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A large economic problem in petroleum processing, the plugging of catalytic hydrocracking units, led to a study of the production of large polycyclic aromatic hydrocarbons (PAHs) in this process. Through that work, many other studies of PAHs happened. These included the analysis of coal tar pitches, hydrothermal-vent bitumens, carbon black, Diesel particulate, and fullerene soots. Many new PAHs were synthesized or isolated during the course of these many studies.

Keywords Large polycyclic aromatic hydrocarbons, catalytic hydrocracking, coal tar, hydrothermal vent, perhydrocoronene, chromatographic retention

INTRODUCTION

I have been involved in many studies involving the large polycyclic aromatic hydrocarbons (PAHs). This article is a brief overview of some of these studies. Many more studies have occurred, including many investigations in which I was not directly involved; however, many of those studies resulted from the availability of these large PAHs through my own work. More detailed examples and discussions are included in

the book *Large (C ≥ 24) Polycyclic Aromatic Hydrocarbons—Chemistry and Analysis* (1).

My research career in the polycyclic aromatic hydrocarbons (PAHs) began in 1980 when I joined Chevron Research Company directly out of graduate school, where my dissertation work had dealt in the observation of isotopic effects of certain small molecules in their gas chromatography retention and in supercritical fluid extraction of carbonaceous materials. One of the first projects with Chevron involved the petroleum process known as catalytic hydrocracking.

I will describe this processing problem, how we solved it, and how this work resulted in many other studies in large PAHs.

Here is the history of the problem. Catalytic hydrocracking aims at turning large saturated hydrocarbons, such as those found in waxes and lubricating oils, into the smaller hydrocarbons sold as motor fuels (gasoline, diesel and jet fuels). The process typically involves two processing stages. A typical process scheme is shown in Figure 1. In the first stage, a feed that has already been treated to remove almost all of its heteroatoms (sulfur, nitrogen, metals, etc.) is passed through a catalytic bed. This catalyst is most often a transition metal loaded surface that cracks the saturated hydrocarbons, i.e., breaks the big ones into much smaller ones. The smaller targeted ones are distilled away and the residue is fed into the second stage, another catalytic bed containing a transition metal or precious metal that further cracks the saturated hydrocarbons. After distillation of the light hydrocarbons, the residue is mixed with first-stage residue and cycled back through the second stage. This is a continuous repetitive process until the catalyst loses its activity or a process problem requires shutdown.
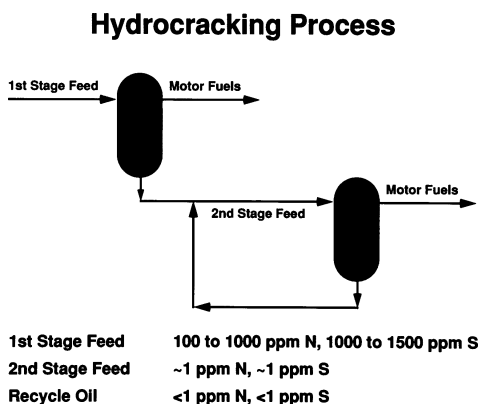
Hydrocracking Process

1st Stage Feed	100 to 1000 ppm N, 1000 to 1500 ppm S
2nd Stage Feed	~1 ppm N, ~1 ppm S
Recycle Oil	<1 ppm N, <1 ppm S

FIGURE 1. A typical two-stage petroleum hydrocracking unit.

In 1980 catalyst lifetimes, as measured in small-scale pilot plants, was 2 to 3 years. A particular process problem, however, mandated shutdowns after months, sometimes as often as every two or three months. A shutdown cost several hundred thousand US dollars to do and in lost production. In its own refineries and through the global licensing of its hydrocracker technology, Chevron had many dozens of hydrocracking units in operation. Thus, this was a multimillion dollar per year problem (2).

What was the nature of the problem? The recycle piping between the two units experienced severe plugging by a reddish-colored solid. It was thought that this residue was some type of PAH deposited there because the piping was cooler than the catalyst bed. The material could be rinsed with an alkane solvent to remove the entrained oil, leaving a red powder, which was insoluble in hot xylene, dichloromethane, acetone, or any other more polar solvent.

ANALYSIS THAT LED TO THE SOLUTION

In order to see what PAHs were present in the recycle oil, reversed-phase liquid chromatography (LC) was used to analyze the PAH fraction isolated from a normal-phase LC separation. A variety of normal phases were used including silica, alumina, Fluorosil, aminopropyl, and nitrile bonded phases. All of these phases were able to separate the PAHs from the saturated hydrocarbons. The reversed-phase material was a polymeric C18, which had been shown to separate PAH isomers. The initial work used a stop-flow scanning UV detector to collect the UV spectra of the PAHs. Later work involved the use of the diode-array UV detector (after it became commercially available in the early 1980s).

A variety of PAHs were found under various process conditions. Initially the PAHs were those found from the first-stage processing including the unsubstituted and lightly methylated versions of benzene, naphthalene, phenanthrene, and pyrene (start-of-run conditions). As the recycle time increased similar species were found of benzo[e]pyrene, benzo[ghi]perylene, and coronene (mid-run conditions). During end-of-run conditions many more large PAHs were observed including benzo[a]coronene, benzo[pqr]naphtho[8,1,2-bcd]perylene, naphtha[8,1,2-abc]coronene, ovalene, dibenzo[cd,lm]perylene, naphtha[8,1,2-bcd]perylene, dinaphtho[2,1,8,7-defg:2′,1′,8′,7′-ijkl]pentaphene and dinaphtho[2,1,8,7-defg:2′,1′,8′,7′-opqr]pentacene. For the latter four compounds there were also partially-hydrogenated intermediates where two rings of the last two PAHs were saturated into versions of the seven-ring structures.
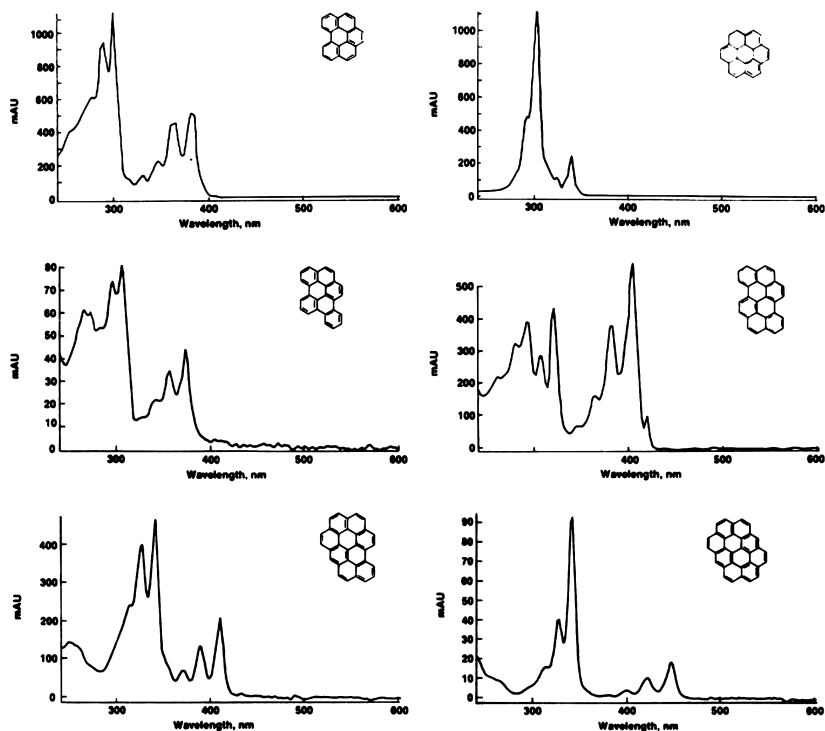
These particular large PAHs point to two separate formation mechanisms. The first is a series of one-ring additions resulting from two specific addition mechanisms. If there is a bay region, two carbons are added to make a six-member ring. Thus, phenanthrene goes to pyrene and benzo[e]pyrene goes to benzo[ghi]perylene. If the PAH has no bay region, then four carbons are added to the outer face of highest electron density. Thus pyrene goes to benzo[e]pyrene and benzo[ghi]perylene

