# Some Reactions with Indane-1,3-dione: A Facile Synthesis of Pentacycline Heterocyclic Analogues

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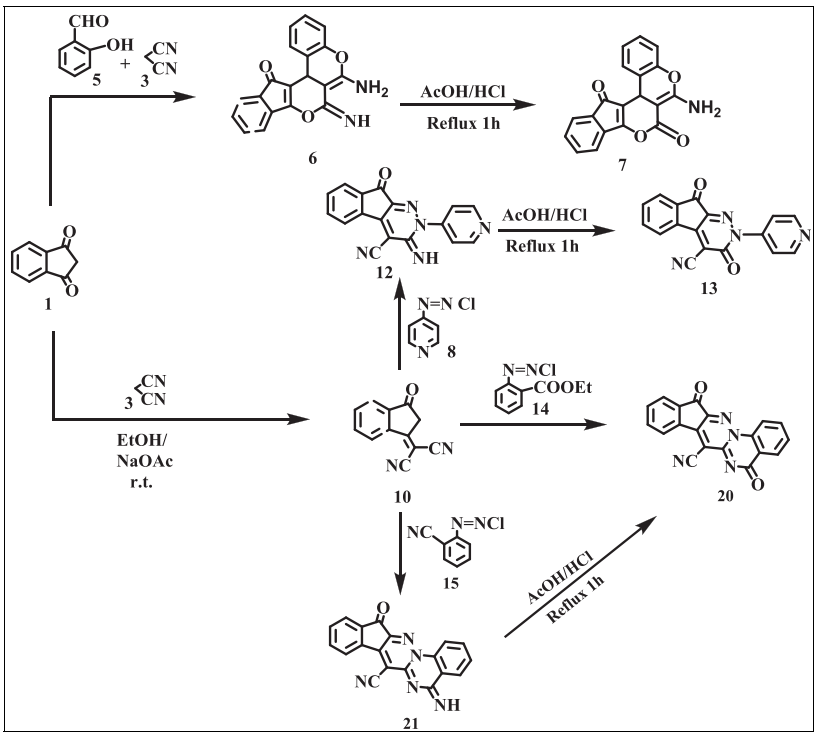



Indane-1,3-dione **1** reacts with salicylaldehyde **5** and malononitrile **3** to afford 6-amino-7-imino-7*H*-indeno-[2′,1′:5,6]-pyrano-[3,4-*c*]-chromene **6**, which could be transformed into the corresponding 7-oxo derivative **7**. 2-(3-Oxoindan-1-ylidene)-malononitrile **10** couples with the diazonium salts **8**, **14**, and **15** to afford after cyclization the indeno-[2,1-*c*]-pyridazine **13** and the indeno-[2′,1′:3,4]-pyridazino-[1,6-*a*]-quinazoline derivatives **20** and **21**, respectively.



