Reactions of amidrazones with 1,4-quinones

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Abstract

Syntheses of various benzo- and naphtho-1,2,4-triazin-6(4*H*)-ones are formed in one step *via* the reactions of amidrazones with benzo- and naphtho-1,4-quinones. In contrast, the reactions of amidrazones with 2,3,5,6-tetrachloro-1,4-benzoquinone or 2,3-dichloro-1,4-naphthoquinone produced the same indazoles, no matter what substituents were present on the nitrogen of the amidrazone.

Keywords: Amidrazones, 1,4-quinones, fused 1,2,4-triazin-6(4*H*)-ones, [3+2]cycloaddition, indazoles

Introduction

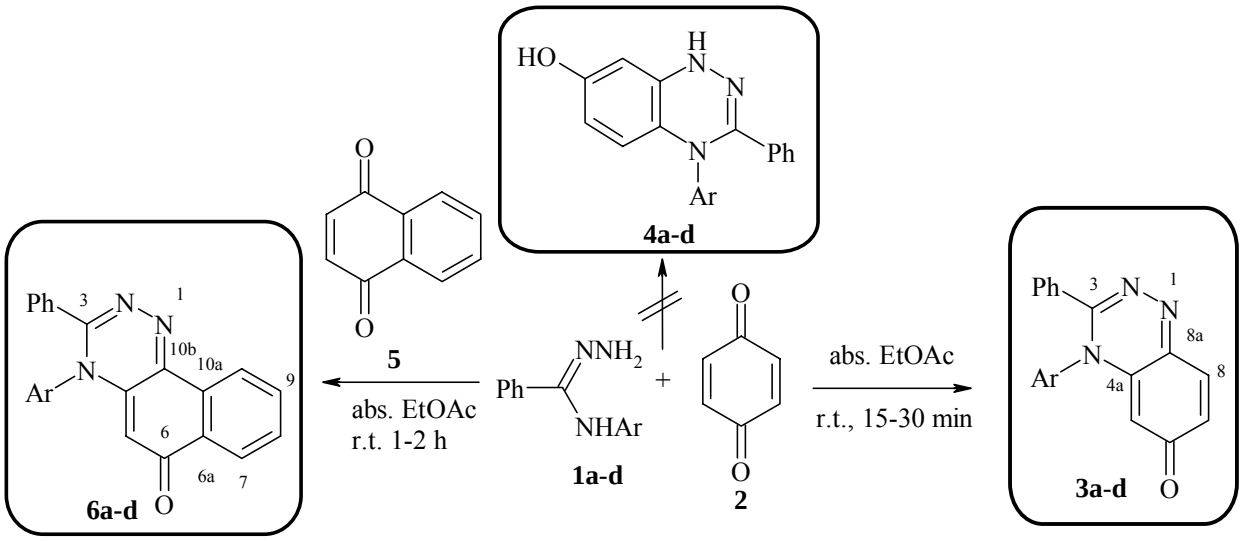
Benzo- and naphth-annulated 1,2,4-triazines are important as pharmaceuticals and agrochemicals. An example is 3-amino-1,2,4-benzotriazine 1,4-dioxide, which has received considerable attention as a new class of antitumor agent.[1,2] The mechanism of DNA cleavage by this type of compound is therefore of biochemical and pharmaceutical interest.[3-5] Known syntheses of this azaaromatic framework involve the reaction of 2-nitroaniline with cyanamide,[6] the base-induced cyclization of 2-nitrophenylurea followed by successive treatment with phosphoryl chloride and gaseous ammonia,[7] and the addition of diisocyanamide to benzofuroxan followed by acidic work-up.[8] Some time ago, a convenient synthesis of 3-amino-1,2,4-benzotriazine derivatives by the reaction of *o*-fluoronitro-benzenes with free guanidine base was developed.[9] Amidrazones are an important class of amidines.[10] Amidrazones display fungistatic, bacteriostatic, and antimycotic activity[11] and also function as herbicides[12] and lipoxygenase-1 inhibitors.[13] In addition, amidrazones can also used to prepare 1,2,4-triazines.[14,15] 2-Pyridyl-carboxamidrazones showed antimicrobacterial activity[16] and anticancer activity.[17] Interestingly, α,β-unsaturated *N*,*N*-dimethylhydrazones can react with quinones at the electron rich δ-position to form indoles and benzofurans.[18,19] α,β-Diketoesters react with amidrazones to yield triazines, generally in good yields.[20] Treatment of amidrazones with alkyl ketones under acidic catalysis lead generally to 4,5-dihydro-1*H*-1,2,4-triazoles.[21] Nitrosation of *N*-formyl amidrazones with

sodium nitrite in aqueous hydrochloric acid gives tetrazoles in good yields.[22] We have investigated the reaction of 2,3-diphenylcyclopropenone with *N*-imidoyl-thioureas as amidine analogues. The reaction was interpreted as a stepwise addition to produce pyrimidin-4(3*H*)-ones.[23] Aly *et al.* have recently reported the syntheses of various naphtha-1,2,4-triazepinediones from the reaction of amidrazones with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile.[24] Amidrazones also react with 2-(1,3-dioxo-indan-2-ylidene)malononitrile to produce 1,2,4-triazoles.[25] In this paper, we describe a straightforward synthesis of benz- and naphth-annulated 1,2,4-triazines in a single step *via* the reaction of amidrazones with 1,4-quinones. Also described are some reactions of amidrazones with electron-deficient quinones, which follow a different reaction path.

