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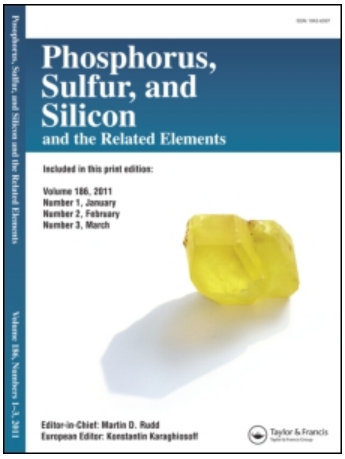


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# NEW ACTIVATION METHOD OF CHLOROENAMINONE QUINONES FOR SYNTHESIS OF POLYNUCLEAR HETEROCYCLIC SYSTEMS

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*The chlorine atom of chloroenamineone in the quinonoid compounds* ***1a–f*** *and* ***7*** *was activated by the reaction with benzenesulphonyl chloride to form naphthoquinonid moiety fused with linear or angular heterocyclic systems as carbazoles* ***2a–c****, phenazines* ***3a,b*** *and* ***5a–c****, phenoxazines* ***3c*** *phenothiazine* ***3d****, quinoxalinophenazine* ***6a****, quinoxalinophenoxazine* ***6b****, quinoxalinophenthiazine* ***6c****, oxadiazine* ***8****, thiadiazine* ***9****, and pyrazole* ***10****. The mechanism of the latter derivative was discussed. Spectroscopic data of all new products are given. Additionally, the antimicrobial activity of some reported compounds was screened.*

*Keywords:* Alkylamino naphthoquinones; heterocyclic naphthoquinones; sulphonylation reaction

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## INTRODUCTION

It is well known that the chlorine atom in chloroenaminone quinones is inert toward nucleophilic substitution reactions.[1,2] Kallmayer and Binger[3–5] reported that acylation or nitrosation reactions of the amino group in this moiety increase the reactivity of the chlorine atom. In this article, we report a new method for activation of this atom by reaction of the amino group with benzenesulphonyl chloride. Interesting heterocyclic quinones containing a sulphonamide group were formed. Analogous quinonoid systems showed excellent anticancer activities.[6–8] On the other hand, the sulphonamide group leads to an increase of the pharmacological activity of the compounds due to in vivo release of this group by metabolic processes.[9–13]

The author thank Dr. Seif-Eldin N. Ayyad for carrying out $^{13}C$ and $^{1}H$-NMR spectra in the Chemistry Department at Minnesota University, Minnesota, USA.

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## RESULTS AND DISCUSSION

2-Chloro-3-(N-arylamino)-1,4-naphthoquinones **1a–f**[14] were used as starting materials. Compounds **1a–c** were smoothly stirred with benzenesulphonyl chloride in the presence of a catalytic amount of triethylamine at room temperature for 5 h to afford the carbazole derivatives **2a–c** with about 80–90% yield. Moreover, linear polynuclear heterocyclic systems as phenazines **3a**,**b**, phenoxazine **3c** and phenothiazine **3d** were immediately achieved by treatment of **1d–f** with benzenesulphonyl chloride in triethylamine respectively (Scheme 1). IR spectra of the products **2a–c** and **3a**,**c**,**d** revealed the absence of NH and C—Cl bands, in addition to the appearance of a sulphonamide band at 1330–1320 $cm^{-1}$. The IR spectrum of **3b** revealed the absence of a C—Cl bond only and the clear appearance of an NH band at 3310 $cm^{-1}$. The $^1H$ NMR spectra of **2a–c** and **3a**,**c**,**d** do not contain signals characteristic for amino groups. The $^1H$ NMR spectrum of **3b** showed a singlet signal at 8.11 ppm due to an NH group. The mass spectra of **2a**,**b** and **3a–c** supported the reported structures. The $^{13}C$ NMR spectrum of **3b** was also consistent with its structure (cf. Experimental part). On the other hand, the cyclized compounds **2d–f** and **3e–g** were not formed when **1a–f** were refluxed for 24 h with triethylamine only. Moreover, **1d** was stirred with concentrated sulfuric acid for 15 h to give the angular phenazine product **4a**, which was reacted subsequently with benzenesulphonyl chloride in triethylamine to give **4b**. The structure of **4a** follows from its IR spectrum which shows an NH band at 3330 $cm^{-1}$ and a strong C—Cl band at 730 $cm^{-1}$. The NH band in the IR spectrum of **4b** disappeared. Instead strong bands at 1330, 1220, and 1630 $cm^{-1}$ due to sulphonamide and C=N groups appeared. The $^{13}C$ and $^1H$ NMR spectra confirmed the structure of **4a**. The mass spectrum of **4b** supported the structure (cf. Experimental part).

