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ANNELLATION EFFECTS IN THE PERYLENE AND CORONENE SERIES

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Abstract—Naphtho(2′:3′, 2:3)perylene (VIII), dinaphtho(2′:3′, 2:3); (2″:3″, 8:9)perylene (VII), anthraceno(1′:4′, 1:12)perylene (IV), 1:12-benzonaphtho(2″:3″, 2:3)perylene (II), 1:12-benzonaphtho (2″:3″, 4:5)perylene (III) and 1:12-benzodinaphtho(2″:3″, 2:3); (2″ :3″, 8:9)perylene (XV) were synthesized. There are two different annellation effects in passing from 1:12-benzoperylene (I) to II or III resp., the one in naphthocoronene (V) lies in between these two effects. The annellation effect in the perylene series cannot be related to the molecular axes but is easily explained by the strict application of Robinsons aromatic sextet.

According to formula (I) the three sextets in 1:12-benzoperylene cannot change their place. Therefore the annellation effect must be quite different if annellation takes place in the position 1′:2′ or 2:3 or 4:5 resp. The fusion of a naphtho complex to the position 2:3 in benzoperylene gives the hydrocarbon (II), which has four sextets. Their interaction produces the aromatic conjugation as indicated by the arrows. This excludes part of the 1:12-benzoperylene complex, just as it is the case in 1:2-benzo-naphtho (2″:3″,6:7) pyrene.[1] Therefore the shift of the p- and β-bands is small in comparison with I.

A much larger shift is observed in passing from I to III. This annellation does not add another sextet. The conjugation as indicated by the arrows includes most of the length of the molecule. Although the hydrocarbons II and III have exactly the same length and breadth the wavelength of their p-bands (3830 and 4500 Å resp) and β-bands (3260 and 3690 Å resp) are quite different. This shows again[1] that the position of the bands cannot be related to the perimeter of the systems and that a classification of the absorption bands based on the molecular axes[2] is impossible.

In the hydrocarbon (IV) all three sextets can change their position as shown by the arrows. The annellation effect in comparison with 1:12-benzoperylene (I) shows a big shift for the p-band and a small shift for the β-band, which is a combination of the shifts in passing to II and III. A comparison of the spectra of the hydrocarbons II, III and IV is presented in Fig. 1.

In naphtho (2′:3′, 1:2) coronene (V)[3] the three sextets become mobil within the coronene complex and the two conjugations V and Va are possible, being analogous to the conjugation in II and III. This is probably the reason why the p-band (4230 Å) and β-band (3410 Å) are in the middle between the p- and β-bands of II and III (middle of p-bands cal: 4165 Å, middle of β-bands cal: 3475 Å). It appears that

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[1] E. Clar, J. F. Guye-Vuillème, I. A. Macpherson and A. McCallum, *Tetrahedron* **19**, 2185 (1963); E. Clar and M. Zander, *Ibid.* **19**, 521 (1963).

[2] J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949); H. B. Klevens and J. R. Platt, *Ibid.* **17**, 470 (1949); W. J. Moffit, *Ibid.* **22**, 320 (1954).

this can only be explained by the strict application of Robinsons aromatic sextet. The coronene complex in V must be considered as a unit capable of a degree of aromatic conjugation which lies in between the one of the hydrocarbons II and III.

3:9-Di-*o*-toluylperylene (VI)[4] obtained from perylene, *o*-toluyl chloride and aluminium chloride was pyrolyzed above 400°. Dinaphthoperylene (VII) was formed together with naphthoperylene (VIII) and perylene. The hydrocarbons can be readily separated by sublimation. Their absorption spectra (Fig. 2) show very similar p-bands. This is completely at variance with the classification of bands based on the molecular axes.[2] Here the p-bands termed L_a bands are associated with polarization across the long molecular axis which becomes very much elongated in passing from perylene to VIII and VII. The bands therefore ought to shift very much to the red which is not the case.

