Tetrahedron Vol. 34, pp. 3219–3224
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0040-4020/1101-3219/$02.00/0

CORRELATIONS BETWEEN PHOTOELECTRON AND ULTRAVIOLET ABSORPTION SPECTRA OF POLYCYCLIC HYDROCARBONS. THE TERRYLENE AND PEROPYRENE SERIES

E. Clar*
Department of Chemistry, University of Glasgow, Glasgow W2, Scotland

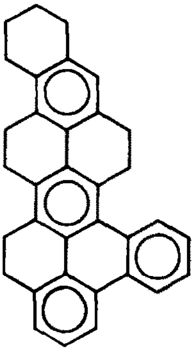
and

W. Schmidt
Institut für Organische Chemie der Universität, Karlstr. 23, D-8 München-2, Germany

(*Received in the UK 24 February 1978; Accepted for publication 14 April 1978*)

Abstract—The photoelectron spectra of terrylene, peropyrene and their benzologues are studied and related to their optical spectra. The analogy to the perylene and pyrene series considered in earlier papers is perfect.

As part of a continued study[1-3] of the relationships between the PE and optical spectra of polycyclic aromatic hydrocarbons, we consider in the present paper the terrylene- and peropyrene-type hydrocarbons. Due to their high melting points and consequent low volatility, these compounds presented difficulties initially in that some of them required probe temperatures up to 600° to yield adequate vapour pressures for PE spectroscopic measurements. These difficulties have now been overcome with the development[4] of a high-powered, all-metal hollow-cathod lamp system in conjunction with a heatable probe made of mu-metal or W–Cu alloy. High-resolution gas-phase PE spectra are now available for the complete set of hydrocarbons, and some representative spectra are shown in Figs. 1–4. The energy scale was calibrated using the α- and β-peaks of Ar, Xe, CH_3I, benzene and naphthalene; particularly useful was the He^+ peak at 4.98 eV. This calibration procedure guarantees an accuracy of ±0.02 eV for the location of the sharp peaks in the spectra. The remarkable stability of the hydrocarbons is borne out by the fact that no decomposition products could be observed.



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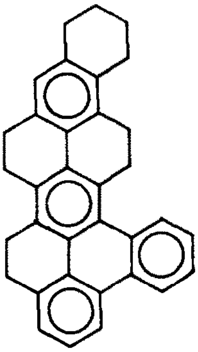

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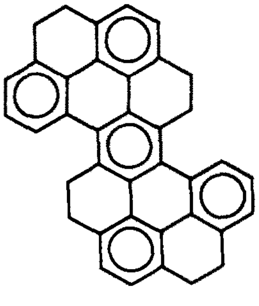
The present PE data allow us to assign unambiguous structures to the two dibenzoperopyrenes which are formed if benzanthrone is condensed with phosphorous oxychloride.[5] The two isomers, for which only the structures 17 and 18 come into question, could be separated by chromatography,[5] but since they have the same number of aromatic sextets,[6] their optical spectra are practically identical as are the first IP's. Comparison of the higher IP's from the PE spectra with the results of Hückel calculations shows that the lower melting (279°) hydrocarbon is the isomer 17 and the higher melting one (334–335°) is the isomer 18. A similar ambiguity exists for the two dinaphthoperopyrenes which are obtained when naphthanthrone is condensed in a zinc dust melt.[7] Structure 19 with five sextets has been assigned[5,8] to the isomer which absorbs at shorter wavelengths; this is in accord with the PE and Hückel results as well as other chemical evidence.[7] The other isomer which absorbs at longer wavelengths can have either structure 20a or 20b.



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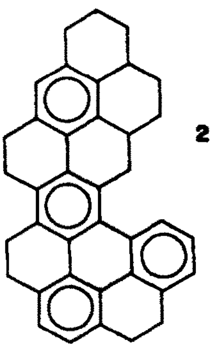

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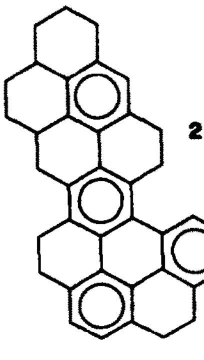

20b

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*Address correspondence to this author at: Punta Chullera Km 144, Estepona Prov. Malaga, Spain.

