Syntheses of New Pyridoxazines, Benzoxa(thia)azines, and Benzoxa(thia)azepines *via* Cyclocondensation and Elimination Reactions between Donors and Acceptors

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Reaction of 3-amino-2-hydroxypyridine and 2-amino(thio)phenols with various selected π-acceptors are herein reported. Different modes of cyclization *via* elimination and/or condensation reactions were observed during the reaction of the donors with 3,4,5,6-tetrachloro-1,2-benzoquinone (**CHL-*o***), 2,3,5,6-tetrachloro-1,4-benzoquinone (**CHL-*p***), 2,3-dicyano-1,4-naphthoquinone (**DCNQ**) and 2-dicyanomethyleneindane-1,3-dione (**CNIND**). A series of pyridoxazines, benzoxa(thia)azines, benzoxa(thia)azepines has been synthesized in good yields.

Key words: 2-Amino(thio)phenols, 3-Amino-2-hydroxypyridine, π-Acceptors, Pyridoxazines, Benzoxa(thia)azines, Benzoxa(thia)azepines

Introduction

The chemistry of quinones is of considerable interest: the class includes many natural products and numerous important synthetic products [1, 2]. A large variety of quinones, including many fused heterocyclic rings have been used as synthetic intermediates in medicine and industrial chemistry. Quinones are particularly important in dye chemistry [3], and many quinones dyes are commercially available. Quinone-type dyestuffs have received increasing attention because of the search for new infrared dyes for optical recording media [4, 5].

Organic molecules containing electron donor and acceptor moieties constitute a very interesting topic due to their interesting optical and electronic properties [6]. Previously, it was reported that 2,3-dichloro-1,4-naphthoquinone as π-acceptor underwent nucleophilic substitution with a variety of binucleophiles, such as *o*-phenylenediamine, *o*-aminothiophenol and dithiooxamide to produce colored phenoxazinones, phenoquinoxalinediones and thiaphenoxazinones [7]. A number of natural and synthetic antiproliferative compounds also contain the benzoxazinone ring system: Indeed, it has been shown that the antineoplastic activity is correlated with the ability of the planar heterocyclic moiety to intercalate into double-stranded DNA. In the actinomycins [8] an important family of antibiotics produced by actinomycetes, the phenoxazinone skeleton is linked to two pentapeptide chains, while meridine and neoamphimedine [9] contain this pharmacophoric moiety within a polycondensed system.

The recent [10, 11] discovery of a novel class of powerful antitumor intercalating phenoxazinone derivatives rekindled the interest for this system, which is involved in an array of biochemical roles ranging from the photochemical response of vision pigments [11] to the production of DNA-damaging radicals by antiproliferative drugs [12].

Sometime ago, we reported an anomalous behavior of 4-arylidene-2-phenyl-5(4*H*)-1,3-oxazolones and tetrazoles towards benzyne and we succeeded to synthesize 1,4-benzoxazepines and benzyltetrazoles, respectively [13a, b]. Subsequently, we examined the reaction of *N*-vinyl-1*H*-imidazole with benzyne and some selected π-deficient compounds which was catalytic under basic conditions [13c]. Recently, diaryl azines have been shown to react with benzyne (*o*-benzyne) to give 10-amino-3-substituted-9(10*H*)-acridinones. On the other hand, 1,1,2,2-tetracyanoethylene reacted with diaryl azines through Michael-addition to yield 5-aryl-pyrazolidine-3,3,4,4-tetracarbonitriles [13d]. On reacting the same azines with dibenzoylacetylene, pyridazine derivatives were obtained *via* Diels-Alder reaction [13d].

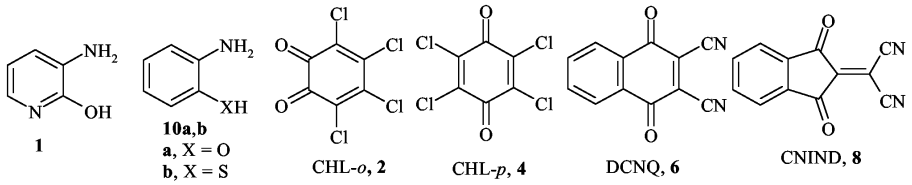


Fig. 1. Structures of donors 3-amino-2-hydroxypyridine (**1**), 1-amino-(thio)phenols (**10a, b**) and acceptors CHL-*o* (**2**), CHL-*p* (**4**), DCNQ (**6**), and CNIND (**8**),

Results and Discussion

In this publication, we report facile syntheses of various pyridoxazinone, phenoxazinones and thiaphenoxazinones, *via* the reactions of both 3-amino-2-hydroxypyridine (**1**) and 2-amino-(thio)phenols (**10a,b**) with 3,4,5,6-tetrachloro-1,2-benzoquinone (**CHL-*o***, **2**), 2,3,5,6-tetrachloro-1,4-benzoquinone (**CHL-*p***, **4**), 2,3-dicyano-1,4-naphthoquinone (**DCNQ**, **6**) and 2-dicyanomethylene-indane-1,3-dione (**CNIND**, **8**) (see Fig. 1).

