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THE NATURE OF PARA-BOND AND OF PARA-COUPLING

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Abstract—The para-coupling in a number of tetracene- and anthracene-derivatives was investigated and found to be not measurable in the middle ring of these compounds. There is also no peri- and epi-coupling between meso-positions. However, there is appreciable coupling between meso- and terminal peri-positions. A very weak para-π-bond is assumed which is very much strengthened in meso-Me derivatives. In this case the Me signals are split into doublets by direct coupling with the proton in the para-position.

THE COUPLING of the para-protons in the terminal rings of polycyclic hydrocarbons is well established by direct observation of the splitting of the signals.[1] However, no direct observations of the splitting resulting from spin–spin coupling of the protons in meso-position have been reported. The singlets of the meso-protons in tetracene derivatives are particularly suitable for this purpose. Fig 1 shows the meso-proton

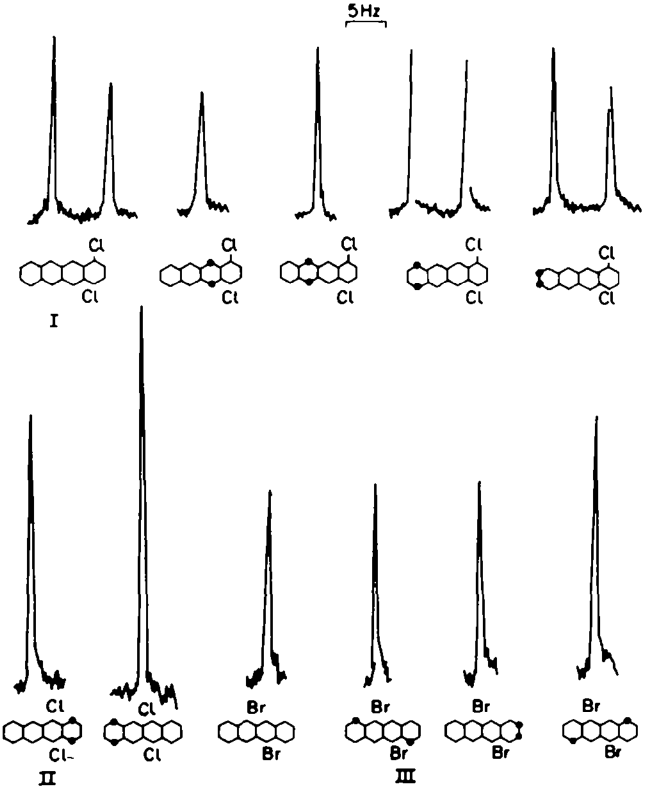
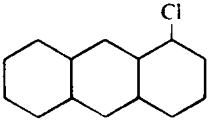
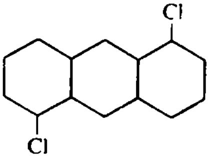
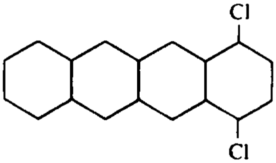
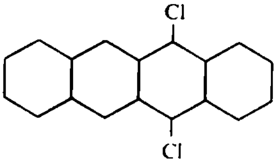
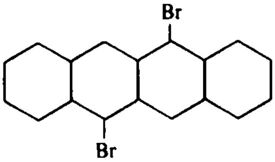
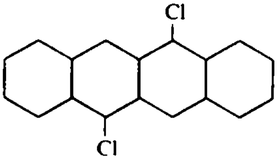
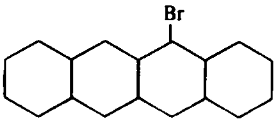
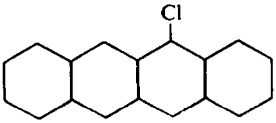


FIG 1. Comparison of singlets of halogen tetracenes with decouplings marked by points.

