

The Influence of the Acyl Side Chain on Pyrene Excimer Formation as a Model for Asphaltene Aggregation

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Asphaltene aggregation mechanism is still a nebulous and controversial issue. Many authors argue that the aggregation of its components is due to π -stacking interactions, nonetheless, alkyl chains, heteroatoms, and even acidic groups are also constituents of asphaltenes and can play an important role in the chemistry of asphaltene. Excimers from pyrene are easily detected by fluorescence and were used in the current study to probe the effect of the side chain on the π -stacking capacity of pyrene. Pyrene was acylated with acyl chains varying from two to twelve carbon atoms, and the effect of the variation of the acyl chain length on excimer formation was followed by fluorescence emission spectroscopy. The results revealed that as the side chain grows from two to twelve carbon atoms the excimer/monomer ratio decreases and the excimer heat of formation drops from $\Delta H = -6.00$ to -1.29 kcal mol⁻¹. Further, the crystal structure of octanoyl pyrene (PC8) indicates that in the crystal structure, the aromatic moiety faces the acyl chain. This result was corroborated by density functional theory (DFT) calculations. Finally, the results were compared with two different asphaltenes and indicate that π -stacking cannot be assumed as the main driving force for asphaltene aggregation.

Keywords: acyl pyrenes, asphaltene, fluorescence, aggregation

Introduction

The importance of oil and gas in the present and future is not a matter of question.¹ The usage of such goods encompasses energy, plastics, solvents, and pharmaceuticals, thus profoundly impacting the entire structure of life in the world. Even the development of new green energies is only possible due to the world's economy based on the petroleum industry.² In fact, enhancing oil technologies will drive humans to the point where it will be possible to decide what kind of future our civilization will live.

Probably, one of the most important aspects in petroleum technology is related to the upstream segment.³ This link in the whole oil chain is responsible for the exploration of oil,

drilling, and production, and accounts for most production costs. So, improving upstream technology directly impacts the future of the world and this study sheds light on the asphaltenes components.

Asphaltenes represent the petroleum fraction that is insoluble in *n*-alkanes (e.g., hexane, heptanes) but soluble in toluene.⁴ This fraction is known to be the cause of problems during extraction, transportation, and refining, as well as being environmentally dangerous due to resistance to chemical transformation.⁵ From an industrial point of view, the principal problem associated with asphaltenes is their capacity to aggregate and precipitate, reducing oil flow, necessitating pipeline cleaning, and thus reducing petroleum production.⁶

From a chemical point of view, asphaltenes have a C/H ratio of about 1:1.2.^{7,8} The sulfur and nitrogen contents can reach 6 and 3% (m/m), respectively, and the

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fused aromatic cores show 4–10 rings.^{9–11} Concerning the asphaltene composition, Strausz *et al.*^{12,13} reported the presence of alkyl groups (side chains in aromatic cores) forming bridges of $-(CH_2)_n-$, $-S-$, $-C(O)-$ and $-O-$ with more than 30 atoms. Thus, alkyl chains, heteroatoms, and even acidic groups can play an important role in asphaltene chemistry.^{14,15} Recently, based on fluorescence and UV-Vis studies, it was proposed that compounds with more than 5 condensed aromatic rings are not present in the asphaltene mixture, namely the “archipelago” model for the asphaltene structure.^{16,17} This model is different from that proposed by Mullins *et al.*¹⁸ which was termed “island”. Experimental and theoretical data indicate that π -stacking is the driving force for asphaltene aggregation.^{19–21} Nevertheless, theoretical methods were assumed in a non-solvent environment, i.e., aromatic compounds, which do not represent asphaltene composition simulated without the aliphatic and non-aromatics structures.²² A second problem concerning aggregation studies is the absence of the initial aggregate’s formation control and, in this case, the best pieces of information are acquired after aggregation is unrolling.²³

Although many sophisticated molecular systems have been synthesized and used as models for asphaltene aggregation,²⁴ there are few studies in the literature that use fluorescent probes to mimic and follow this aggregation. In a previous study,^{5,25} our group showed that asphaltene aggregation can be followed by fluorescence emission spectroscopy due to the high sensitivity of this experimental technique and the capacity to follow the very early stages of aggregation. Our results suggested that, at the beginning of the aggregation process dimerization represents the major contribution, showing an enthalpy (ΔH) value of $-1.3 \text{ kcal mol}^{-1}$ also, in a recent study,²⁵ we were able to hydrogenate the aromatic fraction of asphaltene by a photochemical reaction, by using 1,4-cyclohexadiene as a hydrogen source. After photohydrogenation (increasing ca. 44% in hydrogen content by CHN analysis) the asphaltene aggregation was evaluated by the onset method and the result showed no onset limit change between the hydrogenated and pristine material, indicating that the π -stacking interaction cannot be the main driven force during asphaltene aggregation.^{5,25} Our dimerization enthalpy is in good agreement with that found by Merino *et al.*,²⁶ and others^{27,28} and both values are smaller than the π -stacking energies found for molecules like pyrene, naphthalene, and phenanthrene,²⁹ which is contradictory with the assumption that π -stacking is the driving force for asphaltene aggregation.

