

## Investigations on the photochromic properties of 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone†

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The network of chemical reactions of 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone (BHBC) when subjected to light and different pH values has been investigated. The pH dependent species involved in the chemical network have been identified and characterized by NMR and UV-VIS spectroscopy. Direct pH jumps were carried out by adding a strong acid to equilibrated solutions of *trans*-chalcone (Ct) forming the flavylium cation which was stable only under extremely acidic conditions (pH < 0.5). The single crystal X-ray study and NMR analysis has confirmed the structure of the new flavylium cation. In the case of a reverse pH jump, the Ct species interconverted instantaneously into deprotonated *trans*-chalcone (Ct<sup>2-</sup>) around pH 12. A new colorless compound 3,11-dibromo-7,8-dihydro-6*H*-chromeno[3,2-*d*]xanthene (B–B) isolated from the equilibrated solution of *trans*-chalcone species in methanol after long periods of time (100 h) under dark conditions has been isolated and fully characterized by NMR and X-ray diffraction. The rate of the reaction increased when the solution of *trans*-chalcone was exposed to light and the total conversion of Ct into the spiropyran-like compound (B–B) was achieved in about 30 minutes. The B–B form was stable under neutral and basic conditions, while at low pH values it converts into a cationic AH<sup>+</sup> form.

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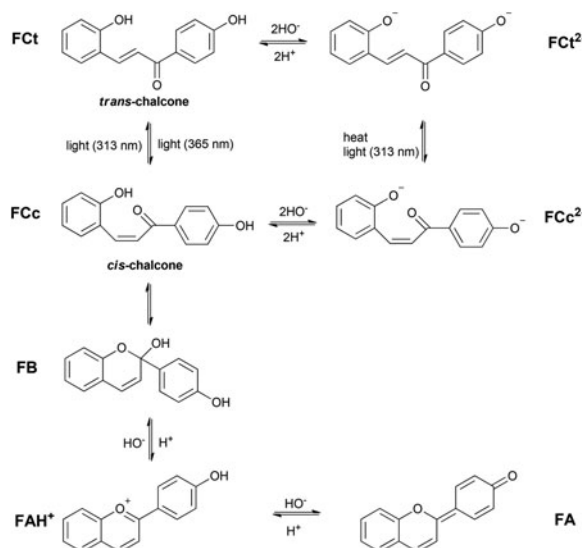
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## Introduction

The development of novel photochromic materials has gained an increased interest in the last few decades due to their industrial applications in optical memory devices, sensors, switches, intelligent windows and displays.<sup>1–6</sup> Flavylium derivatives constitute an attractive family of organic compounds comprising anthocyanins, the natural pigments responsible for the red and blue colors prevailing in flowers, fruits and processed beverages.<sup>7</sup> This class of colorants, including synthetic or natural molecules, are of practical interest with the possibility of achieving reversible changes in color when subjected to different external stimuli, such as light, temperature and pH.<sup>8–12</sup> Moreover, this family of compounds can even mimic the properties of neurons.<sup>13</sup> Generally, all these compounds hold the same 2-arylbenzopyrylium (flavy-

lium) core and follow the same pH-dependent network of reversible chemical reactions. An illustrative example of the chemical reaction network of the flavylium-type compound is illustrated in Scheme 1.<sup>14</sup> The aqueous 4'-hydroxyflavylium can



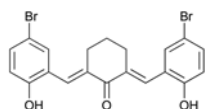
Scheme 1 Structural transformations of the 4'-hydroxyflavylium ion.<sup>14</sup>

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**Scheme 2** Chemical structure of 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone (BHBC).

