Research Article

Crystal Structures of Two Macrocyclic Bischalcones Possessing 26-Membered Rings

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Single crystal X-ray diffraction of two macrocyclic bischalcones, namely, (2*E*,25*E*)-11,17,33,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{18,23}.0^{27,32}]dotetraconta-1(42),2,5,7,9,18,20,22,25,27,29,31,38,40-tetradecaene-4,24-dione (**1**) and (2*E*,24*E*)-11,16,32,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{17,22}.0^{26,31}]dotetraconta-1(42),2,5,7,9,17,19,21,24,26,28,30,38,40-tetradecaene-4,23-dione (**2**), each containing a 26-membered ring, has been studied. Compound **1** belongs to the monoclinic system, space group *C2/c* with *a* = 34.3615(9) Å, *b* = 12.7995(3) Å, *c* = 14.6231(3) Å, β = 96.912(2)°, *V* = 6,384.6(3) Å³, and *Z* = 8. Compound **2** is triclinic, space group *P-1* with *a* = 10.066(2) Å, *b* = 10.670(3) Å, *c* = 16.590(3) Å, α = 85.95(2)°, β = 89.244(14)°, γ = 62.211(13)°, *V* = 1572.0(6) Å³, and *Z* = 2. Intermolecular C–H...O hydrogen bonding interactions are present in both compounds.

1. Introduction

Compounds containing the chalcone (1,3-diphenyl-2-propen-1-one) moiety [1] are known to possess important biological activities such as antimicrobial [2], antiviral [3], antibacterial [4, 5], antihelminthic [5], antimalarial [6, 7], and antitumor [8] activities. Moreover, these compounds can be transformed in a number of ways into other biologically active heterocycles, for example, pyrimidines [9], isoxazole and pyrazole [10], and pyridines [11]. Macrocycles incorporating more than one chalcone moiety have great potential in generating new compounds suitable for molecular recognition [12–15] and photophysical [16, 17] studies. Recently, we reported the synthesis of a new family of 22- to 28-membered macrocycles containing two chalcone moieties. For structural confirmation, an X-ray crystallographic study of one compound of this family has been done [18]. The interesting aspects of that study arising out of the folded nature of the molecule encouraged us to record the X-ray crystallographic data of some other compounds of the family. In this paper, we report the X-ray crystallographic data of two other compounds, (2*E*,25*E*)-11,17,33,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{18,23}.0^{27,32}]dotetraconta-1(42),2,5,7,9,18,20,22,

25,27,29,31,38,40-tetradecaene-4,24-dione (**1**) and (2*E*,24*E*)-11,16,32,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{17,22}.0^{26,31}]dotetraconta-1(42),2,5,7,9,17,19,21,24,26,28,30,38,40-tetradecaene-4,23-dione (**2**), each having a 26-membered ring.

2. Experimental

2.1. Synthesis of 1 and 2. Synthesis of the macrocyclic bischalcones (2*E*,25*E*)-11,17,33,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{18,23}.0^{27,32}]dotetraconta-1(42),2,5,7,9,18,20,22,25,27,29,31,38,40-tetradecaene-4,24-dione (**1**) and (2*E*,24*E*)-11,16,32,37-tetraoxapentacyclo[36.4.0.0^{5,10}.0^{17,22}.0^{26,31}]dotetraconta-1(42),2,5,7,9,17,19,21,24,26,28,30,38,40-tetradecaene-4,23-dione (**2**) (Scheme 1) was completed using the Claisen-Schmidt reaction in highly diluted aqueous methanol solution. The methods for the synthesis of **1** and **2** and their spectral data have been presented in our previous paper [18]. The light yellow single crystals of these compounds were obtained by slow evaporation of solvents from their solutions in *n*-hexane and acetone (1:3, v/v) (melting points: **1**, 182–184°C; **2**, 162–164°C).

TABLE 1: Crystallographic and experimental data for **1** and **2**.