One of the most studied dimerization examples in literature is the observation of π -stacking by the first excited state of pyrene (excimer formation).³⁰ It is important to

stress here that as pyrene aggregation occurs in the excited state, the process is driven by an excited state molecule’s light-induced deficient electronic nature, which drives the dimerization with a non-excited species. In this case, parameters such as time evolution and the related enthalpy are vastly documented in different media and conditions.³¹ π -Stacking dimerization in the excited state is energetically more favorable than that occurring with molecules in the fundamental electronic state and can be used as a model to follow the influence of side chains in aromatic compounds upon aggregation as it begins to occur, as well as the effect of heteroatoms on the side chain.

In the present study, we prepared a series of acyl pyrenes with side chain acyl groups varying from 2 to 10 carbons and studied their dimerization in the singlet excited state by fluorescence emission spectroscopy. The effect of variation of the acyl chain length for acyl pyrene excimer formation was investigated and a comparison with asphaltene aggregation was made.

Experimental

Synthesis

All reagents were purchased from Sigma-Aldrich (St. Louis, USA). All solvents, including deuterated solvents, were bought from Tedia (Fairfield, USA). Acyl pyrenes with the side chain of lengths 2, 4, 6, 8, 10 and 12 carbon atoms (**PC2**,³² **PC4**,³³ **PC6**,³⁴ **PC8**,³⁵ **PC10** and **PC12**,³⁴ respectively) were prepared by direct acylation of pyrene with the respective acyl chloride in the presence of $AlCl_3$ in CH_2Cl_2 , following a literature procedure.³⁶

A sample of asphaltene PetroPhase 2017 was used as received. This sample was prepared by the group of Marianny Y. Combariza at the Industrial University of Santander (Bucaramanga, Colombia).³⁷ A second sample from Venezuela (Merida) crude was obtained following the method described in the literature.³⁸ Both samples were evaluated at room temperature by 500 MHz 1H nuclear magnetic resonance (NMR) in $CDCl_3$.

Structural and optical properties

NMR spectra were recorded at room temperature using 200 and 400 MHz Bruker spectrometers (Karlsruhe, Germany) in $CDCl_3$ as solvent in 5 mm NMR standard tubes. Mass spectrometry studies were done with a mass selective detector Shimadzu GCMS QP2010S (Shimadzu, Kyoto, Japan) interfaced with a capillary gas chromatography. The column used was a DB-5 (0.1 μm film thickness, 0.25 mm internal diameter, 30 m length).

The injection temperature was 280 °C and the split ratio 1:20, the oven was set at 50 °C for 2 min, increasing the temperature to 290 °C with a ramp of 10 °C min⁻¹. N₂ was used as the carrier gas at flow rate of 2 mL min⁻¹. The mass spectrometry (MS) was set with 34.6 µA emission and 70.0 eV electron energy. All mass spectra found the following ions: *m/z* 229 as the main signal peak due to acylium ion [PyCO]⁺ and the following molecular ions M⁺ (*m/z*): 244 (**PC2**), 272 (**PC4**), 300 (**PC6**), 328 (**PC8**), 356 (**PC10**) and 384 (**PC12**).

X-ray diffraction data were collected on a D8 venture diffractometer (Bruker; AXS, Karlsruhe, Germany) equipped with a CMOS (complementary metal-oxide-semiconductor) type detector and Mo anode (Mo K α radiation, λ = 0.71073 Å) at 286 K. The structures were solved by direct methods implemented in SHELXS³⁹ and refined by a full-matrix least-squares procedure based on F² using SHELXL,⁴⁰ in the OLEX2 platform.⁴¹ All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed using appropriate riding model. The ORTEP^{42,43} and Mercury⁴⁴ software were used for figure preparation. Single crystals suitable for the X-ray study were obtained by the slow diffusion of hexane into a dichloromethane solution of **PC8** and the data were collected at room temperature. Crystallographic data for the structure **PC8** were deposited in the Cambridge Crystallographic Data Centre (CCDC) with number 1575395. All calculations were performed using Gaussian C.01⁴⁵ software. Ground state geometries of the molecules considered in this study were optimized in vacuum using density functional theory (DFT) with the M06-2X^{46,47} functional in conjunction with a 6-311+G(d,p) basis set. The initial geometries consisted of five **PC8** dimers differing in their interacting orientations and one single **PC8** molecule optimized for energy reference. These geometries were obtained from the .cif file corresponding to the experimental X-ray structure of a **PC8** molecule through rotations and translations of one randomly selected molecule. The geometries were optimized in the vacuum using the methodology cited and frequencies were computed to check that the structures were true minima. The conformer analysis for 1-acetylpyrene was carried out using the B3LYP/def2svp/gd3bj/[IEFPCM] (dichloromethane (DCM) as solvent) for S₀ and TD-B3LYP/def2svp/gd3bj/[IEFPCM (DCM)] for S₁.