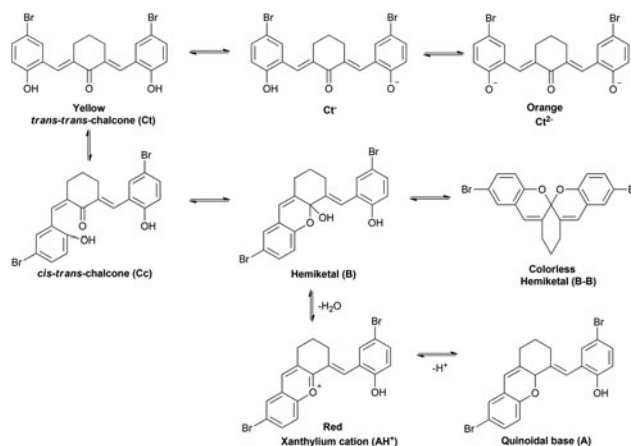
be interconverted into different forms using light excitation or by changing pH.<sup>15</sup> The flavylium cation (FAH<sup>+</sup>) is only stable at pH < 1. When the pH changes from 1 to 7 the cationic species is immediately transformed into the quinoidal base (FA) through a fast proton transfer reaction. At the same time, competitive hydration of FAH<sup>+</sup> can also occur to give the hemiketal (FB) which, after a ring-opening tautomerization, leads to *cis*-2,4'-dihydroxychalcone (FCc). By irradiation at 313 nm isomerization of FCc into *trans*-2,4'-dihydroxychalcone (Fct) takes place. A direct pH jump from 1 to 12 or higher determines the deprotonation of FAH<sup>+</sup> leading to the formation of thermodynamically stable Fct<sup>2-</sup> species.<sup>16</sup> It was also reported that the rates of hydration, tautomerization and isomerization strongly depend on the solvent, and type and position of the functional groups attached to the flavylium core.<sup>17–19</sup> Moreover, it was demonstrated that the change in the colour of FAH<sup>+</sup> solutions depends on the amount of water and flavylium cation concentration in the solution.<sup>20</sup>

It was reported that other three families of structurally related compounds such as styrylflavylium,<sup>21</sup> naphthoflavylium<sup>22</sup> and xanthylum<sup>23–25</sup> follow an identical network of chemical reactions as flavylium derivatives.

The aim of the present work was to discover new photochromic systems based on xanthylum derivatives and to study the influence of substituents on the network of the chemical reactions. The designed molecule was 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone (BHBC) (Scheme 2) which can be further functionalized by attaching certain substituents on 5,5' positions. Our previous studies on the functionalization of open form (Ct) of BHBC led to many products difficult to isolate. We have demonstrated that the B–B form of the compound, without bromine, 2,6-bis(2-hydroxybenzylidene)cyclohexanone, is a stable species under basic conditions.<sup>24</sup> Therefore, in the present study, we focused our attention on the influence of external stimuli on the stability of spiropyran-like species of 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone. The stability of the species involved in the network of chemical reactions of BHBC has been investigated and characterized.

## Results and discussion

In the present study we have investigated the behavior of 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone (BHBC) when subjected to external stimuli. Our attention has been focused on the isolation, identification and characterization of the species involved in the network of chemical reactions,



**Scheme 3** Chemical transformation of BHBC depending on pH conditions.

which are similar to the structurally related flavylium-type compounds.

The synthesis of BHBC was performed under basic conditions according to the procedure described previously for the synthesis of 2,6-bis(2-hydroxybenzylidene)cyclohexanone.<sup>23</sup> The halochromic behavior of the compound considering the changes in color due to the pH shift has been studied. This ability can be attributed to the various species involved in the interconversion of the compound under acidic or basic conditions (Scheme 3).<sup>24,26</sup> In order to identify the stable species, the NMR analyses were performed in different pH media: neutral (pH 6), acidic (pH < 0.5) and basic (pH > 12). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of neutral species are reported in the ESI (Fig. S10 and S11†). The NMR spectra corresponding to the basic conditions, recorded immediately after the addition of deuterated sodium hydroxide, revealed the total conversion of Ct into deprotonated base Ct<sup>2-</sup> (see the ESI, Fig. S7 and S9†). The <sup>1</sup>H-NMR spectrum recorded after 7 days confirmed the stability of the species under basic conditions (ESI, Fig. S8†). The flavylium cation, AH<sup>+</sup>, was detected only in very acidic medium at pH < 0.5. The NMR spectra of this species were recorded after 4 days upon the addition of HClO<sub>4</sub> (70% w/w) when the thermodynamic equilibrium was established and the total conversion of Ct into AH<sup>+</sup> was achieved. After a period of two months, under dark conditions, red crystals suitable for X-ray crystal analysis have been developed from the solution. Complete characterization and assignments of <sup>1</sup>H and <sup>13</sup>C signals for AH<sup>+</sup> was achieved by COSY, HSQC, HMBC and NOESY spectra (see the ESI, Fig. S1–S6†).