Compound **4b** was reacted quickly with *o*-phenylenediamine, *o*-aminophenol and *o*-aminothiophenol in absolute ethanol and a catalytic amount of freshly fused sodium acetate to afford **5a–c** respectively; while **4a** failed to react with these amines under all conditions. The $^1H$-NMR spectra of **5a–c** showed amino protons centered at 10.11–10.54 ppm as singlet signals. Also, the IR spectra of **5a–c** exhibited bands at 3330–3310 due to $NH_2$ groups. The mass spectrum of **5c** showed a molecular ion peak at 509 [$M^+$] and an additional peak of low intensity at 513 [(M + 4), 2%].

Cyclization reactions of **5a–c** with concentrated sulfuric acid gave polynuclear heterocyclic quinones **6a–c**. **6d** was obtained from **6a** under similar conditions as used for the preparation of **4b** from **4a**. The $^1H$ NMR spectra of **6a–c** are consistent with the reported structures. The

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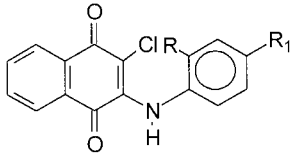
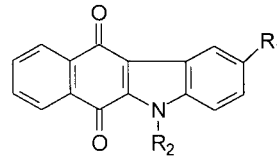


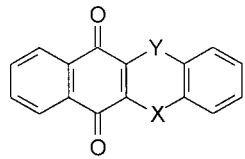
**1**

| | R | $R_1$ |
|---|---|---|
| a | H | H |
| b | H | $CH_3$ |
| c | H | Cl |
| d | $NH_2$ | H |
| e | OH | H |
| f | SH | H |



**2**

| | $R_1$ | $R_2$ |
|---|---|---|
| a | H | $SO_2PH$ |
| b | $CH_3$ | $SO_2Ph$ |
| c | Cl | $SO_2Ph$ |
| d | H | H |
| e | $CH_3$ | H |
| f | Cl | H |



**3**

| | Y | X |
|---|---|---|
| a | $NSO_2Ph$ | $NSO_2Ph$ |
| b | NH | $NSO_2Ph$ |
| c | O | $NSO_2Ph$ |
| d | S | $NSO_2Ph$ |
| e | NH | NH |
| f | O | NH |
| g | S | NH |

**SCHEME 1**

$^{13}C$ NMR spectrum of **6a** and the mass spectrum of **6b** supported also the reported structures (Scheme 2).

Finally, 1,3,4-oxadiazine derivative **8** was accomplished by stirring of the hydrazide derivative **7**[15] with benzenesulphonyl chloride in the presence of triethylamine for 10 h at room temperature. Refluxing of **7** with triethylamine only for 15 h failed to give **8**. Instead the starting material was recovered.

