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THE LOCATION OF DOUBLE BONDS IN FLUORANTHENE PERYLENE AND 1,1'-DINAPHTHYL BY NMR

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Abstract—1-Methyl-, 3-methyl-, 8-methyl-, 1,3-dimethyl-, 7,10-dimethyl-, and 8,9-dimethylfluoranthene were synthesized and their NMR spectra recorded. The results show double bonds in the positions: 2,3-, and 4,5- which are equivalent to the fixed double bond in 9,10-position in phenanthrene. There is a high degree of double bond character in 8,9-position. The electronic spectra of fluoranthene,2,3-benzofluoranthene, naphtho[2':3', 2:3]fluoranthene are compared. This shows that the fluoranthene type of spectrum changes gradually into the phene type spectrum. There are no fixed double bonds in 3,10-dimethylperylene and 4,4'-dimethyl-1,1'-dinaphthyl.

RECENTLY[1] it was shown that the electronic and NMR spectra of polycyclic hydrocarbons are best explained by the distribution of three pairs of π-electrons of any benzenoid ring in three orbitals: one pair being located in a double bond (mobile or fixed), one pair in a circular orbital within the ring and one pair delocalized outside the ring and capable of migrating from one ring to the next.

We are now presenting the application of this model to fluoranthene (I). The NMR spectrum of fluoranthene in carbon tetrachloride and acetone was reported and analysed by Heffernan *et al.*[2] Our own measurements in carbon disulphide agree well with the former ones except for minor deviation resulting from the change of solvent. ($J_{2,3} = 8{\cdot}5$; $J_{1,3} = 1{\cdot}0$; $J_{1,2} = 6{\cdot}7$ c/s) The high value of $J_{2,3}$ already indicates a high degree of double bond character in 2,3-position. This is confirmed by the NMR spectrum of 3-methylfluoranthene, Fig. 1. The Me resonance is split into a doublet with a separation of 1 c/s, which is the same as in 9-methylphenanthrene. If double bond fixation is assumed in the latter case,[3] this must be equally true for fluoranthene. This agrees well with the fact that fluoranthene is oxidized to 2,3-fluoranthenequinone with chromic acid.[4] The doublet becomes sharper if the proton in m-position, H_1, is radiated. (Second band from the right in Fig. 1). It collapses into a sharp singlet (first band from the right) if H_2 is decoupled. The high field doublet of the quartet produced by H_2 and H_1 is split into a multiplet, partly by superposition with the protons H_8 and H_9 and by coupling with the Me protons. If the latter are decoupled a sharp doublet (marked black) is obtained. Only minor changes are observed in the low field doublet (marked black) by the same procedure.

The Me resonance in 1-methylfluoranthene forms a sharp singlet (Fig. 2, first band from the right). The quartet originating from H_2 and H_3 (marked with shadows) is already quite clear in spite of some superposition from H_8 and H_9. Decoupling of the Me protons and the protons H_2 and H_3 resp. produced only a little sharpening of these five bands. This proves that the double bond is not freely mobile between the positions 3,2- and 1,2- resp. but fixed in position 2,3.

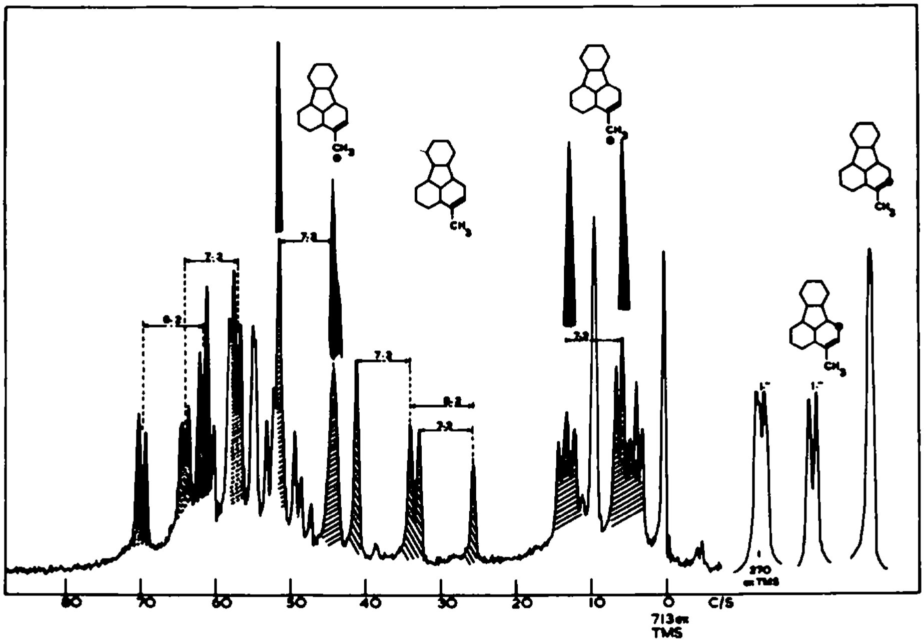


FIG. 1 NMR spectrum of 3-methylfluoranthene in CS_2 at 100 Mc/s. H_1, 760·3; H_2, 722·6; H_{Me}, 270·0, Doublet, separation 1·0 c/s. Decoupling of protons marked with points in the formulae. ABC system marked with different shadows $J_{1,2}$ = 7·2 c/s