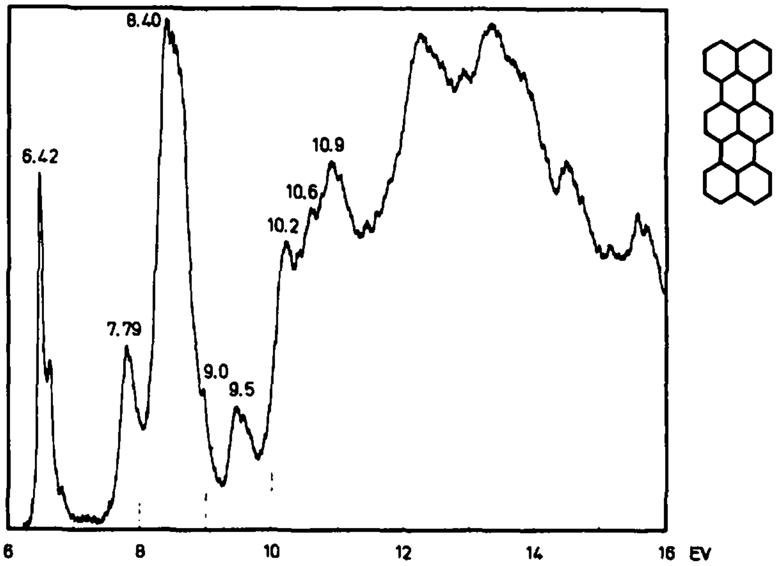


Fig. 1. Gas-phase PE spectrum of terrylene.

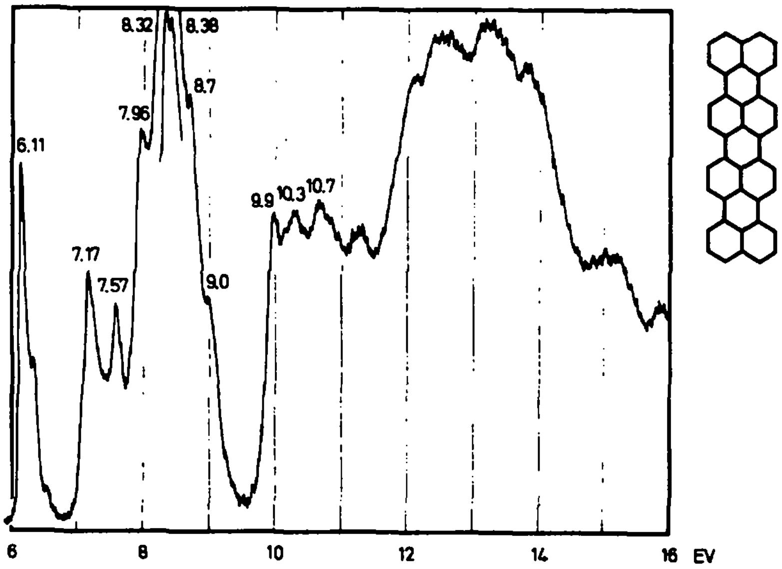
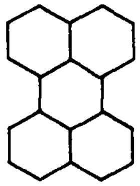
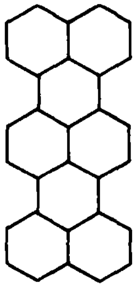


Fig. 2. Gas-phase PE spectrum of quaterrylene.

Since these have both four sextets, their optical spectra (and first IP's) would be very similar so that no decision is possible. Unfortunately, the higher IP's calculated by Hückel theory for **20a** and **20b** show only minor differences in the two isomers. The structure which we have adopted for the longer-wavelength absorbing isomer should therefore be regarded as tentative.

Terrylenes. The parent hydrocarbon **1** is built up of three naphthalene complexes in the same way as perylene is built up of two naphthalenes. Addition of another naphthalene complex gives quaterrylene **11**. The PE and optical spectra reveal surprising similarities; there is a large gap between the first and second PE bands, and the *p*-band is the first band in the optical spectra. The values for IP_p form a converging series: 8.15, 6.97, 6.42 and





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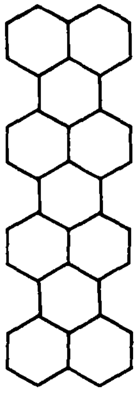

