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Arylazo derivatives of quinoxaline (1,4-benzodiazine), 1,4-benzothiazine, and 1,4-benzoxazine have been prepared by condensation of hydrazidoyl halides with *o*-phenylenediamine, *o*-aminothiophenol, and *o*-aminophenol, respectively (Table I). This method seems to be more general than the approach using coupling of reactive diazonium salts with, *e.g.*, 2*H*-1,4-benzothiazine. Both the spectral data and the results of HMO calculations of bonding energies of the azo compounds obtained in this study indicate that they exist predominantly in the hydrazone tautomeric form.

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Introduction.

Our interest in the synthesis of dyes containing the quinoxaline (1,4-benzodiazine), 1,4-benzothiazine, and 1,4-benzoxazine chromophores has prompted us to reexamine an earlier work carried out by Lozinskii and Pel'kis [2]. These authors have reported that the reaction of *o*-aminothiophenol (**1b**, Z = S) with *C*-chlorocarbonylhydrazidoyl chloride (**2a**, X = Y = Cl) gives *C*-(2-benzothiazolyl)-hydrazidoyl chloride (**3**, Z = S, Y = Cl, Ar = Ph) (Scheme 1). It seemed of interest to use a modification of this reaction that would lead to such dyes. We envisioned the amidrazones of the general structure **4** (Z = NH), the hydraz-

onate esters (**5**, Z = O), or the thiohydrazone esters (**5**, Z = S) as precursors of these systems. For example, depending on the nature of the group X, cyclization of **4** would yield **7** and/or **8**, whereas cyclization of **5** may yield **9** and/or **10**. On the other hand, cyclization of the hydroxy or mercapto derivatives **6** (Z = O or S) would afford **3** and **10** in the acid and alkaline media, respectively (Scheme 1). Accordingly, we have studied the reactions between each of the three α -keto-hydrazidoyl halides, **2b** (X = OEt, Y = Cl), **2c** (X = Me, Y = Cl), and **2d** (X = RC₆H₄, Y = Br), with *o*-phenylenediamine **1a** (Z = NH), *o*-aminothiophenol **1b** (Z = S), and *o*-aminophenol **1c** (Z = O).

