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Synthesis of New Benzo-substituted Macrocyclic Ligands Containing Quinoxaline Subunits

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Abstract—The macrocyclic Schiff bases **20**–**25** were prepared by cyclocondensation of the bis aldehydes **12**–**15** with the appropriate diaminoalkanes **17**–**19**. Reduction of the latter with $NaBH_4$ afforded the corresponding azacrown ethers **27**–**30**. Heating of the aldehydes **12**–**16** in refluxing acetic acid afforded the corresponding 2,3-bis(benzofuranyl)quinoxalines **33**–**37**. Nucleophilic reaction of the bis phenols **45**–**48**, **54**, **56**, **57** with the appropriate dihalo compounds **1**, **38** afforded the corresponding macrocyclic diamides **49**–**52** and 1,ω-bis-[quinoxalino(2,3-*b*)benzoxazepino-13-on-yl]alkanes **60**, **61**, respectively.

Introduction

The continued interest in designing new macrocyclic ligands stems mainly from their use as models of protein–metal binding sites in biological systems,[1–3] as synthetic ionophores, as therapeutic reagents in chelate therapy, as cyclic antibiotics,[4] to study host–guest interactions[5] and in catalysis.[6] Recognition of the importance of macrocyclic compounds and their complexes with metal cations as well as uncharged molecules has led to considerable effort being invested in developing reliable inexpensive synthetic routes to these compounds. In the past few decades, much attention has been directed towards the systematic determination of the parameters that affect complex stability and to understand their stability in terms of thermodynamic and kinetic data for complex formation.[7–9] Various changes have been made to the basic crown ether structure in an attempt to enhance the selectivity of these ligands and the stability of complexes formed with both metal and organic cations. Some of these modifications involve the substitution of the ligand polyether oxygen donor atoms by sulfur and/or nitrogen atoms.[5] Other substitution involved the insertion of functional groups in the ring (e.g. amides, esters).[10–13] One of the most interesting modifications is the incorporation of heterocyclic groups in the macrocyclic ring.[14,15] In some cases these groups were attached to the macrocyclic ring as side arms.[16,17] Heterocyclic groups provide rigidity and are able to participate, in some cases, in complexation through their soft donor atoms. Although many macrocyclic compounds containing heterocycles such as pyridine, bipyridine, pyrimidine, triazole, pyrazole, imidazole and thiophene have been synthesized and studied,[18] very little is known[19,20] about using benzoheterocycles as a subunit of macrocyclic compounds. We are now engaged in a project aimed at the preparation of new macrocyclic ligands fused with benzoheterocycles. Our objective in this project is to study the effect of the rigidity provided by these groups on the ability of the ligands to form stable complexes compared to other macrocyclic analogues. We report here on the synthesis of novel macrocyclic ligands, which are fused to a quinoxaline unit and also discuss the formation of unexpected products in some reactions.

Results and Discussion

We initially aimed to introduce the quinoxaline moiety into macrocycles containing an O_2N_2-donor set and fused with two benzene units. Lindoy and coworkers[21] pioneered the synthesis of dibenzo O_2N_2 macrocycles and studied the kinetic and thermodynamic stability of their complexes with Ni(II) and Cu(II). The synthetic strategy depends on the cyclocondensation between bis amines and the appropriate bis aldehydes, to give the corresponding Schiff bases[22] followed by reduction. The cyclocondensation reactions are known to occur either in the absence or in the presence of metal ions. The latter can serve to direct the condensation preferentially to cyclic rather than oligomeric/polymeric products and to stabilize the macrocycles once formed. The reactions proceed to give '1+1' macrocycles or '2+2' macrocycles depending, together with other factors, on the size of the template ion (when it is used) and the chain length of both of the diamines and the dialdehydes.[23–25]

The synthetic routes to novel macrocycles **20**–**30** is outlined in Scheme 1. The 2,3-dibromomethylquinoxalines **1**, **2**[26] were chosen as the starting materials and their reactivities towards phenoxide anions were first investigated by reaction

Keywords: Schiff base; diaminoalkanes; quinoxaline.

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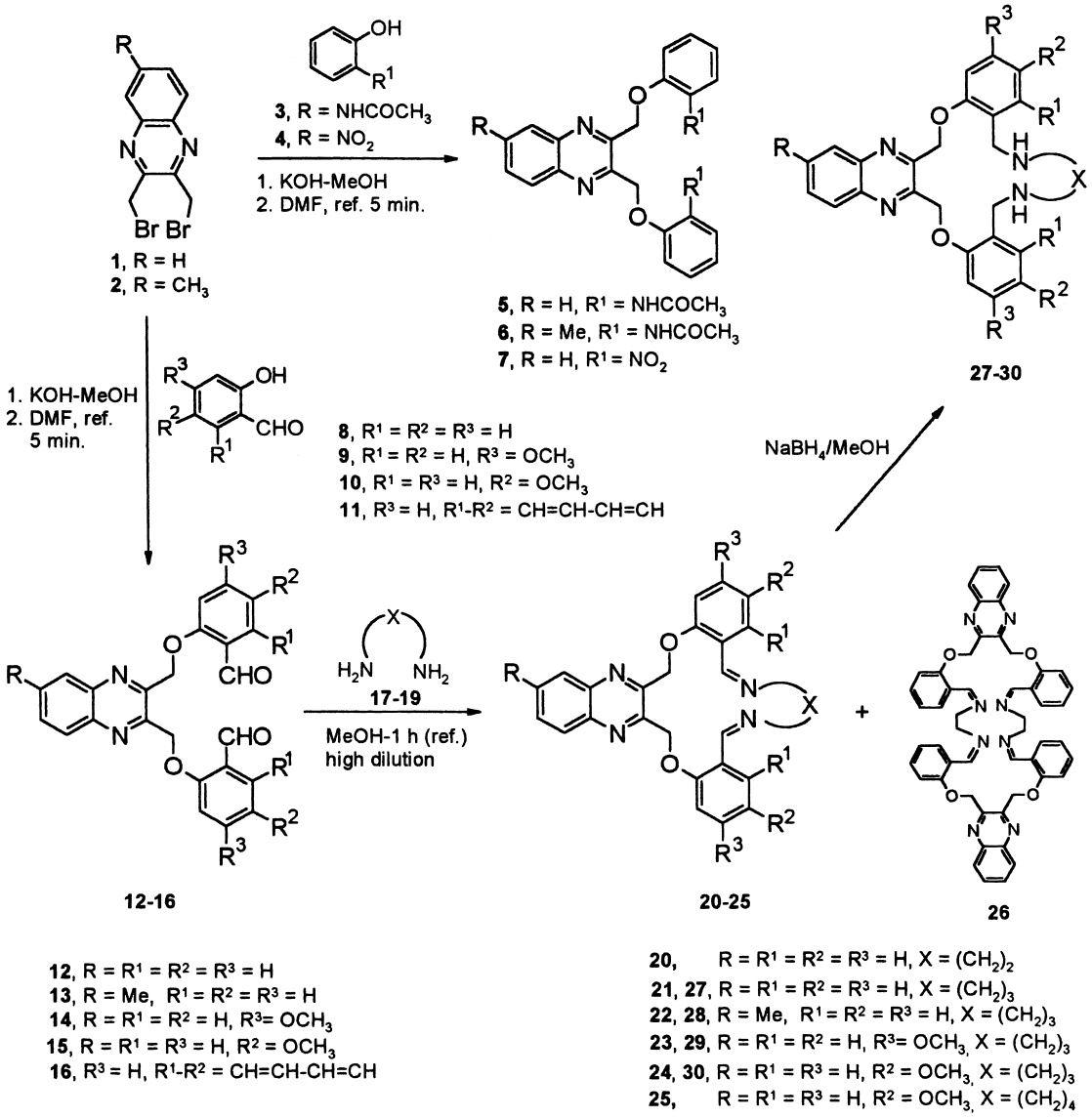
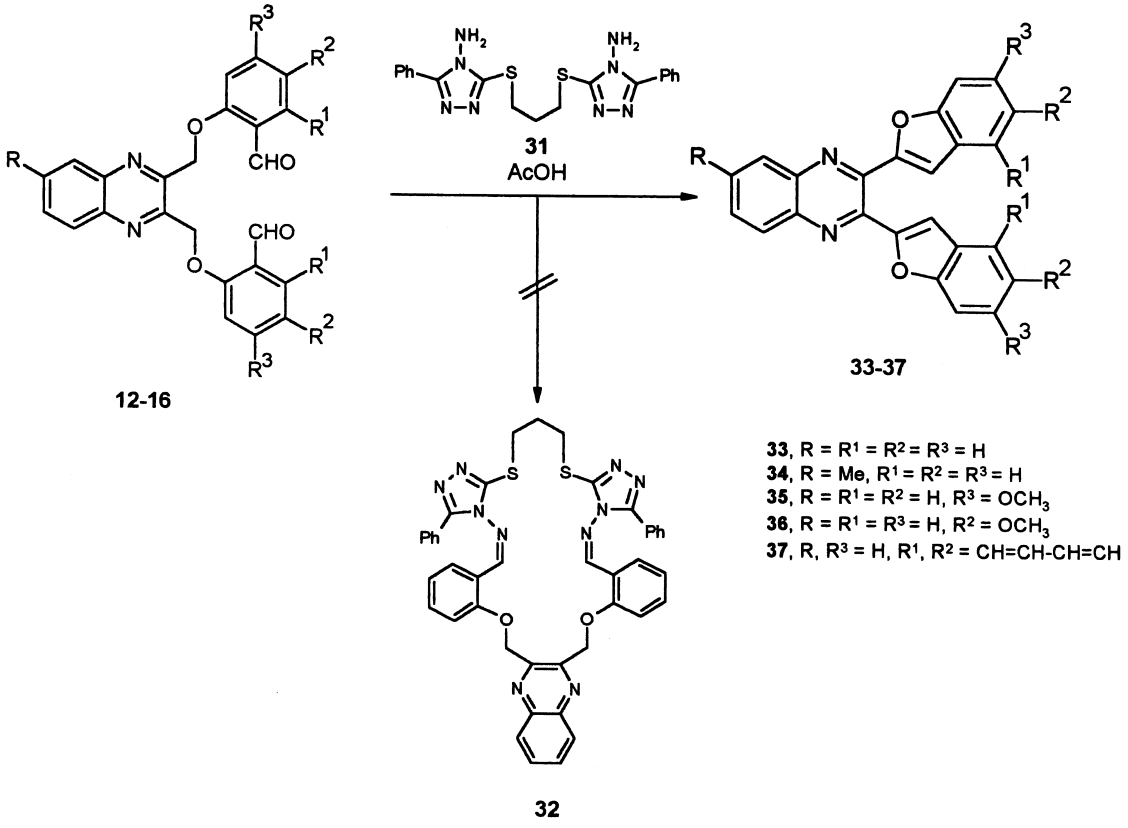