According to single-crystal X-ray diffraction, the AHClO<sub>4</sub>·0.375H<sub>2</sub>O compound crystallizes in the P2<sub>1</sub> space group of the monoclinic system.‡ The crystal is built up from

‡ Crystal data for AHClO<sub>4</sub>·0.375H<sub>2</sub>O: C<sub>20</sub>H<sub>15.75</sub>Br<sub>2</sub>ClO<sub>4</sub> (M<sub>r</sub> = 533.35 g mol<sup>-1</sup>), monoclinic, a = 13.2991(6) Å, b = 20.2762(12) Å, c = 15.0236(7) Å, β = 91.184(5)°, V = 4050.3(3) Å<sup>3</sup>, T = 200 K, space group P2<sub>1</sub>, Z = 8, 37 533 coll. refl., 11 582 indep. (R<sub>int</sub> = 0.0745), Gof = 1.014, R<sub>1</sub> = 0.0758, wR(F<sup>2</sup>) = 0.2093. CCDC 1522904.

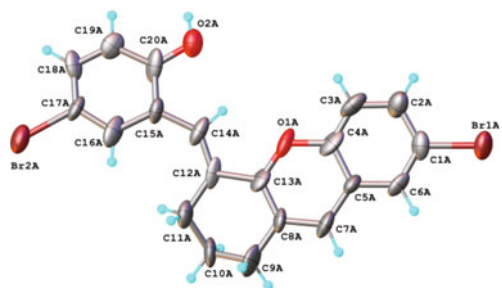


Fig. 1 Crystal structure of the AH<sup>+</sup> cation (component A) with thermal ellipsoids at 50% probability level.

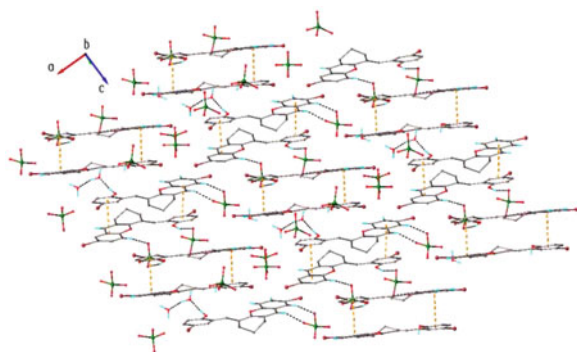


Fig. 2 Partial view of the crystal structure of AH<sup>+</sup> along the *b*-axis. Centroid-to-centroid distances are shown in dashed orange line.

AH<sup>+</sup> cations, ClO<sub>4</sub><sup>-</sup> anions and co-crystallized water molecules in a 1 : 1 : 0.375 ratio. The symmetric part of the unit cell contains four cations, chemically identical but crystallographically independent (denoted as A, B, C and D) with very close geometric parameters. As an example, Fig. 1 shows the structure of cation AH<sup>+</sup>, component A.

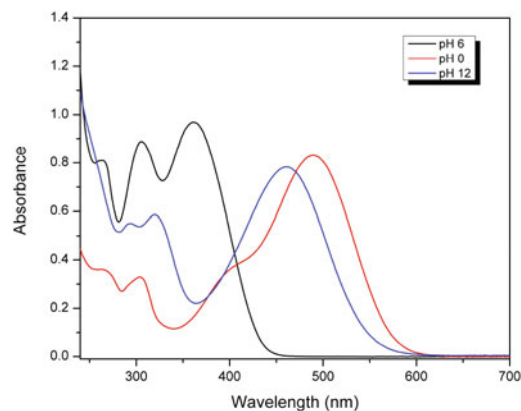
The crystal structure of AHClO<sub>4</sub>·0.375H<sub>2</sub>O is described as a packing of 2D supramolecular layers which grow parallel to *ac* the crystallographic plane through  $\pi$ - $\pi$  stacking interactions (Fig. 2). The values of centroid-to-centroid distances are in the range of 3.489–3.704 Å. Besides this, the intermolecular O–H...O and C–H...O hydrogen bonding involving ClO<sub>4</sub><sup>-</sup> anions and coordinated water molecules provides additional strengthening of the supramolecular motif.

The assignments of the <sup>1</sup>H and <sup>13</sup>C NMR peaks of Ct, Ct<sup>2-</sup> and AH<sup>+</sup> species are reported in Table 1.

