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CRYSTAL STRUCTURE ANALYSIS OF TWO DIFFERENT CHALCONES: EFFECT OF METHOXY GROUP SUBSTITUTION ON DIHEDRAL ANGLE

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ABSTRACT

Two different chalcones *viz.* **1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (chalcone-I)** and **1,3-bis(4-methoxyphenyl)prop-2-en-1-one (chalcone-II)** were synthesized and analyzed using single crystal X-ray crystallography. One chalcone has a methoxy substituent on one of the benzene ring, whereas the other has two methoxy substituents symmetrically situated on both the benzene rings. The chains are linked into a two-dimensional sheet via weak hydrogen bonds. Two benzene rings in chalcone-I make a dihedral angle of 32.93° whereas the dihedral angle between benzene rings in chalcone-II is 4.29°.

Key words: Chalcone, X-ray, crystal structure, dihedral angle.

INTRODUCTION

Chalcones are one of the important groups of natural products (Tomazela, 2000) which have wide pharmacological properties. Some chalcones possess anticancer (Wattenberg, 1994; Dinkova-Kostova, 1998), antimalarial (Ram, 2000) and anti-inflammatory (Ballesteros, 1995) activities. Chalcones also exhibit nonlinear optical (NLO) properties (Fichou, 1988; Uchida, 1998; Tam, 1989). Among several organic compounds having NLO properties, chalcone derivatives are well known for their excellent blue-light transmittance and good crystallizability. The NLO properties of chalcones are due to their typical structure with two planar rings connected through a conjugated double bond. Substitution on either of the benzene rings greatly

influences the non-centrosymmetric crystal packing. X-ray crystallographic study of chalcones have been the subject of interest for last 80 years. Many chalcone shows polymorphic behaviour also (Barsky, 2008). There are several reports on the structure elucidation of various chalcones. For example, Zhengdong (Zhengdong, 1992) reported the structure of 4'-methoxychalcone. Qiu reported the structure of two different chalcones namely (E)-3-(4-Hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one and (*E*)-1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one (Qiu, 2006; Qiu, 2006). Structure of a biphenyl substituted chalcone namely (2*E*)-3-(Biphenyl-4-yl)-1-(4-methoxyphenyl)prop-2-en-1-one has been reported (Fischer; 2007). Lavy studied the crystal structures of 1:2 inclusion compound consist of host molecule 2,5-diphenylhydroquinone and the guest molecules 1-(4-methoxyphenyl)- 3-phenyl-2-propen-1-one in order to study the ability of guest molecules in inclusion compounds to undergo photoreaction (Lavy, 2004). A study on the structural as well as spectroscopic characteristics of $2^{/}$-diethylboryl-$4^{//}$-dimethylaminochalcone and $2^{/}$-ethylenedioxyboryl-$4^{//}$-dimethylaminochalcone with chloro- {2- [(4-dimethylaminostyryl) carbonyl] phenyl} (4-methylphenyl)] bismuthane and $4^{//}$-dimethylaminochalcone was undertaken by Murafuji to understand how formation of an intramolecular coordinate bond affects the molecular structure (Murafuji 1999). We have also reported a study on the structural as well as spectroscopic aspects of $2^{/}$, $4^{/}$-dichlorochalcone (Phukan 2006; Phukan, 2008). Peng reported the crystal structure of 1-(4-Aminophenyl)-3-[2-(trifluoromethyl)phenyl] prop-2-en-1-one (Peng, 2010). The structure of flouring substituted chalcone namely (E)-1-(3,5-difluorophenyl)-3-(2,4- dimethoxyphenyl)prop-2-en-1-one has been reported by Huang (Huang 2010). Cai reported the structure of another methoxy stbstituted chalcone, namely, (E)-1-(4-Methoxyphenyl)-3-(2,4,6- trimethoxyphenyl)prop-2-en-1-one has been reported (Cai, 2011).

