Journal of Crystal Growth 327 (2011) 161–166

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth, characterization, crystal and molecular structure studies of 1-(2′-thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one

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ARTICLE INFO

Article history:
Received 4 January 2011
Received in revised form
1 June 2011
Accepted 3 June 2011
Communicated by M. Fleck
Available online 12 June 2011

Keywords:
B3. Opto-electronics
B3. NLO materials
B3. Z-scan technique
A1. X-ray diffraction
A1. Trigonal plane
A1. Hydrogen bonds

ABSTRACT

1-(2′-Thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one (TTCP) was synthesized by Claisen-Schmidt condensation reaction. FT-IR spectra were recorded to identify the functional groups present in the compound. The NLO test carried out on the sample using Z-scan technique confirms the existence of nonlinearity in the third harmonic generation. Further, the compound is characterized by UV-visible spectral studies for the optical transmission. Finally, the structure of the product obtained was confirmed by the X-ray diffraction studies. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.6170(6)$ Å, $b = 7.6180(5)$ Å, $c = 10.9280(11)$ Å and $\beta = 104.635(3)^\circ$. The thiophene ring shows planar conformation and is affected by π conjugation. The unsaturated keto group is in + *syn-periplanar* conformation. The molecule exhibits both inter and intramolecular hydrogen bonds of the type C–H ⋯ O and C–H ⋯ Cl which can account for the stability of the molecule.

1. Introduction

Thiophene based materials, due to the richness of thiophene chemistry and the general stability of its compounds, have found applications in fields ranging from antistatic coatings to polymer electronics [1]. Non-linearity is the major optical phenomenon among all the other properties which promises a revolutionary change in the field of opto-electronics [2]. The most desirable properties to be the best NLO material are high power conversion efficiency, large transparency extending down to UV region, high melting point, high mechanical stability, high chemical inertness, high damage threshold, phase matching, etc. For the materials to have useful and highly efficient NLO properties, the constituent molecules need to exhibit large molecular hyperpolarizability, which is generally characterized by a highly extended π-conjugated chain with strong electron donor–acceptor pairs at the ends [3].

Organic NLO materials are often formed by weak van der Waals forces and hydrogen bonds and hence posses high degree of delocalization. Due to the overlap of π orbits, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionality of both ends of the π bond system with appropriate electron donor and acceptor groups can enhance the asymmetric electronic distribution in either or both ground and excited states, leading to an increased optical nonlinearity [4]. Hence, the search for new materials exhibiting NLO properties has never ceased. Organic crystals, particulary chalcones, have demonstrated superior second and third order NLO properties in the recent years. Among many organic NLO materials, chalcones show excellent blue light transmittance, good crystallizability and large nonlinear optical coefficients [5–8]. Chalcone and its derivatives have received much attention from physicists, chemists and material scientists who have been extensively investigating their optical, physical and chemical properties for fundamental understanding and technological applications. Owing to their electronic structure, chalcones also find unique applications in fluorescent probes for sensing of metal ions [9]. In continuation of our work on the synthesis of new chalcones and study of their NLO properties [3,4], we report the synthesis, growth and characterization of TTCP.

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doi:10.1016/j.jcrysgro.2011.06.006

2. Experimental procedure

2.1. Synthesis of TTCP

Acetyle thiophen and trichloro-benzaldehyde were used to synthesize the title compound by adopting Claisen-Schmidt condensation reaction method [10]. 0.01 mol solution of acetyle thiophen was mixed with 0.01 mol of trichloro-benzaldehyde in ethanol (20 ml) and the mixture was treated with an aqueous solution of potassium hydroxide (2 ml, 20%). The mixture was stirred well and kept aside for 24 h. The resulting solid mass was collected by filtration and dried. The compound so obtained was purified by repeated recrystallization in ethanol. Schematic diagram of the molecule is as shown in Scheme 1.

