

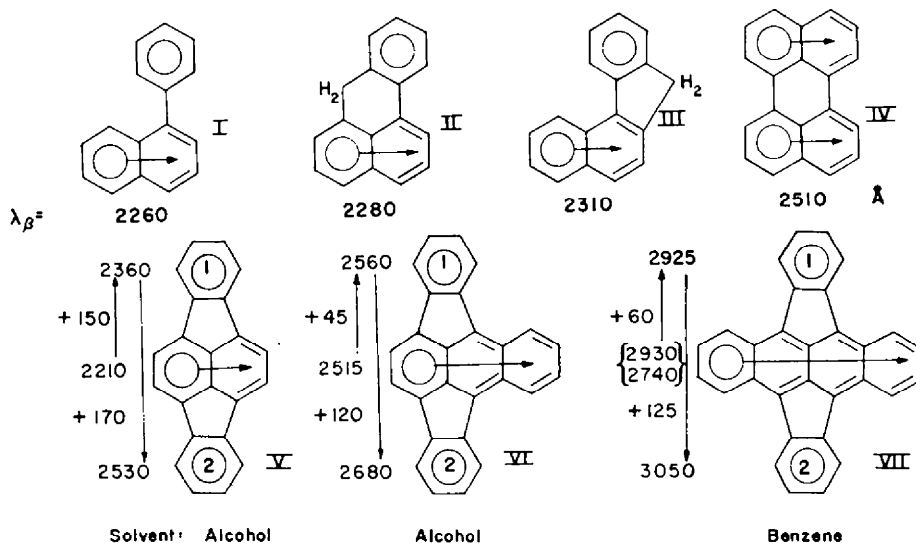
ANNELLATION EFFECTS IN THE FLUORANTHENE SERIES

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Abstract—A systematic study of the absorption spectra of the benzologues of fluoranthene shows that the β - and β' -band of fluoranthene originate from two different absorptions of polarized light. The β' -band at 2360 Å results from polarization along the naphthalene complex and the β -band at 2870 Å from polarization perpendicular to it. A number of higher annellated fluoranthenes have been synthesized: 2:3,6:7-Di(peri-naphthylene)-naphthalene, 2:3,6:7-di(peri-naphthylene)-anthracene and 1:2,3:4-dibenzo-6:7(peri-naphthylene)-anthracene.

THERE is only a very small degree of conjugation between the phenyl and the naphthalene groups in 1-phenyl-naphthalene (I). The situation is very little altered if the phenyl group is forced into a uniplanar position as in benzanthrene (II) and in 3:4-benzo-fluorene (III). This can be shown by the small shifts of the β -bands of these hydrocarbons in comparison with naphthalene. The differences are 50, 70 and 100 Å respectively.¹ Even in perylene (IV) the two single bonds connecting the naphthalene



complexes produce a shift of only 300 Å which is hardly more than double the shift (145 Å) in passing from benzene to diphenyl.

The absorption spectrum of fluoranthene (Fig. 1) shows two β -bands at 2870 and

¹ E. Clar, *Tetrahedron* **16**, 113 (1961).

2360 Å. The latter, the β' -band, is also very little effected by the connection of the phenylene groups 1 and 2, as shown in formula V. The shifts are 150 and 170 Å respectively, if derived from naphthalene. Similar shifts are observed by the *o*-phenylenation of anthracene (VI) and tetracene (VII). A shift of the fluoranthene β -band at 2870 Å cannot be observed with certainty in the hydrocarbons derived from anthracene (VI) and tetracene (VII). Therefore it appears that the β' -bands in V, and the β -bands in VI and VII originate from polarization along the acene system, just as is the case in the acenes themselves.

