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THE ESTABLISHMENT OF DOUBLE BOND CHARACTER IN METHYL DERIVATIVES OF PHENANTHRENE, PYRENE, CHRYSENE AND CORONENE BY NMR

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Abstract—1,6-Dimethylpyrene (V), 2,8-dimethylchrysene (IX) methylcoronene (X) and ethylcoronene have been synthesized. The NMR spectra of 1-methylphenanthrene (III), 2-methylphenanthrene (II) and 9-methylphenanthrene (I) are reported. Whilst the Me-group in the first two hydrocarbons produces sharp singlets as usual in aromatics, 9-methylphenanthrene gives rise to a Me-doublet as in methyl olefins, thus indicating the double bond character of the 9:10-position. An analogous observation can be made in the pyrene series: 3-methylpyrene (VII), 1,2-dimethylpyrene (VIII) and 4,9-dimethylpyrene (VI) give Me-singlets, whilst 1-methylpyrene (IV) and 1,6-dimethylpyrene (V) give Me-doublets. 2,8-Dimethylchrysene (IX) shows a Me-singlet, because the inherent sextets are not fixed as in phenanthrene. Methylcoronene (X) produces a Me-doublet. It must be therefore formulated with three sextets and three double bonds of the double bond type to be found in the middle ring of phenanthrene.

THE NMR spectrum of phenanthrene[1] consists of a group of bands originating from the H atom in the positions 4- and 5-centered at τ 1·3 and a larger group around τ 2·3 with a sharp singlet at τ 2·28, the latter originating from the A_2 system in 9:10 position.

The NMR spectrum of 9-methylphenanthrene (I) is shown in Fig. 1 the two regions of bands are still here, but more complex in appearance. As expected the singlet at τ 2·28 has disappeared. The H atoms of the Me group are recorded at τ 7·45 as a doublet, (separation 1·1 c/s). The latter is caused by coupling of the Me-group with the H atom in position 10. Doublets of this kind are regularly observed in the NMR spectra of methyl olefins and sometimes in methyl derivatives of heterocyclic systems. The formulation of 9-methylphenanthrene (I) with the two sextets gives clearly double bond character to the 9:10-positions.

This is also shown by the NMR spectrum of 3-methylphenanthrene (II) in Fig. 2. Here the methyl group is attached to a sextet and therefore appears as a sharp singlet at τ 7·53 as in methylbenzenes or methylnaphthalenes. The methyl group does not interfere with the sharp singlet at τ 2·49 resulting from the A_2 system in the positions 9 and 10.

The Me-group in 1-methylphenanthrene (III) being in peri-position to the H atom in 10-position causes the H atoms of the 9:10-positions to give rise to a quartet distributed over the whole group of bands centered at τ 2·5. (Fig. 3). The Me-group being attached to a sextet produces a singlet at τ 7·34.

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* The methylcoronene was prepared by M. Zander in the Central Laboratory of Rütgerswerke und Teerverwertung AG. in Castrop-Rauxel.

[1] N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.* **36**, 2443 (1962); R. H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, *Tetrahedron* **20**, 1073 (1964)

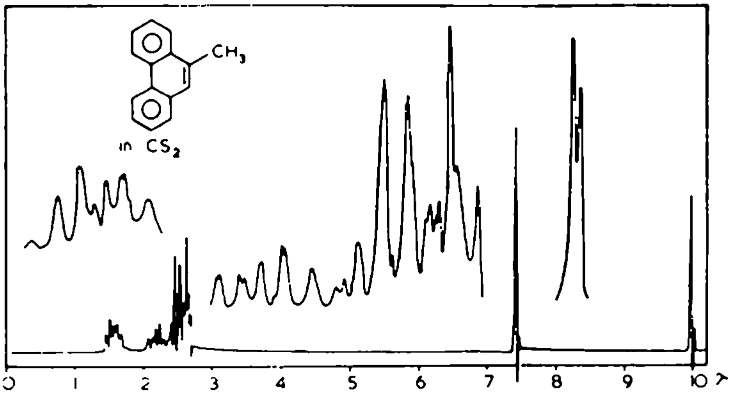

FIG. 1. NMR spectrum of 9-methylphenanthrene in CS_2 at 60 Mc/s with 6 times expansion (Perkin-Elmer R10).

