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CORRELATIONS BETWEEN PHOTOELECTRON AND UV ABSORPTION SPECTRA OF POLYCYCLIC HYDROCARBONS. THE PYRENE SERIES

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Abstract—In continuation of earlier work on the relationships between the PE and optical spectra of polycyclic aromatic hydrocarbons, the PE spectra of 34 pyrene-type molecules are correlated with electronic spectra. As in other series of hydrocarbons considered so far, the p-band in the optical spectra is related to the first IP, whereas the α- and β-bands can be related to higher IP's. Regularities observed in the PE spectra of linearly annellated, plano- and centro-symmetrically annellated pyrenes are discussed.

Earlier papers in this series[1,2] have addressed themselves to the relationships between the PE- and optical spectra of aromatic hydrocarbons. In the present paper we discuss the pyrene-type hydrocarbons.

Linearly annellated pyrenes. The correlation diagram (Fig. 1), contains the IP's related to the p-, α- and β-absorption bands, as well as the corresponding upper levels, defined as $\Delta p = IP_p - E_p$, $\Delta\alpha = IP_\alpha - E_\alpha$ and $\Delta\beta = IP_\beta - E_\beta$ (for the numerical values see Table 1). Here and in the following sereis of hydrocarbons, the energies of the p-, α- and β-absorption bands were taken from the solution spectra,[4-6] a correction being applied to account for the solution shift.[1,3] The IP's come from the high-resolution gas-phase PE spectra[7] and are claimed to be accurate to within ±0.02 eV; most of these data are reported here for the first time.

Passing from diphenyl to phenanthrene with the formation of an induced sextet as indicated by the arrows in Fig. 2 results in a big shift of all absorption bands[3] to the red. A further shift in the same direction is observed when a second ethylene bridge is fused to phenanthrene in passing to pyrene. However, this shift is almost entirely confined to the first PE band (8.38, 7.86 and 7.41 eV) which is related to the p-absorption band, whilst the α- and β-PE bands show only minor changes.

According to formula 1 for pyrene (Fig. 2) the two ethylene double bonds are fixed if the formulation with aromatic sextets is applied. As has been shown with numerous examples,[2-5] annellation effects through fixed double bonds are very small, if compared with the annellation effects in the acene and phene series.[3] This is further confirmed by the PE spectra of benzopyrene 2 and dibenzopyrene 3 shown in Fig. 2. The first PE band which is related to the p-absorption band shifts very little if anything at all. The shifts of the α-bands (8.27, 8.00 and 8.25 eV) and β-bands (9.35, 8.73 and 9.19 eV) are much bigger.

Figure 3 demonstrates the annellation effects starting from 1,2:3,4-dibenzanthracene. As shown earlier,[1] the p-PE band of the phenanthrene complex in dibenzanthracene (boldly drawn in Fig. 2) is found at 7.9 eV; it

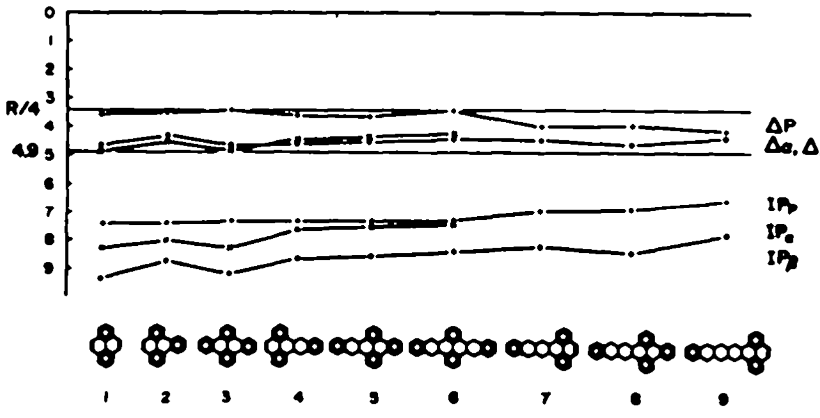

Fig. 1. Term scheme for the linearly annellated pyrenes. For definitions of quantities see text. Here and in Figs. 6–8 all hexagons symbolize aromatic rings; only localized double bonds of the phenanthrene type are marked.