Scheme 1.

with the K-salts of each of *o*-acetamidophenol (**3**)[27] and *o*-nitrophenol (**4**)[27] in refluxing DMF. As expected, the corresponding 2,3-bis[2-(acetamidophenoxy)methyl](quinoxalines **5**, **6** and bis[2-(nitrophenoxy)methyl]quinoxaline (**7**) were obtained, respectively, in 71–75% yields. The latter compounds should undergo acid hydrolysis or reduction, respectively, to give the corresponding bis(amino) derivatives. Further studies utilizing these compounds as precursors in the synthesis of novel macrocyclic formazans, which is one of our recent interests,[28] are now in progress.

We then reacted the K-salt of salicylaldehyde **8** and its derivatives **9**–**11** with the dibromoquinoxalines **1**, **2** in refluxing DMF to give the corresponding new bis aldehydes **12**–**16** in 64–73% yields, respectively. Unfortunately, reaction of **12** with diaminoethane (**17**) in a 1:1 molar ratio in refluxing ethanol under high dilution conditions failed to give pure sample of the corresponding Schiff base **20**. The ^{1}H NMR spectra of the reaction products indicate the presence of a mixture of **20** and **26** in 48% yield. This was also supported by the presence of the characteristic molecular ion peaks in the mass spectrum. All attempts to separate these compounds were unsuccessful. Repeating the above reaction in the absence of high dilution conditions was found by ^{1}H NMR to enhance the formation of one compound with respect to the other but we are still unable to isolate pure samples of each of them.

On the other hand, reaction of **12** with 1,3-diaminopropane in refluxing ethanol under high dilution conditions afforded the corresponding macrocyclic Schiff base **21** in 27% yield as the only reaction product. Reduction of the latter with $NaBH_4$ in methanol afforded the corresponding azacrown ether **27** in 25% yield. Similarly, macrocycles **28**–**30** were obtained in 22–27% yields by $NaBH_4$ reduction of methanolic solution of the corresponding Schiff bases **22**–**24**. The latter were prepared in 25–42% yields, respectively, by cyclocondensation of the appropriate aldehydes **13**–**16** with the corresponding diaminoalkanes **18**, **19**. The above conversion was found to be more easily achieved by one-pot



Scheme 2.

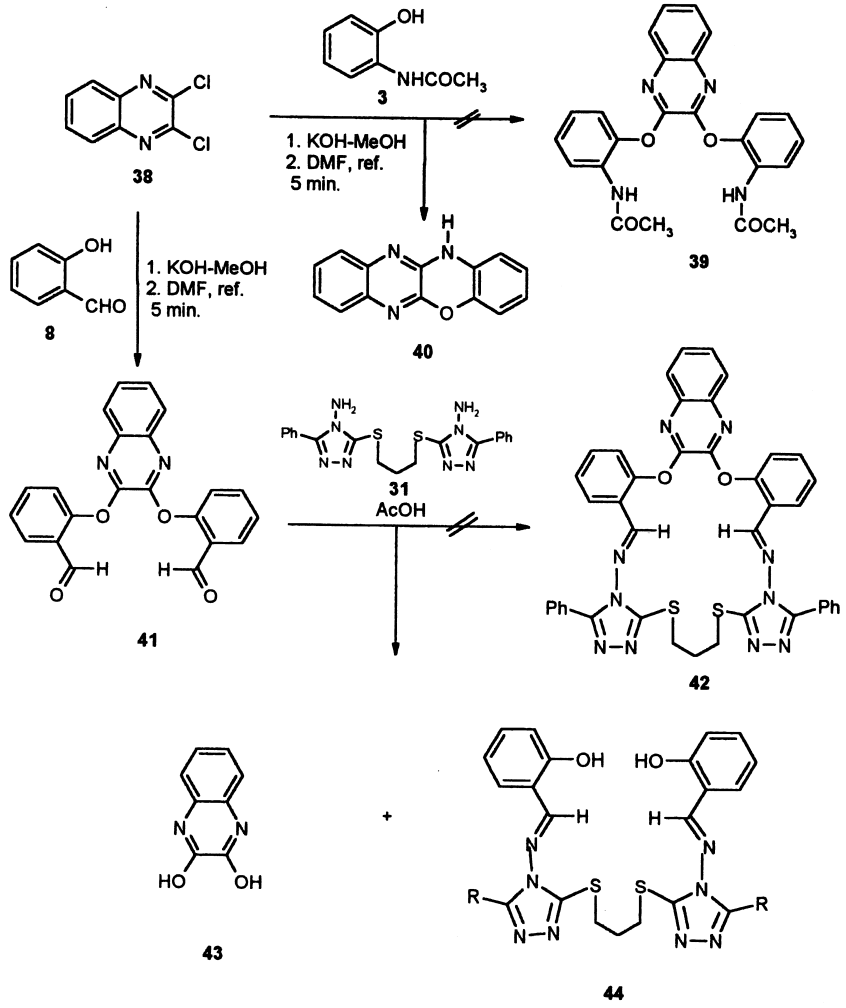
synthesis without isolation of the diimine intermediate. Thus, heating a solution of each of **12**–**15** in refluxing ethanol for 1 h under high dilution conditions followed by addition of $NaBH_4$ to the cold reaction mixture afforded, after work-up, the corresponding **27**–**30** in 31–34% yields, respectively.

