

Study of the Relation existing between Photoresistivity and Substituents Characteristics of some Coumarin Derivatives

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Coumarins has served as the prototype scaffold for the synthesis of a wide variety of analogues in order to investigate their biological activity as well as their use as additives (levelers or/and brighteners) in metal electroplating industrial processes. Several synthetic coumarin derivatives have important pharmacological potential as they proved to be efficient inhibitors of a variety of enzymes. Moreover, coumarin and its derivatives, might also present interesting physical and chemical properties that, in many cases, could be attributed to the development of a π -conjugated system in their molecules. In the present work, a series of coumarin analogues, bearing a substituted phenyl ring on position 3, synthesized via a novel methodology, have been studied as far as concerns their photoconductivity. Specifically, the effect of the nature, the number and the position of substituents, have been investigated. The structure of the molecules was studied by X-ray crystallography. The photoelectrical behavior of the substances was detected using a photoelectrochemical cell (PEC) under a white illumination generated by a halogen lamp and focused in front of the quartz window of the cell. Illumination intensity was approx. 1,000 and 10,000 W/m². It was found that a relation exists between the photoresistivity of the compounds, their molecular structure and the orientation of their crystallites in thin films prepared from them.

1. Introduction

Coumarins are benzopyrone analogues widely distributed in Nature and well known for their biological activity (Roussaki et al., 2010) as well as their use as additives in metal electroplating processes (Macheras et al., 1996). In a previous work (Roussaki et al., 2010) efficiently attained the development in one-step the synthesis of new coumarin analogues. Their biological characterization and a study of their antioxidant behavior were also included.

Coumarin and its derivatives might also present interesting physical and chemical properties that, in many cases, could be attributed to the development of a π -conjugated system, permitting the electron flow through overlapping π -molecular orbitals.

In previous works (Mhaidat et al., 2007 and 2009) the synthesis and the study of photoconductivity of some small molecule semiconductors has been managed. In the present work the study of coumarin derivatives has been selected because of their potential to develop extended π -conjugated systems. Thus, the semiconductivity of two selected coumarin derivatives mentioned in the previous work (Roussaki et al., 2010), has been studied. They, both exhibiting a characteristic antioxidant behavior, present, as rather not expected, a different photoresponse, though the existence of many electrons should favor all these properties. This particular behavior seems to be related with the different spatial arrangement of the molecules.

2. Experimental

2.1 Preparation of the layers

The coumarin derivatives 3-(2-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (1) and 3-(4-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (2) have been prepared and studied as reported (Roussaki et al., 2010). They were taken in the form of films applied on cylindrical Ti substrates, using a solution deposition technique (spin coating) (Mhaidat et al., 2007 and 2009). Films deposited on glass slides were used for X-Ray powder diffraction measurements.

2.2 X-ray study

Structure determination. A crystal of 1 (0.18×0.41×0.42 mm) and one of 2 was taken from the mother liquor and immediately cooled to -113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated CuK α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program package (Rigaku, 2005). The structure was solved by direct methods using SHELXS-97 (Sheldrick, 1997a) and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 (Sheldrick, 1997b). Further experimental crystallographic details for both compounds are given in Table 1S. Hydrogen atoms were either located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

Powder diffraction. The measurements were performed with SIEMENS D500 diffractometer, using CuK α radiation and the following combination of slits: 1.0°/1.0°/1.0° as aperture, 0.15° as detector and 0.15° as diffracted beam monochromator diaphragms. Measured 2θ range was scanned in 5s/0.03° step.

2.3 Photoelectrochemical measurements

They were performed using a Photoelectrochemical Cell (PEC) with three electrode configuration comprising platinum wire rods as counter- and reference- electrodes. An alkaline sulfide-polysulfide solution was the working red-ox electrolyte. The PEC measurements were conducted under a white illumination generated by a halogen lamp. Illumination intensity was approx. 1,000 and 10,000 W/m².