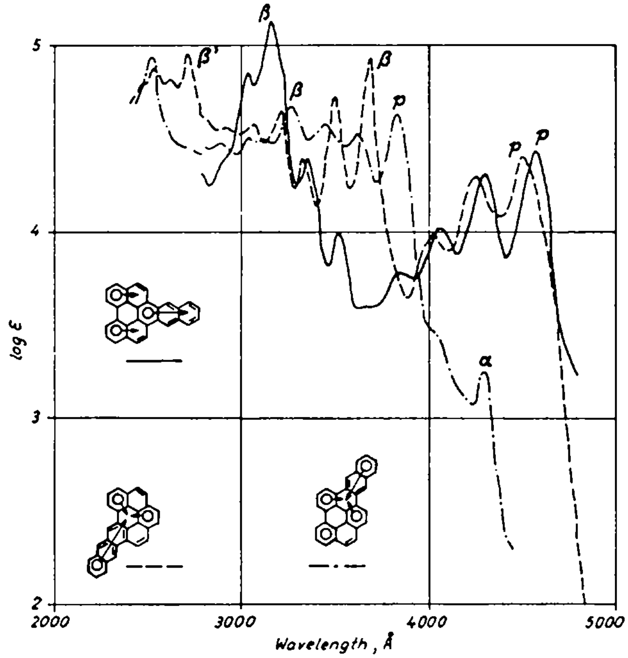

Fig. 1. Absorption max (Å) and log ε in (parentheses).

(———) Anthraceno(1′:4′,1:12)perylene (IV) in benzene: p: 4575 (4·44), 4300 (4·30), 4055 (4·03), 3845 (3·78); 3520 (4·00), 3345 (4·40); β: 3153 (5·14), 3023 (4·86).

(– – – – –) 1:12-Benzo(2″:3″,4:5)naphthoperylene (III) in benzene: p: 4500 (4·40), 4260 (4·30), 4020 (4·00): β: 3690 (4·94), 3500 (4·73), 3330 (4·39); 3220 (4·65), 3060 (4·58), 2920 (4·56); β′: 2710 (4·96), 2620 (4·81), 2540 (4·88).

(– · – · –) 1:12-Benzo(2″:3″,2:3)naphthoperylene (II) in benzene: α: 4300 (3·26), 4040 (3·46); p: 3830 (4·63), 3620 (4·53); 3430 (4·58); β: 3260 (4·67), 3110 (4·50), 3030 (4·50); in cyclohexane: β′: 2520 (4·94).

Naphthoperylene (VIII) reacted with excess maleic anhydride and chloranil as oxidizing agent to form a mixture of the two dianhydrides (IX and X). Sublimation

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[3] E. Clar and M. Zander, *J. Chem. Soc.* 1577 (1958).

[4] A. Pongratz, *Mh. Chem.* **48**, 585 (1927).

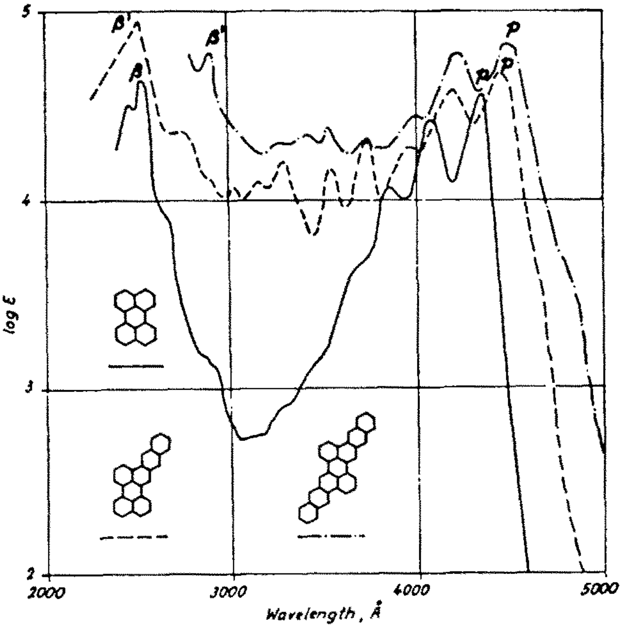

FIG. 2. (———) Perylene in ethanol: p: 4360 (4·55), 4090 (4·42), 3870 (4·06), 3680 (3·63); β: 2530 (4·64), 2460 (4·51).

