Synthesis and structural characterization of 2,6-bis-(N-methylenemorpholino)-4-ter-butylphenol¹

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The crystal and molecular structure of the title compound, $C_{20}H_{32}N_2O_3$, has been determined from X-ray diffraction data using CuK α radiation ($\lambda = 1.5418$ Å). The compound crystallizes in triclinic space group $P\overline{1}$ with a = 8.828(1), b = 18.680(1), c = 6.272(2) Å, $\alpha = 93.42(1)$, $\beta = 90.24(2)$, $\gamma = 77.93(1)^\circ$, V = 1009.4(2)Å³, and Z = 2. The structure was solved by direct methods and the full-matrix least-squares refinement leads the final *R*-factor to 0.065 for 3481 observed reflections with $I \ge 3\sigma(I)$. The phenyl ring is planar and the morpholino rings assume perfect "chair" conformation. The molecules are held together by van der Waals forces.

Introduction

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 ligand characterized by IR, NMR, Mass spectra and X-ray diffraction methods.

Experimental

Synthesis and spectral data

The ligand has been prepared by the modified procedure as given in the literature (Hodgkin, 1984). In a 250 ml round bottomed flask, ethanol (150 ml), tertiary butyl phenol (7.5 g; 0.05 mol) and morpholine (8.7 g, 0.1 mol) were added slowly and heated to reflux and kept at this temperature for 24 hours. During this period, 2.5 ml of formaldehyde was added at 8 hours intervals. The ethanol was evaporated under vacuum and the resulting oil washed with sodium carbonate solution, extracted with diethyl ether and the solvent is removed. The compound was recrystallized from petroleum ether, resulting in colorless crystals (70%) with melting point of 123°C.

The various spectra were recorded using the following instruments: IR—Hitachi 270-50 model using KBr pellet; NMR—Varian EM 390 model (90 MHz) using CDCl₃ as solvent; Mass spectra—Finnigan MAT 8230 GC-MS model.

Crystal structure determination and refinement

A suitable crystal of size $0.2 \times 0.15 \times 0.2$ mm was mounted on an Enraf-Nonius CAD-4 diffractometer employing graphite monochromatized CuK α ($\lambda =$ 1.5418 Å) radiation. Twenty medium angle reflections in the range 25 to 30° provided the cell parameters by least-squares refinement. The intensity data were collected for reflections with $0 \le 2\theta \le 140$ by $\omega/2\theta$ scan mode. A total of 3730 unique reflections were measured, out of which 3481 were found to be observed with $I \ge 3\sigma(I)$. The intensities of standard reflections

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The structure was solved by direct methods using SHELXS-86 (Sheldrick, 1986). The positions of all the nonhydrogen atoms were located. The structure was refined by full-matrix least-squares refinement using SHELX-76 (Sheldrick, 1976). The non-hydrogen atoms were refined anisotropically where as the hydrogen atoms located from the difference Fourier were refined isotropically. In the final cycle of refinement, the reliability factor, R, converged to 0.065 and wR, 0.083.

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 strong absorption band observed at 3200 cm^{-1} in the IR spectrum corresponds to the phenolic-OH

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

| Table 2. | Atomic | coordinates | and equivalent | isotropic thermal | parameters (A | Å ²) fo | r non-hydrogen atoms. |
|----------|--------|-------------|----------------|-------------------|---------------|---------------------|-----------------------|
|----------|--------|-------------|----------------|-------------------|---------------|---------------------|-----------------------|

