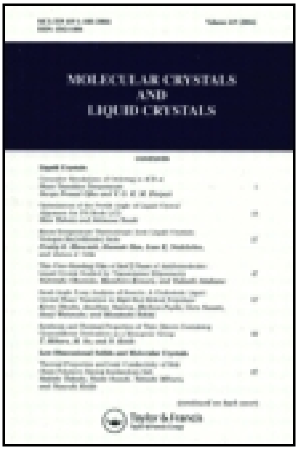

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Synthesis and Phase Transition in New Chalcone Derivatives: Crystal Structure of 1-Phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one

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Synthesis and Phase Transition in New Chalcone Derivatives: Crystal Structure of 1-Phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one

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A series of new chalcone derivatives with a general formula of $CH_3C_nH_{2n}COOC_6H_4CH{:}CHCOC_6H_4$ *where* $n = 10, 12, 14$, *and* 16 *were well synthesized and crystallized from organic solution. The physical properties as well as the chemical formulations of these compounds were determined by the microanalysis and spectroscopic methods (FTIR, and* ^1H *and* ^{13}C *NMR). Crystal structure of* $CH_3C_{10}H_{20}COOC_6H_4CH{:}CHCOC_6H_4$ *was determined by single-crystal X-ray diffraction analysis. The space group of this crystal is triclinic with* $a = 5.8570(3)$ Å, $b = 8.5640(5)$ Å, $c = 24.1592(12)$ Å, $V = 1175.82(11)$ Å^3, *and* $Z = 2$, *and its structure was refined to* $R(F) = 0.055$ *and* $\omega R(F^2) = 0.161$. *The elongated terminal alkyl chain is fully stretched in solid phase. Phase-transition temperatures and the thermal parameters were obtained from differential scanning calorimetry (DSC). The texture observation was carried out with a polarizing optical microscope (POM) over heating and cooling cycles. All of the title compounds except undecylcarbonyloxy analogue exhibit* Cr_1-Cr_2 *transition with smectic-like texture within the* Cr_2 *phase.*

Keywords: chalcone derivatives; differential scanning calorimetry; 1-phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one; polarizing optical microscope; single-crystal X-ray diffraction analysis

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INTRODUCTION

Chalcone is one of the important chemical compounds and is being studied extensively because of its significant use or application in various sectors. In the fields of biology and biochemistry, chalcone has been claimed to be one of the compounds that plays a vital role in antitumor [1,2], antiinflammatory [3,4] and antimalaria [5] activities. It has also been documented that the chalcone possesses a remarkable nonlinear optical (NLO) property, which is an essential element for optical communications devices. The other importance of this compound is its high photosensitivity and thermal stability, which are used in developing various crystalline electro-optical devices [6–8].

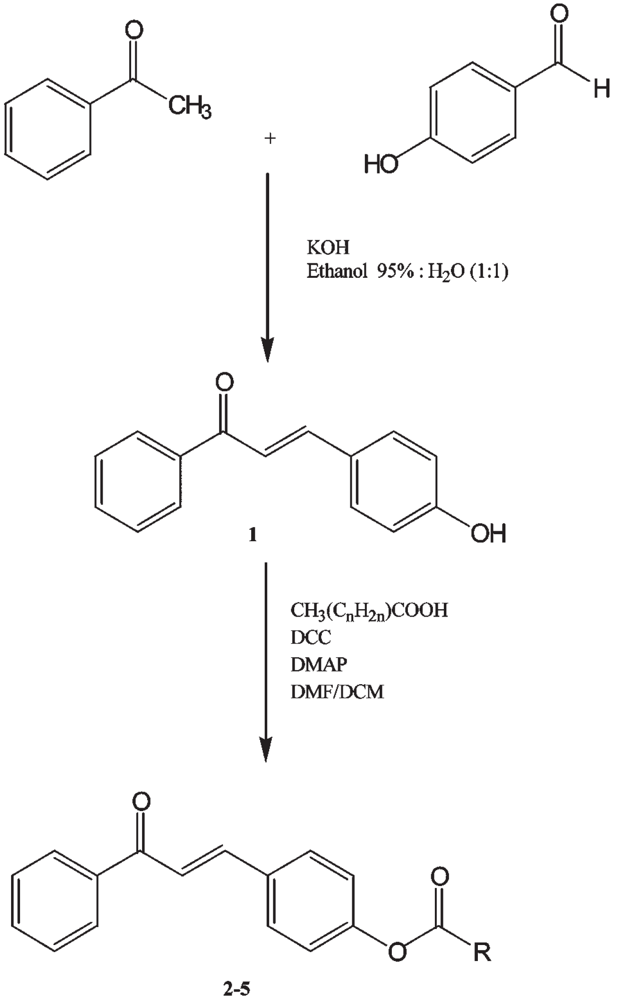
In view of the outstanding behavior of chalcone, a systematic study focusing on the synthesis and characterization of this compound has been carried out in our present laboratory over the past few years [9–11]. A very recent investigation of the molecular structures and characteristics of a series of chalcone derivatives, 1-phenyl-3-(4′-alkyloxyphenyl)-2-propen-1-one with ether and keto bridging groups, has been reported [12]. In this article, we report another series of some newly derived analogues, 1-phenyl-3-(4′-alkylcarbonyloxyphenyl)-2-propen-1-one, of which the ester and keto bonding are essential functional groups. A crystal structure of 1-phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one is reported along with the spectroscopy (IR and NMR), thermal analysis, and texture observation. The method used in the synthesis of all the title compounds is summarized in Scheme 1.