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Table 1. First IP's (IP_1), wavelengths[a] of the p-absorption band (λ_p), p-band energies (E_p), differences $\Delta p = IP_1 - E_p$, and corresponding quantities relating to the α- and β-absorption bands in the linearly annellated pyrenes. Energies in eV, wavelengths in Å

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
Pyrene (1)	7.41	3335 (E)	3.83	3.58	8.27	3715 (E)	3.37	4.90	9.35	2720 (E)	4.67	4.68
1,2-Benzopyrene (2)	7.41	3316 (E)	3.85	3.56	8.00	3660 (E)	3.42	4.58	8.73	2690 (E)	4.40	4.33
1,2:6,7-Dibenzopyrene (3)	7.39	3280 (B)	3.93	3.46	8.25	3720 (B)	3.38	4.87	9.19	2880 (B)	4.45	4.74
Naphtho-(2′,3′:1,2)pyrene (4)	7.35	3450 (B)	3.74	3.61	7.53	4075 (B)	3.09	4.44	8.62	3210 (B)	4.01	4.61
1,2-Benzonaphtho-(2″,3″:6,7)pyrene (5)	7.33	3500 (D)	3.69	3.64	7.50	3980 (D)	3.17	4.33	8.52	3160 (D)	4.07	4.45
Dinaphtho-(2′,3′:1,2);(2″,3″:6,7)pyrene (6)	7.26	3420 (B)	3.77	3.49	7.47	3840 (B)	3.27	4.20	8.43	3160 (B)	4.07	4.36
1,14:4,5-Dibenzopentacene (7)	6.96	4420 (B)	2.96	4.00					8.15	3555 (B)	3.64	4.51
5,6:15,16-Dibenzohexacene (8)	6.91	4390 (B)	2.97	3.94					8.39	3480 (B)	3.71	4.68
1,16:4,5-Dibenzohexacene (9)	6.60[b]	5340 (B)	2.47	4.13					7.80[b]	3770 (B)	3.44	4.36

[a] Solvent given in brackets: E = methanol or ethanol, C = cyclohexane, B = benzene, D = dioxane, T = 1,2,4-trichlorobenzene, N = 1-methylnaphthalene.

[b] Extrapolated using Hückel theory.

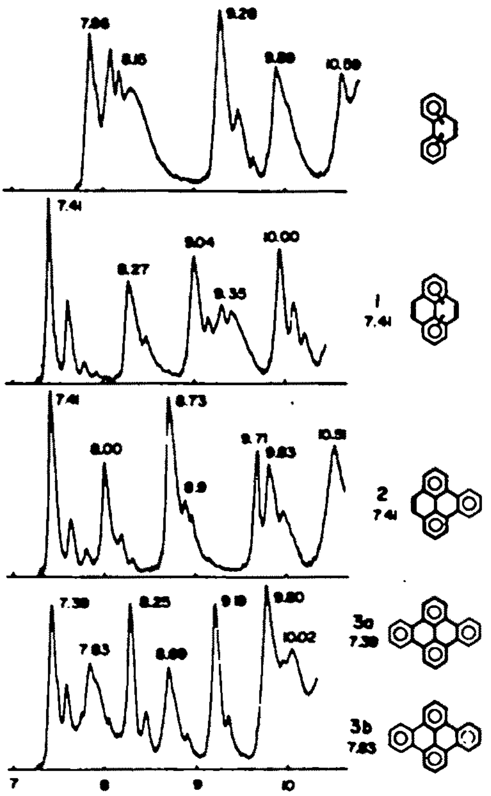


Fig. 2. PE spectra of phenanthrene, pyrene, 1,2-benzopyrene and 1,2:6,7-dibenzopyrene (temps. 98°, 112°, 148° and 230°C, resp.).

