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**FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA**

ONDERWERP: FLUORESCENCE SPECTROSCOPY IN THE CHARACTERISATION OF
SUBJECT: _____

COAL-DERIVED LIQUIDS

AFDELING: CHEMISTRY
DIVISION: _____

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TITLE : FLUORESCENCE SPECTROSCOPY IN
THE CHARACTERISATION OF COAL-
DERIVED LIQUIDS

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FLUORESCENCE SPECTROSCOPY IN THE CHARACTERISATION OF
COAL-DERIVED LIQUIDS

SYNOPSIS

The use of fluorescence spectroscopy as a qualitative analytical technique for the analysis of polyaromatic hydrocarbons in coal-derived liquids is reported. Examples of fluorescence emission and fluorescence excitation spectra obtained from aromatic ring systems in coal hydrogenation oils and solvent extracts are shown. Twelve aromatic ring systems were identified. The separation scheme was simple and, therefore, the method has potential for routine analysis.

INTRODUCTION

Coal-derived liquids, such as those obtained on hydrogenation of coal, are complex mixtures of widely different compounds. They are predominantly aromatic in nature and contain many polyaromatic hydrocarbons. Knowledge of these polyaromatic hydrocarbons is of importance for the further processing of coal hydrogenation liquids, and for environmental and health reasons.

Fluorescence spectroscopic analysis of polyaromatic hydrocarbons is well documented and because of the carcinogenicity of a number of polyaromatic hydrocarbons, fluorescence spectroscopy has been used to detect some of these compounds, especially benzo(a)pyrene, in widely different environments.

Modern fluorescence spectroscopy has found only limited application in the characterisation of coal liquids. The identification of a number of aromatic compounds in coal tar by fluorescence spectroscopy was achieved after a complex separation by Matsushita et al⁽¹⁾. While, Zander has demonstrated the potential of luminescence spectroscopy, especially phosphorescence spectroscopy, for the analysis of coal tars^(2 - 6).

Recently, Popl et al used fluorescence spectroscopy to identify benzo(a)pyrene in coal tars after separation by high pressure liquid chromatography.⁽⁷⁾ However, the use of fluorescence analysis to identify aromatic compounds, or ring systems, in coal hydrogenation liquids or in solvent extracts from coal has not been reported.

This paper demonstrates the potential of fluorescence spectroscopic analysis for the identification of polyaromatic ring systems in coal hydrogenation liquids and coal extracts.

EXPERIMENTAL

Samples

The oils (hexane soluble fraction) from hydrogenation of New Wakefield and Sigma coal, and from soxhlet extraction of Landau, New Wakefield and Sigma coals were analysed. Proximate and ultimate analyses of the coals are given in Table 1.

Hydrogenation was carried out in a fixed bed of coal (0,59 - 0,25 mm mesh), through which hydrogen, at a pressure of 25 MPa, was continuously passed. The volatile products were condensed in a cold trap. The autoclave was heated to 450°C and maintained at that temperature for 1 hour. Tin (1% of the coal), as stannous chloride, was used as the catalyst.

The other samples were obtained from soxhlet extraction on 0,59 - 0,25 mm mesh coal using boiling chloroform/methanol (3:1 by volume) for 100 hours.

The model compounds were obtained commercially.

Separation

The oils were fractionated by adsorption chromatography on silica gel. The column was eluted successively with n-hexane (12 fractions) n-hexane/toluene (increasing proportions of toluene, 5 fractions), toluene, chloroform and methanol.

Spectroscopy

Fluorescence emission and excitation spectra (uncorrected for variations of source and photomultiplier response) were recorded in hexane (spectroscopic grade) using a Perkin-Elmer 512 fluorescence spectrophotometer. The spectra were recorded in very dilute solutions. Typical spectra were recorded at one concentration, the sample diluted tenfold, and the spectra again recorded. This process was repeated until the relative intensities of the bands within each spectrum remained constant.

RESULTS AND DISCUSSION

Identification by fluorescence spectroscopy of aromatic ring systems present in complex mixtures such as coal liquefaction oils requires comparison of the oil sample spectra with those of model ring systems. Though tables of fluorescence emission spectra have been recorded^(8 - 10), solvent, temperature and instrumental variations make comparisons difficult. It was thus decided that it would be more accurate to compare spectra from the oil samples with those of model compounds recorded under identical conditions and at the same time. Fluorescence spectra were recorded in very dilute solutions to avoid concentration quenching and excimer formation.

The separation of the coal-derived oils was achieved by chromatography on silica gel. The oils were separated into twenty fractions of which about ten fractions were of polyaromatic hydrocarbons. It is obvious that complete separation did not occur, nevertheless even after this limited separation quite a number of polyaromatic hydrocarbon structures could be identified.

As a routine procedure ultra-violet spectra were recorded on fractions from the columns. Because of the incomplete separation, ultra-violet analysis was of limited value in the characterisation of these fractions. Though, peaks and even inflections in the ultra-violet spectra are useful as guides for the setting of the fluorescence excitation wavelength. Fluorescence analysis, however, was useful in characterising these fractions, because emission and excitation spectra of different component ring systems could be instrumentally isolated and recorded.

