

X-ray structure determination and analysis of hydrogen interactions in 3,3'-dimethoxybiphenyl

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Abstract. The crystal structure of 3,3'-dimethoxybiphenyl has been determined by X-ray diffraction methods with an aim of describing the hydrogen interaction in biphenyl derivatives. The title compound crystallizes in monoclinic space group $P2_1/c$ with unit cell dimensions, $a = 7.706(1)$, $b = 11.745(2)$, $c = 12.721(2)$ Å, $\beta = 92.31(1)^\circ$, $Z = 4$ and its structure has been refined up to the reliability index of 3.8%. The average torsion angle about the inter-ring C–C bond is 37.5° . The O1 and O1' atoms of the methoxy group are deviated by 0.046(1) Å and 0.234(1) Å from the mean planes of respective rings. The crystal cohesion is pronounced due to three-intermolecular C–H...O hydrogen bonds.

Keywords. Structure analysis; crystal data; packing interactions; symmetry code.

1. Introduction

Biphenyl and its derivatives had been a subject of immense interest to researchers in various fields over the years and the earliest mention of biphenyl investigations date back to 1929 when its molecular configuration in the solid state was first established by the observation that the crystals are monoclinic with 2 molecules in the unit cell of space group $P2_1/a$ (Hengsteberg and Mark 1929; Clark and Pickett 1930, 1931; Dhar 1932). Since then the structure of biphenyl has been investigated by X-ray crystallographic, gas-phase electron diffraction and spectroscopic techniques and it was observed that phenyl rings are coplanar in the solid state (Robertson 1961; Trotter 1961; Hargreaves and Rizvi 1962) unlike the gas phase where it shows a dihedral twist of 42° (Bastianssen and Traetterberg 1962).

During the past few years, a vast amount of data on substituted biphenyl and its derivatives have appeared in the literature (Cailleau *et al* 1979; Brock 1980; Sutherland and Rawas 1983; Brock and Haller 1984a,b; Sutherland *et al* 1985; Brock and Morelan 1986; Sutherland and Ali-Adib 1986; Brock and Minton 1989; Sekine *et al* 1994) and these systems have also been extensively studied because of differences found in the inter ring torsion angle, ϕ (Hargreaves and Rizvi 1962; Charbonneau and Delugeard 1976, 1977; Brock and Minton 1989; Reboul *et al* 1993; Pilati *et al* 2001). There appears to be no well documented study which could lay emphasis on single crystal growth, X-ray structure determination and analysis of packing interactions in this class of materials. As

a part of our ongoing work on the single crystal growth of biphenyl derivatives and their structure analysis (Rajnikant *et al* 1995; Rajnikant 2001), the crystal structure of 3,3'-dimethoxy biphenyl is presented.

2. Experimental

The title compound was obtained in powder form from Aldrich Chemical Company and its initial crystallization was tried with a variety of organic solvent systems but the final crystallization was achieved from acetone and *n*-hexane as white transparent rectangular plates. However, the best grown single crystals were obtained from acetone and the three-dimensional intensity data of a transparent plate-like single crystal ($0.3 \times 0.1 \times 0.1$ mm) were collected on an Enraf-Nonius CAD-4 diffractometer using MoK α radiation ($\lambda = 0.71073$ Å). The title compound crystallized in monoclinic space group $P2_1/c$ with unit cell dimensions, $a = 7.706(1)$, $b = 11.745(2)$, $c = 12.721(2)$ Å, $\beta = 92.31(1)^\circ$ and the number of atoms per unit cell (Z) was 4. The calculated density was 1.237 Mg/m³ and volume of the unit cell was $1150.4(2)$ Å³, respectively. $w/2\theta$ scan mode was employed for data collection with θ ranging from 2.36 – 24.97° . A total of 1690 reflections were measured out of which 1532 were found unique ($0 \leq h \leq 5$, $0 \leq k \leq 13$, $-15 \leq l \leq 15$) and 1532 as observed [$F_0 > 4\sigma(F_0)$]. The reflection data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied.

The structure was determined by direct methods using SHELXS97 program (Sheldrick 1997a). All non-hydrogen atoms of the molecule were located from the E-map. Full-matrix least-squares refinement of the structure was carried out by using SHELXL97 program (Sheldrick 1997b).