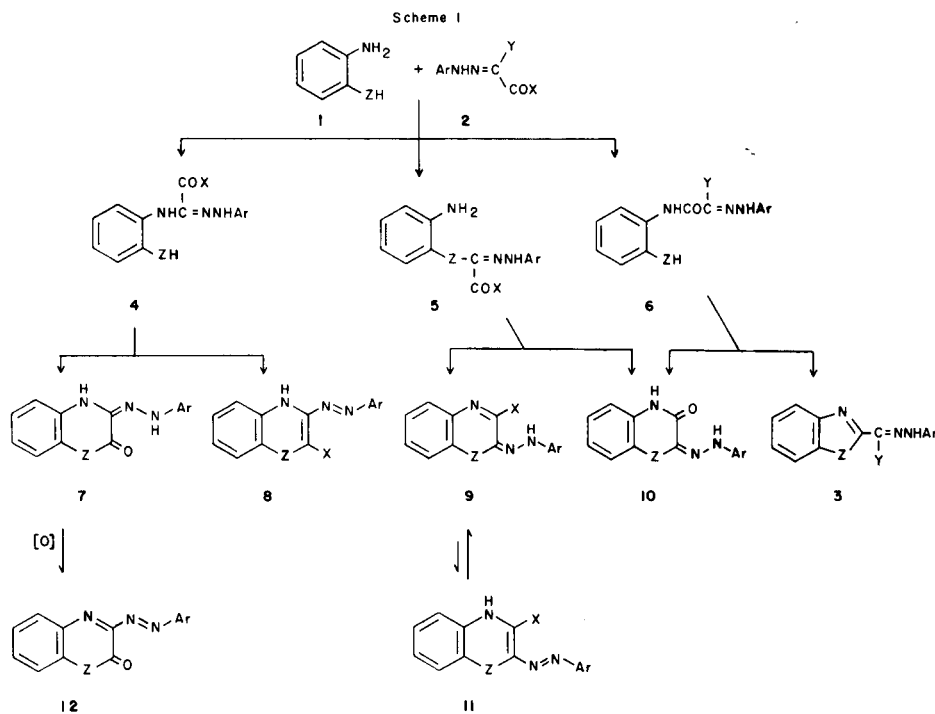


Table I
Synthesized Heterocycles

Compound No.	Z	Ar	X	Mp, °C (Solvent) [a]	Molecular Formula	C, %	Analysis			
							Calcd. (Found)			S, %
							H, %	N, %		
7a	NH	Ph	—	260 (D)	C ₁₄ H ₁₂ N ₄ O	66.65 (66.4)	4.79 (4.5)	22.21 (22.1)	—	
7b	S	Ph	—	288 dec (D)	C ₁₄ H ₁₁ N ₃ OS	62.44 (61.9)	4.12 (3.9)	15.60 (15.8)	11.90 (11.6)	
7c	O	Ph	—	254 dec (D)	C ₁₄ H ₁₁ N ₃ O ₂	66.40 (66.1)	4.38 (4.5)	16.59 (16.9)	—	
9a	NH	Ph	Me	186 (E)	C ₁₅ H ₁₄ N ₄	71.98 (72.1)	5.64 (5.4)	22.38 (22.8)	—	
9b	NH	Ph	Ph	204 (D)	C ₂₀ H ₁₆ N ₄	76.90 (76.7)	5.16 (4.9)	17.94 (18.2)	—	
9c	NH	<i>p</i> -MeC ₆ H ₄	Ph	187 (D)	C ₂₁ H ₁₈ N ₄	77.28 (77.4)	5.56 (5.7)	17.17 (17.3)	—	
9d	NH	Ph	<i>p</i> -MeC ₆ H ₄	158 (D)	C ₂₁ H ₁₈ N ₄	77.28 (77.1)	5.56 (5.4)	17.17 (16.9)	—	
9e	S	<i>p</i> -NO ₂ C ₆ H ₄	Me	218 (A)	C ₁₅ H ₁₂ N ₄ O ₂ S	57.68 (58.0)	3.87 (4.0)	17.94 (18.1)	10.26 (10.2)	
9f	S	Ph	Ph	155 (A)	C ₁₅ H ₁₃ N ₃ S	72.92 (73.0)	4.59 (4.7)	12.77 (13.1)	9.73 (9.6)	
9g	S	<i>p</i> -MeC ₆ H ₄	Ph	165 (A)	C ₂₁ H ₁₇ N ₃ S	73.44 (73.6)	4.75 (4.5)	11.65 (11.3)	8.89 (8.6)	
9h	S	Ph	<i>p</i> -MeC ₆ H ₄	187 (A)	C ₂₁ H ₁₇ N ₃ S	73.44 (73.1)	4.75 (4.6)	11.65 (11.2)	8.89 (8.7)	
9i	S	<i>p</i> -NO ₂ C ₆ H ₄	Ph	239 (A)	C ₂₀ H ₁₄ N ₄ O ₂ S	64.16 (63.9)	3.77 (3.9)	14.96 (15.1)	8.56 (8.1)	
9j	O	<i>p</i> -NO ₂ C ₆ H ₄	Me	270 (D)	C ₁₅ H ₁₂ N ₃ O	60.81 (61.1)	4.08 (3.9)	18.91 (19.1)	—	
9k	O	Ph	Ph	158 (A)	C ₂₀ H ₁₅ N ₃ O	76.66 (76.8)	4.83 (4.4)	13.41 (13.7)	—	
9l	O	<i>p</i> -MeC ₆ H ₄	Ph	141 (D)	C ₂₁ H ₁₇ N ₃ O	77.04 (76.8)	5.23 (4.9)	12.83 (13.1)	—	
9m	O	Ph	<i>p</i> -MeC ₆ H ₄	162 (D)	C ₂₁ H ₁₇ N ₃ O	77.04 (77.1)	5.23 (5.3)	12.83 (12.9)	—	
12	NH	Ph	—	>360 (D)	C ₁₂ H ₁₀ N ₄ O	67.19 (66.9)	4.03 (3.9)	22.39 (21.9)	—	

[a] A, acetic acid; D, dimethylformamide; E, ethanol.