Twelve polyaromatic ring systems were identified in coal liquids by the similarity of their fluorescence excitation and fluorescence emission spectra to those of the standard hydrocarbons. These were anthracene (1a), chrysene (2), pyrene (3a), 1-alkylpyrene (3b), 9,10-dialkylanthracene (1c), benz(a)anthracene (4), benzo(a)pyrene (5), benzo(ghi)perylene (6), dibenzo(def, mno)chrysene (7), perylene (8), coronene (9) and dibenzo(b, def)chrysene (10). The peak maxima of both fluorescence emission and excitation spectra for both the model compounds and the coal liquids are presented in Tables 2 and 3. The most intense band is in *italic* type, and the compounds are listed according to the wavelength of the most intense band in the emission spectrum. A number of representative spectra of both model compounds and those from coal liquids are compared in Figures 1 to 6. With fluorescence analysis, there are two types of spectra, emission and excitation. The similarity of both the emission and excitation spectra allows for definite identification of ring systems. Whereas, for example, benzo(a)pyrene (5) and benzo(ghi)perylene (6) have very similar ultra-violet and fluorescence excitation spectra, they can easily be distinguished by their fluorescent emission spectra.

It was noted that some of the spectra from the coal liquids differed from those of the standards slightly, commonly a red shift of one or two nanometers. It was assumed that this is due to the presence of alkyl substituents. The spectra of these coal liquids were, however, very similar to those of the model compounds and easily recognisable. This is expected, based on the work of Schoental and Scott⁽⁸⁾ on the effects of methyl substitution on the fluorescence spectra of benz(a)anthracene and naphtho(2,1a)fluorene. The effects of methyl substitution on these structures were not large. Van Duuren⁽⁹⁾ confirmed the small effect of methyl substitution on the fluorescence spectra of benz(a)anthracene. McKay et al^(10, 11) also noted that alkyl substituents appear to have only a small effect on the fluorescence spectra of benzo(a)carbazoles in their analysis of these compounds in petroleum distillates. The spectra of 2-methylanthracene were recorded and it was found that this had fluorescence emission and excitation spectra very similar to that of anthracene (see Tables 2 and 3). The perylene containing frac-

tions, for example, were eluted from the columns after those containing the larger coronene structure and well after the fractions that contained benzo(a)pyrene. This indicates that perylene is more heavily substituted than these other polyaromatic hydrocarbons. However, the fluorescence emission and excitation spectra of perylene in the coal liquids were very similar to those of the parent compound (see Tables 2 and 3, and Figure 5). It seems in general, therefore, that alkyl substituents have only a slight effect on the spectra of large aromatic hydrocarbons. This allows mixtures of compounds with the same aromatic nucleus to be identified by fluorescence spectroscopy as a single structure. Unfortunately, however, there are some substituted polyaromatic hydrocarbons which have markedly different spectra to those of their parent hydrocarbon. 9,10-Dialkylanthracenes and 1-alkylpyrenes are notable among these and thus have to be treated as separate hydrocarbon structures from those of their parent hydrocarbon. Van Duuren has reported⁽⁹⁾ that certain methyl derivatives of dibenzo(def, mno)chrysene and fluoranthene also differ significantly from the unsubstituted hydrocarbons.

On examination of Table 2, it will be noticed that except for coronene, all the structures found in the hydrogenation samples were also found in the corresponding solvent extract. All the samples analysed contained the highly carcinogenic hydrocarbons benzo(a)pyrene and dibenzo(b, def)chrysene.

CONCLUSION

Fluorescence spectroscopy is a powerful analytical technique for the characterisation of coal-derived liquids. Separation into fractions is necessary before meaningful data on individual ring systems can be obtained. Adsorption chromatography on silica gel is a relatively simple but, nevertheless, satisfactory separation technique, thus allowing spectrofluorometric analysis to be carried out on a routine basis.

For identification of aromatic ring systems in coal liquids, fluorescence spectroscopy has proved useful for the following reasons. Firstly, emission and excitation spectra of individual ring systems may often

be instrumentally resolved even though the sample contains a mixture of aromatic ring systems. Secondly, alkyl substituents in general, appear to have only a small effect on fluorescence spectra, therefore, allowing fluorescence spectroscopy to be used for the identification of aromatic ring systems rather than individual compounds.

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TABLE 1ANALYSIS OF COALS USED

	COAL		
	Landau	New Wakefield	Sigma
Moisture (% , air dried basis)	2,5	4,9	6,6
Ash (% , air dried basis)	14,3	14,9	29,6
Volatile Matter (% , air dried basis)	23,3	32,8	21,9
Carbon (% , daf)	84,1	79,2	76,7
Hydrogen (% , daf)	4,4	5,4	4,4
Nitrogen (% , daf)	1,9	2,1	1,6
Sulphur (% , daf)	0,6	2,3	1,1

TABLE 2

FLUORESCENCE EMISSION SPECTRA^(a)

