PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

DADOS DE DIFRAÇÃO DE RAIOS-X PARA UM NOVO TIOFENO CHALCONA OBTIDO POR UMA REAÇÃO DE CLAISEN-SCHMIDT

X-RAY POWDER DIFFRACTION DATA FOR A NEW THIOPHENE CHALCONE OBTAINED BY A CLAISEN-SCHMIDT REACTION

DELGADO, Gerzon E.[1*]; DELGADO-NIÑO, Pilar[2]; JAMALIS, Joazaizulfazli[3]

[1] Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Venezuela

[2] Facultad de Ingeniería, Universidad Libre, Bogotá, Colombia

[3] Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Malaysia

** Correspondence author*
e-mail: gerzon@ula.ve

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RESUMO

As chalconas e seus derivados heterocíclicos ganharam considerável importância nos últimos anos devido a sua ampla gama de propriedades farmacológicas, incluindo agentes anti-AIDS, antibacterianos, antimaláricos, anti-inflamatórios, antileishmaniose, antioxidantes, anticâncer, atividade antimicrobiana antituberculose. Estes compostos importantes são convencionalmente sintetizados por reação de condensação de Claisen-Schmidt, em que o aldeído reage com acetofenona na presença de bases alcalinas aquosas. Daí a importância de caracterizar novos derivados utilizando diferentes técnicas tanto espectroscópicas como difratométricas para conhecer sua estrutura molecular e cristalina, mas também técnicas que permitem estudar suas propriedades biológicas para conhecer suas possíveis aplicações. A difração de raios-X em pó é a técnica mais utilizada para a identificação de materiais cristalinos e, portanto, a importância de se reportar padrões de pó no banco de dados de Difração de Pó. Portanto, o objetivo desta investigação foi obter e reportar dados de difração de raios-X de boa qualidade (espaçamento d e intensidade relativa das reflexões de hkl observadas) do novo derivado de chalcona heterercíclico; (E) -3- (5-bromo-tiofen-2-il) -1- (2,5-diclorotiofen-3-il) -2-propen-1-ona. Este novo composto foi sintetizado pelo método de condensação de Claisen-Schmidt entre uma série de chalconas derivadas do tiofeno como potenciais agentes anticancerígenos e antimicrobianos. O padrão em pó foi indexado no grupo de espaço monoclínico $P2_1/n$ com parâmetros de célula unitária a = 4,0323 (7) Å, b = 13,551 (3) Å, c = 23,511 (5) Å, β = 94,27 (1), Z = 4, V = 1281,1 (3) Å3, e figuras de mérito M20 = 18,2 e F30 = 47,6 (0,0143, 44). Todas as linhas medidas foram indexadas e são consistentes com o grupo espacial monoclínico.

Palavras-chave: Difração de raios X, tiofeno chalcona, agente antimicrobiano e anticancerígeno.

ABSTRACT

Chalcones and their heterocyclic derivatives have gained considerable importance in recent years due to their wide range of pharmacological properties including anti-AIDS agents, anti-bacterial, anti-malarial, anti-inflammatory, anti-leishmanial, anti-oxidant, anti-cancer, anti-tuberculosis anti-microbial activity. These important compounds are conventionally synthesized by Claisen-Schmidt condensation reaction in which aldehyde reacted with acetophenone in the presence of aqueous alkaline bases. Hence the importance of characterizing new derivatives using different techniques both spectroscopic and diffractometric to know their molecular and crystalline structure, but also techniques that allow to study their biological properties to know their possible applications. X-ray powder diffraction is the technique most widely used for the identification of crystalline materials and hence the importance of reporting powder patterns in the Powder Diffraction File database. Therefore, the objective of this investigation is to obtain and reported good quality X-ray powder diffraction data (d-spacing and relative intensity of observed hkl reflections) of the new hetererocyclic chalcone derivative; (*E*)-3-(5-bromo thiophen-2-yl)-1-(2,5-dichlorothiophen-3-yl)-2-propen-1-one. This new compound was synthesized by Claisen-Schmidt condensation method among a series of thiophene derivative chalcones as potential anti-cancer and anti-microbial agents. The powder pattern was indexed in the monoclinic space group $P2_1/n$ with unit cell parameters a= 4.0323(7) Å, b= 13.551(3) Å, c= 23.511(5) Å, β= 94.27(1), Z = 4, V= 1281.1(3) Å^3, and figures of merit M_{20}= 18.2 and F_{30}= 47.6 (0.0143, 44). All measured lines were indexed and

are consistent with the monoclinic space group.