| Atom | x | у | z | $U_{\rm eq}^{\ a}$ | Atom | x | у | z | $U_{ m eq}{}^a$ |
|-------|-----------|-----------|-----------|--------------------|-------|------------|-----------|-----------|-----------------|
| C(1) | 0.1432(1) | 0.3138(1) | 0.1716(2) | 0.036 | C(14) | -0.0425(2) | 0.3489(1) | 0.4886(2) | 0.040 |
| C(2) | 0.0629(1) | 0.2930(1) | 0.3414(2) | 0.035 | N(15) | -0.1273(1) | 0.4125(1) | 0.3783(2) | 0.036 |
| C(3) | 0.0860(1) | 0.2192(1) | 0.3825(2) | 0.036 | C(16) | -0.2097(2) | 0.4691(1) | 0.5316(2) | 0.044 |
| C(4) | 0.1891(2) | 0.1653(1) | 0.2620(2) | 0.037 | C(17) | -0.2939(2) | 0.5345(1) | 0.4171(4) | 0.061 |
| C(5) | 0.2662(2) | 0.1876(1) | 0.0939(2) | 0.038 | O(18) | -0.4000(1) | 0.5141(1) | 0.2689(2) | 0.064 |
| C(6) | 0.2449(2) | 0.2609(1) | 0.0464(2) | 0.037 | C(19) | -0.3199(2) | 0.4591(1) | 0.1172(3) | 0.066 |
| C(7) | 0.3263(2) | 0.2831(1) | 0.1454(2) | 0.045 | C(20) | -0.2396(2) | 0.3918(1) | 0.2267(3) | 0.050 |
| N(8) | 0.4735(1) | 0.2332(1) | 0.1955(2) | 0.037 | O(21) | 0.1241(1) | 0.3859(1) | 0.1234(2) | 0.048 |
| C(9) | 0.5919(2) | 0.2449(1) | 0.0442(3) | 0.054 | C(22) | 0.2128(2) | 0.0842(1) | 0.3142(2) | 0.044 |
| C(10) | 0.7418(2) | 0.1909(1) | 0.0948(3) | 0.066 | C(23) | 0.3534(3) | 0.0371(1) | 0.1987(5) | 0.091 |
| O(11) | 0.7934(2) | 0.1966(1) | 0.3056(2) | 0.075 | C(24) | 0.0684(4) | 0.0560(1) | 0.2442(6) | 0.091 |
| C(12) | 0.6765(2) | 0.1861(1) | 0.4543(3) | 0.067 | C(25) | 0.2333(4) | 0.0765(1) | 0.5532(4) | 0.084 |
| C(13) | 0.5269(2) | 0.2406(1) | 0.4101(2) | 0.052 | | | . , | | |

 $^{a}U_{eq} = 1/3\Sigma_{i}\Sigma_{j}U_{ij}a_{i}a_{j}a_{i}^{*}a_{j}^{*}$

group which shows a chemical shift (δ) of 10.6 in the NMR spectrum. The two bands observed at 1350 and 1615 cm⁻¹ are related to the aromatic group having $\delta = 6.75$. The other prominent characteristic peaks observed in the IR and NMR spectra of the compound are given in Table 1. The mass spectral data of the compound are also given in Table 1. The peak correspond-



| Assignment of chemical groups | NMR δ (ppm) | IR (cm ⁻¹) | Mass spectral data [m/e(%)] |
|-----------------------------------|--------------|------------------------|-----------------------------|
| Ar-OH | 10.6 (s, 1H) | 3200 | 349(100), 291(8), |
| Aromatic | 6.75 (s, 2H) | 1350, 1615 | 262(90), 249(25), |
| $O-CH_2-C$ | 3.7 (m, 8H) | | 232(12), 205(45), |
| Ar-CH ₂ -N | 3.5 (s, 4H) | 740, 1460, | 179(60), 161(33), |
| N-CH ₂ -C | 2.4 (m, 8H) | 2860 | 146(16), 86(35), |
| C-(CH ₃) ₃ | 1.28 (s, 9H) | 2960 | 57(8) |

Table 1. Spectral data.