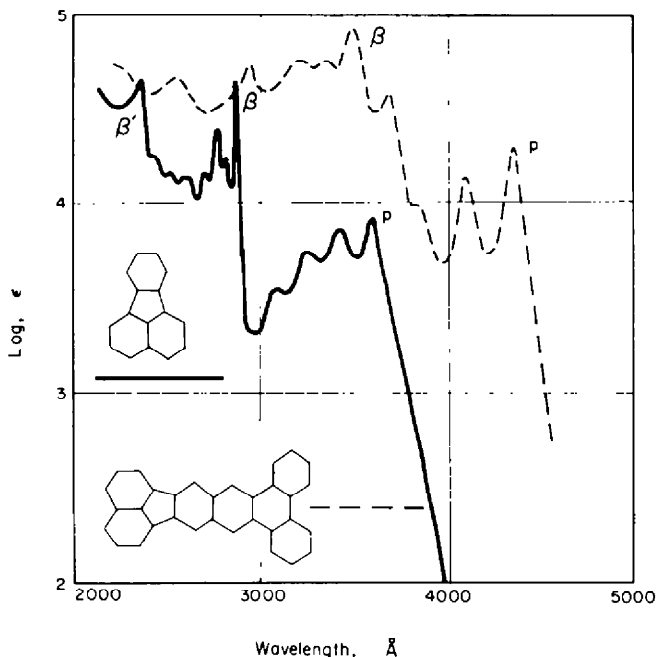
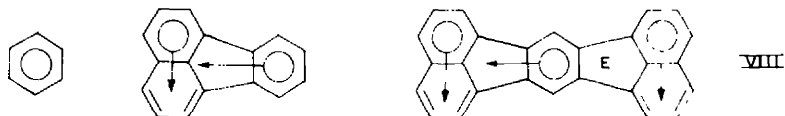


FIG. 1. Absorption max (Å) and log ϵ (in parentheses). Fluoranthene in ethanol, p: 3585 (3.95), 3420 (3.90), 3230 (3.76), 3090 (3.56); β : 2870 (4.66), 2820 (4.26), 2760 (4.40), 2715 (4.17), 2615 (4.16), 2525 (4.17); β' : 2360 (4.66).

6:7-(peri-Naphthylene)-1:2,3:4-dibenzanthracene in benzene, p: 4360 (4.31), 4100 (4.14), 3860 (4.00), 3690 (4.58); β : 3500 (4.92), 3340 (4.76), 3200 (4.78), 2950 (4.74); in cyclohexane: 2540 (4.66).

The β -band of fluoranthene at 2870 Å must be polarized perpendicular to the band at 2360 Å, because it shifts strongly towards the red if the *o*-phenylene ring in fluoranthene is annellated to give 11:12-benzofluoranthene (IX) and naphtho-(2':3';11:12)-fluoranthene (XI). Moreover it can be shown that the successive annellation of two peri-naphthylene complexes to an acene produce a strong asymmetric annellation effect. These are recorded in Å and $\sqrt{\text{Å}}$, the latter being a scale for reciprocal nuclear charges.

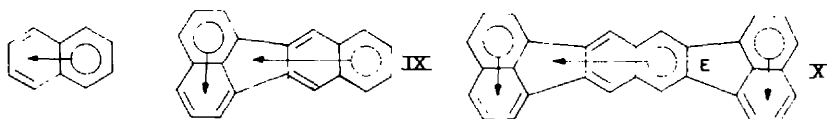
If first one and then two peri-naphthylene complexes are fused to benzene to form fluoranthene and the hydrocarbon (VIII) two very different shifts (1035 and 350 Å) are recorded. If the second shift (in $\sqrt{\text{Å}}$) is subtracted from the β -band of fluoranthene a β -band at 2539 Å is obtained which is almost identical with the β -band of anthracene.



