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Synthesis and Crystal Structure Studies of Novel 4-Tosyloxychalcone Derivative

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4-Tosyloxychalcone derivative, $C_{23}H_{20}O_4S$, was synthesized and characterized by infrared and ^1H NMR spectral studies. Grown crystal was further characterized by single crystal X-ray diffraction studies. The compound crystallizes in monoclinic space group C2/c with unit cell parameters a = 33.431 (6) Å, b = 5.8451 (10) Å, c = 21.439 (4) Å, Z = 8, and V = 3848.2 (12) Å^3. The crystal packing is mainly stabilized by C—H... π interaction. There are no significant intermolecular interactions beyond van der Waals forces observed in the solid state structure of the compound.

Keywords Chalcones; characterization; crystal growth; single crystal studies

Introduction

Chalcones and their derivatives are reported to possess varied biological properties like antimicrobial, antiinflammatory, and anticancer properties[1, 2]. Recent review highlights the potential of such molecules for pharmacological applications[3]. These compounds also find use in material science especially in the area of nonlinear optics[4–6]. Organic compounds having strong donor and acceptor groups at the end of aromatic ring conjugated by the presence of enone function is responsible for nonlinear absorption. Synthetically, these compounds are prepared by Claisen–Schmidtt condensation, wherein one react an aldehyde with ketone in the presence of a base. Many such reactions can be carried out

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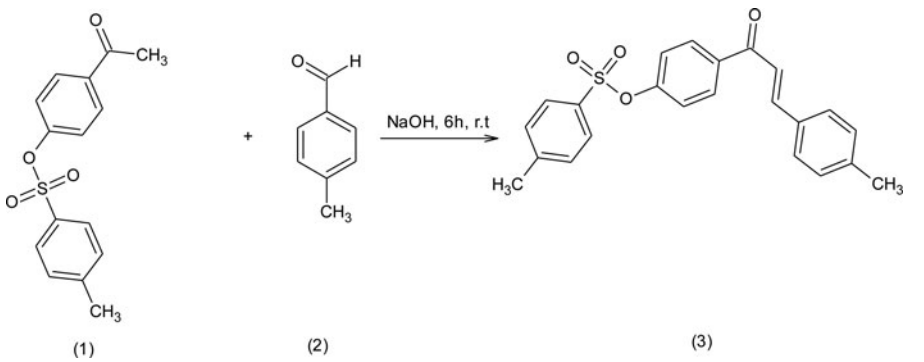
at room temperature and under aqueous ethanolic medium. The simplicity of synthetic method coupled with good yield and reasonable purity during synthesis prompted many researchers to study the crystal growth and optical properties of such compounds. Many chalcone derivatives are also easily crystallisable from cheap and common organic solvents like alcohol, acetone or ethyl acetate. These compounds also possess good thermal and dimensional stability at higher temperatures. We have reported crystal growth and optical property of many chalcone derivatives with varied substituents [7–12]. The objective of the present work is to synthesize the chalcone derivative having a tosyloxy substituent at para position of aromatic ring (Scheme 1), growth of single crystals and its characterization by IR, ^{1}H NMR, and single crystal X-ray diffraction studies. As molecule exhibited centrosymmetric space group, it was not evaluated for second harmonic generation ability but studied for its antimicrobial activities.



Scheme 1. Synthesis of 4-tosyloxychalcone (**3**).

Materials and Methods

The chemicals and solvents required in the synthesis were obtained from commercial sources and were used without further purification. Melting point of the compound was determined using open capillary method and is uncorrected. Thin layer chromatography was carried out using silica gel plates and ethyl acetate:hexane (1:4) solvent system. Infrared spectra were recorded using SHIMADZU-8400S FT-IR spectrometer in the wavenumber range 400–4000 cm^{-1} by KBr pellet technique. ^{1}H NMR spectra was recorded using Bruker 400MHz NMR spectrometer using DMSO-d6 as solvent.

Synthesis of 4-tosyloxychalcone

The required chalcone (3) was prepared by reacting 4-tosyloxyacetophenone (**1**)(10 mmole) and 4-methylbenzaldehyde (**2**) (10 mmole) in a round bottom flask using ethanol as solvent. The reaction was carried out at room temperature and with gradual addition of NaOH solution (Scheme 1). The progress of the reaction was monitored using thin layer chromatography. After continuous stirring for 4h, the reaction was complete. The product was collected by vacuum filtration and is further purified by crystallization from ethanol. A yellow, powdery product with a melting point of 118–20°C (73%) was obtained.