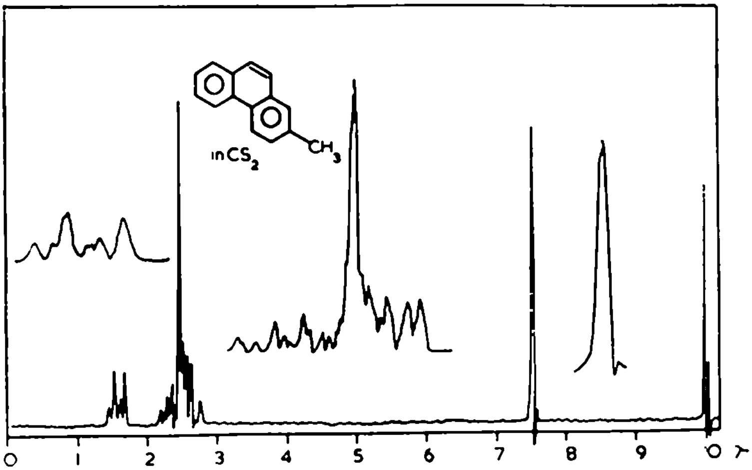

FIG. 2. NMR spectrum of 2-methylphenanthrene in CS_2 at 60 Mc/s with 6 times expansion (Perkin-Elmer R10).

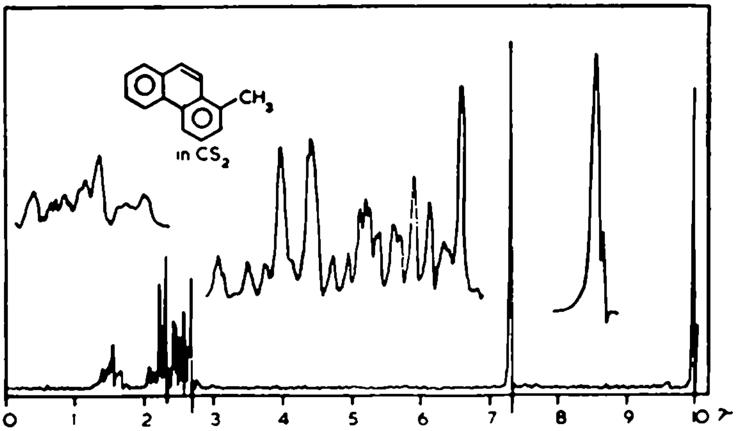

FIG. 3. NMR spectrum of 1-methylphenanthrene in CS_2 at 60 Mc/s with 6 times expansion (Perkin-Elmer R10).

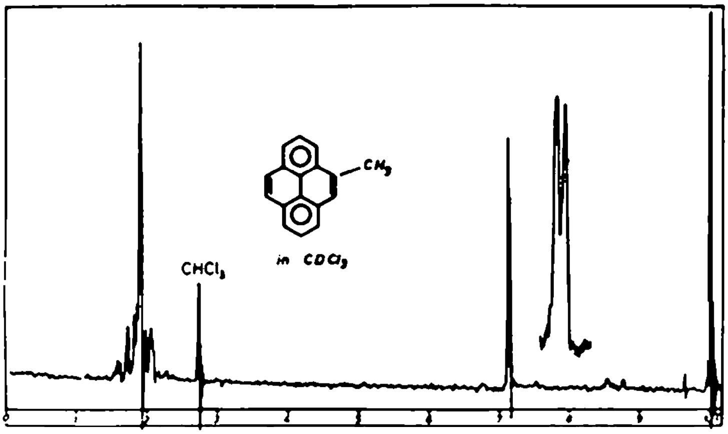

FIG. 4. NMR spectrum of 1-methylpyrene in $CDCl_3$ at 60 Mc/s with 6 times expansion (Perkin-Elmer R10).

