Studies in the Heterocyclic Series. XX. 1,4-Diazaphenoxazine and Related Compounds

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As part of our program on the synthesis of new psychotropic agents, the parent rings of two diazaphenoxazines are described. The reaction of 2-aminophenol and 2,3-dichloropyrazine in alkaline media gave good yields of 1,4-diazaphenoxazine. Replacement of 2,3-dichloropyrazine with 2,3-dichloroquinoxaline gave on the other hand the heterocycle, 1,4-diazabenzo[*b*]phenoxazine. Nitration and *S*-oxide formation were achieved by reaction with mixed nitric and sulfuric acids. Mechanistic pathways to these compounds were also discussed.

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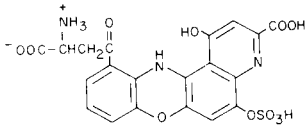
In continuation of our search for pharmaco-active compounds in the phenothiazin class (1-3), we have recently undertaken a study of the aza-analogs of the related phenoxazine. Previous work in this area was concerned mainly with side chain derivatives (4) and the naturally occurring phenoxazines (5). Much of what we know today as natural products derived from phenoxazine ring skeleton are essentially the works of Cavil (6), Butenandt (7), Waksmann (8), Brockmann (9) and Nair (10). From these reports, four classes of natural compounds in these series have emerged. Representative examples are Ommatin D (**1**), cinnabarin (**2**), questiomycin A (**3**) and Actinomycin C (**4**).



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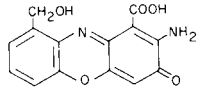

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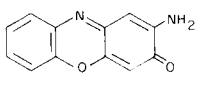
Ommatin D (11) is a red-brown pigment isolated from the small tortoise-shell butterfly, *Vanessa urticae* while cinnabarin is yet another red pigment extracted, this time, from the woodrotting fungi, *Coriolus sanguineus* and *Trametes cinnabarina* (6,12). Questiomycin A (10,13), isolated from the leaves of *Tecoma stans* has no defined uses in contrast to actinomycin C which is an antibiotic produced by species of the genus, *Streptomyces* (14).



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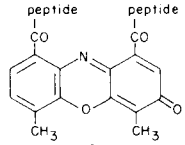

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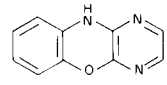
With the exception of the actinomycin antibiotics which have antibacterial and antitumor activities (15), these naturally occurring phenoxazines and phenoxazones are not particularly useful compounds.

Interest in the naturally occurring phenoxazines has as a result declined considerably giving way to a more systematic synthesis of phenoxazine analogs modeled after the biologically active azaphenothiazines (16-22). The synthesis of 1-aza- (23), 2-aza- (24), 3-aza- (25), 4-aza- (26), 3,4-diaza- (27), 1,9-diaza- (28-29), 1,4-diaza- (30) and 1,4,9-triazabenzo[*b*]phenoxazine (31) ring systems have so far been reported. The preparation of the parent rings has been successful in only three cases, namely 1,3-diaza- (25), 1,9-diaza (28,29) and 1,4,9-triazabenzo[*b*]phenoxazines (31). 1,4-Diazaphenoxazine derivatives which are substituted in the 2- and 3- positions were reported in the recent patent literature (30) as having pesticidal, herbicidal and anthelmintic properties. No report, however, was made on the parent compound of this heterocycle. As a continuation of this study we wish to report therefore the successful synthesis of 1,4-diazaphenoxazine (**5**), and 1,4-diazabenzo[*b*]phenoxazine, and their derivatives.



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6

2-Chloropyrazine was converted to 2,3-dichloropyrazine (**6**) by the action of excess sulfuryl chloride in *N,N*-dimethylformamide (DMF) as the solvent (32). When the resulting product was treated with the sodium salt of 2-aminophenol in aqueous *N,N*-dimethylacetamide (DMAC), a creamy white solid melting at 161-162° was isolated after workup. Elemental analysis and molecular weight determination by mass spectroscopy are in agreement with the molecular formula $C_{10}H_7N_3O$. The infrared bands at 3400 (10-NH), 735 (1,2-disubstituted benzene ring) and 1234 cm^{-1} (=C-O-C= of diaryl ethers) (33) are also consistent with the tricyclic structure, **5** (34). Confirmatory evidence was provided by the ^{1}H-nmr spectrum which showed proton signals at τ 1.70 (10-NH) and 3.27 (aromatic protons).

