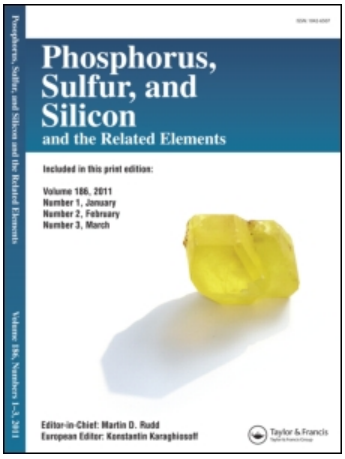


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Complexing Properties of Novel Crown Ethers and Thiacrown Ethers Incorporating New Heterocyclic Moieties

Mehdi Bakavoli[a]; Mohammad Rahimizadeh[a]; Esmaeel Rezaei-Seresht[b]; Majid Mokaber Esfahani[a]; Parisa Ziaee[a]
[a] Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran [b] Department of Chemistry, School of Sciences, Sabzevar Tarbiat Moallem University, Sabzevar, Iran

Online publication date: 24 September 2010

To cite this Article Bakavoli, Mehdi , Rahimizadeh, Mohammad , Rezaei-Seresht, Esmaeel , Esfahani, Majid Mokaber and Ziaee, Parisa(2010) 'Synthesis and Complexing Properties of Novel Crown Ethers and Thiacrown Ethers Incorporating New Heterocyclic Moieties', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 10, 2152 — 2158
To link to this Article: DOI: 10.1080/10426500903544280
URL: http://dx.doi.org/10.1080/10426500903544280

Phosphorus, Sulfur, and Silicon, 185:2152–2158, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903544280

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND COMPLEXING PROPERTIES OF NOVEL CROWN ETHERS AND THIACROWN ETHERS INCORPORATING NEW HETEROCYCLIC MOIETIES

Mehdi Bakavoli,[1] Mohammad Rahimizadeh,[1] Esmaeel Rezaei-Seresht,[2] Majid Mokaber Esfahani,[1] and Parisa Ziaee[1]

[1]*Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran*

[2]*Department of Chemistry, School of Sciences, Sabzevar Tarbiat Moallem University, Sabzevar, Iran*

The synthesis of some novel crown and thiacrown ethers via the reaction of 2,3-bis(4-hydroxyphenyl) or 2,3-bis(4-mercaptophenyl)quinoxalines and pyridopyridazine with diethylene and triethylene glycol ditosylate is described. The complexing ability of compounds 5b and 5h, as the representatives of both groups of compounds, with alkali and alkali earth metal cations were measured by the solvent extraction method. The results showed that crown ether 5b comparatively had more affinity towards the Mg^{2+} cation, while thiacrown ether 5h had greater affinity towards the Ca^{2+} cation.

Keywords Complexing properties; crown ether; pyridopyridazine; quinoxalines; thiacrown ether