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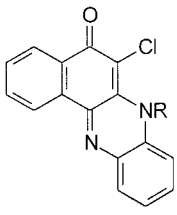
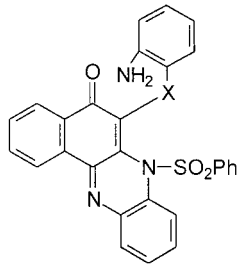


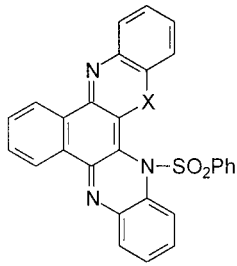

4

| | R |
|---|---|
| a | H |
| b | $SO_2Ph$ |




5

| | X |
|---|---|
| a | NH |
| b | O |
| c | S |




6

| | X |
|---|---|
| a | NH |
| b | O |
| c | S |
| d | $NSO_2Ph$ |

**SCHEME 2**

Compound **8** was subjected to react with phosphorus pentasulfide in xylene for 3 h to give 1,3,4-thiadiazine **9** and the unexpected pyrazole derivative **10**. The formed product **10** can be interpreted in terms of the formation of a 1,3,4-thiadiazine ring with subsequent sulfur-extrusion reaction as shown in the mechanistic consideration (Scheme 3). A similar synthesis type has been reported.[16] The molecular ion peaks in the mass spectra of **8**,**9** and **10** appeared at m/e 430, 446, and 414

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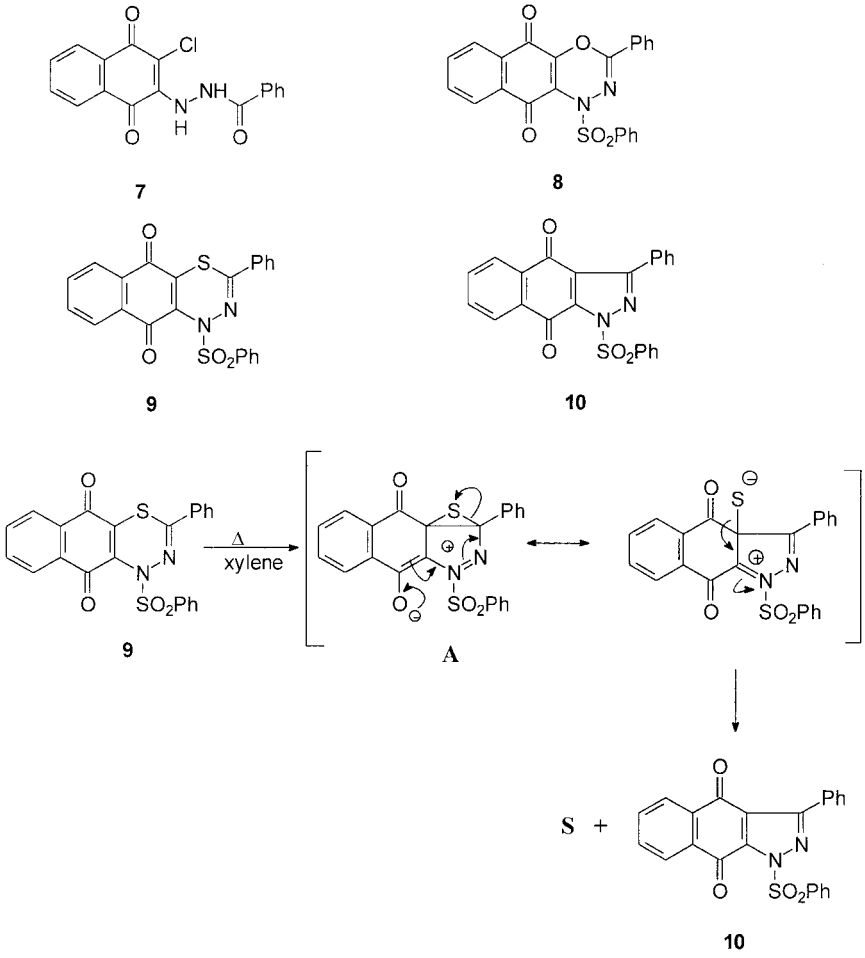


**SCHEME 3**

respectively. The IR spectra of the three compounds **8**,**9** and **10** revealed the absence of NH and C—Cl bonds. Also, the $^{1}H$ NMR spectra of **8–10** showed only the multiplet signals of aromatic protons. The $^{13}C$ NMR spectrum of **9** showed a signal at 165.1 due to $C_2$ of the oxadiazine ring while **10** showed a signal at 134.6 due to $C_3$ of the pyrazole ring (cf. Experimental part).