2.2. Solubility

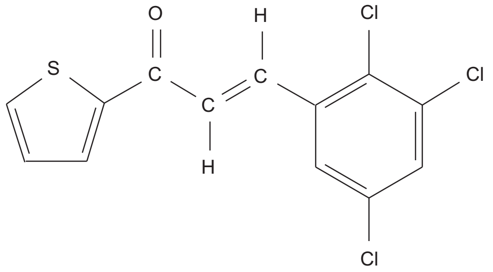
About 15–20 ml of solvent is taken in a clean beaker and heated to a specific temperature. The powdered sample was added slowly to the solvent with continuous stirring to get a saturated solution (till the compound remains un-dissolved). About 10 ml of this clear saturated solution was transferred to a pre-weighed specific gravity bottle and weighed again. The weight of the solution was measured by taking the difference between the weight of the bottle containing the solution and the weight of the empty bottle at constant temperature. The solution from the gravity bottle was transferred to a clean beaker for evaporation to get the actual solute present in the solution. In this study, an electronic balance with an accuracy of 0.001 mg was used for weighing and the temperature was maintained with a good quality temperature controller unit. Knowing the weights of the solute and the solution, the solubility was measured using the following relation:

$$\text{Solubility (wt\%)} = \frac{\text{Weight of the solute} \times 100}{\text{Weight of (solute+solvent)}}$$

The process was repeated for different temperatures. In this case, the solubility of the sample is studied using acetone and 1:1 mixture of acetone and DMF as solvents and the solubility parameters were estimated. The experiment was repeated for 3–4 times at each temperature for better accuracy. The solubility of TTCP was found to be good in both the solvents. The measured solubility of the compound in acetone and 1:1 mixture of acetone and DMF as a function of temperature is shown in Fig. 1. From the solubility data, it was observed that both the solvents are suitable for the crystal growth.

2.3. Crystal growth

The crystals were grown by slow evaporation technique at room temperature using acetone and DMF as solvents. A super-saturated solution of TTCP was obtained by dissolving the sample in a 1:1 mixture of acetone and DMF with continuous stirring at room temperature. This solution was filtered using filter paper, slightly warmed and allowed to evaporate very slowly. After about 5 days, good quality transparent tiny crystals started growing. In order to increase the size of these crystals further, small crystals were used as seeds and larger pale yellow crystals up to a dimension of $7 \times 5 \times 3\ \text{mm}^3$ were grown by slow evaporation method. The grown crystal is shown in Fig. 2.



Scheme 1. Schematic diagram of the molecule.

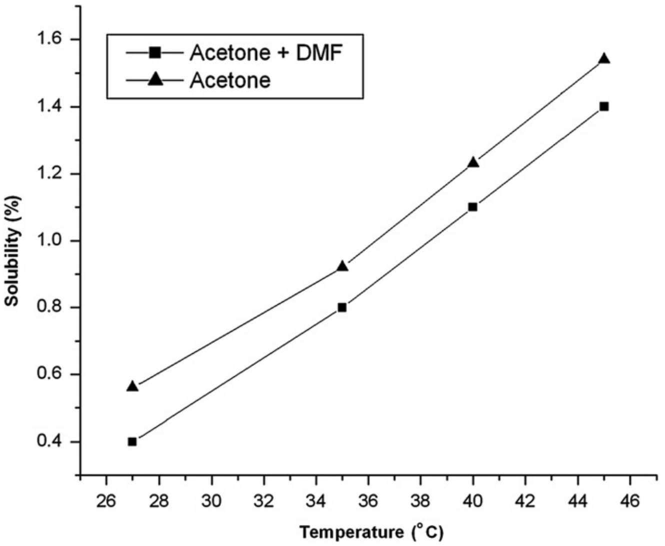


Fig. 1. Solubility curve of TTCP.

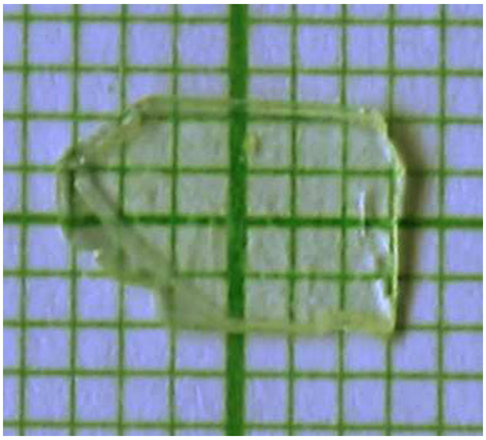


Fig. 2. Single crystal of TTCP.

