

Identification of Six- to Nine-Ring Polycyclic Aromatic Hydrocarbons from the Supercritical Pyrolysis of *n*-Decane

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ABSTRACT: Degradation of hydrocarbon aviation fuels to carbonaceous solid deposits in the pre-combustion environment, due to oxygen-free, high-temperature, high-pressure conditions, represents a limiting factor in the development of increasingly high-performance aircraft. In order to study this phenomenon, we have pyrolyzed the model fuel *n*-decane (critical temperature, 344.5 °C; critical pressure, 20.7 atm), an alkane component of jet fuel, under supercritical conditions at 570 °C, 94.6 atm, and 133 s. The product polycyclic aromatic hydrocarbons (PAH), precursors to the solid deposits, have been analyzed by a two-dimensional high-pressure liquid chromatographic separation technique with ultraviolet-visible absorbance and mass-spectrometric detection. The analyses reveal the presence of 24 unsubstituted PAH products, spanning four isomer families: 15 C₂₄H₁₄ PAH, dibenzo[*a,e*]pyrene, dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*e,l*]pyrene, naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, naphtho[2,3-*e*]pyrene, benzo[*b*]perylene, dibenzo[*a,e*]fluoranthene, dibenzo[*a,k*]fluoranthene, dibenzo[*b,k*]fluoranthene, dibenzo[*j,l*]fluoranthene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*b*]fluoranthene, and naphtho[2,3-*j*]fluoranthene; four C₂₆H₁₄ PAH, dibenzo[*b,ghi*]perylene, dibenzo[*e,ghi*]perylene, dibenzo[*cd,lm*]perylene, and naphtho[1,2,3,4-*ghi*]perylene; four C₂₈H₁₄ PAH, benzo[*a*]coronene, benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, and phenanthro[5,4,3,2-*efghi*]perylene; and one C₃₀H₁₄ PAH, naphtho[8,1,2-*abc*]coronene. Forty-three alkylated derivatives of these PAH have also been identified as products of the *n*-decane pyrolysis experiments. Of the 67 six- to nine-ring PAH products identified, only two had ever before been identified as products of *n*-decane pyrolysis or combustion. The UV spectra establishing the identities of the 24 unsubstituted *n*-decane pyrolysis products are presented.

■ INTRODUCTION

Hydrocarbon fuels play an important role in the removal of waste heat from aircraft engines prior to fulfilling their primary function as a propellant via combustion. Development of higher performance aircraft necessitates increasing the heat load on the fuel in the pre-combustion environment. High pressure is also required to maintain the fuel in a liquid-like, high-density state that ensures sufficient heat transfer from the engine, transfer that would not be possible by a gas-phase fluid. Based on projected requirements, fuels are expected to reach temperatures and pressures as high as 700 °C and 150 atm,¹ conditions that are supercritical for most pure hydrocarbons as well as jet fuels.²

Absorption of waste heat is accomplished not only by simple physical heating but also by conversion of the fuel to lower-molecular-weight, higher-energy products through endothermic chemical reactions.³ Such conversion is advantageous, since the energy that is stored chemically in the fuel may later be released and utilized during combustion. However, through a process not yet fully understood, a small fraction of the fuel is converted to carbonaceous solid deposits. In addition to fouling heat-transfer surfaces, these deposits can also obstruct the flow of the fuel through transfer lines, leading to increased maintenance costs, reduced performance, or even failure.¹

In order to better understand the reactions responsible for solid deposition in the pre-combustion environment, we have conducted supercritical pyrolysis experiments with the model fuel *n*-decane (critical temperature, 344.5 °C; critical pressure, 20.7 atm), an alkane component of jet fuels. A single-component model fuel has the advantage of reducing the number of reactions taking place by reducing the number of

reactants, thereby simplifying the elucidation of individual reaction pathways.

Our work focuses primarily on understanding the formation of polycyclic aromatic hydrocarbons (PAH), a class of compounds that are known not only for their role as environmental pollutants and soot precursors in combustion systems^{4,5} but also recognized as intermediates to the carbonaceous solid deposits formed during supercritical hydrocarbon pyrolysis.^{6–8} A key step in our efforts to discern PAH reaction pathways is the ability to analyze PAH with as much structural specificity as possible. Therefore, we employ high-pressure liquid chromatography (HPLC) combined with diode-array ultraviolet-visible (UV) absorbance and mass-spectrometric (MS) detection—a technique ideally suited for isomer-specific PAH analysis. Previous work^{9,10} in our research group has shown that separation of a large number of PAH, ranging from two to ten aromatic rings, can be achieved by HPLC with the appropriate column and solvent method, and that good component resolution is critical for product identification by UV/MS. However, the products of supercritical *n*-decane pyrolysis consist not only of a large number of unsubstituted PAH but also several alkylated derivatives of each of these PAH. The number of compounds is simply too many for a single HPLC column and method to resolve; therefore, we employ a two-dimensional chromatographic technique. Though the specific details of this technique have been developed by

Received: December 19, 2012

Revised: February 13, 2013

Published: March 11, 2013



Table 1. Reversed-Phase HPLC Solvent Methods Used to Separate Fractions 10–13 of the *n*-Decane Pyrolysis Products

Method	Sequence ^a	Used for Fraction(s)
1	Mobile phase is initially 60/40 H ₂ O/ACN, then ramped for 60 min at a constant gradient to pure ACN and held for 30 min, then ramped for 60 min at a constant gradient to pure DCM and held for 30 min; 30 °C column temperature	10
2	Mobile phase is initially 50/50 H ₂ O/MeOH, then ramped for 40 min at a constant gradient to pure MeOH and held for 160 min; 35 °C column temperature	10
3	Mobile phase is initially 50/50 H ₂ O/ACN, then ramped for 40 min at a constant gradient to pure ACN and held for 30 min, then ramped for 120 min at a constant gradient to pure DCM and held for 30 min; 30 °C column temperature	11
4	Mobile phase is initially 50/50 H ₂ O/ACN, then ramped for 40 min at a constant gradient to pure ACN and held for 30 min, then ramped for 90 min at a constant gradient to pure DCM and held for 30 min; 30 °C column temperature	12, 13

^aACN denotes acetonitrile, DCM denotes dichloromethane, and MeOH denotes methanol.

our research group for the analysis of *n*-decane pyrolysis products, the concept was first established by Wise et al.¹¹ and has been used extensively for the analysis of complex mixtures of PAH.^{12–14}

Application of the two-dimensional HPLC technique has enabled us to identify PAH with as many as nine fused aromatic rings among the supercritical *n*-decane pyrolysis products. The identification of unsubstituted PAH with molecular weight 300 or less and their alkylated derivatives has been documented previously;^{15,16} in this paper we document the identification of 24 individual unsubstituted PAH with molecular weights greater than 300, along with 43 of their alkylated derivatives, from our supercritical *n*-decane pyrolysis experiments. Of the 24 unsubstituted PAH products identified here, 22 have never before been reported as products of *n*-decane pyrolysis or combustion. It is also the first time that any of the 43 alkylated PAH are reported as products of *n*-decane pyrolysis or combustion.

■ EXPERIMENTAL EQUIPMENT AND PROCEDURES

The supercritical *n*-decane pyrolysis experiments are conducted in an isothermal, isobaric flow reactor as described in detail in our previous paper.¹⁶ Prior to an experiment, the *n*-decane fuel ($\geq 99\%$ pure, from Sigma-Aldrich Corporation) is sparged with nitrogen for three hours to remove any dissolved oxygen that could introduce auto-oxidative effects to the reactor system.¹⁷ Once the oxygen is removed, the sparged fuel is loaded into a high-pressure syringe pump for continuous delivery of the fuel through the reactor.