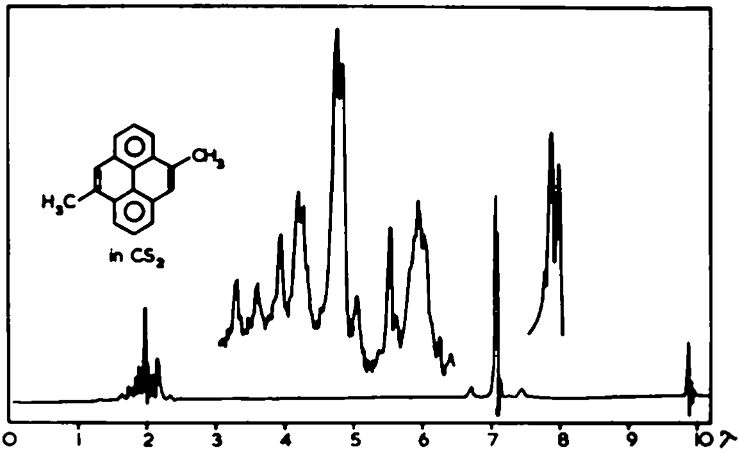

FIG. 5. NMR spectrum of 1.6-dimethylpyrene in CS_2 at 60 Mcps with 6 times expansion (Perkin-Elmer R10).

There is however a very small peak to the right of this singlet. Since it does not appear in 3-methylpyrene (VII) it is probably due to a very small amount of impurity. The double bond character of the 9:10-position in phenanthrene is also shown by the smooth addition of bromine to form phenanthrene dibromide.

1-Methylpyrene (IV) is related to 9-methylphenanthrene (I). The Me-group being attached to a formal double bond again produces a doublet at τ 7·11, with a separation of 1·3 c/s (Fig. 4). The A_2 system in the position 6- and 7- is unaffected by the Me-group and appears as a sharp singlet at τ 1·88.

The NMR spectrum of 1,6-dimethylpyrene (V) is recorded Fig. 5. The two Me-groups on the double bonds produce a doublet at τ 7·20 with a separation of 1·2 c/s. The two H atoms in the positions 2 and 7 appear to give rise to a rather broad band at τ 2·28. Coupling with the three H of the Me group ought to produce a quartet. As in similar cases this cannot be clearly seen.

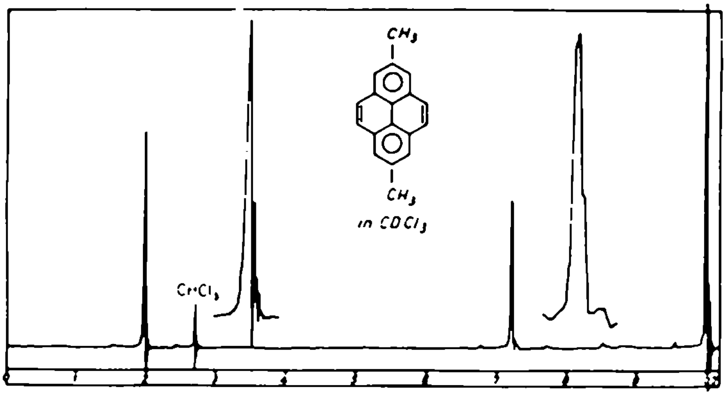

FIG. 6. NMR spectrum of 4,9-dimethylpyrene in $CDCl_3$ at 60 Mcps with 6 times expansion (Perkin-Elmer R10).

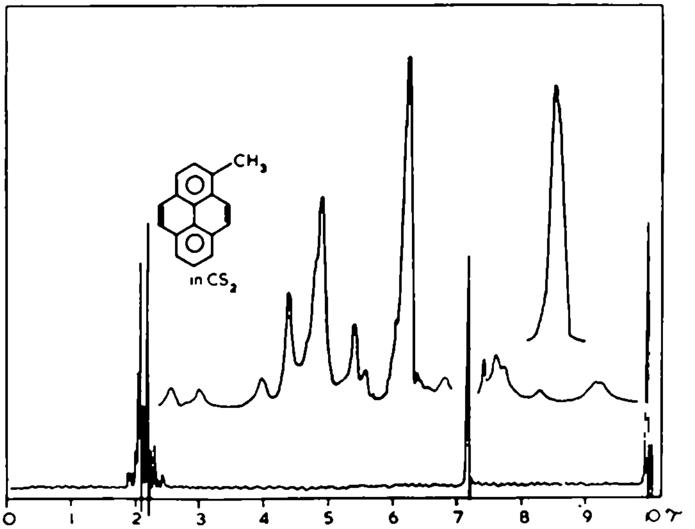

FIG. 7. NMR spectrum of 3-methylpyrene in CS_2 at 60 Mc/s with 12 times expansion (Perkin-Elmer R10).

