCC at a scan rate of 0.1 V s^{-1} were taken in BR buffer solutions containing DMSO–H_2O (1:1) medium in the pH range of 3.5–9.4. Representative voltammograms obtained at pH 3.5 and 9.4 are given in Fig. 3. For HQAB, as can be seen in Fig. 3a, four cathodic and two anodic peaks are discernable in acidic medium, whereas in Fig. 3b, two cathodic and two anodic peaks are visible in the basic medium. The reduction of HQAB at pH 3.5 occurs in four successive steps (peaks I_c, II_c, III_c and IV_c), as shown in Fig. 3a. These peaks appear at about –0.09, –0.40, –0.45 and –0.85 V and two anodic peaks, III_a and I_a, at about –0.45 and –0.15 V, respectively. The second and third reduction peaks, II_c and III_c, were very close to each other, and they become a single peak at very high (>0.5 V s^{-1}) scan rates. At pH 9.4, two cathodic peaks, I_c and II_c, are observed at –0.52 and –0.80 V, and two anodic peaks, II_a and

I_a, at about –0.77 and –0.50 V, respectively (Fig. 3b). The remarkable difference between the reduction potentials of the azo group in the bridge and 1,2-diazene moiety of HQAB is due to the difference in the electron delocalization. Adjacent nitrogen atoms in the heteroaromatic BCC com-

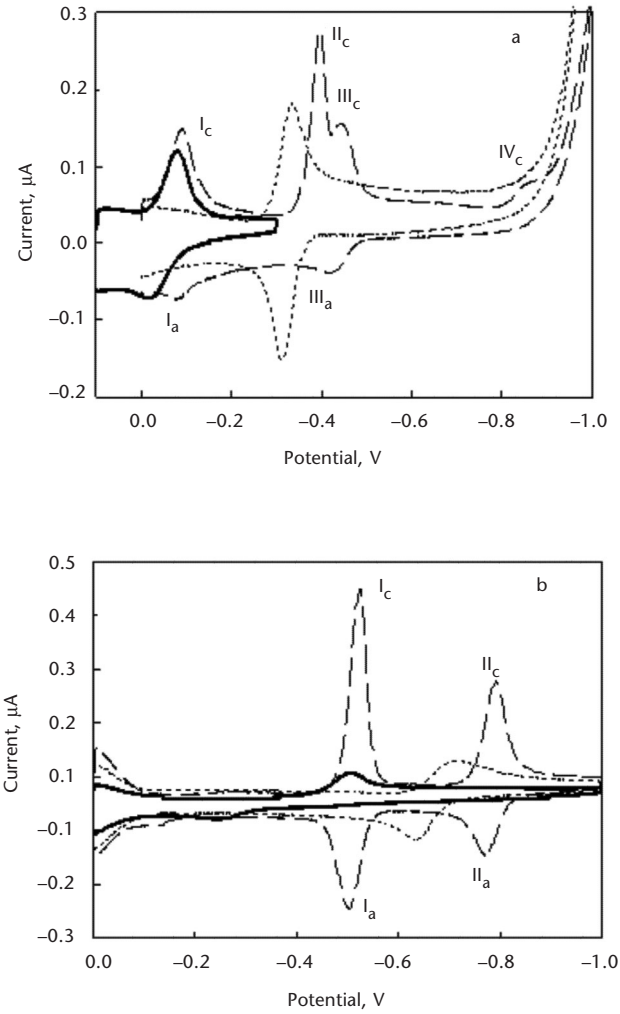


FIG. 3
Cyclic voltammograms of 2.0×10^{-5} M HQAB (– – –), AZB (——) and BCC (· · · ·) at pH 3.5 (a) and 9.4 (b) in DMSO–H_2O (1:1), at scan rate 0.1 V s^{-1}, with HMDE as a working electrode and Ag|AgCl as a reference electrode

ponent of HQAB obviously involve a higher degree of delocalization compared to the bridging azo group. As expected, a higher degree of delocalization would lead to a better stability and therefore, a more negative reduction potential. For AZB and BCC, the cathodic peaks are observed