When 2,3-dichloropyrazine (**6**) was replaced with 2,3-dichloroquinoxaline **7**, R = H, a compound identified as 1,4-diazabenzo[*b*]phenoxazine, **8**, R = H (35), was ob-

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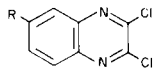
tained. Thus, contrary to the product reported by Kehrmann and Bener (34) in acidic media, a benzo derivative of 1,4-diazaphenoxazine (**8**, R = H) was identified.



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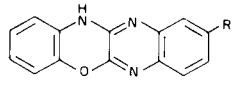

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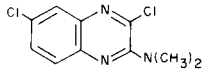
The action of 2,3,6-trichloroquinoxaline (**7**, R = Cl) on 2-aminophenol in aqueous DMF in the presence of near stoichiometric amounts of potassium hydroxide gave two products A and B. Compound A is a greenish yellow, light crystalline material melting at 79-80°. Microanalysis and mass spectroscopy are in agreement with the molecular formula, $C_{10}H_9Cl_2N_3$. Infrared and ^{1}H-nmr data agree with structures **9** and **10**. No product other than the triaza-



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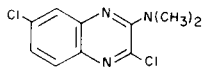

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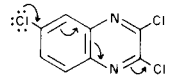
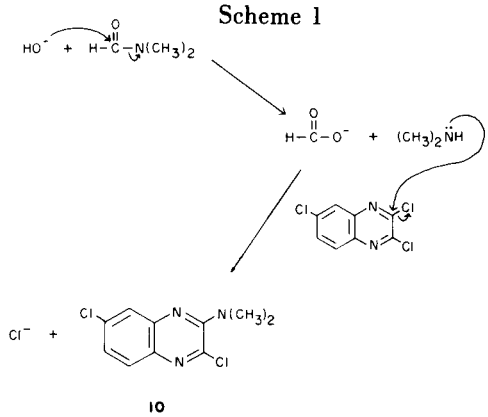
benzophenoxazine, **8**, R = H, was obtained by reacting 2-aminophenol with 2,3-dichloroquinoxaline under similar conditions showing that the +R effect of 6-chlorine atom in structure **7**, R = Cl is the factor responsible for the formation of a second product. It therefore means that the preferred structure of product A is **10** and not **9** because the C-Cl bond in C-2 is strengthened by the +R effect



7 R = Cl

of 7-chlorine atom. This means that the 3-carbon centre will be more susceptible to nucleophilic attack. In the reflux condition that was employed, *N,N*-dimethylformamide was hydrolysed in the aqueous alkaline solution releasing dimethylamine. The dimethylamine thus produced then attacks the more nucleophilic centre, C-3, leading to the formation of 2,6-dichloro-3-[*N,N*-dimethylamino]-quinoxaline, **10**, as shown in Scheme 1.

Scheme 1



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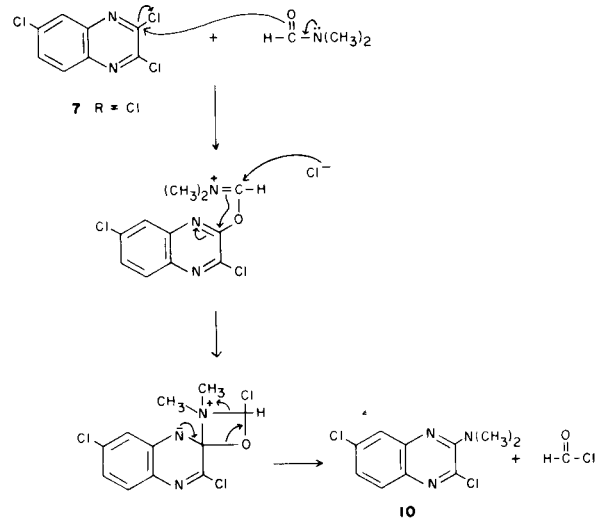
An alternative mechanism involving a nucleophilic attack of the 3-carbon centre by the carbonyl oxygen of the *N,N*-dimethylformamide (36) was also proposed. However,