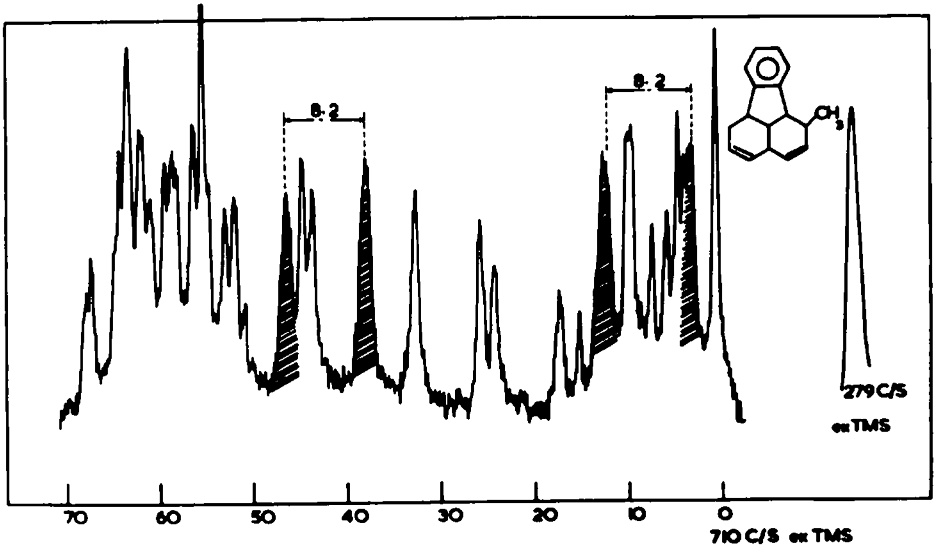


FIG. 2 NMR spectrum of 1-methylfluoranthene in CS_2 at 100 Mc/s. H_2, 718·2; H_3, 751·0; H_{Me}, 279·0 (singlet) ex TMS. $J_{2,3}$ = 8·2 c/s.

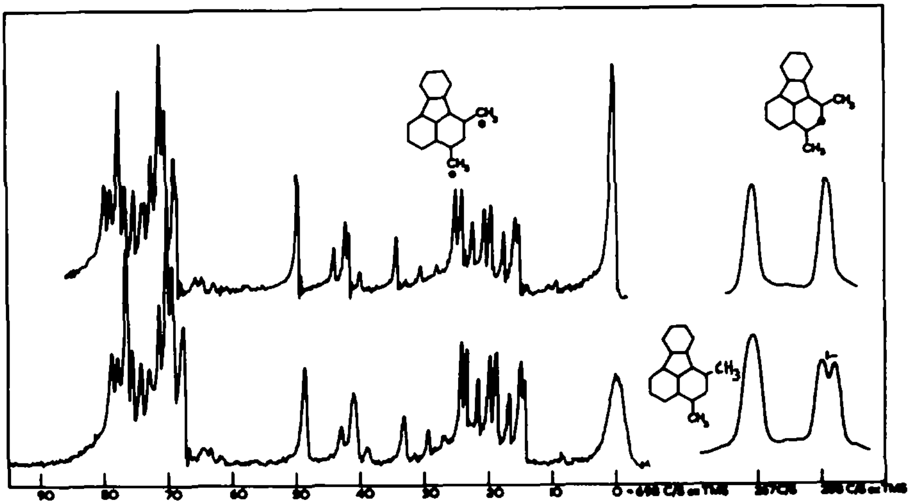


FIG. 3 NMR spectrum of 1,3-dimethylfluoranthene in CS_2 at 100 Mc/s. H_2, 698·0 (singlet), H_{Me}, 267·0 (singlet); H_{Me}, 258·0 (doublet, separation 1·0 c/s). Upper curve after decoupling Me groups and singlet at 698·0 c/s resp.

Further support for this structure is obtained from the NMR spectrum of 1,3-dimethylfluoranthene (Fig. 3). There are two Me resonances, one singlet at 267 c/s and one doublet at 258 c/s (first and second band from the right). The latter collapses into a singlet if H_2 is radiated, whilst the singlet is only slightly sharpened. Both singlets have then the same height. (The upper first two bands from the right). The aromatic singlet originating from H_2 at 698 c/s is rather broad, due to coupling with the Me protons in 3-position. Decoupling produces a sharpening as shown in the upper curve. These features are only compatible with a double bond fixation in 2,3-position.

