Synthesis of phenazone derivatives

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Some new phenazone (antipyrin) derivatives **2—11** have been synthesised by acylation, alkylation, condensation and ring closure reactions of 4-aminophenazone **1**. The structures of the products have been secured by elemental analyses and spectral data (IR, ^{1}H, and ^{13}C NMR).

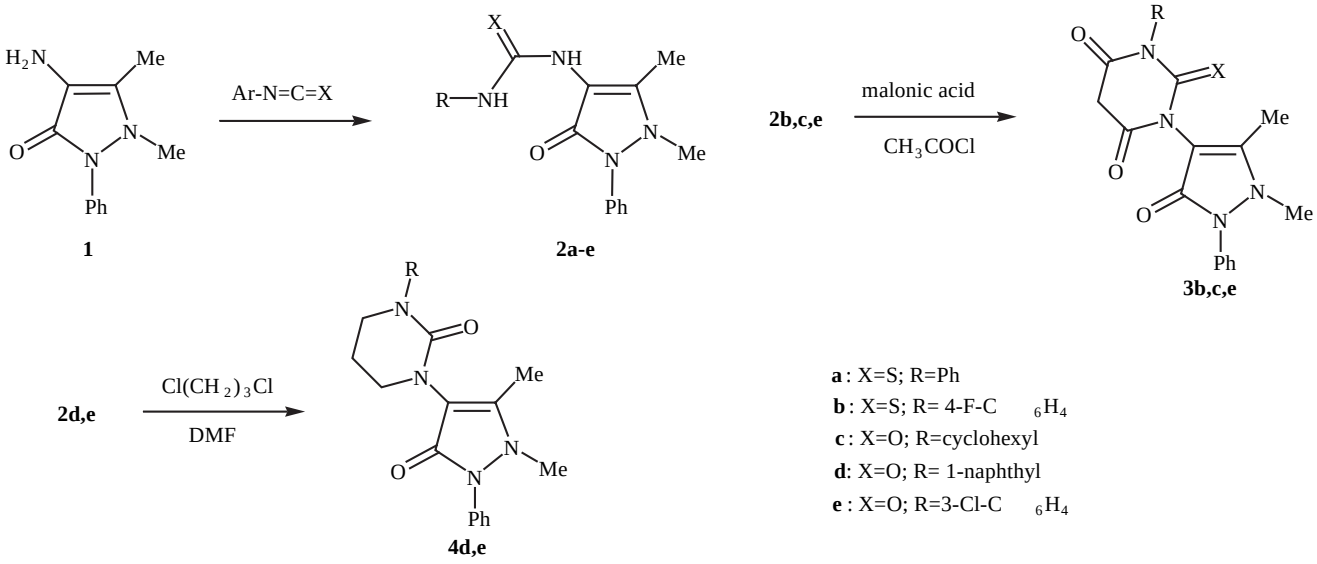
Keywords: phenazone, antipyrin, 1,2,4-triazine, 4-aminophenazone

Pyrazoline derivatives are of interest due to their biological activities[1-3] and as intermediates[4-7] in the syntheses of heterocyclic systems. Here, we describe acylation, alkylation, and condensation reactions of 4-aminophenazone **1** followed by ring closure reactions affording a fluorine substituted heterocyclic systems with possible biological effects. The introduction of fluorine or a CF_3 group into an organic molecule increases its solubility in lipids and fat deposits in the body.[8] Alkylation and acylation products of *N*-arylpyrazolones have been reported to show antimicrobial and anti-inflammatory activities.[1]