Scheme 2



7 R = Cl

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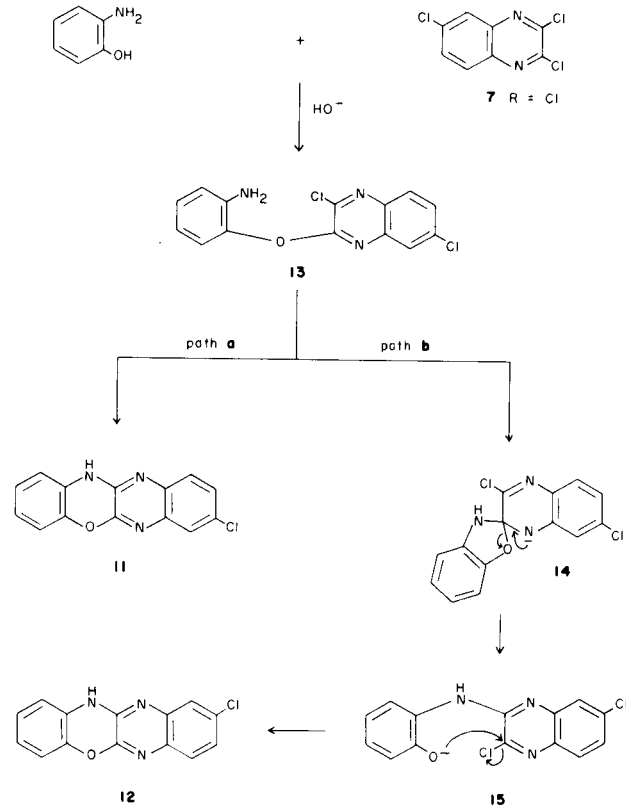
as there was copious evolution of dimethylamine all through the reflux period, this mechanism is untenable. This alternative route (Scheme 2) could have been considered plausible if the reaction were carried out in the absence of potassium hydroxide.

Scheme 3



7 R = Cl

13

path a path b

11

14

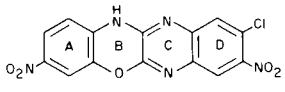
12

15

The second product, B, is a greenish yellow powder melting above 300°. Elemental and mass spectral analyses are in agreement with the molecular formula, $C_{14}H_8ClN_3O$. Infrared, ultraviolet and ^{1}H-nmr spectroscopy are consistent with either 3-chloro- (**11**) or 2-chloro-1,4-diazabenzo-[*b*]phenoxazine (**12**) formed according to routes **a** and **b** in Scheme 3.

In the alkaline medium, the first product formed is the phenylquinoxalinyl ether **13** which reacts further through one of two pathways. In path **a**, cyclization took place directly without rearrangement leading to structure **11**. According to path **b**, compound **13** undergoes a Smiles rearrangement (6, 37-39) leading to the spiro intermediate **14** which rearranges to the phenylquinoxalinyl amine **15** followed by cyclization and formation of compound **12** that is isomeric with structure **11**.

In order to determine the correct structure, product B was treated with mixed concentrated nitric and sulfuric acids at room temperature. A dinitro derivative of molecular formula $C_{14}H_6ClN_5O_5$ was obtained in a good yield. The infrared spectrum of this product gave strong peaks at 1350 (Ar-NO_2), 895 (1,2,4,5-tetrasubstituted ring D), 820 cm^{-1} due to 1,2,4-trisubstitution on ring A. The very strong band at 745 cm^{-1} in the starting material due to 1,2-disubstitution (40) on ring A disappeared. These spectral features show that the structure of the nitration product is **16** and not **17**.



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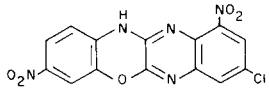

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This structure is also consistent with the results obtained during the nitration of phenoxazine (24) and the related phenothiazine (31, 41-42). Having established that the nitration product is 12-chloro-7,13-dinitro-1,4-diazabenzo-[*b*]phenoxazine, **16**, the precursor is therefore 12-chloro-1,4-diazabenzo[*b*]phenoxazine, **12** which is the product B.

