

DFT and AIM studies of intramolecular hydrogen bonds in dicoumarols

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Abstract

Density functional calculations with Becke's three parameter hybrid method using the correlation functional of Lee, Yang and Parr (B3LYP) were carried out for 3,3'-benzylidenebis(4-hydroxycoumarin) (phenyldicoumarol, PhDC), 3,3'-methylenebis(4-hydroxycoumarin) (dicoumarol, DC) and the parent compound, 4-hydroxycoumarin (4-HC). Different basis sets were tested in the course of the calculations: 6-31G*, 6-31+G** and 6-311G*. In full agreement with available X-ray data, B3LYP/6-31G* calculations of the lowest-energy conformer, PhDC showed two O–H···O asymmetrical intramolecular hydrogen bonds with O···O distances 2.638 and 2.696 Å. The HB energies in PhDC were estimated of –55.46 and –52.32 kJ/mol, respectively. The values obtained correlated with the calculated and experimental O···O distances and predicted difference in the hydrogen bonding strengths in PhDC. The total HB energy in PhDC was calculated of –107.73 kJ/mol. At the same level of theory, both O···O intramolecular distances in DC were calculated identical (2.696 Å) and thus two symmetrical hydrogen bondings were obtained. The single HB strength was estimated of –50.89 kJ/mol and the total one of –101.79 kJ/mol. The electron density (ρ_b) and Laplacian ($\nabla^2\rho_b$) properties, estimated by AIM calculations, showed that both O···H bonds have low ρ_b and positive $\nabla^2\rho_b$ values (consistent with electrostatic character of the HBs), whereas both O–H bonds have covalent character ($\nabla^2\rho_b < 0$). Natural population analysis data for PhDC, DC and 4-HC were used to predict electrostatic interactions in the exocyclic rings. The calculated oxygen natural charges were found to correlate with the O···O distances in PhDC and DC. On the basis of the calculated bond ellipticity, the π -delocalization in the exocyclic rings of PhDC and DC was estimated. The results thus obtained helped to describe the nature of the intramolecular O···H–O bonds and the forces driving their formation. Vibrational study of PhDC at B3LYP/6-31G* optimized geometries showed higher negative (red) shifts for the $\nu(\text{O–H})$ of the O–H involved in the stronger HB (–610 cm^{-1}) in comparison with that obtained for the second O–H which forms the weaker HB in PhDC (–559 cm^{-1}).

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1. Introduction

Hydroxycoumarins and their derivatives possess many diverse applications as colorants, dye laser media, nonlinear optical chromophores as well as biological agents. The electronic structure and electronic absorption spectra of 4- and 7-hydroxycoumarins in their neutral, H-bonded and ionized hydroxyl functions, in

the ground (S_0) and lowest singlet (S_1) and triplet (T_1) excited states were subject of extensive studies [1–7]. At the same time, many oxygenated coumarins, e.g., 4-hydroxycoumarin (4-HC) derivatives, showed marked biological activity, such as enzyme inhibition, hypotoxicity as well as carcinogenicity, anticoagulant and anti-biotic action [8]. The anticoagulant activity shown by many dicoumarols initiated extensive investigations of this class of compounds. It was found that the most promising compounds were those chemically related to 4-hydroxycoumarin [9]. At the same time, 4-HC derivatives are known to have good complexing ability and in

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some cases the complexes obtained showed higher biological activity than their ligands [10].

Both X-ray [11] and NMR [12] studies have shown that 3,3'-benzylidenebis(4-hydroxycoumarin) (phenyldicoumarol, PhDC) and 3,3'-methylenebis(4-hydroxycoumarin) (dicoumarol, DC) are stabilized by two O–H···O intramolecular HBs. In biological systems, strong intramolecular HBs stabilize and hold the compounds in a suitable configuration for binding to an enzyme and hence the HBs contribute to the biological activities of these compounds [12–14]. It was found that large atomic charges give rise to an additional electrostatic stabilization of the system with strong H-bonds [15]. Some compounds with intramolecular HBs are both uncouplers and inhibitors of mitochondrial oxidative phosphorylation, while compounds, which can only form intermolecular HBs, are only uncouplers of oxidative phosphorylation. Thus, a possible relationship between such hydrogen-bonded structures and the biological activity was previously suggested [16].

In this paper, we present DFT study of PhDC, DC and the parent compound, 4-HC at B3LYP/6-31G* level of theory, focusing on the type and the strength of the O–H···O HBs formed. The strength of the HBs was estimated on the basis of the calculated relative energies of structures, with one and both HBs ruptured. Natural population analysis data, the electron density (ρ_b) and Laplacian ($\nabla^2\rho_b$) properties as well as $\nu(\text{O–H})$ red shifts were further used for estimation of the hydrogen-bonding interactions and the forces driving their formation.

2. Computational procedure

All calculations were performed using GAUSSIAN 98 program package [17]. The reliably accurate description of weak interactions like HBs generally requires a treatment of electron correlation. Density functional calculations with Becke's three parameter hybrid method using the correlation functional of Lee, Yang and Parr (B3LYP) have proved quite useful in this regard for studying system with HBs [18–20]. This method has been tested with different basis sets and has successfully been applied for estimation of the relative strengths and preferred geometries of HBs in different systems [21–25]. Density functional theory offers an electron correlation correction frequently comparable to the second-order Møller–Plesset theory (MP2) or in certain cases, and for certain purposes even superior to MP2, but at considerably lower computational cost [20]. Due to the size of the systems investigated in the present study the cost advantage that offers B3LYP method in comparison with MP2 was significant. Moreover, the lower computational cost of B3LYP