EXPERIMENTAL

4-Hydroxybenzaldehyde (Across) and other chemicals including acetophenone, octadecanoic, 4-(dimethylamino)pyridine, and N,N′-dicyclohexylcarbodiimide of 98% purity (Merck) were used without further purification. All the 98–99% pure acids of dodecanoic, tetradecanoic, and hexadecanoic were obtained from a palm-oil factory in Malaysia.

Thin-layer chromatography analyses were performed using aluminium-backed silica-gel plates (Merck 60 F254) and were examined under UV light. Column chromatography was performed under gravity using Aldrich 100–200-mesh silica gel. Melting point of the synthesized compounds were measured by a Gallenkamp melting-point apparatus.

Microanalyses were carried out on 2400 LS series CHNS/O analyzers in the School of Chemical Sciences, Universiti Sains Malaysia. Infrared spectra (KBr pellets) were recorded using a Perkin-Elmer



R= $CH_3(C_nH_{2n})COOH$

Compound	n
2	10
3	12
4	14
5	16

SCHEME 1

system 2000-FTIR over a frequency range of 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were obtained with the use of a Bruker Avance Ultrashield 400 NMR spectrometer. Samples were dissolved in DMSO-d$_6$ (compound **1**) and $CDCl_3$ (compounds **2–5**). Chemical shifts were recorded in parts per million relative to TMS (0.00 ppm) for ^{1}H and ^{13}C NMR. The optical microscopy studies were carried out with an Olympus Vanox (Tokyo, Japan) 200845 polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds were observed by using polarized light with a crossed polarizer with the sample in thin film sandwiched between a glass slide and cover. The thermograms of all derivatives **2–5** were performed in the School of Chemical Sciences, Universiti Sains Malaysia, by using a Perkin-Elmer DSC-50 at heating and cooling rates of 5°C/min and -5°C/min, respectively.

Crystal-structure Analysis

Intensity data for **2** were collected at 293 K in thin-slice (0.3°) ω-scan mode using a Bruker SMART1000 CCD diffractometer (graphite monochromated MoKα radiation, $\lambda = 0.71073$ Å) with the aid of the SMART and SAINT programs [13] to a maximum 2θ value of 55°. The triclinic cell dimensions were refined together with other offset parameters of the diffractometer using 2850 strong reflections with $I > 10\sigma(I)$ measured in the 2θ range 4.88–54.54°. After merging the symmetry equivalent and multiplying measured data, 5381 independent reflections ($R_{int} = 0.022$) were retrieved from the 9769 measured and used for structure determination and refinement.

The structure of **2** was solved by direct methods using SHELXS97, which located all nonhydrogen atoms, and full-matrix nonlinear least-squares refinement on $|F^2|$ was carried out with SHELXL97 [14]. All the H atoms were placed in idealized positions and refined by riding on their carrier atoms with the constraint $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$ (carrier atom) or $U_{\mathrm{iso}}(\mathrm{H}) = 1.5\,U_{\mathrm{eq}}$ (methyl carrier atom) applied, as appropriate. The weighting scheme $\omega = 1/[\sigma^2(F_o^2) + (0.0886P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was used for **2**, resulting in final $R(F)$ and $\omega R(F^2)$ values of 0.055 and 0.161, respectively.

Synthesis

Preparation of 1-Phenyl-3-(4′-hydroxyphenyl)-2-propen-1-one (1)

This compound was prepared via condensation of 4-hydroxybenzaldehyde with acetophenone in the presence of potassium hydroxide.

