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Macrocyclic Dithiomaleonitrile Derivatives Containing Sulfur and Nitrogen Heteroatoms

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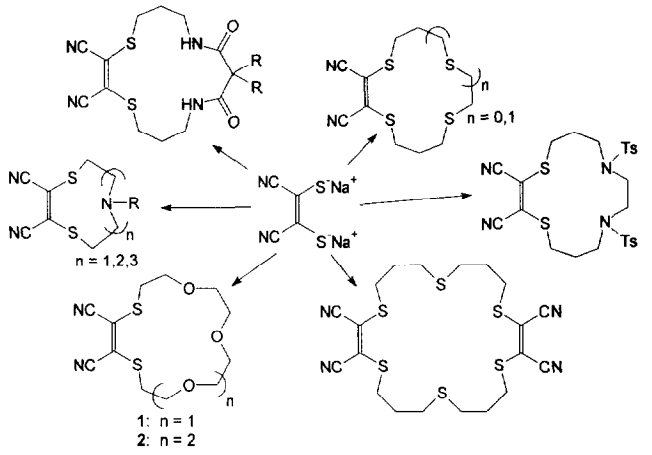
Abstract: A general synthetic method for incorporation of the dithiomaleonitrile unit into macrocycles containing sulfur, oxygen, and nitrogen heteroatoms is presented along with the single-crystal X-ray structures of the thiacrowns. In addition to being new ligands, these macrocycles are direct precursors to peripherally crown functionalized porphyrazines capable of coordinating multiple metal ions.

INTRODUCTION

We[1] and others[2] have studied the metal complexation of the *oxa*-crowned derivatives of dithiomaleonitrile (**1, 2**). These crowns are readily synthesized from disodium dithiomaleonitrile (see inset) and coordinate heavy metal ions, with endocyclic Ag^{I} and Hg^{II} complexes and exocyclic Pd^{II} complexes being known. The electron-withdrawing effect of the maleonitrile unit reduces the sigma-donating ability of the sulfur atoms relative to their fully saturated analogues, and thus the normally thiophilic metal ions, Hg^{II} and Ag^{I}, preferentially coordinate to the macrocyclic oxygen atoms in **2**.

Our interest in synthesizing new macrocycles containing the dithiomaleonitrile unit further stems from their use as precursors to crowned octathioporphyrazines capable of coordinating multiple metal ions.[3,4,5] The ability to functionalize porphyrazines with crowns of different coordinating abilities (S vs O vs N) will allow directed synthesis of molecules that preferentially bind alkali metal, heavy metal, or transition metal ions. Thus, the crowned octathioporphyrazine prepared from **1** forms complexes with Ag^{I} [4,5] and Hg^{II}.[4c] To achieve new crowned derivatives of dithiomaleonitrile having increased affinity for transition metal ions, and thus porphyrazines with this affinity, we have prepared crowns containing only sulfur, as well as with mixed sulfur and nitrogen donor atoms.

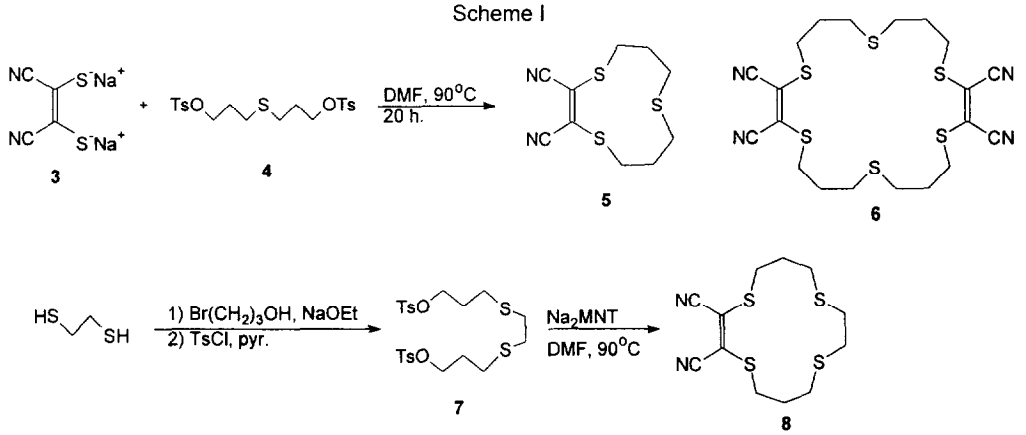


RESULTS AND DISCUSSION

Thiacrown derivatives of MNT.

We have employed the procedure shown in scheme I to prepare crowns **5, 6,** and **8** containing only sulfur donor atoms. This procedure follows our recently reported improved synthesis of **1** and **2** (inset).[1b] The reaction of ditosylate **4**, with disodium dithiomaleonitrile (Na_2MNT) in N,N'-dimethylformamide (DMF) gives macrocycle **5** in 47% yield. In addition, the 2 + 2 addition product, **6**, is formed in 12% yield. The acyclic precursor to tetrathia crown **8** is formed by first reacting ethanedithiol with 3-bromopropanol and then allowing the resulting diol to react with *p*-toluenesulfonyl chloride to give **7**. Reaction of **7** with Na_2MNT gives **8** in 45% yield without the formation of larger rings. The ^1H NMR measurements indicate that **5** and **8** are conformationally constrained at temperatures up to 140 °C (six distinguishable methylene resonances for **5** and seven for **8**), while the larger hexathia crown is conformationally mobile (three methylene resonances) at room temperature.

Scheme I



Structure Descriptions of Thiacrown Derivatives of MNT.

