Structure, tautomerism, and features of 1-(5-acetyl-2,4-dihydroxyphenyl)-3-(furan-2-yl)prop-2-en-1-one (FC) and 1,1′-(4,6-dihydroxybenzene-1,3-diyl)bis[3-(furan-2-yl)prop-2-en-1-one] (FDC)

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Abstract Quantum chemistry studies of various tautomeric/rotameric forms of the furanyl analogues of acetyl dihydroxychalcone (FC) and dihydroxydichalcone (FDC) have shown that the thermodynamically most stable molecules are planar. In the crystalline solid phase, both molecules are more (FDC) or less (FC) non-planar. Two relatively strong intramolecular H-bonds, whose existence is evidenced by X-ray, computational, and spectral investigations, stabilize the planar geometry and influence the features of the lowest energy tautomers/rotamers of both compounds. Extending to the visible region, the electronic absorption of FC and FDC is accompanied by an intramolecular electron density shift, a property that could have analytical implications.

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Introduction

Derivatives of (2E)-1,3-diphenylprop-2-en-1-one (chalcones) are naturally occurring compounds which, due to their biological activity, have been the subject of interest to the food and health sciences [1, 2]. They have been thoroughly investigated in the context of their role in plant growth, human diet, and healthcare [1–7]. Our interest in these compounds arises from the fact that they are precursors in the synthesis of flavonols, which are derivatives of 3-hydroxy-2-phenyl-4H-chromene-4-one [8–10]. Following the synthesis of various chalcones (C) and dichalcones (DC) [derived from (2E,2′E)-1,1′-(1,3-phenylene)bis(3-phenylprop-2-en-1-one)] and related derivatives, we obtained two compounds that were furanyl (F) analogues of these entities, namely, 1-(5-acetyl-2,4-dihydroxyphenyl)-3-(furan-2-yl)prop-2-en-1-one (FC) and 1,1′-(4,6-dihydroxybenzene-1,3-diyl)bis[3-(furan-2-yl)prop-2-en-1-one] (FDC). The molecules of these compounds provide convenient models for studying the properties of intramolecular H-bonds, as there are two sites present in them where a hydroxyl group appears in the vicinity of the carbonyl group and where such bonds can occur. Another interesting property of FC and FDC is that both can exist in several tautomeric and rotameric forms. With these compounds in hand, we can investigate these phenomena. Finally, we may infer from the canonical structures of FC and FDC that both molecules should be planar. Thus, it would be interesting to know how such relatively large molecules are packed in the crystalline solid phase. To shed more light on these issues and to elucidate the properties of both these molecules, we carried out X-ray, spectroscopic, and computational investigations, the results of which are presented in this publication. A search of the Cambridge Structure

Database [11] showed that the structures of several chalcones have been determined by X-ray diffractometry, but that no structures of dichalcones have as yet been established.

Materials and methods

Synthesis and spectral investigations

1-(5-Acetyl-2,4-dihydroxyphenyl)-3-(furan-2-yl)prop-2-en-1-one (FC) and 1,1′-(4,6-dihydroxybenzene-1,3-diyl)-bis[3-(furan-2-yl)prop-2-en-1-one] (FDC) were synthesized by condensation (with removal of H_2O) of commercially available 1,1′-(4,6-dihydroxybenzene-1,3-diyl)diethanone with furan-2-carbaldehyde dissolved in methanol/50 % aqueous NaOH (1/1 v/v) [8, 9, 12]. The reactant mixture was kept at room temperature for 48 h, then diluted twice with distilled water and neutralized with aqueous HCl to pH 5. The resulting precipitate was filtered off, rinsed with hot (333–343 K) water and dried. The products obtained were separated by gravitational column chromatography (Silica Gel 60, ethyl acetate/hexane, 1/2 v/v). Yellow-orange and orange crystals of FC and FDC, respectively, suitable for X-ray and other investigations were grown from an ethanol/n-hexane (4/1 v/v) solution (FC: m.p. 452–453 K, $m/z = 273$ (M–H^+); FDC: m.p. 444–445 K, $m/z = 351$ (M–H^+)).

The relevant spectral grade solvents were used throughout in the spectroscopic investigations. UV spectra were recorded on a Hitachi U3210 spectrophotometer. IR spectra were recorded on a Bruker FTIR IFS 66 spectrophotometer and NMR spectra on a Varian Unity 500 Plus spectrometer operating at a proton frequency of 500 MHz (carbon frequency = 125 MHz).

Single crystal X-ray measurements

X-ray data for the title compounds were collected on an Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer (MoKα radiation, graphite monochromator). Data collection and cell refinement were carried out with CrysAlis CCD and data reduction with CrysAlis RED. Structure solution and refinement was carried out with the SHELXS97 package. All C and O atoms were refined anisotropically. H atoms of C–H bonds were positioned geometrically and constrained to ride on their parent atoms, H atoms involved in O–H···O hydrogen bonds were located on a difference Fourier map and refined isotropically. The asymmetric unit consists of two crystallographically independent molecules of FC and one half of the molecule of FDC.