INTRODUCTION

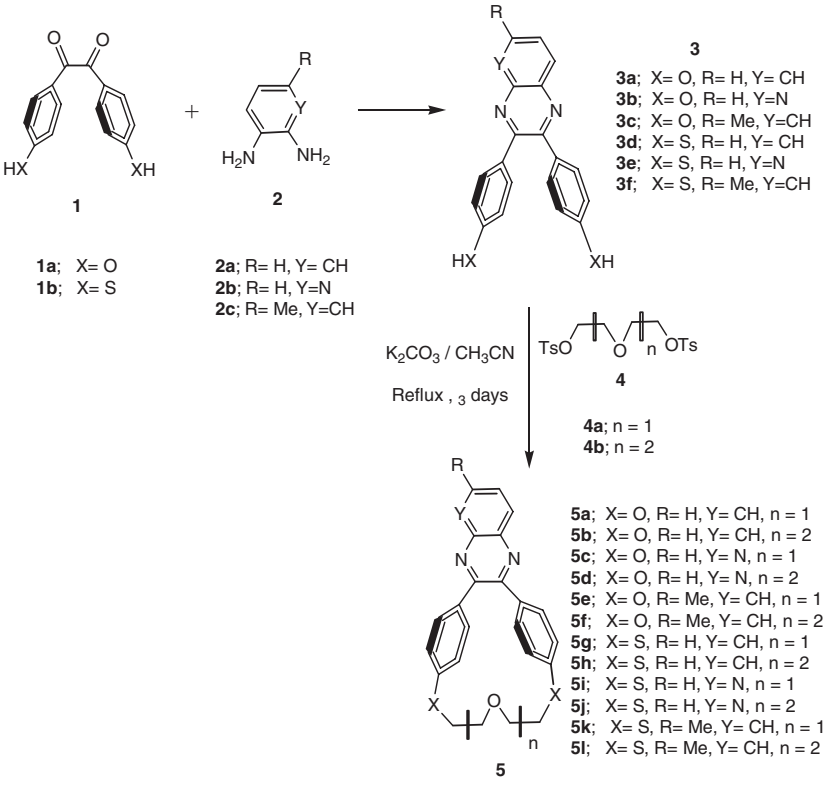
In the course of a program directed toward the synthesis of glycoluril-based receptors for molecular recognition studies, we became interested in 4,4′-disubstituted benzyls, which are valuable synthetic building blocks in the construction of molecular clips with crown ether subunits.[1] Crown ethers have been the focus of much attention since Pedersen's studies in the 1960s.[2] These compounds are important molecular receptors for ionic recognition and are currently used in analytical chemistry and biological model systems, as well as in nuclear medicine.[3,4] Likewise sulfur-substituted crown ethers, or thiacrown ethers**,** have also observed tremendous advances over the past 20 years.[5,6] These compounds are known to coordinate with transition metal cations[5,7] and soft alkaline and earth metal cations,[8] whereas crown ethers prefer to coordinate with hard alkaline and earth metal cations.[9] We report in this article the synthesis of some novel crown and thiacrown ethers derived from 4,4′-disubstituted benzils and their complexing properties with alkali and alkali earth metal

Received 29 July 2009; accepted 7 December 2009.
Address correspondence to Mehdi Bakavoli, Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran. E-mail: mbakavoli@yahoo.com

cations. The complexing abilities of both groups have been exemplified by a representative of each group.

RESULTS AND DISCUSSION

The starting compound **1a**, 4,4′-dihydroxybenzil, was prepared by demethylation of the commercially available 4,4′-dimethoxybenzil using HBr/HOAc mixture as a demethylating agent.[10] Compound **1b**, 4,4′-dimercaptobenzil, was synthesized from 4,4′-dichlorobenzil through an aromatic nucleophilic substitution reaction in the presence of sodium hydrogensulfide in DMF.[11] In the next step, the benzil derivatives **1a** and **1b** were condensed with the aromatic diamines **2a–c** to yield the heterocyclic compounds **3a–f** (Scheme 1). Compound **1a** is comparatively less reactive than **1b**, since p-hydroxy groups have a greater deactivating effect on the electrophilic nature of the carbonyl groups; therefore a condensation reaction of **1a** with diamines was performed under azeotropic distillation to afford the cyclized products **3a–f** (Scheme 1). The latter compounds were reacted with ditosylates **4a** and **4b** under high dilution to obtain the crown and thiacrown ethers **5a–l** (Scheme 1). Spectral evidence and elemental analyses clearly confirmed the formation of these products. For example, the ^{1}H NMR spectrum of thiacrown ether **5g** showed the methylene protons as two triplets at 2.96 and 3.39 ppm (J = 6 Hz). The IR spectrum was devoid of the S–H absorption band at 2520 cm^{-1} of the precursor, but showed a CH_2



Scheme 1

absorption band at 1490 cm^{-1}. The mass spectrum and elemental analysis also confirmed the structure.

