

Orientation in Polyalkylation of Polycyclic Aromatic Hydrocarbons. Structure Determination by NMR Spectroscopy

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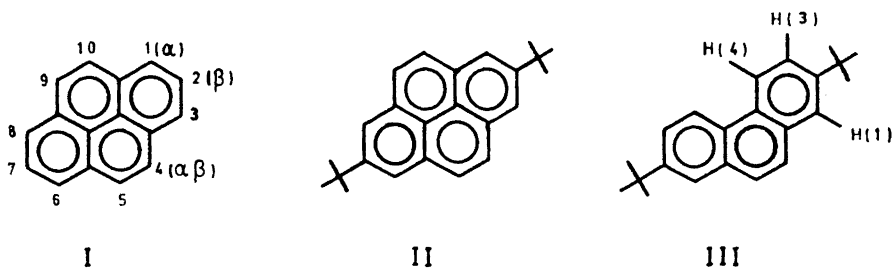
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The orientation in Friedel-Crafts polyalkylation (isopropylation and *tert* butylation) of pyrene and phenanthrene has been studied by NMR spectroscopy. The results suggest that a severe steric effect (*peri*-effect) is operating in *tert*-butylation. H—H as well as ^{13}C —H coupling constants have been obtained from the ^{13}C —H satellite spectra. Calculated spectra of two phenanthrene derivatives are reported.

The polyalkylation of condensed aromatic systems has not been much studied, due to often troublesome separative work involved and the difficulty of identification of the possible isomers. Orientation problems can, however, be successfully attacked by means of NMR spectroscopy.¹ We have studied the orientation in isopropylation and *tert*-butylation of pyrene and in *tert*-butylation of phenanthrene using ^1H —NMR techniques, including ^{13}C —H satellite and double resonance experiments. Some theoretical spectra have been calculated. Our results for phenanthrene do not agree with the literature.

RESULTS

Pyrene (I) reacts with *tert*-butyl chloride and aluminium chloride or bromide to give a di-*tert*-butylpyrene.^{2,3} The orientation of the substituents has been unknown, although by analogy to the products from all other known electrophilic substitution reactions of pyrene^{4,5} the compound has been thought to be the 1,6-derivative.² NMR studies show that it is in fact 2,7-di-*tert*-butylpyrene (II). With *tert*-amyl chloride a dialkylpyrene is likewise formed,³ and in this too the substituents occupy positions 2 and 7.



Secondary alkyl halides (isopropyl, cyclopentyl, cyclohexyl) easily tetraalkylate * pyrene,³ and we have found that the alkyl groups enter the four normal ⁴ positions (1, 3, 6, and 8).

It has been reported² that phenanthrene reacts with *tert*-butyl chloride and aluminium chloride to give a di-*tert*-butylphenanthrene (m.p. 102°–103°; picrate, m.p. 204°) that could be oxidized, with the loss of a *tert*-butyl group, to a compound (m.p. 186–187°) identical with the known⁶ 3-*tert*-butyl-9,10-phenanthrenequinone; this, in turn, could be reduced to the likewise known⁶ 3-*tert*-butylphenanthrene (m.p. 53–54°). The identifications were based on agreement in melting points. From this it was concluded that the alkylation product was 3,9-di-*tert*-butylphenanthrene.

In repeating these reactions we found as the only identifiable alkylation product a compound (yield 60 %) that we, by NMR spectroscopy, could show to be 2,7-di-*tert*-butylphenanthrene (III). The melting point of III is 159.5–160.5°, and the picrate derivative melts at 206–207°. Oxidation of III with chromic anhydride in acetic acid proceeded without loss of an alkyl group to the corresponding 9,10-quinone (IV, m.p. 145.5–146.5°). This structure follows from the NMR spectrum and from the formation of an azine (m.p. 257.5–258.5°) with *ortho*-phenylenediamine. The azine from the previously reported oxidation product had melting point 232° (sintering at 195°).²

NMR SPECTRA

Tetraisopropylpyrene. The NMR spectrum [CDCl_3 , 6 % (w/v)] of this compound is consistent with the 1,3,6,8-orientation of the four isopropyl groups. The aromatic protons appear as two sharp singlets (δ 8.33 and 7.97 ppm, intensity ratio 2:1) corresponding to four $\alpha\beta$ - and two β -protons, respectively (for these symbols,¹ see formula 1). These assignments follow from the facts that $\alpha\beta$ -protons in pyrene⁷ have their chemical shift at slightly lower field than β -protons and that secondary as well as primary alkyl groups shift *ortho*-protons to higher and *peri*-protons to lower field. The chemical shift difference between the two groups of protons in tetraisopropylpyrene (0.36 ppm) is therefore increased over the corresponding difference in pyrene (0.073 ppm).⁷ The aliphatic signals, a well resolved heptet (centered

