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Crystallographic analysis of 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane

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The crystal structure of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane has been determined by X-ray crystallographic technique. The compound crystallized into monoclinic crystal lattice having space group $P2_1/c$ with unit cell parameters, a = 15.023(2) Å, b = 9.924(2) Å, c = 11.620(2) Å, $\alpha = \gamma = 90^0$, β = 112.41(1), V=1601.5(5) Å^3 and Z = 4. Other parameters, such as atomic coordinates, bond lengths, bond angles, torsion angles and geometry of intermolecular interactions are also determined.

Keywords: Bisphenols, Crystal structure, X-ray diffraction

1 Introduction

Bisphenols are important industrial feedstock, especially as a precursor to polycarbonate plastic and epoxy resin[1-3]. Bisphenols have a wide spectrum of biological activity including fungicidal[4], antibacterial[5] and antiviral[6]. The β-fluorinated O-carborane-1, 2-bisphenol has potent antagonistic activity for an estrogen receptor and act as a selective estrogen receptor modulator[7]**.** 1,1-Di(p-hydroxyphenyl) cyclohexane and 1,1,6,6-tetraphenylhexa-2,4-diyne- 1,6-diol has been used for the separation of cyclohexanol and cyclohexanone by complexation[8]. The 1,1'-bis(4-hydroxyphenyl) cyclohexane has been used for the isolation of methylhydrazine from its aqueous solution[9] and proved to be useful for efficient separation of isomers, which could not be separated by the fractional distillation technique because of their narrow boiling points[10,11]. It has been also used to separate the isomers of the cresols[12], phenylenediamines and benzenedilos[13]. These observations prompted to investigate the crystallographic studies of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane (Fig. 1). X-Ray diffraction analysis has been carried out to determine its three-dimensional structure and also to understand the conformation of the cyclohexane ring and phenolic rings. The molecular structure of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane is shown in Fig. 2.

2 Experimental Method

The compound under study was synthesized and crystallized as already done[14]. Good quality single crystals of the compound were grown from methanol solution at 30°C. A colourless prism

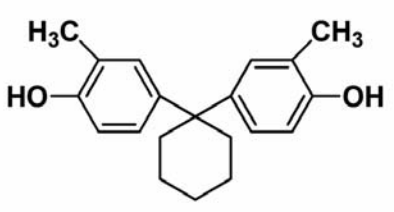

Fig. 1 – Chemical structure of 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane

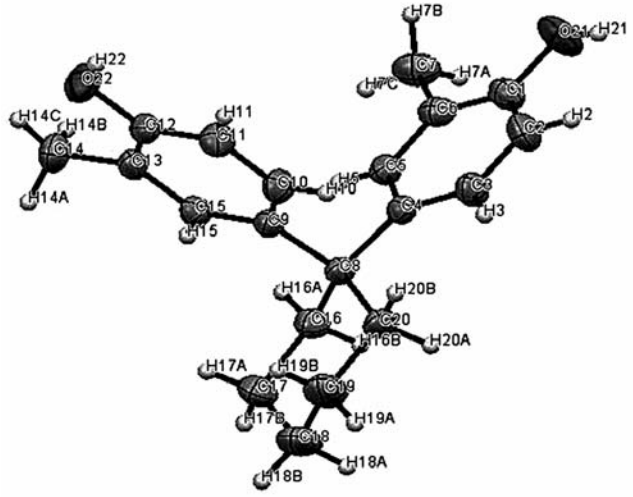

Fig. 2 – Molecular structure of 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane

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shaped crystal with approximate dimensions of 0.660 × 0.480 × 0.350 mm^3 was used for X-ray diffraction study. The mesurements were carried out on a Rigaku SCX mini diffractometer using graphite monochromated Mo-Kα radiation (λ= 0.71075 Å). The diffraction data were collected over the θ range of 3.4 - 27.5°. A total of 15817 reflections were measured, out of which 3658 were found unique and 3164 as observed with $F^2 > 2\sigma(F^2)$. Data were collected and processed using Crystal Clear software (Rigaku)[15]. The reflection data was corrected for Lorentz and polarization effects and no absorption correction was applied. The structure was solved by direct method using SHELXD[16] and refined by full matrix least squares method by using SHELXL-97[17] with anisotropic displacement parameter for all non H-atoms. Refinement of 199 parameters with 3658 unique reflections converged the residuals to R_1 =0.0572. The electron density (Δρ) in the final difference Fourier map ranges from 0.45 to -0.54 $e^-/Å^3$. The value of F(000), i.e., the total number of electrons per unit cell, is 640 and goodness of fit on F^2 was 1.041. The crystal data and structural refinement data are given in Table 1.

