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# Electronically tunable anion $-\pi$ interactions in pyrylium complexes: experimental and theoretical studies<sup>†</sup>

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Noncovalent interactions of anions with electron-deficient aromatic rings that have been studied so far involve non-heteroaromatic or nitrogen-based heteroaromatic systems. Here we report the first case of an organic oxygenated aromatic system, in particular the tri-aryl-pyrylium tetrafluoroborate system, for which noncovalent anion– $\pi$  interactions of the pyrylium cation with the tetrafluoroborate anion have been experimentally detected and demonstrated by means of <sup>19</sup>F NMR spectroscopy in solution. A series of pyrylium tetrafluoroborate salts were synthesized in the presence of BF<sub>3</sub>.Et<sub>2</sub>O, by direct reaction of 4-substituted benzaldehydes with 4-substituted acetophenones or *via* the previously obtained chalcone of the less reactive ketone. Correlations of <sup>19</sup>F NMR chemical shifts of tetrafluoroborate anion molecular weight and the standard substituent Hammett constants, demonstrate anion– $\pi^+$  interaction to act between the polyatomic anion BF<sub>4</sub><sup>-</sup> and the pyrylium aromatic system. DFT calculations reveal that an additional (C–H)<sup>+</sup>–anion hydrogen bond involving the H(5) of pyrylium ring exists for these fluorescent dyes that show a tunable *cup-to-cap* shape cavity. The strong fluorescence emission observed for some representative pyrylium tetrafluoroborates described herein, makes them a promising class of tunable emission wavelength dyes for laser technology applications.

# 1. Introduction

Noncovalent interactions involving aromatic systems play important roles in chemistry and biology.<sup>1</sup> In particular, host–guest and supramolecular systems,<sup>2</sup> design of advanced functional materials,<sup>3,4</sup> and specific biological recognition,<sup>5</sup> including drug-receptor exchanges and protein folding, are the areas of their pivotal significance.

There are different types of reported noncovalent bond interaction in the literature involving both neutral and charged species. Electrostatic, hydrogen bonding,  $\pi$ - $\pi$  stacking, cation coordination including cation- $\pi$  interactions are widely accepted and classical noncovalent bond interactions. Less common are the anion coordination<sup>6</sup> and the anion- $\pi$  interactions. Nevertheless, since 2002, when the term anion- $\pi$  interaction was introduced on the basis of theoretical calculations<sup>7</sup> for designating an attractive force  $(\sim 20 \text{ to } 70 \text{ kJ mol}^{-1})$  between an electron-deficient aromatic  $\pi$  system and an anion, more than three hundred articles about it have been published.<sup>8</sup> Currently, the field of anion- $\pi$  research is highly promising and relevant in the scientific community due to the potential application of an inn- $\pi$  interactions for the design of anion receptors9,10 and anion-templated supramolecular architectures,<sup>11</sup> selective hosts for anions recognition,<sup>8a,12</sup> anion carriers,<sup>13</sup> catalysts,14 and their presumed involvement in biological functions.<sup>5a,15,16a</sup> In comparison with a number of theoretical calculations on anion- $\pi$  interactions,<sup>7,16,17</sup> experimental studies of this exciting noncovalent bond interaction are limited,<sup>9</sup> particularly in solution.<sup>18</sup> It is generally accepted that an ion- $\pi$  interactions can be characterized by anion-ring distances lower than the sum of the van der Waals radii of the participating atoms and at such a position that the anion-ring centroid vector is perpendicular to the plane of the aromatic ring.<sup>19,20</sup>

A comparison of analogous cation– $\pi$  and anion– $\pi$  complexes generally shows the anion– $\pi$  distance to be longer and the

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interaction to be energetically weaker.<sup>21</sup> However, a different picture appears when charged aromatic rings participate in anion- $\pi$  bonding. Positive charges can be easily generated in azine rings by simply adjusting the pH of the medium, and this can be used to increment the anion binding ability of the ring. Several examples of an  $n-\pi$  complexes between aromatic cations (tropylium, quinolizinylium, protonated 2-aminopyrimidine, protonated adenine) and various anions have been reported by Frontera and co-workers along with crystallographic structures that support the theoretical findings.<sup>22</sup> As expected, in these complexes the interaction energies are large (>80 kcal  $mol^{-1}$ ) and electrostatic effects dominate these denoted as an ion- $\pi^+$ interactions.<sup>8e</sup> On the other hand,  $(C-H)^+ \cdots X^-$  hydrogen bonds have been reported in several 1,3-disubstituted imidazolium and a bis(triazolium)-based anion receptors for guest binding.<sup>23</sup> This is a novel type of charged hydrogen bonding wherein the chargecharge electrostatic interaction dominates, in contrast to the wellknown neutral hydrogen bonds that occur in the most positively charged anion receptors which form N-H---anion hydrogen bonds as binding forces.<sup>24</sup> Very recently, taking advantage of both noncovalent anion $-\pi^+/(C-H)^+$  interactions of imidazolium rings with anions as stabilizing forces for crystal packing, Singh and co-workers<sup>4</sup> have designed and reported some self-assembled arrays of cone-shaped calyx[n]imidazolium systems (n = 4, 5) as a new class of positively charged homo-calix compounds for different applications. Moreover, Caballero et al.<sup>23a</sup> have described an unprecedented bidentate triazolium receptor for anion recognition, for which NMR spectroscopic data in solution indicate that one triazolium ring is acting as a hydrogen bond donor, whereas the second triazolium ring behaves as an anion- $\pi$  receptor.

However, despite the progress made in the field in the last few years, all studies about the participation of charged aromatic rings in anion– $\pi$  bonding reported so far involve non-heteroaromatic or nitrogen-based heteroaromatic systems. Here we report the first case of an organic oxygenated aromatic system,<sup>22*a*</sup> in particular a pyrylium-based tri-arylated series of compounds, for which non-covalent anion– $\pi^+/(C-H)^+$  interactions of the pyrylium ring with the tetrafluoroborate anion have been experimentally detected and demonstrated.

