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Research Article

Crystal Structure of Poly[(acetone-O)-3-((3,4-dimethoxyphenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-(2-oxo-2H-chromen-4-olate)sodium]

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The structure of Poly[(acetone-O)-3-((3,4-dimethoxyphenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-(2-oxo-2H-chromen-4-olate)sodium] was determined by X-ray crystallography. The compound crystallizes in an orthorhombic system and was characterized thus P $2_1\,2_1\,2_1$, $a = 9.967(2)$ Å, $b = 11.473(3)$ Å, $c = 22.176(5)$ Å. $Z = 4$, $V = 2535.9(10)$ Å^3. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0601$ and $wR2 = 0.1515$.

Biscoumarin derivatives possess anticoagulant, spasmolytic, bacteriostatic, and rodenticidal activities. Some of them can be used as herbicides. By chemical modifications (different substituents on the aromatic ring) it is possible to obtain a compound with good biological activity, but with lower toxicity and fewer side effects.

The title compound was synthesized from 3,3′-[(3,4-dimethoxyphenyl)-methylidene]-bis(4-hydroxy-2H-chromen-2-one) and water solution of sodium hydroxide at a molar ratio. This compound showed an effect on HIV replication in acutely infected cells by microtiter infection assay. The same substance demonstrated no impact on early stages of HIV-1 replication cycle [1]. The transformation of the compound to sodium salt was a stage for synthesizing complex compounds with lanthanides.

We only succeeded in growing colourless thin needles for single-crystal X-ray diffraction analysis by slow evaporation of an ethanol/acetone solution. Crystallographic data collected at room temperature with an Enraf-Nonius KappaCCD diffractometer using graphite monochromated Mo-$K\alpha$ ($\lambda = 0.71069$ Å) radiation were therefore of limited diffraction quality (Table 1). The solid state structure of the molecule was nonetheless investigated satisfactorily from a chemical/crystallographical point of view.

Crystal unit-cell and orientation parameters were determined by the DENZO [1] auto indexing procedure, as implemented in the data collection monitoring program COLLECT [2]. Intensities recorded up to a diffraction angle, θ_{max}, of 22.1° were also integrated by DENZO, scaled, and then reduced using SCALEPACK-HKL2000 [2], after postrefinement of the unit-cell parameters and absorption correction based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods using SIR97 [3], and all of the nonhydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97 [4]. All hydrogen atoms were located in difference electron-density maps, but refined as riding, with C–H = 0.93, 0.96, 0.97, and 0.98 Å for the aromatic, methyl, and methyne H atoms, respectively, O–H = 0.82 Å for hydroxyl H atoms, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or 1.5 (methyl C). Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of the bond

Table 1: Crystal data and structure refinement for Compound 1.

Identification code	Compound 1
Empirical formula	$C_{30}H_{25}NaO_{10}$
Formula weight	552.49
Temperature	293(2) K
Wavelength	.71069 A
Crystal system, space group	Orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	$a = 9.967(2)$ Å, $\alpha = 90°$ $b = 11.473(3)$ Å, $\beta = 90°$ $c = 22.176(5)$ Å, $\gamma = 90°$
Volume	2535.9(10) Å^3
Z, Calculated density	4, 1.452 g/cm^3
Absorption coefficient	0.124 mm^{-1}
$F(000)$	1152
Crystal size	0.50 × 0.14 × 0.08 mm^3
θ range for data collection	2.00 to 22.11°
Limiting indices	$-10 \le h \le 10$, $-12 \le k \le 12$, $-23 \le l \le 23$
Reflections collected/unique	14591/1822 [R(int) = 0.0407]
Completeness to $\theta = 22.11$	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.86
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1822/23/365
Goodness-of-fit on F^2	1.146
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0585$, $wR2 = 0.1449$/
R indices (all data)	$R1 = 0.0774$, $wR2 = 0.1556$
Extinction coefficient	0.008(2)
Largest diff. peak and hole	0.256 and −0.385 e.Å^{-3}
CCDC	723527