Computations

Geometry optimizations were carried out at the DFT level of theory [13] with the B3LYP functional [14–17] and 6–31G** basis set [18, 19] and, in the case of selected entities, at the MP2 level [20] using the cc-pVDZ basis set [21, 22] and the Gaussian 03 program package [23].
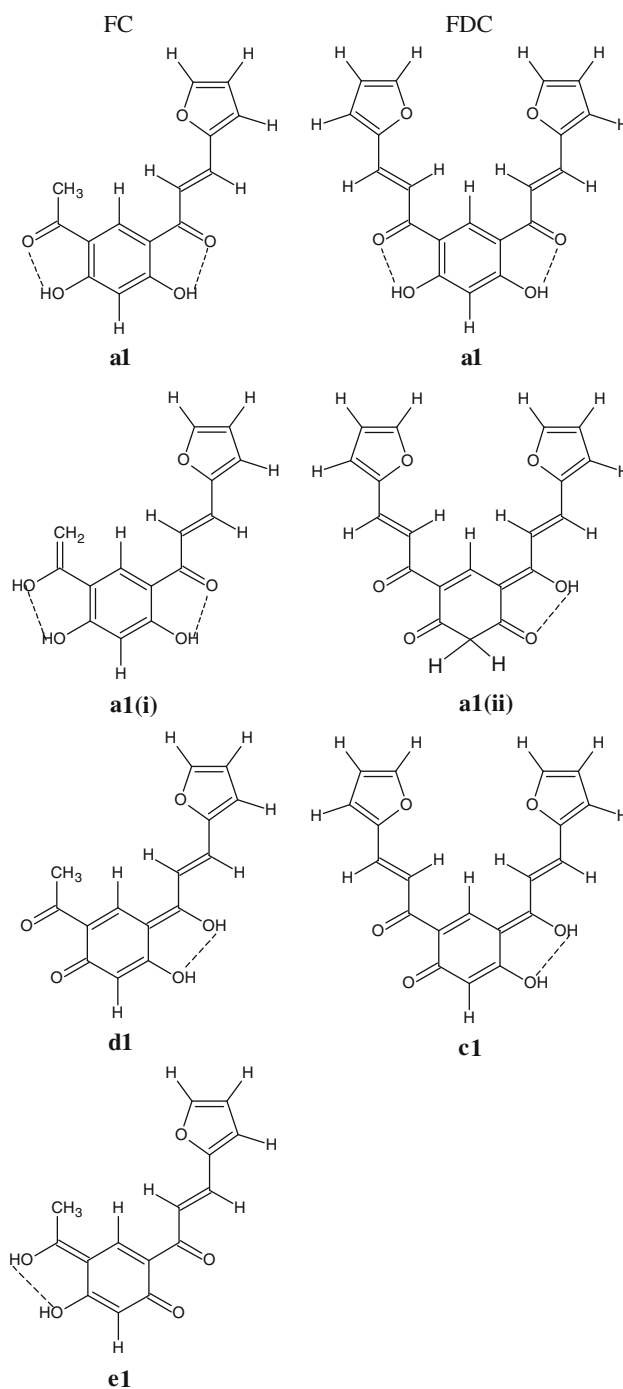

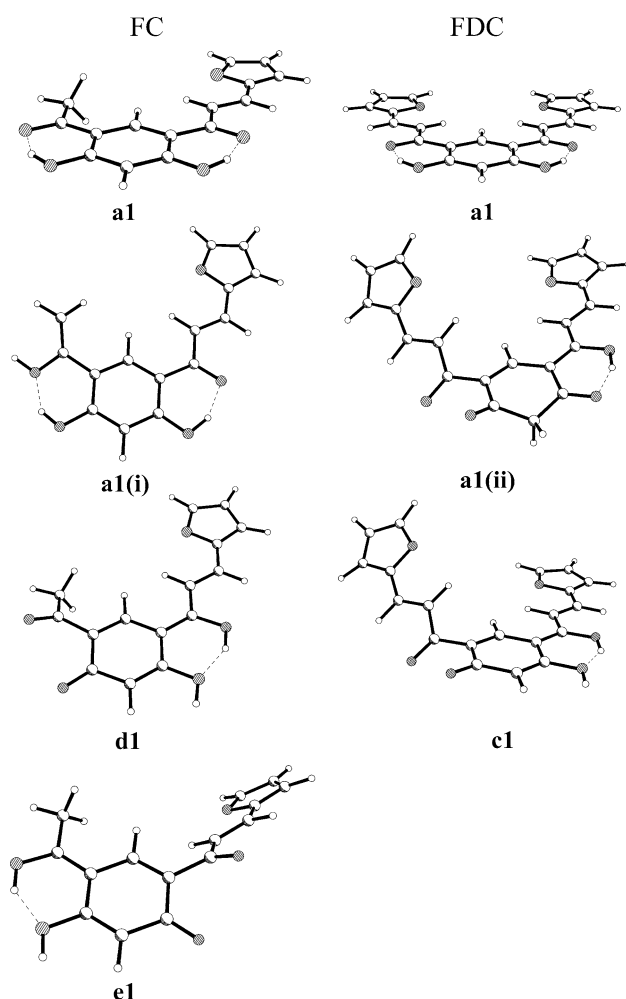Fig. 1 Canonical structures of selected tautomeric forms of FC and FDC