(– – – – –) Naphtho(2′:3′,2:3)perylene (VIII) in benzene: p: 4460 (4·68), 4200 (4·58), 3970 (4·28); 3750 (4·33), 3550 (4·17), 3300 (4·20), 3160 (4·10), 3040 (4·07), 2760 (4·36); in ethanol: β′: 2530 (4·95).

(– · – · –) Dinaphtho(2′:3′,2:3); (2″:3″,8:9)perylene (VII) in trichlorobenzene: p: 4480 (4·83), 4230 (4·77), 4000 (4·45); β: 3730 (4·30); in benzene: 3540 (4·38), 3420 (4·36) 3380 (4·34), 3280 (4·31); β′: 2900 (4·78).

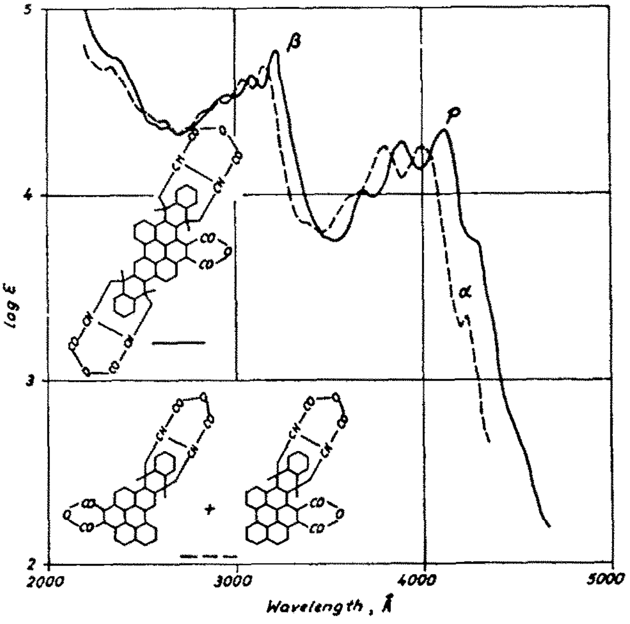

FIG. 3 (———) Hexapotassium salt derived from XIV in 50% ethanol: α: 4280 (3·74); p: 4120 (4·34), 3900 (4·28). 3690 (4·01); β: 3220 (4·76), 3080 (3·64), 2960 (4·53); 2650 (4·36), 2360 (4·74).

(– – – – –) Tetrapotassium salts derived from XI and XII in 50% ethanol: α: 4240 removed the endocyclic complex and gave a mixture of the anhydrides (XI and XII). Decarboxylation with soda lime *in vacuo* yielded the two hydrocarbons (II and III) which could be separated by chromatography. The hydrocarbon (III) which was the minor constituent of the mixture was identical with the 1:12-benzo-naphtho (2″:3″, 4:5)perylene obtained by Zander and Franke[5] by another synthesis. The isomeric hydrocarbon must have therefore the structure of 1:12-benzonaphtho (2″:3″, 2:3)perylene (II).

