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Procedures are given for the preparation of new linear bidentate, tetradentate and tripodal heptadentate ligands incorporating benzimidazole, benzothiazole and pyridyl groups. The compounds were characterized by their nmr, uv and mass spectra. The crystal and molecular structure is reported for a chiral benzothiazole derived from camphoric acid.

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Introduction.

We have been interested in the synthesis and properties of multidentate ligands containing benzimidazole, benzothiazole and pyridine groups for some time [1-4]. As an extension of our earlier work [5-7], we report the syntheses of new heterocycles which are potential ligands for transition metals, Figure 1.

in aqueous hydrochloric acid (Phillips' method [8]). However, insolubility of the acid in aqueous HCl, or its thermal decarboxylation are also determinative factors.

Discussion.

For benzimidazole synthesis in polyphosphoric acid, *N*-phosphorylation usually ensues, and the resulting phos-

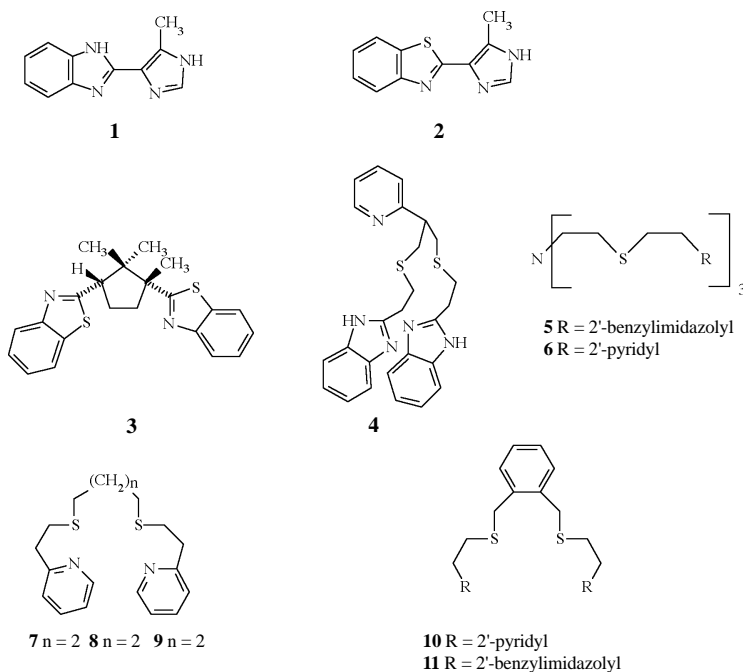


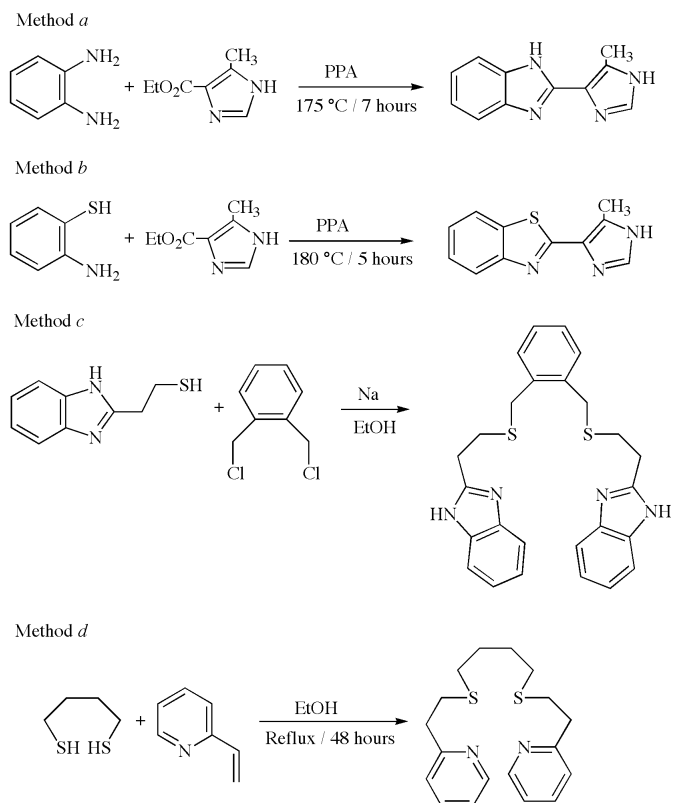
Figure 1. The ligands synthesized.

Benzimidazoles and benzothiazoles are generally preparable by condensation of the carboxylic acid or ester with *o*-phenylenediamines or *o*-aminothiophenols in acid medium [8-12], the choice of the medium determining the reaction time. In polyphosphoric acid the reaction may be achieved in a few hours at the higher accessible temperatures, while it may take days for completion of the reaction

phoramide must be hydrolyzed with a strong base to obtain the free azole; this was the case with **1** and **2**.