That this applies also to the neighbouring ring is shown by the NMR spectrum of 1,3,6-trimethylfluoranthene (II).[5] According to this formula it contains two singlets at 274 and 279·4 c/s and a doublet at 266·3 c/s with a separation of 1·0 c/s.

The Me band at 266 c/s of 7,10-dimethylfluoranthene is a very sharp singlet, only 50% broader than TMS (Fig. 4). The singlet of the aromatic proton H_8 and H_9 at 693 c/s is also very sharp. Decoupling has very little effect. This excludes an appreciable double bond character between the position 7,8 and 9,10. The other part of the spectrum shows a very clear 12 line system originating from the ABC system.

A Me singlet (at 139 c/s at 60 Mc/s) is also observed in 8,9-dimethylfluoranthene (Fig. 5), second band from the right). Decoupling of the 7,10-protons causes some sharpening. This is also the case if the Me protons are decoupled, the aromatic singlet sharpens as indicated by the black area. However, this does not compare with the transformation of a doublet into a singlet as observed in the 1-Me-derivatives, and no double bond character can be deduced from it. From the NMR spectra of 7,10-dimethylfluoranthene (Fig. 4) and 8,9-dimethylfluoranthene (Fig. 5) a double bond fixation can only be deduced for the position 8,9 or for a double bond located between the upper ring and the 5-membered ring. The reactivity of fluoranthene in 8,9-position rather points to the former case.

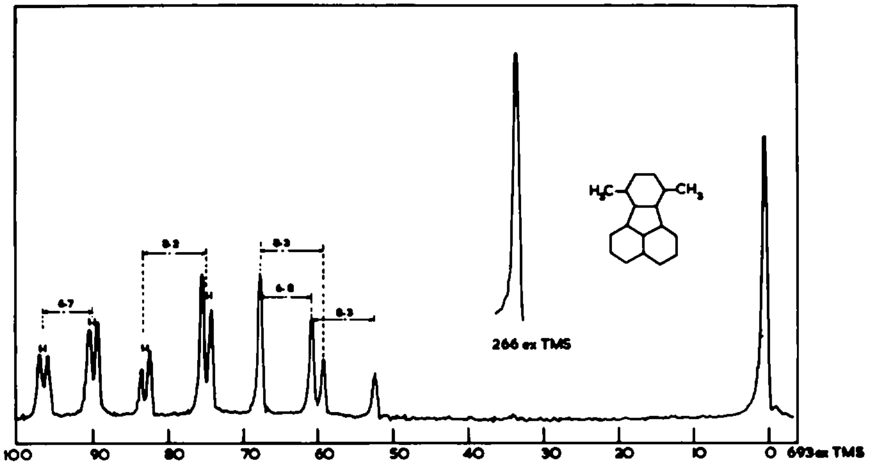


FIG. 4 NMR spectrum of 7,10-dimethylfluoranthene in CS_2 at 100 Mc/s. H_1, 785·4; H_2, 753·0; H_3, 770·4; $H_{8,9}$, 693·0; H_{Me}, 266·0 c/s ex TMS. $J_{1,2} = J_{5,6} = 7{\cdot}3$; $J_{2,3} = J_{4,5} = 8{\cdot}5$; $J_{1,3} = 1{\cdot}0$; $J_{3,1} = 0{\cdot}9$ c/s.

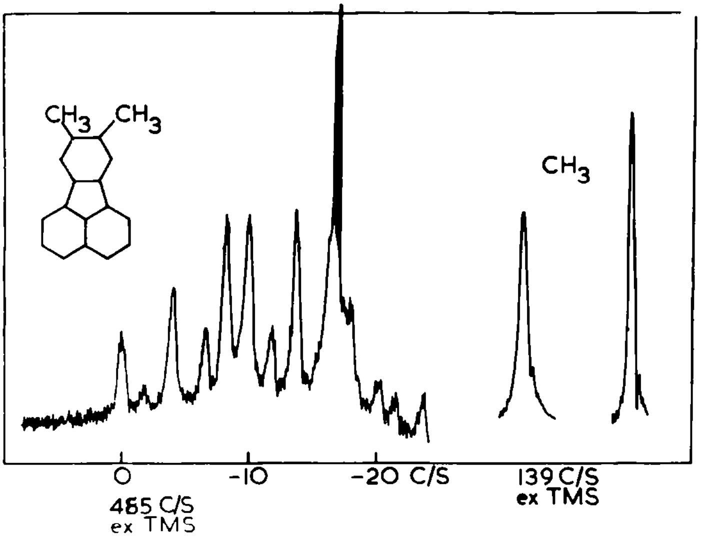


FIG. 5 NMR spectrum of 8,9-dimethylfluoranthene in CS_2 at 60 Mc/s. $H_{7,10}$, 448·4; H_{Me}, 139·0 c/s ex TMS, before and after decoupling of $H_{7,10}$. Black area after decoupling H_{Me}.