The reactor is a silica-lined stainless-steel tube (length, 53 cm; inner diameter, 2.16 mm; outer diameter, 3.17 mm) immersed in a temperature-controlled fluidized alumina bath. The silica lining prevents wall-catalyzed deposit formation that would occur if reactants were to come into contact with bare stainless steel.¹⁸ The fluidized bath maintains the temperature inside the silica-lined stainless-steel tubing (the reaction environment) and ensures isothermality throughout the reactor length.

Two sets of six pyrolysis experiments, each at a residence time of 133 s, have been performed with *n*-decane (critical temperature, 344.5 °C; critical pressure, 20.7 atm). In the first set, pressure is held constant at 94.6 atm, and experiments are conducted at the six temperatures of 530, 540, 550, 560, 565, and 570 °C. In the second set, temperature is held constant at 570 °C, and experiments are conducted at the six pressures of 40, 60, 70, 80, 90, and 94.6 atm.

For each pyrolysis experiment, the reaction products (and any unreacted *n*-decane) are quenched to room temperature and channeled through a stainless-steel filter (hole size, 10 μ m) to trap any solids that may have formed inside the reactor. They then pass through a back-pressure regulator, which maintains constant pressure inside the reactor. Upon leaving the back-pressure regulator, the pyrolysis products and unreacted fuel proceed to the liquid- and gas-phase product collection apparatus, where they are separated by phase for subsequent analyses.

Gas-phase and liquid-phase alkane and alkene products, along with single-ring aromatic products, are analyzed by gas chromatography

coupled to flame-ionization detection and mass spectrometry. PAH products in the liquid phase are analyzed by high-pressure liquid chromatography (HPLC) coupled to ultraviolet-visible spectroscopy and mass spectrometry (UV/MS). This paper documents the identification of six- to nine-ring PAH produced from the experiment at the most severe condition, 570 °C and 94.6 atm, which corresponds to 92 % *n*-decane conversion and the onset of solid deposition in the reaction environment. All PAH produced at experiments conducted at lower temperatures or pressures are also produced at this condition.

To obtain good component resolution among the very large number of unalkylated and alkylated PAH produced during supercritical *n*-decane pyrolysis—resolution that is essential for product identification by UV/MS—we use a two-dimensional HPLC technique. As documented in our previous paper,¹⁶ the first dimension of the technique employs a normal-phase cyano HPLC column and a hexane mobile phase to separate the *n*-decane product mixture into 13 fractions—each fraction containing unsubstituted PAH of a particular isomer group (or molecular weight) and their alkylated derivatives. In the second dimension of the technique, each fraction is injected onto a reversed-phase octadecylsilica HPLC column, which employs a series of mobile-phase solvents to separate the components in the fraction; the resolved components are then identified by UV/MS. Tests of the entire analytical procedure with a mixture of PAH reference standards representative of the supercritical *n*-decane pyrolysis products demonstrate overall individual PAH recovery rates of 91 to 97 %. Our previous paper documents the application of the two-dimensional technique to identify the *n*-decane product PAH (up to seven rings) in Fractions 6–9. In the present paper, the technique is applied to identify the six- to nine-ring PAH products in Fractions 10–13.

As in the case for Fractions 6–9,¹⁶ the reversed-phase HPLC analyses of Fractions 10–13 are achieved by injecting each fraction into an Agilent Model 1100 HPLC coupled to a diode-array ultraviolet-visible (UV) absorbance detector in series with a mass spectrometer (MS). The HPLC utilizes an octadecylsilica (C18) reversed-phase HPLC column (a Restek Pinnacle II PAH column of length, 250 mm; inner diameter, 2.1 mm; and particle size, 4 μ m) and a timed sequence of mobile-phase solvents—each tailored to the composition of a particular fraction or fractions, as indicated in Table 1—to achieve product-component separation. UV absorbance spectra of the separated components are taken every 0.8 s at a resolution of 1 nm.

Because the UV absorbance spectrum of a given PAH is unique to that particular aromatic structure, unsubstituted PAH products can be identified definitively by matching the product's UV absorbance spectrum with that of the appropriate reference standard. Nineteen of the 24 unsubstituted PAH products reported here have been identified by that method—the reference standard of dibenzo[*a,e*]pyrene having been purchased from Columbia Organic Chemicals and those of the other C₂₄H₁₄ PAH, each synthesized as described by Clar¹⁹—dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*e,l*]pyrene, naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, naphtho[2,3-*e*]pyrene, benzo[*b*]perylene, dibenzo[*a,e*]fluoranthene, dibenzo[*a,k*]fluoranthene, dibenzo[*b,k*]fluoranthene, dibenzo[*j,l*]fluoranthene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*b*]fluoranthene, and naphtho[2,3-*j*]fluoranthene—having been acquired from Dr. Werner Schmidt. The reference standards of dibenzo[*cd,lm*]perylene,^{20–22} benzo[*a*]-

coronene,^{23,24} benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene,^{23,24} and naphtho[8,1,2-*abc*]coronene^{22,24} have been provided by Dr. John Fetzer. Each of the remaining five unsubstituted PAH products reported here have been identified by matching the product's UV spectrum with that published for the appropriate compound: dibenzo[*bghi*]perylene,²⁵ dibenzo[*e,ghi*]perylene,²⁶ naphtho[1,2,3,4-*ghi*]perylene,²⁷ benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene,²⁸ and phenanthro[5,4,3,2-*efghi*]perylene.²³

For a PAH with no substituent groups, the UV spectrum alone is sufficient to establish its exact isomer-specific identity. If a PAH has one or more alkyl substituents, however, the UV spectrum looks almost exactly like that of the unsubstituted parent PAH, only shifted a few nanometers to higher wavelengths, with the position(s) and length(s) of the substituent(s) dictating the details of the shift.^{29,30} For PAH that have a multitude of sites at which alkyl groups can be located, one would need reference standards or UV spectra of all possible positional isomers in order to be certain of the exact position(s) of any alkyl substituent(s)—a condition rarely met for large PAH or PAH with multiple alkyl groups. Therefore, to identify alkylated PAH products in situations where the only reference UV spectrum available is that of the unsubstituted PAH, the UV spectrum establishes the aromatic structure of the alkylated PAH product, and mass spectrometry is used to determine the number of alkyl carbon atoms present in the alkyl substituents. The MS employs an atmospheric-pressure photo-ionization (APPI) source equipped with a krypton discharge lamp, with operational parameters optimized¹⁶ to achieve the strongest signal for product PAH. Since APPI is a “soft” ionization technique that does not fragment the analyte,³¹ the mass spectrum consists of a single signal corresponding to the molecular weight of the analyte. Consequently, for each alkylated PAH product identified in this work, there may be uncertainty as to the number, position(s), and/or length(s) of the alkyl substituent(s), but the exact structure of the aromatic portion of the PAH is known (from the UV spectrum), and the total number of carbons associated with the alkyl substituent(s) is known (from the mass spectrum).

For particularly low-yield compounds, single-ion monitoring, in which only one mass-to-charge ratio (m/z) is scanned during an HPLC separation, is used to increase the sensitivity of the MS detector. In these instances, a fraction is injected into the HPLC multiple times, each time scanning a different m/z that corresponds to one of the various possible alkylated derivatives of the unsubstituted products identified in that fraction.

RESULTS AND DISCUSSION

C₂₄H₁₄ PAH and Their Alkylated Derivatives. As indicated in Table 1, Fraction 10 of the products of supercritical *n*-decane pyrolysis at 570 °C and 94.6 atm has been subjected to two reversed-phase HPLC separation methods, Method 1 and Method 2. Even though Method 2 provides better resolution of some of the products of Fraction 10, better overall resolution is achieved by Method 1. Figure 1 therefore presents the reversed-phase HPLC chromatogram that results from the Method-1 separation of Fraction 10. Each peak in Figure 1 that corresponds to an identified product—whether better resolved by Method 1 or by Method 2—has been labeled with the aromatic structure of that product, with unsubstituted PAH shown in black, singly-methylated PAH shown in red, and dimethylated or ethylated PAH shown in blue. (For a given aromatic structure, the APPI mass spectrum of a dimethyl-substituted derivative is indistinguishable from that of an ethyl-substituted derivative.)