Table 1 -Crystal data and structure refinement data

CCDC deposition number	CCDC 953754
Empirical formula	$C_{20}H_{24}O_2$
Formula weight	296.41
Crystal color/shape	Colorless/ prism shaped
Temperature	293K
Wavelength Å	0.71075 Å
Crystal system	Monoclinic
Crystal dimensions	0.660 X 0.480 X 0.350 mm^3
Lattice type	Primitive
Unite cell dimensions	a = 15.023(2) Å, α=90.00 b = 9.924(2) Å, β = 112.41 c = 11.620(2) Å, γ=90.00
Space Group	$P2_1/c$
Volume	1601.5(5) $Å^3$
Z value	4
Calculated density (D_{cal})	1.229 g/cm^3
Absorption coefficient	0.773 cm^{-1}
F_{000}	640.00
θ range for data collection	3.4 - 27.5°
Limiting indices	-19 <= h <= 19, -12 <= k <= 12, -15 <= l <= 15
$2\theta_{max}$	55.0^0
No. of reflections measured	15817
Reflections unique	3658
Observed reflections	3164
Structure solution	SHELXD Direct methods
Refinement	Full-matrix least-squares on F^2
Data/restrains/parameters	3658/0/199
Goodness of fit indicator	1.041
Final R1 (I>2.00σ(I))	0.0572
R indices (All reflections)	0.0639
wR2 (All reflections)	0.1712
Maximum peak in final diff. map	0.45 $e^-/Å^3$
Minimum peak in final diff. map	-0.54 $e^-/Å^3$

3 Results and Discussion

X-Ray diffraction confirmed that compound crystallized in monoclinic crystal lattice having space group $P2_1/c$ with unit cell parameters: *a* = 15.023(2) Å, *b* = 9.924(2) Å, *c* = 11.620(2) Å, α = γ = 90^0, β = 112.41(1), V=1601.5(5) $Å^{-3}$ and Z = 4. Cyclohexane ring adopts the stable chair conformation because it is completely strain-free. The conformation of the cyclohexane ring is described in terms of torsion angles of C_8-C_{16}-C_{17}-C_{18} [-56.5(2)] and C_{18}-C_{19}-C_{20}-C_8 [57.6(3)], respectively indicating that there is greater puckering at C_8 than C_{18}. The dihedral angle between the two phenyl rings is 106.2°. The both phenyl rings are perpendicular to the mean plane of the cyclohexane ring making torsion angles of C_4-C_8-C_{16}-C_{17}= 174.0°, C_4-C_8-C_9-C_{15} = 100.6°, C_9-C_8-C_{20}-C_{19} = 68.9°. Each methyl group present on phenyl rings is oriented in syn-periplanar (*cis*) or anti-periplanar (*trans*) conformation with respect to adjacent C=C of the phenyl rings. The torsion angle O-C=C-C close to 0° corresponds to the *cis* configuration, while it is of 180°, a *trans* configuration. The value of torsion angle is O_{21}-C_1-C_6-C_7 = 0.1°. This value is close to 0°. Thus, the methyl groups adopt a clear *cis* arrangement. The compound links with the neighbouring molecule through strong intermolecular O-H…O hydrogen with O_{21}-H_{21}...O_{22} = 2.868(3) Å, 101.04° and O_{22}-H_{22}…O_{21} = 2.868(3) Å, 156.69° with symmetry code (-*x*+1, *y*+1/2, -*z*+1/2) and (-*x*+1, *y*+1/2-1, -*z*+1/2), respectively. The presence of methyl substituent ortho- to hydroxy group restricts the orientation of the O-H…O bonds along with the concomitant reduction of the bond strengths. The observed O-H…O bond lengths are comparatively higher than O-H…O bond (1.84 Å and 172.5°) of the mother compound[18,19] result shows that the introduction of methyl group affects the strong hydrogen bond network of the

