1 Identification and Quantification of Seven Fused Aromatic Rings C₂₆H₁₄ *Peri*-Condensed
2 Benzenoid Polycyclic Aromatic Hydrocarbons in a Complex Mixture of Polycyclic Aromatic
3 Hydrocarbons from Coal Tar
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Abstract

A methodology for the characterization of groups of Polycyclic Aromatic Hydrocarbons (PAHs) using a combination of Normal Phase Liquid Chromatography with Ultraviolet-Visible Spectroscopy (NPLC/UV-vis) and Gas Chromatography with Mass Spectrometry (GC/MS) was used for the identification and quantification of seven fused aromatic rings $C_{26}H_{14}$ *peri*-condensed benzenoid polycyclic aromatic hydrocarbons, PAHs, in Standard Reference Material (SRM) 1597a, Complex Mixture of PAHs from Coal Tar. The NPLC/UV-vis isolated the fractions based on the number of aromatic carbons and the GC/MS allowed the identification and quantification of five of the nine $C_{26}H_{14}$ PAH isomers; naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene using a retention time comparison with authentic reference standards. For the other four benzenoid isomers with no available reference standards the following two approaches were used. First, the annellation theory was used to achieve the potential identification of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene, and second, the elution distribution in the GC fractions was used to support the potential identification of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene and to reach the tentative identifications of dibenzo[*a,ghi*]perylene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, and anthra[2,1,9,8-*opqra*]naphthacene. It is the first time that naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene are quantified, and the first time that benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene is potentially identified, in any sample, in any context.

Keywords: Coal Tar; Polycyclic Aromatic Hydrocarbons (PAHs); Normal-Phase Liquid Chromatography with Ultraviolet-Visible Spectroscopy (NPLC/UV-vis); Gas Chromatography with Mass Spectrometry (GC/MS); Annellation Theory; ZINDO/S Calculations

1. Introduction

The C₂₆H₁₄ *peri*-condensed benzenoid polycyclic aromatic hydrocarbons (PAHs) with molecular mass 326 Da include the nine compounds illustrated in Figure 1 [1], i.e., dibenzo[*a,ghi*]perylene, naphtho[1,2,3,4-*ghi*]perylene, benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, anthra[2,1,9,8-*opqra*]naphthacene, and dibenzo[*cd,lm*]perylene. In this group, there are five compounds (denoted in black in Figure 1), naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene, with published syntheses procedures. Clar [2] reported the syntheses of naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene, and Zander et al. [7] reported the synthesis of dibenzo[*b,ghi*]perylene. There is no information about the syntheses of dibenzo[*a,ghi*]perylene, benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, and anthra[2,1,9,8-*opqra*]naphthacene. Of the nine members, only dibenzo[*a,ghi*]perylene shows a nonplanar structure and a potential carcinogenic conduct due to the presence of a cove region that resembles the structure of dibenzo[*def,p*]chrysene (also known as dibenzo[*a,l*]pyrene), a widely known carcinogenic PAH [8]. Using reversed-phase liquid chromatography (RPLC) with fluorescence spectroscopy and mass spectrometry (MS), Peaden et al. identified naphtho[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene in carbon black extract [9]. In addition, Fetzer et al. using RPLC/UV-vis (as one of the analytical techniques) identified dibenzo[*b,pqr*]perylene in coal tar pitch, carbon black extract, and oils produced from catalytic hydrocracking [10-12]; naphtho[8,1,2-*bcd*]perylene and dibenzo[*cd,lm*]perylene in coal tar pitch, carbon black extract, and diesel particulate extract [10,11,13]; and naphtho[1,2,3,4-*ghi*]perylene

in carbon black extract [11]. More recently, using RPLC/UV-vis and MS, Oña and Wornat [14] identified the isomer dibenzo[*b,ghi*]perylene as product of the supercritical pyrolysis of toluene and synthetic jet fuel S-8, and Bagley and Wornat [15] identified the isomers naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, and dibenzo[*cd,lm*]perylene as products of the supercritical pyrolysis of *n*-decane. Also, Fetzer and Rechsteiner [11] achieved the separation of the isomer class C₂₆H₁₄ PAHs in coal tar extracts (SRM 1597) using field ionization mass spectrometry and Bergvall et al. [16] accomplished the tentative identification of C₂₆H₁₄ PAHs in urban dust (SRM 1649a) and diesel particulate matter (SRM 1650 and SRM 2975) using normal-phase liquid chromatography (NPLC) with UV-vis and gas chromatography (GC) with MS. Other authors documented the presence of C₂₆H₁₄ PAHs in a variety of samples, e.g, coal tar and zebra mussels from Hamilton Harbour, Canada [17], soot particles [18], and petroleum [19], providing no more than molar mass information as evidence for identification. To the best of our knowledge there is no reference about quantification of C₂₆H₁₄ PAHs in any report published until now.

In a preceding investigation [20], we accomplished the isolation, identification, and quantification of C₂₆H₁₆ *cata*-condensed benzenoid PAHs in Standard Reference Material (SRM) 1597a, a complex mixture of PAHs from coal tar [21,22] (see Certificate of Analysis for SRM 1597a [23]). The objective of the present investigation was the isolation, identification, and quantification of C₂₆H₁₄ *peri*-condensed benzenoid PAHs in SRM 1597a. NPLC/UV-vis was used for the isolation of the fraction containing the C₂₆H₁₄ *peri*-condensed benzenoid PAHs and GC/MS was used for the identification and quantification of five C₂₆H₁₄ PAHs with reference standards available, i.e., naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene. Also, the

combination of RPLC/UV-vis, the annellation theory of Clar [2,24-26], and the Zerner's Intermediate Neglect of Differential Overlap for Spectroscopy (ZINDO/S) semiempirical calculations [3,25,26] were used for the potential identification of one C₂₆H₁₄ PAH with no reference standard available, i.e., benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene. Furthermore, GC elution behavior was used for the confirmation of the potential identification of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene and for the tentative identification of the remaining three C₂₆H₁₄ PAHs with no reference standards available, i.e., dibenzo[*a,ghi*]perylene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, and anthra[2,1,9,8-*opqra*]naphthacene.