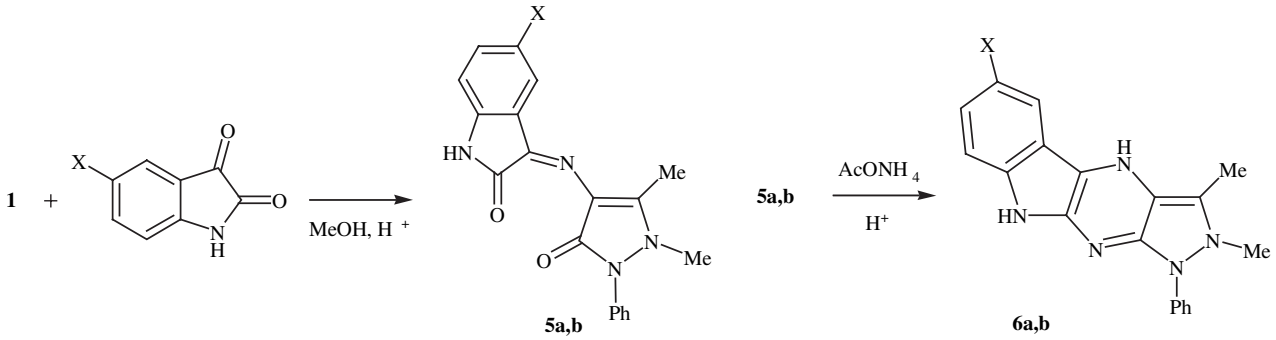
Heterocyclic systems have conveniently been prepared by reactions of isothiocyanates or isocyanates with heterocyclic primary amines.[9] We obtained the thioureas and ureas **2a—e** from the reaction of **1** with phenyl, and 4-fluorophenyl isothiocyanates and with cyclohexyl, 1-naphthyl and 3-chlorophenyl isocyanates. Heterocyclisation of compounds **2b,c,e** via refluxing with malonic acid in the presence of few drops of acetyl chloride and compounds **2d,e** with 1, 3-dichloropropane in boiling DMF furnished *N*,*N*′-disubstituted thiobarbituric acid **3b,c,e** and the *N*,*N*′-disubstituted tetrahydropyrimidine **4d,e** respectively (Scheme 1).

On the other hand, refluxing compound **1** with 5-fluoroisatin or 5-(trifluoromethoxy)isatin in methanol containing a few drops of acetic acid furnished the imines **5a,b**. Refluxing compounds **5a,b** with ammonium acetate in acetic acid produced the heterocycles **6a,b** (Scheme 2).

Pyrazoles are heterocycles showing a broad spectrum of biological activities.[10] 1,2,4-Triazines are used as therapeutic



Scheme 1



Scheme 2

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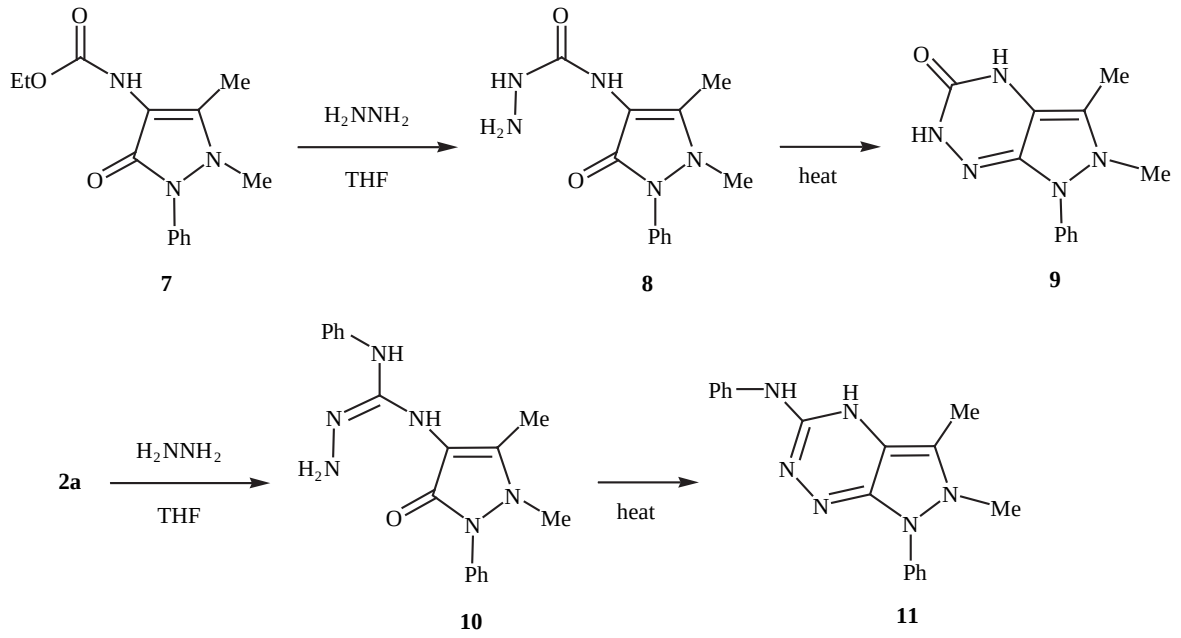