Results and Discussion

Amidrazones **1a-d** reacted with two equivalents of 1,4-benzoquinone (**2**) or 1,4-naphthoquinone (**5**) in absolute ethyl acetate under a N_2 atmosphere to yield compounds **3a-d** (66-85%) and **6a-d** (70-86%), respectively, after chromatographic purification and recrystallization (Scheme 1). We chose amidrazones **1a-d** having aryl groups with either electron-donating or -withdrawing substitutents on the benzene ring, in order to examine their effect on the reaction. Elemental analyses and IR, NMR (^{1}H and ^{13}C) and mass spectra were in good agreement with the assigned product structures. For example, the IR spectrum of the benzotriazin-6-one **3a** had characteristic triazine-C=N bands at ν = 1610 and 1600, and a carbonyl at ν = 1690 cm^{-1}, but no NH absorption. The elemental analysis and mass spectrum of **3a** proved its molecular formula as $C_{19}H_{13}N_3O$. The ^{1}H NMR spectrum of compound **3a** showed the presence of benzotriazine H-5, -7 and -8 at δ = 6.60 (d, *J* =1.0 Hz), 6.80 (dd, *J* = 8.0, 1.2 Hz) and 7.12 (d, *J* = 8.0 Hz), respectively. The ^{1}H NMR spectrum of **3b** contained a methoxy singlet at δ = 3.95 and benzotriazine signals at δ = 6.64 (d, *J* =1.2 Hz; H-5), 6.86 (dd, *J* = 8.0, 1.2 Hz; H-7), and 7.14 (d, *J* = 8.0 Hz; H-8). The ^{13}C NMR spectra of **3a-d** supported the ^{1}H NMR spectral data. For example in **3a**, the carbon signals of C-3 and C-8a appeared at δ = 158.0 and 156.4, respectively.

Direct one-bond attached hydrogen-carbon correlations were established by ^{1}H, ^{13}C- COSY (HETCOR), which correlated the aromatic carbons with their protons in both **3a** and **6a**. In **3a**, there is a correlation between C-6 and quinonoid protons H-5, -7 and -8. In the case of **6a**, the mass spectrum and elemental analysis established its molecular formula as $C_{23}H_{15}N_3O$. The H-5 proton in **6a** resonated at δ = 6.80, and C-5 appeared in the ^{13}C NMR spectrum at δ = 110.0. The ^{13}C NMR spectrum also showed C-3, -6, -6a, and -10a at δ = 158.8, 185.0, 132.0, and 134.0, respectively. Selected chemical shifts of compounds **3a** and **6a** are shown in Figure 1.



1, **3**, **4** and **6**	Ar	Yields of **3** and **6** (%)
a	C_6H_5-	72 and 75
b	4-CH_3O-C_6H_4-	85 and 86
c	4-CH_3-C_6H_4-	80 and 82
d	4-Cl-C_6H_4-	66 and 70

Scheme 1. Synthesis of benzo- and naphtha-1,2,4-triazin-6(4*H*)-ones **3a-d** and **6a-d.**

