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Facile route for the synthesis and characterization of new naphtho[2,3-*f*]quinoxaline-dione, trione and anthra-dione derivatives

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In the present study, addition of nitroso group at position 1 of 2-aminoanthraquinone (1) to yield 2-amino-1-nitroanthraquinone (2) was carried out by the reaction of compound (1) with sodium nitrite in water. Compound (2) was used as starting material to produce many new naphtho[2,3-*f*] quinoxaline-dione, trione, naphtho-pyrazole quinoxaline-dione, anthra-triazine-dione, naphtho-thiazole quinoxaline-dione and anthrabenzo-triazepine-dione derivatives by elimination of one molecule of water as an initial reaction step. The reacting moieties were nitroso and amino function groups to yield a series of compounds. The structures of the products were determined by elemental mass, IR and ^{1}H NMR analysis and the adopted method is efficient to prepare a series of compounds and could possibly be used for the synthesis of new compounds.

Capsule Summary: Addition of nitroso group at position 1 of 2-aminoanthraquinone (1) to yield 2-amino-1-nitroanthraquinone (2) was carried out by the reaction of compound (1) with sodium nitrite in water and adopted method yield was efficient.

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INTRODUCTION

Natural and synthetic anthraquinones have attracted the interest of researches due to their significant biological activities such as antitumour (Chang, 2004; Ge et al., 1997, Hug et al. 2004), anti- inflammatory (Yadav et al., 2010), antimalarial (Sitti et al., 1999, Yadav et al., 2010; Osman et al., 2010), antimicrobial (Xiang et al., 2008, Yadav et al., 2010), antifungal (Rath et al., 1995) antileukemic (Chang and Lee, 1984, Ismail et al., 1997), antiviral and anti-HIV properties (Schinazi et al., 1990, Anderson et al., 1991, Barnad et al., 1992, Alves et al., 2004). Anthraquinone and its derivatives are also used as antioxidants (Yen et L., 2000), dyes (Sokolyuk et al., 1993; Bechtold et al., 1999; Guo et al., 2007; Ahn et al., 2009) or in photoimaging (Ahn et al., 2009) along with various other applications (Atun et al., 2019; Penthala et al., 2019; Ramotowska et al., 2019; Shahid et al., 2019; Sharma et al., 2012; Tikhomirov et al., 2019; Zhang et al., 2019).

Anthraquinone and its derivatives bearing hydroxyl and amino moieties are of remarkable importance in dye industries (Abou-Darwish et al., 2008; Yamping et al., 2009). They have been described as important compounds for decades (Agosti et al., 1962, Bick et al., 1966, Kirk et al., 2005, Mishra, et al., 2007) and are used for the coloration of cotton and cellulose fibers as well as for synthetic materials such as polyamides (Manson et al., 1976). Besides, azo dyes,

they represent the second largest class of textile pigments (Aspland et al., 1997) and unlike these dyes, anthraquinone derivatives are resistant against degradation due to their aromatic structure (Banat et al., 1996). As the synthesis of these dyes is more complicated, their production costs are higher in comparison to azo dyes (Cui et al., 2020; Maliyappa et al., 2020; Putro et al., 2019; Tasli et al., 2020). Therefore, anthraquinone dyes are only used if the required properties and colors are remarkable or when the desired colors cannot be obtained easily by the use of azo dyes. In the present study, addition of nitroso group at position 1 of 2-aminoanthraquinone (1) to yield 2-amino-1-nitroanthraquinone (2) was carried out by the reaction of compound (1) with sodium nitrite in water. Compound (2) was used as starting material to produce many new naphtho[2,3-*f*] quinoxaline-dione, trione, naphtho-pyrazole quinoxaline-dione, anthra-triazine-dione, naphtho-thiazole quinoxaline-dione and anthrabenzo-triazepine-dione derivatives.

MATERIAL AND METHODS

Synthesis of 2–amino-1-nitroanthraquinone (2)

Compound 1 (1.78 g, 8 mmol) was dissolved in 50 ml dimethylformamide, 5 ml from sodium nitrite solution (0.087 g in 5 ml water) was added dropwise during stirring on ice bath for 1/2 hour, the crude product was filtered off and washed by cold water, crystallized from DMF/H_2O.