FC   FDC

a1   a1

a1(i)   a1(ii)

d1   c1

e1

Fig. 2 MP2 optimized structures of selected tautomeric forms of FC and FDC (for canonical structures, see Fig. 1)

Results and discussion

According to the relevant canonical structures (Figs. 1 and 1S, 2S in the Supplementary data), we can expect FC and FDC to have, respectively, five and three tautomeric forms (resulting from the migration of the H atom between two O atoms) with two or one intramolecular H-bond(s) [24]. In the case of only one intramolecular H-bond, four tautomeric/rotameric canonical structures can be expected for both FC and FDC. Rotation of furanyl fragment(s) around a C–C bond, examined to ascertain whether the crystalline phase consists of the lowest energy rotamers, makes it possible for each FC tautomer to occur in two rotameric forms, and each FDC tautomer in three or four such forms. Investigation of the rotation of the O–H group around a C–O bond in four tautomers/rotamers of both FC and FDC enabled us to ascertain whether this would be an adequate reflection of the thermodynamics of H-bonds. Tautomerism may also result from the migration of the H atom between

Table 1 Thermodynamic data for the selected FC and FDC tautomers/rotamers in the gaseous phase

Tautomer/rotamer	ΔH		ΔG	
	DFT	MP2	DFT	MP2
FC				
a1	0.0	0.0	0.0	0.0
a2	7.2	7.8	4.5	4.0
a1(i)	97.4	88.8	98.8	89.5
b1*	148.1	148.4	146.2	147.1
c1*	153.4	156.1	142.5	154.5
d1	154.8	144.8	148.1	138.9
e1	162.2	153.3	155.0	146.7
FDC				
a1	0.0	0.0	0.0	0.0
a2	6.6	1.4	9.9	4.7
a1(ii)	103.3	95.5	104.4	96.5
b1*	148.2	144.6	150.7	152.2
c1	153.0	132.0	152.9	158.1

Values obtained at the DFT(B3LYP)/6–31G** (DFT) or MP2/cc-pVDZ (MP2) levels of theory

ΔH represents the enthalpy of a given tautomer/rotamer (indicated in Figs. 1 and 1S–3S in the Supplementary data) relative to the enthalpy of form **a1** (given in Table 1S in the Supplementary data); ΔG is the Gibbs free energy of a given tautomer/rotamer (indicated in Figs. 1 and 1S–3S in the Supplementary data) relative to the Gibbs free energy of form **a1** (given in Table 1S in the Supplementary data); ΔH and ΔG, in kJ/mol, correspond to 298.14 K and standard pressure

C and O, O and C, or two O atoms [24], which leads to a substantial increase in the number of tautomers. To take into account such a possibility we considered selected structures relevant to the **a1** forms (found to be the lowest energy ones) of FC (fifteen structures) and FDC (four structures) (Fig. 3S in the Supplementary data).

Optimization of the canonical structures **a1**, **b1,** and **c1** of FC or **a1** and **b1** of FDC leads to the most stable molecular structure **a1** for each compound (Fig. 2). An analogous result was obtained for the respective rotamers of FC (**a2**) and FDC (**a2** and **a3**); the relevant molecular structures are shown in Figs. 4S–6S (Supplementary data), also those in which only one H-bond is present (**d** and **e** of FC, and **c** of FDC). The data in Table 1 (Tables 1S, 2S in the Supplementary data) indicate that the thermodynamically most stable tautomer of FC and FDC is predicted to be **a**, which can occur as two rotamers (**a1** and **a2**) in the former compound and three rotamers (**a1**, **a2**, and **a3**) in the latter. The enthalpy and Gibbs free energy differences between the most and the least stable rotamers of **a** are no greater than a dozen or so kJ/mol, which implies that various entities of this kind can occur in equilibrium at room temperature (the equilibrium constants expressing the ratio of the number of molecules of **a2** and **a1** should be

0.201 and 0.152 for FC and FDC, respectively; from MP2 data). Other tautomers/rotamers of both compounds, including those resulting from the migration of the H atom between C–O, O–C, or two O atoms are over 89 kJ/mol thermodynamically less stable than tautomer/rotamer **a1** and cannot be expected to be present in measurable amounts under such conditions.