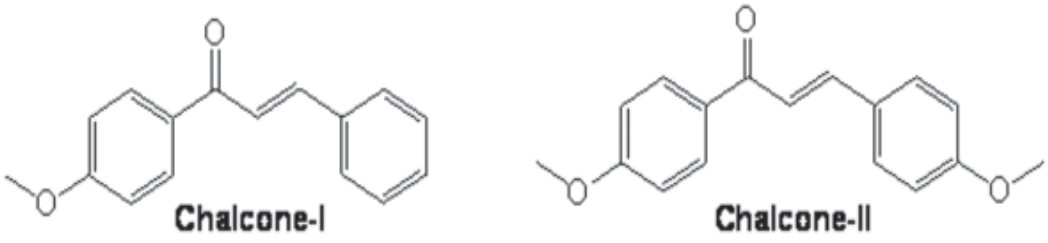

Fig. 1. Chemical structure of the two chalcones

We have prepared two different chalcones namely, 1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (Chalcone-I) and 1,3-bis(4-methoxyphenyl)prop-2-en-1-one **(**Chalcone-II**) (Figure 1)** and reporting herewith a comparative structural analysis of the compounds using single crystal X-ray crystallography.

MATERIALS AND METHODS

(A) Synthesis of compounds

The title compounds were synthesized by mixing benzaldehyde or 4-methoxybenzaldehyde (0.05 mol), with 4-methoxy acetophenone (0.05 mol) and sodium hydroxide (0.1 g, 0.0025 mol) in 50 mL methanol. The reaction mixture was stirred at 298 K for 24 hours. The solution was cooled and the solid precipitated out was collected. A second crop was obtained by evaporating part of the solvent. Finally, the product was recrystallized from methanol to give colourless needle like crystals.

(B) X-ray crystallography

The reflection data for both chalcones were collected at room temperature using a Bruker SMART CCD diffractometer. The SMART programme (Bruker Analytical X-ray Systems, 1994**)** was used for data acquisition and the collected data were integrated using SAINT (Bruker Analytical X-ray Systems, 1994-1996**)** software. Empirical absorption corrections were applied using the programme SADABS (Blessing, 1995) Both structures were solved by direct method (SHELEX-97) and refined by full matrix least squares method using the programme SHELEX-97 (Sheldrick, 1997). Both programmes were used in Windows XP platform by utilizing the WinGX suite of programmes (Farrugia, 1999) that also facilitated the use of PLUTON (Spek, 1990, 2009) and ORTEP-III (Burneo , 1996) for drawing the structural diagrams. All the H atoms in both structures were found in different Fourier maps and were refined with isotopic atomic displacement parameters. The centrosymmetric settings of the space groups were ascertained on the basis of successful solution and refinement of the structures. Details of data collection and refinement for chalcone-I and chalcone-II are presented in Table 1. Position coordinates and isotopic thermal parameters for all atoms in both structures are listed in Table 2 and Table 3.

RESULTS AND DISCUSSION

Two different chalcones were prepared for this study. Both the chalcones contain —OCH_3 group in the benzene ring. We have chosen these chalcones to impart more interactions due to the presence of polar —OCH_3 group. Chalcone-I has only one —OCH_3 group in the 4-position in the one of the two benzene rings of chalcone while the other has two —OCH_3 group in the 4-positions of both the benzene rings. Chalcone-I bearing one –OCH_3 group has an angular structure whereas the other chalcone has almost planner orientation.