Synthesis of 4*H*-2-acetylnaphtho[2,3-*f*]quinoxaline-3,7,12-trione (4)

A mixture of 2 (2 g, 8 mmol) and ethylacetoacetate (1 ml, 8 mmol) in 30 ml dimethylformamide containing 0.1 ml of piperidine was refluxed for 5-7 hours, the reaction mixture was concentrated under reduced pressure and the residue was treated with methanol, then poured onto ice/water and the precipitate forming was collected by filtration, washed well with cold water, crystallized from DMF/H_2O.

Synthesis of 4*H*-2-ethoxycarbonyl-naphtho[2,3-*f*]quinoxalin3,7,12-trione (7)

A mixture of 2 (1 g, 4 mmol), diethylmalonate (0.6 ml, 4 mmol) in 30 ml dimethylformamide containing 0.1 ml of piperidine was refluxed for 6 hours, the solvent was removed by evaporation, the residue was treated with a few amount of hot dimethylformamide and poured onto ice/water, filtered and washed with cold water.

Synthesis of 4*H*-2-cyano-3-oxo-naphtho[2,3-*f*]quinoxaline-3,7,12- trione (9)

A solution of 2 (2 g, 8 mmol), ethylcyanoacetate (0.9 ml, 8 mmol) in 30 ml of dimethylformamide containing 0.1 ml of piperidine was refluxed for 6 hours. The reaction solution was concentrated and the solid formed was treated with methanol, then filtered off and recrystallized DMF/H_2O.

Synthesis of 1*H*-2-amino-naphtho[2,3-*f*]-pyrazolo[3,4-*b*]quinoxaline-8,13-dione (13)

A solution of 2 (2 g, 8 mmol) in 30 ml dimethylformamide, cyanoacetohydrazide (0.79 g, 8 mmol) and 0.1 ml piperidine was refluxed for 6 hours. The reaction solution was concentrated and the solid product treated with methanol, filtered off and recrystallized from DMF/H_2O.

Synthesis of 3-amino-2-cyano-naphtho[2,3-*f*]quinoxaline-7,12- dione (16)

A mixture of 2 (2 g, 8 mmol) and cyanoacetamide (0.69 g, 8 mmol) in 30 ml dimethylformamide containing 0.1 ml of piperidine was refluxed for 5 hours, the reaction mixture was concentrated under reduced pressure, the residue that separated out was treated with methanol collected by filtration and recrystallized from DMF/H_2O.

Synthesis of 3-amino- anthra[1,2-*c*]1,2,4-triazine-7,12-dione (19)

A mixture of 2 (2 g, 8 mmol) and urea/ (0.48 g, 8 mmol), in 30 ml dimethylformamide containing 0.1 ml of piperidine was refluxed for 6 hours. The reaction mixture was concentrated under reduced pressure and the residue was treated with methanol, the product that separated out was filtered off and crystallized from DMF/H_2O. Analogously, compound 2 (2 g, 8 mmol) was reacted with thiourea (0.6 g, 8 mmol) to give 25.