As the structures of Figure 1 reveal, the *n*-decane pyrolysis products in Fraction 10 are composed of 15 unsubstituted six-ring C₂₄H₁₄ PAH—seven pyrene benzologues, one perylene benzologue, and seven fluoranthene benzologues—along with several of their singly-methylated and dimethylated or ethylated derivatives. The UV and mass spectral evidence supporting

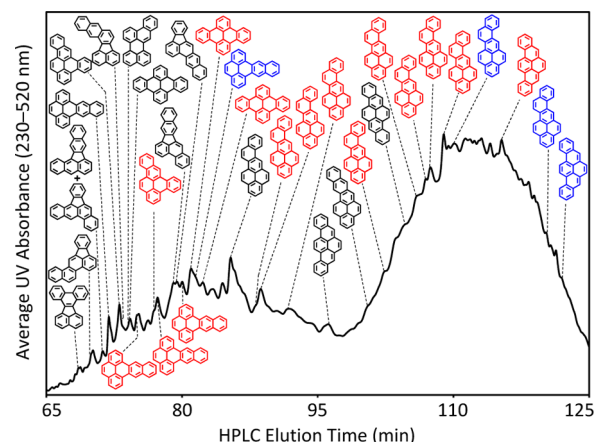


Figure 1. Reversed-phase HPLC chromatogram of Fraction 10 of the products of *n*-decane pyrolysis at 570 °C and 94.6 atm. This fraction contains C₂₄H₁₄ PAH and their alkylated derivatives. Black structures represent unsubstituted PAH, red structures represent singly-methylated PAH, and blue structures represent dimethylated or ethylated PAH.

these product identifications is presented in Figures 2–4. To minimize spectral interference from co-eluting components, each product-component spectrum in Figures 2–4 is taken from the separation method (either Method 1 or Method 2) that provides the better resolution of that component, even though both separation methods provide UV spectra amenable to the identification of the labeled PAH products in Figure 1. In the following, the identifications of the C₂₄H₁₄ pyrene benzologue products of Figure 1 are discussed first, followed by those of the C₂₄H₁₄ perylene and fluoranthene benzologues.

Figure 2a displays the UV spectrum of the *n*-decane pyrolysis product eluting at 71.9 min in the chromatogram of Figure 1, along with the spectrum of a reference standard of naphtho[2,3-*e*]pyrene. The coincidence of the product and reference-standard spectra establishes that the product eluting at 71.9 min in Figure 1 is the C₂₄H₁₄ PAH naphtho[2,3-*e*]pyrene, a six-ring pyrene benzologue. The mass spectrum of the product, displayed in the inset to Figure 2a, shows that this component has a molecular weight of 302, corresponding to the molecular formula C₂₄H₁₄. Therefore, no alkyl substituent is present, and the identity of the product eluting at 71.9 min in Figure 1 is unequivocally established as the unsubstituted naphtho[2,3-*e*]pyrene.

Figure 2b shows the UV spectrum of the product eluting at 77.3 min in the chromatogram of Figure 1, along with the spectrum of a reference standard of naphtho[2,3-*e*]pyrene. Both spectra have the same absorbance features, but those of the product spectrum exhibit a shift to higher wavelengths relative to those of the reference spectrum—suggesting that the product is an alkylated derivative of naphtho[2,3-*e*]pyrene. The mass spectrum of the product, displayed in the inset to Figure 2b, shows that this component has a molecular weight of 316, that of a singly-methylated derivative of a C₂₄H₁₄ PAH. Thus the UV and mass spectra demonstrate unequivocally that the product eluting at 77.3 min is a singly-methylated naphtho[2,3-*e*]pyrene. (The minor deviations between the product and reference-standard UV spectra, particularly evident at 270 nm in Figure 2b, are due to unidentified products eluting at the same time as the identified methylated naphtho[2,3-*e*]pyrene.)

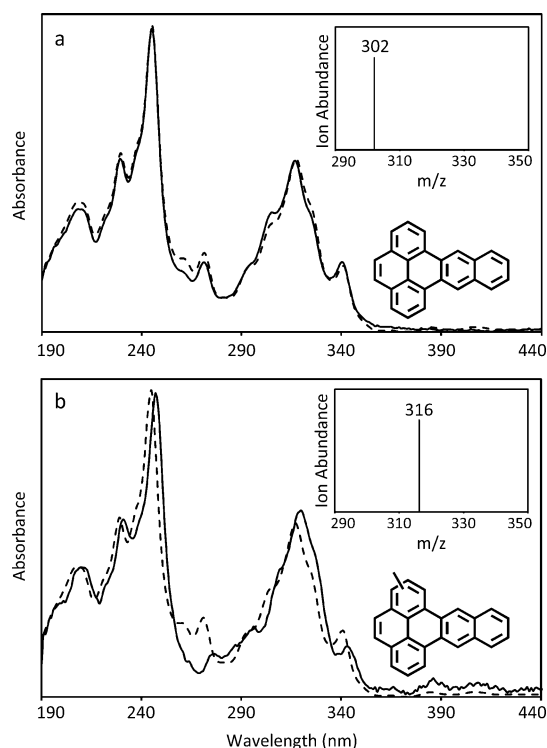


Figure 2. Comparisons of the UV spectrum (dashed lines) of a reference standard of naphtho[2,3-*e*]pyrene to the spectra (solid lines) of the *n*-decane pyrolysis products identified as (a) naphtho[2,3-*e*]pyrene, eluting at 71.9 min, and (b) a singly-methylated naphtho[2,3-*e*]pyrene, eluting at 77.3 min in the chromatogram of Fraction 10 in Figure 1. The position of the methyl group of the product in (b) is unknown. The UV spectra of both product components have been taken with HPLC separation Method 1 in Table 1. Note that, relative to the UV spectrum of the reference standard, the spectrum of the methylated product in (b) is shifted by a few nanometers to higher wavelengths. In (b), the discrepancies between the product and reference spectra, at 257–276 nm, are due to the presence of unidentified co-eluting compounds. The insets to the figure display the mass spectra of the identified products.

Two additional singly-methylated naphtho[2,3-*e*]pyrenes, eluting at 75.0 and 80.0 min in Figure 1, have been identified in the manner just described for Figure 2b. Each of these PAH has a UV spectrum with the same absorbance features as naphtho[2,3-*e*]pyrene, but shifted to higher wavelengths, and each has a mass spectrum that shows that its molecular weight is 316. One dimethylated or ethylated naphtho[2,3-*e*]pyrene, eluting at 85.0 min, has also been identified by its UV and mass spectra. All four of the alkylated naphtho[2,3-*e*]pyrene products have been labeled with the appropriate red or blue structures in the chromatogram of Figure 1.