Scheme 3

agents[11] and as plant protecting agents.[12] 1,2,4-Triazine bearing functional groups are used for determination of metals and to form complexes with transition metals. [13,14]

In compounds **9** and **11** we combined a pyrazole and a 1,2,4-triazine ring in order to test biological effects of these compounds. Thus, treatment of compound **7** with hydrazine hydrate in boiling THF gave the semicarbazide **8**. Heating compound **8** above its melting point resulted in cyclisation to the pyrazolo[4,3-*e*][1,2,4]triazine-5-one **9**. Similarly compound **2a** with hydrazine hydrate in boiling abs. ethanol gave the aminoguanidine **10**. Heating this above its melting point furnished the pyrazolo[4,3-*e*][1,2,4]triazine **11** (Scheme 3).

The structures of the synthesised compounds were confirmed by their spectral data. The IR spectra of compounds **2a–e** showed bands for two NH groups at 3295, 3275, and for CO and CS functional groups at 1685 and 1125 cm^{-1} respectively. IR absorptions were observed characteristic for aliphatic, aromatic and heterocyclic functional groups. The structures of compounds **5a,b** were confirmed by the absorption of two carbonyl groups between 1720 and 1710 cm^{-1}, while no carbonyl bands were observed for compounds **6a,b**, which showed NH stretching bands at 3275 cm^{-1}.

The ^{1}H NMR spectra (*see Experimental*) of the compounds all showed two characteristic signals for Me–C and Me–N, and the expected aryl and NH signals. For compounds **3b,c,e** there were no NH signals but the CH_2 proton signals were observed.

Experimental

All experiments were carried out using anhydrous solvents. M.p.s are uncorrected. IR (KBr) spectra were determined on Perkin–Elmer FTIR 1600 spectrometer. ^{1}H and ^{13}C NMR (295 K, internal reference TMS); were determined on Bruker AC–250 spectrometer.

Preparation of N,N'-disubstituted thioureas/ureas (**2a–e**): *general procedure*: The isothiocyanates or the isocyanates respectively (10 mmol) were added to the solution of compound **1** (10 mmol) in THF (20 ml) containing a few drops of TEA. After boiling under reflux for 2 h the mixture was concentrated under reduced pressure. The solid was filtered off and recrystallised from ethanol.

1-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-3-phenyl-thiourea (**2a**):[15-21] Yellow powder (yield 75%); m.p. 180–182 °C. IR (KBr): 3295, 3275 (NH), 1690 (C=O), 1140 cm^{-1} (C=S). ^{1}H NMR (DMSO-d_6): δ=2.13 (s, CH_3), 3.13 (s, N–CH_3), 7.13–7.90 (m, 10 H, phenyl), 9.37 (br, 2 NH). ^{13}C NMR (DMSO-d_6): δ=10.6 (CH_3), 35.5 (N–CH_3), 114.6, 114.8, 123.7, 126.3, 128.8, 129.1, 134.5, 135.6, 157.3, 160.2 (phenyl), 161.6, 181.8 (C=O, C=S). Anal. Calcd for $C_{18}H_{18}N_4OS$ (338.4): C, 63.88; H, 5.36; N, 16.56. Found: C, 63.70; H, 5.31; N, 16.50.