Compound	Fluorescence emission spectra, wavelength nm		Coal ^(b)	Source ^(c)
	Model compound	Coal liquid		
Chrysene(2)	<u>362</u> 369(s) 381 402 426	<u>361</u> 368(s) 380 400 425	L	SE
1-Methylpyrene(3b)	<u>376</u> 395 415 433(s)	<u>377</u> 397 416 433(s)	NW	H, SE
Anthracene (1a)	<u>378</u> 398 422 446	<u>381</u> 401 424 446(s)	L NW	SE H, SE
2-Methylantracene (1b)	<u>381</u> 403 426 448		S	H, SE
Pyrene (3a)	377 <u>383</u> 393	378 <u>384</u> 393	L NW S	SE H, SE H, SE
Benz(a)anthracene (4)	<u>385</u> 407 433 461	<u>385</u> 406 429 459	NW	H, SE
9,10-Dimethylan- thracene (1c)	<u>399</u> 424 448 474	<u>399</u> 423 449 475	L NW S	SE H, SE H, SE
Benzo(a)pyrene(5) (Benzy(def)chrysene)	<u>403</u> 408(s) 427 453	<u>403</u> 408(s) 427 453	L NW S	SE H, SE H, SE
Benzo(ghi)perylene (6)	397 406 <u>418</u> 427(s) 443	397 406 <u>418</u> 428 443	NW	H, SE
Dibenzo(def,mno) chrysene (7) (Anthanthrene)	<u>431</u> 456 487	<u>433</u> 456 489	L NW S	SE H, SE H, SE
Perylene(8)	<u>437</u> 464 496 536(s)	<u>439</u> 468 496 536(s)	L NW S	SE H, SE H, SE
Coronene (9)	409 420 426 433 <u>444</u> 454 473 483 505	409(s) 419 427(s) 433 <u>445</u> 454 473 483 505	NW S	H H
Dibenzo(b,def) chrysene (10) (3,4,8,9-Dibenzo- pyrene)	<u>448</u> 476 510	<u>449</u> 476 508(s)	L NW S	SE H H, SE

(a) The most intense peak in each spectrum is in italic type. Shoulders are indicated by (s).

(b) L = Landau, NW = New Wakefield, S = Sigma.

(c) H = Hydrogenation, SE = Soxhlet extraction.

TABLE 3

FLUORESCENCE EXCITATION SPECTRA

Compound	Fluorescence excitation spectra, wavelength nm	
	Model compound	Coal liquid
Chrysene(2)	260(s) <u>268</u> 294 306 319	258(s) <u>266</u> 292 306 319
1-Methylpyrene (3b)	243 264 275 312 326 <u>342</u>	246 266 277 313 327 <u>343</u>
Anthracene (1a)	<u>253</u> 311 325 339 356 375	313 327 342 <u>358</u> 377
2-Methylanthracene (1b)	<u>254</u> 312 326 340 358 377	
Pyrene(3b)	231 241 252 262 272 306 318 <u>334</u>	262 273 306 317 <u>334</u>
Benz(a)anthracene (4)	277 <u>287</u> 297 314 327 341 357	290 300 317 330 344 360
9,10-Dimethylanthracene (1c)	325 342 358 377 <u>398</u>	356 376 <u>397</u>
Benzo(a)pyrene (5) (Benzo(def)chrysene)	265 285 <u>296</u> 347 363 383	285 <u>296</u> 347 363 383
Benzo(ghi)perylene (6)	288 <u>299</u> 328 346 363 383	288 <u>299</u> 327 345 363 383
Dibenzo(def,mno)chrysene (Anthanthrene) (7)	258 293 306 362(s) 381 399 404 421 <u>429</u>	295(s) 307 364 379 383(s) 401 421 429
Perlyene (8)	368 387 408 <u>435</u>	366 386 409 <u>435</u>
Coronene (9)	290 <u>302</u> 323 338	290 <u>302</u> 323 338
Dibenzo(b,def)chrysene (10) (3,4,8,9-Dibenzo pyrene)	269 297 <u>310</u> 396 419 445	395 418 447

