Tetrahedron Vol. 35, pp. 2669 to 2672
Pergamon Press Ltd., 1979. Printed in Great Britain

UNUSUAL π-ELECTRON CONJUGATION IN THE PYRENE SERIES

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

and

W. SCHMIDT and T. ZAUNER
Institut für Organische Chemie der Universität, Karlstr. 23, D-8 München-2, Germany

(*Received in UK* 21 *December* 1978)

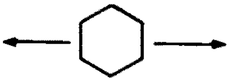
Abstract—The phosphorescence spectra of naphthopyrene 7 and dinaphthopyrene 8, measured at 77 K in organic glasses and at 4.2 K in Shpolskii matrices, are reported. Contrary to expectation, the extension of the π-electron system in 8 relative to 7 produces a small violet rather than a big red shift of the phosphorescence bands. This finding is shown to be fully consistent with the sextet formalism and indicates an interruption of electronic conjugation in 8.

There are three kinds of annellations in aromatic hydrocarbons: The acene type 1 with maximum shifts for all types of UV absorption bands, the phene type 2 with maximum shifts of the α- and β-bands, and the starphene type 3 in which the third branch is ineffective.[1]

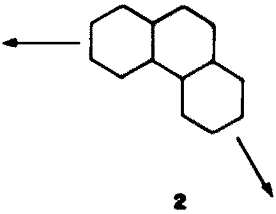
A unique case is represented in pyrene 4 and its linear benzologues[2] 5 and 6. The diphenyl complex in the centre of the pyrene molecule enforces the position of the double bonds. Annellation to these double bonds has very little influence on the positions of the *p*-absorption and phosphorescence bands[3] (λ_p and λ_t, resp.). The shifts are roughly equal for the two benzene rings in going from pyrene 4 to benzopyrene 5 and dibenzopyrene 6.

However, quite different results are obtained by the annellation of naphtho complexes as shown in 4, 7 and 8. The first annellation in going from 4 to 7 causes a considerable positive shift of 115 Å in λ_p whilst the second annellation from 7 to 8 brings a negative shift of −30 Å. This very asymmetric annellation effect reappears in the phosphorescence data where the corresponding values are −152 and −30 Å.

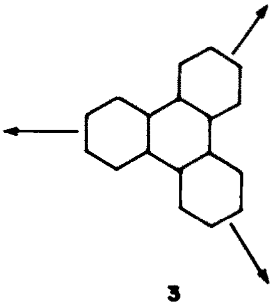
The complete asymmetry is particularly surprising for the triplet state. Here the electrons of one former π-electron pair must have the same spin and one sextet must have been split up because only three π-electron pairs (with opposite spin for the electrons within each



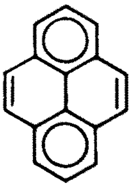
1



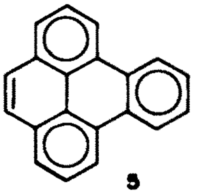
2



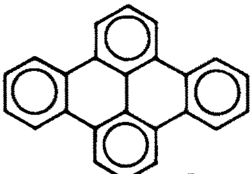
3



4



5



6

$$\lambda_p = 3335\,(E) \xrightarrow{-20} 3315\,(E) \xrightarrow{-35} 3280\,(B) \text{ in Å}$$

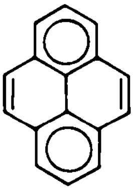
$$E_p = 3.83 \xrightarrow{0.02} 3.85 \xrightarrow{0.08} 3.93 \text{ in eV}$$

$$\lambda_t = 5882\,(E) \xrightarrow{-482} 5400\,(E) \xrightarrow{-490} 4910\,(E) \text{ in Å}$$

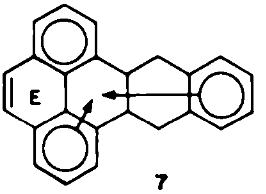
$$E_t = 2.11 \xrightarrow{0.19} 2.30 \xrightarrow{0.23} 2.53 \text{ in eV}.$$

---

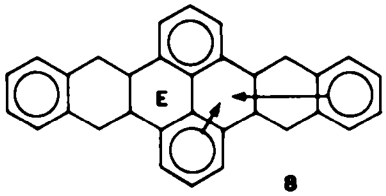
*Present address: Punta Chullera Km 144, Estopona, Prov. Malaga, Spain.