$\lambda_{\beta} =$	1835	$\xrightarrow{+1035}$	2870 (A)	$\xrightarrow{+350}$	3220 (C)
$\sqrt{\lambda_{\beta}} =$	42.84	$\xrightarrow{+10.73}$	53.57	$\xrightarrow{+3.18}$	56.75
$\lambda_{\rho} =$	2068(A)	$\xrightarrow{+1517}$	3585(A)	$\xrightarrow{+575}$	4160 (C)

$$53.57 - 3.18 = 50.39 \quad \sqrt{\text{\AA}} \triangleq 2539 \text{\AA}$$

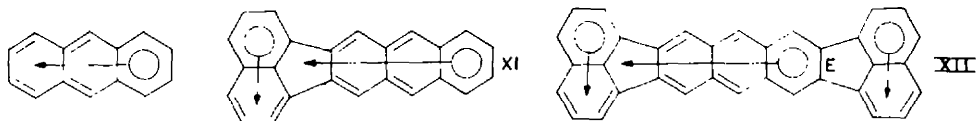
Calc. for 3 annellated rings 2493 \AA



$\lambda_{\beta} =$	2210 (A)	$\xrightarrow{+870}$	3080 (A)	$\xrightarrow{+200}$	3280 (C)
$\sqrt{\lambda_{\beta}} =$	47.01	$\xrightarrow{+8.49}$	55.50	$\xrightarrow{+1.77}$	57.27
$\lambda_{\rho} =$	2850(A)	$\xrightarrow{+1150}$	4000 (A)	$\xrightarrow{+450}$	4450 (B)

$$55.50 - 1.77 = 53.73 \quad \sqrt{\text{\AA}} \triangleq 2887 \text{\AA}$$

Calc. for 4 annellated rings 2803 \AA

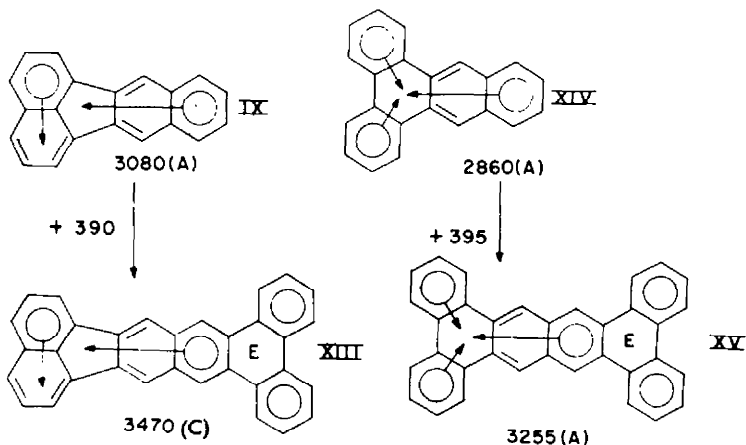


$\lambda_{\beta} =$	2515 (A)	$\xrightarrow{+825}$	3340 (A)	$\xrightarrow{+180}$	3520 (C)
$\sqrt{\lambda_{\beta}} =$	50.15	$\xrightarrow{+7.64}$	57.79	$\xrightarrow{+1.54}$	59.33
$\lambda_{\rho} =$	3745 (A)	$\xrightarrow{+635}$	4380 (A)	$\xrightarrow{+350}$	4730 (B)