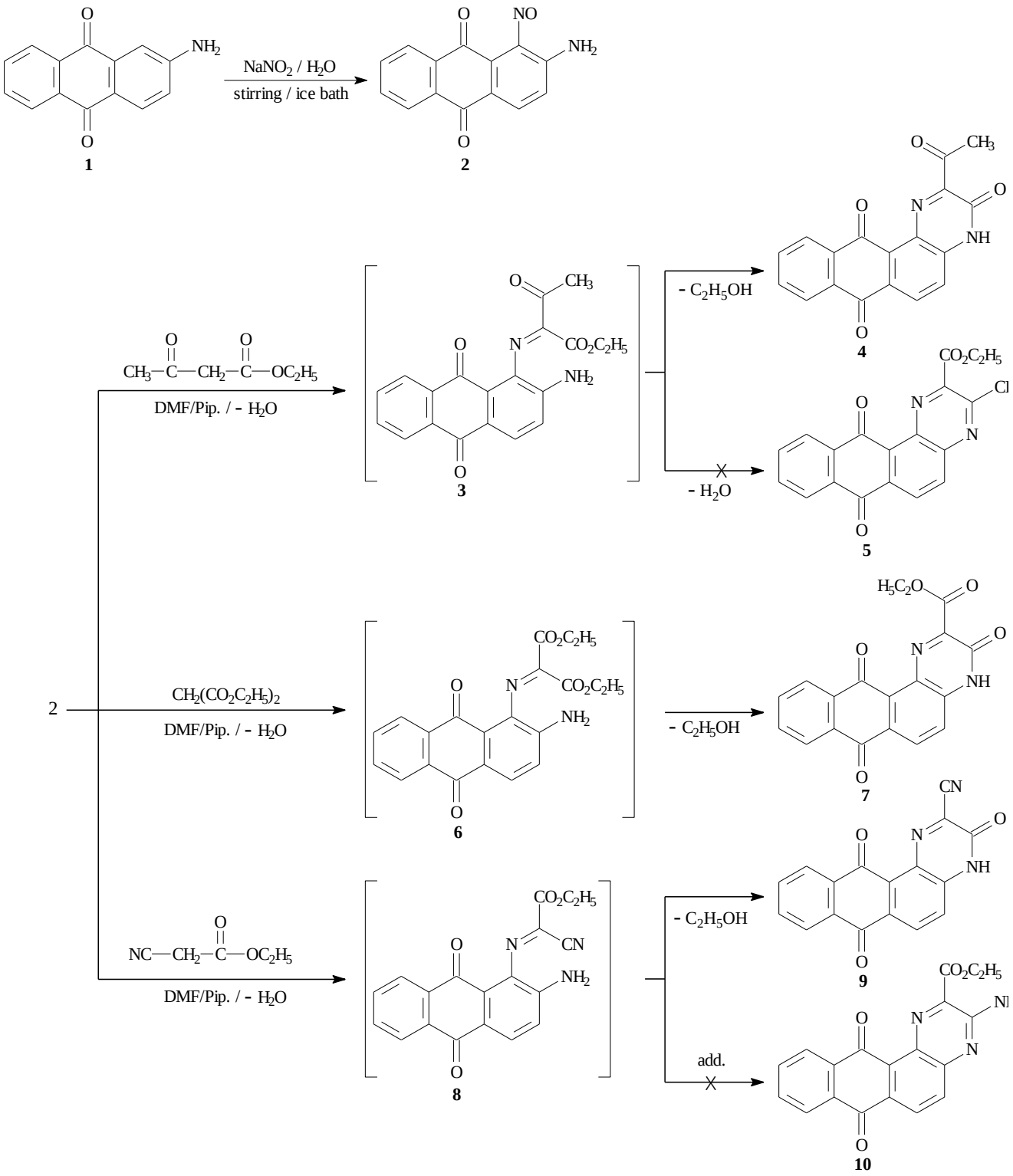
Synthesis of 4-acetyl-naphtho[2,3-*f*]quinoxalie-3,7,12-trione (21)

A mixture of 2 (2 g, 8 mmol) was refluxed in acetic anhydride (30 ml) for 3 hours, then the reaction mixture was concentrated under reduced pressure and the residue was treated with a few amount of hot dimethylformamide and was poured onto ice, the formed product was filtered and washed well with cold water.

Synthesis of 3-cyanometylene-naphtho[2,3-*f*]1,3-thiazolo[4,5-*b*]- quinoxaline 8,13 dione (25)