The NMR spectrum of 8-methylfluoranthene is presented in Fig. 6. The Me band is rather broad (fourth band from the right). It splits into a doublet if H_7 is decoupled. The separation of 0·8 c/s indicates a high degree of double bond character which is in line with the preceding observations. However, decoupling of H_9 also produces a doublet with a smaller separation of 0·6 c/s (third band from the right). Decoupling of H_{10} causes the appearance of a seemingly asymmetric triplet which is formed by superposition of two doublets (first band from the right) The two multiplets between 700 and 720 c/s originate from the superposition of coupling of the proton H_9 with

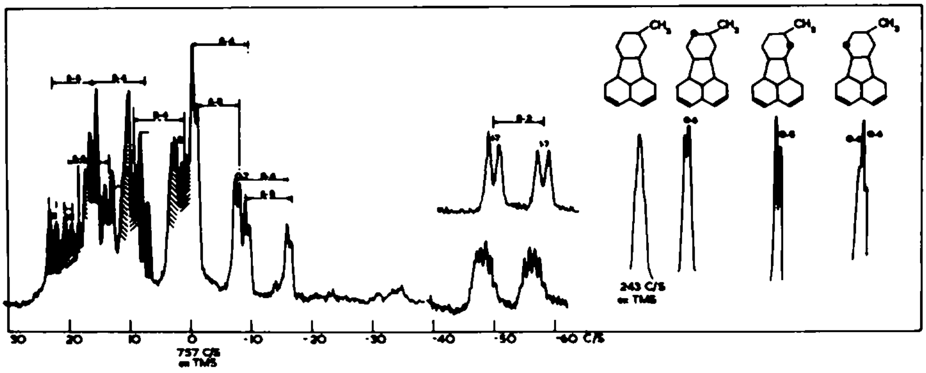


FIG. 6 NMR spectrum of 8-methylfluoranthene in CS_2 at 100 Mc/s. H_9, 705·0; H_{Me}, 243·0 c/s ex TMS. Decoupling of H_9, H_7 and H_{10} marked with points in the formulae. $J_{9,10} = 8{\cdot}2$; $J_{7,9} = 1{\cdot}7$ c/s.

the CH_3 group and meta coupling with H_7. The latter appears clearly after decoupling Me (upper curve). This confirms again a high double bond character between the positions 8 and 9. It is remarkable that the rather distant Me causes the ABC system to appear doubly, as marked by different shadows.

The NMR spectrum of 8-methylfluoranthene, like the preceding spectra, shows that the coupling of the Me protons with the proton in *o*-position (benzylic coupling) can be used for the location of double bond character in polycyclic systems. However, the small double bond character between H_7 and position 8 found in 8-methylfluoranthene, which could not be found in the other Me derivatives urges precaution in the conclusion that the basic π-electronic structure in the parent hydrocarbon and its Me derivatives is always strictly the same. This must be kept in mind before any conclusions by analogy are drawn.

Whilst the methylfluoranthenes show fixation of double bonds in 2,3- and 4,5-position this is not so in the two naphthalene complexes in perylene. The NMR spectrum of 3,10-dimethylperylene[6] (Fig. 7) has a Me doublet at 256 c/s with a separation of 0·6 c/s. This is less than in the fluoranthene series and does not account

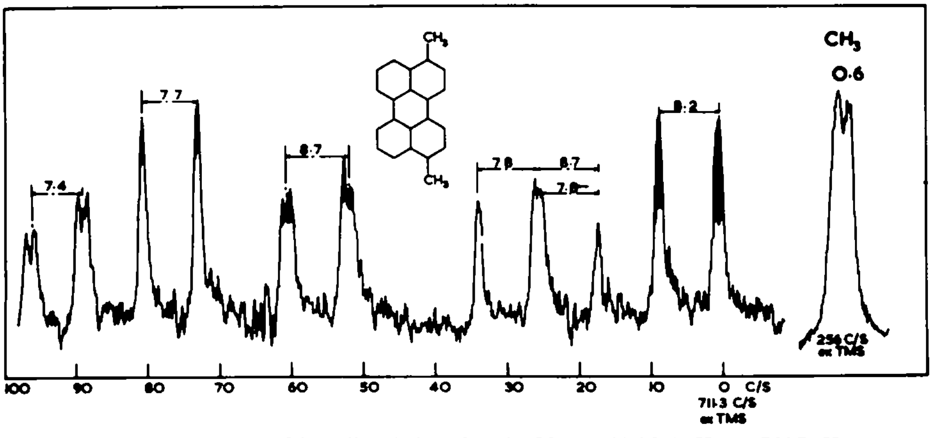


FIG. 7 NMR spectrum of 3,10-dimethylperylene in CS_2 at 100 Mc/s. $H_{1,12}$, 766·7; $H_{2,11}$, 715·8; H_{Me}, 256·0 c/s ex TMS. (Doublet separation 0·6 c/s). $J_{1,2} = J_{11,12} = 8{\cdot}0$ c/s.