The Me-groups in 4,9-dimethylpyrene (VI) are both attached to sextets. They therefore appear as a singlet at τ 7·18 in the NMR spectrum in Fig. 6. This spectrum is remarkably simple, the four H atoms in the positions 1,2,3,5,6,7,8,10 producing a single sharp band at τ 1·97. The Me-groups have only two adjacent H atoms. If in accordance with the VB theory the C—C-bonds in between have each 50% double bond character as compared with 4/6 = 67% in 1,6-dimethylpyrene (V), the Me-group in 4,9-dimethylpyrene ought to appear as a triplet. This cannot be clearly seen. Being of the utmost importance for establishment of the true nature of the aromatic sextet, this and similar cases will be intensively studied in the near future.

The NMR spectrum of 3-methylpyrene (VII; Fig. 7) shows the Me-group as a singlet at τ 7·20, because it is attached to a sextet. It has a strong influence on the H atoms in the positions 1 and 2. These form a quartet difficult to establish with certainty, in the complex spectrum but the A_2 system in the position 6 and 7 is unaffected by it, forming a singlet at τ 2·23. This spectrum has been already reported[2] in the form of a simplified scheme.

If two Me-groups are attached to one formal double bond as in 1,2-dimethylpyrene (VIII) no coupling with the Me-groups can occur and a sharp singlet at τ 7·36 is observed (Fig. 8). The A_2 system in the positions 6 and 7 is undisturbed and forms a singlet at τ 2·24. The two H atoms in the positions 3 and 10 produce a quartet at τ 1·97 with coupling constants $J_{3,5'}$ = 1·8 c/s and $J_{3,4}$ = 7·2 c/s and the H atoms in position 5 and 8 form a quartet at τ 2·15 with coupling constants $J_{5,3}$ = 1·9 and $H_{5,4}$ = 7·6 c/s. The H atom in position 4 and 9 give rise to the bands at τ 2·22, 2·29 and 2·36.

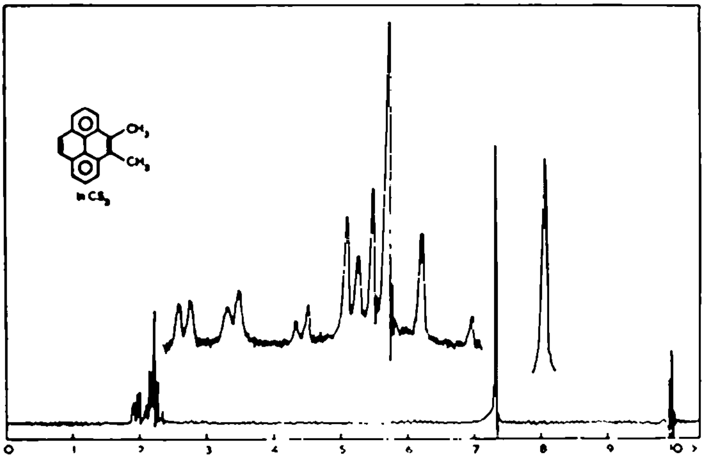

FIG. 8. NMR spectrum of 1,2-dimethylpyrene in CS_2 at 100 Mc/s with 10 times expansion (Varian HA100).

The two inherent sextets in chrysene are not fixed as in phenanthrene. They can move between the rings as indicated by the arrows in 2,8-dimethylchrysene (IX) and therefore the double bonds lose their character as fixed double bonds. As a result of this the two Me-groups in IX do not produce the doublet associated with a fixed double bond but a singlet in the NMR spectrum at τ 7·26 in Fig. 9. The other parts of the spectrum are easy to analyse. The first group of bands at τ 1·44 originates from the two H atoms in positions 6 and 12, the singlet at τ 1·71 belongs to the two H atoms in positions 1 and 7. These obviously do not couple with the Me-groups. The group of bands at τ 2·1 can be related to the two H atoms in positions 3 and 9 and the group at τ 2·55 to the four H atoms in positions 4,5,10,11.