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Results and Discussion

Chemistry

The IR spectrum of compound (**3**) shows characteristic wavenumber at 1651 cm^{-1} due to the presence of C=O stretch of α, β-unsaturated ketone, confirming the formation of the product. The SO_2 group is observed at 1338 and 1173 cm^{-1}, respectively. This indicates that the tosyloxy group is stable under the reaction conditions. Other characteristic peaks were also observed in the spectrum.

The ^{1}H NMR spectrum of 4-tosyloychalcone recorded using DMSO-d6 as solvent and it is in agreement with the structure of the title compound. Proton NMR spectrum of the compound showed two singlets at δ 1.6 and 2.4 integrating for three protons each for CH_3 groups. The multiplets observed in the range 6.8–8 integrating for 14 protons is attributable to aromatic and CH=CH protons.

Antimicrobial Property Evaluation

The title compound was subjected for antimicrobial testing against the *Escherichia coli, Klebsiella pneumonia, Acinetobacter baumanni,* and *Enterobacter cloacae* using standard microbiological techniques using serial dilution method[13]. The title compound was ineffective in inhibiting the growth of these bacterial strains. It may be noted that the presence of free hydroxyl groups may be necessary for exhibiting biological activity as reported by other researchers[3].

Crystal Growth

Good quality single crystals of 4-tosyloxychalcone were grown by slow evaporation technique using a mixture of ethyl acetate, acetone, and ethanol solvent. A saturated solution of the title compound was prepared and filtered to remove any undissolved impurities. The solution was kept undisturbed at room temperature. Yellow, block-shaped single crystals were formed after two days.

X-ray Structure Analysis

Yellow, block-shaped single crystal of the title compound **(3)**, with dimensions of 0.57 mm $\times$ 0.19 mm $\times$ 0.11 mm was selected and mounted on a Bruker APEX-II CCD diffractometer with a fine-focus-sealed tube graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 294 K in the range of $1.3 \leq \theta \leq 30.3^\circ$. The data were processed with SAINT and corrected for absorption using SADABS [14]. A total of 31,696 reflections were collected, of which 5665 were independent and 2765 reflections with $I > 2\sigma(I)$. The structures were solved by direct method using the program SHELXTL[15] and were refined by full-matrix least squares technique on F^2 using anisotropic displacement parameters for all nonhydrogen atoms. All the hydrogen atoms were positioned geometrically [C—H = 0.93−96 Å] and refined using riding model with isotropic displacement parameters set to 1.2 or 1.5 (methyl group) times the equivalent isotropic U values of the parent carbon atoms. A rotating group model was used for methyl groups. The final full-matrix least squares refinement gave R = 0.076 and wR = 0.243 ($w = 1/[\sigma^2(F_o{}^2) + (0.0983P)^2 + 4.4712P]$ where P = ($F_o{}^2$

Table 1. Crystal data and parameters for structure refinement of the title compound

Compound	(3)
CCDC	1029645
Molecular formula	$C_{23}H_{20}O_4S$
Molecular weight	392.45
Crystal system	Monoclinic
Space group	*C*2/*c*
a(Å)	33.431 (6)
b(Å)	5.8451 (10)
c(Å)	21.439 (4)
α (°)	90.00
β(°)	113.280 (6)
γ(°)	90.00
V(Å^3)	3848.2 (12)
Z	8
D_{calc} (g cm^{-3})	1.355
Crystal dimensions (mm)	0.57 × 0.19 × 0.11
μ (mm^{-1})	0.20
Radiation λ (Å)	0.71073
Reflections measured	31696
Ranges/ indices (*h*, *k*, *l*)	−45, 47; −8, 8; −29, 30
θ limit (°)	2.6–23.1
Unique reflections	5665
Observed reflections ($I > 2\sigma(I)$)	2765
Parameters	255
Goodness of fit on F^2	1.03
R1, *w*R2 ($I \geq 2\sigma(I)$)	0.076, 0.243

+ $2F_c^2$)/3, S = 1.03, (Δ/σ)max = 0.001, $\Delta\rho$max = 0.73 e Å^{-3} and $\Delta\rho$min = −0.30 e Å^{-3}. A summary of crystal data and parameters for structure refinement details are given in Table 1. Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre. CCDC No: 1029645 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free-of-charge on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK. Fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