## INTRODUCTION

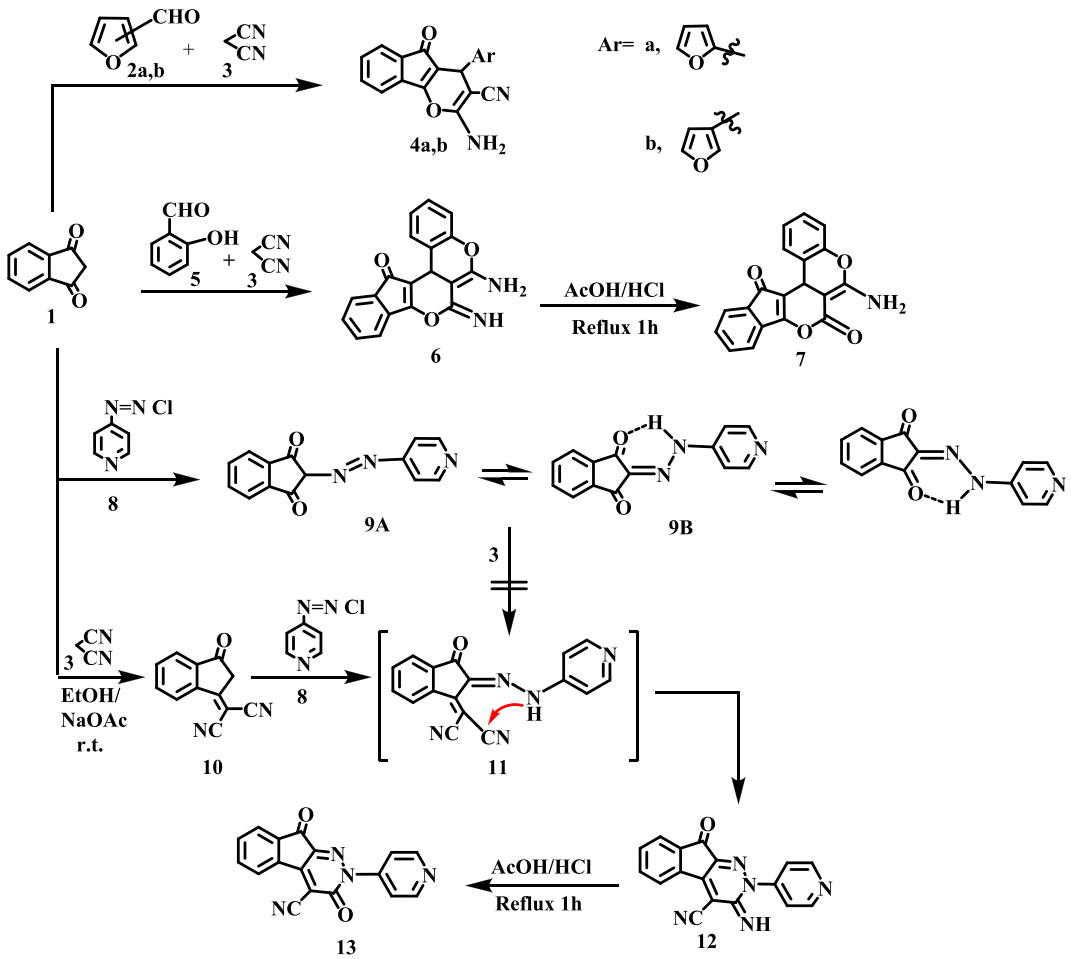
Tetracycline antibiotics have been heavily utilized for the treatment of infectious diseases over the past few decades. However, their excessive use in human and veterinary medicine led to increasing the resistance of many microbial strains that were previously susceptible to tetracycline antibiotics. Therefore, the search for other more potent alternatives attracts much attention and is still under consideration as a major target for chemists and organic chemistry researchers [1–5].

In the past few decades, we were involved in a program aiming at the synthesis of heterocyclic compounds of expected biological activity [6–15]. In the context of this trend and, because of the striking biological activities of tetracycline derivatives, we report here simple syntheses of some new heterocyclic pentacycline derivatives as a novel class of tetracycline analogs starting from indane-1,3-dione.

## RESULTS AND DISCUSSION

Indane-1,3-dione **1** reacts with furanaldehyes **2a**,**b** and malononitrile **3** in a one-pot reaction to afford the indeno-[1,2-*b*]-pyran derivatives **4a**,**b**, respectively (cf. Scheme 1 and Experimental section). Similarly, **1** reacts with salicylaldehyde **5** and malononitrile **3** under the same reaction conditions to afford the indeno-[2′,1′:5,6]-pyrano-[3,4-*c*]-chromene **6**. The IR spectrum of **6** showed absorption bands corresponding to NH, $NH_2$, & C═O functions (cf. Experimental section). The $^1$H NMR

**Scheme 1.** Synthesis of compounds **4**, **6**, **7**, **9**, **12**, and **13**. [Color figure can be viewed at wileyonlinelibrary.com]

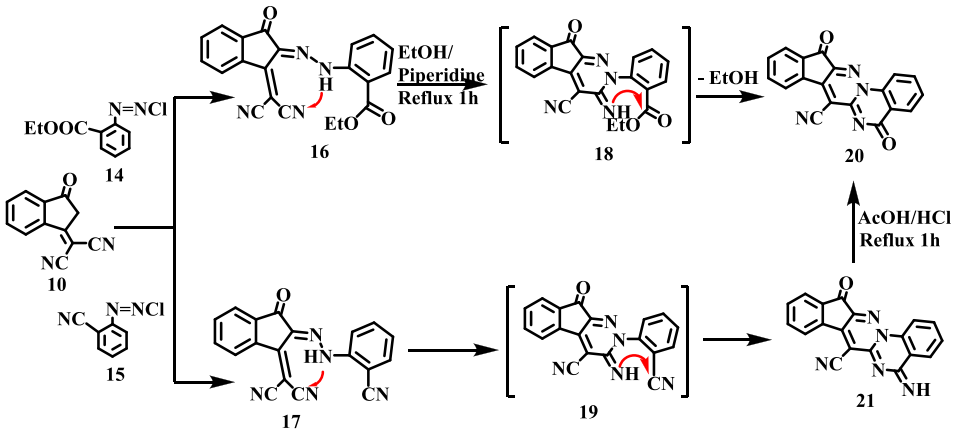



spectrum showed a singlet at $\delta_H$ = 4.03 ppm attributable to the pyran-H4, a multiplet at 7.75–8.5 (10H) assignable to two phenyl rings and the amino group and a singlet at 10.1 (1H) disappeared upon exchange with $D_2O$, which is attributed to the NH. The MS of **6** showed a molecular ion peak at *m/z* = 316. The $^{13}C$ NMR and elemental analyses are coinciding with structure **6**. Refluxing compound **6** in acetic acid/HCl mixture for 1 h furnished the chromene compound **7**. The IR spectrum of **7** showed two carbonyl absorptions at $\nu_{max}$ = 1681 & 1676 $cm^{-1}$. The NH signal at 10.1 ppm (which appeared in **6**) disappeared in the $^1H$ NMR spectrum of **7**.