3. Results and Discussion

The molecular structure of compounds 1 and 2 are given in Figure 1(i) and (ii), correspondingly. Table 1S lists their crystallographic, geometrical parameters and hydrogen bond geometries. The bond length and bond angle values (Table 1S) for the coumarin core are within experimental error of the values given for analogous 3 substituted coumarin derivatives (Vijayakumar et al., 2012). Although the difference in the dihedral angles of the least-squares coumarin ring system and the phenyl rings are not significant, 73.89°(4) for 1 and 71.80°(6) for 2, the different positions of the methoxy group in the modified coumarin molecules (position 2 for 1 and position 4 of the phenyl ring for 2), influences dramatically the packing of molecules in their crystal structure. The structure in 1 is built mainly through C-H $\cdots\pi$ (T-shaped) interactions (Table 1S), as already observed (Vijayakumar et al., 2012). Through the C2-H2 \cdots Cg1 (4.016 Å) and C1-H1 \cdots Cg2 (3.685Å) interactions (Table 1S, Cg1 and Cg2 stands for centroids of O1, C5, C6, C7, C9, C10 and C11, C12, C13, C14, C15, C16 rings, respectively) a bilayer of modified coumarin molecules, parallel to the (001) plane is formed as shown in Figure 1(iii) (top view) and Figure 1 (iv) (side view). These bilayers stack parallel to the *c* (Figure 1v) and interact through C17-H17B \cdots Cg2 (3.652 Å) interactions (Table 1S). The modified coumarin molecules in 2 interact through C1-H1 \cdots O2 (3.309 Å), C2-H2 \cdots O1(3.577 Å), C2-H8C \cdots O3 (3.351 Å) hydrogen bonds (Figure 1vi top and 1vii side view, Table 1S) and form layers parallel to (100) plane. The coumarin core, lying in neighboring layers, interact through π - π interactions, thus forming bilayers (Figure 1vi and 1vii). These π - π interactions are of the offset π -stacked (parallel displaced, [8]) type with the least squares planes of coumarin core of centrosymmetrically related neighboring molecules to be at a distance 3.492(2) Å. Such parallel displaced dimeric structures may have even lower than T-shaped dimers (Janiak, 2000). These bilayers are stacked parallel to the crystallographic axis without any significant interactions.