Extraction Ability

The complex formation ability of crown ethers with metal cations depends on several factors, including cavity size of ligands, cation diameter, special distribution of the ring binding sites, the character of the heteroatoms, and other factors.[12] Crown and thiacrown ethers containing phenyl groups are expected to interact with metal cations through their heteroatoms, as well as π-electron density of the aromatic rings, and form complexes of their own. The complexing capability can be affected by several factors such as the type of heteroatom. Therefore, a quantitative comparison of complexation capability of **5b** as the representative of crown ethers **5a–f** with that of the corresponding thiacrown ether **5h** towards few metal cations was carried out by the method described by Pedersen,[13] and the results are summarized in Table I. As can be seen from Table I, the extractabilities of both crown ether and thiacrown ether for metal cations are varied and can be attributed to the atomic radii of the cations. Na^+ and Mg^{2+} cations, by having smaller atomic radii and being harder compared to their counterparts in the periodic table of elements, K^+ and Ca^{2+}, have more affinity toward crown ether **5b**, while the softer cations K^+ and Ca^{2+} show higher affinity toward thiacrown ether **5h**. Selective extraction of alkaline earth over alkali metal ions is 2.7 (Mg^{+2}:Na^+ extraction ratio) for crown ether **5b**, whereas this ratio for thiacrown ether **5h** is 8.0 (Ca^{+2}:K^+ extraction ratio). However, the high selectivity is attributed to several factors, such as cavity size of the host, conformational behavior, cation radii, and hardness and softness of donor and receptors atoms.

For high extraction efficiency of thiacrown ether **5h**, rather than **5b**, some contribution to the complex's stability may come from the π-interaction between Ca^{2+} and the electron-rich aromatic rings in the crown ether framework. Although, a charge-transfer complex between heterocyclic moiety and the counterion of the cationic guest may be another reason for this observation. Further investigation on the heterocyclic ring's effects in selectivity and extraability of these compounds is in progress in our laboratory. According to this preliminary study, the extraability of thiacrown ether **5h** is greater than **5b**. These two ligands with the same number of donor atoms have different conformational behavior and cavity size due to the differences in atomic radii and bond angles in sulfur and oxygen

Table I Extraction of metal picrates by crown ether **5b** as compared to its thiacrown ether **5h** [solvent system: CH_2Cl_2:H_2O (1:1)]

Crown	Cation	A_o*	A_e*	% Extraction
5b	Na^+	0.32051	0.33365	4.1
	K^+	0.32051	0.32103	1.5
	Mg^{2+}	0.32051	0.35608	11.1
	Ca^{2+}	0.32051	0.32509	1.4
5h	Na^+	0.40594	0.40767	0.4
	K^+	0.40594	0.42508	4.7
	Mg^{2+}	0.40594	0.40800	0.5
	Ca^{2+}	0.40594	0.55955	37.8

*A_o and A_e are the absorbances of the aqueous layer before and after the extraction.

atoms. Probably the binding site of receptors **5b** and **5h** is fitting well only to the small cations, which may be clamped between the two aromatic walls.

In summary, we have synthesized several new crown ethers and thiacrown ethers incorporating new heterocyclic moieties via a convenient route, and the extraction capabilities of these compounds with few alkali and alkali earth metal cations were exemplified by compounds **5b** and **5h**.

EXPERIMENTAL

Toluene was distilled from sodium benzophenon ketyl. MeCN was distilled from $CaCl_2$. CH_2Cl_2 and MeOH were distilled from CaH_2. Silica gel 60 (0.040–0.063 mm, Merck) was used for column chromatography. 4,4′-Dimethoxybenzil was purchased from Merck. Oligoethylene glycol ditosylates (**4a** and **4b**) were prepared according to the literature.[14] Melting points were recorded on an Electrothermal type 9100 melting point apparatus and are uncorrected. The IR spectra were obtained on a 4300 Shimadzu spectrometer. The ^{1}H NMR (100 MHz) spectra were recorded on a Bruker AC 100 spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard; the coupling constant *J* is given in Hertz. The mass spectra were scanned on a Varian Mat. CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer.

General Procedure for the Synthesis of Dihydroxy Compounds 3a–c

A mixture of 4,4'-dihydroxybenzil (**1a**) (7.4 mmol, 1.73 g), aromatic diamine **2** (7.14 mmol), acetic acid (36 mL), and toluene (11 mL) was refluxed with a Dean–Stark apparatus under N_2 atmosphere for 12 h. After cooling, the mixture was poured into an ice-water (144 mL) and HCl (7 mL) mixture. The precipitate was filtered off and recrystallized from ethanol.

