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Ionization and Electroreduction of some Benzthiazin-4-one Azodyes

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pKa values of a series of the titled compounds (**2 a–g**) together with a model compound **3** have been determined spectrophotometrically in alcoholic buffered media. These values were correlated to different σ sets. The polarographic behaviour of the parent **2 a** and its nitro derivative **2 g** was studied in detail. The obtained data showed that **2 a** is reduced via a 2-electron process to the corresponding hydrazo from which was stabilized through hydrogen bonding.

(Keywords: Azo-hydrazo; Hydrazo-azo; Polarography)

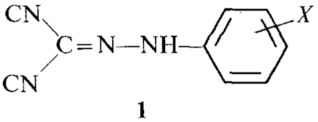
Ionisierung und Elektroreduktion einiger Benzthiazin-4-on-Azofarbstoffe

Es wurden die *pKa*-Werte einer Serie der Titelverbindungen (**2 a–g**) zusammen mit einer Modellverbindung **3** spektrophotometrisch in alkoholischer gepufferter Lösung bestimmt. Diese Werte wurden mit verschiedenen Sets von σ-Werten korreliert. Das polarographische Verhalten der Stammverbindung **2 a** und deren Nitroderivat **2 g** wurde im Detail untersucht. Die Daten zeigen, daß **2 a** über einen Zweielektronenprozeß zur entsprechenden Hydrazo-Verbindung reduziert wird, die durch Wasserstoffbrücken stabilisiert ist.

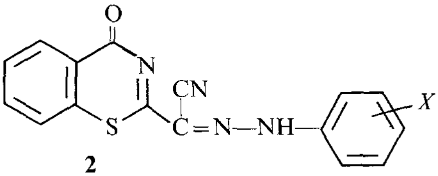
Introduction

Compounds of the general structure **1** have been extensively studied through the last decade[1—4]. This increase of interest is due to the pronounced acid character characteristic of the ionization of their —NH group to form the anion which is usually stabilized through delocalization of the negative charge over the entire molecule. In continuation, we report a spectroscopical and polarographic study of the ionization of a series of 2-(arylazo-cyano)methylbenzthiazin-4-ones **2**.

Since 2-cyanomethylbenzthiazin (**3**) represents the heterocyclic portion of our molecule, it was of interest to use it as model compound for comparison.



1



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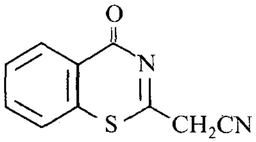


3

2a, $X = H$
2b, $X = m$-Cl
2c, $X = p$-Cl

2d, $X = m$-CH_3
2e, $X = p$-CH_3
2f, $X = m$-NO_2
2g, $X = p$-NO_2

Experimental

The model compound 2-cyanomethylbenzthiazin-4-one (**3**) was prepared by treating equimolecular amounts of thiosalicyclic acid with malononitrile in pirydine for 2 hours, the separated product was crystallized from acetic acid, m.p. 220 °C. On the other hand 2-(arylazo-cyano)-methylbenzthiazin-4-ones **2 a–g** were prepared by coupling an ice-cold solution of the corresponding diazotized amine with a solution of **3** in acetic acid-sodium acetate mixture and then left overnight. The separated product was filtered off and crystallized[5]. The compounds gave correct elemental analyses and IR (3 200 NH, 2 200 $C\equiv N$, 1 680 ring CO and 1 640 $C=N$).

The absorption spectra of the dyes were recorded on a Pye Unicam 1 750 spectrophotometer within the wavelength range 300–500 nm in *Britton-Robinson* buffers[6]. A known volume (0.1 ml) of the stock solution was added to 5 ml of buffer in a 10 ml volumetric flask. The mixture was then continued to the mark with ethanol.

All *pH* measurements were made on an Orion *pH*-meter with an accuracy of ± 0.01 *pH* unit.

The polarograms of 10^{-4} *M* solutions (30% by volume ethanol, 10% *DMF* and 60% buffer) were recorded on a Polarecord type E 506. Half-wave potentials are expressed versus Ag/AgCl/saturated KCl electrode with an accuracy of ± 0.005 V. The capillary had the following characteristics in H_2O open circuit: $t = 3.9$ s/drop, $m = 1.54$ mg/s for $h = 52$ cm. All measurements were carried out at room temperature 25 °C ± 1.

