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CORRELATIONS BETWEEN PHOTOELECTRON AND ULTRAVIOLET ABSORPTION SPECTRA OF POLYCYCLIC HYDROCARBONS. THE PERYLENE, CORONENE AND BISANTHENE SERIES

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Abstract—As in earlier work,[1] the *p*-bands in the optical spectra and the first bands in the PE spectra of polycyclic aromatic hydrocarbons are related to R/4, where R is the Rydberg constant of the hydrogen atom. The α- and β-bands are related to 4.9 eV which is the IP of graphite. These regularities have been tested by means of the UV and PE data of 34 peri-condensed hydrocarbons belonging to the perylene-, 1,12-benzoperylene-, coronene- and bisanthene series.

In continuation of our work directed towards establishing correlations between PE and UV spectra we consider in the present paper, instead of the acenes as before,[1] the perylene-type hydrocarbons. These can be considered as peri-condensed acenes.

In this case the central ring should be empty or almost empty of π electrons. This was supported by NMR which yielded the following chemical shifts for the "bay" protons[2] (in ppm, relative to TMS):

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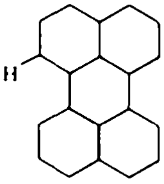
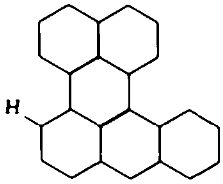
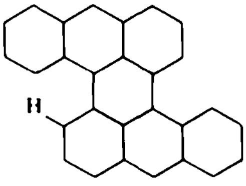
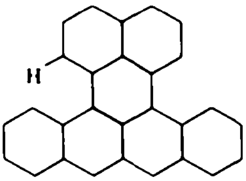


8.03


8.10


8.16


These data indicate that the central ring does not participate appreciably in the ring current. In contrast to this, the "bay" protons in 1,12-benzoperylene and its linear benzologues are at significantly higher values:[2]

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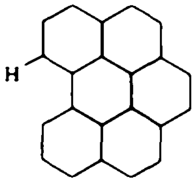
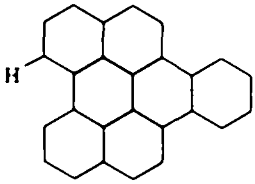
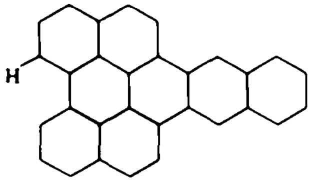


8.71


8.67


In this series, the new middle horizontal branch does of course participate in the π electron migration which reduces the chemical shifts from 8.82 to 8.67 ppm.

In line with these results is the position of the 251 nm band in the UV spectrum of perylene. This band is shifted considerably in the benzologues (to 276, 290 and 302 nm, respectively, in the first above series[3]), suggesting a single bond of the diphenyl type. Surprisingly however, a systematic comparison of the PE spectra in the perylene

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series showed that only the weak band at 337.5 nm in the low-temperature UV spectrum[4] of perylene can be related to the PE band at 8.54 eV. Such a weak UV band is also found in the linearly annellated perylenes[2,3,4] (at 339, 371 and 427 nm, respectively, in the above series) where it appears in the UV spectra even at room temperature. It is obvious that these β-bands, formerly classified as α-bands,[1] are of a partly forbidden character. At present, we are unable to offer an explanation for this and are just reporting the facts as obtained. No such ambiguity exists in the acene and 1,12-benzoperylene series.

Figure 1 shows the PE spectrum of perylene which is amazingly simple. It consists of a band at 6.97 eV which is easily related to the p-band at 434 nm. By subtracting the p-band energy from IP_1, one obtains the upper p level at 4.00 eV which is in line with the principles established in the earlier communication.[1] There is then an unusually wide gap to the next PE band at 8.54 eV which, if compared to the weak 337.5 nm UV band, results in an upper level at 4.76 eV. This is an acceptable value as it comes close to the IP of graphite at 4.9 eV. If the 251 nm band of perylene were used in the above comparison, completely senseless results would be obtained.