Most of the pyridine thioethers **6-10** were synthesized in very good yields in one step, by the addition of the appropriate thiol across the exocyclic double bond of 2-vinylpyridine, Scheme 1. This addition, which follows Markovnikov's rule, can be carried out either by refluxing

Scheme 1



General procedures followed in the synthesis of the ligands. Method *a*: ligands **1** and **3**; method *b*: ligand **3**; method *c*: ligands **4,5** and **11**; method *d*: ligands **6** to **10**.

Table 1

Crystal Data for (1*R*,3*S*)-(+)-*cis*-1,3-Bis(benzothiazol-2'-yl)-1,2,2-trimethylcyclopentane (**3**).

Formula	C ₂₂ H ₂₂ N ₂ S ₂
fw	378.54
Cryst system	Orthorhombic
Cryst size, mm	0.26 × 0.72 × 0.24
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	6.664 (2)
<i>b</i> , Å	19.028 (5)
<i>c</i> , Å	30.229 (8)
<i>V</i> , Å ³	3833 (2)
<i>Z</i>	8
<i>D</i> _{calc} , g cm ⁻³	1.312
<i>F</i> (000)	1600
<i>μ</i> , mm ⁻¹	0.286
(<i>Mo</i> -Kα), Å	0.71073
<i>T</i> , K	293 (2)
<i>R</i> _a , <i>R</i> _w	0.0712; 0.1372

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}.$$

confirmed by X-ray analysis (Table 1). This crystal structure of **3** (with atomic numbering scheme) is shown in Figure 2, while selected bond lengths and bond angles are given in Table 2. This bis-benzothiazole has four each of two inequivalent molecules in the asymmetric unit cell, one of these two molecule types being disordered with respect to the 4,5-positions (C16, C17) of the cyclopentane moiety. In all the molecules, the benzothiazole groups flank the putative camphoryl unit on each side. Due to the configuration of the cyclopentane ring, the benzothiazole

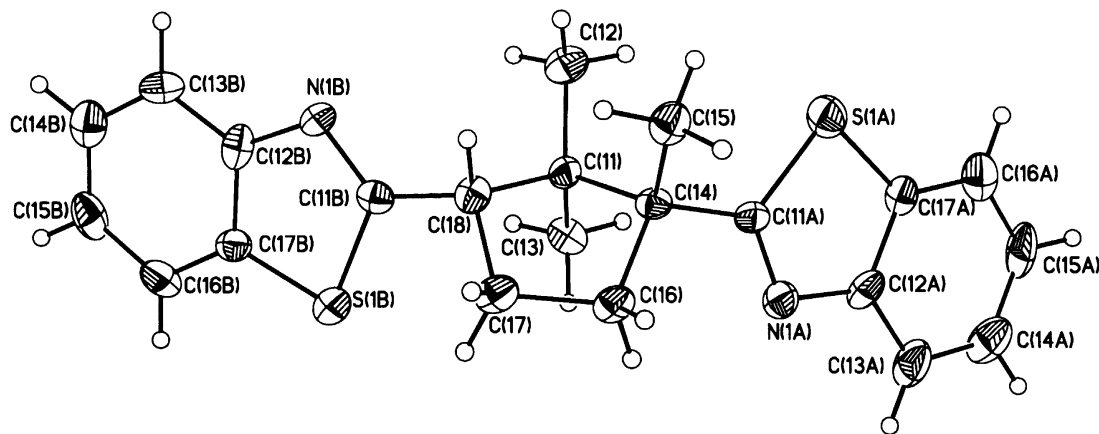


Figure 2. ORTEP diagram of (1*R*,3*S*)-(+)-*cis*-1,3-bis(benzothiazol-2'-yl)-1,2,2-trimethylcyclopentane (**3**), showing atom labeling scheme.

the reactants in ethanol, or by simply stirring the liquid reactants together in the absence of a solvent for a few hours. The ligands **3**, **4** and **11** were prepared by nucleophilic displacement of the halide by the thiolates [13].

The chiral benzothiazole **3** is derived from (1*R*,3*S*)-(+)-camphoric acid, and its structure was unambiguously

ring nitrogen atoms are oriented well away from one another. Consequently, use of the compound as a ligand for preparing mononuclear metal complexes is restricted. However, **3** may be capable of acting as a bridging group; such potentially binuclear nickel complexes are currently under investigation. The average C-C bond length in the

Table 2
Selected Bond Distances and Angles for (1*R*,3*S*)-(+)-*cis*-1,3-Bis(benzothiazol-2'-yl)-1,2,2-trimethylcyclopentane (**3**)