* The fact that pentaalkylpyrenes as well as isomeric tetraalkylpyrenes can be formed³ will be considered in a subsequent paper.

about δ 4.09 ppm, $J=6.9$ Hz [4 H] *) and a doublet (δ 1.53 ppm, $J=6.9$ Hz [24 H]), show that the four isopropyl groups are equivalent, as is obvious from the aromatic signals too. The only other orientation (4,5,9,10) fulfilling this requirement should produce an aromatic AB_2 spectrum.

Di-tert-butylpyrene. The extremely simple NMR spectrum [$CDCl_3$, 8 % (w/v)] consists of only three sharp signals (δ 8.17, 7.98, and 1.57 ppm, intensity ratio 2:2:9). All orientations with two equivalent substituents except the 2,7-orientation (II) should lead to spin-spin splitting, and although fortuitous magnetic equivalence between chemically different protons is possible, it does not seem very probable. Moreover, no indication of line splitting or broadening was observed when the spectrum (expanded, sweep width 50 Hz) was recorded using six different solvents (Table 1), nor was any splitting observable at 100 Mc/s. As the chemical shift of the α -protons in pyrene⁷ falls at slightly lower field than that of the $\alpha\beta$ -protons, and as it has been shown⁸ that the *tert*-butyl group (in *tert*-butylbenzene) causes a shift of *ortho*-protons to lower field, the signals at δ 8.17 and 7.98 ppm were assigned to the α -protons and the $\alpha\beta$ -protons, respectively. The chemical shift difference between α -protons and $\alpha\beta$ -protons in II (see Table 1) is, therefore, increased over that in pyrene (0.10 ppm)⁷ as a result of the perturbing effect of the *tert*-butyl groups on the α -protons.

Table 1. Solvent dependence of the chemical shifts (in ppm, δ -units) of the aromatic protons of 2,7-di-*tert*-butylpyrene.

Solvent	Conc. % (w/v)	δ_α	$\delta_{\alpha\beta}$	$\delta_\alpha - \delta_{\alpha\beta}$
CCl_4	10	8.09	7.92	0.17
CS_2	8	8.04	7.87	0.17
CS_2	18	8.10	7.92	0.18
$CDCl_3$	8	8.16	7.98	0.18
$CDCl_3$	20	8.17	7.99	0.18
1,4-Dioxan	9.5	8.19	8.00	0.19
CH_3COCH_3	11	8.29	8.08	0.21
C_6D_6	10	8.17	7.91	0.26

*Dibromo-di-tert-butylpyrene.*³ Di-*tert*-butylpyrene is brominated to give a dibromo derivative, which, by spectral evidence, is 1,6-dibromo-2,7-di-*tert*-butylpyrene. The NMR spectrum (CS_2 , 1 % (w/v)) is very clear, showing a singlet (δ 8.37 ppm [4 H]) and an AB-system (δ 8.77 and 8.14 ppm, $J=9.2$ Hz [4 H]) in the aromatic part. These signals originate from the 3,8- and 4,5,9,10-protons, respectively. The *tert*-butyl groups show up as a singlet at δ 1.78 ppm.

The crowding of substituents in the 1- and 2- (and 6- and 7-) positions is demonstrated by the change in chemical shift of the proton in position 10 on going from 1,6-dibromopyrene** to the compound in question. The

* Integrated intensity.

** The NMR spectrum of this compound [CS_2 , 1 % (w/v)] will be published in a forthcoming paper.

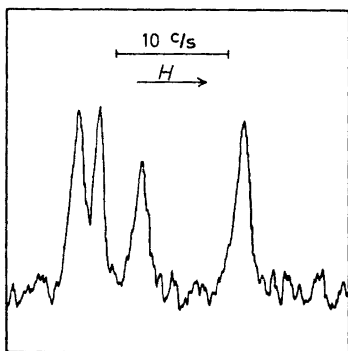


Fig. 1. ^{13}C -H satellites (downfield) of 2,7-di-*tert*-butylpyrene.