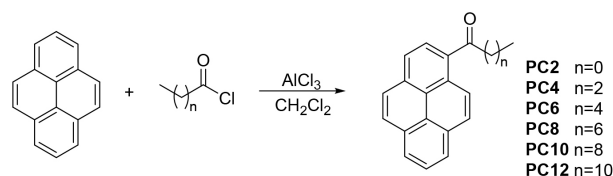
Steady-state UV-Vis absorption spectra were measured at room temperature on a UV-2450 (Shimadzu, Kyoto, Japan), using 1 cm quartz cuvettes (Helma Suprasil). The steady-state emission fluorescence spectra were obtained using an FLS 980 spectrofluorometer (Edinburgh Instruments, Livingston, UK) with front-face geometry.

Fluorescence decay lifetimes were obtained with the same instrument employing single photon counting technique. Fluorescence emission quantum yields were measured using the direct method and pyrene as standard (F_{ru} = 0.65). All solvents used were high performance liquid chromatography (HPLC, Tedia, Fairfield, OH, USA) grade and checked for fluorescent impurities.

Results and Discussion

Synthesis

The acyl pyrenes **PC2**, **PC4**, **PC6**, **PC8**, **PC10** and **PC12** were prepared by a Friedel-Crafts acylation reaction of pyrene with aliphatic acyl chlorides containing chains varying of 2, 4, 6, 8, 10 and 12 carbon atoms, as depicted in Scheme 1. The reactions employed AlCl₃ as catalyst and dichloromethane as solvent at room temperature.



Scheme 1. Synthetic route for the preparation of acyl pyrenes **PC2-PC12**.

Complete conversions were achieved rapidly, giving the crude acylated pyrenes, which were subsequently purified by column chromatography to furnish the corresponding products **PC2-PC12** in excellent yields (92-96%). In all cases, the mono-acylated C1-pyrene derivative was obtained. The initial assignment of structures was based on the coupling constants of the H_{Ar}-2 hydrogen ($J_{\text{H2-H3}}$); for instance, in all the compounds this signal is observed as a doublet with J values of ca. 9.4 Hz. This evidences that a single acylation occurred, and only mono-substituted C1-pyrene is formed.⁴⁸ Spectroscopic data were consistent with the structures and the previously cited literature (see Experimental section).

Optical properties

The UV-Vis spectra of compounds **PC2-PC12** show a bathochromic shift concerning the dipole-allowed S₀→S₂ pyrene absorption band due to the extended π -conjugation between the pyrene and C=O group (Figure 1).

For the acetyl pyrene (**PC2**) two major bands centered at 357 and 389 nm are observed. For all the other compounds, these bands have maxima at 355 and 386 nm, respectively. Furthermore, a loss of spectral resolution is observed which can be attributed to an increase in the number of

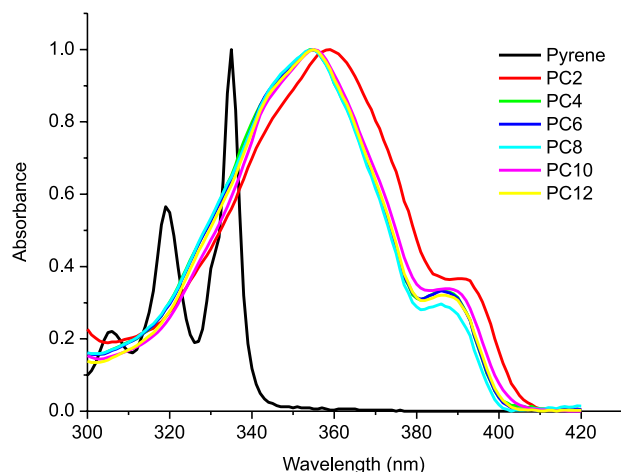


Figure 1. UV-Vis absorption spectra for pyrene and acyl pyrenes **PC2-PC12** recorded in toluene (10^{-6} mol L $^{-1}$).

vibrational modes due to acyl substitution. This is also in line with the diminished symmetry due to the presence of the acyl sidechain. By varying the solvent from toluene to acetonitrile both bands were blue shifted by 4 nm for all compounds. Additionally, the molar absorptivity coefficient (ϵ) was determined by varying the acyl pyrene concentrations from 10^{-5} to 10^{-6} mol L $^{-1}$ which gave values of ϵ around 26000 at 357 nm and 12000 at 390 nm for all compounds (Table 1). The hypsochromic solvent shift and the large values of ϵ are consistent with the $p \rightarrow \pi^*$ character of these electronic transitions.