$$57.79 - 1.54 = 56.25 \quad \sqrt{\text{\AA}} \triangleq 3164 \text{\AA}$$

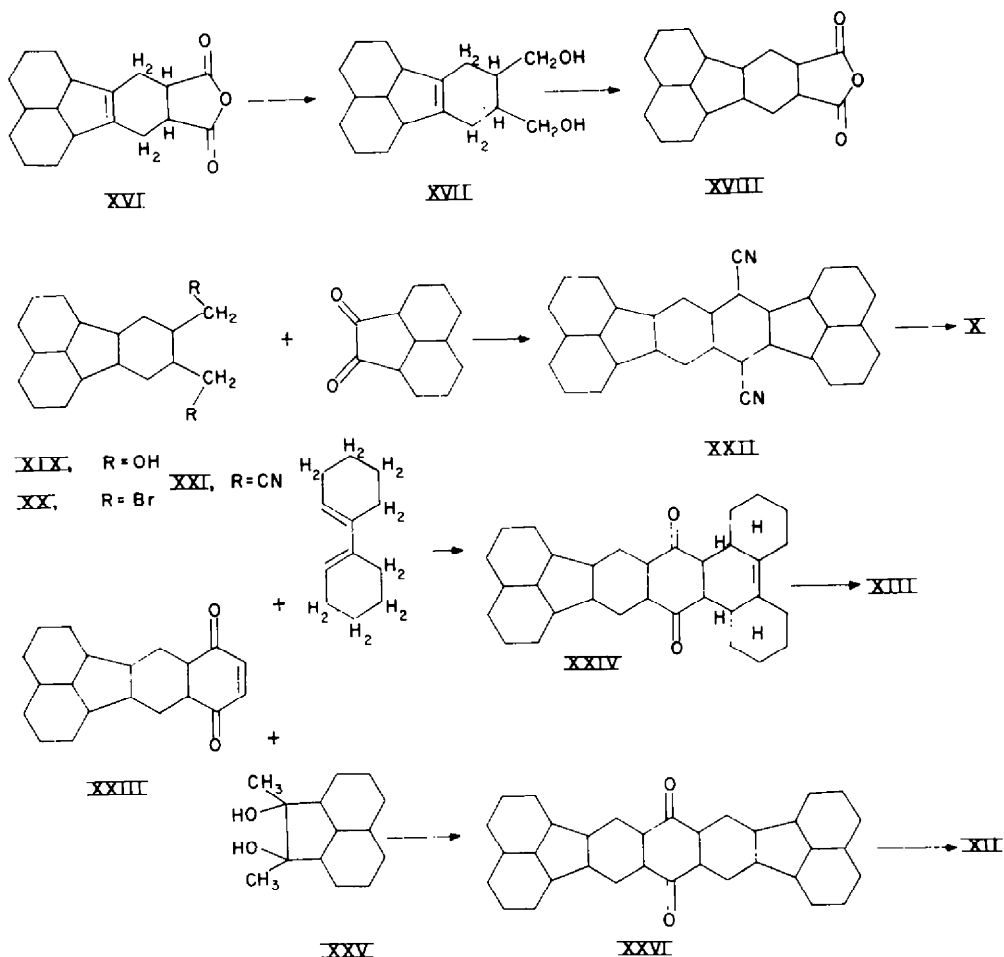
Calc. of 5 annellated rings 3132 \AA

Solvent: A = alcohol, B = benzene, C = cyclohexane



An asymmetric aromatic conjugation must have taken place which extends the aromatic system of benzene to a system with two rings more. The same procedure applied to naphthalene gives 11:12-benzofluoranthene (IX) and the hydrocarbon (X). The annellation effect is again very asymmetric (870 and 200 Å) and the shift subtraction rule² (carried out in units $\sqrt{\text{Å}}$) yields a β -band at 2887 Å, which shows an extension of the aromatic system of naphthalene by two rings. The same observation can be made starting from anthracene and passing to the hydrocarbons XI and XII.

As reported earlier,² the successive fusion of two *o*-diphenylene complexes to an acene system forming first a dibenzo- and then a tetrabenzo-acene is accompanied by



an asymmetric annellation effect which indicates that the initial acene system has been extended by one ring. This is half the effect reported above and it shows that both rings of one *peri*-naphthylene complex participate in aromatic conjugation as indicated by the arrow and that the second annellation produces an empty ring "E". The *p*-bands also show very asymmetric annellation effects.