compared to other correlated methods allowed us to calculate the harmonic vibrational frequencies of the large systems studied here. Different basis sets were tested in the course of the calculations requiring better agreement between the calculated and experimental geometry parameters for the atoms, involved in the hydrogen bondings: 6-31G*, 6-31+G** (diffuse s and p function for oxygen atoms [4s3p1d] and p polarization function for hydrogen atoms [2s1p], Basis (1) and 6-311G* [4s3p1d] for oxygen atoms and [3s] for hydrogen atoms, Basis (2). For all other atoms which were not involved in HBs, 6-31G* basis set was applied. The geometry analysis showed that in general, the calculated structural parameters of the systems studied are in good agreement with experiment when 6-31G* basis set was used: two asymmetrical intramolecular hydrogen-bondings in PhDC and two symmetrical intramolecular hydrogen bondings in DC were calculated with comparatively low deviations from experiment. All stationary points were confirmed as minima via vibrational frequency calculations. Zero-point vibrational energy corrections were included in the calculated HB energies. The initial geometries for the DFT calculations were obtained from preliminary calculations at PM3 level, using PM3 keyword as implemented in GAUSSIAN 98. A conformational analysis of PhDC was performed at the same level and 13 conformers were localized as minima on the potential energy surface.

Analysis of the electronic charge density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) was performed by means of the theory of molecular structure proposed by Bader and coworkers [26–29]. According to this theory, when two neighboring atoms are chemically bonded, a bond critical point appears between them. At the bond critical point, $\nabla\rho_b = 0$, the charge density is a minimum at r_c along the bond path but a maximum along any orthogonal displacement. The sign of the Laplacian of the electron density at a bond critical points, $\nabla^2\rho_b$, reveals whether the charge is concentrated, as in covalent bond ($\nabla^2\rho_b < 0$), or depleted, as in closed shell (electrostatic) interactions ($\nabla^2\rho_b > 0$). The bond ellipticity, ε , was considered as a quantitative measure of the bond π -character [27]. The calculated electron density, ρ_b , its second derivative, $\nabla^2\rho_b$, and the ellipticity, ε , were used for describing the nature of the intramolecular O···H–O bonds. The AIM calculations were performed using the critical point option for the AIM keyword as implemented in GAUSSIAN 98.

The vibrational spectra of the compounds studied were calculated at the B3LYP/6-31G* optimized geometries. In order to assign the calculated frequencies to approximate vibrational descriptor, the vibrational modes have been analyzed by means of the atom movements, calculated in Cartesian coordinates. The

frequency shifts of PhDC and DC vibrational modes, Δv_i , were estimated using the equation

$$\Delta v_i^{\text{scal.}}(\text{PhDC}(\text{DC})) = k_i v_i(\text{PhDC}(\text{DC})) - k_j v_i(4\text{-HC}), \quad (1)$$

where k_i and k_j are the corresponding ‘optimal’ scale factors, determined using the ratio $\nu(\text{O-H})^{\text{exp}}/\nu(\text{O-H})^{\text{calc}}$. The scale factors used are, 0.956 for PhDC and DC and 0.972 for 4-HC.

3. Results and discussion

3.1. Geometry parameters of PhDC, DC and 4-HC

The fully optimized molecular structures of PhDC, DC and 4-HC with atomic numbering, calculated at B3LYP/6-31G* level of the theory, are shown in Fig. 1. Selected calculated and experimental bond distances are given in Table 1. As seen from Table 1, the calculated

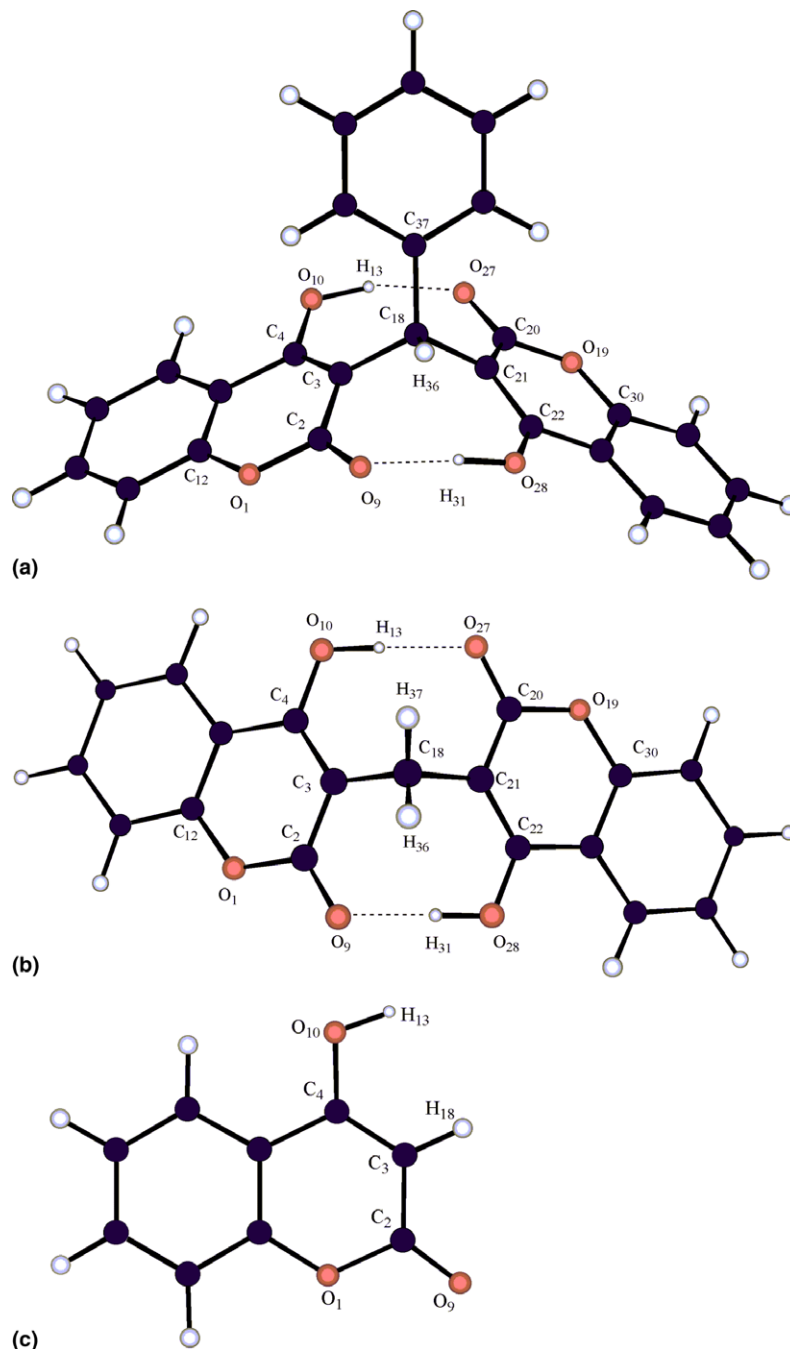


Fig. 1. Optimized geometries of PhDC, DC and 4-HC at B3LYP/6-31G* level of the theory.