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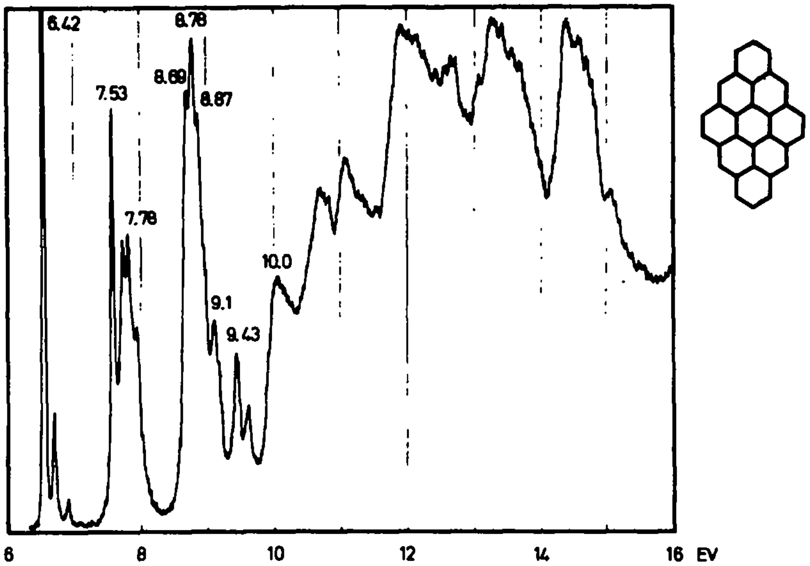


Fig. 3. Gas-phase PE spectrum of 5,6:12,13-dibenzoperopyrene.

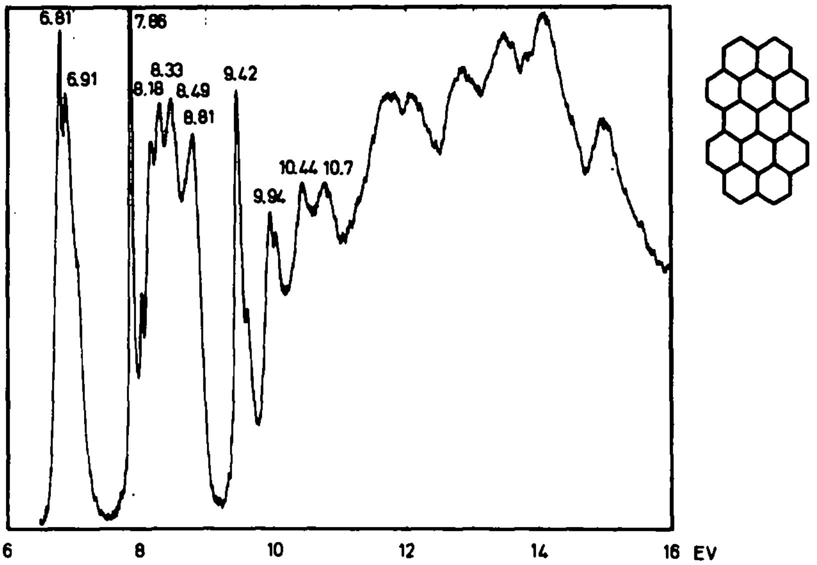


Fig. 4. Gas-phase PE spectrum of circobiphenyl.

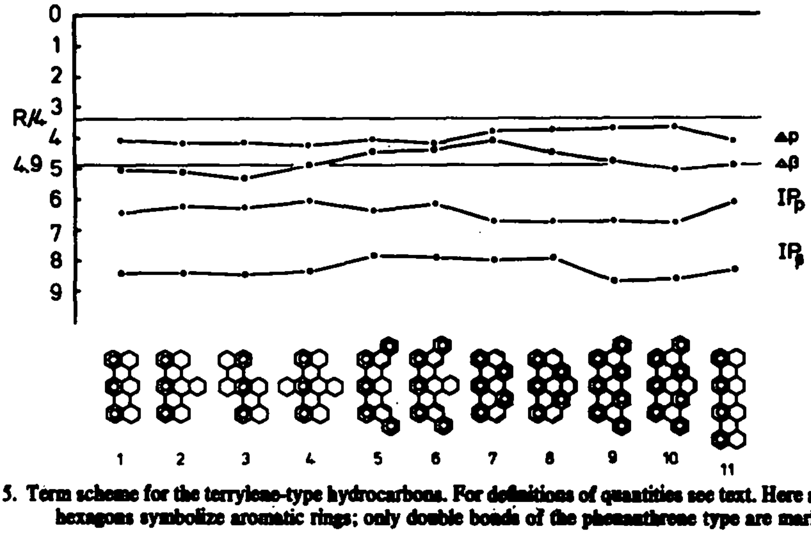


Fig. 5. Term scheme for the terrylene-type hydrocarbons. For definitions of quantities see text. Here and in Fig. 6 all hexagons symbolize aromatic rings; only double bonds of the phenanthrene type are marked.