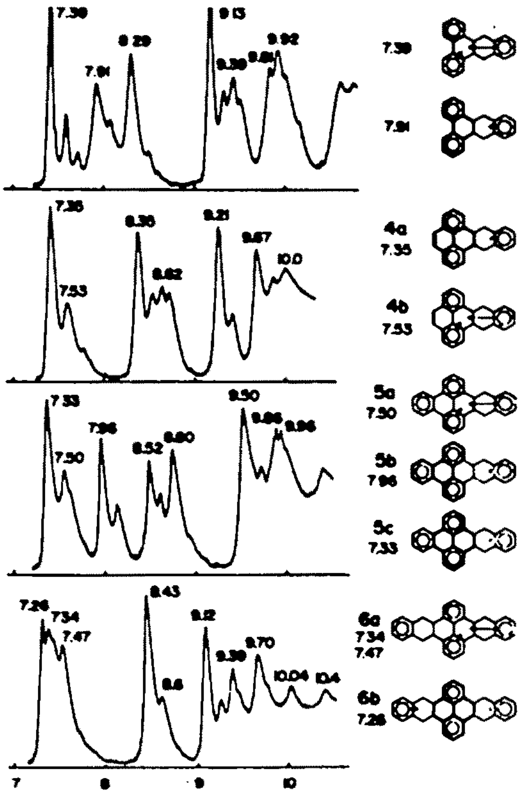


Fig. 3. PE spectra of 1,2:3,4-dibenzanthracene, naphthopyrene, benzonaphthopyrene and dinaphthopyrene (temps. 160°, 225°, 245° and 305°C, resp.).

remains stationary for all phenanthrene and triphenylene complexes. Therefore, this band is also found in benzonaphthopyrene 5 if it has the aromatic conjugation as indicated in formula 5b. The PE spectra of naphthopyrene 4 and dinaphthopyrene 6 do not show this band; instead they have a band at about 7.4 eV which can be related to the pyrene complexes with short-axis polarization (formulas 4a, 5c and 6b). Similar comments apply to Fig. 4. The first PE band at 7.0 eV, which is present in all three hydrocarbons, is related to the tetracene complex, whereas the band at 7.4 eV is related to the pyrene complex which is present only in the conjugation type 7b and 8c. It is particularly remarkable that the triphenylene band at 7.9 eV appears only in 8b.

The upper levels of the p-bands in Fig. 1 remain constant at about R/4 = 3.4 eV, R being the Rydberg

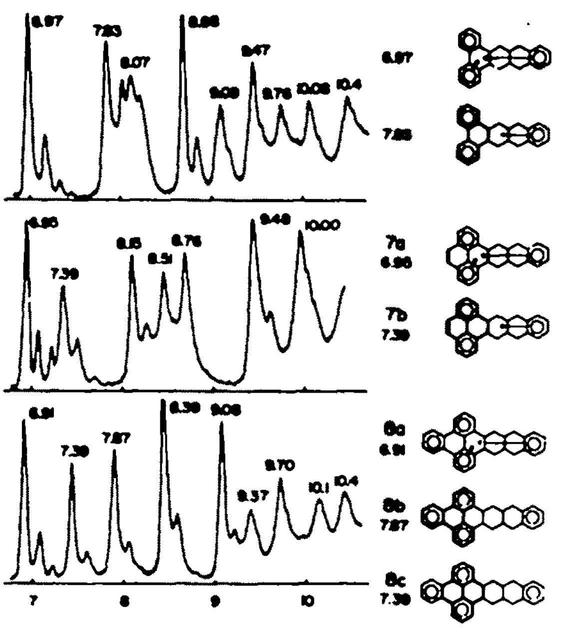


Fig. 4. PE spectra of 1,2:3,4-dibenztetracene, 1,14:4,5-dibenzopentacene and 5,6:15,16-dibenzohexacene (temps. 215°, 232° and 295°C, resp.).

constant of the H atom. As in the acene series,[1] hydrocarbons with low benzenoidity (i.e., low ratio of the number of sextets to the number of π-electrons) tend to deviate from this level toward higher values. The Δα and Δβ values are as expected very near at 4.9 eV, the IP of graphite. The deviations are again as in the acene and benzacene series.[1] It is striking that the only fully benzenoid hydrocarbon in the series, 1,2:6,7-dibenzopyrene 3, shows almost the ideal value of 3.4 eV for the p-band and of 4.9 eV for the α- and β-bands.