The stability of tautomers **a** [**b**, **c**, **a1(i)–a1(vii)**] of FC and **a** (**b**) of FDC should be substantially enhanced by two intramolecular H-bonds (Figs. 1 and 1S–3S in the Supplementary data). In other tautomers of the compounds considered only one such bond occurs. Therefore, the differences between the enthalpy (ΔH) and Gibbs free energy (ΔG) of the respective tautomeric/rotameric forms [**d**, **e** and **a** (**b**, **c**) of FC and **c** and **a** (**b**) of FDC] could tentatively be regarded as relevant thermodynamic characteristics of a single H-bond (tautomeric forms resulting from the migration of the H atom between C and O, O and C or two O atoms cannot be used for such estimations). The ΔH and ΔG values shown in Tables 1 and 2S (Supplementary data) are, however, much higher than those we found earlier for a single H-bond (ΔG for such a bond was estimated to be 78.3 kJ/mol [25]). Presumably, then, the transformation from tautomer **a** to other tautomers of FC (**d**, **e**) and FDC (**c**) is accompanied not only by the disappearance of one H-bond, but also by substantial structural changes (Figs. 2 and 4S–6S in the Supplementary data), which lead to the additional thermodynamic destabilization of the latter molecules. If we compare tautomer **a** with tautomers **d** and **e** of FC, and tautomer **a** with tautomer **c** of FDC, we find that they occur as a result of H atom transfer between non-vicinal sites of the molecules. On the other hand, the forms **b*** and **c*** originating from **b** and **c** of FC and **b*** originating from **b** of FDC, which occur as a result of H atom transfer between vicinal sites of the molecules, are thermodynamically much less stable. The ΔH and ΔG values of the respective latter forms are comparable to the former ones mentioned above, which means that they probably do not reflect thermodynamic characteristics of the single H-bond. The forms **b*** and **c*** of FC and **b*** of FDC can exist since there is an enthalpy and Gibbs free energy barrier to a H atom returning to the position it occupied in tautomers **b** and **c** of FC and **b** of FDC, respectively (the structures of molecules in transition states for such a process are presented in Figs. 7S and 8S, and the activation barriers are given in Table 3S in the Supplementary data).

Crystals of FC and FDC consist of tautomers/rotamers **a1**, as demonstrated by the results of X-ray investigations [the details of the refinement (Tables 4S, 5S) are given in the Supplementary data]. Two structurally similar but crystallographically independent molecules A and B are present in the asymmetric unit of FC (Figs. 3 and 9S in the Supplementary data), while one half of the molecule of C_2

symmetry is present in the asymmetric unit of FDC (Figs. 4 and 10S in the Supplementary data). The molecular structure of FC is stabilized by two $S(6)$ type intramolecular O–H···O H-bonds (Table 6S in the Supplementary data), and the crystal structure of the compound by a network of intermolecular C–H···O interactions (Table 7S and
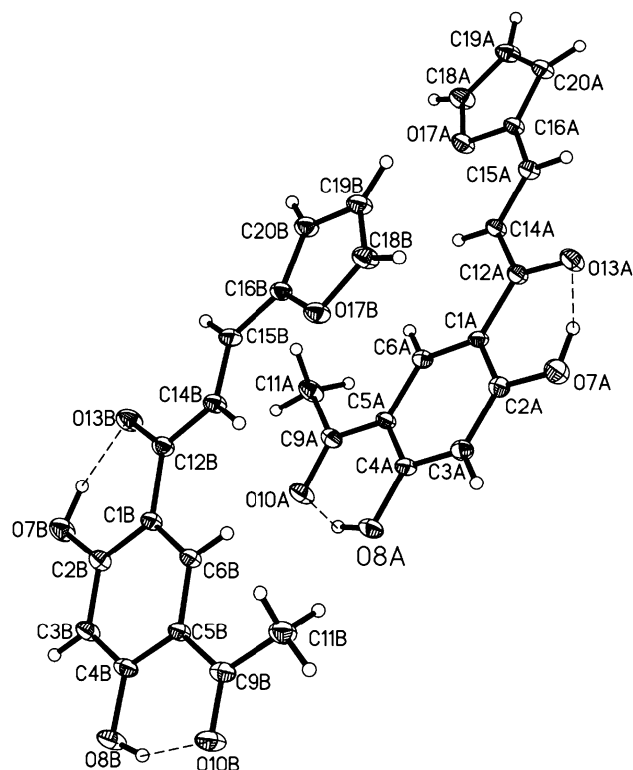