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The positional and thermal parameters of non-hydrogen atoms were refined isotropically with residual index, $R = 0.108$. Further refinement with anisotropic thermal parameters and fixing of hydrogen atoms stereochemically resulted into a final value of the reliability index, $R = 0.038$, with weighted $R(F^2) = 0.093$. The maximum and minimum values for the residual electron density are 0.132 and -0.124 e\AA^{-3} , respectively. The goodness-of-fit on F^2 is 1.023 and the value of $F(000)$ is 256 . Atomic scattering factors have been taken from International tables for Crystallography (1992, Vol. C, tables 4.2.6.8 and 6.1.1.4). The final atomic positions and equivalent isotropic displacement parameters for all the non-hydrogen atoms are listed in table 1.

A general view of the molecule drawn at 50% probability level with atomic numbering scheme is presented in figure 1 (Farrugia 1997). The geometrical calculations were performed by using the PARST program (Nardelli 1995).

3. Results and discussion

The bond distances and bond angles are presented in table 2 and their values were found in good agreement with some analogous structures (Abboud *et al* 1990; Reboul *et al* 1993; Sekine *et al* 1994; Rajnikant *et al* 1995; Nieger *et al* 1998; Kitamura *et al* 2000; Pilati *et al* 2001).

Both the phenyl rings i.e. ring with atoms C1–C6 and ring consisting of atoms C1'–C6', adopt planar conformations with average value of torsion angles $0.7(2)$ and $1.3(2)^\circ$, respectively. The O1 and O1' atoms of the methoxy groups located at positions C3 and C3' are deviated by $0.046(1) \text{ \AA}$ and $0.234(1) \text{ \AA}$ from the mean plane of their respective rings. In the gas phase the average torsion angle about the central C–C bond is $44(1)^\circ$ (Almenningen

et al 1985) while it is at least 10° lower in solution than in the gas phase (Eaton and Steele 1973). This result suggests that the torsion angle may be especially sensitive to intermolecular interactions (Brock and Minton 1989). The value of torsion angle along C1–C1' in the present case is 37.5° . The dihedral angle between the planes of two phenyl rings is $38.1(2)^\circ$ and it is quite close to the value of 42° (Brock 1980).

In the monoclinic space group $P2_1/c$, the molecules of 3,3'-dimethoxy biphenyl are linked by intermolecular C–H...O hydrogen bonds. In intermolecular interactions, the hydrogen donor atoms are C6, C6' and C7' while O1' is the acceptor atom. The C6 (biphenyl)–H and C6' (biphenyl)–H bonds in the molecule form two hydrogen bonds (table 3) with the O1' (methoxy) atom of the molecule. The trifurcated acceptor O1' is linked by three intermolecular atoms C6, C6' and C7' at symmetry related positions $(x, -y - 1/2, z + 1/2)$, $(-x + 1, -y, -z + 1)$ and

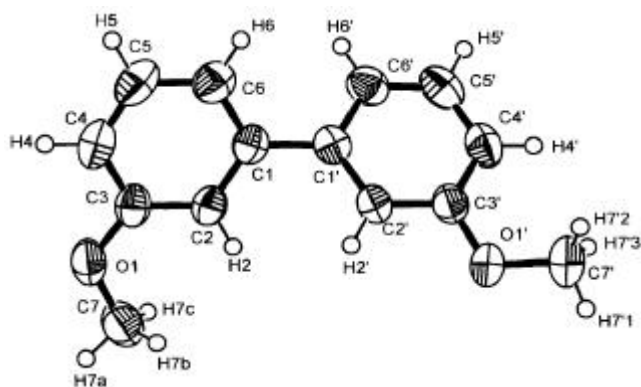


Figure 1. General view of the molecule with atomic numbering scheme.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of non-hydrogen atoms.

Atom	X	Y	Z	* U_{eq}
O1	0.6792(2)	0.1742(1)	0.4741(1)	0.069(1)
C1	0.7121(3)	-0.0617(2)	0.6658(2)	0.047(1)
C2	0.7255(3)	-0.0026(2)	0.5714(2)	0.048(1)
C3	0.6671(3)	0.1091(2)	0.5623(2)	0.052(1)
C4	0.5930(3)	0.1616(2)	0.6466(2)	0.063(1)
C5	0.5802(3)	0.1038(2)	0.7396(2)	0.068(1)
C6	0.6400(3)	-0.0069(2)	0.7504(2)	0.060(1)
C7	0.7605(4)	0.1261(2)	0.3862(2)	0.075(1)
O1'	0.7675(2)	-0.4376(1)	0.5166(1)	0.076(1)
C1'	0.7741(3)	-0.1816(2)	0.6754(1)	0.047(1)
C2'	0.7508(3)	-0.2575(2)	0.5927(1)	0.049(1)
C3'	0.8049(3)	-0.3697(2)	0.6023(2)	0.054(1)
C4'	0.8884(3)	-0.4068(2)	0.6939(2)	0.062(1)
C5'	0.9126(3)	-0.3313(2)	0.7763(2)	0.066(1)
C6'	0.8550(3)	-0.2208(2)	0.7689(2)	0.060(1)
C7'	0.7718(4)	-0.5581(2)	0.5304(2)	0.089(1)