The results of the present report represent the first quantification of naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene, and the first potential identification of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene, in any sample, in any context.

2. Materials and Methods

2.1. Chemicals

SRM 1597a was obtained from the Office of Reference Materials, National Institute of Standards and Technology, Gaithersburg, Maryland. The C₂₆H₁₄ *peri*-condensed benzenoid PAH standards of naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene were obtained from W Schmidt, Institut für PAH-Forschung (Greifenberg, Germany). Hexanes (99.9 %) was purchased from Fisher Scientific (Fair Lawn, NJ, USA) and Methylene Chloride (99.8 %) and Acetonitrile (99.9 %) were purchased from Avantor Performance Materials (Center Valley, PA, USA). High-quality ultrapure water (resistivity value: 18.2 MΩ.cm at 25 °C; ≤ 5 µg/kg) was obtained with a Milli-Q

Advantage A10 water purification system from Merck (Kenilworth, NJ, USA). Coronene (97.0%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and benzo[*a*]coronene (neat) was purchased from Chiron AS (Trondheim, Norway).

2.2. Instrumentation and Chromatographic Columns

The instrumentation and chromatographic columns for NPLC/UV-vis and GC/MS are the same used in an earlier study on the identification and quantification of C₂₆H₁₆ *cata*-condensed PAHs in SRM 1597a [20]; therefore, the reader should refer to that report for further details.

RPLC/UV-vis, was performed using a Dionex Ultimate 3000 Quaternary Analytical LC System composed of pump, column compartment, and diode-array-detector (Thermo Scientific, Sunnyvale, CA, USA) coupled to an Agilent 1100 series autosampler (Agilent, Santa Clara, CA, USA) using a Restek Pinnacle II PAH, 4 µm particle size, 250 mm length, 3.0 mm internal diameter LC Column (Restek, Bellefonte, PA, USA).

2.3. Experimental Methods

The NPLC/UV-vis isolation and GC/MS identification and quantification of C₂₆H₁₄ *peri*-condensed benzenoid PAHs in SRM 1597a follows the same method applied for the qualitative and quantitative analysis of C₂₆H₁₆ *cata*-condensed PAHs in SRM 1597a [20]; therefore, the reader should refer to that report for complete information. Briefly, the NPLC fractionation consisted of the following steps: (i) pre-concentration of the SRM 1597a sample, (ii) solvent exchange from original solvent to NPLC compatible solvent, (iii) dilution of the sample solution in NPLC compatible solvent to the maximum workable level, (iv) injection of aliquots of the sample solution on the normal-phase column at the optimized operating conditions, (v) time-wise collection of the fractions of interest, and (vi) concentration of the collected fractions by

evaporation. The quantification of the identified C₂₆H₁₄ *peri*-condensed PAHs in SRM 1597a was performed using the mass fraction reported in the Certificate of Analysis for SRM 1597a [23] for coronene as an internal standard. For the RPLC/UV-vis analyses, a 5 µL aliquot of the isolated fraction is injected onto the RPLC/UV-vis system with a solvent flow rate of 1.0 mL/min and a temperature of 25 °C. The reversed-phase monitoring wavelength is set to 306 nm. The exiting components are identified by matching UV-vis absorption spectra with those of the C₂₆H₁₄ *peri*-condensed benzenoid PAH reference standards available. The RPLC program, optimized for large PAHs, consists of the following time sequence of solvents: (0-60) min, linear gradient from 60:40 acetonitrile:water to pure acetonitrile; 60 min to 130 min, isocratic acetonitrile. The total run time is 130 min.

2.4. Theoretical Methods

The theoretical method uses the annellation theory [2,24-26] for the calculation of the locations of maximum absorption of the *p* and β bands in the UV-vis absorption spectra of the C₂₆H₁₄ *peri*-condensed benzenoid PAHs. This is the same method used in two earlier investigations about the calculation of the locations of maximum absorbance of the *p* and β bands in the UV-vis absorption spectra of C₂₆H₁₆ *cata*-condensed PAHs [25] and C₃₂H₁₆ *peri*-condensed benzenoid PAHs [26].

The ZINDO/S semiempirical calculations are used as a substantiation method to the annellation theory calculations. The ZINDO/S methodology is well-described elsewhere [3,25,26]. Since the ZINDO/S calculations are semiempirical and the annellation theory calculations are empirical due to the use of reference UV-vis absorption spectra and reference

locations of aromatic sextets, the results from the two methodologies can be adequately compared.

3. Results and Discussion

3.1. Qualitative Analysis

3.1.1. Selection of GC Column for the Separation of the C₂₆H₁₄ *Peri*-Condensed PAHs

The high thermal limit of the stationary phase (360 °C) necessary for the elution of high-molecular mass PAHs and the effectiveness of the phenylmethylpolysiloxane stationary phase for the separation of *cata*-condensed PAHs [20] and *peri*-condensed PAHs [27] suggest that the Rxi-PAH GC column, with a composition very similar to a 50 % phenylmethylpolysiloxane, is an appropriate column for this analysis. The GC/MS chromatogram for the separation of the five C₂₆H₁₄ *peri*-condensed PAHs reference standards available using the Rxi-PAH column is illustrated in Figure 2.