Table 2: Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for Compound 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Na1	1784(3)	7304(3)	6802(2)	60(1)
O2	2236(6)	6062(6)	7570(3)	61(2)
O3	6153(6)	3826(5)	7906(2)	51(2)
O5	−128(5)	7941(5)	7383(3)	54(2)
O7	1537(11)	8625(8)	6001(5)	129(4)
O4	−443(6)	6567(5)	6479(3)	57(2)
O1′	3599(6)	4625(5)	5584(2)	56(2)
O1	2389(6)	4972(5)	8376(2)	53(2)
O2′	2921(6)	6008(5)	6179(2)	52(2)
O3′	6337(5)	3430(4)	6822(2)	49(1)
C10	124(10)	8681(9)	7895(4)	89(4)
C13	−1354(7)	7391(7)	7363(4)	42(2)
C12	−1529(7)	6656(7)	6861(3)	39(2)
C11	−2730(7)	6065(6)	6785(3)	38(2)
C2	2965(9)	5410(7)	7844(4)	46(2)
C16	−3753(7)	6156(6)	7201(3)	36(2)
C15	−3540(8)	6883(7)	7694(4)	49(2)
C14	−2370(8)	7503(7)	7766(3)	47(2)
C8A	3072(9)	4232(7)	8741(4)	47(2)
C3	4296(8)	5051(6)	7692(3)	42(2)
C1	4857(8)	5590(7)	7118(3)	41(2)
C8	2428(9)	3893(8)	9268(4)	58(2)
C7	3050(10)	3147(8)	9659(4)	57(3)
C6	4376(10)	2774(8)	9529(4)	57(2)
C17	1628(13)	9665(13)	5949(6)	107(4)
C5	4985(9)	3103(7)	9002(4)	50(2)
C4A	4361(8)	3869(6)	8606(3)	39(2)
C2′	3692(8)	5212(7)	6133(3)	41(2)
C4	4971(8)	4256(7)	8045(3)	41(2)
C18	2360(16)	10274(14)	5489(8)	186(9)
C19	997(16)	10299(14)	6430(7)	158(7)
C3′	4696(8)	4852(6)	6554(3)	39(2)
C4′	5436(8)	3858(7)	6456(3)	41(2)
C5′	5929(9)	2181(7)	5766(4)	55(2)
C6′	5730(10)	1618(9)	5216(4)	69(3)
C7′	4846(10)	2116(9)	4794(4)	69(3)
C8′	4173(9)	3125(8)	4912(4)	62(3)
C4A′	5233(8)	3209(6)	5891(3)	42(2)
C8A′	4350(8)	3641(7)	5473(3)	45(2)
C9	−592(9)	5917(9)	5946(4)	64(3)

Table 3: Bond lengths (Å) for Compound 1.

Na1–O2	2.267(7)	C16–C15	1.391(10)
Na1–O2′	2.323(7)	C16–C1^{i}	1.541(11)
Na1–O7	2.347(9)	C15–C14	1.376(11)
Na1–O5	2.414(6)	C8A–C4A	1.384(11)
Na1–O4	2.481(7)	C8A–C8	1.388(11)
Na1–O3^{iv}	2.775(6)	C3–C4	1.377(10)
O2–C2	1.206(9)	C3–C1	1.521(10)
O3–C4	1.314(9)	C1–C3′	1.520(10)
O3–Na1^{ii}	2.775(6)	C1–C16^{v}	1.541(11)
O5–C13	1.376(9)	C8–C7	1.367(12)
O5–C10	1.439(10)	C7–C6	1.418(13)
O7–C17	1.202(15)	C6–C5	1.371(11)
O4–C12	1.378(9)	C17–C19	1.435(13)
O4–C9	1.404(9)	C17–C18	1.436(12)
O1′–C8A′	1.376(9)	C5–C4A	1.388(11)
O1′–C2′	1.395(9)	C4A–C4	1.455(11)
O1–C8A	1.356(9)	C2′–C3′	1.429(10)
O1–C2	1.406(9)	C3′–C4′	1.375(10)
O2′–C2′	1.198(9)	C4′–C4A′	1.471(11)
O3′–C4′	1.306(9)	C5′–C6′	1.394(12)
C13–C14	1.357(10)	C5′–C4A′	1.397(11)
C13–C12	1.407(10)	C6′–C7′	1.408(13)
C12–C11	1.385(10)	C7′–C8′	1.364(12)
C11–C16	1.379(10)	C8′–C8A′	1.390(11)
C2–C3	1.429(11)	C4A′–C8A′	1.371(11)

distances, bond angles, torsion angles, and intermolecular H-bond interactions are given as supplementary material (Tables 2, 3, 4, 5, 6, 7, and 8). The bond lengths and bond angles are all within the expected ranges.

The X-ray crystal structure of $Na^{+} \cdot (C_{27}H_{19}O_8)^{-} \cdot (C_3H_6O)$ is formally ionic, containing an anionic bis-coumarin consisting in two 4-hydroxycoumarin moieties (one of it with a deprotonated hydroxyl group) linked through a methylene bridge on which one hydrogen has been replaced by a dimethoxyphenyl residue, Na^{+} ions, and an acetone molecule. However, the structure could be better described as basic fragments of formula $[Na(C_3H_6O)(C_{27}H_{19}O_8)]_n$ forming polymeric chains along the *a* axis with a Na1 ⋯ Na1^{i} separation of 9.967(2) Å

Table 4: Bond angles (°) for Compound 1.

