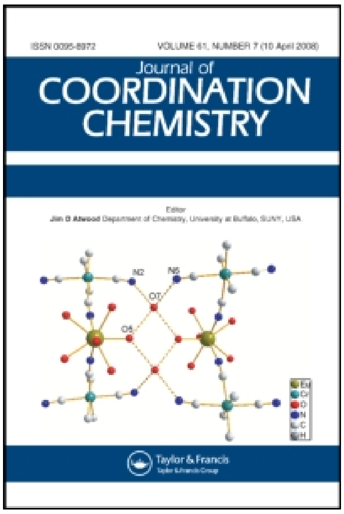

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Hydrogen bonding and π-π stacking in two daidzein derivatives

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Hydrogen bonding and π–π stacking in two daidzein derivatives

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Two daidzein derivatives, hexaaquamagnesium(II) *bis*(7,4′-dimethoxyisoflavone-3′-sulfonate) octahydrate (**1**) and ammonium, diethylamine *bis*(7,4′-diethoxyisoflavone-3′-sulfonate)pentahydrate (**2**) were determined by X-ray diffraction analysis. Crystallographic data for **1**: monoclinic, $P2_1/c$, $a = 18.499(7)$ Å, $b = 7.337(3)$ Å, $c = 18.232(6)$ Å, $\beta = 115.254(4)^\circ$, $V = 2237.8(1)$ Å^3, $Z = 2$. Data for **2**: triclinic, $P\bar{1}$, $a = 11.059(3)$ Å, $b = 15.172(4)$ Å, $c = 15.304(4)$ Å, $\alpha = 98.624(3)^\circ$, $\beta = 108.438(4)^\circ$, $\gamma = 92.752(4)^\circ$, $V = 2395.9(1)$ Å^3, $Z = 2$. The anions of compound **1** have one conformation and those of compound **2** have two conformations. In **1** and **2**, classical hydrogen bonds lead to the formation of hydrophilic regions, columns of the isoflavone moieties form the hydrophobic regions by π–π stacking; with the sulfonate bridging the two regions as well as the inorganic and organic components a three-dimensional supramolecular structure is generated in both systems.

Keywords: Daidzein derivative; Crystal structure; Hydrogen bonding; π–π stacking

1. Introduction

Daidzein (7,4′-dihydroxyisoflavone), a natural soya isoflavone, is biologically active, with resistance to hypoxia and anoxemia [1]. The solubility of the isoflavone is poor, its biological utilization rate is low and the dose is high [2]. In order to improve the solubility of isoflavones, some isoflavones have been sulfonated. Sodium 7-methoxy-4′-hydroxyisoflavone-3′-sulfonate [3] and sodium 7,4′-dihydroxyisoflavone-3′-sulfonate [4] have been synthesized and their crystal structures and biological activities have been studied. The result showed that they possess better biological activity than the parent daidzein. The water-soluble derivatives $Ni(H_2O)_6 \cdot X_2 \cdot 8H_2O$ [5], $Fe(H_2O)_6 \cdot X_2 \cdot 8H_2O$ [6] and $Zn(H_2O)_6 \cdot X_2 \cdot 8H_2O$ [7] ($X = $ 7,4′-dimethoxyisoflavone-3′-sulfonate), $Co(H_2O)_6 \cdot Y_2 \cdot 8H_2O$ [8], $Mg(H_2O)_6 \cdot Y_2 \cdot 8H_2O$ and $Zn(H_2O)_6 \cdot Y_2 \cdot 8H_2O$ [9] ($Y = $ 7,4′-diethoxyisoflavone-3′-sulfonate) have been reported. Two water-soluble daidzein derivatives, hexaaquamagnesium(II) *bis*(7,4′-dimethoxyisoflavone-3′-sulfonate)octahydrate {**1**, $[Mg(H_2O)_6](C_{17}H_{13}O_7S)_2 \cdot 8H_2O$} and ammonium, diethylamine *bis*(7,4′-diethoxyisoflavone-3′-sulfonate)pentahydrate {**2**, $NH_4^+[(C_2H_5)_2NH_2^+](C_{19}H_{17}O_7S)_2 \cdot 5H_2O)$} were synthesized from sodium 7,4′-dimethoxyisoflavone-3′-sulfonate and sodium 7,4′-diethoxyisoflavone-3′-sulfonate (scheme 1), respectively.