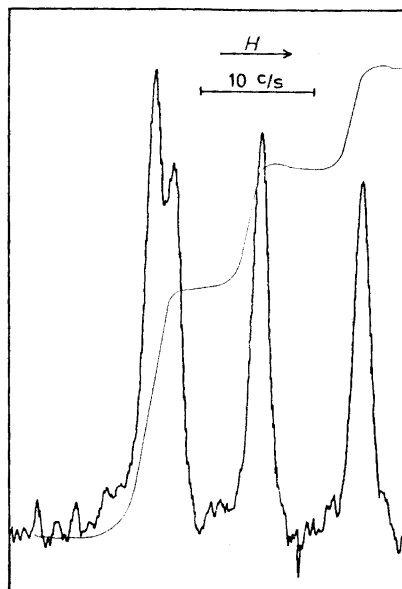


Fig. 2. ^{13}C -H satellites (upfield) of 2,7-di-*tert*-butylpyrene.

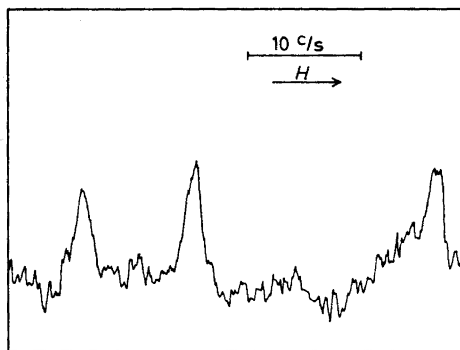


Fig. 3. ^{13}C -H satellites (downfield) of 1,3,6,8-tetraisopropylpyrene.

chemical shift of the *peri*-perturbed H(10) relative to that of H(9) (unperturbed) is 0.63 and 0.32 ppm downfield for 1,6-di-bromo-2,7-di-*tert*-butylpyrene and 1,6-dibromopyrene, respectively. The difference (0.31 ppm) can be taken as a measure of the buttressing effect⁹ of the *tert*-butyl group on the bromo substituent.

The ^{13}C -H satellite spectra of the aromatic parts of di-*tert*-butylpyrene (Figs. 1 and 2) and tetraisopropylpyrene (Fig. 3) confirm the above conclusions.

The upfield as well as the downfield satellites were recorded for di-*tert*-butylpyrene. Each part consists of two doublets. The coupling constants

(1.7 Hz and 8.9 Hz) in these doublets are conclusive evidence of 2,7-orientation (II), one of them (1.7 Hz) being a typical *meta*-coupling constant between two α -protons like that found for a series of 4-substituted pyrenes.¹⁰ The other coupling constant falls outside the range (9.3–9.5 Hz) given by Martin *et al.*¹¹ for *ortho*-coupling between two $\alpha\beta$ -protons. This is also true, however, of the $\alpha\beta$ - $\alpha\beta$ -coupling constant found in the ^{13}C -H satellite spectrum (downfield part only, a singlet and a doublet) of 1,3,6,8-tetraisopropylpyrene (Fig. 3), although for this compound the value (9.8 Hz) is higher than the range cited. This range was obtained from a study of 1-substituted pyrenes,¹¹ and the present results consequently show that $J_{\alpha\beta-\alpha\beta}$ is subject to a greater variation depending on the number and positions of the substituents and, presumably, also on their nature.

From the ^{13}C -H satellite spectra the ^{13}C -H coupling constants for β -protons (~ 154 Hz), α -protons (~ 156 Hz), and $\alpha\beta$ -protons (~ 159 Hz) have been estimated.

It has been shown¹² that the nuclear Overhauser effect can be used as a means of making assignments in NMR spectroscopy. By irradiating the *tert*-butyl protons, which in II will be rather close to the α -protons, the upfield aromatic signal was not affected, whereas the downfield signal was found to increase (20 %) and consequently, from this evidence too, must be assigned to the α -protons.

Di-tert-butylphenanthrene (III). The NMR spectrum (Fig. 4a), [CS_2 , 20 % (w/v)] could be analysed as an ABX spectrum (X=H(4)) with a singlet (H(9), H(10)) superposed on it. Starting from this analysis, the spectrum

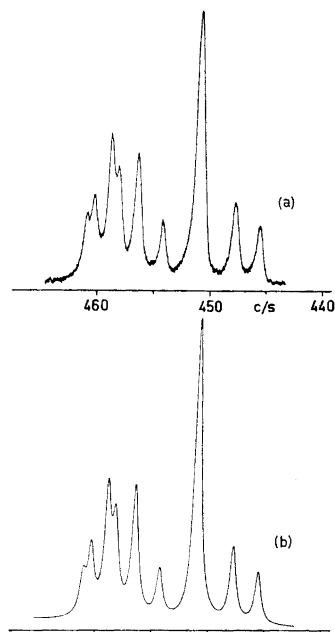


Fig. 4. NMR spectrum (AB-part) of 2,7-di-*tert*-butylphenanthrene. a. Experimental spectrum. b. Calculated spectrum.