O2–Na1–O7	174.5(3)	O1–C8A–C4A	121.7(7)
O2′–Na1–O7	90.9(3)	O1–C8A–C8	116.5(8)
O2–Na1–O5	86.9(2)	C4A–C8A–C8	121.8(8)
O2′–Na1–O5	153.6(3)	C4–C3–C2	120.7(8)
O7–Na1–O5	97.2(3)	C4–C3–C1	124.4(7)
O2–Na1–O4	100.4(2)	C2–C3–C1	114.9(7)
O2′–Na1–O4	92.7(2)	C3′–C1–C3	115.0(6)
O7–Na1–O4	84.8(3)	C3′–C1–C16^{v}	115.3(6)
O5–Na1–O4	63.33(19)	C3–C1–C16^{v}	113.8(6)
O2–Na1–O3^{iv}	94.2(2)	C7–C8–C8A	120.0(9)
O2′–Na1–O3^{iv}	100.4(2)	C8–C7–C6	118.9(8)
O7–Na1–O3^{iv}	81.2(3)	C5–C6–C7	120.2(8)
O5–Na1–O3^{iv}	105.6(2)	O7–C17–C19	113.5(14)
O4–Na1–O3^{iv}	160.9(2)	O7–C17–C18	126.2(15)
C2–O2–Na1	152.5(5)	C19–C17–C18	120.2(15)
C4–O3–Na1^{ii}	147.8(5)	C6–C5–C4A	121.0(8)
C13–O5–C10	116.8(7)	C8A–C4A–C5	118.0(7)
C13–O5–Na1	123.0(5)	C8A–C4A–C4	118.7(7)
C10–O5–Na1	117.5(5)	C5–C4A–C4	123.2(7)
C17–O7–Na1	134.9(11)	O2′–C2′–O1′	113.6(7)
C12–O4–C9	118.3(6)	O2′–C2′–C3′	127.9(7)
C12–O4–Na1	120.0(4)	O1′–C2′–C3′	118.4(7)
C9–O4–Na1	121.2(5)	O3–C4–C3	123.6(7)
C8A′–O1′–C2′	121.1(6)	O3–C4–C4A	117.4(7)
C8A–O1–C2	121.4(7)	C3–C4–C4A	119.0(7)
C2′–O2′–Na1	148.4(5)	C4′–C3′–C2′	120.9(7)
C14–C13–O5	126.7(7)	C4′–C3′–C1	122.3(7)
C14–C13–C12	119.0(7)	C2′–C3′–C1	116.7(7)
O5–C13–C12	114.3(7)	O3′–C4′–C3′	125.7(7)
O4–C12–C11	124.5(7)	O3′–C4′–C4A′	115.7(7)
O4–C12–C13	115.6(7)	C3′–C4′–C4A′	118.6(7)
C11–C12–C13	119.8(7)	C6′–C5′–C4A′	119.7(8)
C16–C11–C12	121.3(7)	C5′–C6′–C7′	118.9(9)
O2–C2–O1	113.4(7)	C8′–C7′–C6′	121.7(9)
O2–C2–C3	128.3(8)	C7′–C8′–C8A′	118.1(9)
O1–C2–C3	118.3(8)	C8A′–C4A′–C5′	119.3(7)
C11–C16–C15	117.3(7)	C8A′–C4A′–C4′	118.8(7)
C11–C16–C1^{i}	123.6(6)	C5′–C4A′–C4′	121.9(7)
C15–C16–C1^{i}	118.8(7)	C4A′–C8A′–O1′	121.7(7)
C14–C15–C16	122.0(7)	C4A′–C8A′–C8′	122.2(8)
C13–C14–C15	120.5(7)	O1′–C8A′–C8′	116.1(7)

Symmetry transformations used to generate equivalent atoms: i: $x-1, y, z$; ii: $1-x, y-1/2, 3/2-z$; iv: $1-x, y+1/2, 3/2-z$; v: $x+1, y, z$.

Table 5: Anisotropic displacement parameters ($A^2 \times 10^3$) for Compound 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + \cdots + 2hka^*b^*U12]$.