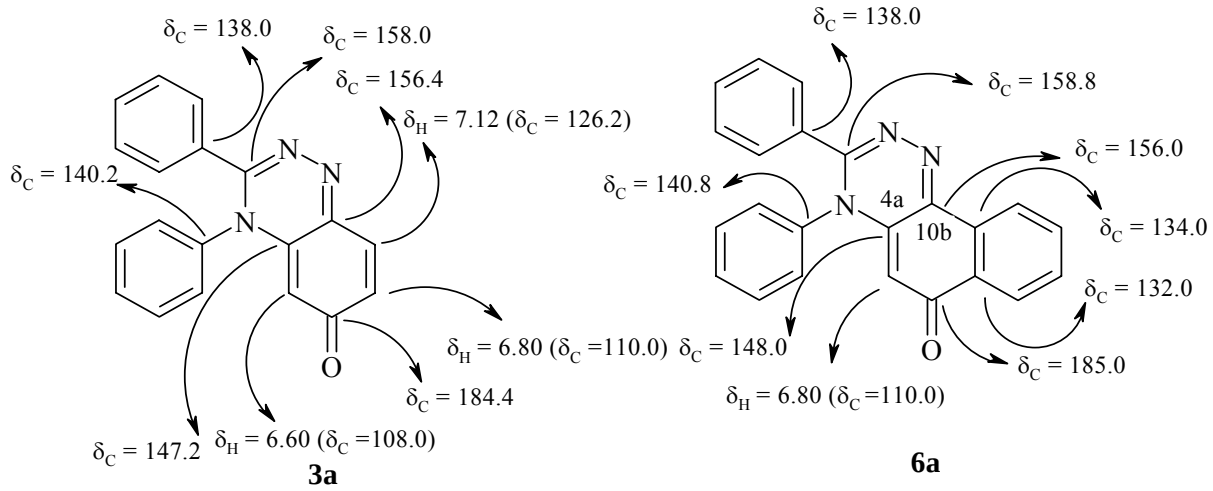
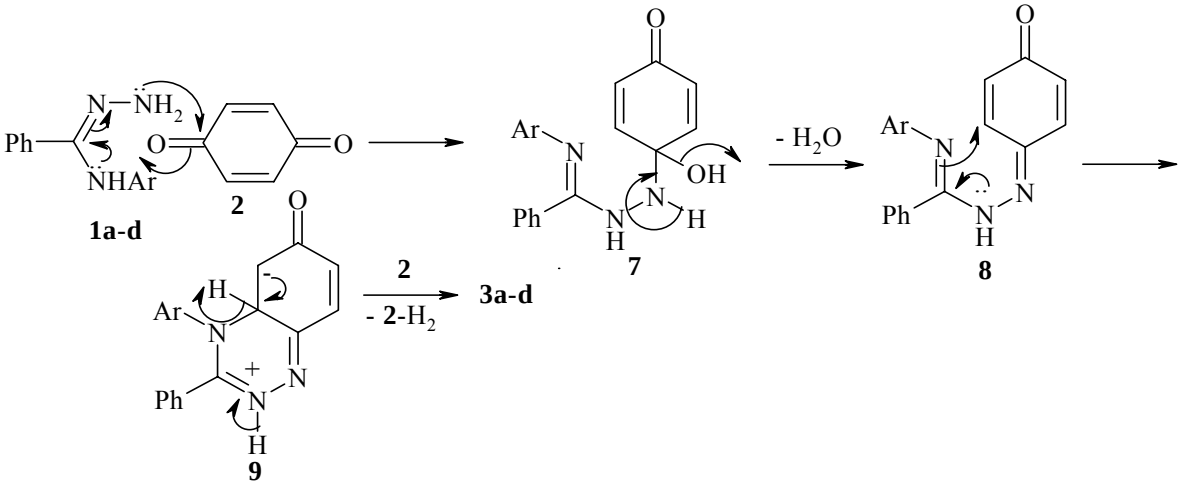


Figure 1. Distinctive δ' values of compounds **3a** and **6a.**

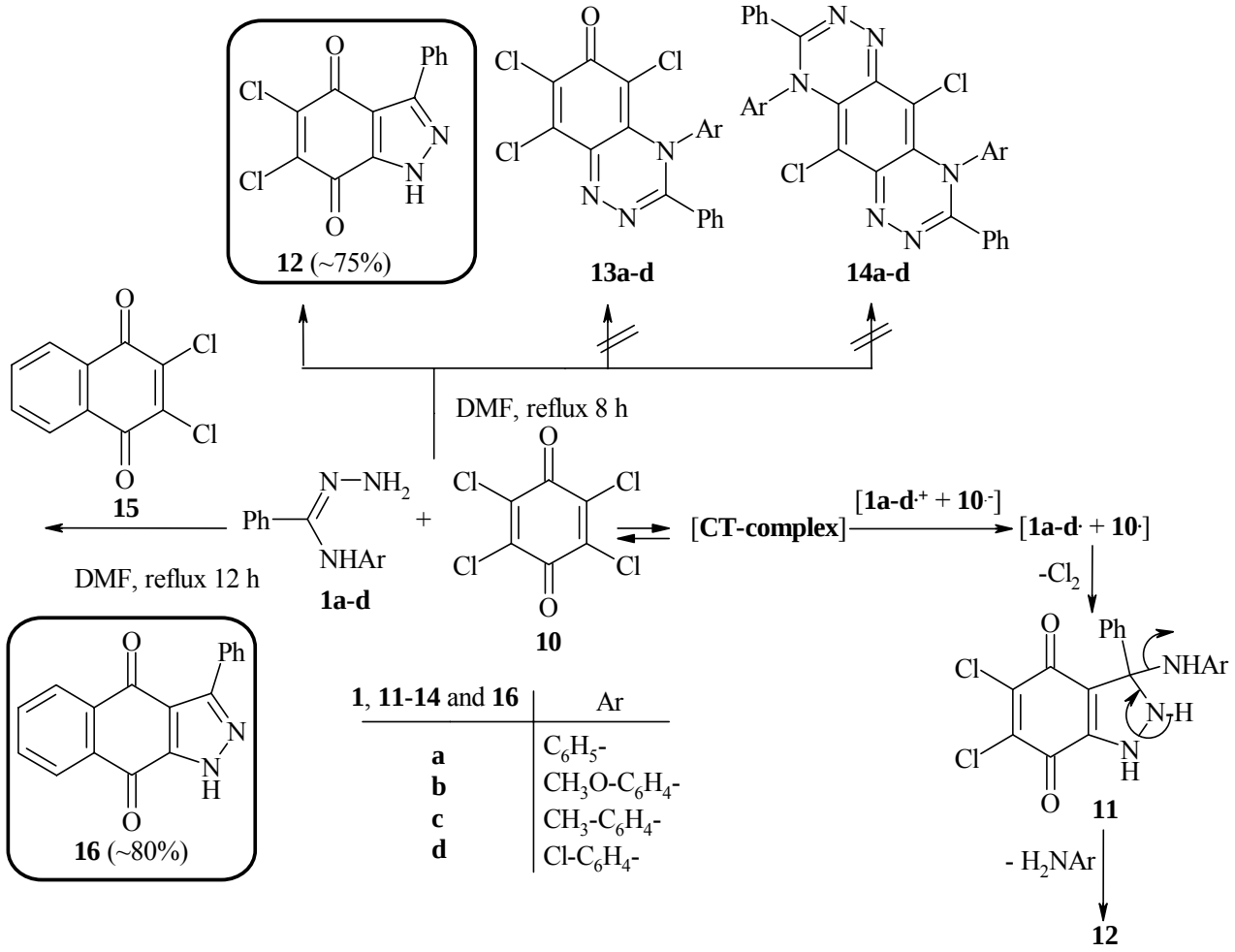
We believe that the hydrazino-NH_2 group is more nucleophilic than the aromatic amine and that the formation of **3a-d** (**or 6a-d**) can be rationalized by initial nucleophilic attack of the terminal hydrazino nitrogen of **1a-d** at one carbonyl group of **2** to form intermediate **7**, followed by elimination of water to produce **8** (Scheme 2). A further nucleophilic amidine-like addition at C-2 of the quinone would form the salt **9**. Finally, we suggest that intermediate **9** is oxidized by