Plane-symmetrically annellated pyrenes. This series reveals interesting new features which are not found in the linearly annellated pyrenes.

In Fig. 5 are shown the PE spectra of picene, pentaphene, 3,4:9,10-dibenzopyrene 11 and dinaphthopyrene 16. The α- and β-bands of picene (7.67 and 8.99 eV, resp.) and pentaphene (7.39 and 8.54 eV, resp.) have already been discussed.[1] It has now been found that the β-bands of both picene and pentaphene reappear in dibenzopyrene 11, namely at 8.90 and 8.49 eV. Only one of the two β-bands can be related to the α-band at 7.70 eV. The conclusion of this comparison is that dibenzopyrene 11 contains the aromatic conjugation of picene with three sextets causing the β-band at 8.90 eV and the pentaphene-type conjugation with the β-band at 8.49 eV. It should be mentioned that this conclusion has already been reached in an earlier paper on the optical spectra of the pyrenes.[5] Thus, the present results further support the validity of the correlation between the PE and the optical spectra.

The PE spectrum of picene shows a redundant band at

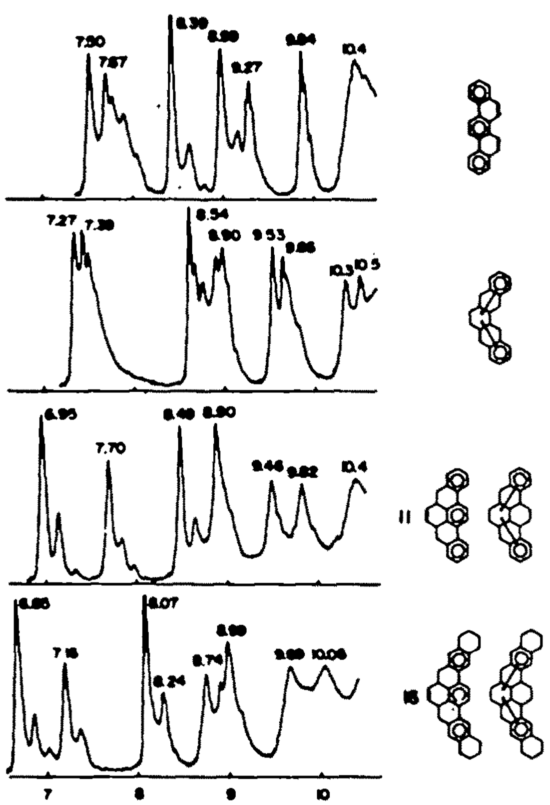


Fig. 5. PE spectra of picene, pentaphene, dibenzopyrene and dinaphthopyrene (temps. 195°, 180°, 200° and 305°C, resp.).

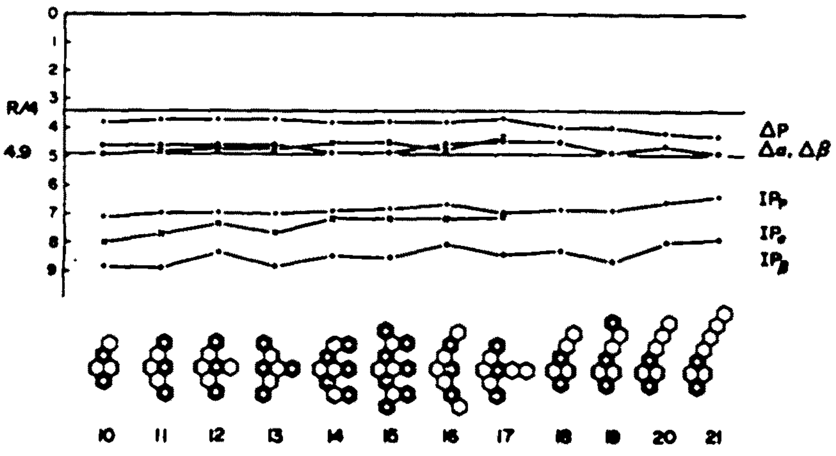


Fig. 6. Term scheme for plane-symmetrically annellated pyrenes.

8.39 eV which will be considered in detail in a forthcoming paper on annellated anthanthrenes.