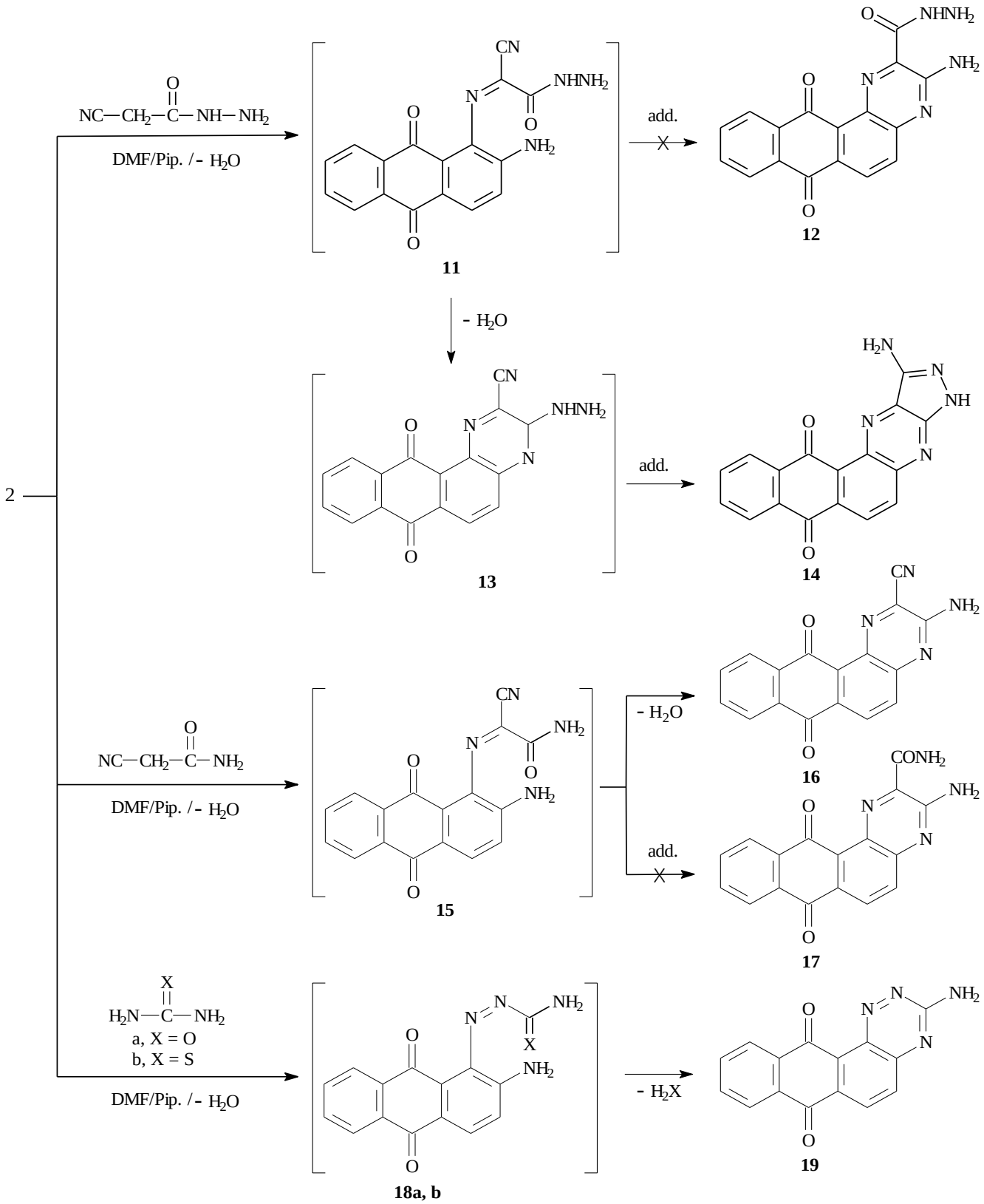
A mixture of 2 (2 g, 8 mmol) and 2-cyanomethylthiazole (1.12 g, 8 mmol) was dissolved in 25 ml dimethylformamide containing 0.1 ml of piperidine as catalyst was warmed at reflux for 6-7 hours and concentrated under vacuum, the residue was poured on 30 ml cold water with rapid stirring, then the product was filtered and recrystallized from DMF/H_2O.

Synthesis of 6*H*-anthra[2,1-*c*]benzo[*f*]1,2,5-triazepine-9,14-dione (27)