TABLE 1

Compound in CS_2 at 100 MHz Aromatics	Chemical shift in τ
	$H_{2,3,6,7}$ 2·84 (m); $H_{4,5,8}$ 2·37 (m) H_{10} 2·10 (s. sharp); H_9 1·40 (s. sharp)
	$H_{2,3,6,7}$ 2·64 (m); $H_{4,8}$ 2·10 (quartet) $H_{9,10}$ 1·27 (s. sharp)
	$H_{2,3}$ 2·73 (s. sharp); $H_{8,9}$ 2·69 (m) $H_{7,10}$ 2·10 (m); $H_{6,11}$ 1·44 (s); $H_{5,12}$ 1·07 (s. sharp)
	$H_{8,9}$ 2·61 (m); $H_{2,3}$ 2·70 (m); $H_{7,10}$ 2·00 (m); $H_{1,4}$ 1·59 (m); $H_{6,11}$ 0·94 (s).
	$H_{2,3,8,9}$ 2·57 (m); $H_{1,7}$ 2·04 (m); $H_{4,10}$ 1·64 (m); $H_{6,12}$ 0·90 (s)
	$H_{2,3,8,9}$ 2·60 (m); $H_{1,7}$ 2·09 (m); $H_{4,10}$ 1·64 (m); $H_{6,12}$ 1·04 (s)
	$H_{2,3,8,9}$ 2·68 (m); $H_{1,7,10}$ 2·17 (m); H_4 1·63 (m); $H_{11,12}$ 1·64 (s. broad); H_6 1·00 (s).
	$H_{2,3,8,9}$ 2·73 (m); $H_{1,7,10}$ 2·17 (m); H_4 1·70 (m); $H_{11,12}$ 1·60 (s. broad); H_6 1·05 (s)

s = singlet, m = multiplet

singlets of 1,4-dichlorotetracene (I). It is striking that the singlet originating from the protons in 6,11-position (adjacent to the non-substituted terminal ring) is shorter and broader than the signal of the 5,12-protons (adjacent to Cl). Decoupling of $H_{5,12}$ does not produce any sharpening of the $H_{6,11}$ signal and *vice versa*. However, the $H_{6,11}$ signal becomes almost equal to the $H_{5,12}$ signal if the protons in peri-position are decoupled. All decouplings are indicated by points. Decoupling of the β-protons restores the ratio of the intensities and widths as in the normal spectrum of the compound. Therefore they cannot have any significant influence. Thus it must be concluded that there is peri- (and/or epi)-coupling between the protons of the terminal ring and the adjacent meso-protons but not between meso-protons in different rings.

This is confirmed by the NMR spectrum of 5,12-dichlorotetracene (II), (Fig 1). The normal meso singlet of $H_{6,11}$ is not changed by decoupling the protons in the terminal ring and adjacent to Cl. However, a big change is observed if the peri-protons adjacent to $H_{6,11}$ are decoupled. Similar observations can be made in the spectrum of 5,11-dibromotetracene (III). No changes are observed by decoupling unless the protons of the terminal ring which are in peri-position to $H_{6,12}$ are decoupled.

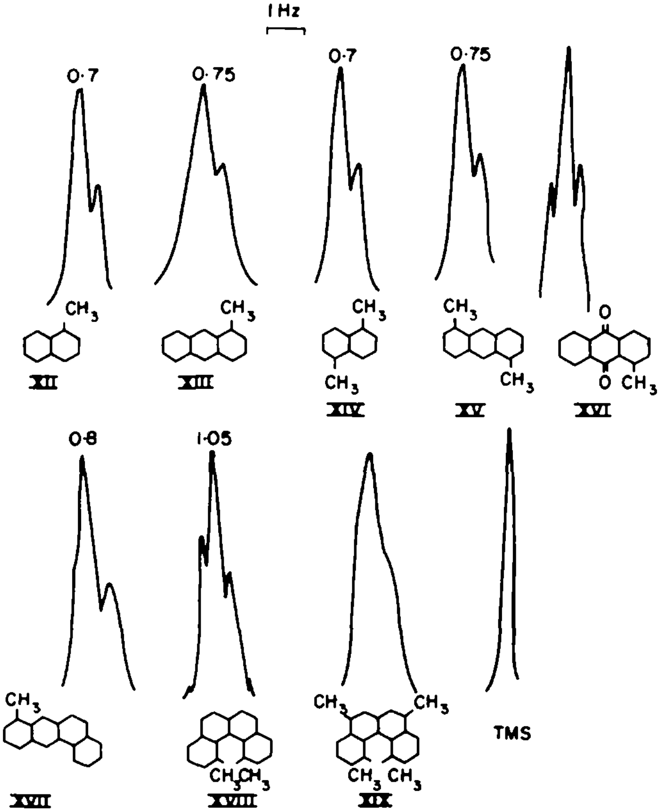
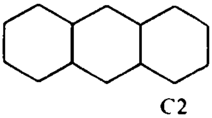
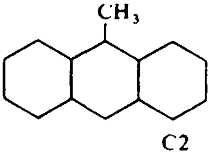


