Formation of indazole derivatives from 2,4-disubstituted thiosemicarbazides and some chloro-*p*-quinones

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The reaction of 2,4-disubstituted thiosemicarbazides with 2,3,5,6-tetrachloro-1,4-benzo-quinone gave 2-aryl-5,6-dichloro-3-(substituted imino)-2,3-dihydro-1*H*-indazole-4,7-diones in 57–66% yield together with smaller amounts of 2-aryl-3-(substituted imino)-4,6,7-trichloro-2*H*-indazole-5(3*H*)-ones (21–25% yield). Reaction of 2,3-dichloro-1,4-naphthoquinone with 2,4-disubstituted thiosemicarbazides provided 2-aryl-3-(substituted imino)-2,3-dihydro-1*H*-benzo[*f*]-indazole-4,9-diones in 63–74% yield. Rationales for these transformations are presented.

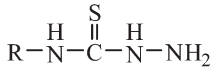
Keywords: 2,4-disubstituted thiosemicarbazides, benzo- and naphthoquinones, indazole, derivatives

Compounds containing a *p*-quinone moiety show strong biological activity due to their interference with metabolic processes of both plant and animal cells.[1,2] In another area benzimidazole-quinones have been investigated for herbicidal activity.[3] The synthesis of indazole derivatives from the reaction of diazoalkanes with some benzo- and naphthoquinones have been investigated.[3–6] Similarly, the analogous Michael addition of N-2 substituted hydrazones, which can be regarded as azaenamines, to 1,4-naphthoquinone, followed by ring closure, gave indazole derivatives.[7] Much less attention has been given to the synthesis of indazole derivatives from the reaction of thiosemicarbazides with benzoquinones.[8–10] 2,3,5,6-Tetrachloro-1,4-benzoquinone **2** and 2,3-dichloro-1,4-naphthoquinone **3** undergo nucleophilic substitution of one or two chlorine atoms by thioacetamide,[11–13] thiourea,[14,15] substituted thioureas,[16] thiocarbazones,[17] hydrazine-1,2-dicarbothioamides,[18] and thiosemicarbazides.[9]

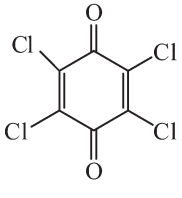
It has been reported that 4-substituted thiosemicarbazides **1a–c** reacted with **2** and **3** in ethyl acetate with admission of air to give compounds **4–6** (Fig. 1).[9]

We report here the results of our investigations on the reaction of 2,4-disubstituted thiosemicarbazides **7a–d** with benzo- and naphthoquinones **2** and **3**. These results are compared with those obtained earlier.[9]

Addition of ethyl acetate solutions of **7a–d** to a solution of **2** in the same solvent resulted in the appearance of a green colour, which gradually changed into brown. When the reaction mixture was monitored spectrophotometrically (at 10 °C), an absorption maximum was observed in the visible region at 565–538 nm, that was assigned to the formation of an unstable charge-transfer complex (CTC), since neither thiosemicarbazide derivatives **7a–d** nor *p*-chloranil **2** alone absorb in this region. After standing for 48 h at room temperature 5,6-dichloro-2-aryl-3-(substituted imino)-2,3-dihydro-1*H*-indazole-4,7-diones **8a–d** (57–66%) and 3-(substituted imino)-4,6,7-trichloro-2-aryl-2*H*-indazole-5(3*H*)-one **9a–d** (21–25%) were isolated by preparative thin layer chromatography (Scheme 1). The structural assignment of the major products **8a–d** is based on the following data: The IR spectrum of 3-(benzylimino)-5,6-dichloro-2-phenyl-2,3-dihydro-1*H*-indazole-4,7-dione **8d** showed broad bands at 3280 cm^{-1} for an



1



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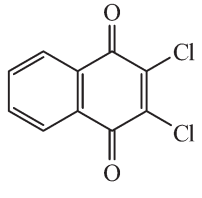

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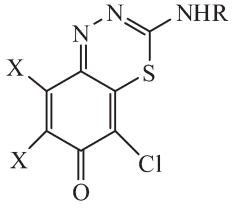
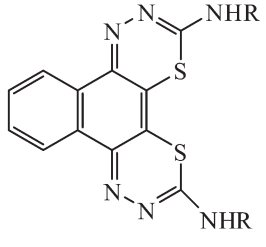


