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From Solid State Photodimers of Ethyl Coumarin-3-carboxylate to their Alcoholysis Derivatives. A Supramolecular Study

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The solid state photodimerization of ethyl coumarin-3-carboxylate and its 6-Cl and 6-Br (1a–c) derivatives as well as the methyl and ethyl alcoholysis derivatives of ethyl coumarin-3-carboxylate photodimer are reported in the context of crystal engineering. Ethyl coumarin-3-carboxylates photodimerize topochemically to form anti head-to-tail stereoisomers (2a–c). The extent of lactone methanolysis of 2a depends on the boiling temperature of the solvent to produce 2-(2-hydroxyphenyl)-3-oxo-8b*H*-4-oxa-cyclobuta[a]naphthalene-1,1,2a-tricarboxylic acid 1,2a-diethyl ester 1-methyl ester (3a) and 2,4-bis-[(2-hydroxyphenyl]cyclobutane-1,1,3,3-tetracarboxylic acid diethyl ester dimethyl ester (4a) in 1:2 proportion, whereas the ethanolysis of 2a only yields 2-(2-hydroxyphenyl)-3-oxo-8b*H*-4-oxa-cyclobuta[a]naphthalene-1,1,2a-tricarboxylic acid triethyl ester (5a). The molecular structure of 2a–c and 3–5a were elucidated by ^{1}H and ^{13}C NMR spectroscopy. Also the molecular and supramolecular structures of 2a,b and 3,4a were studied by X-ray diffraction. Most of the C—H···X (X=O, Ph), π···π and dipolar interactions in the photodimers 2a,b and derivative 3a are preserved from the corresponding original coumarin monomers. Thus the supramolecular structure of ethyl coumarin-3-carboxylate is conserved through this group of compounds as if they would have a "supramolecular memory".

Keywords: Solid state photodimers; Ethyl coumarin-3-carboxylate; Carbonyl–carbonyl interactions; Chlorine–carbonyl interactions; Pi···pi and C—H···pi interactions

INTRODUCTION

The photodimerization of organic molecules in the solid state has been known from the last century [1], however after the pioneering work of Kohlshutter [2] and Schmidt [3,4] on cinnamic acids the reaction was known to be topochemical. It means that the stereochemistry of the products is determined by the relative arrangement of the molecules in the crystal. Thus, this reaction is stereoselective and environmentally friendly, in addition it has been a paradigm to rationalize the factors and forces that appropriately arrange the molecules in the solid to photodimerize. A nice discussion about topochemical postulate can be found elsewhere [5]. A typical example of the use of crystal engineering to organize double bonds is the use of phenyl–perfluorophenyl interactions [6]. Recently, the application of molecular templates to control [2 + 2] photodimerization in the solid state have been described [7].

Coumarins are considered as cinnamic acid derivatives and since the discovery of coumarin photodimerization in solution by sunlight [8], they have been widely studied. Coumarin itself is photoinert in the solid state [9], thus several strategies have been followed to preorganize coumarin molecules through intermolecular forces, which include the formation of solid inclusion complexes with chiral diols [10] or cyclodextrin [11]; forming self-assembled monolayers on polycrystalline gold [12] or grafted into porous materials [13]. Coumarin photoreactivity in solid state has found application as photocuring materials [14] and to impart photostitching capabilities to nanotubes [15].

Several efforts to systematize the structural factors that influence the crystal packing towards

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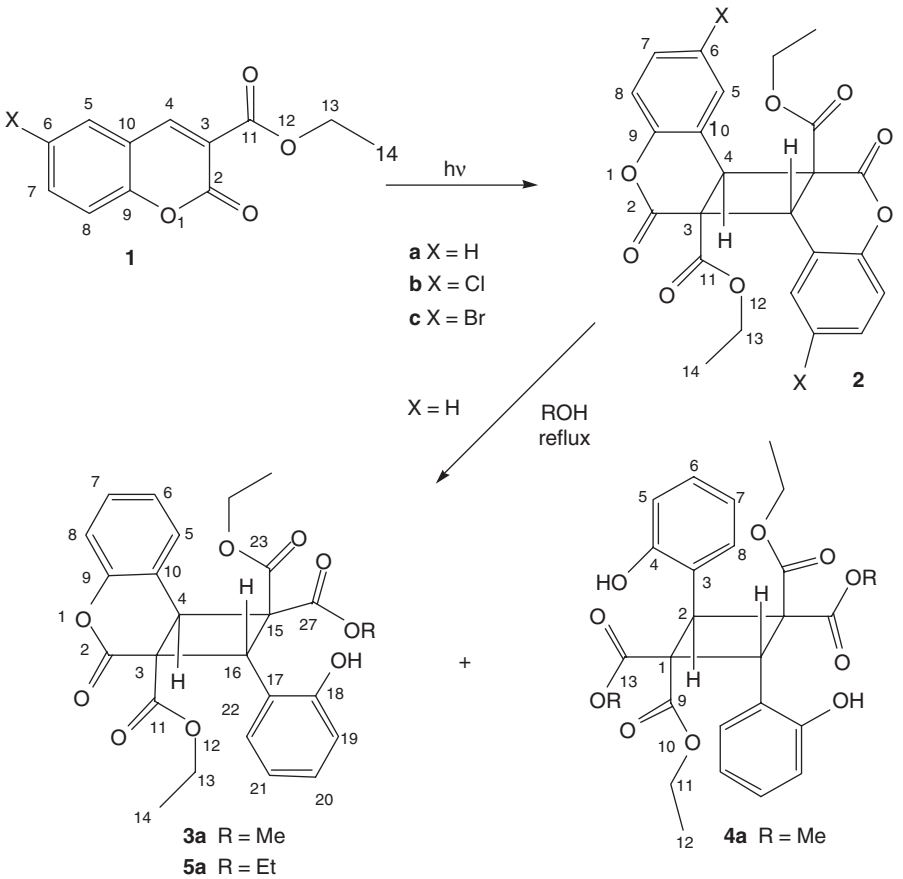
photoreactivity of substituted coumarins have been carried out [16]. A variety of substituted coumarin derivatives at 4, 6 and 7 positions bearing OH, CH_3, Cl, $OCOCH_3$, OCH_3 [9] or F groups [17] has been studied in the solid state. The findings indicate that the reaction is not always topochemical. However the photodimerization of monosubstituted coumarins in the 3-position has not yet been studied so far, in spite of their very well known pharmacological activities. Particularly, 3-carboxycoumarin derivatives have been reported as tautomerase [18], elastase [19], α-chymotrypsin [20] inhibitors and, more recently, also as a very potent thrombin inhibitor [21], although little is known about the forces that regulate the molecular recognition interactions involved. In this context, a study of the supramolecular structure of several 3-carboxy coumarins was reported elsewhere [22–26] in which π-stacking as well as C—H···(X═O, aryl) hydrogen bonding interactions were found as the predominant motifs. In this paper, the photodimerization of ethyl coumarin 3-carboxylate (**1a**) and its 6-Cl (**1b**) and 6-Br (**1c**) derivatives is reported, as well as the crystallographic study of photodimers **2a**, **2b** and **3a**–**5a** alcoholysis derivatives of **2a** (Scheme 1).

RESULTS AND DISCUSSION

Synthesis

Coumarins **1a**–**c** underwent photodimerization in the solid state to form, from the four possible stereoisomers, only the anti head-to-tail one (Scheme 1). These results contrast with the stereoisomer found for 6-Cl and 4-Cl-coumarins, which photodimerize as the syn-head-to-head and as a mixture of anti head-to-head and syn head-to-tail stereoisomers, respectively [9]. Finely pulverized solid samples of **1a** were irradiated for 10 h to achieve 100% of conversion while only 6 h were required for the halogenated derivatives **1b**,**c**. The course of the reaction was monitored by integration of the relative ^{1}H NMR intensities of the H-4 signal for coumarin **1a**–**c** and the corresponding photodimer **2a**–**c** and no induction time was required in any case. Coumarins are preorganized through intermolecular forces in the solid state in order to photodimerization can occur. The packing arrangements of **1a**–**c** correspond to hydrogen-bonded layers centrosymetrically related through π-interactions. The molecular and supramolecular



SCHEME 1

structures of **1a** [22] and **1b**,**c** [27] were published elsewhere. The distance between C3···C4 double bonds are of 3.512(2) Å (along the a axis) for **1a**, 3.602(3) Å for **1b** and 3.592(4) Å for **1c** (along the *c* axis). The above mentioned reaction features are characteristic of a topochemical reaction and the anti-ht stereoisomers are the expected ones [4]. The distance between the neighbouring double bonds is not the only factor that influences the quantum yield of the reaction. The halogen atom exerts a strong influence on the relative quantum yields. This effect could be due to the increased number of intermolecular contacts found in **1b** in relation to **1a**.