Pyrylium salts are a very important class of cationic organic molecules containing a trivalent oxygen atom in a six-membered aromatic ring.<sup>25</sup> The high electronegativity of oxygen is the reason for two experimental observations: (a) pyrylium salts represent the strongest single modification of the electron distribution caused by one heteroatom in a benzene ring, and (b) pyrylium ions have the highest conductivity among the compounds with benzene rings. A number of references are available for this kind of compounds such as crystallographic and structural studies<sup>26</sup> and specially their good absorption, fluorescence, and electron acceptor behaviour.<sup>27</sup> Pyrylium salts can function as intermediates for a variety of syntheses,<sup>28</sup> and have been exploited to design sensors for anions,<sup>29</sup> amines, amino acids and chameleon labels for quantifying proteins,<sup>30</sup> as well as a kind of ionic liquid crystal materials which can be used in the display industry.<sup>31</sup>

Pyrylium ions are less reactive than other oxonium ions. Their improved stability is influenced by the aromaticity of the ring, but it also depends upon the stabilizing effect of the anion. In this communication, the behaviour of the tetrafluoroborate anion in a number of previously synthesized pyrylium salts has been analyzed by <sup>19</sup>F NMR spectroscopy; we have found small but significant variations on chemical shifts from light to heavily modified tri-arylpyrylium cations. From our results, regardless of the classical vision of host–guest interaction, pyrylium tetrafluoroborates can be considered to be "symbiotic" relationships between cations and tetrafluoroborate anions.

## 2. Experimental section

#### <sup>19</sup>F NMR spectroscopy

Spectra were acquired on a Bruker Avance 500 MHz spectrometer equipped with a 5 mm BBFO broadband probehead incorporating a *z*-gradient coil. Spectra were recorded at 300 K in triplicate, and sample concentrations were 20 mM in all cases. DMSO- $d_6$  containing 0.1% TMS was used as the solvent. Spectra were acquired using a high-power 90° pulse of 14.8 µs and a recycle delay of 5 s. The <sup>19</sup>F chemical shifts were referenced indirectly<sup>32</sup> to CCl<sub>3</sub>F ( $\Xi$  = 94.094011).

#### Synthesis of pyrylium tetrafluoroborate salts

#### Route I

General procedure from an aldehyde and a ketone.  $BF_3 \cdot Et_2O$ (3.1 equiv.) was added dropwise under a  $N_2$  atmosphere to a solution of *p*-substituted benzaldehyde\* (1 equiv.) and *p*-substituted acetophenone (3 equiv.). The mixture was heated to 80 °C until the reaction was complete, monitored by TLC (1:4 EtOAc-hexane). The residue was eventually treated with EtOH or  $Et_2O$ . Crystallization from 1,2-dichloroethane or acetone gave the corresponding pure pyrylium tetrafluoroborate.

\*Note: solid *p*-substituted benzaldehydes were previously dissolved in toluene.

#### Route II

General procedure from a chalcone.  $BF_3$ ·Et<sub>2</sub>O (3.1 equiv.) was added dropwise under a N<sub>2</sub> atmosphere to a solution of chalcone (1 equiv.) and *p*-substituted acetophenone (3 equiv.) in anhydrous dichloromethane. The mixture was heated to reflux (45 °C) until the reaction was complete, monitored by TLC (1:4 EtOAc-hexane). Solvents were evaporated to dryness and the residue was eventually washed with H<sub>2</sub>O and EtOH. Crystallization from 1,2-dichloroethane or acetone gave the corresponding pure pyrylium tetrafluoroborate.

## 3. Results and discussion

A series of pyrylium salts (**10–28**) with tunable electronic effects have been synthesized following two approaches (Scheme 1, routes I and II, Table 1), between their different feasible synthetic methods.<sup>33</sup> In the case of symmetrically substituted pyrylium salts, these compounds can be directly synthesized from 4-substituted aldehydes and ketones (route I). Thus, treatment of biphenyl-4-carboxaldehyde and 4-fluoroacetophenone



 Table 1
 Pyrylium salts with tunable electronic effects synthesized following two approaches (Scheme 1, routes I and II)

Compound	Route	$R_1$	$R_2$	R <sub>3</sub> H	
10	I, II	Н	Н		
11	I	Н	Me	Me	
12	II	Ph	Н	Н	
13	II	Ph	Me	Me F H F F H F Me F	
14	II	Н	Н		
15	Ι	F	Н		
16	II	F	F		
17	Ι	Н	F		
18	II	F	F		
19	Ι	$NO_2$	Н		
20	II	$NO_2$	F		
21	II	$NO_2$	Me		
22	I, II	$NO_2$	Me		
23	I, II	$NO_2$	F		
24	II	Ph	Ме	F	
25	Ι	Ph	F	F	
26	II	OMe	Ме	Me	
27	I, II	OMe	F	F	
28	Í	OBz	Me	Me	

with  $BF_3$ ·Et<sub>2</sub>O in toluene gives 4-biphenyl-2,6-di-(4-fluorophenyl)pyrylium tetrafluoroborate **25** in 74% yield. For unsymmetrically substituted systems, the synthesis of a chalcone from the less reactive ketone, as a previous step, is required (Scheme 1, route II). In their turn, *E*-chalcones **1–9** were obtained by Claisen–Schmidt condensation between commercially available aldehydes and ketones.

In both strategies, the Lewis acid  $BF_3 \cdot Et_2O$  was used to mediate cyclization and dehydration steps of the 1,5-dicarbonyl intermediate. For example, treatment of chalcone 2 ( $R_1 = Ph, R_2 =$ H) and acetophenone with  $BF_3 \cdot Et_2O$  in anhydrous  $CH_2Cl_2$  gives 4-biphenyl-2,6-di-phenylpyrylium tetrafluoroborate **12** in 70% yield. The preparation of pyrylium salts from chalcones is a simple process, but the yields are unequal.

Symmetrically substituted pyrylium salts (10,<sup>34</sup> 11,<sup>35</sup> 12,<sup>36</sup> 13, 15,<sup>37</sup> 17,<sup>35</sup> 18,<sup>38</sup> 19,<sup>39</sup> 22, 23, 25, 26,<sup>40</sup> 27, and 28) show in their <sup>1</sup>H NMR spectrum in DMSO- $d_6$  a singlet in the range of 8.93–9.30 ppm for the two typical equivalent protons H-3 and H-5 of the pyrylium ring. For compound 10, a doublet at 8.60 ppm (J = 7.5 Hz) for 6 protons is observed due to the *ortho* protons of three phenyl rings (A, B and C) attached to positions 4, 2 and 6 of the pyrylium ring, respectively. For all the rest of symmetrically substituted derivatives (compounds 11, 12, 13, 15, 17, 18, 19, 22, 23, 25, 26, 27, and 28) two different doublets

are observed for these *ortho* protons in the range of 8.24–8.79 ppm, the most deshielded one corresponding to two *ortho* protons of the phenyl ring A and a second doublet for four protons assigned to *ortho* protons on phenyl rings at pyrylium positions 2 and 6 (rings B and C). When a fluorine atom is present in the phenyl ring (compounds **15**, **17**, **18**, **23**, **25**, **27**), a double doublet is observed instead, due to the coupling with fluorine.