FIGURE 2. One-ring buildup scheme found in hydrocracker oil samples.

FIGURE 3. The HPLC diode-array UV spectra collected that showed the one-ring buildup route.

goes to coronene. Part of the reaction scheme results in the PAHs that Clar called the "naphthalene zigzag" peri-condensed structures of two, four, six, eight, and ten rings that show a pattern of repeated offset condensed of two rings. Figure 2 shows the associated formation route found from these analyses and Figure 3 shows the UV spectra of these typical PAHs.

One specific part of this ring addition scheme was particularly interesting (3). Dibenzo[e,ghi]perylene gas has three bay regions. Addition of two carbons to each results in three different eight-ring isomers (Figure 4). Prior to this work, only two of the isomers were known. The third isomer was isolated, despite eluting extremely close the benzo[a]coronene. Mass spectral analysis showed it to be the expected 350 daltons and comparison to known PAH UV spectra and applying Clar's annelation theory proved that it was the third isomer (Figure 5).

The second reaction is the condensation of two pyrene molecules to form the two nine-ring isomers, dinaphtho[2,1,8,7-defg:2′,1′,8′,
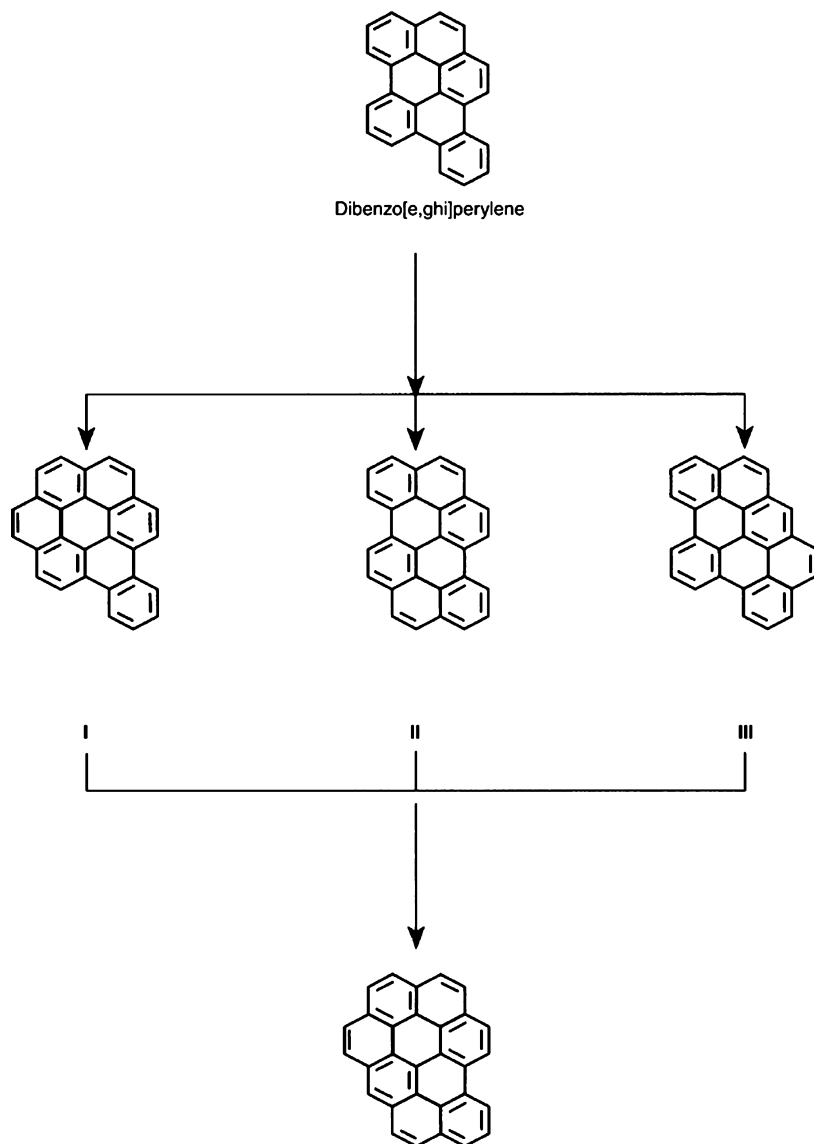
Dibenzo[e,ghi]perylene

I II III

FIGURE 4. Closeup of the conversion of dibenzo[e,ghi]perylene.

7′-ijkl]pentaphene and dinaphtho[2,1,8,7-defg:2′,1′,8′,7′-opqr]penta-
cene. Subsequent hydrogenation of these isomers and removal of those
saturated rings gives the two seven ring PAHs dibenzo[cd,lm]perylene
and naphtha[8,1,2-bcd]perylene. Dibenzo [cd,lm]perylene is heavily
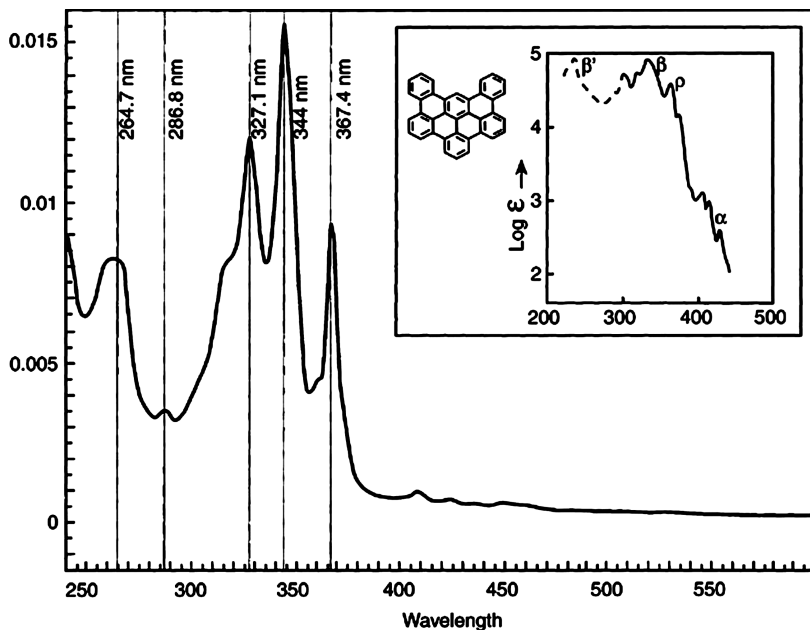
FIGURE 5. The new PAH found in this work and its UV spectrum.

favored in this scheme, being about twenty times greater in abundance. The UV spectra of the large PAHs found and the reaction scheme are shown in Figures 6 and 7.