Table 1
Selected calculated and experimental bond distances (Å), valence and dihedral angles (°) for PhDC, DC and 4-HC

Name definition ^a	PhDC				DC				4-HC			
	Calc. B3LYP/6-31G*	Calc. Basis 1	Calc. Basis 2	Exp. [11]	Calc. B3LYP/6-31G*	Calc. Basis 1	Calc. Basis 2	Exp. [30a]	Calc. B3LYP/6-31G*	Calc. Basis 1	Calc. Basis 2	Exp. [30b]
O ₁₀ ···O ₂₇	2.638	2.610	2.642	2.624	2.696	2.673	2.702	2.632				
O ₉ ···O ₂₈	2.696	2.675	2.702	2.720	2.696	2.673	2.702	2.632				
H ₁₃ ···O ₂₇	1.672	1.634	1.691		1.710	1.685	1.728					
H ₃₁ ···O ₉	1.710	1.688	1.730		1.710	1.685	1.728					
C ₂₀ =O ₂₇	1.229	1.234	1.224	1.221	1.233	1.238	1.227	1.277	1.208	1.214	1.203	1.20
C ₂ =O ₉	1.234	1.238	1.228	1.222	1.233	1.238	1.227	1.268	1.208	1.214	1.203	1.20
O ₁₀ –H ₁₃	1.002	1.003	0.991		1.000	1.000	0.991		0.971	0.967	0.965	
O ₂₈ –H ₃₁	1.000	0.999	0.990		1.000	1.000	0.991		0.971	0.967	0.965	
(C ₂ –O ₁)	1.373	1.368	1.372	1.366	1.374	1.369	1.373	1.297	1.402	1.394	1.403	1.37
(C ₁₂ –O ₁)	1.366	1.368	1.367	1.384	1.368	1.367	1.368	1.443	1.362	1.363	1.362	1.37
(C ₂₀ –O ₁₉)	1.377	1.371	1.376	1.368	1.374	1.369	1.373	1.304	1.402	1.394	1.403	1.37
(C ₃₀ –O ₁₉)	1.367	1.367	1.367	1.379	1.368	1.367	1.368	1.487	1.362	1.363	1.362	1.37
C ₄ –O ₁₀ (–H ₁₃)	1.327	1.327	1.325	1.333	1.332	1.334	1.330	1.444	1.353	1.356	1.350	1.35
C ₂₂ –O ₂₈ (–H ₃₁)	1.330	1.335	1.332	1.339	1.331	1.334	1.330	1.432	1.353	1.356	1.350	1.35
C ₁₈ –C ₃₇	1.540	1.540	1.541	1.538								
C ₄ –O ₁₀ –H ₁₃	112.3	111.8	112.7		112.0	112.6	112.9		109.3	110.2	110.3	
C ₂₂ –O ₂₈ –H ₃₁	112.4	111.9	112.8		112.0	112.6	112.9		109.3	110.2	110.3	
O ₁₀ –H ₁₃ ···O ₂₇	160.6	163.1	159.5		167.7	168.6	166.7					
O ₉ ···H ₃₁ –O ₂₈	168.1	168.8	166.6		167.7	168.7	166.7					
C ₂ –C ₃ –C ₁₈	114.5	114.6	114.4	114.7	116.4	116.5	116.2	115.1				
C ₄ –C ₃ –C ₁₈	126.0	126.2	126.3	126.4	123.4	123.4	123.6	121.7				
C ₁₈ –C ₂₁ –C ₂₀	118.8	119.0	118.7	118.7	116.4	116.5	116.2	114.0				
C ₁₈ –C ₂₁ –C ₂₂	121.7	121.7	121.9	122.0	123.4	123.4	123.6	121.7				
C ₃ –C ₁₈ –C ₂₁	112.3	112.3	112.4	112.7	115.6	115.5	115.8	119.8				
C ₃ –C ₁₈ –C ₃₇ ^b	115.9	115.9	115.8	116.5	109.1	109.1	109.1					
C ₂₁ –C ₁₈ –C ₃₇ ^b	114.7	114.8	114.7	112.8	107.9	108.1	107.9					
H ₃₆ –C ₁₈ –C ₃₇ ^c	101.5	103.2	103.4		106.7	106.5	106.5					
C ₄ –C ₃ –C ₁₈ –C ₂₁	85.3	82.6	85.9	88.2	89.6	88.9	90.0	92.9				
C ₃ –C ₁₈ –C ₂₁ –C ₂₀	–83.3	–85.5	–82.7	–80.1	–89.5	–90.0	–89.2	–90.3				

^a The atom numbering is given in Fig. 1.

^b These are CCH angles in DC.