The above results showed clearly that the formation of **2**,**3**,**5**,**8** and **10** are understandable only in terms of the increasing reactivity of the chlorine atom in the chloroenaminone moiety of the starting material by sulphonylation of the NH group.

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Some newly prepared compounds **2b**,**2c**,**3a**,**4b**,**6a**, and **6b** were tested in vitro for their antimicrobial activity. The microorganisms and the minimum inhibitory concentrations (MIC) in $\mu$g/ml are the following: *Escherichia coli* **2a** 32.2, **2b** 33.1, **3a** 21.7, **3c** 22.8, **4b** 18.1, **6a** 6.3, and **6b** 6.3. A perusal of the literature reveals that, the compounds have a low value of MIC with gram negative bacteria recorded to have antitumor activity.[17] Therefore, the antitumor activity of the compounds **6a**,**b** was investigated in tumor bearing mice. The results shows that these compounds have a relative high toxicity. Maximum tolerance dose is (MTD) = 70, 69 mg/kg body weight respectively.

## EXPERIMENTAL

The purity of the prepared compounds was checked by thin layer chromatography. Melting points were determined using Fisher-Johns apparatus and are not corrected. Infra-red spectra (KBr) were recorded on an SP 2000 Pye-Unicam Spectrophotometer ($\bar{\upsilon}$/cm$^{-1}$). $^1$H NMR spectra were recorded on Varian EM 360 spectrophotometer at 90 MHz using TMS as an internal standard, in $CDCl_3$ or $Me_2SO$-$d_6$, chemical shifts in $\delta$ values (ppm) $^{13}$C NMR spectra at 75 MHz in $CDCl_3$, chemical shifts in $\delta$ values (ppm). Mass spectra were performed on a Varian 111 spectrometer (70 eV). Microanalytical data were determined at microanalytical laboratories in Cairo and Tanta Universities.

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### 2-Alkyl-5-benzenesulphonyl-benzo[b]-5H-carbazole-6,11-dione (2a–c)

To a stirred mixture of **1a–c** (0.01 mmol) and triethylamine (5 ml), benzenesulphonyl chloride (3 ml) was added dropwise with continous smooth stirring for 5 h, cooled, and poured into ice water. The solid that separated was filtered off, washed with water, dried and recrystallized from dioxane to give **2**.

**2a:** m.p. >360°C, 80% yield. IR spectrum ($\bar{\upsilon}$/cm$^{-1}$): 1660, 1645 (2C=O), 1610 (C=C), 1325 ($NSO_2Ph$), 1220 (–$SO_2$–). $^1$H-NMR spectrum ($\delta$/ppm): 7.36–7.78 (br, 13H, Ar). Mass spectrum m/e: 387 [M$^+$] $C_{22}H_{13}NO_4S$ (387.4), Calc. C 68.21, H 3.38, N 8.28, S 3.61. Found C 68.38, H 3.51, N 8.16, S 3.48.

**2b:** m.p. 310°C, 90% yield. IR spectrum ($\bar{\upsilon}$/cm$^{-1}$): 1660, 1650 (2C=O), 1600 (C=C), 1330 ($NSO_2Ph$), 1210 (–$SO_2$–). $^1$H-NMR spectrum ($\delta$/ppm): 1.62 (s, 3H, $CH_3$), 7.15–7.63 (m, 12H, Ar). Mass spectrum m/e: 401 [M$^+$], $C_{23}H_{15}NO_4S$ (401.4), Calc. C 68.81, H 3.77, N 3.49, S 7.99. Found C 68.69, H 3.99, N 3.22, S 8.21.