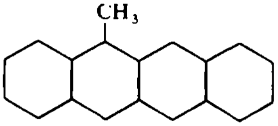
FIG 2. Asymmetric Me signals of α-methylderivatives.



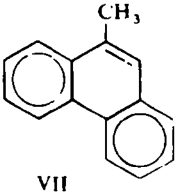
IV



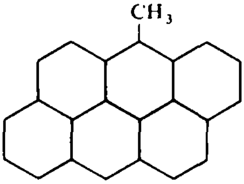
V



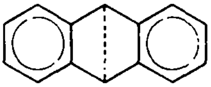
VI



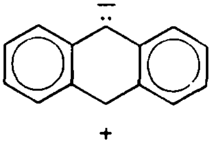
VII



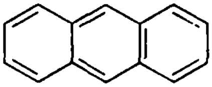
VIII



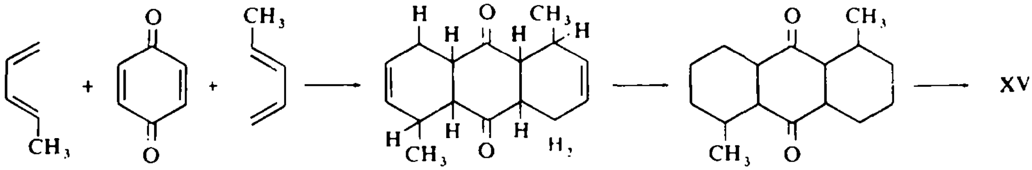
IX



X



XI



XX XXI XXII

All hexagons symbolize aromatic rings

Using the meso singlet of 1-chloroanthracene (IV) it was found that there is no observable para-coupling between H_9 and H_{10}, but there is distinct coupling between these protons and the protons in peri- and epi-positions in the terminal rings. Confirmatory observations were made using other dichloroanthracenes and a number of bromo- and chlorotetracenes, no para-coupling being observed in these cases. It was surprising that 1-chloro-10-methylanthracene (V) shows a clear doublet (separation 0·8 Hz) of the Cl_3 signal, originating from coupling with the para H_9. It is equally surprising to record the even bigger splitting of the Me signal into a doublet (separation 1-Hz) in methyltetracene (VI). This is the same as in 9-methylphenanthrene (VII) where the coupling is transmitted through a double bond. The Me signal of methylanthanthrene (VIII) is not split because there is no para H atom.

Being faced with the fact that there is no evidence for para-coupling in meso rings and considering coupling between meso-protons and peri- and epi-protons in adjacent rings, one must come to the conclusion that there is only a weak bond between the meso-C atoms. This could be a para-π-bond which cannot be symbolized by a line but rather by a dotted line as in formula IX. There could also be a polar bond as in (X), but a Kekulé structure like XI does not account for these facts.