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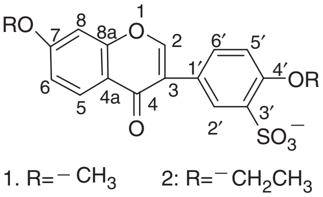

Scheme 1. The structure of anions in compounds **1** and **2**.

2. Experimental

2.1. *Materials*

Reagent-grade chemicals were used directly without further purification. The sodium 7,4′-dimethoxyisoflavone-3′-sulfonate and sodium 7,4′-diethoxyisoflavone-3′-sulfonate were prepared as described in the literature [5, 8].

2.2. *Physical measurements*

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 II analyzer. The infrared spectra were recorded as KBr pellets on a Nicolet 170SX FT-IR spectrophotometer (600–4000 cm^{-1} region).

2.3. *Syntheses of two daidzein derivatives*

For the preparation of compound **1**, sodium 7,4′-dimethoxyisoflavone-3′-sulfonate (0.5 g) was dissolved in water (10 mL), mixed with a saturated $MgSO_4 \cdot 7H_2O$ solution (5 mL) in water. Crystals of **1** were obtained after 5 d in good yield (86%). On recrystallization from water, single crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation. Anal. Calcd for $C_{34}H_{54}MgO_{28}S_2$(%): C, 40.84; H, 5.41. Found: C, 40.97; H, 5.32. IR (KBr): 3386(s), 2968(s), 2880(s), 1633(s), 1567(m), 1444(m), 1287(m), 1207(s), 1091(s), 1024(m) cm^{-1}.

For preparation of compound **2**, sodium 7,4′-diethoxyisoflavone-3′-sulfonate (0.5 g) was dissolved in water (10 mL). The solution was mixed with $NH_4^+Cl^-$ (2 mL) and $(C_2H_5)_2NH_2^+Cl^-$ (2 mL) solution (4 mL, 10%) and a white precipitate appeared. The precipitate was recrystallized from water to give **2** after 7 d in good yield (90%). Anal. Calcd for $C_{42}H_{60}N_2O_{19}S_2$(%): C, 52.45; H, 6.24; N, 2.91. Found: C, 52.38; H, 6.13; N, 3.03. IR (KBr): 3430(s), 2985(s), 2932(s), 2357(s), 1630(s), 1563(m), 1258(s), 1198(s), 1100(s), 1029(m) cm^{-1}.

2.4. *X-ray crystallography*

Single crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by slow evaporation from their aqueous solution. The data were collected with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart-1000 CCD diffractometer at room temperature. The structures were solved using direct methods with the SHELXTL software package [10] and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were treated using a riding model. The structures were refined on F^2 using SHELXTL-97. The crystals used for the diffraction study showed no decomposition during data collection. The crystal and refinement data of **1** and **2** are listed in table 1 and selected bond lengths and bond angles are listed in table 2.

3. Result and discussion

3.1. *Crystal structures of the two daidzein derivatives*

The molecular geometries and the atom-numbering of **1** and **2** are shown in figure 1. Compound **1** consists of a hydrated metal cation $[Mg(H_2O)_6]^{2+}$, two isoflavone sulfate anions ($C_{17}H_{13}O_4SO_3^-$) and eight lattice water molecules (figure 1a). The Mg^{II} atom lies on an inversion center and is coordinated by six water molecules. Compound **2** consists of one NH_4^+ cation, one $(C_2H_5)_2NH_2^+$ cation, two isoflavone sulfate anions and five lattice water molecules (figure 1b). The anions $C_{17}H_{13}O_4SO_3^-$ of compound **1** and $C_{19}H_{17}O_4SO_3^-$ of compound **2** are composed of a benzopyranone moiety, including

Table 1. Crystal data and structure refinement details.