We have solved the X-ray structures of compounds **5**, **6**, and **8**. Bond lengths correspond closely to previous crown structures[6] with carbon-sulfur bonds of the C_{olefin}-S type averaging 1.75Å while the simple C-S bonds average 1.82Å. Structures of macrocyclic thioethers are often characterized according to whether the lone pairs of the sulfur atoms point into or out of the macrocyclic ring, endo- and exocyclic conformations respectively. Uncomplexed aliphatic macrocyclic thioethers commonly adopt the exo conformation[7] and often require large conformational changes to form endocyclic metal complexes. By introducing appropriate ring substituents that force the crown to adopt an endo conformation, increased affinity for Ni^{II} and Cu^{II} metal ions has been observed.[8] The rigidity and size of the maleonitrile unit in the crowns discussed here partially preorganizes the macrocycles towards endocyclic conformation. Thus, in the eleven membered crown, **5**, the sulfur atoms associated with the maleonitrile unit have one lone pair each directed to the center of the macrocyclic ring while the third sulfur donor atom adopts an exo conformation with its lone pairs pointing away (figure 1a). This corresponds closely to the structure of a related crown in which the maleonitrile unit is replaced with a benzene ring.[9]

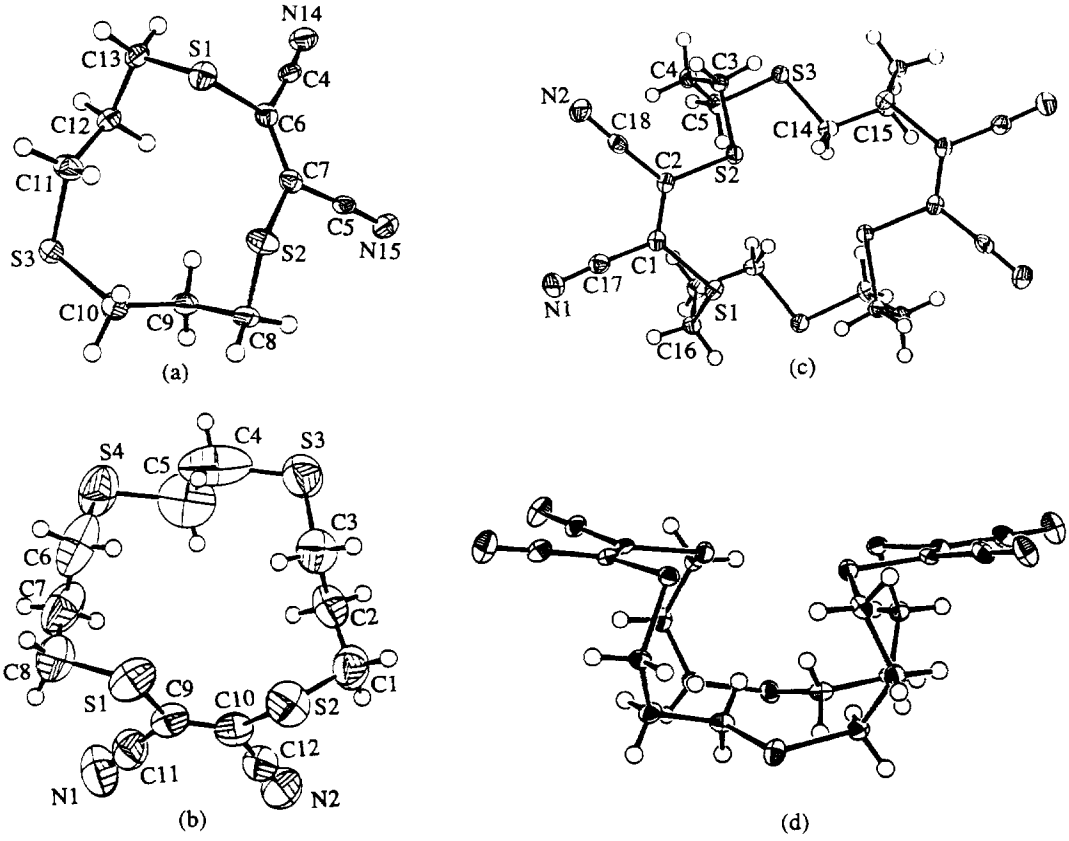


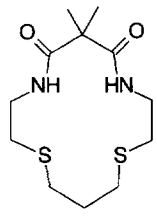
Figure 1: ORTEP representations of compounds of **5** (a), **8** (b) and **6** (c,d).

The tetrathia molecule, **8**, crystallizes in a box-like shape (figure 1b) similar to the fully saturated analog [14]aneS_4.[7b] The sulfur atoms opposite the maleonitrile unit, S3 and S4, are exocyclic and occupy two corner positions of the box. However, in contrast to [14]aneS_4 in which all of the S atoms are exocyclic, the sulfur atoms from the maleonitrile unit contribute one lone pair each to the center of the ring. Examination of torsion angles for the corner sulfur atoms shows the S-C-C-S bond to be anti and both C-S-C-C bonds to adopt gauche conformation. This is typical for thiaether crowns as C-S bonds prefer a gauche conformation.[7a]

In contrast to dibenzo-18aneS_6, which adopts a chair-like conformation,[10] the hexadentate thiacrown, **6**, prefers the basket like structure (figure 1c,d). The molecule sits on a crystallographically imposed C_2 axis that pierces the center of the macrocyclic cavity. The two maleonitrile units are nearly coplanar with their S atoms directed toward the center of the macrocycle. The distances to the center C_2 axis from S1 and S2 are 1.78(2) and 2.98(2) Å respectively. This conformation may have important implications for the coordination chemistry of the macrocycle. The ligand will likely require significant conformational changes in order to complex in an octahedral fashion. However, little conformational change should be required in order to complex in a square planar fashion through the S donors associated with the maleonitrile units.

Amide containing crowned derivatives of MNT

Kimura et al. have recently reported the synthesis and metal binding properties of dithiadioxocyclam, **9**. They have shown the combination of the soft thia donor with the hard amido donors to coordinate Pd^{II} and Pt^{II} exclusively over Cu^{II}, Ni^{II}, and Co^{II} even at elevated pH; whereas the nitrogen analog coordinates these latter metals smoothly and quantitatively at room temperature.[11] The ligand also efficiently removes Pt from cis-platin.[11] We have synthesized the similar, slightly larger macrocycle, **11**, containing the maleonitrile unit in two steps from readily available starting materials. Reaction of diethylmalonyl dichloride with the hydrobromide salt of 3-bromopropylamine in dichloromethane with triethylamine gives the key acyclic crown precurser **10** in 95% yield. The preferred solvent for cyclization is an ethanol/water solution, providing crown **11** in yields of 25-30%. Cyclizations using DMF as the solvent typically yield only 5-8%.



