Convenient Synthesis of New Boric Acid Catalyzed 1,2,4-Triazolopyridinone Derivatives and an Investigation of their Optical Properties

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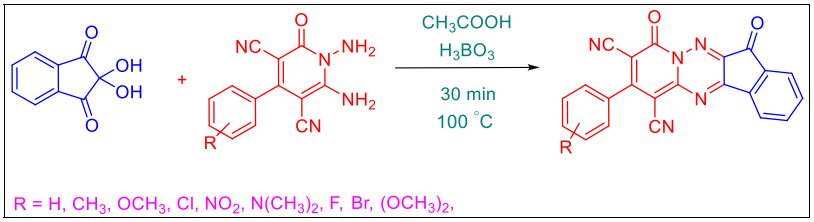

Syntheses of fused heterobicyclic systems containing 1,2,4-triazolopyridinone moieties were accomplished by heterocyclization of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitriles and ninhydrin in ethanol and in the presence of boric acid as a catalyst in 30 min at room temperature. All compounds have been screened for their photophysical properties. Results showed that all compounds exhibit near infrared emissions at 876 nm.

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INTRODUCTION

1,2,4-Triazine derivatives are important classes of heterocyclic compounds which have various biological properties such as anticancer, muscle relaxant, hypnotic, anti-inflammatory, diuretic, and antihypertensive activities [1–4]. In particular, literature studies on 1,2,4-triazoles have shown that the fused 1,2,4-triazoles have a great potential as antifungal [5], antibactericidal [5,6], anxiolytic [7,8], anticonvulsant [9], or herbicidal [10] activities and can act as "antidepressant" reagents [11]. The most widely applicable routes to the synthesis of fused 1,2,4-triazoles mainly involve hydrazones as precursors. However, this method has some limitations on their use, such as toxic reagents like lead tetraacetate [12,13] and bromine [13,14]. Also, the products were isolated in low yield and isolated as salts [15,16].

Recently, fused heterobicyclic systems containing the 1,2,4-triazinopyridinone moiety have been prepared by the heterocyclization of *N*-amino-2-pyridones with different reagents [17]. Meanwhile, reactions of some active carbonyl compounds with 4-aryl-1,6-diamino-2-oxo-1,2-dihydro-pyridine-3,5-dicarbonitrile derivatives have been documented in recent years [18]. Therefore, the development of efficient, clean, and environmentally friendly approaches using new catalysts for the synthesis of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivatives is an important task for organic chemists.

Small molecules with the absorption and fluorescence in the near infrared (NIR) spectral region (e.g., 800–1500 nm) are readily available and have been successfully used in different spectral region. Nearly 50% of solar energy falls in the NIR spectral region, which calls for NIR photovoltaic materials in solar energy conversion [19].

The chromogenic properties of NIR organic materials [20] are expected to receive growing attention for some unique applications, such as NIR variable optical attenuators based on NIR electrochromic organic materials [21], NIR chiral materials for optical switching [22], NIR chemochromic organic materials for chemical sensing [23], and NIR liquid crystalline materials for liquid crystal devices [24]. NIR absorbing pigments are used in laser printers and digital copy machines as the charge-generation material [25] and in optical disks (e.g., CD-R) as the information-storage material [26]. Significant advances in the research and development of NIR organic materials for these existing and emerging applications are certainly expected in the near future. So it was thought worthwhile to incorporate 1,2,4-triazine into the pyridinone ring using 1,6-diaminopyridinone derivatives as starting materials for the building of newly fused heterobicyclic systems.

RESULTS AND DISCUSSION

The starting material 4-(aryl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile derivatives were obtained [27] from cyclocondensation of cyanoacetohydrazide with p-benzilidenemalononitriles under refluxing in absolute ethanol in the presence of piperidine. These 1,2-

biamino compounds are more favored to the ring closure reactions.

