Egypt. J. Chem. **Vol. 65,** No. 3 pp. 501 - 506 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Chemical and Photochemical Studies on 1,8-Diaminonaphthalene

Asma M. Mahran, Sherif S. Ragab*, Dalia A. A. Osman

Photochemistry Department, Chemical Industries Research Division, National Research Centre (NRC), El behouth Street, Dokki, Giza, 12622, Egypt

Abstract

A novel series of naphthodiazepines **4a-e**, **6** were synthesized through the reaction of 1,8-diaminonaphthalene **1** with either hydrazonoyl chlorides **2a-e**, or bis-hydrazonoyl chloride **5**, respectively. Moreover, new derivatives of thiazinoperimidine **9**, triazoloperimidine **13** , and thiazoloperimidines **14,17** were produced upon the interaction of 1*H*-perimidine-2-thiol 7 with the reagents; epichlorohydrin, hydrazonoyl chloride **10,** bis-hydrazonoyl chloride **5**, and α-chloroacetoacetanilide **15**, respectively. Additionally, the irradiation of 1,8-diaminonaphthalene **1** was accomplished at λ > 313 nm using a high-pressure mercury lamp in the presence of oxygen. All the products were characterized using spectroscopic and analytical techniques.

Keywords; naphthodiazepine; bis-hydrazonoyl; perimidine; irradiation.

1. Introduction

It was reported that some naphthalene derivatives [1] demonstrated significant anti-inflammatory, ulcerogenic activities [2-4]. Some others were used as antibacterial, antifungal [5-9], and anticancer agents [10]. On the other hand, compounds 1,4-, 1,5-diazepine derivatives and their analogs have emerged as a successful class of CNS drugs that are used as hypnotics (sleep inducers), anti-anxiety agents, anticonvulsants, muscle relaxants and are being evaluated as therapeutic agents for the treatment of AIDS [11-13]. These common features along with our previous work of using hydrazonoyl halides in the synthesis of interesting fused heterocyclic compounds incorporating different functionalities of biological importance [14-17] have motivated us to seek for straightforward routes for the synthesis of new derivatives of naphthodiazepine, thiazinoperimidine, triazolo-perimidine, and thiazoloperimidine. Moreover, the irradiation of 1,8-diaminonaphthalene **1** was studied using a high-pressure mercury lamp in the presence of oxygen. Details of the experimental results and suggested mechanisms for the formation of the title compounds will be discussed.

2. Experimental:

All melting points were determined on Electrothermal Engineering LTD apparatus and are uncorrected. Infrared spectra were measured on KBr water technique on a Jasco, FT/IR 6100, Japan. ^{1}H-NMR and spectra were obtained using a JEOL, ECA (500 MHz) with TMS as internal standard at National Research Centre. Mass spectra were performed using 70 Kratos on Schimadzu model GC-MSQP 1000 EX equipment at Cairo University. Compound **7** was prepared according to a reported method [18].

General Procedure for the Synthesis of Compounds 3a-e

To a stirred solution of 1,8-diaminonaphthalene **1** (3 mmol) in EtOH, were added portionwise (3 mmol) of the appropriate hydrazonoyl chlorides **2a-e**. Triethylamine (3 mmol) was then slowly added and the stirring was continued at room temperature for about 6-8 hours. The excess solvent was then distilled off under reduced pressure and the formed solid was collected and recrystallized from the proper solvent to give the respective **3a-e** in 70-75% yields.

Ethyl (2E)-[(8-amino-1-naphthyl)amino](phenyl-hydrazono)acetate (3a)

Brown crystals, (0.77 g, 73%, EtOH); m.p. 196°C; IR (KBr) υ_{max} (cm^{-1}): 3315(NH_2), 3120 (NH), 1715

*Corresponding author:e-mail: she2rifx@yahoo.com. (Sherif S. Ragab)

EJCHEM use only: Receive Date: 08 September 2021, Revise Date: 20 September 2021, Accept Date: 22 September 2021

DOI: 10.21608/ejchem.2021.94861.4462

(C=O ester); ^{1}H NMR (DMSO-d_6) δ (ppm): 1.41 (t, 3H, -$CH_2C\underline{H}_3$), 3.88 (s, 2H, NH_2) 4.54 (q, 2H, -$C\underline{H}_2CH_3$), 7.40-7.42 (m, 5H, Ar-H), 8.07-8.08 (m, 6H, Ar-H), 10.9 (s,1H, NH); MS m/z (%): 349 (M^+, 83), 259 (32), 193 (35), 177 (46), 121 (21), 91 (100), 77 (8), 50 (33); Anal. Calcd. for $C_{20}H_{20}N_4O_2$ (348.39): C, 68.95; H, 5.79; N, 16.08. Found: C, 68.79; H, 5.62; N, 16.04 %.