Further annellation in going to dinaphthopyrene **16** does not introduce new aromatic conjugation; as a result of this the PE spectrum is simplified so that there is only one α-band at 7.16 eV and one β-band at 8.07 eV.

The term scheme (Fig. 6) contains the above plane-symmetric pyrenes together with more complicated ones. As in the acene series,[1] the upper level of the p-bands changes from R/4 to 4.9 eV as the number of sextets per number of rings increases. It is remarkable that minor differences in going from **10** (2 sextets) to **11** (3 sextets) come out clearly causing Δp to decrease from 3.76 to 3.68 eV. The number of sextets then remains constant until **13** with 4 sextets is reached, resulting in a fall of Δp to 3.66 eV. In the three overcrowded hydrocarbons **14**, **15** and **17** the E_p values are not sufficiently well defined so that a discussion of the small differences in Δp is unwarranted. The hydrocarbons **18**-**21** show again the expected behaviour, Δp increasing with a decreasing number of sextets.

The upper levels of the α- and β-bands are very close together. In the larger hydrocarbons the $\Delta\beta$ values should be considered with caution as there are too many bands in the PE spectra which could be classified as β-bands. Also, overcrowding limits the accuracy in determining the E_β values.

Centro-symmetrically annellated pyrenes. The term Scheme 7 contains the centro-symmetric pyrenes **22**, **23** and **24**. In accordance with earlier studies[4] of the optical spectra, the p-PE band is always at lower energies than in the corresponding plane-symmetric isomers. Neither the PE nor the electronic spectra show an α-band, confirming again the rule that an α-band must be seen in both types of spectra.

Only by comparison with the centro-symmetric isomers can the β-band in **22** and **23** be identified with some certainty at 8.86 and 8.38 eV, respectively.

The extremest case of centro-symmetry is reached in dinaphthoheptacene **24**. Owing to its extended size, the β-PE band shifts to the very low value of 7.63 eV, the p-PE band to 6.22 eV which is the lowest value found so far in an aromatic hydrocarbon. The electronic spectrum is in perfect agreement with these big shifts. In fact, this hydrocarbon can be considered as a heptacene derivative which explains these low values.

Combined annellation. An interesting annellation series is provided by the four hydrocarbons **11**–**13** and **25**. **13** is derived from **11** by annellation at a fixed double bond in the central pyrene complex. This requires very small shifts for the PE bands which amount to +0.04 eV for the p-band and of −0.04 eV for the one β-band. Practically the same shifts (+0.06 and −0.03 eV, resp.) are observed in the optical spectra.

Annellation of a benzo ring to the other side of **11** to give **12** results in a shift of +0.01 eV for the p-PE band and of −0.12 eV for the first β-PE band. The corresponding shifts for the UV bands are −0.04 and −0.53 eV, respectively. In addition to this an α-band can be detected in both types of spectra.

If these two annellation types are combined, tetrabenzopyrene **25** is obtained. Due to the new sextet the p-PE band shifts to 7.02 eV, whereas the two β-bands appear at practically the same energies as in **11**. There is only one α-band at 7.18 eV.

28 is derived from **10** by annellation at a formally fixed double bond. The resulting shift of the p-PE band (+0.01 eV) is therefore very small. Slightly bigger shifts are observed for the α- and β-PE bands; the former