Results and Discussion

The *pKa* values of the compounds were obtained graphically[7] and are compiled in Table 1. It is clear from the inspection of these values that the coupling products are affected by different substituents on the arylazo

Table 1. *Spectrophotometric pKa of compounds* **2 a–g** *and* **3**

No.	*pKa*	No.	*pKa*
2 a	8.4	**2 e**	8.6
2 b	7.4	**2 f**	6.5
2 c	7.3	**2 g**	4.3
2 d	8.2	**3**	8.5

moiety and are more acidic than the model compound **3**. This can be realized from the fact that the active hydrogen of the cyanomethylene group will ionize in solution to give the anion, the negative charge being delocalized over the whole molecule. This charge is also affected by the arylazo moiety in these molecules. The effects of substituents on *pKa* values are represented graphically in Fig. 1. Results of statistical correlations[8] with different *Hammett* constants (σ, σ°) are given in Fig. 1. From this plot and slope values one may conclude that the *pKa*'s are highly dependent on the nature of the substituent on the aryl moiety. Thus, whereas electron withdrawing substituents significantly decrease the *pKa* values, electron donating substituents have the reverse effect. The strong dependence of *pKa* on σ values reveals that substituents are interfering with both inductive and resonance effects in these molecules. The plot shows that the p-NO_2 substituent deviates from the line. On the other hand if a special σ^- is introduced instead of σ, σ° values the point will fit the

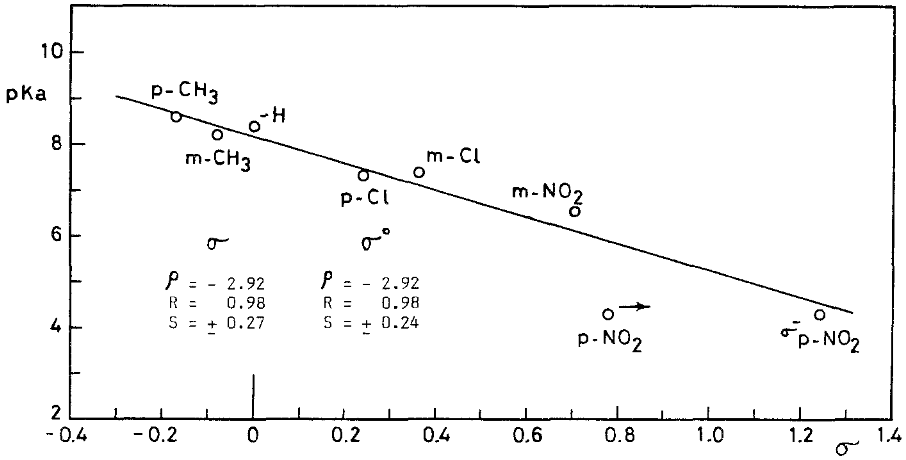
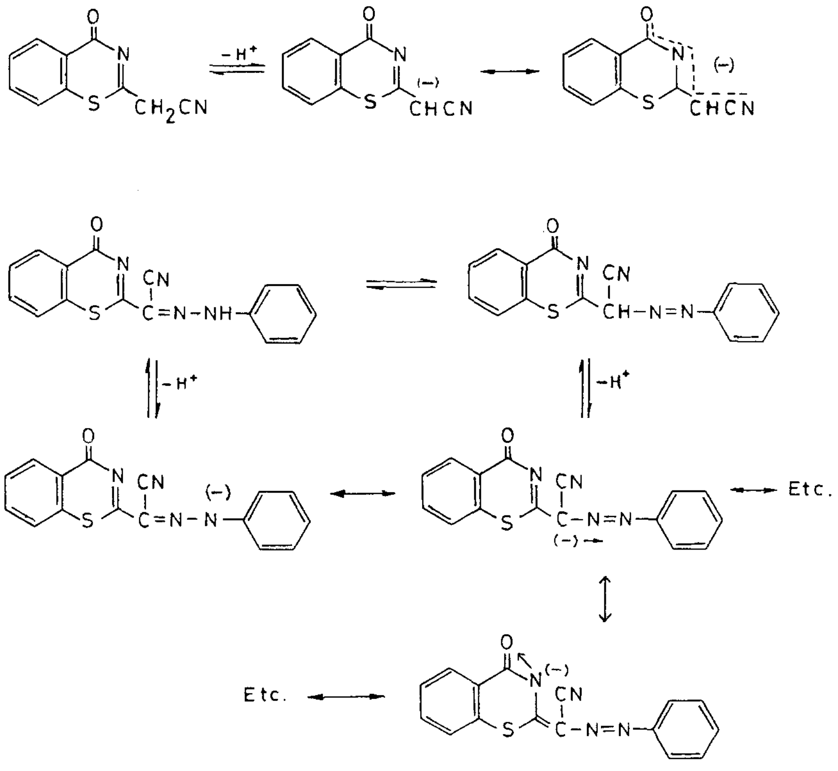


Fig. 1. σ vs. *pKa* plot for 2-arylazo-benzthiazin-4-ones (**2 a–g**)

correlation; this is a further indication that the reaction center is strongly conjugated with the aryl group and the negative charge is built up on the reaction center in the transition state[9] (cf. Scheme 1).