4-[3-(4-Hydroxyphenyl)-2-quinoxalinyl]phenol (3a). Yield 63%; mp > 300 °C; IR (KBr): 609, 762, 735, 981, 1055, 1105, 1143, 1168, 1220, 1278, 1352, 1400, 1438, 1521, 1608, 1666, 1764, 3200, 3520 cm^{-1}; ^{1}H NMR (Acetone-d_6): $\delta = 6.75$ (d, 4H, J = 8 Hz), 7.34 (d, 4H, J = 8 Hz), 7.70 (dd, 2H, J = 2 Hz, J = 7 Hz), 8.05 (dd, 2H, J = 2 Hz, J = 7 Hz), 8.69 (s, 2H, OH); $M^+ = 314$; Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.35; H, 4.33; N, 8.98.

4-[3-(4-Hydroxyphenyl) pyrido [2,3-b] pyrazinyl]phenol (3b). Yield 58%; mp > 300 °C; IR (KBr): 607, 798, 835, 980, 1124, 1174, 1243, 1336, 1386, 1433, 1521, 1556, 1598, 1666, 3257, 3550 cm^{-1}; ^{1}H NMR (Acetone-d_6): $\delta = 6.24$ (d, 4H, J = 8 Hz), 6.89 (d, 4H, J = 8 Hz), 7.34 (dd, 1H, J = 2 Hz, J = 7 Hz), 8.02 (dd, 1H, J = 2 Hz, J = 7 Hz), 8.57 (dd, 1H, J = 4.2 Hz), 9.35 (s, 2H, OH); $M^+ = 315$; Anal. Calcd for $C_{19}H_{13}N_3O_2$: C, 72.37; H, 4.16; N, 13.33. Found: C, 72.35; H, 4.07; N, 13.21.

4-[3-(4-Hydroxyphenyl)-6-methyl-2-quinoxalinyl]phenol (3c). Yield 63%; mp > 300 °C; IR (KBr): 617, 835, 981, 1172, 1240, 1344, 1512, 1558, 1606, 2875, 3520 cm^{-1}; ^{1}H NMR (Acetone-d_6): $\delta = 2.55$ (s, 3H, CH_3), 6.82 (dd, 4H, J = 2 Hz, J = 7 Hz), 7.25–8.09 (m, 7H); $M^+ = 328$; Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.71; H, 4.78; N, 8.41.

General Procedure for the Synthesis of Dimercapto Compounds 3d–f

4,4′-Dimercaptobenzil (**1b**) (10 mmol) was refluxed in ethanol (100 mL) for 30 min. Then a solution of aromatic diamine **2** (11 mmol) in ethanol (50 mL) was added dropwise,

and the reflux was continued for 8 h. After cooling, water (300 mL) was added, and the yellow solid was filtered off, washed with water, and recrystallized from ethanol.

4-[3-(4-Mercaptophenyl)-2-quinoxalinyl]thiophenol (3d). Yield 65%; mp 176–179 °C; IR (KBr): 609, 1111, 1350, 1393, 1660, 2520 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.53$ (s, 2H, SH), 7.23 (d, 4H, J = 7 Hz), 7.41 (d, 4H, J = 7 Hz), 7.79 (dd, 2H, J = 2 Hz, J = 7 Hz), 8.21 (dd, 2H, J = 2 Hz, J = 7 Hz); $M^+ = 346$; Anal. Calcd for $C_{20}H_{14}N_2S_2$: C, 69.36; H, 4.05; N, 8.09; S, 18.50. Found: C, 69.48; H, 3.89; N, 8.31; S, 18.32.