	U11	U22	U33	U23	U13	U12
Na1	51(2)	60(2)	67(2)	7(2)	6(2)	12(2)
O2	45(4)	69(4)	69(4)	14(4)	6(3)	6(4)
O3	52(4)	53(3)	47(3)	3(3)	−3(3)	5(3)
O5	39(3)	53(4)	70(4)	−20(3)	−2(3)	−7(3)
O7	129(8)	95(6)	162(8)	58(7)	6(7)	−4(6)
O4	43(4)	64(4)	63(4)	−17(3)	11(3)	−4(3)
O1′	54(4)	60(4)	55(3)	−14(3)	−16(3)	12(3)
O1	46(4)	54(3)	59(4)	7(3)	8(3)	9(3)
O2′	47(3)	47(3)	64(4)	−8(3)	−12(3)	18(3)
O3′	42(3)	49(3)	56(3)	6(3)	−5(3)	13(3)
C10	60(6)	104(9)	104(8)	−48(7)	−6(6)	−24(6)
C13	28(4)	40(4)	58(5)	−2(4)	−6(4)	−2(4)
C12	32(5)	41(4)	45(4)	0(4)	4(4)	4(4)
C11	38(5)	32(4)	43(4)	−3(4)	−3(4)	0(4)
C2	51(6)	39(5)	47(5)	−1(4)	−2(5)	−7(5)
C16	34(4)	31(4)	44(4)	3(4)	−3(4)	7(4)
C15	33(5)	58(5)	56(5)	−12(4)	5(4)	3(4)
C14	40(5)	48(5)	53(5)	−16(4)	0(4)	1(4)
C8A	47(5)	38(5)	56(5)	2(4)	−3(5)	−2(4)
C3	41(5)	33(4)	51(5)	−8(4)	−3(4)	0(4)
C1	43(5)	36(4)	45(5)	0(4)	6(4)	5(4)
C8	64(6)	55(6)	54(5)	5(5)	10(5)	1(5)
C7	66(7)	65(6)	41(5)	5(4)	9(5)	−8(6)
C6	65(6)	62(6)	43(5)	5(4)	−1(5)	1(5)
C17	78(9)	116(11)	128(10)	25(8)	−17(7)	−4(8)
C5	46(5)	53(5)	52(5)	−6(4)	5(5)	−1(5)
C4A	49(5)	32(4)	35(4)	2(4)	−4(4)	0(4)
C2′	37(5)	42(5)	44(5)	−1(4)	−10(4)	−8(5)
C4	31(5)	40(5)	52(5)	−8(4)	−6(4)	0(4)
C18	123(12)	154(15)	282(19)	121(14)	79(13)	49(12)
C19	122(14)	172(16)	181(14)	−44(13)	−4(10)	−49(12)
C3′	34(5)	40(4)	43(4)	1(4)	−2(4)	2(4)
C4′	31(4)	42(5)	49(5)	6(4)	3(4)	−7(4)
C5′	58(6)	44(5)	62(6)	−5(4)	−4(5)	11(5)
C6′	75(7)	57(6)	75(6)	−17(5)	2(6)	12(6)
C7′	74(7)	67(7)	67(6)	−19(5)	−8(6)	−12(6)
C8′	58(6)	58(6)	71(6)	−12(5)	−12(5)	5(5)
C4A′	38(5)	43(5)	45(5)	−1(4)	2(4)	2(4)
C8A′	37(5)	49(5)	49(5)	−10(4)	−3(4)	3(4)
C9	56(6)	79(7)	56(5)	−13(5)	13(5)	0(5)

Table 6: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for Compound 1.

	x	y	z	U(eq)
H3	6213	3760	7539	61
H10A	−552	9275	7915	133
H10B	991	9038	7853	133
H10C	103	8223	8257	133
H11	−2849	5599	6446	45
H15	−4210	6951	7984	59
H14	−2274	8002	8094	56
H1	4263	6256	7045	50
H8	1574	4173	9355	69
H7	2611	2888	10004	69
H6	4833	2305	9803	68
H5	5828	2809	8907	61
H18A	3175	10580	5656	279
H18B	1822	10903	5337	279
H18C	2570	9747	5166	279
H19A	240	9866	6576	237
H19B	701	11043	6283	237
H19C	1628	10412	6751	237
H5′	6523	1874	6048	66
H6′	6174	924	5130	83
H7′	4718	1748	4425	83
H8′	3611	3458	4625	75
H9A	−881	5142	6044	96

(Figure 2(a)). These chains are interconnected through aromatic π-π stacking interactions involving the methoxyphenyl group and one coumarin group at position $-x$, $1/2 + y$, $3/2 - z$, with $Cg1\cdots Cg5$($Cg1$ = centroid of the O1–C2–C3–C4–C4A–C8A six-membered ring and $Cg5$ = centroid of the C11–C16 six-membered ring) distance of 3.634 Å, and C–H$\cdots\pi$ weak interactions (Table 8), generating a two-dimensional layer architecture parallel to the crystallographic ab plane (Figure 2(b)), and placing the $Na1^{ii}$ at distances from Na1 or $Na1^{i}$ in the range of 7.426–9.143 Å [symmetry codes: (i) $x - 1$, y, z; (ii) $1 - x$, $1/2 + y$, $3/2 - z$]. The layered assembly is merely consolidated in the third-dimension by even weaker C–H$\cdots\pi$ interactions (e.g., methyl groups of acetone ligands and coumarin moieties from adjacent layers) (Figure 2(c)).

The Na1 cation is coordinated by six O atoms in a distorted octahedral geometry, with five oxygen atoms (O2, O2′, $O4^{i}$, $O5^{i}$, $O3^{ii}$) from three molecules of biscoumarin and one O7 from an acetone molecule. The first biscoumarin molecule chelates to the sodium atom through the two atoms from the oxo units, the second molecule through two O atoms from the two methoxy groups of the 3,4-dimethoxyphenyl moiety whereas the third molecule

Table 7: Torsion angles (°) for Compound 1.