Bond distances [Å]			
S(1A)-C(11A)	1.744(11)	S(1B)-C(11B)	1.749(11)
S(1A)-C(17A)	1.709(11)	S(1B)-C(17B)	1.712(11)
N(1A)-C(11A)	1.270(12)	N(1B)-C(11B)	1.304(11)
N(1A)-C(12A)	1.389(13)	N(1B)-C(12B)	1.383(13)
C(12A)-C(17A)	1.394(15)	C(12B)-C(17B)	1.424(16)
Bond Angles [°]			
C(17A)-S(1A)-C(11A)	89.4(6)	C(17B)-S(1B)-C(11B)	90.0(6)
C(11A)-N(1A)-C(12A)	111.2(11)	C(11B)-N(1B)-C(12B)	109.5(10)
N(1A)-C(11A)-S(1A)	115.5(8)	N(1B)-C(11B)-S(1B)	115.9(8)
N(1A)-C(12A)-C(17A)	114.5(11)	N(1B)-C(12B)-C(17B)	116.2(10)
N(1A)-C(12A)-C(13A)	125.2(14)	N(1B)-C(12B)-C(13B)	126.8(14)

aromatic ring is 1.382 Å; the C(12B)-C(17B) bond deviates the most from this, at 1.424(16) Å. Within a given molecule, the C-N bond lengths of the two symmetry-inequivalent benzothiazole units are not identical. For example C(11A)-N(1A) and C(11B)-N(1B) bonds differ by 0.113(12) Å. All the bond distances nonetheless agree closely with previously reported values [14-16].

The CD spectrum of **3** shows a distinct positive Cotton effect around 260 nm (Figure 3b), with two sharper negative bands between 230 and 240 nm. The sign appears consistent with the (+)-designation of the reactant acid being carried through to the product. Normalization of the rotational strength in the spectrum with respect to the associated absorption yields the optical (Kuhn) anisotropy spectrum in Figure 3c. This shows that the greatest anisotropy is associated with the transition(s) around 260-270 nm. In the optical spectra of benzothiazoles, the longer-wavelength transitions are assigned as $n \rightarrow \pi^*$ and the shorter-wavelength ones as $\pi \rightarrow \pi^*$, the demarcation being considered 270 nm [5-7]. As $\pi \rightarrow \pi^*$ transitions are normally magnetic-dipole forbidden, but $n \rightarrow \pi^*$ ones magnetically allowed, it is apparent that the absorption manifold around 265 nm is $n \rightarrow \pi^*$ rather than $\pi \rightarrow \pi^*$ in origin. We note also, that the magnitude of the optical anisotropy and the absence of any indication of a negative Cotton effect component suggest that the two benzothiazoles respond with the same sign for $\Delta\epsilon$, to their vicinal chiral carbons in the molecule.

EXPERIMENTAL

2-Vinylpyridine, polyphosphoric acid (PPA), ethyl 4-methyl-5-imidazole carboxylate, 2-picolyl chloride hydrochloride, 1,4-butanedithiol, 1,2-bis(mercaptomethyl)benzene, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,2-diaminobenzene, α, α' -dichloro-*o*-xylene, 2-aminothiophenol, potassium hydroxide, sodium hydroxide, sodium borohydride and sodium were from Aldrich Chemical Co., Inc. Tris(2'-mercaptoethyl)amine [17], 2-(2'-mercaptoethyl)benzimidazole [18], tris(2'-chloroethyl)amine hydrochloride [19] and 2-(2'-pyridyl)-1,3-dichloropropane

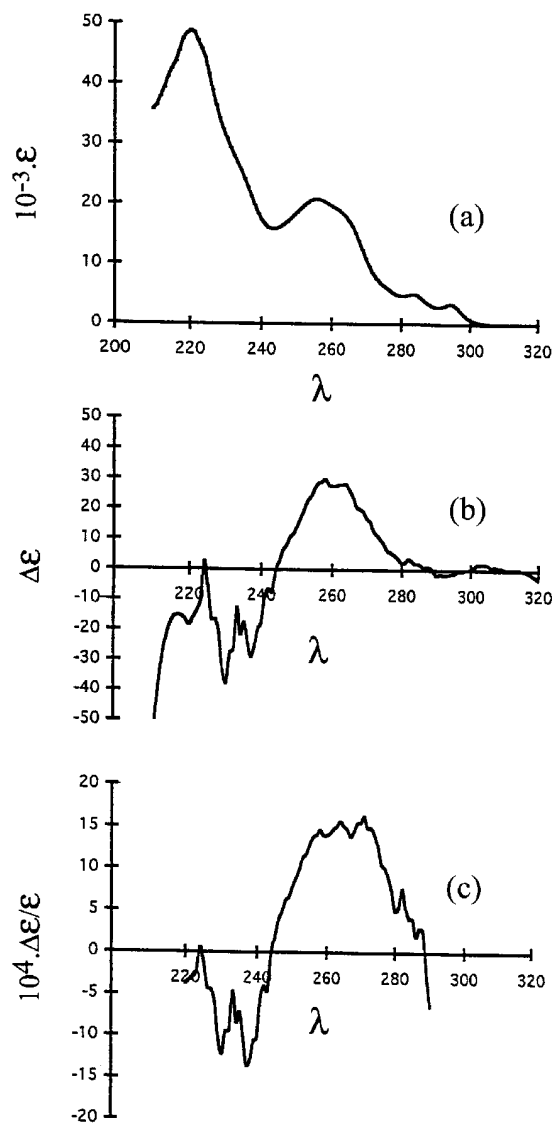


Figure 3. Spectral of (1*R*,3*S*)-(+)-*cis*-1,3-bis(benzothiazol-2'-yl)-1,2,2-trimethylcyclopentane (**3**) in methanol. (a) Electronic spectrum. (b) CD Spectrum. (c) Kuhn anisotropy spectrum. Wavelength scale in nm, while the ϵ and $\Delta\epsilon$ axes are in units of $M^{-1}cm^{-1}$.