**2c:** m.p. 360°C, 85% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 1650, 1640 (2C=O), 1625 (C=C), 1320 ($NSO_2Ph$), 1200 (–$SO_{2-}$). $^1$H-NMR spectrum ($\delta$/ppm): 7.22–7.73 (br, 12H, Ar). $C_{22}H_{12}ClNO_4S$ (421.86), Calc. C 62.63, H 2.87, N 3.32, S 7.60. Found C 62.92, H 3.11, N 3.19, S 7.88.

## 5,12-Dibenzenesulphonyl-benzo[b]-5,12-dihydro-phenazine-6,11-dione (3a), 12-Benzenesulphonylbenzo-[b]-5,12-dihydro-phenazine-6,11-dione (3b), 12-Benzenesulphonylbenzo[b]-12H-phenoxazine-6,11-dione (3c) and 12-Benzenesulphonylbenzo[b]-12H-phenothia-zine-6,11-dione (3d)

To a stirred mixture of **1d–f** (0.02 mmol) and triethylamine (5 ml), benzenesulphonyl chloride (3 ml) was added dropwise at room temperature. The formed gummy products were column chromatographed over silica gel using a mixture of benzene and ethyl acetate (5:1) as an eluent to give **3a** and **3b** from reaction of **1d**. Both **3c** and **3d** were obtained as sole products from reaction of **1e** and **1f** respectively.

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**3a:** m.p. 285°C, 80% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3005 (aromatic CH), 1680, 1675 (2C=O), 1580 (C=C), 1320 ($NSO_2Ph$), 1210 (–$SO_{2-}$). $^1$H-NMR spectrum ($\delta$/ppm): 7.11–7.56 (m, 8H, $H_1$-$H_{10}$), 7.62–798 (br, 10H, $SO_2Ph$). Mass spectrum m/e: 542 [$M^+$]. $C_{28}H_{18}N_2O_6S_2$ (542.6), Calc. C 61.98, H 3.34, N 5.17, S 11.82. Found C 62.12, H 3.53, N 4.93, S 12.12.

**3b:** m.p. 260°C, 10% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3310 (NH), 3000 (aromatic CH), 1675, 1670 (2C=O), 1580 (C=C), 1315 ($NSO_2Ph$), 1220 ($SO_2$), 1100 (C–N–C). $^1$H-NMR spectrum ($\delta$/ppm): 7.21–7.46 (m, 8H, $H_1$-$H_{10}$), 7.58–7.87 (br, 5H, –$SO_2Ar$), 8.11 (s, 1H, NH). $^{13}$C-NMR ($\delta$/ppm): 186.3, 186.1, 149.9, 149.7, 146.7, 146.7, 145.9, 133.4, 131.8, 131.2, 130.8, 124.6, 124.4, 123.5, 123.1, 122.6, 122.3, 121.9, 121.3, 121.0, 120.8. Mass spectrum m/e: 402 [$M^+$]. $C_{22}H_{14}N_2O_4S_2$ (402.4), Calc. C 65.66, H 3.51, N 6.96, S 7.97. Found C 65.36, H 3.69, N 7.23, S 8.19.

**3c:** m.p. 246°C, 85% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3010 (aromatic C–H), 1680, 1670 (2C=O), 1580 (C=C), 1330 ($NSO_2Ph$), 1220 (–$SO_{2-}$), 1220 (C–N–C), 1050 (cyclic C–O–C). Mass spectrum m/e: 403 [$M^+$]. $C_{22}H_{13}NO_5S$ (403.4), Calc. C 65.50, H 3.25, N 3.47, S 7.95. Found C 65.39, H 3.50, N 3.32, S 8.20.

**3d:** m.p. 239°C, 80% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3000 (aromatic C–H), 1675, 1670 (2C=O), 1575 (C=C), 1320 ($NSO_2Ph$), 1210 (–$SO_{2-}$), 1110 (C–S–C). $^1$H-NMR spectrum ($\delta$/ppm): 7.20–7.51 (br, 8H, $H_1$-$H_{10}$), 7.61–7.89 (br, 5H, $SO_2Ph$). $C_{22}H_{13}NO_4S_2$ (419.5), Calc. C 62.99, H 3.12, N 3.34, S 15.29. Found C 63.19, H 2.93, N 3.56, S 15.08.