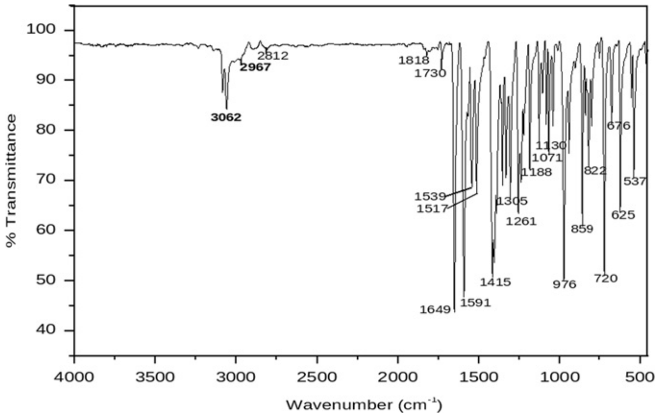


Fig. 3. FT-IR spectrum of TTCP.

2.4. FT-IR analysis

The FT-IR spectrum of the synthesized compound was recorded using Bruker IFS-66 V FT-IR in the wave number range of 400–4000 cm^{-1} using KBr pellet technique and is shown in Fig. 3. The spectrum shows C–H stretching frequency at around 2967 cm^{-1}. The strong peak at 1649 cm^{-1} is due to carbonyl stretch of a,b-unsaturated ketone [4]. Another strong peak around 1591 cm^{-1} due to the C $=$C stretch and C–Cl stretching frequency is observed at 720 cm^{-1}. The peak at 676 cm^{-1} is due to C–S stretching.

3. Results and discussions

3.1. NLO studies

Generally chalcones show very good second order non-linearity. But TTCP exhibits very poor SHG efficiency since the compensation of donor and acceptor groups is very intense. Moreover, TTCP crystallizes in the centrosymmetric space group $P2_1/c$. Hence, the third harmonic generation was tested for TTCP sample using Z-scan technique [11].

The open aperture Z-scan curve for the compound is shown in Fig. 4. The open aperture transmittance curve is symmetric with respect to focus and has minimum transmittance at the focus, indicating the intensity dependent absorption effect. In order to extract the information on nonlinear refraction, the nonlinear transmission was measured as a function of sample position with an aperture placed at the far field. To obtain pure nonlinear refraction, curve division method was employed. The pure NLR graph of the compound is as shown in Fig. 5. The peak and valley configurations of pure NLR curve clearly show that the sign of the nonlinear refractive index is negative.

The third order nonlinear susceptibility is now considered to be a complex quantity

$$\chi^{(3)} = R\chi^{(3)} + i\chi^{(3)}$$

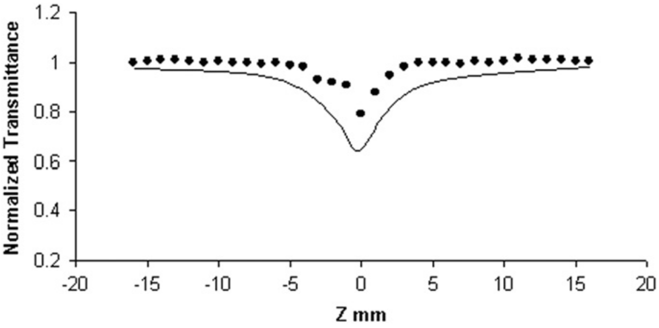


Fig. 4. Open aperture curve for TTCP. Solid line indicates the theoretical curve.