Scheme 1 outlines the reactivity of both **1** and **10a,b** towards **2**, **4**, **6** and **8**. It is interesting to note that the reactions of **1** or **10a,b** with the aforementioned π-acceptors were carried out in dry ethyl acetate at room temp.. Addition of **1** or **10a,b** as electron donors to electron acceptors in ethyl acetate at room temp. leads to complex formation, as indicated by CT-bands in the visible region (Table 1). These CT-complexes gradually disappeared to give the precipitated reaction products. Presumably, CT-complexes exist as intermediates before chemical reactions take place. The reaction time and the λ_{max} of the CT-complexes of **1** and **10a,b** with the former acceptors are given in Table 1.

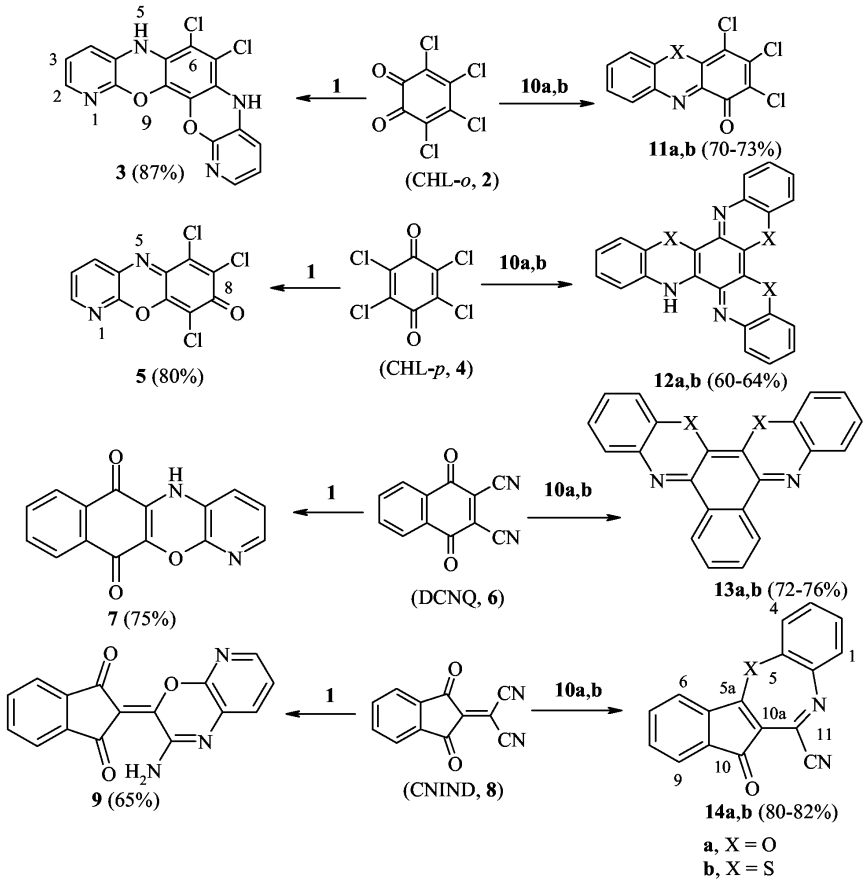
Table 1. Reaction time and absorption maxima for the CT-complexes of **1** and **10a,b** towards various π-acceptors in ethyl acetate at room temp.

Donor	Acceptor	λ_{max} (nm)	Reaction time (h)
1	**2**	420	24
1	**4**	426	24
1	**6**	435	72
1	**8**	438	24
10a	**2**	440	72
10a	**4**	465	24
10a	**6**	468	48
10a	**8**	415	48
10b	**2**	428, 460	24
10b	**4**	472	24
10b	**6**	462	12
10b	**8**	420	12

Treatment of compound **1** with **2** in ethyl acetate at room temp., for 24 h, furnished yellow crystals of **3** in 87% yield (Scheme 1, Table 1). The reaction was followed up by TLC analysis. Thus, it was apparent that the reaction was only completed after addition of two equivalents of **1**. The structure of **3** was proved by spectral data and elemental analysis. Mass spectrometry and elemental analysis proved the molecular formula of **3** as $C_{16}H_8Cl_2N_4O_2$. The IR spectrum of **3** did not reveal any absorptions assigned to the carbonyl group, whereas a strong absorption band at $\tilde{\nu} = 3160$ cm^{-1} corresponding to the absorption of the NH-group (the NH-proton resonated in the ^{1}H NMR spectrum at $\delta = 10.30$). The ^{1}H NMR spectrum of **3** showed two double-doublets at $\delta = 7.35$ and 7.20 ($J = 7.4$, 1.2 Hz) in addition to a triplet at $\delta = 6.25$ ($J = 7.2$, 1.2 Hz) corresponding H-2, H-4 and H-3 of the pyridinyl-protons, respectively. The ^{13}C NMR spectrum proved the symmetrical structure of **3** by the appearance of only eight carbon signals. It is unambiguously proved that the structure of **3** is 6,7-dichloro-5,8-dihydro-13,14-dioxa-1,5,8,12-tetrazapentaphene.