## 6-Chloro-benzo[a]-7H-phenazine-5-one (4a)

To **1d** (0.01 mmol) concentrated sulfuric acid (6 ml, d 1.84) was added with stirring for 15 h. The resulting solution was poured into crushed ice and brought to pH 5 by addition of ammonia. The solid was collected, washed with water, and recrystallized from benzene to give **4a**.

m.p. 250–252°C, 60% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3330 (NH), 1680 (C=O), 1630 (C=N), 730 (C–Cl). $^1$H-NMR spectrum ($\delta$/ppm): 7.11–7.45 (m, 4H, $CH_8$–$CH_{11}$), 7.53–7.99 (m, 4H, $CH_1$–$CH_4$), 10.54 (s, 1H, NH) slowly exchanged with $D_2O$. $^{13}$C NMR ($\delta$/ppm): 186.3, 152.9, 148.4, 144.6, 135.2, 134.4, 133.1, 132.7, 130.6, 130.2, 125.5, 125.3, 124.6, 117.3, 116.4, 104.5. $C_{16}H_9ClN_2O$ (280.71), Calc. C 68.46, H 3.23, N 9.98. Found C 68.17, H 3.39, N 10.21.

## 7-Benzenesulphonyl-6-chloro-benzo[a]-7H-phenazine-5-one (4b)

To a mixture of **4a** (0.01 mmol) and triethylamine (5 ml), benzenesulphonyl chloride (3 ml) was added dropwise at room temperature with stirring for 3 h. The reaction mixture was left to stand overnight, then poured into ice-cold water. The precipitated solid was filtered off and crystallized from benzene to give **4b**.

m.p. 275°C, 50% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 1680 (C=O), 1630 (C=N), 1330 ($NSO_2Ph$), 1220 (–$SO_2$–), 1200 (C–N–C). $^1$H-NMR ($\delta$/ppm): 7.13–7.48 (br, 8H, $H_1$–$CH_{11}$), 7.67–7.96 (m, 5H, –$SO_2$–Ar–H). Mass spectrum m/e: 421 [$M^+$]. $C_{22}H_{13}ClN_2O_3S$ (420.87), Calc. C 62.78, H 3.11, N 6.66, S 7.62. Found C 62.87, H 3.32, N 6.41, S 7.55.

## 7-Benzenesulphonyl-6-[substituted]-benzo[a]-7H-phenazine-5-one (5a–c)

To a stirred mixture of **4b** (0.01 mmol) and anhydrous sodium acetate (0.02 mmol) in absolute ethanol (50 ml), an arylamine derivative (0.01 mmol) was added with continuous stirring. When the color of the reaction mixture turned dark, it was heated under reflux for 4 h cooled, and left overnight. The solid was filtered, washed well with hot water, and finally with aqueous ethanol, and crystallized from ethanol to give **5**.

**5a:** m.p. 272°C, 60% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3330, 3310 ($NH_2$, NH), 1670 (C=O), 1660 (C=N), 1320 ($NSO_2Ph$), 1210 (–$SO_2$–), 1200 (C–N–C). $^1$H-NMR spectrum ($\delta$/ppm): 7.01–7.46 (m, 12H, NAr–H), 7.62–7.85 (br, 5H, $SO_2$Ar–H), 10.54 (br, 3H, $NH_2$, NH). $C_{28}H_{20}N_4O_3S$ (492.48), Calc. C 68.28, H 4.08, N 11.37, S 6.53. Found C 68.07, H 3.89, N 11.51, S 6.39.

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**5b:** m.p. 228°C, 50% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3320 ($NH_2$), 1680 (C=O), 1640 (C=N), 1330 ($NSO_2Ph$), 1220 (–$SO_2$–), 1200 (C–O–C). $^1$H-NMR spectrum ($\delta$/ppm): 7.23–7.64 (br, 12H, NAr–H), 7.81–7.93 (m, 5H, $SO_2Ar$–H), 10.51 (s, 2H, $NH_2$). $C_{28}H_{19}N_3O_4S$ (493.50), Calc. C 68.14, H 3.88, N 8.51, S 6.50. Found C 68.40, H 4.02, N 8.32, S 6.31.

