SYNTHESIS OF NOVEL PYRAZOLE, PYRIDAZINE AND PYRIMIDINE DERIVATIVES CONTAINING SULFONAMIDO MOIETY

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Abstract

Reaction of the hydrazone 2 with hydrazine hydrate, phenylhydrazine, benzoilhydrazine and/or semicarbazide in dioxane afforded the 3,5-diaminopyrazole derivatives 3-6, respectively. Refluxing 3 with acetic anhydride and/or benzoil chloride, furnished the N-acyl derivatives 7 and 8. On the other hand, fusion of 3 with different aromatic aldehydes produced the Schiff bases 9a-c, respectively. Treatment of 2 with urea, thiourea and/or guanidine hydrochloride furnished the pyrimidine and 1,3-thiazine derivatives 10-12, respectively. Reaction of 2 with ethyl cyanoacetate, ethyl acetoacetate, malononitrile and/or piperidine yielded the pyridazine derivatives 14 and 15, pyridopyridazine 17 and the enaminonitrile 18. Treatment of 18 with CS₂ and/or phenylisothiocyanate produced 1,3-thiazine 20, dithioxopyrimidine 21 and the thiopyrimidine derivatives 22, respectively.

Key words:
Sulfonamide, hydrazones, aminopyrazoles, pyrimidines and pyridazines.

Introduction

It is well known that sulfonamides have a variety of biological activities such as antibacterial¹, carbonic anhydrase inhibitory², and antitumor activities³. Also, pyrazoles, pyrimidines and pyridazines possess biological and pharmacological activities⁴-¹¹. Because of these interesting activities and in continuation of our work¹²-¹⁶ on the synthesis of novel heterocyclic systems exhibiting biological activity, we undertook the synthesis of a new series of compounds incorporating the above mentioned biologically active moieties in one molecule.

Results and Discussion

The hydrazone 2 was synthesized by diazotization of sulfamethazine, [N₁-(4,6-dimethyl-2-pyrimidinyl)sulfanilamide], 1 followed by coupling with malononitrile in the presence of sodium acetate at room temperature (Scheme 1). The spectral data revealed that this compound exists in the hydrazone form (b), where, their spectrum displayed a strong band at 2227 cm⁻¹ corresponding to C=N groups. ¹H-NMR spectrum showed two signals at 6.73 and 8.74 (exchangeable) corresponding to two
NH groups and the MS indicated the molecular ion peak at 355, which is in accordance with the molecular formula.

It was reported that β-enaminonitriles reacted with hydrazines producing pyrazole derivatives\(^{17}\). Thus, refluxing 2 with hydrazine hydrate in ethanol, phenylhydrazine, benzylhydrazine and semicarbazide in dioxane afforded the 3,5-diaminopyrazole derivatives 3-6 respectively (Scheme 2).
The structure of compounds 3-6 were elucidated from their elemental analysis and spectral data. (cf experimental part). The $^1$H-NMR spectra of 3 showed two broad peaks (exchangeable) at 6.05 and 6.53 corresponding to two NH$_2$ groups. The presence of a multiplet peak at $\delta$ 8.30-8.80 (10 protons) indicated the presence of phenyl group in compound 4.

Reaction of 3 with acetic anhydride and/or benzoyl chloride under reflux, furnished the N-acyl derivatives 7 and 8. The structures of 7 and 8 were established on the basis of their spectral data, where their spectra showed bands at 1679 and 1672 cm$^{-1}$ corresponding to the carbonyl groups, furthermore, $^1$H-NMR spectrum of 7 showed a band at 2.43 corresponding to COCH$_3$, while that of 8 exhibited a multiplet at 7.48-7.61 for the phenyl group (Scheme 3).

On the other hand, fusion of 3 with different aromatic aldehydes, in the presence of fused sodium acetate, produced the Schiff bases 9a-c respectively. (Scheme 3).