The color shift of the species as a function of pH has been also studied by UV-VIS spectroscopy. The solutions at acid pH values (pH < 0.5) are reddish and exhibit a broad band with a maximum absorption at 498 nm, corresponding to the formation of the AH<sup>+</sup> cation. The solutions are stable for long periods at room temperature. As the pH values increase (1 < pH < 7), the solutions become yellowish, corresponding to the neutral form of the compound. The absorption band of 498 nm is not detectable for the neutral species, and it practically disappears as the pH value increases (Fig. 3). At pH values in the range of 8.2 and 12.5, the 360 nm band of the protonated neutral form (Ct) was gradually shifted to a lower energy 460 nm band at basic pH, due to the formation of the

Table 1 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data for Ct, Ct<sup>2-</sup> and AH<sup>+</sup> species under neutral, basic and acidic conditions

Position of H/C in the molecular structure	Ct = BHBC		Ct <sup>2-</sup>		AH <sup>+</sup>	
	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
1	1.79, m, 2H	23.0	1.80, m, 2H	23.4	1.67, s, 2H	19.7
2	2.85, t, 2H	28.2	2.89, (t, <i>J</i> = 5.3 Hz, 2H)	28.5	2.81, s, 2H	27.2
3	2.85, t, 2H	28.2	2.89, (t, <i>J</i> = 5.3 Hz, 2H)	28.5	2.64, s, 2H	26.2
4	—	132.4	—	132.7	—	133.0
5	—	132.4	—	132.7	—	128.6
6	—	190.4	—	191.2	—	172.3
7	7.86, s, 1H	136.6	8.16, s, 1H	135.8	8.46, s, 1H	151.9
8	—	110.2	—	103.1	—	124.7
9	—	155.9	—	168.4	7.92 (d, <i>J</i> = 2.2 Hz, 1H)	131.0
10	6.80, d, 1H	116.9	7.07 (dd, <i>J</i> = 8.8, 2.7 Hz, 1H)	121.8	—	122.5
11	7.31 (dd, <i>J</i> = 8.7, 2.4 Hz, 1H)	132.1	6.57 (d, <i>J</i> = 8.8 Hz, 1H)	127.1	7.87 (dd, <i>J</i> = 9.1, 2.2 Hz, 1H)	140.5
12	—	125.0	—	132.7	7.62 (d, <i>J</i> = 9.1 Hz, 1H)	119.5
13	7.41 (d, <i>J</i> = 2.4 Hz, 1H)	131.4	7.29 (d, <i>J</i> = 2.7 Hz, 1H)	131.6	—	153.7
14	7.86, s, 1H	136.6	8.16, s, 1H	135.8	8.22, s, 1H	140.3
15	—	110.2	—	103.1	—	111.6
16	7.41 (d, <i>J</i> = 2.4 Hz, 1H)	131.4	7.29 (d, <i>J</i> = 2.7 Hz, 1H)	131.6	7.19 (d, <i>J</i> = 2.0 Hz, 1H)	132.2
17	—	125.0	—	132.7	—	123.0
18	7.31 (dd, <i>J</i> = 8.7, 2.4 Hz, 1H)	132.1	6.57 (d, <i>J</i> = 8.8 Hz, 1H)	127.1	7.00 (dd, <i>J</i> = 8.8, 2.2 Hz, 1H)	135.7
19	6.80, d, 1H	116.9	7.07 (dd, <i>J</i> = 8.8, 2.7 Hz, 1H)	121.8	6.48 (d, <i>J</i> = 8.8 Hz, 1H)	117.4
20	—	155.9	—	168.4	—	155.5



**Fig. 3** UV-VIS spectra of the species in neutral ( $1.2 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH/H $_2$ O = 1 : 1), acidic ( $1.4 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH/H $_2$ O/HClO $_4$  70% = 6 : 1 : 1) and basic pH ( $0.84 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH/NaOH 1 M = 1 : 1).

deprotonated base Ct $^{2-}$ , where the saturation was observed at pH 12.5 (Fig. 4a). Therefore, the successive deprotonation gives rise to an orange shift of the absorption bands. As shown in Scheme 3, the dissociation of Ct to generate Ct $^{2-}$  occurs *via* the formation of Ct $^-$  as reported previously for the non-brominated compound.<sup>24</sup> The superimposed UV-VIS spectra disclose the presence of a slightly distorted isobestic point at ~402 nm which can be due to the similarity of the molar absorption coefficient of the three compounds (Ct, Ct $^-$  and Ct $^{2-}$ ) (Fig. 4a). The compound can be stored at high pH values due to the stability of the solutions at room temperature. The 460 nm absorption at different pHs showed an ideal titration profile with a transition midpoint pK $_a$  at ~9.5 (Fig. 4b).