Chrysene gives only substitution products with bromine in 2- and 8-positions, but no addition reaction is observed. This is in agreement with the above results.

The NMR spectrum of coronene in $CDCl_3$ shows a sharp singlet at τ 1·07[1] and in CS_2 at τ 1·28. The latter does not give any indication of splitting even if 20 times expanded and measured on the Varian HA-100 spectrometer. If coronene is formulated with three inherent sextets and three rings of the type of the middle ring in phenanthrene (analogous to X) then obviously a delocalisation mechanism must exist which makes all the rings equal thus giving rise to a sharp singlet. However the

[2] R. H. Martin, R. Flammang and M. Arbaoui, *Bull. Soc. Chim. Belges* 74, 418 (1965).

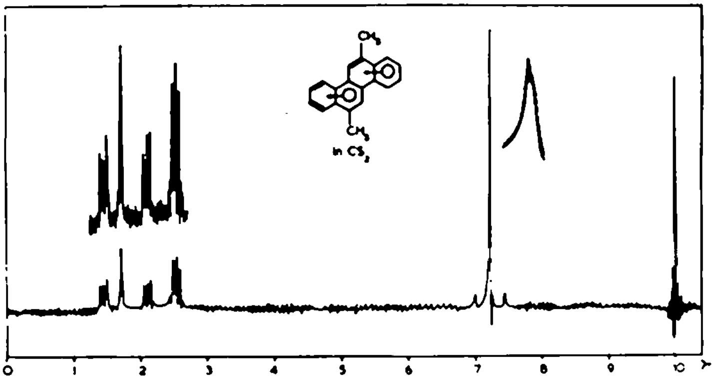

Fig. 9. NMR spectrum of 2,8-dimethylchrysene in CS_2 at 100 Mc/s with 20 times expansion of CH_3 band (Varian HA100).

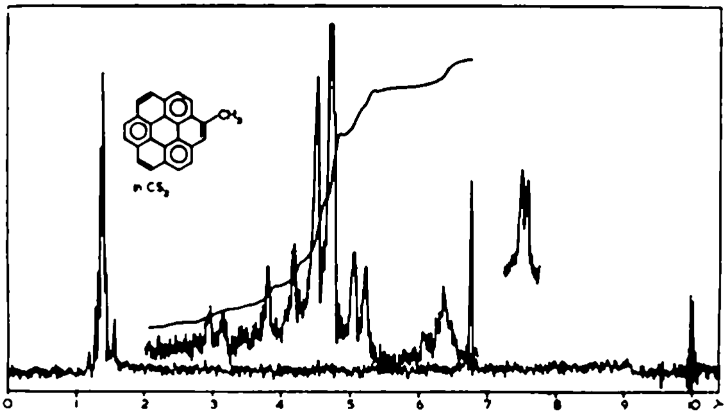

Fig. 10. NMR spectrum of Methylcoronene in CS_2 at 100 Mc/s with 10 times expansion of aromatic H's and 20 times expansion of CH_3 band (Varian HA100).

same mechanism cannot operate in the case of methylcoronene (X). Its NMR spectrum (Fig. 10) shows a doublet at τ 6·76 (separation 0·9 c/s) for the Me-group. As shown above this is typical for a methyl group attached to a double bond like the one in the middle ring of phenanthrene.

The aromatic H atoms in methylcoronene (X) produce 9 distinct peaks. A tentative assignment can be made if the results obtained in the phenanthrene and pyrene series are taken into account: the H atoms in position 2 gives rise to the broad band at τ 1·54, the H atoms in positions 11 and 12 ought to produce a quartet, part of which is at τ 1·20 and 1·22, the other bands being superimposed by the stronger bands. This leaves eight H atoms which cause the appearance of three doublets: two H atoms give bands at 1·28 and 1·32, four H atoms (probably due to the quasi equal H atoms in position 5, 6, 9 and 10) give bands at τ 1·36 and 1·38, and two H atoms give bands at τ 1·40 and τ 1·42. Since neither an A_2 system nor an AB system can produce a doublet, no conventional explanation can be offered.