^c This is HCH in DC.

geometry parameters for PhDC and DC agree with available experimental data [11,30]. X-ray diffraction analysis has shown that PhDC, which is not inherently chiral, crystallized in a polar space group and had an unusually high density [11]. Two O–H···O intramolecular HBs were found; each links a coumarin hydroxyl and carbonyl group (Fig. 1(a)). The structure of PhDC is closely related to those of DC (Fig. 1(b)) [12,30], and dibromodicoumarol (DBrDC) [31]. However, unlike DC and DBrDC, in which the methylene group rests on a two fold axis and the HB system is symmetrical, the HBs in PhDC are unsymmetrical with O···O distances 2.624 and 2.720 Å [11]. The presence of such H-bond system significantly lowers the energy of the PhDC and stabilizes the molecule in the lowest-energy conformation, which was also experimentally observed [11]. At B3LYP/6-31G* level both calculated O···O distances, 2.638 and 2.696 Å, showed comparatively small deviations from the experimental values, 0.014 and 0.024 Å. As seen from Table 1, the addition of diffuse s and p function for oxygen atoms and p polarization function for hydrogen atoms involved in HBs (Basis 1) as well as the split basis set (Basis 2) did not produce significant improvement of the calculated O···O distances in PhDC and DC.

In full agreement with experiment, differences in the exocyclic angles about the coumarin points of attachment to the methylene carbon in PhDC were found with all basis sets applied. According to our B3LYP/6-31G* calculations and in full agreement with experiment, the exocyclic angles about C₃, C₂–C₃–C₁₈ = 114.5° and C₄–C₃–C₁₈ = 126.0° differ by 11.5° (11.9° from experiment), whereas the corresponding angles about C₂₁ differ by only 2.9° (3.3° from experiment). It was previously stated that this asymmetry in the HB could arise from the effects of steric crowding within the molecule or from packing constraints [11]. Since the calculated structural parameters in the frame of our model (which do not include packing effects) confirmed this asymmetry, it obviously arose from inherent properties of the molecule but not from packing constraints. Likewise, all principal bond angles around C₁₈ are widened over normal tetrahedral values, ranging from 112.3 to 115.9. The steric crowding about the methylene carbon may also be responsible for this feature. Although most of the bond distances are of expected length, the calculated C₁₈–C₃₇ distance of 1.540 Å (1.538 Å from experiment) is longer than an unstrained C_(sp³)–C_(Ar) bond, but it is in the range, characteristic of triphenylmethane and related sterically crowded structures [32,33]. The average deviations of the calculated bond lengths and bond angles are: at B3LYP/6-31G*, 0.81% and 0.39%, at B3LYP with Basis 1, 0.75% and 0.38%, and at B3LYP with Basis 2, 0.80% and 0.39%, respectively. The comparison of PhDC and 4-HC calculated structural parameters showed that in PhDC differences were obtained in the O–H, C=O and C–O bond length distances. Due to participation in hydrogen

bonding both hydroxyl and carbonyl groups in PhDC showed longer O–H and C=O bond lengths and shorter C–O bond length: 0.971 Å → 1.002/1.000 Å, 1.208 Å → 1.229/1.234 Å and 1.353 Å → 1.327/1.330 Å, respectively (B3LYP/6-31G* calculations in Table 1).

Using the same levels of the theory (B3LYP/6-31G*, B3LYP/Basis 1 and B3LYP/Basis 2), the geometry of DC was fully optimized and two identical HBs were found. With the exception of some structural parameters in the exocyclic rings, the calculated parameters of DC are very similar to that of PhDC. As it is expected for the symmetrical HBs in DC, the calculated O···O distances do not differ as in the case of PhDC. The B3LYP/6-31G* calculations showed that the O···O distances in DC are identical with the longer O···O in PhDC (2.696 Å) and predicted that the single HB in DC is comparable with the weaker HB in PhDC. Since B3LYP/6-31G* geometry parameters showed sufficient coincidence with experiment and lower computational cost (as compared to B3LYP calculations with Basis 1 and Basis 2), the theoretical study was mainly performed at this level of theory and the results from these calculations will be discussed below.

3.2. Estimation of the single and total HB energies in PhDC and DC: conformational analysis

Preliminary conformational search at PM3 level showed that among all 13 PhDC structures, localized as minima on PES, only one was stabilized by two HBs and its energy was the lowest one, PhDC. Two higher energy structures were stabilized by one HB, PhDC1 and PhDC2. All other structures of PhDC were not stabilized by HBs and hence they showed significantly higher relative energy as compared to that with one and two HBs. B3LYP calculations confirmed the stabilization of PhDC by two HBs with different O···O distances and strengths. To estimate the strengths of the HBs formed, the relative energy of different structures were calculated. The O₂₈–H₃₁···O₉ HB energy was estimated from the PhDC and PhDC1 energy difference, $E(\text{O}_{28}\text{--H}_{31}\cdots\text{O}_9) = E_{\text{PhDC}}^{\text{corr.}} - E_{\text{PhDC1}}^{\text{corr.}}$, and it was calculated of –52.32 kJ/mol (Table 2). The PhDC1 is a global minimum structure with one HB, O₁₀–H₁₃···O₂₇. Both PhDC and PhDC1 energies were obtained by unconstrained DFT minimizations. The O₁₀–H₁₃···O₂₇ HB energy was estimated from the PhDC and PhDC2 energy difference, $E(\text{O}_{10}\text{--H}_{13}\cdots\text{O}_{27}) = E_{\text{PhDC}}^{\text{corr.}} - E_{\text{PhDC2}}^{\text{corr.}}$, and it was calculated of –55.46 kJ/mol (Table 2). The PhDC2 was obtained from the global minimum structure PhDC but the H₁₃ was rotated around C₄–O₁₀ bond until O₁₀–H₁₃···O₂₇ HB rupture occurred. The HB energies thus obtained predicted that the O₁₀–H₁₃···O₂₇ HB is stronger than the O₂₈–H₃₁···O₉ one, the energy difference is $\Delta E = -3.14$ kJ/mol. The total HB energy in PhDC, calculated by the equation $2E_{\text{PhDC}} - (E_{\text{PhDC1}} + E_{\text{PhDC2}})$, was estimated of –107.78

Table 2

Total electronic energies (in hartree) and HB energies (in kJ/mol) of hydrogen bonded conformers of PhDC and DC calculated at B3LYP/6-31G* level of theory

System	Total electronic energy	$\Delta E_{\text{single HB}}^{\text{corr.}}$	$\Delta E_{\text{total HB}}^{\text{corr.}}$
PhDC1	-1413.662499		
	-1413.308141 ^a	-55.46 ^b	-
PhDC2	-1413.662762		
	-1413.306948 ^a	-52.32 ^c	-
PhDC	-1413.683870		
	-1413.328056 ^a	-	-107.78 ^d
DC1	-1182.604406		
	-1182.332287 ^a		-
DC	-1182.646316		
	-1182.371056 ^a	-50.89 ^e	-101.79 ^f

^aZP corrected.