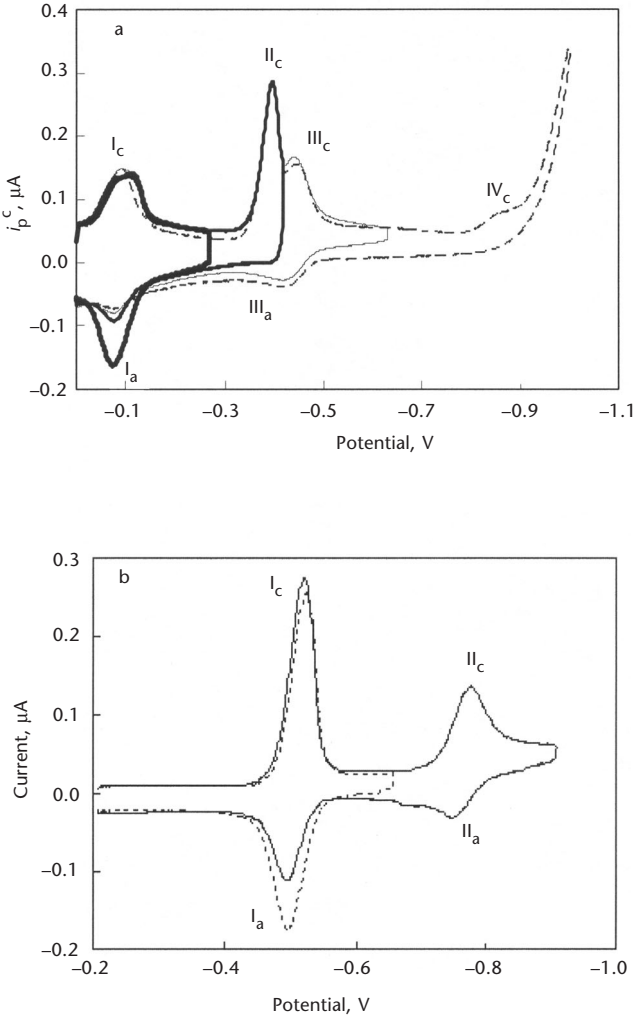


FIG. 4

Cyclic voltammograms of 2.0×10^{-5} M HQAB at different switching potential scans at pH 3.5 (a) and 9.4 (b) in DMSO–H_2O (1:1), at scan rate 0.1 V s^{-1}, with HMDE as a working electrode and Ag|AgCl as a reference electrode

at –0.08 and –0.34 V in acidic medium, and –0.51 and –0.72 V in basic medium, whereas the anodic peaks are observed at –0.01 and –0.31 V in acidic medium, and –0.24 and –0.64 V in basic medium (Fig. 3). In order to judge the reversibility of electrochemical reduction reactions of HQAB, the switching scan studies were carried out after each reduction peak in the acidic and basic media (Fig. 4). When the direction of the scan was reversed at –0.20 V at pH 3.5, an anodic peak corresponding to reoxidation of the first reduction product was observed for every scan rate in acidic medium. The peaks I_c and I_a form a quasi-reversible couple. A reverse scan after the second reduction peak II_c does not display any anodic counterpart, but switching after the third reduction produces the anodic peak III_a. It was concluded that III_a was due to oxidation of the product generated in peak III_c reaction. For the last peak (IVc) in acidic medium, no anodic peak was observed on the reverse scan (Fig. 4a), indicating irreversibility of the last reduction process in acidic medium. At pH 9.4 switching the scan direction after the first cathodic peak (I_c), it was observed to produce an anodic peak (I_a) at about –0.45 V corresponding to the cathodic peak at –0.50 V. For the second cathodic peak (II_c), there is again an anodic peak (II_a) at about –0.75 V corresponding to the second cathodic peak at about –0.80 V (Fig. 4b). Increasing the scan rate from 0.01 to 10 V s^{-1} causes the peak potentials shiftrd to more negative potentials, indicating that the electroreduction steps are not reversible[34]. This conclusion is valid for HQAB as well as for AZB and BCC in acidic and basic media.

Adsorption Properties

The influence of scan rate (v) on the cathodic peak current (i_p) was investigated by CV. The log i_p^c vs log v plots are given in Fig. 5 for HQAB, BCC and AZB. Plots of the logarithm of the peak current versus the logarithm of the scan rate gave a straight line with slopes of 0.64 and 0.74 for HQAB in acidic and basic media, respectively, and 0.74 for BCC in acidic medium. These results indicate that the electrode processes were adsorption controlled[35]. However, plots of the logarithm of the peak current versus the logarithm of the scan rate gave straight lines with slopes of 0.54 and 0.48 for AZB in acidic and basic media, respectively, and 0.57 for BCC in basic medium, very close to the theoretical value of 0.5. Such dependence indicated that the reduction of AZB in acidic and basic media, and the reduction of BCC in basic medium were indeed diffusion controlled.