The UV spectra of the six components of Fraction 10 that have been identified as the other six unsubstituted six-ring pyrene benzologue products of supercritical *n*-decane pyrolysis are shown in Figure 3. Figures 3a, 3b, 3c, 3d, 3e, and 3f present the UV spectra of the Fraction-10 components eluting in the chromatogram of Figure 1 at 73.1, 74.3, 85.4, 96.2, 100.2, and 104.5 min, respectively. Each product-component spectrum in Figure 3 has been overlaid with the spectrum of the corresponding reference standard: (a) dibenzo[*a,e*]pyrene, (b) dibenzo[*e,l*]pyrene, (c) naphtho[2,1-*a*]pyrene, (d) dibenzo[*a,i*]pyrene, (e) naphtho[2,3-*a*]pyrene, and (f) dibenzo[*a,h*]pyrene. The close matching of the UV spectra of

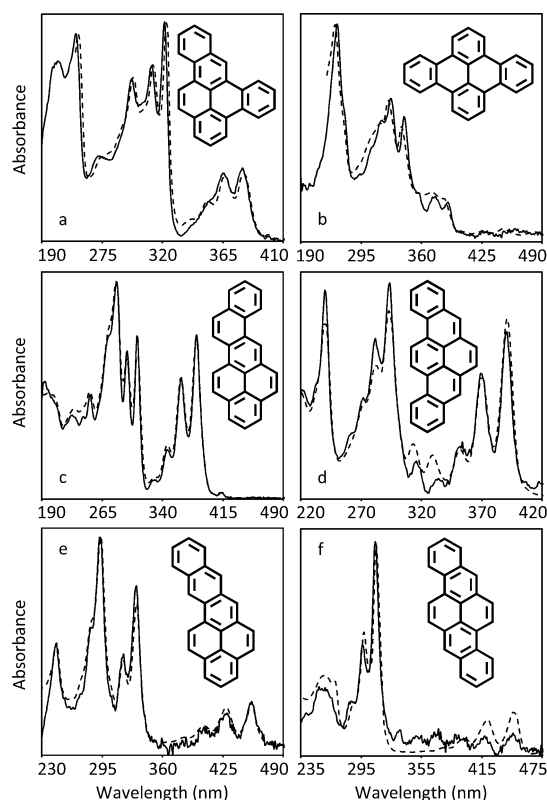


Figure 3. Comparisons of the UV spectra (solid lines) of *n*-decane pyrolysis products from the chromatogram of Fraction 10, in Figure 1, to the spectra (dashed lines) of reference standards. Comparisons are shown for the products identified as (a) dibenzo[*a,e*]pyrene, eluting at 73.1 min, (b) dibenzo[*e,l*]pyrene, eluting at 74.3 min, (c) naphtho[2,1-*a*]pyrene, eluting at 85.4 min, (d) dibenzo[*a,i*]pyrene, eluting at 96.2 min, (e) naphtho[2,3-*a*]pyrene, eluting at 100.2 min, and (f) dibenzo[*a,h*]pyrene, eluting at 104.5 min in Figure 1. The spectra of the product components in (d) and (f) have been taken with HPLC separation Method 2 in Table 1; the remaining four product-component spectra have been taken with Method 1. Additional minor absorbance features in the product-component spectrum in (f) are due to unidentified co-eluting compounds.

each product/standard pair in Figure 3 establishes the identity of each of the six *n*-decane pyrolysis products as the respective $C_{24}H_{14}$ pyrene benzologue shown. In addition, the mass spectral data show that each of these six products has a molecular weight of 302, consistent with an unsubstituted $C_{24}H_{14}$ PAH. The identities of the six products of Figure 3 are thus unequivocally established as the unsubstituted PAH dibenzo[*a,e*]pyrene, dibenzo[*e,l*]pyrene, naphtho[2,1-*a*]pyrene, dibenzo[*a,i*]pyrene, naphtho[2,3-*a*]pyrene, and dibenzo[*a,h*]pyrene.

UV and mass spectral evidence also confirm, among the products of Fraction 10, the presence of 15 alkylated derivatives of these six six-ring pyrene benzologues: one singly-methylated dibenzo[*a,e*]pyrene, two singly-methylated dibenzo[*e,l*]pyrenes, eight singly-methylated naphtho[2,1-*a*]pyrenes, two dimethylated or ethylated naphtho[2,1-*a*]pyrenes, one singly-methylated dibenzo[*a,i*]pyrene, and one dimethylated or ethylated dibenzo[*a,i*]pyrene. Twelve of the red structures and three of the blue structures in Figure 1 stem from these identifications.

Altogether, seven unsubstituted six-ring $C_{24}H_{14}$ pyrene benzologues and 19 of their alkylated derivatives have been identified in Fraction 10 as products of supercritical *n*-decane

pyrolysis. Two of these—dibenzo[*a,e*]pyrene and dibenzo[*a,i*]pyrene—have previously been confirmed as products of *n*-decane pyrolysis,³² whereas the other five—naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, naphtho[2,3-*e*]pyrene, dibenzo[*a,h*]pyrene, and dibenzo[*e,l*]pyrene—are identified here for the first time. Furthermore, none of the 19 alkylated derivatives of the seven pyrene benzologues have ever been reported as pyrolysis products of *n*-decane.

We now consider the remaining identified products in Fraction 10, the six-ring $C_{24}H_{14}$ perylene and fluoranthene benzologues of Figure 1. Figure 4a shows the UV spectrum, obtained by Method 1, of the product eluting at 73.9 min in Figure 1, along with the spectrum of a reference standard of benzo[*b*]perylene. Although there is a difference in intensity of the absorbance between the product and reference spectra, particularly between 270 and 330 nm, the coincidence, between the two spectra, of each absorbance maximum—at 229, 257, 313, 383, 405, and 430 nm—demonstrates unequivocally that the product is the $C_{24}H_{14}$ PAH benzo[*b*]perylene, and mass spectral evidence confirms that it is unsubstituted.

Figures 4b, 4c, 4d, 4e, and 4f show the UV spectra, obtained by Method 1, of the products eluting at 68.6, 70.0, 73.3, 79.1, and 79.4 min, respectively, in Figure 1—along with the spectra of the appropriate reference standards: dibenzo[*j,l*]fluoranthene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*j*]fluoranthene, dibenzo[*b,k*]fluoranthene, and naphtho[2,3-*b*]fluoranthene, respectively. As in the case of benzo[*b*]perylene, there are a few instances of minor discrepancies between the product and reference spectra (e.g., from 190 to 235 nm and from 315 to 367 nm in Figure 4e) due to co-elution. However the otherwise close matching of the UV spectra of each product/standard pair—especially at the absorbance-maxima wavelengths—establishes the identity of each of the five *n*-decane pyrolysis products in Figures 4b–4f as the respective $C_{24}H_{14}$ fluoranthene benzologue shown. The mass spectral data are also consistent with the identifications of these unsubstituted six-ring fluoranthene benzologue products.

Figure 4g shows the UV spectrum of the product eluting at 71.3 min in the chromatogram of Fraction 10 in Figure 1. The mass spectral data reveal a molecular weight of 302, corresponding to a $C_{24}H_{14}$ PAH, but the UV spectrum does not match that of any individual $C_{24}H_{14}$ reference standard available to us or any published spectrum of a single $C_{24}H_{14}$ PAH. The product-component spectrum in Figure 4g does, however, exhibit absorbance maxima at 216, 243, 328, 380, and 400 nm—which are characteristic of the UV absorbance spectrum of dibenzo[*a,e*]fluoranthene, as shown by the dashed-line spectrum of a reference standard of this compound in Figure 4g—and also at 271 nm, the wavelength of maximum absorbance of dibenzo[*a,k*]fluoranthene, whose spectrum (from a reference standard) is shown as the dotted line in Figure 4g. To test if the product-component spectrum in Figure 4g is a result of the co-elution of dibenzo[*a,e*]fluoranthene and dibenzo[*a,k*]fluoranthene, the two reference spectra in Figure 4g have been linearly combined to produce the composite spectrum shown as the dashed line in Figure 4h. The product-component spectrum of Figure 4g is duplicated in Figure 4h as the solid line. The close matching of the solid- and dashed-line spectra in Figure 4h confirms that the product eluting at 71.3 min in Figure 1 is in fact the co-eluting pair, dibenzo[*a,e*]fluoranthene and dibenzo[*a,k*]fluoranthene, two additional $C_{24}H_{14}$ fluoranthene benzologues.

