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-aminophenol and dithiooxamide to produce colored phenoxazinones, phenoquinoniminediethanes and triphenoxazinones [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 neomaphimidine [9] contain this pharmacophoric moiety within a polycondensed system.

The recent [10, 11] discovery of a novel class of powerful antitumor intercalating phenoazaxinone 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(4H)-1,3-oxazolones and tetrazoles towards benzoyne and we succeeded to synthesize 1,4-benzoxazepines and benzyltetrazoles, respectively [13a, b]. Subsequently, we examined the reaction of N-vinyl-1H-imidazole with benzoyne and some selected π-deficient compounds which was catalytic under basic conditions [13c]. Recently, diaryl azines have been shown to react with benzoyne (o-benzoyne) to give 10-amino-3-substituted-9(10H)-acidimones. 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].
Results and Discussion

In this publication, we report facile syntheses of various pyridoxazine, 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-\(\alpha\), 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 \(\pi\)-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 \(\lambda_{\text{max}}\) 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 \(\pi\)-acceptors in ethyl acetate at room temp.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>420</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>426</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>435</td>
<td>72</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>438</td>
<td>24</td>
</tr>
<tr>
<td>10a</td>
<td>2</td>
<td>440</td>
<td>72</td>
</tr>
<tr>
<td>10a</td>
<td>4</td>
<td>465</td>
<td>24</td>
</tr>
<tr>
<td>10a</td>
<td>6</td>
<td>468</td>
<td>48</td>
</tr>
<tr>
<td>10a</td>
<td>8</td>
<td>415</td>
<td>48</td>
</tr>
<tr>
<td>10b</td>
<td>2</td>
<td>428, 460</td>
<td>24</td>
</tr>
<tr>
<td>10b</td>
<td>4</td>
<td>472</td>
<td>24</td>
</tr>
<tr>
<td>10b</td>
<td>6</td>
<td>462</td>
<td>12</td>
</tr>
<tr>
<td>10b</td>
<td>8</td>
<td>420</td>
<td>12</td>
</tr>
</tbody>
</table>

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_{3}Cl_{2}N_{2}O_{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-dioxo-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_{17}H_{3}Cl_{3}N_{2}O_{2}. The \(^1\)H NMR spectrum of 5 is in accordance with the suggested structure and showed two double-doublets at \(\tilde{\nu} = 7.80\) 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, CH-3, CH-4, CH-2, C=N and C-8, respectively. From the results in hand, compound 5 was identified as 6,7,9-trichloro-8H-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_{13}N_{2}O_{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-
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 $\delta = 6.40$ (H = 7.4, 1.2 Hz). The aromatic protons resonated in the $^1$H NMR spectrum as two multiplets (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 $\delta = 122.00$ (CH-3), 134.60 (CH-2) and 138.80 (CH-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, 1H NMR, 13C NMR and mass spectra. Mass spectrometry and elemental analysis confirmed the molecular formula of 12a as C24H13N3O3. 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 1H NMR spectrum as a broad singlet at $\delta = 11.82$) and azomethine groups (these groups resonated very closely in the 13C NMR spectrum as two carbon signals at $\delta = 164.40$ and 164.00, respectively). The 13C 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 C22H12N2O2. 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 13C NMR spectrum. Compounds 13a,b were confirmed and identified as diaza(1,4)diazahexaphenes. Since condensed phenoxazines and phenothiazines are of interest in the preparation of non-linear optical wave materials. 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. 1H and 13C 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 PF254 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 (DCNO, 6) was prepared according to the procedure mentioned in reference [18]. 6-Dicyanoethylenedione-1,3-dione (CNND, 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 aceton and then recrystallized.