Related to non-symmetrical pyrylium derivatives (14, 16, 20, 21, and 24), it was observed that the <sup>1</sup>H NMR spectrum in DMSO- $d_6$  of compound 14 shows a strange lack of peaks as expected for a non-symmetrical compound. A signal for protons H-3 and H-5 of pyrylium cation was observed at 9.16 ppm (a singlet for two protons). Moreover, another main feature of this spectrum is the presence of one doublet for four protons at 8.60 ppm assigned to the ortho protons in phenyl rings at positions 4 and 6 (rings A and C) of the pyrylium cation. Likewise, compound 16 exhibits a multiplet at 8.74-8.66 ppm for these four ortho protons. Substitution patterns of compounds 14 and 16 were confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC experiments. It was first suggested that these features could be caused by solvation effects, but this explanation was discarded when acetone- $d_6$  was used; in this solvent a singlet for H-3 and H-5 was still observed as well as two signals for the ortho protons on phenyl rings A and C, showing virtual <sup>1</sup>H-<sup>1</sup>H coupling (ESI,<sup>†</sup> Fig. S11). We propose that this effect, in solution, may be due to tetrafluoroborate– $\pi^+$ interaction, in such a way that being a fluorine atom of the anion closer to H-3 (or H-5) than H-5 (or H-3) of the pyrylium ring, a change occurs in the expected chemical shift for one of them. A similar experimental effect for H-3 and H-5 (a singlet at 9.14 ppm) is observed for compound 16 but not for the rest of unsymmetrically substituted pyrylium salts 20, 21, and 24.

<sup>13</sup>C NMR corroborated the presence of the pyrylium moiety. Thus, on the spectra of symmetrically substituted derivatives a signal in the range of 167.9–172.7 ppm is observed for C-2 and C-6; C-4 gives rise to a signal at 164.7–167.1 ppm, and C-3 and C-5 generate one signal between 113.0 and 117.7 ppm. As expected, unsymmetrical derivatives give separated signals for each of the pairs C-2/C-6 and C-3/C-5 of the pyrylium ring.

To test our hypothesis, anion exchange was induced by addition of increasing amounts of acid. When compound **14** was treated in a NMR tube with  $H_2SO_4$  or  $HClO_4$  (>500 equiv.), a downshift of the signal for H-3 and H-5 from 9.16 ppm to give separate signals at 8.51 and 8.50 ppm for each proton, was observed (Fig. 1). For the pyrylium perchlorate salts, the new chemical shifts were in the range described in the literature.<sup>41</sup>

If changes in the aromatic protons of the pyrylium cation can be detected as a consequence of the anion–pyrylium system interaction, the corresponding changes must be exhibited in the tetrahedral tetrafluoroborate anion. Using <sup>19</sup>F NMR spectroscopy as a tool for this purpose, we have found a relationship between <sup>19</sup>F chemical shifts and the molecular weight of the pyrylium cation (Fig. 2). From the extensive studies<sup>7a,8d,42</sup> of the physical nature of the anion– $\pi$  interactions it was concluded that electrostatic forces, specifically the quadrupole moment of the arene and ion-induced polarization, are the main energetic contributors to the anion– $\pi$  complex. Accordingly, a molecular





**Fig. 2** Tetrafluoroborate anion chemical shift in <sup>19</sup>F NMR for different pyrylium salts in DMSO- $d_6$  (20 mM) for coupling with <sup>11</sup>B vs. molecular weight of the pyrylium cation. In this graph, triangles correspond to compounds of series (a); circles to series (b); hexagons for series (c); squares to series (d). For coupling with <sup>10</sup>B, see ESI,† Fig. S1.

weight dependence of the quadrupolar molecular moment<sup>43</sup> and/or the ion-induced polarization might be expected to justify our experimental findings.

We realized that <sup>19</sup>F NMR chemical shifts of tetrafluoroborate anion in DMSO- $d_6$ , for most of the synthesized tri-arylpyrylium tetrafluoroborate salts, undergo small but significant changes due to the effect of substituents on the pyrylium cation. To illustrate the magnitude of the effect, which proves significant concentration dependence, we show in Table 2 the  $\Delta\delta(\text{Hz})$ observed for each case relative to the unsubstituted pyrylium dye **10**. For our study, four series of pyrylium salts synthesized can be differentiated: (a) compounds **10**, **11**, **12** and **13**, with only alkyl or aryl substituents; (b) compounds **14**, **15**, **16**, **17** and **18** containing only fluorine atoms as substituent in aromatic rings; (c) nitro-compounds (**19**, **20**, **21**, **22** and **23**) with or without F atoms and (d) hybrid-pyrylium compounds or pyrylium salts **24**, **25**, **26**, **27** and **28** with hybrid electronic effects.

In the second series, (b), due to the electronegativity of the fluorine atom, there is an increased positive charge over the

**Table 2** Series of pyrylium salts synthesized and  $\Delta\delta$ (Hz) observed for each compound relative to the unsubstituted pyrylium dye **10** 

Series	Compound (X)	$\frac{\Delta \delta_{X/10} / \delta_X - \delta_{10} (Hz)^a}{0}$ 0 0.9 4.1 4.3 0.9 10		
a	10	0		
	11	0.9		
	12	4.1		
	13	4.3		
b	14	0.9		
	15	1.9		
	16	3.6		
	17	3.9		
	18	7.3		
C	19	3.5		
-	22	9.4		
	23	8.7		
d	25	3.9		
	26	5.3		
	27	3.7		

<sup>*a*</sup> Corrected values for compounds **19**, **22** and **23** were 4.3, 9.4 and 10.2, respectively.

pyrylium oxygen, which will undergo a higher interaction with the anion. As compared with compound **10**, larger chemical shifts of  $BF_4^-$  are observed. Indeed, a maximized interaction for compound **18** containing three F atoms in the *para* position of each aromatic ring can be achieved.

The position of each substituent group proves to be significant for the interaction. The essential feature was the dependence of the chemical shift value,  $\delta_{\rm F}$ , as a function of fluorine position, which gives rise to small variations among regioisomers, *i.e.*, compounds with the same number of F atoms and  $M_{\rm w}$ . Chemical shift deviations for symmetrically rather than unsymmetrically substituted pyrylium compounds take place, as shown for pairs 17/16 and 15/14: ( $\Delta \delta_{17/16}$  0.3 Hz) and ( $\Delta \delta_{15/14}$  1.0 Hz).

