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Synthesis and structural characterization of 2,6-bis-(N-methylenemorpholino)-4-methylphenol (MMP) and 2,6-bis-(N-methylenemorpholino)-4-bromophenol (MBrP)[1]

S. Shanmuga Sundara Raj,[2] M. N. Ponnuswamy,*[,2] G. Shanmugam,[2] and M. Kandaswamy[3]

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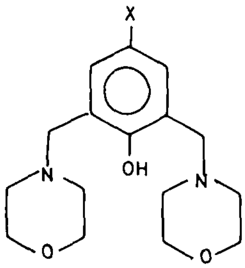
MMP: $C_{17}H_{26}N_2O_3$, $M_r = 306.40$, monoclinic, space group $P2_1/c$, $a = 10.927(2)$, $b = 10.777(2)$, $c = 14.197(2)$ Å, $\beta = 94.04(2)°$, $V = 1667.7(5)$ Å^3, $D_{cal} = 1.22$ Mgm^{-3}, $Z = 4$, $F(000) = 664$, $\mu = 5.93$ cm^{-1}, $T = 293$K. Final $R = 0.049$ and $wR = 0.063$ for 2724 observed reflections. MBrP; $C_{16}H_{23}N_2O_3Br$, $M_r = 371.27$, monoclinic, space group $P2_1/c$, $a = 10.955(1)$, $b = 10.785(1)$, $c = 14.213(1)$ Å, $\beta = 94.54(2)°$, $V = 1674.0(4)$ Å^3, $D_{cal} = 1.48$ Mgm^{-3}, $Z = 4$, $F(000) = 768$, $\mu = 32.35$ cm^{-1}, $T = 293$K. Final $R = 0.055$ and $wR = 0.069$ for 2886 observed reflections. MMP and MBrP are isostructural and in both the molecules the morpholino rings assume a chair conformation.

Introduction

This work forms a part of our study on the conformation of 2,6-bis-(N-methylene) substituted (by $C-(CH_3)_3$, Br, Cl, CH_3, NO_2) morpholino derivatives (Shanmuga Sundara Raj *et al.*, 1993). The study of polymetallic complexes in which coupling between metals is propagated via a bridging molecule has clear application to the design of novel magnetic and electronic solid state materials and to the role of polymetallic sites in biological processes (Willet *et al.*, 1985; Marcus and Sutin, 1985). The nature and the magnitude of interactions depend on the bridge, the metal-metal separation, the bond angles at the bridging atoms, the dihedral angle between the planes containing the metal ions and the stereochemistry around the metal ions. Here we report the synthesis of the bridging ligands (I and II) characterized by IR, NMR, Mass spectra, and X-ray diffraction methods.



I MMP $X = CH_3$
II MBrP $X = Br$

Experimental

In the following text, the quantities in square brackets refer to the MBrP compound. Parameters after which no brackets follow are the same for both the title compounds.

Synthesis

The ligands were prepared by the modified procedure given in the literature (Hodgkin, 1984). To a 250

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[1] DCB Contribution No. 824.

[2] Department of Crystallography and Biophysics, University of Madras, Guindy campus, Madras — 600 025, India.

[3] Department of Inorganic Chemistry, University of Madras, Guindy campus, Madras—600 025, India.

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ml round bottom flask, add 5.4 gm, 0.05 mole methylphenol, [8.6 gm, 0.05 mole bromophenol] in ehanol (150 ml) and 8.7 gm (0.1 mole) of morpholine. The solution was stirred as formaldehyde 3.0 gm (0.1 mole) was added slowly with stirring. The solution was heated to reflux and kept at this temperature for 24 hr. 2.5 ml addition of formaldehyde was added at an approximate time of 8-hr intervals. The ethanol was evaporated under vacuum and the resulting oil washed with sodium carbonate solution, extracted with dimethyl ether and the solvent removed to give a colorless solid (60%, [55%]). The recrystallization from petroleum ether gave colorless crystals. Melting point of the samples is given by 124°C [120°C].

Spectral data

Infrared spectra. Infrared spectra were recorded on a Hitachi 270-50 model spectrophotometer using KBr pellets.

NMR spectra

^{1}H NMR spectra were recorded at room temperature on a Varian EM 390 model (90 MHz) using $CDCl_3$ as solvent.

Mass spectra

The spectra were recorded on a Finningan MAT 8230 GC-MS model spectrophotometer connected to a Data system attached to a PDP-11 computer.