In an attempt to carry out the reaction of **1** with **4**, under the same reaction conditions, the reaction produced **5** in 80% yield (Scheme 1, Table 1). The molecular formula of **5** was elucidated by mass spectrometry and elemental analysis as $C_{11}H_3Cl_3N_2O_2$. The ^{1}H NMR spectrum of **5** is in accordance with the suggested structure and showed two double-doublets at $\delta = 7.80$ and 7.60 ($J = 7.4$, 1.2 Hz) corresponding to H-2 and H-4, respectively. Additionally, a triplet appeared at $\delta = 6.30$ ($J = 7.4$, 1.4 Hz) related to H-3. Most indicatively, the carbon NMR spectra of **5** revealed six distinctive carbon-signals at $\delta = 116.00$, 120.18, 136.90, 137.40, 158.80 and 184.80 corresponding to *C*-9, *C*H-3, *C*H-4, *C*H-2, *C*=N and *C*-8, respectively. From the results in hand, compound **5** was identified as 6,7,9-trichloro-8*H*-pyrido[2,3-*b*][1,4]benzoxazine-8-one.

Interestingly, the reaction between **1** and **6** produced compound **7** in 75% yield after chromatographic purification and recrystallization (Scheme 1). Mass spectrometry and elemental analysis proved the molecular formula of **7** as $C_{15}H_8N_2O_3$. The IR spectrum of the reaction product **7** indicated the presence of a carbonyl ($\tilde{\nu} = 1695-1680$ cm^{-1}), whereas a broad absorption band appeared at $\tilde{\nu} = 3180$ cm^{-1} related to the absorp-



Scheme 1. Reactions of 3-amino-2-hydroxypyridine (**1**) and 2-amino(thio)phenols (**10a, b**) with π-acceptors **2**, **4**, **6** and **8**. X = O, S.

tion of NH group. It is also apparent in the IR spectrum of **7** that there is no absorption bands in relation to the nitrile group. The ^{1}H NMR spectrum of **7** showed the pyridinyl protons as two double-doublets at $\delta = 7.40$ (H-2, $J = 7.4$, 1.2 Hz) and 7.00 (H-4, $J = 7.4$, 1.3 Hz), whereas H-3 appeared as a triplet at $\delta = 6.40$ ($J = 7.4$, 1.2 Hz). The aromatic protons resonated in the ^{1}H NMR spectrum as two muliplets (see the Experimental Section), while the NH-proton appeared as a broad singlet at $\delta = 9.80$. The ^{13}C NMR spectrum revealed the carbonyl carbons as two very close signals at $\delta = 166.20$ and 166.00. The rest of the spectral data of compound **7** unambiguously proved its structure which was identified as 5*H*-12-oxa-1,5-diazanaphthacene-6,11-dione.

Surprisingly, the reaction of equimolar amounts of **1** with **8** furnishes the formation of 2(2-aminopyrido[2,3-*b*]-1,4-oxazin-3-ylidene)indan-1,3-dione (**9**) in 65% yield (Scheme 1). The ^{1}H NMR spectrum revealed two double-doublets and a triplet which were assigned to the pyridinyl-protons, whereas a multiplet at $\delta =$ 7.90–7.70 and a broad singlet at $\delta = 3.80$ related to the fused benzene ring- and the NH_2-protons, respectively. In the ^{13}C NMR spectrum of **9**, the azomethine carbons which resonated at $\delta = 160.00$, whereas the exocyclic vinylic carbons appeared at $\delta = 118.90$ and 158.60. The three carbon signals of the pyridinyl-CH appeared at $\delta = 122.00$ (*C*H-3), 134.60 (*C*H-2) and 138.80 (*C*H-4). Besides, the two carbonyl groups, which absorbed in the IR spectrum at $\tilde{\nu} = 1695$–1680 cm^{-1}, appeared in the ^{13}C NMR spectrum at $\delta = 185.90$ and 184.30.