In going from perylene to 1,2-benzoperylene 2, this pattern is retained, IP_1 decreasing to 6.71 eV. A further decrease, to 6.51 eV, is observed in passing to 1,2:11,12- and 1,2:7,8-dibenzoperylene (3 and 4, respectively). These four hydrocarbons have only two sextets.

The relationship between the PE and UV spectra, for a more comprehensive series of perylene-type hydrocarbons, are reproduced in Fig. 2; for the numerical values see Table 1. Diphenyl was not chosen as a starting point in this annellation series because of its nonplanar carbon skeleton.

In the angularly annellated perylenes, one finds the upper level of the p-bands approaches R/4 at 3.4 eV, as expected by comparison with the acene series. If the β-bands in the UV spectra are correlated with the PE spectra, one finds that this comparison must involve the rather broad band at 8.59 eV in 2,3-benzoperylene 5. In

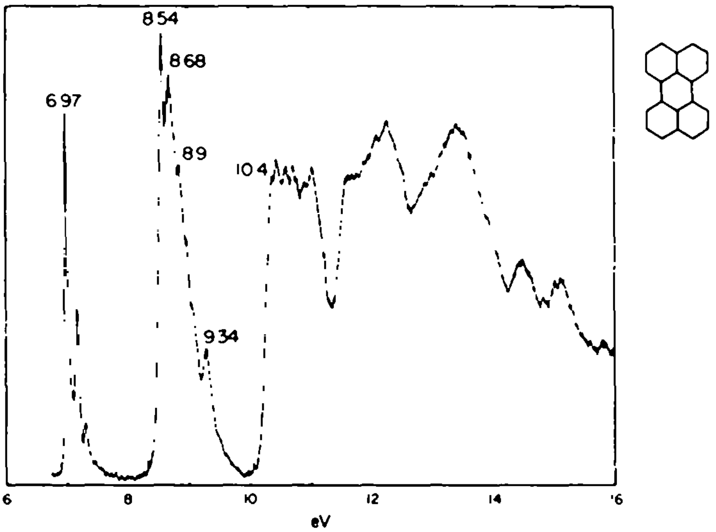

Fig. 1. PE spectrum of perylene at 150°C (Perkin–Elmer PS-16 instrument; calibration: α-, β- and γ-satellites of Xe, Ar, benzene and naphthalene).

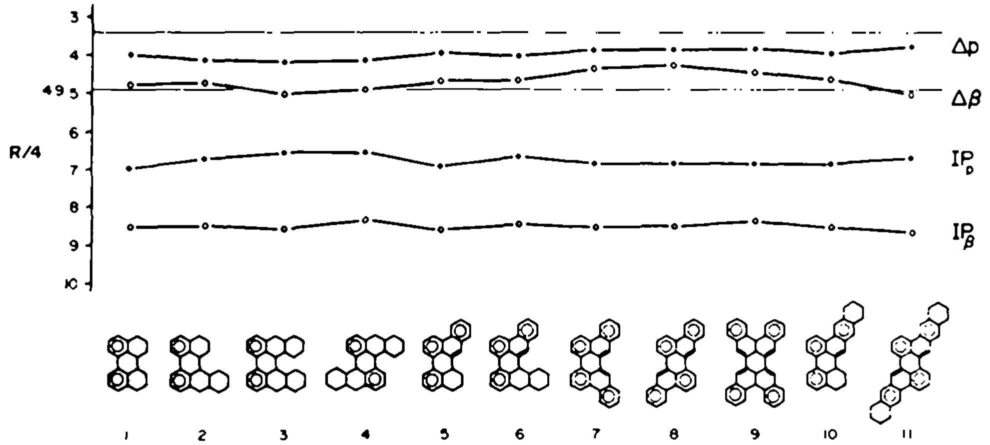

Fig. 2. Relation between the IP's (lower lines) and the upper levels of the p- and β-absorption bands (upper lines) in the perylene series. p-Bands and the corresponding IP's are marked with full circles, β-bands and the corresponding IP's with open circles. All energies in eV. Here and in Figs. 3–5 all hexagons symbolize aromatic rings; only localized double bonds of the phenanthrene-type are marked.