Fluorescence emission spectra were obtained by excitation at 340 nm at 6.5×10^{-6} mol L $^{-1}$ in toluene (Figure 2). Similarly, to the behavior seen in the UV-Vis spectra, the emission spectra are red-shifted relative to pyrene, and the main bands for **PC2** are centered at 375, 395, 412, and 446 nm. These bands are related to the $S_1 \rightarrow S_0$ emission to different ground state vibrational levels. For the other derivatives **PC4** to **PC12** it is worth noting that

the main emission bands seen with pyrene are also present in these acyl derivatives but that there is a loss of the vibrational structure, which can be attributed to the reduced symmetry of these compounds.

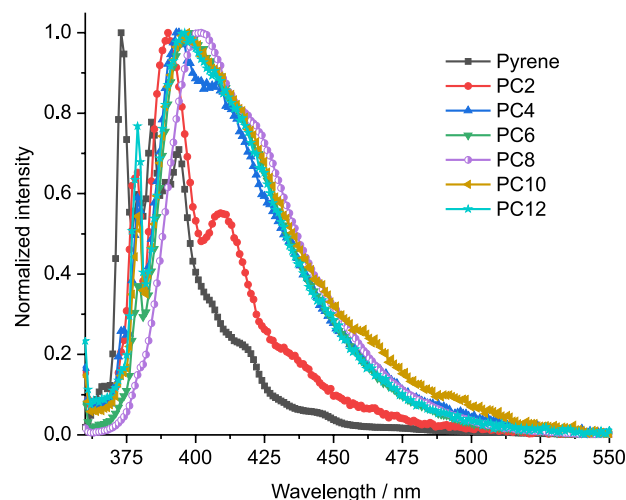


Figure 2. Fluorescence emission spectra (λ_{exc} 340 nm) for acyl pyrenes **PC2-PC12** recorded in toluene (6.5×10^{-6} mol L $^{-1}$).

Notably, the intensity of the 0,0 transition is diminished in relation to pyrene and the same transition diminishes further in the series **PC2**, **PC4**, and **PC6**, whilst with **PC8** the transition is almost absent but can be discerned as a shoulder to the left of the main emission band and with **PC12** the transition is once again evident.

Fluorescence quantum yields were measured by the direct method using pyrene as standard and the results are detailed in Table 1. The fluorescence lifetimes were determined by the single photon counting technique using a pulsed light emitting diode (LED) as a probe. Analysis of the fluorescence decays revealed non-monoexponentially decays which were deconvoluted as a two-component,

Table 1. Photophysical properties for the singlet state for acyl pyrenes **PC2-PC12** in toluene

Compound	Absorption λ_{Max} / nm	Emission λ_{Flu} / nm	ϵ_{Max} / (L mol $^{-1}$ cm $^{-1}$)	$E_{0,0}$ / (kcal mol $^{-1}$)	F_{flu} ^a	t^b / ns
PC2	357	378, 379, 392, 411, 434	26930	75.7	0.03	2.4 (14%) 15.2 (86%)
PC4	355	379, 392, 409	28416	75.5	0.02	0.8 (14%) 15.4 (86%)
PC6	355	379, 398, 416 ^c	29825	71.8	0.02	1.7 (46%) 13.8 (54%)
PC8	355	402, 422 ^c	29044	71.1	0.02	0.8 (6%) 14.6 (94%)
PC10	355	383, 395, 411	21197	71.2	0.02	1.7 (16%) 10.7 (84%)
PC12	355	379, 397	21184	71.8	0.03	0.9 (18%) 8.5 (82%)

^aFluorescence quantum yield; ^bfluorescence decay lifetime; ^cas a shoulder. ϵ : absorptivity coefficient; $E_{0,0}$: transition 0,0.

biexponential, decay. Notably, Cremel and Lianos⁴⁹ found similar values for 1-pyrenaldehyde in different solvents.

A maximum value for the intersystem crossing rate constant (k_{ST}) can be evaluated from equations 1 and 2 by assuming that k_{ST} is equivalent to the sum of all processes, other than fluorescence, leading to deactivation (Sk_d) of the excited state. For compound **PC2**, a fluorescence quantum yield of 0.03 and a fluorescence lifetime for the longest lived, principal component, of 15 ns were measured (Table 1). From these values, values for k_F ($2 \times 10^6 \text{ s}^{-1}$) and k_{ST} ($7 \times 10^7 \text{ s}^{-1}$) can be calculated as:

$$k_F = \Phi_F / \tau_{(S1)} \quad (1)$$

$$\Phi_F = k_F / Sk_d; \text{ where } Sk_d \text{ ca. } k_{ST} = 1/\tau_{(S1)} \quad (2)$$

Therefore, from equation 2, k_{ST} is of the order 10^8 s^{-1} , which is a highly allowed intersystem crossing.