EXPERIMENTAL

Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Uv and visible spectra were recorded on a Pye Unican SP 8000 spectrophotometer using matched 1 cm quartz cells. The solvent is methanol and the absorption maxima are always given in nanometers; the figures in parenthesis are log ϵ values. Ir spectra were obtained on a Perkin Elmer Model 137 spectrophotometer using potassium bromide discs unless otherwise stated. ^{1}H-nmr spectra were determined on a Varian Associates T-60 instrument. Chemical shifts are reported in the τ scale relative to TMS used as an internal standard. The letters b, s, d, t, q, sh and m are used to indicate broad, singlet, doublet, triplet, quartet, shoulder and multiplet respectively. The mass spectra were obtained on an AEI MS-9 double-focusing mass spectrometer at 70 eV.

2-Aminophenol.

2-Aminophenol used for these reactions was repurified by recrystallization (twice) from ethanol after treatment with activated charcoal. Glistening colourless plates of 2-aminophenol were obtained and preserved in a brown bottle wrapped with aluminium foil and kept in a desiccator.

2,3-Dichloropyrazine (**6**).

2-Chloropyrazine (4 ml) was converted to 2,3-dichloropyrazine in 80% yield by the action of sulfuryl chloride in DMF as reported earlier (43). Purification was achieved this time by extraction with chloroform followed by fractional distillation *in vacuo*. This led to a more pure product which was used for the next stage of the reaction, bp 126-129°, literature (44) mp 23-24°, bp 125-130°.

2,3-Dichloroquinoxaline (**7**, R = H).

This compound was prepared from 2,3-dihydroxyquinoxaline by the action of phosphorus oxychloride and phosphorus pentachloride as reported previously (44). Recrystallization from aqueous DMF gave glistening white needles of 2,3-dichloroquinoxaline.

2,3,6-Trichloroquinoxaline (**7**, R = Cl).

4-Chloro-*o*-phenylenediamine was reacted with excess ethyl oxalate as was reported earlier for 2,3-dihydroxyquinoxaline (45). The resulting 6-chloro-2,3-dihydroxyquinoxaline was converted to 2,3,6-trichloroquinoxaline in 69% yield by refluxing with phosphorus pentachloride and phosphorus oxychloride as previously described; mp 143-144°.

1,4-Diazaphenoxazine (**5**).

Purified 2-aminophenol (5.46 g, 50 mmoles) was placed in the reaction flask containing 4 g (100 mmoles) of sodium hydroxide in 50 ml of water. The mixture was warmed until the materials dissolved. Freshly prepared 2,3-dichloropyrazine (10.43 g) (70 mmoles) in 50 ml of DMAC was added in drops during a period of 15 minutes. The entire mixture was refluxed (46) with stirring for 4 hours. It was later poured into a beaker, diluted with water to the 500 ml mark and cooled.

On filtering, the unreacted 2-aminophenol (0.7 g, 6.4 mmoles) was first recovered and recrystallized from ethanol (Norit A); mp 176-177°.

The filtrate after collecting impure 2-aminophenol was further chilled, filtered and the residue crystallized from aqueous DMF after treatment (twice) with Norit A. Glistening creamy-white plates of 1,4-diazaphenoxazine (4.81 g, 52% yield) were obtained; mp 161-162°; uv: λ max 297 (3.7576); ir (potassium bromide): ν max 3400, 3336, 3072, 1646, 1614, 1553, 1520, 1506, 1465, 1400, 1310, 1300, 1265, 1234, 1195, 1170, 1130, 1070, 1060, 1025, 945, 880, 850, 778, 760, 735, 640 cm^{-1}; ^{1}H-nmr (DMSO-d_6): τ 3.27 (multiplet, area 6) (aromatic protons), 1.70 (singlet, area 1) (10-NH); ms: m/e (relative intensity) 91 (11), 92 (8), 93 (6), 94 (2), 131 (23), 158 (25), 185 (M^+, 100%), 186 (13), 187 (2).

Anal. Calcd. for $C_{10}H_7N_3O$: C, 64.87; H, 3.78; N, 22.70. Found: C, 65.00; H, 3.87; N, 22.61.