Table 1. First IP's (IP_1), wavelengths[a] of the p-absorption band (λ_p), p-band energies[b] (E_p), differences $\Delta p = IP_1 - E_p$, IP's relating to the β-absorption band (IP_β), wavelengths[a] of the β-absorption band (λ_β), β-band energies[b] (E_β), differences $\Delta\beta = IP_\beta - E_\beta$ in the perylene series. Energies in eV, wavelengths in Å

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_β	λ_β	E_β	$\Delta\beta$
Perylene **1**	6.97	4340(E)	2.97	4.00	8.54	3375(E)	3.79	4.76
1,2-Benzoperylene **2**	6.71	5030(E)	2.58	4.13	8.51	3390(E)	3.77	4.74
1,2:11,12-Dibenzoperylene **3**	6.51	5580(B)	2.37	4.14	8.53[c]	3710(B)	3.49	5.04
1,2:7,8-Dibenzoperylene **4**	6.51	5460(E)	2.38	4.13	8.34	3710(E)	3.45	4.89
2,3-Benzoperylene **5**	6.89	4350(E)	2.96	3.93	8.58	3200(E)	3.99	4.59
1,2:10,11-Dibenzoperylene **6**	6.64	5025(B)	2.62	4.02	8.43	3410(B)	3.79	4.65
2,3:10,11-Dibenzoperylene **7**	6.85	4400(B)	2.97	3.88	8.56	3020(E)	4.22	4.34
2,3:8,9-Dibenzoperylene **8**	6.86	4335(B)	3.01	3.85	8.51	3035(B)	4.23	4.28
2,3:4,5:8,9:10,11-Tetrabenzoperylene **9**	6.82	4250(B)	3.07	3.75	8.37	3270(B)	3.94	4.43
Naphtho-(2',3':2,3)perylene **10**	6.82	4460(B)	2.93	3.89	8.52	3300(B)	3.91	4.61
Dinaphtho-(2',3':2,3);(2",3":8,9)perylene **11**	6.68	4480(T)	2.94	3.74	8.65	3540(B)	3.65	5.00

[a] Solvent given in brackets: E = methanol or ethanol, C = cyclohexane, B = benzene, T = 1,2,4-trichlorobenzene, M = 1-methylnaphthalene. For the UV spectra of the hydrocarbons see Ref. 3, except for 9 (Ref. 7), and 10 and 11 (Ref. 8).

[b] Corrected for the gas phase, see Refs. 1 and 3.

[c] Value uncertain due to overlap with PE bands of the dihydro compound.

the PE spectra of the other angular benzologues and naphthologues, there is always a band centred at about 8.5 eV. The resulting $\Delta\beta$-values, obtained by subtracting the β-band energies from the PE values, all approach 4.9 eV; this is shown by the second line in Fig. 2.

Similar observations are made in the 1,12-benzoperylene series, see Fig. 3 and Table 2. The upper level of the p-bands again approaches 3.4 eV. This is particularly true for 1,12:2,3:10,11-tribenzoperylene **15** which is the only fully benzenoid hydrocarbon of the