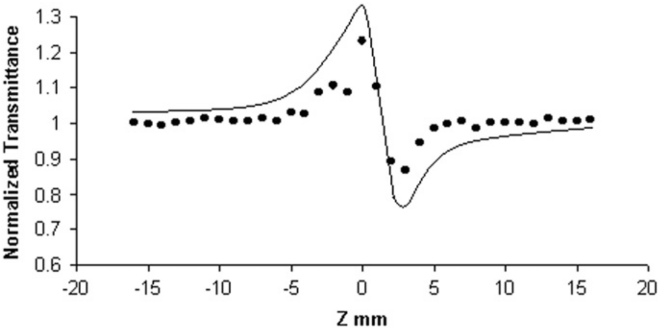


Fig. 5. NLR curve for TTCP. Solid line indicates the theoretical curve.

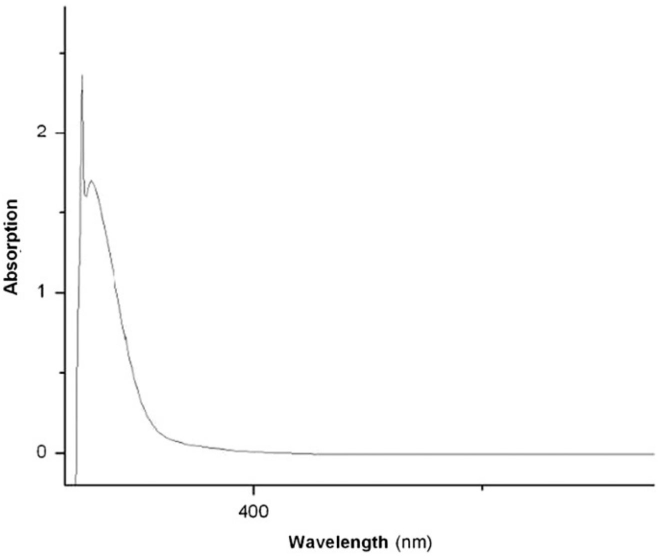


Fig. 6. UV-Visible spectrum of TTCP.

Table 2
Crystal data and structure refinement table.

CCDC	768620
Empirical formula	$C_{13}H_7Cl_3OS$
Formula weight	317.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions	$a = 16.6170(6)$ Å
	$b = 7.6180(5)$ Å
	$c = 10.9280(11)$ Å
	$\beta = 104.635(3)^\circ$
Volume	1338.47(17) Å^3
Z	4
Density (calculated)	1.576 Mg/m^3
Absorption coefficient	0.823 mm^{-1}
F_{000}	640
Crystal size	0.3 × 0.27 × 0.25 mm
Theta range for data collection	2.5°–25.0°
Index ranges	$-19 \le h \le 19$
	$-9 \le k \le 9$
	$-12 \le l \le 12$
Independent reflections	2339 [R(int) = 0.022]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2339/164
Goodness-of-fit on F^2	1.076
Final R indices	$R1 = 0.0395$, $wR2 = 0.1358$
Largest diff. peak and hole	0.28 and −0.34 e.Å^{-3}

Table 1

Sample	n_2 ($\times 10^{-11}$ esu)	β (cm/Gw)	$Re(\chi^{(3)})$ ($\times 10^{-11}$ esu)	$Im(\chi^{(3)})$ ($\times 10^{-11}$ esu)
Title compound	−1.538	2.463	−1.647	0.379