6.11 eV for naphthalene, perylene, terrylene and quaterrylene. This is in perfect agreement with the shifts observed in the optical spectra. The values for IP_β form another converging series: 9.98, 8.54, 8.40 and 8.32 eV.

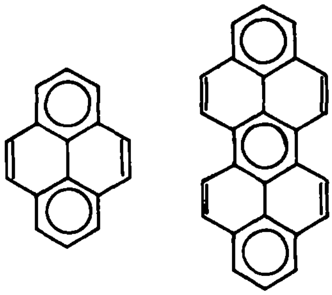
Linear annellation on the middle naphthalene complex of 1 to give anthracene or tetracene complexes as in 2, 3 and 4 lowers IP_p in the same way as in the perylene series: 6.42, 6.22, 6.27 and 6.06 eV. The corresponding values for Δp are as follows: 4.06, 4.14, 4.15 and 4.23 eV. Somewhat smaller changes are observed for IP_β and Δβ (see Table 1). The value of Δβ for hydrocarbon 3 is the highest so far recorded. Hydrocarbon 3 does in fact not belong to the terrylene series;[8] it has only been included because of the surprising similarity of its optical spectrum with that of the isomer 2.

In accordance with the observations made in the acene series,[1] angular annellation as in 5 and 6 has only a minor effect on IP_p. Thus, the IP_p values of 1 and 5, on the one hand, and of 2 and 6, on the other hand, are very similar. However, angular annellation lowers the IP_β values, just as was the case in the acene series.

A new type of terrylenes is represented in the bay-annellated hydrocarbons 7 and 8. Due to the larger number of sextets, their IP_p values are considerably higher than those of 1 and 2. The same comment applies to the pair 9 and 10. It should be noted that 9 is a fully benzenoid hydrocarbon with 7 sextets.

Terrylenes with anthracene complexes react with maleic anhydride first in the meso positions, under more vigorous conditions under *exo* addition. Angular annellation enhances the reactivity of the bay positions; even fourfold addition has been observed.[9]

Peropyrenes. As in pyrene, the aromatic sextets in peropyrene enforce location of the double bonds.[6] Annellation at the fixed double bonds should therefore have little effect on the position of the p-absorption band, whereas drastic effects are expected upon annellation at the sextets. This is amply confirmed by the PE and optical data summarized in Table 2 and Fig. 6.

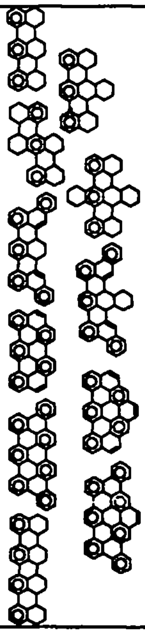


Dibenzoperopyrene 13 and tetrabenzoperopyrene 14 are derived from peropyrene 12 by annellation at fixed double bonds; their IP_p and E_p values are therefore practically unchanged. In isoviolanthrene 15, however, annellation has occurred at two sextets; this causes IP_p and E_p to fall by 0.3 and 0.4 eV, respectively.

The two dibenzoperopyrenes 17 and 18 are intermediate between 13 and 15 in that one benzo ring has been added to a double bond, the other to a sextet. The IP_p and E_p data of 17 and 18 are therefore identical, within experimental error, and lie halfway between those of 13 and 15.

Although isoviolanthrene 15 and violanthrene 16 are both derived from peropyrene by annellation at sextets, they differ in one important respect: 16 can be written with four rather than three sextets so that its IP_p and E_p values are higher than those of its isomer. It should be added that precisely the same observation is made in the pyrene series: the *syn*-dibenzo isomer with three sextets has higher IP_p and E_p values than the *anti* isomer with only two sextets.[3,8]

Table 1. First IP's (IP_p), wavelengths[a] of the p-absorption band (λ_p), p-band energies[b] (E_p), differences $\Delta p = IP_p - E_p$ and corresponding quantities relating to the β-band in the terrylene series. Energies in eV, wavelength in Å