Scheme 1



These observations may be misleading if structurally related molecules[1—4] are compared, since one may conclude that these compounds (**2a–g**) may exist in the hydrazone form. However, UV spectra alone cannot differentiate between the two forms. Thus it seemed necessary to use another tool to confirm the predominating azo or hydrazono forms of these compounds. Therefore the polarograms of 10^{-4} *M* solutions of compounds **2a** and **2g** in 40% (*v*/*v*) ethanolic buffers were recorded under the same experimental conditions. In the whole *pH* range (~2–12) **2a** displayed one well defined irreversible diffusion-controlled wave. The $E_{1/2}$, i_l vs. *pH* plots for this wave are shown in Fig. 2. From the

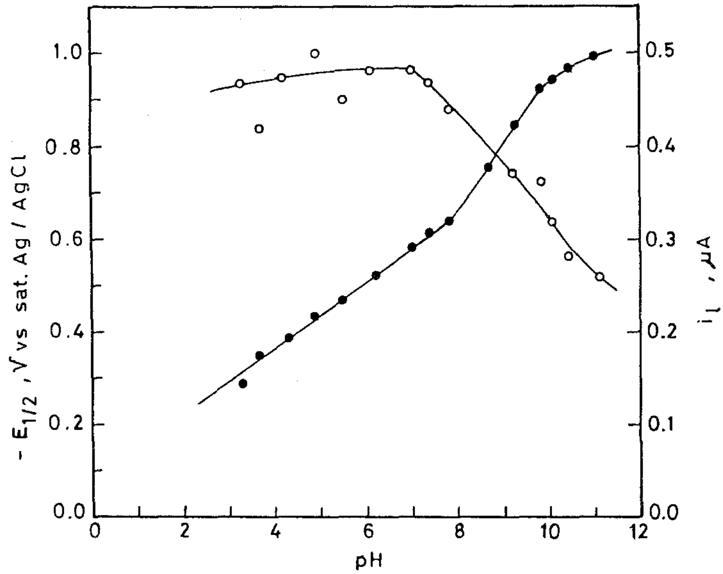


Fig. 2. $E_{1/2}$, i_l vs. *pH* plots of the polarographic wave of 2-phenylazo-benzthiazin-4-one (**2a**)

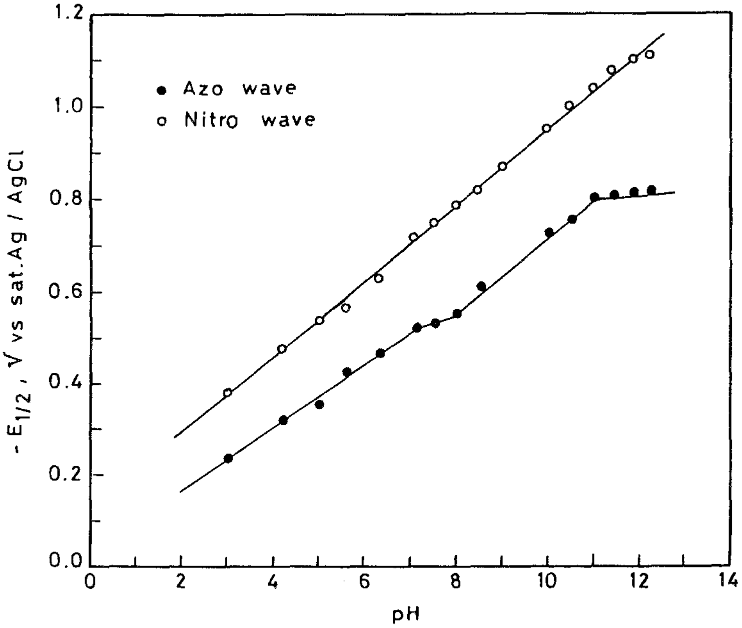
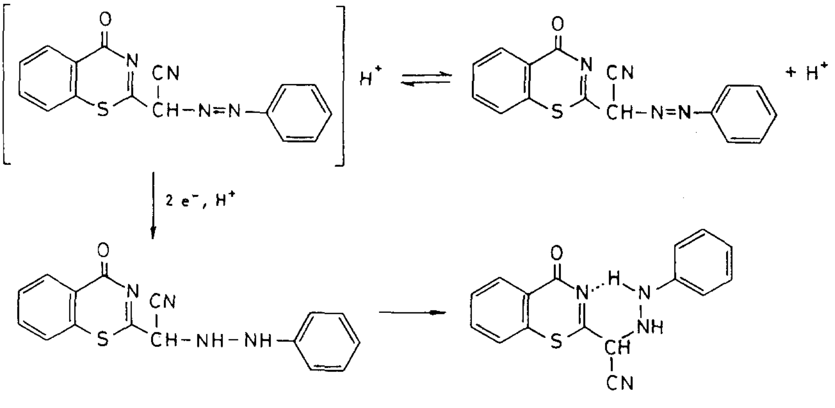