The title compound, 4-[(2E)-3-(4-methylphenyl)prop-2-enoyl]phenyl 4-methylbenzene –1-sulfonate (Fig. 1) is a 4-tosyloxychalcone derivative, which the structure shows three aromatic rings. The central C8−C13 phenyl ring forms the dihedral angles of and with the adjacent C1−C6 and C17−C22 aromatic rings. The molecule is bent at O3 with the C1−S1−O3−C8 torsion angle of 164.3 (2)°. The molecule exists in *E* configuration with respect to the central prop-en-one group which is defined by the C14-C15-C16-C17 torsion angle of 178.5 (3)°. The crystal structure is mainly stabilized by C5—H5A... π interactions (Symmetry code: x, $-y$, $z-1/2$) involving the centroid of the C17—C22 benzene (*Cg*3) ring connecting the molecules into head-to-tail fashion

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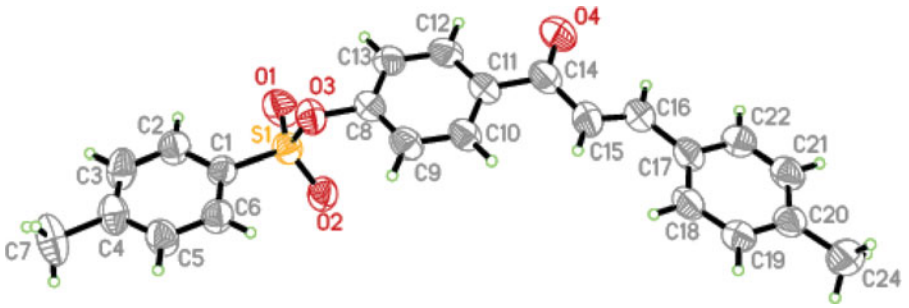

Figure 1. Molecular view of compound (**3**), showing 50% probability displacement ellipsoids and atom labelling scheme.

propagating along *c*-axis direction (Fig. 2). No significant intermolecular hydrogen bonds were found for the investigated structure. The crystal packing is consolidated by van der Waals contacts. The bond length and bond angles agree with the literature values[16] and are comparable with those reported earlier [8, 9,12]. Simulated PXRD diagram for the title compound using *plotCIF* is depicted in Fig. 3.

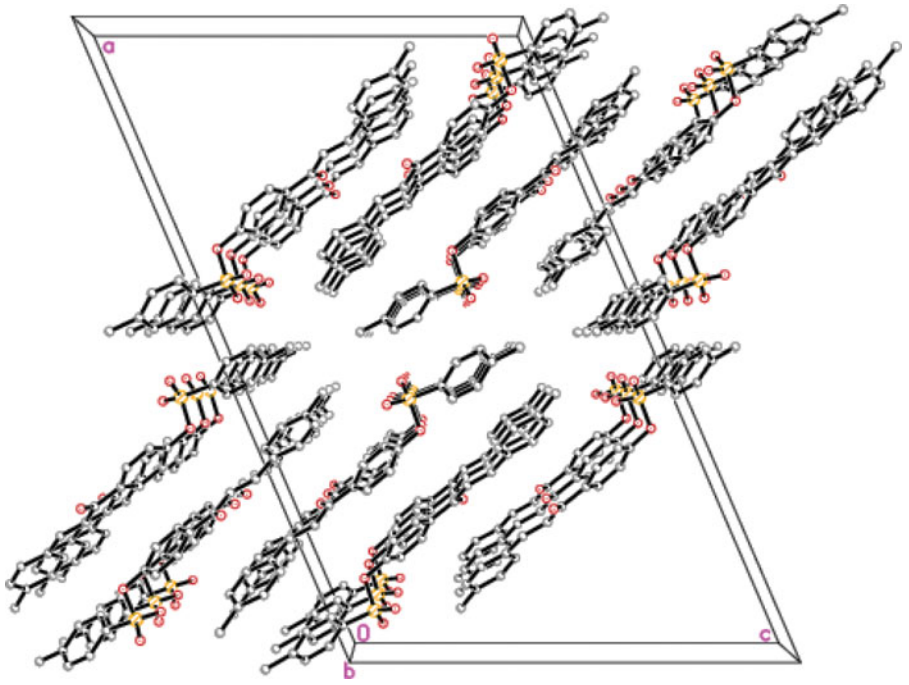

Figure 2. Crystal packing of the title compound (**3**) viewed along *b*-axis. H atoms are omitted for clarity.