The reactions of donors **10a,b** with the same acceptors **2**, **4**, **6** and **8** in ethyl acetate at room temp. is also shown in Scheme 1. When donors **10a,b** reacted with **2**, the phenoxa(thia)azines **11a,b** are successfully obtained in good yields. It was previously indicated that the reaction of acceptor **4** with the donor **1** yielded the corresponding pyrido[2,3-*b*]-1,4-benzoxazine-8-one. However, the reaction of the same acceptor **4** with **10a,b** under the same reaction conditions afforded the trioxa(thia)triazatrinaphthylenes

12a,b in 30% together with recovered **4** (50%). It was noted that the reaction was completed only after addition of three equivalent amounts of **10a,b** relative to **4**. Consequently, addition of three equivalents of **10a,b** to **4** produced blue crystals of compounds **12a,b** in 60 – 64% yield as shown in Scheme 1 and Table 1. The structural proof of compounds **12a,b** was made on the basis of elemental analyses as well as IR, ^{1}H NMR, ^{13}C NMR and mass spectra. Mass spectrometry and elemental analysis confirmed the molecular formula of **12a** as $C_{24}H_{13}N_3O_3$. The IR spectrum of **12a** demonstrated strong absorption bands at $\tilde{\nu} = 3180$ and 1620 cm^{-1} relating to the absorptions of the NH- (the NH-proton appeared in the ^{1}H NMR spectrum as a broad singlet at $\delta = 11.82$) and azomethine groups (these groups resonated very closely in the ^{13}C NMR spectrum as two carbon signals at $\delta = 164.40$ and 164.00, respectively). The ^{13}C NMR spectrum of **12a** confirmed its unsymmetrical structure.

A similar observation was made during the reaction of **10a,b** with **6**, TLC analysis indicated that double amounts of **10a,b** were required to complete the reaction affording **13a,b** in 72 – 76% yield (Scheme 1, Table 1). The elemental analysis and mass spectrum confirmed the molecular formula of **13a** as $C_{22}H_{12}N_2O_2$. The IR spectrum of **13a** did not show any absorption due to the carbonyl, nitrile or NH groups. The symmetric structural feature of **13a** was elucidated on the basis of ^{13}C NMR spectrum. Compounds **13a,b** were confirmed and identified as dioxa(thia)diazahexaphenes. Since condensed phenoxazines and phenothiazines are of interest in the preparation of non-linear optical wave guiding polymer films [14 – 16] therefore, compounds **13a,b** may have prospective electronic industrial applications.

Surprisingly, on reacting **10a,b** with **8**, the reaction afforded **14a,b** (Scheme 1, Table 1). IR spectroscopy of **14a** (as an example) indicated the presence of the nitrile and carbonyl groups as sharp absorption bands at $\tilde{\nu} = 2210$ and 1695 cm^{-1}, respectively. Moreover, mass spectra and elemental analysis confirmed the molecular formula of **14a** as $C_{17}H_8N_2O_2$. The ^{1}H NMR spectrum of **14a** indicated three multiplets for six protons, whereas two separated double-doublets resonated at $\delta = 6.70$ and 7.80 ($J = 7.4$, 1.2 Hz), each for one proton. The ^{13}C NMR spectral data of **14a** revealed four distinctive deshielded carbon signals at $\delta = 148.00$, 156.00, 160.20 and 186.00 assigned to Ar-*C*-O, *C*-11, indenonyl-*C*-O (*C*-5a), and *C*-10 carbons, respectively. The most shielded carbon signals appeared in the ^{13}C NMR spectrum, were found resonating at $\delta = 98.00$ and 114.80, which related to *C*-10a and the nitrile carbons, respectively. The rest of the NMR spectral data confirmed the structure of **14a**, which was ultimately identified as indenonyl[*b*]-1,5-benzoxazepine-11-carbonitrile.

Recently, Müller and co-workers have described the synthesis of 2,4-di(hetero)aryl substituted 2,3-dihydrobenzo[*b*][1,4]heteroazepines as one-pot process initiated by a coupling-isomerization sequence of an electron poor (hetero)aryl halide and a terminal propargyl alcohol subsequently followed by cyclocondensation with 2-mercapto or 2-aminoanilines [17]. The advantage of our methodology is that the reaction of the bi-nucleophilic compounds with our target acceptors **2**, **4**, **6** and **8** directly afforded the corresponding benzoxazepines from readily available starting materials.

In conclusion, we have demonstrated very convenient procedures. For the syntheses of various pyridoxazines, benzoxa(thia)azines and benzoxa(thia) azepines. The advantage of these methodologies are the high yields of the desired products and the facility of the routes.

Experimental Section

Melting points are uncorrected. IR spectra were obtained on Nicolet 320 FT-IR using KBr pellets. ^{1}H and ^{13}C NMR were run at 400 and 100 MHz, respectively using a Bruker AM 400 spectrometer with TMS as internal standard. Mass spectra were run at 70 eV electron impact mode using a Finnigan MAT 8430 spectrometer. For preparative layer chromatography (PLC), glass plates (20×48 cm^2) were covered with a slurry of silica gel Merck PF_{254} and air-dried, using the solvents listed for development. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were performed by Microanalytical unit at Cairo university, Cairo, Egypt.