Table 1S: Crystallographic data for compounds 1 and 2

Crystal data and results of structure refinement	Bond lengths (Å)					
	1		2		1	
Formula	C ₁₇ H ₁₄ O ₃	C ₁₇ H ₁₄ O ₃	C10—O1	1.373(2)	O1—C9	1.378 (2)
Wavelength (Å)	1.54178	1.54178	C5—O1	1.378 (2)	O1—C6	1.384 (2)
	CuKα	CuKα				
Fw	266.28	266.28	C10—O2	1.209 (2)	O2—C9	1.211 (2)
T (K)	160(2)	160(2)	C16—O3	1.365 (1)	O3—C14	1.369 (2)
Crystal system	Monoclinic	Monoclinic	C17—O3	1.426 (2)	O3—C17	1.431 (3)
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>c</i>	C7—C9	1.353 (2)	C7—C10	1.351 (2)
a (Å)	7.6462 (1)	9.8976 (2)	C9—C10	1.464 (2)	C9—C10	1.462 (3)
b (Å)	9.0608 (2)	16.0754 (3)	C9—C11	1.490 (2)	C10—C11	1.492 (2)
c (Å)	18.8955 (3)	9.3254 (2)	C11—C16	1.405 (2)	C11—C16	1.384 (3)
β (°)	97.665 (1)	116.001 (2)	C11—C12	1.390 (2)	C11—C12	1.392 (3)
Volume (Å ³)	1297.40 (4)	1333.57 (5)	C12—C13	1.389 (2)	C12—C13	1.381 (3)
Z	4	4	C13—C14	1.380 (2)	C13—C14	1.389 (3)
D(calc), Mg m ⁻³	1.363	1.326	C14—C15	1.389 (2)	C14—C15	1.383 (3)
Abs. coef., μ, mm ⁻¹	0.76	0.74	C15—C16	1.386 (2)	C15—C16	1.389 (3)
(Δρ) _{max} /(Δρ) _{min} e/Å ³	0.18/0.18	0.21/-0.22	C10— O1—C5	121.82 (9)	C9—O1— C6	121.8 (2)
Goodness-of-fit on F ²	1.07	1.00	C16— O3—C17	117.6 (1)	C14— O3—C17	117.2(2)
θ _{max} (°)	65°	65°	O1—C5— C6	121.0 (1)	O1—C6— C5	120.6 (2)
Reflections collected	11671	9331	C7—C9— C10	120.7 (1)	C7— C10—C9	121.0 (2)
Unique reflections	2185	2145	C12— C11—C16	118.8 (1)	C16— C11—C12	118.1 (2)
parameters	216	216	C13— C12—C11	120.8 (1)	C13— C12—C11	120.7 (2)
R1	0.031a	0.0495b	C14— C13—C12	119.5 (1)	C12— C13—C14	120.5 (2)
wR2	0.0764a	0.1302b	C13— C14—C15	121.1 (1)	C15— C14—C13	119.4 (2)
R1 (for all data)	0.03339	0.0730	C16— C15—C14	119.1 (1)	C14— C15—C16	119.5 (2)
wR2 (for all data)	0.0783	0.1491	C15— C16—C11	120.7 (1)	C11— C16—C15	121.7 (2)
Hydrogen bond geometry for compound 1						
D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)		
C2-H2...Cg1 ⁱ	0.99	3.14	4.016 (1)	149		
C1-H1...Cg2 ⁱⁱ	0.99	2.77	3.685 (1)	154		
C17-H17B...Cg2 ⁱⁱⁱ	0.98	2.73	3.652 (1)	156		
Hydrogen bond geometry for compound 2						
C1-H1...O2 ^{iv}	0.93	2.37	3.309 (3)	152		
C2-H2...O1 ^{iv}	0.97	2.79	3.577 (3)	139		
C8-H8C...O3 ^v	0.98	2.60	3.351 (2)	134		