^b $E_{\text{PhDC}}^{\text{corr.}} - E_{\text{PhDC2}}^{\text{corr.}}$

^c $E_{\text{PhDC}}^{\text{corr.}} - E_{\text{PhDC1}}^{\text{corr.}}$

^d $2E_{\text{PhDC}}^{\text{corr.}} - (E_{\text{PhDC1}}^{\text{corr.}} + E_{\text{PhDC2}}^{\text{corr.}})$

^e $(E_{\text{DC}}^{\text{corr.}} - E_{\text{DC1}}^{\text{corr.}})/2$

^f $E_{\text{DC}}^{\text{corr.}} - E_{\text{DC1}}^{\text{corr.}}$

kJ/mol (Table 2). It was not possible to determine the total HB energy in PhDC from the relative energy of a conformer with both HBs ruptured. When both HBs are absent simultaneous rotations of the coumarin moieties about C₃–C₁₈ and C₂₁–C₁₈ bonds as well as of the benzene about C₁₈–C₃₇ bond occurred to avoid repulsion between the negative charges of the hydroxyl and carbonyl oxygen atoms. Due to the rotation, mentioned above, the geometries obtained are far from the geometry of the lowest energy conformer and they could not be used for estimation of the total HB energy of PhDC.

A stable structure with both HBs ruptured (DC1) was localized on the PES of DC, and the total HB energy in DC was calculated as a difference between the energy of DC and the energy of DC1, -101.79 kJ/mol. Since the HBs in DC are symmetrical (molecular C₂ symmetry), the single HB energy in DC was calculated as a half of the total HB energy, -50.89 kJ/mol. This value predicted that the HB in DC approached in strength the weaker one in PhDC (-52.32 kJ/mol).

The calculated HB energy values for PhDC (-55.46 and -52.32 kJ/mol) and for DC (-50.89 kJ/mol) are slightly higher than those calculated for normal HB (8–42 kJ/mol) [13]. They are, however, below the values, obtained for some negative charge assisted O–H···O hydrogen bonds, where the energy gain by HBs formation in the active site of enzymes could be up to 84 kJ/mol, depending strongly on the nature (hydrophobicity, electrostatics, etc.) of the active site [13–15].

3.3. Molecular properties of PhDC, DC and 4-HC

While the nuclear positions compare well with the experiment for PhDC and DC, an additional check of the theoretical model was performed by natural popu-

lation analysis and computation of the electron density properties at the bond critical points of the PhDC, DC and 4-HC. The O–H···O bonding is homonuclear in nature and permits avoidance of the complications introduced by the different donor and acceptor electronegativities. It is also unique for the wide range of strengths and lengths of the bonds formed and thus comparison of its characteristics and strength with those of other compounds is possible [15].

3.3.1. Natural population analysis of PhDC, DC and 4-HC

Natural population analysis data helped us to study the charge changes going from the parent compound, 4-HC, to DC and PhDC. The calculated natural charges for selected atoms involved in the exocyclic rings of PhDC and DC are compared with the charges of the corresponding atoms in 4-HC in Table 3. For symmetry reasons the carbonyl oxygen atoms in DC have identical charges (-0.651) but they were larger as compared to 4-HC (-0.570). The same results were obtained for the hydroxyl oxygen atoms (-0.671 → -0.687).

For PhDC, less negative natural charges were found on the oxygen atoms, involved in HB in the upper exocyclic ring, O₁₀ and O₂₇ (-0.680, -0.637) as compared to the natural charges obtained on O₂₈ and O₉ in the lower exocyclic ring (-0.690, -0.654). The less negative charges on both the carbonyl and hydroxyl oxygen atoms in the upper exocyclic ring explained the shorter O₁₀···O₂₇ distance in comparison with the O₉···O₂₈. As it is expected, the hydroxyl oxygen atoms (O₁₀ and O₂₈) have more negative natural charges (-0.680 and -0.690) as compared to the carboxyl oxygen atoms (O₉ and O₂₇) (-0.654 and -0.637). The results thus obtained suggested that a substantial electrostatic interaction is present in both HBs of PhDC and from purely electro-

Table 3

Selected natural charges (q_i) of PhDC, DC and 4-HC, calculated at B3LYP/6-31G* level of theory

Atom ^a	PhDC	DC	4-HC
O ₁₀ (-H ₁₃)	-0.680	-0.687	-0.671
O ₂₇ (=C ₂₀)	-0.637	-0.652	-0.570
H ₁₃	0.531	0.527	0.500
O ₂₈ (-H ₃₁)	-0.690	-0.687	-0.671
O ₉ (=C ₂)	-0.654	-0.651	-0.570
H ₃₁	0.527	0.527	0.500
C ₂	0.801	0.797	0.771
C ₃	-0.248	-0.246	-0.448
C ₄	0.438	0.436	0.401
C ₁₈	-0.298	-0.498	
C ₂₀	0.801	0.797	0.771
C ₂₁	-0.244	-0.246	-0.448
C ₂₂	0.438	0.436	0.401
O ₁₉	-0.488	-0.487	-0.509
O ₁	-0.486	-0.487	-0.509

^aThe atom numbering is given in Fig. 1.

static arguments the $O_{10}-H_{13}\cdots O_{27}$ bonding in the upper ring is predicted to be stronger as compared to the $O_9\cdots H_{31}-O_{28}$ one.