4-Hydroxybenzaldehyde (41.0 mmol, 5.00 g) and acetophenone (41.0 mmol, 4.90 g) were added to an aqueous solution of potassium hydroxide (9.20 g in 60 mL of a mixture of 95% ethanol/water 1:1). The mixture was stirred well and left standing overnight. The solution was then evolved in an ice bath and neutralized with dilute HCl, whereupon the product was isolated. The product was filtered and recrystallized from ethanol. Yield (84%). Elemental analysis (%): C = 80.36, H = 5.28 (found), C = 80.34, H = 5.39 (calculated). IR (KBr pellet): 3225 cm^{-1} (O–H), 3021 cm^{-1} (C–H Ar), 1649 cm^{-1} (C=O keto), 1559, 1512 cm^{-1} (C=C Ar). ^{1}H NMR ($CDCl_3$): 10.14 ppm (s, 1H, OH), 6.89–8.11 ppm (9H, Ar–H), 7.72 (d, 2H, olefinic-H). ^{13}C NMR ($CDCl_3$): 116.76 ppm (Ar–C), 119.36 ppm and 145.44 ppm (olefinic-C), 189.92 ppm (C=O keto).

Preparation of 1-Phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one (2)

This compound was synthesized from 1-phenyl-3-(4′-hydroxyphenyl)-2-propen-1-one with dodecanoic acid. 1-phenyl-3-(4′-hydroxyphenyl)-propen-1-one (1 mmol, 1.12 g) and dodecanoic acid (5 mmol, 1.00 g) were dissolved in dichloromethane/dimethylformamide (1:1). To this solution was added dicyclohexylcarbodiimide, DDC (10 mmol, 2.06 g), and 4-dimethylaminopyridine (DMAP, 1 mmol, 0.12 g) before the mixture was stirred for 1 h at 0°C and continued 12 h at room temperature. The solution was filtered and the filtrate was left standing overnight. The crystal thus formed was washed by using petroleum ether. Yield: 76.2%. Elemental analysis (%): C = 80.01, H = 8.34 (found), C = 79.76, H = 8.43 (calculated). IR (KBr pellet): 3055 cm^{-1} (C–H Ar), 2916 cm^{-1} (C–H alkyl), 1755 cm^{-1} (C=O ester), 1658 cm^{-1} (C=O keto). ^{1}H NMR ($CDCl_3$): 0.91 ppm (t, 3H, CH_3), 2.59 ppm (t, 2H, $CH_2C{=}O$), 1.65–1.78 ppm (18H, CH_2), 7.51 and 7.81 ppm (2H, olefinic-H), 7.14–8.03 ppm (9H, Ar–H). ^{13}C NMR ($CDCl_3$): 14.51 ppm (CH_3), 23.09–34.81 ppm (CH_2), 122.53–152.85 ppm (Ar–C), 172.39 ppm (C=O ester), 190.79 ppm (C=O keto).

Preparation of Other Compounds

The preparation and characterization for compound **3–5** were carried out using a similar method. The analytical data obtained are summarized as follows:

*Preparation of 1-Phenyl-3-(4′-tridecylcarbonyloxyphenyl)-2-propen-1-One **(3)**.* Yield: 74.8%. Elemental analysis (%): C = 80.36, H = 8.66 (found), C = 80.14, H = 8.81 (calculated). IR (KBr pellet): 3053 cm^{-1} (C–H Ar), 2917 cm^{-1} (C–H alkyl), 1752 cm^{-1} (C=O ester), 1658 cm^{-1} (C=O keto). ^{1}H NMR ($CDCl_3$): 0.89 ppm (t, 3H, CH_3), 2.58 ppm (t, 2H, $CH_2C{=}O$), 1.29–1.78 ppm (22H, CH_2), 7.51 and 7.81 ppm (2H, olefinic-H), 7.16–8.03 ppm (9H, Ar–H). ^{13}C NMR ($CDCl_3$): 14.51 ppm (CH_3), 23.09–34.81 ppm (CH_2), 122.53–152.84 ppm (Ar–C), 172.39 ppm (C=O of ester), 190.79 ppm (C=O keto).

*Preparation of 1-Phenyl-3-(4′-pentadecylcarbonyloxyphenyl)-2-propen-1-one (**4**).* Yield: 77.3%. Elemental analysis (%): C = 80.28, H = 9.08 (found), C = 80.48, H = 9.15 (calculated). IR (KBr pellet): 3054 cm^{-1} (C–H aromatic), 2916 cm^{-1} (C–H alkyl), 1756 cm^{-1} (C=O of esther), 1658 cm^{-1} (C=O keto). ^{1}H NMR ($CDCl_3$): 0.90 ppm (t, 3H, CH_3), 2.58 ppm (t, 2H, $CH_2C{=}O$), 1.28–1.77 ppm (26H, CH_2), 7.51 and 7.81 ppm (2H, olefinic-H), 7.18–8.03 ppm (9H, Ar–H). ^{13}C NMR ($CDCl_3$): 14.51 ppm (CH_3), 23.09–34.81 ppm (CH_2), 122.52–152.85 ppm (Ar–C), 172.41 ppm (C=O ester), 190.81 ppm (C=O keto).