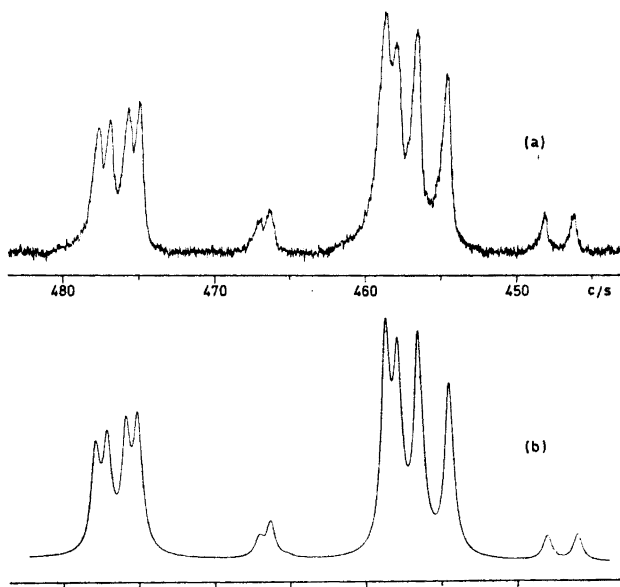


Fig. 5. NMR spectrum (AB- and X-parts) of 2,7-di-*tert*-butyl-9,10-phenanthrenequinone. a. Experimental spectrum. b. Calculated spectrum.

was calculated as an ABC spectrum and refined (Fig. 4b). The parameters used are shown in Table 2. Only the AB-part of the spectrum is shown in Fig. 4. The X-part consists of two broad peaks.

Di-tert-butylphenanthrenequinone (IV). The NMR spectrum (CS₂, 20 % (w/v)) of this compound (Fig. 5a) was treated in the same way as described for III; here X is the 1-proton. The parameters for the calculated spectrum (Fig. 5b) are shown in Table 2.

Table 2. NMR parameters (calculated spectrum) of 2,7-di-*tert*-butylphenanthrene (III) and (III)-9,10-quinone. Chemical shifts in Hz at 60 Mc/s. ^a Coupling constants in Hz.

	III	III-9,10-quinone
H(1)	459.2 ± 0.5	476.2 ± 0.5
H(3)	451.5 ± 0.5	453.3 ± 0.5
H(4)	500.5 ± 0.5	460.5 ± 0.5
<i>J</i> ₁₃	+2.18 ± 0.04	+2.35 ± 0.05
<i>J</i> ₁₄	+0.48 ± 0.04	+0.30 ± 0.05
<i>J</i> ₃₄	+8.80 ± 0.05	+8.40 ± 0.05

^a Chemical shifts of H(9) and H(10) in III: 450.8.

Double resonance (partial decoupling) experiments indicate that the coupling constants in both III and IV have the same sign, and as *ortho*-coupling constants usually are positive¹³ all three will be positive.

DISCUSSION

The 2,7-orientation of tertiary alkyl groups in Friedel-Crafts alkylation of pyrene is remarkable because it represents the first clearly observed deviation from the otherwise strictly followed orientation rules of pyrene.⁴ It appears that four isopropyl groups easily enter the 1,3,6,8-positions without any trace of a 2,7-derivative being formed. Obviously a steric factor must be operating in *tert*-butylation; the *tert*-butyl group, unlike the isopropyl group, is bulky on all sides, which makes the transition state for substitution in the normal positions less favourable. This steric factor probably involves the *peri*-hydrogens in positions 4, 5, 9, and 10. The possibility that the abnormal orientation is the result of a rearrangement following initial attack on the adjacent (normal) positions seems not very likely. If this rearrangement occurs, it must be extremely rapid. Even when the reaction is run under mild conditions (low temperature and short reaction time) only the 2,7-product, besides unreacted pyrene, can be isolated. If the hypothetical rearrangement was not very fast, 1,6- and 1,8-di-*tert*-butylpyrene and even 1,3,6,8-tetra-*tert*-butylpyrene should be among the products, and they could hardly, even in small concentrations, escape discovery by the separative technique used (thin layer and column chromatography).