| | Atom 1 | Atom 2 | Distance | Atom 1 | | Atom 2 | Distance | |
|--------------|--------|----------------|----------------------|---------------------|--------|-----------------|----------------------|----------------------|
| | C(1) | -C(2) | 1.399(2) | C(10) | | -0(11) | 1.417(2) | |
| | C(1) | -C(6) | 1.393(2) | O(11) | | -C(12) | 1.425(3) | |
| | C(1) | -O(21) | 1.374(3) | C(12) | | -C(13) | 1.504(2) | |
| | C(2) | -C(3) | 1.390(3) | C(14) | | -N(15) | 1.474(2) | |
| | C(2) | -C(14) | 1.514(2) | N(15) | | -C(16) | 1.461(2) | |
| | C(3) | -C(4) | 1.394(2) | N(15) | | -C(20) | 1.465(2) | |
| | C(4) | -C(S) | 1.38/(2) | C(16) | | -C(17) | 1.510(3) | |
| | C(4) | -C(22) | 1.540(5) | C(17) | | -0(18) C(10) | 1.410(3) | |
| | C(3) | -C(0) | 1.595(5) | C(18) | | -C(20) | 1.430(2) | |
| | C(0) | -C(7) -N(8) | 1.525(2) | C(13) | | -C(23) | 1.510(5) | |
| | N(8) | $-\Gamma(0)$ | 1.455(2) | C(22) | | -C(23) | 1.521(5) 1.531(4) | |
| | N(8) | -C(13) | 1 451(2) | C(22) | | -C(25) | 1.531(4) | |
| | C(9) | -C(10) | 1.508(2) | 0(22) | | 0(25) | 1.521(5) | |
| 44 | A. 0 | | | | | | | |
| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | | Atom 2 | Atom 3 | Angle |
| Q (4) | | | Be | ond angles (°) | | 2 /10) | - <i></i> | |
| C(6) | -C(1) | -0(21) | 118.4(1) | C(9) | | -C(10) | -0(11) | 111.3(2) |
| C(2) | -C(1) | =0(21) | 121.5(1) | C(10) | | -0(11) | -C(12) | 109.9(1) |
| C(2) | -C(1) | -C(0) | 120.1(2) 121.0(1) | N(8) | | -C(12) | -C(13) | 111.0(2) 100.3(1) |
| C(1) | -C(2) | -C(3) | 110 1(1) | C(2) | | -C(13) | -C(12) -N(15) | 112 2(1) |
| C(3) | -C(2) | -C(14) | 118.9(1) | C(14) | | -N(15) | -C(20) | 113.3(1) 111.8(2) |
| C(2) | -C(3) | -C(4) | 122.0(1) | C(14) | | -N(15) | -C(16) | 110.8(1) |
| C(3) | -C(4) | -C(22) | 120.4(1) | C(16) | | -N(15) | -C(20) | 108.5(1) |
| C(3) | -C(4) | -C(5) | 117.5(2) | N(15) | | -C(16) | -C(17) | 110.4(1) |
| C(5) | -C(4) | -C(22) | 122.1(1) | C(16) | | -C(17) | -O(18) | 111.0(2) |
| C(4) | -C(5) | -C(6) | 122.2(1) | C(17) | | -O(18) | -C(19) | 109.7(1) |
| C(1) | -C(6) | -C(5) | 119.2(1) | O(18) | | -C(19) | -C(20) | 111.0(2) |
| C(5) | -C(6) | -C(7) | 120.8(2) | N(15) | | -C(20) | -C(19) | 108.9(2) |
| C(1) | -C(6) | -C(7) | 120.1(2) | C(4) | | -C(22) | -C(25) | 110.5(2) |
| C(6) | -C(7) | -N(8) | 112.4(1) | C(4) | | -C(22) | -C(24) | 108.3(2) |
| C(7) | -N(8) | -C(13) | 111.9(1) | C(4) | | -C(22) | -C(23) | 111.9(2) |
| C(7) | -N(8) | -C(9) | 111.3(1) | C(24) | | -C(22) | -C(25) | 108.6(2) |
| N(8) | -C(9) | -C(10) | 110.3(2) | C(23) | | -C(22) | -C(24) | 108.8(2) |
| | | Atom 1 | Atom 2 | Atom 3 | Atom 4 | A | Angle | |
| | | | Some selec | cted torsion angles | (°) | | | |
| Ring-A | | | | | | | | |
| | | C(9) | -N(8) | -C(13) | -C(12) | : | 58.2(2) | |
| | | C(13) | -N(8) | -C(9) | -C(10) | -: | 58.0(2) | |
| | | N(8) | -C(9) | -C(10) | -O(11) | : | 57.8(2) | |
| | | C(9) | -C(10) | -O(11) | -C(12) | -: | 56.8(2) | |
| | | C(10) | -O(11) | -C(12) | -C(13) | : | 57.9(2) | |
| Dine D | | O(11) | -C(12) | -C(13) | -N(8) | -: | 59.0(2) | |
| кıng-В | | C(16) | -N(15) | -C(20) | -C(10) | | 58 5/2) | |
| | | C(20) | -N(15) | -C(20) | -C(19) | _ | 57 9(2) | |
| | | N(15) | -C(16) | -C(17) | -0(18) | | 58.5(2) | |
| | | C(16) | -C(17) | -0(18) | -C(19) | | 58.4(2) | |
| | | C(17) | -O(18) | -C(19) | -C(20) | | 59.9(2) | |
| | | O(18) | -C(19) | -C(20) | -N(15) | -(| 60.2(2) | |