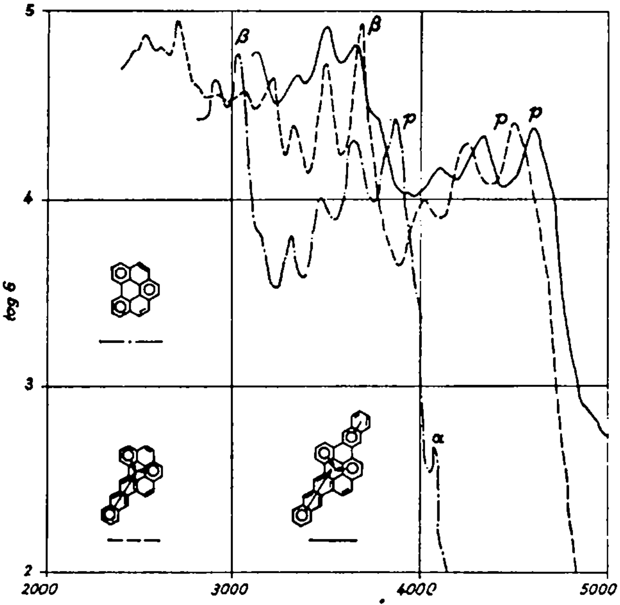

FIG. 4. (———) 1:12-Benzodinaphtho(2″:3″,2:3); (2″:3″, 8:9)perylene (XV) in trichlorobenzene: p: 4600 (4·38), 4340 (4·34), 4100 (4·16); β: 3650 (4·82), 3500 (4·93), 3340 (4·66); 3130 (4·78).

(– – – – –) 1:12-Benzo(2″:3″,4:5)naphthoperylene (III) in benzene: p: 4500 (4·40), 4260 (4·30), 4020 (4·00); β: 3690 (4·94), 3500 (4·73), 3330 (4·39); 3220 (4·65), 3060 (4·58), 2920 (4·56); β′: 2710 (4·96), 2620 (4·81), 2540 (4·88).

(–·–·–) 1:12-Benzoperylene (I) in benzene: α: 4080 (2·68); p: 3870 (4·42), 3650 (4·32) 3480 (4·00), 3320 (3·80); β: 3030 (4·78), 2910 (4·64).

Tetrahydro-1:1′-dinaphthyl condensed with naphthoquinone to form the anthraquinone derivative (XIII) under partial dehydrogenation. This reaction was formerly carried out as a pure addition reaction.[6] A zinc dust melt of this quinone resulted in reduction and simultaneous cyclization to anthraceno (1′:4′, 1:12) perylene (IV).

Dinaphthoperylene (VII) yielded the trianhydride (XIV) when condensed with maleic anhydride and chloranil. Its absorption spectrum as hexapotassium salt (Fig. 3) shows the 1:12-benzoperylene type as do the tetrapotassium salts of the anhydrides (IX and X).

The trianhydride (XIV) gives 1:12-benzo-dinaphtho(2:″3″, 2:3); (2‴:3‴, 8:9)

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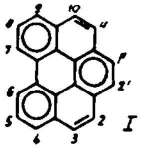
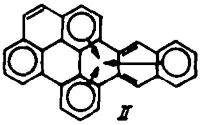
[5] M. Zander and W. H. Franke, *Chem. Ber.* 99, 1275 (1966).

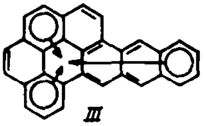
[6] F. Bergmann, H. E. Eschinazi and M. Neeman, *J. Org. Chem.* 8, 179 (1943).