On the other hand, coupling of indan-1,3-dione **1** and pyridine-4-diazonium chloride **8** according to literature methods [16,17] afforded the azo/hydrazo derivative **9A**–**9B**, which was subjected to react with malononitrile **3** in order to obtain the combined azo/condensation derivative **11**. However, using this route, we could not obtain the acyclic derivative **11** or its cyclized derivatives **12**. This is apparently due to the presence of the NH in **9B**, which is involved in making the N—H … O═C hydrogen bonds [17], thus blocking the C═O group against nucleophilic attacks. Therefore, we have followed the alternative route allowing indane-1,3-dione **1** to condense firstly with malononitrile **3** according to a known literature method [18] to afford 2-(3-oxoindan-1-ylidene)-malononitrile **10**. This last compound **10** couples smoothly with **8** to afford directly compound **12** presumably *via* the intermediate **11**, which undergoes cyclization under the coupling conditions. Refluxing the indeno-[2,1-*c*]-pyridazine-3-imine compound **12** in acetic acid/HCl mixture (1:1) afforded the pyridazin-3-one derivative **13**. Spectral data and element analyses of **12** and **13** are in full agreement with their suggested structures.

Following the same route 2-(3-oxoindan-1-ylidene)-malononitrile **10** underwent the coupling reaction with the diazonium salts **14** and **15** (freshly prepare by diazotization of ethyl anthranilate and anthranilonitrile,

**Scheme 2.** Synthesis of compounds **16**, **17**, **20**, and **21**. [Color figure can be viewed at wileyonlinelibrary.com]




respectively) to afford the hydrazo derivatives **16** and **17**, respectively (Scheme 2).

The IR spectra of **16** showed absorption band at $\nu_{max}$ = 3110 & 3067, 2187, 1714, and 1682 $cm^{-1}$ due to NH, CN, ester C═O, and ring C═O, respectively. The $^1H$ NMR spectrum revealed the ester triplet and quartet at 1.4 and 4.5 ppm and a singlet at 15.3 ppm due to the hydrazone NH beside the other signals at their expected positions. The IR spectrum of **17** showed absorption bands at $\nu_{max}$ = 3215 & 3164, 2186 & 2205, and 1680 $cm^{-1}$ assignable to the NH, two CN, and the ring C═O, respectively. The $^1H$ NMR spectrum revealed the aromatic multiplet beside the NH singlet at 13.25 ppm. The $C^{13}$ NMR data, mass spectra, and elemental analyses are in complete agreement with the proposed structures (cf. Experimental section).

Compounds **16** or **17** could be easily cyclized into the required indeno-[2′,1′:3,4]-pyridazine-[1,6-*a*]-quinazoline derivatives **20** and **21**, upon reflux in ethanol presumably *via* the intermediates **18** and **19**, respectively. The cyclization was catalyzed by addition of two drops of piperidine where the color changes promptly from dark red to yellow to afford **20** and **21**, respectively. The IR of **20** showed absorption bands at $\nu_{max}$ = 2210, 1676 & 1689 $cm^{-1}$ corresponding for the cyano group and two ring carbonyl functions, respectively. The $^1H$ NMR spectrum revealed only an aromatic multiplet.

The IR of **21** showed absorption bands at $\nu_{max}$ = 3225 & 3185, 2218, 1680 $cm^{-1}$ assignable to NH, CN, and C═O, respectively. The $^1H$ NMR spectrum revealed the aromatic multiplet 7.30–7.75 and a singlet at 9.38 ppm assignable to NH. The $^{13}C$ NMR, MS, and elemental analyses are in full agreement with the proposed structure.

The 5-imino compound **21** could be smoothly transformed into the corresponding 5-oxo compound **20** upon reflux in acetic acid/HCl mixture (1:1). The identity was deduced from matching melting points, TLC, and IR spectra.