For the first series (a), an also positive, but lower slope than those observed for series (b) with increasing  $M_w$  is observed. A weaker contact of the guest with the pyrylium cation is evidenced from the reference state (compound **10**, Table 2). Compounds **25** and **27** from series (d) correlate acceptably well with this straight line, but not **26** (compounds **24** and **28** not studied).

The trend for nitro-compounds (c) was not satisfactory at first because a  $\delta_{\rm F}$ , lower than expected, was found as a consequence of the spontaneous decrease of the tri-arylpyrylium salt concentration in the sample. These nitro-containing structures evolve to an equilibrium state between pyrylium compounds (Scheme 2), for example **23** and the corresponding substituted pent-2-en-1,5-dione



Table 3 Equilibrium ratio between nitro-containing pyrylium dyes and the corresponding substituted pent-2-en-1,5-diones (by  $^1{\rm H}$  NMR)

$R_2$	$R_3$	Pyrylium/dione ratio
Н	Н	1:0.4
F	Н	1:1.4
Me	F	1:0.8
Me	Ме	1:0.3
F	F	1:1.3
	R <sub>2</sub> H F Me Me F	R2         R3           H         H           F         H           Me         F           Me         Me           F         F           Me         F           F         F

23a (23/23a, 1:1.3 by <sup>1</sup>H NMR), so that the <sup>1</sup>H NMR spectrum in DMSO- $d_6$  now exhibits a singlet for the olefinic proton (H-2) at 7.74 ppm and a singlet at 4.86 ppm assigned to methylene protons in an  $\alpha$  position to the carbonyl group (H-4 and H-4'). This ringopening process is not complete after several days. According to the substituent that stabilizes the pyrylium cation, the formation of the corresponding pent-2-ene-1,5-dione (19a) from compound 19 is less acute (19/19a, 1:0.4) than that observed for fluorinecontaining phenyl B and C rings (Table 3). In the case of pent-2ene-1,5-dione 22a derived from compound 22, the ratio (22/22a) was 1:0.3, <sup>1</sup>H NMR spectrum showing singlets at 7.69 and 4.85 ppm for H-2 and H-4/H-4', respectively. For all 1,5-diones, no perceptible changes in the aromatic regions are observed. A predictable decrease of  $\delta_{\rm F}$  based on the calculated ratio of pyrylium/dione was observed (Table 3). For these compounds,  $\delta_{\rm F}$ exclusively due to the pyrilium contribution has been calculated taking into account the reported pyrilium/dione ratios and these resulting corrected  $\delta_{\rm F}$  values have been employed for being represented in Fig. 2. The described behaviour of nitrocompounds can be considered as a strong evidence of "symbiotic relationship" of both ions in the pyrylium-tetrafluoroborate complex. To further highlight this special relationship, when pyrylium cation is separated from  $BF_4^-$  by solvent, it prefers to decompose itself rather than being disconnected from its anion. DMSO- $d_6$ , whose capability of solvating cations and splitting ionic aggregates is well known, was used as a solvent in this NMR study.

Relevant information can be obtained using linear free energy relationships. Thus, assigned tetrafluoroborate anion <sup>19</sup>F chemical shifts ( $\delta$ , ppm) for different pyrylium salts in DMSO- $d_6$  have been correlated with the standard Hammett constants<sup>44</sup> for summed *para* position substituents ( $\sum \sigma_p$ ). The plot obtained using the classical Hammett equation, type:  $\delta = \rho \sigma + h$ , is shown in Fig. 3. Two straight lines are clearly observed in the plot, with an abrupt change of slope. While a poor correlation coefficient ( $r^2 = 0.714$ ) was obtained for compounds **12**, **13** and **25–27**, from series (a) and (d), respectively, a satisfactory correlation ( $r^2 = 0.911$ ) was found for pyrylium salts having only fluorine as the substituent in the phenyl rings [series (b), compounds **14–18**]. Compound **11** and nitro-compounds [series (c), compounds **19**, **22** and **23**] failed to correlate.

These results reveal quantitative correlation between the  $\sigma$  constants of substituent groups in the pyrylium cation and the tetrafluoroborate–pyrylium cation interaction. Compounds that show this correlation giving a small negative  $\rho$  value have an electron-donating (+R) substituent group at the phenyl ring A (R<sub>1</sub> = Ph, OMe). Substituent groups of this kind stabilize the cation since they disperse the positive charge of the oxygen atom



**Fig. 3** Plot of tetrafluoroborate anion chemical shift in <sup>19</sup>F NMR for different pyrylium salts at a constant concentration of 20 mM in DMSO*d*<sub>6</sub> (for coupling with <sup>11</sup>B) vs. substituent Hammett constants ( $\sum \sigma_p$ ). For coupling with <sup>10</sup>B, see ESI,† Fig. S2.

of the pyrylium ring, in such a way that the anion– $\pi^+$  interaction is relatively small. In other words, a minor anion contribution is required to stabilize the pyrylium system. As a consequence, the sensitivity of the anion–cation interaction to the substituent group nature will be limited, as it is deduced in fact from the plot.

However, for only fluorine-containing pyrylium salts [series (b), compounds **14–18**] a higher and positive slope results. A strong electron deficiency is caused now by the substituents on the pyrylium cation. The electrostatic interaction  $O \cdots B$  is not strong enough for maintaining the complex anion–cation in a solvent like DMSO, thus requiring a fluorine atom of the anion to interact more effectively with the  $\pi$ -system. The higher the electron deficiency caused at the pyrylium system by the substituents, the more significant is this anion– $\pi^+$  interaction. The limit situation was found in nitro-pyrylium salts where extreme electron-withdrawing (–I, –R) effects induced considerable instability, and the consequent correlation failure related to the pyrylium salt concentration decrease in the sample.

These results confirm those inferred from the tetrafluoroborate anion <sup>19</sup>F chemical shifts ( $\delta$ , ppm) *vs.* pyrylium cation molecular weight, described above.

Additionally, on the basis of our experimental results (Table 3) and Hammett correlations we propose a stability range for the studied pyrylium tetrafluoroborate complexes between -0.61 and 0.40 of the corresponding  $\sigma$  value. Compound 22 proved to be more stable ( $\sigma_{\text{para}} 0.44$ ) than **19** ( $\sigma_{\text{para}} 0.78$ ) thanks to donating methyl groups and, of course more stable than **21**, **23** and **20**.

From these results, the lowest value of  $\sum \sigma_{\rm p}$  for anion- $\pi^+$  interaction seems to be a value of at least 0.0. Values under 0.0 can be understood as a sole electrostatic interaction and for values higher than the stated range of stability (-0.61 to 0.4 for  $\sum \sigma_{\rm p}$ ) an enhancement of decomposition products is expected.