Keywords: X-ray powder diffraction, thiophene chalcone, anti-microbial, anti-cancer agent.

1. INTRODUCTION

Heterocyclic compounds, such as rhodanines, thiazolidinediones, thiohydantoins and hydantoins, have been widely studied because of their significant properties and applications in organic and medicinal chemistry. Some examples of their biological applications include their use as anti-convulsant, muscle relaxant, anti-platelet, anti-inflammatory, anti-hyperglycaemic, aldose reductase inhibitory, anti-microbial, and anti-cancer agents (Meusel and Gutschow, 2004; Tomasic and Masic, 2009; Vengurlekar *et al*., 2012; Jain *et al*., 2013).

Among these compounds, chalcones and their heterocyclic derivatives have gained the remarkable importance in recent years due to their wide range of pharmacological properties including anti-AIDS agents (Cheenpracha *et al*., 2006), anti-bacterial (Kumar *et al*., 2013a), anti-malarial (Wu *et al*., 2002; Domínguez *et al*., 2001; Kumar *et al*., 2013b), anti-inflammatory (Won et al., 2005), anti-leishmanial (Kayser and Kiderlen, 2001), anti-oxidant (Ahmad *et al*., 2011), anti-cancer (Lawrence *et al*., 2006; Bandgar *et al*., 2010, Shin *et al*., 2013), anti-tuberculosis (Lin *et al*., 2002) and anti-microbial (Asiri and Khan, 2011) activity. Heterocyclic chalcones are conventionally synthesized by Claisen-Schmidt condensation reaction in which aldehyde reacted with acetophenone in the presence of aqueous alkaline bases (Rao *et al*., 2004; Kumar *et al*., 2013b). Chalcones have also been synthesized using Friedel-Crafts acylation (Nasir *et al*., 2013), microwave irradiation (Jayapal and Sreedhar, 2010), ultrasonic irradiation (Li *et al*., 2002), grinding technique (Zangade *et al*., 2011) and by Suzuki coupling reaction (Eddarir *et al*., 2003).

On the other hand, X-ray powder diffraction is a non-destructive method for characterization of crystalline solids. This technique is most widely used for the identification of unknown crystalline materials (e.g., minerals, inorganic and organic compounds). X-ray diffraction patterns are very useful for the identification of new materials and hence the importance of reporting in the appropriate database: Powder Diffraction File of the International Centre for Diffraction Data (ICDD, 2017).

With the interested in the structural characterization of compounds with possible pharmacological activity (Vizcaya *et al*., 2012; Gonzalez *et al*., 2012; Delgado *et al*., 2015; Delgado *et al*., 2016; Delgado *et al*., 2018a; 2018b), the present work is focused on report the X-ray powder diffraction data for the new heterocyclic chalcone (*E*)-3-(5-bromo thiophen-2-yl)-1-(2,5-dichlorothiophen-3-yl)-2-propen-1-one, which was prepared among a series of thiophene derivative chalcones as potential anti-cancer and anti-microbial agents (Al-Maqtari *et al*., 2015). Its crystal structure was recently reported and crystallizes in the monoclinic space group $P2_1/n$ (Delgado *et al*., 2018b). A search in the ICDD Powder Diffraction File (ICDD, 2017) not contains any entry for this chalcone derivative. Therefore, the goal of this investigation was to obtain and report a good quality X-ray powder pattern, reliable values of d-spacing and relative intensity of observed *hkl* reflections, of the title compound.