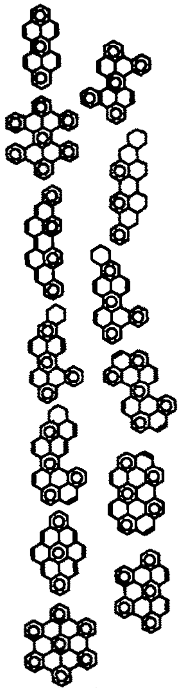


Hydrocarbon	IP_p	λ_p	E_p	Δp	IP_β	λ_β	E_β	Δβ
Terrylene 1	6.42	5600 (B)	2.36	4.06	8.40	3860 (B)	3.36	5.04
7,8-Benzoterrylene 2	6.22	6435 (B)	2.08	4.14	8.41	3920 (B)	3.31	5.10
1,9:5,10-Di-(peri-naphthylene)-anthracene 3	6.27	6300 (B)	2.12	4.15	8.44	4120 (B)	3.16	5.28
7,8:15,16-Dibenzoterrylene 4	6.06	7375 (B)	1.83	4.23	8.40	3725 (B)	3.48	4.92
2,3:12,13-Dibenzoterrylene 5	6.40	5600 (X)	2.36	4.04	7.86	3810 (X)	3.40	4.46
2,3:12,13:15,16-Tribenzo-terrylene 6	6.18	6420 (X)	2.08	4.10	7.90	3680 (X)	3.52	4.38
3,4:5,6:7,8-Tribenzoperopyrene 7	6.74	4460 (T)	2.95	3.79	8.00	3310 (T)	3.92	4.08
3,4:5,6:7,8:12,13-Tetrabenzo-peropyrene 8	6.76	4380 (T)	3.00	3.76	7.95	3780 (T)	3.45	4.50
1,16:2,3:12,13:14,15-Tetrabenzo-terrylene 9	6.72	4350 (T)	3.02	3.70	8.69	3310 (T)	3.92	4.77
1,2:3,4:5,6:7,8:9,10:12,13-Hexa-benzoperopyrene 10	6.79	4220 (T)	3.11	3.68	8.62	3680 (T)	3.54	5.08
Quaterrylene 11	6.11	6730 (N)	2.03	4.08	8.32	3830 (N)	3.42	4.90

[a] Solvent given in brackets: B = benzene, X = xylene, T = 1,2,4-trichlorobenzene, N = 1-methylnaphthalene.

[b] Corrected to the gaseous state, see Refs. 1 and 8.

Table 2. PE and UV data of the peropyrene-type hydrocarbons. For definitions of quantities see Table 1



Hydrocarbon	IP_p	λ_p	E_p	Δp	IP_β	λ_β	E_β	$\Delta\beta$
Peropyrene 12	6.72	4435 (B)	2.94	3.78	8.78	3260 (B)	3.95	4.83
4, 5: 11, 12-Dibenzoperopyrene 13	6.71	4450 (B)	2.94	3.78	8.51	3480 (B)	3.71	4.80
4, 5: 6, 7: 11, 12: 13, 14-Tetrabenzoperopyrene 14	6.71	4670 (B)	2.80	3.91	8.44	3530 (B)	3.66	4.78
Isoviolanthrene 15	6.42	5230 (N)	2.56	3.86	8.46	3640 (N)	3.59	4.87
Violanthrene 16	6.48	4920 (N)	2.71	3.77	8.65	3275 (N)	3.97	4.68
1, 2: 6, 7-Dibenzoperopyrene 17	6.59	4720 (B)	2.78	3.81	8.59	3580 (B)	3.61	4.98
1, 2: 11, 12-Dibenzoperopyrene 18	6.59	4820 (B)	2.72	3.87	8.66	3630 (B)	3.56	5.10
Dinaphtho-(7', 1': 1, 13); (1'', 7'': 6, 8)-peropyrene 19	6.50	5100 (B)	2.58	3.92	8.60	3670 (B)	3.53	5.07
Dinaphtho-(7', 1': 1, 13); (1'', 7'': 9, 11)-peropyrene 20	6.38	5330 (B)	2.48	3.91	8.14	3960 (B)	3.28	4.86
Circobiphenyl 21	6.61	4190 (T)	3.13	3.68	8.33	3640 (T)	3.58	4.75
5, 6: 12, 13-Dibenzoperopyrene 22	6.42	5240 (N)	2.55	3.87	8.69	3620 (N)	3.61	5.08
3, 4: 11, 12-Dibenzobisanthene 23	6.82	4170 (B)	3.12	3.70	8.58	3580 (B)	3.61	4.97
1, 12: 2, 3: 4, 5: 6, 7: 8, 9: 10, 11-Hexabenzocoronene 24	6.87	3875 (T)	3.37	3.50	8.34	3600 (T)	3.62	4.72