6,7-Dichloro-5,8-dihydro-13,14-dioxa-1,5,8,12-tetraza-phenanthrene (3): Compound 3 (0.62 g, 87%) as yellow crystals (Rf 0.3, CH2Cl2), m. p. 160 – 162 °C. – (acetoni- trile). – UV/Vis (CH3CN): λmax (lg ε) = 380 nm (3.70). – IR (film): ν = 3160 (NH), 3030 – 2985 (Ar-CH), 1580 (C=N) cm⁻¹. – 1H NMR (400.134 MHz, CDCl3): δ = 6.25 (t, J = 7.4 Hz, 1 H, py-H-3), 7.20 (dd, J = 7.4 Hz, 1 H, 2 H, py-H-4), 7.35 (dd, J = 7.4 Hz, J = 1.2 Hz, 2 H, py-H-5), 3.72 (t, J = 7.2 Hz, 2 H, py-H-2). m. p. 220 – 222 °C (CH2Cl2), 292 (22), 228 (40), 182 (28), 170 (20), 144 (24), 72 (20). – C15H8N2O3 (264.24): calcd. C 68.18, H 3.06, N 14.43; found C 68.00, H 3.06, N 14.33.

1H NMR (100.6 MHz, DMSO-d 6): 13C δ (ppm) = 116.00 (2py-C-3), 132.80 (2Ar-C-7), 139.00 (q C-11), 7.80 (dd, J = 4 Hz, 2 H, py-H-2), 10.30 (br s, 2 H, 2NH).

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 was 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 aceton and recrystallized from the stated solvents.

5H-12-Oxa-1,5-diazanaphthacene-6,11-dione (7): Compound 7 (0.40 g, 75%) as orange crystals (Rf 0.2, CH2Cl2), m. p. 220 – 222 °C (EtOH). – UV/Vis (CH3CN): λmax (lg ε) = 410 (4.10). – IR (film): ν = 3180 (NH), 3050 – 2900 (Ar-CH), 1695 – 1680 CO), 1590 (C=N) cm⁻¹. – 1H NMR (400.134 MHz, DMSO-d6): δ = 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). – 13C [1H] NMR (100.6 MHz, DMSO-d6): δ = 118.80 (py-CH-3), 126.90 (Ar-CH), 128.00, 130.00, 131.60 (qC), 132.00 (qC-Ar), 132.90, 133.80 (Ar-CH), 134.60 (qC-Ar), 134.60, 134.60, 134.60 (qC-CH), 152.90 (py-CH-4), 154.00, 154.00, 166.20 (CO). – 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). – C16H12N2O2 (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-oxazin-3-ylidene)-inden-1,3-dione (9): Compound 9 (0.38 g, 65%) as yellow crystals (Rf 0.3, CH2Cl2), m. p. 138 °C (acetoni- trile). – UV/Vis (CH3CN): λmax (lg ε) = 300 – 3180 (NH, NH2), 3030 – 2985 (Ar-CH), 1695 – 1680 (CO), 1590 (C=N) cm⁻¹. – 1H NMR (400.134 MHz, DMSO-d6): δ = 3.80 (br s, 2 H, NH2), 6.30 – 7.40 (m, J = 1.3 Hz, 2 H, py-H-5), 3.70 (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). – 13C [1H] NMR (100.6 MHz, DMSO-d6): δ = 118.90, 120.60 (2py-C), 123.80 (2Ar-C), 136.60 (CO), 151.80 (q C-11), 154.00, 166.00, 166.20 (C=N). – 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). – C16H12N2O2 (291.26): calcd. C 68.18, H 3.11, N 14.43; found C 68.00, H 3.00, N 14.38.
tonitrile). – UV/Vis (CH3CN): λmax(ε) = 390 nm (3.80), 
– IR (film): ν = 3050–2990 (Ar-CH), 1680 (C=O), 1580 (C=C) cm⁻¹; 
13C NMR (400.134 MHz, CDCl3): δ = 7.40 – 7.26 (m, 3 H), δ = 7.80 – 7.70 (m, 1 H). – 13C[1]H NMR (100.6 MHz, CDCl3): δ = 118.00 (q, C=O), 120.00, 128.90 (Ar-CH), 130.28, 130.90 (q, C=O), 132.00, 134.20 (Ar-CH), 135.00, 136.00 (q, C=O), 150.90 (Ar-C=O), 152.00 (C=O), 182.00 (C=O) – MS (EI, 70 eV): m/z (%) = 390 (100) [M]+, 281 (16), 247 (80), 186 (12), 174 (52), 136 (14), 124 (80), 97 (62), 76 (30), 55 (85), – C2H5H2N2S3 (439.58): calcld. C 65.58, H 2.98, N 9.56, S 21.81; found C 65.40, H 2.90, N 9.45, S 21.71.