Compound	**1**	**2**
Chemical formula	$C_{34}H_{54}MgO_{28}S_2$	$C_{42}H_{60}N_2O_{19}S_2$
CCDC deposit no.	601777	601776
Colour/shape	Colourless/acerose	Colourless/rhombus
Formula weight	999.20	961.04
Crystal size (mm^3)	$0.63 \times 0.34 \times 0.09$	$0.34 \times 0.29 \times 0.23$
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	18.499(7)	11.059(3)
b (Å)	7.337(3)	15.172(4)
c (Å)	18.232(6)	15.304(4)
α (°)	98.624(3)	
β (°)	115.254(4)	108.438(4)
γ (°)	92.752(4)	
Volume (Å^3)/Z	2237.8(1), 2	2395.9(1), 2
Density (calculated) (g cm^{-3})	1.483	1.332
Absorption coefficient (mm^{-1})	0.229	0.187
θ range for data collection	2.24–25.00°	1.79–25.01°
Limiting indices	$-22 \le h \le 16$, $-8 \le k \le 8$, $-19 \le l \le 21$	$-13 \le h \le 6$, $-17 \le k \le 18$, $-17 \le l \le 18$
Reflections collected/unique	11211/3933	12560/8282
Data/restraints/parameters	3933/0/295	8282/101/628
Goodness-of-fit on F^2	1.025	0.997
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0394$, $\omega R_2 = 0.0951$	$R_1 = 0.0660$, $\omega R_2 = 0.1650$
R indices (all data)	$R_1 = 0.0633$, $\omega R_2 = 0.1120$	$R_1 = 0.1418$, $\omega R_2 = 0.2169$
Largest diff. peak and hole (e Å^{-3})	0.355 and −0.329	0.724 and −0.388

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

Compound	Bond	Length	Bond	Angle
1	Mg(2)–O(8)#	2.0546(17)	O(8)#–Mg(2)–O(8)	180.00(6)
	Mg(2)–O(8)	2.0546(17)	O(8)#–Mg(2)–O(10)#	90.76(7)
	Mg(2)–O(10)#	2.0593(18)	O(8)–Mg(2)–O(10)#	89.24(7)
	Mg(2)–O(10)	2.0593(18)	O(8)#–Mg(2)–O(10)	89.24(7)
	Mg(2)–O(9)	2.0759(17)	O(8)–Mg(2)–O(10)	90.76(7)