**5c:** m.p. 236°C, 70% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3310 ($NH_2$), 1680 (C=O), 1630 (C=N), 1320 ($NSO_2Ph$), 1210 (–$SO_2$–), 1210 (C–S–C). $^1$H-NMR spectrum ($\delta$/ppm): 7.76–7.89 (m, 5H, $SO_2Ar$–H), 10.11 (s, 2H, $NH_2$). Mass spectrum m/e: 509 [$M^+$]. $C_{28}H_{19}N_3O_3S_2$ (509.58), Calc. C 65.99, H 3.76, N 8.25, S 12.58. Found C 66.21, H 3.68, N 8.35, S 12.72.

## 6-Benzenesulphonyl-benzo[a]-6H-quinoxalino-[3,2-c]phenazine (6a), 6-Benzenesulphonyl-6H-benzo-[a]quinoxalino[3,2-c]phenoxazine (6b) and 6-Benzenesulphonylbenzo[a]6H-quinoxalino[3,2-c]-phenothiazine (6c)

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A mixture of **5a–c** (0.01 mmol) and concentrated sulfuric acid (10 ml) was stirred for 4 h. The mixture was treated with sodium bicarbonate solution, the precipitated solid was filtered. The residue was washed with water and crystallized from benzene to give **6a–c**.

**6a:** m.p. 360°C, 40% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 3310 (NH), 2900 (Ar–CH), 1630, 1620 (2C=N), 1600 (C=C), 1380 (C–N–C), 1320 ($NSO_2Ph$). $^1$H-NMR spectrum ($\delta$/ppm): 7.05–7.23 (br, 12H, Ar–H), 7.35–8.14 (m, 5H, $SO_2Ph$), 10.33 (s, 1H, NH). $^{13}$C-NMR ($\delta$/ppm): 149.8, 149.3, 146.7, 146.3, 142.7, 142.1, 136.4, 136.2, 134.8, 134.5, 134.1, 131.2, 130.6, 130.2, 130.0, 125.8, 125.7, 125.5, 124.9, 121.3, 121.1, 120.8, 125.3, 124.7, 124.6, 122.7. $C_{28}H_{18}N_4O_2S$ (474.52), Calc. C 70.87, H 3.82, N 11.81, S 6.76. Found C 71.07, H 4.09, N 12.03, S 6.92.

**6b:** m.p. 256°C, 60% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 2880 (Ar–CH), 1640, 1625 (2C=N), 1600 (C=C), 1330 ($NSO_2Ph$), 1200 (C–O–C). $^1$H-NMR ($\delta$/ppm): 7.12–7.43 (br, 12H, Ar–H), 7.55–7.91 (m, 5H, $SO_2Ar$–H). Mass spectrum m/e: 476 [$M^+$]. $C_{28}H_{17}N_3O_3S$ (475.51), Calc. C 70.72, H 3.61, N 8.84, S 6.74. Found C 70.59, H 3.88, N 9.02, S 6.51.

**6c:** m.p. 287°C, 35% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 2995 (Ar–CH), 1635, 1630 (2C=N), 1610 (C=C), 1320 ($NSO_2Ph$), 1205 (C–S–C). $^1$H-NMR ($\delta$/ppm): 7.23–7.45 (br, 12H, Ar–H), 7.49-7.92 (m, 5H, $SO_2Ar$–H). $C_{28}H_{17}N_3O_2S_2$ (491.57), Calc. C 68.40, H 3.49, N 8.55, S 13.05. Found C 68.23, H 3.68, N 8.80, S 12.79.