The structure of photodimers were elucidated from NMR data and their stereochemistry confirmed by X-ray analysis. The structure was numbered according the original coumarin monomers for comparison purposes, as shown in Scheme 1. The cyclobutane proton H-4 appears as a singlet around 4.9 ppm, in contrast to the singlet observed at 8.1 ppm in the monomers. In ^{13}C NMR spectra, the signals for cyclobutane carbon atoms C-3 and C-4 appear near to 52 ppm and 46 ppm, approximately, in contrast to corresponding vinyl carbon atoms, in **1a–c** which appear near to 118 ppm and 147 ppm, respectively. A summary of ^{1}H and ^{13}C NMR data for **2a–c** is listed in Table I.

The lactone ring of photodimer **2a** is prone to thermal alcoholysis; the extent of it depends on the boiling temperature of the solvent. The photodimer **2a** was refluxed in methyl alcohol for 2 days to form a mixture of products identified as **3a** and **4a** in 1:2 ratio. When ethyl alcohol is used, product **5a** was isolated as the only one after two days of reaction time. In the case of **3a** and **4a**, trans-esterification was not observed. Products **3a** and **5a** show two singlets for cyclobutane protons; one broad at ca. 5.2 ppm and the other sharp at ca. 5.5 ppm, assigned to H-4 and H-16 protons, respectively. The assignment was done by the nOe effect of H-16 on H-5 and H-22 protons. The broad signal for H-4 points out the increased flexibility of the cyclobutane ring due to the partial release of the ring tension as the result of lactone ring opening. The four ^{13}C NMR signals for cyclobutane ring carbon atoms C-3, C-4, C-15 and C-16 appear in the expected range of 63–42 ppm. The ^{1}H NMR spectrum of **4a** shows one sharp singlet at 5.96 ppm for cyclobutane proton H-2, strongly deshielded due to ester carbonyls nearby. Because of symmetry, only two signals are observed for cyclobutane carbon atoms at 60.5 and 42.6 for C-1 and C-2, respectively.

Molecular and Supramolecular Structures of 2a and 2b

Crystals suitable for X-ray analysis were obtained from $CHCl_3$ solutions of **2a** and **2b**, in the case of **2c** only microcrystalline powder was obtained. The X-ray analysis of **2a** and **2b** allowed us to confirm their anti-ht stereochemistry. A summary of bond lengths and angles is listed in Table II and the molecular structures are shown in Figs. 1(a) and 2(a), respectively. Coumarin skeleton geometric parameters are comparable with those values reported for similar structures [28]. In both molecules the cyclobutane ring bond distance C3—C4 is significantly shorter than C3—C4a (between the two photodimerized coumarin rings), however they are in the expected range for C(sp^3)—C(sp^3) bond length of 1.554(21) Å [29], in contrast to C3(sp^2)—C4(sp^2) mean double bond length of 1.343(10) Å in the monomers. In general, the cyclobutane ring is not a perfect square in coumarin photodimers, as have been also observed for syn-ht 7-OMe (1.539 and 1.570(2) Å (mean)) [7]; and anti-ht 7-Me (1.55(2) and 1.59(2) Å mean) [30] coumarin photodimers. However the corresponding C3—C4a distance is always longer than C3—C4 distance. Such difference in length is larger for C3 or C4 substituted coumarins than for non substituted ones, probably due to steric effects.

The angles C4—C3—C4a and C3—C4—C3a take values very close to 90° showing the high ring tension characteristic for a four membered ring. The complementary angles around C3 take the following values for **2a**: C2C3C11 = 109.58(15), C4C3C11 = 115.39(13), C11C3C4a = 114.08(15); and C3C4C10 = 115.40(13), C10C4C3a = 118.19(14), indicating distorted tetrahedron geometry around both atoms. This is also observed for **2b**. In both compounds the lactone and carboxyethyl carbonyls adopt an alternated conformation to avoid electron repulsion with torsion angles O2C2C3C11 = 56.2(3) and

TABLE I Selected ^{1}H and ^{13}C chemical shifts (δ) for compounds **2a–c** and **3–5a**

Compound	H4	H16	OH	C3	C4	C15(1)†	C16(2)†
2a	4.92			52.9	46.8		
2b	4.84			52.4	46.4		
2c	4.85			52.5	46.3		
3a	5.24	5.51	6.1	61.5	52.1	61.5	43.5
4a‡	5.96		9.5			60.5	42.6
5a	5.21	5.51	6.4	62.5	52.1	61.4	42.5

† The numbering in brackets corresponds to compound **4a**. ‡ [$^{2}H_6$]DMSO was used as solvent.

TABLE II Selected bonding geometric parameters for **2a**,**b** and **3**,**4a**

Atoms	**2a**	**2b**	**3a**	Atoms	**4a**
			Bond lengths/Å		
Cl1—C6		1.734(4)			
C3—C4	1.551(2)	1.539(4)	1.537(4)		
C3—C4a(16)†	1.590(2)	1.580(4)	1.576(4)		
C4—C15			1.566(4)	C1—C2a	1.567(5)
C15—C16			1.577(4)	C1—C2	1.574(5)
O1—C9	1.396(3)	1.380(4)	1.387(4)	C4—O4	1.377(5)
C3—C11	1.518(2)	1.504(5)	1.514(4)		
C2—C3	1.512(3)	1.515(4)	1.528(4)		
C4—C10	1.488(2)	1.483(4)	1.498(4)	C2—C3	1.501(6)
			Bond angles/(°)		
C4C3C4a(16)†	89.45(12)	89.4(2)	91.0(2)		
C3C4C3a(15)	90.54(11)	90.6(2)	89.4(2)		
C3C16C15			87.6(2)	C1C2C1a	89.4(3)
C4C15C16			89.9(2)	C2C1C2a	90.6(3)
C2C3C11	109.58(15)	109.2(3)	106.6(2)		
C4C3C11	115.39(13)	115.6(3)	115.7(2)		
C3C4C10	115.40(13)	115.8(2)	116.2(2)		
C10C4C3a(15)†	118.19(14)	118.8(3)	121.6(2)		
C2C3C4a(16)†	109.73(14)	109.9(3)	110.0(2)		
C16C15C23			109.7(2)	C2C1C9	111.7(3)
C2O1C9	123.88(17)	123.7(3)	123.1(2)		
O1C2O2	117.42(2)	118.3(3)	118.3(3)		
C2C3C4	117.26(15)	117.2(3)	114.5(2)		
O1C2C3	119.31(17)	118.7(3)	117.8(3)		
C15C16C17			121.3(2)		
C11C3C4a(16)†	114.08(15)	114.3(3)	118.8(2)		
			Torsion angles/(°)		
C4a(16)†C3C4C3a(15)†	0.00(14)	0.0(2)	−11.3(2)	C2aC1C2C1a	0.0(3)
O2C2C3C11	56.2(3)	−61.1(4)	75.1(4)	O13C13C1C9	−112.9(4)
C2C3C11O11	−8.2(3)	12.4(5)	103.3(4)		
C3C16C17C18			54.0(4)		
C16C15C27O27			127.9(3)	C2C1C13O13	−121.1(4)
C16C15C23O23			−27.9(5)	C2C1C9O9	−17.8(5)
C27C15C23O23			−161.3(4)	C13C1C9O9	112.6(4)
C23C15C27O27			−103.8(4)	C9C1C13O13	112.9(4)
C15C16C17C18			−52.9(4)	C1C2C3C4	61.7(6)
C4C15C23O23			69.6(5)		

† Numbering in brackets correspond to compound **3a**.