4, X= Cl
5, X-X= CH=CH-CH=CH



6

1, 4-6: a, R = C_6H_5
b, R = $C_6H_5CH_2$
c, R = CH_2=CH-CH_2

Fig. 1

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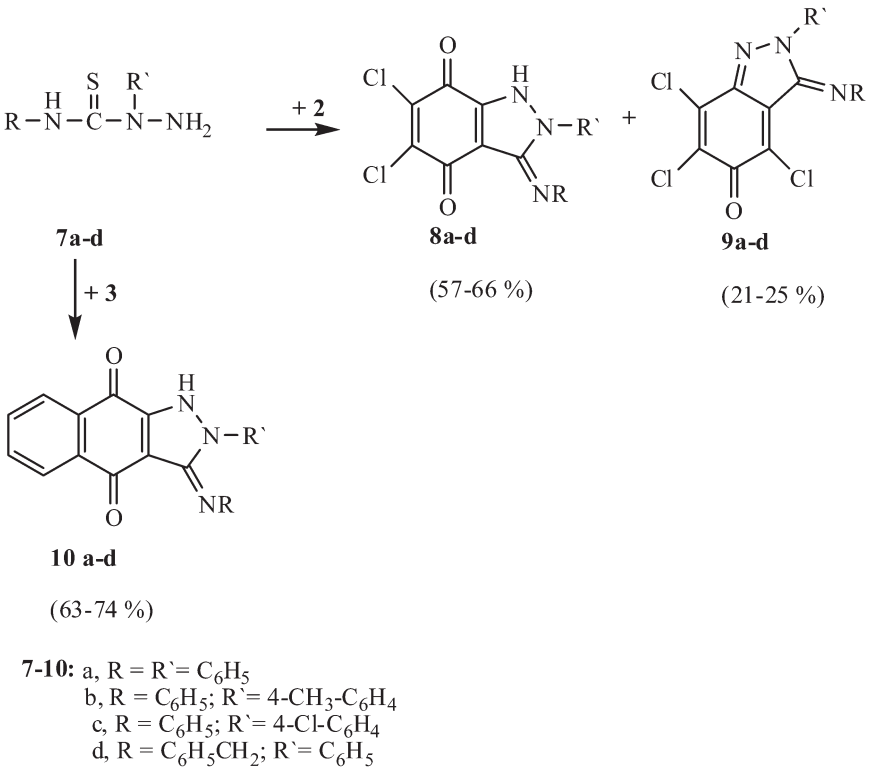