Starting materials

3-Amino-2-hydroxypyridine (**1**), 2-aminophenol (**10a**) and 2-aminothiophenol (**10b**) were commercially used from Fluka. 3,4,5,6-Tetrachloro-1,2-benzoquinone (**CHL-*o***, **2**) and 2,3,5,6-tetrachloro-1,4-benzoquinone (**CHL-*p***, **4**) were bought from Aldrich. 2,3-Dicyano-1,4-naphthoquinone (**DCNQ**, **6**) was prepared according to the procedure mentioned in reference [18]. 2-Dicyanomethyleneindane-1,3-dione (**CNIND**, **8**) was prepared following the procedure mentioned in reference [19].

Reaction of **1** *with acceptors* **2**, **4**, **6** *and* **8**

General procedure: A solution of **1** (0.22 g, 2 mmol) in dry ethyl acetate (40 ml) was added dropwise to a solution of the acceptor **2**, **4**, **6** or **8** (2 mmol) in dry ethyl acetate (40 ml) was stirred at the room temp. for 24 – 72 h (Table 1) until the consumption of the starting materials was finished (the reaction progress was monitored by TLC analysis). The solvent was evaporated *in vacuo* and the residue was purified by plates chromatography using toluene: ethyl acetate (10:1) as eluent. The obtained zones were extracted by acetone and then recrystallized.

6,7-Dichloro-5,8-dihydro-13,14-dioxa-1,5,8,12-tetrazapentaphene (**3**): Compound **3** (0.62 g, 87%) as yellow crystals (R_f 0.3, CH_2Cl_2), m. p. 160 – 162 °C. – (acetonitrile). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 380$ nm (3.70). – IR (film): $\tilde{\nu} = 3160$ (NH), 3030 – 2985 (Ar-CH), 1580 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, $CDCl_3$): $\delta = 6.25$ (t, $J = 7.2$ Hz, $J = 1.2$ Hz, 2 H, py-H-3), 7.20 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 2 H, py-H-4), 7.35 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 2 H, py-H-2), 10.30 (br s, 2 H, 2NH). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 118.00$ (2*C*-6), 120.60 (2py-*C*H-3), 131.00 (2q*C*), 132.90 (2q*C*), 136.80 (2py-*C*H-4), 138.90 (2py-*C*H-2), 151.80 (2*C*=N), 156.00 (2*C*-O). – MS (EI, 70 eV): *m/z* (%) = 360 (38) [M+2], 359 (100) [M^+], 357 (40), 324 (18), 288 (80), 286 (44), 266 (22), 228 (40), 182 (28), 180 (20), 144 (24), 72 (20). – $C_{16}H_8Cl_2N_4O_2$ (359.17): calcd. C 53.51, H 2.25, Cl 19.74, N 15.60; found C 53.50, H 2.20, Cl 19.68, N 15.47.

6,7,9-Trichloro-8*H*-pyrido[2,3-*b*]-1,4-benzoxazine-8-one (**5**): Compound **5** (0.48 g, 80%) as red violet crystals (R_f 0.4, CH_2Cl_2), m. p. 170 – 172 °C (acetonitrile). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 400$ (3.90). – IR (film): $\tilde{\nu} = 3040$ – 2990 (Ar-CH), 1690 (CO), 1575 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta = 6.30$ (t, $J = 7.4$ Hz, $J = 1.4$ Hz, 1 H, py-H-3), 7.60 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, py-H-4), 7.80 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, py-H-2). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 116.00$ (*C*-9), 120.18 (py-*C*H-3), 136.90 (py-*C*H-4), 137.40 (py-*C*H-2), 139.00 (q*C*-Cl), 140.00 (q*C*-N), 141.00 (q*C*-Cl), 154.00 (q*C*-O), 156.00, 158.80 (*C*=N), 184.80 (*C*-8). – MS (EI, 70 eV): *m/z* (%) = 301 (100) [M^+], 289 (82), 287 (46), 285 (20), 266 (20), 228 (38), 78 (20). – $C_{11}H_3Cl_3N_2O_2$ (301.52): calcd. C 43.82, H 1.00, Cl 35.27, N 9.29; found C 43.75, H 0.94, Cl 35.20, N 9.30.