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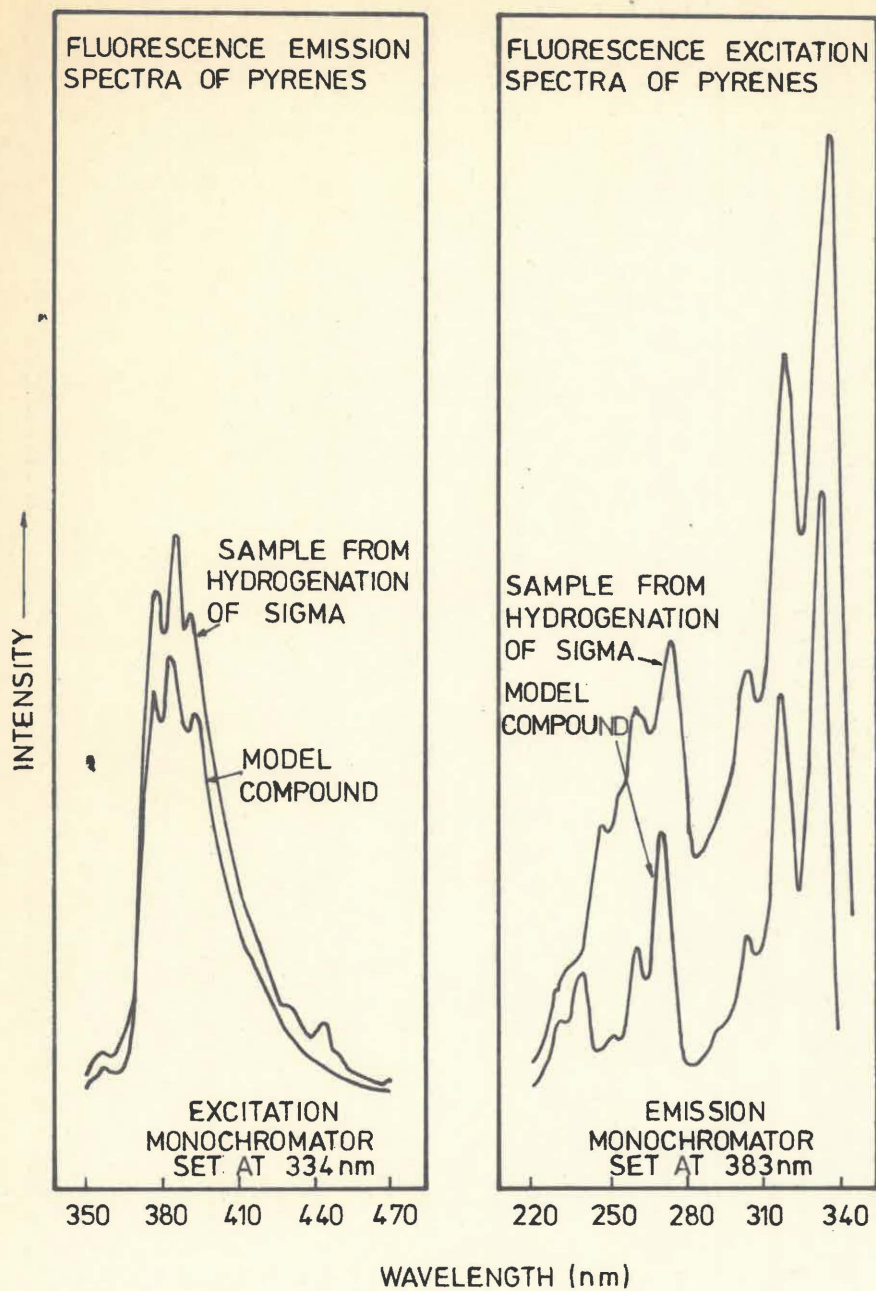


FIGURE 1 FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF PYRENES (3a)