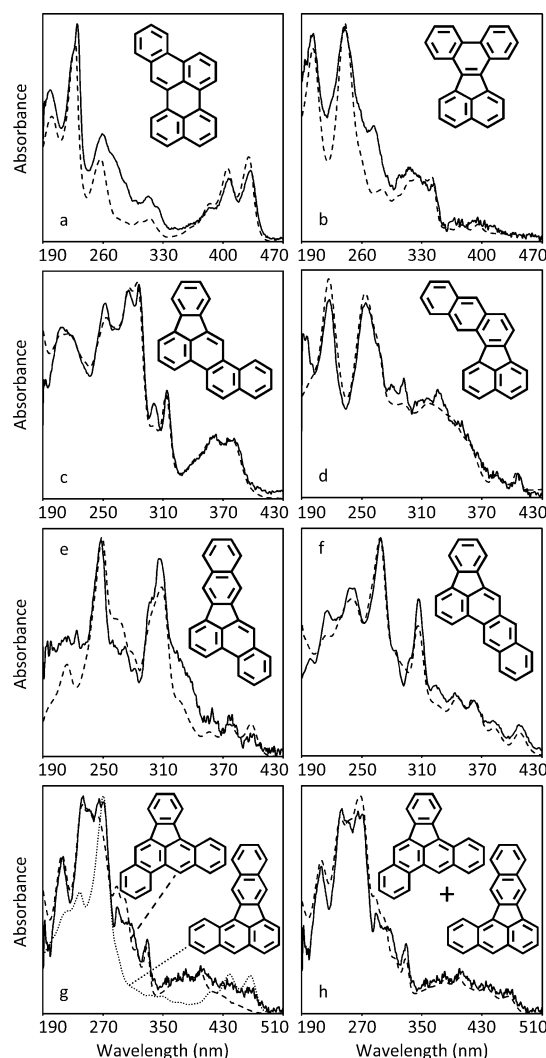


Figure 4. Comparisons of the UV spectra (solid lines) of *n*-decane pyrolysis products from the chromatogram of Fraction 10, in Figure 1, to the spectra (dashed lines) of reference standards. Comparisons are shown for the products identified as (a) benzo[*b*]perylene, eluting at 73.9 min, (b) dibenzo[*j,l*]fluoranthene, eluting at 68.6 min, (c) naphtho[1,2-*b*]fluoranthene, eluting at 70.0 min, (d) naphtho[2,3-*j*]fluoranthene, eluting at 73.3 min, (e) dibenzo[*b,k*]fluoranthene, eluting at 79.1 min, and (f) naphtho[2,3-*b*]fluoranthene, eluting at 79.4 min in Figure 1. The spectrum of the two products co-eluting at 71.3 min is shown in (g) with the spectra of the reference standards of dibenzo[*a,e*]fluoranthene (dashed line) and dibenzo[*a,k*]fluoranthene (dotted line) and in (h) with the composite spectrum (dashed line) of the two reference standards. The UV spectra of the product components have been taken with HPLC separation Method 1 in Table 1. Additional minor absorbance features in the product-component spectra are due to unidentified co-eluting compounds.

Altogether, one unsubstituted six-ring perylene benzologue, benzo[*b*]perylene, and seven unsubstituted six-ring fluoranthene benzologues—dibenzo[*a,e*]fluoranthene, dibenzo[*a,k*]fluoranthene, dibenzo[*b,k*]fluoranthene, dibenzo[*j,l*]fluoranthene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*b*]fluoranthene, and naphtho[2,3-*j*]fluoranthene—have been identified in Fraction 10 as products of supercritical *n*-decane pyrolysis. None of these $C_{24}H_{14}$ PAH have been identified previously as products of *n*-decane pyrolysis or combustion.

$C_{26}H_{14}$ PAH and Their Alkylated Derivatives. As indicated in Table 1, the Fraction-11 products of supercritical

n-decane pyrolysis at 570 °C and 94.6 atm have been separated by Method 3, and the reversed-phase HPLC chromatogram resulting from that separation appears in Figure 5. As in the

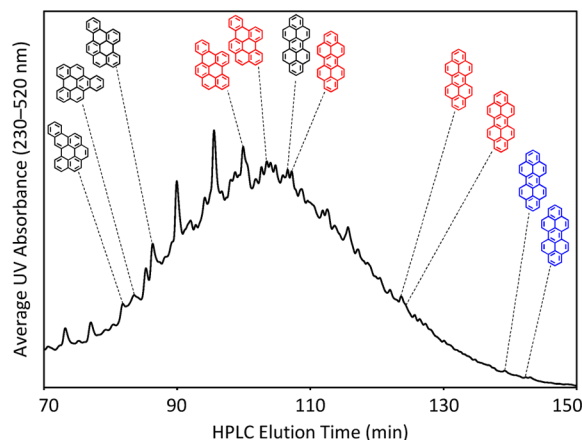


Figure 5. Reversed-phase HPLC chromatogram of Fraction 11 of the products of *n*-decane pyrolysis at 570 °C and 94.6 atm. This fraction contains $C_{26}H_{14}$ PAH and their alkylated derivatives. Black structures represent unsubstituted PAH, red structures represent singly-methylated PAH, and blue structures represent dimethylated or ethylated PAH.

case of Figure 1, each peak in Figure 5 that corresponds to an identified product has been labeled with the aromatic structure of that product, with unsubstituted PAH shown in black, singly-methylated PAH shown in red, and dimethylated or ethylated PAH shown in blue. As the structures of Figure 5 reveal, the *n*-decane pyrolysis products identified in Fraction 11 are composed of four unsubstituted $C_{26}H_{14}$ seven-ring perylene benzologues and seven of their alkylated derivatives. The UV spectra supporting these identifications are presented in Figure 6, as discussed in the following.

Figure 6a presents the UV spectrum of the Fraction-11 *n*-decane pyrolysis product eluting at 106.6 min in Figure 5, along with the UV spectrum of a reference standard of the $C_{26}H_{14}$ PAH dibenzo[*cd,lm*]perylene. The close matching of the product UV spectrum and the reference-standard spectrum in Figure 6a establishes that the product eluting at 106.6 min is dibenzo[*cd,lm*]perylene. Mass spectral evidence also establishes the molecular weight of this product as 326, consistent with the molecular formula $C_{26}H_{14}$ for the unsubstituted dibenzo[*cd,lm*]perylene. As indicated by three of the red structures and the two blue structures in Figure 5, three singly-methylated and two dimethylated or ethylated dibenzo[*cd,lm*]perylenes have also been identified among the components of Fraction 11.