C2C3C11O11 = −8.2(3) in **2a** and −61.1(4) and 12.4(5) in **2b**, respectively. Lactone carbonyl is out of the mean plane defined by O1C2C3C4C5C6C7C8C9C10 by 4.61(7)° in **2a** and 9.13(11)° in **2b**, probably due to its involvement in intermolecular interactions.

The two monomers **1a** and **1b** are isomorphs and crystallize in the monoclinic space group $P2_1/c$, whereas photodimer **2a** crystallizes in the triclinic space group P-1 and **2b** does it as a monoclinic $P2_1/c$ system. It is interesting to note that even when the molecular structure of both photodimers is very similar, the replacement of a single H atom in **2a** by Cl atom in **2b**, dramatically alters not only the crystallization behaviour but also the molecular packing. The supramolecular structure of **2a** is given by self complementary C4—H4···O2^{i} interactions [C4···O2 = 3.379(2) Å, C4—H4···O2 = 158(1)°, symmetry code (*i*) 1 + x, y, z] to form $R_2^2(10)$ rings [31]. This motif develops along the (0 7 6) direction forming tapes interlinked by C13—H13A···O11^{ii} interactions [C13···O11 = 3.283(7) Å, C13—H13A···O11 = 137(1)°, symmetry code (*ii*) 1 − x, 2 − y, 1 − z] to form $R_2^2(10)$ rings along the (001) direction, giving rise to the second dimension, Fig. 1(b). Hydrogen bonding geometry is listed in Table III. The third dimension is achieved through face to face π···π stacking [32], along the (−4 8 17) direction, between the π-deficient lactone ring [*Cg*(*1*)] and the π-rich bencenoid ring [*Cg*(*2*)], as shown by the *Cg*(*1*)···*Cg*(*2*)^{iii} intercentroid and interplanar distances as well as torsion angle of 3.8480(15), 3.602(2) Å, and −0.22(2)° [symmetry code (*iii*) 1 − x, 1 − y, −z], respectively, Fig. 1(c). The set of C—H···O and face to face π···π stacking interactions strongly resemble the supramolecular structure of the monomer **1a** [22].

The supramolecular structure of the isostructural compound **2b** is given by C—H···O and dipolar interactions. Hydrogen bonding geometry is listed in Table III. Self complementary C7—H7···O2^{iv} [C7···O2 = 3.339(5) Å, C7—H7···O2 = 141(1)°] and C8—H8···O11^{iv} [C8···O11 = 3.418(5) Å, C8—H8···O11 = 154(1)°, symmetry code (*iv*) 2 − x, $-\frac{1}{2}$ + y, $\frac{1}{2}$ + z] soft interactions form a $R_2^2(9)$ ring. Each consecutive ring alternate in the family of planes [4 −8 −13] and [3 8 −25] to form twisted tapes. The set of inversion-reflection related tapes conform

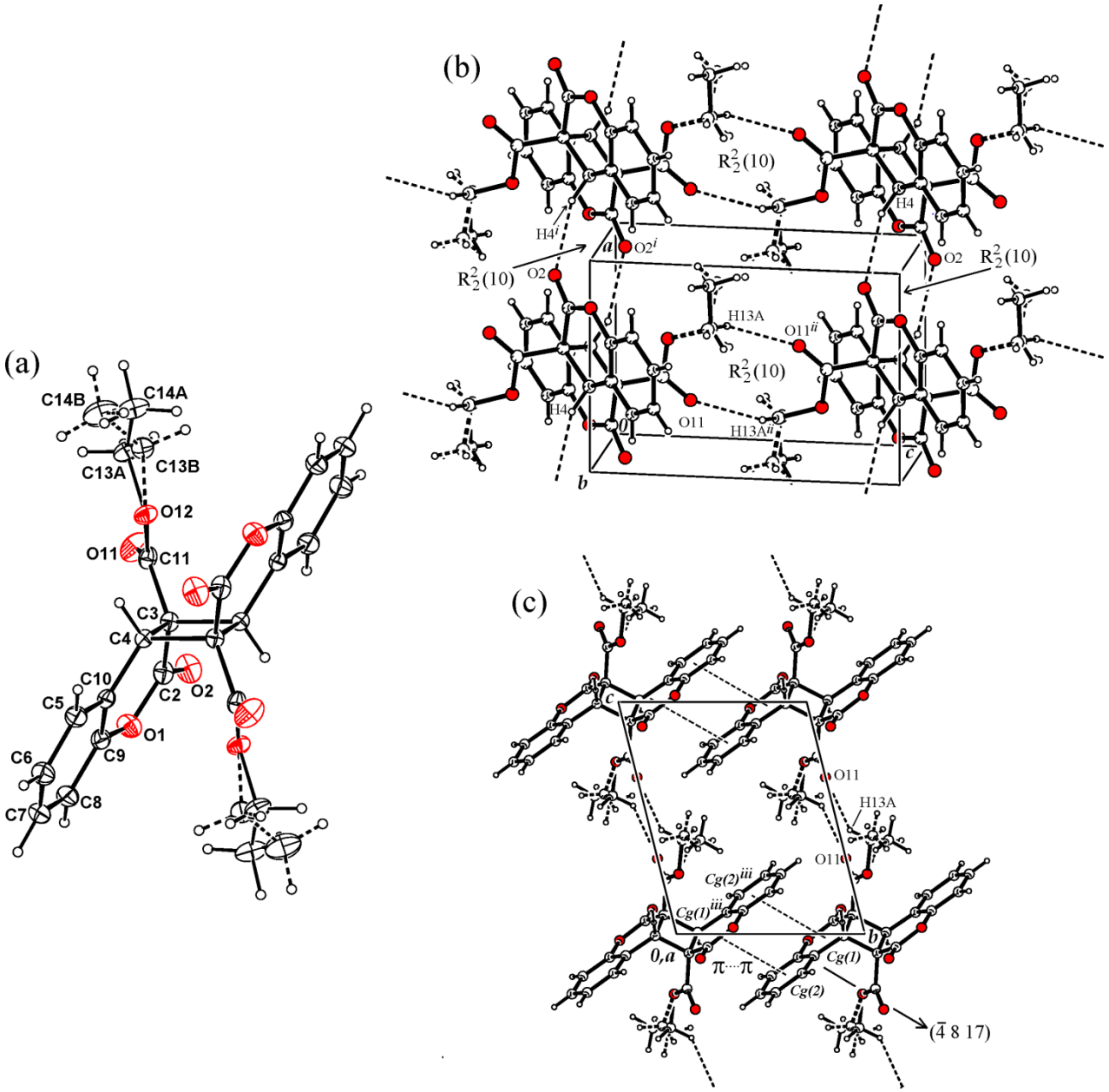


FIGURE 1 (a) Molecular structure of compound **2a**. Supramolecular structure of compound **2a**: (b) partial view showing two different $R_2^2(10)$ motifs; (c) view on the *bc* plane of $Cg(1)\cdots Cg(2)^{iii}$ interactions that propagate along the (−4 8 17) direction.