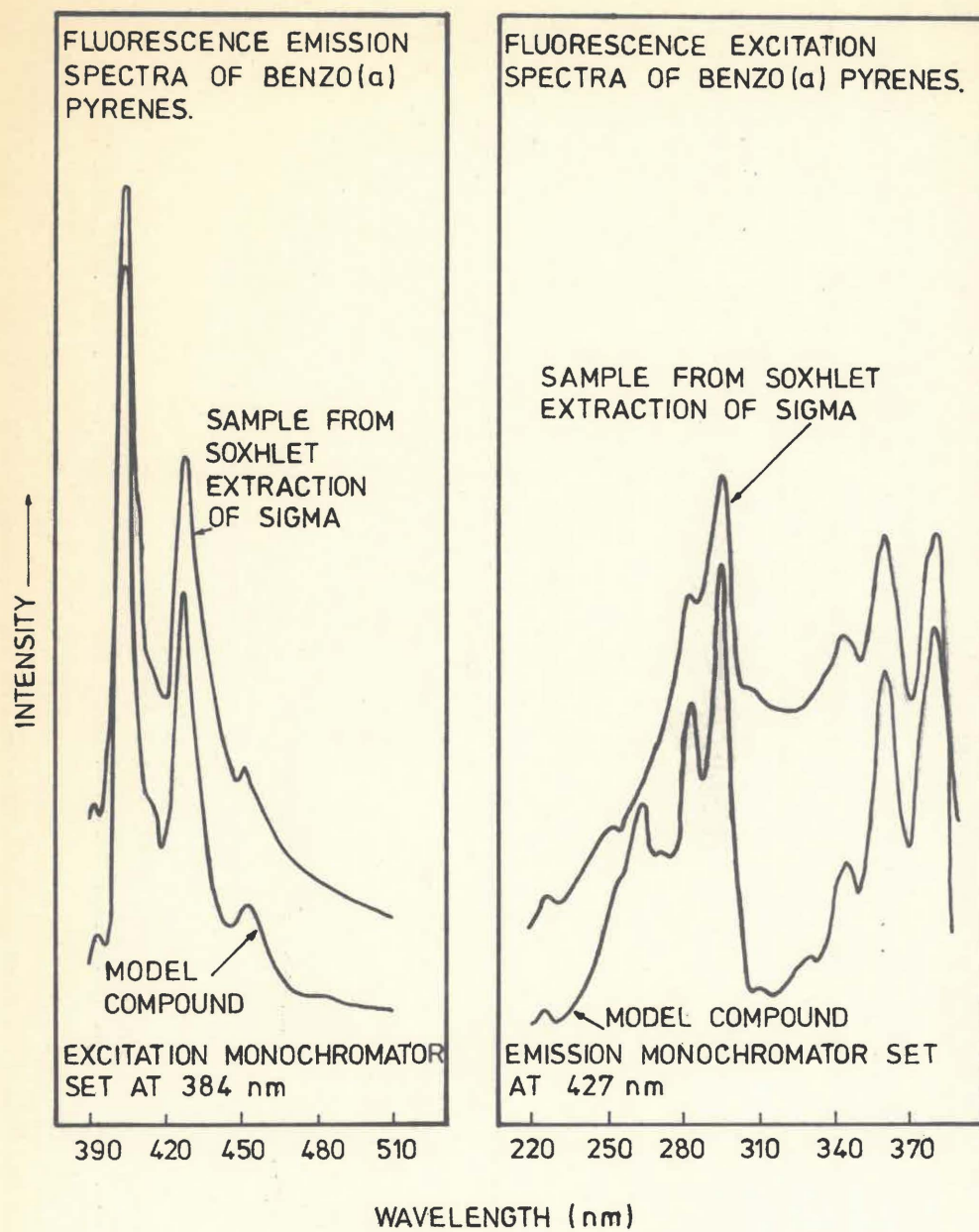


FIGURE 2 FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF BENZO(a) PYRENES (5)

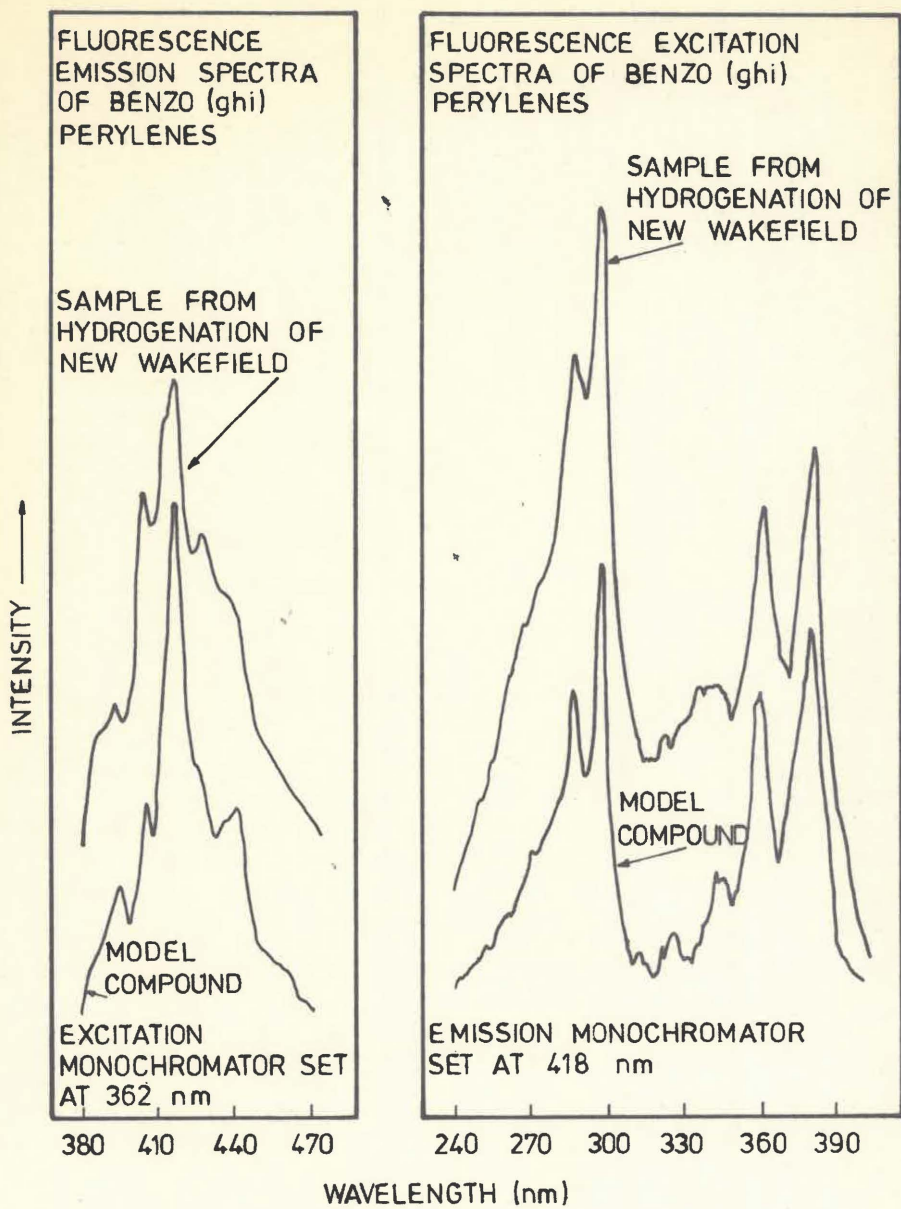


FIGURE 3 FLUORESCENCE EMISSION AND EXCITATION
SPECTRA OF BENZO (ghi) PERYLENES (6)