O2′–Na1–O2–C2	41.3(13)	O1–C2–C3–C4	2.8(11)
O7–Na1–O2–C2	−26(4)	O2–C2–C3–C1	1.5(12)
O5–Na1–O2–C2	−164.4(13)	O1–C2–C3–C1	−178.4(6)
O4–Na1–O2–C2	133.5(12)	C4–C3–C1–C3′	83.3(10)
O3^{iv} –Na1–O2–C2	−58.9(13)	C2–C3–C1–C3′	−95.5(8)
O2–Na1–O5–C13	−86.1(6)	C4–C3–C1–C16^{v}	−52.9(9)
O2′–Na1–O5–C13	−9.4(9)	C2–C3–C1–C16^{v}	128.4(7)
O7–Na1–O5–C13	97.5(6)	O1–C8A–C8–C7	180.0(8)
O4–Na1–O5–C13	17.1(5)	C4A–C8A–C8–C7	−2.4(13)
O3^{iv} –Na1–O5–C13	−179.6(5)	C8A–C8–C7–C6	2.8(13)
O2–Na1–O5–C10	74.8(6)	C8–C7–C6–C5	−3.9(13)
O2′–Na1–O5–C10	151.6(7)	Na1–O7–C17–C19	−44(2)
O7–Na1–O5–C10	−101.5(7)	Na1–O7–C17–C18	132.0(15)
O4–Na1–O5–C10	178.1(7)	C7–C6–C5–C4A	4.6(13)
O3^{iv} –Na1–O5–C10	−18.6(7)	O1–C8A–C4A–C5	−179.5(7)
O2–Na1–O7–C17	−71(4)	C8–C8A–C4A–C5	3.0(12)
O2′–Na1–O7–C17	−138.5(14)	O1–C8A–C4A–C4	−2.7(11)
O5–Na1–O7–C17	66.7(14)	C8–C8A–C4A–C4	179.8(7)
O4–Na1–O7–C17	128.9(14)	C6–C5–C4A–C8A	−4.1(11)
O3^{iv} –Na1–O7–C17	−38.1(14)	C6–C5–C4A–C4	179.3(8)
O2–Na1–O4–C12	65.7(6)	Na1–O2′–C2′–O1′	160.9(7)
O2′–Na1–O4–C12	153.2(5)	Na1–O2′–C2′–C3′	−22.1(15)
O7–Na1–O4–C12	−116.2(6)	C8A′–O1′–C2′–O2′	−175.6(7)
O5–Na1–O4–C12	−15.4(5)	C8A′–O1′–C2′–C3′	7.1(10)
O3^{iv} –Na1–O4–C12	−73.3(9)	Na1^{ii} –O3–C4–C3	−176.9(6)
O2–Na1–O4–C9	−105.7(6)	Na1^{ii} –O3–C4–C4A	3.6(12)
O2′–Na1–O4–C9	−18.2(7)	C2–C3–C4–O3	174.7(7)
O7–Na1–O4–C9	72.4(7)	C1–C3–C4–O3	−3.9(12)
O5–Na1–O4–C9	173.2(7)	C2–C3–C4–C4A	−5.7(10)
O3^{iv} –Na1–O4–C9	115.3(8)	C1–C3–C4–C4A	175.6(7)
O2–Na1–O2′–C2′	−18.1(10)	C8A–C4A–C4–O3	−174.8(7)
O7–Na1–O2′–C2′	156.8(10)	C5–C4A–C4–O3	1.8(11)
O5–Na1–O2′–C2′	−94.9(11)	C8A–C4A–C4–C3	5.7(11)
O4–Na1–O2′–C2′	−118.4(10)	C5–C4A–C4–C3	−177.7(7)
O3^{iv} –Na1–O2′–C2′	75.6(10)	O2′–C2′–C3′–C4′	174.8(8)
C10–O5–C13–C14	2.2(12)	O1′–C2′–C3′–C4′	−8.4(11)
Na1–O5–C13–C14	163.3(6)	O2′–C2′–C3′–C1	−2.8(12)
C10–O5–C13–C12	−178.4(7)	O1′–C2′–C3′–C1	174.0(6)
Na1–O5–C13–C12	−17.3(9)	C3–C1–C3′–C4′	−72.1(10)
C9–O4–C12–C11	5.9(11)	C16^{v} –C1–C3′–C4′	63.3(9)
Na1–O4–C12–C11	−165.7(6)	C3–C1–C3′–C2′	105.4(8)
C9–O4–C12–C13	−175.2(7)	C16^{v} –C1–C3′–C2′	−119.1(8)
Na1–O4–C12–C13	13.2(9)	C2′–C3′–C4′–O3′	−177.2(7)
C14–C13–C12–O4	−178.6(7)	C1–C3′–C4′–O3′	.3(12)
O5–C13–C12–O4	1.9(9)	C2′–C3′–C4′–C4A′	3.7(11)
C14–C13–C12–C11	.4(11)	C1–C3′–C4′–C4A′	−178.8(7)
O5–C13–C12–C11	−179.1(7)	C4A′–C5′–C6′–C7′	1.3(14)
O4–C12–C11–C16	177.0(7)	C5′–C6′–C7′–C8′	−.7(15)
C13–C12–C11–C16	−1.9(11)	C6′–C7′–C8′–C8A′	−1.9(14)
Na1–O2–C2–O1	176.4(9)	C6′–C5′–C4A′–C8A′	.8(12)

Table 7: Continued.