7-10: a, R = R`= C_6H_5
b, R = C_6H_5; R`= 4-CH_3-C_6H_4
c, R = C_6H_5; R`= 4-Cl-C_6H_4
d, R = $C_6H_5CH_2$; R`= C_6H_5

Scheme 1

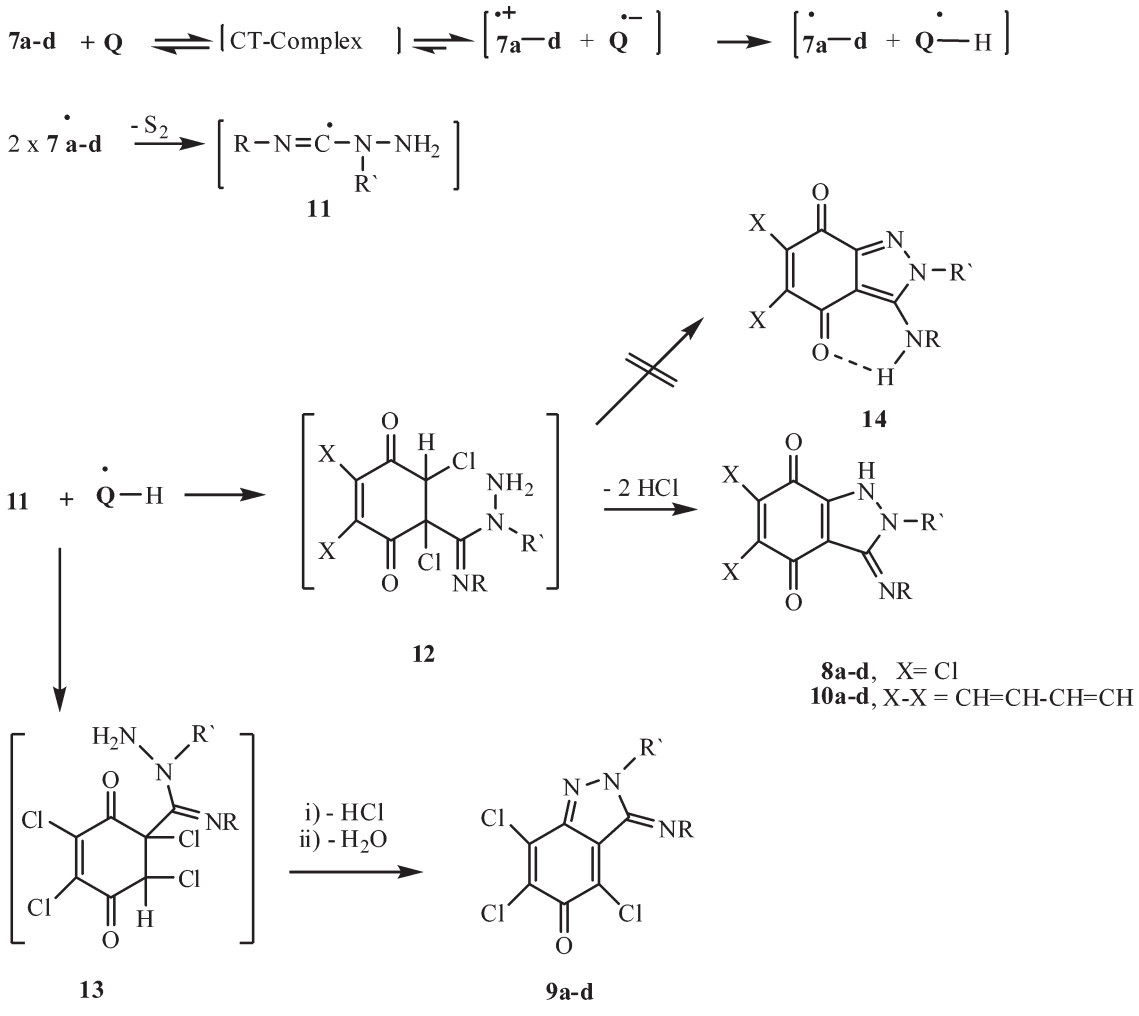
NH group, with sharp bands at 1675 (CO) and at 1610 (C=N) cm^{-1}. The ^1H NMR spectrum of **8d** showed one broad singlet at 11.18 ppm, due to the indazole-NH proton (11.14–11.21 for compounds **8a–c**). On the other hand, the alternative tautomer **14** was ruled out on the basis of δ values for the exocyclic-NHR groups which are dependent on the nature of RNH (*ca* 9.5 ppm when R = Ph, 7.8 ppm when R = benzyl).[19] Also present in the spectrum was another singlet at 4.57 ppm due to the CH_2-Ph group, as well as multiplets at 7.48–7.56 and 7.61–7.64 ppm, which are characteristic of phenyl protons. In its ^{13}C NMR spectrum, **8d** displayed the characteristic resonances for carbonyl groups in chlorinated benzoquinones at 173.48 and 173.55 ppm.[20] The decoupled carbon spectrum of **8d** showed signals at 119.18, 158.12 and 153.07 ppm, assigned to C-3a, C-7a and C-3, respectively. In addition, a signal for C-5 and C-6 was present at 140.28 ppm.

The presence of a benzyl methylene group was also evident from the ^{13}C DEPT NMR spectrum which exhibited a negative signal at 51.38 ppm. The constitution of compounds **8a–d** was further confirmed by EI-mass spectrometry. The following features of the fragmentation patterns provided additional support for the assigned structures. The mass spectra were characterised by loss of 28 a.m.u (dinitrogen or carbonyl group), followed by loss of R–NC and Cl which were common to the spectra of all of the compounds.