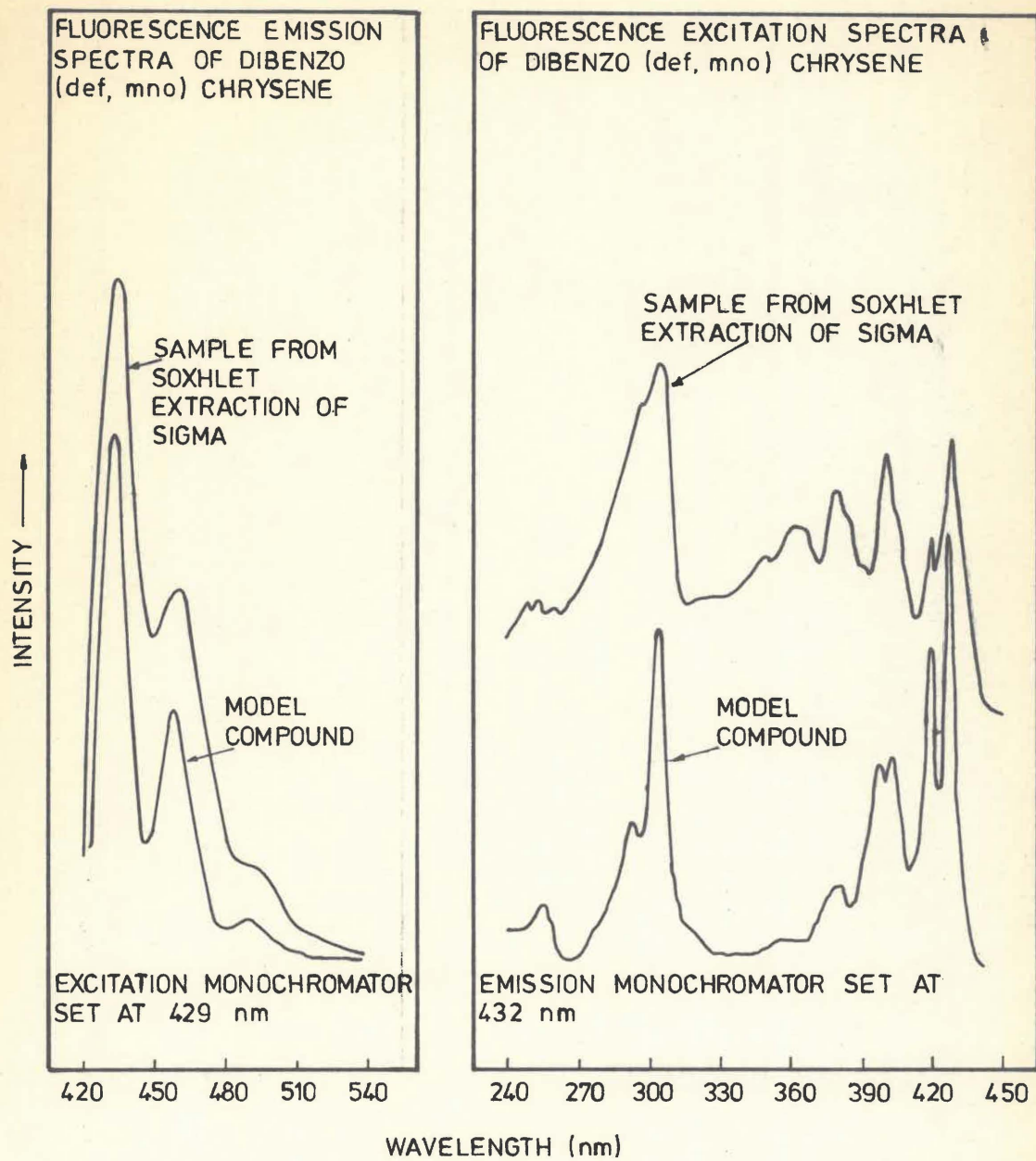


FIGURE 4 FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF DIBENZO (def, mno) CHRYSENES (7)