another mol of **2** to give **3a-d** (Scheme 2). Isolation of 1,4-dihydro-benzo- and/or naphthoquinones supports the proposed mechanism. Spectroscopic data proved unambiguously the structure of compounds **3a-d** and excluded any other posssibilities such the formation of compounds **4a-d** (Scheme 1). Since amidrazones can be described as amino derivatives of *N*-substituted hydrazones,[26] the proposed mechanism is supported by literature precedent, which indicated that aromatic amines can react with 1,2- and 1,4-benzoquinones *via* condensation and elimination processes.[27]



Scheme 2. Rational formation of triazin-6(4*H*)-ones **3a-d.**

In the light of the aforementioned results, our attention turned to the reactions of **1a-d** with 2,3,5,6-tetrachloro-1,4-benzoquinone (**10**) and 2,3-dichloro-1,4-naphthoquinone (**15**) (Scheme 3) in dry DMF. The reaction of each of **1a-d** with **10** produced the same product, the spectroscopic and analytical data for which showed it to be 5,6-dichloro-3-phenyl-1*H*-indazole-4,7-dione (**12**) (Scheme 3). In the same manner, the reaction of **1a-d** with **15** all yielded **16**, which was identified as 3-phenyl-1*H*-benzo[*f*]indazole-4,9-dione (**16**) (Scheme 3). Mass spectrometric and elemental analysis of **12** proved the molecular formula to be $C_{13}H_6Cl_2N_2O_2$. The IR spectrum of **12** had two broad peaks at ν = 3220 and 1700-1682 cm^{-1} assigned to the NH and carbonyl groups, respectively. The ^1H NMR spectrum of **12** showed a broad singlet at δ = 12.40. From analytical and spectroscopic data, it could be concluded that the reaction between **1a-d** and **10** was accompanied by the overall loss of one molecule of Cl_2 and one of the corresponding aromatic amine. In the ^{13}C NMR spectrum of **12**, the two carbonyl carbons resonated at δ = 175.8 and 176.4; C-5 and -6 resonated at δ = 124.5 and 126.8; and C-3 and -3a appeared at δ = 155.8 and 132.0. One might have also expected the formation of triazines **13a-d** or **14a-d** (Scheme 1), however, this possibility is excluded by the spectroscopic data discussed above.



Scheme 3. Synthesis of indazoles **12** and **16.**

The structure assignment of **16** is based on analytical and spectral data: its IR spectrum contained an NH signal at about $\nu = 3200$ cm^{-1}, in addition to broad carbonyl absorption at $\nu =$ 1700-1685 cm^{-1}. The NMR spectra of **16** are in accordance to the proposed structure (Scheme 3) thus the ^{13}C NMR spectrum contained signals for C-3, -4 and -9 at $\delta = 156.0$, 175.8 and 176.8, respectively (see also the Experimental Section). We suggest that formation of these products can be rationalized by the mechanism shown in Scheme 3: an unstable CTC is formed, in the case of reaction between **1a-d** with **10,** followed by the formation of radicals **1a-d**$^{\cdot+}$ and **10**$^{\cdot-}$ (Scheme 3). Combination of the two radicals and extrusion of a chlorine molecule would form **11** (Scheme 3). Finally, elimination of a molecule of arylamine from **11** would give the observed product **12** (Scheme 3). Similar reactivity between donors and acceptors (i.e. **11** and **15**) has been recently discussed by us.[28]