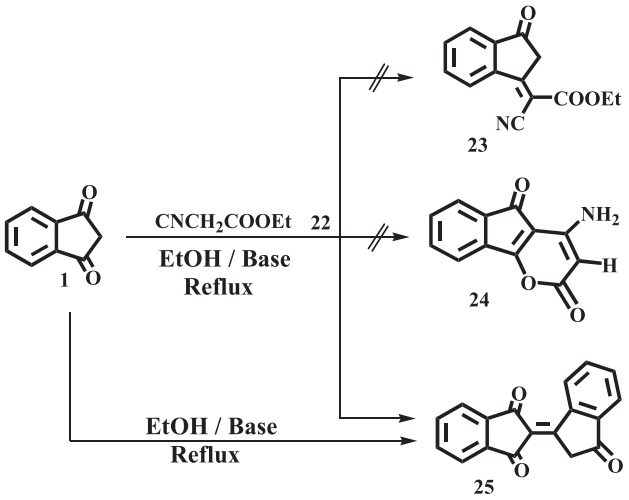
On the other hand, ethyl 2-cyan-2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)acetate **23** was required for further reactions. Reacting indanedione **1** with ethyl cyanoacetate **22** according to the reported method [19,20], we could not obtain the required compound **23** or its alternative indeno[1,2-*b*]pyran derivative **24**.

Repeating the reaction with different basic catalysts and under different conditions we obtained always one and the same product (TLC and mp). Elemental analysis and mass spectrum showed that this product consists of two molecules of **1** after elimination of one water molecule. Thus, the self-condensation structure **25** (Scheme 3) was assigned to this product. Spectral data are in favor of this structure (cf. Experimental section). The same product was also obtained upon refluxing **1** alone in ethanol using the same catalyst. This structure was further confirmed by X-ray crystallography [21] as shown in Figure 1, which showed two molecules of indane-1,3-dione condensed through the carbonyl group of one molecule with the active methylene of the other. The X-ray shows two molecules of the product.

## EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus (Kleinfeld, Gehrden, Germany) and are uncorrected. FT-IR spectra (KBr) were obtained on a Nicolet 205 spectrophotometer (Nicolet, Madison, WI, USA). $^1H$ NMR and $^{13}C$ NMR spectra were obtained on a Bruker AC 300 P ($^1H$: 300 MHz, $^{13}C$: 75 MHz; Bruker, Rheinstetten, Germany) in $CDCl_3$ unless mentioned

**Scheme 3.** Synthesis of [1,2`]biindenylidene-3,1`,3`-trione **25**.



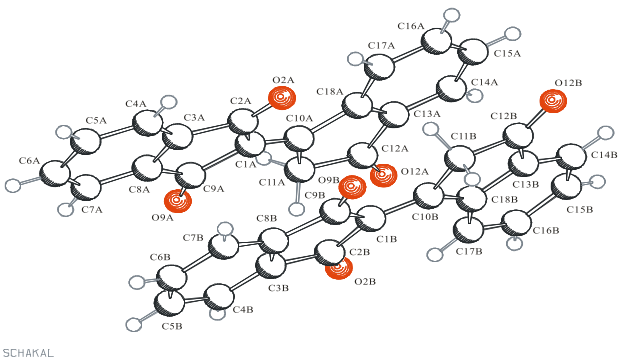



**Figure 1.** X-ray crystallography of **25**. [Color figure can be viewed at wileyonlinelibrary.com]

otherwise using TMS as internal reference. Chemical shifts are expressed in δ (ppm) values. $^{13}$C NMR multiplicities were determined using DEPT and off resonance pulse sequences. Spectral and elemental analyses were carried out in the organic microanalytical laboratory of the Department of Chemistry, Technical University of Dresden and the Microanalytical Center at Cairo University.

**Synthesis of the 4-furanyl-4,5-dihydroindeno[1,2-*b*]pyrans 4a**,**b**. A mixture of indanedione **1** (1.46 g; 0.01 mol) and each of 2- or 3-furanaldehyde **2a** or **2b** (0.96 g; 0.01 mol) and malononitrile **3** (0.66 g; 0.01 mol) in ethanol (25 mL) was heated to reflux. Triethylamine (two drops) were added, and the reflux was continued for 1 h and left to cool to overnight. The reaction mixture was then poured onto ice-cold water and neutralized with drops of conc. HCl till acid reaction (pH paper). The dark brown solids that precipitated were filtered off and recrystallized from acetonitrile to give **4a**,**b**.