Our study was extended to investigate the reactivity of the, now available, bis(aldehydes) **12**–**16** towards the bis(aminotriazole) **31**[29] in an attempt to obtain the corresponding novel macrocycle **32**. Unfortunately, the reaction of **12** with **31** in refluxing acetic acid under high dilution conditions did not lead to the formation of **32**. Instead, the reaction gave 2,3-bis[benzo(b)furan-2-yl]quinoxaline (**33**) in 76% yield. The formation of **33** prompted us to study the generality of the reaction. This was done by repeating the above reaction with other derivatives. Thus, heating **13**–**16** in refluxing acetic acid for 30 min afforded 72–83% yields of the corresponding 2,3-bis[benzo(*b*)-furan-2-yl]quinoxaline derivatives **34**–**37** (Scheme 2). This reaction provided a new and easy access to dibenzofuranylquinoxaline derivatives.

The reaction proceeds via intramolecular cyclocondensation of the active methylene with the aldehyde group. The enhanced electrophilicity of C-2 and C-3 in the quinoxaline ring caused by protonation of the nitrogen atom under the acidic condition activate the methylene group towards the condensation reaction. It is important to mention that Sarodnick et al.[30] reported the synthesis of some 2-[benzo(*b*)furan-2-yl]quinoxaline derivatives by heating the corresponding 2-[2-(formylphenoxy)methyl]quinoxalines in the presence of strong base under reflux for 2–3 h in the appropriate solvent.

We have also attempted to prepare new quinoxaline containing macrocyclic ligands in which the ether oxygens are attached directly to the heteroring as outlined in Scheme 3.

2,3-Dichloroquinoxaline[31] (**38**) was chosen as the starting material and its reactivity towards phenoxide derivatives was now investigated. Thus, reaction of the potassium salt of **3** with **38** in refluxing DMF for 15 min did not afford the expected 2,3-bis(2-acetamidophenoxy)quinoxaline (**39**). Instead, the reaction gave 12*H*-quinoxalino[2,3-*b*][1,4]benzoxazine (**40**) in 75% yield. Agarwal et al.[32] reported the synthesis of **40** in 90% yield by heating a solution of 2-aminophenol and **38** in refluxing DMF–H_2O mixture containing KOH for 3 h. On the contrary, heating the potassium salt of **8** with **38** in refluxing DMF for 15 min afforded the corresponding bis(aldehyde) **41** in 34% yield. Reaction of **41** with a series of diaminoalkanes **17**–**19** in refluxing ethanol under high dilution conditions gave mixtures of polymeric products that were not easily handled. Also, cyclocondensation of **41** with the bis(aminotriazole) derivative **31** in refluxing acetic acid under high dilution conditions did not lead to the formation of the corresponding macrocyclic Schiff base **42**. Instead, the reaction gave 40% yield of 2,3-dihydroxyquinoxaline (**43**) together with 9% yield of 1,3-bis[4-(2-hydroxybenzylideneamino)-5-phenyl-1,2,4-triazol-3-ylsulfanyl]propane (**44**).[29] The reaction proceeds via initial cyclocondensation followed by attack of the water molecules produced on the C-2 and C-3 of quinoxaline. Protonation of the quinoxaline



Scheme 3.

nitrogens under acidic conditions enhanced the electrophilicity of the quinoxaline carbons C-2 and C-3 and facilitated the attack of water molecules. This suggestion was confirmed by the possible formation of **43** in 51% yield upon heating the bis(aldehyde) **41** in refluxing acetic acid containing traces of H_2O.

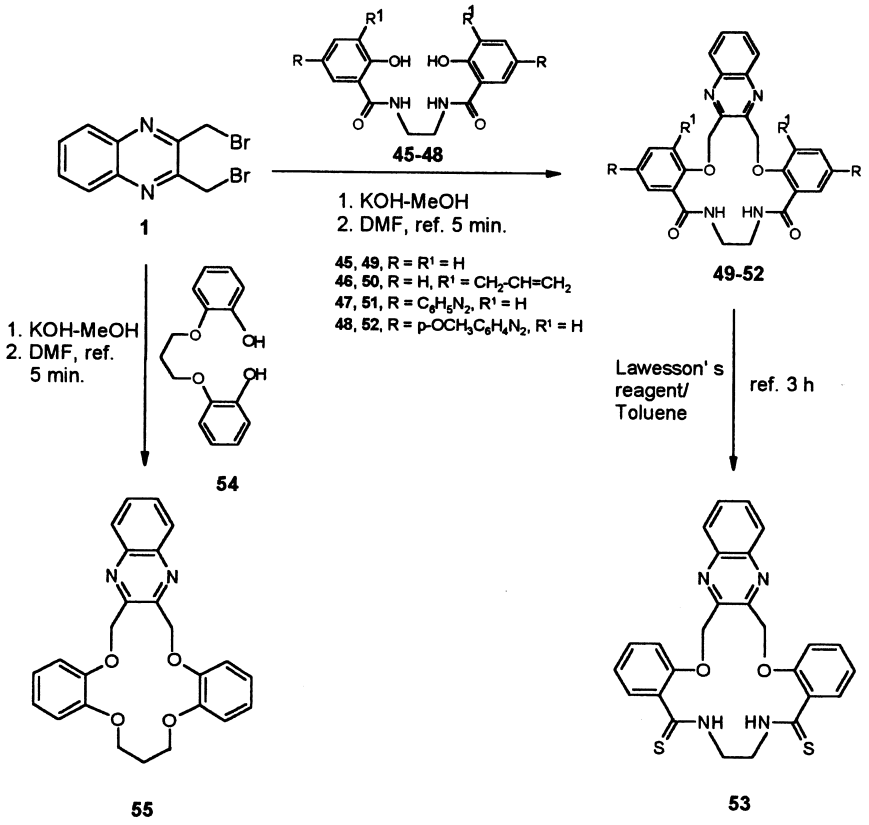
We studied the utilization of the bis halides **1**, **38** as intermediates in the synthesis of new macrocyclic diamides. The synthesis of these systems have recently attracted much attention[33] not only for being precursors in the preparation of azacrown compounds,[34] but also for their recent use as catalysts in organic reactions.[35] The synthetic approach to the new macrocyclic diamides **49**–**52** is outlined in Scheme 4.

Thus, reaction of the diphenols **45**–**48**[36,37] 33g, with KOH in anhydrous methanol generated the corresponding dianion in quantitative yield. Heating of the latter with 2,3-dibromomethylquinoxaline (**1**) in refluxing DMF for 5 min afforded the corresponding macrocyclic diamides in 49–58% yields. The reaction proceeds in a short time to give moderate to good yields of the macrocycles without using the high dilution conditions. Compound **49** was transformed to the corresponding dithiodiamide **53** upon treatment with Lawesson's reagent in refluxing toluene. The new macrocyclic ether **55** was similarly obtained in 60% yield by reaction of the dipotassium salt of **54** (obtained upon treatment of **54** with methanolic KOH) with **1** in refluxing DMF.