In conclusion, our method is a convenient procedure to synthesize fused 1,2,4-triazines. Its advantages are the reasonable yields, and the ease with which the reaction can be carried out as a

one-pot procedure. Additionally, amidrazones react with halogenated quinones to give indazoles. possibly *via* CT-complexes.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker AM 400, ^{1}H: 400.13 MHz, ^{13}C:100.6 MHz) were obtained from $CDCl_3$ solutions; the chemical shifts are given relative to internal standard TMS. For preparative thin layer chromatography (PLC), glass plates (20 x 48 cm) were covered with a slurry of silica gel Merck PF_{254} and air dried and developed using the solvents listed. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were carried in the Assiut Microanalysis Center of Assiut University. Mass spectrometry was performed by electron impact at 70 eV, with a Finnigan Mat 8430 spectrometer in the Institute of Organic Chemistry, TU-Braunschweig. Germany. IR spectra were run on a Shimadzu 470 spectrometer using KBr pellets. Ultraviolet (UV) spectra were obtained of acetonitrile solutions, on a Perkin Spectrometer.

Starting materials. Amidrazones **1a-d** were prepared according to reference 10. Benzo- and naphtho-1,4-quinones (**2** and **5**) were obtained from Fluka, whereas 2,3,5,6-tetrachloro-1,4-benzoquinone (**10**) and 2,3-dichloro-1,4-naphthoquinone (**15)** were obtained from Aldrich.

Reaction of amidrazones 1a-d with 2 and 5

General procedure. A 250 ml two-necked round-bottom flask was flame-dried under N_2 and then cooled to room temperature. Under an N_2 atmosphere, dry absolute ethyl acetate (30 mL) containing a mixture of **1a-d** (1 mmol) and **2** (or **5**) (2 mmol) was added. The mixture was stirred at room temperature (the reaction was followed by TLC analysis). The solvent was then removed under vacuum and the residue was separated by preparative plates chromatography (silica gel, toluene: ethyl acetate 5:2). The obtained products **3a-d** or **6a-d** were isolated as the fastest migrating zones, whereas 1,4-dihydro benzo- and/or naphtho-quinone as the slowest zones. The products were recrystallized from the stated solvents, whereas the dihydroquinones were identified by comparison using authentic samples by TLC analyses along with m.p. measurements.

3,4-Diphenyl-1,2,4-benzotriazin-6(4*H*)-one (3a). Orange crystals (0.22 g. 72%); R_f = 0.4 (CH_2Cl_2), m.p. 238 °C (ethyl acetate). - IR (KBr): ν = 3060-3010 (Ar-CH), 1690 (C=O), 1610, 1600 (C=N), 1590 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 410 (4.10). - ^{1}H NMR ($CDCl_3$): δ = 6.60 (d, 1 H, *J* = 1.0 Hz, H-5), 6.80 (dd, 1 H, *J* = 8.0, 1.2 Hz, H-7), 7.12 (d, 1 H, *J* = 8.0 Hz, H-8), 7.20-7.28 (m, 3 H, Ar-H), 7.43-7.60 (m, 5 H, Ar-H), 7.66-7.70 (m, 2 H, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 108.0 (CH-5), 110.0 (CH-7), 126.2 (CH-8), 126.8, 127.2 (*p*-Ar CH), 127.8, 128.0, 128.4, 128.6 (Ar 2 CH), 138.0 (Ph C), 140.2 (*N*-Ph C), 147.2 (C-4a), 156.4 (C-8a), 158.0 (C-3),

184.4 (C-6). - MS (EI, 70 eV): *m/z* (%) = 299 [M^+] (100), 295 (20), 257 (18), 222 (42), 194 (20), 180 (60), 178 (30), 118 (24), 91 (26), 77 (44), 56 (14). - $C_{19}H_{13}N_3O$ (299.33): Calcd. C, 76.24; H, 4.38; N, 14.04. Found: C, 76.14; H, 4.30; N, 14.00.