A Me group strengthens the para-bond through hyperconjugation to such an extent that the para-bond in Me derivatives becomes comparable with the π-bond between meso-C atoms in phenanthrene. This particular kind of para-bond becomes important in terminal rings with an α-Me group. Fig 2 shows a number of asymmetric Me signals which consist of a singlet and a doublet or two doublets one of which originates from para-coupling as proved by decoupling. The asymmetry could become so strong in non-planar hydrocarbons like dimethylbenzophenanthrene (Fig 2, XVIII), that the Me signal appears as a triplet. In this case decouplings transform the triplet into two doublets originating from para-coupling (0·5 Hz) and ortho-coupling (0·5 Hz). In some Me derivatives even interring coupling has been considered.[2]

There is a long history of formulae with para-bonds, beginning with the Dewar structure of benzene, followed by the Anschütz formula of anthracene which comes very near to formula IX and which was used for a long time until X-ray measurements made such a long bond unlikely. However, it has been revived with justification not so long ago[3] and may still play an important role in the future.

EXPERIMENTAL*

The halogen derivatives of tetracene were prepared following the description by Clar *et al.*[4] and methyltetracene (VI) according to Clar and Wright.[5]

1-*Chloro*-10-*methylanthracene* (V). 1-Chloroanthrone (3·6 g) was dissolved in dry benzene (20 ml) and an ethereal soln of Mg (2 g) and MeI (10 g) added dropwise. After refluxing for 1 hr the green yellow soln was cooled and decomp with ice and dil AcOH. The organic layer was refluxed for 1 hr with AcOH (30 ml) and a few drops of conc HCl. Water was added to the mixture and the ppt dissolved in xylene. This soln was concentrated and chromatographed over Grade 1 Alumina. Eluting with light petrol (60–80°) gave a pale yellow green band with a purple fluorescence. Concentration of these fractions gave pale yellow crystals (1·4 g) which recrystallized from EtOH formed yellow prisms, m.p. 72–73° and dissolved in conc H_2SO_4 to give an olive green soln. (Found: C, 79·2; H, 4·7. $C_{15}H_{11}Cl$ requires: C, 79·5; H, 4·8%).

Preparation of 6-*methylanthanthrene* (VIII). This was carried out as described by Buu-Hoï and Lavit[6] with some alteration aimed to prevent unreacted anthanthrene being carried through the reaction.

6-*Formylanthanthrene.* Anthanthrene (4 g), N-methylformanilide (2·4 g) and $POCl_3$ (2·8 g) in *o*-dichlorobenzene (8 ml) were gently refluxed for 4 hr. The mixture was poured into a soln of NaOAc and stirred with further *o*-dichlorobenzene (50 ml). After steam distilling off the dichlorobenzene the dark green solid (3·8 g) was filtered off.

Hydrazone. The crude aldehyde (2 g) was dissolved in boiling pyridine (100 ml) and hydrazine hydrate (50%, 20 ml) was added. After boiling for 5 min, water (50 ml) was added. This dilution ensures that unreacted anthanthrene is not carried on through the further stages. The hot soln was filtered and the hydrazone precipitated by addition of a further quantity of water (300 ml). The light brown hydrazone (1·1 g) was filtered and dried, m.p. 195° dec. It dissolved in conc H_2SO_4 to form a deep purple soln. (Found: C, 86·7; H, 4·6; N, 8·6. $C_{23}H_{14}N_2$ requires: C, 86·8; H, 4·4; N, 8·8%).

6-*Methylanthrene* (VIII). The above hydrazone (0·35 g) was dissolved in diethylene glycol (35 ml), hydrazine hydrate (2 ml) was added and the mixture heated to 210° under N_8. After cooling to 150° KOH (0·4 g) was added and refluxed for 30 min. The water formed was removed from the condenser and the temp allowed to rise to 220°. After cooling to 100°, water was added and the yellow-green hydrocarbon filtered off and redissolved in xylene. The dried soln was chromatographed over Grade I Alumina. Concentration of the soln yielded orange leaflets (150 mg), m.p. 188–190° (lit. 192°) which dissolved in conc H_2SO_4 to form a brown soln. (Found: C, 94·9; H, 4·9. $C_{23}H_{14}$ requires: C, 95·2; H, 4·8%).

1,5-*Dimethylanthracene* (XV) was prepared by a diene synthesis using benzoquinone and 1,3-pentadiene XX via XXI and XXII.