1-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-3-(4-fluorophenyl) thiourea (**2b**): Pale yellow powder (yield 80 %); m.p. 188–190 °C. IR (KBr): 3275 (NH), 1685 (C=O), 1125 (C=S) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ=2.19 (s, CH_3), 3.11 (s, N–CH_3), 7.13–7.70 (m, 9 H, aryl), 9.27 (br, 2 NH). ^{13}C NMR (DMSO-d_6): δ=10.7 (CH_3), 35.5 (N–CH_3), 114.6, 114.8, 123.7, 126.3, 128.9, 129.0, 134.8, 135.9, 157.9, 160.4, (aryl), 161.5 (C=O), 181.6 (C=S). Anal. Calcd for $C_{18}H_{17}FN_4OS$ (356.4): C, 60.66; H, 4.81; N, 15.72. Found: C, 60.49; H, 4.73; N, 15.59.

1-Cyclohexyl-3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)urea (**2c**): Orange powder (yield 78 %); m.p. 243–245 °C. IR (KBr): 1665 (NCON), 1682 cm^{-1} (C=O). ^{1}H NMR (DMSO-d_6): δ=1.12–1.79 (m, 10 H, cyclohexyl), 2.15 (s, CH_3), 2.98 (s, N–CH_3), 3.44 (m, 1 H, HC-NH), 6.20 (d, 1H, N*H*-CH, *J*=7.8 Hz), 7.05 (s, 1 H, NH), 7.27–7.50 (m, 5 H, phenyl). ^{13}C NMR (DMSO-d_6): δ=11.3 (CH_3), 24.3, 25.2, 32.9, 36.3, 47.9 (cyclohexyl and N–CH_3), 109.3, 123.1, 125.8, 128.9, 135.1, 150.8 (phenyl, C=C), 155.3, 162.2 (2C=O). Anal. Calcd for $C_{18}H_{24}N_4O_2$ (328.4): C, 65.83; H, 7.37; N, 17.06. Found: C, 65.80; H, 7.30; N, 17.00.

1-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-3-(1-naphthyl)urea (**2d**): Colourless powder (yield 65 %); m.p. 208–210 °C. IR (KBr): 1660 (NCON), 1690 cm^{-1} (C=O). ^{1}H NMR (DMSO-d_6): δ=2.27 (s, CH_3), 3.05 (s, N–CH_3), 7.31–8.17 (m, 12 H, aryl), 8.94 (s, 2 NH). ^{13}C NMR (DMSO-d_6): δ=11.3 (CH_3), 36.1 (N–CH_3), 108.5, 117.1, 121.3, 122.7, 123.4, 125.5, 125.8, 126.1, 128.3, 129.0, 133.6, 134.6, 134.9, 151.1 (aryl), 153.9, 162.1 (2 C=O). Anal. Calcd for $C_{22}H_{20}N_4O_2$ (372.4): C, 70.95; H, 5.41; N, 15.04. Found: C, 70.98; H, 5.47; N, 15.20.

1-(3-Chlorophenyl)-3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)urea (**2e**): Colourless powder (yield 60 %); m.p. 215–217 °C. IR (KBr): 1665 (NCON), 1695 cm^{-1} (C=O). ^{1}H NMR (DMSO-d_6) δ=2.21 (s, CH_3), 3.05 (s, N–CH_3), 6.98 (d, *J*=4.9 Hz, NH), 7.00–7.69 (m, 9 H, aryl), 9.00 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ=11.1 (CH_3), 36.0 (N–CH_3), 107.8, 116.4, 117.4, 121.2, 123.4, 126.1, 128.9, 130.2, 133.1, 134.9, 141.4, 151.7 (aryl, C=C), 153.4, 162.0 (2 C=O). Anal. Calcd for $C_{18}H_{17}ClN_4O_2$ (356.8): C, 60.59; H, 4.80; N, 15.70. Found: C, 60.50; H, 40.70; N, 15.66.