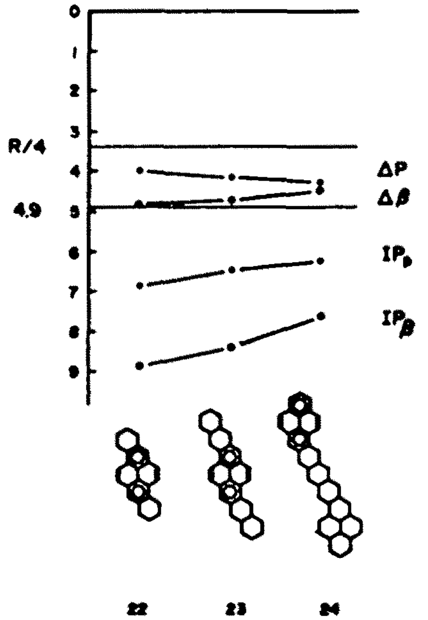
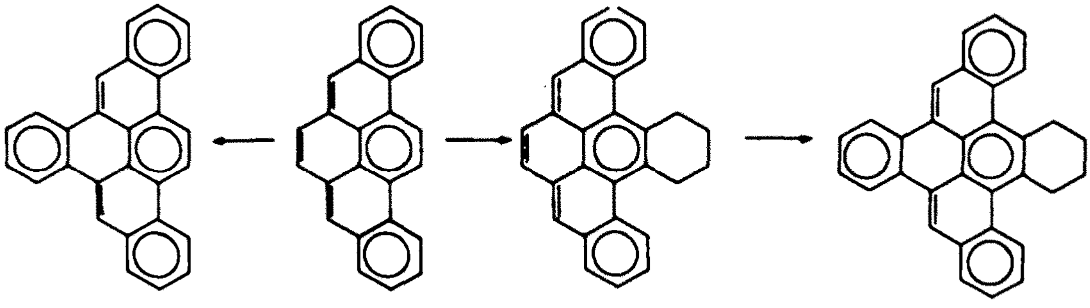


Fig. 7. Term scheme for centro-symmetrically annellated pyrenes.



	13	11	12	25
IP$_p$	6.99	6.95	6.96	7.02
IP$_\alpha$	7.65	7.70	7.33	7.18
IP$_\beta$	8.86	8.49/8.90	8.37/8.79	8.50/8.79

Scheme 1.

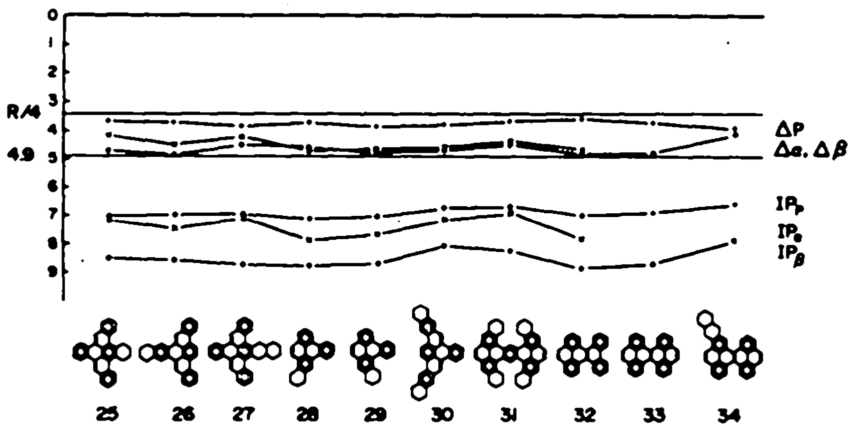


Fig. 8. Term scheme for pyrenes of mixed annellation.

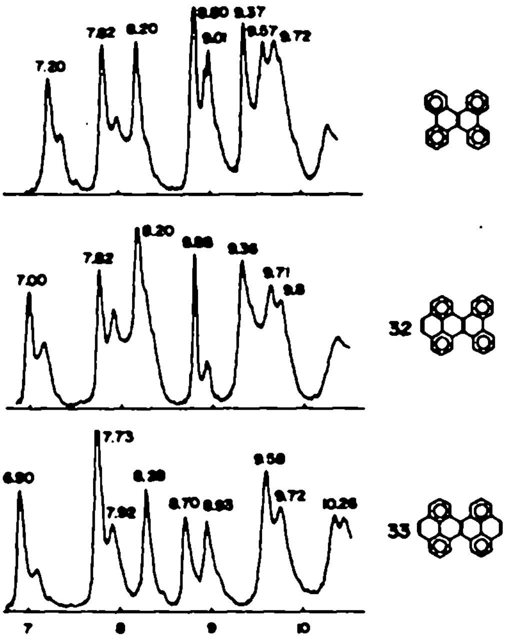


Fig. 9. PE spectra of 1,2:7,8-dibenzochrysene, phenanthrenopyrene and pyrenopyrene (temps. 190°, 220° and 240°C).

moving from 8.01 to 7.87 eV, the latter from 8.88 to 8.77 eV.