3.1.2. Calculation of Retention Indices

The retention indices were calculated following the method of Lee et al. [28] with the extension for large molecular mass PAHs proposed by Bemgard et al. [29] that uses two retention index standards, coronene (retention index 100) and benzo[*a*]coronene (retention index 200). The next PAH in the phenanthrene-chrysene-picene series of Lee et al. [28], benzo[*b*]picene, was not chosen as a GC marker because its GC elution range [20] is shorter than the GC elution range of the C₂₆H₁₄ PAHs investigated. Other C₂₆H₁₆ PAHs, e.g., benzo[*a*]pentacene and hexacene, and larger PAH isomers, e.g., C₃₀H₁₈, were not chosen due to their null solubility in GC compatible solvents and due to the high temperature requirement (above 350 °C) for their GC elution.

Furthermore, no other C₂₆H₁₄ PAHs besides the PAHs analyzed in this report, are available to act as GC markers for the calculation of the retention indices. The calculated retention indices for the five C₂₆H₁₄ *peri*-condensed benzenoid PAHs with reference standards available are shown in Table 1. This is the first time that the GC retention indices of naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene have been reported.

3.1.3. Normal-Phase Liquid Chromatography with Ultraviolet-Visible Spectroscopy and Gas Chromatography with Mass Spectrometry Analyses

To simplify the complex PAH mixture, the sample was fractionated using NPLC on an aminosilane phase to isolate PAH isomers based on number of aromatic carbons as described previously [30]. The NPLC/UV-vis chromatogram from the fractionation of SRM 1597a and the distribution of the ions in each fraction are the same as reported in our previous study on C₂₆H₁₆ *cata*-condensed PAHs [20]. As described in that study [20], of the six fractions collected, only fractions **F1**, **F2**, **F3**, and **F4** showed response related to the presence of C₂₆H₁₄ PAHs; thus, fraction **F0** and fraction **F5** were disregarded as fractions of interest for the identification of C₂₆H₁₄ *peri*-condensed benzenoid PAHs. In addition, the same study [20] demonstrated that C₂₆H₁₄ *peri*-condensed PAHs are more abundant in fraction **F3** than in any other fraction. Furthermore, qualitative analysis of the elution behavior of the C₂₆H₁₄ *peri*-condensed benzenoid PAH reference standards using NPLC/UV-vis indicated that dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene elute in fraction **F3**.

Illustrated in Figure 3 are the GC/MS chromatograms with SIM for the m/z 326 ion from the analyses of SRM 1597a with no NPLC fractionation and of fraction **F3** that indicate the presence of 31 and 20 $C_{26}H_{14}$ PAHs, respectively, with molecular mass 326 Da. Of the 31 and 20 peaks, five $C_{26}H_{14}$ *peri*-condensed benzenoid PAHs (dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene) were identified based on comparison of retention times with the five $C_{26}H_{14}$ benzenoid PAH reference standards shown in Figure 2. As it is observed, the m/z 326 ion chromatogram from the analysis of the unfractionated coal tar (Figure 3A) and fractionated coal tar (fraction **F3**) (Figure 3B) are very similar, particularly for retention times greater than 53 min. However, the NPLC fractionation does simplify the complexity of the chromatogram in the region with retention times between 40 min and 48 min, which may contain primarily fluoranthenoid PAHs. This comparison for the m/z 326 ion chromatograms (Figures 3A and 3B) is in stark contrast to the comparison of m/z 328 ion from the analysis of unfractionated coal tar where only two peaks could be identified compared to 13 peaks identified in the NPLC fractionated coal tar [Figure 3, Figure 6D, Figure 7C, and Figure 7D in reference 20].

The GC/MS chromatograms of the analyses of fractions **F1**, **F2**, **F3**, and **F4** with SIM for the m/z 326 ion are shown in Figures 4B, 4C, 4D, and 4E and they are compared with the five $C_{26}H_{14}$ *peri*-condensed benzenoid PAH reference standards and with the three $C_{26}H_{14}$ fluoranthenoid PAH reference standards (in order of elution: acenaphtho[1,2-*k*]fluoranthene, acenaphtho[1,2-*j*]fluoranthene, and rubicene) illustrated in Figure 4A.

3.1.3.1. Fraction 1, **F1**

218 The GC/MS chromatogram of the analysis of fraction **F1** for the m/z 326 ion illustrated in Figure
219 4B shows the presence of three unknown peaks *AP-AR* which could not be identified based on
220 retention times compared with the available reference standards of the $C_{26}H_{14}$ benzenoid and
221 fluoranthenoid PAHs. A tentative identity of the unknown peak *AQ*, the most abundant in
222 fraction **F1**, is the only nonplanar $C_{26}H_{14}$ *peri*-condensed benzenoid PAH dibenzo[*a,ghi*]perylene
223 for which a reference standard was not available. Dibenzo[*a,ghi*]perylene (molecular
224 thickness=5.06 [1]) would be expected to elute in fraction **F1** based on the nonplanarity elution
225 argument mentioned in section 1 and on the elution behavior of dibenzo[*def,p*]chrysene, a
226 nonplanar $C_{24}H_{14}$ *peri*-condensed PAH that elutes in fraction **F1** [20], which structure with one
227 ring less is identical to the structure of dibenzo[*a,ghi*]perylene.