1,4-Diazabenzo[*b*]phenoxazine (**8**, R = H).

To a solution of 4 g (71 mmoles) of potassium hydroxide in 50 ml of water, 5.00 g (46 mmoles) of 2-aminophenol and 30 ml of DMF were added. The entire mixture was warmed until it dissolved and 5.97 g (30 mmoles) of 2,3-dichloroquinoxaline **7**, R = H, was added slowly during 10 minutes. The hot mixture was refluxed on a heating mantle for 3 hours. Brown precipitate occurred followed by a scanty oily brown product which appeared after about 20 minutes. The amount of oil increased as refluxing continued and was followed by considerable darkening of the reaction mixture.

At the end of the reflux period, the mixture was poured into a beaker and cooled overnight. The oil which solidified was collected by filtration. The residue was washed thoroughly with boiling methanol to remove unreacted 2,3-dichloroquinoxaline.

The washed residue was crystallized from methanol-DMF mixture after treatment with activated charcoal to give 5.85 g (83% yield) of 1,4-diazabenzo[*b*]phenoxazine **8**, R = H, as glistening yellow crystalline powder, mp > 300°; this product gave a bluish-green fluorescence in toluene, methanol, ethanol, benzene, DMAC, and DMF solutions; uv: λ max 380 (4.4502), 298 (4.1116), 275 (4.1116), 234 (5.0363); ir (potassium bromide): ν max 3400, 1610, 1574, 1557, 1527, 1500, 1490, 1460, 1450, 1384, 1333, 1303, 1290, 1270, 1245, 1230, 1200, 1140, 1106, 1025, 940,

920, 875, 780, 764, 742, 720 cm^{-1}; ^{1}H-nmr (DMSO-d$_6$): τ 3.08 (singlet, area 4) (ring A protons), 2.55 (singlet, area 4) (ring D protons) −0.37 (very broad, area 1) (10-NH); ms: m/e (relative intensity) 70 (4), 73 (2), 76 (5), 77 (3), 78 (4), 79 (8), 82 (2), 89 (1), 90 (10), 91 (3), 92 (1), 95 (2), 102 (6), 103 (3), 104 (2), 117 (2), 118 (4), 130 (1), 144 (1), 179 (2), 180 (1), 181 (1), 206 (6), 207 (2), 234 (8), 235 [M$^+$, 100%], 236 (21), 237 (2).

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.49; H, 3.83; N, 17.87. Found: C, 71.21; H, 3.80; N, 17.80.

12-Chloro-1,4-diazabenzo[*b*]phenoxazine (**8**, R = Cl).

A mixture of 6.98 g (64 mmoles) of 2-aminophenol, 7 g of potassium hydroxide and 100 ml of water was warmed until it dissolved. Dimethylformamide (DMF) (50 ml) and 9.34 g (40 mmoles) of 2,3,6-trichloroquinoxaline were later added. The mixture was refluxed with a heating mantle with constant stirring for 3 hours. After about 5 minutes of refluxing the largely non-homogeneous dark mixture gave a very dark solution followed by massive precipitation of a greenish yellow material. The precipitate gave a light dark green solution.

The reaction mixture was poured into a beaker containing 400 ml of water. The mixture was cooled overnight, filtered and the residue crystallized from aqueous DMAC after treatment with Norit A. 12-Chloro-1,4-diazabenzo[*b*]phenoxazine **8**, R = Cl (7.76 g, 72% yield) was obtained as greenish yellow powder, mp > 300°; uv: λ max 236 (4.6019), 275 (3.4934), 385 (3.9311); ir (potassium bromide): ν max 3270, 3060, 3034, 1638, 1612, 1580, 1529, 1514, 1502, 1490, 1466, 1443, 1410, 1396, 1332, 1310, 1292, 1270, 1248, 1220, 1207, 1200, 1114, 1073, 1032, 954, 930, 922, 883, 860, 843, 825, 820, 798, 770, 745, 724, 690 cm^{-1}; ^{1}H nmr (DMSO-d$_6$): τ 3.55 (6-H, 7-H, 8-H, 9-H), 2.90 (11-H, 13-H, 14-H), 0.83 (very broad, 10-NH); ms: m/e (relative intensity) 104 (7), 105 (8), 149 (100), 151 (11), 212 (10), 269 (74, M$^+$), 270 (2) 271 (M$^+$, + 2, 24).