4-[3-(4-Mercaptophenyl)pyrido[2,3-b]pyrazinyl]thiophenol (3e). Yield 63%; mp > 300 °C; IR (KBr): 823, 1095, 1323, 1392, 1456, 1588, 2520, 2864, 2919, 3419 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.54$ (s, 2H, SH) 7.15–7.55 (m, 8H), 7.70 (dd, 1H, J = 2 Hz, J = 7 Hz), 8.48 (dd, 1H, J = 2 Hz, J = 7 Hz), 9.16 (dd, 1H, J = 2 Hz, J = 7 Hz); $M^+ = 347$; Anal. Calcd for $C_{19}H_{13}N_3S_2$: C, 65.70; H, 3.74; N, 12.10; S, 18.46. Found: C, 65.61; H, 3.58; N, 12.37; S, 18.44.

4-[3-(4-Mercaptophenyl)-6-methyl-2-quinoxalinyl]thiophenol (3f). Yield 58%; mp158 °C; IR (KBr): 815, 1183, 1330, 1589, 1630, 2540, 2930, 3423 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.59$ (s, 3H, CH_3), 3.50 (m, 2H, SH), 7.20 (d, 4H, J = 8 Hz), 7.38 (d, 4H, J = 8 Hz), 7.53 (t, 1H, J = 8 Hz), 7.89 (s, 1H), 8.00 (d, 1H, J = 8 Hz); $M^+ = 360$; Anal. Calcd for $C_{21}H_{16}N_2S_2$: C, 70.00; H, 4.44; N, 7.78; S, 17.78. Found: C, 69.94; H, 4.26; N, 7.68; S, 18.12.

General Procedure for the Synthesis of Crown Ethers and Thiacrown Ethers 5a–l

Ditosylate **4** (0.3 mmol) was added in small portions during a period of 12 h to a refluxing mixture of **3** (0.3 mmol) and K_2CO_3 (0.14 g, 1 mmol) in dry MeCN (20 mL). The reflux was continued for 36 h. Then the solvent was evaporated in vacuo, and the residue was partitioned between aqueous NaOH (5%, 25 mL) and CH_2Cl_2 (25 mL). The organic layer was washed with water (2 × 25 mL), dried (Na_2SO_4), and evaporated to dryness. After column chromatography (eluent: CH_2Cl_2:MeOH, 98:2, v/v), compound **5** was obtained as pure powder.

(2,3-Diphenylquinoxaline)-4′,4″-dioxy diethylene glycol (5a). This compound was obtained according to the general procedure starting with **3a** and **4a**. Yield 53%; mp 230 °C; IR (KBr): 883, 978, 1134, 1176, 1247, 1473, 1604, 1666, 1764, 2871, 3381 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.96$ (t, 4H, J = 6 Hz), 4.18 (t, 4H, J = 6 Hz), 6.90 (d, 4H, J = 8 Hz), 7.45 (d, 4H, J = 8 Hz), 7.77 (dd, 2H, J = 4 Hz, J = 6 Hz), 8.13 (dd, 2H, J = 4 Hz, J = 6 Hz); $M^+ = 384$; Anal. Calcd for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.95; H, 5.16; N, 7.32.

(2,3-Diphenylquinoxaline)-4′,4″-dioxy triethylene glycol (5b). This compound was obtained according to the general procedure starting with **3a** and **4b**. Yield 60%; mp 187–190 °C; IR (KBr): 675, 761, 737, 781, 928, 974, 1051, 1134, 1173, 1249, 1296, 1344, 1390, 1440, 1506, 1604, 1666, 1699, 1715, 1764, 2335, 2869 cm^{-1}; ^1H NMR: ($CDCl_3$) δ: 3.61 (s, 4H), 3.70 (t, 4H, J = 5 Hz), 4.05 (t, 4H, J = 5 Hz), 6.70 (d, 4H, J = 8Hz), 7.32 (d, 4H, J = 8 Hz), 7.55 (dd, 2H, J = 4 Hz, J = 7 Hz), 7.86 (dd, 2H, J = 4 Hz, J = 7 Hz); $M^+ = 428$; Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.88; H, 5.65; N, 6.54. Found: C, 72.85; H, 5.71; N, 6.63.