![Scheme 3](image)

Treatment of 2 with urea, thiourea, and guanidine hydrochloride, in ethanol-ethoxide, produces the 4,6-diaminopyrimidin-2-one 10, 2-imino-4,6-diaminothiazine 11 and triaminopyrimidine derivatives 12$^{18}$, respectively (Scheme 4). The formation of these products is assumed to proceed through the cycloaddition of NH$_2$ or SH groups to the cyano functions of 2. The spectral data of 10, 11 and 12 confirmed the proposed structures, where, the is spectra showed bands at 3444, 3382, 3229 and 1660 cm$^{-1}$, corresponding to NH$_2$, NH and CO groups and the MS of 10 exhibited molecular ion peak at 415 which is in agreement with the molecular formula.
The reactivity of 2 towards some active methylene reagents was studied. Thus, compound 2 reacted with ethyl cyanoacetate and/or ethyl acetoacetate in refluxing ethanol containing triethylamine to yield the pyridazine derivatives 14 and 15 via the intermediate 13. The structures of 14 and 15 were approved by their IR and 1H NMR spectra, where, the 1H NMR of 15 indicated the presence of a peak at δ 2.3 corresponding to COCH₃ protons. On the other hand, the reaction of 2 with two moles of malononitrile in refluxing ethanol/Et₃N solution afforded the pyridopyridazine derivative 17 through the intermediate 16 (Scheme 4). The structure was elucidated through elemental analysis and MS.
Refluxing 2 with piperidine in ethanol produced the acyclic enaminonitrile 18. The $^1$HNMR spectrum displayed the characteristic peaks of the piperidine ring at 1.62 (m, 6H) and 3.49 (m, 4H). Furthermore, compound 18 underwent acidic hydrolysis to produce the corresponding enaminocarboxylic acid derivative 19. Also, the behaviour of 18 towards carbon disulfide at different conditions was studied. Thus, reaction of 18 with carbon disulfide in pyridine at room temperature yielded 1,3-thiazine 20, while, upon reflux dithioxopyrimidine 21 were formed. Finally, the pyrimidine derivative 22 was obtained when 18 was fused with phenylisothiocyanate, in an oil bath, at 140°C (Scheme 6). The structures of 19-22 were elucidated from their elemental analysis, MS and $^1$HNMR spectra.

Scheme 6

Experimental:

Melting points are uncorrected. The infrared absorption spectra were determined with a Pye Unicam SP 2000 infrared spectrophotometer with KBr Wafer Technique. The mass spectra were run on Shimadzu GC-NS-QP 1000 EX instrument operating at 70 ev. The $^1$H-NMR spectra were determined on a Varian Gemini 200 $^1$NMR
spectrophotometer using DMSO-d₆ as solvent, (chemical shift in δ, ppm) and TMS as internal standard. Elemental analyses were carried out by the Microanalytical Research Center, Faculty of Science, Cairo University, Egypt [satisfactory analytical data (± 0.3) were obtained for all compounds].

**3,5-Diamino-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazomalononitrile (2).**

Sulfonamide 1 (10 mmol, 2.78 g) were dissolved in a mixture of concentrated HCl (5 mL) and water (5 mL) and cooled to 5-10°C in an ice bath. A cold aqueous solution of sodium nitrite (10 mmol, 5 mL) was then added with stirring. The diazonium salt so obtained was filtered into a cold mixture of sodium acetate (4 g) and malononitrile (10 mmol, 0.66 g) in ethanol (25 mL) with stirring for one h. The resulting solid was washed with water (150 mL) and recrystallized from ethanol to afford 2 (Table 1). IR: 3243, 3192 (NH), 3001 (CHar), 2889 (C–H al), 2227 (C=N), 1623 (C=N), 1600 (C=C), 1543 (N=N), 1327, 1150 cm⁻¹ (SO₂). ¹H-NMR (DMSO-d₆): 2.25 (s, 6H, 2 CH₃), 6.73 (s, 1H, NH exchangeable), 7.57-8.05 (m, 5H, ar–H + 1H pyrimidine ring), 8.74 (s, 1H, NH, exchangeable). MS (%): molecular ion peak at 355 (3.5) and M+ 1 at 356 (3.7).

**3,5-Diamino-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (3).**

To a solution of 2 (4 mmol, 1.42 g) in ethanol (50 mL), hydrazine hydrate (5 mmol, 0.25 mL) was added and the reaction mixture was refluxed for 2 h. The solid product which formed on heating was collected and recrystallized from the proper solvent to give 3 (Table 1). IR: 3474, 3370, 3203 (NH₂, NH), 1621 (C=N), 1561 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.27 (s, 6H, 2 CH₃), 6.73 (s, 1H, NH exchangeable), 7.57-8.05 (m, 5H, ar–H + 1H pyrimidine ring), 8.74 (s, 1H, NH, exchangeable). MS (%): 389 (3.1) M+2, 388 (2.5) M+1, 387 (1.8) M⁺.