4



7



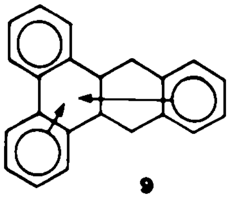
8

$\lambda_p = 3335\,(E) \xrightarrow{115} 3450\,(B) \xrightarrow{30} 3420\,(B)$

$E_p = 3.83 \xrightarrow{0.09} 3.74 \xrightarrow{0.03} 3.77$

$\lambda_t = 5882\,(E) \xrightarrow{152} 5730\,(C) \xrightarrow{30} 5700\,(U)$

$E_t = 2.11 \xrightarrow{0.05} 2.16 \xrightarrow{0.03} 2.19$



9

3490 (E) in Å
3.66 in eV
5630 (E) in Å
2.20 in eV

Solvents: E = ethanol or EPA, B = benzene, C = methylcyclopentane/-hexane, U = n-undecane.

pair) can form an aromatic sextet. In the triplet state one would expect the odd electrons of 7 to go into different branches because of the Coulomb forces.

There is also very little change in going from 7 to 9. Thus, the double bond in 7 which is marked does not enter in aromatic conjugation with the rest of the system. Moreover, the six linearly annellated benzene rings in 8 should cause a shift of about 2000 Å (relative to 7) for the p-bands and much more for the phosphorescence bands if they were in aromatic conjugation. There is also hardly any shift of the α- and β-bands in going from 7 to 8.

All these facts indicate an electronic interruption of the aromatic conjugation by the central aromatic sextets and the formation of empty rings marked "E". MO theory[4] also yields very similar triplet energies for 7 and 8 (2.29 and 2.36 eV, resp.) but does not offer an explanation for these surprising facts. However, the above results are enforced by the aromatic sextets in the central diphenyl system and the formation of induced sextets as indicated by the arrows. Such an arrangement appears to be energetically more favourable than a symmetric distribution of the π-electrons.

In addition to the flashlamp excited[5] low-resolution phosphorescence spectra measured at 77 K, we have also recorded the high-resolution line spectra of 7 and 8 at

Table 1. Vibrational peaks in the line spectra of 7 and 8, with tentative analysis for 8

Naphthopyrene 7			Dinaphthopyrene 8			
No.	Intensity	$\Delta\tilde{\nu}$ [cm^{-1}]	No.	Intensity	$\Delta\tilde{\nu}$ [cm^{-1}]	Possible assignment
1	vs	0	1	max	0	0–0 peak, site A
2	vw	26	2	vs	8	0–0 peak, site B
3	vw	138	3	vs	88	0–0 peak, site C or ν_1
4	w	278	4	w	145	0–0 peak, site D
5	w	301	5	s	180	0–0 peak, site E
6	m	313	6	vs	225	ν_1
7	m	377	7	vw	288	ν_2
8	m	411	8	m	341	ν_3
9	w	454	9	w	411	ν_4
10	vw	482	10	vw	451	$2\nu_1 = 450$
11	w	527	11	vw	530	ν_5
12	vw	545	12	m	591	ν_6
13	m	590	13	m	745	ν_7
14	s	748	14	vw	822	ν_8 or $\nu_1+\nu_6 = 816$
15	m	827	15	s	879	ν_9
16	m	842	16	w	976	ν_{10}
17	s	882	17	w	1 155	ν_{11}
18	w	951	18	w	1 227	ν_{12}
19	m	973	19	w	1 264	$\nu_2+\nu_{10} = 1264$
20	w	1 152	20	w	1 328	$2\nu_1+\nu_9 = 1329$
21	m	1 236	21	m	1 403	ν_{13} or $\nu_1+2\nu_6 = 1407$
22	vw	1 281	22	w	1 546	$3\nu_1+\nu_9 = 1554$
23	w	1 326	23	m	1 571	$\nu_{12}+\nu_3 = 1568$
24	s	1 401	24	m	1 581	ν_{14}
25	m	1 416	25	s	1 612	ν_{15}
26	w	1 474	26	vs	1 637	ν_{16}
27	s	1 569				
28	s	1 593				
29	w	1 610				
30	max	1 641				