(2,3-Diphenylpyrido[2,3-b]pyrazine)-4′,4″-dioxy diethylene glycol (5c). This compound was obtained according to the general procedure starting with **3b** and **4a**. Yield 32%; mp > 300 °C; IR (KBr): 673, 976, 1128, 1176, 1249, 1384, 1442, 1601, 1664,

1724, 2871 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.95$ (t, 4H, J = 4 Hz), 4.20 (t, 4H, J = 4 Hz), 6.88 (dd, 4H, J = 4 Hz), 7.43–7.63 (m, 5H), 8.48 (dd, 1H, J = 2 Hz, J = 8 Hz), 9.13 (dd, 1H, J = 2 Hz, J = 8 Hz); $M^+ = 385$; Anal. Calcd for $C_{23}H_{19}N_3O_3$: C, 71.67; H, 4.97; N, 10.90. Found: C, 71.61; H, 4.81; N, 10.91.

(2,3-Diphenylpyrido[2,3-b]pyrazine)-4′,4″-dioxy triethylene glycol (5d). This compound was obtained according to the general procedure starting with **3b** and **4b**. Yield 48%; mp 210 °C; IR (KBr): 673, 979, 1592, 1664, 1726 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.73$ (s, 4H), 3.90 (t, 4H, J = 4 Hz), 4.15 (t, 4H, J = 4 Hz), 6.85 (dd, 4H, J = 4 Hz, J = 7 Hz), 7.41–7.67 (m, 5H), 8.41 (dd, 1H, J = 2 Hz, J = 8 Hz), 9.11 (dd, 1H, J = 2 Hz, J = 8 Hz); $M^+ = 429$; Anal. Calcd for $C_{25}H_{23}N_3O_4$: C, 69.92; H, 5.40; N, 9.78. Found: C, 69.78; H, 5.18; N, 9.79.

(2,3-Diphenylquinoxaline)-6-methyl-4′,4″-dioxy diethylene glycol (5e). This compound was obtained according to the general procedure starting with **3c** and **4a**. Yield 54%; mp 130 °C; IR (KBr): 835, 978, 1134, 1174, 1249, 1342, 1512, 1554, 1681, 2873, 3421 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.58$ (s, 3H, CH_3), 3.90 (t, 4H, J = 6 Hz), 4.15 (t, 4H, J = 6 Hz), 6.85 (dd, 4H, J = 2 Hz, J = 6 Hz), 7.15–8.11 (m, 7H); $M^+ = 398$; Anal. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.31; H, 5.64; N, 6.97.

(2,3-Diphenylquinoxaline)-6- methyl-4′,4″-dioxy triethylene glycol (5f). This compound was obtained according to the general procedure starting with **3c** and **4b**. Yield 44%; mp 236 °C; IR (KBr): 979, 1132, 1176, 1244, 1512, 1606, 2868, 3448 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.95$ (s, 3H, CH_3), 3.56 (s, 4H), 3.78 (t, 4H, J = 6 Hz), 4.22 (t, 4H, J = 6 Hz), 6.88 (dd, 4H, J = 4 Hz, J = 8 Hz), 7.15–8.10 (m, 7H); $M^+ = 442$; Anal. Calcd for $C_{27}H_{26}N_2O_4$: C, 73.28; H, 5.92; N, 6.33. Found: C, 73.21; H, 5.79; N, 6.31.

(2,3-Diphenylquinoxaline)-4′,4″-dithio diethylene glycol (5g). This compound was obtained according to the general procedure starting with **3d** and **4a**. Yield 52%; mp > 300 °C; IR (KBr): 665, 761, 784, 816, 923, 946, 1013, 1091, 1170, 1190, 1219, 1352, 1397, 1490, 1555, 1586, 1663, 2923 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.96$ (t, 4H, J = 6 Hz), 3.39 (t, 4H, J = 8 Hz), 7.19 (d, 4H, J = 8 Hz), 7.36 (d, 4H, J = 8 Hz), 7.82 (dd, 2H, J = 4 Hz, J = 7 Hz), 8.20 (dd, 2H, J = 4 Hz, J = 7 Hz); $M^+ = 416$; Anal. Calcd for $C_{24}H_{20}N_2OS_2$: C, 69.20; H, 4.84; N, 6.72; S, 15.40. Found: C, 69.14; H, 4.77; N, 6.58; S, 15.44.