In comparison, the solutions of Ct in methanol under dark conditions are not stable and in a slow process an interesting colorless species is formed according to the spectral modifications shown in Fig. 5a. The spectral changes indicate that the Ct species leads to the formation of a product lacking absorption in the visible region, showing a disruption of  $\pi$ - $\pi^*$  conjugation of the aromatic ring. During a period of 100 h, the absorption band at 360 nm is blue shifted due to the presence of Ct, Cc, B and B-B species. Under dark conditions, the color of the solution changes from yellow to colorless, forming transparent crystals suitable for single X-ray crystal analysis. The crystals have been washed with methanol, dried at room temperature for 24 h and solubilized in CD $_3$ OD in order to yield the spectrum shown in Fig. 6.

Complete characterization and assignments of  $^1$ H and  $^{13}$ C signals for the formed colorless product was achieved by COSY, HSQC, HMBC and NOESY spectra (see the ESI, Fig. S12–S17 $^\dagger$ ) and allowed us to identify a spiro- $\pi$ - $\pi^*$  structure linked by a propano-bridge, 3,11-dibromo-7,8-dihydro-6H-chromeno[3,2-d] xanthene (Fig. 7). In the IR spectrum (see the ESI, Fig. S18 $^\dagger$ ) the absorption band at 951 cm $^{-1}$  could be assigned to the presence of stretching vibrations  $\nu$ O–C–O corresponding to the spiro form according to the

literature.<sup>27–29</sup> The compound has been henceforth named B–B.

The X-ray crystallographic analysis confirms that the compound B–B is able to crystallize in the  $P\bar{1}$  space group of the triclinic system and its molecular crystal structure consists of the isolated neutral molecules, as shown in Fig. 7. No co-crystallized solvent has been found in the crystal. $\S$

The ring-closure reaction of Ct to form B–B species has been accelerated by incubating the solution of BHBC in methanol at 55 °C. The total conversion of Ct into B–B was reached after 7 hours as shown in Fig. 5b.

Surprisingly, by exposing a fresh solution of BHBC at neutral pH to light irradiation at 365 nm, the product exhibits the same absorption spectrum of the cyclic ketal B–B. Under these conditions, the total conversion of BHBC into B–B was achieved within only 30 minutes (Fig. 5c). In conclusion, we can affirm that photoirradiation and high temperatures can have a significant influence on the formation of B–B by increasing the rate of the process.

In order to investigate the stability of this compound, the equilibrated solutions of B–B at neutral pH were subjected to pH jumps to the basic and acidic regions. In basic medium, B–B was stable, while under very acidic conditions (pH < 0.5) it was quickly transformed into the flavylum cation. The absorption spectra of B–B from neutral pH to acidic pH values are represented in Fig. 8. The AH $^+$  species started to form immediately (10 seconds) after the addition of HClO $_4$  (70 wt%). The kinetics of the transformation of B–B into AH $^+$  was studied in time (~8 h) until the system reached the equilibrium. It was observed that at pH values higher than 1, B–B is very stable, while increasing the pH does not give any Ct back.