$$*U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

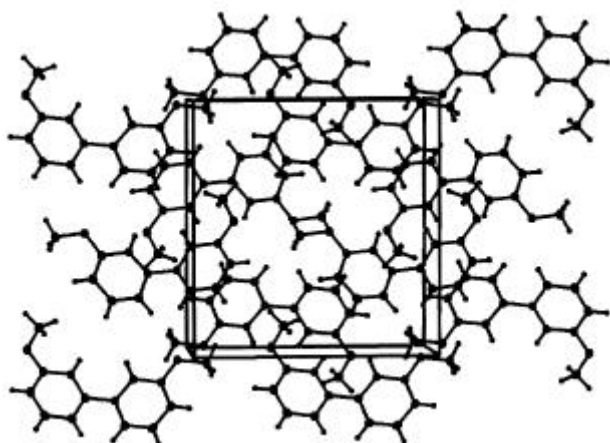
Table 2. Bond lengths [\AA] and angles [$^\circ$] for 3,3'-dimethoxy biphenyl.

O1–C3	1.364(2)	O1–C7	1.420(3)
C3–C4	1.381(3)	C3–C2	1.390(3)
C2–C1	1.394(3)	C1–C6	1.388(3)
C1–C1'	1.491(3)	C6–C5	1.385(3)
C5–C4	1.371(3)	O1'–C3'	1.373(2)
O1'–C7'	1.426(2)	C3'–C4'	1.378(3)
C3'–C2'	1.386(3)	C2'–C1'	1.385(3)
C1'–C6'	1.398(3)	C6'–C5'	1.374(3)
C5'–C4'	1.379(3)		
C3–O1–C7	118.1(2)	O1–C3–C4	115.6(2)
O1–C3–C2	124.4(2)	C4–C3–C2	119.9(2)
C3–C2–C1	120.5(2)	C6–C1–C2	118.9(2)
C6–C1–C1'	120.7(2)	C2–C1–C1'	120.4(2)
C5–C6–C1	120.0(2)	C4–C5–C6	120.9(2)
C5–C4–C3	119.8(2)	C3'–O1'–C7'	118.4(2)
O1'–C3'–C1'	124.3(2)	O1'–C3'–C2'	115.5(2)
C4'–C3'–C2'	120.2(2)	C1'–C2'–C3'	121.1(2)
C2'–C1'–C6'	118.3(2)	C2'–C1'–C1	121.0(2)
C6'–C1'–C1	120.7(2)	C5'–C6'–C1'	120.0(2)
C6'–C5'–C4'	121.5(2)	C3'–C4'–C5'	118.9(2)

Table 3. Geometry of intermolecular interactions (e.s.d.'s are given in parentheses).

X-H...A	$d(\text{H}\dots\text{A})(\text{\AA})$	$D(\text{X}\dots\text{A})(\text{\AA})$	$q(\text{X}-\text{H}\dots\text{A})(^\circ)$
C6-H6...O1 ⁽ⁱ⁾	2.756(1)	3.548(2)	144.9(2)
C6'-H6'...O1 ⁽ⁱⁱ⁾	2.881(2)	3.744(1)	154.8(1)
C7'-H7'3...O1 ⁽ⁱⁱⁱ⁾	2.865(3)	3.625(2)	136.8(2)

Symmetry code: (i) $x, -y - 1/2, +z + 1/2$, (ii) $-x + 1, -y, -z + 1$ and (iii) $-x + 2, -y - 1, -z + 1$

**Figure 2.** Unit cell packing view of the molecules.

($-x + 2, -y - 1, -z + 1$), respectively. Based on the pioneering work of Desiraju and Steiner (1999) on the weak hydrogen bond in structural chemistry and biology, hydrogen bonds for organic molecular assemblies have been classified as very strong, strong and weak. The distinction between the strength of hydrogen bonds has been made on the basis of distance [$D(\text{X}\dots\text{A}), d(\text{H}\dots\text{A})$] and angle [$q(\text{X}-\text{H}\dots\text{A})$] cut-off criteria. In the present case all the three hydrogen bonds are weak and results are in consonance with the finding of Desiraju and Steiner (1999). Geometrical details of hydrogen bonds are given in table 3.