The solid lines in Figures 6b, 6c, and 6d present the UV spectra of the Fraction-11 product components eluting at 81.9, 83.6, and 86.3 min, in Figure 5. The mass-spectral data show that each of these products has a molecular weight of 326, corresponding to unsubstituted $C_{26}H_{14}$ PAH. We do not have reference standards of $C_{26}H_{14}$ PAH whose UV spectra match those in Figures 6b–6d; however, the literature provides spectra of the three $C_{26}H_{14}$ PAH whose UV spectra do match those of the products in Figures 6b, 6c, and 6d: dibenzo[*b,ghi*]perylene,²⁵ naphtho[1,2,3,4-*ghi*]perylene,²⁷ and dibenzo[*e,ghi*]perylene.²⁶ At least a portion of each of these three published spectra has been recorded in the solvent benzene, which has a higher index of refraction than the Method-3

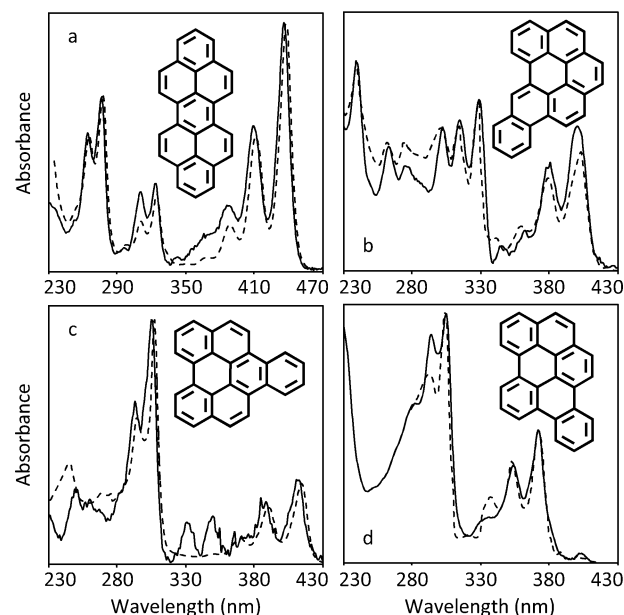


Figure 6. Comparisons of the UV spectra (solid lines) of *n*-decane pyrolysis products from the chromatogram of Fraction 11, in Figure 5, to reference spectra (dashed lines). Comparisons are shown for the products identified as (a) dibenzo[*cd,lm*]perylene, eluting at 106.6 min, (b) dibenzo[*b,ghi*]perylene, eluting at 81.9 min, (c) naphtho[1,2,3,4-*ghi*]perylene, eluting at 83.6 min, and (d) dibenzo[*e,ghi*]perylene, eluting at 86.3 min in Figure 5. The reference spectrum in (a) is from a reference standard of dibenzo[*cd,lm*]perylene. The reference spectra in (b), (c), and (d) are those published for dibenzo[*b,ghi*]perylene,²⁵ naphtho[1,2,3,4-*ghi*]perylene,²⁷ and dibenzo[*e,ghi*]perylene,²⁶ respectively, with a 4 nm shift applied to each spectrum or spectrum portion taken in benzene, as explained in the text. The UV spectra of the product components have been taken with HPLC separation Method 3 in Table 1. Additional minor absorbance features in the product-component spectra are due to unidentified co-eluting compounds.

mobile phase of acetonitrile/dichloromethane, the solvent mixture corresponding to the product-component spectra of Figures 6b–6d. As demonstrated by Oña and Wornat,^{33,34} due to benzene's higher index of refraction, the UV spectrum of a PAH taken in benzene is shifted about 4 nm to higher wavelengths, relative to the spectrum of the same PAH taken in acetonitrile/dichloromethane. Therefore, to compare UV spectra taken with these two different solvent compositions, one should shift the UV spectrum taken in benzene approximately 4 nm to lower wavelengths. In accordance with those findings,^{33,34} the published UV spectra (taken in benzene) of naphtho[1,2,3,4-*ghi*]perylene²⁷ and dibenzo[*e,ghi*]perylene²⁶ have each been digitized and shifted 4 nm to lower wavelengths, and the resulting reference spectra appear as the dashed lines in Figures 6c and 6d, respectively. In the case of the published spectrum of dibenzo[*b,ghi*]perylene,²⁶ only the portion above 280 nm was taken in benzene; the portion below 280 nm was in ethanol, whose index of refraction does not differ substantially from that of acetonitrile/dichloromethane. Therefore, in that case, only the benzene portion of the published spectrum²⁶ has been shifted 4 nm to lower wavelengths, and the resulting reference spectrum appears as the dashed line in Figure 6b. Despite a few minor interferences from unidentified components (particularly at 331 and 350 nm in Figure 6c), Figures 6b, 6c, and 6d each portray good agreement between the product-component spectrum and the

reference spectrum, and the identities of these three $C_{26}H_{14}$ products of *n*-decane pyrolysis are therefore established as dibenzo[*b,ghi*]perylene, naphtho[1,2,3,4-*ghi*]perylene, and dibenzo[*e,ghi*]perylene, respectively. As indicated by two of the red structures in Figure 5, UV and mass spectral evidence has also led to the identification of two singly-methylated dibenzo[*e,ghi*]perylene among the Fraction-11 products.

Altogether, four unsubstituted $C_{26}H_{14}$ seven-ring perylene benzologues—dibenzo[*cd,lm*]perylene, dibenzo[*b,ghi*]perylene, naphtho[1,2,3,4-*ghi*]perylene, and dibenzo[*e,ghi*]perylene—and seven of their alkylated derivatives have been identified in Fraction 11 as products of supercritical *n*-decane pyrolysis. None of the four $C_{26}H_{14}$ PAH or their alkylated derivatives have ever before been identified as products of *n*-decane pyrolysis.

$C_{28}H_{14}$ and $C_{30}H_{14}$ PAH and Their Alkylated Derivatives. As indicated in Table 1, Fractions 12 and 13 of the products of *n*-decane pyrolysis at 570 °C and 94.6 atm have each been analyzed by separation Method 4, and the resulting HPLC chromatograms appear in Figures 7 and 8, respectively.

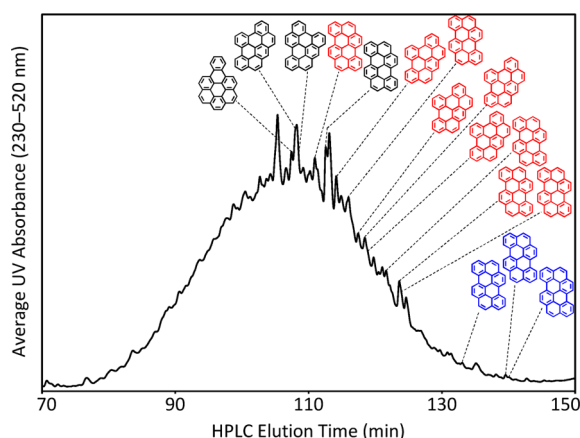


Figure 7. Reversed-phase HPLC chromatogram of Fraction 12 of the products of *n*-decane pyrolysis at 570 °C and 94.6 atm. This fraction contains $C_{28}H_{14}$ PAH and their alkylated derivatives. Black structures represent unsubstituted PAH, red structures represent singly-methylated PAH, and blue structures represent dimethylated or ethylated PAH.

Each peak in Figures 7 and 8 that corresponds to an identified product has been labeled with the aromatic structure of that product, with unsubstituted PAH shown in black, singly-methylated PAH shown in red, and dimethylated or ethylated PAH shown in blue. As the structures in Figures 7 and 8 reveal, the identified products in Fraction 12 are composed of four unsubstituted $C_{28}H_{14}$ eight-ring perylene benzologues and some of their alkylated derivatives; those in Fraction 13 are composed of an unsubstituted $C_{30}H_{14}$ nine-ring PAH and some of its methylated derivatives. The UV spectra establishing the identifications of the products in Figures 7 and 8 appear in Figure 9.