Table 1. Crystal data and structure refinement for chalcones I and II

Crystal data	**Chalcone**	
	$[C_{16}H_{14}O_2]$ I	$[C_{17}H_{16}O_3]$ II
Formula weight	238.27	268.30
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.5411(8) Å	a = 5.2976(2) Å
	b = 10.9259(13) Å	b = 8.6573(4) Å
	c = 30.543(4) Å	c = 30.7062(14) Å
	α = 90°	= 90°
	= 90°	= 90°
	= 90°	= 90°
Volume	2516.5(5) $Å^3$	1408.28(11) $Å^3$
Radiation	Mo-K	Mo-K
Wavelength	0.71073 Å	0.71073 Å
Z	8	4
Density (calculated)	1.258 Mg/m^3	1.265 Mg/m^3.
Absorption coefficient	0.082 mm^{-1}	0.086 mm^{-1}
F(000)	1008	568
Crystal size	0.37 × 0.25 × 0.17 mm^3	0.33 × 0.21 × 0.12 mm^3
Theta range for data collection	3.80 to 28.36°	2.44 to 28.35°
Index ranges	-10 h 10, -14 k 12,	-7 h 7, -11 k<=9,
	-36 l 40	-35 l 40
Reflections collected	19300	17961
Independent reflections	3097 [R(int) = 0.0831]	3506 [R(int) = 0.0385]
Completeness to theta=28.36°	98.4 %	99.7 %

(Cont...)

Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3097 / 0 / 165	3506 / 0 / 184
Goodness-of-fit on F^2	1.004	0.974
Final R	R1 = 0.0499,	
wR2 = 0.0914	R1 = 0.0498,	
wR2 = 0.0852		
R indices (all data)	R1 = 0.1071,	
wR2 = 0.1138	R1 = 0.0943,	
wR2 = 0.0994		
Extinction coefficient	0.0072(9)	0.0082(13)
max	0.134 e.Å^{-3}	0.107 e.Å^{-3}
min	-0.131 e.Å^{-3}	-0.114 e.Å^{-3}
( )max	0.000	0.001

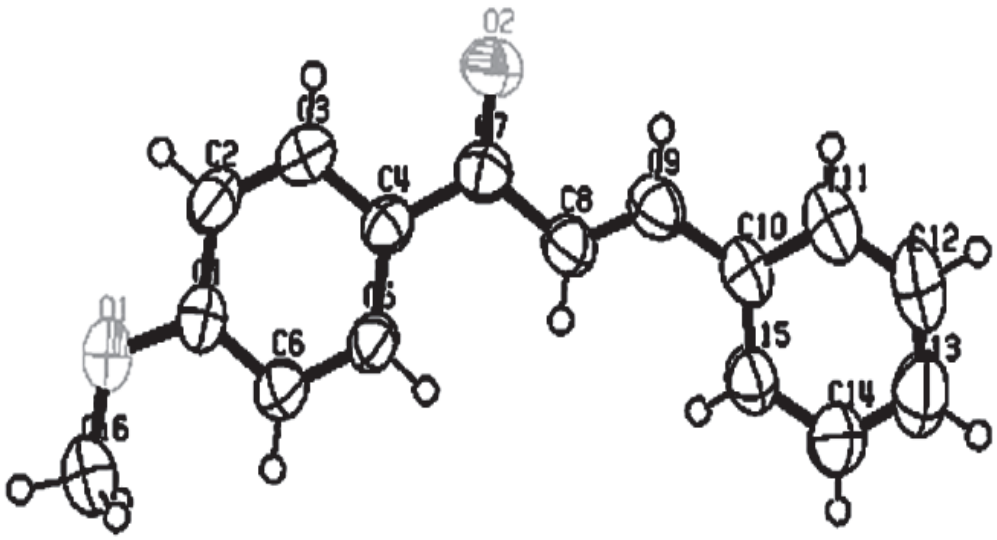

Fig. 1. ORTEP view of chalcone-I with 50% probability level

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Chalcone-I.