## 6,7-Dibenzenesulphonyl-6,7-dihydro-benzo[a]quinoxalino[3,2-c]phenazine (6d)

**6d** was prepared as mentioned above in the preparation of **4b**.

m.p. >360°C, 30% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 2930 (Ar—CH), 1630, (C=N), 1600 (C=C), 1320 ($NSO_2Ph$), 1210 (—$SO_{2^-}$). $^1$H-NMR ($\delta$/ppm): 7.11–7.34 (m, 12H, Ar—H), 7.55–8.26 (m, 10H, $SO_2Ar$—H). Mass spectrum m/e: 615 [M$^+$]. $C_{34}H_{22}N_4O_4S_2$ (614.68), Calc. C 66.43, H 3.61, N 9.12, S 10.43. Found C 66.29, H 3.82, N 8.97, S 10.32.

## 4-Benzenesulphonyl-2-phenyl-naphtho[2,3-e]-1,3,4-oxadiazine-5,10-dione (8)

To a solution of **7** (0.01 mmol) in DMF (20 ml), triethylamine (5 ml), and benzenesulphonyl chloride (3 ml) were added dropwise. The mixture was refluxed with stirring for 10 h and left overnight. The precipitated solid was filtered, washed well with water, dried, and recrystallized from ethanol to give **8**.

m.p. 241–243°C, 65% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 1680, 1660 (2C=N), 1320 ($NSO_2Ph$), 1210 (—$SO_{2^-}$), 1200 (C—O—C). $^1$H-NMR ($\delta$/ppm): 7.12–8.13 (br, 14H, Ar—H). Mass spectrum ($\delta$/ppm): 430 [M$^+$]. $C_{23}H_{14}N_2O_5S$ (430.43), Calc. C 64.18, H 3.27, N 6.51, S 7.45. Found C 63.97, H 3.38, N 6.40, S 7.63.

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## 4-Benzenesulphonyl-2-phenyl-naphtho[2,3-e]-1,3,4-thiadiazine-5-,10-dione (9), 1-Benzenesulphonyl-3-phenylnaphtho[2,3-d]pyrazole-4,9-dione (10)

To a solution of **8** (0.01 mmol) in xylene (50 ml), phosphorus pentasulfide (0.02 mmol) was added. The mixture was boiled under reflux for 3 h, and the mixture was then filtered while hot and allowed to cool. The solid was filtered off, dried, and crystallized from xylene to give **9**. The filtrate was concentrated by evaporation. The solid that separated was crystallized from dioxane to give **10**.

**9:** m.p. >360°C, 40% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 1680, 1660 (2C=N), 1330 ($NSO_2Ph$), 1260 (C—S—C). $^{13}$C NMR ($\delta$/ppm): 186.3, 186.1, 165.1, 149.8, 149.6, 146.5, 145.9, 133.2, 130.2, 129.7, 128.8, 128.6, 128.3, 128.2, 127.6, 127.2, 126.9, 126.5, 125.8, 125.5, 125.1. Mass spectrum m/e: 446 [M$^+$]. $C_{23}H_{14}N_2O_4S_2$ (446.49), Calc. C 61.87, H 3.16, N 6.28, S 14.36. Found C 61.69, H 3.36, N 6.09, S 14.18.

**10:** m.p. 210°C, 30% yield. IR spectrum ($\bar{\nu}$/cm$^{-1}$): 1660 (C=O), 1620 (C=N), 1580 (C=C), 1320 ($NSO_2Ph$). $^1$H-NMR ($\delta$/ppm): 7.00–7.56 (m, 14H, Ar—H). $^{13}$C NMR ($\delta$/ppm): 186.5, 186.2, 149.9, 149.6, 146.4, 145.8, 134.6, 132.7, 130.2, 130.0, 129.8, 128.7, 128.4, 128.3, 128.1, 127.8, 127.5, 127.1, 126.7, 125.9, 124.8, 124.5. Mass spectrum m/e: 414 [M$^+$]. $C_{23}H_{14}N_2O_4S$ (414.43), Calc. C 66.65, H 3.40, N 6.76, S 7.74. Found C 66.91, H 3.62, N 7.01, S 7.52.

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