^a2003 reflections with $I > 2\sigma(I)$; ^b1369 reflections with $I > 2\sigma(I)$

(i): 2-x, -0.5+y, 0.5-z; (ii): 1-x, -0.5+y, 0.5-z; (iii): 1-x, 1-y, -z; (iv): x, 0.5-y, -0.5+z; (v): x, -0.5-y, -0.5+z

Crystallographic data for the structures presented in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 975837, 975838. Copies of data can be obtained free of charge, on application to CCDC, 12Union Road, Cambridge CB2 1Ez, UK.

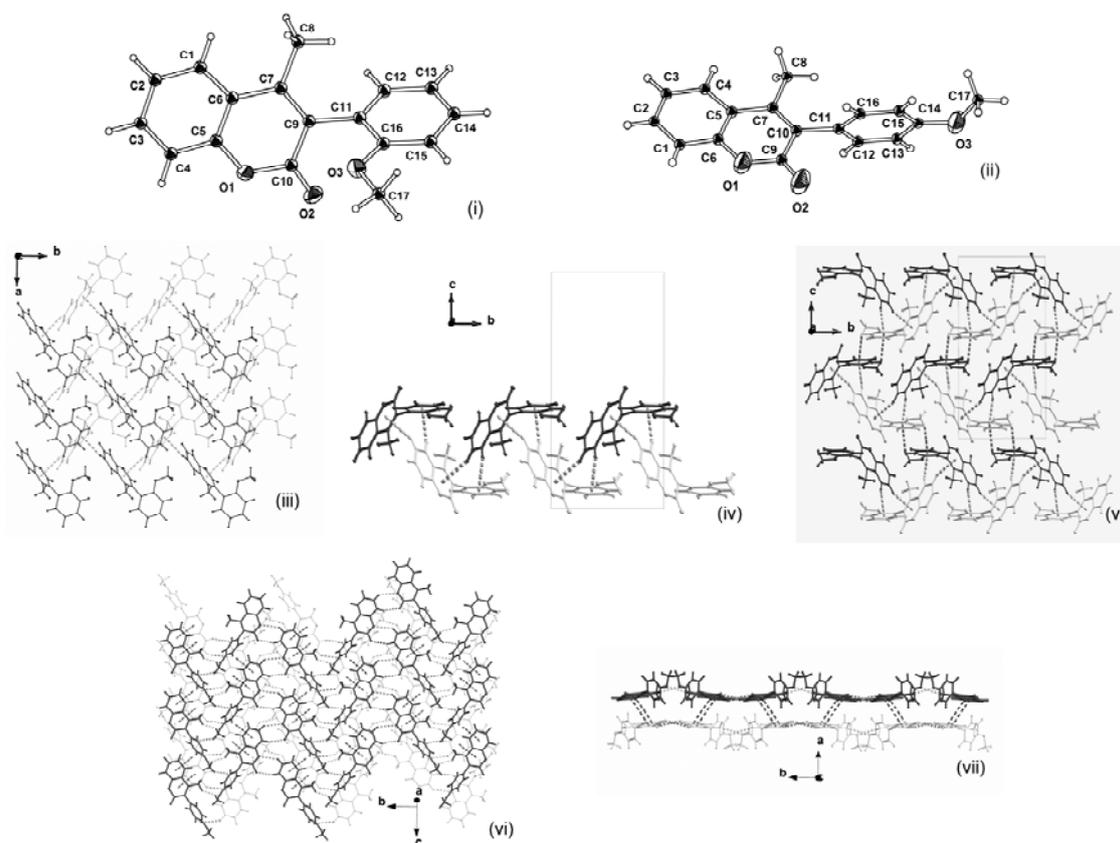


Figure 1: (i) and (ii) Ortep diagrams (thermal ellipsoid probability is 50%) for compound 1 and 2, respectively, (iii) top view and (iv) side view of bilayers formed by ortho-modified coumarin molecules of structure 1, (v) stacking of bilayers in 1 along *c* crystallographic axis formed through *Cg...* interactions, (vi) Top view and (vii) side view of bilayers of meta-modified coumarin molecules in structure of compound 2.

X-ray powder diffraction measurements on samples prepared on substrate glass, from solutions in dichloromethane give diffractograms with characteristics of a random oriented polycrystalline film in the case of 1 (Figure 2(i)) and a highly oriented one in the case of 2 (Figure 2(ii)). Powder diagrams recorded from a polycrystalline sample prepared from the batch which gave the studied single crystal gave diagrams which match that of the theoretical one (exp. powder, Fig. 1i). The peaks recorded from the powder deposited on the PEC unit (powder from PEC, Fig. 1i), from thin films on glass (film on glass, Fig. 1i) and the same material in the form of powder (powder from glass, Fig. 1i) does not match those corresponding to theoretical ones, which indicate a possible crystal structure transformation of 1, a result which is currently under further investigation. In the films prepared from 2, according to Figure 2(ii), as far as the only observed peaks are those with $(0k0)$ and $k=2n$, the crystallites are oriented with the *b* crystallographic axis normal to the film. Taking into account the structure of 2 (Figures 1(vi) and (vii)) the layers of 2 are normal to substrate surface. The highly oriented crystallites in the glass films of 2 are further supported by rocking curve XRD measurements which give a curve with $\text{FWHM}=1.25^\circ$ (inset in Figure 2(ii)).