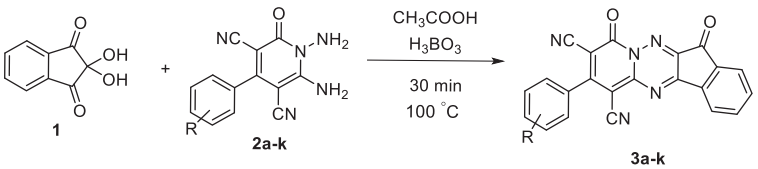
Dihydroindeno[1,2-*e*]pyrido[1,2-*b*][1,2,4]triazine-1,3-dicarbonitrile derivatives (**3a**–**k**) were easily prepared from the readily available 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivatives by reaction with ninhydrin in the presence of boric acid as a catalyst and acetic acid as a solvent (Scheme 1, Table 1).

Structure assignments of new products have been established on the basis of elemental analysis and spectral data. For example, the IR spectrum of compound **3b** showed absorption bands at 1689 and 1740 cm^{-1} assigned to C=O groups and bands at 2216 cm^{-1} assigned to CN groups. The ^{1}H-NMR spectrum of **3b** showed a singlet signal for the methyl protons at δ = 2.47 ppm. In addition, doublets at δ = 7.50 ppm and δ = 7.62 ppm and multiples at δ = 8.09–8.16 ppm and δ = 8.20–8.24 ppm and δ = 8.35–8.39 ppm correspond to nine protons present in the molecule. The ^{13}C-NMR spectrum of **3b** displayed a downfield signal at δ = 172.53 ppm and δ = 183.68 ppm for the two carbonyl groups and at δ = 21.58 ppm for the methyl carbon. Also, two signals at δ = 91.81 ppm and δ = 99.64 ppm correspond to CN groups.

The pathway to the products can be explained by firstly the activation of ninhydrin and then the formation of intermediate A. Formation of target compounds occur *via* a nucleophilic addition–elimination reaction of the 6-position -NH2 group. It is plausible that the amino group in the 6-position is more reactive than that attached to the ring nitrogen in the 1-position. Attack of the primary 6-position amino group on the hydrate form of the central carbon of the ninhydrin molecule can account for the formation of intermediate A, and this is followed by nucleophilic attack of the second -NH2 present in the system on the carbonyl group to yield the final products (Scheme 2).

The photophysical properties of compounds **3a**–**k** were studied by ultraviolet–visible and fluorescence spectroscopies. Absorption and emission spectra of 3×10^{-6} M solutions (solvent: dimethylformamide) of compounds are shown in Figures 1 and 2 , respectively. The absorption behaviors of all the samples were quite similar to each other meaning that the optical band gap

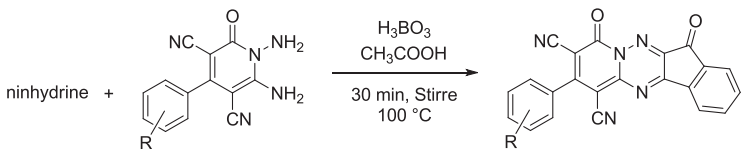
Scheme 1. Synthesis of dihydroindeno[1,2-*e*]pyrido[1,2-*b*][1,2,4]triazine-1,3-dicarbonitrile derivatives.



R = H, CH_3, OCH_3, Cl, NO_2, $N(CH_3)_2$, F, Br, $(OCH_3)_2$,

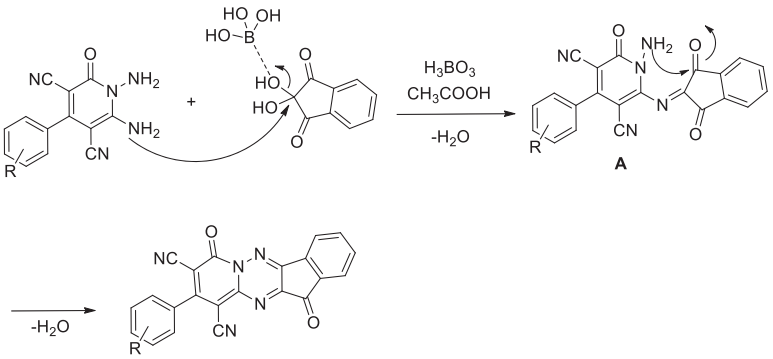
Table 1

Synthesis of dihydroindeno[1,2-*e*]pyrido[1,2-*b*][1,2,4]triazine-1,3-dicarbonitrile derivatives (**3a**–**k**).