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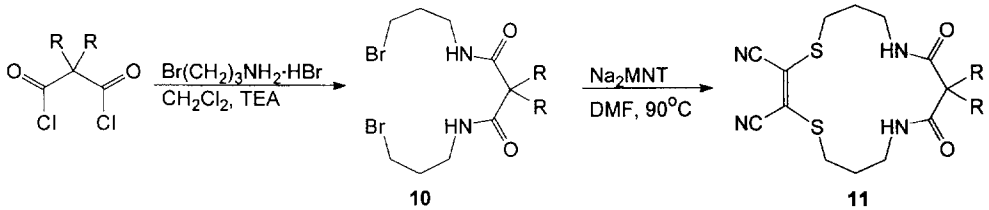
Scheme II



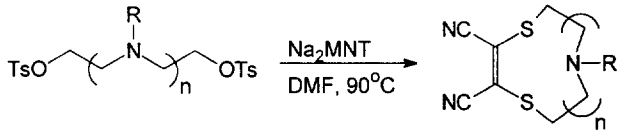
10 **11**

N-protected crowns

The synthesis of the aza-crown derivatives of dithiomaleonitrile begins with the protection of the N atoms. We have investigated the use of two protecting groups, toluene-4-sulfonyl (tosyl) and diethyl phosphoryl. Both protecting groups are stable to the basic conditions used for porphyrazine formation.[3] The tosyl group is well-known to be successful in a varity of aza-crown systems, but deprotecting it typically requires harsh conditions. Therefore, we have also prepared the macrocycles with the more readily cleaved diethyl phosphoryl group.[12]

The first step in preparing these macrocycles involves the synthesis of the acyclic precursors **12-16**. The acyclic pertosylated amines **12**, **14**, and **16** are readily prepared from literature methods.[13] Because the phosphorylation of alkanolamines in the presence of weak inorganic bases is fully chemoselective,[14] we were able to extend Zwierzak and coworkers' procedure for protection of diethanolamine to ethylenediamine diethanol as well. Once obtained, the N-protected diols are then converted to the corresponding ditosylates, **13** and **15**.

Scheme III



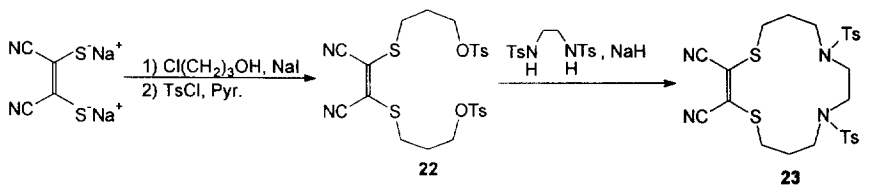
12: n=1, R=Ts
13: n=1, R=PO(OEt)$_2$
14: n=2, R=Ts
15: n=2, R=PO(OEt)$_2$
16: n=3, R=Ts

17: n=1, R=Ts
18: n=1, R=PO(OEt)$_2$
19: n=2, R=Ts
20: n=2, R=PO(OEt)$_2$
21: n=3, R=Ts

The acyclic precursors, **12-16**, are reacted with Na_2MNT using the cyclization conditions described for the thia-crown derivatives, and give the macrocycles, **17-21**, respectively, in yields of 22-38%. The one exception is **18** which forms in only 6% yield. Interestingly, in the synthesis of both **17** and **18**, the formation of the larger tetranitrile-containing macrocycles (2 + 2 addition products) was observed in minor amounts. This is analogous to that seen in the synthesis of **5**.

To this point all of the crown syntheses discussed involve the synthesis of an appropriate acyclic precursor and reaction with the nucleophile Na_2MNT. An alternative method, as shown in scheme IV, is based on the classic method of Richman and Atkins[13] for aza-crown synthesis. To use this procedure the maleonitrile-containing unit is converted into the electrophilic component of the cyclization reaction as follows. Disodium dithiomaleonitrile is first alkylated with 3-chloro-1-propanol and then reacted with *p*-

Scheme IV



22 **23**

toluenesulfonyl chloride to afford the key acyclic precurser, **22**. Reaction of **22** with the disodium salt of N,N'-bis(*p*-toluenesulfonyl)ethylenediamine forms the tosyl protected macrocycle, **23**, in 32% yield.

Conclusion:

We have previously reported a synthetic method for oxa-crowned derivatives of dithiomaleonitrile. We have now generalized this method to macrocyclic derivatives of dithiomaleonitrile containing all sulfur, and mixed sulfur and nitrogen heteroatoms. X-ray crystallography of the thiacrowns suggests that the S atoms of the maleonitrile unit are preorganized for metal coordination in an endocyclic manner. In fact, the S atoms of the dithiomaleonitrile units adopt endo conformations in all three cases, while all of the simple aliphatic S atoms are exo. Future work will explore the coordination chemistry of this unique class of macrocycles and study the peripheral crown appended porphyrazines.

EXPERIMENTAL SECTION

Materials and Apparatus. Disodium dithiomaleonitrile was prepared according to literature procedures.[15] All other reagents and solvents were of reagent grade quality, obtained from Aldrich, and were used as obtained. Proton and carbon NMR spectra were recorded on either Varian Gemini-300 (300 MHz) or Varian VXR-300 (300 MHz) spectrometers. Infrared spectra were recorded on a Mattson Instruments Alpha Centauri FTIR spectrometer. EI and FAB mass spectra were recorded using a VG-70-250SE instrument.

Preparation of 4-thianonane-1,9-di-p-toluenesulfonate (**4**). The synthesis but not the characterization of compound **4** has been previously reported by Riley and Oliver.[16] Using their method, **4** was prepared in 63% yield: mp 64-66 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (4H, quint, -$CH_2CH_2CH_2$-), 2.45 (10H, m, -Ar-CH_3, -CH_2S-), 4.10 (4H, t, -CH_2O-), 7.35 (2H, d, *Ar*), 7.78 (2H, d, *Ar*); ^{13}C NMR ($CDCl_3$) δ 21.5, 27.5, 28.5, 68.6, 127.7, 129.8, 132.5, 144.8; MS *m/e* 458 (M+).

Preparation of 1,5,8-trithiacycloundec-6-en-6,7-dicarbonitrile (**5**). Disodium dithiomaleonitrile (1.62g, 8.7 mmol) and **4** (4.0g, 8.7 mmol) were added together to rapidly stirring anhydrous N,N'-dimethylformamide (DMF) (1L) heated at 90°C. After 20 hours the DMF was removed under reduced pressure and the residue taken up in chloroform (200ml) and filtered. The filtrate was washed 3 times with water, dried over Na_2SO_4, filtered, and the solvent removed by rotary evaporation to leave a golden brown solid. The product (1.04g, 47%) was purified by column chromatography on silica gel (eluent $CHCl_3$) and was isolated as a yellow crystalline solid: mp 152-155 °C; ^{1}H NMR ($CDCl_3$) δ 2.05 (4 H, m, -$CH_2CH_2CH_2$-), 2.68 (4H, t, -CH_2SCH_2-) 3.09 (4 H, t, -$CSCH_2CH_2$-); ^{13}C NMR ($CDCl_3$) δ 29.3, 33.0, 36.3, 112.6, 128.2; HR EI MS *m/e* 256.0143 (M+) (calcd for $C_{10}H_{12}N_2S_3$, *m/e* 256.0163).