Both hydroxyl and carbonyl oxygen charges in DC have values, which are closer to those of the hydroxyl and carbonyl oxygen atoms involved in the weaker HB in PhDC, O_{28} and O_9 (Table 3) and these results confirmed the suggestion that the HBs in DC approach the weaker HB in PhDC.

3.3.2. Electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) at the bond critical points of PhDC, DC and 4-HC

The property of the Laplacian of the electron density to determine regions of concentration and depletion of the electron charge density forms a basis for the classification of the atomic interactions [29]. The atomic interactions were classified in two general classes, shared interactions and closed-shell interactions. The shared interactions (as covalent and polar bonds) are caused by a contraction of the charge density towards the line of interaction linking the nuclei. For these interactions the electronic charge is concentrated in the internuclear region and $\nabla^2\rho_b < 0$. The closed-shell interactions (as HBs, ionic bonds, and van der Waal's molecules) are governed by the contraction of the charge density toward each of the interacting nuclei. In this case, the electronic charge is depleted in the interatomic surface and $\nabla^2\rho_b > 0$ [29].

The calculated electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) at bond critical points for PhDC, DC and 4-HC are given in Table 4. The calculated electron density properties of PhDC and DC showed that both $O\cdots H$ bondings have low ρ_b , (ranging from 0.0444 to 0.0483), and positive $\nabla^2\rho_b$ values (ranging from 0.1366 to 0.1524). These properties are typical for closed-shell interactions as HBs and indicate electrostatic character of the $O\cdots H$ bondings [29]. The HBs in DC are symmetrical and the calculated ρ_b , and $\nabla^2\rho_b$, for both $O\cdots H$ bondings are obtained identical and comparable

with the values of the weaker HB in PhDC (Table 4). The HBs in PhDC are unsymmetrical and the calculated ρ_b , and $\nabla^2\rho_b$, for the $O\cdots H$ bonding in the upper exocyclic ring were found higher (0.0483 and 0.1524, respectively) than those in the lower exocyclic ring (0.0444 and 0.1371). The results thus obtained are consistent with more electrostatic $O\cdots H$ bonding and increasing bond strength in the upper exocyclic ring (as it was found from the calculated HB energies) and they are in full agreement with the correlation between ρ_b and $\nabla^2\rho_b$ from one side, and the H-bond strength from the other. This correlation was first reported by Carroll and Bader [34] and confirmed later by many authors [35,36].

The calculated Laplacian at the critical points of both $O-H$ bonds in PhDC have negative values, $O_{10}-H_{13} = -1.557$ and $O_{28}-H_{31} = -1.576$, thus pointing out that both $O-H$ bonds in PhDC have covalent character, the first one ($O_{10}-H_{13}$) with lower covalent contribution (has lower negative value). The obtained lower covalent character of the $O_{10}-H_{13}$ bond in the upper exocyclic ring (as compared to that of the $O_{28}-H_{31}$ in the lower ring) correlated with more electrostatic $O_{10}-H_{13}\cdots O_{27}$ HB in which H_{13} participates in the upper exocyclic ring of PhDC. Identical and negative values for the Laplacian at both $O-H$ bond critical points were found for DC (-1.567) indicating no differences in the $O-H\cdots O$ bondings in this compound. Comparison of the Laplacian at the $O-H$ bond critical points for PhDC and DC with the Laplacian at the $O-H$ bond critical point for the parent compound, 4-HC (-1.811), showed that the participation of the hydroxyl hydrogen in HBs in PhDC and DC led to lowering of the negative Laplacian values and hence to lowering of the covalent contribution to both $O-H$ bonds.

Going from 4-HC to DC and PhDC, the electron density at both $C_{22}-O_{28}(-H_{31})$ and $C_4-O_{10}(-H_{13})$ bond critical points showed more positive values whereas the Laplacians – more negative values, indicating more covalent character of these bonds in PhDC and DC as

Table 4

Properties of the electron density at bond critical points, ρ_b and its Laplacian, $\nabla^2\rho_b$, (a.u.) for PhDC, DC and 4-HC, calculated at B3LYP/6-31G* level of theory

Bond ^a	ρ_b			$\nabla^2\rho_b$		
	PhDC	DC	4-HC	PhDC	DC	4-HC
<i>Upper exocyclic ring</i>						
$O_{10}-H_{13}$	0.3041	0.3059	0.3430	-1.5570	-1.5670	-1.8110
$C_4-O_{10}(-H_{13})$	0.3156	0.3119	0.2947	-0.3355	-0.3424	-0.3166
$C_{20}=O_{27}$	0.4004	0.3978	0.4193	-0.0797	-0.1120	-0.1047
$H_{13}\cdots O_{27}$	0.0483	0.0445		0.1524	0.1366	
<i>Lower exocyclic ring</i>						
$O_{28}-H_{31}$	0.3070	0.3059	0.3430	-1.5760	-1.5670	-1.8110
$C_{22}-O_{28}(-H_{31})$	0.3106	0.3119	0.2947	-0.3552	-0.3424	-0.3166
$C_2=O_9$	0.3973	0.3978	0.4193	-0.1168	-0.1120	-0.1047
$O_9\cdots H_{31}$	0.0444	0.0445		0.1371	0.1366	

^a The atom numbering is given in Fig. 1.

compared to 4-HC. As compared to 4-HC, in PhDC and DC the electron density at the $C_2=O_9$ and $C_{20}=O_{27}$ bond critical points have lower values and correlated with the lengthening of these bonds.

