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X-ray structure analysis of 1-(4-bromophenyl)-3-(4-chlorophenyl)-prop-2-en-1-one

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The title compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 15.6239(15)$ Å, $b = 14.0537(14)$ Å, $c = 5.8396(5)$ Å, $\beta = 92.666(3)°$, $V = 1280.8$ (2) Å^3, and $Z = 4$. The final reliability index is 0.0538 for 2921 observed reflections. Two phenyl rings of the title molecule are not coplanar, with a dihedral angle of 46.3(0)°. The molecular planarity of this substituted chalcone is strongly affected by the 4′-bromo group. The crystal cohesion is accentuated by $\pi \cdots \pi$, C–H···Br interactions and R_3^1 (11) hydrogen bond.

KEY WORDS: Chalcone; crystal structure; organic compound; hydrogen bond.

Introduction

Chalcones are renowned for their potent and diverse photochemical activities.[1] With appropriate substitutents, they are also a class of nonlinear optical materials.[2] As a part of our on-going work on the synthesis and structure elucidation of substituted chalcones and in view of their nonlinear optical properties, the crystal structure of 4′-bromo-4-chlorochalcone has been determined. In this paper we report the X-ray structure of the title compound and possible role of hydrogen bonding.

Experimental

The synthesis of the title compound was carried out according to the procedure of Migrdichian.[3] An aqueous solution of sodium hydroxide (10%, 10 mL) was added to a solution of 4-bromoacetophenone (0.02 mol) and 4-chlorobenzaldehyde (0.02 mol) in 95% ethanol (30 mL). The reaction mixture was stirred at room temperature for 4 hours and yielded a light-white solid, and the mixture was then neutralized with hydrochloric acid (10%) and water. The product was recrystallized three times from dry acetone. After seven days, ivory-white crystals were obtained by slow evaporation from dry acetone at 293 K. The chemical structure assigned to the title compound as shown in Fig. 1. Element analysis

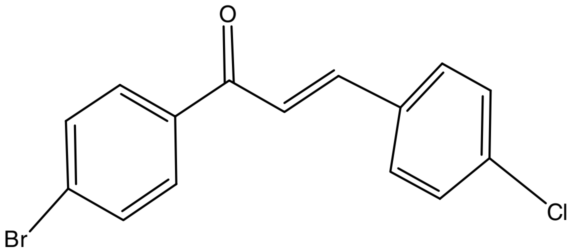

Fig. 1. Chemical structure of the title compound.

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Table 1. Crystal Data and Structure Refinement Details

Empirical formula	$C_{15}H_{10}Br\,ClO$
CCDC reference no.	277112
Formula (wt.)	321.59
Temperature (K)	293.1(1)
Wavelength (Å)	0.7107
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	15.6239(15)
b (Å)	14.0537(14)
c (Å)	5.8396(5)
β (°)	92.666(3)
Volume (Å^3)	1280.8(2)
Z, Calculated density (kg/m^3)	4, 1.668
F000	640
Crystal dimensions (mm)	0.39 × 0.30 × 0.10
θ Range for data collection (°)	3.18–27.48
Limiting indices	$-20\text{-} \leq h \leq 20$, $-18 \leq k \leq 18$, $-7 \leq l \leq 6$
Reflections collected/unique	2921/2582
Data/restraints/parameters	2921/0/164
Goodness-of-fit on F^2	1.180
R indices (all data)	0.0538
Final R indices [$I > 2\sigma(I)$]	0.0460, $wR2 = 0.1035$

(Perkin-Elmer 240C elemental analyzer): Calcd. for $C_{15}H_{10}BrClO$ (%), C 55.99, H 3.11. Found: C 56.23, H 3.22. IR (FT-IR Spectrometer with KBr pellets, cm^{-1}): 1657 (–C=O), 1604 (–CH=CH–), 1563 (Ph), 816 (Ar–H).^{1}H NMR (Bruker AV-400 NMR Spectrometer, $CDCl_3$, 399.97 MHZ, ambient temperature, p.p.m.): 7.40 (d, 2H, Ph), 7.45 (d, H, –CH=CH–), 7.58 (d, 2H, Ph), 7.65 (d, 2H, Ph), 7.77 (d, H, –CH=CH–), 7.89 (d, 2H, Ph).