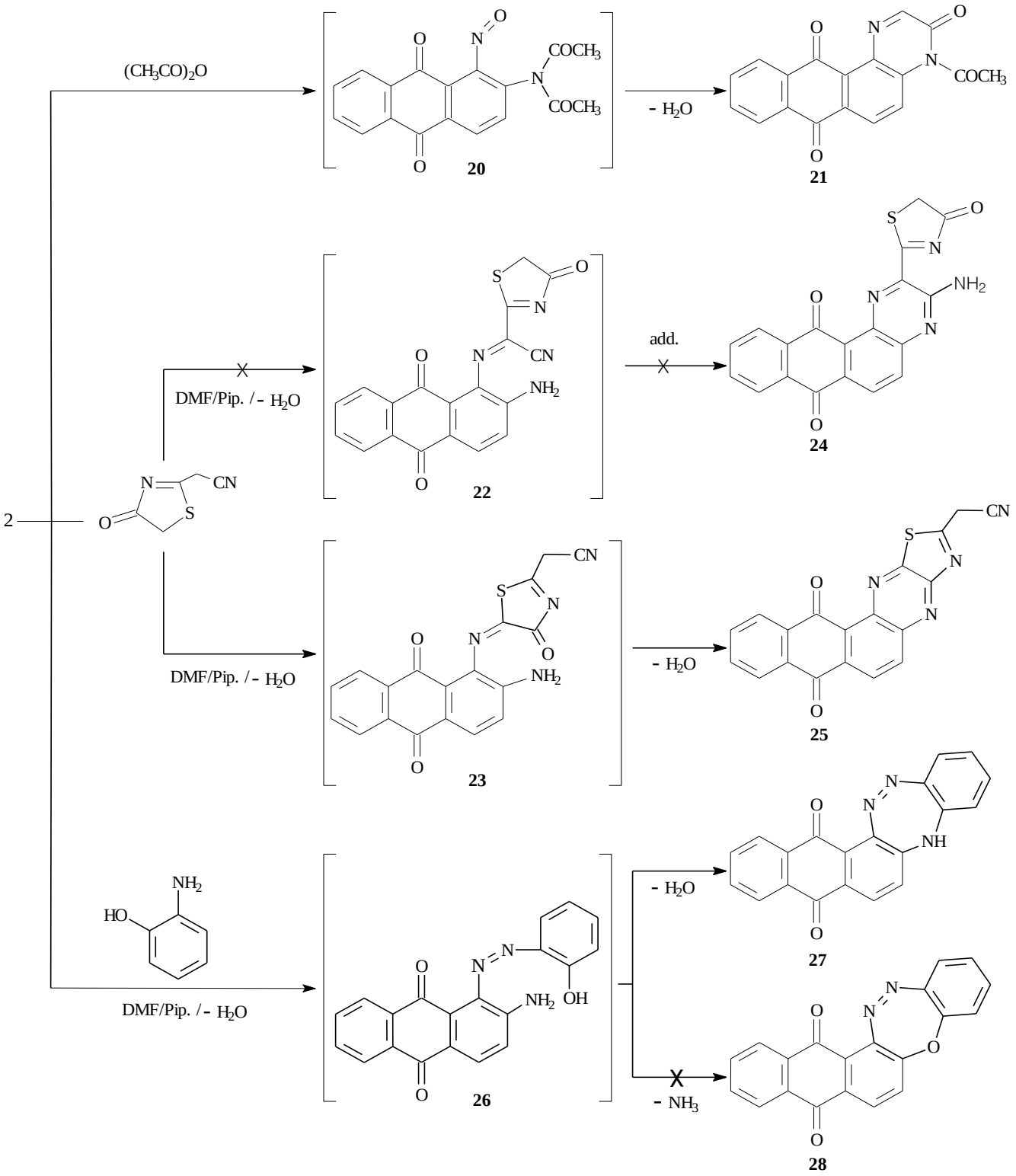


Scheme 1: Synthesis scheme

To a solution of 2 (2 g, 8 mmol) in 30 ml dimethylformamide and 0.1 ml of piperidine, o-aminophenol (0.87 g, 8 mmol) was added with refluxing for 7 hours, the reaction mixture was concentrated under vacuum, the residue was triturated by methanol and collected by filtration, recrystallized from DMF/H_2O.



Scheme 1: Continue...



Scheme 1: Continue…

Analysis

All the melting points of prepared compounds are measured using Electro thermal 15 V,45W A9100 melting point apparatus, and are uncorrected. Elemental analysis was carried out at the Micro analytical Center of Cairo University by an automatic analyzer (Vario EL111 Germany) .^{1}H NMR spectra accomplished using Varian Gemini-300 MHZ

Table 1: Characterization of the prepared compounds (2, 4, 7, 9, 13, 16, 19, 21, 25 and 27)