Preparation of 1,5,8,12,16,19-hexathiacyclodocos-6,17-dien-6,7,17,18-tetracarbonitrile (**6**). The hexathia product (0.278g, 12%), **6**, was obtained as a byproduct from the synthesis of **5**, eluting immediately after **5** by column chromatography: mp 129-132 °C; ^{1}H NMR δ ($CDCl_3$) 2.02 (8H, quint., $CH_2CH_2CH_2$), 2.67 (8H, t, -CH_2SCH_2-), 3.29 (8H, t, -$CSCH_2$-); ^{13}C NMR δ ($CDCl_3$) 28.9, 29.8, 33.5, 111.8, 121.3; HR EI MS m/e 512.0358 (M+) (calcd for $C_{20}H_{24}N_4S_6$, m/e 512.0325).

Preparation of 4,7-dithiadecane-1,10-di-p-toluenesulfonate (**7**). A solution of 4,7-dithiadecane-1,10-diol[17] (3.25g, 15 mmol) in pyridine (50 ml) was cooled to 0°C with stirring and *p*-toluenesulfonyl chloride (3.8g, 20 mmol) in pyridine (50 ml) was added dropwise over a 30 minute period. The solution was kept stirring for an additional 4 h at 0°C and after this time it was placed in a freezer at -10°C for 24 hours with occasional swirling. After 24 hours the reaction solution was poured over crushed ice (300g) in conc HCl (150 ml) and stirred for 30 minutes. The aqueous mixture was extracted with $CHCl_3$ (3 times, 200ml), the organics combined, dried over $MgSO_4$, and filtered. The chloroform was removed by rotary evaporation to leave a partially solidified oil. The product (4.8g, 62%) was isolated as a white crystalline solid after purification by column chromatography on silica gel (eluent, $CHCl_3$): mp 68-71°C; ^{1}H NMR ($CDCl_3$) δ 1.91(4h, quint., -$CH_2CH_2CH_2$-), 2.45(6H, s, ArCH_3), 2.55(4H, t, -$CH_2CH_2CH_2$S-), 2.61(4H, s, -SCH_2CH_2S-), 4.12(-OCH_2CH_2-), 7.35(4H, d, aromatic), 7.75(4H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.6, 27.8, 28.8, 68.6, 127.8, 129.9, 132.7, 144.9; EI MS *m/e* 518 (M+).

Preparation of 1,4,8,11-tetrathiacyclotetradec-9-en-9,10-dicarbonitrile (**8**). Disodium dithiomaleonitrile (1.6g, 8.59 mmol) was allowed to react with **7** (4.45g, 8.59 mmol) as described for **5** above. The product (1.27g, 45%) was isolated as a yellowish crystalline solid after purification by column chromatography on silica gel (eluent, $CHCl_3$): mp 125-127 °C; ^{1}H NMR ($CDCL_3$) δ 1.98 (4 H, m, -$CH_2CH_2CH_2$-), 2.56 (4 H, m, -$CH_2CH_2CH_2$S-), 2.62 (4 H, s, -SCH_2CH_2S-), 3.22 (4 H, m, -CSCH_2CH_2-); ^{13}C NMR ($CDCl_3$) δ 29.4, 31.7, 33.0, 111.9, 123.2; HR EI MS *m/e* 316.0175 (M+) (calcd for $C_{12}H_{16}N_2S_4$ 316.0196).

Preparation of 1,11-dibromo-4,8-diaza-6,6-diethyl-5,7-dioxoundecane (**10**). Diethylmalonyl dichloride (12g, 61mmol) and 3-bromopropylamine hydrobromide (25g, 122mmol) were added to methylene chloride (100 ml) cooled to 0°C with stirring. A solution of methylene chloride (60 ml) and triethylamine (51 ml, 366 mmol) was then added dropwise to the slurry over 30 minutes. Methylene chloride was added as necessary to keep the mixture stirring. The mixture was stirred an additional 15 minutes and then extracted with dilute HCl until the washings remained acidic. The organic layer was dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to leave a white crystalline product. The product (22.4g, 92%) was purified by recrystallization from methanol: mp 109-111°C; ^{1}H NMR ($CDCl_3$) δ 0.82 (6 H, t, -CH_3), 1.85 (4 H, q, -CCH_2CH_3), 2.10 (4 H, q, -$CH_2CH_2CH_2$-), 3.45 (8 H, m, BrCH_2-, -NCH_2-), 7.5 (2 H, t, -N*H*); ^{13}C NMR $CHCl_3$ δ 9.9, 30.3, 30.7, 31.9, 37.9, 57.8, 173.3; EI MS *m/e* 400 (M+).

Preparation of 1,5-diaza-3,3-diethyl-2,4-dioxo-9,12-dithiacyclopentadec-10-en-10,11-dicarbonitrile (**11**). Disodium dithiomaleonitrile (2.5g, 0.013 mmol) and **10** (5.36g, 0.013 mmol) were added to a refluxing solution of ethanol (900 ml) and water (200 ml). After 20 hours the solvent was removed by rotary evaporation to leave a yellowish colored solid. The solid was taken up in chloroform, filtered and the solvent removed by rotary evaporation. The product (1.68g, 33%) was purified by column chromatography on silica gel (eluent, 2% MeOH/$CHCl_3$): mp 181-184 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (6 H, t, CH_3), 1.88 (4 H, q, CCH_3), 1.97 (4 H, m, CH_2), 3.25 (4 H, t, SCH_2), 3.5 (4 H, q, NCH_2), 7.08 (2 H, t, NH); ^{13}C NMR ($CDCl_3$) δ 9.5, 28.5, 28.7, 34.2, 39.5, 58.3, 112.2, 123.0, 173.1; HR FAB+ MS *m/e* 381.1370 (M+H) (calcd for $C_{17}H_{25}N_4O_2S_2$, *m/e* 381.1418); IR 1637 (CO) cm^{-1}, 2204 (CN) cm^{-1}.