O2′–Na1–O2–C2	41.3(13)	O1–C2–C3–C4	2.8(11)
Na1–O2–C2–C3	−3.4(19)	C6′–C5′–C4A′–C4′	−178.1(8)
C8A–O1–C2–O2	−179.6(7)	O3′–C4′–C4A′–C8A′	−176.8(7)
C8A–O1–C2–C3	.3(10)	C3′–C4′–C4A′–C8A′	2.4(11)
C12–C11–C16–C15	1.3(11)	O3′–C4′–C4A′–C5′	2.0(11)
C12–C11–C16–C1^{i}	175.6(7)	C3′–C4′–C4A′–C5′	−178.8(7)
C11–C16–C15–C14	.8(11)	C5′–C4A′–C8A′–O1′	177.4(7)
C1^{i} –C16–C15–C14	−173.8(7)	C4′–C4A′–C8A′–O1′	−3.7(11)
O5–C13–C14–C15	−178.9(7)	C5′–C4A′–C8A′–C8′	−3.5(12)
C12–C13–C14–C15	1.6(12)	C4′–C4A′–C8A′–C8′	175.4(8)
C16–C15–C14–C13	−2.3(12)	C2′–O1′–C8A′–C4A′	−1.1(11)
C2–O1–C8A–C4A	−.2(11)	C2′–O1′–C8A′–C8′	179.8(7)
C2–O1–C8A–C8	177.4(7)	C7′–C8′–C8A′–C4A′	4.0(13)
O2–C2–C3–C4	−177.3(8)	C7′–C8′–C8A′–O1′	−176.8(8)

Symmetry transformations used to generate equivalent atoms: i: $x-1, y, z$; ii: $1-x, y-1/2, 3/2-z$; iv: $1-x, y+1/2, 3/2-z$; v: $x+1, y, z$.

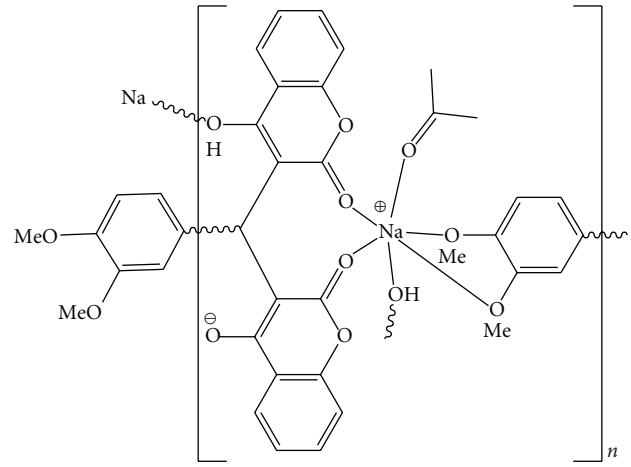

Figure 1

Table 8: Hydrogen bonds for Compound 1 (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	⟨(DHA)⟩
O3–H3···O3′	0.82	1.64	2.453(7)	171.9
C5′–H5′···Cg1^{ii}	0.82	3.05	3.714(9)	129.5
C6′–H6′···Cg4^{ii}	0.82	3.22	3.893(11)	130.6
C19–H19C···Cg5^{iii}	0.96	2.81	3.669(16)	148.9

*Cg*1, *Cg*4 and *Cg*5 are the centroids of the O1–C2–C3–C4–C4A–C8A, O1–C4A–C8A–C5–C6–C7–C8, and C11–C16 six-membered rings, respectively. symmetry-code: ii: $1-x, y-1/2, 3/2-z$; iii: $-x, 1/2+y, 3/2-z$.

through the hydroxyl atom O3^{ii}. The six oxygen atoms are at distances from the cation in the range of 2.267(7)–2.774(6) Å, the longest distance being observed with the hydroxyl oxygen atom.

Unlike nonionic structures of biscoumarin compounds [5–7] for which the two 4-hydroxycoumarin moieties are also intramolecularly hydrogen bonded between hydroxyls and carbonyls, the coumarin residues here are arranged in such a way that hydroxyl O3 and O3′ atoms are brought