**2-Amino-4-furan-2-yl-5-oxo-4,5-dihydro-indeno[1,2-*b*] pyran-3-carbonitrile 4a**. Dark brown flakes, mp 197–198°C ($CH_3CN$); yield (2.26 g; 78%). $\nu_{max}$ cm$^{-1}$: 3152–3128 ($NH_2$), 2215 (CN), 1681 (C═O). $\delta_H$: 4.17 (s, 1H, pyran 4-H), 6.8–7.7 (m, 9H, Ar + $NH_2$). $\delta_c$: 26.7 (d), 58.2 (s), 102.4 (s), 106.7 (d), 110.5 (d), 118.2 (s), 123.7 (d), 126.1 (d), 128.3 (d), 134.5 (d), 136.7 (s), 137.5 (s), 142.0 (d), 152.3 (s), 159.5 (s), 171.4 (s), 192.4 (s). MS: *m/z* = 290. Calcd for $C_{17}H_{10}N_2O_3$ (290.28): C, 70.34; H, 3.47; N, 9.65; found: C, 70.50; H, 3.55; N, 9.54.

**2-Amino-4-furan-3-yl-5-oxo-4,5-dihydro-indeno[1,2-*b*] pyran-3-carbonitrile 4b**. Dark brown flakes, mp 163–165°C ($CH_3CN$); yield (2.35 g; 81%). $\nu_{max}$ cm$^{-1}$: 3147–3124 ($NH_2$), 2205 (CN), 1678 (C═O). $\delta_H$: 4.25 (s, 1H, pyran-4H), 6.25 (d, 1H, *J* = 4 Hz, furan-4H), 6.8 (s, 2H,

$NH_2$), 7.18 (s, 1H, furan-2H), 7.3 (d, 1H, $J$ = 4 Hz, furan-5H), 7.5–7.68 (m, 4H, ArH). $\delta_c$: 33.1 (d), 57.5 (s), 102.3 (s), 111.2 (d), 117.2 (s), 118.5 (s), 126.8 (d), 128.2 (d), 129.5 (d), 134.2 (d), 134.5 (s), 135.9 (s), 138.2 (d), 141.5 (d), 160.9 (s), 176.5 (s), 187.2 (s). MS: *m/z* = 290. Calcd for $C_{17}H_{10}N_2O_3$ (290.28): C, 70.34; H, 3.47; N, 9.65; found C, 70.55; H, 3.40; N, 9.59.

**Synthesis of the indeno-pyrano-chromenes 6 & 7**. To a mixture of the indanedione **1** (1.46 g; 0.01 mol), salicylaldehyde **5** (1.22 g; 0.01 mol), and malononitrile **3** (0.66 g; 0.01 mol) in ethanol (25 mL) was added two drops of triethylamine, and the reaction mixture was stirred at 60°C for 1 h. The reaction mixture was then diluted with cold water acidified by conc. HCl where a yellow precipitate appeared, filtered off, and recrystallized from the proper solvent to afford the imino-chromene derivative **6**. Refluxing **6** (1.58 g; 0.005 mol) in AcOH/HCl solution for 1 h furnished the chromene—compound **7**.

**6-Amino-7-imino-7*H*-indeno[2′,1′:5,6]pyrano[3,4-*c*] chromene-13(13*bH*)-one 6**. Yellow powder, mp >300°C ($CH_3CN$); yield (2.53; 80%). $\nu_{max}$ $cm^{-1}$: 3186–3124 (NH & $NH_2$), 1676 (C═O). $\delta_H$: 4.03 (s, 1H, pyran-H), 7.75–8.5 (m, 10H, 8ArH + $NH_2$), 10.1 (s, 1H, NH). $\delta_c$: 26.7 (d), 73.3 (s), 97.6 (s), 117.0 (d), 122.7 (d), 123.7 (d), 124.0 (s), 126.1 (d), 126.3 (d), 128.2 (d), 129.6 (d), 134.5 (d), 136.5 (s), 137.7 (s), 153.0 (s), 154.3 (s), 160.5 (s), 191.9 (s), 198.3 (s). MS: *m/z* = 316. Calcd for $C_{19}H_{12}N_2O_3$ (316.31): C, 72.15; H, 3.82; N, 8.86; found C, 72.32; H, 3.48; N, 8.65.

**6-Amino-7*H*-indeno[2′,1′:5,6]pyrano[3,4-*c*]chromene-7,13(13*bH*)-dione 7**. Yellow crystals, mp >300°C (dioxane); yield (1.3 g; 82%). $\nu_{max}$ $cm^{-1}$: 3175–3125 ($NH_2$), 1681 & 1676 (2C═O). $\delta_H$: 4.1 (s, 1H, pyran-H), 7.72–8.42 (m, 10H, 8ArH + $NH_2$). $\delta_c$: 34.3 (d), 76.8 (s), 105.9 (s), 117.2 (d), 122.8 (d), 123.6 (d), 124.1 (s), 126.2 (d), 126.4 (d), 128.3 (d), 129.7 (d), 134.5 (d), 136.5 (s), 137.7 (s), 154.1 (s), 162.8 (s), 164.1 (s), 164.3 (s), 192.0 (s). MS: *m/z* = 317. Calcd for $C_{19}H_{11}NO_4$ (317.29): C, 71.92; H, 3.49; N, 4.41; found C, 72.62; H, 3.47; N, 4.62.