The condensation of pyrene on alumina is a well-known organic reaction, a variation of the Scholl condensation, which is a Freidel-Crafts type reaction. This reaction was first done in 1905 by reacting naphthalene in heated aluminum chloride to yield perylene. A few other PAHs undergo Scholl condensation, including coronene. Boente reported that coronene gives a red, highly insoluble product, which he trivially named "dicoronylene" (benzo[1,2,3-bc:4,5,6-b′c′]dicoronene) (Figure 8).

This intractable molecule is sparingly soluble in hot 1,2,4-trichlorobenzene. When an authentic sample of dicoronylene was compared to a solution of the red hydrocracker deposit, the fluorescence excitation spectra matched (Figure 9). A mass spectrum of the deposit could now be obtained, knowing that it needed to be vaporized directly into the mass spectrometer source with high temperature. This analysis gave the mass spectrum with the characteristic ion at 596. There is one additional main product found in the deposits besides dicoronylene and its polymethyl derivatives. Ovalene produced in the one-ring buildup also
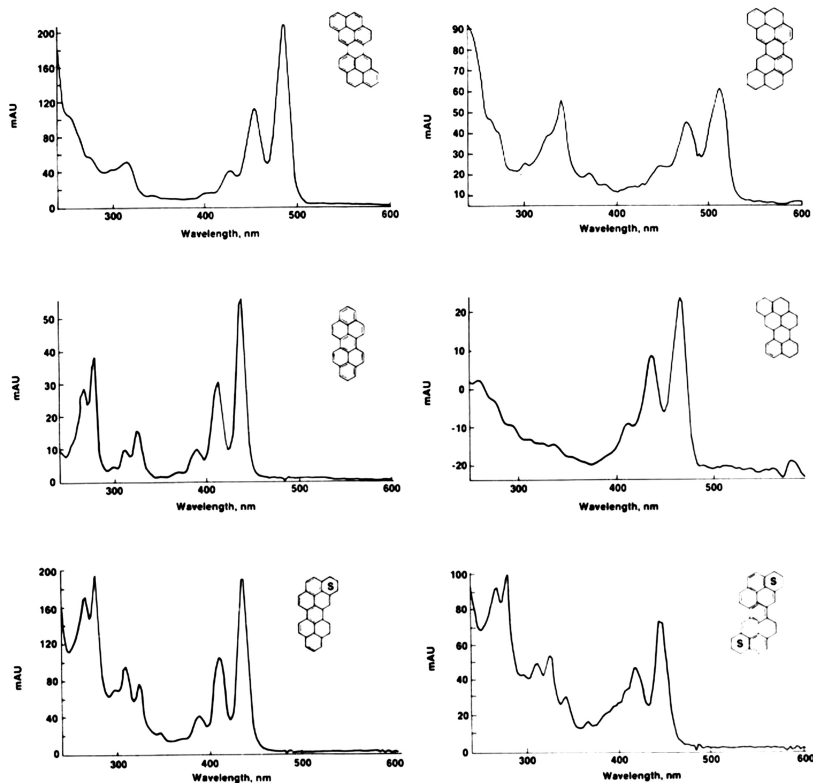
FIGURE 6. HPLC diode-array UV spectra collected at end-of-run conditions showing the additional PAHs.

is subject to Scholl condensation and the cross-product with coronene is seen in the mass spectrum at 684 daltons. This 18-ring PAH has a high wavelength fluorescence band at 545 nm.

With such specific composition of the deposit, the large number of hydrocracker plants worldwide, and a production rate of several hundred kilograms of deposit per hydrocracker, dicoronylene and the larger coronylovalene are produced in many metric tons per year and the accumulated amounts of these large PAHs must be in the thousands of metric tons.

With the identity of the deposit now known, monitoring methods using synchronous-scanning fluorescence were developed, as well as an approach to its prevention. Within a few years these deposits were no longer a major refining issue (4, 5).
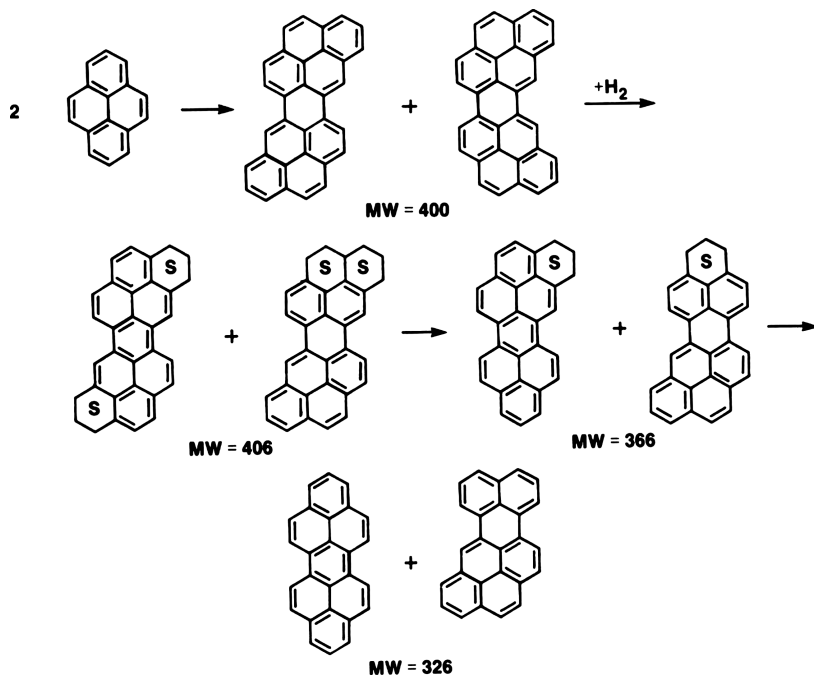
FIGURE 7. The second reaction scheme, seen at end-of-run, and involving condensation of pyrene and subsequent hydrogenation of the product PAHs.