As can be seen in Table 1, only compound **PC2** shows defined emission maxima in the series with a well-structured spectrum. By adding a butanoyl group to pyrene to form **PC4**, the emission spectrum is less well resolved in comparison to **PC2** and only three bands can be discerned. With longer acyl chains **PC6-PC12**, the emission spectra are dominated by two bands due to the multitude of solvated conformers and their respective vibrational states, which result in the loss of spectral resolution. All the synthesized acyl pyrenes have an S_1 state less energetic than pyrene (S_1 energy $76.5 \text{ kcal mol}^{-1}$ in toluene)⁵⁰ and this is due to the extended conjugation between the pyrene core and the C=O group.

A closer look at the UV-Vis and fluorescence spectra reveals that the emission spectra of **PC2**, **PC4**, and **PC12** are not mirror images of the first absorption band in the UV-Vis spectrum (Figure 3). This can be attributed to the loss of symmetry in the acyl derivatives and to different conformations of the acyl group bonded to the

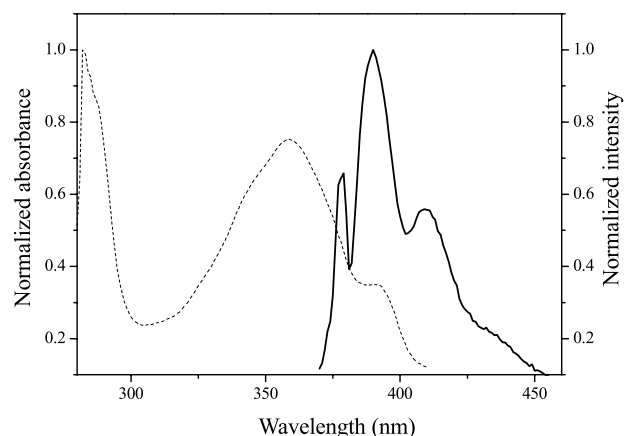


Figure 3. Normalized UV-Vis (dashed) and fluorescence (line) spectra for **PC2** recorded in toluene ($6.5 \times 10^{-6} \text{ mol L}^{-1}$).

pyrene moiety. Further, the energy separation between the emission bands for **PC2**, **PC4** and **PC12** varies between $860\text{--}996 \text{ cm}^{-1}$ and can be related to the vibrational deformation of aromatic CH bonds, therefore providing further evidence of a $p\pi^*$ excited state.

The most interesting characteristic of the acyl pyrene structures is the diminishing capacity to form the respective excimer as the side chain's carbon atoms increase. For comparison, emission spectra for compounds **PC2-PC12** and pyrene were taken at the same concentration (Figure 4). It is well documented that the pyrene excimer can be detected at low concentrations such as $10^{-4} \text{ mol L}^{-1}$ as a broad band centered at 450 nm and the enthalpy related to the excimer formation is $7.3 \text{ kcal mol}^{-1}$. As can be seen in Figure 4, despite the small fluorescence quantum yields (ca. 0.03) and the short fluorescence lifetimes (ca. 2 and 15 ns) the acyl pyrenes also form excimers, but to the extent that is inversely related to the number of CH_2 groups in the side chain (Table 2). Additionally, excimer formation is only significant at one order of magnitude greater concentration relative to pyrene (right in Figure 4)

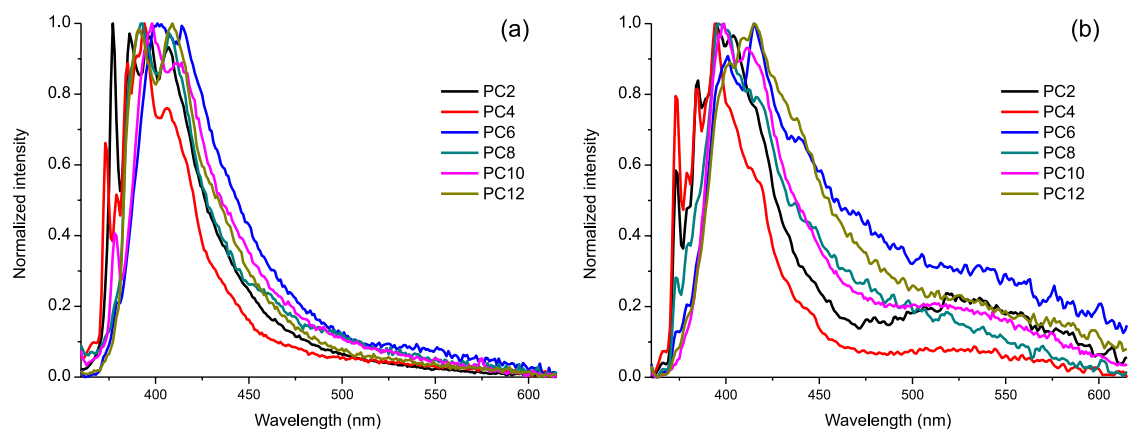
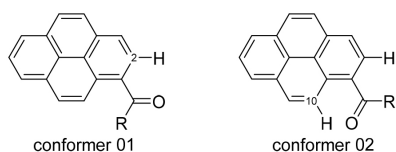