Results and Discussion.

Treatment of the hydrazidoyl chloride **2b** with *o*-phenylenediamine in ethanol in the presence of triethylamine gave one isolable product whose mass spectral data and elemental analysis indicated a molecular formula C₁₄H₁₂N₄O. Thus, the structures **3** (Z = NH, Y = Cl, Ar = Ph) and the corresponding open structures **4-6** could be excluded. Also, the structures **8** and **9** (X = OEt, Ar = Ph)

were discarded as the nmr spectrum of the isolated product did not contain the characteristic signals of the ethoxy group protons. The ir spectrum of the product showed absorption bands near 3200 and 1680 cm⁻¹ attributable to the NH and CO groups, respectively (Table II) and the uv spectrum contained absorption bands at 332 and 336 nm due to the presence of the carbonyl group (Table III). On the basis of these data, the product was assigned the structure of 3-oxo-2-arylhydrazono-1,4-dihydroquinoxaline **7a** or **10a** (Z = NH, Ar = Ph). Oxidation of this compound with hydrogen peroxide gave the corresponding 3-oxo-2-phenylhydrazonoquinoxaline **12** (Scheme 1). The difference between **2a** (X = Y = Cl, Ar = Ph) and **2b** (X = OEt, Y = Cl, Ar = Ph) in their reaction with *o*-phenylenediamine seems to result from the difference in chemical reactivities of the ethoxycarbonyl, chlorocarbonyl, and hydrazidoyl chloride groups. It could be postulated that due to the lower reactivity of the ethoxycarbonyl group than the hydrazidoyl chloride group, nucleophilic substitution of the latter occurs prior to the aminolysis of the ester group. This assumption is substantiated by the results obtained from the reactions of **2b** with *o*-aminothio-

Table II

The Infrared Spectral Data for Selected Compounds [a]

Compound No.	$\tilde{\nu}$ C=O, cm ⁻¹	$\tilde{\nu}$ NH, cm ⁻¹
7a	1680	3200, 3350
7b	1650	3220
7c	1700	3300
9a-9c	—	3280
9j	—	3350
12	1680	—

[a] In nujol.

Table III

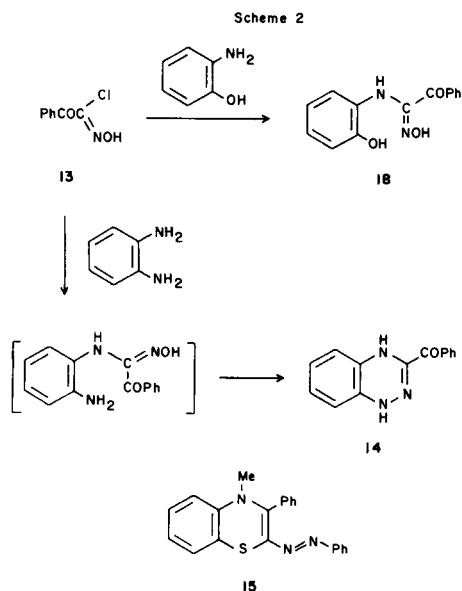
The Electronic Absorption Spectral Data for Compounds under Study [a]

Compound No.	λ max, nm (log ϵ) [b]
7a	336 (4.02), 332 (4.05), 263 (4.90)
7b	356 (4.41), 278 (4.04)
7c	360 (4.42), 270 (4.20)
9a	410 (broad) (3.82), 348 (3.84), 283 (4.25), 245 (4.44)
9b	448 (4.12), 364 (4.40), 256 (4.55)
9c	454 (4.04), 360 (4.36), 255 (4.63)
9e	415 (4.66), 265 (4.50), 236 (4.36)
9f	392 (4.45), 266 (4.55)
9g	396 (4.44), 266 (4.55)
9j	412 (4.69), 267 (4.69)
9k	384 (4.32), 262 (4.18)
9l	388 (4.36), 264 (4.21)
12	334 sh (3.60), 315 sh (3.98), 263 (4.49)

[a] In ethanol. [b] Sh indicates a shoulder.