	x	y	z	U(eq)
O(1)	998(2)	5996(1)	3698(1)	72(1)
O(2)	1998(2)	4214(1)	1755(1)	72(1)
C(5)	745(2)	6591(1)	2520(1)	51(1)
C(4)	1375(2)	5493(1)	2355(1)	47(1)
C(7)	1526(2)	5231(2)	1881(1)	53(1)
C(6)	596(2)	6802(2)	2965(1)	54(1)
C(3)	1841(2)	4590(2)	2656(1)	58(1)
C(10)	112(2)	6776(2)	808(1)	57(1)
C(2)	1701(3)	4787(2)	3097(1)	64(1)
C(8)	1063(2)	6189(2)	1562(1)	57(1)
C(1)	1084(2)	5895(2)	3254(1)	54(1)
C(9)	690(2)	5933(2)	1152(1)	60(1)
C(11)	-611(3)	6304(2)	424(1)	72(1)
C(15)	192(3)	8037(2)	854(1)	64(1)
C(12)	-1254(3)	7070(3)	103(1)	84(1)
C(16)	485(3)	7143(2)	3879(1)	74(1)
C(14)	-467(3)	8792(2)	531(1)	79(1)
C(13)	-1191(3)	8309(3)	156(1)	85(1)

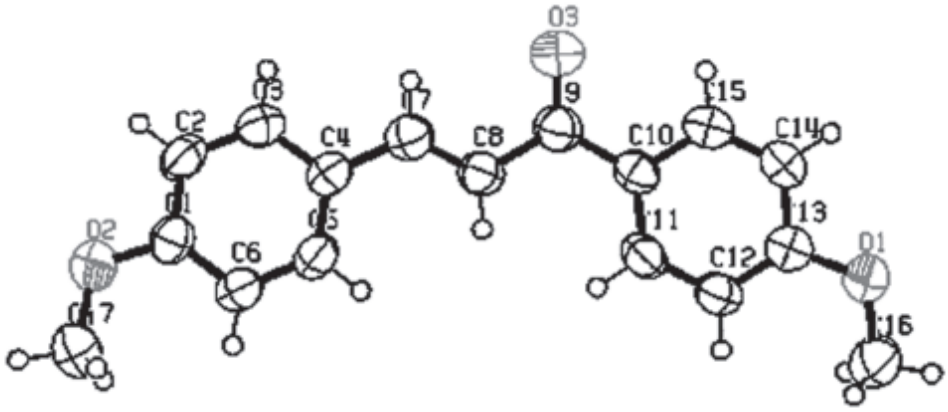

Fig. 2. ORTEP view of chalcone-II with 50% probability level

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) Chalcone-II.

	x	y	z	U(eq)
O(1)	10107(3)	10521(2)	10272(1)	70(1)
O(2)	4052(3)	7543(2)	6359(1)	76(1)
C(10)	10613(3)	8287(2)	9078(1)	53(1)
C(8)	9223(4)	7675(2)	8299(1)	60(1)
C(4)	8061(3)	7190(2)	7520(1)	55(1)
C(13)	10153(4)	9838(2)	9873(1)	54(1)
C(1)	5277(4)	7483(2)	6748(1)	58(1)
C(9)	10975(4)	7441(2)	8663(1)	65(1)
C(7)	9579(4)	7026(2)	7913(1)	62(1)
C(11)	8695(4)	9350(2)	9150(1)	62(1)
C(14)	12087(4)	8789(2)	9806(1)	60(1)
C(15)	12319(4)	8030(2)	9417(1)	59(1)
C(5)	6092(4)	8237(2)	7482(1)	66(1)
C(3)	8578(4)	6296(2)	7157(1)	67(1)
C(12)	8452(4)	10122(2)	9542(1)	64(1)
C(6)	4730(4)	8396(3)	7104(1)	68(1)
C(2)	7202(5)	6421(2)	6779(1)	69(1)
C(17)	2332(4)	8789(3)	6289(1)	80(1)
C(16)	7967(4)	11424(3)	10384(1)	88(1)
O(3)	12760(3)	6543(2)	8625(1)	110(1)