N,N'-Disubstituted barbituric acids (**3b,c,e**): *General procedure*: A mixture of one of the compounds **2b,c,e** (10 mmol) and malonic acid (10 mmol) with a few drops of acetyl chloride was kept at 100°C (water-bath) for 10 h. The solid, which separated on cooling to 25°C, was isolated by filtration. Recrystallisation from EtOH afforded a colourless powder.

3-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-1-(4-fluorophenyl)-2-thio-1H,5H-pyrimidine-4,6-dione (**3b**): Yield 65 %; m.p. 256–258 °C. IR (KBr): 1180 (C=S), 1665, 1685 cm^{-1} (2 C=O). ^1H NMR (DMSO-d_6): δ=2.13 (s, CH_3), 2.97 (s, N–CH_3), 3.58 (s, CH_2), 6.99–7.62 (m, 9 H, aryl). ^{13}C NMR (DMSO-d_6): δ=13.5, 34.5, 35.3 (CH_3, CH_2, N–CH_3), 104.3, 113.3, 115.7, 118.9, 122.0, 129.2, 133.7, 136.4, 142.2, 157.7 (aryl, C=C), 160.7, 167.3, 168.2 (3 C=O); 177.5 (C=S). Anal. Calcd for $C_{21}H_{17}FN_4O_3S$ (424.4): C, 59.42; H, 4.04; N, 13.20. Found: C, 59.39; H, 4.21; N, 13.35.

1-Cyclohexy1-3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-pheny1-1H-pyrazol-4-yl)-1H,5H-pyrimidine-2,4,6-trione (**3c**): Yield 70%; m.p. 250–252 °C. IR (KBr): 1668, 1680, 1690 cm^{-1} (3 C=O). ^1H NMR (DMSO-d_6): δ=1.44–1.66 (m, 11 H, cyclohexyl), 2.51 (s, CH_3), 2.97 (s, N–CH_3), 3.07 (s, CH_2), 6.67–7.50 (m, 5 H, phenyl). ^{13}C NMR (DMSO-d_6): δ=12.2 (CH_3), 21.6, 27.1, 30.3, 35.3, 36.5, 43.5 (cyclohexyl, N–CH_3, CH_2), 103.9, 112.2, 118.9, 129.8, 133.7, 142.8 (phenyl), 152.8, 160.7, 162.3, 168.6 (4 C=O). Anal. Calcd for $C_{21}H_{24}N_4O_4$ (396.4): C, 63.62; H, 6.10; N, 14.13. Found: C, 63.69; H, 6.18; N, 13.89.

1-(3-Chlorophenyl)-3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-1H,5H-pyrimidine-2,4,6-trione (**3e**): Yield 70 %; m.p. 260–262 °C. IR (KBr): 1660, 1675, 1685 cm^{-1} (3 C=O). ^1H NMR (DMSO-d_6): δ=1.98 (s, CH_3), 2.98 (s, N–CH_3), 3.52 (s, CH_2), 6.98–7.65 (m, 9 H, aryl). ^{13}C NMR (DMSO-d_6): δ=13.9, 35.6, 35.9 (CH_3, N–CH_3, CH_2), 104.6, 113.2, 118.5, 118.9, 120.9, 124.5, 129.0, 130.2, 133.7, 134.3, 142.6, 142.8 (aryl, C=C), 147.3, 160.7, 165.3, 166.8 (4 C=O). Anal. Calcd for $C_{21}H_{17}ClN_4O_4$ (424.8): C, 59.37; H, 4.03; N, 13.19. Found: C, 59.07; H, 3.89; N, 12.98.

1,3-Disubstituted perhydro-pyrimidine-2-ones (**4d,e**): *General procedure*: A mixture of compound **2d** or **2e** (10 mmol) and 1,3-dichloropropane (10 mmol) in DMF (20 ml) was boiled under reflux for 4 h. After cooling to 25 °C, the reaction mixture was poured on ice. The precipitated solid was filtered off. Recrystallisation from DMF/EtOH furnished a pale yellow powder.