*Preparation of 1-Phenyl-3-(4′-heptadecylcarbonyloxyphenyl)-2-propen-1-one (**5**).* Yield: 70.2%. Elemental analysis (%): C = 80.98, H = 9.33 (found), C = 80.77, H = 9.45 (calculated). IR (KBr pellet): 3056 cm^{-1} (C–H aromatic), 2917 cm^{-1} (C–H alkyl), 1750 cm^{-1} (C=O of ester), 1658 cm^{-1} (C=O keto). ^{1}H NMR ($CDCl_3$): 0.90 ppm (t, 3H, CH_3), 2.59 ppm (t, 2H, $CH_2C{=}O$), 1.28–1.76 ppm (30H, CH_2), 7.51 and 7.81 ppm (2H, olefinic-H), 7.18–8.04 ppm (9H, Ar–H). ^{13}C NMR ($CDCl_3$): 14.51 ppm (CH_3), 23.09–34.82 ppm (CH_2), 122.52–152.85 ppm (Ar–C), 172.38 ppm (C=O ester), 190.79 ppm (C=O keto).

RESULTS AND DISCUSSION

Physical Characterization

The IR spectra for the chalcone **1** and its derivaties **2–5** were summarized for comparison. The presence of a new band at 2916–2917 cm^{-1} in **2–5** is a strong indication of the introduction of the long alkyl chain into intermediary compound 1-phenyl-3-(4′-hydroxyphenyl)-2-propen-1-one. The presence of a new C=O in the ester linkage of **2–5** within the frequency range 1750–1756 cm^{-1} can also substantiate the formation of the title compounds.

The ^{1}H and ^{13}C NMR assignments were made from high-resolution ^{1}H and ^{13}C NMR spectra based on the chemical shifts, multiplicities, and electronic effects. The ^{1}H NMR spectrum of compound **1** shows a single resonance at 10.14 ppm, indicating the presence of hydroxyl proton. This peak is absent upon formation of compounds **2–5**. Instead, the new peaks attributed to the methylene protons in the alkyl chain in compounds **2–5** were found within the chemical shift range of

1.28–1.78 ppm. Although the methylene protons adjacent to the C=O ester group appeared as a quintet at 2.58–2.59 ppm, the protons from the methyl group gave rise to a triplet at $\delta = 0.89$–0.91 ppm. The presence of the C=O ester group in the elongated chalcones can also be substantiated by the new ^{13}C signal observed at 172.39 ppm, 172.39 ppm, 172.41 ppm, and 172.38 ppm in compounds **2**, **3**, **4**, and **5**, respectively.

The melting point for compound **2** is much lower than that of **1** (170°C) indicating the absence of hydroxyl group OH. This strong piece of evidence indicates that intermolecular hydrogen bonding was reduced to minimal, leading to the anisotropic motion of the compound **2** using the heating process. This phenomenon is similar to that reported for *p*-alkoxycinnamic acids [15] and *p*-n-octadecanyloxybenzylidine-*p*-hydroxyaniline [16]. The same characteristics with respect to the bonding mode were observed for other analogue compounds **3–5**.

TABLE 1 Crystal Data and Structure Refinement for Compound **2**

Parameter	Value
Empirical formula	$C_{27}H_{34}O_3$
Formula weight	406.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 5.8570(3) Å, $\alpha = 98.305(1)^\circ$ b = 8.5640(5) Å, $\beta = 95.200(1)^\circ$ c = 24.1592(12) Å, $\gamma = 99.148(1)^\circ$
Volume	1175.82(11) Å^3
Z	2
Density (calculated)	1.148 Mg/m^3
Absorption coefficient	0.073 mm^{-1}
F(000)	440
Crystal size	$0.45 \times 0.25 \times 0.13$ mm^3
Theta range for data collection	2.44 to 27.55°.
Index ranges	$-7 \le h \le 7,\ -11 \le k \le 11,\ -31 \le l \le 30$
Reflections collected	9769
Independent reflections	5381 [R(int) = 0.0223]
Completeness to theta = 27.55°	98.9%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.980 and 0.968
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5381/0/272
Goodness-of-fit on F^2	0.980
Final R indices [I > 2sigma(I)]	R1 = 0.0547, wR2 = 0.1411
R indices (all data)	R1 = 0.0941, wR2 = 0.1606
Largest diff. peak and hole	0.161 and −0.238 e.Å^{-3}

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound **2** (U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor)