Figures 9a, 9b, and 9c present the UV spectra of the Fraction-12 products of *n*-decane pyrolysis that elute at 107.4, 108.0, and 112.6 min, respectively, in Figure 7; Figure 9d presents the UV spectrum of the Fraction-13 product eluting at 128.7 min in Figure 8. Along with the product-component spectra in Figures 9a, 9c, and 9d are the UV spectra of reference standards of the $C_{28}H_{14}$ benzo[*a*]coronene, the $C_{28}H_{14}$ benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, and the $C_{30}H_{14}$

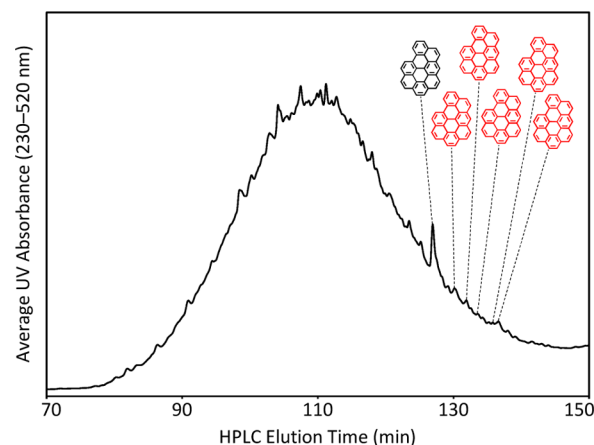


Figure 8. Reversed-phase HPLC chromatogram of Fraction 13 of the products of *n*-decane pyrolysis at 570 °C and 94.6 atm. This fraction contains $C_{30}H_{14}$ PAH and their alkylated derivatives. Black structures represent unsubstituted PAH, and red structures represent singly-methylated PAH.

naphtho[8,1,2-*abc*]coronene, respectively. Figure 9b includes the published spectrum²³ of the $C_{28}H_{14}$ phenanthro[5,4,3,2-*efghi*]perylene, which has been recorded in a mixture of solvents (ethyl acetate and dichloromethane) whose refractive indices do not differ substantially from that of the acetonitrile/dichloromethane mixture used for the product-component spectrum in Figure 9b; hence no shifting of the published spectrum²³ is necessary. The close matching of the UV spectra of each product/standard pair in Figure 9a–9d establishes the identity of each of the four *n*-decane pyrolysis products as the respective eight- and nine-ring PAH shown. Mass spectral data reveal that the molecular weight of each of the products in Figure 9a–9c is 350 and that the molecular weight of the product in Figure 9d is 374—confirming that each of these identified PAH products is unsubstituted.

Figure 9e presents the UV spectrum of the Fraction-12 product eluting in Figure 7 at 108.2 min, slightly later than, but still co-eluting with, the product identified in Figure 9b as phenanthro[5,4,3,2-*efghi*]perylene. Using the same combination of HPLC stationary and mobile phases as in Method 4, McClaine et al.³⁵ have shown that—relative to the other identified $C_{28}H_{14}$ products of Figure 7—the $C_{28}H_{14}$ PAH benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene, a product of the supercritical pyrolysis of a synthetic jet fuel,³⁵ exhibits the same co-elution and elution behavior as the product component of Figure 9e. Included therefore with the product-component spectrum in Figure 9e are the published UV spectra of benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene²⁸ and phenanthro[5,4,3,2-*efghi*]perylene,²³ the co-elutant. Because these two published spectra have each been recorded in solvents whose refractive indices do not differ significantly from that of the acetonitrile/dichloromethane mobile phase used for the product component, neither published spectrum has been shifted in Figure 9e. As for the case of the co-eluting dibenzofluoranthenes in Figures 4g and 4h, the two published spectra in Figure 9e have been linearly combined to produce the composite reference spectrum shown as the dashed line in Figure 9f. The product-component spectrum from Figure 9e is duplicated as the solid line in Figure 9f. Aside from some minor discrepancies due to an unidentified co-eluting species, the composite and product spectra of Figure 9f match, establishing the identity of the product eluting at 108.2 min in Figure 7 as

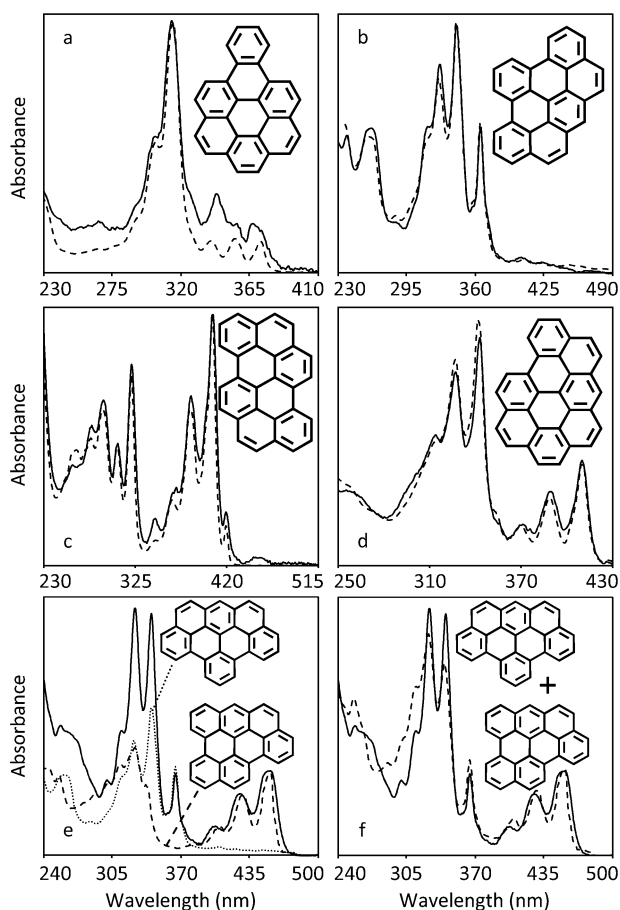


Figure 9. Comparisons of the UV spectra (solid lines) of *n*-decane pyrolysis products from the chromatograms of Fractions 12 and 13, in Figures 7 and 8, to reference spectra (dashed lines). Comparisons are shown for the products identified as (a) benzo[*a*]coronene, eluting at 107.4 min, (b) phenanthro[5,4,3,2-*efghi*]perylene, eluting at 108.0 min, and (c) benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, eluting at 112.6 min in Figure 7, as well as (d) naphtho[8,1,2-*abc*]coronene, eluting at 128.7 min in Figure 8. The spectrum of the two products co-eluting at 108.2 min in Figure 7 is shown in (e) with the reference spectra of benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene (dashed line) and phenanthro[5,4,3,2-*efghi*]perylene (dotted line) and in (f) with the composite (dashed line) of the two reference spectra. The reference spectra in (a), (c), and (d) are from reference standards of benzo[*a*]coronene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, and naphtho[8,1,2-*abc*]coronene, respectively. The reference spectra of phenanthro[5,4,3,2-*efghi*]perylene²³ in (b) and (e) and of benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene²⁸ in (e) are taken from the literature. The UV spectra of the product components have been taken with HPLC separation Method 4 in Table 1. Additional minor absorbance features in the product-component spectra in (a) and (f) are due to unidentified co-eluting compounds.

benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene, which partially co-elutes with the product already identified in Figure 9b as phenanthro[5,4,3,2-*efghi*]perylene. The mass spectral data reveal a molecular weight of 350, consistent with each of the co-eluting C₂₈H₁₄ products being unsubstituted.

As suggested by the red and blue structures in Figure 7, UV and mass spectral data additionally reveal the presence of several alkylated derivatives of two of the C₂₈H₁₄ PAH products in Fraction 12: five singly-methylated benzo[*pqr*]naphtho[8,1,2-*bcd*]perylenes, four singly-methylated phenanthro[5,4,3,2-*efghi*]perylenes, and three dimethylated or ethylated

benzo[*pqr*]naphtho[8,1,2-*bcd*]perylenes. Likewise, the five red structures in Figure 8 show that five singly-methylated naphtho[8,1,2-*abc*]coronenes have also been identified in Fraction 13.

Interestingly, one of the methylated derivatives in Fraction 12, the product eluting at 110.2 min in Figure 8, actually elutes before its unsubstituted parent, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene. The UV and mass spectral evidence confirm this identification, but the elution order is unusual among alkylated PAH. Typically, a methyl group causes a PAH to elute after its unalkylated parent compound, when the HPLC column and solvent combinations used in the present analyses are employed.³⁶ The most likely explanation for a methylated benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene eluting before its unsubstituted parent would be for the methyl group to be attached to a carbon that is in one of the two bay regions of the benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene structure. In such a case, the close proximity of an aryl hydrogen in the bay region would cause methyl-H/aryl-H interactions that would slightly distort, away from planar, the benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene aromatic structure. Non-planar PAH are known to elute earlier than planar PAH of the same molecular weight on C18 HPLC columns;³⁷ hence the early elution of a methylated benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene.