for any double bond fixation. Therefore it must be assumed that the double bond can be localized in any α,β-position as indicated by full and dashed lines in formula (III). This is also the case in naphthalene[1] and it shows that the central six membered ring does not impose any double bond fixation in the naphthalene complexes, as it is the case with the five membered ring in fluoranthene. The latter case appears to be related to the Mills Nixon effect[7] in hydrindene derivatives.

Formula III for perylene which omits the symbolisation of other π-electrons than those belonging to double bonds accounts well for the diene reactivity in 1,12- and 6,7-positions[8] and for the benzylic coupling with the protons in *o*-positions. That this is so, can be proved by decoupling the high field doublet which causes the Me doublet to collapse. Decoupling of H_1 and H_{12} produces a considerable sharpening of the Me doublet. To a lesser degree this is also the case by decoupling the peri-protons H_4 and H_9. Therefore there must be a measurable degree of coupling between Me and the *meta*- and *peri*-protons. Decoupling of the Me protons has the greatest effect on the *o*-protons H_2 and H_{11} and a smaller affect on H_1 and H_{12}. The increase in intensity is marked in black in Fig. 7. There is also a ABX system in this spectrum which is of the same 12 line type as the one in perylene itself.[9]

No double bond fixation can be observed in 4,4′-dimethyl-1,1′-dinaphthyl (IV).[9] The Me resonance at 272 c/s consists of a doublet with a separation of only 0·4 c/s, showing that the double bonds may not be equally distributed between the α,β-positions.

The distribution of double bonds in fluoranthene as shown in formula I is supported by the very asymmetric annellation effect as observed by the electronic spectra of naphthalene, fluoranthene and 3,4-*o*-phenylene-fluoranthene which is recorded in formula (V). The red shift of the β-bands in going from naphthalene to fluoranthene (+ 660 Å) is much bigger than passing on to phenylene-fluoranthene (+ 55 Å). The first very big shift can only be explained if the 5-membered ring participates in the aromatic conjugation as shown in formula I. This formula does not show the two π-electrons on the highest level which can migrate over the whole system. Such a participation is not possible for the second five membered ring in V because the system has not enough π-electrons to fill this ring and still leave two electrons for the migration over the system. Therefore there must be an empty 5-membered ring "E". The distribution of double bonds in (V) makes the second anellation one without aromatic conjugation and causing only a small red shift, due to the two single bonds in the ring "E".

The fixed double bond in the phenylene ring of fluoranthene (I) also causes the asymmetric annellation effect in passing from benzene to fluoranthene (+ 1035Å) and to *peri*-naphthylene-fluoranthene (VI) (shift + 350 Å). The double bond between the five-membered ring and the second *peri*-naphthylene system must cut off the latter from aromatic conjugation as in the starphene series.[1] This results in the formation of an empty ring "E" and two single bonds which produce the small shift of + 350 Å.

These observations have been reported before[10] but they gain additional significance in connection with the location of double bonds by NMR, which makes the asymmetry of the π-electron system in V and VI obvious.

If rings are annellated to the 2,3-positions in fluoranthene there are two possibilities for aromatic conjugation. Either the double bond remains fixed in 2,3-position, then the annellation must be ineffective and the fluoranthene character retained as in VII, or the naphthalene complex is transformed into a phenanthrene complex, then the double bond must shift as shown in VIII. If both conjugations take place one would expect an electronic transition which consists of two perpendicular polarized bands, β- and β'-bands, which is shown in formula IX and actually found in fluoranthene (Fig. 8). In going to 2,3-benzofluoranthene both bands shift toward the red, 150 and 210 Å resp., however, the β-bands less than the β'-bands, so that the differences between both diminishes from 520 to 450 Å. Simultaneously the inclination of the polarization axes decreases as shown in formula X. This is even more so in passing further to naphthofluoranthene (XI), the difference between β and β'-bands being reduced to 350 Å (Fig. 8).