2. MATERIALS AND METHODS

2.1. Synthesis

The title compound was synthesized by the Claisen-Schmidt condensation method (Kumar *et al*., 2013b) (Figure 1) using a methodology recently reported (Al-Maqtari *et al*., 2015). A mixture of 3-acetyl-2,5-dichlorothiophene (1) (0.03 mmol) and 5-bromo-2-thiophenecarboxaldehyde (2) (0.03 mmol) was dissolved in methanol (25mL). Aqueous sodium hydroxide (15 mL) was added dropwise and the resulting mixture was stirred overnight at room temperature. The precipitate was collected, dried and purified by recrystallization from ethanol to give the new thiophene chalcone (**3**). Yield: 83.6% (m.p. 373-375 K).

2.2. Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR)

The FT-IR absorption spectrum was obtained as KBr pellet using a Perkin-Elmer spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance II spectrometer in $CDCl_3$ solution. The infrared spectrum showed stretching vibrations; 3078 cm^{-1} (Ar-H), 1644 cm^{-1} (C=O), 1579 cm^{-1}, 1512 cm^{-1} (Ar-C=C), 1020 cm^{-1} (C-Cl); and nuclear magnetic resonance; ^{1}H NMR

($CDCl_3$): δ 7.07(1H, d, *J* =4 Hz, H-5), δ 7.08 (1H, d, *J*=15.2 Hz, H-2), δ 7.12 (1H, d, *J* =4 Hz, H-6), δ 7.19 (1H, s, H-11), δ 7.76 (1H, d, *J* =15.2 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 117.20 (C-7), δ 122.56 (C-5), δ 127.08 (C-11), δ 127.12 (C-8), δ 131.28 (C-9), δ 131.49 (C-2), δ 132.86 (C-6), δ 136.61 (C-3), δ 137.60 (C-10), δ 141.61 (C-4), δ 182.84 (C-1).

2.3. X-ray powder diffraction data

Powder diffraction data was collected at room temperature 298(1) K. A small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powder, sieved to 106 μm, was mounted in a zero background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction (XRPD) pattern was recorded with a Siemens D5005 diffractometer operating in Brag-Brentano geometry equipped with a Cu target X-ray tube (40 kV and 30 mA) and a diffracted beam graphite monochromator. The specimen was scanned from 5-50° 2θ, with a step size of 0.02° and counting time of 10 s. Quartz was used as an external standard. The software package Highscore Plus v2.0 was used to eliminate the $K\alpha_2$ component, establish the positions of the peaks and determine the peak intensities of the diffraction peaks.

3. RESULTS AND DISCUSSION:

The X-ray powder pattern of thiophene chalcone (**3**) is shown in Figure 2. The 20 first peak positions were indexed using the program DICVOL04 (Boultif and Louër, 2004), which gave a unique solution in a monoclinic cell. This result confirms the crystal structure reported (Delgado *et al*., 2018b).