Ethyl (2E)-[(8-amino-1-naphthyl)amino][(4-methylphenyl)hydra-zono]acetate (3b)

Brown powder, (0.81 g, 74%, $CHCl_3$/pet. ether 60/80); m.p. 132-125°C; IR (KBr) υ_{max} (cm^{-1}): 3317 (NH_2), 3211 (NH), 1713 (C=O ester), 1591 (C=N); ^{1}H NMR (DMSO-d_6) δ (ppm): 1.34 (t, 3H, -$CH_2C\underline{H}_3$), 2.34 (s, 3H, CH_3), 4.0 (s, 2H, NH_2) 4.22 (q, 2H, -$C\underline{H}_2CH_3$), 6.79-7.15 (m, 4H, Ar-H), 7.07-7.58 (m, 6H, Ar-H), 10.77 (s, 1H, NH). MS m/z (%): 362 (M^+, 20), 342 (27), 206 (29), 200 (100), 80 (40), 64 (100); Anal. Calcd. for $C_{21}H_{22}N_4O_2$ (362.44): C, 69.59; H, 6.12; N, 15.46. Found: C, 69.00; H, 5.99; N, 15.31%.

Ethyl (2E)-[(8-amino-1-naphthyl)amino][(4-chlrophenyl) hydrazono] acetate 3c

Dark brown powder, (0.87 g, 75% chloroform/pet ether 60/80); m.p. 127-129°C; IR (KBr) υ_{max} (cm^{-1}): 3313 (NH_2), 3212 (NH), 1713 (C=O ester), 1591 (C=N); ^{1}HNMR (DMSO-d_6) δ (ppm): 1.38-1.41 (t, 3H, -CH_2CH_3), 4.44 (s, 2H, NH_2), 4.54-4.55 (q, 2H, -CH_2CH_3), 7.40-7.42 (m, 4H, Ar-H), 8.07-8.08 (m, 6H, Ar-H), 10.58 (s, 1H, NH); MS m/z (%): 383 (M^+, 10), 351 (38), 292 (48), 256 (32), 210 (25), 168 (82), 111 (100), 75 (35); Anal. Calcd. for $C_{20}H_{19}ClN_4O_2$ (382.85): C, 62.75%; H, 5.00 %; N, 14.63 %. Found: C, 61.80%; H, 4.92 %; N, 14.08%.

Ethyl (2E)-[(8-amino-1-naphthyl)amino][(4-nitrophenyl)hydrazono]-acetate (3d)

Brown powder, (0.88 g, 74 % chloroform/pet ether 60/80); m.p. 145°C. IR (KBr) υ_{max} (cm^{-1}): 3313 (NH_2), 3212 (NH), 1713 (C=O ester), 1591 (C=N); ^{1}HNMR (DMSO-d_6) δ (ppm): 1.38 (t, 3H, -CH_2CH_3), 4.11 (s, 2H, NH_2), 4.54 (q, 2H, -CH_2CH_3), 6.89-7.12 (m, 4H, Ar-H), 7.37-7.68 (m, 6H, Ar-H), 10.68 (s, 1H, NH). MS m/z (%): 394 (M^++1, 50), 393 (M^+, 2), 392 (29), 365 (8), 351 (37), 292 (48), 256 (31), 210 (24), 168 (82), 138 (100), 111(98), 75 (35); Anal. Calcd. for $C_{20}H_{19}N_5O_4$ (393.39): C, 61.64%; H, 4.87%; N, 17.80 %. Found: C, 60.74%; H, 4.65 %; N, 17.71%.

Ethyl (2E)-[(8-amino-1-naphthyl)amino][(2-methoxyphenyl) hydra-zono]acetate (3e)

Dark brown powder, (0.8 g, 70%, chloroform/pet. ether 60/80); m.p. 120-122°C; IR (KBr) υ_{max} (cm^{-1}): 3391 (NH_2), 3212 (NH), 1725 (C=O ester), 1620 (C=N); ^{1}H NMR (DMSO-d_6) δ (ppm): 1.38 (t, 3H, -CH_2CH_3), 3.68 (s, 3H, -OCH_3), 4.42 (s, 2H, NH_2), 4.54 (q, 2H, -CH_2CH_3), 6.94-7.02 (m, 4H, Ar-H), 7.37-7.68 (m, 6H, Ar-H), (NH); MS m/z (%): 378 (M^+, 10), 351 (38), 292 (48), 256 (32), 210 (25), 168 (82), 111 (100), 75 (35). Anal. Calcd. for $C_{21}H_{22}N_4O_3$ (378.42): C, 66.65; H, 5.86; N, 14.81. Found: C, 6.50; H, 5.32; N, 14.68%.