#### 3.1 Photophysical properties

The UV-vis absorption and fluorescence properties of some representative synthesized pyrylium tetrafluoroborates (10, 13,

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14, 15, 22, 23, 26, 27 and 28) were studied. All studied compounds showed one UV-vis absorption band in the range 406-439 nm in acetone (ESI,† Table S2). Some of them showed a second absorption band (10, 14, 15 and 28 at 357, 356, 358 and 368 nm, respectively) in acetone. Previously, Suresh and co-workers reported theoretical studies of absorption bands denoted as "x" and "y" bands<sup>27</sup> for pyrylium salts. Two independent chromophores assigned to the x-band (2,6-diarylpyrylium moieties, longer wavelength) and the y-band (4-arylpyrylium moiety, shorter wavelength) act on pyrylium salts. A hypsochromic shift of the absorption bands to shorter wavelengths occurs when solvent polarity is increased. Thus, the absorption spectrum of compound 10 in CH<sub>2</sub>Cl<sub>2</sub> shows the same two bands (417 and 369 nm) red-shifted reported in the literature,<sup>45</sup> whereas the absorption spectrum of compound 14 in MeOH shows two bands at 254 and 322 nm. When compound 14 was treated with increasing amounts (0.2, 0.6, 1.0, 1.5 and 4.0 equiv.) of HClO<sub>4</sub>, AcOH and TFAA, (ESI,† Fig. S3) a bathochromic shift of the absorption bands (357 and 409 nm) resulted. Addition of 0.2 equiv. of HClO<sub>4</sub> was sufficient for the completion of this displacement. Adding up to 4 equiv. any changes with respect to 0.2 equiv. were observed. The same procedure was applied for TFAA and AcOH. TFAA and HClO<sub>4</sub> cause a hypochromic effect on UV spectra while the presence of AcOH has the opposite effect. Unfortunately, in our opinion, any evidence of the nature of anion-cation interactions can be extracted from the just exposed absorption experiments.

Nevertheless, interesting photophysical changes in different solvents were observed, in particular related to the stability of synthesized complexes. For example, in compound **10**, three absorption bands with time-dependence intensity were attributed to the x-band (412 nm), y-band (359 nm) and another one at 298 nm located in the carbonyl absorption region (ESI,† Fig. S4). Furthermore, treatment of compound **10** in DMSO- $d_6$  with 10 cycles of UV radiation showed an increase of the blue shifted band (298 nm) and respectively, loss of intensity in the pyrylium bands. Subsequently, the <sup>1</sup>H NMR spectrum reveals a ring-opening compound (1,5-di-ketone) (ESI,† Fig. S5).

All complexes showed fluorescence characteristics in acetone solution due to the extended  $\pi$ -conjugation. The wavelength emission band of the investigated pyrylium tetrafluoroborates (10, 13, 15, 22, 23, 26, 27 and 28) was in the range 464-533 nm depending on the substituent in the para position of phenyl rings A, B and C attached to the pyrylium core (see Table S2 in the ESI<sup>†</sup>). From these results we concluded that, in general, incorporation of substituent groups at these para positions causes a red-shift in the emission band. Furthermore, changing the conjugation length, *i.e.* the length of the oligophenyl moiety as in compound 13 ( $\lambda_e$  533 nm,  $R_1$  = Ph,  $R_2$  = Me,  $R_3$  = Me), or introducing different substituent groups in the aromatic rings, the maximum emission can be controlled. Thus, it is noteworthy that replacing two methyl groups by fluorine atoms in rings B and C (pairs 22/23 and 26/27) causes shifts in the maximum emission to shorter wavelengths (14 and 20 nm, respectively) while introducing a fluorine atom the in phenyl ring A (pair 10/15) does not even remotely affect the emission band wavelength.



Fig. 4 Colour perception and brightness of pyrylium tetrafluoroborates **10**, **12**, **13**, **15** and **22** in acetone solution.

In its turn, replacing an electron-withdrawing group like NO<sub>2</sub> in the phenyl ring A by an electron-donating group, like OMe (pairs 22/26 and 23/27) or OBz (pair 22/28), also provides a blue shift in maximum emission to shorter wavelengths ( $\Delta\lambda_e = 22$  to 28 nm) as a consequence of electronic reorganization and subsequent displacement of the positive charge to the methoxy or benzyloxy group, and then tetrafluoroborate should move towards the phenyl ring A during electronic excitation.

All complexes are stable with the exception of **15** ( $R_1 = F$ ,  $R_2 = H$ ,  $R_3 = H$ ) and **26** ( $R_1 = OMe$ ,  $R_2 = Me$ ,  $R_3 = Me$ ), fluorescence intensities of which slowly decay with time ( $t_{1/2} = 214.2$  min and 272.2 min, respectively), probably due to some photoinstability of the complex, and specially, pyrylium salt **22** ( $R_1 = NO_2$ ,  $R_2 = Me$ ,  $R_3 = Me$ ), which is highly unstable. In this case, the maximum fluorescence emission peak becomes null ( $t_{1/2} = 166.3 \text{ min}$ ) (ESI,† Fig. S6).

On the other hand, most of the investigated pyrylium tetrafluoroborate salts showed blue to orange emission colours, as it is shown in Fig. 4 for compounds **10**, **12**, **13**, **15** and **22**. Furthermore, the strong fluorescence emission of these pyrylium tetrafluoroborate salts makes them a promising class of tunable emission wavelength dyes for laser technology applications.<sup>46</sup>

#### 3.2 Theoretical calculations

To establish the theoretical disposition of  $BF_4^-$ , density functional theory (DFT) calculations with the Becke 3 Lee-Yang-Park (B3LYP) exchange correlation functional at the 6-31G(d) level of theory were employed. During the optimization process no symmetry constraints were enforced.<sup>47</sup> This basis set proved to be more in agreement with our experimental results as compared with B3LYP/6-31+G(d,p). Other levels of this theory, such as MP2/6-31++G\*\*, B3LYP/DZVP or/and MP2/aug-cc-pVDZ, have been previously reported for this kind of interactions.<sup>11,12</sup> TD-DFT calculations to support the UV-vis results to substantiate the mode of binding of the anion has been applied for other systems.<sup>48</sup> Particularly, for pyrylium compounds B3LYP/ LanLsDZ or ZINDO/S methods have been also applied.<sup>27,49</sup> These theoretical calculations by B3LYP/6-31G(d) are in excellent agreement with the correlation and experimental results observed.