Fig. 3 ORTEP view of two structurally similar but crystallographically independent A and B molecules in the asymmetric unit of the crystalline solid phase of FC (*dashed lines* H-bonds)
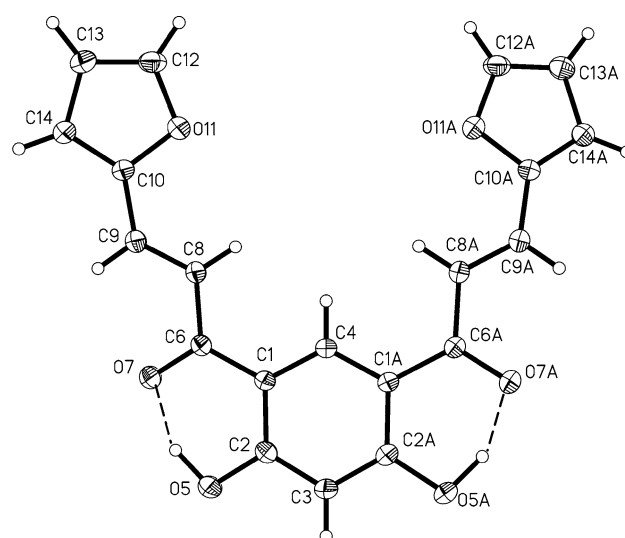

Fig. 4 ORTEP view of the FDC molecule in the crystalline solid phase (*dashed lines* H-bonds)

Table 2 Comparison of experimental (X-ray) and predicted (DFT(B3LYP)/ 6–31G** and MP2/cc-pVDZ levels of theory) lengths of C–C, C–O and C=O bonds (in Å) in FC

Bond[a]	X-ray[b]		DFT[c]		MP2[c]	
	A	B		δ[d]		δ[d]
C1–C2	1.417 (4)	1.414 (4)	1.442	1.764/1.980	1.437	1.411/1.627
C1–C6	1.386 (4)	1.385 (4)	1.398	0.866/0.939	1.406	1.443/1.516
C1–C12	1.457 (4)	1.463 (4)	1.471	0.961/0.547	1.481	1.647/1.230
C2–C3	1.372 (4)	1.373 (4)	1.395	1.676/1.602	1.402	2.187/2.112
C2–O7	1.344 (4)	1.350 (4)	1.329	1.116/1.556	1.339	0.372/0.815
C3–C4	1.363 (4)	1.373 (4)	1.393	2.201/1.457	1.400	2.715/1.966
C4–C5	1.416 (4)	1.403 (4)	1.439	1.624/2.566	1.434	1.271/2.210
C4–O8	1.344 (4)	1.347 (4)	1.331	0.967/1.113	1.341	0.223/0.445
C5–C6	1.387 (4)	1.386 (4)	1.398	0.793/0.865	1.404	1.226/1.299
C5–C9	1.444 (4)	1.458 (4)	1.464	1.385/0.412	1.479	2.424/1.440
C9–O10	1.241 (3)	1.243 (3)	1.243	0.161/0.0	1.243	0.161/0.0
C9–C11	1.499 (4)	1.497 (4)	1.516	1.134/1.269	1.516	1.134/1.269
C12–O13	1.246 (4)	1.251 (4)	1.255	0.722/0.320	1.251	0.401/0.0
C12–C14	1.454 (4)	1.448 (4)	1.470	1.309/1.519	1.482	2.132/2.348
C14–C15	1.332 (4)	1.336 (4)	1.353	1.577/1.272	1.362	2.252/1.946
C15–C16	1.423 (4)	1.409 (4)	1.430	0.492/1.490	1.440	1.195/2.200
C16–O17	1.361 (4)	1.367 (3)	1.376	1.102/0.658	1.370	0.661/0.219
C16–C20	1.353 (4)	1.353 (4)	1.377	1.774/1.774	1.392	2.882/2.882
O17–C18	1.355 (4)	1.361 (4)	1.357	0.148/0.294	1.362	0.517/0.073
C18–C19	1.330 (4)	1.334 (4)	1.365	2.632/2.324	1.381	3.835/3.523
C19–C20	1.401 (4)	1.391 (4)	1.424	1.642/2.372	1.428	1.927/2.660
Average				1.240/1.254		1.525/1.513

[a] The atom numbering is given in Fig. 9S

[b] A and B denote two structurally similar but crystallographically independent molecules in the asymmetric unit of the compound (Fig. 9S)

[c] For **a1** structure, see Figs. 1S, 4S and 6S

[d] δ=|X-ray bond length–DFT or MP2 bond length|/X-ray bond length × 100 (in %)

Fig. 11S in the Supplementary data). The molecular structure of FDC is also stabilized by two S(6) type intramolecular O–H···O H-bonds (Table 8S in the Supplementary data). In the crystal structure, the parallel FDC molecules interacting via C=O···π contacts (Table 9S in the Supplementary data) are arranged in columns along the a axis; the inverted columns in which molecules are in contact via C–H···O interactions (Table 10S in the Supplementary data) form pairs of columns, each of which interacts dispersively with four adjacent pairs of columns stabilizing the crystal lattice (Figs. 12S, 13S in the Supplementary data).