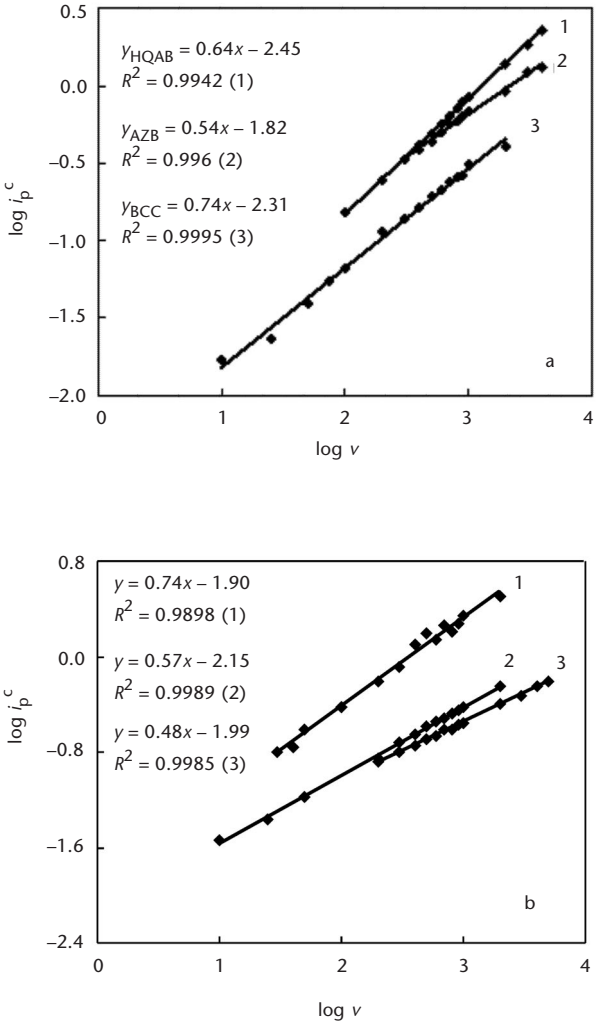


FIG. 5
Log i_p^c vs log v plots of 2.0 × 10^{-5} M HQAB, AZB and BCC at pH 3.5 (a) and 9.4 (b)

Number of Electrons Transferred in Electrode Reaction, Diffusion Coefficient and Standart Rate Constants

The numbers of electrons (n) transferred at various stages of the electroreduction were determined by CPE data. The potentials chosen for the CPE procedures are indicated in Fig. 3. Exactly the same procedures are carried out for AZB and BCC to judge by the active sites in HQAB undergoing reduction at each step.

The n values were calculated by the equation $Q = nFn'$, Q being the electric charge spent, n' the number of moles electrolyzed, F the Faraday constant and n total number of electrons transferred in electrode reaction. The n values found for peaks I_c, II_c and III_c, and IV_c at pH 3.5 and 9.4, and diffusion coefficient (D) and standart rate constants (k_s) are presented in Table I. If steps II_c and III_c are counted as a single step, the number of electrons involved in each step of the reduction of HQAB appears to be 2.0. The ambient temperature (25 °C) diffusion coefficients of HQAB and BCC at pH 3.5 (DMSO–H_2O 1:1) were calculated from the cyclic voltammetric data using the method developed by Garrido et. al.[36], because at pH 3.5 HQAB and BCC are found to be adsorbed at HMDE electrode as described under adsorption properties. The diffusion coefficients for AZB at pH 3.5 and 9.4, and BCC at pH 9.4 were calculated from under the diffusion-controlled conditions by the use of the Cottrell equation (Table I). The standard rate constants of HQAB, BCC and AZB were calculated by two different methods, namely Klingler–Kochi method[37] for diffusion-controlled current and Laviron method[38] for adsorption on the electrode surface.

pH Effect on Peak Potentials

The electrochemical behavior of HQAB was investigated as a function of pH. The pH dependence of CV of HQAB is evident from Fig. 6. Peak potentials of the cathodic peak (I_c) shift towards more negative values as the pH increases. The influence of the pH on the second and third reduction peaks (II_c and III_c) is similar. Cathodic peak currents also change with changing pH, which is not a surprise as the reaction products are known to change with the adjusted pH. The shift in cathodic peak potentials to more negative values and the change in cathodic currents with increasing pH indicate that hydrogen ions are involved in electrode reactions. These results are in agreement with data reported in refs[27,29,31,33].