1-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-3-(1-naphthyl)-tetrahydro-2(1H)pyrimidinone (**4d**): Yield 55 %; m.p. 235–237 °C. IR (KBr): 1665 (NCON), 1680 cm^{-1} (C=O). ^1H NMR (DMSO-d_6): δ=1.78 (s, CH_3), 1.98 (m, CH_2); 2.97 (s, N–CH_3), 3.16 (t, 2 CH_2), 6.88–7.99 (m, 12 H, aryl). ^{13}C NMR (DMSO-d_6): δ=12.8, 31.2, 35.3, 49.8, 54.7 (CH_3, 3 CH_2, N–CH_3), 103.9, 109.5, 113.0, 118.7, 118.9, 120.7, 123.9, 124.6, 125.6, 126.2, 128.3, 129.5, 133.7, 134.2, 142.5, 142.8 (aryl, C=C), 153.3, 160.7 (2 C=O). Anal. Calcd for $C_{25}H_{24}N_4O_2$ (412.5): C, 72.80; H, 5.86; N, 13.58. Found: C, 72.78; H, 5.81; N, 13.29.

3-(3-Chlorophenyl)-1-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-tetrahydro-2(1H)pyrimidinone (**4e**): Yield 67 %; m.p. 228–230 °C. IR (KBr): 1660 (NCON); 1685 cm^{-1} (C=O). ^1H NMR (DMSO-d_6): δ=1.80 (s, CH_3), 1.98 (m, CH_2), 2.98 (s, N–CH_3), 3.26 (t, 2 CH_2), 6.98–7.86 (m, 9 H, aryl). ^{13}C NMR (DMSO-d_6): δ=12.6 (CH_3), 31.1, 35.3, 49.8, 54.3 (N–CH_3, 3 CH_2), 104.0, 112.8, 118.6, 118.9, 120.8, 124.5, 129.5, 130.1, 133.7, 134.5, 139.6, 142.8 (aryl, C=C), 153.3, 160.7 (2 C=O). Anal. Calcd for $C_{21}H_{21}ClN_4O_2$ (396.9): C, 63.55; H, 5.33; N, 14.12. Found: C, 63.90; H, 5.32; N, 14.23.

3-Iminoindol-2-ones (**5a,b**): *General procedure*: An equimolar mixture of compound **1** and 5-fluoroisatin or 5-trifluoromethoxy-isatin in dry MeOH (20 ml) containing a few drops of AcOH was boiled under reflux for 2 h. After cooling the precipitated solid was filtered off. Recrystallisation from EtOH afforded red powders.

1,3-Dihydro-3-(2,3-dihydro-1,5-Dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-ylimino)-5-fluoro-2H-indol-2-one (**5a**):[22] Yield 56 %; m.p. 233–235 °C. IR (KBr): 1705, 1715 cm^{-1} (2 C=O). ^1H NMR (DMSO-d_6): δ=2.40 (s, CH_3), 3.20 (s, N–CH_3), 6.83–7.56 (m, 8 H, aryl), 8.59 (br, NH). ^{13}C NMR (DMSO-d_6): δ=11.98, 35.19 (CH_3, N–CH_3), 110.5, 114.9, 116.6, 118.0, 118.9, 125.7, 127.6, 129.2, 134.2, 141.1, 150.2, 155.2 (aryl, C=C), 156.5, 158.5, 164.9 (2 C=O, C=N). Anal. Calcd for $C_{19}H_{15}FN_4O_2$ (350.3): C, 65.14; H, 4.32; N, 15.99. Found: C, 65.43; H, 4.05; N, 15.87.