Hydrogen bonded sufaces interlinked by C4—H4···O2^{v} contacts [C4···O2 = 3.429(4) Å, C4—H4···O2 = 163(1)°, symmetry code (*v*) −1 + x, y, z] which form $R_2^2(10)$ motifs, Fig. 2(b), as well as by Cl···π, Cl···CO and CO···CO dipolar interactions of (δ −)···(δ +) type along the *c* axis direction. The chlorine atom simultaneously donates electronic density to the lactone ring *Cg(1)* and to the carboxyethyl carbon C11 atom, both electron π-deficient moieties, forming a three centered interaction π(δ +)···Cl(δ −)···C(δ +), described as a $R_1^2(3)$ motif. The geometric parameters for C—Cl···*Cg(1)*^{vi} and C—Cl···C11O11^{vi} interaction are: CCl···*Cg(1)* = 3.3429(19) Å, C—Cl···*Cg(1)* = 126.82(12)° and CCl···C11O11 = 3.535(20) Å, C—Cl···C11 = 90.01(12)°, respectively [symmetry code (*vi*) = 1 − x, $-\frac{1}{2}$ + y, $\frac{1}{2}$ − z]. Both interactions are in the range of distance and show an almost perpendicular arrangement between the donor and the acceptor groups, in agreement with the "side-on" geometry proposed for C—X···E (X = halogen, E = electrophyle) [33,34] interactions, Fig. 2(c). Finally, C═O···C═O dipolar interactions with C2O2···C2O2^{vii} distance of 3.429(20) Å and C2═O2···C2^{vii} angle of 120.53(12)° [symmetry code (*vii*) = 2 − x, −y, −z], are in agreement with the sheared parallel type [35], complementing the crystal packing, Fig. 2(b). It is worthy to note that the above mentioned dipolar interactions strongly resemble the supramolecular structure of the monomer **1b** [27],

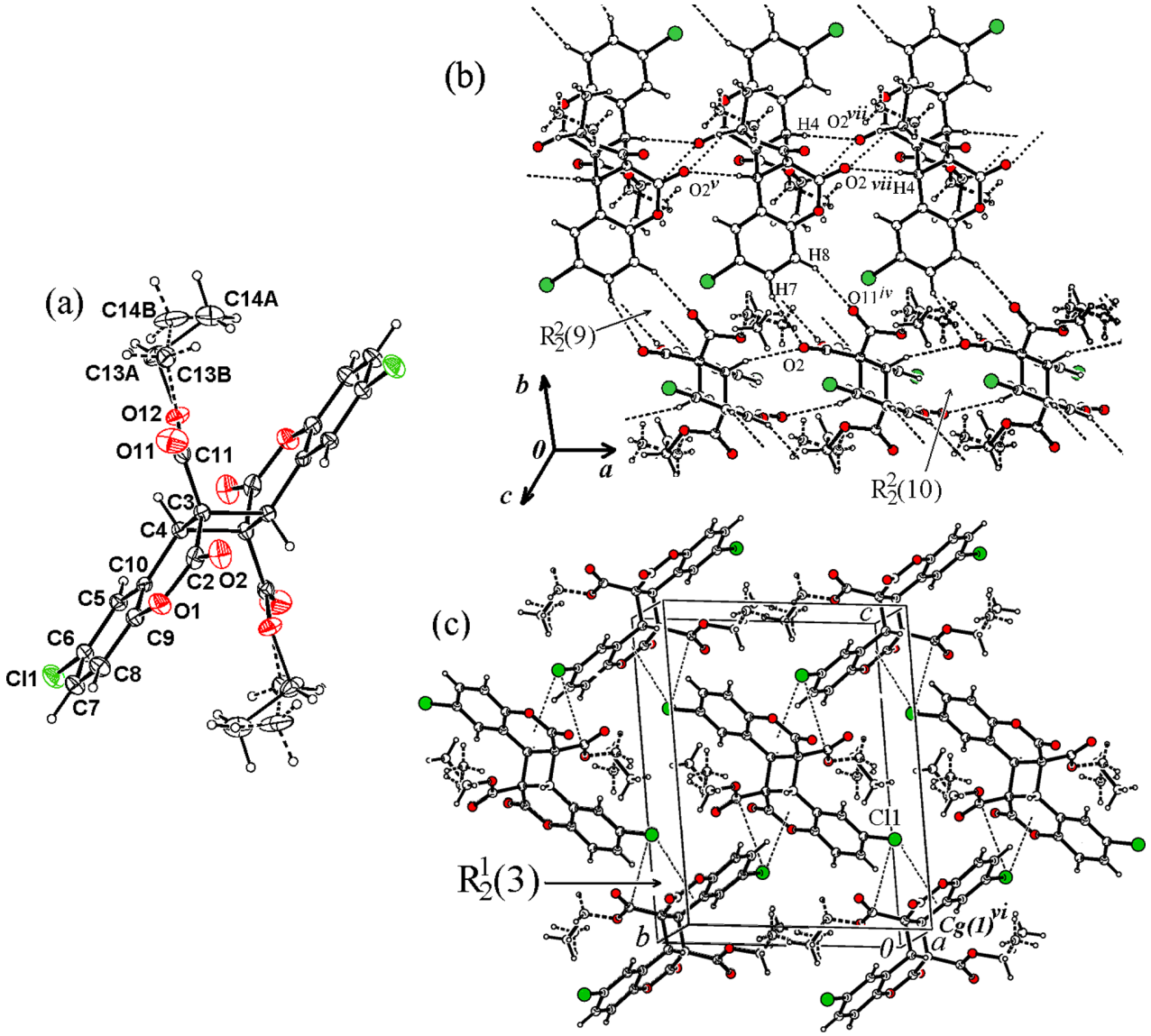


FIGURE 2 (a) Molecular structure of compound **2b**. Supramolecular structure of compound **2b**: (b) view showing $R_2^2(9)$ motifs that propagate in the family of planes [4 −8 −13] and [3 8 −25], $R_2^2(10)$ motifs propagating along the *a* axis and C2═O2···C2═2^{vii} dipolar interactions; (c) view on the *bc* plane of dipolar three centered $R_1^2(3)$ motif.

as was noticed before for **2a**. In the course of the photoreaction, van der Waals contacts between C3═C4 double bonds are converted to chemical bonds; and thus a dimensional mismatch between the product and reactant lattices exists, so it is expected that **2a**–**c** are formed as amorphous solids. However, photodimers **2a**,**b** crystallize in such way that most of the motifs of the original monomers are preserved, as if they would have a "supramolecular memory".

Molecular and Supramolecular Structure of 3a and 4a

Thermal methanolysis of 6-methylcoumarin photodimer was reported elsewhere [36], however to the best of our knowledge there are no reports on the molecular or the supramolecular structure of these types of compound.

The molecular structures of **3a** and **4a** are shown in Figs. 3(a) and 4(a), respectively, and a summary of bond lengths and angles is listed in Table II. The opening reaction of only one lactone ring by methyl alcohol generates that the four pro-chiral cyclobutane carbon atoms in **2a** become chiral, thus **3a** is formed as a racemic mixture. As discussed before for **2a**,**b**, the cyclobutane ring is not a perfect square, the value of C3—C4 length of 1.537(4) Å, corresponding to the lactone ring fusion is significantly shorter than length of the others sides. The angles of cyclobutane ring are very close to 90° being C3—C16—C15 the closer one with a value of 87.6(2)°. In contrast to photodimers **2a**,**b**, the cyclobutane ring in **3a** adopts a non planar conformation as the torsion angle C16—C3—C4—C15 of −11.3(2)° indicates. This distortion is similar to that found for syn-ht photodimer derivative of 7-OMe coumarin (19.3°) [9].

TABLE III Geometric parameters of intermolecular contacts for **2a**,**b** and **3**,**4a**

D—X···A	D—X(Å)	X···A(Å)	D···A(Å)	D—X···A(°)	Motif
		Intermolecular contacts for **2a**			
C4—H4···O2^{i}	0.98	2.45	3.379(2)	158(1)	$R_2^2(10)$
C13A—H13A···O(11)^{ii}	0.97	2.51	3.283(7)	137(1)	$R_2^2(10)$
		Intermolecular contacts for **2b**			
C7—H7···O2^{iv}	0.98	2.57	3.339(5)	141(1)	
C8—H8···O11^{iv}	0.93	2.56	3.418(5)	154(1)	$R_2^2(9)$
C4—H4···O2^{v}	0.98	2.48	3.429(4)	163(1)	$R_2^2(10)$
C6—Cl···*Cg*(1)^{vi}		3.3429(19)	4.596(4)	126.82(12)	
C—Cl···C11O11^{vi}		3.535(20)		90.01(12)	$R_1^2(3)$
		Intermolecular contacts for **3a**			
O18—H18···O27^{viii}	0.82	2.00	2.818(3)	179(1)	$R_2^2(16)$
C13—H13B···O2^{iii}		2.70	3.357(4)	126(1)	$R_2^2(14)$
C21—H21···O11^{v}	0.93	2.37	3.374(6)	166(1)	
C22—H22···*Cg*(2)^{v}		2.97	3.606(4)	127(1)	$R_2^2(9)$
		Intermolecular contacts for **4a**			
O4—H4···O9^{i}	0.84	1.90	2.735(3)	174	
C15—H15B···O9^{x}	0.98	2.51	3.346(5)	144	$R_2^2(14)$

Symmetry codes: (*i*) [1 + x,y,z], (*ii*) [1 − x, 2 − y,1 − z], (*iii*) [1 − x, 1 − y, − z], (*iv*) [2 − x, $-\frac{1}{2}$ + y, $\frac{1}{2}$ − z], (*v*) [−1 + x, y, z], (*vi*) [1 − x, $-\frac{1}{2}$ + y, $\frac{1}{2}$ − z], (*vii*) [2 − x, − y, − z], (*viii*) [1 − x, − y, − z], (*ix*) [1 − x, 1 − y, 1 − z], (*x*) [− x, 2 − y, 1 − z], (*xi*) [− x, 1 − y, − z].