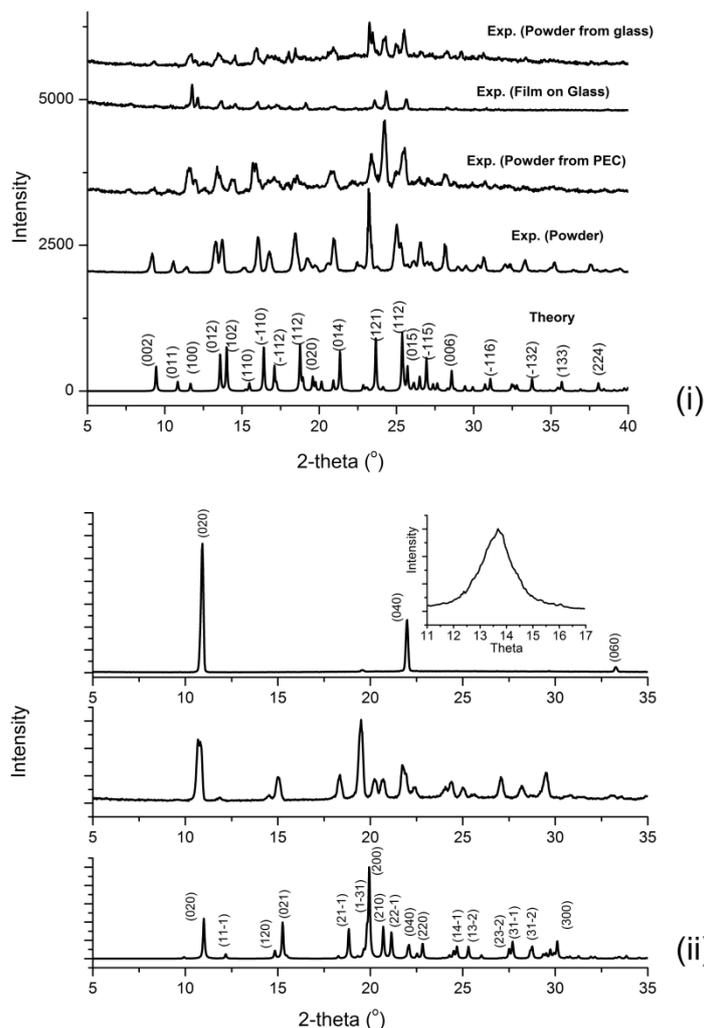


Figure 2: (i) X-ray powder diffraction diagrams from 1, theoretical based on the structure model determined at 160 K, experimental at RT, experimental on films. (ii) X-ray powder diffraction diagrams from 2, theoretical based on the structure model determined at 160 K, experimental at RT, experimental on films.

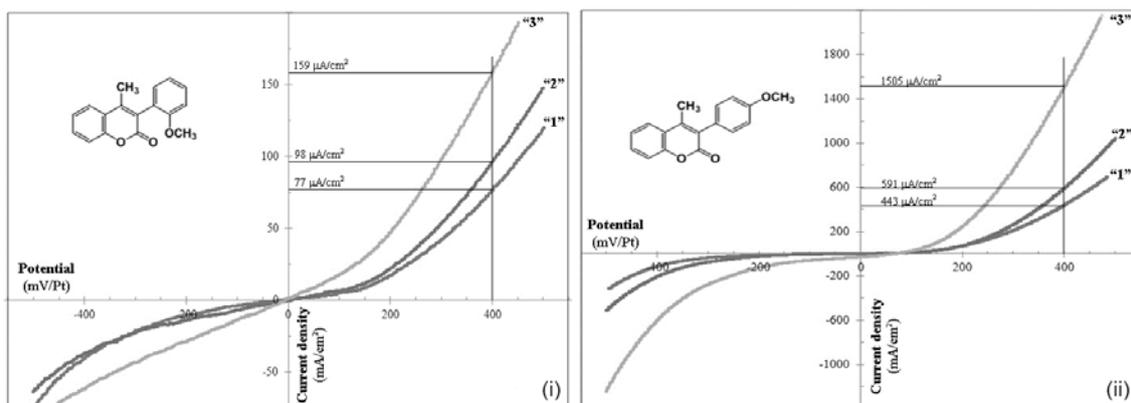


Figure 3: (i) and (ii) Current density vs. electrochemical potential given by 1 and 2, respectively, used directly as absorbed electrodes in a conventional PEC in the dark: "1" and under illumination of 1,000 W/m²: "2" and 10,000 W/m²: "3".

Concerning their photoelectrochemical behavior, as derived by the Figs. 3(i) and 3(ii), **2** presents an obviously higher current density (more than ten times higher) in comparison to **1**, especially in the area of positive potentials. The importance of crystal structure, molecule arrangement, orientation and isomerization on optoelectronic properties have also been reported (Saito et al., 1997 & Wang et al., 2013).

4. Conclusions

The coumarin derivatives 3-(2-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (**1**) and 3-(4-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (**2**) have been studied as far as concern their molecular structure and photoresistivity, attributed to the existence of extended π -conjugated systems in their molecules. However, **2** exhibits more than ten times higher photoconductivity.

This significant deviation, as derived by their crystallographic evaluation, seems to be correlated to a different spatial arrangement of the molecules. Consequently, their final construction is greatly affected by steric forces. This fact is probably reinforced by the impulsions between the electron clouds of the carbonyl and methoxy groups, as well.

Thus, the selection of the appropriate substituents in the various positions at the aromatic ring can affect not only the physicochemical properties, such as the semiconductive behavior of the corresponding compounds, but also can modify the spatial arrangement of their molecules.

Acknowledgement

Financial support by the Basic Research Committee Programme 'PEBE 2009, 65/1796' concerning the synthesis and photoelectrochemical study of the compounds, is gratefully acknowledged.

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