Table 3. Molecular geometry

ing to the molecular weight of the molecule obtained 349(100) tallies with the roughly calculated molecular weight of 348.

The final atomic coordinates and the anisotropic temperature factors of the nonhydrogen atoms are given in Table 2. Figure 1 shows a view of the molecule and the numbering scheme of the atoms. The bond lengths, bond angles and some selected torsion angles of interest are given in Table 3.

The two morpholino rings assume perfect "chair" conformation (Table 3) with the torsion angles in the range $\pm 56.8(2) - \pm 59.0(2)^{\circ}$ and $\pm 57.9(2)$ $\pm 60.2(2)^{\circ}$. In the morpholino rings the bond distances C-N = 1.451(2)-1.465(2)Å, C-C = 1.504(2) – 1.510(3)Å and C-O = 1.410(3)-1.430(2)Å agree with those found in related systems (Andreetti et al., 1979; Baydar et al., 1984; Ponnuswamy and Trotter, 1984; Swaminathan et al., 1980). The phenyl ring is planar (maximum deviation $\pm 0.008(1)$ Å). The best least-squares plane through the morpholino rings omit N and O atoms. The atoms N(8) and O(11) deviate by -0.673(2) and 0.639(2)Å from the plane of the atoms C(9), C(10), C(12), and C(13) of the morpholino ring A whereas the atoms N(15) and O(18) deviate by 0.684(1) and -0.656(1)Å from the plane of the atoms C(16), C(17), C(19) and C(20) of the morpholino ring B. The planes of these morpholino rings A and B are oriented by 117.4(1) and 120.8(1)° with respect to the phenyl ring. In addition they are inclined by $42.2(1)^{\circ}$ with each other.

The t-boc group is in staggered conformation. The C-O bond distance [=1.374(3) Å] is comparable with the average value of 1.364 Å reported in the literature (Allen *et al.*, 1987).

The packing of the molecules are shown in Fig. 2. An intramolecular hydrogen bond between the atoms O(21) and N(15) (O(21)-N(15) = 2.682(1)Å, H(21)-N(15) = 1.94(4)Å and O(21)-H(21) $\cdots N(15) = 142(3)^{\circ}$) controls the crystal packing in addition to the van der Waals forces. The molecules run in a linear fashion in the c-direction. The shortest inter molecular distance observed between C(3) and O(11) (x - 1, y, z + 1) is 3.357(2)Å.

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Fig. 2. Packing of the molecules in the unit cell down a-axis.

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Hydrogen atom parameters, anisotropic thermal parameters, torsion angles, plane results and structure factors for the compound have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication no. 67129 (22 pages).