THE LARGE PAH RESEARCH THAT ALSO RESULTED

In the course of the work described previously, several authentic standards of large PAHs were synthesized. As a consequence of these syntheses, many more large PAHs were either made in similar reactions or obtained through bartering with other researchers.

The reaction to make the standard of dibenzo[cd,lm]perylene is known as the Clar reaction. It involves the condensation and reduction of the three-ring cyclic ketone perinaphthenone (Figure 10). Clar also used other similar benzologous ketones to make several other PAHs. In these
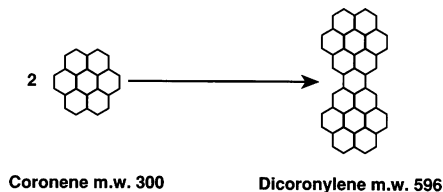

FIGURE 8. The Scholl condensation of coronene.
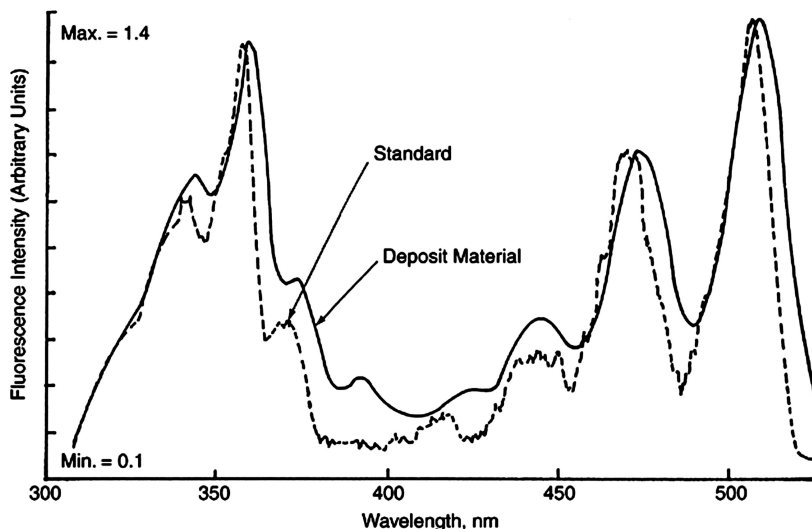
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FIGURE 9. The fluorescence spectrum of an authentic dicoronylene sample and of a hydrocracker deposit.

syntheses only one ketone was used in each reaction, while for the new work binary mixtures were used (6). This work was replicated, but the products were separated using LC and characterized by more modern spectroscopic techniques than were available to Clar (7). Figure 11 shows the four ketones used in these syntheses. In these repeated syntheses two previously missed isomers of nine and eleven rings (molecular weights 426 and 474) were found (8). In these cases, the structures of the newly found isomers were very similar to one found by Clar, but not separable by the adsorption chromatography technique that he and his coworkers used. Modern reversed-phase LC with polymeric C-18 separated the isomers. Clar also did not see these isomers because their UV and fluorescence bands are very similar to the other isomer.

Cross reaction of mixtures of two ketones resulted in over thirty new PAHs being found (9). Isolation with the LC techniques and
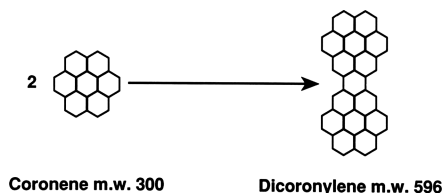

Coronene m.w. 300   Dicoronylene m.w. 596

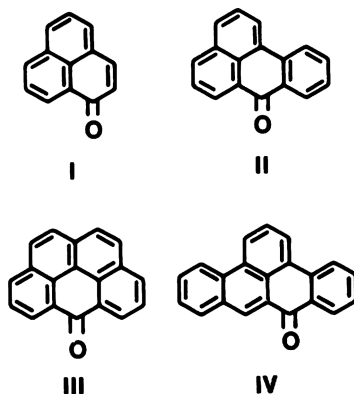**FIGURE 10.** The Clar reaction to for dibenzo[cd,lm]perylene.

FIGURE 11. The four ketones used in the syntheses.

characterization using spectrometric methods were much simpler and definitive than in the earlier work of Clar. Figure 12 shows three PAHs synthesized, with the middle isomer being a new structure. Some of the more interesting of these reactions will be described individually.

The reaction of perinaphthenone and benzo[fg]naphthacenone gave the expected tetrabenzo[a,cd,f,lm]perylene. Its nonplanarity made it elute very early. After isolation, however, an anomaly was found. Although the fluorescence excitation spectrum appeared to be the expected pattern of increasing intensity for the bands in the highest wavelength group, the UV spectrum showed a different pattern (Figure 13). The highest wavelength band was much smaller than in the fluorescence excitation spectrum and did not have the expected pattern of increasing intensity found for most similar PAHs. Molecular modeling hinted at an answer. When the structure is reduced to its lowest strain conformation, two structures result that differ only by small energies (the value varied with the modeling program, but was typically less than 5 kcal). One structure reduced the steric strain through twisting in the center ring, while the other folded in this area (Figure 14 and 15). Subsequent collaborations using both Shpol'skii spectrometry (11) and polarized light spectrometry (12) found that both isomers are present in the room temperature solution. The UV anomaly arises through interconversion.

