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CORRELATIONS BETWEEN PHOTOELECTRON AND PHOSPHORESCENCE SPECTRA OF POLYCYCLIC HYDROCARBONS

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Abstract—Comparison of the first IP's obtained from the photoelectron spectra of polycyclic hydrocarbons with the phosphorescence bands and the p-, α- and β-bands in the absorption spectra shows that only the first IP's, the first p-bands and the first phosphorescence bands are related to each other. The first triplet level T can be calculated from the difference $IP_1 - E_t = T$, where E_t is the energy of the first phosphorescence band. The first triplet level T approaches 4.9 eV which is the vertical IP of graphite. Any deviation from this value is strictly related to the number of aromatic sextets in polycyclic systems. This applies to kata- and peri-condensed hydrocarbons. The asymmetric annellation effects reported in earlier work are again supported by the phosphorescence spectra. Contrary to the observations with the α-, β- and p-bands, there is considerable interaction with the third branch in linear benzologues of triphenylene (starphenes) when the t-bands are formed, and the T level shifts towards higher energies (lower eV values).

In a recent paper[1] the α-, p- and β-bands in the visible and UV spectra of polycyclic aromatic hydrocarbons have been correlated to the photoelectron spectra, and it was shown that the p-bands are in direct relation to the first photoelectron bands, whereas the α- and β-bands are related to higher photoelectron bands. The upper level of the p-bands, defined as $\Delta p = IP_1 - E_p$ (where E_p is the energy of the first p-band), was shown to be R/4 = 3.4 eV, R being the IP of the hydrogen atom.

Since it has been demonstrated earlier[2] that the energies of the lowest triplet state (E_t), as obtained from the phosphorescence spectra, correlate with the p-band energies, one should expect a relation between E_t and IP_1. The present paper shows that this is the case indeed. Furthermore, the connection between the upper level of the phosphorescence bands, defined as $T = IP_1 - E_t$, and the IP of graphite (4.9 eV) is pointed out.

Figures 1 and 2 (see also Table 1) give, for 34 hydrocarbons, the first IP's and the upper levels of the p-absorption and phosphorescence bands, Δp and T. Most of the phosphorescence and photoelectron data were taken from Refs. 2–5; some are reported here for the first time.

It is seen that the deviations of the Δp and T values from the two lines at 3.4 and 4.9 eV are profoundly influenced by the number of aromatic sextets in the various hydrocarbons. As one would expect, the greatest deviations are observed in benzene. This molecule has six π electrons on its own, not sharing some of them with neighbouring rings. The deviations are reduced in naphthalene, where the sextet is shared between two rings.[6]

There are two sextets in phenanthrene, chrysene and 3,4-benzophenanthrene; their Δp and T values are correspondingly very close together. The hydrocarbons with 3 sextets (picene, 3,4:5,6-dibenzophenanthrene and triphenylene) have again very similar Δp and T values, except that triphenylene has the highest IP in the series, as one would expect for a fully benzenoid hydrocarbon.[8] Moreover, the T value comes close to the IP of graphite, 4.9 eV, just as Δp approaches closest R/4 amongst these three hydrocarbons.

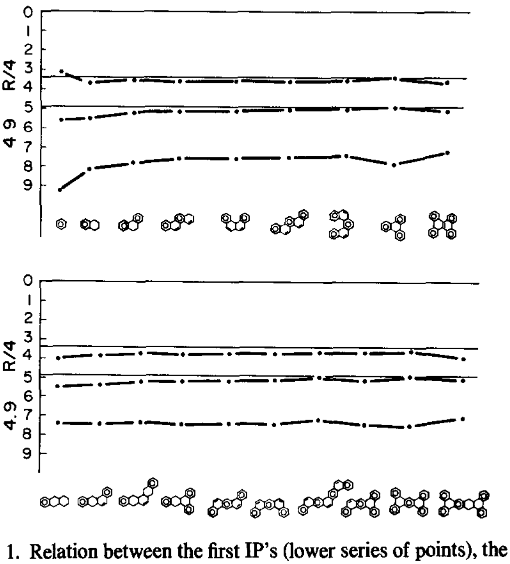

Fig. 1. Relation between the first IP's (lower series of points), the Δp values near R/4, and the first triplet levels T near 4.9 eV of kata-condensed hydrocarbons. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked.

1,2:7,8-Dibenzochrysene does not reach triphenylene in that respect. Although it has four aromatic sextets, it is not a fully benzenoid hydrocarbon.