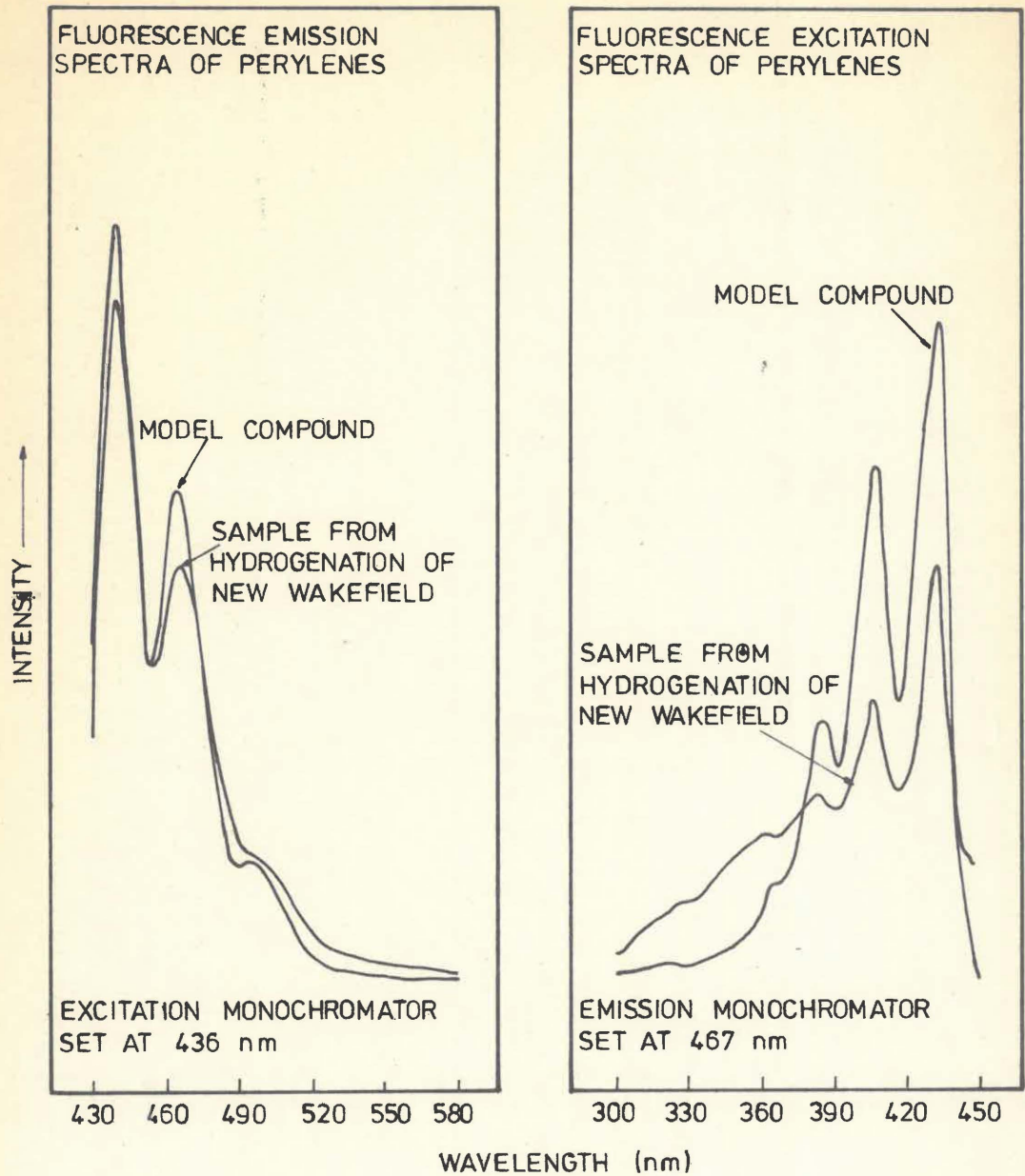


FIGURE 5 FLUORESCENCE EMISSION AND EXCITATION SPECTRA OF PERYLENES (8)

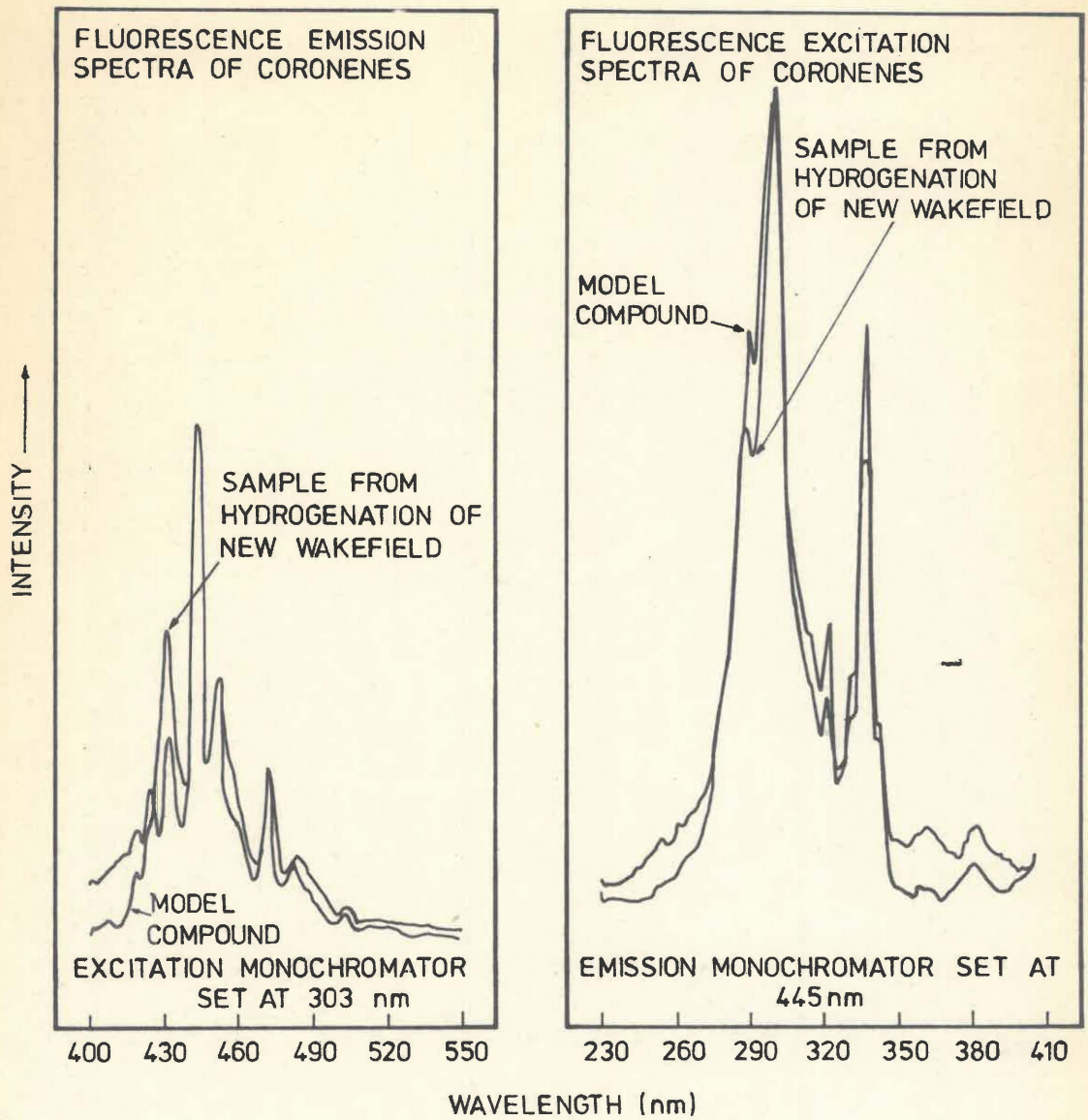
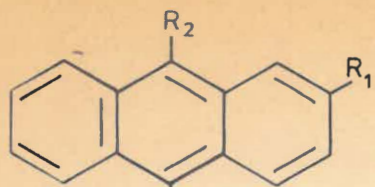