Fig. 3. $E_{1/2}$, i_l vs. *pH* plots of the polarographic waves of 2-nitrophenyl-benzthiazin-4-one (**2g**)

$E_{1/2}$-pH dependence it was found that $dE_{1/2}/dpH$ is 0.080 V per pH unit, a value which indicates that protons are involved in the electrode process. Applying the equation[10] $dE_{1/2}/dpH = -(0.059/\alpha n)\ P^+$, the value of P^+ was found to be ~ 1 indicating that one proton is consumed; hence, the rate of protonation is the rate determining step. Surprisingly, the polarograms of this compound were typical for azo compounds[11—13] and not for hydrazones[1—4] and a $2\,e^-$ wave was obtained in contrary to a four electron wave typical for hydrazones. Also, the nitro derivative **2g** displayed (in addition to the predominant wave of compound **2a** another $4\,e^-$ irreversible wave (Fig. 3) which can be described by $E_{1/2} = -0.15 - 0.08\,pH$. The behaviour of this wave is similar to the well known behaviour of aromatic nitro derivatives[14, 15]. Model compound **3** is polarographically inactive in the whole pH range. The product of controlled potential electrolysis in $10^{-2}\,M$ HCl-ethanol (50% v/v at —0.32 V vs. Ag/AgCl) did not give any dye test for aniline[16]. Moreover, analysing the product by TLC using aniline as reference gave no indication for the presence of aniline. Finally by applying the logarithmic analysis technique on the wave we obtained values of αn varying between 0.405 and 0.619 indicating that the process proceeds irrrversibly. This can only be true if one assumes the formation of a compound which is stabilized through hydrogen bonding towards oxidation (see Scheme 2).

Scheme 2



References

[1] *Elnagdi M. H., Fahmy H. M., Morsi M. A.*, J. Electroanal. Chem. **68**, 237 (1976).

[2] *Fahmy H. M., Morsi M. A., Elnagdi M. H.*, Gazz. Chim. Ital. **107**, 565 (1977).

[3] *Fahmy H. M., Elnagdi M. H., Kandeel Z. E., Pierre G.,* J. Chem. Tech. Biotechnol. **31**, 688 (1981).
[4] *Morsi M. A., Fahmy H. M., Elnagdi M. H., Abdel Azzem M.,* J. Electroanal. Chem. **133**, 269 (1982).
[5] *Abed N. M., El-Sayed A. M.,* Ind. J. Text. **1984**, 91.
[6] *Britton H. T. S.,* Hydrogen Ions, 4th. edn., Vol. 1, p. 365. London: Chapman and Hall. 1951.
[7] *Issa R. M., Hamman A. S., Etaiw S. H.,* Z. Phys. Chem. **251**, 177 (1972).
[8] *Jaffe H. H.,* Chem. Rev. **53**, 191 (1953).
[9] *Jackson R. A.,* Mechanism, an Introduction to the Study of Organic Reactions, p. 110. Oxford: Clarendon Press. 1972.
[10] *Mairanovskii S. G.,* J. Electroanal. Chem. **4**, 166 (1962).
[11] *Fahmy H. M., Elnagdi M. H., Ibrahim L. I.,* Ind. J. Chem. **198**, 644 (1980).
[12] *Darwish S., Fahmy H. M., Aziz M. A., El Maghraby A. A.,* J. Chem. Soc. Perk. II **1981**, 344.
[13] *Sakla A. B., Fahmy H. M., Aboutabl M. A.,* J. Electroanal. Chem. **90**, 261 (1978).
[14] *Pearson J.,* Trans. Faraday Soc. **44**, 683 (1943).
[15] *Lund H.,* in: Cathodic Reduction of Nitro Compounds in Organic Electrochemistry (*Baizer M. M.,* ed.), Ch. 7, p. 315. New York: Marcel Dekker. 1973.
[16] *Feigl F.,* Spot Tests in Organic Analysis, p. 243. New York: Elsevier. 1983.