**2-(2-(Pyridin-4-yl)hydrazono)-1*H*-indene-1,3(2*H*)-dione 9**. These were prepared according to the reported method [16,17]. Dark brown crystals, mp 276–277°C (dioxane); yield (1.91 g; 76%). $\nu_{max}$ $cm^{-1}$: 3114 & 3069 (NH), 1695 (ring C═O). $\delta_H$: 6.95 (d, 2H, $J$ = 12.6 Hz, pyridine), 7.62 (d, 2H, Ph), 7.74 (m, 2H, Ph), 8.45 (d, 2H, $J$ = 12.6 Hz, pyridine), 11.85 (s, 1H-$D_2O$ exchangeable, NH). MS: *m/z* = 251. Calcd for $C_{14}H_9N_3O_2$ (251.25): C, 66.93; H, 3.61; N, 16.73; found C, 66.73; H, 3.85; N, 16.80.

**2-(3-Oxoindan-1-ylidene)-malononitrile 10**. Prepared according to literature method; mp 228°C (lit. mp 232°C [18]).

**3-Imino-9-oxo-2-(pyridine-4-yl)-3,9-dihydro-2*H*-indeno[2,1-*c*]pyridazine-4-carbonitrile 12**. To a solution of indan-1-ylidene malononitrile **10** (1.94 g; 0.01 mol) in ≈30 mL of pyridine was added dropwise a solution of the diazonium salt **8** (freshly prepared by diazotization [0.94 g; 0.01 mol] of 4-aminopyridine/conc. hydrochloric acid with sodium nitrite [0.69 g, 0.01 mol] solution 1:1 in an ice bath at 0°C). After complete addition of the diazonium salt solution (≈10 min), a dark brown solid precipitate appeared. Stirring was continued at room temperature for further 1 h. The reaction mixture was diluted with cold water (≈30 mL), filtered off, washed thoroughly with water, dried, and recrystallized from ethanol/DMF 1:1. Dark brown crystals, mp 209–210°C (EtOH/DMF); yield (2.7 g; 76%). $\nu_{max}$ $cm^{-1}$: 3215–3165 (NH), 2228 (CN), 1678 (C═O). $\delta_H$: 7.1 (d, 2H, $J$ = 12.5 Hz, pyridine), 7.32–7.75 (m, 4H, Ar), 8.48 (d, 2H, $J$ = 12.5 Hz, pyridine), 8.45 (br s, 1H, NH). MS: *m/z* = 299. Calcd for $C_{17}H_9N_5O$ (299.29): C, 68.22; H, 3.03; N, 23.40; found C, 68.40; H, 3.15; N, 23.62.

**3,9-Dioxo-2-pyridin-4-yl-3,9-dihydro-2*H*-indeno[2,1-*c*] pyridazine-4-carbonitrile 13**. Compound **12** (1.49 g; 0.005 mol) was refluxed in acetic acid/HCl (1:1) for 1 h, then cooled and neutralized with ammonia solution. The solid precipitate that appeared was filtered off, washed thoroughly with water, dried, and recrystallized from dioxane to afford reddish brown crystals, mp 269–270°C (dioxane); yield (1.29 g; 86%). $\nu_{max}$ $cm^{-1}$: 2224 (CN), 1672 & 1686 (2C═O). $\delta_H$: 7.05 (d, 2H, $J$ = 12.5 Hz, pyridine-3, 5H), 7.32–7.42 (m, 3H, Ph), 7.78 (t, 1H, Ph), 8.47 (d, 2H, $J$ = 12.5 Hz, pyridine-2, 6H). $\delta_c$: 109.1 (d), 115.5 (s), 123.3 (s), 126.24 (d), 127.12 (d), 128.45 (d), 131.92 (d), 136.7 (s), 137.75 (s), 137.72 (s), 150.32 (d), 155.5 (s), 161.1 (s), 162.25 (s), 162.32 (s), MS: *m/z* = 300. Calcd for $C_{17}H_8N_4O_2$ (300.27): C, 68.00; H, 2.69; N, 18.66; found C, 68.25; H, 2.62; N, 18.55.

**Preparation of the hydrazo derivatives 16 & 17**. To a solution of indan-1-ylidene malononitrile **10** (1.94 g; 0.01 mol) in ≈30 mL of pyridine was added dropwise a solution of the diazonium salts **14** or **15** (freshly prepared by diazotization [1.65 g; 0.01 mol] of ethyl anthranilate or [1.18 g; 0.01 mol] anthranilonitrile/conc. hydrochloric acid with sodium nitrite solution 1:1 in an ice bath at 0°C). After complete addition of the diazonium salt solution (≈10 min), dark red solid precipitates appeared, respectively. Stirring was continued at room temperature for further 1 h. The reaction mixture was diluted with cold water (≈30 mL), filtered off, washed thoroughly with water, dried, and recrystallized from ethanol/DMF 1:1 to afford **16** and **17**, respectively.