The structures of the minor products **9a–d** (25–21 %) were delineated from their spectroscopic properties and gross compositions. 2-(4-Methylphenyl)-3-(phenylimino)-4,6,7-trichloro-2*H*-indazol-5(3*H*)-one **9b** was obtained as characteristically reddish brown crystals. Its molecular structure is supported by the following findings: The gross formula $C_{20}H_{12}Cl_3N_3O$ represents a product derived from one molecule of **7b** and one molecule of **2** with loss of sulfur, HCl and H_2O. The IR spectrum of **9b** showed a sharp absorption band characteristic of a carbonyl group at 1675 cm^{-1} and the absence of NH_2 or NH groups. Also, upon transformation of **2** into **9b**, one of the benzoquinone-CO absorptions was replaced by a new IR band at υ_{max} 1630 cm^{-1} due to C=N. The ^1H NMR spectrum of **9b** clearly indicated a methyl group singlet at 2.24 ppm, in addition to multiplets at 7.43–7.54 ppm, due to the phenyl protons. In the ^{13}C NMR spectrum of **9b**, the signal characteristic of a chlorinated benzoquinone carbonyl group appeared at 174.26 ppm,[20] whilst the other carbonyl carbon was replaced by signal at 150.12 ppm (C-7a).[20] In addition, the indazole-C-3 carbon was observed at 156.57 ppm, and a methyl signal resonated at 20.87 ppm. Other signals were observed which clearly indicated the presence of Cl–C= and Cl–C= C–Cl fragments at 140.07, 141.14 and 141.36 ppm, respectively. The formation of **9b** was further confirmed by mass spectrometry; besides the molecular ion at 421/415, the fragment ion patterns characteristic of substituted trichloro compounds were observed.[21]

2,3-Dichloro-1,4-naphthoquinone **3** was chosen to compare its reactivity towards 2,4-disubstituted thiosemicarbazides **7a–d** with that of *p*-chloranil **2**. It has been reported that **3** resembles **2** in most of its substitution reactions, especially with nitrogen nucleophiles (amines, amino acids, pyrazoles, imidazoles, *etc.*).[22–30] From this point of view one might expect that **7a–d** should react with **3** in a similar manner to **2**.

Mixing equimolar amounts of **7a–d** and **3** in ethyl acetate for 72 h led to the formation of benzo[*f*]indazol-4,9-dione derivatives **10a–d** (Scheme 1). In the IR spectra of **10a–d** one carbonyl band was seen in the range 1680–1675 cm^{-1}, and a band between 1620 and 1630 cm^{-1} was assigned to a C=N vibration, besides a broad band between 3305 and 3295 cm^{-1} due to an NH group. The ^1H NMR spectra of compounds **10a–d** did reveal an indazole-NH signal between 11.28 and 11.20 ppm, whilst the aromatic protons resonated at 7.17 and 7.26 ppm, for the Ar3',5'-H protons, two multiplets at 7.65–7.83 for Ar6,7-H and at 8.09–8.27 for Ar5, 8-H. Furthermore, multiplets were observed for Ar2`,6` and other phenyl protons in the region 7.29–7.61 ppm. In the case of **10b**, the ^{13}C NMR spectrum showed signals at 178.74 and 179.37 for (C-4 and C-9), 156.83 (C-3), 151.06 (C-9a), 111.94 (C-3a) and 21.27 (CH_3) ppm.



Scheme 2

The benzo[*f*]indazole-4,9-diones **10a–d** underwent mass spectral fragmentation by loss of ArNC and ArN_2 as well as loss of mass 28 due to N_2 or CO.

The formation of indazole derivatives **8–10** may be rationalised as shown (Scheme 2). At first an unstable CTC is formed followed by the formation of radicals (**7a–d**) and Q-H**˙**. The radicals (**7a–d**)˙ being a precursor to **11**.[8–10,17,31–33] The latter reacts with the semiquinone Q-H˙ with elimination two molecules of HCl to give the indazole derivatives **8a–d** or **10a–d** *via* the intermediate **12**. On the other hand, elimination of HCl and H_2O from the intermediate **13** affords the indazole derivatives **9a–d.**

Conclusion

The products obtained from the nucleophilic substitution reactions of 2,4-disubstituted thiosemicarbazides **7a–d** to chlorinated benzo- and naphthoquinones **2** and **3** followed by cyclisation are neither thiahetrocycles nor heterocyclic thiones, but indazole derivatives. Whilst neither the S–C–N–N + C_2 nor the N–C(S)–N–N + C_2 mode of reaction was found in this study, a novel C–N–N + C_2 addition mode was observed. The reactivity of 2,4-disubstituted thiosemicarbazides **7a–d** is thus markedly different to that observed for the 4-substituted thiosemicarbazides **1a–d**.