Interaction energies of the pyrylium complexes have been also calculated at the M06-2X/6-31G(d)<sup>50</sup> level, which has been successfully employed in different molecular systems<sup>51</sup> and provides more accurate values in our case. From the inspection of the results shown in Table 4, several interesting points arise. First, the unsubstituted compound 10 shows a theoretical distance  $R_{B...O}$  of 3.023 Å. For all the other investigated pyrylium salts this distance increases ( $\Delta R_{B...O} = 0.214$  to 0.543 Å, being maximum for 27), with the exception of compound 12 ( $R_1 = Ph$ ,  $R_2 = H$ ,  $R_3 = H$  where  $R_{B \dots O} = 3.005$  Å). In addition, the anion distance to the aromatic pyrylium centroid  $(R_e)$  diminished with respect to  $\mathbf{10}$  ( $R_e = 3.453$  Å) in a range of 0.132–0.239 Å (minimum value for 28), with the exception of compound 12 ( $R_e = 3.467$  Å). That indicates that the incorporation of a sole phenyl group at the para position of phenyl ring A (e.g. pairs 10/12 and 11/13 and 17/25) [ $\Delta R_{B...O} = 0.018$ , -0.113 and 0.033 Å, respectively;  $\Delta R_e =$ -0.014, 0.018 and -0.010 Å, respectively;  $\Delta R_{\text{F}\cdots\text{C}(5)} = -0.038$ , 0.002 and -0.018 Å, respectively;  $\Delta R_{F \cdots C(3)} = 0.018$ , 0.035 and -0.002 Å, respectively;  $\Delta R_{F \cdots H(5)} = -0.044$ , 0.037 and -0.045 Å, respectively; and  $\Delta R_{F \cdots H(3)} = 0.028$ , 0.161 and -0.030 Å, respectively] has a poor influence on the anion- $\pi^+$  interaction, while the dispersion of charge through the cation, in general, favours the anion-cation interaction. Thus, a maximum dispersion of charge in 27 ( $R_1$  = OMe,  $R_2$  =  $R_3$  = F) could be correlated with the lowest electrostatic interaction and justify the maximum  $R_{B...O}$ distance observed for this compound.

From compound **10** to compound **13**, series (a), a slight reduction of  $R_{\text{F}\cdots\text{H}(5)}$  (3.511 and 3.162 Å, respectively) and  $R_{\text{F}\cdots\text{H}(3)}$  (3.722 and 2.911 Å, respectively) was observed (Table 4). For this series, the anion is practically over the trivalent oxygen atom and two fluorine atoms of BF<sub>4</sub><sup>-</sup> are almost equidistant to electropositive C-2 and C-6 atoms (2.714 and 2.543 Å, respectively for compound **10**) (Fig. 5).

When fluorine atoms were incorporated into the molecule, the  $R_{B...O}$  distance increased up to a maximum value of 3.480 Å and the anion was directly positioned over C-6 (Fig. 6).

An increasingly shorter distance for  $F \cdots H(5)$  in the pyrylium framework was calculated. This reinforcement of interaction with the positive charge of the cation provides a non-covalent



**Fig. 5** A superimposition of structures based on DFT calculations for compounds of series (a).



Fig. 6 A superimposition of structures based on DFT calculations for compounds of series (b) in comparison with compound **10**.

interaction anion– $\pi^+$ . In fluorine compounds (14 to 18) a maximized contact with a distance shorter than  $\Delta R_{vdw}$  for  $F \cdots C(5)$  in comparison with C-5 in series (a), is observed. In the case of compound 18, the lowest value for  $R_{F \cdots H(5)}$  (2.821 Å) is indicative of the higher anion– $\pi^+$  interaction suggested. It is noteworthy that taking for comparison the  $R_{F \cdots H(5)}$  and  $R_{F \cdots H(3)}$  values for compounds 14 and 16, these distances are identical for compound 16, while there is a difference of 0.195 Å in the case of 14, all of that in accordance with the observations in the

Table 4	Theoretical calculations by	B3LYP/6-31G(d) method o	distances and dihedral angles	s for some pyrylium tetrafluoroborates <sup>a</sup>
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Compound	$R_{\mathrm{B}\cdots\mathrm{O}}$ (Å)	$R_{\mathrm{F}\cdots\mathrm{C}(5)}$ (Å)	$R_{\mathrm{F}\cdots\mathrm{C}(3)}\left(\mathrm{\AA}\right)$	$R_{\mathrm{F}\cdots\mathrm{H}(5)}$ (Å)	$R_{\mathrm{F}\cdots\mathrm{H}(3)}$ (Å)	$R_{\rm e}$ (Å)	$\phi_2 (^\circ)$	$\phi_4 \left( ^\circ  ight)$	$\phi_6 (^\circ)$	$\Delta E_{\rm int}^{\ b}  ({\rm kcal}  {\rm mol}^{-1})$
10	3.023	3.048	3.297	3.511	3.722	3.453	11.1	-4.7	-15.2	-72.1(-78.8)
11	3.287	2.824	2.881	3.199	3.072	3.258	-26.5	7.2	-16.9	-72.9 (-79.0)
12	3.005	3.086	3.279	3.555	3.694	3.467	15.8	-1.0	-16.6	-67.8(-75.2)
13	3.400	2.822	2.846	3.162	2.911	3.240	-26.8	0.8	24.0	-71.1 (-77.9)
14	3.247	2.972	2.847	3.122	3.317	3.321	-27.2	9.0	-4.5	-77.8 (-84.5)
15	3.346	2.891	2.882	2.907	3.353	3.301	-30.0	5.4	17.1	-76.9 (-83.6)
16	3.310	2.812	2.849	3.086	3.098	3.255	-27.0	7.0	-16.4	-77.6 (-83.8)
17	3.246	2.821	2.870	3.144	3.132	3.264	-25.0	6.8	-17.7	-78.2(-84.4)
18	3.480	2.874	2.979	2.821	3.395	3.272	-28.7	8.4	24.7	-79.1 (-86.1)
25	3.279	2.803	2.868	3.099	3.102	3.254	-23.5	5.9	-17.2	-74.9(-81.8)
26	3.549	2.863	3.042	2.768	3.417	3.277	-27.5	5.8	28.7	-70.6 (-77.6)
27	3.566	2.860	3.058	2.753	3.442	3.281	-28.1	5.8	26.9	-74.9(-82.2)
28	3.488	2,781	2.845	2.777	3.120	3.214	-25.8	-5.2	23.1	-67.4(-75.3)

<sup>*a*</sup> All calculated contacts between aromatic rings and protons have been qualitatively confirmed by 2D NOESY experiments where NOE enhancements for compounds **10**, **14**, **16** and **28** were observed. <sup>*b*</sup> Interaction energies (without BSSE correction) were calculated from  $\Delta E_{int} = E_{complex} - E(BF_4^-) - E(PF_4^+)$ . In parentheses the interaction energies at M06-2X/6-31G(d) level of theory are shown.