Preparation of N-p-toluenesulfonyl-1-aza-4,7-dithiacyclonon-5-en-5,6-dicarbonitrile (**17**). Disodium dithiomaleonitrile (2g, 11.0 mmol) was allowed to react with N-(*p*-toluenesulfonyl)-4-azaheptane-1,7-di-*p*-

toluenesulfonate[18] (6.25g, 11.0 mmol) by the method described for **5**. The product (1.52 g, 38%) was isolated following column chromatography (eluent, $CHCl_3$): mp 235-240 °C (dec.);^{1}H NMR ($CDCl_3$) δ 2.46 (3H, s, CH_3Ar), 3.55 (8H, m, -NSH_2CH_2S-), 7.35 (2H, d, aromatic), HR EI MS *m/e* 365.0313 (M+) (calcd for $C_{15}H_{15}N_3S_3O_2$ m/e 365.0326).

Preparation of N,N'-bis(p-toluenesulfonyl)-3,6-diazaoctane-1,8-di-p-toluenesulfonate (**14**). *N,N'*-bis(2-hydroxyethyl)ethylenediamine (5g, 0.034 mol) was reacted with *p*-toluenesulfonyl chloride (38g, 0.203 mol) by the method described for **7**. The product (7.8g, 30%) was isolated following recrystallization of the crude solid from ethanol: mp 148-152 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s), 3.30 (s), 3.35 (m), 4.15 (t), 7.32 (d), 7.75 (m); ^{13}C NMR ($CDCl_3$) δ 21.5, 21.6, 49.8, 68.9, 127.2, 127.3, 128.0, 129.8, 129.9, 132.3, 134.9, 143.9, 145.1; FAB MS *m/e* 765 (M+).

Preparation of N,N'-bis(p-toluenesulfonyl)-1,4-diaza-7,10-dithiacyclododec-8-en-8,9-dicarbonitrile (**19**). Disodium dithiomaleonitrile (2.37g, 12.7 mmol) was allowed to react with **14** (9.75g, 12.7 mmol) by the method described for **5**. The product (2.1g, 30%) was isolated as a white solid following repeated recrystallizations of the crude residue from methanol: mp 247-249 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (6 H, s, -CH3Ar), 3.32 (4 H, t, -SCH_2-), 3.36 (4 H, t, -NCH_2CH_2S-), 3.57 (4 H, s, -NCH_2CH_2N-), 7.34 (4 H, d, aromatic), 7.68 (4 H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.6, 36.6, 48.6, 49.7, 111.7, 127.2, 130.0, 135.5, 144.2; EI MS m/e 562 (M+), 407 (M - Ts); HR FAB MS *m/e* 563.0931 (M+H) (calcd for $C_{24}H_{27}N_4S_4O_4$, 563.0915).

Preparation of N,N',N"-tris(p-toluenesulfonyl)-3,6,9-triazaundecane-1,11-di-p-toluenesulfonate (**16**). N,N',N"-tris(p-toluenesulfonyl)-3,6,9-triazaundecane-1,11-diol[13] (10g, 15.3 mmol) was reacted with *p*-toluenesulfonyl chloride (7.3, 38.2 mmol) by the method described for **7**. The product (7.06g, 48%) was isolated following recrystallization of the crude solid two times from methanol: mp 153-156 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (m), 3.27 (s), 3.40 (t), 3.45 (s), 4.15 (t), 7.30 (m), 7.75 (m); ^{13}C NMR ($CDCl_3$) δ 21.5, 21.6, 48.9, 49.3, 49.5, 68.8, 127.4, 127.5, 128.0, 130.0, 132.3, 135.0, 143.8, 143.9, 145.1; FAB MS *m/e* 962 (M+H).

Preparation of N,N',N"-tris(p-toluenesulfonyl)-1,4,7-triaza-10,13-dithiacyclopentadec-11-en-11,12-dicarbonitrile (**21**). Disodium dithiomaleonitile (2.19g, 11.7mmol) was allowed to react with **16** (11.3g, 11.7mmol) by the method described for **5**. The product (3.0g, 34%) was isolated as a white solid following purfication by column chromatography on silica gel (eluent, $CHCl_3$): mp 213-216 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 2.43 (6 H, s, CH_3Ar), 2.45 (3 H, s, CH_3Ar), 3.19 (4 H, t, -SCH_2-), 3.34 (4 H, br t, -NCH_2CH_2S-), 3.39 (4 H, br t, -SCH_2CH_2NCH_2-), 3.53 (4 H, t, -SCH_2CH_2NCH_2CH_2N-), 7.33 (6 H, m, aromatic), 7.74 (4 H, d, aromatic), 7.80 (2 H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.5, 37.2, 51.3, 51.8, 53.1, 111.5, 121.4, 127.5, 129.9, 130.0, 133.8, 134.3, 143.9, 144.2; FAB MS *m/e* 760 (M + H), 604 (M-Ts), HR FAB MS m/e 760.1458 (M+H) (calcd for $C_{33}H_{37}N_5S_5O_6$, 760.1426).

Preparation of N-diethylphosphoryl-4-azaheptane-1,7-di-p-toluenesulfonate (**13**). N-diethylphosphoryl-4-azaheptane-1,7-diol[14] (18g, 75 mmol) was reacted with *p*-toluenesulfonyl chloride (35.6g, 187 mmol) by the method described for **7**. The crude oil was purified by silica gel chromatography (eluent, 3% MeOH/$CHCl_3$): yield 18g, 44%; ^{1}H NMR ($CDCl_3$) δ 1.20 (6 H, t, CH_3CH_2-), 2.42 (6 H, s, CH_3Ar), 3.26 (4 H, m, -NCH_2-), 3.89 (4 H, m, -OCH_2CH_3), 4.03 (4 H, t, TsOCH_2-), 7.33 (4 H, d, aromatic), 7.74 (4 H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.8, 15.9, 16.0, 21.3, 21.5, 21.6, 46.1, 62.2, 62.4, 62.4, 62.6, 68.6, 68.7, 68.8, 127.7, 127.8, 129.8, 129.9, 132.4, 145.0; EI MS *m/e* 550 (M+).