228 3.1.3.2. Fraction 2, **F2**

229 The GC/MS chromatogram of the analysis of fraction **F2** for the m/z 326 ion illustrated in Figure
230 4C shows the presence of 14 unknown peaks *AS-BF*. Due to the close retention times (time
231 difference=0.3 min) of peak *BE* from fraction **F2** and peak *AQ* from fraction **F1** (tentatively
232 identified as dibenzo[*a,ghi*]perylene previously), a tentative identity for peak *BE* could also be
233 dibenzo[*a,ghi*]perylene. In this case, it is supposed that during the NPLC fractionation, the
234 elution of dibenzo[*a,ghi*]perylene matches with the transition time between fraction **F1** and
235 fraction **F2** and thus part of dibenzo[*a,ghi*]perylene goes to fraction **F1** and the other part goes to
236 fraction **F2**. In addition to peak *BE*, the second most abundant peak in fraction **F2** is peak *BF*. A
237 closer look of the retention time of peak *BF* in fraction **F2** reveals that it approximately matches
238 with the retention time of the peak of the reference standard of naphtho[1,2,3,4-*ghi*]perylene
239 (time difference=0.3 min) illustrated in Figure 4A, however, the lack of standards for the other
240 three $C_{26}H_{14}$ *peri*-condensed PAHs not yet assigned to any peak, benzo[*qr*]naphtho[3,2,1,8-

241 *defg*]chrysene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, and anthra[2,1,9,8-*opqra*]naphthacene
242 makes the direct assignment of the identity of peak *BF* to naphtho[1,2,3,4-*ghi*]perylene
243 ambiguous. In this sense, the following two arguments will help to narrow the possible choices
244 for the identity of peak *BF*. First, theoretical analysis, discussed later, demonstrates the presence
245 of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene in fraction **F3** and, second, the long and planar
246 structure of anthra[2,1,9,8-*opqra*]naphthacene (length-to-breadth ratio=1.601, molecular
247 thickness=3.888 [1]) that makes it more likely to be in later NPLC fractions. Therefore, besides
248 naphtho[1,2,3,4-*ghi*]perylene, among the three additional choices for the identity of peak *BF*,
249 naphtho[7,8,1,2,3-*pqrst*]pentaphene emerges as the most suitable candidate.

250 3.1.3.3. Fraction 3, **F3**

251 The GC/MS chromatogram of the analysis of fraction **F3** shown in Figure 4D (which is a
252 repetition of Figure 3B) contains most of the C₂₆H₁₄ *peri*-condensed benzenoid PAHs. As stated,
253 of the 20 peaks, five C₂₆H₁₄ *peri*-condensed benzenoid PAHs (dibenzo[*b,ghi*]perylene,
254 dibenzo[*b,pqr*]perylene, naphtho[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-*bcd*]perylene, and
255 dibenzo[*cd,lm*]perylene) were identified based on comparison of retention times with the five
256 C₂₆H₁₄ benzenoid PAH reference standards. Moreover, this result is confirmed by the NPLC
257 elution analysis of the C₂₆H₁₄ standards mentioned in section 3.1.3. that indicates
258 dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-
259 *bcd*]perylene, and dibenzo[*cd,lm*]perylene elute in fraction **F3**. Additionally, as illustrated in
260 Figure 4D, peaks *AA* and *AC* are tentatively identified as acenaphtho[1,2-*k*]fluoranthene and
261 acenaphtho[1,2-*j*]fluoranthene by matching their retention times with the retention time of the
262 standards. Conclusive identifications of acenaphtho[1,2-*k*]fluoranthene and acenaphtho[1,2-
263 *j*]fluoranthene could not be accomplished because of the large number of possible C₂₆H₁₄

fluoranthenoid PAHs (>100). As illustrated in Figure 4D, the 13 remaining unknown peaks *AB* and *AD-AO* could not be identified based on retention times compared with the remaining C₂₆H₁₄ PAH reference standard available, i.e., rubicene.

The GC/MS chromatogram of Figure 4A demonstrates the trend of the C₂₆H₁₄ fluoranthenoid PAHs to elute in the early part of the chromatogram (below 48 min) which is corroborated by the higher abundances of C₂₆H₁₄ fluoranthenoid PAHs versus C₂₆H₁₄ benzenoid PAHs (fluoranthene versus pyrene) measured and illustrated in the analysis of SRM 2975 [16,31]. Thus, the only peaks available for assignment of C₂₆H₁₄ *peri*-condensed benzenoid PAHs in the GC/MS chromatogram of Figures 3B and 4D would be peaks *AJ-AN*. As it will be demonstrated later in this report using RPLC/UV-Vis, annellation theory, and ZINDO/S calculations, benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene elutes in fraction **F3**, consequently, one of the still unassigned peaks *AJ-AN* in fraction **F3** should be benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene.

3.1.3.4. Fraction 4, **F4**

The GC/MS analysis of fraction **F4** for the *m/z* 326 ion illustrated in Figure 4E shows the presence of 16 unknown peaks *BG-BV* which could not be identified based on retention times compared with the available reference standards of the C₂₆H₁₄ benzenoid and fluoranthenoid PAHs. The two most abundant peaks in fraction **F4**, i.e., *BG* and *BH*, are tentatively assigned to C₂₆H₁₄ fluoranthenoid PAHs because of the elution arguments explained in fraction **F3**. As far as the identity of the third most abundant peak in fraction **F4**, i.e., *BT*, it is most probably the last C₂₆H₁₄ *peri*-condensed benzenoid PAH not yet assigned, anthra[2,1,9,8-*opqra*]naphthacene, whose long and planar shape would make it suitable for elution in fraction **F4** and not suitable for elution in fractions **F1-F3**.