The fact that the very strict substitution scheme of pyrene is broken in the case of *tert*-alkylation suggests that a similar steric effect will be connected with the *peri*-positions in other polycyclic aromatic hydrocarbons also. This is known to be the case for naphthalene, which is alkylated by the Friedel-Crafts reaction preferentially in the 2-position.¹⁴ With *tert*-butyl chloride and aluminium chloride only 2,6- and 2,7-di-*tert*-butyl naphthalene could be detected.¹⁵

We have not been able to confirm the claim of Buu-Hoï and Cagniant² that 3,9-di-*tert*-butylphenanthrene, which has one of the *tert*-butyl groups in a *peri*-position, is formed in the *tert*-butylation of phenanthrene. That this cannot be so in the present study is seen from the oxidation of the hydrocarbon to a disubstituted 9,10-quinone, and also from the fact that the NMR spectrum must originate from a symmetrical molecule. The *tert*-butyl groups do not occupy the 1,8- or the 4,5-positions because in both these cases the three-spin system would involve two *ortho*-coupling constants instead of only one. Moreover, the 4,5-positions are strongly disfavoured on steric grounds. The X-proton can only be the "bay"-proton (H(4)),⁷ and the fact that a typical *ortho*-coupling constant can be assigned to the coupling between H_X and one of the other protons shows that the *tert*-butyl groups occupy the 2,7-positions. This being the case, H_X in the quinone must be identical with H(1), since H_X does not couple with an *ortho*-coupling constant to any of the other protons. The deshielding of H(1) is partly due to the

anisotropic effect of the *ortho*-carbonyl group, and this effect is particularly pronounced when the carbonyl group is part of a six-membered ring.¹⁶

A. C. Hazell and J. G. Lomborg at this institute have confirmed the structure of the 2,7-di-*tert*-butylpyrene by a three-dimensional X-ray analysis. This examination will be published independently at a later time.

There has been one more reason, besides the unusual orientation of the substituents, for scrutinizing this structural problem. Studies by J. H. Eggers at this institute on molecular geometry and dichroism of compounds dissolved in stretched films had thrown some doubt on the 2,7-orientation, which was directly inferred from the NMR spectrum. Whereas experimental results (unpublished) for 2,7-di-carbethoxypyrene were in agreement with empirical structure-dichroism relations, the results for the di-*tert*-butylpyrene were not. The reason for this is perhaps to be sought in the shape of the *tert*-butyl group, which in contrast to the carbethoxy group cannot be forced to have its whole skeleton coplanar with the aromatic nucleus.

EXPERIMENTAL

The NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. Temperature $35^{\circ} \pm 2^{\circ}$. The chemical shifts are downfield from TMS as internal standard. The ¹³C-H satellite spectra were obtained from saturated solutions in CS₂ using a Varian C-1024 Time Averaging Computer. The double resonance experiments were performed by means of a Varian V-6058 A Spin Decoupler.

The 100 Mc/s spectrum of 2,7-di-*tert*-butylpyrene was kindly recorded by professor E. Clar, Glasgow, on a Varian HA 100 (frequency sweep mode; temperature 33°).

In the nuclear Overhauser experiment the solution was carefully degassed and sealed under vacuum.

1,3,6,8-Tetraisopropylpyrene and *2,7-di-tert-butylpyrene* were prepared as previously described³ and further purified by chromatography on silica impregnated with caffeine.¹⁷

2,7-Di-tert-butylphenanthrene. The procedure of Buu-Hoi and Cagniant² for preparing the postulated 3,9-di-*tert*-butylphenanthrene was closely followed. When chromatography on silica with caffeine was used instead of distillation in working up the rawmaterial better yields (60%) were obtained. In the residual oil (mainly polymerisation products arising from *tert*-butyl chloride) only 2,7-di-*tert*-butylpyrene could be detected (spectroscopical evidence). M.p. 159.5–160.5°. Picrate (from hot ethanol), m.p. 206–207°.

2,7-Di-tert-butyl-9,10-phenanthrenequinone. 2,7-Di-*tert*-butylphenanthrene (3.0 g) was oxidized following Buu-Hoi and Cagniant.² The crude product (2.0 g) had m.p. 125–35°. After crystallization from methanol, sublimation *in vacuo*, and repeated crystallization, m.p. was 145.5–146.5°. (Found: C 82.9; H 7.47. Calc. for C₂₂H₂₄O₂: C 82.46; H 7.55).

2,7-Di-tert-butyl-dibenzo[a,c]phenazine. The quinone (0.3 g), dissolved in boiling ethanol, was mixed with a hot solution of phenylenediamine (0.1 g). The precipitated product was recrystallized from ethanol-ethylacetate (1:1) yielding 0.21 g, m.p. 257.5–258.5°. (Found: C 85.68; H 7.04; N 7.25. Calc. for C₂₈H₂₈N₂: C 85.67; H 7.19; N 7.14).

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Received July 1, 1968.