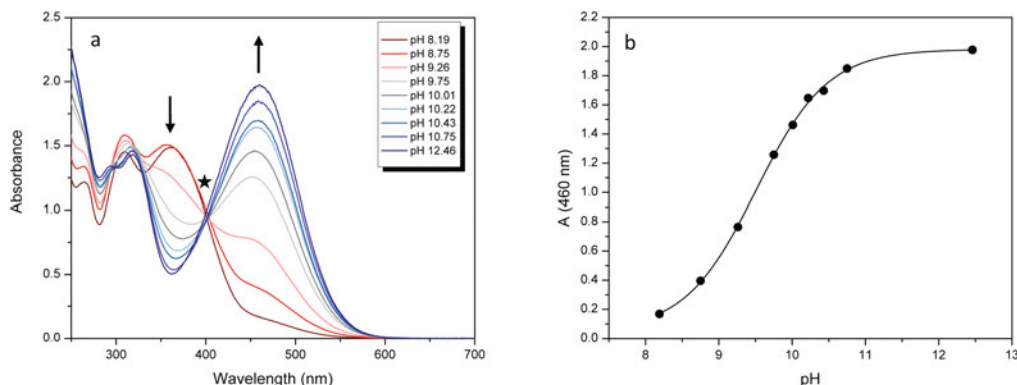
## Experimental

### Materials and methods

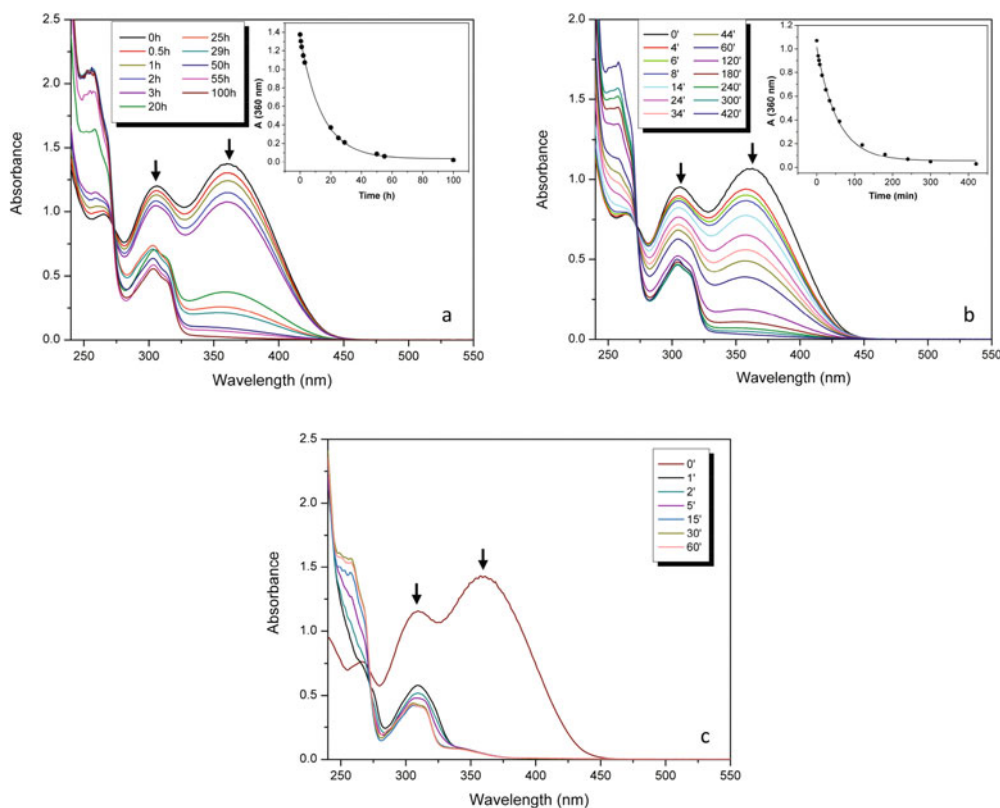
5-Bromo-2-hydroxybenzaldehyde and hydrochloric acid were purchased from Merck & Co. Sodium hydroxide was from Lach-Ner (CZ) and cyclohexanone was purchased from Chimopar (RO). All the other reagents and solvents were of analytical grade.

Elemental analysis was performed on an elemental analysis system VarioMICRO cube from Elementar Analyses. The NMR spectra were recorded on a Bruker Advance III 500 spectrometer (500.13 MHz for  $^1$ H, 125.77 MHz for  $^{13}$ C) at 298 K. The center of the solvent signal was used as an internal standard, which was related to TMS with  $\delta$  3.31 ppm for  $^1$ H and  $\delta$  49.15 ppm for  $^{13}$ C. Chemical shifts  $\delta$  are reported in ppm, coupling constants are reported in Hz and following abbreviations are used for splitting pattern: s (singlet), d (doublet), dd

$\S$  Crystal data for B–B: C $_{20}$ H $_{14}$ Br $_2$ O $_2$  ( $M_r$  = 446.13 g mol $^{-1}$ ), triclinic,  $a$  = 6.9626(10) Å,  $b$  = 11.1199(15) Å,  $c$  = 11.382(2),  $\alpha$  = 75.755(14) $^\circ$ ,  $\beta$  = 89.506(14) $^\circ$ ,  $\gamma$  = 83.992(12) $^\circ$ ,  $V$  = 849.3(2) Å $^3$ ,  $T$  = 293 K, space group  $P\bar{1}$ ,  $Z$  = 2, 6057 coll. refl., 3003 indep. ( $R_{int}$  = 0.0620), Gof = 0.986,  $R_1$  = 0.0406,  $wR(F^2)$  = 0.0785. CCDC 1509599.