	Mg(2)–O(9)#	2.0759(17)	O(10)#–Mg(2)–O(10)	180.0(6)
	O(1)–C(1)	1.354(3)	O(8)#–Mg(2)–O(9)	90.68(7)
	O(1)–C(9)	1.375(3)	O(8)–Mg(2)–O(9)	89.32(7)
	O(2)–C(3)	1.237(3)	O(10)#–Mg(2)–O(9)	90.94(8)
	O(3)–C(7)	1.360(3)	O(10)–Mg(2)–O(9)	89.06(8)
	O(3)–C(16)	1.424(3)	O(8)#–Mg(2)–O(9)#	89.32(7)
	O(4)–C(13)	1.358(3)	O(8)–Mg(2)–O(9)#	90.68(7)
	O(4)–C(17)	1.422(3)	O(10)#–Mg(2)–O(9)#	89.06(8)
	O(5)–S(1)	1.4415(18)	O(10)–Mg(2)–O(9)#	90.94(8)
	O(6)–S(1)	1.4588(18)	O(9)–Mg(2)–O(9)#	180.00(7)
	O(7)–S(1)	1.4495(18)	C(1)–O(1)–C(9)	117.92(19)
			C(7)–O(3)–C(16)	117.7(2)
			C(13)–O(4)–C(17)	118.24(19)
2	N(1)–C(39)	1.471(10)	C(39)–N(1)–C(41)	101.7(7)
	N(1)–C(41)	1.477(11)	C(1)–O(1)–C(9)	117.9(4)
	O(1)–C(1)	1.350(5)	C(7)–O(3)–C(16)	118.6(4)
	O(1)–C(9)	1.375(5)	C(13)–O(4)–C(18)	119.1(4)
	O(2)–C(3)	1.232(5)	C(20)–O(8)–C(28)	118.2(4)
	O(3)–C(7)	1.361(6)	C(26)–O(10)–C(35)	117.6(4)
	O(3)–C(16)	1.433(6)	C(32)–O(11)–C(37)	119.7(4)
	O(4)–C(13)	1.350(5)	O(5)–S(1)–O(7)	110.9(2)
	O(4)–C(18)	1.407(6)	O(5)–S(1)–O(6)	113.5(3)
	O(5)–S(1)	1.443(4)	O(7)–S(1)–O(6)	112.1(3)
	O(6)–S(1)	1.446(4)	O(5)–S(1)–C(12)	107.3(2)
	O(7)–S(1)	1.443(4)	O(7)–S(1)–C(12)	107.3(2)
	O(8)–C(20)	1.344(6)	O(6)–S(1)–C(12)	105.3(2)
	O(8)–C(28)	1.382(6)	O(14)–S(2)–O(13)	111.8(2)
	O(9)–C(22)	1.232(5)	O(14)–S(2)–O(12)	13.0(2)
	O(10)–C(26)	1.358(6)	O(13)–S(2)–O(12)	112.6(2)
	O(10)–C(35)	1.431(6)	O(14)–S(2)–C(31)	105.5(2)
	O(11)–C(32)	1.353(6)	O(13)–S(2)–C(31)	106.6(2)
	O(11)–C(37)	1.420(6)	O(12)–S(2)–C(31)	106.8(2)
	O(12)–S(2)	1.448(4)	C(2)–C(1)–O(1)	126.7(4)
	O(13)–S(2)	1.444(4)	C(1)–C(2)–C(3)	18.0(4)
	O(14)–S(2)	1.437(4)	C(1)–C(2)–C(10)	119.9(4)