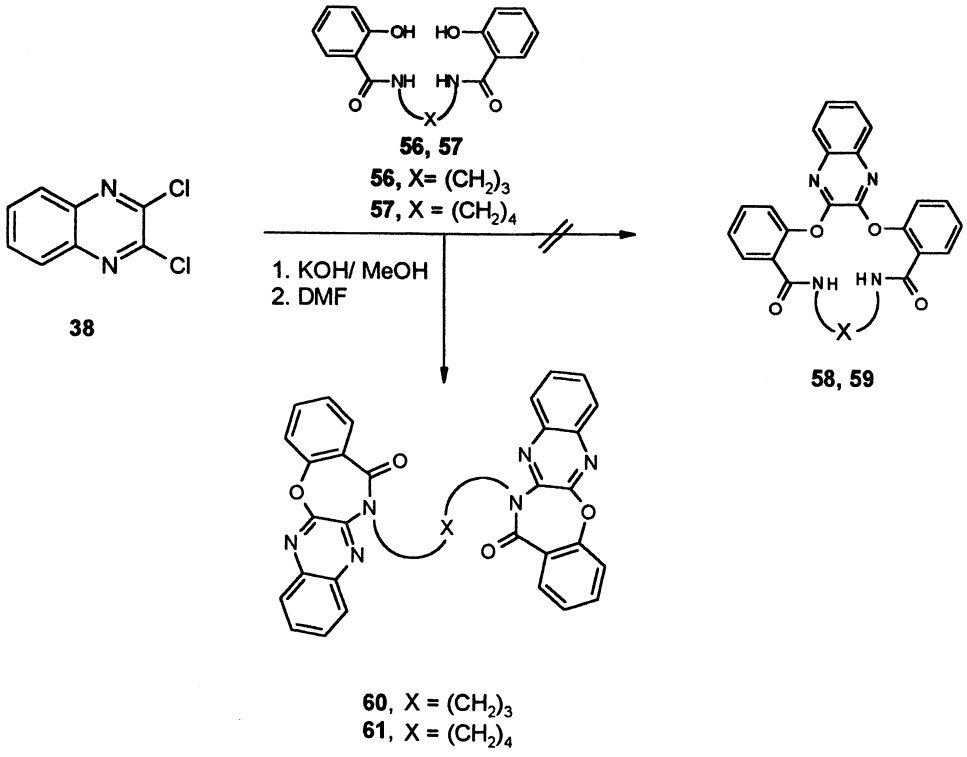
In contrast to the behavior of **1** towards the bis phenols **45**–**48**, heating the dipotassium salt of each of **56** and **57**[38] with **38** in refluxing DMF did not lead to the formation of the corresponding macrocyclic diamides **58**, **59**. Unexpectedly, the reaction gave the corresponding 1,ω-bis[quinoxalino(2,3-*b*)benzoxazepino-13-on-12-yl]alkanes **60** and **61** in 36% and 29% yields, respectively (Scheme 5).

The structure proposed for these new compounds are consistent with the data obtained from their elemental analyses, IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry.

In conclusion, we could prepare the first macrocyclic ligands, which are fused to quinoxaline at the 2,3-position. A study of the complexing properties of the new macrocycles will be described in detail when that work is finished. We have also described the effect of the enhanced electrophilicity of C-2 and C-3 of the quinoxaline moiety under acidic conditions on the formation of unexpected products.



Scheme 4.



Scheme 5.

Experimental

All melting points are uncorrected. IR spectra (KBr) were recorded on a Perkin–Elmer 1430 spectrometer. NMR spectra were measured with a Brucker WM-300 instrument and chemical shifts are given in ppm downfield from TMS. Mass spectra were recorded on a Varian 311A instrument. Elemental analyses were performed with a Perkin–Elmer 240 elemental analyzer.

Synthesis of the K-salt of 3, 4, 8–11

A solution of each of compounds **3**, **4**, **8**–**11** (10 mmol) and KOH (1.14 g, 20 mmol) in ethanol (10 ml) was stirred at room temperature for 10 min. The solvent was removed in vacuo and the remaining solvent was triturated with dry ether, collected and dried. It was then used in the next steps without further purification.

Synthesis of compounds 5–7, 12–16, 40, 41

A solution of each of the potassium salt of **3**, **4**, **8**–**11** (20 mmol) and the appropriate dihalide **1**, **38** (10 mmol) in DMF (20 ml) was heated under reflux for 5 min during which time KCl was precipitated. The solvent was then removed in vacuo and the remaining material was washed with water (50 ml) and crystallized (for solvents see below) to give compounds **5**–**7**, **12**–**16**, **40** and **41**, respectively.

2,3-Bis[2-(acetamidophenoxy)methyl]quinoxaline (5). With the use of the general procedure, compound **1** and the potassium salt of **3** gave crude **5**, which crystallized from ethanol as grey crystals (72%), mp 126–128°C; IR: ν 3380 (NH), 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (s, 6H, CH_3CO), 5.6 (s, 4H, OCH_2), 6.99–8.33 (m, 14H, ArHs, NH) ppm. Anal. for $C_{26}H_{24}N_4O_4$ (456.49) Calcd: C, 68.41; H, 5.29; N, 12.27. Found: C, 68.40; H, 5.30; N, 11.90.

6-Methyl-2,3-bis[2-(acetamidophenoxy)methyl]quinoxaline (6). With the use of the general procedure, compound **2** and the potassium salt of **3** gave crude **6**, which crystallized from methanol as gray crystals (75%), mp 127–129°C; IR ν 3318 (NH), 1668 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (s, 6H, $NHCOCH_3$), 2.63 (s, 3H, $CH_3C_6H_3$), 5.50, 5.51(2 s, 4H, OCH_2), 6.99–8.31 (m, 13H, ArHs, NH) ppm; ^{13}C NMR ($CDCl_3$) δ 22.08, 24.77 ($CH_3C_6H_3$, CH_3CO), 71.15 (OCH_3), 112.94, 112.99, 121.15, 122.74, 123.91, 124.11, 127.99, 128.54, 128.68, 133.56 (ArCHs), 140.14, 141.76, 142.08, 147.14, 149.05, 149.96(ArCs), 168.51 (C=O) ppm. Anal. for $C_{27}H_{26}N_4O_4$ (470.525) Calcd: C, 68.92; H, 5.57; N, 11.91. Found: C, 69.10; H, 5.40; N, 11.60.

2,3-Bis[2-(nitrophenoxy)methyl]quinoxaline (7). With the use of the general procedure, compound **1** and the potassium salt of **4** gave crude **7**, which crystallized from ethanol as pale yellow crystals (71%), mp 156–158°C; IR: ν 1610, 1522 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.83 (s, 4H, $C_6H_4OCH_2$), 6.97–8.15 (m, 12H, ArHs); ^{13}C NMR ($CDCl_3$) δ 76.70 (OCH_2), 114.72, 120.97, 125.87, 129.27, 130.97, 134.67 (ArCHs), 139.59, 141.33, 149.83, 151.69 (ArCs) ppm. Anal. for $C_{22}H_{16}N_4O_6$ (432.392) Calcd: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.40; H, 3.70; N, 13.00.

2,3-Bis[2-(formylphenoxy)methyl]quinoxaline (12). With the use of the general procedure, compound **1** and the potassium salt of **8** gave crude **12**, which crystallized from ethanol as colorless crystals (69%), mp 138–140°C; IR ν 1684 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63 (s, 4H, OCH_2), 6.95–8.62 (m, 12H, ArHs), 10.25 (s, 2H CHO) ppm. Anal. for $C_{24}H_{18}N_2O_4$ (398.416) Calcd: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.40; H, 4.70; N, 7.30.

6-Methyl-2,3-bis[2-(formylphenoxy)methyl]quinoxaline (13). With the use of the general procedure, compound **2** and the potassium salt of **8** gave crude **13**, which crystallized from ethanol as colorless crystals (65%), mp 188–190°C; IR ν 1682 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.64 (s, 3H, $CH_3C_6H_3$), 5.68 (s, 4H, OCH_2), 6.91–8.05 (m, 11H, ArHs), 10.5 (s, 2H, CHO) ppm. Anal. for $C_{25}H_{20}N_2O_4$ (412.44) Calcd: C, 72.80; H, 4.88; N, 6.79. Found: C, 72.70; H, 4.50; N, 7.00.

2,3-Bis[(5-methoxy-2-formylphenoxy)methyl]quinoxaline (14). With the use of the general procedure, compound **1** and the potassium salt of **9** gave crude **14**, which crystallized from ethanol as pale yellow crystals (70%), mp 161–163°C; IR ν 1666 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 6H, OCH_3), 5.68 (s, 4H, OCH_2), 6.52–8.16 (m, 10H, ArHs), 10.17 (s, 2H, CHO) ppm; ^{13}C NMR ($CDCl_3$) δ 55.80 (OCH_3), 70.77 (OCH_2), 99.05, 107.38, 129.27, 131.11, 131.60 (ArCHs), 119.11, 141.44, 149.99, 162.13, 166.20 (ArCs), 187.73 (C=O) ppm. Anal. for $C_{26}H_{22}N_2O_6$ (458.468) Calcd: C, 68.11; H, 4.83; N, 6.11. Found: C, 68.30; H, 5.10; N, 5.90.