1,3-Dihydro-3-(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-ylimino)-5-trifluoromethoxy-2H-indol-2-one (**5b**): Yield 55 %; m.p. 270–272 °C. IR (KBr): 1710, 1725 cm^{-1} (2 C=O). ^1H NMR (DMSO-d_6): δ=2.43 (s, CH_3), 3.23 (s, N–CH_3), 6.92 (d, *J*=9.0 Hz, 1 H, aryl), 7.32(d, *J*=9.0 Hz 1 H, aryl), 7.37–7.57(m, 6 H, aryl), 8.80 (s, NH). ^{13}C NMR (DMSO-d_6): δ=12.7, 35.3 (CH_3, N–CH_3), 110.8, 118.9, 121.5, 124.5, 125.5, 127.6, 129.2, 134.4, 134.6, 142.8, 143.6, 143.8, (aryl, C=C), 149.8, 155.5 (2 C=O). Anal. Calcd for $C_{20}H_{15}F_3N_4O_3$ (416.4): C, 57.69; H, 3.63; N, 13.46. Found: C, 57.43; H, 3.25; N, 13.57.

{(3,4-Dihydro-4,5-dimethyl-3-phenylpyrazolo)[2a,5a-b]-(4H-pyrazolino)}-8-fluoro-[1a,6a-b]-indole) (**6a**): A mixture of **5a** (10 mmol) and CH_3COONH_4 (15 mmol) in AcOH (10 ml) was boiled under reflux for 4 h. After cooling the mixture was poured on ice. The precipitated solid was isolated by filtration and washed with a 5% aq. solution of $NaHCO_3$ and with H_2O. Crystallisation from EtOH afforded a pale brown powder (yield 65%); m.p. 260–262 °C. IR (KBr): 3275 cm^{-1} (NH). ^1H NMR (DMSO-d_6): δ=2.30 (s, CH_3), 2.97 (s, N–CH_3), 4.25 (br, NH), 6.67–7.51 (m, 8 H, aryl), 10.50 (s, NH). ^{13}C NMR (DMSO-d_6): δ=10.9, 35.6 (CH_3, N–CH_3), 102.5, 107.8, 108.2, 109.2, 112.5, 113.0, 118.9, 124.8, 126.0, 129.6, 129.8, 131.2, 142.4, 155.0, 164.3 (aryl, C=C, C=N). Anal. Calcd for $C_{19}H_{16}FN_5$ (333.4): C, 68.46; H, 4.84; N, 21.01. Found: C, 68.43; H, 4.59; N, 20.98.

{(3,4-Dihydro-4,5-dimethyl-3-phenylpyrazolo)[2a,5a-b]-(4H-pyrazolino)}-8-trifluoromethoxy-[1a,6a-b]-indole) (**6b**): Yield 70% brown powder; m.p. 268–270 °C. ^1H NMR (DMSO-d_6): δ=2.29 (s, CH_3), 2.94 (s, N–CH_3), 4.50 (br, NH), 6.76–6.86 (m, 8 H, aryl), 10.50 (s, NH). ^{13}C NMR (DMSO-d_6): δ=11.0, 35.8 (CH_3, N–CH_3), 102.4, 105.2, 106.0, 109.5, 112.2, 112.5, 118.9, 122.3, 124.0, 126.0, 128.2, 129.5, 129.9, 142.2, 155.0, 164.5 (aryl, C=C, C=N, OCF_3){aryl, C=C, C=N and OCF_3 (decoupling)}. Anal. Calcd for $C_{20}H_{16}F_3N_5O$ (399.4): C, 60.15; H, 4.04; N, 17.54. Found: C, 60.20; H, 4.08; N, 17.28.

N-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)hydrazine carboxamide (**8**): A mixture of **7** (10 mmol) and hydrazine hydrate (99%; 15 mmol) in THF (20 ml) was boiled under reflux for 2 h. After cooling and concentration under reduced pressure the precipitated solid was filtered off. Recrystallisation from EtOH furnished colourless crystals (yield 60%); m.p. 165–167 °C. IR (KBr): 3310, 1690, 1665 cm^{-1} (NH, 2 C=O). ^1H NMR (DMSO-d_6): δ=1.90 (s, CH_3), 2.20 (br, NH_2), 2.96 (s, N–CH_3), 6.40 (s, 2 NH), 6.80–7.58 (m, 5 H, phenyl). ^{13}C NMR (DMSO-d_6): δ=13.9, 35.5 (CH_3, N–CH_3), 104.5, 113.1, 118.9, 129.0, 133.7, 142.8, (phenyl, C=C), 154.8, 160.7 (2 C=O). Anal. Calcd for $C_{12}H_{15}N_5O_2$ (261.3): C, 55.16; H, 5.79; N, 26.80. Found: C, 55.08; H, 6.00; N, 26.98.