Crystal structure determination and refinement

Suitable crystals of size 0.3 × 0.4 × 0.1 [0.4 × 0.1 × 0.25] mm were used for the intensity data collection on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Cu$K\alpha$ (λ = 1.5418 Å) radiation. The accurate cell parameters were obtained by least-squares refinement using 25 medium angle reflections with $16 \leq \theta \leq 25$ [$20 \leq \theta \leq 30$]. The data were collected in the range $0 \leq 2\theta \leq 140$ by $\omega/2\theta$ scan mode. Out of 3040 [3123] reflections collected 2724 [2886] reflections were regarded as $I \geq 3\sigma$ (I) and used for structure solution and refinement. The intensities of three standard reflections monitored every 2 hr showed no significant change during data collection (1.6% [1.2%]). The intensities were corrected for Lorentz and polarization effects and for empirical absorption. The absorption correction were applied using PSI scan where the transmission factor varies from 0.94 [0.92] to 0.98 [0.99].

The trial structure was obtained by direct methods using SHELXS-86 (Sheldrick, 1986). The structure was refined by full-matrix least-squares procedure using SHELX-76 (Sheldrick, 1976). All the nonhydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. In the final cycles of refinement, the maximum and minimum electron densities were found to be 0.18 e$Å^{-3}$ [0.42 e$Å^{-3}$] and −0.21 [−1.1] e$Å^{-3}$. The sigma weighting scheme was applied and is given by $w = 1/(\sigma^2(F) + 0.0067\ F^2)$ [$w = 1/\sigma^2(F) + 0.067\ F^2)$]. A total of 303 [287] parameters were refined with 2724 [2886] reflections to the final R-factor of 0.049 [0.055] and wR of 0.063[0.069].

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The figures and the geometrical calculations were done by using PLUTO (Motherwell and Clegg, 1978) and PARST (Nardelli, 1983), respectively. All the calculations were performed on VAX730 and Micro VAX II computers available in the department.

Discussion

The spectroscopic data are presented in Table 1. The absorption peaks observed at 2840 cm^{-1} [2820

Table 1. Spectral data

Assignment	MMP	MBrP
IR data	cm^{-1}	
Ar OH	2840	2820
Aromatic		
C−C st	1340 1610	1350 1620
Ar−CH_2−N	742 1480	760 1455
C−Br		662
NMR data	δ (ppm)	
Ar−OH	10.6(1H,s)	10.75(1H,s)
Aromatic proton	6.6(2H,s)	6.93(2H,s)
O-CH_2	3.5-3.6(8H,m)	3.6-3.7(8H,m)
N−CH_2	2.3-2.5(4H,m)	2.3-2.4(4H,m)
C−CH_2−C	3.4(2H,s)	3.4(2H,s)
Mass spectral data	m/e[%]	
	307[30], 306[100], 220[80], 206[25], 190[18], 175[22], 161[35], 149[35], 134[26], 106[32], 86[75]	372[90], 371[100] 355[36], 340[28], 301[15], 290[32], 270[25], 255[22], 230[18], 201[31], 170[40], 100[15], 86[46], 80[10]

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2$) for nonhydrogen atoms

	MMP				MBrP			
Atom	x	y	z	$B_{eq}{}^{a}$	x	y	z	$B_{eq}{}^{a}$
C1	8810(1)	838(1)	7890(1)	3.57(5)	8891(2)	820(2)	7894(2)	3.19(5)
C2	8971(1)	−13(1)	7163(1)	3.58(5)	9045(2)	−30(2)	7169(2)	3.12(5)
C3	7950(2)	−604(1)	6728(1)	4.04(4)	8035(2)	−637(2)	6743(2)	3.52(4)
C4	6776(2)	−387(2)	7013(1)	4.37(4)	6883(3)	−400(3)	7067(2)	3.93(4)
C5	6655(2)	429(2)	7760(1)	4.29(5)	6737(3)	401(2)	7800(2)	3.86(5)
C6	7650(1)	1055(1)	8201(1)	3.86(5)	7747(3)	1031(2)	8226(2)	3.51(6)
C7	7459(2)	1961(1)	8993(1)	4.55(5)	7584(3)	1928(2)	9025(2)	4.16(8)
N8	6784(1)	1403(1)	9737(1)	3.67(5)	6860(2)	1401(2)	9747(2)	3.34(5)
C9	6514(2)	2334(2)	10444(1)	4.50(5)	6620(3)	2334(3)	10456(2)	4.09(7)
C10	5816(2)	1740(2)	11208(1)	5.06(5)	5894(3)	1754(4)	11206(2)	4.93(1)
O11	6484(1)	747(1)	11654(1)	5.80(4)	6504(3)	746(3)	11645(2)	6.15(8)
C12	6759(2)	−164(2)	10969(1)	5.51(7)	6734(5)	−188(3)	10950(2)	5.87(2)
C13	7472(2)	395(2)	10208(1)	4.68(5)	7505(3)	367(3)	10214(2)	4.38(8)
C14	10240(1)	−290(1)	6868(1)	3.77(5)	10302(2)	−312(2)	6867(2)	3.31(5)
N15	10936(1)	853(1)	6690(1)	3.37(5)	10991(2)	834(2)	6685(1)	3.00(5)
C16	10313(1)	1596(1)	5939(1)	3.83(5)	10333(2)	1585(2)	5944(2)	3.44(5)
C17	11063(2)	2718(2)	5726(1)	4.60(5)	11089(3)	2704(2)	5728(2)	4.14(8)
018	12248(1)	2370(1)	5457(1)	5.16(5)	12237(2)	2349(2)	5426(2)	4.76(5)
C19	12864(2)	1679(2)	6198(1)	5.16(5)	12900(3)	1648(3)	6151(3)	4.68(8)
C10	12158(1)	520(2)	6412(1)	4.17(5)	12201(2)	495(2)	6385(2)	3.71(5)
O21	9803(1)	1461(1)	8307(1)	4.49(4)	9885(2)	1462(2)	8294(1)	4.05(4)
C22	5675(2)	−1017(3)	6515(2)	6.36(7)				
Br					5512(1)	−1235(1)	6461(1)	6.34(3)