5*H*-12-Oxa-1,5-diazanaphthacene-6,11-dione (**7**): Compound **7** (0.40 g, 75%) as orange crystals (R_f 0.2, CH_2Cl_2), m. p. 220-222 °C (EtOH). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) =$ 410 (4.10). – IR (film): $\tilde{\nu} = 3180$ (NH), 3050 – 2900 (Ar-CH), 1695 – 1680 CO), 1590 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta = 6.40$ (t, $J = 7.4$ Hz, $J =$ 1.2 Hz, 1 H, py-H-3), 7.00 (dd, $J = 7.4$ Hz, $J = 1.3$ Hz, 1 H, py-H-4), 7.40 (dd, $J = 7.4$ Hz, $J = 1.4$ Hz, 1 H, py-H-2), 7.70 – 7.50 (m, 2 H), 8.20 – 8.00 (m, 2 H), 9.80 (br s, 1 H, NH). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta =$ 118.80 (py-CH-3), 126.90 (Ar-*C*H), 128.00, 130.00, 131.60 (q*C*), 132.00 (q*C*-Ar), 132.90, 133.80 (Ar-*C*H), 134.60 (q*C*-Ar), 136.40, (py-*C*H-4), 137.40 (py-*C*H-2), 152.90 (q*C*-O), 154.00, 166.00, 166.20 (*CO*). – MS (EI, 70 eV): *m/z* (%) = 264 (100) [M^+], 232 (46), 206 (18), 180 (22), 168 (20), 154 (24), 140 (16), 106 (22), 92 (24), 78 (16), 50 (12), 24 (14). – $C_{15}H_8N_2O_3$ (264.24): calcd. C 68.18, H 3.05, N 10.60; found C 68.00, H 3.00, N 10.56.

2-(2-Aminopyrido[2,3-*b*]-1,4-oxazine-3-ylidene)-indan-1,3-dione (**9**): Compound **9** (0.38 g, 65%) as yellow crystals (R_f 0.3, CH_2Cl_2), m. p. 138 °C (acetonitrile). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 400$ (3.90). – IR (film): $\tilde{\nu} = 3220$ – 3180 (NH, NH_2), 3030 – 2985 (Ar-CH), 1695 – 1680 (CO), 1590 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta = 3.80$ (br s, 2 H, NH_2), 6.30 (t, $J = 7.4$ Hz, $J = 1.3$ Hz, 1 H, py-H-3), 7.40 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, py-H-4), 7.60 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, py-H-2), 7.90 – 7.70 (m, 4 H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 118.90$, (exocycl. CO-*C*=C), 122.00 (py-*C*H-3), 128.50 (2Ar-*C*H), 132.80 (2Ar-*C*H), 134.60 (py-*C*H-4), 136.60 (q*C*), 137.50 (2q*C*), 138.80 (py-*C*H-2), 150.90 (q*C*), 158.60 (exocycl. CO-C=*C*), 160.00 (H_2N-*C*=N), 184.30, 185.90 (*C*O). – MS (EI, 70 eV): *m/z* (%) = 291 (100) [M^+], 232 (46), 206 (18), 180 (22), 168 (20), 154 (24), 140 (16), 106 (22), 92 (24), 78 (16), 50 (12), 24 (14). – calcd. $C_{16}H_9N_3O_3$ (291.26): calcd. C 65.98, H 3.11, N 14.43; found C 65.80, H 3.00, N 14.38.

Reaction of **10a**, **b** *with acceptors* **2**, **4**, **6** *and* **8**

General procedure: To a solution of either **10a** or **10b** in dry ethyl acetate (30 ml) was dropwise added to a solution of the acceptor **2**, **4**, **6** and **8** in dry ethyl acetate (40 ml) was stirred at the room temp. for 12 – 72 h until the consumption of the starting materials were finished (the reaction progress was monitored by TLC analysis). In case of the reaction of **10a,b** with **4**, three moles of the donors were led to react with one mole of the acceptor. While the reaction of **10a,b** with **6** was completed after addition two moles of the donors to one mole of the acceptor. Finally, the reaction of **10a,b** with **8**, equimolar amounts of both the donor and the acceptor were used to complete the reaction. The solvent was evaporated *in vacuo* and the residue was applied on PC using toluene as eluent as in case of the reaction of **10a,b** with **2**. In case of the reaction of **10a,b** with **4** or **6**, toluene: ethyl acetate (1:1) was used as eluent, whereas, in case of the reaction of **10a,b** with **8**, toluene was used to purify the obtained products **14a,b**. The obtained zones were extracted with acetone and recrystallized from the stated solvents.

2,3,4-Trichlorophenoxazine-1-one (**11a**): (0.21 g, 70%) as orange crystals (R_f 0.5, CH_2Cl_2), m. p. 186 – 188 °C (ace-

tonitrile). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 390$ nm (3.80). – IR (film): $\tilde{\nu} = 3050-2990$ (Ar-CH), 1680 (CO), 1580 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, $CDCl_3$): 7.40–7.26 (m, 3 H), $\delta = 7.80-7.70$ (m, 1 H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 118.00$ (q*C*-Cl), 120.00, 128.90 (Ar-*C*H), 130.28, 130.90 (q*C*), 132.00, 134.20 (Ar-*C*H), 135.00, 136.00 (q*C*), 150.90 (Ar-*C*-O), 152.00 (*C*=N), 182.00 (*C*O). – MS (EI, 70 eV): *m/z* (%) = 300 (100) [M^+], 298 (80), 296 (54), 294 (22), 264 (40), 228 (20), 192 (24), 144 (30), 108 (18), 72 (20). – $C_{12}H_4Cl_3NO_2$ (300.53): calcd. C 47.96, H 1.34, Cl 35.39, N 4.66; found C 47.78, H 1.30, Cl 35.28, N 4.60.