Entry	Products	R	Melting point
1	**3a**	H	324–327
2	**3b**	4-Me	325–328
3	**3c**	4-OMe	326–330
4	**3d**	4-Cl	326–329
5	**3e**	3-NO_2	310–314
6	**3f**	4-N (Me)2	330–334
7	**3g**	4-F	319–322
8	**3h**	2-Cl	327–330
9	**3i**	4-Br	320–324
10	**3j**	3-Cl	320–324
11	**3k**	2,4-dimethyl	324–329

Scheme 2. A possible mechanism for the synthesis of dihydroindeno[1,2-*e*]pyrido[1,2-*b*][1,2,4]triazine-1,3-dicarbonitrile derivatives.



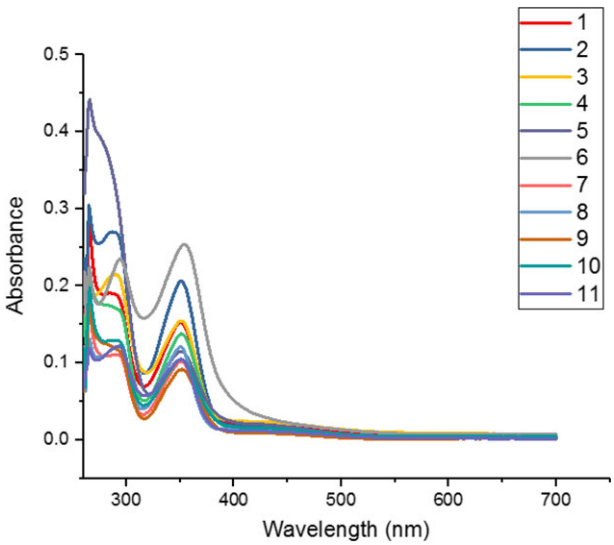


Figure 1. Absorption spectra of the synthesized compounds (**1**–**11**). [Color figure can be viewed at wileyonlinelibrary.com]

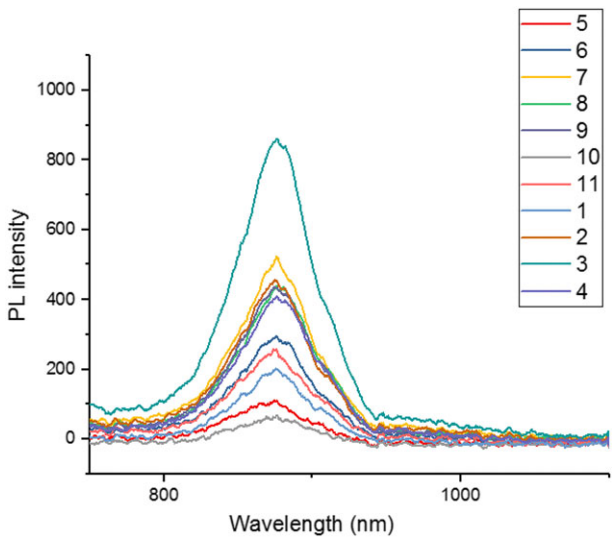


Figure 2. Fluorescence emission spectra of the synthesized compounds (**3a**–**k**). [Color figure can be viewed at wileyonlinelibrary.com]

of the molecules originates from a unit structure. Also, emission maxima and molar extinction coefficient are reported (Table 2). According to Table 2, the maximum absorption of all the **3a**–**k** compounds was located at 350–353 nm. The emission spectra of all the **3a**–**k** compounds were very similar, with their emission maxima within a narrow range around 876 nm (Figure 2).

In conclusion, an efficient, general, and simple methodology for the synthesis of dihydroindeno[1,2-*e*] pyrido[1,2-*b*][1,2,4]triazine-1,3-dicarbonitrile derivatives from 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile and ninhydrin in the presence of boric acid is reported. In this way, the procedure offers several advantages including cleaner reaction profiles, excellent yields, shorter reaction time, and higher purity products. Also, according to their emission spectra, they exhibit NIR emissions at 876 nm.