Figure 4. (a) Fluorescence emission (front face geometry) of acyl pyrenes **PC2-PC12** ($3.3 \times 10^{-4} \text{ mol L}^{-1}$) in toluene. Excitation at 340 nm . (b) Emission from solutions at $1.2 \times 10^{-3} \text{ mol L}^{-1}$.

and at substantially higher concentrations (10^{-2} mol L $^{-1}$) the excimer predominates.

A direct comparison of the properties of the acyl pyrene compounds can be made as the fluorescence quantum yields (0.025 on average) and lifetimes are all similar and therefore other excited state deactivation processes for these compounds will also be closely related, i.e., the excited S_1 states for these compounds are essentially equivalent. Notably, as detailed in Table 1, the fluorescence decays for the acylpyrene compounds were best fitted using two exponential functions, where the two components had average values of 19% (1.3 ns lifetime) and 81% (13.5 ns lifetime). That a bi-exponential function was required to fit the fluorescence decays is consistent with the fact that the carbonyl group of the acyl pyrenes can generate at least two different conformers 01 and 02 as shown in Scheme 2, where conformer 02 is the lowest S_0 energy. The conformer 02 for **PC2** in the ground state (S_0) is $\Delta G = -3.30$ kcal mol $^{-1}$ more stable than conformer 01. Additionally, the respective S_1 excited states were optimized and a similar difference in energy was observed (Figures S16-S17, Supplementary Information (SI) section).



Scheme 2. Acyl pyrene conformers for **PC2**.

Therefore, considering that the photophysical behavior of the acyl pyrene compounds is similar, it is possible to directly compare the excimer/monomer ratio at different concentrations. Table 2 details the excimer/monomer ratio for pyrene and acyl pyrenes. For the acyl pyrenes, this ratio can be followed by comparing the excimer and monomer emission intensities measured at 515 and 410 nm, respectively, at different concentrations.

As can be seen from Table 2, even at 10^{-4} mol L $^{-1}$ (ca. 80 mg L $^{-1}$), excimer formation by the acyl pyrenes was observed and the proportion of excimer to monomer shows a dependence upon the alkyl chain length. It is worthwhile to note that this concentration falls in the range found for the critical nano aggregation of asphaltene (below 100 mg L $^{-1}$)⁵¹ as proposed by the Yen-Mullins model. For the acyl pyrene series, the excimer/monomer ratio differences found are mainly due to a low signal/noise ratio in dilute solutions but considering an average value of 0.1 for all acyl pyrene ratios at the most diluted concentration, it turns out that **PC2** excimer emission increases by a factor of 23 from a solution of concentration 10^{-4} mol L $^{-1}$ to a solution of concentration 10^{-2} mol L $^{-1}$. For pyrene, this ratio increases by a factor of 87 over the same concentration range. Among the acyl pyrenes studied, **PC12** shows the smallest excimer/monomer ratio enhancement factor of 15. Also, following the **PC** series from **PC2** to **PC12** at 10^{-2} mol L $^{-1}$ a reduction of the excimer/monomer ratio occurs revealing that in relatively concentrated solutions, the alkyl side chain interferes with the dynamics for achieving the appropriate intermolecular arrangement for excimer formation via π -stacking interactions.

The same behavior can be seen by following the measured melting points for **PC2-PC12**, Table 2. The solid-state structures for pyrene and **PC2** show mainly π -stacking interactions, so Table 2 indicates that as CH_2 groups are added to the pyrene side chain, the intermolecular interactions in the **PC** series progressively change. The **PC8** crystal structure shows that the pyrene core has intermolecular interactions with the CH_2 chain (*vide infra* and SI section). These results reinforce the role of the saturated hydrocarbon side chain with respect to reducing the π -stacking capacity of the compounds **PC2-PC12**. In general terms, the results reveal that the larger the side chain, the less efficient the π -stacking interaction.