Comp No.	Nature of products			Molecular formula (M.Wt)	Analysis (%)					
					Calculated			Found		
	Colour	yield %	MP C°		C	H	N	C	H	N
2	Orange	60	218-220	$C_{14}H_8N_2O_3$ (252.23)	66.67	3.2	11.11	66.69	3.34	11.21
4	Orange	73	215-218	$C_{18}H_{10}N_2O_4$ (318.29)	67.89	3.17	8.8	67.92	3.23	8.78
7	Yellow	70	170-173	$C_{19}H_{12}N_2O_5$ (348.29)	65.52	3.47	8.03	65.46	3.36	8.12
9	Yellow	70	225-227	$C_{17}H_7N_3O_3$ (301.09)	67.78	2.34	13.95	67.73	2.22	13.87
13	Orange	56	160-163	$C_{17}H_9N_5O_2$ (315.11)	64.71	2.84	22.19	64.7	2.79	22.31
16	Red	79	150-153	$C_{17}H_8N_4O_2$ (300.28)	67.99	2.68	18.65	67.87	2.57	18.54
19	Red	66	232-235	$C_{15}H_8N_4O_2$ (276.25)	65.22	2.91	20.28	65.31	2.86	20.36
21	Deep orange	59	238-240	$C_{18}H_{10}N_2O_4$ (318.28)	67.92	3.16	8.8	67.88	3.24	8.71
25	Deep orange	56	253-254	$C_{19}H_8N_4O_2S$ (356.36)	64.03	2.26	15.72	64.12	2.34	15.67
27	Red	59	233-235°	$C_{20}H_{11}N_3O_2$ (325.33)	73.84	3.4	12.91	73.77	3.34	12.86

Spectrometer. Mass spectroscopy was recorded on GC-2010 Shimadzy spectrometer. Infra-red spectra were measured with a FT/IR(4100 jaso).

RESULTS AND DISCUSSION

A facile and convenient route was reported to prepare 2-amino-1-nitroanthraquinone, which is considered as a key intermediate for the synthesis of new heterocyclic compounds containing different rings, such as triazine, triazepine, pyrazine, pyrazole, thiazole, thiazine, pyrmidine, pyridine. The structures of all products were evaluated by IR, ^{1}H NMR, Mass spectroscopy and elemental analysis.

Thus, the addition of nitroso group in position 1 of 2-aminoanthraquinone (1) to yield 2-amino-1-nitroanthraquinone (2) was carried out by the reaction of compound (1) with sodium nitrite in water. Compound (2) considers good and available starting material to produce many new anthraquinone derivatives, since it contains nitroso and amino active function groups, (Scheme 1).

Thus, the reaction of compound (2) with ethylacetoacetate in refluxing dimethylformamide in presence of catalytic amount of piperidine gave intermediate (3) through condensation reaction, which cyclized *via* elimination of ethanol molecule to yield compound (5) rather than releasing of water molecule. Also, condensation reaction between compound (2) and diethylmalonate in dimethylformamide with presence of few catalytic amount of piperidine at reflux for 6 hours gave intermediate (6) through condensation reaction, followed by cyclization *via* losing one ethanol molecule to yield(7), the reaction of compound (2) with ethylcyanoacetate was carried out under reflux in dimethylformamide/piperidine to give intermediate (8) through condensation reaction which cyclized *via* releasing of ethanol molecule to yield (9), rather than addition of amino function onto cyano group to give compound (10), Condensation reaction of compound (2) with cyanoaceto-hydrazide afforded compound(13) rather than forming of compound (14). Compound (13) may be proceeded through formation of intermediate (11), followed by losing water molecule to give intermediate (16) which undergo intramolecular cyclization *via* nucleophilic addition of amino function onto cyano group. Reaction of compound (2) with cyanoacetamide gave intermediate (15), then cyclization may be carried out by releasing of water molecule or by addition of amino function onto cyano group to yield compound (16) or compound (17), respectively; the structure of the resulting product was established based on spectral and elemental analysis seemed that (16) was formed .The reaction of compound (2) with urea and/or thiourea gave intermediate (18a,b) *via* losing water molecule followed by cyclization through releasing of water molecule and /or hydrogen sulfide molecule yielded compound (19). Compound (2) reacted with acetic anhydride affording compound (21). The formation of compound (21) may be proceeded *via* acetylation of two hydrogen of amino group through intermediate (20) which cyclized *via* losing water molecule. Reaction of compound (2) with 2-cyanomethylthiazole by the expected way through condensation of nitroso group of compound (2) with active methylene of carbonitrile of thiazole derivative followed by addition reaction of amino function onto cyano group to yield compound (24) was rout out. The compound obtained had been proven by the spectral and elemental analysis that may be formed by the condensation between