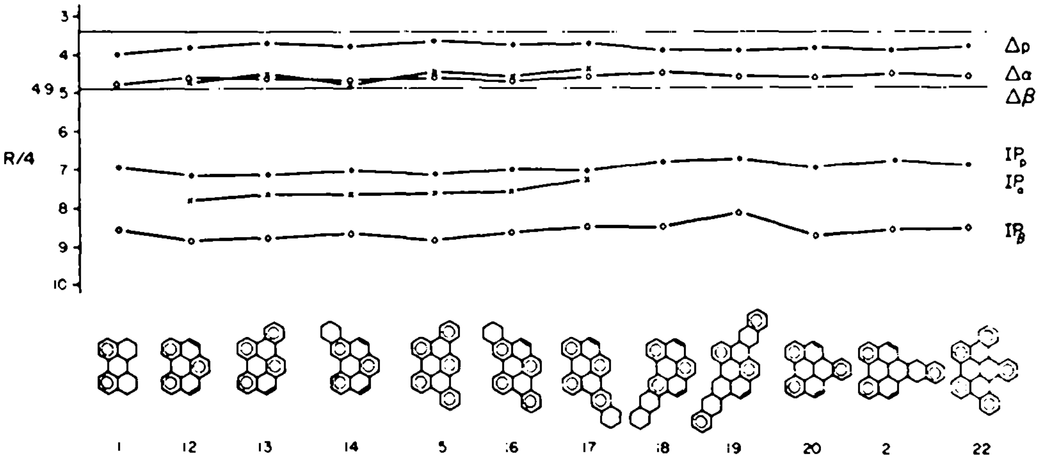

Fig. 3. Relation between the IP's (lower lines and the upper levels of the p-, α- and β-absorption bands (upper lines) in the 1,12-benzoperylene series. α-Bands and the corresponding IP's are marked with crosses.

Table 2. PE and UV data of the 1,12-benzoperylene-type hydrocarbons.[a] For definition of quantities see Table 1. IP_α, λ_α, E_α and $\Delta\alpha$ refer to the α-absorption bands if visible in the UV spectra

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
1,12-Benzoperylene **12**	7.15	3875(B)	3.35	3.80	7.81	4065(B)	3.09	4.72	8.83	3030(B)	4.24	4.59
1,12:2,3-Dibenzoperylene **13**	7.12	3775(B)	3.43	3.69	7.68	4050(B)	3.11	4.58	8.73	3095(B)	4.16	4.58
1,12:4,5-Dibenzoperylene **14**	6.99	4070(B)	3.20	3.80	7.61	4290(B)	2.93	4.68	8.53	3330(B)	3.87	4.66
1,12:2,3:10,11-Tribenzoperylene **15**	7.13	3740(T)	3.49	3.64	7.60	4010(T)	3.14	4.46	8.58	3000(E)	4.24	4.34
1,12:2,3:8,9-Tribenzoperylene **16**	6.97	4020(B)	3.23	3.74	7.57	4210(B)	2.99	4.58	8.51	3290(B)	3.92	4.59
1,12-Benzo-naphtho-(2',3':2,3) perylene **17**	7.04	3830(B)	3.39	3.65	7.40	4300(B)	2.93	4.32	8.48	3260(B)	3.95	4.53
1,12-Benzo-naphtho-(2',3':4,5) perylene **18**	6.78	4500(B)	2.90	3.88					8.48	3220(B)	4.00	4.48
1,12-Benzo-dinaphtho(2',3':2,3); (2",3":8,9)perylene **19**	6.72	4600(T)	2.87	3.85					8.14	3650(T)	3.57	4.57
1,12-o-Phenyleneperylene **20**	6.96	4180(B)	3.12	3.85					8.75	3105(B)	4.14	4.61
Anthraceno-(1',4':1,12)perylene **21**	6.77	4575(B)	2.86	3.91					8.60	3153(B)	4.08	4.52
1,12-o-Phenylene-2,3;10,11-dibenzo-perylene **22**	6.84	4260(B)	3.06	3.78					8.49	3260(B)	3.95	4.54

[a] For UV spectra of the hydrocarbons see Ref. 3, except for 17, 18, 19 and 21 (Ref. 8).

series, i.e. all its π electrons can be accommodated in aromatic sextets.[5]

A number of hydrocarbons in Fig. 3 also show well-defined α-bands in the optical spectra. The PE spectra of these hydrocarbons also show α-bands from which the upper level can be determined; the resulting values are very close to the upper levels of the β-bands (see Fig. 3 and Table 2).