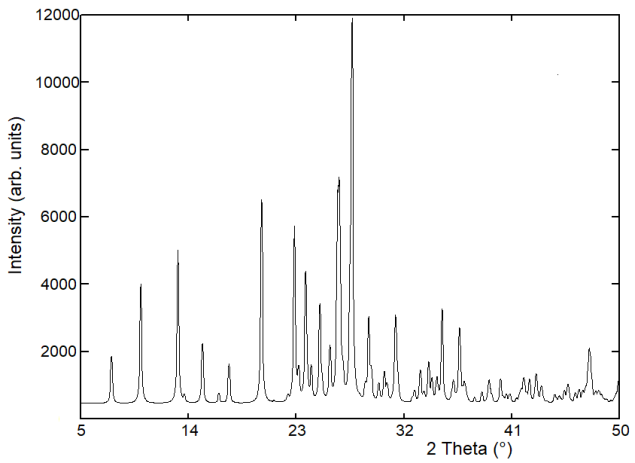

***Figure 2**. X-ray powder diffraction pattern of the thiophene chalcone (**3**).*

The complete powder diffraction dataset was reviewed in the monoclinic space group $P2_1/n$, using the program NBS*AIDS83 (Mighell *et al*. 1981). All measured lines were indexed and were consistent with the mentioned space group. From this analysis, the refined unit cell parameters obtained were: *a*= 4.0323(7) Å, *b*= 13.551(3) Å, *c*= 23.511(5) Å, *β*= 94.27(1), *V*= 1281.1(3) $Å^3$, Z = 4, with figures of merit M_{20}= 18.2 (de Wolff, 1968) and F_{30}= 47.6 (0.0143, 44) (Smith and Snyder, 1979). The resulting X-ray powder diffraction data for (*E*)-3-(5-bromo thiophen-2-yl)-1-(2,5-dichlorothio phen-3-yl)-2-propen-1-one, together with the observed and calculated 2θ, the d-spacing's as well as the relative intensities of the reflections, are given in Table 1.

In order to confirm the unit cell parameters, a Le Bail refinement (Le Bail, 2005) was carried out using the Fullprof program (Rodríguez-Carvajal, 2018). Figure 3 shows the very good fit between the observed and calculated patterns.

4. CONCLUSIONS:

The new thiophene chalcone, (*E*)-3-(5-bromo thiophen-2-yl)-1-(2,5-dichlorothio phen-3-yl)-2-propen-1-one, was synthesized by Claisen-Schmidt condensation. The spectroscopic studies confirmed the molecular structure of the chalcone compound. The X-ray powder diffraction data for the title compound is reported and will be included in the PDF database. All lines of powder pattern data were indexed and are consistent with the $P2_1/n$ monoclinic space group. The indexed yielded the following unit cell parameters: *a*= 4.0323(7) Å, *b*= 13.551(3) Å, *c*= 23.511(5) Å, *β*= 94.27(1), Z = 4, *V*= 1281.1(3) $Å^3$, and figures of merit M_{20}= 18.2 and F_{30}= 47.6 (0.0143, 44). This is a new chalcone derivative with potential anti-microbial and anti-cancer properties.

5. ACKNOWLEDGMENTS:

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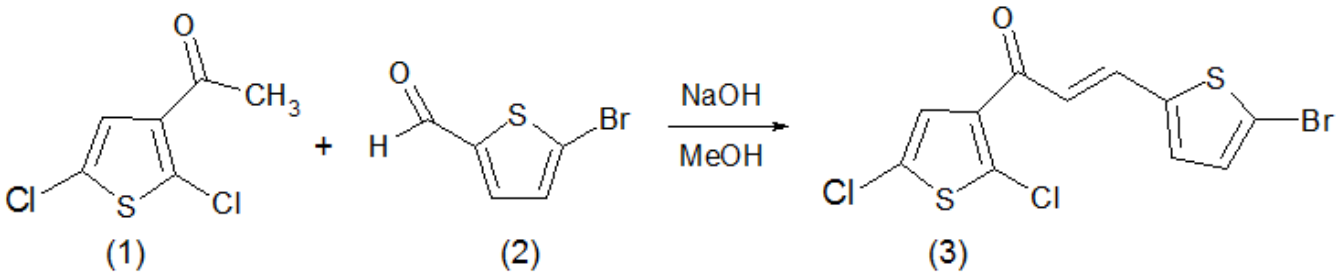