(2,3-Diphenylquinoxaline)-4′,4″-dithio triethylene glycol (5h). This compound was obtained according to the general procedure starting with **3d** and **4b**. Yield 41%; mp > 300 °C; IR (KBr): 665, 761, 784, 816, 923, 946, 1013, 1091, 1170, 1190, 1219, 1352, 1397, 1490, 1555, 1586, 1663, 2923 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.04$ (t, 4H, J = 7 Hz), 3.45–3.8 (m, 8H), 7.32 (d, 4H, J = 12 Hz), 7.46 (d, 4H, J = 12Hz), 7.77 (dd, 2H, J = 4 Hz, J = 7 Hz), 8.13 (dd, 2H, J = 4 Hz, J = 7 Hz); $M^+ = 460$; Anal. Calcd for $C_{26}H_{24}N_2O_2S_2$: C, 67.80; H, 5.25; N, 6.08; S, 13.92. Found: C, 67.79; H, 4.92; N, 6.06; S, 14.14.

(2,3-Diphenylpyrido[2,3-b]pyrazine)-4′,4″-dithio diethylene glycol (5i). This compound was obtained according to the general procedure starting with **3e** and **4a**. Yield 57%; mp 226–228 °C; IR (KBr): 836, 1013, 1081, 1176, 1319, 1374, 1428, 1547, 1594 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.98$ (t, 4H, J = 6 Hz), 3.41 (t, 4H, J = 8 Hz), 7.22 (d, 4H, J = 9 Hz), 7.37 (d, 4H, J = 9 Hz), 7.77 (dd, 1H, J = 4 Hz, J = 7 Hz), 8.55 (dd, 1H, J = 2 Hz, J = 7 Hz), 9.21 (dd, 1H, J = 2 Hz, J = 7 Hz); $M^+ = 417$; Anal. Calcd for $C_{23}H_{19}N_3OS_2$: C, 66.16; H, 4.59; N, 10.06; S, 15.36. Found: C, 66.09; H, 4.43; N, 9.94; S, 15.40.

(2,3-Diphenylpyrido[2,3-b]pyrazine)-4′,4″-dithio triethylene glycol (5j). This compound was obtained according to the general procedure starting with **3e** and **4b**. Yield 39%; mp 98–101 °C; IR (KBr): 607, 727, 765, 794, 827, 973, 1011, 1032, 1094, 1189, 1242, 1333, 1386, 1442, 1541, 1592, 1653, 1717, 2361, 2855, 3420 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.06$ (t, 4H, J = 7 Hz), 3.6 (t, 8H, J = 7 Hz), 7.37 (d, 4H, J = 10 Hz), 7.49 (d, 4H, J = 10 Hz), 7.71 (dd, 1H, J = 4 Hz, J = 7 Hz), 8.52 (dd, 1H, J = 4 Hz, J = 7 Hz), 9.19 (dd, 1H, J = 2 Hz, J = 4 Hz); $M^+ = 461$. Anal. Calcd for $C_{25}H_{23}N_3O_2S_2$: C, 65.05; H, 5.02; N, 9.10; S, 13.89. Found: C, 65.02; H, 4.94; N, 9.03; S, 13.93.

(2,3-Diphenylquinoxaline)-6-methyl-4′,4″-dithio diethylene glycol (5k). This compound was obtained according to the general procedure starting with **3f** and **4a**. Yield 63%; mp 255–260 °C; IR (KBr): 622, 740, 767, 799, 835, 925, 979, 1013, 1054, 1080, 1094, 1185, 1301, 1330,1348, 1395, 1427, 1495, 1548, 1596, 1621, 2931 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.63$ (s, 3H), 2.96 (t, 4H, J = 6 Hz), 3.36 (t, 4H, J = 8 Hz), 7.18 (d, 4H, J = 8 Hz), 7.33(d, 4H, J = 8 Hz), 7.64 (d, 1H), 7.96 (s, 1H), 8.07 (d, 1H, J = 8 Hz); $M^+ = 430$; Anal. Calcd for $C_{25}H_{22}N_2OS_2$: C, 69.73; H, 5.15; N, 6.51; S, 14.89. Found: C, 69.69; H, 5.13; N, 6.55; S, 14.87.