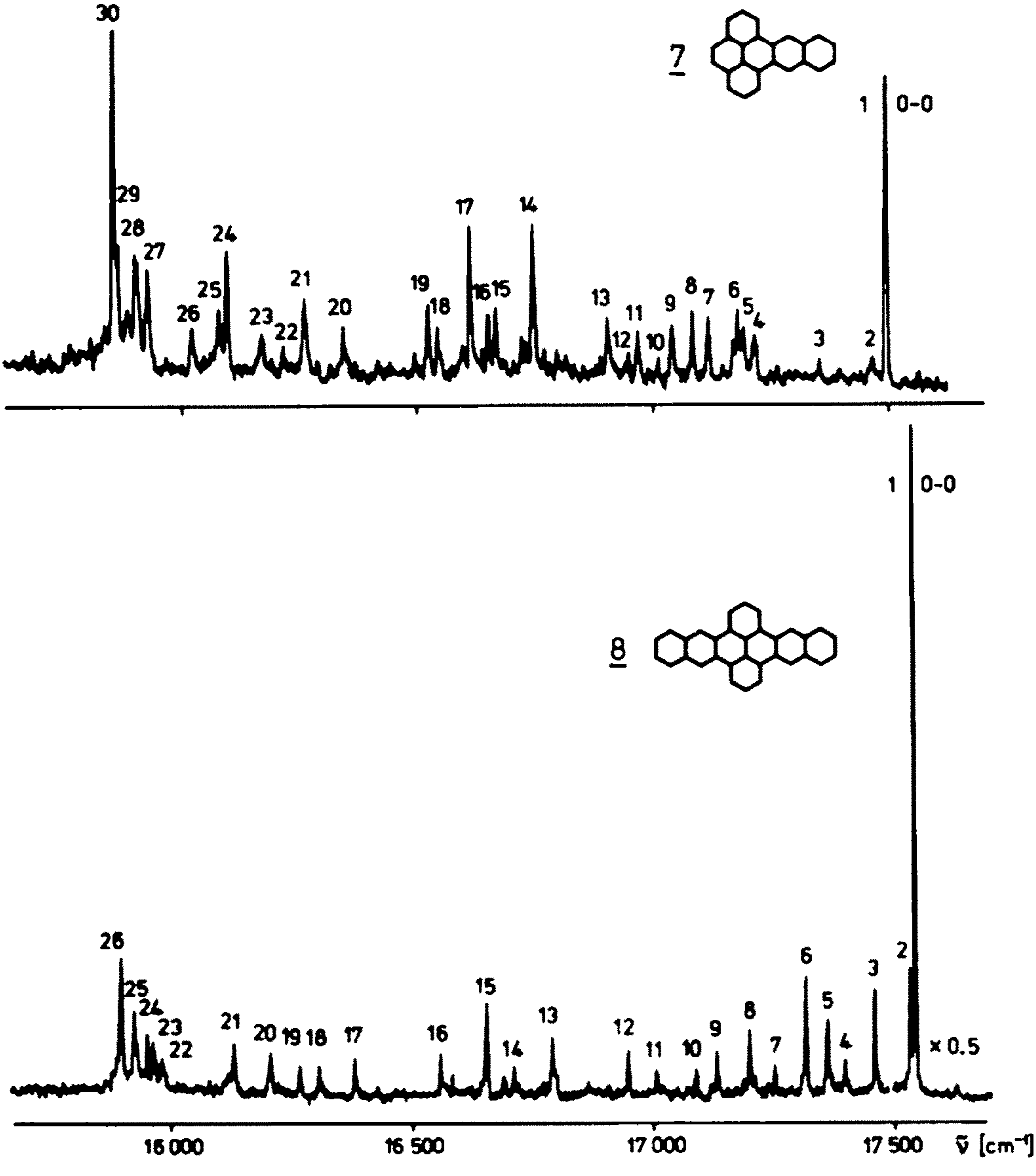


Fig. 1. Phosphorescence spectra of 7 and 8 measured at 4.2 K in *n*-octane and *n*-dodecane, respectively. Concentration *ca.* 10^{-5} mole/L. The O–O bands (site A) are at 17,496 cm^{-1} ≙ 5716 Å for 7 and at 17,535 cm^{-1} ≙ 5703 Å for 8.

4.2 K in Shpolskii matrices (see Fig. 1). The apparatus[6] includes a high-pressure 200 W mercury lamp, a SPEX 1802 double monochromator equipped with a Peltier-cooled RCA C 31034 PMT detector and an ORTEC 5C1 photon counting system. Suitable mercury lines (365 nm for 7, 313 nm for 8) were selected for excitation with the aid of a monochromator and filters.

Both spectra are essentially phonon-less and largely devoid of multiplet structure, but less rich in lines than those of 5 and 6 which we have also studied. The triplet half-lifetimes, as measured in site A of the O–O bands, are 0.46 sec for 7 and 0.44 sec for 8.

The peaks in the particularly well resolved spectrum of 8, labelled 1 to 26 for easy reference, have been tentatively interpreted as harmonics and combinations of 16 fundamentals (Table 1). It is noteworthy that overtones appear relatively weak, presumably because the T_1 and S_0 potential surfaces are very similar so that the Franck–Condon factors for transitions to higher vibrational levels of the S_0 state are vanishingly small. The most active fundamentals are CC stretching frequencies with $\Delta\tilde{\nu} \gg 1400\ cm^{-1}$. No CH stretching frequencies are observed. Interestingly, whereas the O–O peak is by far the most intense in the spectrum of 8, it is comparatively weak in 7. The same holds for the pair 6 and 5.