4-(4′-Methoxyphenyl)-3-phenyl-1,2,4-benzotriazin-6(4*H*)-one (3b). Orange crystals (0.28 g. 85%); R_f = 0.5 (CH_2Cl_2), m.p. 258 °C (ethanol). - IR (KBr): ν = 3080-3030 (Ar-CH), 2980-2860 (aliph-CH), 1692 (C=O), 1612, 1604 (C=N), 1594 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 420 (4.12). - ^{1}H NMR ($CDCl_3$): δ = 3.95 (s, 3 H, OCH_3), 6.64 (d, 1 H, *J* = 1.2 Hz, H-5), 6.70 (dd, 2 H, *J* = 8.0, 1.2 Hz, OCH_3-Ph), 6.86 (dd, 1 H, *J* = 8.0, 1.0 Hz, H-7), 7.14 (d, 1 H, *J* = 8.0 Hz, H-8), 7.40-7.60 (m, 5 H, Ar-H), 7.80-7.90 (dd, 2 H, *J* = 8.0, 1.0 Hz, OCH_3-Ph). – ^{13}C NMR ($CDCl_3$): δ = 51.0 (OCH_3), 108.4 (CH-5), 110.6 (CH-7), 126.6 (CH-8), 126.8, (*p*-Ar CH), 127.4 (OCH_3-Ph 2CH), 128.6, 128.8 (Ar 2CH), 132.0 (OCH_3-Ph 2CH), 137.4 (OCH_3-Ph C), 138.6 (Ph C), 140.4 (*N*-Ph C), 147.0 (C-4a), 156.2 (C-8a), 158.4 (C-3), 184.5 (C-6). – MS (EI, 70 eV): *m/z* (%) = 330 [M + 1] (22), 329 [M^+] (100), 314 (20), 298 (40), 252 (28), 238 (24), 221 (26), 212 (32), 185 (36), 144 (36), 118 (32), 109 (26), 78 (40), 56 (24). – $C_{20}H_{15}N_3O_2$ (329.36): Calcd. C, 72.94; H, 4.59; N, 12.76. Found: C, 73.04; H, 4.50; N, 12.70.

4-(4′-Methylphenyl)-3-phenyl-1,2,4-benzotriazin-6(4*H*)-one (3c). Orange crystals (0.25 g. 80%); R_f = 0.45 (CH_2Cl_2), m.p. 218 °C (methanol). - IR (KBr): ν = 3065-3010 (Ar-CH), 2986-2870 (aliph-CH), 1690 (C=O), 1610, 1600 (C=N), 1596 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 416 (4.10). - ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 6.60 (d, 1 H, *J* = 1.0 Hz, H-5), 6.80 (dd, 1 H, *J* = 8.0, 1.0 Hz, H-7), 7.10 (d, 1 H, *J* = 8.0 Hz, H-8), 7.20-7.40 (m, 7 H, Ar-H), 7.60-7.68 (m, 2 H, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 32.8 (CH_3), 108.4 (CH-5), 110.6 (CH-7), 126.4 (CH-8), 127.0 (*p*-Ar CH), 128.0, 128.6, 128.8, 130.0 (Ar 2CH), 132.2 (CH_3-Ph C), 138.2, 140.0 (*N*-Ph C), 146.8 (C-4a), 156.0 (C-8a), 158.0 (C-3), 184.2 (C-6). – MS (EI, 70 eV): *m/z* (%) = 313 [M^+] (100), 298 (36), 220 (24), 210 (34), 144 (30), 92 (40), 77 (30), 56 (26). – $C_{20}H_{15}N_3O$ (313.36): Calcd. C, 76.66; H, 4.82; N, 13.41. Found: C, 76.60; H, 4.78; N, 13.36.

4-(4′-Chlorophenyl)-3-phenyl-1,2,4-benzotriazin-6(4*H*)-one (3d). Pale orange crystals (0.22 g, 66%); R_f = 0.25 (CH_2Cl_2), m.p. 168 °C (ethanol). - IR (KBr): ν = 3050-3008 (Ar-CH), 1690 (C=O), 1606 (C=N), 1590 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 398 (3.8). - ^{1}H NMR ($CDCl_3$): δ = 6.56 (d, 1 H, *J* = 1.2 Hz, H-5), 6.70-6.76 (m, 3 H, Ar-H, H-7), 7.08 (d, 1 H, *J* = 8.0 Hz, H-8), 7.22-7.38 (m, 7 H, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 108.0 (CH-5), 110.0 (CH-7), 126.2 (CH-8), 126.8 (Cl-Ar 2CH), 127.4 (*p*-Ar CH), 127.6, 128.0, (Ar 2CH), 128.4 (Cl-Ar C), 128.8 (Cl-Ar 2CH), 138.0 (Ph C), 140.0 (*N*-Ph C), 146.5 (C-4a), 156.0 (C-8a), 157.4 (C-3), 184.0 (C-6). – MS (EI, 70 eV): *m/z* (%) = 335 [M + 2] (34), 333 [M^+] (100), 300 (34), 298 (32), 222 (28), 220 (24), 212 (30), 210 (34), 145 (26), 115 (38), 113 (36), 77 (26), 56 (20). – $C_{19}H_{12}ClN_3O$ (333.78): Calcd. C, 68.37; H, 3.62; Cl, 10.62; N, 12.59. Found: C, 68.20; H, 3.68; Cl, 10.55; N, 12.56.