The experimentally determined structural parameters of the **a1** forms of the compounds investigated compared well with the predicted values (Tables 2, 3) according to the criteria we applied earlier [25]. The lowest energy forms (**a1**) of both FC and FDC (C_{2v} symmetry) should be planar in the gaseous phase (Table 4). In the crystalline solid phase both compounds are less (FC) and more (FDC) non-planar. Other tautomers/rotamers of FC and FDC are predicted to be either planar (**a2** and **c1*** of FC, and **a2** and **a3** of FDC) or non-planar (Tables 4 and 11S in the Supplementary data). Low energy rotamers resulting from the rotation of furanyl fragment(s) around a C–C bond (**a1** and **a2** of FC, and **a1**, **a2** and **a3** of FDC) are predicted to be

Table 3 Comparison of experimental (X-ray) and predicted (DFT(B3LYP)/6–31G** and MP2/cc-pVDZ levels of theory) lengths of C–C, C–O and C=O bonds (in Å) in FDC

Bond[a]	X-ray	B3LYP[b]		MP2[b]	
			δ[c]		δ[c]
C1–C2, C1A–C2A	1.417 (4)	1.442	1.764	1.437	1.411
C1–C4, C1A–C4	1.384 (3)	1.398	1.012	1.406	1.590
C1–C6, C1A–C6A	1.461 (4)	1.470	0.616	1.480	1.300
C2–C3, C2A–C3	1.384 (3)	1.393	0.650	1.401	1.228
C2–O5, C2A–O5A	1.346 (3)	1.330	1.189	1.339	0.520
C6–O7, C6A–O7A	1.248 (3)	1.255	0.561	1.251	0.240
C6–C8, C6A–C8A	1.457 (4)	1.472	1.030	1.482	1.716
C8–C9, C8A–C9A	1.331 (4)	1.352	1.578	1.362	2.329
C9–C10, C9A–C10A	1.429 (4)	1.430	0.070	1.440	0.770
C10–O11, C10A–O11A	1.367 (3)	1.375	0.585	1.370	0.219
C10–C14, C10A–C14A	1.337 (4)	1.377	2.992	1.392	4.114
O11–C12, O11A–C12A	1.372 (4)	1.357	1.093	1.362	0.729
C12–C13, C12A–C13A	1.320 (4)	1.365	3.409	1.381	4.621
C13–C14, C13A–C14A	1.412 (4)	1.424	0.850	1.428	1.133
Average			1.243		1.566

[a] The atom numbering is given in Fig. 10S

[b] For **a1** structure, see Figs. 2S, 5S and 6S

[c] δ=|X-ray bond length–DFT or MP2 bond length|/X-ray bond length × 100 (in %)

Table 4 Structural features of selected (Table 1) tautomers/rotamers of FC and FDC

Tautomer[a]	Method[b]	A[c]	Bond lengths[d]			
			C–O		C=O	
			B	D	B	D
FC						
a1	X-ray	0.0352 (2); 0.0465 (2)[e]	1.346 (4)		1.245 (4)	
	MP2	0.0002	1.340		1.247	
	DFT	0.0000	1.330		1.249	
a2	MP2	0.0000	1.340		1.246	
	DFT	0.0000	1.330		1.248	
a1(i)	MP2	0.1026	1.362		1.251	
	DFT	0.0948	1.358		1.256	
b1*	MP2	0.1600	1.349	1.347	1.241	1.237
	DFT	0.1764	1.342	1.342	1.240	1.234
c1*	MP2	0.0000	1.347	1.343	1.248	1.237
	DFT	0.0000	1.339	1.338	1.251	1.234
d1	MP2	0.0841	1.365			1.229
	DFT	0.0813	1.362			1.223
e1	MP2	0.4159	1.361			1.232
	DFT	0.4149	1.359			1.227
FDC						
a1	X-ray	0.1774 (2)	1.346 (3)		1.248 (3)	
	MP2	0.0000	1.339		1.251	
	DFT	0.0000	1.330		1.255	
a2	MP2	0.0000	1.339		1.251	
	DFT	0.0000	1.329		1.254	
a1(ii)	MP2	0.3144	1.330		1.248	
	DFT	0.3223	1.323		1.251	
b1*	MP2	0.2682	1.348	1.348	1.248	1.237
	DFT	0.2446	1.340	1.343	1.251	1.234
c1	MP2	0.3782	1.365			1.232
	DFT	0.3929	1.363			1.228

[a] For canonical structures, see Figs. 1 and 1S–3S in the Supplementary data

[b] MP2 (MP2/cc-pVDZ), DFT (DFT(B3LYP)/6–31G**) levels of theory

[c] A—average deviation from planarity of the molecular system involving all C and O atoms

[d] Mean lengths of the C–O(H) and C=O bonds (in Å) when O atoms are engaged (B) and non-engaged (D) in intramolecular H-bonds