15.16-Dioxo-5,10-diazahexaphene (13a): (0.48 g, 72%) as green crystals (EtOH), m.p. 210 – 212 ºC – UV/Vis (CH3CN): λmax(ε) = 424 nm (4.20). – IR (film): ν = 3060–3020 (Ar-CH), 1640 (C=O) cm⁻¹. – 1H NMR (400.134 MHz, DMSO-d6): δ = 7.40 – 7.10 (m, 8 H, Ar-H), 7.90 – 7.78 (m, 4 H, Ar-H). – 13C NMR (100.6 MHz, DMSO-d6): δ = 129.00 (2Ar-CH), 127.20 (2Ar-CH), 129.70 (2Ar-C=O), 132.80 (2Ar-CH), 134.90 (2Ar-C=O), 137.80 (2q, C=O), 147.80 (2q, C=O), 150.20 (2q, C=O), 164.50 (2q,C=O). – C2H5H2N2S3 (336.35): calcld. 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 ºC (decolor). – UV/Vis (CH3CN): λmax(ε) = 424 nm (4.20). – IR (film): ν = 3060–3020 (Ar-CH), 1648 (C=O) cm⁻¹. – 1H NMR (400.134 MHz, DMSO-d6): δ = 7.44 – 7.18 (m, 8 H, Ar-H), 8.05 – 7.84 (m, 4 H, Ar-H). – 13C NMR (100.6 MHz, DMSO-d6): δ = 122.00 (2Ar-CH), 122.90 (2Ar-CH), 125.00 (2Ar-CH), 127.90 (2Ar-C=O), 129.60 (2q, C=O), 132.90 (2Ar-CH), 134.94 (2Ar-C=O), 137.62 (2q, C=O), 149.80 (2q, C=O), 150.40 (2q, C=O), 164.00 (2q,C=O). – C2H5H2N2S3 (368.48): calcld. C 71.71, H 3.28, N 7.60; found C 71.58, H 3.20, N 7.55.

Indene-10-oneyl[1,4-benzoxazepine-11-carbonitrile (14a): (0.44 g, 80%) as yellow crystals (acetonitrile), m.p. 174 – 176 ºC. – UV/Vis (CH3CN): λmax(ε) = 390 nm (3.80). – IR (film): ν = 3056–3008 (Ar-CH), 2210 (CN), 1695 (CO), 1620 (C=O) cm⁻¹. – 1H NMR (400.134 MHz, DMSO-d6): δ = 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). – 13C NMR (100.6 MHz, DMSO-d6): δ = 98.00 (indenonyl-C=O), 114.80 (CN), 122.70 (Ar-C=O), 124.00, 126.10, 126.60, 129.70 (2Ar-C=O), 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). – C17H10N2O2 (272.27): C 75.00, H 2.96, N 10.29; found C 75.20, H 2.90, N 10.34.

Indene-10-oneyl[1,4-benzothiazepine-11-carbonitrile (14b): (0.47 g, 82%) as yellow crystals (acetonitrile), m.p. 190 – 192 ºC. – UV/Vis (CH3CN): λmax(ε) = 398 nm (3.90). – IR (film): ν = 3050–3010 (Ar-CH), 2212 (CN), 1690 (CO), 1618 (C=O) cm⁻¹. – 1H NMR (400.134 MHz, CDCl3): δ = 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). – 13C\textsuperscript{1H} NMR (100.6 MHz,
CDCl\textsubscript{3}): \(\delta = 98.40\) (indenonyl-C(O), C-10a), 114.90
(CN), 122.80 (Ar-CH), 124.30, 126.40, 126.70, 127.60,
129.00, 132.08, 132.60, 135.20 (q CN), 137.40, 141.60, 148.64
(Ar-C=O), 156.50 (C-11), 160.60 (indenonyl-C(O)), 186.40
(C-10). – C\textsubscript{17}H\textsubscript{8}N\textsubscript{2}O\textsubscript{5} (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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