As with the smaller PAHs, non-planarity in the large PAHs affects the retention in reversed-phase LC. Some of the large PAHs produced eluted extremely early on polymeric reversed-phase LC columns. For example hexabenzo[a,cd,f,j,lm,o]perylene eluted close to pyrene, although it has eleven rings to pyrene's four.
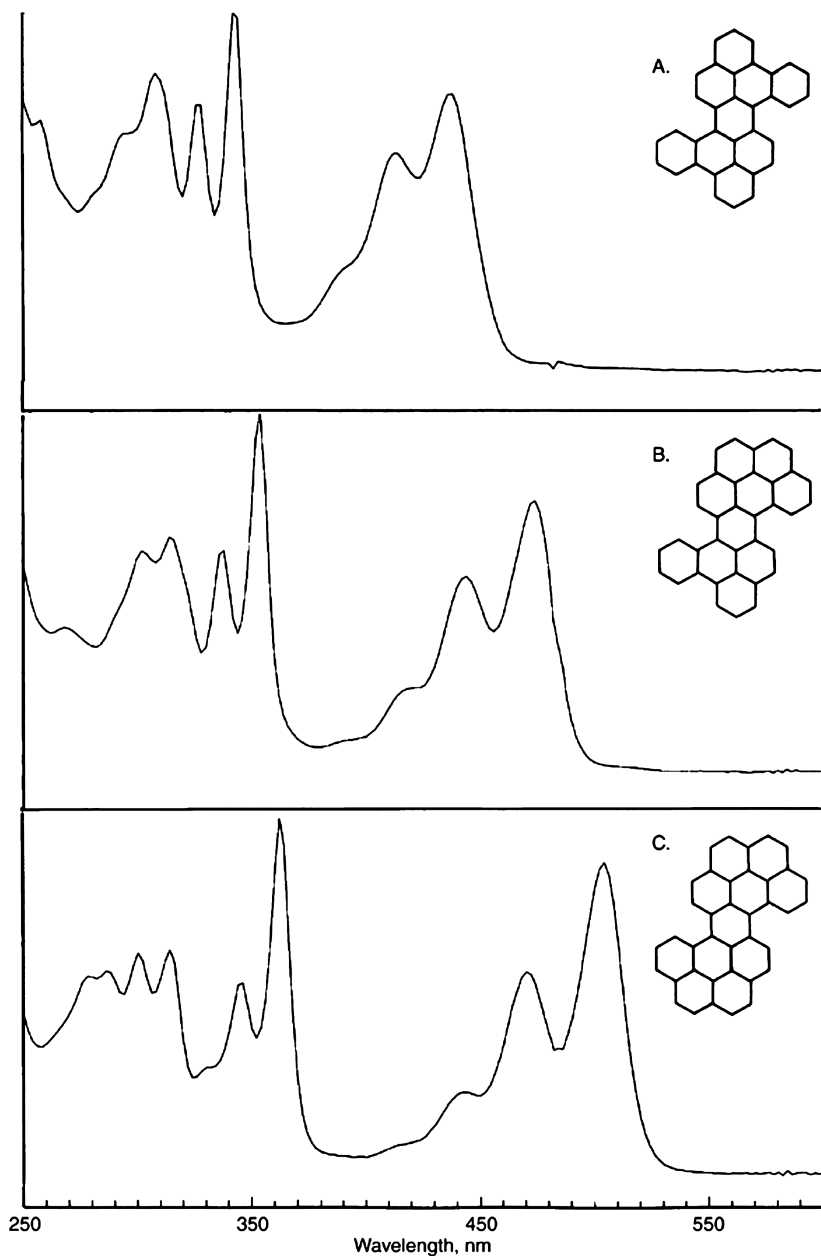
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FIGURE 12. Three of the PAHs synthesized. The middle one isomer was a previously unidentified new PAH.
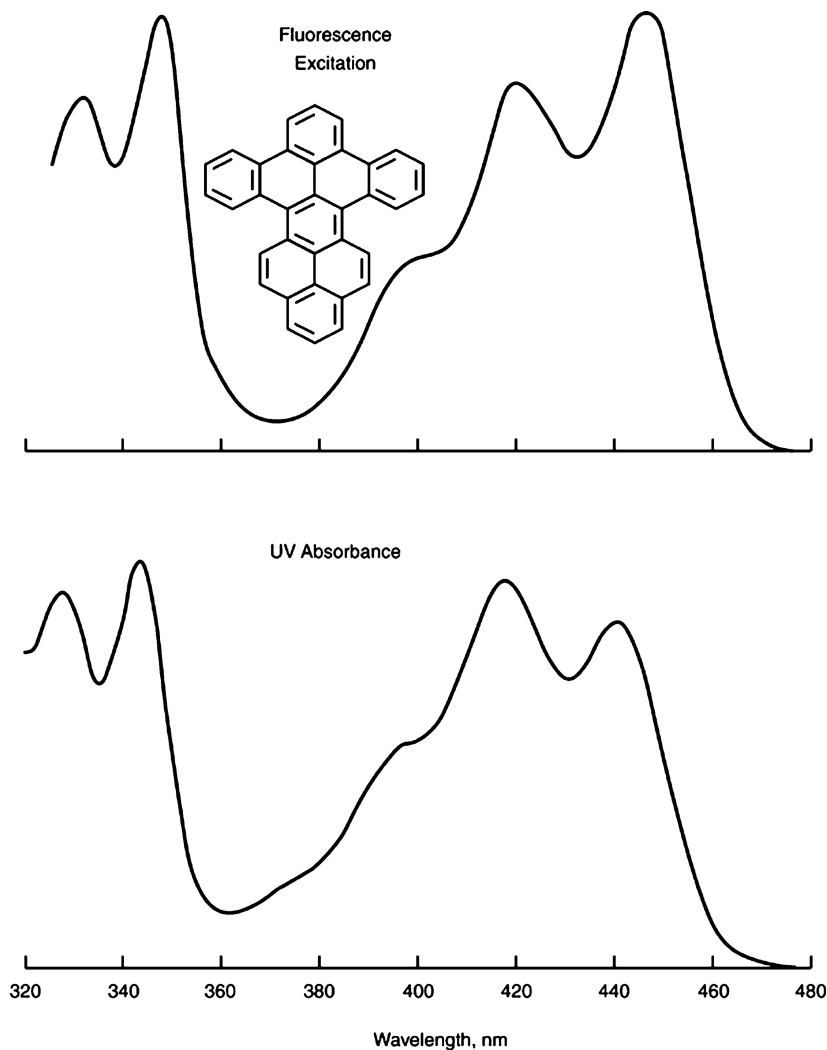
FIGURE 13. Anomalous UV spectra pattern of tetrabenzo[a,cd,f,lm] perylene.

Another interesting PAH was found serendipitously because of the extreme retention differences of nonplanar and planar isomers. In the cross reaction of perinaphthenone and benzanthrone, the main new product was tribenzo[a,cd,lm]perylene. There were also the individual PAHs resulting from each ketone reacting with another molecule of its kind. After numerous LC runs, the column was cleaned by flushing
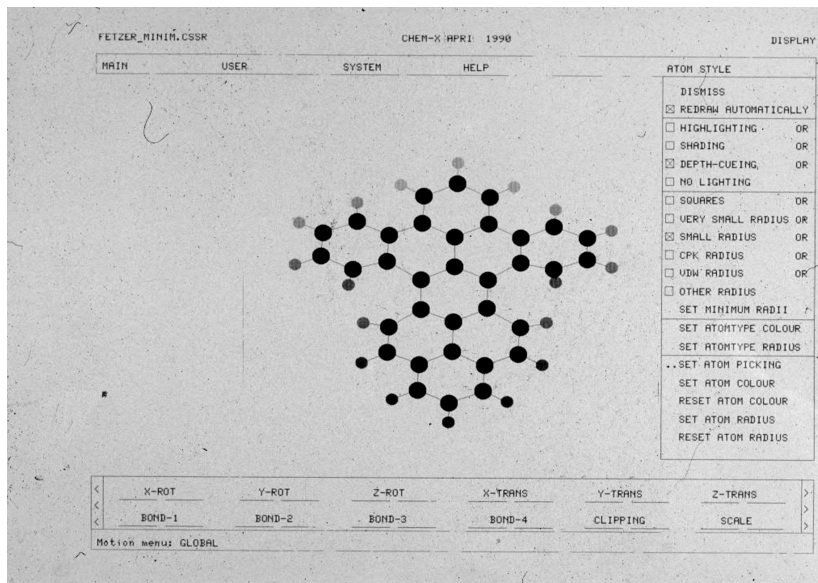
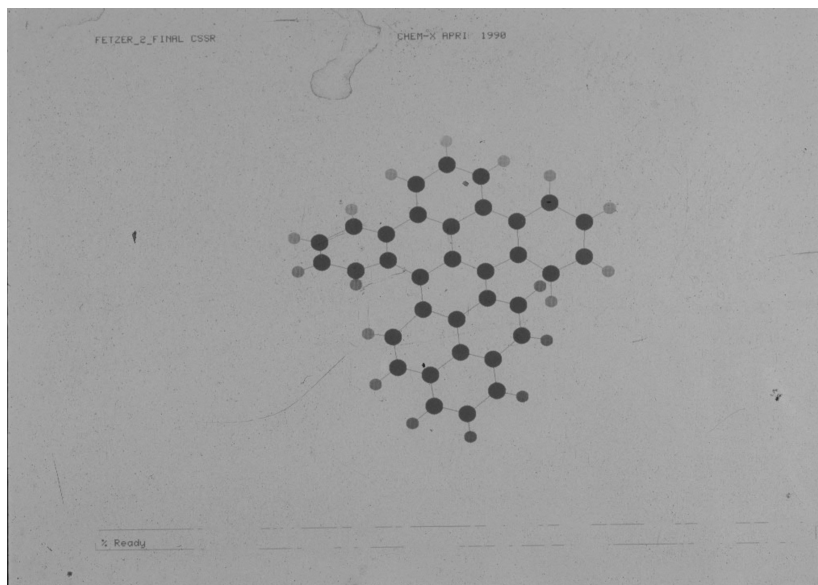**FIGURE 14.** The folded configuration of tetrabenzo[a,cd,f,lm]perylene.