[e] Values for molecules A (first) and B (second) in Fig. 3

planar, whereas rotamers arising from the rotation of the OH group around a C–O bond (**b1***, **b2*** and **c2*** of FC, and **b1***, **b2***, **b3*,** and **b4*** of FDC) ought to be non-planar. It is thus evident that the disappearance of one of the H-bonds in the latter rotamers is accompanied by a loss of planarity. Another reason for the loss of planarity is the partial disappearance of resonance conjugation from the molecular systems of FC [in tautomers **a1(vi)**, **a1(vii)**, **a1(x)**, **a1(xi)**, **a1(xiv)**, and **a1(xv)**] and FDC [**a1(iii)** and **a1(iv)**] (Fig. 3S in the Supplementary data). The thermodynamic measure of this effect can be given by the difference in Gibbs free energies of the relevant tautomers of the series **a1(i)**–**a1(xv)** of FC and **a1(i)**–**a1(iv)** of FDC. The lowest such differences [i.e. relevant to **a1(x)**–**a1(viii)** and **a1(xv)**–**a1(xiii)** of FC, and **a1(iii)**–**a1(ii)** of FDC], ranging from 24 to 32 kJ/mol, reflect the extent of the thermodynamic destabilization of both molecules caused by the partial disappearance of conjugation in them.

C=O bonds in molecules in which O atoms are involved in (C)O···H–O interactions, whose geometry is described in Tables 6S and 8S (Supplementary data) and demonstrated in Figs. 2 and 4S–6S (Supplementary data), are usually longer than those not engaged in such interactions (Tables 4 and 11S in the Supplementary data). On the other hand, the C–O bond length, if the O atom is a part of the hydroxyl group, is not affected by the involvement or non-involvement of this group in H-bonding interactions. The involvement of the above mentioned fragments of FC and FDC molecules in intramolecular O–H···O bonds is confirmed by IR and NMR spectral data: the wavenumbers of the C=O and O–H stretching vibrations determined experimentally agree qualitatively with the predicted values (Table 5) [25, 26], and the ^{1}H signals of H atoms from hydroxyl groups engaged in such interactions appear at relatively high chemical shifts (Table 6) [25, 27].

Table 5 Infrared absorption data (in cm^{-1}) for FC and FDC

Method	Vibration/wavenumber[a]			
FC				
	C(9)=O(10)	C(12)=O(13)	O(7)–H	O(8)–H
Exp	1,630	1,610	3,420 (broad)	
Theor[b]	1,663	1,651	3,283	3,349
FDC				
	C(6/6A)=O(7/7A)		O(5/5A)–H	
Exp	1,699		3,440 (broad)	
Theor[b]	1,702		3,297	

Exp—experimental values from IR spectra recorded in KBr pellets; Theor—values predicted for isolated molecules at the MP2/cc-pVDZ level of theory

[a] The atom numbering (in parentheses) is given in Figs. 9S and 10S

[b] Stretching vibrations in structures **a1**

Extension of the electronic absorption of FC and FDC to the visible region (Figs. 5, 6) confirms that both molecular systems are conjugated and planar. The long wavelength absorption accompanied by an electron density shift from 4,6-dihydroxy-1,3-phenylene (in both FC and FDC) to the one (FC) or two (FDC) (1*E*)-1-(furan-2-yl)-3-oxoprop-1-en-3-yl fragments, as reflected by changes in the sum of the atomic partial charges of these fragments (Table 7) and the contours of the HOMO and LUMO orbitals of molecules in the ground and electronically excited states (Figs. 14S, 15S in the Supplementary data), is similar in both compounds (falling within the 370–380 nm range). This implies that the extent of conjugation does not affect the spectral behaviour of FDC. Electronic excitation is also accompanied by loss of planarity in both FC and FDC (Fig. 16S in the Supplementary data). Such substantial structural and electron density changes accompanying electronic excitation make these compounds potential absorption spectral
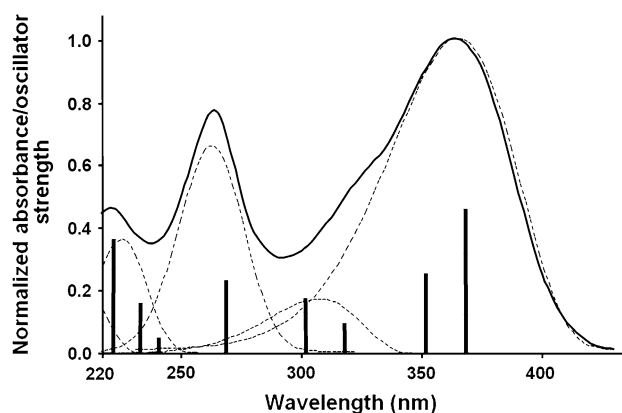