Altogether, one unsubstituted nine-ring C₃₀H₁₄ PAH, naphtho[8,1,2-*abc*]coronene, four unsubstituted eight-ring C₂₈H₁₄ PAH—benzo[*a*]coronene, phenanthro[5,4,3,2-*efghi*]perylene, benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene, and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene—along with 17 alkylated derivatives of these eight- and nine-ring PAH have been identified in Fractions 12 and 13 of the products of supercritical *n*-decane pyrolysis at 570 °C and 94.6 atm. None of these unsubstituted eight- or nine-ring PAH or their alkylated derivatives have ever previously been reported as products of *n*-decane pyrolysis.

Unresolved Aromatic Products. Inspection of the Fractions' chromatograms in Figures 1, 5, 7, and 8 reveals that most of the *n*-decane pyrolysis products whose resolution is sufficient to produce sharp chromatographic peaks and clean UV spectra have been identified. However, each Fraction's chromatogram also contains a broad "hump" of unresolved material that comprises a significant portion of that Fraction's composition. It is clear that the product components responsible for each hump are aromatic because they absorb UV light strongly (a property not shared with the primary products of *n*-decane pyrolysis, alkanes and alkenes) and because they interact with the cyano stationary phase of the HPLC column used in the first dimension of product separation. (Otherwise they would not elute off the cyano column at the same time as the identified products in these fractions.) However, beyond this basic information, little else is known about the composition of this undifferentiated material.

One possibility is that it is simply made up of additional alkylated derivatives of the PAH already identified as products of *n*-decane pyrolysis, especially as there are so many available positions for alkyl groups on the identified six- to nine-ring PAH. Many such alkylated derivatives would exhibit a high degree of structural similarity and would consequently not be easily differentiated by any HPLC column. The combination of a very high number of analytes and a lack of chromatographic resolution would lead to a single, amorphous hump, rather than sharp peaks.

Alternatively, the undifferentiated material could be PAH products that are neither benzenoid (having only six-membered rings, such as pyrene and perylene benzologues) nor fluoranthene benzologues (having six-membered rings and one internal five-membered ring). One such class of PAH is the fluorene benzologues, each of which contains a CH₂ methylene group in a five-membered ring. Fluorene and the methyl fluorenes are major PAH products of supercritical toluene pyrolysis;⁸ certain dibenzofluorenes and their methylated derivatives are major PAH products of supercritical 1-methylnaphthalene pyrolysis.³⁶ Given that unsubstituted and methylated fluorenes, benzofluorenes, dibenzofluorenes, and naphthofluorenes are among the three-, four-, and five-ring PAH already identified as products of supercritical *n*-decane pyrolysis,¹⁶ unsubstituted and methylated fluorene benzologues composed of six, seven, and eight or more rings are very likely products as well. With the huge number of possible isomers of such benzologues, it is unlikely that a complex mixture of unsubstituted and methylated fluorene-benzologue products would be resolved into well-defined peaks.

A third possibility is that bi-aryls (two aromatic groups joined by a single carbon-carbon bond) are formed in the supercritical *n*-decane pyrolysis environment. Bi-aryls and their methylated derivatives are among the highest-yield aromatic products of supercritical toluene pyrolysis⁸ and supercritical 1-methylnaphthalene pyrolysis,³⁶ at temperatures and pressures similar to those in the supercritical *n*-decane pyrolysis experiments. *n*-Decane would potentially form a far greater variety of bi-aryls than either toluene or 1-methylnaphthalene, due to the far greater variety of aromatic building blocks available in the supercritical *n*-decane pyrolysis environment. The very high number of possible unsubstituted and methylated bi-aryl products would make full chromatographic separation extremely difficult.

Of course, any combination of the above three possibilities, as well as another unconsidered alternative, could be responsible for the observed undifferentiated material. Considerable improvement in separation techniques would be necessary to permit any further determinations.

SUMMARY AND CONCLUSIONS

In order to improve understanding of the formation of solids in the pre-combustion environment of future high-speed aircraft, we have performed supercritical pyrolysis experiments with the model fuel *n*-decane in a flow reactor at temperatures between 530 and 570 °C and pressures between 40 and 94.6 atm. The PAH products of these experiments—precursors to solid deposits—have been separated by a two-dimensional HPLC technique and identified by UV/MS. The product analyses have led to the identification of 24 unsubstituted PAH with molecular weights greater than 300, and 43 of their alkylated derivatives.

The 24 identified unsubstituted products are composed of 15 six-ring C₂₄H₁₄ PAH, dibenzo[*a,e*]pyrene, dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*e,l*]pyrene, naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, naphtho[2,3-*e*]pyrene, benzo[*b*]perylene, dibenzo[*a,e*]fluoranthene, dibenzo[*a,k*]fluoranthene, dibenzo[*b,k*]fluoranthene, dibenzo[*j,l*]fluoranthene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*b*]fluoranthene, and naphtho[2,3-*j*]fluoranthene; four seven-ring C₂₆H₁₄ PAH, dibenzo[*b,ghi*]perylene, dibenzo[*cd,lm*]perylene, dibenzo[*e,ghi*]perylene, and naphtho[1,2,3,4-*ghi*]perylene; four eight-ring C₂₈H₁₄ PAH, benzo[*a*]coronene, benzo[*cd*]naphtho[3,2,1,8-

pqra]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, and phenanthro[5,4,3,2-*efghi*]perylene; and one nine-ring C₃₀H₁₄ PAH, naphtho[8,1,2-*abc*]coronene. Of the 24 unsubstituted products, only two, the six-ring PAH dibenzo[*a,e*]pyrene and dibenzo[*a,i*]pyrene, have been identified³² before as products of *n*-decane pyrolysis. None of the remaining 22 unsubstituted PAH and none of the 43 alkylated PAH have ever before been identified as products of *n*-decane pyrolysis or combustion. It is also the case that, for each of the nine unsubstituted and 24 alkylated seven- to nine-ring PAH identified here, it is the first time that any has been identified as a product of the pyrolysis of any pure alkane fuel.

The present work, in combination with our previous paper,¹⁶ has established the identities of 48 unsubstituted and 130 alkylated five- to nine-ring PAH products of supercritical *n*-decane pyrolysis at 570 °C, 94.6 atm, and 133 s. The fact that such large PAH can form from pyrolysis of an alkane at a temperature as low as 570 °C is a direct result of the high pressure that characterizes the supercritical *n*-decane pyrolysis environment. No alkane fuel, when pyrolyzed at atmospheric pressure, has ever been shown to produce such large PAH at such a low temperature. The relatively low temperature also ensures that no acetylene is formed, as our experiments confirm, so acetylene-addition mechanisms,³⁸ for the formation and growth of PAH under high-temperature conditions, play no role in the production of PAH in the supercritical *n*-decane pyrolysis experiments performed here. The mechanisms that are responsible for PAH formation in the supercritical *n*-decane pyrolysis environment are the subject of ongoing research and will be reported in future publications, along with the temperature- and pressure-dependent product yields of the PAH whose identities have now been established.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the United States Air Force Office of Scientific Research for support of this research: Grants FA9550-05-1-0253, FA9550-07-1-0033, FA9550-08-1-0281, and FA9550-10-1-0056. They also thank Dr. Arthur Lafleur and Ms. Elaine Plummer, of the Massachusetts Institute of Technology, and Dr. John Fetzer, of FETZPAHS, for reference standards and UV spectra of PAH.

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