The correctness of this view can be tested with the hydrocarbon (XIII; Absorption

Spectrum S, Fig. 1) which is built up by fusing an *o*-diphenylene and a peri-naphthylene system to naphthalene. If the latter annellation can account for the extension of the aromatic system of naphthalene by two rings and the former annellation for only one ring, then aromatic conjugation must exist between the two naphthalene complexes, as indicated by the arrow, and not between the central naphthalene system and the *o*-diphenylene system. There must be an empty ring "E". This can be shown by the comparison of the shifts observed when 11:12-benzofluoranthene (IX) is fused with an *o*-diphenylene system to form XIII.² This shift is +390 Å and is almost the same as the one recorded in passing from 1:2:3:4-dibenzanthracene (XIV) to 1:2,3:4,7:8,9:10-tetrabenzotetracene (XV) which is 395 Å. In both cases an empty ring "E" is produced. This must also be considered as a proof for the electronic asymmetry in formally symmetric systems as reported before.²

The syntheses of the hydrocarbons. The spectra of the hydrocarbons (V, VI, VII, VIII, IX, XIV and XV)³ have been recorded before. The anhydride (XVI)⁴ was reduced to the diol (XVII) with lithium aluminium hydride. However, this gave only a resin when treated with phosphorus tribromide. The aromatic anhydride (XVIII)⁴ yielded the diol (XIX) when reduced with lithium aluminium hydride. The dibromide (XX) was obtained with phosphorus tribromide and the dinitrile (XXI) by treatment with potassium cyanide. The condensation with acenenaphthenequinone yielded the dinitrile (XXII) which on sublimation with potassium hydroxide and soda-lime gave di-2:3,6:7-(peri-naphthylene)-naphthalene (X).

The quinone (XXIII)⁴ was submitted to a diene synthesis with octahydrodiphenyl. This resulted in the formation of the hydrogenated quinone (XXIV) from which 1:2,3:4-dibenzo-6:7-(peri-naphthylene)-anthracene (XIII) was obtained by a melt with sodium chloride and zinc chloride, followed by dehydrogenation with copper powder.

Condensation of the quinone (XXIII) with the *cis*-form of dimethyl-dihydroxy-acenaphthene (XXV) yielded the quinone (XXVI) as described by Campbell and Gow.⁴ It can be reduced to 2:3,6:7-di-(peri-naphthylene)-anthracene (XII) by the pyridine, zinc dust, acetic acid method or by a zinc dust melt. The absorption spectra of the hydrocarbons (VIII, X and XII) are recorded in Figs. 2, 3 and 4.

EXPERIMENTAL*

10,11,12,13-Tetrahydro-11,12-bishydroxymethylfluoranthene (XVII). To a stirred suspension of LiAlH₄ (0.8 g) in anhydrous tetrahydrofuran (50 ml) was added during the course of 20 min a solution of XVI⁴ (5 g) in tetrahydrofuran (75 ml). The reaction mixture, after boiling for 2 hr, was cooled and decomposed with ice and dil. H₂SO₄. Extraction with ether and concentration of the dried (Na₂SO₄) ether extract gave the diol as an oil which solidified after trituration with 100–120° pet. ether. The diol (2.6 g) crystallized from xylene in yellow leaflets m.p. 185–186°. (Found: C, 81.2; H, 6.8%. C₁₈H₁₈O₂ requires: C, 81.2; H, 6.8%).

11,12-Bishydroxymethylfluoranthene (XIX). Compound XVIII⁴ (3.8 g) in tetrahydrofuran (160 ml) was added during 15 min to a stirred suspension of LiAlH₄ (0.84 g) in tetrahydrofuran (30 ml) and the mixture heated under reflux for 2 hr. A deep red colour developed immediately and persisted. The reaction mixture was decomposed by cautious addition of water and after acidification with dil. H₂SO₄ the mixture was extracted with ether. Evaporation of the dried (Na₂SO₄) ether extract

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

² E. Clar, *Tetrahedron* 5, 98, 355 (1959); 9, 202 (1960).

³ E. Clar, *Polycyclic Hydrocarbons* Vol. II; pp. 339, 341, 344, 359, 316, 325; Vol. I, pp. 327, 415. Academic Press (1964).