In addition, the monotosylated product (5.2g, 17.5%), N-diethylphosphoryl-4-azaheptane-1,7-diol *p*-toluenesulfonate, was isolated in pure form as a slower moving fraction: ^{1}H NMR ($CDCl_3$) δ 1.24 (6H, t, -CH_2CH_3), 2.42 (3H, s, ArCH_3), 3.18 (2H, t, -CH_2N-), 3.28 (2H, m, -CH_2N-), 3.62 (2H, t, TsOCH_2-), 3.97 (4H, q, -OCH_2CH_3), 4.07 (2H, t, HOCH_2-), 7.32 (2H, d, aromatic), 7.75 (2H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.9, 21.6, 45.9, 50.0, 62.7, 68.6, 127.8, 129.9, 132.5, 145.0; FAB MS *m/e* 396 (M+H).

Preparation of N-diethylphosphoryl-1-aza-4,7-dithiacyclonon-5-en-5,6-dicarbonitrile (**18**). Disodium dithiomaleonitrile (1.7g, 9 mmol) was allowed to react with **13** (5.0g, 9 mmol) by the method described for **5**. The product (0.19g, 6%) was isolated as a white solid following purification by column chromatography on silica gel (eluent $CHCl_3$): mp 190-193 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 1.37 (6 H, t, -CH_3CH_2-), 3.18-3.38 (8 H, m, -SCH_2-, -NCH_2-), 4.10 (4 H, q, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 16.3, 16.4, 34.3, 49.1, 49.1, 63.1, 63.1, 111.2, 121.3; EI MS *m/e* 347. (M+).

Preparation of N,N'-bis(diethylphosphoryl)-3,6-diazaoctane-1,8-di-p-toluenesulfonate (**15**). Using the method of Zwierzak et al.,[15] N,N'-bis(2-hydroxyethyl)ethylenediamine (10.5g, 71 mmol) was allowed to react with diethylphosphite (18.25 ml, 142 mmol) to give N,N'bis(diethylphosphoryl)-3,6-diazaoctane-1,8-diol: yield 25.4g, 85%; ^{1}H NMR ($CDCl_3$) δ 1.27 (12 H, t, CH_3CH_2-), 3.09-3.20 (8 H, m, -CH_2N-), 3.63 (4 H, t, -CH_2OH), 3.77 (2 H, br, -O*H*), 3.94-4.06 (8 H, m, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.1, 46.8, 50.1, 50.2, 61.2, 62.4, 62.5; FAB MS *m/e* 421 (M + H). N,N'bis(diethylphosphoryl)-3,6-diazaoctane-1,8-diol (36.3g, 86 mmol) was reacted with *p*-toluenesulfonyl chloride (41g, 215 mmol) to give **15** by the method described for **7**. The product (37g, 59%) was isolated as a partially solidified oil following purification by column chromatography on silica gel (eluent $CHCl_3$): ^{1}H NMR ($CDCl_3$) δ 1.20 (12 H, t, CH_3CH_2-), 2.36 (6 H, s, CH_3Ar), 3.03 (4 H, m, -CH_2N-), 3.22 (4 H, m, -CH_2N-), 3.88 (8 H, m, -OCH_2CH_3), (4 H, m, -CH_2OTs), 7.29 (4 H, d, aromatic), 7.71 (4 H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.8, 15.9, 16.0, 45.3, 45.5, 62.1, 62.2, 62.3, 62.3, 62.4, 68.7, 127.7, 127.8, 129.7, 129.7, 132.3, 144.8; FAB MS *m/e* 729 (M + H), 557 (M - OTs^-).

Preparation of N,N'-bis(diethylphosphoryl)-1,4-diaza-7,10-dithiacyclododec-8-en-8,9-dicarbonitrile (**20**). Disodium dithiomaleonitrile (4.16g, 22 mmol) was reacted with **15** (16.3g, 22 mmol) by the method described for **5**. The product (2.6g, 22%) was isolated as a waxy white solid following purification by column chromatography on silica gel (eluent $CHCl_3$): ^{1}H NMR ($CDCl_3$) δ 1.31 (12 H, t, CH_3CH_2), 3.22-3.40 (12 H, m, SCH_2, NCH_2), 3.94-4.10 (8 H, m, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 16.2, 37.0, 47.6, 47.6, 48.6, 62.5, 62.6, 62.6, 62.7, 62.8, 112.0, 126.0; HR EI MS *m/e* 526.1218 (M+) (calcd for $C_{18}H_{22}N_4O_6P_2S_2$, 526.1239).

Preparation of 5,8-dithiadodec-6-en-6,7-dicarbonitrile-1,2-di-p-toluenesulfonate (**22**). To a rapidly stirred suspension of NaI (0.1g) and Na_2MNT (5.08g, 27mmol) in acetone (75 ml) was added 3-chloro-1-propanol (5.36 g, 57 mmol) by syringe. The mixture was then heated at reflux for 20 hours under nitrogen. After this time the acetone was removed by rotary evaporation. The residue was extracted with chloroform (3 xs 150 ml), dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation. Pure 5,8-dithiadodec-6-en-6,7-dicarbonitrile-1,2-diol (5.71g, 81%) was obtained as a yellow oil following column chromatography on silica gel (eluent, 3-5% MeOH/$CHCl_3$): ^{1}H NMR ($CDCl_3$) δ 1.95(4H, quint, -$CH_2CH_2CH_2$-), 2.26(2H, s, -O*H*), 3.25(4H, t, -SCH_2), 3.75(4H, t, -OCH_2); ^{13}C NMR ($CDCl_3$) δ 31.6, 32.3, 60.2, 112.1, 121.2; EI MS *m/e* 258 (M+). 5,8-dithiadodec-6-en-6,7-dicarbonitrile-1,2-diol (4.86g, 19 mmol) was reacted with *p*-toluenesulfonyl chloride (9.03g, 47.5 mmol) to give **22** by the method described for **7**.

The product (6.7g, 63%) was isolated as a yellow solid following purification by column chromatography on silica gel: mp 76-78 °C; ^{1}H NMR ($CDCl_3$) δ 2.03(4H, quint, -$CH_2CH_2CH_2$-), 2.43(6H, s, CH_3Ar), 3.12(4H, t, -SCH_2-), 4.12(4H, t, -OCH_2-), 7.35(4H, d, aromatic), 7.75(4H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.5, 28.8, 30.7, 67.3, 111.6, 120.9, 127.7, 129.9, 132.2, 145.1; EI MS *m/e* 566 (M+), 411 (M-Ts), 395 (M-OTs).