Symmetry code, #: $1-x$, $1-y$, $1-z$.

A-ring and C-ring, a phenyl moiety B-ring and a sulfonate. For compound **2**, the anions have two conformations, which can be labeled as X1(C1–C19, O1–O7, S1) and X2(C20–C38, O8–O14, S2). The benzopyranone moiety is nearly coplanar, as indicated by the mean deviation from the least square plane of 0.0129 Å for compound **1** and 0.0058 (X1), 0.0222 Å (X2) for compound **2**. To avoid steric conflicts, the two rigid ring systems, the benzopyranone moiety and the phenyl moiety, are rotated by 57.17° in **1** and 33.95 (X1), −27.52° (X2) with respect to each other in **2**. The methoxy group bonded to a C13 of **1** is almost coplanar with its attached phenyl plane with a C17–O4–C13–C12 torsion angle of 177.44°. However, the methoxy group bonded to C7 is displaced from the benzopyranone plane, indicated by the C16–O3–C7–C6 torsion

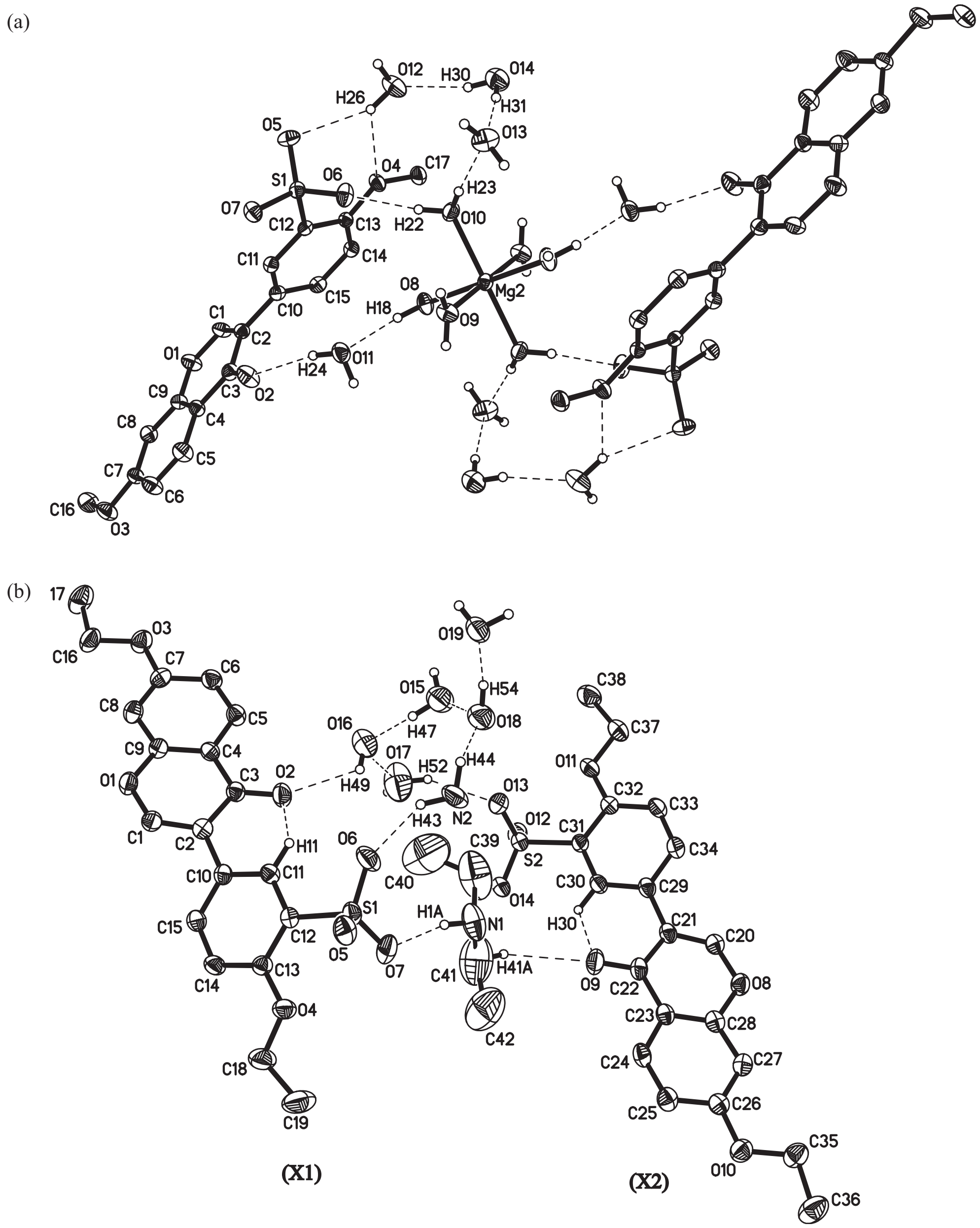

Figure 1. The molecular structures of compounds **1** (a) and **2** (b), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level. Thin dashed lines indicate the hydrogen bonds. For clarity, some H atoms have been omitted.

angle of 153.52°. For compound **2**, all ethoxy groups are slightly twisted out of the benzopyranone moiety or phenyl ring with small torsion angles.

Eight hydrogen bonds of **1** and eleven hydrogen bonds of **2** exist between the anions, the cations, and the lattice water molecules as shown in figure 1(a) and (b), respectively.

Table 3. Hydrogen-bonding geometry of **1** and **2** (Å, °).