EXPERIMENTAL

General information. All chemicals and solvents were purchased from commercial sources and used without further purification unless otherwise stated. Melting points were determined on a Melt-Tem II melting point apparatus and are uncorrected. IR spectra were obtained on a Matson-1000 FTIR spectrometer. Peaks are reported in wave numbers ($cm^{-}1$) All of the NMR spectra were recorded on a Bruker model DRX-400 AVANCE (^{4}H: 300, ^{13}C: 100 MHz) and on a Varian model (^{1}H: 500, ^{13}C: 125 MHz) NMR spectrometer. Chemical shifts of ^{1}H and ^{13}C-NMR are reported in parts per million (ppm) from tetramethylsilane as an internal standard in DMSO-d_6 as a solvent and. Ultraviolet–visible and fluorescence (PL) spectra were measured using a Perkin Elmer and Avantes spectrometer (AvaSpec-2048 TEC), respectively.

Table 2

Ultraviolet–visible absorption data compounds **3a**–**k**.

Compound	λmax (nm)	ε_{max}	Compound	λmax (nm)	ε_{max}
3a	350	33441	**3g**	351	23048
3b	350	40573	**3h**	350	22409
3c	351	39959	**3j**	351	21930
3d	351	19425	**3i**	351	21698
3e	351	28315	**3k**	351	25249
3f	353	60619			

General procedure for the synthesis of compounds 3a–k. In a typical experimental procedure, 50 mL of round bottomed flask was charged with 15 mL of acetic acid, 0.2 mmol of boric acid, 2 mmol of ninhydrin, and 2 mmol of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivatives. The mixture was stirred at room temperature for 30 min. After completing the reaction (30 min, indicated by thin-layer chromatography), the solid formed was filtered and washed with water to obtain pure product.

4,7-Dioxo-2-phenyl-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3a). Prepared according to the general procedure, Orange solid, M. *P* = 324–327°C, Yield = 88%, IR (KBr, cm^{-1}):1467 (C=C), 1700, 1735. (C=O), 2222 (CN). ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.68–7.75 (m, 5H, H_{Ar}), 8.10–8.16 (m, 2H, H_{Ar}), 8.21–8.24 (m, 1H. H_{Ar}), 8.36–8.40 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6) δ = 91.80, 99.83 (CN), 114.90, 115.37, 124.89, 125.71, 125.99, 128.67, 129.42, 131.67, 137.22, 137.78, 138.13, 138.96, 141.04, 148.40, 151.30 (Ar), 156.22, 160.52 (C=N), 160.76, 183.67 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_9N_5O_2$: C, 70.40; H, 2.42; N, 18.66%, Value found: C, 70.33; H, 2.39; N, 18.61%.

4,7-Dioxo-2-(p-tolyl)-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3b). Prepared according to the general procedure, Orange solid, M. *P* = 325–328°C, Yield = 86%, IR (KBr, cm^{-1}):1465 (C=C), 1689, 1740 (C=O), 2216 (CN). ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 2.47 (S, 3H, Me), 7.50 (d, 2H, *J* = 8 Hz), 7.62 (d, 2H, *J* = 8 Hz), 8.09–8.16 (m, 2H, H_{Ar}), 8.20–8.24 (m, 1H, H_{Ar}), 8.35–8.39 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (100 MHz, DMSO-d_6) δ = 2158 (CH3), 91.81, 99.64 (CN), 114.60, 115.59, 125.71, 125.96, 128.93, 129.96, 130.85, 137.22, 138.10, 138.56, 141.02, 141.83, 148.32, 151.28, 156.25, 160.46, 160.81 (C=N), 172.53, 183.68 (C=O) ppm. Elemental analysis: Value calculated for $C_{23}H_{11}N_5O_2$: C, 70.95; H, 2.85; N, 17.99%, Value found: C, 70.78; H, 2.80; N, 17.89%.