⁴ N. Campbell and R. S. Gow, *J. Chem. Soc.* 1555 (1949).

and crystallization from xylene furnished the diol (1.97 g, 54%) as colourless needles m.p., 180–181°. (Found: C, 82.1; H, 5.3. $C_{18}H_{14}O_2$ requires: C, 82.4; H, 5.4%).

11,12-Bisbromomethylfluoranthene (XX). A suspension of XIX (1.97 g) in dry benzene (250 ml) was treated with PBr_3 (4.8 g) and the mixture heated under reflux for 2 hr. The benzene solution was then washed with water and $NaHCO_3$ aq dried (Na_2SO_4) and evaporated. The residue of XX (1.9 g, 65%) crystallized from benzene in small pale yellow prisms, m.p. 186–192°. Repeated crystallization from benzene gave the dibromide as thick pale yellow prisms, m.p. 197–198° (Found: C, 56.3; H, 3.3; Br, 40.15. $C_{18}H_{12}Br_2$ requires: C, 55.7; H, 3.1; Br 41.20%).

11,12-Biscyanomethylfluoranthene (XXI). Potassium cyanide (370 mg) was dissolved in as little water as possible and ethanol (80 ml) added. The mixture was heated to boiling and finely divided

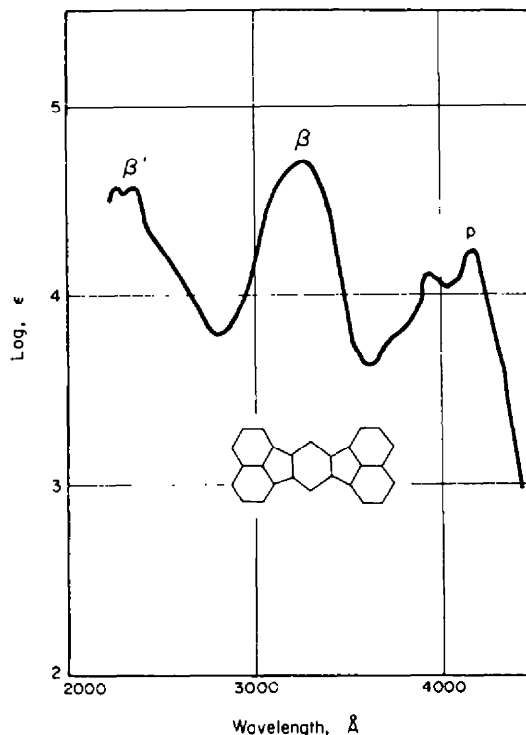


FIG. 2. Absorption max (Å) and log ϵ (in parentheses) of 11:12-(peri-Naphthylene)-fluoranthene in benzene, p: 4170 (4.24), 3940 (4.10); β , 3250 (4.72); in cyclohexane, β' : 2360 (4.58).

XX (1.0 g) added in portions. After refluxing 2 hr, the cooled reaction mixture was poured into water and the precipitated dicyanide (100 mg, 14%) crystallized from benzene in colourless needles or leaflets, m.p. 229–230° (Found: N, 10.0. $C_{20}H_{12}N_2$ requires: N, 10.0%).

Di-2:3,6:7-(peri-naphthylene)-naphthalene-1,4-dicyanide (XXII). Compound XXI (100 mg) and acenaphthenequinone (70 mg) were dissolved in pyridine (10 ml) and piperidine (0.5 ml) added. The solution was refluxed for 15 min during which time the yellow condensation product precipitated from solution. The precipitated yellow solid (120 mg, 79%) was filtered off and crystallized from nitrobenzene as yellow needles of XXII, m.p. > 500°. (Found: C, 89.7; H, 3.4; N, 6.3. $C_{22}H_{14}N_2$ requires: C, 90.1; H, 3.3; N, 6.6%).