2,3,4-Trichlorophenothiazine-1-one (**11b**): (0.23 g, 73%) as orange crystals (R_f 0.4, CH_2Cl_2), m. p. 140–142 °C (EtOH). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 400$ nm (3.90). – IR (film): $\tilde{\nu} = 3060-2994$ (Ar-CH), 1682 (CO), 1584 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, $CDCl_3$): $\delta = 7.44-7.22$ (m, 3 H), 7.84–7.72 (m, 1 H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 118.60$ (q*C*-Cl), 120.40, 128.80 (2Ar-*C*H), 130.20, 131.10 (q*C*), 132.40, 134.40 (2Ar-*C*H), 135.20, 136.20 (q*C*), 150.60 (Ar-*C*-O), 152.40 (*C*=N), 182.80 (*C*O). – MS (EI, 70 eV): *m/z* (%) = 316 (100) [M^+], 314 (78), 312 (52), 310 (20), 284 (20), 282 (24), 280 (34), 244 (30), 210 (18), 208 (24), 124 (14), 108 (22), 72 (24). – $C_{12}H_4Cl_3NOS$ (316.59): calcd. C 45.53, H 1.27, Cl 33.59, N 4.42; found C 45.40, H 1.22, Cl 33.52, N 4.40.

17*H*-5,6,12-Trioxa-11,17,18-triazatrinaphthylene (**12a**): (0.70 g, 60%) as blue crystals (EtOH), m. p. 260–262 °C. – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 420$ nm (4.10). – IR (film): $\tilde{\nu} = 3180$ (NH), 3080–3000 (Ar-CH), 1620 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta =$ 6.40 (dd, $J = 8.4$ Hz, $J = 1.4$ Hz, 2 H), 6.70 (dd, $J = 8.4$ Hz, $J = 1.4$ Hz, 2 H), 7.24–7.08 (m, 3 H, Ar-H), 7.72–7.52 (m, 5 H, Ar-H), 11.82 (br, s, 1 H, NH). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 115.30$ (q*C*), 116.00 (Ar-*C*H), 118.60, 118.80, 123.40, 123.60, 123.80 (q*C*), 124.00, 124.90, 126.60 (Ar-*C*H), 126.70, 127.50, 128.00, 128.90, 134.00 (Ar-*C*H), 134.70, 137.00 (q*C*), 137.50, 138.90 (q*C*), 140.50, 152.00 (Ar-*C*-O), 156.00 (Ar-*C*-O), 164.00, 164.40 (*C*=N). – MS (EI, 70 eV): *m/z* (%) = 391 (100) [M^+], 282 (60), 268 (24), 252 (18), 222 (20), 196 (34), 112 (20), 98 (16). – $C_{24}H_{13}N_3O_3$ (391.39): calcd. C 73.65, H 3.35, N 10.74; found C 73.50, H 3.25, N 10.58.

17*H*-5,6,12-Trithia-11,17,18-triazatrinaphthylene (**12b**): (0.84 g, 64%) as blue crystals (EtOH), m. p. 300–302 °C. – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 440$ nm (4.28). – IR (film): $\tilde{\nu} = 3160$ (NH), 3070–3010 (Ar-CH), 1622 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta =$ 6.60 (dd, $J = 8.4$ Hz, $J = 1.4$ Hz, 2 H), 6.80 (dd, $J =$ 8.2 Hz, $J = 1.4$ Hz, 2 H), 7.24–7.10 (m, 3 H, Ar-H), 7.70–7.48 (m, 5 H, Ar-H), 11.80 (br, s, 1H, NH). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 115.30$ (q*C*), 118.00 (Ar-*C*H), 118.90, 120.00, 123.60, 123.80, 123.94 (q*C*), 124.20, 124.98, 126.70 (Ar-*C*H), 126.90, 127.70, 128.20, 128.98, 134.30, 134.80, 137.40 (q*C*), 137.60, 139.10, 140.70, 152.20 (Ar-*C*-O), 156.40, 164.20, 164.50 (Ar-*C*=N). – MS (EI, 70 eV): *m/z* (%) = 439 (100) [M^+], 314 (60), 281 (16), 247 (80), 186 (12), 174 (52), 136 (14), 124 (80), 97 (62), 76 (30), 55 (85). – $C_{24}H_{13}N_3S_3$ (439.58): calcd. C 65.58, H 2.98, N 9.56, S 21.88; found C 65.40, H 2.90, N 9.45, S 21.71.