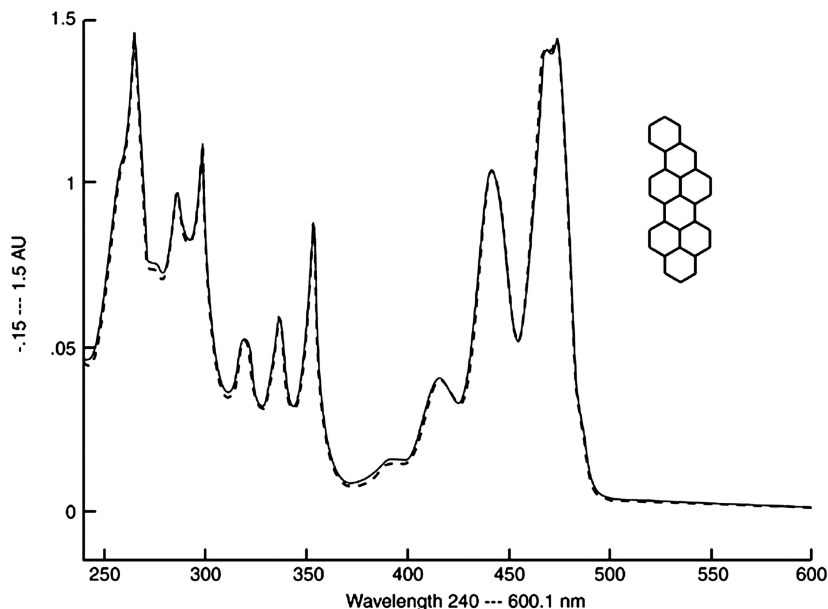**FIGURE 15.** The twisted configuration of tetrabenzo[a,cd,f,lm]perylene.

FIGURE 16. The PAH discovered by accident. The long structure eluted much later than any other product.

with pure dichloromethane. After several column volumes of this very strong solvent, strongly retained impurities were eluted. A chance look at the detector output showed a UV spectrum characteristic of a PAH (Figure 16). This compound was collected through several preparative runs using dichloromethane as the eluent. It was found to be the very long and planar isomer benzo[rst]naphtha[8,1,2-cdepentaphene (7).

The solvent interaction with some of these nonplanar PAHs can also create interesting retention in LC. Weaker solvent interactions are reflected in more steric interaction and more nonplanarity. Strong solvents resulted in a more planar configuration. This resulted in retention reversals of similarly structured PAHs as solvent composition was changed (Figure 17). Subsequent NMR studies showed that the steric interactions were less in strong solvent (8, 9, 13).