<sup>1</sup>H NMR spectrum of **14** described above. In general, the incorporation of a fluorine atom at the para position of the phenyl ring A (pair 10/15) causes, apart from an increase of  $R_{\rm B}$ ...O ( $\Delta R_{\rm B}$ ...O = 0.323 Å), also a decrease of  $R_{\rm e}$  ( $\Delta R_{\rm e}$  = -0.152 Å),  $R_{\rm F...C(5)} (\Delta R_{\rm F...C(5)} = -0.157 \text{ Å}), R_{\rm F...C(3)} (\Delta R_{\rm F...C(3)} = -0.415 \text{ Å}),$  $R_{\text{F}\dots\text{H}(5)} (\Delta R_{\text{F}\dots\text{H}(5)} = -0.604 \text{ Å}), \text{ and } R_{\text{F}\dots\text{H}(3)} (\Delta R_{\text{F}\dots\text{H}(3)} = -0.369 \text{ Å});$ analogously, the incorporation of two fluorine atoms at the para position of phenyl rings B and C (e.g. pairs 10/17 and 12/25) provokes not only a diminution of  $R_e$  ( $\Delta R_e = -0.189$  and -0.213 Å, respectively), but also of  $R_{\text{F}\cdots\text{C}(5)}$  ( $\Delta R_{\text{F}\cdots\text{C}(5)} = -0.227$  and, -0.283 Å, respectively),  $R_{F \cdots C(3)}$  ( $\Delta R_{F \cdots C(3)} = -0.427$  and -0.411 Å, respectively),  $R_{\text{F}\cdots\text{H}(5)}$  ( $\Delta R_{\text{F}\cdots\text{H}(5)} = -0.367$  and, -0.456 Å, respectively), and specially  $R_{F \cdots H(3)}$  ( $\Delta R_{F \cdots H(3)} = -0.590$  and, -0.592 Å, respectively). As a conclusion, the incorporation of fluorine atoms at the para position of phenyl rings A, B and C, apart from diminishing  $R_{\rm e}$ , strongly decreases the distance between fluorine atoms of the tetrafluoroborate anion and C(3)/C(5) as well as H(3)/H(5) of the pyrylium ring. That can be interpreted in terms of effective anion- $\pi^+$ , and  $(C-H)^+ \cdots F^-$  hydrogen bonds interactions, respectively. It is worth mentioning that the incorporation of two methyl groups at the para position of both phenyl rings B and C has a similar effect to that shown by the presence of fluorine atoms.

A different disposition of the BF<sub>4</sub><sup>-</sup> anion in series (d) of compounds (**26**, **27** and **28**) resulted. The incorporation of electron donating groups such as OMe or OBz promotes the migration of guest tetrafluoroborate over C-4 (Fig. 7) with the boron atom positioned in the centroid ( $R_e$  3.214–3.281 Å), one of its F atoms over C-4, and other F atoms perpendicular to C(5)–C(6) bonds. From the data in Table 4, the incorporation of a methoxy group at the *para* position of the phenyl ring A (pairs **11/26** and **17/27**) causes, apart from an increase of  $R_{B...O}$  ( $\Delta R_{B...O} = 0.262$  and 0.320 Å, respectively), a slight increase of  $R_e$  ( $\Delta R_e = 0.019$  and 0.017 Å), an increasing of  $R_{F...C(5)}$  ( $\Delta R_{F...C(5)} = 0.039$  Å for both cases),  $R_{F...C(3)}$  ( $\Delta R_{F...C(3)} = 0.161$  and 0.188 Å),  $R_{F...H(3)}$  ( $\Delta R_{F...H(3)} = 0.345$  and 0.310 Å) and a decrease of  $R_{F...H(5)}$  ( $\Delta R_{F...H(5)} = -0.431$  and -0.391 Å).

On the other hand, the dihedral angles on geometryoptimized structures by B3LYP/6-31G(d) calculations are dependent on the substituent groups at the *para* position of the aromatic ring attached to C-2 and C-6 (rings B and C). Thus, for the unsubstituted compound **10**, the phenyl rings of pyrylium



Fig. 7 A superimposition of structures based on DFT calculations for compounds of series (d) in comparison with compound **10**.



Fig. 8 A perspective view of compounds **10** and **27** showing *cup-to-cap* shape cavity.

at *ortho* positions (rings B and C) present dihedral angles of  $11.1^{\circ}$  and  $-15.2^{\circ}$  with the pyrylium core. The phenyl ring A is also rotated at  $-4.7^{\circ}$ . The aromatic rings are rotated with respect to the pyrylium cation, forming a simulated cavity in the attempt to accommodate the anion. Nevertheless, the cavity shape changing from the *cup-to-cap* form (Fig. 8) is determined by the substituent groups nature and electronic effects as it is shown for compound **27**, having an electron-donating methoxy group at the *para* position of the phenyl ring A.

A comparison of the interaction energies calculated using the B3LYP/6-31G(d) method or at the M06-2X/6-31G(d) level (Table 4) shows that, although there is a parallelism between both groups of data, the B3LYP/6-31G(d) values underestimate the noncovalent interaction, as has been described for other cases previously.<sup>51b,c</sup> An analysis of these interaction energies for our different pyrylium tetrafluoroborate complexes reveals that compound 18 has the highest anion-cation binding energy with calculated B3LYP/6-31G(d) [M06-2X/6-31G(d)] values of -79.1 kcal mol<sup>-1</sup> [-86.1 kcal mol<sup>-1</sup>], as expected due to its three strongly electron-withdrawing fluorine substituents. In contrast, an electron-donating (+R effect) methoxy group as the substituent, to lead a larger electron density at the aromatic system, it should result in a weaker binding energy of the pyrylium cation with the tetrafluoroborate anion. Nevertheless, we realize that compound 26 ( $R_1 = OMe$ ,  $R_2 = R_3 = Me$ ) has an interaction energy, -70.6 kcal mol<sup>-1</sup> [-77.6 kcal mol<sup>-1</sup>], similar to that calculated for compound 13,  $(R_1 = Ph, R_2 = R_3 = Me)$ -71.1 kcal mol<sup>-1</sup> [-77.9 kcal mol<sup>-1</sup>], and higher than those for compound 12,  $(R_1 = Ph, R_2 = R_3 = H) - 67.8 \text{ kcal mol}^{-1}$  $[-75.2 \text{ kcal mol}^{-1}]$ . Moreover, the interaction energy for compound 27 is the same [B3LYP  $(-74.9 \text{ kcal mol}^{-1})$ ] or slightly higher  $[M06-2X (-82.2 \text{ kcal mol}^{-1})]$  than for compound 25  $[B3LYP (-74.9 \text{ kcal mol}^{-1}) \text{ and } M0-62X (-81.8 \text{ kcal mol}^{-1})].$ This unexpected behaviour can be explained in terms of the so called cooperativity, a feature observed previously in structures stabilized by weak noncovalent interactions.<sup>51a</sup> Thus, the presence of a methyl group in the methoxy group attached to ring A in compound 26, leads to a cooperative stabilization of the otherwise weakly stable anion- $\pi$  complex by bending of the side group toward the anion to facilitate (C-H)<sup>+</sup>-anion interactions. Additionally, we have found a relationship between <sup>19</sup>F chemical shifts and the interaction energies calculated at the M06-2X/ 6-31G(d) level, (ESI,† Fig. S7). Two straight lines are observed in the plot. While a satisfactory correlation  $(r^2 = 0.938)$  with a higher and negative slope results for only fluorine-containing