In order to further investigate the effect of the acyl side chain on the π -stacking capacity of the acyl pyrenes, the

Table 2. Excimer/monomer emission ratio at different concentrations for acyl pyrenes **PC2-PC12**

Comp.	mp / °C	Excimer/monomer emission intensity ratios (515/410 nm)		
		1.2×10^{-4} mol L $^{-1}$	1.2×10^{-3} mol L $^{-1}$	1.2×10^{-2} mol L $^{-1}$
Pyrene ^a	145-146	0.04	0.40	3.51
PC2	88-89	0.06	0.14	2.28
PC4	70-71	0.08	0.17	1.97
PC6	90-91	0.15	0.35	2.15
PC8	72-74	0.11	0.32	1.25
PC10	61-63	0.13	0.26	1.38
PC12	58-59	0.10	0.26	1.46

^aMonomer and excimer emissions at 372 and 470 nm, respectively.

heat of formation of the respective excimers and of pyrene was measured following the methodology of Birks *et al.*,⁵² Table 3. Considering that:

$$-RT \ln K_{eq} = \Delta H^\circ - T\Delta S \quad (3)$$

$$I_E/I_M = K_{eq} \quad (4)$$

where I_E is the emission intensity of the excimer and I_M the emission intensity of the monomer, T the temperature, R the gas constant, K_{eq} the equilibrium constant, ΔS the entropy and ΔH the enthalpy, then, a plot of $\ln(I_E/I_M) \times 1/T$ gives ΔH for the respective excimer in toluene. Figure 5 illustrates the effect of temperature on the monomer $\rightleftharpoons$ excimer equilibrium for **PC2**.

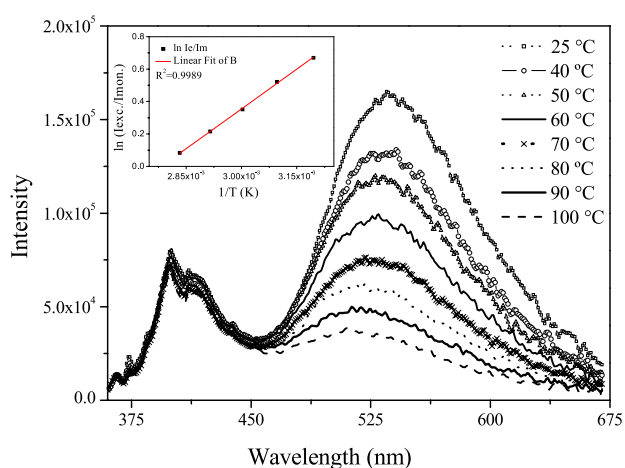


Figure 5. Temperature effect for the monomer $\rightleftharpoons$ excimer equilibrium of **PC2** compound at 10^{-2} mol L^{-1} in toluene.

Figure 5 clearly shows that as the temperature rises from 10–100 °C, the excimer emission intensity diminishes gradually to almost one-quarter of the initial value, indicating a relationship between excimer emission and temperature. The inset in Figure 5 reveals the linear correlation over the temperature range studied and the heat of formation of the excimer is given in Table 3.

The data in Table 3 reveal that pyrene has the largest ΔH value in the series. As mentioned above for the melting point analysis, if one considers that the excimer emission requires to some extent a π -stacking type arrangement,⁵³ then a symmetrical compound like pyrene offers the largest number of possible overlap structures for a dimer. However, the inclusion of an increasingly larger acyl side chain systematically diminishes the extent of possible intermolecular π -stacking type arrangements due to the alkyl chains. So, the reduced number of possible dimer geometries and the increased possibility of non- π -stacking interactions offer an explanation for the diminishing values of ΔH for excimer formation with increasing alkyl side

Table 3. Heat of excimer formation for pyrene, **PC2–PC12**, and asphaltene samples in toluene

Compound	Concentration / (mol L^{-1})	ΔH° / (kcal mol^{-1})
Pyrene	1.5×10^{-2}	–7.20
PC2	1.2×10^{-2}	–6.00
PC4	1.1×10^{-2}	–4.15
PC6	1.0×10^{-2}	–3.08
PC8	9.1×10^{-3}	–2.35
PC10	1.2×10^{-2}	–1.56
PC12	7.8×10^{-3}	–1.39
Asphaltene from PetroPhase	0.08 g L^{-1}	–1.79
Asphaltene from Venezuela	0.08 g L^{-1}	–1.31

^aPyrene was analyzed at 390 nm (monomer) and 475 nm (excimer); acyl pyrenes were analyzed at 410 nm (monomer) and 550 nm (excimer). ΔH : enthalpy.

chain length. In the case of **PC12**, ΔH for excimer formation was found to be almost one-fifth of that for pyrene. In fact, the crystal structures for pyrene and acetyl pyrene reveal that π -stacking interactions are the principal intermolecular interaction in the respective crystals.