3.1.4. Reversed-Phase Liquid Chromatography with Ultraviolet-Visible Spectroscopy

The GC/MS analyses shown in Figure 4 indicate that fraction **F3** contains the largest number of $C_{26}H_{14}$ PAHs; therefore, fraction **F3** was analyzed using RPLC/UV-vis to examine the UV-vis spectral features of the $C_{26}H_{14}$ PAHs that do not match with the UV-vis absorption spectra of the reference standards available. The RPLC/UV-vis chromatogram of the analysis of fraction **F3**, shown in Figure 5, indicates the presence of 14 peaks. As illustrated in Figure 6, five of the 14 peaks observed in the chromatogram of Figure 5 are identified by matching the UV-vis absorption spectra with the UV-vis absorption spectra of the reference standards of dibenzo[*b,ghi*]perylene, naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene, respectively. The UV-vis spectral identifications of dibenzo[*b,ghi*]perylene, naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene confirm the GC/MS identifications in Figures 3B and 4D. The remaining peaks *BW-CE* in Figure 5 could not be identified based on comparison with the $C_{26}H_{14}$ fluoranthenoid PAH reference standards available. Furthermore, among the unknown peaks, the UV-vis absorption spectrum of peak *BX*, illustrated in Figure 7, was analyzed using the approach described in the following section.

3.1.5. Annellation Theory and ZINDO/S Semiempirical Calculations

As stated in section 2.4., the calculation of the locations of maximum absorbance in the UV-vis absorption spectra of the $C_{26}H_{14}$ *peri*-condensed PAHs where no reference standards are available followed the same approach described by J. Oña-Ruales and Y. Ruiz-Morales for the calculation of the locations of maximum absorbance of the *p* and β bands in the UV-vis absorption spectra of the $C_{26}H_{16}$ *cata*-condensed PAHs [25] and $C_{32}H_{16}$ *peri*-condensed

benzenoid PAHs [26]. As illustrated in Figure 8, four PAHs (PAHs 1, 2, and 3 with UV-vis absorption spectra available and PAH 4 with UV-vis absorption spectrum not available) were connected by two analogies. Analogy 1 connects PAH 1 and PAH 3 using an aromatic and structural enclosure and analogy 2 connects PAH 1 and PAH 2, and PAH 3 and PAH 4 using an aromatic and structural relationship. In addition to analogies 1 and 2, to accomplish the arrangement of the PAH structures, the difference between the total number of rings of PAH 4 and PAH 3 and total number of rings of PAH 1 and PAH 2 was maximized. The elucidation of the locations of maximum absorbance of the p and β bands in the UV-vis absorption spectrum of PAH 4 consists in the addition of the difference between the locations of maximum absorbance of PAH 2 and PAH 1 to the locations of maximum absorbance of PAH 3. The Validation-Elucidation-Substantiation scheme previously reported [25,26] is used in the following analysis for the calculation of the locations of maximum absorbance in the UV-vis absorption spectra of the $C_{26}H_{14}$ *peri*-condensed PAHs where reference standards are not available.

3.1.5.1. Validation

As described in Figure 9, the calculation of the locations of maximum absorbance of the p and β bands in the UV-vis absorption spectra of the five $C_{26}H_{14}$ *peri*-condensed PAHs with reference standards available is achieved with the mathematical procedure based on the annellation theory shown in Figure 8. For purposes of comparison, the experimental locations of maximum absorbance of the p_{41} , p_{42} , p_{43} , β_{41} , β_{42} , and β_{43} bands, if any, are also described in Figure 9 in parentheses. Average differences of -7.2 nm, -6.2 nm, and -1.8 nm are evidenced for the p_{41} , p_{42} , and p_{43} bands and average differences of +1.6 nm and -3.3 nm are evidenced for the β_{41} and β_{42} bands. There is not sufficient data to calculate the locations (and therefore the average differences) of the β_{43} bands. The calculated average differences (2-7 nm) for the p and β bands

are related to the solvent effects in the UV-vis absorption spectra which are associated to the refractive indices of the solvents as explained in reference 14. The UV-Vis spectra of the PAHs in Case C of Figure 9 are presented in Figure S1 (Supporting Information). As it is observed in Figure S1, in addition to the spectral shifts already described, the UV-Vis spectra of benzo[*e*]pyrene (left top), dibenzo[*e,l*]pyrene (right top), benzo[*ghi*]perylene (left bottom), and dibenzo[*b,pqr*]perylene (right bottom) are mutually similar in terms of spectral shape showing as distinctive features high prominent β' bands, intermediate prominent β bands, and less prominent *p* bands. Besides this spectral shape agreement, two types of annellation effects are observed in Figure S1. First, the addition of a benzenoid ring to an isolated π double bond, e.g., from benzo[*e*]pyrene to dibenzo[*e,l*]pyrene and from benzo[*ghi*]perylene to dibenzo[*b,pqr*]perylene, does not shift significantly the location of the β and *p* spectral bands (± 10 nm), and second, the addition of an isolated π double bond to a bay region, e.g., from benzo[*e*]pyrene to benzo[*ghi*]perylene and from dibenzo[*e,l*]pyrene to dibenzo[*b,pqr*]perylene, shift the locations of the β bands and *p* bands approximately 20 nm and 50 nm to longer wavelengths, respectively.

3.1.5.2. Elucidation

The procedure used in the validation section demonstrated the suitability of the mathematical procedure of Figure 8 for the calculation of the locations of maximum absorbance of the *p* and β bands in the UV-vis absorption spectra of the C₂₆H₁₄ *peri*-condensed PAHs; therefore, the same technique is used for the calculation of the locations of maximum absorbance of the *p* and β bands in the UV-vis absorption spectra of the four C₂₆H₁₄ *peri*-condensed PAHs for which reference standards are not available as shown in Figure 10.