2,3-Dimethyl-1-phenyl-1,2,4,6-tetrahydro-5H-pyrazolo[4,3-e][1,2,4] triazin-5-one (**9**):[23] Compound **8** (1.0 g) was heated above its melting point for 30 min. The product was treated with MeOH and recrystallised from EtOH to give a pale brown powder (yield 65 %); m.p. 198–200 °C. IR (KBr): 3280, 1670 cm^{-1} (NH, C=O). ^1H NMR (DMSO-d_6): δ=2.13 (s, CH_3), 3.02 (s, N–CH_3), 7.14–7.68 (m, 5 H, phenyl), 8.15 (br, 2 NH). ^{13}C NMR (DMSO-d_6): δ=10.4, 35.5 (CH_3, N–CH_3), 107.9, 123.3, 126.1, 128.9, 135.2, 152.7 (phenyl, C=C), 155.5, 162.2 (C=O and C=N). Anal. Calcd for $C_{12}H_{13}N_5O$ (243.3): C, 59.25; H, 5.39; N, 28.79. Found: C, 59.08; H, 5.10; N, 28.98.

N'-(2,3-Dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)-N-phenyl-hydrazinecarboximidamide (**10**): A mixture of **2a** (10 mmol) and hydrazine hydrate (99%) (20 mmol) in Me_2CHOH (20 ml) was refluxed for 2 h. After cooling to 25 °C the mixture was neutralised with a few drops of acetic acid. The solid obtained was filtered off and recrystallised from EtOH to give a colourless powder (yield 76 %); m.p. 160–162 °C. IR (KBr): 3350–3150 (br, NH); 1690 cm^{-1} (C=O). ^1H NMR (DMSO-d_6): δ=2.10 (s, CH_3); 2.50 (br, 3 H, NH, NH_2) 3.03 (s, N–CH_3); 4.50 (s, 1 H, NH); 6.66–7.65 (m, 10 H, phenyl). ^{13}C NMR (DMSO-d_6): δ=11.5 (CH_3), 35.5 (N–CH_3), 110.1, 112.0, 116.2, 118.5, 119.5, 129.0, 129.5, 143.5, 146.7, 150.2 (phenyl), 160.7, 163.5 (C=O and C=N). Anal. Anal. Calcd for $C_{18}H_{20}N_6O$ (336.4): C, 64.27; H, 5.99; N, 24.98. Found: C, 64.29; H, 5.68; N, 24.90.

5-Anilino-2,4-dihydro-2,3-dimethyl-1-phenyl-1H-pyrazol[4,3-e][1,2,4] triazine (**11**): Compound 10 (1.0 g) was heated above its melting point for 30 min. After cooling the solid was treated with MeOH and recrystallised from EtOH/DMF to give a pale brown powder (yield 60 %); m.p. 184–186 °C. IR (KBr): 3280 cm^{-1} (NH). ^1H NMR (DMSO-d_6): δ=2.10 (s, CH_3), 2.98 (s, N–CH_3), 4.20 (s, NH), 6.66–7.70 (m, 10 H, phenyl), 8.20 (br, NH). ^{13}C NMR (DMSO-d_6): δ=11.2, 35.6 (CH_3, N–CH_3), 109.0, 112.0, 115.5, 118.5, 118.9, 129.0, 129.3, 134.2, 145.2, 146.7 (phenyl, C=C), 156.0, 163.0 (2 C=N). Anal. Calcd for $C_{18}H_{18}N_6$ (318.4): C, 67.90; H, 5.70; N, 26.40. Found: C, 67.80; H, 5.60; N, 26.73.

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