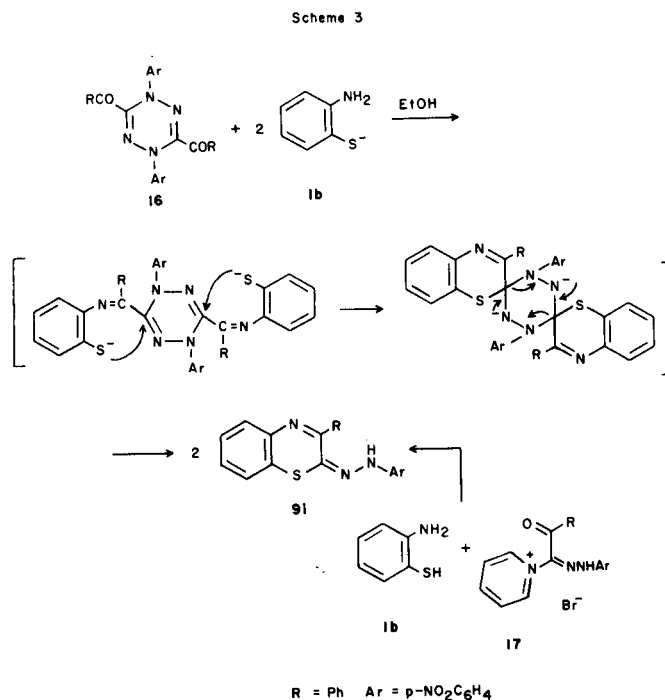
phenol and *o*-aminophenol as described in the following section.

Reaction of the hydrazidoyl chloride **2c** or the hydrazidoyl bromides **2d-2f** with *o*-phenylenediamine in ethanol under reflux yielded the corresponding new dyes **9a** (X = Me, Z = NH) and **9b-9d** (X = RC₆H₄, Z = NH) in good yields, respectively. The structures of these dyes follow from their elemental analyses and spectral data. Thus, the ir spectra of **9a-9d** (Table II) revealed the absence of carbonyl absorption and the presence of a weak NH band near 3280 cm⁻¹. The compounds may possess either the structure **9** or its tautomeric azo structure **11**. The hydrazone structure **9** seems to be the predominant form on the basis of the following information: a) the mass spectrum of **9b** (Z = NH, Ar = Ph) shows a strong peak for (M⁺ - PhNH); b) its electronic absorption spectrum in ethanol is that of a typical hydrazone (an intense absorption maximum near 370 nm; cf. Table III), and the HMO calculations of the bonding energies for the two tautomeric forms **9** and **11** indicate that **9** is the more stable isomer. For example, the bonding energies of **9b** and **11b** are 37.303β and 36.983β, respectively [3,4]. The behavior of the related hydroxamoyl chloride **13** towards *o*-phenylenediamine **1a** is different. It was reported [5] that **13** reacts with **1a** and gives 3-benzoyl-1,4-dihydro-1,2,4-benzotriazine **14** (Scheme 2).



The hydrazidoyl chloride **2b** reacts readily with *o*-aminothiophenol **1b**. When refluxed with **1b** in ethanol, **2b** yielded a colored product identified as **7b**. The structure of the latter was derived from its elemental analysis and the spectral data. The ir spectrum of this compound showed a carbonyl absorption near 1650 cm⁻¹ and an NH band near 3220 cm⁻¹ (Table II), and the uv spectrum possessed an intense absorption band at 356 nm (a hydrazone) (Table III).

A similar reaction of **1b** with the hydrazidoyl halides **2c-2g** afforded the corresponding 1,4-benzothiazine derivatives which can be formulated as **8e-8i** or **9e-9i**, respectively. To determine which isomeric structure predominates, a comparison was made between the electronic absorption spectra of the above compounds and of the spectrum of **15** prepared by condensation of *o*-(*N*-methylamino)thiophenol with **2d**. The electronic absorption spectrum of **15** in ethanol contains an intense (log ε > 4) maximum near 505 nm, whereas the spectra of the products obtained from **1b** and **2c-2g** exhibit, in each case, a maximum near 426 nm. This finding excludes the azo chromophoric system present in structures of the types **8** and **11**. The structure **11** was further discarded on the basis of an alternative synthesis of **9i** by condensation of the tetrazine **16** with the sodium salt of *o*-aminothiophenol which probably proceeds as shown in Scheme 3. Furthermore, when **17** was refluxed with **1b** in ethanol, a product identical in



all respects with **9i** (the melting point, mixed mp, the spectra) was obtained (Scheme 3). The HMO calculations indicate that the hydrazone form **9** is more stable than the azo form **11**. Thus, the values of the bonding energies of **9f** and **11** were found to be 38.240β and 37.934β, respectively [3,4].