LARGE PAH OCCURRENCE STUDIES

In addition to the work on hydrocracker oils, several other types of materials were analyzed for large PAHs including extracts of diesel exhaust particulate (14, 15), coal tar pitches (16), carbon black (17), fullerene
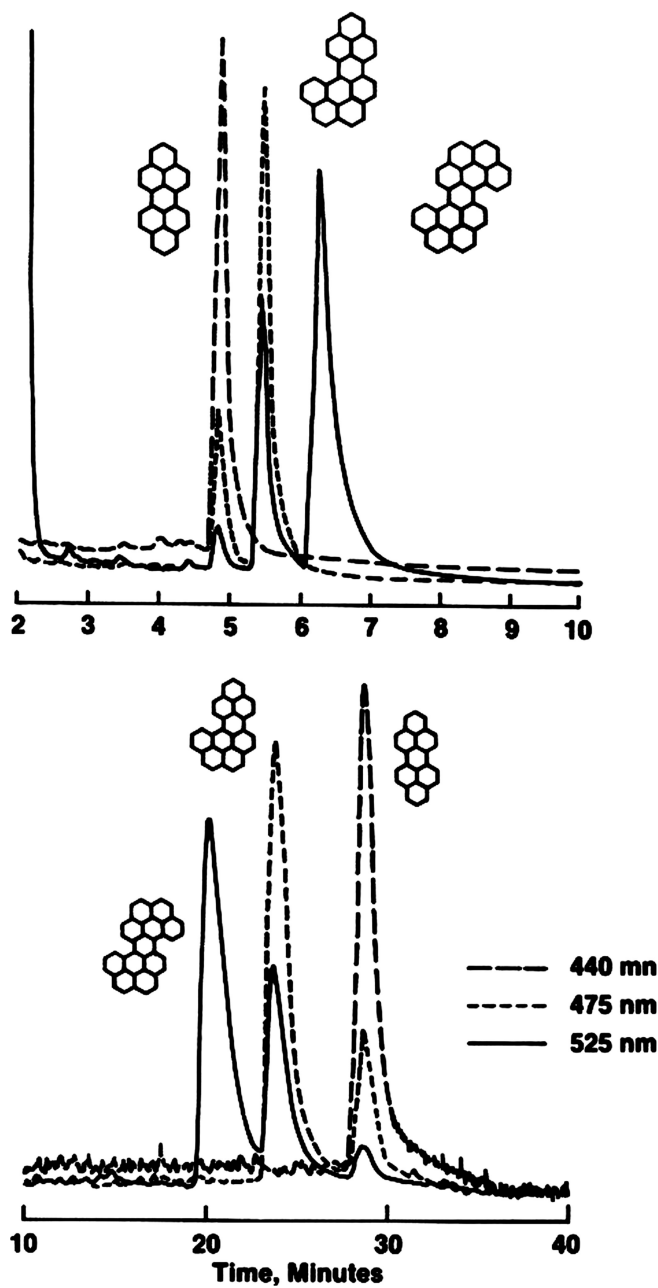
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FIGURE 17. The retention reversal of three PAHs when the mobile phase is changed from weak to strong.
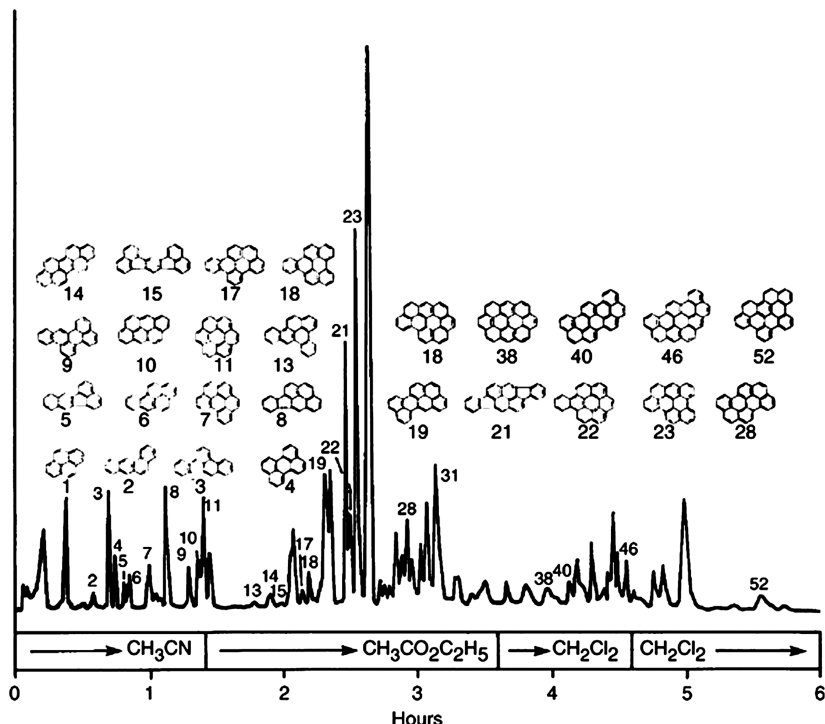
FIGURE 18. The many large PAHs found in a carbon black extract through comparison to authentic standard PAHs.

soot (18), and deep-sea hydrothermal vent bitumens (19–21). A chromatogram of the carbon black extract is shown in Figure 18.

Basic studies into polarized light spectrometry (22–24), matrix-isolation narrow-line spectrometry in perhydrocoronene (25–27), X-ray edge spectrometry (28), radical cation solution chemistry (29), fluorescence behavior (30–33), and liquid chromatography retention (34–36) also resulted from the sharing of these large PAHs.

REFERENCES

1. J. C. Fetzer, *The Chemistry and Analysis of the Large Polycyclic Aromatic Hydrocarbons*, New York: John Wiley and Sons, (2000), pp. 1–288.
2. J. C. Fetzer, The Production of Large Polycyclic Aromatic Hydrocarbons During Catalytic Hydrocracking in M. Absi-Halabi, J. Besharah, H. Qabazard, and A. Stanislaus (Eds.), *Catalysts in Petroleum and Petrochemical Processing 1995*, Amsterdam: Elsevier (1996) p. 263–271.

 3. J. C. Fetzer and W. R. Biggs, Identification of a New Eight-Ring Condensed Poly-cyclic Aromatic Hydrocarbon, *Polycyclic Arom. Compd.* 5 (1994):193–199.

 4. J. C. Fetzer and D. G. Lammel, Hydrocracking Process With Polynuclear Aromatic Dimer Foulant Adsorption, US Patent 5,190,633, March 2, 1993.

 5. J. C. Fetzer, J. M. Rosenbaum, R. W. Bachtel, D. R. Cash, and D. G. Lammel, Hydro-cracking Process With Polycyclic Aromatic Dimer Removal, US Patent 5,232,577, August 3, 1993

 6. J. C. Fetzer and W. R. Biggs, The Synthesis of Peropyrene Type Polycyclic Aromatic Hydrocarbons, *Org. Prep. Proced. Intern.* 20 (1988):223–230.

 7. J. C. Fetzer, Beyond Clar: The Use of Modern Analytical Methods for Large Poly-cyclic Aromatic Hydrocarbons, *Polycyclic Arom. Compd.* 14 (1999):1–10.

 8. J. C. Fetzer and W. R. Biggs, Liquid Chromatographic Retention Behavior of Large Fused Polycyclic Aromatics: Normal Bonded Phases, *J. Chromatogr.* 346 (1985):81–92.

 9. J. C. Fetzer and W. R. Biggs, Retention Behavior of Large Polycyclic Aromatics in Bonded Phase High Performance Liquid Chromatography, *J. Chromatogr.* 386 (1987):87–101.

10. J. C. Fetzer and W. Schmidt, Comparison of the Electronic Spectrometry of Two Similar Tetrabenzoperylene Isomers, *Spectrochim. Acta A* 45A (1989):503–505.

11. F. J. Morgan, R. Lamotte, P. Garrigues, and J. C. Fetzer, Resolved Absorption and Fluorescence Spectra of Two Tetrabenzoperylene Isomers in n Alkane Matrices at Low Temperature: Evidences for Non Planar Conformations, *Polycyclic Arom. Compds.* 2 (1991):141–153.

12. J. Waluk, J. Fetzer, S. J. Hamrock, and J. Michl, Evidence for Confor-mational Equilibrium in an Unsubstituted Benzenoid Hydrocarbon, Tetra-benzo[a,cd,f,lm]perylene, *J. Phys. Chem.* 95 (1991):8660–8663.

13. K. Jinno, S. Shimura, N. Tanaka, M. Kimata, J. C. Fetzer, and W. R. Biggs, Planarity Recognition of Large Polycyclic Aromatic Hydrocarbons by Various Octadecyl Stationary Phases in Non Aqueous Reversed Phase Liquid Chromatography, *Chro-matographia* 27 (1989):285–291.

14. J. C. Fetzer, W. R. Biggs, and K. Jinno, HPLC Analysis of the Large Polycyclic Aromatic Hydrocarbons in a Diesel Particulate, *Chromatographia* 21 (1986):439–442.

15. K. Jinno, J. C. Fetzer, and W. R. Biggs, Identification of Naphtho[8,1,2abc]coronene in the Extract of Diesel Particulate Matter by Non Aqueous Reversed Phase Liquid Chromatography with Multichannel Detector, *Chromatographia* 21 (1986):274–276.