A colorless thin plate crystal with dimensions 0.39 mm × 0.30 mm × 0.10 mm was selected for X-ray diffraction. Data were collected at -80 ± 1 °C with a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). A total of 14097 unique ($R_{\text{int}} = 0.033$) reflections were collected in the range of $6.4° < 2\theta < 55°$ with ω scans mode and used in the refinement. The structure was solved by direct methods[4] and expanded using Fourier techniques.[5] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically using the riding model. All calculations were performed using the Crystal Structure Analysis Package,[6,7] SHELTX-86 and SHELTX-93 programs.[8,9]

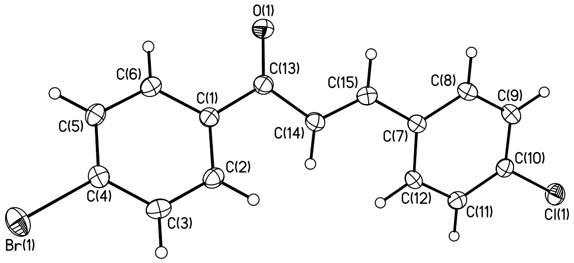

Fig. 2. General view of the molecule with thermal ellipsoids drawn at 30% probability level.

Table 2. The Dihedral Angles in this Study (°)

Compound	Substituents	A_{12}	A_{13}	A_{23}
BRCHAL[a]	4′-Br	50.0(0)	14.7(2)	36.0(3)
TARCIY	4-Br	48.6(1)	22.3(0)	26.5(0)
PUQSOJ	4′-Cl	48.2(1)	21.0(0)	27.6(3)
LEBGUU	4-Cl	14.4(2)	12.6(0)	9.8(1)
BZYACO		11.4(3)	4.2(1)	14.2(0)
Title compound	4′-Br, 4-Cl	46.3(0)	11.1(0)	35.2(0)

[a] Reference code in CSD (version 5.26, 2004; November).

Results and discussion

Precise crystal data and other structure refinement parameters of the title compound are presented in Table 1. General view of the molecule

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for Non-hydrogen Atoms

Br1–C4	1.885(3)	C7–C15	1.467(4)
Cl1–C10	1.732(3)	C13–C14	1.480(4)
O1–C13	1.229(4)	C14–C15	1.336(4)
C1–C13	1.485(4)		
C6–C1–C13	118.5(3)	O1–C13–C14	121.3(3)
C2–C1–C13	122.8(3)	O1–C13–C1	120.4(3)
C5–C4–Br1	119.7(2)	C14–C13–C1	118.3(3)
C3–C4–Br1	119.0(2)	C15–C14–C13	120.4(3)
C8–C7–C15	118.9(3)	C14–C15–C7	127.2(3)
C12–C7–C15	122.4(3)	C9–C10–Cl1	120.3(2)
C11–C10–Cl1	118.8(2)		
C2–C3–C4–Br1	176.4(2)	C15–C7–C8–C9	−175.6(3)
C15–C7–C12–C11	175.2(3)	C6–C1– C13–O1	20.7(4)
C6–C1–C13–C14	−158.6(3)	C2–C1–C13–C14	23.4(4)
O1–C13–C14–C15	16.4(4)	C1–C13–C14–C15	−164.3(3)
C13–C14–C15–C7	−174.3(3)	C8–C7–C15–C14	−174.9(3)

Table 4. Geometries of $\pi\cdots\pi$ Interaction (Å) (°)

	Dp^{a}	Dc^{b}	θ^{c}	Symmetry code
PL3-PL3	3.49	4.44	38.3	$-x$, $1-y$, $1-z$

^{a}Dp is the interplanar distance between two phenyl rings.
^{b}Dc is the distance between two centers of two phenyl rings.
$^{c}\theta$ is the angle of the Dp and Dc vectors.

with atomic labeling (thermal ellipsoids drawn at 40% probability) is shown in Fig. 2.