$^{a}B_{eq} = 8\pi^2/3\Sigma_i\Sigma_j U_{ij}a_i \cdot a_j a_i^* a_j^*$.

cm^{-1}] in the IR spectrum corresponds to aromatic-OH group which shows a chemical shift of 10.6 ppm [10.75 ppm] in the NMR spectrum. The two bands observed at 1340 cm^{-1} [1350 cm^{-1}] and 1610 cm^{-1} [1620 cm^{-1}] are related to the aromatic group having $\delta = 6.6$ ppm [6.93 ppm]. The peaks at 742 cm^{-1} [760 cm^{-1}] and 1480 cm^{-1} [1455 cm^{-1}] correspond to methylene groups (2.3-2.5 ppm [2.3-2.4 ppm]). The m + 1 peak 307 [372] tallies exactly with the calculated molecular weight of the compound. The final atomic coordinates of the nonhydrogen atoms are given in Table 2. The bond lengths, bond angles and some selected torsion angles of interest are given in Table 3.

Figure 1 shows a view of the molecule and the numbering scheme of the atoms. The two morpholino rings assume chair conformation (Table 4) with the torsion angles in the range ±56.1(3)–±60.4(4)° [±56.5(2)–±59.8(2)°]. In the morpholino rings the bond distances C—N = 1.453(4)—1.478(3) Å [1.457(2)—1.479(2) Å], C—C = 1.506(3)—1.511(5) Å [1.503(2) – 1.512(3) Å], C—O = 1.397(5)—1.433(4) Å [1.419(2)—1.429(2) Å] agree with those values found in the related system (Andreetti *et al.*, 1979; Baydar *et al.*, 1984; Ponnuswamy and Trotter, 1984; Shanmuga Sundara Raj *et al.*, 1993; Swaminathan *et al.*, 1980).

The phenyl rings are planar (maximum deviation ±0.015(3) Å [±0.013(1) Å]). The methyl carbon C22 [Br] atom deviates from the plane by 0.062(3) Å [0.050(4) Å]. The morpholino ring is in chair conformation and orients at an angle of 50.2(1)° (MMP) and 57.4(1)° (MBrP) with each other. The C—O bond distance 1.391(2) Å [1.375(3) Å] is in agreement with the reported values 1.364 Å (Allen *et al.*, 1987).

Intermolecular interactions correspond to van der Waals interactions. The shortest intermolecular distance observed between C19 and C10 ($x + 1, -y + 1/2, z - 1/2$) is 3.647(3) Å [3.701(5) Å].

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Table 3. Molecular geometry

Atoms	MMP	MBrP
(a) Bond lengths(Å)		
C1–C2	1.401(2)	1.399(4)
C1–C6	2.391(2)	1.392(4)
C1–O21	1.374(2)	1.375(3)
C2–C3	1.391(2)	1.383(3)
C2–C14	1.506(2)	1.505(3)
C3–C4	1.392(3)	1.401(4)
C4–C5	1.391(3)	1.372(4)
C4–C22	1.513(3)	—
C4–Br	—	1.898(3)
C5–C6	1.390(2)	1.395(4)
C6–C7	1.515(2)	1.513(4)
C7–N8	1.460(2)	1.461(4)
N8–C9	1.464(2)	1.463(4)
N8–C13	1.457(2)	1.452(4)
C9–C10	1.512(3)	1.515(5)
C10–O11	1.419(2)	1.397(5)
O11–C12	1.429(2)	1.447(5)
C12–C13	1.502(3)	1.519(5)
C14–N15	1.479(2)	1.482(3)
N15–C16	1.463(2)	1.471(3)
N15–C20	1.464(2)	1.470(3)
C16–C17	1.503(2)	1.509(4)
C17–O18	1.426(3)	1.414(4)
O18–C19	1.419(2)	1.429(4)
C19–C20	1.510(3)	1.511(4)