[20] were prepared by published procedures. Elemental microanalyses were performed by Robertson Microanalytical Laboratories (Madison, NJ) or by the Microanalytical Laboratory of the University of Pennsylvania. All reactions involving thiols were carried out under a nitrogen atmosphere. The compounds **1-5** and **11**, which were obtained as solids were dried overnight in a desiccator over sulfuric acid, while the compounds **6-10** were obtained as colorless oily liquids. The ^1H nmr and ^{13}C nmr spectra were recorded on a Bruker AC250 spectrometer using CDCl_3 (deuteriochloroform) or $\text{DMSO}-d_6$ (deuterio-dimethyl sulfoxide) as solvent, with TMS (tetramethylsilane) as internal standard. Infrared spectra were recorded on a Perkin-Elmer 1610 FT-IR. Electronic spectra were obtained on a Perkin-Elmer Lambda-2 UV-visible spectrophotometer. Mass spectra are from a VG-ZABHF high resolution double-focusing mass spectrometer operating in the FAB mode and using 2-nitrobenzyl alcohol as the sample matrix. Circular dichroism (CD) spectra were recorded on an Aviv Associates 60DS spectrophotometer and the optical rotation was measured in a Perkin Elmer 341 Digital Polarimeter.

4-Methyl-5-(benzimidazol-2'-yl)imidazole (**1**).

To 70 ml of polyphosphoric acid stirring at 100 °C was added a powdered mixture of ethyl 4-methyl-5-imidazole carboxylate (7.7 g, 50 mmol) and *o*-phenylenediamine (5.41 g, 50 mmol). The temperature was slowly raised and kept at 175 °C for 7 hours. The green reaction mixture was cooled to 80 °C, and poured slowly into 200 ml of vigorously stirred ice-cold concentrated sodium hydroxide solution. After stirring overnight, the pale brown precipitate obtained was isolated by filtration and recrystallized from methanol as colorless needles. Yield 6.9 g (35 mmol, 70%). ^1H nmr ($\text{DMSO}-d_6$): δ 1.78 (s, 3H, $-\text{CH}_3$); 6.19-6.26 (m, 2H, aro); 6.53-6.56 (m, 1H, aro); 6.67-6.70 (m, 1H, aro); 6.84 (s, 1H, aro). ^{13}C nmr ($\text{DMSO}-d_6$): δ 10.8, 110.8, 118.0, 121.1, 127.5, 127.7, 133.9, 134.5, 149.5. FAB-MS m/z : 221 $[\text{M}+\text{Na}]^+$ (36%), 199 $[\text{M}+\text{H}]^+$ (100%). IR (KBr): ν_{max} cm^{-1} 3460 w (N-H stretching), 3040 m (C-H aromatic stretching), 2942 m (C-H aliphatic stretching), 1625 s (C=C ring stretching), 1547 s (C=N ring stretching). UV (methanol): 307 (17400), 295 (23100), 261 (8700), 237 (15200), 203 (28600); mp > 295 °C (decomp).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_4$: C, 66.6; H, 5.09; N, 28.3. Found: C, 66.2; H, 5.23; N, 27.9.

4-Methyl-5-(benzothiazol-2'-yl)imidazole (**2**).

A mixture of 3.4 g (22 mmol) of ethyl 4-methyl-5-imidazole carboxylate and 2.76 g (22 mmol) of 2-aminothiophenol was heated in 60 ml of polyphosphoric acid at 180 °C for 4.5 hours. The reaction mixture was cooled to 80 °C, poured into 200 ml of ice-cold concentrated potassium hydroxide solution and allowed to stir for 1 hour. The resulting grey precipitate was isolated by filtration and recrystallized from methanol (charcoal), giving 2.9 g (13.5 mmol, 60%) of pale yellow flakes. ^1H nmr ($\text{DMSO}-d_6$): δ 2.68 (s, 3H, $-\text{CH}_3$); 7.32-7.38 (m, 1H, aro); 7.43-7.49 (m, 1H); 7.73 (s, 1H); 7.93 (d, $J = 8.1$ Hz, 1H, aro); 8.05 (d, $J = 7.8$ Hz, 1H, aro). ^{13}C nmr ($\text{DMSO}-d_6$): δ 10.9, 121.8, 124.2, 125.9, 128.0, 130.5, 133.6, 135.2, 154.2, 165.1. FAB-MS m/z : 238 $[\text{M}+\text{Na}]^+$ (100%), 216 $[\text{M}+\text{H}]^+$ (35%), 199 (16%). IR (KBr): ν_{max} cm^{-1} 3342 w (N-H stretching), 3070 m (C-H aromatic stretching), 2956 m (C-H aliphatic stretching), 1603 s (C=C ring stretching), 1547 s (C=N ring stretching). UV (methanol): 307 (19800); 255 (7100); 247 (7400); 209 (22000); mp 168-170 °C.

Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{N}_3\text{S}$: C, 61.4; H, 4.21; N, 19.5. Found: C, 61.0; H, 4.17; N, 19.4.

(1*R*,3*S*)-(+)-*cis*-1,3-Bis(benzothiazol-2'-yl)-1,2,2-trimethylcyclopentane (**3**).

To *o*-aminothiophenol (8.8 g, 70 mmol) in 30 ml of polyphosphoric acid at 130 °C was added 7.0 g (35 mmol) of (1*R*,3*S*)-(+)-camphoric acid. The reaction mixture was stirred at 110-140 °C for 5 hours and allowed to cool to *ca.* 70 °C. It was then poured slowly into 500 ml of vigorously stirred ice-cold 4 *M* potassium hydroxide solution. After the suspension had cooled, the product was isolated by filtration, washed with water, recrystallized from acetonitrile (charcoal), and dried *in vacuo* over sulfuric acid to give 4.7 g (12.5 mmol, 35%) of effloresced cream powder. ^1H nmr ($\text{DMSO}-d_6$): δ 0.43 (s, 3H, $-\text{CH}_3$); 1.42 (s, 3H, $-\text{CH}_3$); 1.58 (s, 3H, $-\text{CH}_3$); 1.95-2.05 (m, 1H, $-\text{CH}-$); 2.32-2.48 (m, 1H, $-\text{CH}-$); 2.55-2.69 (m, 1H, $-\text{CH}-$); 2.96-3.09 (m, 1H, $-\text{CH}-$); 3.93 (t, $J = 9.5$ Hz, $-\text{CH}-$); 7.42-7.53 (m, 4H, aro); 7.99-8.02 (m, 2H, aro); 8.08 (d, $J = 7.5$ Hz, 2H, aro). ^{13}C nmr ($\text{DMSO}-d_6$): δ 20.9, 22.1, 25.5, 26.2, 35.3, 48.6, 52.1, 54.8, 121.9, 122.3, 122.5, 124.8, 124.9, 126.1, 134.1, 134.2, 152.5, 152.7, 175.1. FAB-MS m/z : 481 $[\text{M}+\text{Na}]$ (29%), 379 $[\text{M}+\text{H}]$ (100%). IR (KBr): ν_{max} cm^{-1} 3444 w and 3350 w (N-H stretching), 3073 m (C-H aromatic stretching), 2930 m (C-H aliphatic stretching), 1605 s (C=C ring stretching), 1456 and 1477 s (C=N ring stretching). UV (methanol): 294 (3350), 283 (4950), 255 (20800), 220 (48900); mp 115-116 °C. $[\alpha]_D^{20} = +9.4$ (0.5, MeOH).

Anal. Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{S}_2$: C, 69.8; H, 5.86; N, 7.40; S, 16.9. Found: C, 69.3; H, 5.82; N, 7.41. When a hot butyronitrile solution of **3** was allowed to cool and stand for 2 days, colourless prisms suitable for X-ray diffraction were obtained.

1,9-Bis(benzimidazol-2'-yl)-5-(2"-pyridyl)-3,7-dithianonane (**4**).

To 10.7 g (60 mmol) of 2-(2'-mercaptoethyl)benzimidazole in ethanol were added firstly 0.5 g of sodium borohydride and then 3.36 g (60 mmol) of potassium hydroxide. To this solution 6.79 g (30 mmol) of 2-(2'-pyridyl)-1,3-dichloropropane hydrochloride in ethanol was added. It was stirred overnight and then heated on a steam bath for 30 minutes. After treatment with Norit-A decolorizing carbon, the solvent was removed at reduced pressure and the resulting yellow powder was isolated by filtration, recrystallized from methanol to yield a white solid. Yield 5.7 g (12 mmol, 40%). ^1H nmr ($\text{DMSO}-d_6$): δ 2.95 (t, $J = 6.9$ Hz, 4H, $-\text{CH}_2-$); 3.10 (t, $J = 6.9$ Hz, 4H, $-\text{CH}_2-$); 3.23-3.56 (m, 5H, $-\text{CH}-$ and $-\text{CH}_2-$); 7.11-7.14 (m, 5H, aro); 7.29 (d, $J = 7.7$ Hz, 2H, aro); 7.43-7.48 (m, 4H, aro); 7.72 (t, $J = 7.7$ Hz, 1H, aro). ^{13}C nmr ($\text{DMSO}-d_6$): δ 28.9, 29.0, 36.7, 121.1, 121.2, 137.6, 153.5, 158.1. FAB-MS m/z : 238 $[\text{M}+\text{Na}]^+$ (100%), 216 $[\text{M}+\text{H}]^+$ (38%), 199 (17%). IR (KBr): ν_{max} cm^{-1} 3342 w (N-H stretching), 3048 m (C-H aromatic stretching), 2946 m and 2840 m (C-H aliphatic stretching), 1618 s and 1589 (C=C ring stretching), 1541 s (C=N ring stretching). UV (methanol): 281 (21700); 274 (21700); 251(14300); 244 (15300); mp 167-168 °C.

Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{N}_5\text{S}_2$: C, 65.9; H, 5.75; N, 14.8. Found: C, 65.6; H, 5.54; N, 14.8.

Tris[5-(benzimidazol-2'-yl)-3-thiapentyl]amine (**5**).

This compound was prepared in a manner similar to that of **4**, using 6.02 g (25 mmol) of tris(2-chloroethyl)amine hydrochloride and 13.4 g (75 mmol) of 2-(2'-mercaptoethyl)benzimidazole. The yield of white solid was 7.07 g (11.2 mmol, 45%). ^1H nmr ($\text{DMSO}-$

d_6): δ 2.51-2.61 (m, 12H, $-\text{CH}_2-$); 2.98 (t, $J = 6.1$ Hz, 6H, $-\text{CH}_2-$); 3.06-3.08 (m, 6H, $-\text{CH}_2-$); 7.09-7.13 (m, 6H, aro); 7.45-7.49 (m, 6H, aro). ^{13}C nmr (DMSO- d_6): 29.2, 29.6, 53.4, 56.2, 114.6, 121.4, 138.7, 153.7. FAB-MS m/z : 652 $[\text{M}+\text{Na}]^+$ (100%), 630 $[\text{M}+\text{H}]^+$ (28%), 474 (25%), 452 (28%). IR (KBr): ν_{max} cm^{-1} 3376 w (N-H stretching), 3078 m (C-H aromatic stretching), 2918 m and 2846 m (C-H aliphatic stretching), 1623 m (C=C ring stretching), 1455 s and 1467 s (C=N ring stretching). UV (methanol): 281 (24500), 274 (23400), 244 (18900); mp 103-104 °C.

Anal. Calcd. for $\text{C}_{33}\text{H}_{39}\text{N}_7\text{S}_3 \cdot 2\text{H}_2\text{O}$: C, 59.5; H, 6.51; N, 14.7. Found: C, 59.5; H, 6.61; N, 14.6.

Tris[5-(2'-pyridyl)-3-thiapentyl]amine (6).

Tris(2'-mercaptoethyl)amine, 4.5 g (22.6 mmol) and 7.1 g (67.9 mmol) of 2-vinylpyridine were refluxed in 100 mL anhydrous ethanol for two days. The reaction mixture was treated with Norit-A decolorizing carbon and the solvent was removed at reduced pressure, leaving 10.5 g of yellow oil. Chromatography on silica gel with a hexane/acetonitrile/ethanol mixture gave 8.15 g (15.9 mmol, 70%) of colorless oil. ^1H nmr (CDCl_3): δ 2.54-2.62 (m, 6H, $-\text{CH}_2-$); 2.65-2.72 (m, 6H, $-\text{CH}_2-$); 2.91-2.97 (m, 6H, $-\text{CH}_2-$); 3.02-3.08 (m, 6H, $-\text{CH}_2-$); 7.10-7.19 (m, 6H, aro); 7.56-7.63 (m, 3H, aro); 8.52-8.54 (m, 3H, aro). ^{13}C nmr (CDCl_3): 30.0, 31.9, 38.5, 53.9, 121.4, 123.1, 136.3, 149.3, 159.8. FAB-MS m/z : 513 $[\text{M}+\text{H}]^+$ (100%), 408 (14%), 391 (12%), 374 (38%), 360 (65%), 269 (35%), 195 (56%), 166 (59%). IR (neat): ν_{max} cm^{-1} 3064 m and 3007 m (C-H aromatic stretching), 2960 s and 2919 s (C-H aliphatic stretching), 1592 s and 1569 s (C=C ring stretching), 1473 s and 1435 s (C=N ring stretching). UV (methanol): 268 (9900), 262 (12000), 255 (10500), 243 (9000), 234 (9100), 202 (28400).

Anal. Calcd. for $\text{C}_{27}\text{H}_{36}\text{N}_4\text{S}_3 \cdot 0.25\text{CH}_3\text{CN} \cdot 0.5\text{CH}_3\text{OH}$: C, 62.4; H, 7.25; N, 11.0. Found: C, 62.6; H, 7.45; N, 11.1.

The compounds **7-10** were prepared and purified by adopting a procedure similar to that used for the preparation of **6**, in all instances ethanol being used as the solvent.

1,10-Bis(2'-pyridyl)-3,8-dithiadecane (7).