pyrylium salts [series (b), compounds **14–18**], a poor correlation line ( $r^2 = 0.409$ ) with a near zero slope was obtained for compounds **12**, **13** and **25–27**, from series (a) and (d), respectively. Thus, the higher the electron deficiency is at the pyrylium system provoked by the substituents, the greater is the interaction energy of the complex, while an interplay of cooperativity between anion– $\pi$  and (C–H)<sup>+</sup>–anion interactions could justify the results obtained for compounds from series (a) and (d).

The effect of the solvent (DMSO) on the tetrafluoroboratepyrylium cation interaction was also investigated by using Polarizable Continuum Method (PCM)<sup>52</sup> coupled to B3LYP/ 6-31G(d) by means of Gaussian 09.53 In general, DMSO causes higher lengths between pyrylium cation and BF<sub>4</sub><sup>-</sup> anion as expected of the intrinsic effects on the cation by this solvent and very small interaction energies. Thus, by using the B3LYP/ 6-31G(d) level, the calculated  $\Delta E_{int}$  for compounds 10, 14 and 18 were -7.5, -6.7 and -8.1 kcal mol<sup>-1</sup>, respectively. For compound **10** the predicted  $B \cdots O^+$  distance increased ~ 0.35 Å  $(\sim 0.36 \text{ Å for } R_{\rm e})$  in the PCM model. A second point observed in this model was an enhanced rotation of A, B and C aryl rings with respect to the cation core  $(-31.4, -29.6 \text{ and } 30.7^\circ, \text{ respec-}$ tively). For fluorinated compound 14 a major distance for  $B \cdots O^+$ (3.390 Å) was also calculated in the PCM model. A similar rotation to that described for compound 10 was observed  $(-30.9^{\circ} \text{ in the C-2 ring})$ . However, the phenyl ring at the C-6 position, which contains the fluorine atom, is rotated over  $-15.8^{\circ}$  less than the phenyl ring in **10**. In general, BF<sub>4</sub><sup>-</sup> in this model is situated over charged oxygen but is much closer to ortho protons in phenyl rings B and C with a distance shorter than  $\Delta R_{\rm vdw}$  F···H (2.242 and 2.245 Å for B and C, respectively) (Fig. 9). Certainly, the aforementioned model brings to light a (C-H)<sup>+</sup>-anion interaction between H-6b of the aromatic ring in B and a fluorine atom of the anion (and H-6c for the aromatic ring C). By incorporating fluorine atoms into pyrylium salts, the calculated Mülliken charges over H-3, H-5, H-6b and H-6c change significantly. Thus, an increase of positive charge from 0.190 (compound 10) to 0.200 (compound 18) is observed for H-6b that indicates in this last case an enhanced (C-H)<sup>+</sup>-anion interaction involving this proton. It is worthy of note that by using this procedure, compound 14 shows the same charge (0.212) in fictitious equivalent H-3 and H-5 protons.

On the basis of DFT calculations, two situations can be observed for this interaction. First, an anion– $\pi^+$  contact involving F atoms of the anion with acidic C-5, and in the second place, (C–H)<sup>+</sup>–anion between the same F atoms and H-5 of the



Fig. 9 Structures based on DFT calculations including solvent effects (PCM) for compounds **10**, **14** and **18**.

pyrylium cation (for which the Mülliken charge shows to be the more electropositive of the pyrylium salt protons) is inferred. In most cases, C-3 and H-3 in host pyrylium are not involved in any interaction.

# Conclusions

We have found that <sup>19</sup>F NMR chemical shifts of tetrafluoroborate anions at a constant concentration in DMSO- $d_6$  for most of the here described tri-arylpyrylium tetrafluoroborate salts undergo small but significant changes caused by the effect of substituents on the pyrylium cation. Correlations of these parameters with both the pyrylium cation molecular weight and the standard substituent Hammett constants, demonstrate that an anion- $\pi^+$ interaction between the polyatomic anion BF<sub>4</sub><sup>-</sup> and the pyrylium aromatic system does exist. Two trends are shown by the complexes depending on the substituents: electron-withdrawing substituent groups like fluorine enhance the magnitude of the anion- $\pi^+$  non-covalent interaction, while electron-donating groups, such as OMe or Ph, have a poor global effect.

DFT calculations are in excellent agreement with the observed correlations and experimental results. Furthermore, apart from corroborating the anion– $\pi^+$  interaction by means of calculated  $R_e$  distances, from the boron atom to the centroid of the pyrylium moiety, shorter than  $R_{B-\cdot\cdot O}$  distances, suggests the existence of: (1) an additional non covalent anion– $\pi^+$  contact involving a fluorine atom of the anion with acidic C(5), in practically all of the substituted pyrylium salts described here (exceptions are compounds **10** and **12**), (2) a (C–H)<sup>+</sup>–anion interaction between a F atom of BF<sub>4</sub><sup>-</sup> and H(5) of the pyrylium ring in some cases (compounds **15**, **18** and **26–28**), and (3) an arrangement of the aromatic rings A, B and C, which are rotated with respect to the pyrylium ring, to conform to a *cup-to-cap* shape cavity, depending on the nature and electronic effects of the substituent groups.

On the other hand, although the study on photophysical properties gave no evidence of the investigated anion– $\pi^+$  interaction, the strong fluorescence emission of some representative pyrylium tetrafluoroborates described herein makes them a promising class of tunable emission wavelength dyes for laser technology applications.

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