The T values in the anthracene series show similar

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Table 1. First IP's (IP$_1$) from the photoelectron spectra, wavelengths[a] of the p-absorption bands (λ_p), p-band energies[b] (E_p), differences $\Delta p = IP_1 - E_p$, wavelengths of the lowest triplet states (λ_t) from the phosphorescence spectra,[c] triplet state energies (E_t), and differences $T = IP_1 - E_t$. Energies in eV, wavelengths in Å

Hydrocarbon	IP$_1$	λ_p	E_p	Δp	λ_t	E_t	T
Benzene	9.24	2038 (G)	6.08	3.16	3401 (E)[4]	3.65	5.59
Naphthalene	8.15	2850 (E)	4.46	3.69	4695 (P)[4]	2.64	5.51
Phenanthrene	7.86	2925 (E)	4.35	3.51	4621 (E)[2]	2.68	5.18
Chrysene	7.59	3190 (E)	4.00	3.59	4990 (E)[2]	2.49	5.11
3,4-Benzophenanthrene	7.60	3150 (E)	4.05	3.55	4995 (E)[2]	2.48	5.12
Picene	7.52	3290 (B)	3.92	3.60	4980 (E)[2]	2.49	5.03
3,4:5,6-Dibenzophenanthrene	7.51	3290 (E)	3.88	3.63	5051 (E)[2]	2.46	5.06
Triphenylene	7.88	2840 (E)	4.48	3.40	4202 (H)[4]	2.95	4.93
1,2:7,8-Dibenzochrysene	7.20	3510 (E)	3.64	3.56	5790 (E)[2]	2.14	5.06
Anthracene	7.41	3745 (E)	3.42	3.99	6803 (P)[4]	1.82	5.59
1,2-Benzanthracene	7.41	3590 (B)	3.60	3.81	6053 (E)[2]	2.05	5.36
Pentaphene	7.27	3560 (E)	3.59	3.68	5907 (E)[2]	2.10	5.17
1,2:3,4-Dibenzanthracene	7.39	3490 (E)	3.66	3.73	5627 (E)[2]	2.20	5.19
1,2:5,6-Dibenzanthracene	7.38	3500 (E)	3.65	3.73	5476 (E)[2]	2.26	5.12
1,2:7,8-Dibenzanthracene	7.40	3510 (B)	3.68	3.72	5405 (E)[2]	2.29	5.11
3,4:9,10-Dibenzopentaphene	7.11	3680 (B)	3.52	3.59	5682 (E)[2]	2.18	4.93
1,2:3,4:5,6-Tribenzanthracene	7.40	3450 (B)	3.74	3.66	5163 (E)[2]	2.40	5.00
Tetrabenzanthracene	7.43	3335 (B)	3.87	3.56	4866 (E)[2]	2.55	4.88
Tetrabenzotetracene	7.00	4190 (T)	3.13	3.87	6042 (E)[6]	2.05	4.95
Perylene	6.97	4340 (E)	2.97	4.00	7937 (H)[4]	1.56	5.41
1,12-Benzoperylene	7.15	3875 (B)	3.35	3.80	6180 (E)[2]	2.01	5.14
Coronene	7.29	3415 (B)	3.78	3.51	5252 (E)[2]	2.36	4.93
1,2-Benzocoronene	7.08	3760 (B)	3.45	3.63	5500 (M)	2.25	4.83
1,2:7,8-Dibenzocoronene	6.92	4010 (T)	3.27	3.66	6000 (T)	2.07	4.85
1,2:5,6-Dibenzocoronene	7.04	3790 (T)	3.45	3.60	5490 (T)	2.26	4.78
1,2:3,4:5,6-Tribenzocoronene	6.88	4070 (B)	3.20	3.69	6000 (T)	2.07	4.81
Circobiphenyl	6.90	4190 (T)	3.13	3.77	6098 (T)[3]	2.03	4.87
Pyrene	7.41	3335 (E)	3.83	3.58	5935 (E)[2]	2.09	5.32
1,2-Benzopyrene	7.41	3315 (E)	3.85	3.56	5402 (E)[2]	2.30	5.11
1,2:6,7-Dibenzopyrene	7.39	3280 (B)	3.93	3.46	4912 (E)[2]	2.52	4.87
1,12:2,3:10,11-Tribenzoperylene	7.13	3740 (T)	3.49	3.64	5350 (E)[10]	2.32	4.81
1,2:3,4:5,6:10,11-Tetrabenzanthanthrene	7.10	3650 (T)	3.57	3.53	5440 (D)[10]	2.28	4.82
1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene	6.89	3875 (T)	3.37	3.52	5750 (T)[10]	2.16	4.73
1,2:3,4:5,6:7,8:9,10:11,12-Hexabenzocoronene	6.78	4020 (T)	3.26	3.52	6160 (M)	2.01	4.77