molecules due to the non-polar character. These bonds link molecules into endless helical chains and help in stabilizing the crystal structure. The presence of the cyclohexane ring also affects conformation of the molecule. The value of dihedral angle is dramatically increased as the size of bridge atom (S =104.21°, $C(CH_3)_2$=108.9°, CH_2=114.8°, O = 118.8°) decreased, reflecting the fact that the shorter the C-X (X= bridging atom) distance, the greater is the steric interaction between the phenyl ring but results show that dihedral angle is 106.2° is quite similar to $C(CH_3)_2$ and bond length value is 1.544 Å, which is similar to the typical C-C bond length (1.54 Å) show less steric effect between phenyl rings[20,21]. Corresponding distances of C-H….π interactions between cyclohexane ring units of one molecule and phenyl ring units of adjacent molecules with the distances of 2.864 and 2.849 Å, respectively and π….π interaction is observed between the two phenyl ring units of neighbouring molecule with the distance of 3.598 Å, which also helps to stabilize the molecule as illustrated in Fig. 3. All the molecules are interconnected in a 3D network through weak interactions as shown in Fig. 4. The atomic coordinates and equivalent isotropic displacement parameters for various carbon and oxygen atoms are reported in Table 2. The bond lengths, bond angles and torsion angles of non-hydrogen atoms are presented in Tables 3 and 4, respectively. The geometry of intermolecular interactions is presented in Table 5.

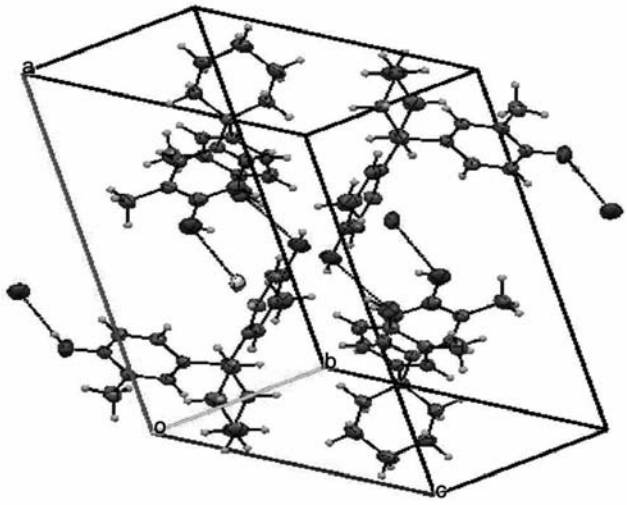

Fig. 3 – Diagram showing the C-H…π and π-π interactions between the adjacent molecules