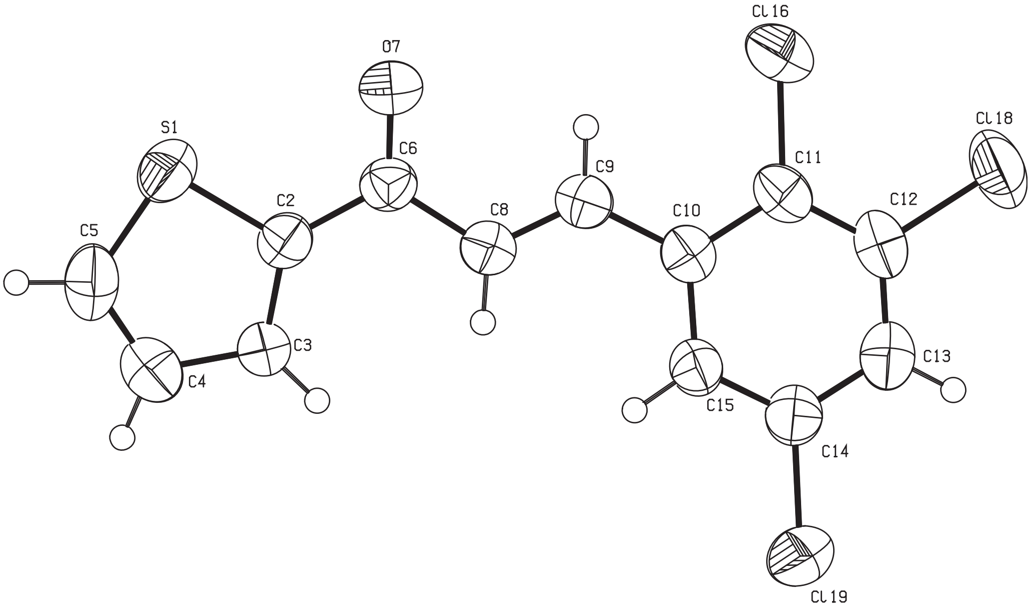


Fig. 7. ORTEP diagram of the molecule with thermal ellipsoids drawn at 50% probability.

Table 3
Bond lengths (Å).

Atoms	Length	Atoms	Length
C11–C12	1.385(4)	C9–C8	1.318(3)
C11–C10	1.399(3)	C8–C6	1.476(3)
C11–Cl16	1.729(3)	C6–O7	1.226(3)
C12–C13	1.380(4)	C6–C2	1.461(3)
C12–Cl18	1.734(3)	C2–C3	1.402(3)
C13–C14	1.377(4)	C2–S1	1.707(2)
C14–C15	1.367(4)	C3–C4	1.410(4)
C14–Cl19	1.738(3)	C4–C5	1.340(4)
C15–C10	1.405(3)	C5–S1	1.689(4)
C10–C9	1.459(3)		

where the imaginary part is related to the two photon absorption coefficients β through

$$\Im(\chi^{(3)}) = \frac{n_0^2 \varepsilon_0 c}{\omega}\beta$$

and the real part is related to γ through

$$\Re(\chi^{(3)}) = 2n_0^2 \varepsilon_0 c\gamma$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space, and c is the velocity of light in vacuum, γ is the nonlinear refractive index. The real and imaginary part of the third order nonlinear susceptibility can be calculated using above equations. The nonlinear refractive index n_2 (in esu) can be obtained by the conversion formula

$$n_2 = \frac{cn_0}{40\pi}\gamma \ (\mathrm{m}^2/\mathrm{W})$$

The experimentally determined values of β, n_2, $\Re(\chi^{(3)})$ and $\Im(\chi^{(3)})$ are given in Table 1.

3.2. UV-visible studies

The UV-visible spectra were recorded using SHIMADZU UV-Visible spectrophotometer in the range of 195–1000 nm in the crystal form. Generally, it is known that the chalcones absorb light in the UV region and transmit in the remaining region. The recorded spectrum is shown in Fig. 6. In this case, the maximum absorption peak is observed at 324 nm, which can be assigned to $n{-}\pi^*$ transition and may be attributed to the excitation in the aromatic ring and C=O group [12]. It is also observed from Fig. 6 that the TTCP crystal is transparent in the entire visible and IR region. The absence of the absorption in the visible region is a key factor as the compound is to be exploited for NLO applications at the room temperature [12].