Compounds	1	2
Empirical formula	C ₃₈ H ₃₆ O ₆	C ₃₈ H ₃₆ O ₆
Color/shape	Light yellow	Light yellow
Formula weight	588.67	588.67
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	$a = 34.3615(9) \text{ \AA}, \alpha = 90$	$a = 10.066(2) \text{ \AA}, \alpha = 85.95(2)$
	$b = 12.7995(3) \text{ \AA}, \beta = 96.912(2)$	$b = 10.670(3) \text{ \AA}, \beta = 89.244(14)$
	$c = 14.6231(3) \text{ \AA}, \gamma = 90$	$c = 16.590(3) \text{ \AA}, \gamma = 62.211(13)$
Volume	6384.6(3) Å ³	1572.03(125) Å ³
Z	8	4
Density (calculated)	1.225 g cm ⁻³	1.24 g cm ⁻³
Absorption coefficient	0.082 mm ⁻¹	0.083 mm ⁻¹
F(000)	2496	624
Crystal size	0.12 × 0.09 × 0.11 mm ³	0.12 × 0.09 × 0.11 mm ³
Theta range for data collection	1.2–27.6	2.2–27.7
Limiting indices	−44 ≤ <i>h</i> ≤ 44, −16 ≤ <i>k</i> ≤ 16, −18 ≤ <i>l</i> ≤ 18	−12 ≤ <i>h</i> ≤ 12, −13 ≤ <i>k</i> ≤ 13, −18 ≤ <i>l</i> ≤ 20
Reflections collected	50677	20993
Independent reflections	7,334 [<i>R</i> (int) = 0.038]	5673 [<i>R</i> (int) = 0.093]
Reflections observed (<i>I</i> > 2σ(<i>I</i>))	3677	1534
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7,334/1/413	5673/1/413
Goodness-of-fit on <i>F</i> ²	1.00	0.567
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.047, <i>wR</i> ₂ ^b = 0.105	<i>R</i> ₁ = 0.0657, <i>wR</i> ₂ = 0.155
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.114, <i>wR</i> ₂ = 0.130	<i>R</i> ₁ = 0.242, <i>wR</i> ₂ = 0.260
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + 0.0537P]^2 + 0.8426P]$	$w = 1/[\sigma^2(F_o^2) + 0.2000P]^2 + 0.0000P]$
Largest diff. peak and hole	0.13 and −0.17 eÅ ⁻³	0.17 and −0.15 eÅ ⁻³

$$^a R = (\sum [|F_o| - |F_c|] / (\sum |F_o|)); ^b wR_2 = \{[\sum (w[(F_o^2 - F_c^2)^2] / [\sum (w(F_o^2)^2)])]^{1/2}.$$

SCHEME 1: Synthesis of **1** and **2**.

2.2. Single Crystal X-Ray Crystallography. A summary of the crystallographic data and conditions is given in Table 1. The selected bond lengths and bond angles of **1** and **2** are listed in Table 2. The structures of **1** and **2** as well as the packing arrangement in a unit cell of these compounds are shown in Figures 1 and 2, respectively. X-ray single crystal data collection and cell refinement were carried out at room temperature using a “Bruker SMART CCD-detector” diffractometer equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and

refined by full-matrix least-squares based *F*² using SHELXS 97 set of programs [19]. ORTEP-3 for Windows [20] and PLATON [21] programs were used for molecular graphics. The structures were drawn with Mercury for Windows [22].

3. Results and Discussion

The molecular structures of **1** and **2** are shown in Figure 1. Hydrogen bonding in the molecules is summarized in Table 2. For compound **1**, the distances C15–C16 (1.458(3) Å), C17–C18 (1.458(3) Å), and C18–C19 (1.359(13) Å) and, for

TABLE 2: Selected bond lengths (Å) and bond angles (°) of **1** and **2**.

Selected bond lengths for 1		Selected bond lengths for 2	
C(15)–C(16)	1.458(3)	C(16)–C(17)	1.424(6)
C(16)–C(17)	1.324(3)	C(17)–C(18)	1.378(6)
C(17)–C(18)	1.458(3)	C(18)–C(19)	1.438(7)
C(18)–C(19)	1.359(3)	C(11)–O(2)	1.343(5)
O(1)–C(1)	1.359(13)	C(10)–O(2)	1.425(5)
O(1)–C(7)	1.426(11)	C(19)–O(3)	1.263(4)
Selected bond angles for 1		Selected bond angles for 2	
C(6)–C(38)–C(37)	127.07(19)	C(1)–C(38)–C(37)	130.30(4)
C(15)–C(16)–C(17)	128.36(16)	C(36)–C(37)–C(38)	127.00(4)
C(17)–C(18)–C(17)	119.03(15)	C(16)–C(17)–C(18)	127.31(5)
C(35)–C(36)–C(37)	122.38(15)	C(17)–C(18)–C(19)	123.50(5)
C(7)–C(8)–C(9)	114.60(19)	C(7)–C(8)–C(9)	114.80(4)
C(25)–C(26)–C(27)	113.83(15)	C(8)–C(9)–C(10)	113.30(4)
C(26)–C(27)–C(28)	112.85(15)	C(26)–C(27)–C(28)	116.00(4)
C(27)–C(28)–C(29)	114.31(17)	C(27)–C(28)–C(29)	113.10(4)
C(29)–O(5)–C(30)	120.22(14)	C(6)–O(1)–C(7)	121.32(4)
C(24)–O(4)–C(25)	119.39(13)	C(10)–O(2)–C(11)	122.42(4)
C(9)–O(2)–C(10)	118.99(14)	C(30)–O(5)–C(29)	120.05(3)
C(1)–O(1)–C(7)	117.07(17)	C(25)–O(4)–C(26)	118.66(6)

FIGURE 1: Molecular structure and atom numbering of compounds **1** and **2**. (Displacement ellipsoids are drawn at the 50% probability level.)

compound **2**, the distances C16–C17 (1.424(6) Å), C18–C19 (1.438(7) Å), and C19–C20 (1.484(7) Å) are shorter than the normal C–C single bond (1.53 Å). However, the C16–C17 (1.324(3) Å) distance for compound **1** is a bit shorter while C17–C18 (1.378(6) Å) distance for compound **2** is somewhat longer than the normal C–C double bond (1.34 Å). Again, in the case of compound **1**, the C18–C19 bond length is very close to that of a C–C single bond. In both **1** and **2** each of the two phenyl rings attached to the >C=O is not coplanar with the α,β -unsaturated carbonyl moiety. All these may be

due to accommodation of the polymethylene linkers in the molecules.