Experimental

Melting points have been determined using open capillaries on a Gallenkamp melting point apparatus and uncorrected. Elemental analyses were determined by the Microanalytical Centre, Cairo University, Egypt. The IR spectra were recorded with a Shimadzu 408 instrument using potassium bromide discs. Both 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra were recorded for DMSO-d_6 solutions on a Bruker Avance DRX 500 spectrometer. Chemical shifts are expressed as δ [ppm] with reference to tetramethylsilane as an internal standard, s = singlet, d = doublet, m = multiplet and br = broad. ^{13}C NMR assignments were made with the aid of distortionless enhancement by polarisation transfer (DEPT) 135/90 spectra (qc = sp^2 quaternary carbon atoms). Mass spectra were recorded on a Varian MAT CH-7 instrument in EI mode at 70 eV ionisation energy. Preparative layer chromatography (PLC) used air dried 1.0 mm thick layers of slurry applied silica gel (Merck Pf_{254}) on 48 cm wide and 20 cm high glass plates using the solvents listed. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light and were isolated by extraction with acetone.

2,4-Disubstituted thiosemicarbazides **7a–d** were synthesised by reaction of the appropriate hydrazine hydrochloride with the appropriate isothiocyanate derivative according to published procedures.[34] 2,3,5,6-Tetrachloro-1,4-benzoquinone (*p*-chloranil, **2**) and 2,3-dichloro-1,4 naphthoquinone **3** (Aldrich) were used as received.

*Reactions of 2,4-disubstituted thiosemicarbazides (***7a–d***) with p-chloranil (***2***)*

To a solution of **2** (246 mg, 1 mmol) in dry ethyl acetate (15 mL), was added the appropriate 2,4-disubstituted thiosemicarbazides **7a–d** (1 mmol) in dry ethyl acetate (10 mL) dropwise with stirring at room temperature. The colour of the reaction changed gradually from green to brown. Stirring was contained for 48 h with admission of air to complete the reaction. The reaction mixture was concentrated and the residue was then separated by PLC using toluene/ethyl acetate (3:1) as eluent, to give numerous zones, the two most intense of which were removed and extracted. The faster migrating zone contained

2-aryl-5,6-dichloro-3-(substituted imino)-2,3-dihydro-1*H*-indazole-4,7-diones **8a–d**. The slowest migrating zone contained 2-aryl-3-(substituted imino)-4,6,7-trichloro-2*H*-indazol-5(3*H*)-ones **9a–d**. The zones were extracted with acetone and recrystallisation from suitable solvents afforded the pure compounds **8a–d** and **9a–d**.

*5,6-Dichloro-2-phenyl-3-(phenylimino)-2,3-dihydro-1*H*-indazole-4,7-dione* (**8a**): Reddish brown crystals (0.242 g, 63 %), m.p. 279–281 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.21 (br, 1H, indazole-NH), 7.52–7.62 (m, 10H, ArH). ^{13}C NMR (DMSO-d_6): δ = 173.44, 173.52 (CO), 158.17 (C-7a), 152.98 (C-3), 146.84, 140.27 (C-5,6), 137.66 (ArC), 129.67, 129.55, 127.63, 127.45, 126.97, 126.84 (Ph-CH), 119.28 (C-3a). IR (KBr): ν (cm^{-1}) 3285 (NH), 1680 (CO), 1615 (ArC=N), 1585 (ArC=C). MS: *m/z* (%) = 387/383 [M$^+$] (46), 355 (31), 319 (28), 283 (23), 180 (42), 105 (54), 77 (100), 65 (57). $C_{19}H_{11}Cl_2N_3O_2$ (384.22): Calcd: C, 59.39; H, 2.89; Cl, 18.45; N, 10.94. Found: C, 59.52; H, 3.02; Cl, 18.38; N, 11.12%.

*5,6-Dichloro-2-(4-methylphenyl)-3-(phenylimino)-2,3-dihydro-1*H*-indazole-4,7-dione* (**8b**): Reddish brown crystals (0.263 g, 66 %), m.p. 291–293 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 11.21 (br, 1H, indazole-NH), 7.54–7.62, 7.46–7.50, (m, 9H, ArH), 2.23 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ = 173.41, 173.47 (CO), 158.09 (C-7a), 153.11 (C-3), 140.16 (C-5, 6), 137.61, 133.12 (ArC), 129.62, 127.57, 127.41, 126.85, 126.79 (ArCH), 119.37 (C-3a), 20.71(CH_3). IR (KBr): ν (cm^{-1}) 3300 (NH), 1680 (CO), 1610 (ArC=N), 1590 (ArC=C). MS: *m/z* (%) = 401/397 [M$^+$] (34), 382 (36), 354 (27), 283 (41), 180 (28), 91 (100), 77 (78), 76 (71), 65 (42). $C_{20}H_{13}Cl_2N_3O_2$ (398.24): Calcd: C, 60.32; H, 3.29; Cl, 17.80; N, 10.55. Found: C, 60.19; H, 3.38; Cl, 17.94; N, 10.41%.