Atom	x	y	z	U(eq)
O(1)	8915(2)	968(2)	1464(1)	65(1)
O(2)	7237(2)	1149(2)	2261(1)	87(1)
O(3)	−2560(2)	−4109(2)	−791(1)	73(1)
C(1)	25448(4)	10298(3)	6332(1)	113(1)
C(2)	22971(4)	9465(3)	6133(1)	89(1)
C(3)	22597(3)	8703(2)	5522(1)	74(1)
C(4)	20135(3)	7873(2)	5317(1)	72(1)
C(5)	19728(3)	7118(2)	4704(1)	72(1)
C(6)	17248(3)	6301(2)	4500(1)	73(1)
C(7)	16820(3)	5570(2)	3887(1)	73(1)
C(8)	14334(3)	4726(2)	3690(1)	73(1)
C(9)	13940(3)	4003(2)	3077(1)	68(1)
C(10)	11485(3)	3091(2)	2872(1)	66(1)
C(11)	11269(3)	2354(2)	2263(1)	59(1)
C(12)	8897(3)	1446(2)	2021(1)	56(1)
C(13)	6930(3)	72(2)	1129(1)	52(1)
C(14)	4924(3)	693(2)	1042(1)	55(1)
C(15)	3151(3)	−176(2)	652(1)	53(1)
C(16)	3341(3)	−1631(2)	341(1)	47(1)
C(17)	5393(3)	−2234(2)	447(1)	51(1)
C(18)	7159(3)	−1388(2)	843(1)	53(1)
C(19)	1437(3)	−2479(2)	−79(1)	50(1)
C(20)	1461(3)	−3691(2)	−481(1)	54(1)
C(21)	−651(3)	−4425(2)	−874(1)	52(1)
C(22)	−408(3)	−5566(2)	−1384(1)	48(1)
C(23)	−2315(3)	−6722(2)	−1622(1)	57(1)
C(24)	−2187(3)	−7786(2)	−2097(1)	69(1)
C(25)	−185(4)	−7686(2)	−2351(1)	74(1)
C(26)	1715(3)	−6539(2)	−2122(1)	71(1)
C(27)	1634(3)	−5497(2)	−1638(1)	59(1)

Crystal data of **2** are given in Table 1. The final coordinates and equivalent isotropic displacement parameters are given in Table 2, and the selected bond lengths, angles, and torsion angles are given in Table 3. The molecular structure with the atom-numbering scheme and packing for **2** are shown in Figs. 1 and 2, respectively.

It is clearly shown in Fig. 1 that the conformation of C19-C20 is also E, which resembles that observed in 1-phenyl-3-(4′-hydroxyphenyl)-2-propene-1-one [11]. The angle made by the ring [C13-C14-C15-C16-C17-C18] with the plane defined by C19-C20-C21 [14.6(2)°] is found to be higher than that in the intermediary chalcone [8.5(2)°]. This observation could be ascribed to the long alkyl chain of