This compound was prepared from 2.8 g (23 mmol) of 1,4-butanedithiol and 4.7 g (46 mmol) of 2-vinylpyridine, as a colorless oil in 69% yield. ^1H nmr (CDCl_3): δ 1.63-1.69 (m, 4H, $-\text{CH}_2-$); 2.50-2.55 (m, 4H, $-\text{CH}_2-$); 2.88-2.95 (m, 4H, $-\text{CH}_2-$); 3.02-3.09 (m, 4H, $-\text{CH}_2-$); 7.11-7.19 (m, 4H, aro); 7.61 (td $J = 1.8$ Hz, 7.6 Hz, 2H, aro); 8.54 (d, $J = 4.6$ Hz, 2H, aro). FAB-MS m/z : 333 $[\text{M}+\text{H}]^+$ (100%), 226 (28%), 194 (19%). IR (neat): ν_{max} cm^{-1} 3063 m and 3007 m (C-H aromatic stretching), 2922 s and 2853 s (C-H aliphatic stretching), 1592 s and 1568 s (C=C ring stretching), 1474 s and 1435 s (C=N ring stretching). UV (methanol): 268 (6600), 262 (8400), 255 (7100), 202 (18000).

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{S}_2$: C, 65.0; H, 7.28; N, 8.42. Found: C, 65.0; H, 7.36; N, 7.98.

1,11-Bis(2'-pyridyl)-3,9-dithiaundecane (8).

The reaction of 3.91 g (28.6 mmol) of 1,5-pentanedithiol with 6.01 g (57.2 mmol) of 2-vinylpyridine gave 7.8 g (23 mmol, 79%) of the product. ^1H nmr (CDCl_3): δ 1.40-1.50 (m, 2H, $-\text{CH}_2-$); 1.59 (q, $J = 7.3$ Hz, 4H, $-\text{CH}_2-$); 2.52 (t, $J = 7.2$ Hz, 4H, $-\text{CH}_2-$); 2.89-2.96 (m, 4H, $-\text{CH}_2-$); 3.02-3.09 (m, 4H, $-\text{CH}_2-$); 7.12-7.20 (m, 4H, aro); 7.61 (td $J = 1.8$ Hz, 7.7 Hz, 2H, aro); 8.55 (d, $J = 4.0$ Hz, 2H, aro). ^{13}C nmr (CDCl_3): δ 27.9, 29.0, 31.5, 31.9, 38.4, 121.3, 122.9, 136.2, 149.2, 159.9. FAB-MS m/z : 347

$[\text{M}+\text{H}]^+$ (100%), 256 (7%), 240 (23%), 208 (12%), 167 (8%). IR (neat): ν_{max} cm^{-1} 3064 m and 3006 m (C-H aromatic stretching), 2925 s and 2852 s (C-H aliphatic stretching), 1592 s and 1568 s (C=C ring stretching), 1473 s and 1435 s (C=N ring stretching). UV (methanol): 268 (8700), 262 (10500), 256 (9200), 204 (25600).

Anal. Calcd. for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{S}_2 \cdot 0.5\text{C}_2\text{H}_5\text{OH}$: C, 65.0; H, 7.91; N, 7.58. Found: C, 65.0; H, 7.77; N, 7.93.

1,12-Bis(2'-pyridyl)-3,10-dithiadodecane (9).

The reaction of 2.98 g (19.8 mmol) of 1,2-hexanedithiol and 4.17 g (39.6 mmol) of 2-vinylpyridine produced 6.02 g (16.7 mmol, 84%) of **9** as a colorless oil. ^1H nmr (CDCl_3): δ 1.33-1.39 (m, 4H, $-\text{CH}_2-$); 1.55-1.61 (m, 4H, $-\text{CH}_2-$); 2.52 (t, $J = 7.3$ Hz, 4H, $-\text{CH}_2-$); 2.89-2.96 (m, 4H, $-\text{CH}_2-$); 3.02-3.09 (m, 4H, $-\text{CH}_2-$); 7.1-7.20 (m, 4H, aro); 7.61 (td $J = 1.8$ Hz, 7.7 Hz, 2H, aro); 8.53-8.56 (m, 2H, aro). ^{13}C nmr (CDCl_3): δ 28.1, 29.2, 31.4, 31.9, 38.3, 121.2, 122.9, 136.1, 149.1, 159.8. FAB-MS m/z : 361 $[\text{M}+\text{H}]^+$ (100%), 256 (40%), 222 (13%). IR (neat): ν_{max} cm^{-1} 3064 m and 3007 m (C-H aromatic stretching), 2924 s and 2853 s (C-H aliphatic stretching), 1591 s and 1568 s (C=C ring stretching), 1473 s and 1435 s (C=N ring stretching). UV (methanol): 268 (7900), 262 (9600), 255 (8200), 203 (24000).

Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{S}_2 \cdot 0.5\text{C}_2\text{H}_5\text{OH}$: C, 65.7; H, 8.15; N, 7.30. Found: C, 65.6; H, 8.26; N, 7.48.

1,2-Bis[4-(2'-pyridyl)-2-thiabutyl]benzene (10).