Compound	D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry code
1	O8–H18···O11	0.86	1.89	2.737	171	
	O8–H19···O7	0.85	2.02	2.853	167	$x, y+1, z$
	O9–H20···O14	0.84	2.11	2.904	157	$x, 1/2-y, z-1/2$
	O9–H21···O6	0.84	2.01	2.830	165	$-x+1, -y, -z+1$
	O10–H22···O6	0.84	1.96	2.775	162	
	O10–H23···O13	0.86	2.03	2.887	174	
	O11–H24···O2	0.87	1.96	2.808	165	
	O11–H25···O12	0.86	1.93	2.782	173	$x, -y+1/2, z-1/2$
	O12–H26···O5	0.87	2.28	3.085	153	
	O12–H26···O4	0.87	2.38	2.959	125	
	O12–H27···O14	0.88	1.98	2.792	153	$-x+1, -y, -z+1$
	O13–H28···O7	0.87	2.13	2.989	171	$-x+1, -y, -z+1$
	O13–H29···O11	0.89	2.01	2.839	155	$-x+1, -y, -z+1$
	O14–H30···O12	0.86	1.99	2.816	161	
	O14–H31···O13	0.89	1.91	2.793	174	
	C8–H8···O5	0.93	2.49	2.868	164	$-x, 1/2+y, 1/2-z$
2	N1–H1A···O7	0.90	1.93	2.809	164	
	N1–H1B···O5	0.90	2.02	2.841	151	$x, -1+y, z$
	N2–H43···O6	0.88	2.00	2.725	139	
	N2–H44···O18	0.88	1.77	2.523	143	
	N2–H46···O7	0.88	2.05	2.837	149	$x, -1+y, z$
	O15–H47···O16	0.85	1.86	2.607	146	
	O15–H48···O13	0.85	2.12	2.729	128	$1-x, 1-y, 1-z$
	O16–H49···O2	0.85	2.23	2.768	121	
	O16–H50···O17	0.85	1.87	2.658	154	
	O17–H51···O12	0.85	2.16	2.864	140	$-1+x, y, z$
	O17–H52···O13	0.85	2.16	2.909	147	
	O18–H53···O15	0.85	1.62	2.442	161	
	O18–H54···O19	0.85	1.76	2.567	158	
	O19–H55···O12	0.85	1.95	2.801	179	$1-x, 1-y, 1-z$
	O19–H56···O14	0.85	1.89	2.745	178	$-1+x, y, z$
	C6–H6···O10	0.93	2.60	3.519	170	$1-x, -y, -z$
	C11–H11···O2	0.93	2.38	2.880	114	
	C27–H27···O5	0.93	2.49	3.391	163	$1-x, 1-y, -z$
	C30–H30···O9	0.93	2.34	2.890	118	
	C41–H41A···O9	0.97	2.48	3.272	139	

H atoms of $[Mg(H_2O)_6]^{2+}$, the eight lattice water molecules in compound **1** and the five lattice water molecules in compound **2** act as donors, leading to the formation of the hydrogen bonds. Details of the remaining hydrogen bonds of **1** and **2** are given in table 3. In **1**, one supramolecular synthon $R_5^5(12)$ ring exists between the sulfonate O5 and O6, bridged by O12–H26···O5, O14–H30···O12, O14–H31···O13, O10–H23···O13 and O10–H22···O6 hydrogen bonds. Hydrogen bonds O12–H26···O4 and O12–H26···O5, and the atom H26 act as donors forming three-centered hydrogen bonding. The atoms O5, O6, O7, O11, O12, O13 and O14 of **1** and O2, O5, O7, O9, O12 and O13 of **2** are all trifurcated by hydrogen bonds. In **2**, two independent C11–H11···O2 and C30–H30···O9 intramolecular hydrogen bonds separately form a characteristic intramolecular *S*(6) motif. In figure 2(a), the isoflavone skeletons are arranged in an anti-parallel mode and π–π stacking interactions exist between the A-rings (C4–C9) forming a column along the *b*-axis. The A-rings of the isoflavone skeleton stack with those of the neighboring isoflavone skeletons with Cg···Cg# = 3.773 Å and Cg···Cg* = 3.656 Å, where Cg is the center of A-ring at