Fig. 5 The UV–vis absorption (*solid line*) and deconvoluted (using Spectral Data Lab software [35]) (*dashed lines*) spectra of FC (dissolved in methanol) together with predicted (at the TDDFT(B3LYP)/6–31G** level of theory for structure **a1**) electronic absorption transitions (*bars*)
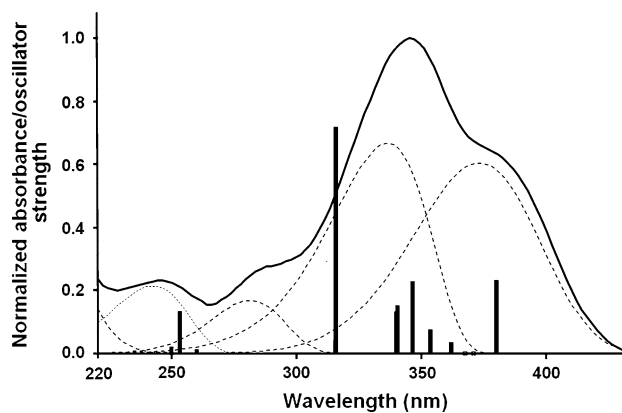

Fig. 6 The UV–VIS absorption (*solid line*) and deconvoluted (using Spectral Data Lab software [35]) (*dashed lines*) spectra of FDC (dissolved in methanol) together with predicted (at the TDDFT(B3LYP)/6-31G** level of theory for structure **a1**) electronic absorption transitions (*bars*)

Table 6 ^{1}H chemical shifts (in ppm) for FC and FDC

Method	Hydrogen atom number[a]/chemical shift								
FC									
	3	6	7/8	11	14	15	18	19	20
Exp	6.39	8.52	13.04	2.69	7.63	7.77	7.95	6.72	7.16
Theor[b]	6.23	8.41	14.46/13.25	2.35/2.19/2.34	6.95	8.24	7.57	6.44	6.85
FDC									
	3	4	5/5A	8/8A	9/9A	12/12A	13/13A	14/14A	
Exp	6.44	8.66	13.24	7.63	7.77	7.95	6.72	7.16	
Theor[b]	6.25	8.71	14.46/14.46	7.10/7.10	8.24/8.25	7.61/7.61	6.45/6.45	6.84/6.84	

Exp—experimental values from ^{1}H spectra recorded in DMSO-d_6; Theor—values predicted for isolated molecules at the GIAO MP2/cc-pVDZ level of theory [20–22, 28–31]

[a] Identical with the carbon or oxygen atom number to which it is attached (the atom numbering is given in Figs. 9S and 10S)

[b] Values for structures **a1**

Table 7 Sum of Mulliken [32, 33] and MEP fitted [34] atomic partial charges of selected fragments of FC and FDC in the ground and excited electronic states

Fragment	Sum of atomic partial charges			
	Ground state		Excited state	
	Mulliken	MEP fit	Mulliken	MEP fit
FC				
A	0.1620	−0.1641	0.3625	0.1380
B	−0.0922	0.0940	−0.0461	0.1075
C	−0.0698	0.0701	−0.3164	−0.2455
FDC				
A	0.1570	−0.0935	0.3266	0.1465
B	−0.0785	0.0392	−0.1633	−0.0732
C	−0.0785	0.0543	−0.1633	−0.0733

indicators for physicochemical and analytical investigations. On the other hand, the compounds investigated do not luminesce, so they cannot be used as fluorescent probes.
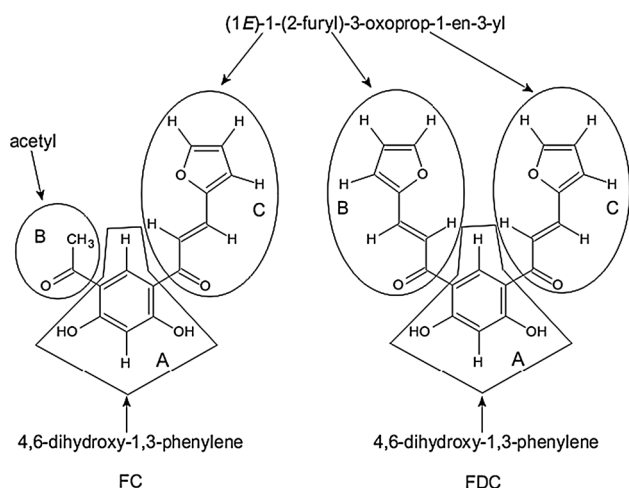
Conclusions

To summarize, only one tautomeric/rotameric form of FC and FDC has been found in the crystalline solid phase, which corresponds to the lowest energy form of the isolated molecules. Two intramolecular H-bonds influencing the crystal structures of FC and FDC also occur in the liquid phase and affect the spectral properties of both molecules. The quite large FC and FDC molecules, predicted to be planar in the ground state become non-planar in the electronically excited state. Electronic excitation, accompanied by a substantial interfragmental shift of electron density, makes these compounds potential spectral indicators for physicochemical and analytical applications.

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