16. J. C. Fetzer and J. R. Kershaw, The Identification of Large PAHs in a Coal Tar Pitch, *Fuels* 74 (1995):1533–1536.

17. J. C. Fetzer and C. E. Rechsteiner, The Analysis of the Large PAH in Various Pyrolytic Products, *Polynuclear Aromatic Hydrocarbons: Eleventh International Symposium*, M. Cooke, K. Loening, and J. Merritt (Eds.), Columbus, Ohio: Battelle Press, (1991), pp. 259–270.

18. M. T. Beck, J. C. Fetzer, and S. Keki, Formation of PAHs and C-60 as Intermediates in the Carbonization of Liquid Toluene and Benzene Upon the Effect of Electric Discharges, *Carbon* 32 (1994):795–799.

19. J. C. Fetzer, B. R. T. Simoneit, H. Budzinski, and P. Garrigues, Identification of Large PAHs in Bitumens from Deep-Sea Hydrothermal Vents, *Polycyclic Arom. Compd*. 9 (1996):109–120.

20. B. R. T. Simoneit and J. C. Fetzer, High Molecular Weight Polycyclic Aromatic Hydrocarbons in Hydrothermal Petroleums, *Organic Geochememistry: Developments and Applications to Energy, Climate, Environment and Human History*, J. O. Grimalt and C. Dorronsoro, (Eds.), A. I. G. O. A., Donostia, San Sebastian, Spain (1995), pp. 414–417.

21. B. R. T. Simoneit and J. C. Fetzer, High Molecular Weight Polycyclic Aromatic Hydrocarbons in Hydrothermal Petroleums from the Gulf of California and Northeast Pacific Ocean, *Org. Geochem*. 24 (1996):1065–1077.

22. J. Marczyk, J. Waluk, and J. Fetzer, Electronic States and Structure of Benzo[lm]Phenanthro[5,4,3-abcd]perylene, *Acta Physica Polonica*. 88 (1995): 295–304.

23. J. Marczyk, J. Waluk, and J. C. Fetzer, Determination of Structure of Nonplanar Polycyclic Aromatic Hydrocarbons by Polarized Spectroscopy, *Polycyclic Arom. Compd*. 9 (1996):283–290.

24. J. Marczyk, J. C. Fetzer, J. Szubiakowski, and J. Waluk, Luminescence Anisotropy and Linear Dichroism Studies of Large Polycyclic Aromatic Hydrocarbons Based on the Perylene Chromophore, *J. Luminesc*. 72–74 (1997): 517–519.

25. J. C. Fetzer and M. Zander, The Fluorescence, Phosphorescence, and E Type Delayed Fluorescence of Hexabenzo[bc,ef,hi,kl,no,qr}coronene, *Z. Naturforsch., A: Phys. Sci*. 45 (1990):727–729.

26. J. C. Fetzer and M. Zander, On the Use of Perhydrocoronene as a Matrix in the Luminescence Spectroscopy of Polycyclic Aromatic Hydrocarbons, *Z. Naturforsch., A: Phys. Sci*. 45 (1990): 814–816, correction Z. Naturforsch., *A: Phys. Sci*., 45 (1990):1218.

27. J. C. Fetzer, W. R. Biggs, and M. Zander, Preparation and Purification of Perhydrocoronene for Use as a Spectroscopic Matrix, *Z. Naturforsch., A: Phys. Sci*. 46 (1991):291–292.

28. U. Bergmann, H. Groenzin, O. C. Mullins, P. Glatzel, J. C. Fetzer, and S. P. Cramer, Carbon K-Edge X-Ray Raman Spectroscopy Applied to Aromatic Hydrocarbons and Asphaltenes, *Chem. Phys. Lett*. 369 (2003):184–191.

29. K. K. Laali, M. Tanaka, and J. C. Fetzer, Persistent Oxidation Dications of Dialkyl- and Tetraalkylperylenes and Dibenzo[cd.lm]perylene; Charge Distribution Mode, Substitution Effects and Conformational Aspects, *J. Chem. Soc., Perkin Trans* 2 (1997):1315–1318.

30. R. Waris, M. A. Rembert, D. M. Sellers, W. E. Acree, Jr., K. W. Street, Jr., C. F. Poole, P. H. Shetty, and J. C. Fetzer, Polycyclic Aromatic Hydrocarbon Solvent Probes: Effect of Solvent Polarity on the Ovalene and Benzo[ghi]perylene Florescence Emission Fine Structures, *Appl. Spectrosc*. 42 (1988):1525–1531.

31. R. Waris, K. W. Street, Jr., W. E. Acree, Jr., and J. C. Fetzer, Polycyclic Aromatic Hydrocarbons Solute Probes: 4. Effect of Solvent Polarity on the Fluorescence Emission Fine Structures of Select Pyrene and Pentaphene Derivatives, *Appl. Spectrosc*. 43 (1989):845–850.

32. K. W. Street, Jr., W. E. Acree, Jr., J. C. Fetzer, P. H. Shetty, and C. F. Poole, Poly-
     cyclic Aromatic Hydrocarbons Solute Probes: 5. Fluorescence Spectra of Pyrene,
     Ovalene, Coronene and Benzo[ghi]perylene Dissolved in Liquid Alkylammonium
     Thiocyanate Organic Salts, *Appl. Spectrosc.* 43 (1989):1149–1153.

33. S. A. Tucker, W. E. Acree, Jr., K. W. Street, Jr., and J. C. Fetzer, Polycyclic Aro-
     matic Hydrocarbons Solute Probes: 3. Fluorescence Emission Spectra of Pyrene,
     Ovalene, Benzo[ghi]perylene, and Coronene Dissolved in Liquid Tetrabutylammo-
     nium Sulfonate Salts, *Appl. Spectrosc.* 43 (1989):162–164.

34. K. Jinno, T. Ibuki, H. Lamparczyk, M. Okamoto, N. Tanaka, J. C. Fetzer, and
     W. R. Biggs, Study on Retention Behavior of Peropyrene Type Polycyclic Aromatic
     Hydrocarbons with Various Bonded Stationary Phases in Reversed Phase Liquid
     Chromatography, *Chromatographia* 25 (1988):483–486.

35. K. Jinno, T. Katoh, M. Okamoto, J. C. Fetzer, and W. R. Biggs, Retention Pre-
     diction of Large and Condensed Polycyclic Aromatic Hydrocarbons in Reversed
     Phase Microcolumn Liquid Chromatography with Diphenyl Silica Stationary Phase,
     J. High Resol. Chromatogr. Chromatogr. Commun. 11 (1988):33–38.

36. K. Jinno, T. Ibuki, J. C. Fetzer, W. R. Biggs, P. R. Griffiths, and J. M. Ollinger, Spec-
     troscopic Investigation on Planarity Recognition of Polycyclic Aromatic Hydrocar-
     bons with Polymeric Octadecylsilica in Reversed Phase Liquid Chromatography,
     J. Chromatogr. 461 (1989):209–227.