*2-(4-Chlorophenyl)-5,6-dichloro-3-(phenylimino)-2,3-dihydro-1*H*-indazole-4,7-dione* (**8c**): Pale brown crystals (0.256 g, 61 %), m.p. 307–309 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.14 (br, 1H, indazole-NH), 7.58–7.71 (m, 9H, ArH). IR (KBr): ν (cm^{-1}) 3290 (NH), 1675 (CO), 1615 (ArC=N), 1590 (ArC=C). MS: *m/z* (%) = 424/417 [M$^+$] (44), 383 (32), 355 (21), 319 (25), 283 (17), 180 (24), 77 (100), 65 (49). $C_{19}H_{10}Cl_3N_3O_2$ (418.66): Calcd: C, 54.51; H, 2.41; Cl, 25.40; N, 10.04. Found: C, 54.31; H, 2.52; Cl, 25.50; N, 10.23%.

*3-(Benzylimino)-5,6-dichloro-2-phenyl-2,3-dihydro-1*H*-indazole-4,7-dione* (**8d**): Brown crystals (0.229 g, 57 %), m.p. 286–288 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.18 (br, 1H, indazole-NH), 7.61–7.64, 7.48–7.56 (m, 10H, ArH), 4.57 (s, 2H, CH_2-Ph). ^{13}C NMR (DMSO-d_6): δ = 173.48, 173.55 (CO), 158.12 (C-7a), 153.07 (C-3), 140.28 (C-5,6), 137.61, 135.82, 133.15 (ArC), 129.66, 129.36, 128.86, 127.89, 127.46, 127.27 (ArC), 119.18 (C-3a), 51.38 (CH_2Ph). IR (KBr): ν (cm^{-1}) 3280 (NH), 1675 (CO), 1610 (ArC=N), 1590 (ArC=C). MS: *m/z* (%) = 401/397 [M$^+$] (39), 369 (22), 298 (18), 180 (25), 91 (100), 77 (81), 65 (66). $C_{20}H_{13}Cl_2N_3O_2$ (398.24): Calcd: C, 60.32; H, 3.29; Cl, 17.80; N, 10.55. Found: C, 60.19; H, 3.36; Cl, 17.97; N, 10.46%.

*2-Phenyl-3-(phenylimino)-4,6,7-trichloro-2*H*-indazole-5(3*H*)-one* (**9a**): Brown crystals (0.092 g, 23 %), m.p. 294–296 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 7.49–7.58 (m, 10H, ArH). ^{13}C NMR (DMSO-d_6): δ = 174.31 (CO), 156.49 (C-3), 150.26 (C-7a), 141.42, 141.19, 140.12 (C-4,6,7), 147.17, 137.55, 131.22 (ArC), 129.35, 129.26, 127.85, 127.41, 126.93, 126.79 (ArCH). IR (KBr): ν (cm^{-1}) 1680 (CO), 1625 (ArC=N), 1600 (ArC=C). MS: *m/z* (%) = 407/401 [M$^+$] (39), 365 (27), 329 (21), 293 (41), 190 (35), 167 (15), 91 (83), 77 (100), 65 (46). $C_{19}H_{10}Cl_3N_3O$ (402.66): Calcd: C, 56.67; H, 2.50; Cl, 26.41; N, 10.44. Found: C, 56.81; H, 2.42; Cl, 26.54; N, 10.61%.

*2-(4-Methylphenyl)-3-(phenylimino)-4,6,7-trichloro-2*H*-indazole-5(3*H*)-one* (**9b**). Reddish brown crystals (0.091 g, 22 %), m.p. 316–318 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 7.43–7.54 (m, 9H, ArH), 2.24 (s, 3H, CH_3), ^{13}C NMR (DMSO-d_6): δ = 174.26 (CO), 156.57 (C-3), 150.12 (C-7a), 141.36, 141.14, 140.07 (C-4,6,7), 147.22, 137.61, 131.86, 131.42 (ArC), 129.41, 127.74, 127.36, 127.01, 126.86 (ArCH), 20.87 (CH_3). IR (KBr): ν (cm^{-1}) 1675 (CO), 1630 (ArC=N), 1600 (ArC=C). MS: *m/z* (%) = 421/415 [M$^+$] (37), 400 (28), 364 (25), 328 (29), 292 (18), 189 (27), 161 (17), 103 (61), 91(100), 77 (86), 65 (43). $C_{20}H_{12}Cl_3N_3O$ (416.69): Calcd: C, 57.65; H, 2.90; Cl, 25.52; N, 10.08. Found: C, 57.81; H, 3.01; Cl, 25.41; N, 9.94%.