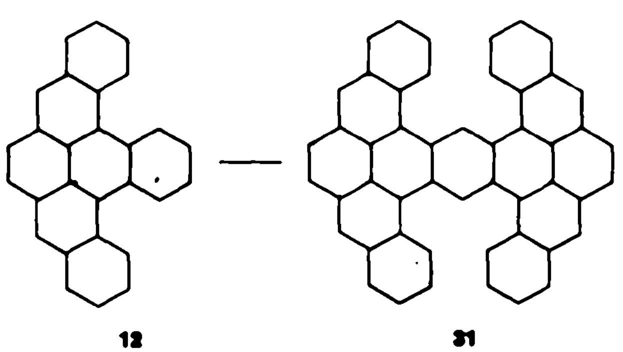
A combination of benzo and naphtho annellation gives the overcrowded hydrocarbon 17, with the p-PE band lying at 6.94 eV and the β-band at 8.44 eV.

For the PE and electronic spectral data of a wider range of hydrocarbons with mixed annellation see Table 4 and Fig. 8.

There is a striking similarity of the PE spectra of the three hydrocarbons shown in Fig. 9. All three hydrocarbons have four sextets, the only difference being additional formal double bonds. This causes a shift of the p-PE band from 7.20 to 7.00 to 6.90 eV, and for the β-bands from 9.01 to 8.88 to 8.70 eV. It is remarkable that only the first two hydrocarbons have α-bands at 7.82 eV while there is none in 33, just as is the case in the electronic spectrum. In addition to the above hydrocarbons, Table 4 contains also naphthopyrenopyrene 34 which shows the p-PE band at 6.58 eV and the β-band at 7.84 eV.

The following comparison shows a highly complex scheme (see Scheme 2 below).

The complete PE spectra, not presented here, reveal a surprising similarity. In view of the modest shifts of the PE bands, one is forced to the conclusion that essentially only one half of the molecule including the central benzene ring is responsible for the PE spectrum.



	12	31
IP_p	6.98	6.70
IP_α	7.33	6.9
IP_β	8.37	8.28

Scheme 2.

Table 2. PE- and UV-data of the plane-symmetrically annellated pyrenes. For definition of quantities see Table 1

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
3, 4-Benzopyrene (10)	7.10	3845 (E)	3.34	3.76	8.01	4030 (E)	3.11	4.90	8.88	2965 (E)	4.29	4.59
3, 4: 9, 10-Dibenzopyrene (11)	6.95	3970 (B)	3.27	3.68	7.70	4330 (B)	2.91	4.79	8.90	2970 (B)	4.32	4.58
1, 2: 3, 4: 9, 10-Tribenzopyrene (12)	6.92	3930 (E)	3.23	3.69	7.33	4610 (E)	2.72	4.61	8.37	3375 (E)	3.79	4.58
1, 2: 4, 5: 8, 9-Tribenzopyrene (13)	6.99	3860 (C)	3.33	3.66	7.65	4180 (C)	3.00	4.65	8.86	2965 (C)	4.29	4.57
1, 2-Benzodinaphtho-(1″, 2″: 3, 4);(1‴, 2‴: 9, 10)-pyrene (14)	6.88	4200 (C)	3.10	3.78	7.17	4700 (B)	2.68	4.49	8.49	3520 (B)	3.67	4.82
1, 2-Benzodiphenanthreno-(9″, 10″: 3, 4); (9‴, 10‴: 9, 10) pyrene (15)	6.80	4250 (C)	3.03	3.77	7.16	4680 (C)	2.68	4.48	8.52	3470 (C)	3.69	4.83
Dinaphtho-(2′, 3′: 3, 4); (2″, 3″: 9, 10) pyrene (16)	6.65	4580 (T)	2.89	3.76	7.16	5150 (T)	2.45	4.71	8.07	3655 (T)	3.57	4.50
3, 4: 9, 10-Dibenzonaphtho-(2′, 3′: 1, 2) pyrene (17)	6.94	3950 (B)	3.29	3.65	7.10	4530 (B)^a	2.79	4.31	8.44	3120 (B)	4.12	4.32
Naphtho-(2′, 3′: 3, 4) pyrene (18)	6.82	4580 (B)	2.86	3.96					8.30	3360 (B)	3.85	4.45
Phenanthreno-(2′, 3′: 3, 4) pyrene (19)	6.83	4500 (B)	2.90	3.93					8.67	3370 (B)	3.83	4.84
Naphtho-(1′, 7′: 2, 1) pentacene (20)	6.57	5410 (B)	2.44	4.13					7.99	3820 (B)	3.39	4.60
Naphtho-(1′, 7′: 2, 16) hexacene (21)	6.36	6390 (T)	2.11	4.25					7.88	4360 (T)	3.02	4.86