2,3-Bis[(4-methoxy-2-formylphenoxy)methyl]quinoxaline (15). With the use of the general procedure, compound **1** and the potassium salt of **10** gave crude **15**, which crystallized from ethanol as pale yellow crystals (73%), mp 172–173°C; IR ν 1677 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (s, 6H, OCH_3), 5.63 (s, 4H, OCH_2), 7.05–8.17 (m, 10H, ArHs), 10.33 (s, 2H, CHO) ppm; ^{13}C NMR ($CDCl_3$) δ 55.91 (OCH_3), 71.24 (OCH_2), 111.30, 114.92, 123.38, 129.31, 131.05 (ArCHs), 125.53, 141.49, 150.13, 154.36, 155.19 (ArCs), 188.91 (CHO) ppm. Anal. for $C_{26}H_{22}N_2O_6$ (458.468) Calcd: C, 68.12; H, 4.84; N, 6.11. Found: C, 68.30; H, 4.50; N, 6.20.

2,3-Bis[(1-formyl-2-naphthoxy)methyl]quinoxaline (16). With the use of the general procedure, compound **1** and the potassium salt of **11** gave crude **16**, which crystallized from ethyl acetate–hexane (1:1) as pale yellow crystals (64%), mp 174–175°C; IR ν 1668 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.74 (s, 4H, OCH_2), 7.29–9.09 (m, 16H, ArHs), 10.8 (s, 2H, CHO) ppm. Anal. for $C_{32}H_{22}N_2O_4$ (498.536) Calcd: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.10; H, 4.50; N, 5.80.

12*H*-Quinoxalino[2,3-*b*][1,4]benzoxazine (40). With the use of the general procedure, the potassium salt of **3** and compound **38** gave **40** (76%); mp >300°C (lit.[32] mp >300°C); ^1H NMR (DMSO) δ 6.77–7.46 (m, 8H, ArHs), 10.45 (br s, 1H, NH) ppm.

2,3-Bis(formylphenoxy)quinoxaline (41). With the use of the general procedure, the potassium salt of **8** and compound

38 gave crude **41**, which crystallized from ethanol as pale yellow crystals (34%); mp 191–193°C; IR ν 1688 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.09–8.04 (m, 12H, ArHs), 10.30 (s, 2H, CHO) ppm; ^{13}C NMR ($CDCl_3$) δ 123.62, 126.40, 127.12, 128.21, 130.67, 135.66 (ArCHs), 128.58, 137.65, 149.14, 154.30 (ArCs), 188.98 (C=O) ppm. Anal. for $C_{22}H_{14}N_2O_4$ (370.362) Calcd: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.40; H, 4.00; N, 7.20.

Synthesis of the macrocyclic Schiff bases 20–26

A solution of the appropriate bis aldehydes **12**–**15** (10 mmol) in ethanol (10 ml) was added to a solution of the corresponding 1,ω-diaminoalkanes **17**–**19** (10 mmol) in ethanol (400 ml). The reaction mixture was heated under reflux for 2 h. The solvent was then removed in vacuo and the remaining solid [in case of (**20**, **26**), **24**, **25**] was collected and crystallized from the proper solvent. Otherwise, the remaining oily materials [in case of **21**, **22**, **23**] were dissolved in hot ethyl acetate, filtered hot, the volume reduced by rotary evaporation to 10 ml and then hexane (10 ml) was added. The solid obtained upon cooling was collected and crystallized (solvents given below).

6,13,22,23-Tetrahydro-21*H*-dibenzo[*b,k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (21). With the use of the general procedure, compounds **12** and **18** gave crude **21**, which crystallized from ethyl acetate–hexane (1:1) as colorless crystals (27%), mp 176–178°C; ^1H NMR ($CDCl_3$) δ 2.17 (quin., 2H, J=5.3 Hz, NCH_2CH_2), 3.57 (t, 4H, J=5.2 Hz, NCH_2), 5.62 (s, 4H, OCH_2), 7.09–8.18 (m, 12H, ArHs), 8.70 (s, 2H, CH=N) ppm. Anal. for $C_{27}H_{24}N_4O_2$ (436.511) Calcd: C, 74.29; H, 5.54; N, 12.83. Found: C, 74.40; H, 5.20; N, 13.10.

8-Methyl-6,13,22,23-tetrahydro-21*H*-dibenzo[*b,k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (22). With the use of the general procedure, compounds **13** and **18** gave crude **22**, which crystallized from ethyl acetate–hexane (1:1) as colorless crystals (25%); mp 170–172°C; IR ν 1636 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (quin., 2H, J=4.8 Hz, NCH_2CH_2), 2.62 (s, 3H, $CH_3C_6H_3$), 3.56 (t, 4H, J=4.9 Hz, NCH_2), 5.59 (s, 4H, OCH_2), 7.03–8.04 (m, 11H, ArHs), 8.69 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$) δ 22.02 ($CH_3C_6H_3$), 28.80 (NCH_2CH_2), 57.09 (NCH_2), 71.21 (OCH_2), 114.44, 121.99, 127.52, 128.12, 128.82, 131.86, 133.28 (ArCHs), 125.65, 140.05, 141.67, 149.67, 150.54, 158.14 (ArCs), 158.94 (CH=N) ppm. Anal. for $C_{28}H_{26}N_4O_2$ (450.538) Calcd: C, 74.65; H, 5.82; N, 12.43. Found: C, 74.70; H, 5.50; N, 12.40.

3,16-Dimethoxy-6,13,22,23-tetrahydro-21*H*-dibenzo[*b,k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (23). With the use of the general procedure, compounds **14** and **18** gave crude **23**, which crystallized from ethyl acetate as colorless crystals (32%); mp 218–220°C; MS: *m/z* (M^+, 496); IR ν 1636 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (quin., 2H, J=5.0 Hz, NCH_2CH_2), 3.53 (t, 4H, J=5.2 Hz, OCH_2), 3.92 (s, 6H, OCH_3), 5.57 (s, 4H, OCH_2), 6.53–8.17 (m, 12H, ArHs), 8.57 (s, 2H, CH=N); ^{13}C NMR ($CDCl_3$) δ 29.08 (NCH_2CH_2), 55.69, 56.92 (NCH_2, OCH_3), 70.98 (OCH_2), 100.64, 107.55, 128.60, 129.32, 130.99 (ArCHs), 118.64, 141.53, 150.52, 159.28, 162.92 (ArCs), 157.64 (CH=N) ppm. Anal. for $C_{29}H_{28}N_4O_4$ (496.563) Calcd: C, 70.15; H, 5.68; N, 11.28. Found: C, 70.30, H, 5.40; N, 11.10.

2,17-Dimethoxy-6,13,22,23-tetrahydro-21*H*-dibenzo[*b,k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (24). With the use of the general procedure, compounds **15** and **18** gave crude **24**, which crystallized from ethanol as colorless crystals (42%); mp 220–222°C; IR ν 1636 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (quin., 2H, J=5.2 Hz, NCH_2CH_2), 3.61 (t, 6H, J=5.2 Hz, NCH_2CH_2), 3.83 (s, 6H, OCH_3), 5.57 (s, 4H, OCH_2), 6.97–8.17 (m, 10H, ArHs), 8.69 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$) δ 28.87 (NCH_2CH_2), 55.93 (NCH_2), 57.08 (OCH_3), 72.33(OCH_2), 110.39, 116.81, 118.92, 129.29, 130.77 (ArCHs), 126.56, 141.41, 150.71, 152.44, 154.80 (ArCs), 158.15 (CH=N) ppm. Anal. for $C_{29}H_{28}N_4O_4$ (496.563) Calcd: C, 70.15; H, 5.68; N, 11.32. Found: C, 70.30; H, 5.70; N, 11.10.