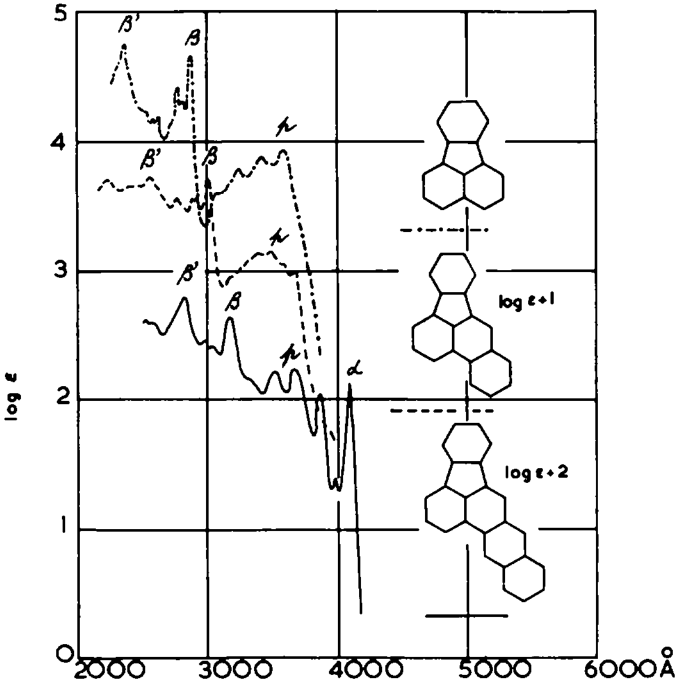


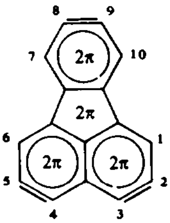
FIG. 8 Absorption spectra in cyclohexane with max (Å) and log ε in parentheses.

-·-· Fluoranthene: *p*, 3580 (3·93), 3410 (3·90), 3240 (3·79), 3090 (3·61); β, 2870 (4·66), 2770 (4·42), 2630 (4·19), 2530 (4·22); β', 2360 (4·74).

------ 2,3-Benzofluoranthene: *p*, 3690 (3·99), 3500 (4·16), 3420 (4·14); β, 3020 (4·72), 2930 (4·57), 2890 (4·57), 2770 (4·57); β', 2570 (4·74), 2460 (4·67), 2400 (4·66), 2230 (4·71).

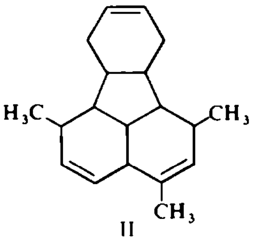
——— Naphtho[2':3', 2:3]fluoranthene: α, 4100 (4·13), 3880 (4·06); *p*, 3680 (4·24), 3520 (4·22); β, 3180 (4·65), 3040 (4·43), 2970 (4·36); β', 2830 (4·80), 2540 (4·62).

This makes it desirable to extend the series to the next member, anthracenofluoranthene, where a further reduction of the difference between β- and β'-band ought to be observed. However, we have not succeeded in the attempt to synthesize this hydrocarbon. The dinitrile (XII) could be readily condensed with fluoranthenequinone to the anthracenofluoranthene-dinitrile (XIII) but the two nitrile groups could not be eliminated by hydrolysis and decarboxylation, without complete decomposition. Even sublimation with soda-lime which gave good results in similar cases[10] failed.

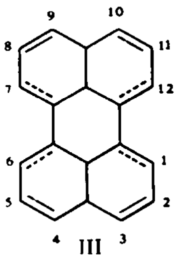


I

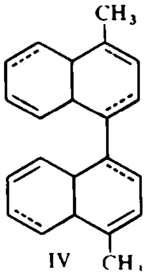
There are also 2π-electrons to migrate freely over the system.