2-(4-Methoxyphenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3c). Prepared according to the general procedure, Orange solid, M. *P* = 326–330°C, Yield = 90%, IR (KBr, cm^{-1}): 1157 (C-O), 1462 (C=C), 1689, 1741 (C=O), 2217(CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 3.88 (S, 3H, OMe), 7.22 (d, 2H, *J* = 10 Hz), 7.68 (d, 2H, *J* = 10 Hz), 8.07–8.12 (m, 2H, H_{Ar}), 8.17–8.20 (m, 1H, H_{Ar}), 8.33–8.35 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 55.97 (O-CH_3), 91.78, 99.34 (CN), 114.65, 114.77, 115.60, 125.55, 125.64, 125.89, 130.96, 137.22, 138.01, 138.51, 140.97, 148.18, 151.20 (Ar), 156.22, 160.37 (C=N), 162.02, 183.64 (C=O) ppm. Elemental analysis: Value calculated for $C_{23}H_{11}N_5O_3$: C, 68.15; H, 2.74; N, 17.28%, Value found: C, 68.07; H, 2.71; N, 17.19%.

2-(4-Chlorophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3d). Prepared according to the general procedure, Orange solid, M. *P* = 326–329°C, Yield = 87%, IR (KBr, cm^{-1}): 1478 (C=C), 1592, 1642 (C=N), 1711, 1733 (C=O), 2220 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.72–7.77 (m, 4H, H_{Ar}), 8.09–8.12 (m, 2H, H_{Ar}), 8.17–8.20 (m, 1H, H_{Ar}), 8.35 (S, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.65, 99.90 (CN), 114.31, 115.15, 125.65, 125.96, 129.57, 130.81, 132.58, 136.60, 137.19, 138.11, 138.50, 141.03 (Ar), 156.02, 159.59 (C=N), 160.56, 183.54 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8ClN_5O_2$: C, 64.48; H, 1.97; N, 17.09%, Value found: C, 64.39; H, 1.93; N, 17.16%.

2-(3-Nitrophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3e). Prepared according to the general procedure, Orange solid, M. *P* = 310–314°C, Yield = 93%, IR (KBr, cm^{-1}): 1352, 1467 (C-NO_2), 1700, 1735 (C=O), 2219 (C=N). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.98–8.02 (m, 1H, H_{Ar}), 8.10–8.13 (m, 2H, H_{Ar}), 8.17–8.21 (m, 2H, H_{Ar}), 8.37 (S, 1H, H_{Ar}), 8.51–8.54 (m, 1H, H_{Ar}), 8.64 (d.d, 1H, *J* = 2.5, 2.5 HZ) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.72, 100.34 (CN), 109.99, 114.23, 115.00, 123.93, 125.66, 126.01, 126.27, 131.43, 135.21, 135.43, 138.18, 138.50, 141.07, 148.17 (Ar), 151.26, 155.91 (C=N), 158.39, 183.50 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8N_6O_4$: C, 62.86; H, 1.92; N, 19.99%, Value found: C, 62.79; H, 1.89; N, 19.91%.

2-(4-(Dimethylamino)phenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3f). Prepared according to the general procedure, Orange solid, M. *P* = 330–334°C, Yield = 85%, IR (KBr, cm^{-1}): 1151, 1381 (N-CH_3), 1525, 1603 (C=N), 1698, 1733 (C=O), 2210 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 3.06 (S, 6H, N-CH3), 6.09 (d, 2H, *J* = 10 Hz), 7.60(d, 2H, *J* = 5 Hz), 8.06–8.12 (m, 2H, H_{Ar}), 8.17–8.19 (m, 1H, H_{Ar}), 8.32–8.34 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.41, 97.61 (CN), 111.03, 115.03, 116.25, 119.23, 125.60, 125.79, 130.93, 137.23, 137.83, 138.49, 140.90, 147.73 (Ar), 151.23, 152.67 (CN), 156.44, 160.14 (N-CH_3), 160.26, 183.73 (C=O) ppm.

Elemental analysis: Value calculated for $C_{24}H_{14}N_6O_2$: C, 68.89; H, 3.37; N, 20.09%, Value found: C, 68.79; H, 3.32; N, 19.97%.