3.3.3. AIM ellipticity (ϵ_b) and π -delocalization in PhDC, DC and 4-HC

The calculated AIM ellipticities for PhDC, DC and 4-HC are presented in Table 5. On the basis of the calculated ellipticity data, the changes in the π -delocalization going from the parent compound, 4-HC to DC and PhDC were estimated. As it is expected for the symmetric HBs in DC, the calculated ellipticities of the bonds in both exocyclic rings are identical. For PhDC the ellipticities of the bonds in the upper and lower exocyclic rings differ in agreement with the asymmetry of the HBs discussed above. As seen from the results given in Table 5, in comparison with 4-HC, the calculated ellipticities for both $C=O$ bonds in DC and PhDC are lower in agreement with the calculated longer $C=O$ distances (Table 1). With the exception of C_4-O_{10} bond, the ellipticities for both $C-O$ bonds in PhDC and DC are larger, as compared to 4-HC and this finding is consistent with the calculated slightly shorter $C-O$ distances in comparison with 4-HC (Table 1). The deviation of the C_4-O_{10} ellipticity value from the correlation obtained could not be explained. It should be mentioned, however, that the ellipticity is calculated as a ratio between two second derivatives of the electron density, and thus it is a feature that is very difficult to be determined accurately for such large-size molecules. As seen from Table 5, there is slightly higher π -delocalization over the left coumarin ring in PhDC, $O_9=C_2-C_3-C_4-O_{10}$, in comparison with the π -delocalization over the right coumarin ring $O_{27}=C_{20}-C_{21}-C_{22}-O_{28}$. The calculated ellipticities for the $O-H$ bonds showed that in comparison with 4-HC (0.0158), there is only weak, if any, π -delocalization over the $O-H$ bonds in PhDC (0.0129 and 0.0120) and DC (0.0125).

Table 5
Selected AIM ellipticities (a.u.) calculated at B3LYP/6-31G* level of theory for PhDC, DC and 4-HC

Bond ^a	PhDC	DC	4-HC
$C_2=O_9$	0.1232	0.1265	0.1447
$C_{20}=O_{27}$	0.1338	0.1265	
C_4-O_{10}	0.0304	0.0375	0.0365
$C_{22}-O_{28}$	0.0452	0.0375	
$O_{10}-H_{13}$	0.0120	0.0125	0.0158
$O_{28}-H_{31}$	0.0129	0.0125	
$C_3-C_4(-O_{10}-H_{13})$	0.3216	0.3251	0.3545
$C_{21}-C_{22}(-O_{28}-H_{31})$	0.3307	0.3251	
$C_3-C_2(=O_9)$	0.2271	0.2225	0.1897
$C_{21}-C_{20}(=O_{27})$	0.2164	0.2226	
$O_9 \cdots H_{31}$	0.0284	0.0243	
$O_{27} \cdots H_{13}$	0.0243	0.0243	

^aThe atom numbering is given in Fig. 1.

3.4. Estimation of the HB strength in PhDC and DC from $\nu(O-H)$ vibrational shifts

The correlation between frequency shifts and the HB strength is well known and could be successfully applied for estimation of HB strength of many systems [37–40]. To give reliable assignment of the hydrogen-bonding vibrational modes and to use their shifts further for estimation of the $O \cdots H$ bonding strength in PhDC and DC, at the starting point we performed detailed vibrational analysis of 4-HC at B3LYP/6-31G* optimized geometry. The $O-H$ and $C=O$ groups in 4-HC are free (not involved in HB interactions) and thus the calculated and experimental gas-phase IR spectrum of 4-HC [41] supplied information about the $\nu(O-H)$ and $\nu(C=O)$ positions. In PhDC and DC both $O-H$ and $C=O$ are H-bonded and their $\nu(O-H)$ and $\nu(C=O)$ modes showed negative (red) frequency shifts. The observed frequency shifts of selected vibrational modes of PhDC and DC as compared to 4-HC are presented in Table 6. The calculated frequency shifts were obtained as a difference between the scaled wavenumbers of PhDC and DC and the corresponding scaled wavenumbers of 4-HC (Eq. (1), Section 2). As it is expected, due to complexation of the $O-H$ and $C=O$ groups in PhDC and DC, negative (red) $\nu(O-H)$ and $\nu(C=O)$ shifts were observed in comparison with 4-HC. Conversely, the deformational modes of the HBs, $\delta(COH)_{i.p.}$, $\delta(COH)_{o.o.p.}$ as well as $\nu(C-O)$, showed positive (blue) frequency shifts [42]. In PhDC higher negative shift was obtained for the $\nu(O_{10}-H_{13})$, -610 cm^{-1} (exp. shift, -602 cm^{-1}) in comparison with the shift of $\nu(O_{28}-H_{31})$, -559 cm^{-1} (exp. shift, -560 cm^{-1}). The higher red shift of $\nu(O_{10}-H_{13})$ is consistent

Table 6
Frequency shifts of selected vibrational modes ($\Delta\nu_i$ and $\Delta\delta_i$ in cm^{-1}) and selected bond length changes (Δr_i in Å) of PhDC and DC

Vibrational mode ^a	PhDC		DC	
	Calc. ^b	Exp.	Calc. ^b	Exp.
$\Delta\nu(O_{28}-H_{31})$	-559	-560	-562	-601
$\Delta\nu(O_{10}-H_{13})$	-610	-602	-566	-601
$\Delta r(O_{28}-H_{31})$	0.029		0.029	
$\Delta r(O_{10}-H_{13})$	0.031		0.029	
$\Delta\nu(C_{20}=O_{27})$	-126	-154	-130	-174
$\Delta\nu(C_2=O_9)$	-151	-197	-148	-174
$\Delta r(C_{20}=O_{27})$	0.021	0.02	0.025	0.05
$\Delta r(C_2=O_9)$	0.026	0.02	0.025	0.05
$\Delta\nu(C_4-O_{10}(H))$	+106	+114	+112	+114
$\Delta\nu(C_{22}-O_{28}(H))$	+103		+109	
$\Delta\delta(C_4O_{10}H_{13})_{i.p.}$	+129	+111	+130	+136
$\Delta\delta(C_{22}O_{28}H_{31})_{i.p.}$	+115	+102	+111	+115
$\Delta\delta(C_4O_{10}H_{13})_{o.o.p.}$	+334		+362	
$\Delta\delta(C_{22}O_{28}H_{31})_{o.o.p.}$	+323		+349	

^a $\Delta\nu_i$, $\Delta\delta_i$ for PhDC and DC were calculated in agreement with Eq. (1).