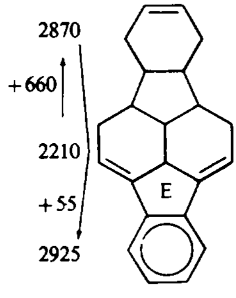
II



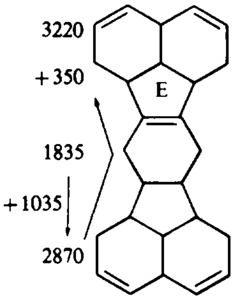
III



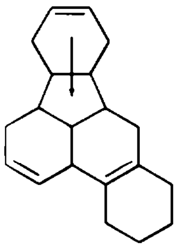
IV



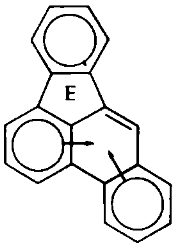
V



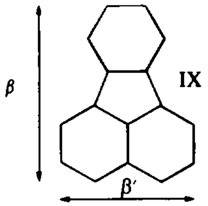
VI



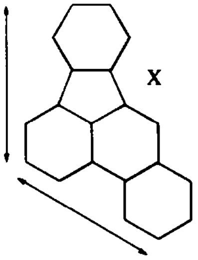
VII



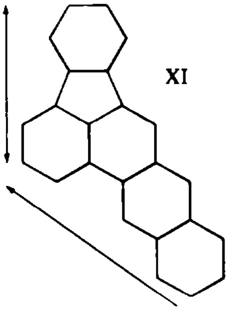
VIII



IX



X

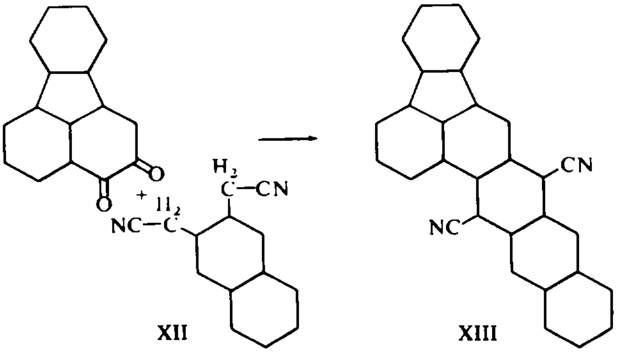


XI

$\beta = 2870 \xrightarrow{150} 3020 \xrightarrow{160} 3180$ Å

$\beta' = \underline{2360} \xrightarrow{210} 2570 \xrightarrow{260} 2830$ Å

Diff = 520 450 350



XII XIII

All Hexagons symbolize aromatic rings. Double bonds are only marked where they can be proved or for discussion. All other π-electrons are not symbolised.

1-Methylfluoranthene was prepared following the method of Campbell and Wang[11] with minor variations. 3-Methyl- and 8-methylfluoranthene were obtained from fluoranthene via the mixed 3- and 8-aldehydes by a Rieche synthesis. Their reduction by a Huang-Minlon reaction gave mainly 3-methylfluoranthene and only about 10% 8-methylfluoranthene. 7,10-Dimethylfluoranthene was synthesized by the method of Campbell and Gow[12] which was considerably simplified. 8,9-Dimethyl-tetrahydrofluoranthene was obtained by a condensation of acenaphthylene with 2,3-dimethylbutadiene.[13] The dehydrogenation was carried out with chloranil.

Naphtho[2′:3′, 2:3]fluoranthene (XI) was prepared by reduction of its 1′,4′-quinone[11] with zinc dust, pyridine and acetic acid.

EXPERIMENTAL*

3-*Methyl- and* 8-*methylfluoranthene*. Titanium tetrachloride (60 ml) was dropped into a soln of dichloromethyl-n-butyl-ether (10 g) and fluoranthene (10 g) in CS_2 (150 ml) at room temp. The yellowish brown mixture was stirred for 3½ hr, left over night without stirring and then decomposed with ice and dil HCl. CS_2 was distilled off and the residue washed with dil HCl and water. This mixture of aldehydes was dissolved in hot EtOH (125 ml), hydrazine hydrate (80%, 20 ml) added and refluxed for 3 min. The ppt was filtered off and washed with little MeOH, yield 2·7 g. This product was used for the preparation of 3-methylfluoranthene.

Concentration of the mother liquor yielded 4·3 g of a mixture of crystals, consisting of orange brown compact ones and lighter yellow ones. These were separated mechanically. The yields of the yellow part was 0·42 g and used for the preparation of 8-methylfluoranthene.

The first hydrazone (1 g), dimethylene glycol (15 ml) and NaOH (3 g) were heated under N_2 for 3 hr, water and excess hydrazine were removed frequently from the condenser. The mixture was diluted with water and the hydrocarbon (0·35 g) filtered off. The picrate was formed in EtOH and recrystallized 3 times from EtOH. It formed long orange needles (0·38 g) m.p. 174–175° dec. (Lit.[14] 171–173°). (Found: N, 9·15. $C_{23}H_{15}O_7N_3$ requires: N, 9·43%).

After decomposition of the picrate the hydrocarbon was recrystallized from EtOH. 3-Methylfluoranthene formed pale yellow plates (0·11 g), m.p. 66·67° (lit.[14] 66°). (Found: C, 94·4; H, 5·5. $C_{17}H_{12}$ requires: C, 94·4; H, 5·6%).

The yellow hydrazone (0·42 g) from the second crystallization, diethylene glycol (8 ml) and NaOH (1·5 g) were refluxed as above. The hydrocarbon (0·35 g) was dissolved in pet. ether (80–100°) and chromatographed on alumina. The crystals obtained from the eluate were transformed into the picrate in EtOH soln. Recrystallization gave orange-yellow needles, m.p. 159–162° dec. (lit.[14] 156–157°). Decomposition with dil ammonia gave a hydrocarbon which consisted of a mixture of 8-methylfluoranthene (75%) and 3-methylfluoranthene (25%) as found by NMR and GLC. The mixture (50 mg) was separated by the use of a Pye, Series 105 chromatograph all glass preparative GLC (Column 10 ft; 3% APL; temp 230°, carrier gas 150 ml; sensitivity 1×10^3) and 20 mg of pure 8-methylfluoranthene, m.p. 90 (lit.[14] 88–90) were obtained.