The NMR spectrum of ethylcoronene (Fig. 11) shows a similar splitting of the aromatic H atoms: one H (position 2) at τ 1·56 and at τ 1·18 part of quartet (or double

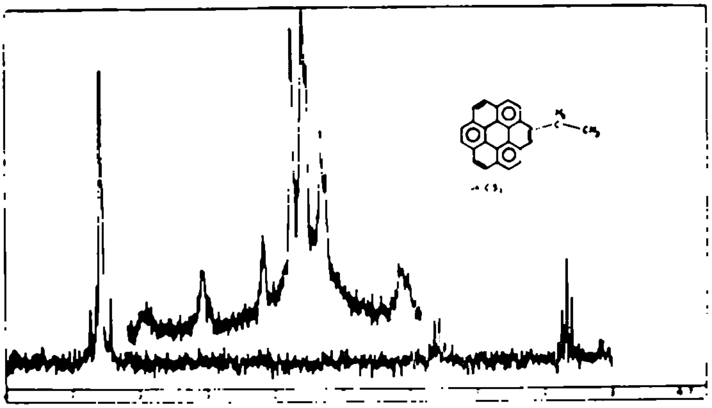

FIG. 11. NMR spectrum of ethylcoronene in CS_2 at 100 Mc/s with 10 times expansion (Varian HA100).

quartet), two H at τ 1·26 and 1·36, four H at τ 1·40 and 1·42, two H at 1·44 and 1·45 τ. Owing to the low solubility the bands of the CH_2 and Me group are too weak for an expansion.

Summarizing it can be stated that there is no connection between the occurrence of the splitting of the Me-band the degree of separation of the doublet and the precentage of double bond character in the Me—C=CH— system as calculated by the valence bond theory. The strict application of Robinson's aromatic sextet shows that splitting is observed if the Me-group is connected with a double band which cannot participate in an inherent sextet. This does, of course, not exclude that the same ring contains other delocalised π-electrons as in an induced aromatic sextet[3] of type as in the middle ring of phenanthrene.

EXPERIMENTAL*

1,6-*Dicyano*-3,4,5,8,9,10-*hexahydropyrene*. This was prepared by a modified version of Vollmann's method:[4] 1,6-dibromo-3,4,5,8,9,10-hexahydropyrene (40 g) and CuCN (25 g) were ground together, suspended in quinoline (500 ml) and refluxed for 3½ hr. The cooled mixture was filtered and the ppt washed with EtOH. The brown ppt was extracted with boiling nitrobenzene, the Cu salts filtered off and the soln concentrated. The yellow ppt was recrystallized from nitrobenzene and gave colourless needles, m.p. 303°, (lit.[4] m.p., 303°). It sublimed at 240–250°/0·025 mm and dissolved in conc H_2SO_4 with a yellow green colour. (Found: N, 10·88. $C_{18}H_{14}N_2$ requires: N, 10·85%.)

Pyrene-1,6-*dinitrile*. 1,6-Dicyano-3,4,5,8,9,10-hexahydropyrene (20 g), Se (20 g) and dibenzofuran (60 g) were refluxed for 20 hr. The excess Se forming a lump was removed and the soln allowed to solidify. The separation of dibenzofuran and pyrenedinitrile was achieved by vacuum sublimation. The pyrene-1,6-dinitrile yielded yellow needles (m.p., 401, lit.[4] 406°) from trichlorobenzene and did not dissolve in cold conc. H_2SO_4. (Found: N, 11·20. $C_{18}H_8N_2$ requires: N, 11·11%.)

1,6-*Dimethylpyrene* (V). The above nitrile (0·1 g) hydrazine hydrate (80%, 2·5 ml) and xylene (5 ml) were heated in a sealed tube at 200° for 30 hr. The solid was filtered from the xylene-hydrazine mixture, which was then diluted with water, the xylene separated and combined with the xylene soln of the solid residue. The concentrated, dried soln was chromatographed on grade I alumina. Elution with benzene and concentration yielded colourless crystals (from 4 tubes 96 mg hydrocarbon) which after recrystallization from benzene formed colourless plates, m.p., 195°. These dissolved in

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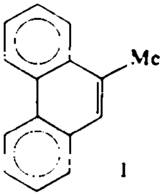
* M.ps are uncorrected and were taken in evacuated capillaries.