3.1.5.3. Substantiation

As observed in Table 2, the results for the locations of maximum absorbance of the last *p* band in the UV-vis absorption spectra of the four C₂₆H₁₄ *peri*-condensed PAHs with no available reference standards achieved using the ZINDO/S methodology show close resemblance with the results obtained using the annellation theory with an average difference of +5.5 nm. A ZINDO/S effect explained elsewhere [3,25,26] that involves the reconfiguration of the solvent cage for the ground electronic state once the excited PAH molecule undergoes photoemission, also known as Stokes shift [3], could be the reason of the differences between the ZINDO/S semiempirical values and the annellation theory results. The *p* band, which is associated to the HOMO-LUMO gap (energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) in the PAH molecules was calculated, using the theoretical chemistry method ZINDO/S. The calculation with the ZINDO/S method was carried out considering a single “frozen” molecule of PAH in the gas phase at a temperature of 0 K without corrections for thermal motions and solvent effects. On the other hand the estimate of the *p* band with the annellation theory involves the use of experimental data that has been measured in a solvent. The difference between the theoretical ZINDO/S and annellation values is due to the solute-solvent interactions of the solute’s ground and excited states, which are not considered in the ZINDO/S calculation. The reconfiguration of the solvent cage for the ground electronic state once the excited molecule of PAH undergoes photoemission (Stokes Shift) is reported to be around 10-45 nm for solvents with low polarity [34, 35]. The highest difference shown in Table 2 of +14 nm can be considered negligible.

An important point to support this theoretical procedure is the reasonable match between the calculated location of maximum absorbance of the last *p* band (*p*₄₃) in the UV-vis absorption spectrum of anthra[2,1,9,8-*opqra*]naphthacene in Figure 10 – Case D, 506 nm, and the prediction

of the location of the last *p* band in the UV-vis absorption spectrum of anthra[2,1,9,8-*opqra*]naphthacene discerned with another procedure based on UV-vis spectral comparisons used by McClaine et al. [36], ≈ 500 nm.

3.1.6. Identification of Benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene using the Annellation Theory

The locations of maximum absorbance of the *p* and β bands in the UV-vis absorption spectrum of peak *BX* in Figure 7 are compared with the locations of maximum absorbance of the *p* and β bands calculated using the annellation theory for benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene in Figure 10 – Case B. The comparison shows a direct similarity between the locations of maximum absorbance in the UV-vis absorption spectrum of peak *BX* (425, 403, 373, 318, 310, and 290 nm) and the locations of maximum absorbance calculated by means of the annellation theory in Figure 10 – Case B (426, 404, 381, 320, 308, and 290) nm. The other locations of maximum absorbance in the UV-vis absorption spectrum of peak *BX* in Figure 7, i.e., 418 and 396 nm, which are not present in the calculations of Figure 10 – Case B are explained due to the double band behavior observed in the last two *p* bands of the UV-vis absorption spectrum of anthanthrene [2] (one of the reference PAH used in Figure 10 – Case B). The double band behavior consists in the appearance of secondary peaks at lower wavelengths (≈ 7 nm from the primary peaks) in the last two *p* bands of the UV-vis absorption spectrum. Due to the close structural resemblance between anthanthrene and benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene, it is anticipated that the UV-vis absorption spectrum of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene will also present the double band behavior; therefore, the secondary peaks in the calculation of the locations of maximum absorbance in the UV-vis absorption spectrum of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene in Figure 10 – Case B will appear at 418 and 396 nm. Since the eight locations of maximum absorbance observed in the UV-vis absorption spectrum of

peak *BX* denoted in Figure 7 match closely the locations of maximum absorbance calculated using the annellation theory (six locations) and using the double band behavior (two locations), there is a high likelihood that the UV-vis absorption spectrum of benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene is indeed the UV-vis absorption spectrum of peak *BX*.

3.2. Quantitative Analysis

The alternative semi-quantitative approach successfully used in the quantification of the C₂₆H₁₆ *cata*-condensed PAHs [20] was used in this investigation for the quantification of the C₂₆H₁₄ *peri*-condensed PAHs in fraction **F3**. Coronene which was previously quantified in SRM 1597a [21-23] and which elutes in fraction **F1**, was used as a reference internal standard for quantification. Further details of the semi-quantitative methodology are discussed in our previous publication [20]. The results for the calculated mass fractions (mg/kg) for the five identified C₂₆H₁₄ *peri*-condensed PAHs are presented in Table 3 – Case A. As observed in Table 3 – Case A, the mass fractions for the 326 Da molecular mass isomers range from 0.34 mg/kg (dibenzo[*cd,lm*]perylene) to 2.48 mg/kg (dibenzo[*b,pqr*]perylene). The most abundant 326 Da molecular mass isomer, dibenzo[*b,pqr*]perylene, is more than 4 times lower than the mass fraction of the most abundant molecular mass 302 Da PAHs, dibenzo[*b,k*]fluoranthene, more than 30 times lower than benzo[*a*]pyrene, and more than 400 times lower than naphthalene [23]. Contrary to the trend observed for C₂₆H₁₆ *cata*-condensed PAHs [20], there is not a conceivable relation between the planarity (based on molecular thickness) of C₂₆H₁₄ *peri*-condensed PAHs [1] and their abundance in SRM 1597a.

Table 3 – Case B contains the mass fractions (mg/kg) for the five identified C₂₆H₁₄ *peri*-condensed PAHs determined by direct GC/MS analysis (no NPLC fractionation) also using

coronene as reference internal standard. The quantitative results determined with fractionation and with no fractionation are in good agreement for three of the five C₂₆H₁₄ *peri*-condensed PAHs with differences of 0.15 mg/kg (7 %) for dibenzo[*b,ghi*]perylene, 0.07 mg/kg (3 %) for dibenzo[*b,pqr*]perylene, and 0.32 mg/kg (25 %) for naphtho[8,1,2-*bcd*]perylene. The largest discrepancies occur for naphtho[1,2,3,4-*ghi*]perylene and dibenzo[*cd,lm*]perylene with differences of 0.76 mg/kg (143 %) and 0.21 mg/kg (62 %), respectively. Although the discrepancy for naphtho[1,2,3,4-*ghi*]perylene could be associated to the presence of peak *BF* in fraction **F2** (whose identity could also be naphtho[1,2,3,4-*ghi*]perylene as explained in section 3.1.3.2.), the large discrepancies for naphtho[1,2,3,4-*ghi*]perylene and dibenzo[*cd,lm*]perylene are presumably related to the presence of multi-methylated C₂₆H₁₄ PAHs (with molecular mass 326 + 14x, Da, where x=1,2,3,...etc.) in the coal tar standard material that co-elute with naphtho[1,2,3,4-*ghi*]perylene and dibenzo[*cd,lm*]perylene generating a *m/z* 326 ion in the direct GC/MS analysis.