**3,5-Diamino-1-phenyl-4[f4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (4).**

A mixture of 2 (4 mmol, 1.42 g) in dioxane (30 mL) and phenylhydrazine (4 mmol, 0.43 mL) was refluxed for 3 h., concentrated and left to cool at room temperature. The solid deposited was filtered off, dried and crystallized from proper solvent to produce 4 (Table 2). IR: 3395, 3276, 3205, 3163 (NH₂, NH), 1622 (C=N), 1558 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 3.06 (s, 6H, 2 CH₃), 4.11 and 4.36 (s., 2 NH₂, exchangeable), 6.87 (s, 1H, NH exchangeable), 7.76-8.06 (m, 5H, ar–H + 1H pyrimidine ring). MS (%): 389 (3.1) M+2, 388 (2.5) M+1, 387 (1.8) M⁺.
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3,5-Diamino-1-benzoyl-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (5).

To 40 mL of dioxane containing the hydrazone 2 (4 mmol, 1.42 g), benzyldihydrazone (4 mmol, 0.54 g) was added and the mixture was refluxed for 6 h., concentrated and left to cool at room temperature. The solid product so formed was filtered off, dried and crystallized from proper solvent to yield 5 (Table 1). IR: 3443, 3324, 3210, (NH₂, NH), 1687 (C=O), 1604 (C=N), 1541 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.28 (s, 6H, 2 CH₃), 6.78 and 7.07 (s, 4H, 2 NH₂, exchangeable), 7.58-8.19 (m, 10H, ar-H + IH pyrimidine ring), 10.52 (br, IH, NH exchangeable).

3,5-Diamino-1-benzoyl-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (6).

A solution of hydrazone 2 (4 mmol, 1.42 g), semicarbazide.HCl (4 mmol, 0.45 g and triethylamine (0.5 mL) in dioxane (40 mL) was heated under reflux for 12 h. The solid product which precipitated on heating was collected and crystallized from proper solvent to give 6 (Table 2). IR: 3404, 3302, 3207, (NH₂, NH), 1680 (C=O), 1608 cm⁻¹ (C=N).

3-amino-5-acetylaminoo-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (7) and 3-amino-5-benzoylamino-4-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrazole (8).

A mixture of pyrazole 3 (5 mmol, 1.93 g) and acetic anhydride and/or benzoyle chloride (15mL) was refluxed for 1 h. The solid product which precipitated after cooling was filtered off, washed with water (100 mL), dried and recrystallized from proper solvent to produce 7 and 8.

(Table 1). Compound 7, IR: 3379, 3269, 3208, 3177 (NH₂, NH), 1679 (C=O), 1620 (C=N), 1603 (C=C), 1563 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.26 (s, 6H, 2 CH₃), 2.43 (s, 3H, COCH₃), 3.57 (s, 2H, NH₂, exchangeable), 6.34, 6.77 (s, 2H, 2 NH exchangeable), 7.74-8.04 (m, 5H, ar-H + IH pyrimidine ring), 8.35 (br, 1H, NH exchangeable).

Compound 8, IR: 3437, 3289, 3212, 3172 (NH₂, NH), 1672 (C=O), 1627 (C=N), 1595 (C=C), 1562 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.25 (s, 6H, 2 CH₃), 3.57 (s, 2H, NH₂, exchangeable), 6.37, 6.77 (s, 2H, 2 NH exchangeable), 7.48-8.14 (m, 10H, ar-H + IH pyrimidine ring), 8.58 (br., 1H, NH exchangeable).
3-Amino-5-[4-substitutedbenzal] amino-4-[4-N-(4,6-dimethylpyrimidin-2-yl) sulfamoyl Jheny1azopyrazole (9a-c)

Fused sodium acetate (2 g) was added to a mixture of 3 (5 mmol, 1.93 g) and different aromatic aldehydes (4 mmol) namely, 4-chlorobenzaldehyde, 4-N,N-dimethylaminobenzaldehyde and/or 4-methoxybenzaldehyde. The reaction mixture was grinded and heated in a sand bath at 200-210°C for 3h. The solid product so obtained was washed with water, triturated with dioxane, filtered off, dried and crystallized from the proper solvent to furnish 9a-c, respectively (Table 1). IR (9a): 3423, 3374, 3214 (NH₂, NH), 1622 (C=N), 1590 (C=C), 1540 cm⁻¹ (N=N). §H-NMR (9a) (DMSO-d₆): 2.11 (s, 6H, 2 CH₃), 6.28 (s, 2H, NH₂ exchangeable), 7.33 (br, IH, NH exchangeable), 7.61 8.04 (m, 10H, ar-H + IH pyrimidine + N=CH), 9.26 (s., IH, NH exchangeable).