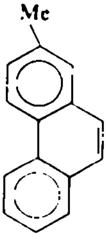
[3] E. Clar, *Tetrahedron*, **9**, 206 (1960); **18**, 1471 (1962).

[4] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Liebigs Ann.* **531**, 145 (1937).



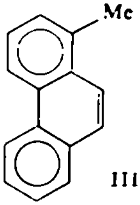
I

Me Doublet



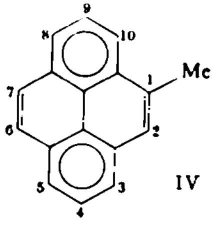
II

Me Singlet



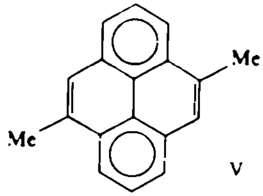
III

Me Singlet



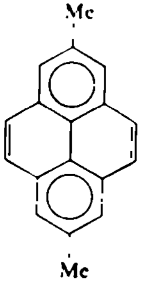
IV

Me Doublet



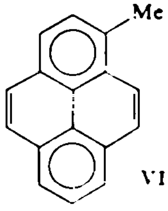
V

Me Doublet



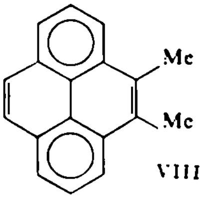
VI

Me Singlet



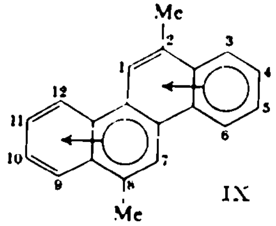
VII

Me Singlet



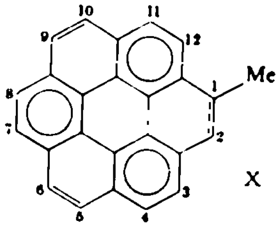
VIII

Me Singlet



IX

Me Singlet



X

Me Doublet

conc. H_2SO_4 with a yellowish green colour. (Found: C, 93·7; H, 6·03. $C_{18}H_{14}$ requires: C, 93·88; H, 6·12%.)

2,8-*Dimethylchrysene* (IX). Chrysene-2,8-dinitrile[4] (100 mg), hydrazine hydrate (2·5 ml) and xylene (1 ml) were heated in a sealed tube at 200° for 30 hr. The crystals were filtered from the liquids, the xylene layer separated and combined with a xylene soln of the crystals. This soln was dried and chromatographed on grade I alumina. Elution with benzene and concentration yielded colourless

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[4] K. Funke, E. Müller, L. Vadasz, *J. prakt. Chem.* (N.F.) **144**, 265 (1936).

needles (100 mg from 4 tubes), which after recrystallization from benzene had m.p. 236–237°. This hydrocarbon was identical with the 2,8-dimethylchrysene prepared by a different synthesis.[6]

Coronene-aldehyde. This compound was prepared by the method of Reimlinger *et al.*[7] although far more drastic conditions had to be applied. Dichloromethyl-n-butylether (25 g) and titanium tetrachloride (150 ml) were added to a soln of coronene (5 g) in CS_2 (2500 ml) at room temp. The blue mixture was stirred for 50 hr then decomposed with ice and dil HClaq. The crude aldehyde (3 g) was filtered off washed with dil HClaq, water and then ammonia. The CS_2 soln, after concentration and adding ether, gave a further portion of aldehyde (2·2 g). Repeated crystallization from xylene yielded yellow needles, m.p., 340–342° (lit.[7] >360°) which gave a red violet soln with conc. H_2SO_4. (Found: C, 91·5; H, 3·75. $C_{25}H_{12}O$ requires: C, 91·44; H, 3·68%.)