Phenol ring and both carboxyl groups occupy an alternated conformation with respect to cyclobutane ring with torsion angles C3—C16—C17—C18 = 54.0(4)°, C4—C15—C23—O23 = 69.6(5)° and C16—C15—C27—O27 = 127.9(3)°. These last two carbonyls are antiperiplanar between each other with torsion angles C27—C15—C23—O23 = −161.3(4)° and C23—C15—C27—O27 = −103.8(4)°.

The phenol moiety, as the best H-donor in the molecule, directs the formation of H-bonded dimers through self complementary interactions with the carboxymethyl moiety of a neighbouring molecule:

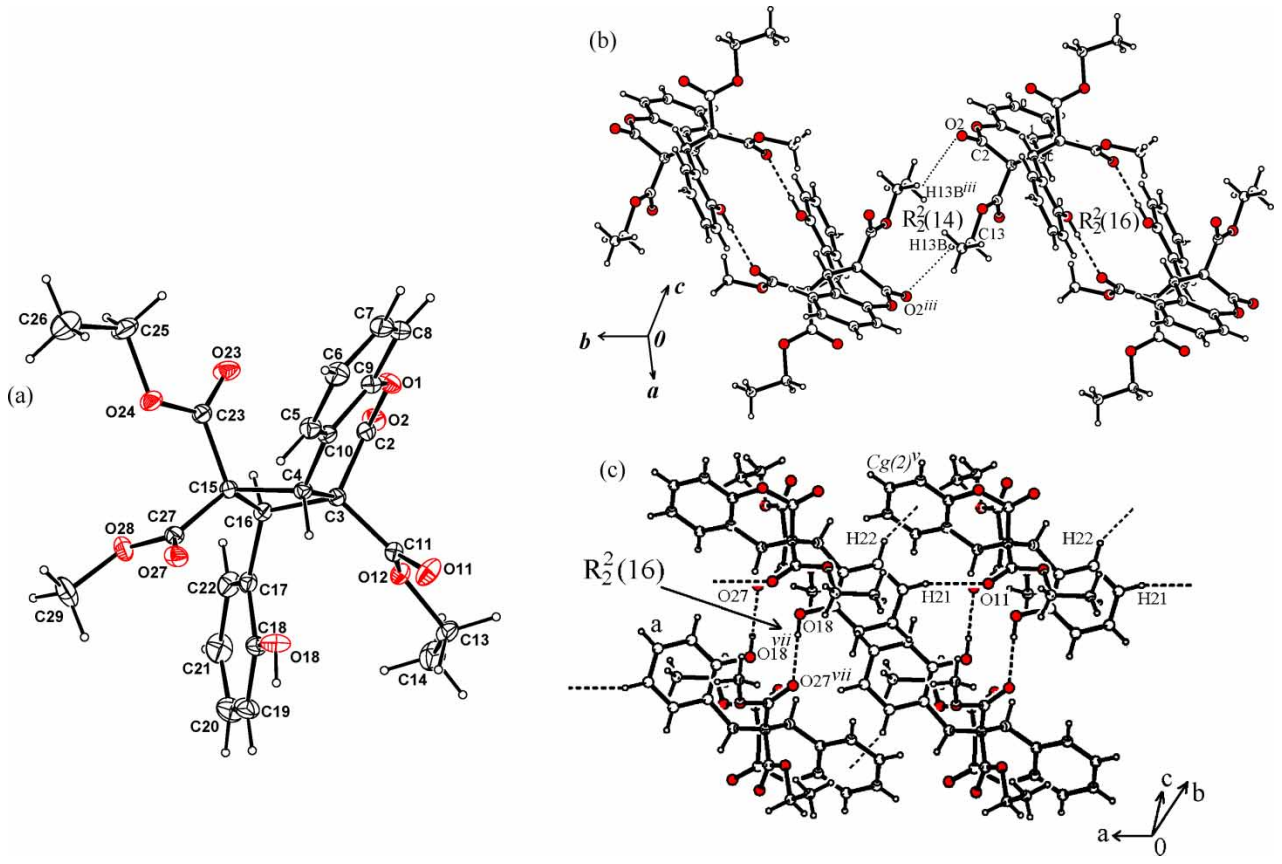


FIGURE 3 (a) Molecular structure of compound **3a**. Supramolecular structure of compound **3a**: (b) view of hydrogen bonded zig-zagging tape formed by $R_2^2(16)$ and $R_2^2(14)$ motifs on the *bc* plane; (c) view of C21—H21···O11^{v} and C22—H22···*Cg*(2)^{v} interactions.