[a] Solvent given in brackets: G = gas phase, E = methanol or ethanol or EPA, D = dioxane, H = heptane, M = methylcyclohexane/isopentane or methylcyclopentane/methylcyclohexane, P = liquid paraffin, B = benzene, T = 1,2,4-trichlorobenzene.

[b] Corrected for the gas phase, see Refs. 1 and 6.

[c] Measured at 77°K. Figures after the solvent are the same as for the References. Unmarked values result from new measurements.

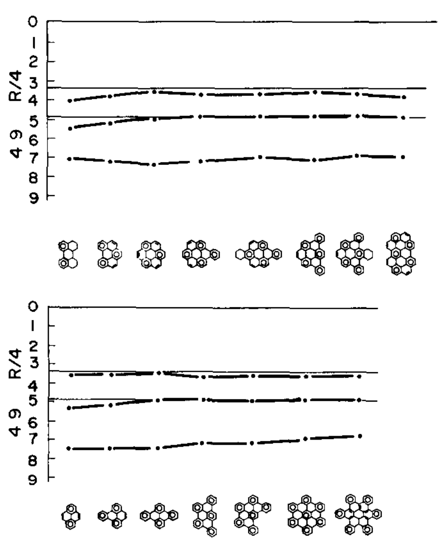

Fig. 2. Relation between the first IP's (lower series of points), the Δp values near R/4, and the first triplet levels T near 4.9 eV of peri-condensed hydrocarbons. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked.

trends as the Δp values discussed in our recent paper.[1] Thus, the greatest deviation is encountered in anthracene; it is gradually reduced in passing to 1,2-benzanthracene and pentaphene (each having two sextets), and further in progressing to the three isomeric dibenzanthracenes which have three sextets in five rings. The deviation from the ideal value is further reduced in 3,4:9,10-dibenzopentaphene, tribenzanthracene and tetrabenzanthracene, the latter again being a fully benzenoid hydrocarbon and as such reaching exactly 4.9 eV. It is most remarkable that tetrabenzotetracene, which is the only tetracene derivative where phosphorescence has been observed, deviates considerably from the ideal value because it is not a fully benzenoid hydrocarbon. We think that this example constitutes a severe test for the usefulness of the concept of the aromatic sextet.

Figure 2 contains the peri-condensed hydrocarbons beginning with perylene. It came as a big surprise that the complex band centred at 8.7 eV in its photoelectron spectrum could be only correlated with the weak band at 3375 Å in the low-temperature ultraviolet spectrum.[6] This is supported by the photoelectron spectra of 1,2-benzoperylene and 1,2:11,12-dibenzoperylene. As will be shown in a future communication, this is also the case with bisanthene and terrylene, i.e. hydrocarbons with formally empty rings connected in peri-positions.

Just as the p-band of perylene shows the biggest deviation within the perylene-type hydrocarbons, this applies also to the phosphorescence band. The introduction of a further sextet in 1,12-benzoperylene reduces the deviation which disappears practically in coronene. Due to its superaromaticity,[9] coronene behaves like a fully benzenoid hydrocarbon. In the following benzologues of coronene: 1,2-benzocoronene, 1,2:7,8-dibenzocoronene, 1,2:5,6-dibenzocoronene, 1,2:3,4:5,6-tribenzocoronene and circobiphenyl the upper level of the first phosphorescence band T remains almost unchanged around 4.9 eV (see Fig. 2). However, there are increasing deviations from the R/4 level towards higher values. It appears possible that in very large hydrocarbons both upper levels converge at 4.9 eV, i.e. the IP of graphite.

The lower series in Fig. 2 begins with pyrene. Here again the introduction of additional sextets in going to 1,2-benzopyrene and 1,2:6,7-dibenzopyrene (the latter being fully benzenoid) reduces the deviations and brings the Δp and T values to 3.4 and 4.9 eV, respectively. The following hydrocarbons: 1,12:2,3:10,11-tribenzoperylene, 1,2:3,4:5,6:10,11-tetrabenzanthanthrene and hexa-peri-benzocoronene are fully benzenoid. Their upper levels are very similar with hardly any deviation from 4.9 eV and a distinct deviation towards higher values of the Δp level. This trend is increased in going to the not fully benzenoid 1,2:3,4:5,6:7,8:9,10:11,12-hexabenzocoronene. In that respect there is complete agreement between the two series of hydrocarbons. In both cases the two upper levels appear to be approaching the same value.