The torsional angle of chalcone-**I** is 17.94° for O(2)—C(7)—C(8)—C(9) of the C_2H_2CO group, whereas for chalcone-**II** the torsional angle for the same set of atoms was found to be 4.63. The H atoms are *trans* in the —C=C— group. C=C bond distance for 1 is 1.313Å whereas the bond length for the other is slightly longer with a value of 1.327 Å. Two benzene rings in chalcone-**I** make a dihedral angle of 32.93°. This is because of the methoxy substituent present in 4 -position of one of the benzene rings. However, a significant enhancement of coplanarity was observed when both the benzene rings were substituted in 4-position (chalcone-**II**). In this case, the dihedral angle between benzene rings is 4.29°.

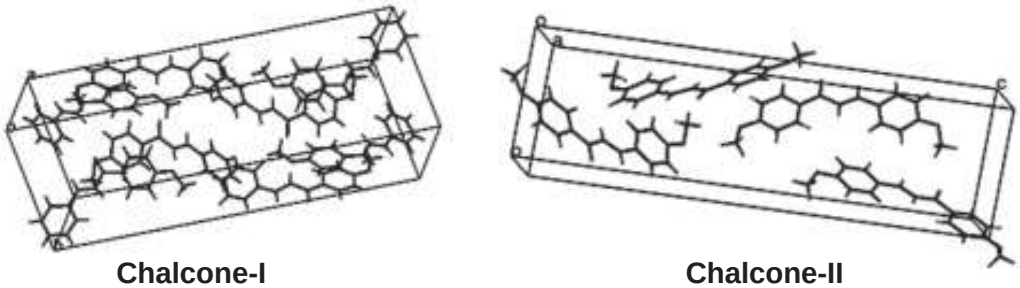

Fig. 3. Packing of chalcone I & II in the unit cell

In case of chalcone-I, the oxygen atom of the methoxy group is not taking part in crystal packing. Interestingly, out of two methoxy substituents in case of chalcone-II, only O2 establishes short contacts through the oxygen atom (Figure 4b). Hence, O2—C1 bond length (1.361Å) is slightly longer than O1—C13 bond length (1.359Å) However O2—C17 bond (1.428Å) is slightly longer than O1—C16 bond (1.420Å).

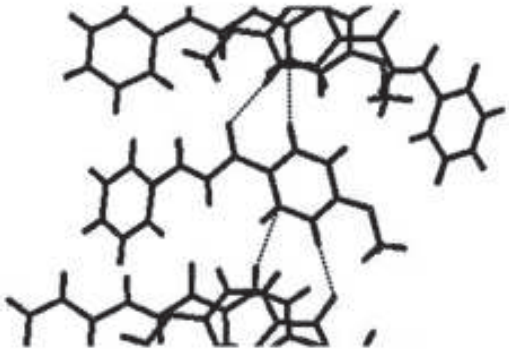

Fig. 4a. Short contacts of chalcone-I

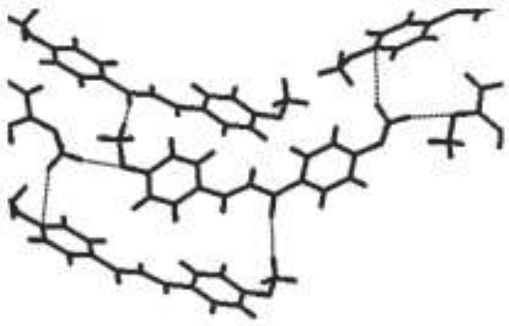

Fig. 4b. Short contacts of chalcone-II

CONCLUSION

Single crystal X-ray crystallography of two different methoxy-substituted chalcones were performed to examine the impact of methoxy-substituents on structural differences. The dihedral angle between the rings in each case is different from the other. When both the benzene rings of a chalcone are symmetrically substituted by the same functional group, the compound orients itself in planner geometry, whereas compound having mono substitution have a bent structure having a higher dihedral angle between the rings.

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