3.3. Crystal structure determination

A single crystal of the title compound with dimensions 0.3 × 0.27× 0.25 mm was chosen for X-ray diffraction study. The data were collected on a DIPLabo Image Plate system equipped with a normal focus, 3 kW sealed X-ray source [graphite monochromated MoK_α]. The crystal-to-detector distance is fixed at 120 mm with a detector area of 441 × 240 mm^2. Thirty six frames of data were collected at room temperature by the oscillation method. Each exposure of the image plate was set to a period of 400 s. Successive frames were scanned in steps of 5° per minute with an oscillation range of 5°. Image processing and data reduction were done using Denzo [13]. The reflections were merged with Scalepack [14]. All the frames could be indexed using a primitive monoclinic lattice. The structure was solved by direct methods using SHELXS-97 [15]. All of the non-hydrogen atoms were revealed in the first Fourier map itself. Full-matrix least squares refinement using SHELXL-97 [15], with isotropic temperature factors for all the nonhydrogen atoms converged the residual $R1$ to 0.1985. Refinement of the non-hydrogen atoms with anisotropic parameters was started at this stage. The hydrogen atoms were placed at chemically acceptable positions and were allowed to ride on the parent atoms. One hundred and sixty-four parameters were refined with 2339 unique reflections which saturated the residuals to $R1{=}0.0395$. The details of the crystal data and refinement are given in Table 2.[1] Fig. 7 represents the ORTEP [16]

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[1] CCDC 768620 consists of the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK); Fax: +45 1223 336033): e-mail: deposit@ccdc.cam.ac.uk.

Table 4
Bond angles (°).

Atoms	Angle	Atoms	Angle
C12–C11–C10	120.5(2)	C15–C10–C9	121.0(2)
C12–C11–Cl16	119.1(2)	C8–C9–C10	126.8(2)
C10–C11–Cl16	120.4(2)	C9–C8–C6	121.4(2)
C13–C12–C11	121.2(2)	O7–C6–C2	120.6(2)
C13–C12–Cl18	118.3(2)	O7–C6–C8	122.1(2)
C11–C12–Cl18	120.5(2)	C2–C6–C8	117.3(2)
C14–C13–C12	118.1(2)	C3–C2–C6	129.8(2)
C15–C14–C13	122.2(2)	C3–C2–S1	110.9(2)
C15–C14–Cl19	118.8(2)	C6–C2–S1	119.3(2)
C13–C14–Cl19	119.0(2)	C2–C3–C4	111.0(2)
C14–C15–C10	120.3(2)	C5–C4–C3	113.2(3)
C11–C10–C15	117.7(2)	C4–C5–S1	112.9(2)
C11–C10–C9	121.2(2)	C5–S1–C2	92.0(1)