**Ethyl 2-(2-(1-(dicyanomethylene)-3-oxo-1,3-dihydro-2*H*-inden-2-ylidene)hydrazinyl)-benzoate 16**. Red crystals, mp 310–312°C (EtOH/DMF); yield (3.14 g; 85%). $\nu_{max}$ $cm^{-1}$: 3110 & 3067 (NH), 2187 (CN), 1714 (ester C═O),

1682 (ring C=O). $\delta_H$: 1.4 (t, 3H, $J$ = 7.5 Hz, $CH_3$), 4.5 (q, 2H, $J$ = 7.5 Hz, $CH_2$), 7.6–7.8 (m, 4H, Ph), 7.9 (d, 1H, $j$ = 8.1 Hz, Ph), 8.05 (dd, 1H, Ph), 8.28 (d, 1H, $J$ = 8.1 Hz, Ph), 8.59 (d, 1H, $J$ = 8.1 Hz, Ph), 15.3 (s, 1H, NH). $\delta_c$: 14.32 (q), 61.93 (t), 69.90 (s), 114.05 (s), 114.38 (s), 115.78 (s), 116.88 (d), 124.39 (d), 125.18 (d), 125.59 (d), 131.08 (d), 131.54 (s), 134.72 (d), 135.16 (d), 135.64 (d), 138.91 (s), 143.70 (s), 156.09 (s), 167.01 (s), 184.55 (s). MS: $m/z$ = 370. Calcd for $C_{21}H_{14}N_4O_3$ (370.37): C, 68.10; H, 3.81; N, 15.13; found C, 68.29; H, 3.65; N, 15.25.

**2-(2-(2-(2-Cyanophenyl)hydrazono)-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile 17**. Red crystals, mp 298–301°C (EtOH/DMF); yield (2.78 g; 86%). $\nu_{max}$ $cm^{-1}$: 3215 & 3164 (NH), 2186 & 2205 (2CN), 1680 (ring C=O). $\delta_H$: 7.32–7.36 (m, 3H, Ph), 7.62–7.74 (m, 3H, Ph), 7.91–7.93 (m, 2H, Ph), 13.25 (s, 1H, NH). $\delta_c$: 69.95 (s), 101.05 (s), 115.75 (s; CN), 115.28 (d), 117.76 (s; Ph-CN), 119.39 (d), 126.18 (d), 126.88 (d), 128.38 (d), 131.74 (d), 132.95 (d), 133.76 (d), 136.54 (s), 137.58 (s), 137.73 (s), 144.30 (s), 162.36 (s), 170.65 (s). MS: $m/z$ = 323. Calcd for $C_{19}H_9N_5O$ (323.32): C, 70.58; H, 2.81; N, 21.66; found C, 70.65; H, 2.65; N, 21.45.

**Cyclization of compounds 16** and **17**. Compounds **16** (1.85 g) or **17** (1.615 g) (0.005 mol of each) in ethanol (25 mL) was heated to reflux, and two drops of piperidine was added where the color changes promptly from dark red to yellow. The reaction mixture was left to cool overnight where a yellow precipitate appeared in each case, filtered off, and washed thoroughly with ethanol and recrystallized from dioxane to afford **20** and **21**, respectively.

**5,12-Dioxo-5,12-dihydroindeno[2′,1′:3,4]pyridazino[1,6-*a*]quinazoline-7-carbonitrile 20**. Yellow crystals, mp 318–320°C (dioxane); yield (1.38 g; 85%). $\nu_{max}$ $cm^{-1}$: 2210 (CN), 1676 & 1689 (two ring C=O). $\delta_H$: 7.70–8.20 (m, 3H), 8.18–8.21 (d, 1H, $J$ = 8 Hz), 8.24–8.32 (t, 1H, $J$ = 8 Hz), 8.35–8.63 (m, 2H), 8.87–8.93 (d, 1H, $J$ = 8 Hz). $\delta_c$: 114.75 (d), 115.78 (s), 122.82 (s), 126.12 (s), 126.22 (d), 126.85 (d), 127.18 (d), 128.04 (d), 128.50 (d), 131.76 (d), 136.64 (s), 137.70 (s), 137.73 (s), 138.89 (d), 146.18 (s), 157.55 (s), 158.93 (s), 162.36 (s), 167.75 (s). MS: $m/z$ = 324. Calcd for $C_{19}H_8N_4O_2$ (324.29): C, 70.37; H, 2.49; N, 17.28; found C, 70.29; H, 2.63; N, 17.35.