Figure 4 and Table 3 contain the UV and PE data of the coronene-type hydrocarbons. Coronene **23** can be considered as a benzologue of perylene **1**. However, the two rings filling the bay positions in perylene produce a profound change because the three sextets can now migrate throughout the whole system. Due to this superaromaticity,[6] which is also evident in the NMR, coronene **23** behaves like a fully benzenoid hydrocarbon. This is apparent by the fact that the upper level of the p-band, 3.51 eV, comes very close to R/4. Subtraction of the β-band energy from 9.13 eV results in 4.92 eV which is almost exactly the IP of graphite. In order to obtain the upper level of the α-band, we have to subtract the α-band energy from the energy of the first PE band which, due to the sixfold symmetry of coronene, accommodates two IP's. The resulting value of 4.35 eV compares well with those gathered in Table 2.

The deviations of the upper levels from the ideal values increase as benzo rings are annellated to the coronene system. Here again the rule is valid that the highest number of sextets brings the upper value of the p-bands closest to R/4. The only fully benzenoid hydrocarbon in the coronene series is hexa-peri-benzocoronene **30**. The upper values of the p-, α- and β-bands are 3.50, 4.60 and 4.72 eV, respectively, values which are perfectly satisfactory. It should be added that α-type bands in the PE spectra can only be observed if they occur in the optical spectra, and *vice versa*. Keeping this in mind, Fig. 4 requires no further explanation.

The UV and PE data of the bisanthene-type hydrocarbons are summarized in Fig. 5 and Table 4. Bisanthene (meso-naphthodianthrene, **31**) is derived from two anthracene complexes in the same way as perylene from naphthalene. Its PE spectrum shows a similar unusually

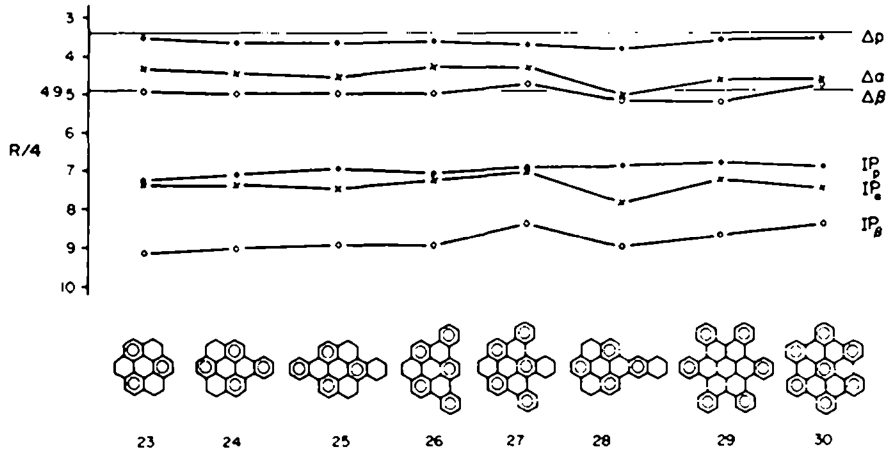

Fig. 4. Relation between the IP's and the upper levels of the p-, α- and β-absorption bands in the coronene series. For symbols see legends to Figs. 2 and 3.

Table 3. PE and UV data of the coronene-type hydrocarbons.* For definition of quantities see Tables 1 and 2

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
Coronene **23**	7.29	3415(B)	3.78	3.51	7.29	4280(B)	2.94	4.35	9.13	3050(B)	4.21	4.92
1,2-Benzocoronene **24**	7.08	3760(B)	3.45	3.63	7.35	4320(B)	2.91	4.44	9.02	3200(B)	4.02	5.00
1,2:7,8-Dibenzocoronene **25**	6.92	4010(T)	3.27	3.65	7.43	4350(T)	2.90	4.53	8.89	3300(T)	3.93	4.96
1,2:5,6-Dibenzocoronene **26**	7.04	3790(T)	3.45	3.60	7.18	4335(T)	2.91	4.27	8.92	3280(T)	3.95	4.97
1,2:3,4:5,6-Tribenzocoronene **27**	6.88	4070(B)	3.20	3.68	7.02	4640(B)	2.72	4.30	8.38	3540(B)	3.65	4.73
Naphtho-(2',3':1,2)coronene **28**	6.88	4230(B)	3.08	3.80	7.86	4440(B)	2.84	5.02	8.97	3410(B)	3.78	5.19
1,2:3,4:5,6:7,8:9,10:11,12-Hexabenzocoronene **29**	6.75	4020(B)	3.23	3.53	7.16	4860(B)	2.59	4.57	8.59	3760(B)	3.45	5.14
1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene **30**	6.87	3875(T)	3.37	3.50	7.44	4440(T)	2.84	4.60	8.34	3600(T)	3.62	4.72