TABLE 3 Bond Lengths (Å), Angles (°), and Torsion Angles (°) for Compound **2**

O(1)-C(12)	1.350(2)	C(13)-C(14)	1.376(2)
O(1)-C(13)	1.401(2)	C(14)-C(15)	1.377(2)
O(2)-C(12)	1.188(2)	C(15)-C(16)	1.385(2)
O(3)-C(21)	1.219(2)	C(16)-C(17)	1.399(2)
C(1)-C(2)	1.513(3)	C(16)-C(19)	1.458(2)
C(2)-C(3)	1.508(3)	C(17)-C(18)	1.374(2)
C(3)-C(4)	1.508(2)	C(19)-C(20)	1.319(2)
C(4)-C(5)	1.510(3)	C(20)-C(21)	1.481(2)
C(5)-C(6)	1.513(2)	C(21)-C(22)	1.490(2)
C(6)-C(7)	1.504(3)	C(22)-C(23)	1.388(2)
C(7)-C(8)	1.519(2)	C(22)-C(27)	1.390(2)
C(8)-C(9)	1.500(3)	C(23)-C(24)	1.375(2)
C(9)-C(10)	1.525(2)	C(24)-C(25)	1.368(3)
C(10)-C(11)	1.502(2)	C(25)-C(26)	1.376(3)
C(11)-C(12)	1.501(2)	C(26)-C(27)	1.373(2)
C(13)-C(18)	1.371(2)		
C(12)-O(1)-C(13)	121.2(1)	C(15)-C(16)-C(17)	117.7(1)
C(3)-C(2)-C(1)	113.6(2)	C(15)-C(16)-C(19)	120.0(1)
C(4)-C(3)-C(2)	114.2(2)	C(17)-C(16)-C(19)	122.3(1)
C(3)-C(4)-C(5)	114.8(2)	C(18)-C(17)-C(16)	120.5(2)
C(4)-C(5)-C(6)	114.6(2)	C(13)-C(18)-C(17)	119.9(1)
C(7)-C(6)-C(5)	114.9(2)	C(20)-C(19)-C(16)	128.3(2)
C(6)-C(7)-C(8)	114.5(2)	C(19)-C(20)-C(21)	121.4(2)
C(9)-C(8)-C(7)	113.8(2)	O(3)-C(21)-C(20)	121.6(2)
C(8)-C(9)-C(10)	115.0(2)	O(3)-C(21)-C(22)	119.8(1)
C(11)-C(10)-C(9)	111.4(2)	C(20)-C(21)-C(22)	118.6(1)
C(12)-C(11)-C(10)	115.2(2)	C(23)-C(22)-C(27)	118.7(2)
O(2)-C(12)-O(1)	123.4(2)	C(23)-C(22)-C(21)	118.6(1)
O(2)-C(12)-C(11)	128.1(2)	C(27)-C(22)-C(21)	122.7(1)
O(1)-C(12)-C(11)	108.6(1)	C(24)-C(23)-C(22)	120.7(2)
C(18)-C(13)-C(14)	121.2(2)	C(25)-C(24)-C(23)	120.1(2)
C(18)-C(13)-O(1)	116.7(1)	C(24)-C(25)-C(26)	119.8(2)
C(14)-C(13)-O(1)	121.7(2)	C(27)-C(26)-C(25)	120.8(2)
C(13)-C(14)-C(15)	118.4(2)	C(26)-C(27)-C(22)	119.9(2)
C(14)-C(15)-C(16)	122.2(2)		
C(1)-C(2)-C(3)-C(4)	–179.8(2)	C(19)-C(16)-C(17)-C(18)	179.2(1)
C(2)-C(3)-C(4)-C(5)	179.4(2)	C(14)-C(13)-C(18)-C(17)	2.1(3)
C(3)-C(4)-C(5)-C(6)	–179.5(2)	O(1)-C(13)-C(18)-C(17)	−171.1(1)
C(4)-C(5)-C(6)-C(7)	179.0(2)	C(16)-C(17)-C(18)-C(13)	−1.1(2)
C(5)-C(6)-C(7)-C(8)	179.0(2)	C(15)-C(16)-C(19)-C(20)	166.0(2)
C(6)-C(7)-C(8)-C(9)	–180.0(2)	C(17)-C(16)-C(19)-C(20)	−14.0(3)
C(7)-C(8)-C(9)-C(10)	177.7(2)	C(16)-C(19)-C(20)-C(21)	179.7(1)
C(8)-C(9)-C(10)-C(11)	–177.8(2)	C(19)-C(20)-C(21)-O(3)	−11.4(3)
C(9)-C(10)-C(11)-C(12)	–179.3(2)	C(19)-C(20)-C(21)-C(22)	168.2(2)
C(13)-O(1)-C(12)-O(2)	0.0(3)	O(3)-C(21)-C(22)-C(23)	−26.5(2)
C(13)-O(1)-C(12)-C(11)	179.2(1)	C(20)-C(21)-C(22)-C(23)	153.9(1)

(*Continued*)

TABLE 3 Continued

C(10)-C(11)-C(12)-O(2)	–5.8(3)	O(3)-C(21)-C(22)-C(27)	152.1(2)
C(10)-C(11)-C(12)-O(1)	175.0(2)	C(20)-C(21)-C(22)-C(27)	–27.5(2)
C(12)-O(1)-C(13)-C(18)	–122.4(2)	C(27)-C(22)-C(23)-C(24)	0.4(2)
C(12)-O(1)-C(13)-C(14)	64.4(2)	C(21)-C(22)-C(23)-C(24)	179.1(2)
C(18)-C(13)-C(14)-C(15)	–1.1(3)	C(22)-C(23)-C(24)-C(25)	–1.8(3)
O(1)-C(13)-C(14)-C(15)	171.8(1)	C(23)-C(24)-C(25)-C(26)	1.4(3)
C(13)-C(14)-C(15)-C(16)	–1.0(3)	C(24)-C(25)-C(26)-C(27)	0.4(3)
C(14)-C(15)-C(16)-C(17)	1.9(2)	C(25)-C(26)-C(27)-C(22)	−1.8(3)
C(14)-C(15)-C(16)-C(19)	–178.1(2)	C(23)-C(22)-C(27)-C(26)	1.4(2)
C(15)-C(16)-C(17)-C(18)	−0.8(2)	C(21)-C(22)-C(27)-C(26)	–177.2(2)

which the rotation about the C12-C13 bond led to the deviation from the planarity of the entire molecule. The free phenyl ring [C22-C23-C24-C25-C26-C27] is also found to be deviated from the same plane by 34.86(15)°, which is greater than that found in the intermediate