The packing diagram drawn to emphasize the structural features (figure 2) illustrates that the molecular packing is typical of monoclinic system with molecules lying in reversed orientations. The overlap of methoxy groups of the molecules results into intermolecular interactions of the type C-H...O which are described in table 3. The molecules appear to be staggering along the bc -plane giving rise to a broad view of the molecules linked together by C-H...O hydrogen bonds.

4. Conclusions

- (I) X-ray diffraction quality single crystals of 3,3'-dimethoxybiphenyl have been obtained from acetone.
- (II) The structure of 3,3'-dimethoxybiphenyl has been determined in the monoclinic space group $P2_1/c$.

(III) The inter-ring torsion angle, γ , along C1-C1' and the dihedral angle, t , between planes of the two rings, by and large, have values close to the reported value of 44.1° and 42° , respectively.

(IV) Packing interactions have been analysed on the basis of equivalent positions as occupied by the symmetry related molecules.

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References

- Abboud K A, Minton M A, Whitesell J K and Davis R E 1990 *Acta Crystallogr.* **C46** 1553
- Almenningen A, Bastiansen O, Fernholt L, Cyvin B N, Cyvin S J and Samdal S J 1985 *J. Mol. Struct.* **128** 59
- Bastiansen O and Traetterberg M 1962 *Tetrahedron* **17** 147
- Brock C P 1980 *Acta Crystallogr.* **B36** 968
- Brock C P and Haller K L 1984a *J. Phys. Chem.* **88** 3570
- Brock C P and Haller K L 1984b *Acta Crystallogr.* **C40** 1387
- Brock C P and Morelan G L 1986 *J. Phys. Chem.* **90** 5631
- Brock C P and Minton R P 1989 *J. Am. Chem. Soc.* **111** 4586
- Cailleau H, Baudour J L and Zeyen C M E 1979 *Acta Crystallogr.* **B35** 426
- Charbonneau G P and Delugeard Y 1976 *Acta Crystallogr.* **B32** 1420
- Charbonneau G P and Delugeard Y 1977 *Acta Crystallogr.* **B33** 1586
- Clark G L and Picket L W 1930 *Proc. Nat. Acad. Sci. USA* **16** 20
- Clark G L and Picket L W 1931 *J. Am. Chem. Soc.* **53** 167
- Dhar J 1932 *Indian J. Phys.* **7** 43
- Desiraju G R and Steiner T 1999 *The weak hydrogen bond in structural chemistry and biology*, IUCr (Oxford: Oxford University Press) p. 48
- Eaton V J and Steele D 1973 *J. Chem. Soc. Faraday Trans.* **2** 1601
- Farrugia L J 1997 *J. Appl. Cryst.* **30** 565
- Hargreaves A and Rizvi S H 1962 *Acta Crystallogr.* **15** 365
- Hengsteberg J and Mark H 1929 *Z. Krist.* **70** 285
- Kitamura C, Yamamoto S, Ouchi M and Yoneda A 2000 *J. Chem. Res. (S)* **IX** 46
- Nardelli M 1995 *J. Appl. Cryst.* **28** 659
- Nieger M, Hupfer H and Bolte M 1998 *Acta Crystallogr.* **C54** 656
- Pilati T, Metrangolo P and Giuseppe R 2001 *Acta Crystallogr.* **C57** 113
- Rajnikant, Watkin David and Tranter George 1995 *Acta Crystallogr.* **C51** 1452, 2071, 2161, 2637
- Rajnikant 2001 *Mol. Mater.* **14** 165
- Reboul J P, Pepe G, Siri D, Oddon Y, Caranoni C, Rahal H, Soyfer J C and Barbe J 1993 *Acta Crystallogr.* **C49** 735
- Robertson G B 1961 *Nature (London)* **191** 593

- Sekine A, Ohashi Y Y, Oshimura K, Yagi M and Higuchi J 1994 *Acta Crystallogr.* **C50** 1101
- Sheldrick G M 1997a *SHELXS97 program for the solution of crystal structures* (Germany: University of Gottingen)
- Sheldrick G M 1997b *SHELXS97 program for the refinement of crystal structures* (Germany: University of Gottingen)
- Sutherland H H and Rawas A 1983 *Acta Crystallogr.* **C39** 1568
- Sutherland H H and Ali-Adib Z 1986 *Acta Crystallogr.* **C42** 432
- Sutherland H H, Rawas A and Mottram M J 1985 *Acta Crystallogr.* **C41** 926
- Trotter J 1961 *Acta Crystallogr.* **C14** 1135