TABLE I
Number of electrons (n), diffusion coefficients (D) and standard rate constants (k_s) for heterogeneous electron transfers at pH 3.5 9.4 in DMSO–H_2O (1:1) for 2.00×10^{-5} M HQAB, AZB and BCC

Compound	pH	Number of electrons n			Diffusion coefficient $D \times 10^6$, $cm^2\ s^{-1}$	Standard rate constant $k_s \times 10^2$, cm^{-1}	
		Ic	II_c and III_c	IV_c	I_c	I_c	II_c and III_c
HQAB	3.5	2.2 ± 0.03	1.9 ± 0.3	1.8 ± 0.2	$0.147 \pm 1.22 \times 10^{-2}$ [a]	$0.132 \pm 4.58 \times 10^{-3}$ [c]	$0.120 \pm 1.04 \times 10^{-3}$ [c]
	9.4	1.7 ± 0.07	1.7 ± 0.1		$1.66 \pm 4.59 \times 10^{-3}$ [a]	4.99 ± 2.38 [c]	4.73 ± 2.67 [c]
AZB	3.5	1.8 ± 0.2			$40.1 \pm 3.74 \times 10^{-3}$ [b]	$9.4 \pm 5.3 \times 10^{-1}$ [d]	
	9.4	1.8 ± 0.2			$7.55 \pm 9.80 \times 10^{-1}$ [b]	$4.1 \pm 2 \times 10^{-1}$ [d]	
BCC	3.5	1.7 ± 0.1			$1.43 \pm 7.40 \times 10^{-1}$ [a]	$0.139 \pm 1.13 \times 10^{-3}$ [c]	
	9.4	1.8 ± 0.1			$5.41 \pm 8.66 \times 10^{-1}$ [b]	$8.04 \pm 4.8 \times 10^{-1}$ [d]	

± Values are $ts/\sqrt{N}$ at 95% confidence level. [a] Garrido method. [b] Cotrell method. [c] Laviron method. [d] Klingler–Kochi method.

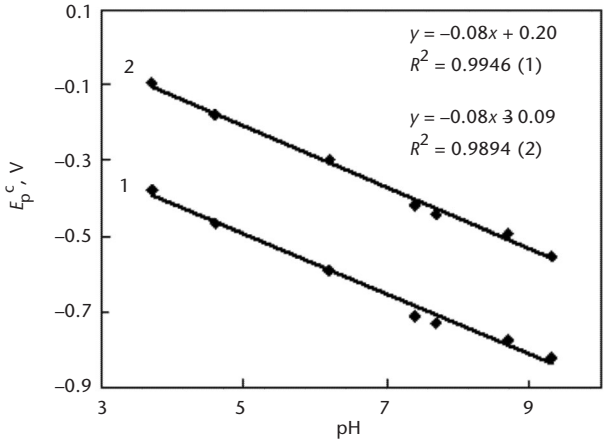
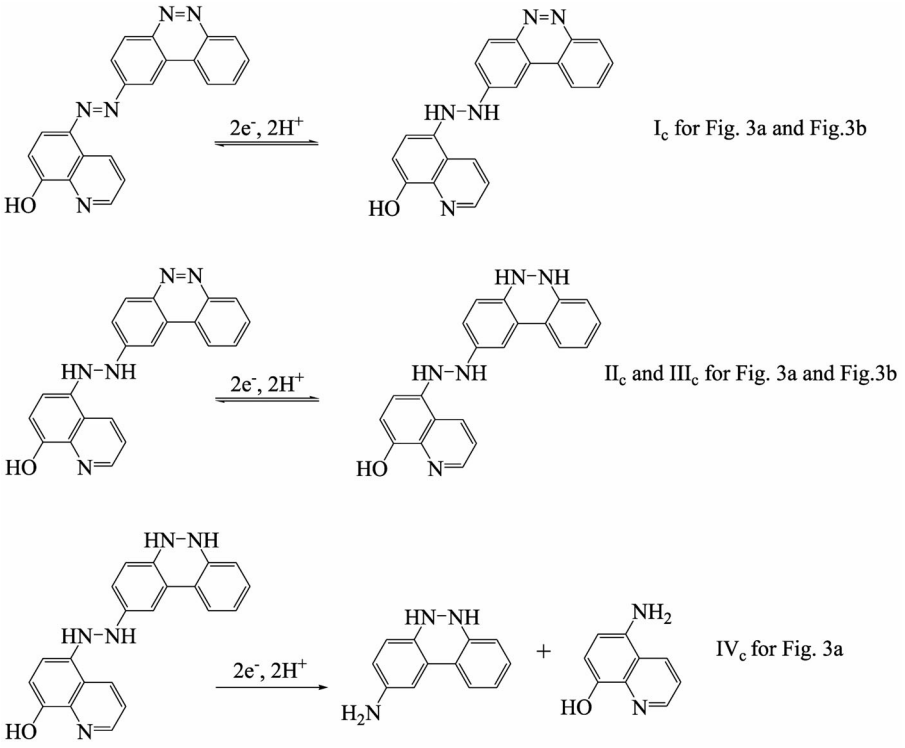