2-(4-Fluorophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e] pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3g). Prepared according to the general procedure, Orange solid, M. *P* = 319–323°C, Yield = 76%, IR (KBr, cm^{-1}): 1238 (C-F), 1466 (C=C), 1560, 1605 (C=N), 1695, 1739 (C=O), 2218 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.50–7.54 (m, 2H, H_{Ar}), 7.76–7.80 (m, 2H, H_{Ar}), 8.08–8.13 (m, 2H, H_{Ar}), 8.17–8.20 (m, 1H, H_{Ar}), 8.33–8.36 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.82, 99.98 (CN), 114.39, 115.25, 116.51, 116.69, 125.65, 125.95, 130.15, 1313.58, 131.65, 137.20, 138.09, 138.51, 141.02, 148.41, 151.19 (Ar), 156.06, 159.78 (C=N), 160.53, 183.58 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8FN_5O_2$: C, 67.18; H, 2.05; N, 17.81%, Value found: C, 67.12; H, 1.98; N, 17.87%.

2-(2-Chlorophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e] pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3h). Prepared according to the general procedure, Orange solid, M. *P* = 327–330°C, Yield = 69%, IR (KBr, cm^{-1}): 668 (C-Cl), 1694, 1731 (C=O), 2232, 2353 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.63–7.71 (m, 3H, H_{Ar}), 7.78–7.80 (m, 1H, H_{Ar}), 8.09–8.13 (m, 2H, H_{Ar}), 8.19–8.22 (m, 1H, H_{Ar}), 8.35–8.37 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.99, 109.98 (CN), 113.76, 125.74, 128.60, 130.40, 130.53, 131.04, 132.89, 133.11, 137.14, 138.64 (Ar), 140.98, 151.38 (C=N), 183.53, 220.11 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8ClN_5O_2$: C, 64.48; H, 1.97; N, 17.09%, Value found: C, 64.35; H, 1.93; N, 17.15%.

2-(4-Bromophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e] pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3j). Prepared according to the general procedure, Orange solid, M. *P* = 320–334°C, Yield = 73%, IR (KBr, cm^{-1}): 1478 (C=C), 1711, 1732 (C=O), 2219, 2237 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.67 (d, 2H, *J* = 5 HZ), 7.9 (d, 2H, *J* = 10), 8.08–8.13 (m, 2H, H_{Ar}), 8.18–8.21 (m, 1H, H_{Ar}), 8.34–8.37 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.58, 99.81 (CN), 114.34, 115.18, 125.44, 125.66, 125.98, 130.95, 132.51, 132.96, 137.19, 138.12, 138.51, 141.04, 148.56, 151.26 (Ar), 156.03, 159.63 (C=N), 160.58, 183.56 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8BrN_5O_2$: C, 58.17; H, 1.78; N, 15.42%, Value found: C, 58.05; H, 1.69; N, 15.44%.

2-(3-Chlorophenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e] pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3i). Prepared according to the general procedure, Orange solid, M. *P* = 320–324°C, Yield = 80%, IR (KBr, cm^{-1}): 1467 (C=C), 1697, 1741 (C=O), 2218 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.66–7.77 (m, 3H, H_{Ar}), 7.82–7.83 (m, 1H, H_{Ar}), 8.03–8.13 (m, 2H, H_{Ar}), 8.18–8.22 (m, 1H, H_{Ar}), 8.35–8.38 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 91.66, 100.04 (CN), 114.25, 115.06, 125.67, 126.00, 127.61, 128.53, 131.47, 133.93, 135.70, 137.20, 138.14, 138.52, 141.04, 148.58, 151.20 (Ar), 155.98, 159.10 (C=N), 160.64, 183.55 (C=O) ppm. Elemental analysis: Value calculated for $C_{22}H_8ClN_5O_2$: C, 64.48; H, 1.97; N, 17.09%, Value found: C, 64.43; H, 1.95; N, 17.01%.