In case of compound **1**, for the first chalcone moiety, the α,β -unsaturated carbonyl unit (C16–C17–C18) is almost coplanar with the phenyl ring C10–C11–C12–C13–C14–C15 (angle 3.69(5)°) but is not so with the phenyl ring C19–C20–C21–C22–C23–C24 (angle 69.69(12)°), while, for the second chalcone moiety, the α,β -unsaturated carbonyl unit (C36–C37–C38) is not coplanar with any of the two phenyl rings C30–C31–C32–C33–C34–C35 and

TABLE 3: Intermolecular hydrogen bonds, intramolecular C–H...O, and C–H... π supramolecular interactions in **1** and **2**.

	D–H...A	Symmetry	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
Compound 1	C8–H8B...O2	$3/2 - x, 1/2 - y, 1 - z$	0.9700	2.5400	3.469(3)	162
	C14–H14...O6	$x, 1 - y, -1/2 + z$	0.9300	2.6000	3.411(2)	146
	C16–H16...O2	—	0.931(15)	2.295(15)	2.717(2)	107
	C29–H29B...O6	$x, 1 - y, 1/2 + z$	0.9700	2.4500	3.382(2)	161
	C37–H37...O5	—	0.970(17)	2.243(17)	2.726(2)	109
	C38–H38...O1	—	1.01(2)	2.323(19)	2.717(3)	101
	C7–H7B...phenyl ring	$x, -y, -1/2 + z$	0.9700	2.8500	3.708(2)	148
Compound 2	C8–H8B...O2	—	0.9700	2.4800	2.852(11)	103
	C9–H9B...O1	—	0.9700	2.4100	2.809(10)	104
	C21–H21...O3	$-x, 2 - y, 1 - z$	0.9300	2.5100	3.407(13)	161
	C34–H34...O6	$1 - x, -y, -z$	0.9300	2.4700	3.371(13)	164
	C14–H14...phenyl ring	$1 - x, -y, 1 - z$	0.9300	2.8200	3.735	167

FIGURE 2: The packing arrangement in the unit cells of **1** and **2**.

C1–C2–C3–C4–C5–C6 (angles 16.82(9) and 22.90(11)°, resp.). On the other hand, in compound **2**, arrangement is the same in both chalcone moieties. In each case the α,β -unsaturated carbonyl unit is almost coplanar with one phenyl ring C1–C2–C3–C4–C5–C6 or C11–C12–C13–C14–C15–C16 (angle 1.20(3) or 3.33(4)°) while it makes an angle of nearly 67° with the other phenyl rings C30–C31–C32–C33–C34–C35 or C20–C21–C22–C23–C24–C25. It is therefore apparent that the extent of electron delocalization between the phenyl ring attached to carbonyl and the remaining part of the chalcone moiety is very poor for both compounds **1** and **2**. The aliphatic chains O1–C7–C8–C9–O2 and O4–C25–C26–C27–C28–C29–O5 in **1** and O1–C7–C8–C9–C10–O2 and O4–C26–C27–C28–C29–O5 in **2** are mostly in staggered arrangement with the dihedral angles ranging from 57 to 64°. Antiarrangements were observed for C25–C26–C27–C28 and C26–C27–C28–C29 in **1** and C7–C8–C9–C10 in **2** (dihedral angles 177.32(17), 176.19(17), and 175.10(9)°, resp.). It is interesting to note that the arrangements for the apparently

similar units C7–C8–C9–C10 and C26–C27–C28–C29 in **2** are somewhat different in the crystalline state. For the first unit it is anti while for the second unit it is staggered. In the unit cell containing two molecules of **2** (Figure 2), two anti units are much closer than two staggered ones.

The salient feature of the crystal packing of **1** and **2** is that both of them form intermolecular hydrogen bonding networks (Figure 2). For the crystal of each compound there are two types of C–H...O intermolecular hydrogen bonds and one type of C–H... π supramolecular interactions (Table 3). In the crystal lattices, all the abovementioned hydrogen bonds and intermolecular interactions play a significant role in stabilizing the crystal structures. The intermolecular hydrogen bonds in **1** and **2** are summarized in Table 3.

Supplementary full crystallographic information for compounds **1** (CCDC 999278) and **2** (CCDC 999279) can be obtained via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK.

4. Conclusions

Several interesting structural aspects of two macrocyclic bischalcones **1** and **2**, each containing a 26-membered ring, in the solid state were evident from their single crystal X-ray diffraction studies.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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