Crystals of **PC8** suitable for X-ray diffraction analysis were obtained by recrystallization from a dichloromethane-hexane solution. Crystal quality gave a weak diffraction pattern; however, the structure is consistent with the chemical analysis (SI section). Compound **PC8** crystallizes in the triclinic P1 space group, the asymmetric units consist of eight molecules. The supramolecular arrangement shows the main interaction, being a non-classical Csp^3 - π -stacking between two aromatic cores and the alkyl chain (CH–C: 2.88 Å) forming a trimer instead of a π -stacking between two pyrene moieties (Figure 6). Furthermore, similar interactions were observed between alkyl chains (CH–C: 2.35 Å).

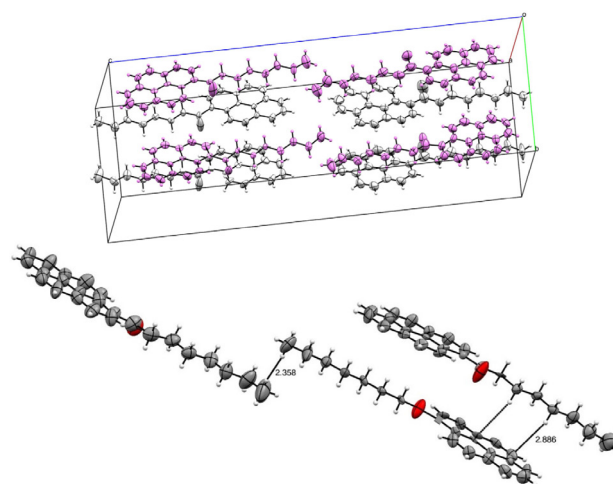
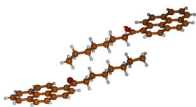
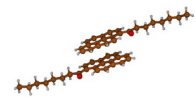
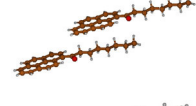
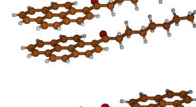
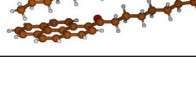


Figure 6. ORTEP packing arrangement in **PC8**: unit cell (top), and view of intermolecular interactions (down). Thermal ellipsoids are drawn at 50% probability.

Theoretical calculations

To further clarify the acyl pyrene interaction, quantum-mechanical DFT calculations of five possible, gas phase, interaction geometries for **PC8** dimers were performed. Comparison (see Table 4) of the energies of the optimized geometries with reference energy for a pair of non-interacting molecules shows that the most stable orientation is obtained via a double cross-interaction of the acyl chain with the conjugated system (orientation E) instead of a π -stacking interaction (orientations B or D). Even though solvent is not included in the calculations, the energy gap between the least energetic structure and the π -stacked ones (at least 0.6 kcal mol⁻¹) suggests that the driving forces for the dimerization of the acyl pyrene molecules are not π -stacking interactions but are van der Waals interactions.

Table 4. Interaction energy (ΔE) and the energy relative to the minimum energy orientation ($\Delta\Delta E$) for the five types of acylpyrene dimers for **PC8** considered in the quantum-mechanical calculations

Orientation	$\Delta E /$ (kcal mol ⁻¹)	$\Delta\Delta E /$ (kcal mol ⁻¹)
A 	-13.30	12.28
B 	-18.56	7.02
C 	-15.19	10.38
D 	-24.89	0.69
E 	-25.58	0.00

The results in Table 4 clearly show that van der Waals interactions are more important than π -stacking for **PC8**. Comparing the theoretical results of Table 4 and the experimental results from Table 3 (values are related to the respective excited state dimer formation), it can be expected that the larger the acyl chain the less important the π -stacking interaction between substituted pyrenes in the encounter complexes. Thus, it can be inferred that the aggregation energy for asphaltenes, where alkyl chains can reach over 30 CH₂ groups, cannot be governed only by the π -stacking

interaction. One can assume that van der Waals interactions have greater importance for aggregation. In this sense, it is reasonable to assume that the archipelago-like structure is the most representative of the asphaltene structure.

Conclusions

The results of the present study indicate that acyl side chains bonded to a pyrene core significantly decrease excimer formation, and the longer the acyl group the less excimer formed. Considering the size of the side chain, our results show that from two to twelve carbon atoms the ΔH for excimer formation falls ca. 4.3 times indicating the weakening of the π -stacking interaction along the series. Therefore, the side chains of the aromatic compounds of asphaltenes indicate that π -stacking interactions are not the main force during molecular aggregation.

Supplementary Information

Supplementary information (¹H and ¹³C NMR spectra, mass spectra and DRX) is available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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Author Contributions

S.D.S.A., R.S.T., R.S.S., Y.M.H.G., B.C.H., J.A.G.G. were responsible for conceptualization, data curation, validation, visualization, and writing-review; S.J.G., J.S.B.F., E.S.R., R.J.C., for writing original draft, investigation, writing-review, resources, and editing.

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