2-(2,4-Dimethoxyphenyl)-4,7-dioxo-4,7-dihydroindeno[1,2-e]pyrido[1,2-b][1,2,4]triazine-1,3-dicarbonitrile (3k). Prepared according to the general procedure, Orange solid, M. *P* = 324–329°C, Yield = 77%, IR (KBr, cm^{-1}): 1211, 1233 (O-CH_3), 1469 (C=C), 1554, 1609 (C=N), 1686, 1749 (C=O), 2219 (CN). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 3.87 (S, 3H, OMe), 3.89 (S, 3H, OMe), 6.78 (d. d, 1H, *J* = 5, 2.5 Hz), 6.83 (d, 1H, *J* = 2.5 Hz), 7.45 (d, 1H, *J* = 8.5 Hz), 8.07–8.12 (m, 2H, H_{Ar}), 8.17–8.19 (m, 1H, H_{Ar}), 8.32–8.34 (m, 1H, H_{Ar}) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6) δ = 56.07, 56.35 (OCH_3), 92.99, 99.54 (CN), 100.62, 106.51, 109.99, 114.47, 114.86, 115.31, 125.65, 125.86, 131.46, 137.26, 137.96, 138.59, 140.84, 148.01, 150.79, 156.12, 157.83 (Ar), 158.71, 160.14 (C=N), 163.74, 183.72 (C=O) ppm. Elemental analysis: Value calculated for $C_{24}H_{13}N_5O_4$: C, 66.21; H, 3.01; N, 16.09%, Value found: C, 66.25; H, 2.97; N, 16.15%.

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REFERENCES AND NOTES

[1] Li, F.; Feng, Y.; Meng, Q.; Li, W.; Wang, Q.; Tao, F. ARKIVOC 2007, 1, 40.

[2] Abdel-Rahman, R. M.; Morsy, J. M.; El-Edfawy, S.; Ameneand, H. A. Pharmazie 1999, 54, 347.

[3] Abdel-Rahman, R. M.; Morsy, J. M.; Hanafy, F.; Abdel-Salam, H. A. Pharmazie 1999, 54, 347.

[4] Abdel-Halim, A. M.; El-Gendy, Z.; Abdel-Rahman, R. M. Pharmazie 1995, 50, 726.

[5] El-Hawash, S. A.; Habib, N. S.; Fanaki, N. H. Pharmazie 1999, 45, 808.

[6] Brown, D. J.; Iwai, Y. Aust J Chem 1979, 32, 2727. https://doi.org/10.1071/CH9792727.

[7] Tarzia, G.; Ocelli, E.; Toja, E.; Barone, D.; Corsico, N.; Gallico, L.; Luzzani, F. J Med Chem 1988, 31, 1115. https://doi.org/10.1021/jm00401a010.

[8] Trust, R. I.; Albrigh, J. D. U S Patent, 1980, 242.

[9] Tarzia, G.; Ocelli, E.; Barone, D. IL Farmaco 1989, 44, 3.

[10] (a) Peignier, R.; Cheme, A.; Cantregril, R.; Mortier, J. Eur Patent 441718 Chem Abstr 1991, 115, 208000; (b) Cantegriil, R.; Chem, A.; Mortier, J.; Peignier, R. Eur Patent 483027 Chem Abstr 1992, 117, 131214.

[11] Sarges, S.; Howard, H. R.; Browne, R. G.; Lbel, L. A.; Seymour, P. A.; Koe, B. K. J Med Chem 1990, 33, 2240. https://doi.org/10.1021/jm00170a031.

[12] Bower, J. D.; Doyle, F. P. J Chem Soc 1957 727. https://doi.org/10.1039/jr9570000727.

[13] Pollak, A.; Tisler, M. Tetrahedron 1966, 22, 2073. https://doi.org/10.1016/S0040-4020(01)82127-X.

[14] Gibson, M. S. Tetrahedron 1963, 19, 1587. https://doi.org/10.1016/S0040-4020(01)99232-4.

[15] Hadi, A.; Martin, N.; Seoane, C.; Soto, J. L.; Albert, A.; Cano, F. J Heterocyclic Chem 1992, 29, 1229.

[16] Al-Najjar, A. A.; Amer, S. A. R.; Riad, M.; Elghamry, I.; Elnagdi, M. H. J Chem Res 1996 296.

[17] Abdel-Monem, W. R. Chem Pap 2004, 58, 276.

[18] Harb, A. A. Chem Pap 2004, 58, 260.