Hydrazone. Coronene aldehyde (3 g) was dissolved in boiling pyridine (125 ml) and hydrazine hydrate (50%, 13 ml) and then water (30 ml) were added. The hot soln was filtered from a small amount of insoluble material and the hydrazone precipitated from the solution with water (150 ml). Yield 2·6 g. The hydrazone had m.p., 360°, dec. (Found: N, 7·9. $C_{25}H_{14}N_2$ requires: N, 8·2%.)

Methylcoronene (X). The above hydrazone (2 g), diethylene glycol (30 ml) and KOH (6 g) were heated under N_2 at 230–240°. The water formed was distilled off. After heating for 6½ hr, the mixture was diluted with water and the hydrocarbon filtered off (1·9 g). Sublimation at 300°/10^{-3} mm yielded pale yellow needles, which were dissolved in xylene and chromatographed on alumina grade I. The different fractions from the eluate showed hardly any difference in m.p., and UV spectrum, yield 1·3 g. The middle fractions were transformed into the picrate with picric acid in xylene soln. The picrate was recrystallized from xylene containing picric acid. The dark red needles had m.p., 258-260°, dec. (Found: N, 7·8. $C_{31}H_{17}N_3O_7$ requires: N, 7·7%.)

The picrate was decomposed with NH_4OH and the hydrocarbon recrystallized from xylene. Methylcoronene forms pale yellow needles, m.p., 317·5–318° which do not dissolve in cold conc. H_2SO_4. (Found: C, 95·3; H, 4·65. $C_{25}H_{14}$ requires: C, 95·5; H, 4·5%.) UV spectrum in benzene: (wavelength in Å with log ε in parenthesis) α: 4310 (2·48), 4220 (2·08), 4120 (2·60), 4060 (2·58), 3910 (2·36), 2860 (2·34), 3800 (2·30), 3700 (2·18); p: 3440 (4·72), 3280 (4·36), β: 3080 (5·34), 2950 (4·88).

Acetylcoronene. To a finely ground mixture of coronene (1 g) and $AlCl_3$ (4 g) in nitrobenzene (50 ml) was added acetyl chloride (1 ml) in nitrobenzene (10 ml). The soln which changed from yellow to reddish-brown was shaken for 10 hr with glass beads and then decomposed with dil HClaq. The nitrobenzene was removed by steam distillation, and the residue repeatedly recrystallized from xylene. Acetylcoronene (0·95 g) formed yellow needles, m.p., 207–208°, (lit.[7] 206–207°). (Found: C, 91·0; H, 4·38. $C_{26}H_{14}O$ requires: C, 91·24; H, 4·66%.) Acetylcoronene in pyridine formed readily a hydrazone with hydrazine hydrate and piperidine. If water was added this hydrolysed gradually back to acetylcoronene. In this way any trace of coronene could be removed in the first stage of the dilution.

Ethylcoronene. Acetylcoronene (0·5 g), NaOH (0·18 g), hydrazine hydrate (80%, 0·3 ml) in diethylene glycol (10 ml) were refluxed for 1 hr. Water and excess hydrazine were then distilled off until the temp rose to 200°. The mixture was then refluxed for a further 3 hr, water added and the hydrocarbon filtered off and washed. It was chromatographed in xylene soln on alumina grade I. Concentration of the soln gave yellow needles which were purified through the picrate. Decomposition with ammonia and repeated crystallization from xylene gave long pale yellow needles (0·3 g) of ethylcoronene, m.p., 203–204°, which did not dissolve in conc H_2SO_4. (Found: C, 94·9; H, 4·70. $C_{26}H_{16}$ requires: C, 95·09; H, 4·91%.)

Acknowledgements—We wish to thank Dr. A. L. Porte for valuable discussions. We are also indebted to Professor H. Dannenberg for a sample of 1,2-dimethylpyrene, to Dr. W. Carruthers for a sample of 1-methylpyrene, to Messrs. Rütgerswerke und Teerverwertung AG for samples of 1-, 2- and 9-methylphenanthrene and 3-methylpyrene and 4,9-dimethylpyrene.

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[6] H. J. Lewis, G. R. Ramage and R. Robinson, *J. Chem. Soc.* 1414 (1935).

[7] H. Reimlinger, J. P. Golstein, J. Jadot and P. Jung, *Chem. Ber.* **97**, 349 (1964).