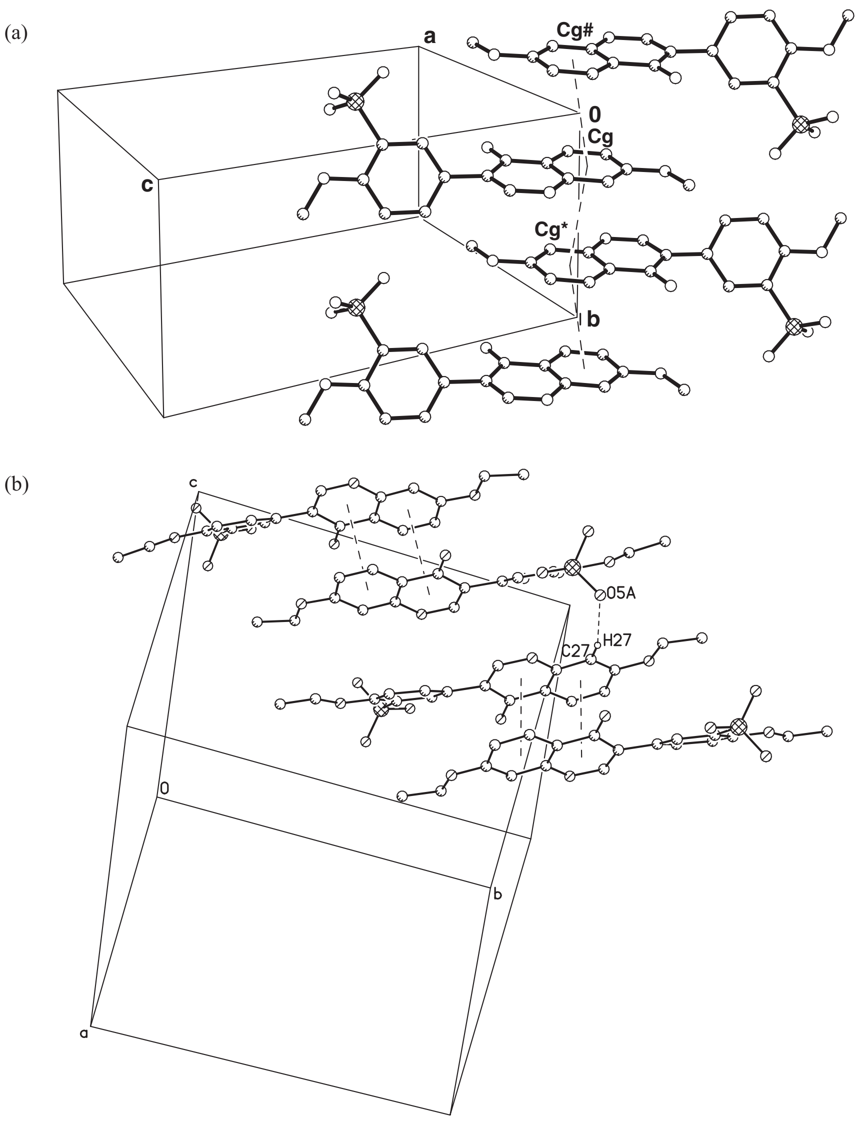

Figure 2. Part of the crystal structures of **1** (a), and **2** (b), columns viewed down the *b*-axis of compound **1** and the *c*-axis of compound **2** are generated by hydrogen bonds and other intermolecular interactions. For clarity, some H atoms bonded to atoms not involved in the motif shown have been omitted. Thin dashed lines indicate the hydrogen-bonding and π–π stacking interactions.

(x, y, z), Cg# and Cg* are the centers of the A-rings of the neighboring isoflavone skeleton at $(-x, -y, -z)$ and $(-x, 1-y, -z)$, respectively. The corresponding interplanar spacings are 3.5480 and 3.5802 Å. The π–π stacking interactions have been observed in $[Zn(H_2O)_6](C_{17}H_{13}O_7S)_2 \cdot 8H_2O$ [7]. In figure 2(b), two kinds of π–π interaction dimers are formed between the adjacent benzopyranone moieties of X1 and X2 with an almost anti-parallel manner with rings A and C, of which the dihedral angles are 0.3 and 2.1° and the intercentroid distances are 3.432 and 3.626 Å, respectively. A normal range for such interaction is 3.3–3.8 Å [11]. The strong hydrogen