***Figure 2**. Chemical synthesis of the title chalcone (**3**) by the Claisen-Schmidt reaction.*

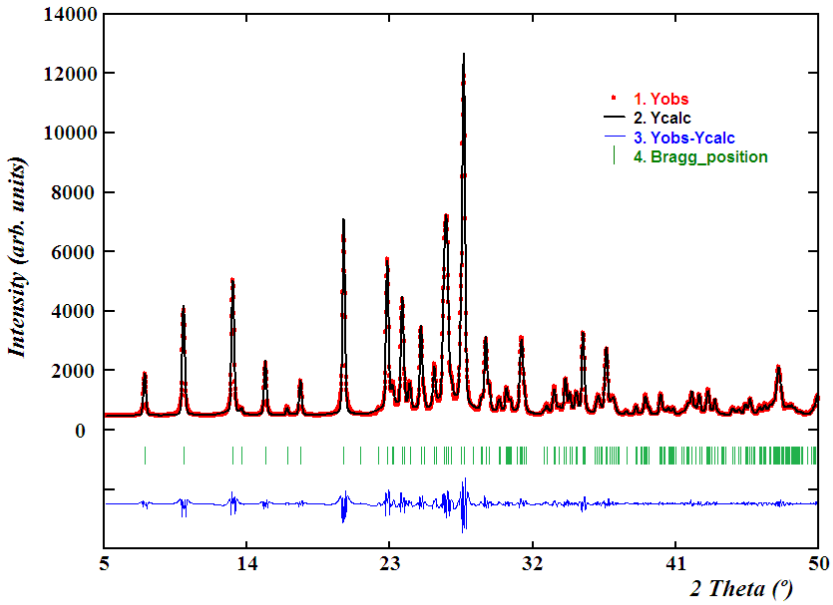

***Figure 3.** Le Bail refinement of the thiophene chalcone (3).*

***Table 1.** X-ray powder diffraction data of (E)-3-(5-bromo thiophen-2-yl)-1-(2,5-dichlorothiophen-3-yl)-2-propen-1-one.*

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	*h*	*k*	*l*	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
7.529	11.7324	104	0	1	1	7.529	11.7324	0.000
9.973	8.8621	1000	0	1	2	9.969	8.8657	-0.004
13.116	6.7447	307	0	1	3	13.067	6.770	-0.049
13.589	6.5109	51	0	2	1	13.593	6.5092	0.004
15.100	5.8626	324	0	0	4	15.103	5.8614	0.003
16.462	5.3805	42	0	1	4	16.465	5.3797	0.003
17.304	5.1206	182	0	2	3	17.308	5.1194	0.004
20.023	4.4309	986	0	1	5	20.021	4.4313	-0.002
21.059	4.2152	10	0	3	2	21.061	4.2149	0.002
22.150	4.01	17	-1	0	1	22.131	4.0134	-0.019