1,5-*Dimethyl*-1,4,5,8,4a,8a,9a,10a-*octahydro-anthraquinone* (XXI). Benzoquinone (8 g), 1,3-pentadiene (20 ml) and dry xylene (10 ml) were heated together in a sealed tube at 150° for 8 hr. The light brown viscous soln from 4 such tubes was then heated under vacuum to remove the solvent and excess pentadiene. The resulting gum was refluxed with alcoholic KOH soln for 15 min giving crystals and a rubber like resin. The crystals were filtered off, washed with little alcohol and water and dried, yield 20 g. Recrystallisation

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

from AcOH gave long thin colourless needles, m.p. 190–210° subl., which did not dissolve in conc H_2SO_4. (Found: C, 78·5; H, 8·3. $C_{16}H_{20}O_2$ requires: C, 78·7; H, 8·3%).

1,5-*Dimethylanthraquinone* (XXII). The crude hydroderivative (5 g) was dissolved in boiling diethylene glycol (20 ml). KOH (10 g) was added and the dark green-brown soln refluxed for 20 min. On cooling under access to air, yellow brown needles (3 g) crystallized, which were recrystallized from xylene, m.p. 188–189°. They dissolved in conc H_2SO_4 to give an orange soln. (Found: C, 81·5; H, 5·3. $C_{16}H_{12}O_2$ requires: C, 81·4; H, 5·1%).

1,5-*Dimethylanthracene* (XV). An intimate mixture of 1,5-dimethylanthraquinone (500 mg) and Zn dust (5 g) and a few drops of water were heated together in a sealed tube at 250° for 12 hr. The contents of the tubes were powdered and extracted with xylene. The dried soln was chromatographed over Grade I alumina and the hydrocarbon eluted with light petrol (60–80°). Concentration gave the hydrocarbon (105 mg) which was dissolved in EtOH and picric acid added. The picrate was recrystallized from EtOH and yielded crimson needles, m.p. 167° (lit[7] m.p. 168–169°). (Found: C, 60·9; H, 4·0; N, 9·7. $C_{22}H_{17}N_3O_7$ requires: C, 60·7; K, 3·9; H, 9·7%). A soln of the picrate in xylene was shaken with dil ammonia. The xylene layer was washed with water, dried and the solvent evaporated. Recrystallization from EtOH gave yellow-platelets m.p. 135–137° (lit.[7] 139–140°) which dissolved in conc H_2SO_4 to give an olive green soln. (Found: C, 93·0; H, 7·0. $C_{16}H_{14}$ requires: C, 93·2; H, 6·8%).

Acknowledgements—We are indebted to Prof. S. Newman for samples of 5,4′-dimethyl-3,4-benzophenanthrene and 2,5,9,4′-tetramethyl-3,4-benzophenanthrene and to Messrs Rütgerswerke and Teerverwertung AG for a sample of 1,5-dimethylnaphthalene.

REFERENCES

[1] C. W. Haig and R. B. Mallion, *Mol. Phys.* **18**, 737 (1970).

[2] K. D. Bartle, D. W. Jones and R. S. Matthews, *Tetrahedron* **25**, 2701 (1969); P. M. E. Lewis, *Tetrahedron Letters* No 21, 1859 (1971)

[3] J. L. Ferrari, I. M. Hunsberger and H. S. Gutowsky, *J. Am. Chem. Soc.* **67**, 1247 (1965)

[4] C. Marschalk and C. Stumm, *Bull. Soc. chim. Fr.* (5) **15**, 418, 777 (1948); E. Clar and C. Marschalk, *Ibid.* (5) **17**, 433 (1950); C. Marschalk, *Ibid.* 800 (1952)

[5] E. Clar and J. W. Wright, *Nature, Lond.* **63**, 921 (1949)

[6] N. P. Buu-Hoï and D. Lavitt, *Rec. Trav. Chim.* **76**, 200 (1957)

[7] 1,5-Dimethylanthracene was also obtained by R. D. Haworth and G. Sheldrick, *J. Chem. Soc.* 1950 (1934), as a by-product during the attempted synthesis of 4,5-dimethylphenanthrene.