(2,3-Diphenylquinoxaline)-6-methyl-4′,4″-dithio triethylene glycol (5l). This compound was obtained according to the general procedure starting with **3f** and **4b**. Yield 51%; mp 250–255 °C; IR (KBr): 620, 664, 780, 816, 832, 911, 980, 1013, 1094, 1131, 1176, 1295, 1330, 1395, 1484, 1594, 2867 cm^{-1}; ^1H NMR ($CDCl_3$):$\delta = 2.62$ (s, 3H, CH_3), 3.04 (t, 4H, J = 10 Hz), 3.50–3.70 (m, 8H), 7.38 (t, 8H, J = 12 Hz), 7.60 (d, 1H, J = 9 Hz), 7.93 (s, 1H), 8.05 (d, 1H, J = 9 Hz); $M^+ = 474$; Anal. Calcd for $C_{27}H_{26}N_2O_2S_2$: C, 68.32; H, 5.25; N, 5.90; S, 13.51. Found: C, 68.36; H, 4.98; N, 6.01; S, 13.47.

REFERENCES

1. M. Rahimizadeh, E. Rezaei Seresht, M. Bakavoli, and M. Pordel, *Can. J. Chem.*, **85,** 964 (2007).
2. C. J. Pedersen, *J. Am. Chem. Soc.*, **89,** 7017 (1967).
3. G. W. Gokel, W. M. Leevy, and M. E. Weber, *Chem. Rev.*, **104,** 2723 (2004).
4. J. C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, **34,** 1048 (2005).
5. (a) S. R. Cooper, *Acc. Chem. Res.*, **21,** 141 (1988); (b) A. J. Blake and M. Schroder, *Adv. Inorg. Chem.*, **35,** 1 (1990); (c) S. R. Cooper and S. C. Rawle, *Struct. Bonding*, **72,** 1 (1990).
6. (a) J. Buter and R. M. Kellogg, *Org. Synth.*, **65,** 150 (1987); (b) R. E. Wolf Jr., J. R. Hartman, L. A. Ochrymowycz, and S. R. Cooper, *Inorg. Synth.*, **25,** 122 (1989); (c) P. J. Blower and S. R. Cooper, *Inorg. Chem.*, **26,** 2009 (1987).
7. (a) C. J. Pedersen, *J. Org. Chem.*, **36,** 254 (1971); (b) S. G. Murray and F. R. Hartley, *Chem. Rev.*, **81,** 365 (1981).
8. (a) B. Russell, *J. Org. Magn. Reson.*, **4,** 433 (1972) (b) J. Meijer, P. Vermeer, H. D. Verkruijsse, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **92,** 1326 (1973); (c) R. C. Long and J. H. Goldstein, *J. Mol. Spectrosc.*, **40,** 632 (1971); (d) K. K. Deb, J. E. Bloor, and T. C. Cole, *Inorg. Chem.*, **10,** 2428 (1972); (e) N. V. Bojkova and R. S. Glass, *Tetrahedron Lett.*, **39,** 9125 (1998).
9. (a) C. J. Pedersen, *J. Am. Chem. Soc.*, **89,** 2495 (1967); (b) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93,** 600 (1971); (c) N. S. Poonia, *J. Am. Chem. Soc.* **96,** 1012 (1974); (d) R. M. Izatt, K. Pawlak, and J. S. Bradshaw, *Chem. Rev.*, **91,** 1721 (1991).
10. C. R. Moylan, R. Wortmann, R. J. Twieg, and I. H. McComb, *Chem. Mater.*, **5,** 1499 (1993).
11. Y. Ding and A. S. Hay, *Macromolecules*, **29,** 6386 (1996).
12. F. Dejong and D. N. Reihoult, *Stability and Reaction of Crown Ether Complexes* (Academic Press, New York, 1981).
13. C. J. Pedersen, *Federation Proceedings*, **27,** 1305 (1968).
14. M. Ouchi, Y. Inoue, T. Kanzaki, and T. Hakushi, *J. Org. Chem.*, **49,** 1408 (1984).