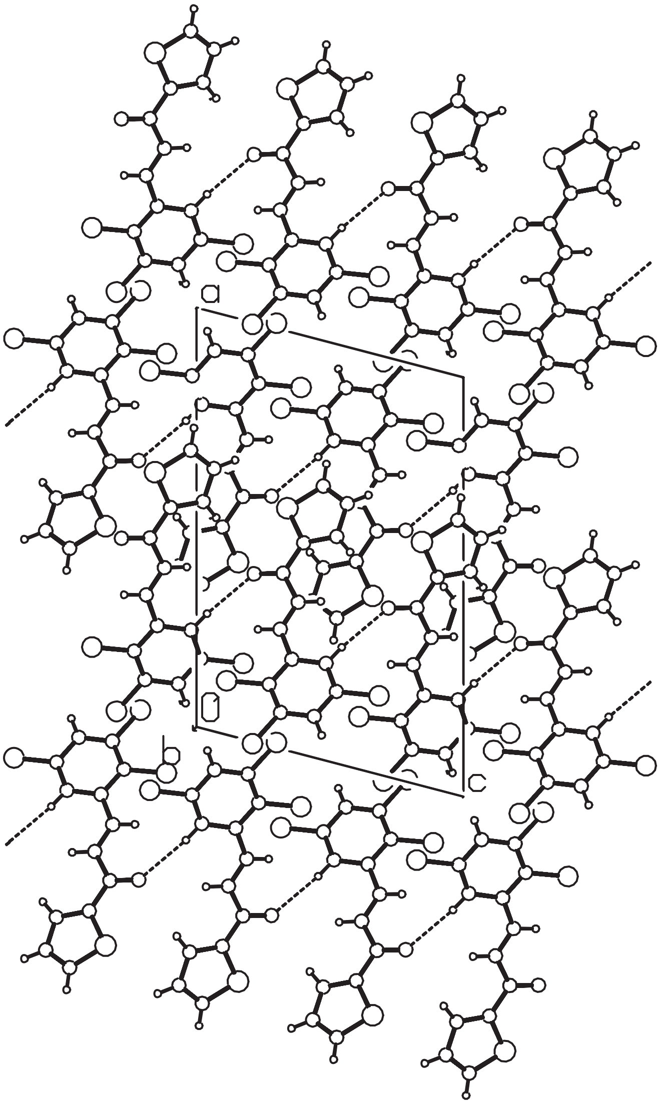

Fig. 8. Packing of the molecule down the *b* axis. The dashed lines represent the intermolecular hydrogen bonds.

diagram of the molecule with thermal ellipsoids drawn at 50% probability.

Bond lengths and bond angles are listed in Tables 3 and 4, respectively, and are in good agreement with the standard values. The molecular structure consists of one thiophene ring and one trichlorophenyl ring. These two rings are linked by propenone chain at 1,3-position. The molecule is nonplanar with the dihedral angle between two rings being 13.92(19) Å, which is different from the values of 11.0(1) Å and 19.25(10) Å, reported for 1-(2-Hydroxy-4-methoxyphenyl)-3(2,3,4-trimethoxyphenyl) prop-2-one [17] and 1-(4-Methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one [2], respectively. The unsaturated keto group is in +*syn-periplanar*(+*sp*) conformation which is evident from the torsion angle value of −5.3(4)° for the atoms O7–C6–C8–C9. This value differs from the value of −9.9(3)° reported for 1-(4-fluorophenyl)-3-(3,4,5-trimethoxyphenyl)-2-propen-1-one [18]. Both aromatic rings of the molecule are in planar conformation within the experimental limits with maximum deviations being 0.003(3) and 0.002(3) Å for atoms C4 and C10, respectively from the least squares plane. The thiophene ring is affected by the π conjugation. This can be explained by the longer C=S values of 1.707(2) and 1.689(4) Å for C2=S1 and C5=S1, respectively. The bond angle values of 122.1(2)°, 120.6(2)° and 117.33(19)° about C6 indicates that the carbon atom is in a distorted trigonal plane which is due to steric hindrance of the oxygen atom. The structure exhibits both intermolecular and intramolecular hydrogen bonds of the type C–H ··· O and C–H ··· Cl. The intermolecular hydrogen bond C15–H5 ··· O7 has a bond length of 3.421(3) Å and an angle of 174° with symmetry code $x,3/2-y,-1/2+z$. Further, the structure is stabilized by the C–H ··· π(phenyl) interactions. The stability of the crystal structure can be accounted for by these hydrogen bonds. Crystal packing indicates that the molecules are stacked in pairs and exhibit layered stacking when viewed down the *b* axis as shown in Fig. 8.

4. Conclusion

The nonlinear optical chalcone derivative 1-(2′-Thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one was synthesized by Claisen-Schmidt condensation reaction and single crystals were grown by slow evaporation technique using acetone and DMF as solvents. FT-IR spectral studies were carried out to confirm the functional groups of the TTCP. Single crystal X-ray diffraction study reveals that the π-conjugation in the thiophen ring accounts for the increase in the optical nonlinearity. Also, the crystal structure of TTCP is stabilized by the hydrogen bonds of the type C–H ··· O and the π interactions involving the phenyl ring. TTCP crystals have a transparency range with UV cutoff wavelength at 324 nm. NLO test using Z-scan technique shows that TTCP exhibits large and negative nonlinear optical properties. Due to the presence of wide transparency range and third harmonic efficiency, the TTCP crystal may be used for NLO applications.

Acknowledgements

The authors are grateful to DST, Government of India and University of Mysore for financial assistance. The authors also thank Prof. G. Umesh, Department of Physics, National Institute of Technology, Surathkal, Karnataka for providing the laser facility. HRM thanks UGC-BRS and University of Mysore for the award of fellowship.

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