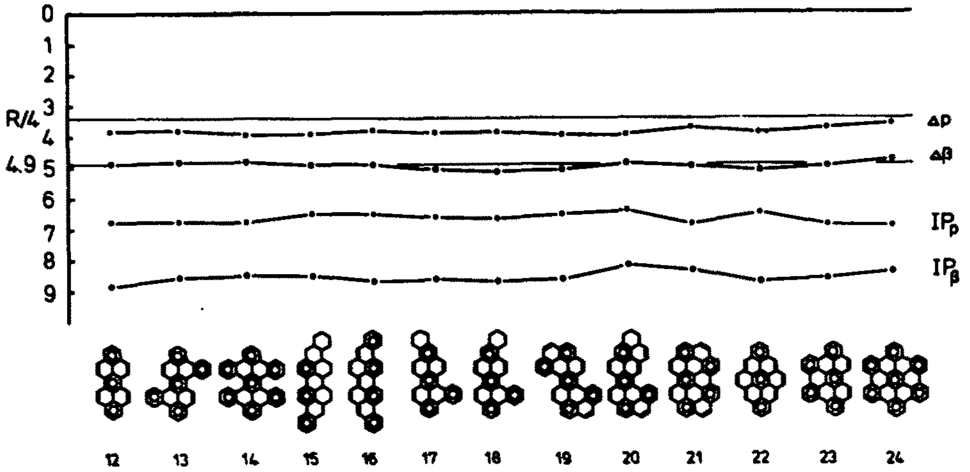
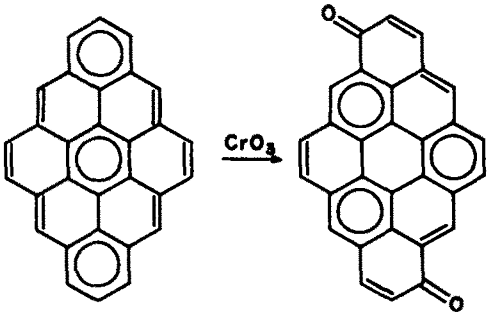
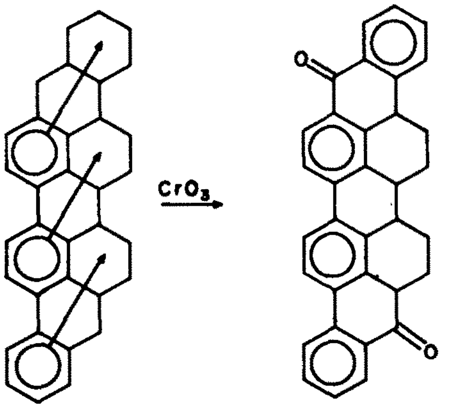


Fig. 6. Term scheme for the peropyrene-type hydrocarbons.





Using the same argument, the different IP_p and E_p data of the isomeric dinaphthoperopyrenes **19** (five sextets) and **20** (four sextets) can be rationalized.

Due to its superaromaticity,[6] circobiphenyl **21** displays extreme stability, high IP_p and E_p values, and phosphorescence of long life.

Dibenzoperopyrene **22** and isoviolanthrene **15** have both three sextets; as a result of this the PE and optical spectra of these "isotopic" hydrocarbons are very similar. However, whereas the sextets are fixed in **22**, they are free to move in **15**. This explains why oxidation with chromic acid gives quinones in which the CO groups occupy different positions.

In conclusion, the sextet concept proves to be very useful in rationalizing and correlating spectroscopic and chemical properties of aromatic hydrocarbons.

A more detailed description of the PE spectra of the present hydrocarbons will appear elsewhere.

REFERENCES

[1] E. Clar and W. Schmidt, *Tetrahedron* 31, 2263 (1975).
[2] E. Clar and W. Schmidt, *Ibid.* 33, 2093 (1977).
[3] E. Clar and W. Schmidt, 34, In Press (1978).
[4] H. J. Lempka, Helectros Developments, Beaconsfield, Bucks., England.
[5] E. Clar, G. S. Fell, C. T. Ironside and A. Balsillie, *Tetrahedron* 10, 26 (1960).
[6] E. Clar, *The Aromatic Sextet.* Wiley, London (1972).
[7] E. Clar, W. Kelly, J. Montheath Robertson and M. G. Rossmann, *J. Chem. Soc.* 3878 (1956).
[8] E. Clar, *Polycyclic Hydrocarbons*, Vol. 2. Academic Press, New York (1964).
[9] E. Clar and A. Mullen, *Tetrahedron* 27, 5239 (1971).