7,10-*Dimethylfluoranthene*. The diol (20 g), obtained from acenaphthenquinone and EtMgBr, and maleic anhydride (80 g) were refluxed in Ac_2O for 5 hr. Nitrobenzene (400 ml) was added and the mixture distilled until the temp reached 210°. Then iodine (2 g) was added and refluxed for a further 5 hr. Concentration and cooling gave dark yellow needles (11·5 g) of 7,10-dimethylfluoranthene-8,9-dicarboxylic anhydride, m.p. 313–315°.

This anhydride (2 g), basic copper carbonate (2 g) and quinoline (25 ml) were refluxed under N_2 for 24 hr. The mixture was boiled with dil HCl and the residue filtered, washed and extracted with dil NaOH. The residue was dissolved in hot xylene, humidity removed by boiling, and chromatographed on alumina using benzene as eluant. Concentration yielded pale yellow needles (1·05 g), m.p. 210–212° (lit.[12] 210–211°). This method gave much better results than sublimination with soda-lime.

8,9-*Dimethylfluoranthene*. The method of Kloetzel and Mertel[13] was used to prepare 8,9-dimethyltetrahydrofluoranthene. 3 sealed tubes gave 6·1 g of this hydrocarbon, m.p. 69–70°. It was dissolved in xylene (100 ml), chloranil (10 g) added and refluxed for 5 hr. The mixture was added to dil NaOH (5%, 300 ml)

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* M.ps are uncorrected and were taken in evaluated capillaries.

and refluxed with stirring for 4 hr. The mixture was filtered and the organic layer separated. The soln was concentrated to a small volume, diluted with light petroleum (100–120°) and chromatographed on alumina. The hydrocarbon after three recrystallization from EtOH formed long yellowish needles (4 g), m.p. 144–145°. (Found: C, 93·7; H, 6·3. $C_{18}H_{14}$ requires: C, 93·9; H, 6·1%).

2,3-Bis-cyanomethyl-naphthalene (XII). A modification of the method of Ried and Bodem[15] was used which gave a higher yield. KCN (10 g) was dissolved in a minimum of water, EtOH (150 ml) added and refluxed. 2,3-Bisbromomethyl-naphthalene (10 g) was added in portions and refluxed for 2 hr. After cooling the mixture was poured into water (2 l) and the ppt filtered off. Recrystallization from benzene–light petroleum (100–120°) gave needles (4·7 g), m.p. 156–157°.

1′,4′-Dicyano-anthraceno[2′:3′, 2:3]*fluoranthene* (XIII). The above dicyano compound (0·2 g) was dissolved in dry EtOH (20 ml) and added to a soln of fluoranthenequinone[4] (0·23 g) in dry EtOH. The soln was boiled and KOH (0·05 g) in EtOH (3 ml) added. The mixture which became immediately dark and precipitated red needles was cooled and filtered after 2 hr. The needles (0·1 g) were recrystallized from dry benzene and sublimed at 300°/4 × 10^{-2} mm. The soln in benzene showed the following absorption bands: *p*, 5220 (4·92), 4860 (4·93), 4580(4·84); 4350 (4·73); *β*, 3620 (5·84), 3540 (5·87); 2850 (5·69). (Found: C, 89·7; H, 3·6; N, 6·73. $C_{30}H_{14}N_2$ requires: C, 89·5; H, 3·5; N, 6·96%). Mol. wt. mass spect $m^+/e = 402$. Cal.: 402.

Naphtho[2′:3, 2:3]*fluoranthene* (XI). The crude quinone (17·4 g) obtained from 9-methyl-9-hydroxyfluoranthene and naphthoquinone, following the description of Campbell and Wang,[11] was dissolved in pyridine (200 ml) and filtered from a white residue, which was washed with pyridine (50 ml). The combined soln was refluxed with Zn dust (50 g), and AcOH (80%, 50 ml) was added dropwise over a period of 3 hr. The colour of the soln changed from rust red to violet red then finally to pale yellow. After 5 hr the soln was decanted from the Zn and acidified with AcOH. The ppt (2·5 g) was filtered off and washed with water. More ppt appeared after prolonged standing. The first portion (2·5 g) was dissolved in hot xylene (500 ml), concentrated to removed water and chromatographed on alumina. Concentration of the eluate showed that the crystals were not uniform. Therefore the picrates were prepared from different fractions and orange needles of the pure picrate (0·219 g) obtained. Decomposition with dil ammonia gave the hydrocarbon which was recrystallized from xylene. It formed pale yellow crystals, m.p. 228–229° (lit.[11] 229°).

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