^bVibrational frequencies of PhDC and DC scaled by 0.956, and of 4-HC by 0.972.

with higher lengthening of the $r(\text{O}_{10}\text{--H}_{13})$, 0.031 Å, in comparison with that of $r(\text{O}_{28}\text{--H}_{31})$, 0.029 Å. The higher red shift of $\nu(\text{O}_{10}\text{--H}_{13})$ and the higher lengthening of $r(\text{O}_{10}\text{--H}_{13})$ in PhDC are in excellent agreement with the other molecular properties discussed in the previous sections (lower covalent character of $\text{O}_{10}\text{--H}_{13}$ bond, more positive charge on H_{13} , smaller negative charges on O_{10} and O_{27} , and shorter $\text{O}_{10}\cdots\text{O}_{27}$ distance). All these properties together with the estimated HB energies (–55.46 and –52.32 kJ/mol) pointed out that the HB in the upper exocyclic ring of PhDC is stronger. The longer $\text{C}_2=\text{O}_9$ bond showed larger negative shift, -151 cm^{-1} , than the shorter one, -126 cm^{-1} . In agreement with shorter C--O(H) bond lengths in PhDC as compared to 4-HC, positive (blue) shifts were observed for $\nu(\text{C}_4\text{--O}_{10}(\text{H}))$ and $\nu(\text{C}_{22}\text{--O}_{28}(\text{H}))$ modes in PhDC: $+106$ and $+103\text{ cm}^{-1}$, respectively (Table 6). The values obtained correlated with the observed shift in the experimental spectrum, $+114\text{ cm}^{-1}$. In agreement with the stronger $\text{O}_{10}\text{--H}_{13}\cdots\text{O}_{27}$ HB, the blue shifts of the $\delta(\text{C}_4\text{O}_{10}\text{H}_{13})\text{i.p.}$ and $\delta(\text{C}_4\text{O}_{10}\text{H}_{13})\text{o.o.p.}$ modes were obtained higher (Table 6).

By reasons of symmetry and in agreement with the calculations, identical lengthening of the O--H bonds in DC was obtained (0.029 Å) Table 6. The O--H lengthening in DC is comparable with the lengthening of the O--H , involved in the weaker HB in PhDC, ($\Delta r(\text{O}_{28}\text{--H}_{31}) = 0.029\text{ Å}$). In consequence, the negative shifts for the $\nu(\text{O--H})$ in DC, $\Delta\nu(\text{O}_{28}\text{--H}_{31})$ and $\Delta\nu(\text{O}_{10}\text{--H}_{13})$ were found comparable (-562 and -566 cm^{-1} , respectively), with $\Delta\nu(\text{O}_{28}\text{--H}_{31})$ in PhDC (-559 cm^{-1}). The results obtained were in agreement with the calculated HB energies, which also predicted that the HB in DC is comparable with the weaker one in PhDC.

4. Conclusions

The molecular structures of PhDC and DC were optimized at B3LYP level, using different basis sets for the atoms involved in HBs, 6-31G*, 6-31+G** and 6-311G*. In full agreement with available X-ray data, two asymmetrical intramolecular HB in PhDC were found with $\text{O}\cdots\text{O}$ distances 2.638 and 2.696 Å. For DC, both intramolecular $\text{O}\cdots\text{O}$ distances were calculated identical, 2.696 Å and hence symmetrical HBs were predicted. According to the calculations and in coincidence with the experiment, the exocyclic angles about C_3 , $\text{C}_2\text{--C}_3\text{--C}_{18} = 114.5^\circ$ and $\text{C}_4\text{--C}_3\text{--C}_{18} = 126.0^\circ$ differ by 11.5° (11.9° from the experiment), whereas the corresponding angles about C_{21} differ by only 2.9° (3.3° from the experiment). The HB energies in PhDC, estimated of –55.46 and –52.32 kJ/mol, correlated with the calculated and experimental $\text{O}\cdots\text{O}$ distances and predicted by –3.14 kJ/mol stronger HB in the upper exocyclic ring. The HB energy in DC was estimated of –50.89 kJ/mol

and this value suggested that the HB in DC is comparable with the weaker HB in PhDC (–52.32 kJ/mol). The total stabilization HB energy in DC (–101.79 kJ/mol) was by –5.98 kJ/mol smaller than the total stabilization HB energy in PhDC (–107.78 kJ/mol). Natural population analysis data predicted less negative oxygen atom charges and stronger HB in the upper exocyclic ring of PhDC, which is in agreement with the experimental and calculated shorter $\text{O}\cdots\text{O}$ distance in this ring. The calculated electron density and Laplacian properties for PhDC and DC showed that both $\text{O}\cdots\text{H}$ bondings have lower ρ_b and positive $\nabla^2\rho_b$ values, which is typical for closed-shell interactions as HBs and indicated electrostatic $\text{O}\cdots\text{H}$ bondings. Lower covalent character of the O--H -bond and more electrostatic HB were predicted in the upper exocyclic ring of PhDC. The calculated ellipticities were consistent with π -delocalization in both exocyclic rings and are in full agreement with the differences in their structural parameters obtained from X-ray analysis. The higher lengthening of $\text{O}_{10}\text{--H}_{13}$ bond (as compare to that of $\text{O}_9\text{--H}_{31}$) in PhDC and the higher $\nu(\text{O}_{10}\text{--H}_{13})$ red shift are in excellent agreement with the lower covalent character of the $\text{O}_{10}\text{--H}_{13}$ bond, more positive charge on H_{13} , smaller negative charges on O_{10} and O_{27} and shorter $\text{O}_{10}\cdots\text{O}_{27}$ distance. All these properties together with the estimated HB energies (–55.46 and –52.32 kJ/mol) pointed out that the HB in the upper exocyclic ring of PhDC is stronger.

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