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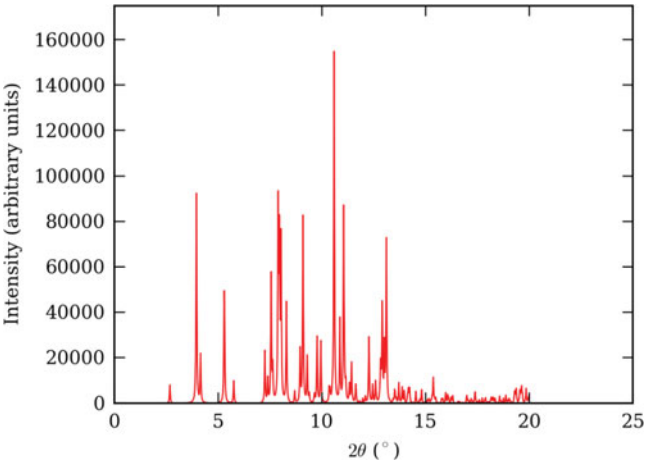

Figure 3. Simulated PXRD diagram for the title compound using *plotCIF*.

Conclusions

A novel 4-hydroxy chalcone is synthesized and crystals of this compound were successfully grown by the solution growth technique. The functional groups present in the synthesized compound were identified using FTIR and ^{1}H NMR spectra. Single crystal XRD studies confirm the conformation of the investigated compound. The molecule does not exhibit significant antimicrobial properties. There exists ample scope for synthesis and crystal growth studies on other chalcone derivatives possessing tosyloxy derivatives which might show better biological activities or optical properties.

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References

[1] Nowakowska, Z. (2007). *Eur. J. Med. Chem.*, *42*, 125.
[2] Dhar, D. N. (1981). *The Chemistry of Chalcones and Related Compounds*, Wiley: New York.
[3] Singh, P., Anand, A., & Kumar, V. (2014). *Eur. J. Med. Chem.*, *85*, 758.
[4] Dsilva, E. D., Podagatlapalli, G. K., Rao, S. V., & Dharmaprakash, S. M. (2011). *Cryst. Growth Design*, *11*, 5362.
[5] Patil, P. S., Bhumannavar, V. M., Banuur, M. S., Kulkarni, H. N., & Bhagavannarayana, G. (2013). *J. Cryst. Process. Tech.*, *3*, 108.
[6] Kiran, M. S., Anand, B., Sai, S. S. S., & Rao, G. N. (2014). *J. PhotoChem. Photobio-A: Chem.*, *290*, 38.
[7] Prabhu, A. N., Jayarama, A., Upadhyaya, V., & Subrahmanya Bhat, K. (2013). *Mat. Chem. Phy.*, *138*, 179.

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[8] Shubhalaxmi, Hahne, S., Jayarama, A., & Subrahmanya Bhat, K. (2013). *Chem. Sci. Trans.*, *2*(3), 829.
[9] Shubhalaxmi, Hahne, S., Carl, Zschille, Jayarama, A., & Subrahmanya Bhat, K. (2013). *Chem. Sci. Trans.*, *2*(3), 841.
[10] Prabhu, A. N., Jayarama, A., Subrahmanya Bhat, K., & Upadhyaya, V. (2013). *J. Mol. Struct.*, *1031*, 79.
[11] Prabhu, A. N., Jayarama, A., Subrahmanya Bhat, K., Manjunatha, K. B., Umesh, G., & Upadhyaya, V. (2013). *Ind. J. Mat. Sci.*, Article ID 151230, 5 pages.
[12] Prabhu, S. R., Jayarama, A., Upadhyaya, V., Bhat, K. S., & Ng, S. W. (2015). *Mol. Cryst. Liq. Cryst., 607*, 200.
[13] Cruickshank, R., Marmion, J. P., & Swain, R. H. A. (1975). *Med. Microbiol.*, *11*, 190.
[14] Bruker. (2009). *APEX2, SAINT and SADABS*. Bruker AXS Inc.: Madison, WI, USA.
[15] Sheldrick, G. M. (2008). *A Short History of SHELX*. *Acta Cryst.*, *A64*, 112–122.
[16] Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G., & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.*, *2*, S1–S19.

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