*2-(4-Chlorophenyl)-3-(phenylimino)-4,6,7-trichloro-2*H*-indazole-5(3*H*)-one* (**9c**): Pale brown crystals (0.109 g, 25 %), m.p. 333–335 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 7.52–7.69 (m, 9H, ArH), ^{13}C NMR (DMSO-d_6): δ = 174.15 (CO), 156.44 (C-3), 150.23 (C-7a), 141.35, 141.26, 140.16 (C-4,6,7), 147.11, 137.67, 131.55, 130.86 (ArC), 129.36, 127.65, 127.26, 126.97, 126.81 (ArCH). IR (KBr): ν (cm^{-1}) 1680 (CO), 1630 (ArC=N), 1595 (ArC=C). MS: *m/z* (%) = 443/435 [M$^+$] (29), 399 (32), 363 (27), 292 (41), 264 (28), 161 (33), 91 (62), 77 (100), 65 (81). $C_{19}H_9Cl_4N_3O$ (437.11): Calcd: C, 52.21; H, 2.08; Cl, 32.44; N, 9.61. Found: C, 51.98; H, 1.96; Cl, 32.57; N, 9.75%.

*3-(Benzylimino)-2-phenyl-4,6,7-trichloro-2*H*-indazole-5(3*H*)-one* (**9d**): Brown crystals (0.087 g, 21 %), m.p. 311–313 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 7.61–7.64, 7.43–7.62, (m, 10H, ArH), 4.61 (s, 2H, CH_2-Ph). ^{13}C NMR (DMSO-d_6): δ = 174.36 (CO), 156.29 (C-3), 150.16 (C-7a), 141.28, 141.15, 140.26 (C-4,6,7), 147.26, 137.71, 131.12 (ArC), 129.25, 129.18, 127.55, 127.17, 126,93, 126.85 (ArCH). IR (KBr): ν (cm^{-1}), 1680 (CO), 1625 (ArC=N), 1590 (ArC=C) cm^{-1}. MS: *m/z* (%) = 415/421 [M$^+$] (36), 379 (25), 243 (29), 307 (25), 190 (27), 117 (54), 91 (100), 77 (74), 65 (65). $C_{20}H_{12}Cl_3N_3O$ (416.64): Calcd: C, 57.65; H, 2.90; Cl, 25.52; N, 10.08. Found: C, 57.76; H, 3.02; Cl, 25.41; N, 9.93%.

*Reactions of 2,4-disubstituted thiosemicarbazides (***7a–d***) with 2,3-dichloro-1,4-naphthoquinone (***3***)*

A solution of **7a–d** (1.0 mmol) in dry ethyl acetate (15 mL) was added dropwise with stirring to a solution of **3** (1.0 mmol) in dry ethyl acetate (15 mL). The reaction mixture was stirred for 72 h, during which time it turned from orange into green and finally to brown in colour. The reaction mixture was concentrated and subjected to PLC using toluene/ethyl acetate (2:1) as eluent to give only one zone which was removed and extracted to give the substituted imino-2-aryl-2,3-dihydro-1*H*-benzo[*f*]indazole-4,9-diones **10a–d**.

*2-Phenyl-3-(phenylimino)-2,3-dihydro-1*H*-benzo[f]indazole-4,9-dione* (**10a**): Reddish brown crystals (0.259 g, 71 %), m.p.267–269 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.26 (br, 1H, indazole-NH), δ = 8.09–8.25 (m, 2H, Ar5,8-H), 7.67–7.83 (m, 2H, Ar6,7-H), 7.33–7.51 (m, 10 H, ArH). ^{13}C NMR (DMSO-d_6): δ = 179.34, 178.78 (CO), 156.87 (C-3), 150.93 (C-9a), 147.64, 137.57, 131.66, 130.84 (ArC), 129.68, 129.64, 127.93, 127.78, 127.67, 127.35, 126.89, 126.64 (ArCH), 112.22 (C-3a). IR (KBr): ν (cm^{-1}) 3305 (NH), 1680 (CO), 1625 (ArC=N), 1600 (ArC=C). MS: *m/z* (%) = 365 [M$^+$] (51), 262 (36), 157 (39), 129 (17), 105 (37), 103 (76), 77 (100), 65 (42). $C_{23}H_{15}N_3O_2$ (365.38): Calcd: C, 75.60; H, 4.14; N, 11.50. Found: C, 75.46; H, 4.02; N, 11.67%.