[a] The weak band at 4610 Å in the UV spectrum[5] of 17 could be due to an impurity.

Table 3. PE- and UV-data of centro-symmetrically annellated pyrenes. For definitions see Table 1

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_β	λ_β	E_β	$\Delta\beta$
3, 4: 8, 9-Dibenzopyrene (22)	6.82	4510 (B)	2.90	3.92	8.86	3135 (B)	4.10	4.76
Dinaphtho-(2′, 3′: 3, 4); (2″, 3″: 8, 9) pyrene (23)	6.42	5830 (N)	2.32	4.10	8.38	3530 (N)	3.70	4.68
Dinaphtho-(1′, 7′: 2, 18); (7″, 1″: 9, 11) heptacene (24)	6.22	6830 (T)	1.99	4.23	7.63	4070 (T)	3.22	4.41

Table 4. PE- and UV-data of the pyrenes of mixed annellation type. For definitions see Table 1

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
1, 2: 3, 4: 6, 7: 9, 10-Tetrabenzopyrene (25)	7.03	3800 (C)	3.37	3.66	7.18	4140 (C)	3.03	4.15	8.50	3360 (C)	3.80	4.70
3, 4: 9, 10-Dibenzonaphtho-(2′, 3′: 6, 7) pyrene (26)	6.99	3840 (T)	3.40	3.59	7.43	4260 (T)	2.96	4.48	8.60	3470 (T)	3.75	4.85
3, 4: 6, 7: 9, 10-Tribenzonaphtho-(2′, 3′: 1, 2)-pyrene (27)	6.96	4080 (C)	3.16	3.80	7.09	4300 (C)	2.91	4.18	8.72	3020 (C)	4.22	4.50
1, 2: 4, 5-Dibenzopyrene (28)	7.11	3780 (B)	3.43	3.68	7.87	3960 (B)	3.17	4.70	8.77	3065 (B)	4.19	4.58
1, 2: 3, 4-Dibenzopyrene (29)	7.07	3970 (E)	3.23	3.84	7.72	4200 (E)	2.98	4.74	8.54	3190 (E)	4.00	4.54
1, 2-Benzodinaphtho-(2″, 3″: 4, 5); (2‴, 3‴: 8, 9)-pyrene (30)	6.74	4430 (T)	2.97	3.77	7.14	4930 (T)	2.56	4.58	8.09	3760 (T)	3.47	4.62
Tetranaphtho-(2, 4: 1, 14); (2′, 4′: 4, 5); (1″, 3″: 7, 8); (2‴, 4‴: 11, 12) pentacene (31)	6.70	4300 (T)	3.06	3.64	6.9	5010 (T)	2.52	4.38	8.26	3400 (T)	3.82	4.44
Phenanthreno-(9′, 10′: 1, 2) pyrene (32)	7.00	3740 (C)	3.43	3.57	7.82	3980 (C)	3.15	4.67	8.68	3140 (C)	4.06	4.62
Pyreno-(1′, 2′: 1, 2) pyrene (33)	6.90	4000 (C)	3.21	3.69					8.70	3260 (C)	3.92	4.79
Naphtho-(2″, 3″: 4, 5)-pyreno-(1′, 2′: 1, 2)-pyrene (34)	6.58	4850 (B)	2.71	3.87					7.84	3420 (B)	3.77	4.07

A detailed description of the PE spectra will be published elsewhere.

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