Preparation of N,N'-bis(p-toluenesulfonyl)-1,4-diazacyclotetradec-9-en-9,10-dicarbonitrile (**23**). A solution of N,N'-bis(*p*-toluenesulfonyl)ethylenediamine[19] (4.66g, 12.8 mmol) and NaH (1.04g, 60% dispersion in mineral oil) were added to anhydrous DMF. The solution was then heated to 90°C for 1 hour under a N_2 atmosphere. After cooling the reaction to 75 °C, **22**, dissolved in DMF, was added dropwise over the course of 2 hours. Over the 2 hour addition period the reaction color changed from purple to a deep brown. Following further heating for 24 hours the DMF was removed under high vacuum. The residue was taken up in chloroform and washed with water. Column chromatography on silica (1% $CH_3OH/CHCl_3$) produced pure **23** (2.36 g, 32%) as an off-white solid: mp 252-255 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 1.88 (4 H, br quintet, -$SCH_2CH_2CH_2$N-), 2.47 (6 H, s, CH_3Ar), 3.09 (4 H, t, -SCH_2-), 3.15 (4 H, s, -NCH_2CH_2N-), 3.23 (4 H, t, -$NCH_2CH_2CH_2$-), 7.34 (4 H, d, aromatic), 7.68 (4 H, d, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.6, 29.6, 32.5, 47.1, 48.1, 111.6, 123.9, 127.2, 130.0, 136.1, 143.9; EI MS *m/e* 590 (M+), 435 (M - Ts), HR FAB MS *m/e* 591.1177 (M+H) (calcd for $C_{26}H_{31}N_4S_4O_4$, 591.1228).

X-Ray diffraction data collection.

Crystals suitable for X-ray analysis of compounds **5**, **6**, and **8** were grown by slow evaporation from toluene. Crystallographic data for all three structures are summarized in table 1. Selected bond lengths and angles are collected in tables 2-7. Crystals of **5** and **6** were mounted on glass fibers using oil (Paraton-N, Exxon), a crystal of **8** was mounted to the glass fiber using epoxy. All data sets were collected using the ω-θ scan technique by means of an Enraf-Nonius Cad-4 diffractometer with graphite monochromated Mo Kα radiation. Unit cell parameters and orientation matrices were determined from a least squares refinement using the setting angles of 25 carefully centered reflections widely distributed in reciprocal space. Orientation and intensity standards were measured every 90 minutes. No decomposition was observed during data collection for any of the crystals. The data were corrected for Lorentz and polarization efffects and analytical absorption corrections were applied (transmission factors for **5, 6** and **8**, 0.84-0.97, 0.90-0.95, 0.90-0.92, respectively). Compounds **5** and **6** showed secondary extinction (coefficients, 0.442e-6 and 0.297e-6 respectively) and corrections were applied. Compound **8** showed no secondary extinction.

All three structures were solved by direct methods[20] (SHELXS 86) and refined by the full-matrix least squares technique (TEXSAN 5.0). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms for **5** and **6** were included in idealized positions. For **6** the hydrogen atoms were refined isotropically. All calculations were performed using the TEXSAN[21] crystallographic software package of Molecular Structures Corporation. Neutral atom scattering factors were taken from Cromer and Waber.[22] Cycles of difference fourier maps and least squares refinment were continued to convergance in all cases.[23]

Table 1. Crystallographic data for compounds **5, 6** and **8**.

cpd	**5**	**6**	**8**
mol. wt.	256.40	512.80	316.51
space group	$P2_1/n$	C2/c	$P\bar{1}$
a, Å	8.761(1)	21.765(4)	8.450(1)
b, Å	9.252(2)	6.437(1)	9.856(2)
c, Å	14.800(4)	18.303(4)	10.172(1)
α, deg			78.78(2)
β, deg	91.24(2)	114.12(2)	71.18(1)
γ, deg			79.67(2)
vol., $Å^3$	1199.4(7)	2340(2)	780.3(4)
$d_{calcd.}$	1.420	1.455	1.347
Z	4	4	2
λ	0.71069 (Mo)	0.71069 (Mo)	0.71069 (Mo)
F(000)	536	1072	332
μ, cm^{-1}	5.63	5.77	5.7
crystal size, mm	0.41x0.30x0.06	0.48x0.16x0.12	0.25x0.24x0.17
tot no. of refl coll	2153	2328	2305
no. of unique data I>3.00σ(I)	1390	1619	1284
2θ max	47.9	49.9	45.9
final R^a	0.030	0.028	0.049
final $R_w{}^b$	0.034	0.034	0.054
GOF	1.35	1.32	1.95
no. of var.	185	137	163
temp, °C	-120	-120	20
max. peak on diff. Fourier map, $e^-/Å^3$	0.30	0.37	0.36
scan rate, deg/min	3.0-16.0	3.0-16.0	3.0-16.0
mode	ω-θ	ω-θ	ω-θ

$^aR = \Sigma| \ |F_o| - |F_c| \ | / \Sigma |F_o|$, $^bR_w = [(\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2}$.

Table 2: Intramolecular Bond Distances and Angles for **5**[a]

	Bond Angles (deg)				Bond Distances (Å)		
C6-S1-C13	99.2(1)	C7-S2-C8	98.9(1)	S1-C6	1.755(3)	C9-C10	1.518(4)
C10-S3-C11	100.9(2)	N14-C4-C6	175.3(3)	S1-C13	1.825(3)	S2-C7	1.757(3)
N15-C5-C7	176.7(3)	S1-C6-C4	116.3(2)	S2-C8	1.829(3)	S3-C10	1.817(3)
S3-C11-C12	114.4(2)	S1-C6-C7	123.2(2)	S3-C11	1.821(3)	C11-C12	1.509(4)
C4-C6-C7	120.6(3)	S2-C7-C5	116.6(2)	N14-C4	1.148(4)	N15-C5	1.144(3)
S2-C7-C6	123.6(2)	C5-C7-C6	119.8(3)	C4-C6	1.431(4)	C12-C13	1.525(4)
S2-C8-C9	112.6(2)	C11-C12-C13	113.5(3)	C5-C7	1.435(4)	C6-C7	1.362(4)
C8-C9-C10	113.0(3)	S1-C13-C12	113.1(2)	C8-C9	1.523(4)		
S3-C10-C9	116.7(2)						

[a]Estimated standard deviations are given in parentheses.