4. Conclusions

The advantage of the fractionation approach using NPLC/UV-vis in combination with the identification and quantification using GC/MS versus the direct analysis approach using only GC/MS was demonstrated in this report for the identification and quantification of the C₂₆H₁₄ *peri*-condensed benzenoid PAHs in an environmental combustion sample. Five out of the nine members of the C₂₆H₁₄ *peri*-condensed PAHs, naphtho[1,2,3,4-*ghi*]perylene, dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]perylene were identified and quantified. The other four PAHs were analyzed using the annellation theory and chromatographic GC elution analysis. In this group, benzo[*qr*]naphtho[3,2,1,8-*defg*]chrysene was potentially identified by matching the locations of

maximum absorbance in the UV-vis spectrum with the locations calculated using the annellation theory and with GC elution analysis, and dibenzo[*a,ghi*]perylene, naphtho[7,8,1,2,3-*pqrst*]pentaphene, and anthra[2,1,9,8-*opqra*]naphthacene were tentatively identified using GC elution analysis.

As described in our previous paper [20] and demonstrated in the present report, the experimental procedure NPLC/UV-vis followed by GC/MS is suitable for the analysis of PAHs with molecular masses greater than 300 Da. It is anticipated that future experimental and theoretical approaches will reveal the identities and abundances of other isomer groups of PAHs such as C₂₈H₁₄ and C₂₈H₁₆ *peri*-condensed benzenoid PAHs.

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7. Notes

The authors declare no competing financial interest. Certain commercial equipment, instruments, or materials (or suppliers, or software, ...) are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Figure Captions

Fig. 1. The nine $C_{26}H_{14}$ *peri*-condensed benzenoid PAHs [1]. The structures in black denote the compounds with known UV–vis spectra and the structures in red denote the compounds with unknown UV–vis spectra.

Note 1: The locations, number, and migrating behavior of the sextets in the PAHs have been achieved by means of the information provided in reference 2 and the Y-rule method [3-6]. The black lines connecting rings denote the movement of the aromatic sextets.

Fig. 2. GC/MS chromatogram of the five $C_{26}H_{14}$ *peri*-condensed PAH standards available with SIM for the m/z 326 ion in the Rxi-PAH column. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 3. A. GC/MS chromatogram of the analysis of the unfractionated SRM 1597a with SIM for the m/z 326 ion. **B.** GC/MS chromatogram of the analysis of NPLC fraction **F3** with SIM for the m/z 326 ion. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 4. GC/MS analyses of the following samples: **A.** The three $C_{26}H_{14}$ fluoranthenoid PAH standards available and the five $C_{26}H_{14}$ *peri*-condensed benzenoid PAH standards illustrated in Figure 2 with SIM for the m/z 326 ion, **B.** Fraction **F1** with SIM for the m/z 326 ion, **C.** Fraction **F2** with SIM for the m/z 326 ion, **D.** Fraction **F3** with SIM for the m/z 326 ion, and **E.** Fraction **F4** with SIM for the m/z 326 ion. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 5. RPLC/UV-Vis chromatogram of fraction **F3**. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 6. A. UV-Vis absorbance spectra for a coal tar product (dotted line) and for the reference standard of dibenzo[*b,ghi*]perylene in acetonitrile (solid line). **B.** UV-Vis absorbance spectra for a coal tar product (dotted line) and for the reference standard of naphtho[1,2,3,4-*ghi*]perylene in acetonitrile (solid line). **C.** UV-Vis absorbance spectra for a coal tar product (dotted line) and for the reference standard of dibenzo[*b,pqr*]perylene in acetonitrile (solid line). **D.** UV-Vis absorbance spectra for a coal tar product (dotted line) and for the reference standard of naphtho[8,1,2-*bcd*]perylene in acetonitrile (solid line). **E.** UV-Vis absorbance spectra for a coal tar product (dotted line) and for the reference standard of dibenzo[*cd,lm*]perylene in acetonitrile (solid line). For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 7. UV-Vis absorption spectrum of peak *BX*. Only the β and *p* bands are labeled.

Fig. 8. Annellation theory methodology for the prediction of the locations of maximum absorbance of the *p* and β bands in the UV-Vis spectra of the *cata*-condensed [25] and *peri*-condensed [26] PAHs. Red line denotes structural and aromatic enclosure. Black line denotes structural and aromatic relationship. The symbol *i* denotes the three locations of maximum absorbance of the *p* and β bands in the UV-vis spectra of PAH₁, PAH₂, PAH₃, and PAH₄.