General Procedure for the Synthesis of Compounds (4a-e)

To a stirred EtONa solution (230 mg of Na in 50 ml EtOH), a mixture of each of **3a-e** (0.01 mole) in EtOH/dioxane mixture was added and the mixture was then refluxed for 4-6 h and work up of the reaction by TLC analysis. The filtered solid crystallized from the proper solvent. The isolated products **4b** and **4c** proved identical in all respects (MP, mixed mp, IR) as literature reported [19].

3-(phenyl-hydrazono)-3,4-dihydro-1H-naphtho[1,8-ef][1,4]diazepin-2-one (4a)

Brown powder, (1.82 g, 60%, EtOH); m.p. 300 °C; IR (KBr) υ_{max} (cm^{-1}): 3312, 3231, 3211 (3NH), 1665, 1612 (C=N); ^{1}H-NMR (DMSO-d_6) δ (ppm): 6.90-7.11 (m, 6H, naphthalene-H), 7.23-7.35 (m, 5H, Ar-H), 8.11(s, 1H, NH), 10.12 (s, 1H, NH), 10.68 (s, 1H, NH); MS m/z (%): 303 (M^++1, 8), 302 (M+, 10), 207 (10), 182 (41), 125 (21), 107 (3), 86 (100), 77 (7); Anal. Calcd. for $C_{18}H_{14}N_4O$ (302.33): C, 71.51; H, 4.67; N, 18.53 . Found: C, 71.50; H, 4.65; N, 1.49 %.

3-(**4-nitrophenyl-hydrazono)-3,4-dihydro-1H-naphtho[1,8-ef][1,4]-diazepin-2-one (4d)**

Brown powder, (2.2 g, 63%, EtOH); m.p. 292-294 °C; IR (KBr) υ_{max} (cm^{-1}): 3312, 3231, 3211 (3NH), 1665, 1612 (C=N); ^{1}H-NMR (DMSO-d_6) δ (ppm): 6.90-7.11 (m, 6 H, naphthalene-H), 7.23-7.35 (m, 4H, Ar-H), 8.11 (s, 1H, NH), 10.12 (s, 1H, NH), 10.68 (s, 1H, NH); MS m/z (%): 347 (M^++1, 8), 302 (M+, 10), 207 (10), 182 (41), 125 (21), 107 (3), 86 (100), 77 (7); Anal. Calcd. for $C_{18}H_{13}N_5O_3$ (347.32): C, 62.42; H, 3.77; N, 20.16 . Found: C, 62.50; H, 3.65; N, 20.10 %.

3-(2-methoxyphenyl-hydrazono)-3,4-dihydro-1*H*-naphtho[1,8-e*f*]-[1,4]diazepin-2-one (4e)

Red powder, yield (2.58 g, 77%); m.p. 160°C ($CHCl_3$/n-hexane). IR (KBr) υ_{max} (cm^{-1}): 3329, 3217, 3210 (3NH), 1662 (C=O), 1610 (C=N); ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.38 (s, 3H, -OCH_3), 6.90-7.11 (m, 6H, naphthyl-H), 7.23-7.35 (m, 4H, Ar-H, NH), 8.11 (s, 1H, NH amide), 10.0 (s, 1H, NH), 10.56 (s, 1H, NH); MS m/z (%): 333 (M^++1, 1), 332 (M+, 2), 207 (10), 182 (41), 125 (21), 107 (3), 86 (100), 77 (7); Anal. Calcd. for $C_{19}H_{16}N_4O_2$ (332.35): C, 68.66; H, 4.85; N, 16.86. Found: C, 68.54; H, 4.65; N, 16.69 %.

Synthesis of (2*Z*,3*Z*)-naphtho[1,8-*ef*][1,4]diaze-pine-2,3(1*H*,4*H*)-dione bis(phenylhydrazone) (6)

To a stirred EtONa solution (115 mg of Na in , 50 ml EtOH) was added a solution of **1** (5 mmol, 0.79 g) and bis-hydrazonoyl chloride **5** (5 mmol, 1.53 g) in EtOH/dioxane mixture. The reaction mixture was

heated under reflux for 10 hours, The deep brown precipitate formed was collected by filtration washed with H_2O , air dry crystallized from (EtOH/dioxane); yield (1.2 g, 61 %); mp 245° C; IR (KBr) υ_{max} (cm^{-1}): 3242-2920 (NH),1627 (C=N), ^{1}H NMR (DMSO-d_6) δ (ppm): 6.90-8.46 (m, 16H, Ar-H), 10.61 (s, 2H, NH),11.00 (s, 2H, 2NH). MS m/z (%): 392.26 (9.0%), 373.12 (7.0%), 334.31 (5.0%), 294.23 (17.00), 277 (40), 95 (40), 69 (53), 57 (88); Anal. Calcd. for $C_{24}H_{20}N_6$ (392.546): C, 73.45; H, 5.14; N, 21.41. Found: C, 73.23; H, 5.01; N, 21.39 %.