*For UV spectra of the hydrocarbons see Ref. 3, except for 29 (Ref. 9).

Table 4. PE and UV data of the bisanthene-type hydrocarbons.* For definition of quantities see Tables 1 and 2

Hydrocarbon	IP_1	λ_p	E_p	Δp	IP_α	λ_α	E_α	$\Delta\alpha$	IP_β	λ_β	E_β	$\Delta\beta$
Bisanthene **31**	6.30	6625(B)	2.02	4.28					7.90	4240(B)	3.07	4.83
1,14-Benzobisanthene **32**	6.50	5355(B)	2.46	4.04					8.54	3450(B)	3.74	4.80
Ovalene **33**	6.71	4560(M)	2.91	3.81	7.33	4650(M)	2.72	4.61	8.66	3490(M)	3.74	4.92
3,4:11,12-Dibenzobisanthene **34**	6.82	4170(B)	3.12	3.70	7.20	4660(B)	2.70	4.50	8.49	3580(B)	3.61	4.88

*For UV spectra of the hydrocarbons see Ref. 3.

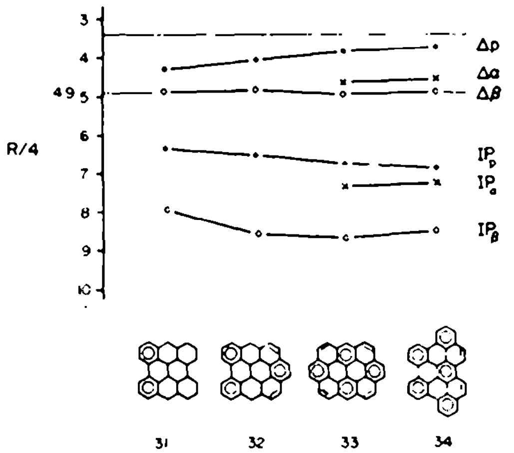

Fig. 5. Relation between the IP's and the upper levels of the p-, α- and β-absorption bands in the bisanthene series. For symbols see legends to Figs. 2 and 3.

wide gap between the first and second bands (6.30 and 7.90 eV, respectively) as does perylene. Therefore, one would expect the IP's in the series bisanthene, 1,14-benzobisanthene **32** and ovalene **33** to show the same trends as in the series perylene, 1,12-benzoperylene **12** and coronene **23** which is the case indeed. IP_1 increases from 6.30 to 6.50 to 6.71 eV; the corresponding upper levels change from 4.28 to 4.04 to 3.81 eV, thus approaching R/4 due to increased benzenoidity (ovalene has four sextets). The same observation is made in the perylene series. This is also reflected in the IP's of the β-type PE bands which move from 7.90 to 8.54 to 8.66 eV, thus showing increased stability with the number of sextets. The upper level of the β-bands is again kept constant at about 4.9 eV. In addition to this, ovalene **33** and 3,4:11,12-dibenzobisanthene **34** show α-type PE bands at 7.33 and 7.20 eV, respectively. The upper levels are close to those of the β-bands, namely at 4.61 eV in ovalene **33** and at 4.54 eV in dibenzobisanthene **34**. Thus, in all cases where α-bands are observed in the optical spectra they can also be seen in the PE spectra.

A detailed description of the PE spectra in terms of MO theory will be published elsewhere.

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