By means of ODMR experiments, the symmetries of the more prominent vibrations have been determined. This subject will be dealt with by Bräuchle *et al.*,[7] as will be the line spectra of a more comprehensive series of pyrene-type hydrocarbons.[8]

Acknowledgement—We thank Dr. H. Kabza (Physikalisch-Chemisches Institut der Universität) for taking the phosphorescence spectra at 4.2 K.

REFERENCES

[1] E. Clar and A. McCallum, *Tetrahedron* 10, 171 (1960); E. Clar, *Polycyclic Hydrocarbons*, Vol. I, p. 70, Academic Press (1964); E. Clar, *The Aromatic Sextet* p. 32. Wiley, New York (1972).

[2] E. Clar, J. F. Guye-Vuillème, A. McCallum and I. A. MacPherson, *Tetrahedron* 19, 2185 (1963).

[3] E. Clar and M. Zander, *Chem. Ber.* 89, 749 (1956). For the line spectra of pyrene and benzopyrene see E. W. Shpolskii and E. Girdzhiyauskaite, *Opt. i Spektr.* 4, 620 (1958); E. W. Shpolskii, L. A. Klimova and R. J. Personov, *Ibid.* 13, 341 (1962).

[4] PPP procedure using standard parameters and bond-order geometries as defined in R. Boschi, E. Clar and W. Schmidt, *J. Chem. Phys.* 60, 4406 (1974).

[5] T. Zauner, Diplomarbeit, Universität München (1977).

[6] Ch. Bräuchle, Dissertation, Universität München (1977).

[7] Ch. Bräuchle, H. Kabza and J. Voitländer, manuscript in preparation.

[8] E. Clar, W. Schmidt and T. Zauner, to be published.