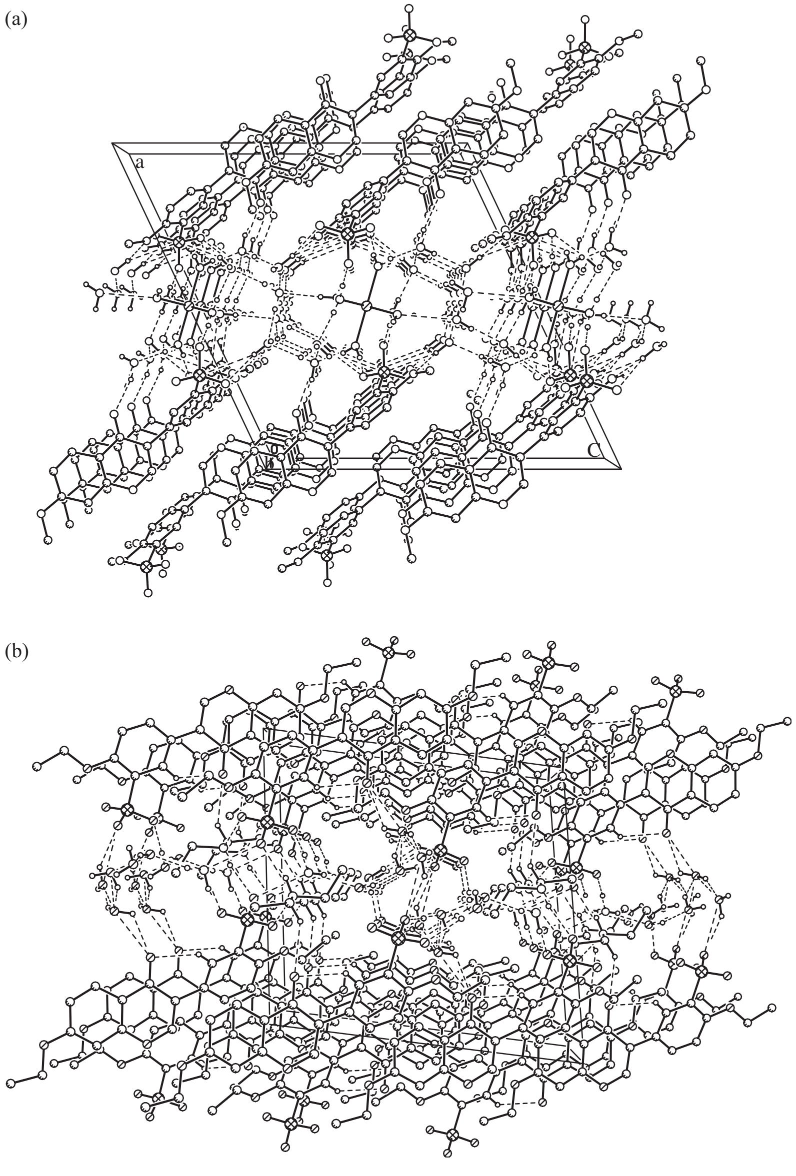

Figure 3. Unit cell packing diagrams of **1**, (a) and **2**, (b), viewed down the *b*-axis and *c*-axis, respectively.

bonds C27–H27 $\cdots$ O5A $(1-x, 1-y, -z)$ link the two dimers into a column along the *c*-axis.

In **1** and **2**, the hydrophilic regions are dominated by classical hydrogen bonds, while the columns of the isoflavone moieties generate the hydrophobic regions by π–π stacking, with the sulfonate bridging the two regions, as well as organic and inorganic components as shown in figure 3(a) and (b), respectively. This combination of the hydrogen bonds, π–π stacking and electrostatic interactions between the cations and anions of compounds **1** and **2** lead to the formation of three-dimensional supramolecular structures in these two daidzein derivatives.

3.2. *Infrared spectra*

In the IR spectrum of compound **1**, bands at 1567(m) and 1091(s) cm^{-1} can be assigned to ν(–C=O) and $\nu(-SO_3^-)$ of the isoflavone. For compound **2**, ν(N–H) bonds of the NH_4^+ and $(C_2H_5)_2NH_2^+$ can be seen separately at 3430(s) and 2357(s) cm^{-1}. Bonds at 1563(m) and 1100(s) cm^{-1} originate from ν(–C=O) and $\nu(-SO_3^-)$ of the isoflavone, respectively.

Supplementary material

CCDC-601777 and CCDC-601776 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retriev-ing.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk)].

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