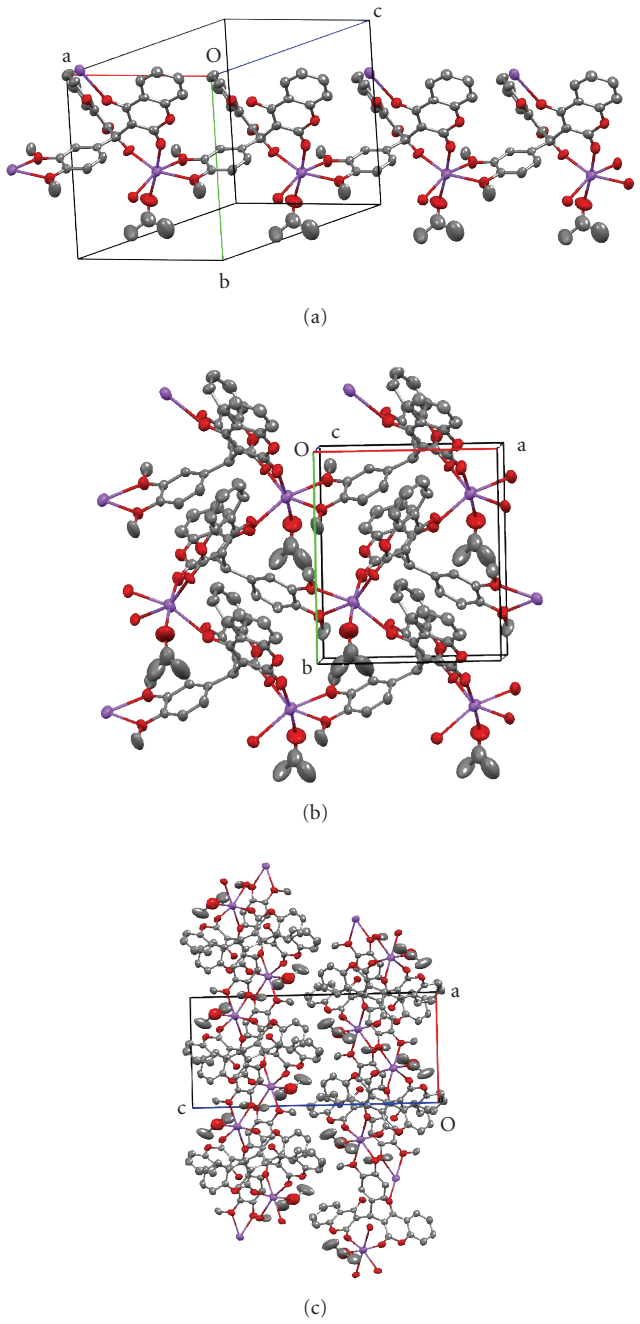

Figure 2: (a) View of the polymeric chain propagating along the *a* direction. (b) Bidimensional array parallel to the *ab* plane. (c) View of the crystal structure down the *b* axis.

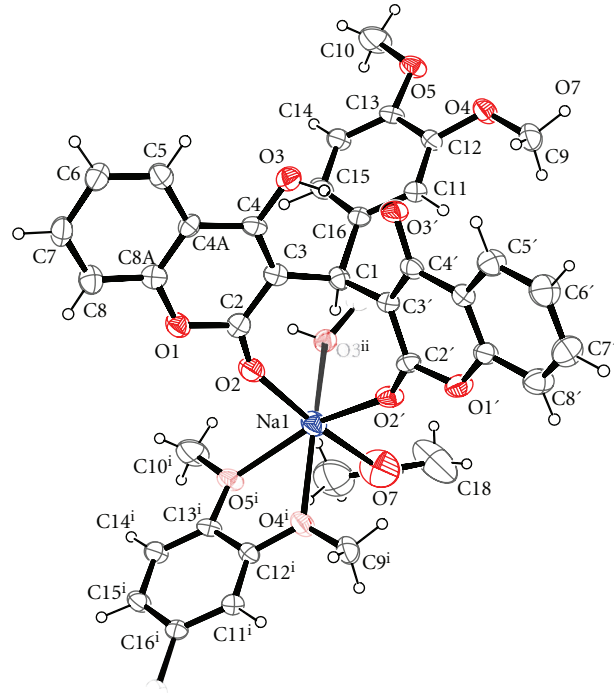

Figure 3: A view of the coordination sphere around the Na^+ ion in compound 1 with 30% probability displacement ellipsoids is displayed with the numbering scheme. The complete coordination of the Na atom is shown. Symmetry-related atoms are shown in transparency with symmetry codes: i: $x-1, y, z$, ii: $-x+1, y+1/2, -z+3/2$.