Di-2:3,6:7-(peri-naphthylene)-naphthalene (X). An intimate mixture of the above dicyanide (100 mg) and soda lime was made into a thick paste with saturated KOH aq and then heated for 5 min at 400° (atm. of N_2). Traces of yellow sublimate were observed at this temp and the major portion of the hydrocarbon was sublimed from the soda lime *in vacuo*. The yellow sublimate was dissolved in benzene and chromatographed on alumina. Development of the chromatogram gave a

single yellow band which was eluted with benzene. Evaporation of the solvent and crystallization of the yellow solid thus obtained from xylene gave X (20 mg) as yellow needles or leaflets, m.p. 368–370°. The hydrocarbon shows a strong blue fluorescence in organic solvents and dissolves very slowly in conc. H_2SO_4 to give a green solution. (Found: C, 95.6; H, 4.55. $C_{30}H_{18}$ requires: C, 95.7; H, 4.3%.)

Decahydro-1:2,3:4-dibenzo-6:7-(peri-naphthalene)-anthraquinone (XXIV). Octahydrodiphenyl (1.9 g) and XXIII⁴ (3.3 g) were melted together and the resulting deep red viscous oil heated to boiling for a few sec. The deep red glass which formed on cooling gave, after repeated crystallization from xylene, XXIV (530 mg) as bright yellow needles, m.p. 300–301°. The quinone gives a violet vat with

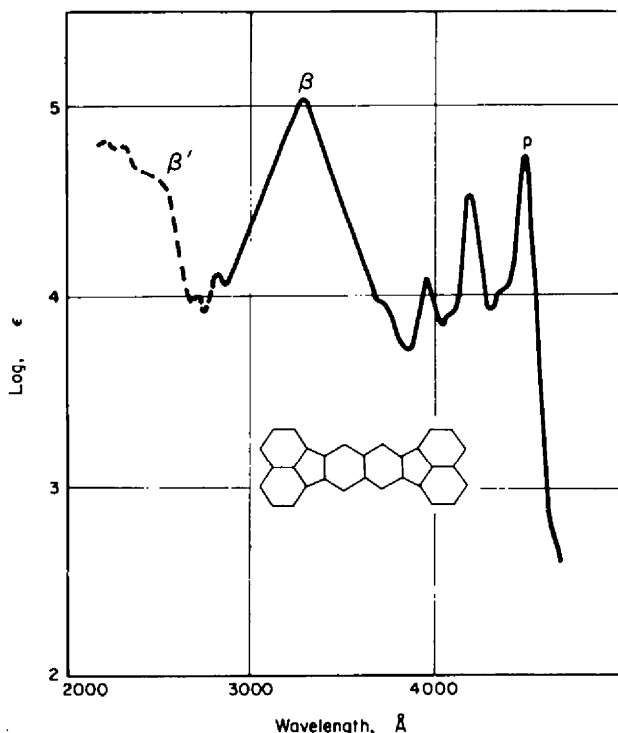


FIG. 3. 2:3,6:7-Di-(peri-naphthylene)-naphthalene in benzene, p : 4450 (4.74), 4180 (4.54), 3940 (4.09); β : 3290 (5.04), 2850 (4.10), in cyclohexane; β' : 2320 (4.80)

alkaline sodium dithionite and dissolves in conc. H_2SO_4 to give a dark green solution which changes to violet on standing (Found: C, 86.7; H, 5.9. $C_{32}H_{24}O_2$ requires: C, 86.8; H, 5.9%).

1:2,3:4-Dibenzo-6:7-(peri-naphthalene)-anthracene (XIII). The above quinone (850 mg) and NaCl (850 mg) were ground together. Zinc chloride (4.25 g) was added and the mixture melted, the temp being raised to 320° for 4 min. The colour of the melt was red brown. The $ZnCl_2$ was removed with dil. acetic acid, the residue washed with ammonia and water, dried and dehydrogenated with Cu powder at 300° under CO_2 for 4 min. Sublimation *in vacuo* gave XII (200 mg) as small yellow needles which crystallized from xylene as thin bright yellow needles, m.p. 344–346° (Found: C, 95.2; H, 4.6. $C_{32}H_{18}$ requires C, 95.5; H, 4.5%). The hydrocarbon exhibits a blue fluorescence in organic solvents and dissolves very slowly in conc. H_2SO_4 to give a yellow brown solution.