Independent from the above rules the lifetime of the phosphorescence depends entirely on the number of sextets or, in the case of coronene, on superaromaticity. The longest life of the phosphorescence is found in fully benzenoid hydrocarbons; it is gradually reduced with the number of formal double bonds or π electrons which are not accommodated in sextets. Thus, 1,2:5,6-dibenzocoronene has a phosphorescence of longer life than the isomeric 1,2:7,8-dibenzocoronene.

The establishment of the upper phosphorescene level T makes it worthwhile to consider again the asymmetric annellation effects in the acene series.[1] This is done for the acenes, the 1,2:3,4-dibenzacenes and tetrabenzacenes in Fig. 3. The asymmetric annellation effect is again confirmed, now including the phosphorescence bands. It is similar as for the p-bands.

However, the annellation effect on the Δp and T levels is different (see Fig. 4). Whilst in the former case the observed shifts are small for the two terminal benzo-rings, they are much stronger for the T level. This comparison shows also that the third branch of a linear benzologue of triphenylene does participate considerably in the T level. This is easily understandable. In the triplet state one pair of π electrons is split up and the two odd electrons with the same spin prefer to migrate in different branches because of the Coulomb repulsion.

This being the case the asymmetric annellation effect for the first phosphorescence bands in the series benzene, phenanthrene and 1,2:5,6-dibenzanthracene must be bigger than in the series benzene, triphenylene and tetrabenzanthracene. According to Figs. 5 and 3 these shifts are −0.97 and −0.42 eV for the former series, and −0.70 and −0.40 eV for the latter series. This shows the importance of the number of sextets in the T level and the participation in the interaction with the third branch.

We intend to study the threefold interaction on the T level with other hydrocarbons.

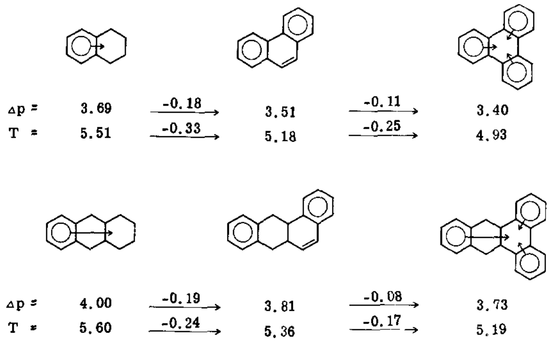

Fig. 4. Annellation effects of the upper levels of the p-bands, Δp, and the first triplet levels, T, in the series acene, 1,2-benzacene and 1,2:3,4-dibenzacene. Symbolization of double bonds as before.

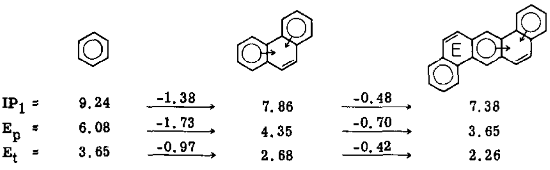

Fig. 5. Asymmetric annellation effects of the first IP's, IP_1, the p-band energies, E_p, and the first phosphorescence band energies, E_t. Symbolization of double bonds as before.

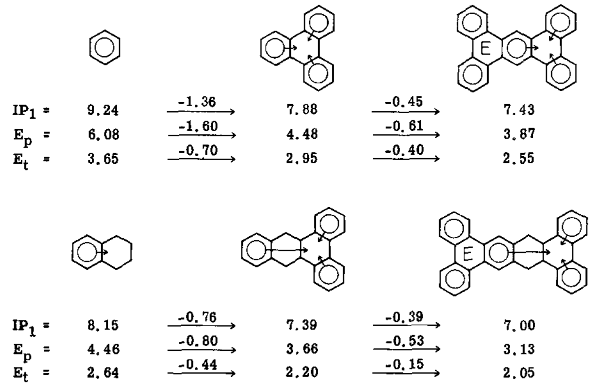

Fig. 3. Asymmetric annellation affects of the first IP's, IP_1, the p-band energies, E_p, and the first phosphorescence band energies, E_t. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked.

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