2,17-Dimethoxy-6,13,21,22,23,24-hexahydrodibenzo[*b,l*]1,14,5,10-dioxadiazacyclooctadeceno[16,17-*b*]quinoxaline (25). With the use of the general procedure, compounds **15** and **19** gave crude **25**, which crystallized from ethyl acetate as colorless crystals (38%), mp 198–200°C; MS: *m/z* (M^+, 510); ^1H NMR ($CDCl_3$) δ 1.25 (br s, 4H, NCH_2CH_2), 3.61 (br s, 4H, CH_2N=CH), 3.79 (s, 6H, OCH_3), 5.43 (s, 4H, OCH_2), 6.80–8.23 (m, 10H, ArHs), 8.61 (s, 2H, CH=N) ppm; ^{13}C NMR ($CDCl_3$) δ 26.41 (NCH_2CH_2), 55.9 (CH_2N=CH), 59.39 (OCH_3), 71.99, (OCH_2), 110.29, 115.94, 118.67, 129.41, 130.85 (ArCHs), 126.38, 141.81, 150.29, 152.61, 154.91 (ArCs), 156.87 (C=N) ppm. Anal. for $C_{30}H_{30}N_4O_4$ (510.59) Calcd: C, 70.57; H, 5.92; N, 10.97. Found: C, 70.60; H, 6.00; N, 11.10.

6,13,21,22-Tetrahydrodibenzo[*b, j*]1,12,5,8-dioxadiazacyclohexadeceno[14,15-*b*]quinoxaline (20); 7,8,16,23,31,32,40,47-Octahydrotetrabenzo[*b, j, r, z*]1,12,17,28,5,8,21,24-tetraoxatetrazacyclodotriacontino[14,15-*b*:31,30-*b*]quinoxaline (26). With the use of the general procedure, compounds **12** and **17** gave a crude mixture of **20** and **26**, which crystallized from ethanol as colorless crystals (48%); mp 235–239°C; MS: *m/z* [423 (M^++1, 100%), compound **20**]; [845 (M^++1, 20%), compound **26**]; ^1H NMR ($CDCl_3$) δ 3.6, 4.1 (2 s, 12H, NCH_2), 5.47, 5.58 (2 s, 12H, OCH_2), 6.84–8.17 (m, 36H, ArHs), 8.49, 8.76 (2 s, 6H, CH=N); ^{13}C NMR ($CDCl_3$) δ 59.33, 61.83 (NCH_2), 71.05, 71.93 (OCH_2), 112.50, 115.71, 121.66, 122.57, 127.65, 128.78, 129.26, 130.78, 131.62, 158.27, 159.34 (ArCHs), 125.02, 126.48, 129.35, 131.99, 141.37, 141.67, 150.68, 157.45, 157.91 (ArCs, C=N) ppm.

Synthesis of the macrocycles 27–30

General procedure A. To a stirred warm (40–50°C) solution of each of **21**–**25** (10 mmol) in methanol (20 ml) was added carefully sodium borohydride (30 mmol) in incremental amounts. After the effervescence had stopped, the solvent was then removed in vacuo and water (20 ml) was added to the residues, and the macrocycles extracted into CH_2Cl_2 (2×20 ml). The CH_2Cl_2 solution was combined, washed with water (20 ml), separated and dried over anhydrous $MgSO_4$. The CH_2Cl_2 was removed in vacuo to

leave a pale yellow viscous oil. This was dissolved in hot ethyl acetate, filtered hot, the volume reduced by rotary evaporator (ca. 10 ml) and hexane (10 ml) was added; the solid obtained upon cooling was collected and crystallized from ethyl acetate–hexane to give pale yellow crystals of **27**–**30**.

General procedure B. A solution of the appropriate bis-(aldehydes) **12**–**15** (10 mmol) in ethanol (10 ml) was added to a solution of 1,3-diaminopropane (**18**) (10 mmol) in ethanol (400 ml). The reaction mixture was refluxed for 2 h, cooled to 40–50°C, then solid $NaBH_4$ (30 mmol) was added carefully in incremental amounts. After the effervescence had stopped, the solution was filtered. The solvent was then removed in vacuo and water (200 ml) was added to the residue. The macrocycles were extracted into CH_2Cl_2 (2×50 ml) followed by the same work-up as in general procedure A.

6,13,19,20,22,23,24,25-Octahydro-21*H*-dibenzo-[*b*,*k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (27). (a) With the use of the general procedure A, compounds **21** gave **27** (25%), mp 83–85°C; MS: *m*/*z* (M^++1, 441); IR: ν 3436 (NH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (quin., *J*=5.9 Hz, 2H, $NHCH_2CH_2$), 2.77 (t, 4H, *J*=6.0 Hz, $NHCH_2$), 3.82 (s, $C_6H_4CH_2N$), 4.69 (br s, 2H, NH), 5.67 (s, 4H, OCH_2), 6.89–8.18 (m, 12H, ArHs); ^{13}C NMR ($CDCl_3$) δ 28.91 ($NHCH_2CH_2$), 47.67 ($NHCH_2$), 51.03 ($NHCH_2C_6H_4$), 71.62 (OCH_2), 113.43, 121.76, 128.72, 129.17, 130.53, 131.23 (ArCHs), 141.32, 151.12, 157.20 (ArCs) ppm. Anal. for $C_{27}H_{28}N_4O_2$ (440.543) Calcd: C, 73.61; H, 6.41; N, 12.72. Found: C, 73.70; H, 6.20; N, 13.00.

(b) With the use of the general procedure B, compound **27** was obtained in 34% yield based on **12**.

9-Methyl-6,13,19,20,22,23,24,25-octahydro-21*H*-dibenzo-[*b*,*k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]-quinoxaline (28). (a) With the use of the general procedure A, compound **22** gave **28** (22%), mp 109–111°C; IR ν 3440 (NH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (quin., 4H, *J*=5.9 Hz,$NHCH_2CH_2$), 2.70 (br s, 2H, NH), 2.62 (s, 6H, CH_3), 2.77 (t, 4H, *J*=5.9 Hz, $NHCH_2$), 3.8 (s, 4H, $C_6H_4CH_2NH$), 5.66 (s, 4H, OCH_2), 6.82–8.05 (m, 11H, ArHs) ppm; ^{13}C NMR ($CDCl_3$) δ 22.02 ($C_6H_3CH_3$), 28.86 (CH_2CH_2NH), 47.61 (CH_2N), 51.26 ($C_6H_4CH_2NH$), 71.20 (OCH_2), 113.3, 121.74, 128.07, 128.70, 128.80, 131.27, 132.97 (ArCHs), 129.08, 139.81, 141.35, 141.45, 150.13, 151.02, 157.23 (ArCs) ppm. Anal. for $C_{28}H_{30}N_4O_2$ (454.57) Calcd: C, 73.98; H, 6.65; N, 12.32. Found: C, 73.60; H, 6.50; N, 12.10.

(b) With the use of the general procedure B, compound **28** was obtained in 30% yield based on **13**.

3,16-Dimethoxy-6,13,19,20,22,23,24,25-octahydro-21*H*-dibenzo[*b*,*k*]1,13,5,9-dioxadiazacycloheptadeceno-[15,16-*b*]quinoxaline (29). (a) With the use of the general procedure A, compound **23** gave **29** (27%), mp 110–112°C; IR: ν 3440 (NH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (quin., *J*=5.7 Hz, 2H, $NHCH_2CH_2$), 2.1 (br s, 2H, NH), 2.75 (t, *J*=5.6 Hz,4H, $NHCH_2CH_2$), 3.75 (s, 6H, OCH_3), 3.77 (d, 4H, *J*=2.9 Hz, $C_6H_4CH_2NH$), 5.54 (s, 4H, OCH_2), 6.52–8.16 (m, 10H, ArHs) ppm; ^{13}C NMR ($CDCl_3$) δ 28.87 ($NHCH_2CH_2$), 47.60 ($NHCH_2$), 50.45 ($C_6H_3CH_2NH$), 55.36 (OCH_3), 71.28 (OCH_2), 101.48, 105.48, 105.96, 130.55, 131.61, 132.02 (ArCHs), 121.57, 141.32, 150.99, 158.00, 160.17 (ArCs) ppm. Anal. for $C_{29}H_{32}N_4O_4$ (500.595) Calcd: C, 69.58; H, 6.44; N, 11.19. Found: C, 69.90; H, 6.60; N, 11.40.