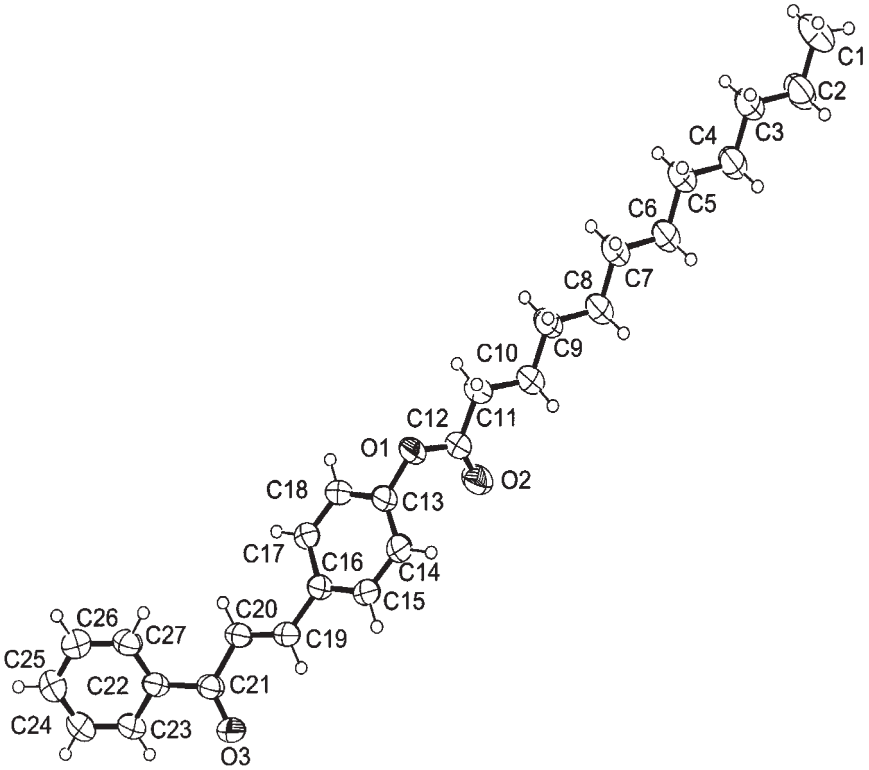


FIGURE 1 Molecular structure with atomic numbering scheme for compound **2**.

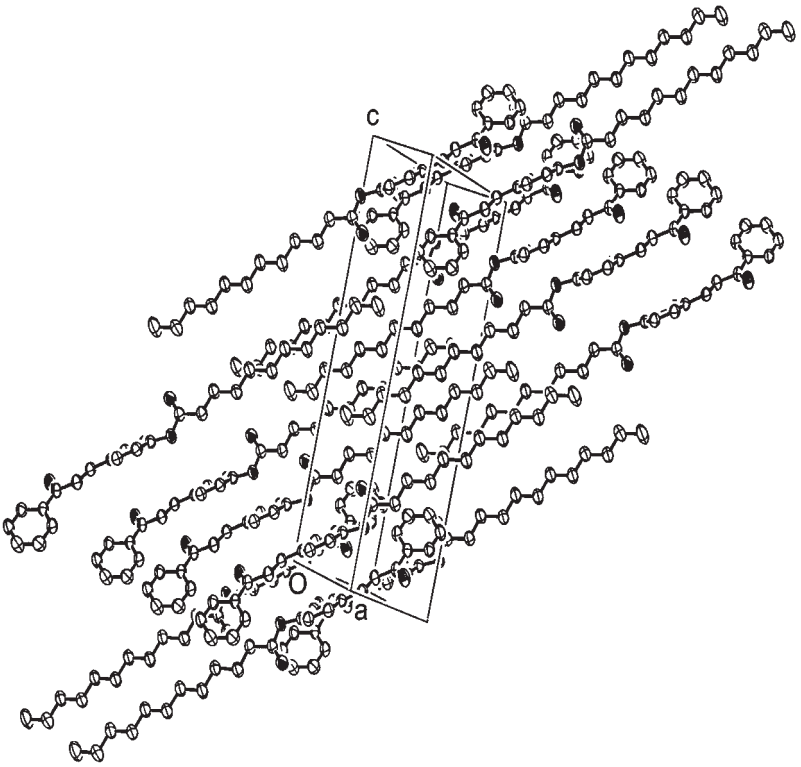


FIGURE 2 Molecular packing of compound **2**.