15,16-Dioxa-5,10-diazahexaphene (**13a**): (0.48 g, 72%) as green crystals (EtOH), m. p. 210–212 °C. – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 428$ nm (4.18). – IR (film): $\tilde{\nu} =$ 3060–3020 (Ar-CH), 1640 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta = 7.40-7.10$ (m, 8 H, Ar-H), 7.90–7.78 (m, 4 H, Ar-H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 120.90$ (2Ar-*C*H), 122.70 (2Ar-*C*H), 124.80 (2Ar-*C*H), 127.70 (2Ar-*C*H), 129.10 (2q*C*), 132.80 (2Ar-*C*H), 134.90 (2Ar-*C*H), 137.50 (2q*C*), 148.70 (2q*C*), 150.20 (2q*C*), 164.50 (2q*C*=N). – $C_{22}H_{12}N_2O_2$ (336.35): calcd. C 78.56, H 3.60, N 8.33; found C 78.43, H 3.54, N 8.21.

15,16-Dithia-5,10-diazahexaphene (**13b**): (0.56 g, 76%) as green crystals (EtOH), m. p. 260 °C (decop.). – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 424$ nm (4.20). – IR (film): $\tilde{\nu} =$ 3060–3020 (Ar-CH), 1648 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz- DMSO-d_6): $\delta = 7.44-7.18$ (m, 8 H, Ar-H), 8.05–7.84 (m, 4 H, Ar-H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 122.00$ (2Ar-*C*H), 122.90 (2Ar-*C*H), 125.00 (2Ar-*C*H), 127.90 (2Ar-*C*H), 129.60 (2q*C*), 132.90 (2Ar-*C*H), 134.94 (2Ar-*C*H), 137.62 (2q*C*), 148.90 (2q*C*), 150.40 (2q*C*), 164.00 (2q*C*=N). – $C_{22}H_{12}N_2S_2$ (368.48): calcd. C 71.71, H 3.28, N 7.60; found C 71.58, H 3.20, N 7.55.

Indene-10-one-yl[*b*]-1,4-benzoxazepine-11-carbonitrile (**14a**): (0.44 g, 80%) as yellow crystals (actetonitrile), m. p. 174–176 °C. – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 390$ nm (3.80). – IR (film): $\tilde{\nu} = 3056-3008$ (Ar-CH), 2210 (CN), 1695 (CO), 1620 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, DMSO-d_6): $\delta = 6.70$ (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, Ar-H), 7.08–6.90 (m, 2 H, Ar-H), 7.40–7.24 (m, 2 H, Ar-H), 7.70–7.52 (m, 2 H, Ar-H), 7.80 (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, Ar-H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): $\delta = 98.00$ (indenonyl-*C*-CO), 114.80 (*C*N), 122.70 (Ar-*C*H), 124.00, 126.10, 126.60, 127.70, 128.90, 132.00, 132.80, 135.10 (q*C*), 137.50, 141.70, 148.00 (Ar-*C*-O), 156.00 (*C*-11), 160.20 (indenonyl-*C*-O, *C*-5a), 186.00 (*C*-10). – $C_{17}H_8N_2O_2$ (272.27): C 75.00, H 2.96, N 10.29; found C 75.20, H 2.90, N 10.34.

Indene-10-one-yl[*b*]-1,4-benzothiazepine-11-carbonitrile (**14b**): (0.47 g, 82%) as yellow crystals (actetonitrile), m. p. 190–192 °C. – UV/vis (CH_3CN): $\lambda_{max}(\lg\varepsilon) = 398$ nm (3.90). – IR (film): $\tilde{\nu} = 3050-3010$ (Ar-CH), 2212 (CN), 1690 (CO), 1618 (C=N) cm^{-1}. – ^1H NMR (400.134 MHz, $CDCl_3$): $\delta = 6.70$ (dd, $J = 7.4$ Hz, $J = 1.2$ Hz, 1 H, Ar-H),

7.12 – 6.94 (m, 2 H, Ar-H), 7.50 – 7.34 (m, 2 H, Ar-H), 7.80 – 7.60 (m, 3 H, Ar-H). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 98.40 (indenonyl-*C*-CO, *C*-10a), 114.90 (*C*N), 122.80 (Ar-*C*H), 124.30, 126.40, 126.70, 127.60, 129.00, 132.08, 132.60, 135.20 (q*C*), 137.40, 141.60, 148.64 (Ar-*C*-O), 156.50 (*C*-11), 160.60 (indenonyl-*C*-O), 186.40 (*C*-10). – $C_{17}H_8N_2OS$ (288.33): calcd. C 70.82, H 2.80, N 9.72; found C 70.70, H 2.80, N 9.64.

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