FIGURE 6 FLUORESCENCE EMISSION AND EXCITATION
SPECTRA OF CORONENES (9)

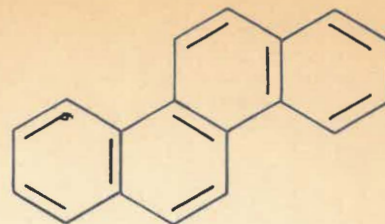


(1)

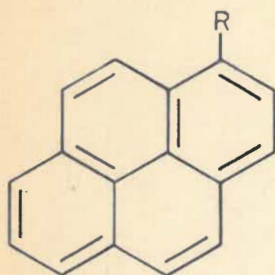
(a) $R_1 = R_2 = H$

(b) $R_1 = CH_3$; $R_2 = H$

(c) $R_1 = H$; $R_2 = CH_3$



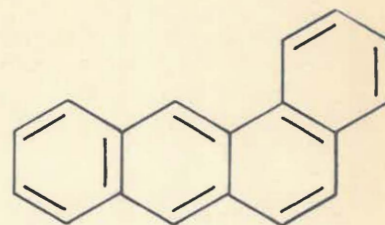
(2)



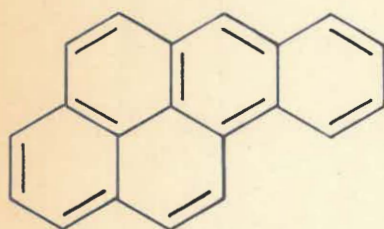
(3)

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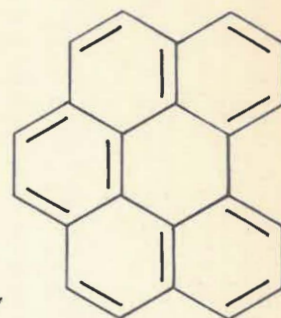
(b) $R = CH_3$



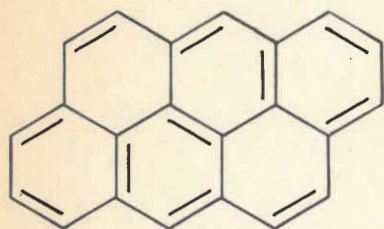
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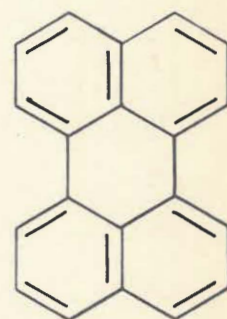
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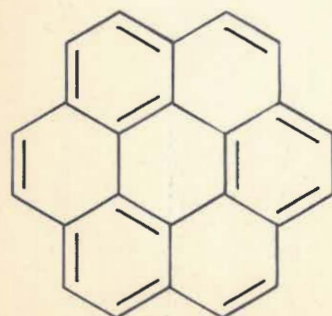
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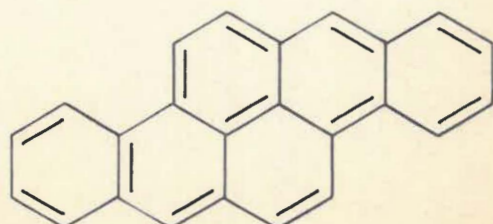
(7)



(8)



(9)



(10)