[19] Qian, G.; Wang, Z. Y. Chemistry–An Asian Journal 2010, 5, 1006. https://doi.org/10.1002/asia.200900596.

[20] Wang, Z. Y.; Zhang, J. D.; Wu, X. G.; Birau, M.; Yu, G. M.; Yu, H. G.; Qi, Y. H.; Desjardins, P.; Meng, X. S.; Gao, J. P.; Todd, E.; Song, N. H.; Bai, Y. M.; Beaudin, A. M. R.; LeClair, G. Pure Appl Chem 2004, 76, 1435. https://doi.org/10.1351/pac200476071435.

[21] (a) Qi, Y. H.; Desjardins, P.; Wang, Z. Y. J Opt A 2002, 4, 273; (b) Qi, Y.; Wang, Z. Y. Macromolecules 2003, 36, 3146. https://doi.org/10.1021/ma021018s; (c) Rastegar, M. F.; Todd, E. K.; Tang, H. D.; Wang, Z. Y. Org Lett 2004, 6, 4519. https://doi.org/10.1021/ol048021b; (d) Zhang, J. D.; Yu, H. A.; Wu, M. G.; Wang, Z. Y. Opt Mater 2004, 27, 265. https://doi.org/10.1016/j.optmat.2004.04.002; (e) Wang, S.; Todd, E. K.; Birau, M.; Zhang, J. D.; Wan, X. H.; Wang, Z. Y. Chem Mater 2005, 17, 6388; (f) Wang, S.; Li, X. Z.; Xun, S. D.; Wan, X. H.; Wang, Z. Y. Macromolecules 2006, 39, 7502. https://doi.org/10.1021/ma061751+; (g) LeClair, G.; Wang, Z. Y. J Solid State Electrochem 2009, 13, 365. https://doi.org/10.1007/s10008-008-0562-y.

[22] (a) Li, D.; Wang, Z. Y.; Ma, D. G. Chem Commun 2009 1529. https://doi.org/10.1039/b819270g; (b) Zheng, J.; Qiao, W. Q.; Wan, X. H.; Gao, J. P.; Wang, Z. Y. Chem Mater 2008, 20, 6163. https://doi.org/10.1021/cm8014644; (c) Deng, J.; Song, N. H.; Liu, W.; Zhou, Q. F.; Wang, Z. Y. Chemphyschem 2008, 9, 1265.

[23] (a) Qian, G.; Li, X. Z.; Wang, Z. Y. J Mater Chem 2009, 19, 522. https://doi.org/10.1039/B813478B; (b) Xun, S. D.; LeClair, G.; Zhang, J. D.; Chen, X.; Gao, J. P.; Wang, Z. Y. Org Lett 2006, 8, 1697. https://doi.org/10.1021/ol060344f.

[24] (a) Li, X. Z.; Liu, A. H.; Xun, S. D.; Qiao, W. Q.; Wan, X. H.; Wang, Z. Y. Org Lett 2008, 10, 3785. https://doi.org/10.1021/ol801345r; (b) Marshall, K. L.; Klehn, B.; Watson, B.; Griffin, D. W. In in Advanced Characterization Techniques for Optics, Semiconductors, and Nanotechnologies, Vol. 5188, Duparr, A.; Singh, B. Eds.; SPIE: Bellingham, WA, 2003, pp. 48–60; (c) Marshall, K. L.; Schudel, B.; Lippa, I. A. In in Liquid Crystals VII, Vol. 5213, Khoo, I.-C. Ed.; SPIE: Bellingham, WA, 2003, pp. 201–212; (d) Guardalben, M. J.; Ning, L.; Jain, N.; Battaglia, D. J.; Marshall, K. L. Appl Opt 2002, 41, 1353. https://doi.org/10.1364/AO.41.001353.

[25] Law, K. Y. Chem Rev 1993, 93, 449. https://doi.org/10.1021/cr00017a020.

[26] Peng, Z.; Geise, H. J. Bull Soc Chim Belg 1996, 105, 739.

[27] Al-Najjar, A. A.; Abdul Rahman, A. S.; Riad, M.; Elghamary, I.; Elnagdi, M. H. J Chem Res 1996 296.