**5-Imino-12-oxo-5,12-dihydroindeno[2′,1′:3,4]pyridazino[1,6-*a*]quinazoline-7-carbonitrile 21**. Yellow crystals, mp 312–314°C (dioxane); yield (1.4 g; 87%). $\nu_{max}$ $cm^{-1}$: 3225–3185 (NH), 2218 (CN), 1680 (C=O). $\delta_H$: 7.30–7.75 (m, 8H, Ar), 9.38 (s, 1H, NH). $\delta_c$: 114.65 (d), 115.75 (s), 117.84 (s), 126.14 (s), 126.25 (d), 126.88 (d), 130.16 (d), 118.74 (d), 128.56 (d), 131.76 (d), 136.55 (s), 137.68 (s), 137.71 (s), 135.85 (d), 145.38 (s), 157.48 (s), 158.83 (s). 162.39 (s), 164.25 (s). MS: $m/z$ = 323. Calcd for $C_{19}H_9N_5O$ (323.31): C, 70.58; H, 2.81; N, 21.66; found C, 70.49; H, 2.95; N 21.60.

**Transformation of 21** into **20**. Compound **21** (1.615 g; 0.005 mol) refluxed in AcOH/HCl (1:1) for 1 h, then cooled and neutralized with ammonia solution. The solid precipitate that appeared was filtered off, washed thoroughly with water, dried, and recrystallized from dioxane and found to be **20** (1.46 g; 90%) (identical mp, TLC, and IR).

**[1,2′]Biindenylidene-3,1′,3′-trione 25**. Compound **1** (1.46 g; 0.01 mol) was refluxed for 30 min in ethanol (25 mL) catalyzed by one drop of triethylamine. After cooling to room temperature, the flask contents were poured on ice-cold water and neutralized with drops of HCl. The precipitated solid was filtered off and recrystallized from dioxane.

Yellow crystals turn into dark blue in acetone and to rose red on contact with water, mp 212–213°C (dioxane); yield (1.23 g; 90%). $\nu_{max}$ $cm^{-1}$: 1713.5, 1681 & 1654 (3C=O). $\delta_H$: 3.25 (s, 2H, $CH_2$), 7.47 (d, 1H, $J$ = 8 Hz), 7.56 (t, 1H, $J$ = 8 Hz), 7.70–7.73 (m, 4H), 7.77 (t, 1H, $J$ = 8 Hz), 7.95 (d, 1H, $J$ = 8 Hz). $\delta_c$: 43.41 (t), 124.62 (d), 125.85 (d), 126.82 (s), 131.66 (d), 133.05 (d), 135.32 (d), 135.58 (d), 140.39 (s), 141.24 (s), 145.88 (s), 159.26 (s), 190.35 (s), 196.45 (s). MS: $m/z$ = 274. Calcd for $C_{18}H_{10}O_3$ (274.26): C, 78.83; H, 3.68; found C, 78.69; H, 3.63.

X-ray crystallographic data: yellow crystals, $C_{18}H_{10}O_3$ ($M_r$ = 274.26 g*$mol^{-1}$), crystal dimensions = 0.28*0.26*0.17 mm. Molecules per unit cell $Z$ = 32, $D_{calcd}$ = 1.482 g*$cm^{-3}$. F(000) = 4544e, crystal system: orthorhombic, space group Fdd2 (No. 43), cell constants with standard deviations: $a$ = 18.003 (2) Å, $b$ = 20.933 (2) Å, $c$ = 26.101 (3) Å, α[°] = 90.00, β[°] = 90.00 (1), γ[°] = 90.00; $V$[Å$^3$] = 9836.2 (18). Data were collected using a Bruker Nonius area detector at T [K] = 100 (2), with graphite monochromator multi-layer with Mo Kα radiation (λ = 0.71073 Å) using the CCD data collection and SADABS absorption correction method; absorption coefficient μ = 0.101 $cm^{-1}$; the final difference Fourier ρ = 0.44 (−0.34)e Å$^{-3}$. Max. resolution [sin θ/λ]$_{max}$ = 0.70 Å$^{-1}$/99.9%. Absorption correction min. 97.2%; max. 98.3%. Total number of reflections collected and counted were 143,426, number of independent reflections 7522, and number of observed reflections 7110. $R_{av}$ = 0.160. The final R and $R_W^2$ = 0.042 and 0.114, respectively.

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[21] Crystallographic data (excluding structure factors) for the structure **25** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1886200. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (Internat.)] + 441223/336–033; e-mail: deposit@ccdc.cam.ac.uk].