(b) With the use of the general procedure B, compound **29** was obtained in 32% yield based on **14**.

2,17-Dimethoxy-6,13,19,20,22,23,24,25-octahydro-21*H*-dibenzo[*b*,*k*]1,13,5,9-dioxadiazacycloheptadeceno[15,16-*b*]quinoxaline (30). (a) With the use of the general procedure A, compound **24** gave **30** (26%); mp 105–107°C; IR ν 3446 (NH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (quin., 2H, *J*=5.8 Hz, $NHCH_2c$), 1.90 (br s, 2H, NH), 2.76 (t, 4H, *J*=5.9 Hz, NCH_2), 3.76, 3.77 (2 s, 10H, OCH_2, $C_6H_3CH_2NH$), 5.58 (s, 4H, OCH_2), 6.59–8.18 (m, 10H, ArHs) ppm. Anal. for $C_{29}H_{32}N_4O_4$ (500.595) Calcd: C, 69.58; H, 6.44; N, 11.19. Found: C, 69.40; H, 6.10; N, 11.20.

(b) With the use of the general procedure B, compound **30** was obtained in 31% yield based on **15**.

Action of acetic acid to compounds 12–16

A solution of each of **12**–**16** in acetic acid (10 ml) was heated under reflux for 1 h. The solid obtained upon cooling was collected and crystallized from the proper solvent to give **33**–**37**, respectively.

2,3-Bis[benzo(*b*)furan-2-yl]quinoxaline (33). With the use of the general procedure, compound **12** gave crude **33**, which crystallized from ethanol as pale yellow crystals (76%), mp 114–116°C; MS: *m*/*z* (M^+, 362); ^1H NMR ($CDCl_3$) δ 7.20–8.27 (m, ArHs, furan Hs) ppm. Anal. for $C_{24}H_{14}N_2O_2$ (362.386) Calcd: C, 79.55; H, 3.89; N, 7.73. Found: C, 79.50; H, 3.60; N, 7.80.

6-Methyl-2,3-bis[benzo(*b*)furan-2-yl]quinoxaline (34). With the use of the general procedure, compound **13** gave crude **34**, which crystallized from ethanol as pale yellow crystals (72%), mp 176–178°C; ^1H NMR ($CDCl_3$) δ 2.63 (s, 3H, $CH_3C_6H_3$), 7.15–8.13 (m, 13H, ArHs, furan Hs) ppm; ^{13}C NMR ($CDCl_3$) δ 22.14 ($C_6H_3CH_3$), 109.53, 112.01, 121.99, 123.46, 125.89, 128.27, 128.97, 133.59 (ArCHs, furan CHs), 103.33, 125.95, 128.37, 139.57, 142.02, 152.71, 155.43 (ArCs, furan Cs) ppm. Anal. for $C_{25}H_{16}N_2O_2$ (376.413) Calcd: C, 79.77; H, 4.28; N, 7.44. Found: C, 80.00; H, 4.30; N, 7.60.

2,3-Bis[6-methoxybenzo(*b*)furan-2-yl]quinoxaline (35). With the use of the general procedure, compound **14** gave crude **35**, which crystallized from AcOH as pale yellow crystals (74%), mp 207–208°C; ^1H NMR ($CDCl_3$) δ 3.86 (s, 6H, OCH_3), 6.81–8.21 (m, 12H, ArHs, furan Hs); ^{13}C NMR ($CDCl_3$) δ 55.82 (OCH_3), 96.06, 109.84, 113.20, 122.23, 129.33, 130.77 (ArCHs, furan CHs), 121.70, 140.86, 143.01, 151.81, 156.71, 159.44 (ArCs, furan Cs) ppm. Anal. for $C_{26}H_{18}N_2O_4$ (422.438) Calcd: C, 73.92; H, 4.30; N, 6.63. Found: 73.70; H, 4.40; N, 6.90.

2,3-Bis[5-methoxybenzo(*b*)furan-2-yl]quinoxaline (36). With the use of the general procedure, compound **15** gave **36**, which crystallized from acetic acid as yellow crystals (79%); mp 180–182°C; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 6H, OCH_3), 6.96–8.24 (m, 12H, ArHs, furan CHs) ppm; ^{13}C NMR ($CDCl_3$) δ 55.96 (OCH_3), 103.62, 109.79, 112.60, 115.43, 129.45, 131.08 (ArCHs, furan CHs), 128.80, 141.02, 143.09, 150.59, 153.24, 156.44 (ArCs, furan Cs) ppm. Anal. for $C_{26}H_{18}N_2O_4$ (422.438) Calcd: C, 73.92; H, 4.30; N, 6.62. Found: C, 73.90; H, 4.10; N, 6.20.

2,3-Bis[naphtho(8,1-*b*)furan-2-yl]quinoxaline (37). With the use of the general procedure, compound **16** gave **37**, which crystallized from DMF as yellow crystals (83%); mp >250°C; MS: *m*/*z* (M^+, 463); ^{1}H NMR ($CDCl_3$) δ 7.50–8.23 (m, 18H, ArHs, furan Hs); ^{13}C NMR ($CDCl_3$) δ 108.62, 112.58, 123.53, 125.02, 126.80, 127.19, 128.98, 129.33, 130.85 (ArCHs, furan CH), 123.00, 127.91, 130.57, 140.011, 142.87, 152.26, 153.43 (ArCs, furan Cs) ppm. Anal. for $C_{32}H_{18}N_2O_2$ (462.506) Calcd: C, 83.10; H, 3.92; N, 6.06. Found: C, 83.30; H, 4.20; N, 6.10.

Synthesis of compound 44

A solution of each of **41** (10 mmol) and **31** (10 mmol) in acetic acid (100 ml) was heated under reflux for 3 h. The solid obtained upon cooling was filtered and proved to be **43** (40% based on **41**); mp >300°C (lit.[31] mp >300°C). The mother liquor was then evaporated in vacuo and the remaining material was dissolved in hot benzene (10 ml) and filtered hot to remove the undissolved polymeric materials. Then, *n*-hexane (5 ml) was added, the solid obtained was collected and proved to be **44** (9%) (mp 92–94°C; lit.[29] mp 95°C); ^{1}H NMR ($CDCl_3$) δ 2.37 (m, 2H, SCH_2CH_2), 3.48 (br s, 4H, SCH_2), 6.9–7.8 (m, 18H, ArHs), 8.64 (s, 2H, CH=N), 10.28 (br s, 2H, OH) ppm.

Synthesis of compounds 49–52, 55, 60, 61

A solution of the potassium salt of each of **45**–**48**, **54** (10 mmol) and the appropriate dihalide **1**, **38** (10 mmol) in DMF (20 ml) was heated under reflux for 15 min during which KCl was precipitated. The solvent was then removed in vacuo and the remaining material was washed with water (50 ml) and crystallized from the proper solvent to give compound **49**–**52**, **55**, **60**, **61**, respectively.

6,13,21,22-Tetrahydrodibenzo[*b*, *j*]1,12,5,8-dioxadiazacyclopentadeceno[14,15-*b*]quinoxaline-19,24(20*H*,23*H*)-dione (49). With the use of the general procedure, compounds **1** and **45** gave crude **49**, which crystallized from ethanol as colorless crystals (58%); mp 225–228°C; MS: *m*/*z* (M^+, 454); IR ν 3400 (NH), 1635 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.8 (br s, 4H, $NHCH_2$), 5.66 (s, 4H, OCH_2), 6.94–8.18 (m, 14H, ArHs, NH) ppm. Anal. for $C_{26}H_{22}N_4O_4$ (454.482) Calcd: C, 68.71; H, 4.88; N, 12.33. Found: C, 68.70; H, 4.50; N, 12.00.