3,4-Diphenyl-naphtho[2,1-*e*]-1,2,4-triazin-6(4*H*)-one (6a). Red crystals (0.26 g 75%); R_f = 0.5 (CH_2Cl_2), m.p. 288 °C (ethyl acetate). - IR (KBr): ν = 3040-3000 (Ar-CH), 1700-1685 (C=O), 1600 (C=N), 1595 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 400 (3.8). - ^{1}H NMR ($CDCl_3$): δ = 6.80 (s, 1 H, H-5), 7.18-7.30 (m, 5 H, Ar-H), 7.50-7.60 (m, 7 H, Ar-H), 7.94 (dd, 2 H, *J* = 8.0,

1.2 Hz, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 110.0 (CH-5), 126.6, 127.0 (*p*-Ar CH), 127.6 (Ar-CH), 128.0, 128.2, 128.6, 129.0 (Ar 2CH), 129.4, 130.0, 131.0 (Ar CH), 132.0 (C-6a), 134.0 (C-10a), 134.4 (Ph C), 140.8 (*N*-Ph *C*), 148.0 (C-4a), 156.0 (C-10b), 158.8 (C-3), 185.0 (C-6). - MS (EI, 70 eV): *m/z* (%) = 349 [M^+] (100), 272 (46), 195 (20), (32), 180 (42), 116 (28), 91 (20), 77 (60), 51 (20). – $C_{23}H_{15}N_3O$ (349.40): Calcd. C, 79.07; H, 4.33; N, 12.03. Found C, 79.00; H, 4.29; N, 12.00.

4-(4\-Methoxyphenyl)-3-phenyl-naphtho[2,1-*e*]-1,2,4-triazin-6(4*H*)-one (6b). Red crystals (0.31 g, 86%); R_f = 0.40 (CH_2Cl_2), m.p. 182 °C (methanol). - IR (KBr): ν = 3066-3008 (Ar-CH), 2980-2860 (aliph-CH), 1702-1690 (C=O), 1610 (C=N), 1596 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 436 (4.2). - ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3 H, OCH_3), 6.82 (s, 1 H, H-5), 6.90 (dd, 2 H, *J* = 8.0, 1.0 Hz, CH_3OPh-H), 7.24-7.50 (m, 7 H, Ar-H), 7.80 (dd, 2 H, *J* = 8.0, 1.2 Hz, CH_3OPh-H), 7.98 (dd, 2 H, *J* = 8.0, 1.2 Hz, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 51.9 (OCH_3), 110.4 (CH-5), 126.4 (*p*-Ar CH), 127.0 (Ar CH), 127.2 (OCH_3-Ph 2CH), 128.5, 128.8 (Ar 2CH), 129.0, 130.4, 131.2 (Ar CH), 131.6 (OCH_3-Ph 2CH), 132.2 (C-6a), 134.4 (C-10a), 134.6 (Ph C), 140.4 (*N*-Ph C), 148.4 (C-4a), 150.0 (CH_3O-Ph C) 156.0 (C-3), 156.6 (C-10b), 185.5 (C-6). - MS (EI, 70 eV): *m/z* (%) = 379 [M^+] (100), 348 (22), 332 (20), 286 (24), 272 (40), 194 (26), 180 (40), 166 (24), 108 (34), 92 (30), 77 (50), 50 (18). – $C_{24}H_{17}N_3O_2$ (379.42): Calcd. C, 75.98; H, 4.52; N, 11.07. Found C, 75.80; H, 4.50; N, 11.00.

4-(4\-Methylphenyl)-3-phenyl-naphtho[2,1-*e*]-1,2,4-triazin-6(4*H*)-one (6c). Pale red crystals (0.30 g, 82%); R_f = 0.25 (CH_2Cl_2), m.p. 240 °C (acetonitrile). - IR (KBr): ν = 3100-2996 (Ar-CH), 2980-2860 (Aliph-CH), 1700-1684 (C=O), 1600 (C=N) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 426 (4.1). - ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 6.84 (s, 1 H, H-5), 7.24-7.36 (m, 7 H, Ar-H), 7.50-7.60 (m, 4 H, Ar-H), 7.90 (dd, 2 H, *J* = 8.0, 1.0 Hz, Ar-H). - ^{13}C NMR($CDCl_3$): δ = 32.0 (CH_3), 110.6 (CH-5), 126.6 (*p*-Ar CH), 127.2, 128.0, 128.5, 128.8 (Ar 2*C*H), 130.0, 130.6, 132.0, 132.4 (Ar CH), 132.8 (C-6a), 133.6 (Ph C), 134.0 (C-10a), 136.0 (CH_3Ph C), 140.0 (*N*-Ph C), 148.4 (C-4a), 156.4 (C-3), 158.0 (C-10b), 185.2 (C-6). - MS (EI, 70 eV): *m/z* (%) = 296 [M^+] (4), 331 (4), 252 (9), 248 (100), 246 (80), 210 (22), 175 (24), 147 (32), 87 (44). - MS (EI, 70 eV): *m/z* (%) = 363 [M^+] (100), 348 (22), 272 (40), 194 (26), 180 (40), 166 (24), 118 (34), 92 (30), 77 (50), 50 (18). – $C_{24}H_{17}N_3O$ (363.42): Calcd. C, 79.32; H, 4.72; N, 11.56. Found C, 79.20; H, 4.69; N, 11.48.