General Procedure for the Synthesis of Compounds 9, 13, 14 and 17

To a stirred EtONa solution (115 mg of Na in 50 ml EtOH) of **7** (5 mmol, 1 g) were added dropwise (5 mmol) of each of the appropriate reagents; epichlorohydrin, hydrazonoyl chloride **10**, bis-hydrazonoyl chloride **5** and α-chloroacetoacetanilide **15**. The mixture was then refluxed for 8-10 h. The solvent was evaporated and the residue was triturated with MeOH. The solid was collected by filtration, washed with water, air-dried, and recrystallized to afford the corresponding derivatives **9**, **13**, **14** and **17**.

10,11-dihydro-9H-[1,3]thiazino[3,2-a]perimidin-10-ol (9)

Brown crystals, (0.7 g, 55%), EtOH/dioxane), m.p. 322°C; IR (KBr) υ_{max} (cm^{-1}): 3380 (OH), 2890 (CH_2); ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.00-3.22 (m, 2H, S-CH_2), 3.31-3.58 (m, 2H, N-CH_2), 3.66 (d, 1H, OH), 3.85-4.2 (m, 1H, C<u>H</u>-OH), 6.68-7.42 (m, 6H, Ar-H); MS m/z (%): 256 (M^+,11 %); Anal. Calcd. for $C_{14}H_{12}N_2OS$ (256.324): C, 65.60; H, 4.72; N, 10.93; S,12.51 Found: C, 65.41; H, 4.49; N, 10.70; S,12.11 %.

10-Naphthalen-1-yl-8-phenyl-8H-7,8,9,10a-tetraaza-cyclopenta[a]-phenalene (13)

Grey powder, yield (1.1 g, 53 %) from EtOH /dioxane), mp 295°C; IR (KBr) υ_{max} (cm^{-1}): 1425 (C=N); ^{1}H-NMR (DMSO-d_6) δ (ppm): 6.73-7.24 (m, 6H, Ar-H), 7.55-7.64 (m, 7H, Ar-H), 7.95-8.14 (m, 5H, Ar-H); MS m/z (%): 410.29 (M^+, 5.0), 366.22 (7.21), 308.17 (4.76), 200.04 (100), 172.00 (10.45), 166 (63.91), 139.03 (15,13), 113.03 (10.58), 69.99 (14.23); Anal. calcd for $C_{28}H_{18}N_4$ (410.47): C, 81.93; H, 4.42; N, 13.65, Found: C, 8.78; H, 4.32; N, 13.35 %.

(9Z,10E)-9,10-bis(2-phenylhydrazono)-9,10-dihydrothiazolo[3,2-a]perimidine (14)

Green powder yield (1.35 g, 60%) from EtOH, mp 306° C; IR (KBr) υ_{max} (cm^{-1}): 3300-3180 (NH); ^{1}H NMR (DMSO-d_6) δ (ppm): 6.86-7.11 (m, 6H, Ar-H), 7.22-7.29 (m, 10H, Ar-H), 10.20 (s, H, NH), 11.12 (s, 1H, NH): MS m/z (%): 434.01 (M^+, 12.0), 315.15 (3%), 284.12 (10.0), 256.08 (1.0), 166.23 (7.0),139 (14.0), 118 (48), 91 (30), 77 (50), 63 (100); Anal. calcd for $C_{25}H_{18}N_6S$ (434.44): C, 69.10; H, 4.18; N, 19.34; S, 7.38. Found: C, 69.37; H, 4.21; N, 1.29, S, 7.22 %.

10-methyl-N-phenylthiazolo[3,2-a]perimidine-9-carboxamide (17)

Dark Color, yield (1.2 g, 67%, EtOH), m.p. 330°C; IR (KBr) υ_{max} (cm^{-1}): 3312 (NH), 1603 (C=O); ^{1}HNMR (DMSO-d_6) δ (ppm): 2.23 (s, 3H, CH_3), 6.74-7.22 (m, 6H, Ar-H), 7.41-7.72 (m, 5H, Ar-H), 10.13 (s, 1H, NH). MS m/z (%): 357 (M^+, 0.4); Anal. calcd for $C_{21}H_{15}N_3OS$ (357.429): C, 70.57; H, 4.23; N, 11.76, S, 8.97. Found: C, 69.99; H, 4.26; N, 11.59; S, 8.52 %.

Irradiation (photooxidation) of 1,8-naphthalene-diamine 1

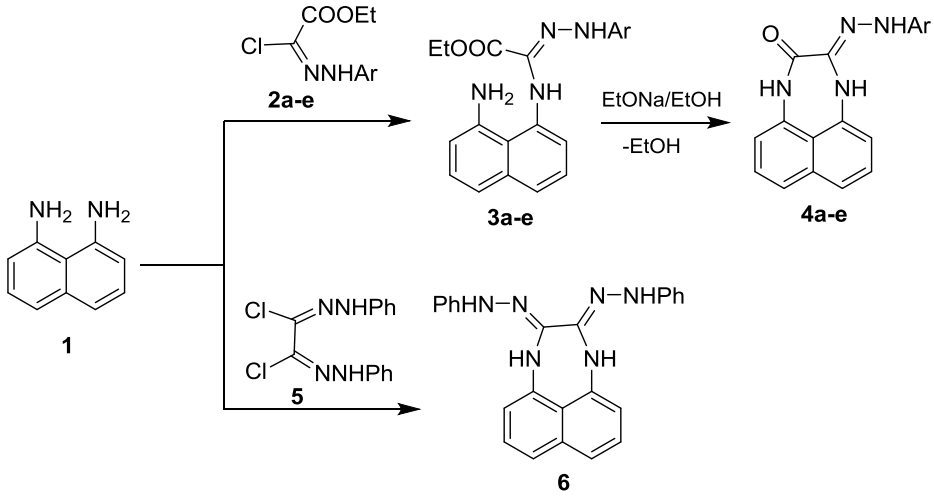
A solution of **1** (5 mmol) in 250 ml of EtOH was irradiated using a high pressure mercury lamp/pyrex vessel, λ > 313 nm for 20 hrs. The reaction process was followed by TLC. The solvent was then evaporated at room temperature. The formed product was collected by filtration, dried and recrystallized from EtOH to give product **18**.

Compound **18** formed dark powder. Yield: (1.08 g,70 %), m.p 140 ^{0}C (EtOH), IR (KBr) υ_{max} (cm^{-1}): 3358 (NH), 1591 (C=N) cm^{-1}. MS m/z (%): 312 (M^+, 14), 310 (M^+-2, 24), 282 (21), 270 (59), 168 (100), 153 (21), 140 (45), 115 (29), 93 (12), 77 (8); Anal. Calcd. for $C_{20}H_{16}N_4$ (312.35): C, 77.40; H, 4.55; N, 18.05. Found: C, 77.29; H, 4.48; N, 18.07 %.

3. Results and discussions

1,8-Diaminonaphthalene **1** reacted with ethyl (Z)-2-chloro-2-(2-arylhydrazono)acetates **2a-e** [20] in (EtONa/EtOH) solution at ambient temperature to furnish a single product based on the TLC analysis of the crude product. Both spectroscopic (MS, IR, ^{1}H-NMR) and elemental analytical data (c.f. Experimental) were consistent with (E)-ethyl-2-((8 aminonaphthalen-1-yl)amino)-2-(2-arylhydrazono) acetates **3a-e** (Scheme 1). The mass spectrum of **3a** taken as an example showed a molecular ion peak at m/z (%) 349 (M^+, 83%) corresponding to $C_{20}H_{20}N_4O_2$. Also, the IR spectra of all new compounds **3a-e** revealed the presence of characteristic C=O ester band in the range 1713-1725 cm^{-1} and (NH_2) in the range 3315-3329 cm^{-1}. Attempts to cyclize these hydrazono acetates **3a-e** could be achieved by their refluxing in EtONa/EtOH solution that furnished the respective naphthadiazepinones **4a-e** (Scheme 1). The ^{1}H-NMR spectra of **4a-e** revealed the absence of the corresponding signals of ethyl protons which were existed in the spectra of their parent compounds **3a-e**. The formation of compounds **4a-e** was supported by the suggested mechanism that is depicted in Scheme 1, thus the reaction pathway starts with S_N2 nucleophilic substitution reaction of 1,8-

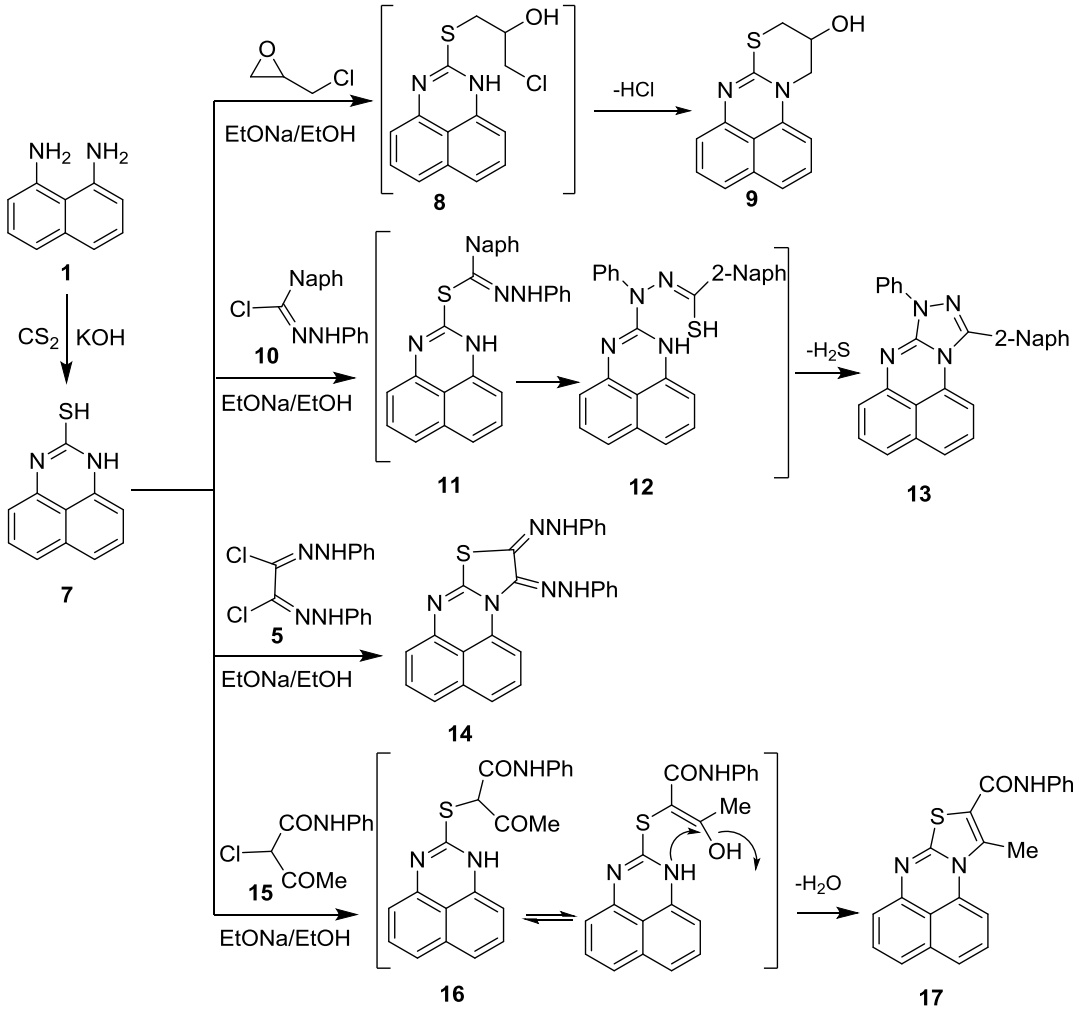
diaminonaphthalene **1** with (*Z*)-ethyl-2-chloro-2-(2-arylhydrazono)acetates **2a-e** to give compound **3** which cyclized upon boiling in EtONa to yield **4** as end product *via* elimination of EtOH molecule. Subjecting equimolar quantities of **1** and bis-hydrazonoyl chloride **5** [21] to the same previous conditions afforded the naphthodiazepine **6** whose structure was identified on the basis of its spectral and elemental analysis. Specifically, the mass spectrum of **6** revealed the molecular ion peak at *m/z* 392 (27%) while the elemental analysis showed that the product has the molecular formula of $C_{24}H_{20}N_6$. Moreover, the ^{1}H-NMR spectrum of **6** showed a development of signals at δ 6.90-8.46 ppm corresponding to additional ten aromatic protons compared to whose of its parent compound.



Ar: **a**, C_6H_5; **b**, 4-Me-C_6H_4; **c**, 4-Cl-C_6H_4; **d**, 4-NO_2-C_6H_4; **e**, 4-MeO-C_6H_4

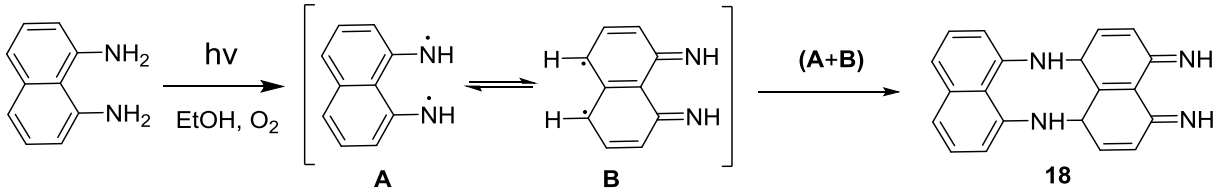
Scheme 1. Reactions of **1** with hydrazonoyl chlorides

Continuously to the aim of this study, the starting 1*H*-perimidine-2-thiol **7** was prepared by refluxing 1,8-diaminonaphthalene **1** with carbon disulfide in ethanol in the presence of KOH as previously reported [18]. When epichlorohydrin was allowed to react with **7** in EtONa/EtOH solution it afforded thiazinoperimidine derivative **9**. The ^{1}H-NMR of **9** revealed a singlet at 3.66 ppm corresponding to (-O<u>H</u>) in addition to the protons of S-C<u>H</u>$_2$, N-C<u>H</u>$_2$ around 3.10 and 3.41 ppm respectively, while the multiplet of C<u>H</u>-OH appeared at 3.85 ppm. While the OH stretching is evidently clear from the IR spectrum as a broad band at 3380 cm^{-1} and thus the structure was assigned as 10,11-dihydro-9H-[1,3]thiazino[3,2-a]perimidin-10-ol. The direct formation of **9** from reaction of **7** with epichlorohydrin indicates that the initially formed **8** underwent *in situ* dehydrative cyclization under the employed reaction condition via loss of HCl molecule [22]. When **7** reacted with hydrazonoyl chloride **10** in refluxing EtONa/EtOH solution for 8-10 hrs, it afforded a single product whose structure was established from its spectral data, and was evidently identified as 10-naphthalen-1-yl-8-phenyl-8*H*-7,8,9,10a-tetraaza-cyclopenta[a]-phenalene **13**. The proposed mechanism for the reaction of **7** with **10** proceeds in two steps; firstly acylation of **7** occurred *via* nucleophilic substitution of chloride in **10** to generate 1*H*-perimidin-2-yl(E)-N-phenylnaphthalene-2-carbohyd-razonothioate **11**. The latter undergoes *in situ* Smiles rearrangement [15] providing the thiohydrazide intermediate **12**, which in turn was cyclized with loss of H_2S molecule to furnish the respective **13** as end product (Scheme 2). Treatment of equimolar quantities of **7** and bis-hydrazonoyl chloride **5** [20] in EtOH/dioxane in the presence of EtONa delivered **14** whose mass spectra showed a molecular ion peak at [*m/z* 434 (M^+)] and its microanalysis data is consistent with the molecular formula $C_{25}H_{18}N_6S$. The reaction of **7** with α-chloroacetoacetanilide **15** in refluxing EtONa/EtOH solution gave the respective **17** (scheme 2). The IR spectrum exhibited the existence of (-NH) and (C=O) bands at υ = 3312, υ =1603 cm^{-1} respectively. The ^{1}H-NMR spectrum showed two characteristic signals at δ 2.20, 2.2.28 corresponding to CH_3 and NH respectively. The formation of **17** from reaction of **7** with **15** was supported from the reaction pathway outlined in (Scheme 2) which suggested the reaction to proceed with the initial generation of the respective intermediates **16** which undergo *in situ* cyclization with elimination of H_2O molecule to deliver the final product **17.**



Scheme 2. Synthesis of Thiazolo-, Thiazino-, and Triazoloperimidine Derivatives

Finally, in continuation to our work concerning the photochemical studies of heterocycles [23-25] and diamino compounds [26], we studied the photolysis of 1,8-diaminonaphthalene **1**. Specifically, when a solution of **1** in ethanol was irradiated using a high-pressure mercury lamp ($\lambda > 313$ nm) in the presence of oxygen for 20 hrs, it furnished a single product (evidenced from TLC). The Spectral and elemental analytical data of the product were in conformity with the assigned structure **18**. For example, its molecular formula $C_{20}H_{16}N_4$ with molecular ion peak at 312 (M^+, 24), while the IR spectrum revealed the appearance of (NH) stretching and (C=N) at 3358 and 1591 cm^{-1} respectively. The suggested mechanism for the photochemical synthesis of **18** involves the two hydrogen abstractions [27] from each amino group in **1** to give the diradical species **A**, which undergo tautomerization giving another diradical species **B.** The two diradicals **A, B** could combine together leading to the formation of **18** (Scheme 3).



Scheme 3. Irradiation of 1,8-diaminonaphthalene **1**

4. Conclusion

In the current study we investigated the chemical and photochemical study of 1,8-diaminonaphthalene **1** and the outcomes were novel series of naphthodiazepines, thiazinoperimidine, triazolo-perimidine, and thiazoloperimidines. While, the

irradiation of 1,8-diaminonaphthalene **1** was accomplished at λ > 313 nm using a high-pressure mercury lamp in the presence of oxygen. Due to the expected biological importance of the title compounds it will be interesting if they could be subjected to evaluation as bioactive agents.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgments

The authors are grateful to Prof. Dr. Afaf Ali Nada (the founder of photochemistry department) for her help and support not only during the current study but also throughout their careers.

5. References

[1] Ziarani G. M., Mohajer F., Mali S. N., *Comb. Chem. High Throughput Screen.,* **24**(10) 1702-1713 (2021).

[2] Palaska E., Sahin G., Kelicen P., Tugba N., *Farmaco*, **57**, 101–107 (2002).

[3] Pandya A.B., Prajapati D.G., Pandya S. S., *J. Appl. Pharm. Sci.*, **2**, 226–232 (2012).

[4] Bansal E., Srivastava V., Kumar A., *Eur. J. Med. Chem*., **36**, 81–92 (2001).

[5] Rokade Y.B., Sayyed R. Z., *Rasayan J, Chem* **2**(4), 972-980 (2009).

[6] Huang M., Wu S., Wang J., Lin C., Lu S., Liao L., Shen A., *Drug Dev. Res*., **60**, 261–269 (2003).

[7] Bassyouni F. A., Abu-Bakr S. M., Hegab K. H., El-Eraky W., El Beih A. A., Abdel Rehim M. E., *Res. Chem. Intermed*. **38**, 1527–1550 (2012). DOI 10.1007/s11164-011-0482-9

[8] Goksu S., Tansu M., Ozdemir H., Secen H., *Turk. J. Chem*., **29**,199-205 (2005).

[9] Ryu C., Chae M., *Arch. Pharm. Res*., **28**, 750-755 (2005). doi.org/10.1007/BF02977337

[10] Antonini, I.; Polucci, P.; Magnano, A.; Sparapani, S.; Martelli, S. Rational. *J. Med. Chem*., **47**, 5244–5250 (2004).

[11] Hamor T. A., Martin I. L., in progress in medicinal chemistry, 20, " eds. G. P. Ellis and G. B West, Elsevier Science Publishers, Amsterdam 1983.

[12] Hsu M. C., Schutt A. D., Holly M., Slice L. W., Sherman M. I., Richman D. P., Potash M. J., Volsky D. J., *Science*, **254**, 1799 (1991).

[13] Fujii T., Saito T., T. Fujisawa, *Heterocycles*, , **27**, 1163 (1988). DOI: 10.3987/COM-88-4519.

[14] Mahran A. M., Farghaly T. A., Nada A. A., *Res. Chem. Intermed.*, **41**: 2961-9 (2015).

[15] Mahran A. M, Ragab S. S., Hashem A. I., Ali. M. M., Nada A. A., *Eur J. Med. Chem*., **90**: 568-78 (2015). DOI: 10.1016/j.ejmech.2013.12.007.

[16] Mahran A. M., Hassan N. A., *Arch. Pharm. Res*., **29** (1):46-59 (2006).

[17] Shawali A. S., Mahran A. M., Nada A. A., *J Heteroatom Chemistry*, **18** (4), 393-8 (2007).

[18] Dolzhenko A. V., Chui W., Dolzhenko A. V., *Heterocycles*, **68**(4), 821-828 (2006). DOI: 10.3987/COM-06-10678

[19] Farghaly T. A., Abbas E. M. H., Dawood K. M., El-Naggar T. B. A., *Molecules*, **19**, 740-755 (2014).

[20] a) Favrel G., *Bull. Soc.Chim. Fr*. **31**,150 (1904).
b) Grundmann, C., Datta, S. K., Sprecher R. F., *Liebigs Ann. Chem*., **88,** 744, (1971).

[21] Bakavoli M., Ghorbani M. H., Rahimzadeh M., Ghassemzadeh M., Heravi M. M., *Phosphorus. Sulphur and Silicon*. **170**, 135-138 (2001).

[22] Mahran A. M., Hassan N. A., Osman D. A. A., Ragab S. S., Hassan A. A., *Z. Naturforsch*., **71**(5-6)c: 133–140 (2016). DOI 10.1515/znc-2015-0265.

[23] Nada A. A., Mahran A. M., Shawali A. S., *Phosphorus, Sulfur and Silicon*, **180**, 2111-2117 (2005).

[24] Mahran A. M., Nada A. A., Ragab S. S., *Egypt. J. Chem*., **50** (5), 683-689 (2007).

[25] Nada A. A., Mohamed N. R.. Mahran A. M., Ibrahim Y. A., *J. Het. Commun*., **4** (3), 271-276 (1998).

[26] Ragab S. S., Badawy A. A., El Nazer H. A., *J Chin. Chem. Soc*., **66**:719-724 (2019). DOI: 10.1002/jccs.201800355.

[27] Okamura T., Akai N., Nakata M., *J. Phys. Chem. A*, **121**, 1633 (2017).