*2-(4-Methylphenyl)-3-(phenylimino)-2,3-dihydro-1*H*-benzo[f]indazole-4,9-dione* (**10b**): Reddish brown crystals (0.280 g, 74 %), m.p. 278–280 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.22 (br, 1H, indazole-NH), 8.13–8.27 (m, 2H, Ar5,8-H), 7.65–7.79 56 (m, 2H, Ar6,7-H), 7.17 (d, 2H, Ar3`,5`-H), 7.38–7.56 (m, 7H, ArH), ^{13}C NMR (DMSO-d_6): δ = 179.37, 178.74, (CO), 156.83 (C-3), 151.06 (C-9a), 147.59, 137.64, 131.83, 130.79 (ArC), 129.60, 129.55, 127.89, 127.68, 127.41, 126.86, 126.61 (ArCH), 111.94 (C-3a), 21.27 (CH_3). IR (KBr): ν (cm^{-1}) 3295 (NH), 1680 (CO), 1630 (ArC=N), 1595 (ArC=C). MS: *m/z* (%) = 379 [M$^+$, 44], 364 (37), 261 (43), 156 (16), 128 (8), 103 (47), 91 (100), 77 (64), 65(54). $C_{24}H_{17}N_3O_2$ (379.41): Calcd: C, 75.97; H, 4.52; N, 11.08. Found: C, 76.11; H, 4.43; N, 10.95%.

*2-(4-Chlorophenyl)-3-(phenylimino)-2,3-dihydro-1*H*-benzo[f]indazol-4,9-dione* (**10c**): Brown crystals (0.271 g, 68 %), m.p. 293–295 °C (methanol). ^{1}H NMR (DMSO-d_6): δ = 11.28 (br, 1H, indazole-NH), 8.10–8.22 (m, 2H, Ar5,8-H), 7.68–7.83 (m, 2H, Ar6,7-H), 7.43–7.61 (m, 7H, ArH), 7.26 (d, 2H, Ar3′,5′-H). ^{13}C NMR (DMSO-d_6): δ = 179.41, 178.69, (CO), 156.78 (C-3), 150.94 (C-9a), 147.65, 137.59, 132.78, 131.59, 130.66 (ArC), 129.68, 129.62, 127.93, 127.55, 127.38, 126.82, 126.75 (ArCH), 112.16 (C-3a). IR (KBr): ν (cm^{-1}) 3300 (NH), 1675 (CO), 1630 (ArC=N), 1590 (ArC=C). MS: *m/z* (%) = 399/401 [M$^+$, 32], 363 (54), 260 (29), 155 (13), 103 (49), 77 (100), 65 (57). $C_{23}H_{14}ClN_3O_2$ (399.83): Calcd: C, 69.09; H, 3.53; Cl, 8.87; N, 10.51. Found: C, 68.94; H, 3.45; Cl, 9.02; N, 10.66%.

*3-(Benzylimino)-2-phenyl-2,3-dihydro-1*H*-benzo[f]indazol-4,9-dione* (**10d**): Brown crystals (0.239 g, 63 %), m.p. 273–275 °C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 11.20 (br, 1H, indazole-NH), 8.13–8.26 (m, 2H, Ar5,8-H), 7.65–7.80 (m, 2H, Ar6,7-H), 7.29–7.48 (m, 10H, ArH), 4.62 (s, 2H, CH_2Ph). ^{13}C NMR (DMSO-d_6): δ = 179.41, 178.73 (CO), 156.78 (C-3), 151.09 (C-9a), 147.59, 137.62, 131.73, 130.76 (ArC), 129.64, 129.57, 128.12, 127.84, 127.73, 127.41, 126.92, 126.61 (ArCH), 111.88 (C-3a), 52.64 (CH_2-Ph). IR (KBr): ν (cm^{-1}) 3295 (NH), 1680 (CO), 1620 (ArC=N), 1585 (ArC=C). MS: *m/z* (%) = 379 [M$^+$, 24], 262 (32), 157 (26), 129 (19), 117 (63), 91 (100), 77 (58), 65 (46). $C_{24}H_{17}N_3O_2$ (379.41): Calcd: C, 75.97; H, 4.52; N, 11.08. Found: C, 76.12; H, 4.63; N, 10.99%.

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