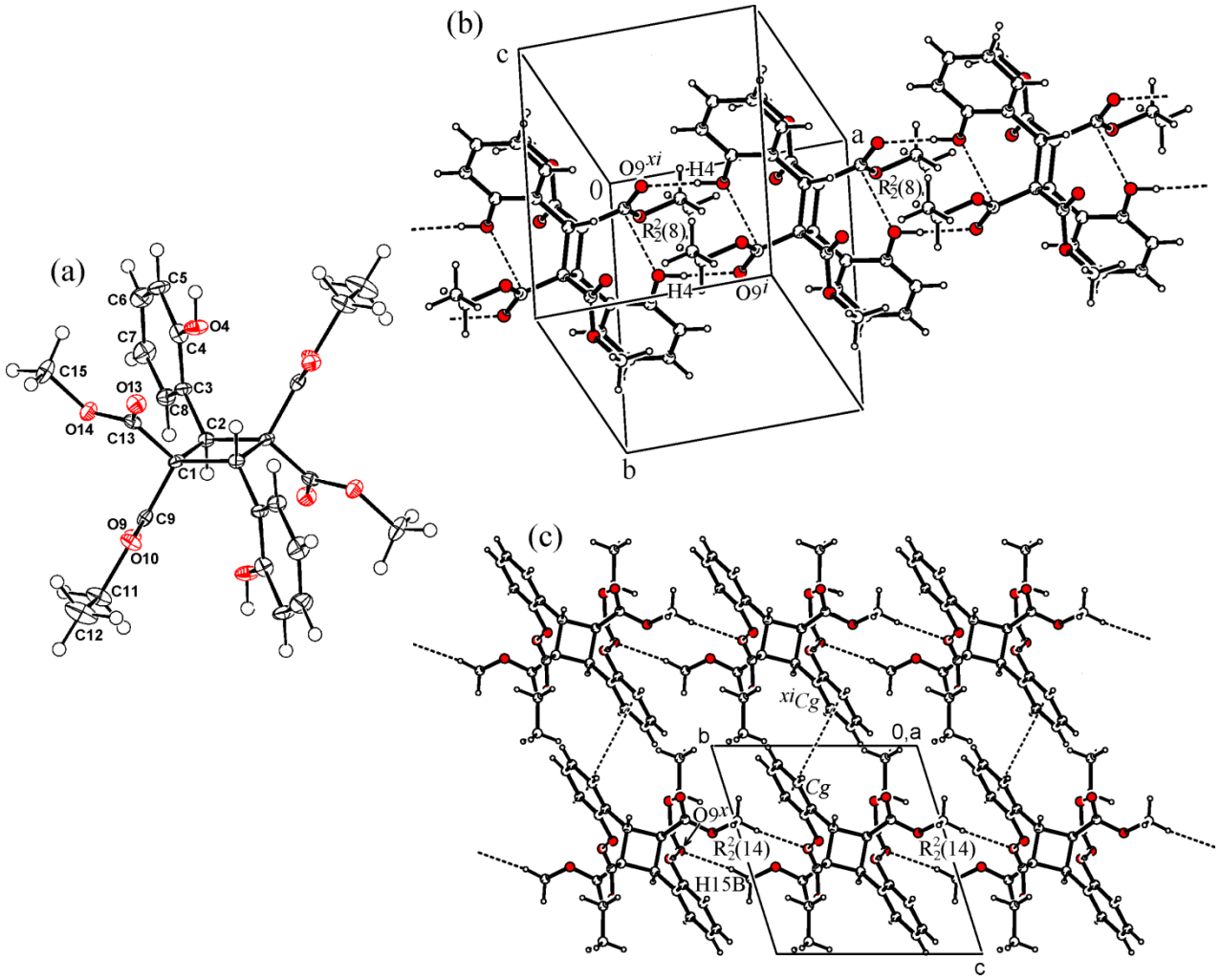


FIGURE 4 (a) Molecular structure of compound **4a**. Supramolecular structure of compound **4a**: (b) O4—H4···O9^{i} and dipolar H4O4···C9O9^{ix} hydroxy–carbonyl interactions forming $R_2^2(8)$ motifs that propagate as ladders along the (0 2 16) direction; (c) view along the *b* axis of C15—H15(B)···O9^{x} interactions forming $R_2^2(14)$ motifs and *Cg(1)*···*Cg(1)*^{xi} parallel displaced π···π stacking.

O18—H18···O27^{viii} [O18···O27 = 2.818(3) Å, O18—H18···O27 = 179(1)°, symmetry code (*viii*) 1 − x, − y, − z]. Thus a sixteen membered ring whose graph descriptor is $R_2^2(16)$ is formed. A hydrogen bonded zig-zagging tape on the *bc* direction is developed by very weak C13—H13B···O2^{iii} interactions [C13···O2 = 3.357(4) Å, C13—H13B···O2 = 126(1)°, symmetry code (*iii*) 1 − x, 1 − y, − z] that form $R_2^2(14)$ motifs, Fig. 3(b). The H-bonding geometric parameters are listed in Table III. These tapes are interlinked through soft C21—H21···O11^{v} [C21···O11 = 3.374(6) Å, C21—H21···O11 = 166(1)°] and C22—H22···*Cg*(2)^{v} [C22···*Cg*(2) = 3.606(4) Å, C22—H22···*Cg*(2) = 127(1)°, *Cg*(2) is the benzene ring of coumarin moiety] interactions to form nine membered rings $R_2^2(9)$ that propagate as tapes along the (001) direction, Fig. 3(c).

Complete methanolysis of **2a** to form **4a**, again produces an inversion-reflection plane of symmetry restarting the planarity of the cyclobutane ring and almost equalizing the ring angles [C2—C1—C2a = 90.6(3)° and C1—C2—C1a = 89.4(3)°] and distances [C1—C2 = 1.574(5) and C1—C2a = 1.567(5) Å]. Both distances are shorter than the equivalent distances found for other cyclobutane rings substituted with phenyl ring and one carboxy group [C1—C2 = 1.582(1) Å, C1—C2a = 1.552(1) Å [37,38]. The molecular structure of **4a** is shown in Fig. 4(a). The phenol ring and carboxymethyl pendant groups occupy an alternated conformation in relation to the cyclobutane ring C1—C2—C3—C4 = 61.7(6)° and C2—C1—C13—O13 = − 121.1(4)°, respectively whereas the carboxyethyl pendant group occupies an almost staggered conformation with C2—C1—C9—O9 = − 17.8(5)°. This situation positions both carbonyl groups almost antiparallel to each other with torsion angles C13—C1—C9—O9 = 112.6(4)° and C9—C1—C13—O13 = 112.9(4)°.

In this molecule the presence of two phenol rings determines the supramolecular structure. The combination of a strong H-bonding O4—H4···O9^{i}

[O4···O9 = 2.735(3) Å, O4—H4···O9 = 174(1)°] hydroxy–carbonyl interaction, and dipolar H4O4···C9O9^{ix} hydroxy–carbonyl interaction, forms $R_2^2(8)$ motifs that propagate as ladders along the (0 2 16) direction. The geometric parameters for this last interaction are H4O4···C9O9 distance of 2.668(6) Å and O4···C9═O9 angle of 91.0(4)° [symmetry code (*ix*) 1 − x, 1 − y, 1 − z], Fig. 4(b). The crystal packing is complemented by weak self complementary C15—H15(B)···O9^{x} [C15···O9 = 3.346(5) Å, C15—H15(B)···O9 = 144(1)°, symmetry code (*x*) −x, 2 − y, 1 − z] contacts [39] between a methyl proton and a CO from carboxyethyl group to form $R_2^2(14)$ rings, which develop tapes that propagate along the (010) direction. Besides, parallel displaced π···π stacking [40] between neighbouring phenyl rings *Cg*(*1*)···*Cg*(*1*)^{xi} with intercentroid and interplanar distances, as well as torsion and slippage angles of 4.606(3) Å, 3.230(3) Å and 0.02(2)°, 45.5(1)° [symmetry code (*xi*) −x, 1 − y, −z], respectively, Fig. 4(c), complete the supramolecular architecture along the *b* axis.

The analysis of the supramolecular architecture of **3a** and **4a** reveals that in spite of the presence of one —OH group in **3a** or two of them in **4a**, a strong H-bonding donor, the supramolecular architecture is mainly structured by C—H···X (X═O, Ph), π···π and dipolar interactions.

CONCLUSIONS

The halogen atom exerts a strong influence on the quantum yields. This effect could be due to influence of the increased number of intermolecular contacts found in **1b** in relation to **1a**. The set of C—H···X (X═O, Ph), π···π stacking and dipolar interactions in **2a** and **2b** strongly resemble the supramolecular architecture of the respective monomer **1a** and **1b**, but slipped by the formation of the cyclobutane ring.

In general, on going from **2a** to its methanolysis derivatives **3a** and **4a**, the hydrogen bonding capability is increased, because of the transformation of the lactone moiety into a hydroxy and an ester group. Therefore the OH···O═C motif directs the supramolecular organization into dimers (**3a**) or polymers (**4a**). However most of the C—H···X (X═O, Ph), π···π and dipolar interactions are preserved from the original coumarin monomer **1a**. Therefore the supramolecular architecture of 3-ethylcoumarin carboxylate is preserved through its photodimers **2a**,**b** and derivative **3a** as if they would have a "supramolecular memory".

EXPRIMENTAL SECTION

General

Ethyl coumarin 3-carboxylates **1a**–**c** were prepared as described in the literature [22,27]. Photodimers **2a**–**c** were synthesized following the synthetic procedure described below. ^{1}H and ^{13}C NMR assignments of all compounds were achieved on the basis of COSY and HETCOR experiments. All chemicals and solvents were of reagent grade and used as received (Aldrich).

Instrumental Methods

Melting points were measured on an Electrothermal IA 9100 apparatus and were uncorrected. IR spectra were recorded in KBr disks using a Perkin–Elmer 16F PC IR spectrophotometer. Elemental analyses were performed on a Perkin–Elmer 2400 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (^{1}H, 300.08; ^{13}C, 75.46 MHz) equipment in [$^2H_6$]DMSO or $CDCl_3$ solution, measured with $SiMe_4$ as internal reference following standard techniques.