4,6-Diamino-5-[4-N-(4,6-dimethylpyrimidin-2-yl) sulfamoyl]phenylazopyrimidin-2(1H)-one(10), 4,6-Diamino-2-imino-5-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazo-1,3-thiazine (11) and 2,4,6-Triamino-5-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyrimidine (12).

To a mixture of 2 (4 mmol, 1.42 g) and the proper amino compound (6 mmol) (urea 0.36 g, thiourea 0.46 g, or guanidine 0.58 g) in absolute ethanol (40 mL), sodium ethoxide (0.23 g of Na in 10 mL ethanol) was added. The reaction mixture was refluxed for 6-8 h, concentrated and cooled. The separated solid was filtered off, washed with water and crystallized from the proper solvent to afford compounds 10-12 (Table 1).

Compound (10), IR: 3437, 3372, 3224, 3154 (NH₂, NH), 1670 (CO), 1628 (C=N), 1598 (C=C), 1548 (N=N). §H-NMR (DMSO-d₆): 2.27 (s, 6H, 2 CH₃), 6.77 (s, 2H, NH₂ exchangeable), 7.40 (br, 2H, NH₂ exchangeable), 7.56-8.19 (m, 4H, ar-H + 1H pyrimidine), 8.40, 8.84 (br, 2H, 2NH exchangeable).

Compound (11), IR: 3444, 3382, 3228 (NH₂, NH), 1631 (C=N), 1603 (C=C), 1543 (N=N). §HNMR (DMSO-d₆): 2.27 (s, 6H, 2 CH₃), 6.78 (s, 2H, NH₂ exchangeable), 7.72 (br, 2H, NH₂ exchangeable), 7.92-8.15 (m, 4H, ar-H + 1H pyrimidine), 8.70, 11.95 (br, 2H, 2NH exchangeable). Compound (12), IR: 3433, 3354, 3189 (NH₂, NH), 1621 (C=N), 1599 (C=C), 1553 cm⁻¹ (N=N). §HNMR (DMSO-d₆): 2.29 (s, 6H, 2 CH₃), 6.61, 6.79 and 7.47 (br, 6H, 3NH₂ exchangeable), 7.63-8.24 (m, 4H, ar-H + 1H pyrimidine), 8.83 (br., H, NH exchangeable).
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4-Amino-3,5-dicyano-1-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyridazin-6-one (14), 5-Acetyl-4-amino-3-cyano-1-[4-N-(4,6dimethylpyrimidin-2-yl)sulfamoyl]phenylazopyridazin-6-one (15) and 6,8-diamino-4,7-dicyano-3-imino-2-[4-N-(4,6-dimethylpyrimidin-2-yl)-sulfamoyl]phenylazopyrido[3,2-c]pyridazine (17).

A solution of 2 (4 mmol, 1.42 g) and the proper active methylene compound (ethyl cyanoacetate 4 mmol, 0.4 mL, ethyl acetoacetate 4 mmol, 0.5 mL and/or malononitrile 8 mmol, 0.53 g) in ethanol (50 mL) containing a catalytic amount of Et3N (5 drops) was heated under reflux for 7-10 h. The solid product so obtained on cooling was collected by filtration and crystallized from the appropriate solvent to give compounds 14, 15 and 17, respectively (Table 1).

Compound (14), IR: 3433, 3371, 3232, 3196 (NH2, NH), 2224 (C=N), 1671 (CO), 1621 (C=N), 1602 (C=C), 1549 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.26 (s, 6H, 2 CH₃), 6.76 (s, 2H, NH₂ exchangeable), 7.58-8.19 (m, 4H, ar-H + IH pyrimidine), 8.67 (br, H, NH exchangeable).

Compound (15), IR: 3448, 3381, 3275, 3106 (NH₂, NH), 2230 (C=N), 1677, 1661 (2CO), 1628 (C=N), 1595 (C=C), 1547 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.27 (s, 6H, 2 CH₃), 2.64 (s, 3H, COCH₃), 6.68 (s, 2H, NH₂ exchangeable), 7.51-8.20 (m, 4H, ar-H + IH pyrimidine), 9.31 (br, H, NH exchangeable).

Compound (17), IR: 3458, 3377, 3231, 3195 (NH₂, NH), 2225 (C=N), 1627 (C=N), 1595 (C=C), 1546 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 2.27 (s, 6H, 2 CH₃), 6.68, 6.76 (s, 4H, 2NH₂ exchangeable), 7.59-8.22 (m, 4H, ar-H + IH pyrimidine), 10.34, 11.53 (br, 2H, 2NH exchangeable).