4,15-Diallyl-6,13,21,22-tetrahydrodibenzo[*b*, *j*]1,12,5,8-dioxadiazacyclopentadeceno[14,15-*b*]quinoxaline-19,24(20*H*,23*H*)-dione (50). With the use of the general procedure, compounds **1** and **46** gave crude **50**, which crystallized from ethyl acetate as colorless crystals (41%); mp 205°C; MS: *m*/*z* (M^+, 534); IR: ν 3269 (NH), 1636 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.41 (m, 4H, $NHCH_2$), 3.48 (d, 4H, J=6.6 Hz,CH_2–CH=), 4.97–5.08 (m, 4H, CH=CH_2), 5.48 (s, 4H, OCH_2), 5.87–6.00 (m, 2H, C*H*=CH_2), 7.16–8.16 (m, 10H, ArHs, NH) ppm. Anal. for $C_{32}H_{30}N_4O_4$ (534.612) Calcd: C, 71.89; H, 5.66; N, 10.48. Found: C, 71.90; H, 5.70; N, 10.20.

2,17-Diphenylazo-6,13,21,22-tetrahydrodibenzo[*b*, *j*]1,12,5,8-dioxadiazacyclopentadeceno[14,15-*b*]quinoxaline-19,24(20*H*,23*H*)-dione (51). With the use of the general procedure, compounds **1** and **47** gave crude **51**, which crystallized from dioxane as orange crystals (38%); mp 227–229°C; IR: ν 3404 (NH), 1642 (C=O) cm^{-1}; ^{1}H NMR (DMSO) δ 3.50 (br s, 4H, NCH_2), 5.81 (s, 4H, OCH_2), 7.54–8.53 (m, 22H, ArHs, NH) ppm; ^{13}C NMR (DMSO) δ 38.50 ($NHCH_2$), 72.19 (OCH_2), 114.54, 123.37, 123.62, 125.18, 127.13, 129.03, 129.38, 131.26, 131.41, 140.70, 146.03, 150.22, 151.77, 158.15 (ArCs, quinoxaline Cs), 164.56 (C=O) ppm. Anal. for $C_{38}H_{30}N_8O_4$ (662.702) Calcd: C, 68.87; H, 4.56; N, 16.91. Found: C, 68.90; H, 4.20; N, 16.60.

2,17-Di-*p*-methoxyphenylazo-6,13,21,22-tetrahydrodibenzo[*b*, *j*]1,12,5,8-dioxadiazacyclopentadeceno[14,15-*b*]quinoxaline-19,24(20*H*,23*H*)-dione (52). With the use of the general procedure, compounds **1** and **48** gave crude **52**, which crystallized from DMF/ethanol as orange crystals (36%); mp >250°C; MS: *m*/*z* (M^+, 722); IR ν 3402 (NH), 1660 (C=O) cm^{-1}; ^{1}H NMR (DMSO) δ 3.86 (s, 6H, OCH_3), 5.80 (s, 4H, OCH_2), 6.8–8.5 (m, 14H, ArHs) ppm; ^{13}C NMR (DMSO) δ 38.58 (CH_2NH), 55.56 (OCH_3), 72.19 (OCH_2), 114.53, 123.26, 124.36, 125.10, 126.70, 128.80, 131.38, 140.68, 146.0, 146.12, 150.28, 157.60, 161.79, 162.27 (ArCs, quinoxaline Cs), 164.64 (C=O) ppm. Anal. for $C_{40}H_{34}N_8O_6$ (722.754) Calcd: C, 66.47; H, 4.74; N, 15.50. Found: C, 66.70; H, 4.80; N, 15.30.

6,13,20,21-Tetrahydro-22*H*-dibenzo[*b*, *j*]1,4,8,11-tetraoxapentadeceno[13,14-*b*]quinoxaline (55). With the use of the general procedure, compounds **1** and **54** gave crude **55** which was purified by chromatography over a short silica column using CH_2Cl_2–MeOH (20:1) as an eluent to give colorless crystals (39%); mp 192°C; MS: *m*/*z* (M^+, 414); ^{1}H NMR ($CDCl_3$) δ 2.16 (quin., 2H, *J*=5.1 Hz, OCH_2CH_2), 4.29 (t, 4H, *J*=5.0 Hz, OCH_2), 5.69 (s, 4H, OCH_2C=N), 6.77–8.10 (m, 12H, ArHs) ppm; ^{13}C NMR ($CDCl_3$) δ 29.40 (OCH_2CH_2), 68.05 (OCH_2CH_2), 72.38 (OCH_2C=N), 114.19, 119.22, 121.45, 123.40, 129.24, 130.18 (ArCHs), 141.37, 148.23, 150.51, 151.59 (ArCs, quinoxaline Cs) ppm. Anal. for $C_{25}H_{22}N_2O_4$ (414.459) Calcd: C, 72.45; H, 5.35; N, 6.76. Found: C, 72.40; H, 5.20; N, 6.5

1,3-Bis[quinoxalino(2,3-*b*)benzoxazepin-13-on-12-yl]propane (60). With the use of the general procedure, compounds **38** and **56** gave crude **60**, which crystallized from methanol as colorless crystals (36%); mp 208–209°C; MS: *m*/*z* (M^+, 566); IR: ν 1660 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (quin., 2H, *J*=6.9 Hz, NCH_2CH_2), 4.60 (t, 4H, *J*=7.0 Hz, NCH_2), 7.24–7.91 (m, 16H, ArHs); ^{13}C NMR ($CDCl_3$) δ 26.85 (NCH_2CH_2), 45.21 (NCH_2), 120.91, 126.32, 127.86, 127.99, 129.71, 129.95, 132.34, 134.43 (ArCHs), 125.54, 137.97, 139.95, 143.82, 151.69,

155.41, 165.32 (ArCs, quinoxaline Cs) ppm. Anal. for $C_{33}H_{22}N_6O_4$ (566.571) Calcd: C, 69.96, H, 3.91; N, 14.83. Found: C, 70.30; H, 3.70; N, 14.50.

1,4-Bis[quinoxalino(2,3-*b*)benzoxazepin-13-on-12-yl]-butane (61). With the use of the general procedure, compounds **38** and **57** gave crude **61**, which crystallized from ethyl acetate as colorless crystals (29%); mp 245°C; MS: *m*/*z* (M^+, 580); IR: ν 1654 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (m, 4H, NCH_2CH_2), 4.64 (m, 4H, NCH_2CH_2), 7.26–7.93 (m, 16H, ArHs) ppm; ^{13}C NMR ($CDCl_3$) δ 25.8 (NCH_2CH_2), 47.4 (NCH_2CH_2), 120.91, 126.39, 127.90, 128.07, 129.73, 130.01, 132.35, 134.39 (ArCHs), 125.81, 137.99, 140.04, 143.94, 151.64, 155.40, 165.38 (ArCs, quinoxaline Cs) ppm. Anal. for $C_{34}H_{24}N_6O_4$ (580.598) Calcd: C, 70.34; H, 4.17; N, 14.47. Found: C, 70.40; H, 4.30; N, 14.50.

6,13,21,22-Tetrahydrodibenzo[*b*, *j*]1,12,5,8-dioxadiaza-cyclopentadeceno[14,15-*b*]quinoxaline-19,24(20*H*,23*H*)-dithione (53). To a solution of **49** (10 mmol) in boiling toluene (20 ml) was added, Lawesson's reagent (20 mmol). The reaction mixture was heated under reflux for 3 h. The solid obtained upon cooling was collected and crystallized from ethanol as brown crystals (60%); mp 229–231°C; MS: *m*/*z* 487 (M^++1, 4%), 455 (100%), 421 (89%), 375 (18%), 286 (100%), 179 (73%), 137 (60%), 77 (65%); ^1H NMR (DMSO) δ 4.1 (s, 4H, NCH_2), 5.6 (s, 4H, OCH_2), 6.9–8.1 (m, 12H, ArHs), 10.33 (br s, 2H, NH) ppm; ^{13}C NMR (DMSO) δ 44.51 (CH_2NH), 72.18 (OCH_2), 113.48, 121.08, 128.8, 131.01, 131.16, 150.78 (ArCHs), 116.62, 119.13, 140.38, 153.20 (ArCs, quinoxaline Cs), 195.13 (C=O) ppm. Anal. for $C_{26}H_{22}N_4O_2S_2$ (486.484) Calcd: C, 64.19; H, 4.56; N, 11.52; S, 13.15. Found: C, 64.30; H, 4.20; N, 11.50; S, 13.40.

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