General Procedure for Photodimerization

50 mg of finely powdered ethyl 2-oxo-2H-1-benzopyran-3-carboxylate (**1a**), ethyl 6-chloro-2-oxo-2H-1-benzopyran-3-carboxylate (**1b**), or ethyl 6-bromo-2-oxo-2H-1-benzopyran-3-carboxylate (**1c**) were placed between two glass plates. A total of 20 assemblies were equidistantly located at *ca* 20 cm from the ACE quartz 450-W medium pressure mercury arc lamp. Uniform temperature in the irradiation chamber was ensured using a cooling water-ice bath jacket around the lamp during the irradiation time. Progress of the reaction was monitored by TLC using a mixture of ethyl acetate–hexane 6:4 as eluent and ^{1}H NMR at different time intervals. Percentage of conversion was deduced from the integrations of the olefinic and cyclobutyl protons in the NMR spectrum of the irradiated sample.

6-Oxo-6b*H*,12b*H*-5,11-dioxa-dibenzo[a,b]biphenylene-6a,12a-dicarboxylic acid diethyl ester (**2a**). The photoconversion of **1a** was completely achieved at 10 h of irradiation to quantitatively obtain 1.0 g of **2a** as a white solid, mp 190–192°C, no further purification was required. Crystals suitable for X-ray analysis were obtained after recrystallization from a diluted $CHCl_3$ solution. ^{1}H NMR (δ, $CDCl_3$): 7.34 (t, 1H, ^3J = 7.2 Hz and 8.2 Hz, H-7), 7.29 (d, 1H, ^3J = 7.8 Hz, H-5), 7.16 (t, 1H, ^3J = 7.8 Hz and 7.2 Hz, H-6), 7.08 (d, 1H, ^3J = 8.2 Hz, H-8), 4.92 (s, 1H, H-4), 3.99 (m, 2H, AA′BB′, OCH_2), 1.03 (t, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 166.2 (C-11), 163.9 (C-2), 151.9 (C-9), 130.7 (C-7), 128.8 (C-5), 125.4 (C-6), 117.6 (C-8), 116.0 (C-10), 63.4 (OCH_2), 52.9 (C-3), 46.8 (C-4), 13.8 (CH_3); IR/ν (cm^{-1}): 1765.3, 1727 (C═O); 1609 (Ar); 1211.1, 1183.0 (C—O). Anal. Calcd. for $C_{24}H_{20}O_8$: 66.06, C; 4.63, H %. Found: 66.04, C; 4.58 H %.

2,8-Dichloro-6-Oxo-6b*H*,12b*H*-5,11-dioxa-dibenzo[a,b]biphenylene-6a,12a-dicarboxylic acid diethyl

ester (**2b**). The photoconversion of **1b** was completely achieved at 6 h of irradiation to quantitatively obtain 1.0 g of **2b** as a white solid, mp 208–209°C, no further purification was required. Crystals suitable for X-ray analysis were obtained after recrystallization from a diluted $CHCl_3$ solution. ^{1}H NMR (δ, $CDCl_3$): 7.33 (dd, 1H, $^3J = 8.8$, $^4J = 2.5$ Hz, H-7), 7.27 (d, 1H, $^4J = 2.5$ Hz, H-5), 7.05 (d, 1H, $^3J = 8.8$ Hz, H-8), 4.84 (s, 1H, H-4), 4.08 (m, 2H, AA′BB′, OCH_2), 1.12 (t, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 165.9 (C-11), 163.1 (C-2), 150.4 (C-9), 130.8 (C-5), 130.6 (C-7), 128.5 (C-6), 119.0 (C-8), 117.2 (C-10), 63.8 (OCH_2), 52.4 (C-3), 46.4 (C-4), 13.9 (CH_3); IR/ν (cm^{-1}): 1765, 1710 (C═O); 1206, 1172, 1126, 1089 (C—O); 815 (C—Cl). Anal. Calcd. for $C_{24}H_{18}O_8Cl_2$: 57.05, C; 3.60, H %. Found: 57.07, C; 3.58 H %.

2,8-Dibromo-6-Oxo-6b*H*,12b*H*-5,11-dioxa-dibenzo[a,b]biphenylene-6a,12a-dicarboxylic acid diethyl ester (**2c**). Obtained as described for **2b**. White solid, mp 205–207°C, no further purification was required. Crystals suitable for X-ray analysis were obtained after recrystallization from a diluted $CHCl_3$ solution. ^{1}H NMR (δ, $CDCl_3$): 7.45 (dd, 1H, $^3J = 8.8$ Hz, $^4J = 2.0$ Hz, H-7), 7.41 (d, 1H, $^4J = 2.0$ Hz, H-5), 6.99 (d, 1H, $^3J = 8.8$ Hz, H-8), 4.85 (s, 1H, H-4), 4.06 (m, 2H, AA′BB′, OCH_2), 1.13 (t, 3H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 165.9 (C-11), 163.0 (C-2), 151.0 (C-9), 133.8 (C-5), 131.4 (C-7), 119.4 (C-8), 118.0 (C-6), 117.7 (C-10), 63.9 (OCH_2), 52.5 (C-3), 46.3 (C-4), 13.9 (CH_3); IR/ν (cm^{-1}): 1717, 1705 (C═O); 1615 (Ar); 1246, 1206, 1154 (C—O); 811 (C-Br). Anal. Calcd. for $C_{24}H_{18}O_8Br_2$: 48.35, C; 3.39, H %. Found: 48.32, C; 3.36, H %.

General Procedure for Alcoholysis

In a 250 mL flask were added 1.00 g (2.29 mmol) of compound **2a** and 100 mL of the corresponding alcohol. Progress was followed by TLC using a mixture of ethyl acetate-hexane 6:4 as eluent. The mixture was refluxed to complete 48 h and then the solvent was evaporated to dryness.

2-(2-Hydroxyphenyl)-3-oxo-8b*H*-4-oxa-cyclobuta[a]naphthalene-1,1,2a-tricarboxylic acid 1,2a-diethyl ester 1-methyl ester (**3a**). It was obtained from **2a** and methyl alcohol. The reaction mixture was extracted with three consecutive portions (20 mL, 12 mL and 8 mL) of chloroform. Chloroform extracts were joined together, the volume was reduced to one half and filtered off and after slow evaporation 0.272 g (0.58 mmol, 25% yield) of **3a** were obtained as a white crystalline powder mp 161–163°C. Crystals suitable for X-ray analysis were obtained after recrystallization from methyl alcohol. ^{1}H NMR (δ, $CDCl_3$): 7.46 (dd, 1H, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, H-5), 7.28 (ddd, 1H, $^3J = 7.5$ Hz and 7.7 Hz, $^1J = 1.5$ Hz, H-7), 7.15 (d, 1H, $^3J = 8.7$ Hz, H-22), 7.15 (ddd, 1H, $^3J = 6.8$ Hz, H-20), 7.13 (ddd, 1H, $^3J = 7.5$ Hz, $^1J = 1.1$ Hz, H-6), 7.01 (d, 1H, $^3J = 8.3$ Hz, H-8), 6.88 (t, 1H, $^3J = 7.5$ Hz, H-21), 6.85 (t, 1H, $^3J = 9.9$ Hz, H-19), 6.1 (b, 1H, —OH), 5.51 (s, 1H, H-16), 5.24 (b, 1H, H-4), 3.89 (m, 4H, —OCH_2), 3.46 (s, 3H, OCH_3), 0.84 and 0.83 (each: t, 3H, $^3J = 7.2$ Hz, CH_3); ^{13}C NMR (δ, $CDCl_3$): 169.8 (C-23 and C-27), 169.5 (C-11), 165.4 (C-2), 154.8 (C-18), 152.4 (C-9), 130.0 (C-7), 129.7 (C-20, C-22), 129.6 (C-5), 124.9 (C-6), 122.6 (C-17), 120.7 (C-21), 117.6 (C-10), 117.1 (C-8), 115.7 (C-19), 62.8 (OCH_2), 61.5 (C-3, C-15), 52.7 (OCH_3), 52.1 (C-4), 43.5 (C-16), 13.5 y 13.5 ($2CH_3$). IR/ν (cm^{-1}): 3410 (OH), 1766, 1729, 1702 (C═O), 1655 (Ar), 1242, 1208, 1149 (C—O), 762 (OH). Anal. Calcd. for $C_{25}H_{24}O_9$: 64.10, C; 5.18, H %. Found: 64.07, C; 5.12, H %.