FIG. 6
Effect of pH on the first peak (I_c) (*1*) and the second peak pair (II_c and III_c) (*2*) potentials obtained from cyclic voltammetric data for 2.0×10^{-5} M HQAB versus Ag|AgCl reference electrode

Proposed Mechanism in Acidic Medium

The electroreduction mechanism of HQAB in acidic medium is tentatively suggested in Scheme 1. The stability of the hydrazo intermediate generated in the electroreduction processes of HQAB depends strongly on pH. The hydrazo derivatives of azo compounds in general, are reported to be stable in basic medium, but in acidic medium, decomposition to amines is known to be accelerated via acid catalysis[31]. Each of the first (I_c) and second (II_c and III_c) stages of reduction involve the uptake of 2 e^-, 2 H^+ giving the corresponding hydrazo intermediates at pH 3.5. The last stage (IVc) of reduction occurs only in acidic medium, but no anodic peak was observed for the last reduction step of HQAB which supports the last step of the mechanism in Scheme 1. CVs of AZB and BCC were obtained under identical condition to judge the reduced part of HQAB at each stage (Fig. 3a and Scheme 1). By comparison with the CV of HQAB, these voltammograms indicate that the first reduction peak (I_c) of HQAB corresponds to 2 e^- reduction of azo group while the second reduction peak pair (II_c and III_c) corresponds to the 2 e^- reduction of 1,2-diazene moiety of HQAB. This conclusion is also consistent with the literature reports[29,33]. The third electroreduction peak (IV_c) of HQAB is attributable to cleavage to amine with the consumption of 2 e^-

and 2 H^+. Furthermore, the determination of reduction products was taken TLC chromatogram. The TLC chromatogram of the mixture obtained by the CPE was compared with that of 5,6-dihydrobenzo[*c*]cinnolin-2-amine. The retention factor (R_F) values of 5,6-dihydrobenzo[*c*]cinnolin-2-amine and one of the reduction products were found to be equal. Hence, it appears reasonable to conclude that the azo linkage in the bridge breaks in peak IV_c step in acidic medium. It was observed that 5,6-dihydrobenzo-[*c*]cinnolin-2-amine was formed in step IV.



SCHEME 1
The proposed electrochemical reduction mechanism of HQAB

Proposed Mechanism in Basic Medium

At pH 9.4, the hydrazo intermediate appears to be stable enough to resist reductive cleavage to amines at potentials as negative as –1.0 V (Fig. 3b and Scheme 1). Similar behavior was reported for other azo compounds[27,29,33,34].

The coulometric studies indicate that the number of electrons involved in the reduction at pH 9.4 is 4, and this supports that hydrazo intermediate is relatively stable in basic medium (Table I). CVs of AZB and BCC were taken at pH 9.4 and at scan rate of 0.1 V s^{-1} (Fig. 3b). These CVs indicate that the first reduction peak of HQAB corresponds to 2 e^- reduction of azo group in the bridge while the second reduction peak corresponds to the 2 e^- reduction of 1,2-diazene moiety of HQAB (Scheme 1). These results show that the reduction of HQAB starts at the azo group first as is also the case in acidic media. In conclusion, the electroreduction of HQAB in basic medium involves the same steps as in the acidic medium except for the reductive cleavage into amines being now much more difficult.

CONCLUSIONS

A novel azo dye 2-[8-hydroxyquinoline-5-yl)azo]benzo[*c*]cinnoline (HQAB) was syntesized and characterized. The electroreductions of HQAB on hanging mercury drop electrode in DMSO–H_2O medium buffered at pH 3.5 and 9.4 were investigated. In acidic medium, a three step reduction corresponding to 2 e^- reductions of the bridging –N=N– to –NH–NH–, cinnolinic –N=N– to –NH–NH– and of the bridging hydrazino intermediate to amines was revealed. In basic medium, the last step is found to be absent, supporting the konown stability of the hydrazo bridge above pH 8.

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