(b) Bond angles(°)

Atoms	MMP	MBrP
C6–C1–O21	119.4(1)	118.8(2)
C2–C1–O21	120.1(1)	119.8(2)
C2–C1–C6	120.6(1)	121.4(2)
C1–C2–C14	120.0(1)	120.6(2)
C1–C2–C3	119.2(1)	119.6(2)
C3–C2–C14	120.7(1)	119.8(2)
C2–C3–C4	121.4(1)	118.7(2)
C3–C4–C22	120.5(2)	—
C3–C4–Br	—	117.7(2)
C3–C4–C5	117.8(2)	121.8(3)
C5–C4–C22	121.7(2)	—
C5–C4–Br	—	120.5(2)
C4–C5–C6	122.5(2)	120.0(3)
C1–C6–C5	118.5(1)	118.5(3)
C5–C6–C7	120.2(2)	120.0(3)
C1–C6–C7	121.4(1)	121.5(3)
C6–C7–N8	112.0(1)	112.4(2)
C7–N8–C13	111.6(1)	110.4(2)
C7–N8–C9	110.5(1)	110.7(2)
C9–N8–C13	108.6(1)	108.7(2)
N8–C9–C10	109.8(2)	109.5(3)
C9–C10–O11	111.7(2)	112.1(3)
C10–O11–C12	109.9(1)	109.9(3)
O11–C12–C13	111.0(2)	109.4(3)
N8–C13–C12	110.6(2)	109.9(3)
C2–C14–N15	112.2(1)	111.8(2)
C14–N15–C20	109.4(1)	109.1(2)
C14–N15–C16	111.2(1)	110.9(2)
C16–N15–C20	108.9(1)	109.3(2)
N15–C16–C17	110.8(1)	109.9(2)
C16–C17–O18	111.1(2)	111.2(2)
C17–O18–C19	109.4(1)	109.8(3)
O18–C19–C20	111.2(1)	110.9(3)
N15–C20–C19	109.9(1)	110.1(2)

(c) Some selected torsion angles(°)

Atoms	Angle	
	MMP	MBrP
Ring A		
C9–N8–C13–C12	58.0(2)	59.4(3)
C13–N8–C9–C10	−57.2(2)	−57.3(3)
N8–C9–C10–O11	58.4(2)	58.3(4)
C9–C10–O11–C12	−57.9(2)	−58.9(4)
C10–O11–C12–C13	57.7(2)	59.2(4)
O11–C12–C13–N8	−58.8(2)	−60.2(4)
Ring B		
C16–N15–C20–C19	56.5(2)	56.0(3)
C20–N15–C16–C17	−56.2(2)	−56.1(3)
N15–C16–C17–O18	58.1(2)	59.0(3)
C16–C17–O18–C19	−59.0(2)	−60.2(3)
C17–O18–C19–C20	59.8(2)	59.8(3)
O18–C19–C20–N15	−59.5(2)	−58.1(3)

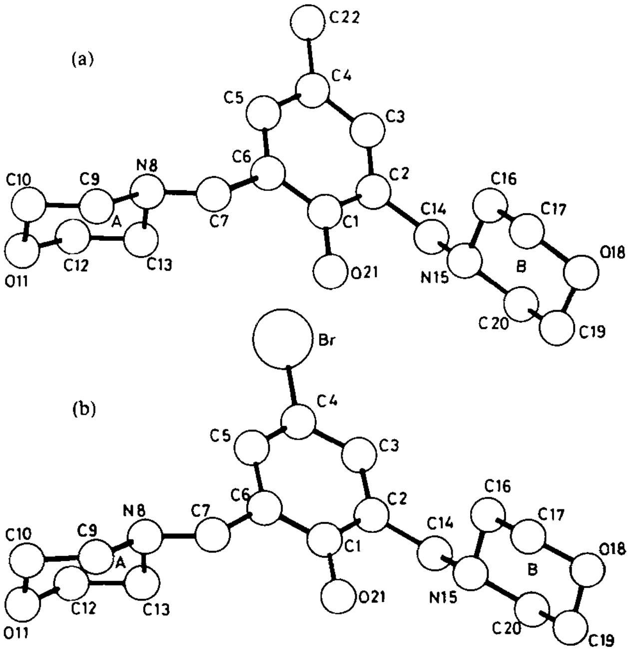

Fig. 1. Perspective view of the molecules showing the numbering scheme of atoms.

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