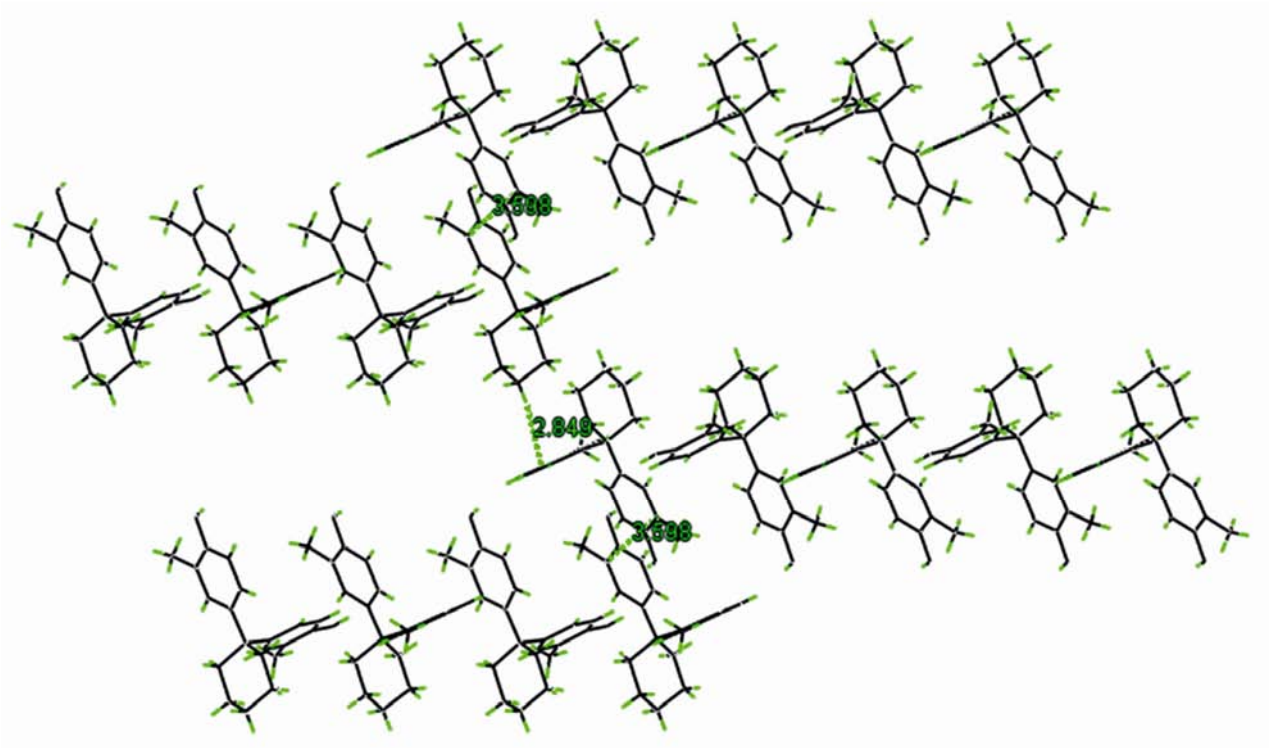

Fig. 4 – Diagram showing the 2D architecture of 1,1'-bis(3-methyl-4-hydroxyphenyl)-cyclohexane

Table 2 – Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atoms	X	Y	Z	U_{eq}*
O21	0.4145(1)	0.7537(2)	-0.1336(2)	4.31(4)
O22	0.7145(1)	0.2211(2)	0.5064(2)	3.70(3)
C1	0.5071(2)	0.7284(2)	-0.0491(2)	2.98(4)
C2	0.5443(2)	0.8144(2)	0.0508(2)	3.29(4)
C3	0.6358(2)	0.7929(2)	0.1404(2)	2.80(3)
C4	0.6917(1)	0.6850(2)	0.1316(2)	2.17(3)
C5	0.6518(1)	0.5998(2)	0.0290(2)	2.42(3)
C6	0.5602(2)	0.6187(2)	-0.0627(2)	2.63(3)
C7	0.5192(2)	0.5224(3)	-0.1702(2)	3.68(4)
C8	0.7917(1)	0.6537(2)	0.2325(2)	2.10(3)
C9	0.7762(1)	0.5382(2)	0.3120(2)	2.03(3)
C10	0.7329(2)	0.5631(2)	0.3971(2)	2.55(3)
C11	0.7125(2)	0.4593(2)	0.4628(2)	2.78(3)
C12	0.7337(1)	0.3274(2)	0.4443(2)	2.48(3)
C13	0.7773(1)	0.2977(2)	0.3604(2)	2.36(3)
C14	0.8012(2)	0.1545(2)	0.3404(2)	3.36(4)
C15	0.7974(1)	0.4043(2)	0.2964(2)	2.22(3)
C16	0.8620(1)	0.6153(2)	0.1693(2)	2.61(3)
C17	0.9663(2)	0.5963(2)	0.2605(2)	3.39(4)
C18	1.0040(2)	0.7212(3)	0.3392(3)	4.14(5)
C19	0.9378(2)	0.7600(3)	0.4052(2)	3.77(4)
C20	0.8343(2)	0.7797(2)	0.3134(2)	2.75(3)

U_{eq} = 8/3 $\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*) \cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*) \cos\alpha]$

Table 3 – Bond lengths (Å) and bond angles (°)

Bond	Bond lengths (Å)	Bond	Bond angles (°)
O21-C1	1.386(2)	O21-C1-C2	117.38(18)
O22-C12	1.370(3)	O21-C1-C6	121.61(16)
C1-C2	1.376(3)	C2-C1-C6	121.00(15)
C1-C6	1.394(3)	C1-C2-C3	120.28(19)
C2-C3	1.389(3)	C2-C3-C4	121.17(16)
C3-C4	1.388(3)	C3-C4-C5	117.03(13)
C4-C5	1.397(2)	C3-C4-C8	122.71(14)
C4-C8	1.544(2)	C5-C4-C8	120.19(14)
C5-C6	1.395(2)	C4-C5-C6	123.24(16)
C6-C7	1.505(3)	C1-C6-C5	117.28(15)
C8-C9	1.544(3)	C1-C6-C7	121.32(14)
C8-C16	1.546(3)	C5-C6-C7	121.38(17)
C8-C20	1.549(3)	C4-C8-C9	106.15(12)
C9-C10	1.398(3)	C4-C8-C16	109.39(13)
C9-C15	1.394(3)	C4-C8-C20	110.83(13)
C10-C11	1.385(3)	C9-C8-C16	112.78(13)
C11-C12	1.383(3)	C9-C8-C20	110.97(14)
C12-C13	1.397(3)	C16-C8-C20	106.76(14)
C13-C14	1.506(3)	C8-C9-C10	120.58(14)
C13-C15	1.391(3)	C8-C9-C15	122.44(16)
C16-C17	1.531(2)	C10-C9-C15	116.81(16)
C17-C18	1.516(3)	C9-C10-C11	121.28(17)
C18-C19	1.519(4)	C10-C11-C12	120.38(19)
C19-C20	1.526(3)	C11-C12-C13	120.36(17)
		C12-C13-C14	120.67(17)
		C12-C13-C15	117.88(16)
		C14-C13-C15	121.45(19)
		C9-C15-C13	123.29(18)
		C8-C16-C17	113.89(15)
		C16-C17-C18	111.42(16)
		C17-C18-C19	110.19(18)
		C18-C19-C20	111.60(17)
		C8-C20-C19	113.31(15)
		O22-C12-C13	116.97(15)
		O22-C12-C11	122.66(19)