I



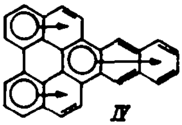
II



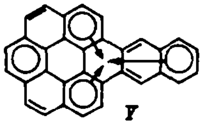
III

λ_p = 3875 3830 4500 Å

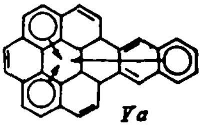
λ_β = 3030 3260 3690 Å



IV



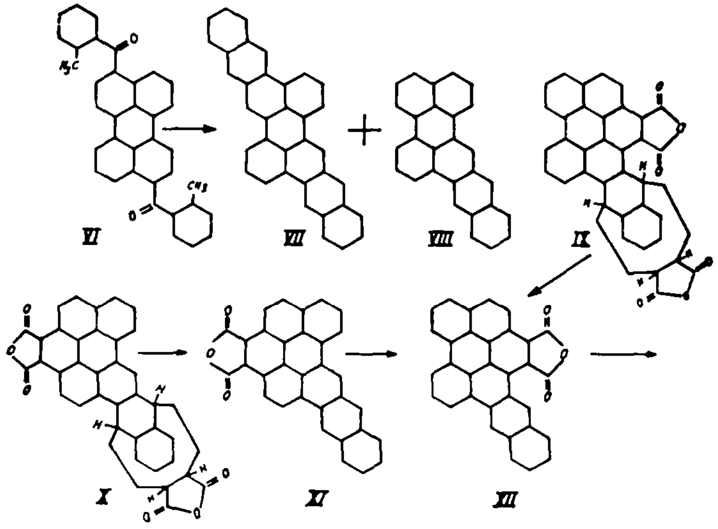
V

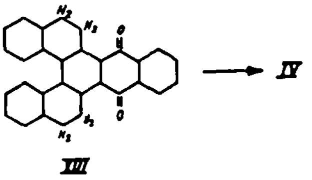


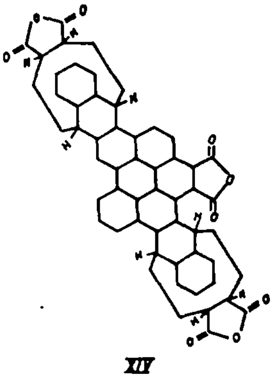
Va

λ_p = 4575 4230 Å cal. 4165 Å

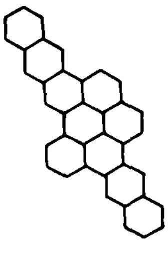
λ_β = 3153 3410 Å cal. 3475 Å







XIV



XV

perylene (XV) on sublimation with soda lime. A comparison of the absorption spectra (Fig. 4) of this hydrocarbon with the spectra of I and III shows a big shift of p- and β-bands for the annellation of the first naphtho complex in passing from 1:12-benzoperylene (I) to III. No further direct aromatic conjugation can be achieved in going to benzo-dinaphtho-perylene (XV) as indicated by the small shifts. The sextets and the arrows (Fig. 4) demonstrate this clearly while a classification of the p-bands as L_a bands based on polarization across the long molecular axis required another similar big shift towards the red, which is not observed.

EXPERIMENTAL*

Naphtho(2′:3′, 2:3)*perylene* (VIII) *and dinaphtho*(2′:3′, 2:3); (2″:3″, 8:9)*perylene* (VII). Compound VI[4] (74 g) was dissolved in hot 1-methylnaphthalene, filtered, the solvent distilled off and the residue heated at 400° under CO_2. After 20 min the pyrolysate was distilled at 300°/0·1 mm in order to remove perylene. The residue (50 g) was sublimed in a vacuum (0·1 mm). Compound VIII sublimed below 370° (2·6 g) and was resublimed and recrystallized from pseudocomene (2·2 g) as yellow needles, m.p. 271–272° which dissolved in conc H_2SO_4 to form a green solution which changed to blue and then to violet. (Found: C, 95·6; H, 4·6. $C_{28}H_{16}$ requires: C, 95·4; H, 4·6%,) See Fig. 2 for the absorption spectrum.

The residue from the above sublimation was sublimed at 390° and 10^{-3} mm. In order to remove a further quantity of VIII the sublimate was extracted with pseudocumene, resublimed (1·1 g) and then recrystallized from 1-methylnaphthalene under CO_2 (0·96 g). Compound VII formed brownish-yellow needles, m.p. 404–406°, which dissolved in conc H_2SO_4 to give a green solution changing to blue and then violet on standing. (Found: C, 95·8; H, 4·5. $C_{34}H_{20}$ requires: C, 95·6; H, 4·5%.) In another experiment the residue (75 g) from the above vacuum distillation of the perylene was dissolved in xylene (4000 ml), filtered from the insoluble part containing the hydrocarbon (VII) and chromatographed on alumina. Yield 11 g of the hydrocarbon (VIII).