By reaction of 3.48 g (20.4 mmol) of 1,2-bis(mercaptoethyl)benzene and 4.3 g (40.9 mmol) of 2-vinylpyridine, 6.07 g (15.9 mmol, 78%) of **10** was obtained as a colorless oil. ^1H nmr (CDCl_3): δ 2.85-2.92 (m, 4H, $-\text{CH}_2-$); 3.01-3.07 (m, 4H, $-\text{CH}_2-$); 3.87 (s, 4H, $-\text{CH}_2-$); 7.1-7.24 (m, 8H, aro); 7.59 (td $J = 1.8$ Hz, 7.4 Hz, 2H, aro); 8.53 (dd, $J = 1.6$ Hz, 5.3 Hz, 2H, aro). ^{13}C nmr (CDCl_3): δ 31.5, 33.7, 38.1, 121.4, 123.1, 127.2, 130.5, 136.3, 149.3, 159.8. FAB-MS m/z : 403 $[\text{M}+\text{Na}]^+$ (100%), 381 $[\text{M}+\text{H}]^+$ (87%), 349 (21%), 305 (19%), 278 (15%), 261 (15%), 242 (15%). IR (neat): ν_{max} cm^{-1} 3063 m and 3008 m (C-H aromatic stretching), 2921 s and 2855 s (C-H aliphatic stretching), 1591 s and 1568 s (C=C ring stretching), 1473 s and 1435 s (C=N ring stretching). UV (methanol): 268 (7600), 262 (9700), 255 (8600), 207 (28600).

Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{S}_2 \cdot 0.25\text{H}_2\text{O}$: C, 68.6; H, 6.41; N, 7.28. Found: C, 68.7; H, 6.54; N, 6.90.

1,2-Bis[4-(benzimidazol-2'-yl)-2-thiabutyl]benzene (11).

To 4.76 g (26.7 mmol) of 2-(2'-mercaptoethyl)benzimidazole in 50 ml of ethanol was added 0.61 g (26.7 mmol) of metallic sodium. After the sodium had dissolved, an ethanolic solution of 2.34 g (13.4 mmol) of α,α' -dichloro-*o*-xylene was added dropwise. After the mixture had been stirred overnight, heated on the steambath for 0.5 hour and the sodium chloride was filtered off, the solvent was removed by rotary evaporation. The brown solid obtained was recrystallized from aqueous ethanol (charcoal) to give 3.9 g (8.2 mmol, 61%) of white flakes. ^1H nmr (DMSO- d_6): δ 2.93 (t, $J = 7.3$ Hz, 4H, $-\text{CH}_2-$); 3.12 (t, $J = 7.2$ Hz, 4H, $-\text{CH}_2-$); 3.89 (s, 4H, $-\text{CH}_2-$); 7.09-7.12 (m, 4H, aro); 7.13-7.21 (m, 2H, aro); 7.22-7.31 (m, 2H, aro); 7.35-7.52 (m, 4H, aro). ^{13}C nmr (DMSO- d_6): δ 29.1, 29.5, 32.5, 127.2, 130.4, 136.3, 153.4. FAB-MS m/z : 481 $[\text{M}+\text{Na}]^+$ (87%), 459 $[\text{M}+\text{H}]^+$ (43%), 433 (18%), 393 (27%), 261 (51%), 217 (37%), 199 (100%). IR (KBr): ν_{max} cm^{-1} 3384 w (N-H stretching), 3048 m (C-H aromatic stretching), 2917 m and 2840 m

(C-H aliphatic stretching), 1621 m and 1589 m (C=C ring stretching), 1455 s and 1435 s (C=N ring stretching). UV (methanol): 281 (18700), 274 (18000), 244 (156001); mp >226 °C (decomp.).

Anal. Calcd. for $C_{26}H_{26}N_4S_2 \cdot H_2O$: C, 65.5; H, 5.92; N, 11.8. Found: C, 65.8; H, 5.50; N, 11.5.

Structure Analysis.

For X-ray diffraction, a suitable crystal of **3** was mounted on a glass fiber with epoxy cement and attached to the goniometer head in a Siemens P4S diffractometer employing graphite-monochromated Mo-K α radiation ($\lambda = 0.7103$ Å). Cell constants and orientation matrices were obtained by least-squares refinement of setting angles of 25 randomly selected reflections. SHELXA as found in the SHELXTL package was used to provide an empirical absorption correction [21]. The structure was solved by a combination of the Patterson and direct methods and refined by full-matrix least-squares on F^2 . A total of 3599 reflections was collected ($0 \leq h \leq 18$, $-26 \leq k \leq 0$, $-14 \leq l \leq 12$) in the range of 2.16° to 27.50° , with 3469 being unique ($R_{int} = 0.0292$). The empirically derived transmission coefficient ranged from 0.623 to 0.524.

Hydrogens were included in structure factor calculations in calculated positions and refined using a riding model. Thermal ellipsoids are displayed at 20% probability level for clarity, and hydrogen atoms are shown as spheres of arbitrary size [22].

Conclusion.

The oligodentate ligands reported here were prepared in good yields by straightforward procedures. The electronic spectra of these compounds show intense absorption in 230–280 nm region. For the benzothiazoles, the $\pi \rightarrow \pi^*$ transition is observed below 250 nm and the weak absorption above 250 nm is attributed to the $n \rightarrow \pi^*$ transition [23]. The proton nmr spectra were consistent with the expected structures. The metal complexes of these ligands are presently under investigation.

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