Fig. 9. Calculation of the locations of maximum absorbance of the *p* and β bands in the UV-Vis spectra of the five *peri*-condensed C₂₆H₁₄ PAHs with reference standards available using the annellation theory method of Figure 8. The wavelengths inside of the parentheses correspond to experimental measurements. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

Fig. 10. Calculation of the locations of maximum absorbance of the p and β bands in the UV-Vis spectra of the four *peri*-condensed C₂₆H₁₄ PAHs with reference standards not available using the annellation theory method of Figure 8. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

$C_{26}H_{14}$ PAH	Average Retention Index ^a
	100
	131.40 ± 0.04
	134.80 ± 0.05
	136.75 ± 0.05
	138.77 ± 0.02
	145.47 ± 0.03
	200

^a Based on 4 determinations

Table 1

Average retention indices and standard deviations for the five $C_{26}H_{14}$ *peri*-condensed PAHs with standards available. Coronene ($C_{24}H_{12}$) and Benzo[*a*]coronene ($C_{28}H_{14}$) are used as the retention index standards. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

C ₂₆ H ₁₄ PAH	Location of last <i>p</i> band, nm		δ
	Annellation Theory	ZINDO/S
438	433	+5
426	423	+3
449	449	0
506	492	+14

Table 2

Comparison of the locations of maximum absorbance of the last *p* bands in the UV-vis spectra of the four C₂₆H₁₄ *peri*-condensed PAHs with no reference standards available using the annellation theory and the ZINDO/S methodologies. The symbol δ is defined as the difference between annellation theory and ZINDO/S. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

	NPLC Fractionation (Case A)	Direct Analysis (Case B)
	Coronene 8.7 mg/kg $\pm$ 1.8 mg/kg [18]	
	Mass Fraction ^a mg/kg	Mass Fraction ^a mg/kg
1.98 $\pm$ 0.60	1.83 $\pm$ 0.42
2.48 $\pm$ 0.77	2.41 $\pm$ 0.52
0.53 $\pm$ 0.13	1.29 $\pm$ 0.35
1.29 $\pm$ 0.32	1.61 $\pm$ 0.44
0.34 $\pm$ 0.08	0.55 $\pm$ 0.26

^a Based on 3 replicates

Table 3

Calculated mass fractions (mg/kg) of the five identified C₂₆H₁₄ *peri*-condensed PAHs dibenzo[*b,ghi*]perylene, dibenzo[*b,pqr*]perylene, naphtho-[1,2,3,4-*ghi*]perylene, naphtho[8,1,2-*bcd*]perylene, and dibenzo[*cd,lm*]-perylene using NPLC Fractionation (Case A) and Direct Analysis (Case B) with coronene as reference internal standard . Measured uncertainties are mean standard deviations from the number of replicates stated in the table. All PAHs identified in fraction **F3**. For the characterization of the aromatic sextets see Note 1 in the caption of Figure 1.

dibenzo[*a,ghi*]
perylene

naphtho[1,2,3,4-
ghi]perylene

benzo[*qr*]naphtho
[3,2,1,8-*defg*]chrysene

dibenzo[*b,ghi*]
perylene

dibenzo[*b,pqr*]
perylene

naphtho[8,1,2-*bcd*]
perylene

naphtho[7,8,1,2,3-
pqrst]pentaphene

anthra[2,1,9,8-
opqra]naphthacene

dibenzo[*cd,lm*]
perylene

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

$$\left. \begin{aligned} p_{4i} &= (p_{2i} - p_{1i}) + p_{3i} \\ \beta_{4i} &= (\beta_{2i} - \beta_{1i}) + \beta_{3i} \end{aligned} \right\} i = 1, 2, 3$$

A. UV-Vis Bands Calculated for naphtho[1,2,3,4- <i>ghi</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	293	251		319	267
	281	242		306	259
	274			295

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	388	303		414 (412)	319 (306)
	367	292		392 (390)	309 (293)
	348			369 (371)	(282)

B. UV-Vis Bands Calculated for dibenzo[<i>b,ghi</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	293	251		319	267
	281	242		306	259
	274			295

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	388	303		414 (401)	319 (330)
	367	292		392 (383)	309 (315)
	348			369 (363)	(303)

C. UV-Vis Bands Calculated for dibenzo[<i>b,pqr</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	332	289		328	288
	317	278		315	278
	304	267

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	388	303		384 (372)	302 (306)
	367	292		365 (355)	292 (295)
	348			(340)	(283)

D. UV-Vis Bands Calculated for naphtho[8,1,2- <i>bcd</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	293	251		334	272
	281	242		318	262
	274			305	251

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	435	260		476 (464)	281 (292)
	408	230		445 (435)	250
	385			416 (411)	

E. UV-Vis Bands Calculated for dibenzo[<i>cd,lm</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ³²	λ_p , nm	λ_β , nm
	329	287		381	308
	315	274		362	295
	304	256		345

UV-Vis ³²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	381	308		433 (436)	329 (324)
	362	295		409 (409)	316 (310)
	345			386 (388)	(297)

A. UV-Vis Bands Calculated for dibenzo[<i>a,ghi</i>]perylene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	284	257		334	286
	273	249		321	277
				308

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	388	303		438	332
	367	292		415	320
	348				

B. UV-Vis Bands Calculated for benzo[<i>qr</i>]naphtho[3,2,1,8-<i>defg</i>]chrysene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	385	297		433	310
	364	284		408	297
	347	274		385	287

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	378	307		426	320
	360	295		404	308
	343	277 ^a		381	290

C. UV-Vis Bands Calculated for naphtho[7,8,1,2,3-<i>pqrst</i>]pentaphene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	329	287		397	297
	315	274		375	285
	304	256		357

UV-Vis ³²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	381	308		449	318
	362	295		422	306
	345			398	

D. UV-Vis Bands Calculated for anthra[2,1,9,8-<i>opqra</i>]naphthacene

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis ²	λ_p , nm	λ_β , nm
	385	297		433	310
	364	284		408	297
	347	274		385	287

UV-Vis ²	λ_p , nm	λ_β , nm	UV-Vis	λ_p , nm	λ_β , nm
	458	335		506	348
	431	320		475	333
	406			444	

^aUV-Vis spectral point from Reference 33 with the correction for the solvent effect shift following the arguments of Reference 14.