[17.2(2)°]. The dihedral angle between the planes of the phenyl ring [C22-C23-C24-C25-C26-C27] and the esterified ring [C13-C14-C15-C16-C17-C18] is 46.93(15)°. This value is almost double of that observed in 1-phenyl-3-(4-hydroxyphenyl)-2-propene-1-one [25.2(1)°] [11]. It is also shown in Fig. 1 that the long alkyl chain attached to the ring via an ester bond is fully stretched with zigzag conformation made up by the methylene group. The bond length of the olefinic group C19-C20 [1.319(2) Å] is much shorter than that in its reported chalcone [1.333(4) Å]. One of the probable explanation pertinent to this observation is that the introduction of the elongated methylene chain into the *para*-hydroxyl group increased the electron density within the aromatic ring, which was in turn conjugated with the exocyclic olefinic group. The packing of the molecules (Fig. 2) shows that they lie collinear to each other. The molecules are arranged in layers and they seem to be stacked along the b axis.

There are no anomalously short intermolecular contacts in crystal **2**. Apart from normal van der Waals' contacts, there may be a weak $\pi \cdots \pi$ stacking interactions between the phenyl rings made up of atoms C13-C14-C15-C16-C17-C18. This could be substantiated by both the centroid…centroid separation of 4.002 Å (symmetry operation to generate second molecule = 1−x, −y, −z), and their lateral displacement of 1.81 Å.

Phase Transition and Liquid Crystallinity of 1-Phenyl-3-(4′-alkylcarbonyloxyphenyl)-2-propen-1-one

The data inferred from the DSC thermograms for the title compounds **2–5** during heating cycles (Table 4) show only one peak that can be ascribed to direct isotropization process. A further examination of DSC data also illustrates the evolution of the Cr-I transition with the lengthening of terminal chains. The melting temperatures for compounds **2–4** increases as the alkyl chain of $CCH_2C_nH_{2n+1}$ elongates in the range of $n = 10$–14. This observation could be attributed to the increase of van der Waals attraction when the alkyl chains of the title compounds ($CCH_2C_nH_{2n+1}$) varied from 10 to 12 and 14. The least intermolecular interaction in compound **2** in comparison to its analogues **3** and **4** can explain why there is no unusual contact as that described in the molecular structure of crystal **2**. However, the melting temperature of compound **5** is found to be lower than those of **2–4**. The lowering of the melting temperature in compound **5** wherein $n = 16$

TABLE 4 Transition Temperatures and Associated Enthalpies of Compound **2–5** upon Heating and Cooling (DSC)

Compound	Cycle	Transition	Temperature(°C)	ρH_t (J/g)
2	Heating	Cr-I	94.6	148.0
	Cooling	I-Cr	77.0	142.4
3	Heating	Cr_1-Cr_2	86.2	—
		Cr_2-I	97.7	153.3
	Cooling	I-Cr	76.8	148.1
4	Heating	Cr_1-Cr_2	85.5	—
		Cr_2-I	99.9	141.1
	Cooling	I-Cr	83.0	144.1
5	Heating	Cr_1-Cr_2	83.7	—
		Cr_2-I	92.6	149.8
	Cooling	I-Cr	79.8	158.3

Cr = Crystal.
I = Isotropic.

could probably be due to the repulsive (steric) forces leading to larger intermolecular distance. One of the reasons that can explain the repulsion among the molecules in compound **5** is the probable deviation from the linearity of the terminal alkoxyl chain. Although the molecular structure for compounds **2–4** may be fully stretched, the long molecular axis of compound **5** could be distorted from linearity, which entails molecular packing as reported for the azomethines containing terminal cycloalkyl ring systems [17].

Furthermore, the observation under polarized microscope showed the presence of subphases within the crystal region especially in compounds **3**, **4**, and **5** of which the Cr_1-Cr_2 transitions occurred at 86.2°C, 85.5°C, and 83.7°C, respectively. The identification of Cr_1 and Cr_2 phases is not clear even though the molecules have seemingly shown smectic-like texture in Cr_2 region.

CONCLUSION

A series of new chalcone derivatives, 1-phenyl-3-(4′-alkylcarbonyloxyphenyl)-2-propen-1-one, has been synthesized and characterized. The physical properties as well as their mesomorphic behaviors were studied by using spectroscopic techniques (microanalysis, IR, and NMR). The conformation of their representative compound, 1-phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propen-1-one, has also been ascertained by X-ray diffraction, which revealed for the first time the conformation of 1-phenyl-3-(4′-undecylcarbonyloxyphenyl)-2-propene-1-one wherein the exocyclic methylene chain is elongated without being kinked at the ester linkage.

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