Table 4 – Torsion angles (°)

O21-C1-C2-C3	178.46(17)	O21-C1-C6-C5	-178.39(17)
O21-C1-C6-C7	0.1(3)	C2-C1-C6-C5	0.3(3)
C2-C1-C6-C7	178.72(18)	C6-C1-C2-C3	-0.3(3)
C1-C2-C3-C4	0.1(3)	C2-C3-C3-C4	0.1(3)
C2-C3-C4-C8	-176.99(17)	C3-C4-C5-C6	-0.0(3)
C3-C4-C8-C9	100.31(18)	C3-C4-C8-C16	-137.74(17)
C3-C4-C8-C20	-20.3(3)	C5-C4-C8-C9	-76.62(19)
C5-C4-C8-C16	45.3(2)	C5-C4-C8-C20	162.79(15)
C8-C4-C5-C6	177.09(14)	C4-C5-C6-C1	-0.1(3)
C4-C5-C6-C7	-178.59(16)	C4-C8-C9-C10	-74.53(15)
C4-C8-C9-C15	100.55(14)	C4-C8-C16-C17	174.01(12)
C4-C8-C20-C19	-173.45(14)	C9-C8-C16-C17	-68.11(15)
C16-C8-C9-C10	165.70(10)	C16-C8-C9-C15	-19.22(16)
C9-C8-C20-C19	68.87(18)	C20-C8-C9-C10	45.97(16)
C20-C8-C9-C15	-138.95(13)	C16-C8-C20-C19	-54.39(17)
C20-C8-C16-C17	54.03(16)	C8-C9-C10-C11	175.56(11s)
C8-C9-C15-C13	-175.02(10)	C10-C9-C15-C13	0.23(19)
C15-C9-C10-C11	0.21(19)	C9-C10-C11-C12	-0.8(2)
C8-C9-C15-C13	-179.60(12)	C10-C11-C12-C13	0.9(2)
O22-C12-C13-C14	0.07(19)	O22-C12-C13-C15	-179.99(11)
C11-C12-C13-C14	179.55(12)	C11-C12-C13-C15	-0.50(19)
C12-C13-C15-C9	-0.1(2)	C14-C13-C15-C9	179.86(12)
C8-C16-C17-C18	-56.5(2)	C16-C17-C18-C19	55.0(3)
C17-C18-C19-C20	-55.8(3)	C18-C19-C20-C8	57.6(3)

Table 5 – Geometry of intermolecular interactions

Donor	D...A(Å)	D-H(Å)	H...A(Å)	D-H...A(°)
O21- H21- O22^1	2.868(3)	0.82	2.60	101.04
O21- H21- O22^2	2.868(3)	0.82	2.10	156.69

Symmetry codes: (i) -X+1, Y+1/2, -Z+1/2 (ii) -X+1, Y+1/2-1, -Z+1/2

4 Conclusions

Good quality prism shaped single crystal of 1, 1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane was developed from methanol solution at 30°C.Crystal structure was determined by X-ray diffraction using Mo-Kα radiation (λ= 0.71075 Å). The diffraction data were collected over the θ range of 3.4-27.5°.The compound crystallized into monoclinic crystal lattice having space group $P2_1/c$ with unit cell parameters: a = 15.023(2) Å, b = 9.924(2) Å, c = 11.620(2) Å, α = γ = 90^0, β = 112.41(1), V = 1601.5(5) Å^3 and Z = 4. Atomic coordinates, bong lengths, bond angles, torsion angles and geometry of intermolecular interactions are also determined.

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