22.715	3.9115	432	0	3	3	22.719	3.9108	0.004
22.786	3.8995	222	0	0	6	22.738	3.9076	-0.048
23.027	3.8592	67	0	2	5	23.048	3.8558	0.021
23.095	3.848	67	-1	1	1	23.094	3.8481	-0.001
23.675	3.7551	418	0	1	6	23.678	3.7546	0.003
23.744	3.7443	184	-1	1	2	23.758	3.7422	0.014
24.113	3.6878	69	-1	0	3	24.105	3.6891	-0.008
24.841	3.5814	231	0	3	4	24.866	3.5779	0.025
25.055	3.5513	62	-1	1	3	24.996	3.5595	-0.059
25.652	3.47	91	1	0	3	25.637	3.472	-0.015
25.722	3.4607	53	1	2	0	25.742	3.458	0.020
26.319	3.3835	386	0	2	6	26.307	3.385	-0.012
26.396	3.3738	450	-1	2	2	26.38	3.3759	-0.016
26.504	3.3603	279	1	1	3	26.48	3.3633	-0.024
26.588	3.3499	113	0	4	1	26.563	3.3529	-0.025
26.742	3.3309	60	-1	1	4	26.734	3.3319	-0.008
27.312	3.2627	183	1	2	2	27.331	3.2605	0.019
27.398	3.2527	381	0	3	5	27.394	3.2532	-0.004
27.514	3.2392	819	-1	2	3	27.507	3.2400	-0.007
28.567	3.1222	21	1	1	4	28.586	3.1202	0.019
28.648	3.1135	26	0	4	3	28.697	3.1083	0.049
28.886	3.0884	129	-1	1	5	28.89	3.0879	0.004
29.106	3.0656	56	-1	2	4	29.107	3.0655	0.001
29.743	3.0013	30	-1	3	1	29.755	3.0002	0.012
30.220	2.955	57	0	3	6	30.218	2.9552	-0.002
30.471	2.9313	35	0	0	8	30.477	2.9307	0.006
31.126	2.8711	119	1	3	2	31.123	2.8713	-0.003
31.287	2.8567	119	-1	3	3	31.280	2.8573	-0.007
31.390	2.8475	119	-1	1	6	31.387	2.8478	-0.003
32.572	2.7468	10	0	4	5	32.581	2.7461	0.009
32.714	2.7352	22	-1	3	4	32.712	2.7354	-0.002
33.129	2.7019	23	1	2	5	33.132	2.7017	0.003
33.333	2.6858	46	0	2	8	33.282	2.6899	-0.051
33.926	2.6402	74	0	5	2	33.922	2.6406	-0.004
34.167	2.6222	27	-1	1	7	34.159	2.6228	-0.008
34.522	2.596	25	-1	3	5	34.528	2.5955	0.006
34.609	2.5897	27	-1	4	1	34.622	2.5888	0.013
35.025	2.5599	169	0	4	6	35.027	2.5597	0.002
35.100	2.5546	73	-1	4	2	35.083	2.5558	-0.017
35.833	2.504	16	1	4	2	35.824	2.5046	-0.009
35.971	2.4947	25	-1	4	3	35.963	2.4952	-0.008
36.400	2.4663	52	1	3	5	36.380	2.4676	-0.020
36.516	2.4587	130	0	3	8	36.518	2.4586	0.002
36.626	2.4516	36	-1	3	6	36.681	2.4480	0.055
36.78	2.4416	18	1	1	7	36.752	2.4435	-0.028
36.933	2.4319	31	0	2	9	36.939	2.4315	0.006
37.750	2.3811	16	0	4	7	37.738	2.3818	-0.012
38.336	2.346	23	0	5	5	38.329	2.3465	-0.007

38.833	2.3172	11	-1	4	5	38.867	2.3152	0.034
38.951	2.3104	32	0	1	10	38.954	2.3102	0.003
39.101	2.3019	11	-1	3	7	39.124	2.3006	0.023
39.953	2.2547	36	0	3	9	39.918	2.2567	-0.035
40.062	2.2489	22	0	6	1	40.076	2.2481	0.014
41.639	2.1673	14	1	2	8	41.618	2.1683	-0.021
41.817	2.1584	27	-1	3	8	41.817	2.1584	0.000
42.292	2.1353	15	1	5	3	42.270	2.1364	-0.022
42.763	2.1129	13	1	4	6	42.757	2.1131	-0.006
42.883	2.1072	33	0	6	4	42.878	2.1075	-0.005
42.952	2.104	14	0	1	11	42.919	2.1055	-0.033
43.234	2.0909	10	1	1	9	43.247	2.0903	0.013
44.340	2.0413	10	1	3	8	44.334	2.0416	-0.006
45.068	2.01	11	2	0	0	45.055	2.0106	-0.013
45.432	1.9948	17	1	5	5	45.437	1.9946	0.005
45.498	1.992	17	-2	1	1	45.448	1.9941	-0.050
46.939	1.9342	15	0	1	12	46.948	1.9338	0.009
47.026	1.9308	14	1	6	2	47.034	1.9305	0.008
47.121	1.9271	33	-2	1	4	47.123	1.927	0.002
47.200	1.9241	49	-2	2	2	47.20	1.9241	0.000
47.378	1.9173	18	1	3	9	47.413	1.9159	0.035
47.469	1.9138	12	1	5	6	47.462	1.914	-0.007
48.041	1.8923	10	1	6	3	48.018	1.8932	-0.023
49.549	1.8382	10	0	7	4	49.549	1.8382	0.000
49.660	1.8344	14	-2	3	2	49.675	1.8339	0.015
49.741	1.8316	10	1	5	7	49.749	1.8313	0.008