Anal. Calcd. for $C_{14}H_8ClN_3O$: C, 62.34; H, 2.97; Cl, 13.17; N, 15.58. Found: C, 62.70; H, 3.15; Cl, 13.18; N, 15.47.

2,6-Dichloro-3-(*N,N*-dimethylamino)quinoxaline (**10**).

From the reaction of 2-aminophenol and 2,3,6-trichloroquinoxaline in the presence of potassium hydroxide and aqueous DMAC described above the first product that was obtained from crystallization with aqueous DMAC was 12-chloro-1,4-diazabenzo[*b*]phenoxazine (**8**, R = Cl). The aqueous DMAC filtrate, after collecting product **8**, R = Cl, was chilled further for several days at −10° and filtered. The product was recrystallized twice from methanol-DMF mixture and after treatment with activated charcoal to give 1.53 g of 2,6-dichloro-3-(*N,N*-dimethylamino)quinoxaline, **10**, (6.3 mmoles, 16% yield), mp 78-79°; uv: λ max 219 (5.0274), 264 (4.7640), 369 (4.3838); ir (potassium bromide): ν max 2940, 1602, 1560, 1544, 1535, 1480, 1460, 1400, 1359, 1396, 1280, 1232, 1205, 1170, 1130, 1064, 1050, 955, 913, 870, 820, 772, 743, 726, 698, 680 cm^{-1}; ^{1}H-nmr (DMSO-d$_6$): τ 6.90 (singlet, area 6) (3-N(CH$_3$)$_2$), 2.40 (multiplet, area 2) (7-H, 8-H), 2.30 (singlet, area 1) (5-H).

Anal. Calcd. for $C_{10}H_9Cl_2N_3$: C, 49.59; H, 3.72; Cl, 29.34. N, 17.36. Found: C, 49.65; H, 3.75; Cl, 29.09; N, 17.24.

12-Chloro-7,13-dinitro-1,4-diazabenzo[*b*]phenoxazine (**16**).

To 28 ml of concentrated sulfuric acid (d. 1.84) precooled at 0° was added 2.70 g (10 mmoles) of 12-chloro-1,4-diazabenzo[*b*]phenoxazine, **8**, R = Cl. Concentrated nitric acid (d. 1.42) also precooled at 0° was added to the resulting dark brown solution in droplet during 15 minutes while cooling the stirred mixture in an ice-salt bath. The mixture was stirred at 0° for 2 hours and at room temperature for 24 hours.

The dark brown mixture was poured into a beaker containing 200 g of ice and neutralized with cooling with concentrated ammonia. The solid product was filtrated and crystallized from ethanol after treatment with activated charcoal. 12-Chloro-7,13-dinitro-1,4-diazabenzo[*b*]phenoxazine, **16** (3.13 g, 87% yield) was collected as a yellow powder, mp 286-287°; uv: λ max 281 (4.2089), 350 (4.0331); ir: ν max 3380, 2920, 1630, 1580, 1560, 1545, 1507, 1465, 1413, 1383, 1350(b), 1330, 1270, 1240, 1228, 1155, 1124, 1090, 1054, 1007, 974, 930, 920, 900, 895, 850, 820, 785, 756, 727 cm^{-1}.

Anal. Calcd. for $C_{14}H_6ClN_5O$: C, 46.73; H, 1.67; Cl, 9.88. Found: C, 46.99; H, 1.54; Cl, 10.04, N, 19.39.

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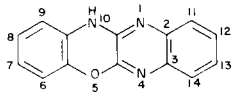

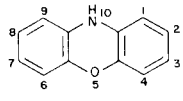

The nomenclature used is consistent with what is used in the current literature of phenoxazine chemistry as it brings out the structural relationship with the parent heterocycle, phenoxazine numbered as shown. 1,4-Diazabenzo[*b*]phenoxazine can also be named, quinoxalino[2,3-*b*]-[1,4]benzoxazine and numbered as indicated.

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