1:12-*Benzonaphtho*(2″:3″, 2:3)*perylene* (II). Compound VIII (5 g), maleic anhydride (75 g) and chloranil (15 g) were refluxed for 10 min. The mixture of IX and X crystallized during the reaction as red needles (6 g). The suspension was diluted with hot xylene (300 ml) and the crystals filtered hot and washed with xylene, benzene and ether. A further quantity of red crystals was obtained on standing (1·3 g). The mixture of IX and X was sublimed at 400°/5·10^{-3} mm. The sublimate formed a mixture of XI and XII, m.p. 356–358°, dec. (Found: C, 86·3; H, 3·2. $C_{32}H_{14}O_3$ requires: C, 86·1; H, 3·2%.)

Decarboxylation can be combined with the above sublimation. A mixture of IX and X (3 g) was powdered with sodalime (9 g) and heated under N_2 at 400° for 15 min. This was followed by vacuum sublimation at 400°/10^{-3} mm. The sublimate (1·2 g) contained a mixture of II and III, which were separated by crystallization or chromatography of the solution in xylene. Compound III[5] was the minor constituent and remained in the xylene mother liquor or was longer retained in the chromatographic column. It was identified by its absorption spectrum. Compound II formed yellow needles from xylene, m.p. 292–294°, which dissolved slowly in conc H_2SO_4 with a brown colour. (Found: C, 95·7; H, 4·2. $C_{30}H_{16}$ requires: C, 95·7; H, 4·3%.) See Fig. 1. for the absorption spectrum.

1:12-*Benzodinaphtho*(2″:3″,2:3); (2‴:3‴,8:9)*perylene* (XV). Compound VII (0·35 g), maleic anhydride (5 g) and chloranil (0·5) were heated under reflux for 20 min. The hot mixture was diluted with boiling xylene and XIV (0·4 g) filtered and washed with benzene. The very sparingly soluble trianhydride which could not be recrystallized without decomposition was mixed with sodalime and decarboxylated and sublimed at 450°/2·10^{-3}mm. The hydrocarbon sublimate (56 mm) yielded orange crystals, m.p. 435–438°, which dissolved slowly in conc H_2SO_4 to give a green solution. (Found: C, 95·7; H, 4·0, $C_{38}H_{20}$ requires: C, 95·8, H, 4·2%.) See Fig. 4 for the absorption spectrum.

Anthraceno(1:4′,1:12)*perylene* (IV). The quinone (XIII) was prepared as described[6] with the modification that nitrobenzene was added to the reaction mixture and distilled off after completion of the reaction.

The quinone (XIII; 2·0 g) was fused with NaCl (4·0 g) and $ZnCl_2$ (20 g) and was kept at 300° for 8 min, with constant stirring. The product was washed in the normal manner, dried and sublimed at

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* All m.p.s are uncorrected and were taken in evacuated capillaries.

360°/0·1 mm. It gave a small amount of dinaphthyl and a larger amount of a dark red solid. The red impurity could not be removed by crystallization, but chromatography on alumina gave 3 pure fractions: (a) light yellow needles readily soluble in benzene and absorbing at 438 and 428mμ, (b) yellow needles of IV, m.p. 356°, moderately soluble in benzene and slowly soluble with a green colour in conc H_2SO_4. (Found: C, 95·5; H, 4·1. $C_{30}H_{16}$ requires: C, 95·7; H, 4·3%.) The spectrum of this hydrocarbon is shown in Fig. 1. The third fraction contained the red impurity.

Repetition of this $ZnCl_2$ melt with the addition of Zn dust gave none of the red by-product.