4-(4\-Chlorophenyl)-3-phenyl-naphtho[2,1-*e*]-1,2,4-triazin-6(4*H*)-one (6d). Red crystals (0.25 g, 70%); R_f = 0.5 (CH_2Cl_2), m.p. 162 °C (ethanol). - IR (KBr): ν = 3220 (NH), 3070-3000 (Ar-CH), 1700-1690 (CO), 1600 (C=N), 1598 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 402 (4.0). - ^{1}H NMR ($CDCl_3$): δ = 6.70 (s, 1 H, H-5), 6.80 (dd, 2 H, *J* = 8.0, 1.0 Hz, ClPh-H), 7.20-7.50 (m, 7 H, Ar-H), 7.60 (dd, 2 H, *J* = 8.0, 1.2 Hz), 7.92 (dd, 2 H, *J* = 8.0, 1.0 Hz, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 108.6 (CH-5), 124.0, 126.0 (Cl-Ph 2CH), 126.4 (*p*-Ar CH), 127.0 (Cl-Ph C), 127.6, 128.0 (Ar 2CH), 128.40, 128.60, 130.0, 130.4 (Ar CH), 131.4 (Ph C), 132.2 (C-6a), 134.2 (C-10a), 135.2 (Cl-*N*-Ph C), 148.0 (C-4a), 154.0 (C-3), 156.0 (C-10b), 185.0 (C-6). - MS (EI, 70 eV): *m/z* (%) = 384 [M+1] (32), 383 [M^+] (100), 381 (28), 348 (20), 346 (30), 272 (34), 270 (38),

196 (28), 194 (24), 118 (30), 116 (34), 77 (42). – $C_{23}H_{14}ClN_3O$ (383.84): Calcd. C, 71.97; H, 3.68; Cl, 9.24; N, 10.95. Found C, 71.82; H, 3.60; Cl, 9.16; N, 11.08.

Reaction of amidrazones 1a-d with 10 and 15. General procedure

A 250 ml two necked bottom flask was flame-dried under N_2 atmosphere and then cooled to room temperature Under N_2 atmosphere, dry DMF (30 mL) containing a mixture of **1a-d** (1 mmol) and **10** or **15** (1 mmol) is placed. The mixture was stirred with reflux (the reaction was followed by TLC analysis). The solvent was evaporated to its half volume. The obtained products **12** and **16** were filtered and recrystallized from the stated solvents.

5,6-Dichloro-3-phenyl-1*H*-indazole-4,7-dione (12). Red crystals (0.22 g, 75%); R_f = 0.3 (CH_2Cl_2), m.p. 280 °C (ethyl acetate). - IR (KBr): ν = 3220 (NH), 3070-2996 (Ar-CH), 1700-1690 (C=O), 1610, 1600 (C=N), 1590 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 410 (4.1). - ^1H NMR ($CDCl_3$): δ = 7.00-7.28 (m, 5 H, Ph-H). 12.40 (s, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 124.5, (C-5), 126.8 (C-6), 127.2 (*p*-Ph CH), 127.6, 128.4 (Ar 2CH), 130.0 (Ph C), 132.0 (C-3a), 133.0 (C-7a), 155.8 (C-3), 175.8 (C-4), 176.4 (C-9). - MS (EI, 70 eV): *m/z* (%) = 295 [M+2] (12), 294 [M+1] (34), 293 [M^+] (100), 258 (30), 256 (34), 224 (34), 222 (28), 218 (34), 120 (22), 118 (28), 80 (44), 77 (34). - $C_{13}H_6Cl_2N_2O_2$ (293.11): Calcd. C, 53.27; H, 2.06; Cl, 24.19; N, 9.56. Found: C, 53.16; H, 2.00; Cl, 24.10; N, 9.50.

3-Phenyl-1*H*-benzo[*f*]indazole-4,9-dione (16). Red crystals (0.22 g, 80%); R_f = 0.5 (CH_2Cl_2), m.p. 250 °C (ethyl acetate). - IR (KBr): ν = 3200 (NH), 3120-2990 (Ar-CH), 1700-1685 (C=O), 1610, 1600 (C=N), 1590 (C=C) cm^{-1}. - UV (CH_3CN): λ_{max} (log ε) = 420 (4.16). - ^1H NMR ($CDCl_3$): δ = 7.10-7.36 (m,7 H, Ph-H). 7.74 (dd, 2 H, *J* = 8.0, 1.2 Hz, Ar-H), 12.30 (s, 1H, NH).- ^{13}C NMR ($CDCl_3$): δ = 126.8 (*p*-Ph CH), 127.8, 128.2 (Ar 2CH), 128.4, 128.8, 129.6, 130.0 (Ar CH), 130.4 (C-4a), 130.8 (Ph C), 132.4 (C-3a), 132.0 (C-8b), 134.2 (C-8a), 156.0 (C-3), 175.8 (C-4), 176.8 (C-9). – MS (EI, 70 eV): *m/z* (%) = 274 [M^+] (100), 196 (30), 156 (60), 120 (22), 118 (34), 80 (40), 77 (36). - $C_{17}H_{10}N_2O_2$ (274.28): Calcd. C, 74.45; H, 3.67; N, 10.21. Found: C, 74.36; H, 3.60; N, 10.10.

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