2,4-Bis-[(2-hydroxyphenyl]cyclobutane-1,1,3,3-tetracarboxylic acid diethyl ester dimethyl ester (**4a**). It was obtained from the remnant solid after the isolation of **3a**. Compound **4a** was recrystallized from methyl alcohol to obtain 0.56 g (1.12 mmol, 49% yield) of a white crystalline solid, suitable to X-ray analysis, mp 219–220°C. ^{1}H NMR (δ, [$^2H_6$]DMSO): 9.50 (s, 1H, OH), 7.00 (d, 1H, $^3J = 8.1$ Hz, H-8), 6.9 (d, 1H, $^3J = 6.6$ Hz, H-5), 6.73 (t, 1H, $^3J = 7.6$ Hz and 8.1 Hz, H-7), 6.66 (t, 1H, $^3J = 6.6$ Hz and 7.4 Hz, H-6), 5.96 (s, 1H, H-2), 3.70 (m, 2H, OCH_2), 3.26 (s, 3H, OCH_3), 0.68 (t, 3H, $^3J = 7.1$ Hz, CH_3); ^{13}C NMR (δ, [$^2H_6$]DMSO): 169.9 (C-13), 169.2 (C-9), 156.7 (C-4), 129.8 (C-8), 129.2 (C-6), 123.1 (C-3), 118.7 (C-7), 115.4 (C-5), 61.5 (OCH_2), 60.5 (C-1), 52.7 (OCH_3), 42.6 (C-2), 13.9 (CH_3). IR/ν (cm^{-1}): 3320 (OH); 1743, 1707 (C═O); 1617 (Ar), 1263, 1242, 1206 (C—O), 758 (OH). Anal. Calcd. for $C_{26}H_{28}O_{10}$: 62.40, C; 5.65, H %. Found: 62.42, C; 5.60, H %.

2-(2-Hydroxyphenyl)-3-oxo-8b*H*-4-oxa-cyclobuta[a]naphthalene-1,1,2a-tricarboxylic acid triethyl ester (**5a**). It was obtained from **2a** and ethyl alcohol which was evaporated to dryness. The solid was dissolved in 40 mL of hot $CHCl_3$, treated with activated charcoal and filtered. After $CHCl_3$ evaporation 1.01 g (2.09 mmol, 91% yield) of **5a** were obtained as a white solid, mp 178–182°C. ^{1}H NMR (δ, $CDCl_3$): 7.46 (d, 1H, H-5), 7.28 (t, 1H, $^3J = 7.9$ Hz and 7.6 Hz, H-7), 7.18 (d, 1H, $^3J = 7.3$ Hz, H-22), 7.14 (t, 1H, ^3J = H-20), 7.13 (t, 1H, $^3J = 6.2$ Hz and 7.6 Hz, H-6), 7.00 (d, 1H, $^3J = 8.2$ Hz, H-8), 6.86 (t, 1H, $^3J = 7.6$ Hz, H-21), 6.84 (d, 1H, $^3J = 7.9$ Hz, H-19), 6.4 (b, 1H, OH), 5.51 (s, 1H, H16), 5.21 (b, 1H, H-4), 3.92 (q, 4H, $^3J = 7.0$ Hz, CH_2O), 3.85 (q, 2H, $^3J = 7.0$ Hz, CH_3O), 0.86 (t, 3H, $^3J = 7.0$ Hz, CH_3), 0.83 (t, 6H, $^3J = 7.0$ Hz, $2CH_3$); ^{13}C NMR (δ, $CDCl_3$): 169.6 (C-23 and C-27), 169.3 (C-11), 165.4 (C-2), 154.9 (C-18), 152.4 (C-9), 129.9 (C-7), 129.7 (C-20 and C-22), 129.6 (C-5), 124.9 (C-6), 122.6 (C-17), 120.7 (C-21), 117.8 (C-10), 117.1 (C-8), 115.7 (C-19), 62.9 (OCH_2), 62.8 (OCH_2), 62.5 (C-3), 62.0 (OCH_2), 61.4 (C-15), 52.1 (C-4), 43.5 (C-16), 13.6 ($2CH_3$), 13.5 (CH_3); IR/ν (cm^{-1}): 3335.6 (OH); 1750.5, 1735, 1721 (C═O); 1242.6, 1194.8 (C—O). Anal. Calcd. for $C_{26}H_{26}O_9$: 64.73, C; 5.44, H %. Found: 64.20, C; 5.20, H %.

TABLE IV Details of data collection and structure refinement for **2a**,**b** and **3**,**4a**

	2a	**2b**	**3a**	**4a**
Formula	$C_{24}H_{20}O_8$	$C_{24}H_{18}O_8Cl_2$	$C_{25}H_{24}O_9$	$C_{26}H_{28}O_{10}$
Mw	436.4	505.3	468.5	500.5
Crystal colour/shape	Colourless/rectangular	Colourless/block	Colourless/block	Colourless/rectangular
Crystal size (mm)	0.37 × 0.29 × 0.22	0.22 × 0.18 × 0.16	0.24 × 0.20 × 0.17	0.16 × 0.10 × 0.06
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	P $2_1/c$	P $2_1/c$	P-1
T (K)	273	273	173	273
a (Å)	6.7483(15)	6.7056(16)	9.0387(10)	7.8132(10)
b (Å)	7.9882(18)	11.0830(30)	13.9428(15)	8.9533(11)
c (Å)	10.0018(22)	16.0610(40)	19.8179(18)	9.5556(12)
α (°)	103.472(3)	90.0	90.0	106.406(2)
β (°)	92.243(4)	109.027(9)	111.641(4)	97.859(2)
γ (°)	99.803(4)	90.0	90.0	95.388(2)
V (Å^3)	514.92(6)	1128.41(37)	2321.50(40)	629.01(5)
Z	1	2	4	1
F (000)	228	520	983.9	264
ρ_{calc} (gcm^{-1})	1.41	1.49	1.34	1.32
μ (cm^{-1})	0.107	0.337	0.102	0.102
θ (min, max)	2.1, 27.5	2.3, 26.0	1.8, 25.0	2.3, 24.0
Data Colleted	4381	5662	21848	5656
Unique data	2265	2188	4086	1964
R_{int}	0.020	0.058	0.036	0.083
Obs data [I > 2σ(I)]	1967	1653	3029	1393
Parameters	164	174	307	166
R_1 (observed data)	0.063	0.079	0.067	0.079
*w*R2 (all data)	0.170	0.195	0.226	0.145
S	1.035	1.092	1.058	1.134
Max/min residual e density(eÅ^{-3})	0.291/−0.318	0.510/−0.335	0.584/−0.659	0.266/−0.335

X-ray Crystal Structure Determination

Single-crystal X-ray diffraction data for molecules **2a**–**4a** were collected on a Bruker Apex II CCD diffractometer at the ambient and low temperature with Mo Kα radiation, λ = 0.71073 Å. A semiempirical absorption correction was applied using SADABS [41], and the program SAINT [42] was used for integration of the diffraction profiles. The structures were solved by direct methods using SHELXS [42] program of WinGX package [43]. The final refinement was performed by full-matrix least-squares methods on F^2 with SHELXL [42] program. Hydrogen atoms bonded to carbon were placed geometrically using a riding mode with an isotropic displacement parameter fixed at 1.2 times *U*eq of the parent atoms symmetry. For the minor orientational component, the two methyl groups were constrained to be regular methyl group, with C13A—C14A and C13B—C14B bond distances of 1.54 Å. A common isotropic displacement parameter was applied to C13 and C14 atoms. The site-occupancy factors for the two orientations then refined to 0.706(2) and 0.294(2) for **2a** and 0.648(5) and 0.352(5) for **2b**.

Hydrogen atoms bonded were located in difference Fourier maps and then fixed in the given positions. All hydrogen atoms are included in the final refinement. Detailed crystallographic data and structural refinement parameters are summarized in Table IV. The crystallographic (cif-file) data have been deposited to the Cambridge Crystallographic Data Centre with numbers CCDC-635290 (**2a**), CCDC-635291 (**2b**), CCDC-635292 (**3a**) and CCDC-635293 (**4a**).

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