3-Amino-2-[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazo-3-(piperidin-1-yl) acrylonitrile (18).

Equimolar amounts of 2 (10 mmol, 3.55 g) and piperidine (10 mmol, 1 mL), in absolute ethanol (70 mL), were refluxed for 1 h. The solid product so formed while hot was filtered off and crystallized to give 18 (Table 1). IR: 3400, 3317, 3227, 3202 (NH₂, NH), 2188 (C=N), 1629 (C=N), 1600 (C=C), 1568 cm⁻¹ (N=N). ¹H-NMR (DMSO-d₆): 1.65 (s, 6H, 3 CH₂), 2.27 (s, 6H, 2 CH₃), 3.27 (s, 4H, -CH₂-N-CH₂-), 3.60 (br, 2H, NH₂ exchangeable), 6.74 (s, IH, NH exchangeable), 7.537.92 (m, 4H, ar-H + IH pyrimidine). MS (%): 440 [M+] (0.9), 441 [M+ 1] (2.9), 442 [M+2] (2.7).
A mixture of 18 (5 mmol, 2.2 g) and hydrochloric acid (2 M, 50 ml) was refluxed for 6 h., concentrated and left to cool. The solid deposited was collected by filtration, dried and crystallized to afford 19 (Table 1). IR: broad 3459-2723 (OH, NH$_2$), 1650 (CO acid), 1620 (C=N), 1594 (C=C), 1545 cm$^{-1}$ (N=N). 1H-NMR (DMSO-d$_6$): 1.69 (s, 6H, 3 CH$_2$), 2.23 (s, 6H, 2 CH$_3$), 3.24 (s, 4H, -CH$_2$-N-CH$_2$-), 3.73 (br, 2H, NH$_2$ exchangeable), 7.40-7.88 (m, 4H, ar-H + IH pyrimidine), 9.63 (s, IH, NH exchangeable), 13.42 (s, IH, COOH).

A mixture of 18 (5 mmol, 2.2 g), carbon disulfide (4 mL) and dry pyridine (10 mL) was stirred at room temperature for 24h. The reaction mixture was poured onto ice/water and neutralized by dilute HCl. The solid product was filtered off, washed with water (3x50), dried and crystallized to yield 20 (Table 1). IR: 3320, 3229, 3205 (NH), 1629 (C=N), 1599 (C=C), 1569 cm$^{-1}$ (N=N). 1H-NMR (DMSO-d$_6$): 1.67 (s, 6H, 3 CH$_2$), 2.27 (s, 6H, 2 CH$_3$), 3.60 (s, 4H, -CH$_2$-N-CH$_2$-), 6.74 (s, IH, NH exchangeable), 7.55-7.94 (m, 4H, ar-H + IH pyrimidine), 8.84, 9.63 (br, 2H, 2NH exchangeable). MS (%): 290 [M-226] (44).

A mixture of 18 (5 mmol, 2.2 g), carbon disulfide (4 mL) and dry pyridine (15 mL) was refluxed for 3h. The reaction mixture was poured onto ice/water and neutralized by dilute HCl. The solid product was filtered off, washed with water (3x50), dried and crystallized to produce 21 (Table 1). IR: 3319, 3227, 3203 (NH), 1626 (C=N), 1598 (C=C), 1567 cm$^{-1}$ (N=N). MS (%): 290 [M-226] (44).

Phenyl isothiocyanate (5 mmol, 0.6 mL) was added to a stirred mixture of 18 (5 mmol, 2.20 g) and powdered sodium hydroxide (0.8 g) in dioxane (40 mL). After stirring for 4h., the reaction mixture was refluxed for another 4 h., then poured onto dilute acetic acid (15%, 40 mL). The precipitated solid was filtered and crystallized to afford 22 (Table 1). IR: 3322, 3223, 3209 (NH), 1626 (C=N), 1593 (C=C), 1559
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1H-NMR (DMSO-d_6): 1.64 (s, 6H, 3 CH_2), 2.25 (s, 6H, 2 CH_3), 3.62 (s, 4H, -CH_2-N-CH_2-), 6.78 (s, 1H, NH exchangeable), 7.55-8.17 (m, 9H, ar-H + 1H pyrimidine), 8.89, 9.54 (br, 2H, 2NH exchangeable).

Table 1: Physical and analytical data of compounds 2-22

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* E = Ethanol  
** M/T = Methanol-Toluene mixture  
*** D = Dioxane  
**** D/E = Dioxane-Ethanol mixture
References: