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Gas-phase thermolysis of condensed-1,2,4-triazines: interesting routes toward heterocyclic ring systems

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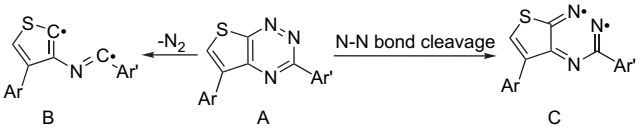
Abstract—Gas-phase thermolysis of thieno[2,3-*e*][1,2,4]triazines gave benzonitrile, isothiazole, pyridazine, and thieno[2,3-*d*]thiazole derivatives. Similar transformation of benzo[1,2,4]triazine and phenanthro[9,10-*e*][1,2,4]triazine derivatives into their corresponding condensed thiazoles has been achieved by heating at 350 °C with sulfur. A mechanism for these pyrolytic transformations was proposed.

1. Introduction

Pyrolysis of N=N heterocyclic compounds has been shown to start mainly by N_2 loss leading to reactive diradical intermediates which undergo subsequent transformation leading to many interesting products. These pyrolytic reactions have been reported for five-membered heterocyclic rings including pyrazoles,[1] thiadiazoles,[2] triazoles,[3] and tetrazoles[4] and also six-membered heterocyclic rings including benzotriazoles,[5] naphtho[1,8-*de*][1,2,3]triazines,[6] cinnolines,[7] 1,2,3-benzotriazines,[8] and 1,2,4-benzotriazines.[9]

The primary step in the pyrolysis of cinnolines,[7] 1,2,3-benzotriazines,[8] 1,2,4-benzotriazines,[9] benzotriazoles,[5] and naphtho[1,8-*de*][1,2,3]triazines[6] involves mainly N_2 elimination, yielding the corresponding diradical intermediates which subsequently combine intramolecularly into the corresponding condensed cyclobutenes or benzazetes, or undergo further rearrangement or fragmentation before yielding the final products.

Recently,[10] we have shown that pyrolysis of thieno[3,2-*e*]-[1,2,4]triazines **A** takes, in addition to nitrogen extrusion ($-N_2$), a different main fragmentation route by cleavage of the N–N bond leading to reactive diradical intermediates **B** and **C** (Scheme 1), which explains the formation of the pyrolytic reaction products resulting from this ring system.[10]

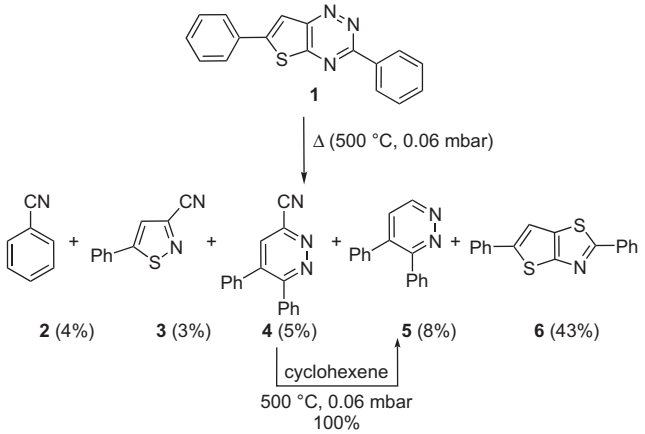


Scheme 1.

In the present investigation we report our results on the pyrolysis products of thieno[2,3-*e*][1,2,4]triazine **1** in order to compare the pyrolytic behavior of this ring system with its isomeric derivative **A** and the benzo analogs as well as their synthetic potentialities.

2. Results and discussion

Reaction products from complete gas-phase pyrolysis of thieno[2,3-*e*][1,2,4]triazine **1** (Scheme 2) were obtained at optimal reactor conditions of temperature, pressure (0.06 mbar), and substrate residence time compatible with >98% reaction established for completed pyrolysis as evident from HPLC analysis. The products of pyrolysis of **1** were separated by preparative HPLC and by column chromatography. These products were characterized using GC–MS, LCMS, ^{1}H, ^{13}C NMR, and 2D NMR spectroscopy. Thus, compound **1** upon pyrolysis gave benzonitrile **2**, 5-phenyl-3-cyanoisothiazole **3**, 5,6-diphenylpyridazine-3-carbonitrile **4**, 3,4-diphenylpyridazine **5**, and 2,5-diphenylthieno[2,3-*d*]thiazole **6**.



Scheme 2.

Keywords: Pyrolysis; Triazines; Thiazoles; Imidazoles; Heterocycles.
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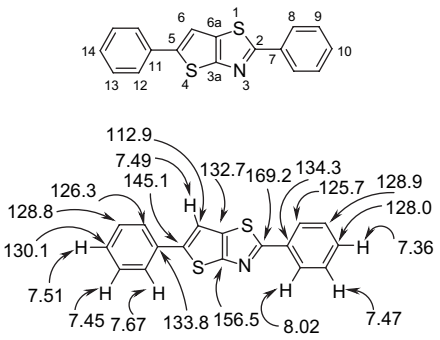


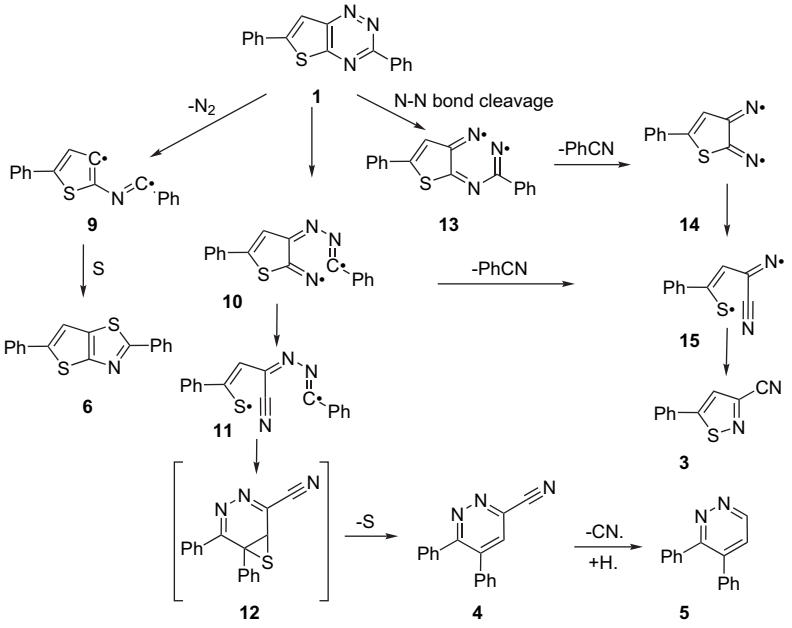
Figure 1. ^{1}H and ^{13}C NMR spectroscopy assignment of **6**. The HMBC correlation showed the following proton carbon cross peaks: H^{6} at δ 7.49 correlates with C^{3a} (at δ 156.5) and C^{5} (at δ 145.1), H^{13} at δ 7.47 correlates with C^{11} (at δ 133.8), H^{12} at δ 7.67 correlates with C^{5} (at δ 145.1), H^{8} at δ 8.02 correlates with C^{2} (at δ 169.2), and H^{9} at δ 7.47 correlates with C^{7} (at δ 134.3).

Assignments of the heterocyclic ring protons and carbons of compound **6** along with the numbering used in the NMR correlations are shown in Figure 1. These assignments were made based on H,H-COSY, HMQC, and HMBC experiments.

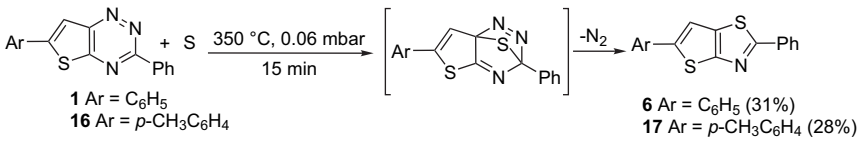
Scheme 3 illustrates possible mechanistic routes explaining the formation of **2**–**6** obtained in the present pyrolytic studies of compound **1**. The first route starts by extrusion of N_2 to give the diradical **9** which then captures sulfur from the decomposition products to give compound **6**. The second route which explains the formation of the pyridazines starts by initial C3–N4 bond cleavage to give the diradical **10** which rearranges to the cyano diradical **11**. The latter combines to give the intermediate **12** which aromatizes via loss of S to give **4**. The latter via thermal loss of CN and replacement with H radical gives the corresponding 3,4-diphenylpyridazine **5**. This was substantiated by the fact that pyrolysis of **4** in the presence of cyclohexene (as a hydrogen source) at 500 °C gave **5**.

The third route starts by N–N cleavage to give the diradical **13** which fragments further to give benzonitrile **2** and the diradical **14**. The latter rearranges to the cyano diradical **15**. The latter cyclizes intramolecularly via diradicals bonding to give **3**.

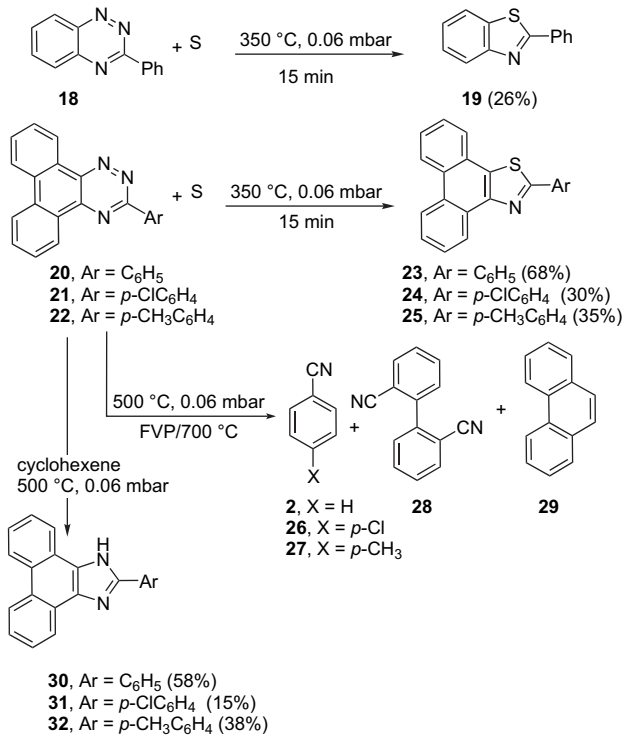
Alternatively, the formation of compound **6** has been proposed to take place by cycloaddition of sulfur (generated from decomposition of some of the starting compound or through conversion of the proposed intermediate **12** to **4**) to the starting triazine **1** followed by nitrogen extrusion (Scheme 4). This presumption has been verified by reacting compound **1** with sulfur (in different molar ratio) at different temperature (extending from 500 °C to 250 °C) in a static pyrolyzer. The optimum condition was found to be the use of 1.5 equiv of sulfur and heating at 350 °C. Higher temperatures or a higher sulfur ratio gave large amounts of decomposition products whereas lower temperatures gave very low



Scheme 3.



Scheme 4.



Scheme 5.

yields. This led to the exclusive formation of compound **6** together with the recovered **1**. The fact that compound **1** did not undergo pyrolysis alone below 500 °C, but, in the presence of sulfur, compound **6** was formed at 350 °C, indicates that compound **6** was formed mainly, through cycloaddition of sulfur to the starting triazine **1** followed by nitrogen extrusion (Scheme 4) and most probably not as postulated in Scheme 3.

This cycloaddition of sulfur to the 1,2,4-triazine ring was further investigated by reacting 3-phenylbenzo-1,2,4-triazine **18** with sulfur under the previous conditions whereby 2-phenylbenzothiazole **19** was obtained along with benzonitrile (the normal pyrolysis product obtained in absence of sulfur in the FVP)[9] (Scheme 5). Moreover, extension of this cycloaddition of sulfur to 3-arylphenanthro[9,10-*e*]-[1,2,4]triazines **20**–**22** led to the formation of the corresponding 2-arylnaphtho[9,10-*d*]thiazoles **23**–**25**. Pyrolysis of **20**–**22** in absence of sulfur occurred at 700 °C by FVP and at 500 °C under static conditions to give the corresponding benzonitrile derivatives **2**, **26**, **27**, biphenyl-2,2′-dicarbonitrile **28**, and phenanthrene **29**. The formation of the latter could have been resulted from the addition of two hydrogen atoms to the expected intermediate 9,10-phenanthryne. The dimmer of the latter (tetrabenzobiphenylene) was only detected by its mass spectrum (MS: m/z=352) in the pyrolysis products (this compound is not stable enough for purification and identification as reported).[11] On the other hand, static pyrolysis of **20**–**22** in the presence of cyclohexene (in an attempt to force a possible cycloaddition reaction) occurred only at 500 °C and led to the exclusive formation of the corresponding 2-aryl-1*H*-phenanthro[9,10-*d*]imidazoles **30**–**32**, respectively (Table 1).

Table 1. Pyrolysis conditions and reaction products

Entry	Starting triazine	Pyrolysis conditions	Products/yield (%)
1	**1**	A	**2**/4, **3**/3, **4**/5, **5**/8, **6**/43
2	**4**	B	**5**/80
3	**1**	C	**6**/31[a]
4	**16**	C	**17**/28[b]
5	**18**	C	**19**/26[c]
6	**20**	C	**23**/68[d]
7	**21**	C	**24**/30[e]
8	**22**	C	**25**/35[f]
9	**20**	A	**2**/38, **28**/11, **29**/5
10	**21**	A	**26**/35, **28**/8, **29**/3
11	**22**	A	**27**/36, **28**/12, **29**/4
12	**20**	D	**2**/53, **28**/19, **29**/6
13	**21**	D	**26**/43, **28**/15, **29**/7
14	**22**	D	**27**/63, **28**/18, **29**/9
15	**20**	B	**30**/58
16	**21**	B	**31**/15
17	**22**	B	**32**/38

For conditions A, B, C, D see Section 4.
[a] Recovered starting **1** (30%).
[b] Recovered starting **16** (35%).
[c] Recovered starting **18** (25%).
[d] Recovered starting **20** (15%).
[e] Recovered starting **21** (40%).
[f] Recovered starting **22** (46%).

3. Conclusions

The present study offers interesting new routes toward heterocyclic compounds, some of which are new derivatives. The present study also shows that thienotriazines behave differently from the corresponding benzo analogs in the sense that the pyrolytic liberated sulfur could undergo cycloaddition reaction to the 1,2,4-triazine ring systems, which opened a new synthetic route to condensed thiazoles. Moreover, this study also showed the effect of the more electron rich five-membered condensed thiophene ring on the pyrolytic behavior involving mechanistic pathways which are different from their corresponding benzo analogs.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded in KBr disks on a Perkin Elmer System 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400, 400 MHz, Avance^{II} 600, 600 MHz super-conducting NMR spectrometers. Mass spectra were measured on VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer. Separation of reaction products was performed using preparative HPLC WATER PREP 4000 series with PDA detector WATER 2996. The starting triazines **1**,[12] **16**,[12] **18**,[13] and **20**[14] were prepared as reported.

4.2. 3-Arylphenanthro[9,10-*e*][1,2,4]triazines 20–23. General procedure

To a mixture of the appropriate *N*-aminobenzamidine hydrochloride derivatives[15] (12 mmol) in methanol (15 mL) was

added with stirring at room temperature a suspension of phenanthraquinone (2.1 g, 10 mmol) in methanol (10 mL), the reaction mixture was allowed to stir at room temperature overnight. The precipitate was then collected, washed with ethanol, and recrystallized from the proper solvent.

4.2.1. 3-Phenylphenanthro[9,10-*e*][1,2,4]triazine (20). Yellow needles from ethanol, yield 50%, mp 185–186 °C (lit.[14] mp 187 °C). LCMS: *m*/*z*=308 (M+1). ^{1}H NMR ($CDCl_3$) δ 9.53 (d, 1H, *J*=7.6 Hz), 9.46 (d, 1H, *J*=7.6 Hz), 8.89 (dd, 2H, *J*=7.6, 1.6 Hz), 8.66 (dd, 2H, *J*=7.6, 1.6 Hz), 7.92 (t, 1H, *J*=7.7 Hz), 7.86 (m, 2H), 7.66–7.47 (m, 4H).

4.2.2. 3-*p*-Chlorophenylphenanthro[9,10-*e*][1,2,4]triazine (21). Yellow needles from DMF, yield 64%, mp 235–237 °C. LCMS: *m*/*z*=342 (M+1), 343 (M+2). MS: *m*/*z*=341 (M^+, 15%), 312 (60%), 176 (100%). IR: 3292, 3070, 2850, 1603, 1503, 1399, 1366, 1298, 1066, 1094, 1012, 820, 760. ^{1}H NMR ($CDCl_3$) δ 9.53 (d, 1H, *J*=7.6 Hz), 9.45 (d, 1H, *J*=8.0 Hz), 8.84 (d, 2H, *J*=8.4 Hz), 8.66 (t, 2H, *J*=6.9 Hz), 7.96 (t, 1H, *J*=7.6 Hz), 7.93–7.82 (m, 3H), 7.63 (d, 2H, *J*=8.4 Hz). ^{13}C NMR (DMSO-d_6) δ 160.7 (C), 145.7 (C), 143.6 (C), 137.7 (C), 135.2 (C), 134.7 (C), 134.1 (CH), 132.3 (CH), 131.9 (C), 130.8 (2CH), 130.4 (2CH), 130.1 (CH), 129.7 (CH), 128.3 (C), 128.0 (C), 127.3 (CH), 125.1 (CH), 125.0 (2CH). Anal. Calcd for $C_{21}H_{12}ClN_3$ (341.8): C 73.80; H 3.54; N 12.29. Found: C 73.88; H 3.68; N 12.27.

4.2.3. 3-*p*-Tolylphenanthro[9,10-*e*][1,2,4]triazine (22). Yellow needles from DMF, yield 56%, mp 187–189 °C. MS: *m*/*z*=321 (M^+, 15%), 293 (90%), 176 (100%). IR: 3067, 3014, 2858, 1607, 1504, 1488, 1404, 1366, 1299, 1063, 1034, 817, 758. ^{1}H NMR ($CDCl_3$) δ 9.52 (dd, 1H, *J*=7.6, 1.6 Hz), 9.45 (d, 1H, *J*=7.6 Hz), 8.77 (d, 2H, *J*=8.2 Hz), 8.63 (m, 2H), 7.94 (t, 1H, *J*=7.6 Hz), 7.91–7.79 (m, 3H), 7.46 (d, 2H, *J*=8.2 Hz), 2.53 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ 166.4, 150.1, 148.2, 147.6, 139.2, 138.7, 138.2, 136.8, 136.4, 135.6, 134.7, 134.4, 133.8, 133.2, 132.8, 132.0, 131.8, 129.6, 128.8, 27.0. Anal. Calcd for $C_{22}H_{15}N_3$ (321.4): C 82.22; H 4.70; N 13.07. Found: C 82.10; H 4.67; N 13.04.

4.3. Pyrolysis reaction conditions: general procedures

Condition A: compound **1** (0.2 g) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar), and placed in the pyrolyzer for 15 min at 500 °C, a temperature that is required for complete pyrolysis of the substrate as indicated by a preliminary HPLC study. The pyrolyzate was then separated by preparative HPLC using an ABZ+column with a solvent mixture of acetonitrile and water (50:50) and the collected fractions were evaporated and subjected to ^{1}H NMR and GC–MS and LCMS studies. Also, the products were separated on column chromatography using Merck Al-silica gel 60 F_{254}, with EtOAc/pet. ether (40–60) (1–15% of EtOAc) to give successively **6** followed by **3**, **5**, and **4**.

Condition B: *pyrolysis of **4** and **20–22** with cyclohexene*. A mixture of each of **4** and **20–22** (1.0 mmol) and cyclohexene (2 mmol) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed, and pyrolyzed as described for compound **1** for 15 min at 500 °C. The product showed by HPLC, ^{1}H NMR, LCMS the formation of compounds **5** and **30–32**, respectively.

Condition C: *pyrolysis of 1,2,4-trizines in the presence of sulfur*. Each of the triazines **1**, **16**, **18**, **20–22** (0.25 g), and sulfur (1.5 mol equiv) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar), and placed in the pyrolyzer for 15 min at 350 °C, a temperature that is required for obtaining the optimum yield of the corresponding thiazole derivatives. After cooling the reaction tube, the product was extracted with $CDCl_3$ and analyzed by ^{1}H NMR and GC–MS and LCMS. The pure products were separated on column chromatography using Merck Al-silica gel 60F_{254}, with EtOAc/pet. ether (40–60) (1–15% of EtOAc).

Condition D: *flash vacuum pyrolysis*. The apparatus used was similar to the one which has been described in our recent publications.[5,6,7a] The sample was volatilized from a tube in a Buchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 700 °C, the temperature being monitored by Pt/Pt-13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap and cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gage situated between the cold trap and pump. Under these conditions the contact time in the hot zone was estimated to be 10 ms. The different zones of the product collected in the U-shaped trap were analyzed by ^{1}H, ^{13}C NMR, IR, and GC–MS. Relative and percent yields were determined from NMR.

4.4. Pyrolysis products

4.4.1. Benzonitrile (2). LCMS: *m*/*z*=104 (M+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[16]

4.4.2. 3-Cyano-5-phenylisothiazole (3). White needles from pet. ether (40–60) (TLC, R_f=0.74, EtOAc/pet. ether 40–60 1:19), mp 90–92 °C. MS: *m*/*z*=186. IR: 3080, 2236, 1595, 1478, 1447, 1380, 1308, 1283, 1075, 977, 852, 827, 760, 696. ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 7.88 (d, 2H, *J*=7.5 Hz), 7.74 (t, 1H, *J*=7.5 Hz), 7.54 (d, 2H, *J*=7.6 Hz). Anal. Calcd for $C_{10}H_6N_2S$ (186.2): C 64.49; H 3.25; N 15.04; S 17.22. Found: C 64.78; H 3.20; N 14.88; S 17.16.

4.4.3. 3-Cyano-5,6-diphenylpyridazine (4). Colorless needles from ethanol (TLC, R_f=0.48, EtOAc/pet. ether 40–60 1:19), mp 138–142 °C. MS: *m*/*z*=257 (M^+, 100%). IR: 2949, 2922, 2220, 1729, 1565, 1528, 1459, 1375, 1347, 1260, 1074, 1027, 876, 802, 750. ^{1}H NMR ($CDCl_3$) δ 8.62 (dd, 2H, *J*=7.4, 1.5 Hz), 8.26 (dd, 2H, *J*=7.4, 1.5 Hz), 7.93 (s, 1H), 7.64–7.54 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 116.8 (CN), 118.0 (CH), 128.0 (2CH), 129.3 (2CH), 129.4 (2CH), 129.9 (2CH), 132.5 (CH), 132.9 (CH), 135.7 (C), 136.7 (C), 142.9 (C), 148.8 (C), 166.5 (C). Anal. Calcd

for $C_{17}H_{11}N_3$ (257.3): C 79.36; H 4.31; N 16.33. Found: C 79.25; H 4.16; N 16.20.

4.4.4. 3,4-Diphenylpyridazine (5). Colorless needles from ethanol (TLC, R_f=0.65, EtOAc/pet. ether 40–60 1:19), mp 105–106 °C (lit.[17] mp 106–107 °C). MS: *m*/*z*=232 (M^+, 100%). IR: 3031, 1549, 1421, 1378, 1347, 1165, 1069, 1023, 837, 745, 687. ^{1}H NMR ($CDCl_3$) δ 8.87 (d, 1H, *J*=5.2 Hz), 8.63 (dd, 2H, *J*=7.8, 1.2 Hz), 8.26 (dd, 2H, *J*=7.8, 1.2 Hz), 7.61 (d, 1H, *J*=5.2 Hz), 7.55 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 115.1 (CH), 127.8 (2CH), 128.9 (2CH), 129.1 (2CH), 129.5 (2CH), 131.3 (CH), 131.6 (CH), 137.5 (C), 138.4 (C), 158.5 (CH), 164.5 (C), 165.2 (C). Anal. Calcd for $C_{16}H_{12}N_2$ (232.3): C 82.73; H 5.21; N 12.06. Found: C 82.65; H 5.16; N 12.00.

4.4.5. 2,5-Diphenylthieno[2,3-*d*]thiazole (6). Yellow plates from acetonitrile (TLC, R_f=0.80, EtOAc/pet. ether 40–60 1:19), mp 235–236 °C. MS: *m*/*z*=293 (M^+, 100%). IR: 3053, 2922, 1628, 1595, 1507, 1454, 1301, 1220, 998, 813, 750, 684. ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, 2H, *J*=7.8, 1.4 Hz), 7.67 (d, 2H, *J*=7.6 Hz), 7.52 (m, 1H), 7.49 (s, 1H), 7.47 (m, 2H), 7.45 (t, 2H, *J*=7.7 Hz), 7.36 (t, 1H, *J*=7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 112.9 (CH), 125.7 (2CH), 126.3 (2CH), 128.0 (CH), 128.8 (2CH), 128.9 (2CH), 130.1 (CH), 132.7 (C), 133.8 (C), 134.3 (C), 145.1 (C), 156.5 (C), 169.2 (C). Anal. Calcd for $C_{17}H_{11}N_2S$ (293.4): C 69.59; H 3.78; N 4.77; S 21.86. Found: C 69.45; H 3.36; N 4.56; S 22.00.

4.4.6. 2-Phenyl-6-*p*-tolylthieno[3,2-*d*]thiazole (17). Yellow plates from ethanol, mp 280–282 °C. LCMS: *m*/*z*=308 (M+1). MS: *m*/*z*=307 (M^+, 100%), 154 (10%), 115 (10%). IR: 3056, 3024, 2954, 2918, 2850, 1633, 1523, 1456, 1303, 1220, 1120, 999, 912, 877, 804, 756, 686. ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, 2H, *J*=8.0, 1.6 Hz), 8.57 (d, 2H, *J*=7.8 Hz), 7.52–7.46 (m, 3H), 7.44 (s, 1H), 7.25 (d, 2H, *J*=7.8 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 148.8 (C), 145.4 (C), 139.4 (C), 138.2 (C), 134.0 (C), 132.7 (C), 131.7 (C), 130.1 (CH), 129.8 (2CH), 129.0 (2CH), 126.4 (2CH), 125.7 (2CH), 112.6 (CH), 21.2 (CH_3). Anal. Calcd for $C_{18}H_{13}N_3S_2$ (307.1): C 70.32; H 4.26; N 4.56; S 20.86. Found: C 70.28; H 4.41; N 4.38; S 20.71.

4.4.7. 2-Phenylbenzothiazole (19). Yellow plates from ethanol, mp 113–114 °C (lit.[18] mp 112–113 °C). LCMS: *m*/*z*=212 (M+1). ^{1}H NMR ($CDCl_3$) δ 8.13 (m, 2H), 8.09 (d, 1H, *J*=8.0 Hz), 7.93 (d, 1H, *J*=8.0 Hz), 7.52 (m, 4H), 7.41 (t, 1H, *J*=7.4 Hz).

4.4.8. 2-Phenylphenanthro[9,10-*d*]thiazole (23). Yellow plates from pet. ether 60–80, mp 150–152 °C. R_f=0.46 (EtOAc/pet. ether 60–80 1:9). LCMS: *m*/*z*=312 (M+1). MS: *m*/*z*=311 (100%), 208 (30%), 156 (15%). IR: 3322, 3236, 3081, 2945, 1723, 1653, 1562, 1418, 1317, 1199, 972, 941, 741. ^{1}H NMR ($CDCl_3$) δ 8.99 (dd, 1H, *J*=7.6, 1.4 Hz), 8.75 (dd, 1H, *J*=7.8, 1.6 Hz), 8.72 (d, 1H, *J*=8.2 Hz), 8.25(d, 2H, *J*=7.6 Hz), 8.08 (dd, 1H, *J*=8.2, 1.6 Hz), 7.77 (m, 2H), 7.69 (m, 2H), 7.57–7.52 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 166.6 (C), 149.7 (C), 133.9 (2C), 130.8 (C), 130.6 (CH), 129.9 (2C), 129.1 (2CH), 128.3 (C), 127.4 (2CH), 127.2 (2CH), 126.9 (CH), 126.7 (CH), 126.1 (CH), 124.9 (CH), 123.8 (CH), 123.1 (CH). Anal. Calcd for $C_{21}H_{13}NS$ (311.4): C 81.00; H 4.21; N 4.50; S 10.30. Found: C 80.88; H 4.21; N 4.58; S 10.11.

4.4.9. 2-*p*-Chlorophenylphenanthro[9,10-*d*]thiazole (24). Yellow plates from ethanol, mp 218–220 °C. R_f=0.60 (EtOAc/pet. ether 60–80 1:8). LCMS: *m*/*z*=346 (M+1), 347 (M+2). IR: 3435, 3232, 3043, 2907, 1632, 1592, 1461, 1393, 1161, 973, 821, 750. ^{1}H NMR ($CDCl_3$) δ 8.97 (dd, 1H, *J*=7.6, 1.6 Hz), 8.76 (dd, 2H, *J*=7.8, 1.6 Hz), 8.19 (d, 2H, *J*=8.4 Hz), 8.07 (dd, 1H, *J*=7.6, 1.6 Hz), 7.78–7.66 (m, 4H), 7.53 (d, 2H, *J*=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ 166.6 (C), 145.4 (C), 138.2 (C), 134.7 (C), 134.4 (C), 133.0 (CH), 131.6 (C), 131.3 (CH), 130.2 (2CH), 129.7 (2CH), 129.2 (CH), 128.6 (CH), 128.4 (C), 128.2 (C), 128.0 (C), 127.0 (CH), 125.4 (CH), 123.6 (CH), 123.5 (CH). Anal. Calcd for $C_{21}H_{12}NSCl$ (345.8): C 72.93; H 3.50; N 4.05; S 9.27. Found: C 72.88; H 3.41; N 4.00; S 9.21.

4.4.10. 2-*p*-Tolylphenanthro[9,10-*d*]thiazole (25). Yellow plates from ethanol, mp 210–212 °C. R_f=0.68 (EtOAc/pet. ether 60–80 1:9). LCMS: *m*/*z*=326 (M+1). MS: *m*/*z*=325 (M^+, 70%), 307 (80%), 293 (30%). IR: 3224, 3045, 2920, 2882, 1723, 1601, 1493, 1467, 1378, 1257, 1113, 1060, 906, 807, 749. ^{1}H NMR ($CDCl_3$) δ 8.99 (d, 1H, *J*=7.5 Hz), 8.74 (m, 2H), 8.14 (d, 2H, *J*=8.4 Hz), 8.07 (m, 1H), 7.76 (m, 2H), 7.69 (m, 2H), 7.36 (d, 2H, *J*=8.4 Hz), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 161.6 (C), 145.4 (C), 143.4 (C), 142.8 (C), 134.5 (C), 133.9 (C, CH), 133.5 (C), 132.1 (2CH), 131.7 (CH), 130.9 (CH), 130.0 (2CH), 129.6 (C), 129.0 (C), 128.5 (CH), 128.1 (CH), 127.2 (CH), 124.9 (2CH), 22.2 (CH_3). Anal. Calcd for $C_{22}H_{15}NS$ (325.4): C 81.20; H 4.65; N 4.30; S 9.85. Found: C 81.08; H 4.48; N 4.30; S 9.81.

4.4.11. *p*-Chlorobenzonitrile (26). LCMS: *m*/*z*=137 (M+1). ^{1}H NMR ($CDCl_3$) δ 7.49 (d, 2H, *J*=8.4 Hz), 7.63 (d, 2H, *J*=8.4 Hz).[19]

4.4.12. *p*-Tolylbenzonitrile (27). MS: *m*/*z*=117 (M^+, 100%). ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 2H, *J*=8.0 Hz), 7.56 (d, 2H, *J*=8.0 Hz).[20]

4.4.13. Biphenyl-2,2′-dicarbonitrile (28). Colorless needles from ethanol, mp 170–172 °C (lit.[21] mp 173–174 °C). LCMS: *m*/*z*=205 (M+1). MS: *m*/*z*=204 (M^+, 100%). IR: 3061, 2969, 2916, 2229, 1663, 1566, 1489, 1449, 1394, 1334, 1230, 1115, 1056, 889, 760, 695. ^{1}H NMR ($CDCl_3$) δ 7.85 (m, 2H), 7.77 (dt, 2H, *J*=7.8, 1.4 Hz), 7.62–7.52 (m, 4H).

4.4.14. Phenanthrene (29). Colorless needles from pet. ether (40–60), mp 98–100 °C (lit.[22] mp 100 °C). MS: *m*/*z*=178 (M^+, 100%). ^{1}H NMR ($CDCl_3$) δ 8.72 (d, 2H, *J*=8.2 Hz), 7.92 (dd, 2H, *J*=7.8, 1.5 Hz), 7.77 (s, 2H), 7.69 (t, 2H, *J*=7.8 Hz), 7.61 (t, 2H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ 122.6 (CH), 126.6 (CH), 126.9 (CH), 128.6 (CH), 129.2 (CH), 130.3 (C), 132.0 (C).

4.4.15. 2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazole (30). Yellow needles from acetonitrile, mp 322–324 °C (lit.[14] mp 325 °C). LCMS: *m*/*z*=295 (M+1). IR (KBr): 3432, 3119, 1611, 1455, 1440, 751, 735. ^{1}H NMR (DMSO-d_6) δ 13.53 (br s, 1H, NH), 8.87 (m, 2H), 8.58 (dd, 2H, *J*=8.2,

1.5 Hz), 8.32 (d, 2H, J=7.4 Hz), 7.73 (m, 2H), 7.67–7.59 (m, 4H), 7.50 (t, 1H, J=7.4). Anal. Calcd for $C_{21}H_{14}N_2$ (294.4): C 85.69; H 5.23; N 9.08. Found: C 85.58; H 5.18; N 9.00.

4.4.16. 2-*p*-Chlorophenyl-1*H*-phenanthro[9,10-*d*]imidazole (31). LCMS: m/z=328 (M+1), 329 (M+2).

4.4.17. 2-*p*-Tolyl-1*H*-phenanthro[9,10-*d*]imidazole (32). Yellow needles from DMF, mp 328–330 °C. LCMS: m/z=309 (M+1). IR: 3326, 3148, 3060, 2956, 1705, 1614, 1483, 1457, 1359, 1280, 1127, 755, 725. ^{1}H NMR (DMSO-d_6) δ 13.39 (br s, 1H, NH), 8.86 (m, 2H), 8.56 (dd, 2H, J=8.0, 1.6 Hz), 8.21 (d, 2H, J=8.0 Hz), 7.76–7.61 (m, 4H), 7.43 (d, 2H, J=8.0 Hz), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 161.1 (C), 142.8 (C), 142.2 (C), 133.9 (C), 133.3 (CH), 132.9 (CH), 131.5 (CH), 131.1 (C), 130.3 (2CH), 130.2 (C), 129.3 (CH), 129.0 (CH), 128.5 (C, 2CH), 127.9 (C), 127.5 (C), 126.6 (CH), 124.6 (CH), 124.3 (2CH), 21.6 (CH_3). Anal. Calcd for $C_{22}H_{16}N_2$ (308.4): C 85.69; H 5.23; N 9.08. Found: C 85.58; H 5.18; N 9.00.

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References and notes

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