**Fig. 4** (a) Absorption spectra of BHBC in various pH buffer solutions ( $2.1 \times 10^{-4}$  mol L $^{-1}$  BHBC in buffer/MeOH 1 : 1). The increase and decrease in intensities with increase in pH are indicated in arrows; (b) Absorption at 460 nm at different pH values.



**Fig. 5** (a) Formation of B-B from equilibrated solution of BHBC under dark conditions ( $1.7 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH); (b) formation of B-B from equilibrated solution of BHBC at 55 °C ( $1.3 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH); (c) formation of B-B from equilibrated solution of BHBC upon irradiation at 356 nm ( $1.7 \times 10^{-4}$  mol L $^{-1}$  BHBC in MeOH).

(doublet of doublets), t (triplet), and m (multiplet). NMR assignments have been carried out on the basis of  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT 135 and 2D NMR spectra: DQF-COSY, standard multiplicity-edited HSQC (HSQCDETGPSISP) and standard HMBC (HMCETGPL3ND). The NMR measurements: (i) basic pH of the BHBC solution in deuterated methanol (0.7 ml) was reached by adding 40  $\mu\text{l}$  of 40 wt% NaOD solution in  $\text{D}_2\text{O}$ ; and (ii) the acidic pH of BHBC in deuterated methanol (0.2 ml) was reached by adding 0.5 ml of 40 wt%  $\text{DClO}_4$  solution in

$\text{D}_2\text{O}$ . The NMR spectra of B-B species was recorded in  $\text{CDCl}_3$ . The FTIR spectra were recorded on a Cary 630 FTIR from Agilent Technologies, recorded using KBr pellets. The UV-VIS absorption spectra were recorded on an Agilent Cary 60 spectrophotometer. The pH of the solutions was measured using an Oakton pH/ $^{\circ}\text{C}$  meter pH 10 series. The BHBC solutions were prepared using distilled water and methanol. Experiments involving pH jumps were performed by adding 1 mL of a solution of BHBC in methanol (0.43 mM) to 1 mL of

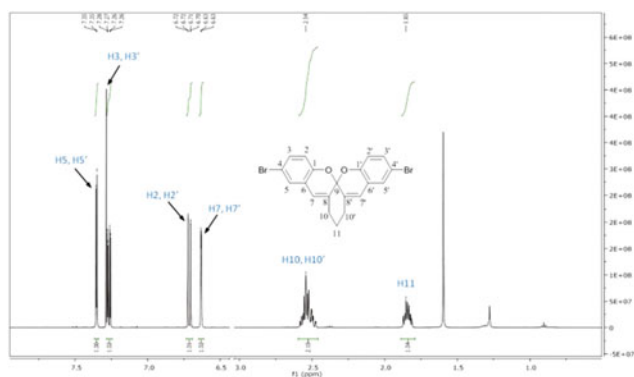


Fig. 6  $^1\text{H}$  NMR spectrum of B-B crystals in  $\text{CDCl}_3$ .

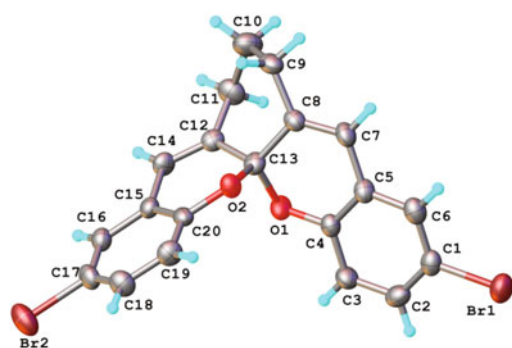


Fig. 7 X-ray molecular structure of B-B. Thermal ellipsoids are drawn at 50% probability level.

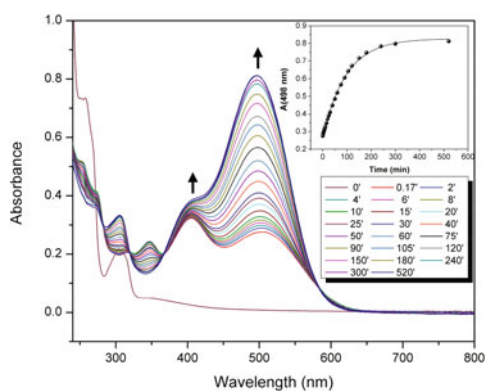


Fig. 8 Spectral variation upon pH jumps from equilibrated solutions of B-B in methanol to lower pH values. The spectra were obtained by adding 2.5 ml  $\text{HClO}_4$  (70 wt%) to 1 ml solution of B-B in MeOH (0.43 mM).