nitroso group of (2) and methylene group of thiazole ring forming intermediate (23) which lost another molecule of water to yield (25) (Mahmoud N. A., 2018). Reaction of compound (2) with *o*-aminophenol may proceeded *via* elimination of water molecule to give intermediate (26) which cyclized by elimination of another water molecule to give compound (27) or by losing an ammonia molecule to give compound (28). The structure of the resulting product was established based on the spectral and elemental analysis which proved that (27) was formed. Using adopted used for synthesis a series of many five, six and seven fused rings from naphtho[2,3-*f*] quinoxaline-dione, trione, naphtho-pyrazole quinoxaline-dione, anthra-triazine-dione, naphtho-thiazole quinoxaline-dione and anthrabenzo-triazepine-dione derivatives due to the presence of amino and nitroso function groups, through elimination of water molecule followed by releasing ethanol molecule (4, 7, 9) or releasing water molecule (16, 21, 25, 27), or addition reaction (14), and releasing water or dihydrogensulphide molecule (19). The compounds which was obtained was conformed for spectral

Table 2: IR and ^{1}H NMR (Mass) spectral data of the prepared compounds (3), (4b) and (5b)

Comp. No	IR Spectrum (KBr, Cm^{-1})	^{1}H NMR Spectrum (DMSO, δ); and Mass data
2	1581 (NO), 3500 (NH_2)	4.02 (s, 2H, NH_2), 7.01-7.94 (m, 6H, Ar-H). (M-1): 251
4	1714(C=O), 1730 (C=O), 3360 (NH)	2.20 (s, 3H, CH_3), 7.55-7.90 (m, 6H, Ar-H), 8.01 (s, 1H, NH). (M+2): 320
7	1714(C=O), 1744 (C=O), 3357 (NH)	1.30 (t, 3H, CH_3), 4.20 (q, 2H, CH_2), 7.55- 7.90 (m, 6H, Ar-H), 8.01 (s, 1H, NH). 350 (M+2): 350
9	1715 (C=O), 2218 (CN), 3342 (NH).	7.55-7.90 (m, 6H, Ar-H), 8.01(s, 1H, NH). (M+1): 302
13	3363 (NH), 3487 (NH_2)	^{1}H NMR (DMSO) δ: 4.00 (s, 2H, NH_2), 7.55-8.36 (m, 6H, Ar-H), 13.7 (s, 1H, NH). (M-2): 313
16	2226 (CN), 3498 (NH_2).	4.00 (s, 2H, NH_2), 7.55-8.40 (m, 6H, Ar-H). (M+): 300
19	3489 (NH_2)	4.00 (s, 2H, NH_2), 7.55-7.80 (m, 6H, Ar-H). (M-1): 275
21	1713 (C=O), 1725 (C=O).	2.40 (s, 3H, CH_3), 7.50 (s, 1H, CH pyrazine), 7.55-7.80 (m, 6H, Ar-H). (M+2): 320
25	2215 (CN)	3.67 (s, 2H, CH_2), 7.55-8.36 (m, 6H, Ar-H). (M+1): 357.
27	3430 (NH).	4.00 (s, 1H, NH), 6.66-7.80 (m, 10H, Ar-H). 327 (M+2): 327

scheme, a series of new anthraquinone derivatives were prepared. The described approach opens up access to several derivatives of based on anthraquinones, which can be extended for the preparation of class of compounds for different applications (Cardoso et al., 2019; Devi et al., 2020; Li et al., 2017; Nagia and El-Mohamedy, 2007; Orbán et al., 2008; Penthala et al., 2019; Ramotowska et al., 2019; Rybczyńska-Tkaczyk et al., 2018; Shan et al., 2015; Tapeinou et al., 2018; Veremeichik et al., 2019; Zarren et al., 2019; Zhang et al., 2019).

CONCLUSIONS

In the present investigation, 2-aminoanthraquinone was used to synthesis 2-amino-1-nitroanthraquinone which was and elemental analysis and the method adopted was efficient synthesis of series of compounds and future study will be focused on the applications of synthesize dyes.

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