The reaction of **2b-2g** with *o*-aminophenol **1c** in the presence of triethylamine seems to proceed in a similar manner and gives the corresponding 2-arylhydrazono-1,4-benzoxazine derivatives **7c** and **9j-9m**, respectively, in almost quantitative yields. In the absence of triethylamine,

the yields of **9j-9m** were low (lower than 30%). Both the elemental analyses and the spectral data for **7c** and **9j-9m** were in agreement with the assigned structures. The isomeric structure of 3-arylhydrazono-1,4-benzoxazine **8** ($Z = O$) was excluded by analogy with **8** ($Z = S$). Also, the tautomeric structure **11** ($Z = O$) was rejected as the bonding energies of the structures **9k** and **11k** are 36.394β and 36.053β , respectively [3,4]. It seems worth mentioning here that the related hydroxamoyl chloride **13** also reacts differently with *o*-aminophenol and gives the open-chain oxime **18** [5] (Scheme 2).

EXPERIMENTAL

All melting points are uncorrected and were determined on a Thomas-Hoover melting point apparatus. The ir spectra were recorded in nujol on a Perkin-Elmer 580B spectrophotometer with a CDS data station. The electronic absorption spectra were measured in ethanol using a Cary 118 spectrophotometer. The nmr spectra were recorded on a Varian EM-360 instrument in chloroform-*d* solutions at 60 MHz, with tetramethylsilane as the internal reference. The mass spectra were obtained with a Perkin-Elmer RMU-6E spectrometer at 70 eV. Elemental microanalyses were carried out by the Microanalytical Laboratory, University of Cairo, Giza, Egypt. The hydrazidoyl halides **2b-2d** were prepared as previously described [6-9].

Preparation of **7**, **9** and **11**.

General Method.

Equivalent amounts of a hydrazidoyl halide (0.005 mole), an appropriate amine (0.005 mole), and triethylamine (0.006 mole) in ethanol (50 ml) were refluxed for 3-4 hours and then cooled. The precipitated solid was collected and washed with water. The products **7**, **9**, and **11** were obtained in almost quantitative yields (Table I).

Preparation of **9i**.

Method A.

A mixture of phenylglyoxylyl-2-(*p*-nitrophenyl)hydrazone-2-pyridinium bromide (**17**) [10] (2.1 g, 0.005 mole) and **1b** (0.63 g, 0.005 mole) in ethanol (50 ml) was refluxed for 2 hours and then cooled. The obtained solid was collected and crystallized from acetic acid.

Method B.

To an ethanolic solution of sodium ethoxide prepared by dissolving sodium (0.11 g, 0.005 g-atom) in ethanol (25 ml), **1b** (0.63 g, 0.005 mole) was added with stirring. 3,6-Dibenzoyl-1,4-bis(*p*-nitrophenyl)-1,4-dihydro-tetrazine (**16**) [11] (2.6 g, 0.005 mole) was added and stirring was conti-

nued for 25 hours at room temperature. The solution was acidified with diluted hydrochloric acid and the precipitated solid was collected and recrystallized from acetic acid. The product obtained by either of the two procedures (Method A or Method B) was identical with the corresponding product obtained by the General Method described above.

Oxidation of **7a** to **12**.

A mixture of **7a** (0.5 g) in ethanol (20 ml) and 3 ml of hydrogen peroxide (30%) was stirred for 24 hours at room temperature. The solvent was evaporated under reduced pressure, the solid (**12**) was collected and recrystallized from aqueous dimethylformamide, mp $>360^\circ$.

HMO Treatment.

The HMO calculations were carried out in the usual way on an IBM 4331 computer. The values of the parameters employed in this work were the same as in our previous publications [4,12,13].

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