Di-2:3,6:7-(peri-naphthylene)-anthracene (XII). Compound XXVI⁴ (1 g) was ground together with Zn dust (1 g), NaCl (1 g) and moist $ZnCl_2$ (5 g) added. The temp was raised with constant stirring to 320° for 4 min. After cooling the melt was digested with dil. acetic acid aq, the Zn dust dissolved in conc. HCl and the residue washed with ammonia and finally water. Sublimation *in vacuo* followed by crystallization of the brown yellow sublimate from nitrobenzene gave XII as golden

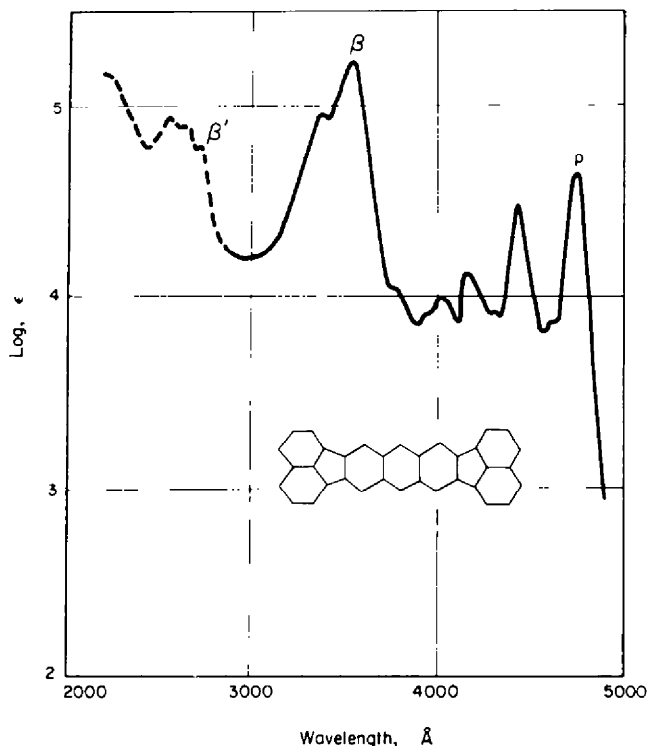


FIG. 4. 2:3,6:7-Di-(peri-naphthylene)-anthracene in benzene, β : 4730 (4.66), 4420 (4.46), 4160 (4.12), 4030 (4.00); β : 3540 (5.22), 3380 (4.96); in cyclohexane, β' : 2700 (4.80), 2570 (4.98).

yellow leaflets (100 mg), m.p. 460°. (Found: C, 95.55; H, 4.3. $C_{24}H_{18}$ requires: C, 95.7; H, 4.3%). The hydrocarbon shows a green fluorescence in organic solvents and dissolves very slowly in conc. H_2SO_4 to give a red-brown solution.

Compound XXVI (1 g) and Zn dust (5 g) were refluxed in pyridine (50 ml), contact with air being prevented by a mercury valve. Dil. acetic acid (95%, 14 ml) was added in portions at intervals of 1 hr over 6 hr. The solution, initially orange yellow in colour, became red and this colour persisted. After 6 hr, the pyridine mother liquor was poured into dil. HCl aq and the precipitated yellow solid filtered off and washed with ammonia and water. After drying the reduction product was heated together with Cu powder at 320° under CO_2 for 5 min. The hydrocarbon (80 mg) was sublimed from the Cu *in vacuo* and was identical to the sample obtained in the Zn dust melt, m.p. and mixed m.p. 460°.