Table 3: Torsion or Conformation Angles for **5**[a]

				Angle					Angle
S1	C6	C4	N14	-51(4)	N15	C5	C7	C6	-174(5)
S1	C6	C7	S2	1.8(4)	C4	C6	S1	C13	58.2(2)
S1	C6	C7	C5	-174.9(2)	C4	C6	C7	C5	4.4(4)
S1	C13	C12	C11	64.6(3)	C5	C7	S2	C8	-51.0(2)
S2	C7	C5	N15	9(5)	C6	S1	C13	C12	63.2(2)
S2	C7	C6	C4	-178.9(2)	C6	C7	S2	C8	132.2(3)
S2	C8	C9	C10	-70.7(3)	C7	S2	C8	C9	-68.3(2)
S3	C10	C9	C8	148.4(2)	C7	C6	S1	C13	-122.4(2)
S3	C11	C12	C13	-167.1(2)	C9	C10	S3	C11	-84.7(3)
N14	C4	C6	C7	130(4)	C10	S3	C11	C12	100.5(3)

[a]Estimated standard deviations are given in parentheses, angles are in degrees.

Table 4: Intramolecular Bond Distances and Angles for **8**[a]

	Bond Angles				Bond Distances			
C8-S1-C9	103.3(3)	C1-S2-C10	101.5(3)	S1-C8	1.794(6)	S1-C9	1.738(5)
C3-S3-C4	104.3(3)	S4-C5-C4	110.4(7)	C4-C5	1.36(1)	S2-C1	1.806(6)
C5-S4-C6	99.8(3)	S2-C1-C2	113.6(4)	S2-C10	1.751(5)	S3-C3	1.800(6)
S4-C6-C7	111.5(6)	C1-C2-C3	112.3(5)	S3-C4	1.84(1)	S4-C5	1.902(9)
C6-C7-C8	108.2(6)	S3-C3-C2	114.8(4)	C6-C7	1.46(1)	S4-C6	1.800(9)
S1-C8-C7	112.6(4)	S3-C4-C5	112.8(7)	N1-C11	1.125(7)	N2-C12	1.141(6)
S1-C9-C10	122.3(4)	S1-C9-C11	118.0(4)	C7-C8	1.585(9)	C1-C2	1.520(8)
C10-C9-C11	119.5(5)	S2-C10-C9	121.7(4)	C2-C3	1.511(8)	C9-C10	1.344(7)
S2-C10-C12	117.5(4)	C9-C10-C12	120.6(5)	C9-C11	1.445(8)	C10-C12	1.436(8)
N1-C11-C9	179.1(7)	N2-C12-C10	178.2(6)				

[a]Estimated standard deviations are given in parentheses.

Table 5: Torsion angles for **8**[a]

				Angle					Angle
S1	C8	C7	C6	-73.0(6)	C1	S2	C10	C9	-136.4(5)
S1	C9	C10	S2	3.0(7)	C1	S2	C10	C12	47.9(5)
S1	C9	C10	C12	178.6(4)	C2	C1	S2	C10	69.8(5)
S1	C9	C11	N1	44(2)	C2	C3	S3	C4	102.9(5)
S2	C1	C2	C3	64.9(5)	C3	S3	C4	C5	-80.8(6)
S2	C10	C9	C11	-171.5(4)	C4	C5	S4	C6	-78.7(7)
S2	C10	C12	N2	-48(9)	C5	S4	C6	C7	-93.3(6)
S3	C3	C2	C1	172.1(4)	C7	C8	S1	C9	-67.5(5)
S3	C4	C5	S4	177.7(4)	C8	S1	C9	C10	161.0(5)
S4	C6	C7	C8	171.1(4)	C8	S1	C9	C11	-24.4(5)
N1	C11	C9	C10	-141(4)	C11	C9	C10	C12	4.1(8)
N2	C12	C10	C9	136(19)					

[a]Estimated standard deviations are given in parentheses, angles are in degrees.

Table 6: Intramolecular Bond Distances and Angles for **6**[a]

Bond Angles (deg)				Bond Distances(Å)			
C1-S1-C16	100.5(1)	C2-S2-C3	103.0(1)	S1-C1	1.757(2)	C4-C5	1.517(3)
C5-S3-C14	101.9(1)	S1-C1-C2	121.7(2)	S1-C16	1.823(2)	S2-C2	1.750(2)
S1-C1-C17	117.5(2)	C2-C1-C17	120.8(2)	S2-C3	1.815(2)	S3-C5	1.816(2)
S2-C2-C1	121.1(2)	S2-C2-C18	118.5(2)	S3-C14	1.817(2)	C14-C15	1.526(3)
C1-C2-C18	120.3(2)	S2-C3-C4	115.3(2)	N1-C17	1.143(3)	N2-C18	1.141(3)
C3-C4-C5	116.0(2)	S3-C5-C4	113.7(2)	C1-C2	1.353(3)	C15-C16	1.514(3)
N2-C18-C2	177.6(2)	S3-C14-C15	110.8(2)	C1-C17	1.440(3)	C2-C18	1.443(3)
C14-C15-C16	114.9(2)	S1-C16-C15	113.9(2)	C3-C4	1.520(3)		
N1-C17-C1	177.4(2)						

[a]Estimated standard deviations are given in parentheses.

Table 7: Torsion Angles for **6**[a]

				Angle					Angle
S1	C1	C2	S2	2.7(3)	N2	C18	C2	C1	-158(6)
S1	C1	C2	C18	-174.7(2)	C1	S1	C16	C15	71.0(2)
S1	C1	C17	N1	-13(6)	C1	C2	S2	C3	161.9(2)
S1	C16	C15	C14	59.3(2)	C2	S2	C3	C4	-65.5(2)
S2	C2	C1	C17	179.1(2)	C2	C1	S1	C16	-120.3(2)
S2	C2	C18	N2	25(6)	C3	S2	C2	C18	-20.7(2)
S2	C3	C4	C5	-57.8(2)	C4	C5	S3	C14	114.0(2)
S3	C5	C4	C3	-63.8(2)	C5	S3	C14	C15	-159.7(2)
S3	C14	C15	C16	63.2(2)	C16	S1	C1	C17	63.2(2)
N1	C17	C1	C2	171(6)	C17	C1	C2	C18	1.7(3)

[a]Estimated standard deviations are given in parentheses, angles are in degrees.

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