0.1 M glycine/0.1 M NaOH buffer solution (pH previously adjusted) in order to obtain the final desired pH value. Irradiation of BHBC was performed at 365 nm using a TLS – 260 from Newport equipped with a 350 W Mercury arc-lamp.

### X-ray crystal for compound B-B

X-ray diffraction data were collected with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated  $\text{MoK}\alpha$  radiation. Single crystals were positioned at 40 mm from the detector, and 592 and 376 frames were measured each of 5 and 100 s over  $1^\circ$  scan for  $\text{AH}^+$  and B-B, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.<sup>30</sup> The structures were solved by direct methods using Olex2<sup>31</sup> software with the SHELXS structure solution program and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>32</sup> Hydrogen atoms attached to carbon were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding non-hydrogen atoms. Positional parameters of the H attached to O atoms were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. Two of four asymmetric  $\text{ClO}_4^-$  anions were found to be disordered and their positional parameters were refined in combination with PART and SADI restraints and the displacement parameters for paired components were constrained to be equivalent.

### Synthesis of BHBC

4.0 g 5-bromo-2-hydroxybenzaldehyde (20 mmol) was dissolved in 40 mL ethanol, while stirring at room temperature. 1.03 mL of cyclohexanone (0.981 g, 10 mmol) were then added and the mixture was stirred vigorously for 1 h. 24 g of a NaOH 20% (w/w) solution were added dropwise, slowly, by maintaining the temperature below  $40^\circ\text{C}$  and the reaction was carried out at room temperature for 24 h. Then, 100 mL of distilled water was added and the mixture was neutralized to pH 5.5–6.0 by using 6 M HCl solution. An orange precipitate was formed which was filtered, dried and recrystallized from methanol/water while adjusting the pH of the solution to 1.5–2.0 using 6 M HCl solution. A yellowish powder was obtained,  $\eta = 65.4\%$ . Elemental analysis calcd for  $\text{C}_{20}\text{H}_{16}\text{Br}_2\text{O}_3$ : C 51.75, H 3.47, found: C 51.82, H 3.44%.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ),  $\delta$  (ppm): 8.16 (s, 1H), 7.29 (d,  $J = 2.7$  Hz, 2H), 7.07 (dd,  $J = 8.8, 2.7$  Hz, 2H), 6.57 (d,  $J = 8.8$  Hz, 2H), 2.89, (t,  $J = 5.3$  Hz, 4H), 1.80 (m, 2H).

$^{13}\text{C}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ),  $\delta$  (ppm): 191.2, 168.4, 135.8, 132.7, 131.6, 127.1, 121.8, 103.1, 28.5, 23.4.

FTIR ( $\text{cm}^{-1}$ ): 3368, 3938, 2865, 2359, 2328, 1655, 1604, 1560, 1489, 1474, 1412, 1286, 1259, 1218, 1168, 1144, 1113, 981, 926, 877, 815, 755, 626, 569.

## Conclusions

In spite of the fact that only a few studies of the pH network of chemical reaction involving xanthylium compounds have been reported, we proved that the new compound 2,6-bis(5-bromo-2-hydroxybenzylidene)cyclohexanone follows the same network of the chemical reaction as flavylium derivatives. This new photochromic system can be selectively “locked” in three

different species: xanthylium cation ( $AH^+$ ), chromeno-xanthene (B–B) and deprotonated trans-chalcone ( $Ct^{2-}$ ).

The *trans*-chalcone form is transformed into the xanthylium cation (red color) at very low values of pH, but reverts back to the yellowish *trans*-chalcone at pH values higher than 0.5. The structure of  $AH^+$  was confirmed by a single crystal X-ray study. At basic pH values, *trans*-chalcone is spontaneously transformed into an anionic form, displaying an orange color. An interesting feature of this system is related to the formation of xanthylium cation *via* a stable chromeno-xanthene intermediate, which was isolated and fully characterized by NMR. The structure of B–B was confirmed by an X-ray study on single crystal and it can be transformed into other species only in very acidic media.

The presence of bromine atoms on the molecule determines the formation of  $AH^+$  species at lower pH values compared to the mother molecule 2,6-bis(2-hydroxybenzylidene)cyclohexanone.

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