The molecule consisits of two phenyl rings and central part –CH=CH–C (=O)–. The average value of the bond distances [1.388(6) Å] and exocyclic bond angles [120.6(8)°] in the phenyl rings have normal values which agrees quite well with the values reported in the literature for some analogous structures.[10–14] The molecule as such is non-planar. Taking the C7–C12 phenyl ring as plane 1 (PL1), the C1–C6 phenyl ring as plane 2 (PL2) and the central C7–C15=C14–C13 as plane 3 (PL3), the dihedral angles between them, A_{12}, A_{13} and A_{23}, are 46.3, 11.1 and 35.2°, respectively, showing that the two phenyl rings are rotated in opposite directions with respect to the central part, plane 3. The C7–C15=C14–C13 torsion angle is -174.3 (3)°. The angle between the C=O bond and plane 3 is 13.9°.

Comparing our results with those of litertures (Table 2),[10–14] it can be seen that the planarity of such substituted chalcone molecule is strongly affected by bromo group. When 4- or 4′-position was substituted by a bromine atom, the angles between the planes of the two phenyl groups are nearly 50°. On the other hand, if mono-substituent in 4-position has a chloro group, the molecule is close to planar. This seems to mean that the bromo group has larger effect for molecular planarity than chloro group. Further geometric parameters are given in Table 3.

Table 5 Geometries of Hydrogen Bond (Å) (°)

D–H···A	D–H	H···A	D···A	< D–H···A	Sym. code
C2–H2···O1	0.95	2.814	3.615	142.5	x, y, $z-1$
C12–H12···O1	0.95	2.857	3.696	147.7	x, y, $z-1$
C14–H14···O1	0.95	2.789	3.702	161.4	x, y, $z-1$
C9–H9···Br1	0.95	3.140	3.940	142.4	$x-1$, y, z

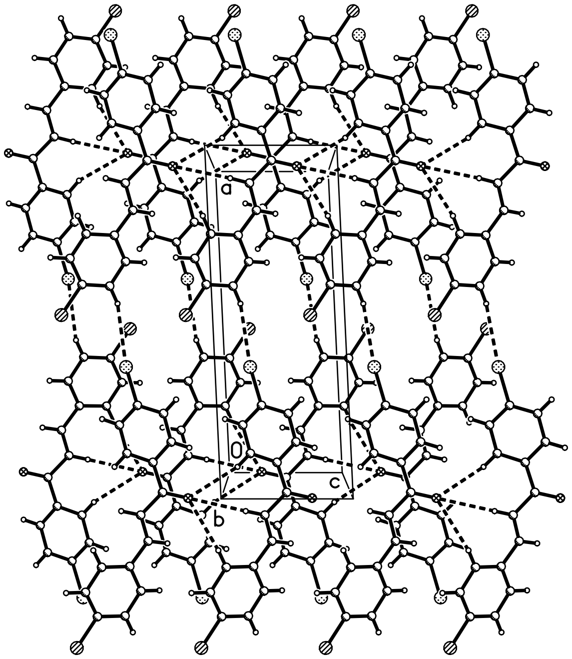

Fig. 3. Crystal packing diagram for the title compound, viewed down the *b* axis.

In the crystal structure of the title compound, molecules are paired through $\pi\cdots\pi$ interactions[15] (Table 4). The paired molecules interact via three C–H···O interactions[16] (Table 5) that form a ring with graph set notation R_3^1 (11),[17,18] then build hydrogen-bonded molecular chains along [001]. These chains interact further through C-H···Br[19] hydrogen bonds (Table 5) forming (0 10) molecular layers. In the third direction, [0 10], there are only weak ordinary van der Waals interactions (Fig. 3).

Supplementary material CCDC 277112 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request_cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336033.

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