close enough to form an intramolecular hydrogen bond. This feature seems characteristic of biscoumarin structures with a deprotonated hydroxyl since it was previously noted with the following salt structure, $C_5H_{12}N^+$ $C_{29}H_{23}O_6^-$ [8]. Limited crystallographic data resolution and long hydroxyl C–O bond lengths >1.3 Å are in favour of a 50/50 donor/attractor character in both residues. For the sake of the model refinement, O3 has been chosen to act as the donor (Table 8). Otherwise, the geometric parameters of the biscoumarin agree with closely related structures [5–8]. All of the twelve non-H atoms of the coumarin rings are essentially coplanar, with r.m.s deviation of 0.032 and 0.056 Å, respectively. The plane of the dimethoxyphenyl ring is inclined at angles of 78.49(19)° and 67.17(18)° to the coumarin moieties. The dihedral angle between the two coumarin moieties is 58.65(16)°. The orientations of the coumarins about C1 may be described in terms of the torsion angles C3–C1–C3′–C4′ of −72.1(10)°, and C4–C3–C1–C3′ of 83.2(9)°. The bond angles C3′–C1–C3, 115.1(6), C3–C1–C16, 113.7(6), and C3′–C1–C16, 115.4(6)° at C1 are also widened in comparison with standard tetrahedral values. Steric crowding around this atom may be invoked to explain this feature, as well as in the case of the C1–C16 distance of 1.541(11) Å, longer as expected than an unstrained C_{sp2}–C_{ar} bond [5]. The exocyclic bond angles at C3 [C2–C3–C1, 114.9(7)°, and C4–C3–C1, 124.4(7)°] and those at C3′ [C2′–C3′–C1, 116.8(6)° and C4′–C3′–C1, 122.4(7)°] do not differ very significantly (9.5 and 5.6°, resp.) in comparison with dicoumarols [5].

Acknowledgments

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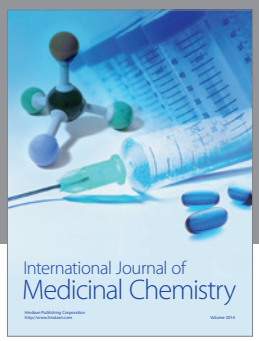

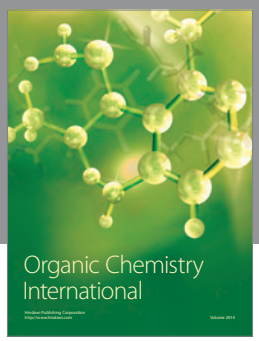

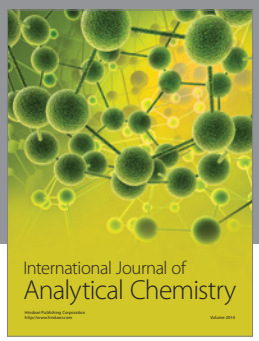

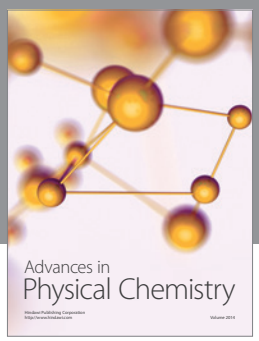

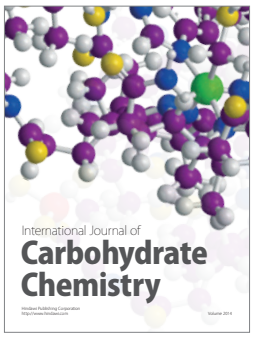

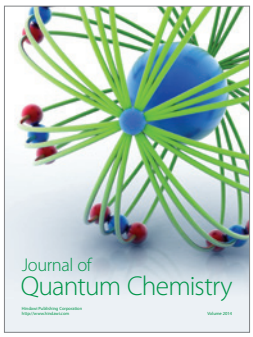

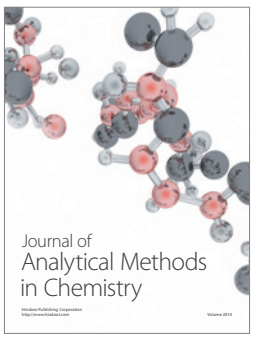

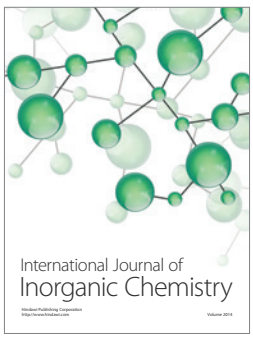

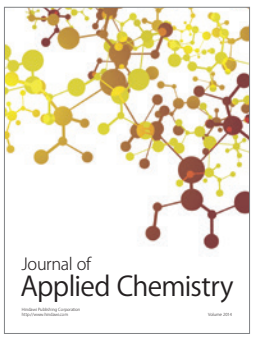

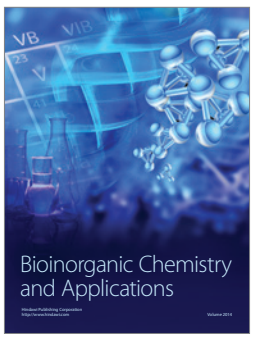

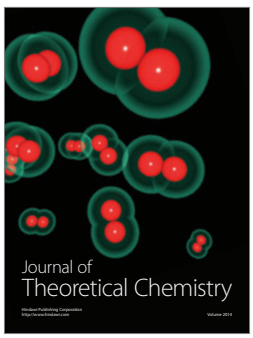

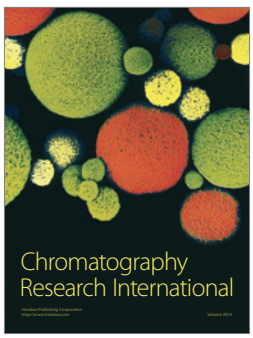

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