Electrophilic Aromatic Substitution. Part 28.[1] Rate Factors for Protiodetritiation of all Positions of Hexahelicene (Benzo[*c*]naphtho-[1,2-*g*]phenanthrene): the Reactivity of Bent Benzene Rings

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The first study of the quantitative electrophilic aromatic reactivity of hexahelicene has been made through preparation of each of the eight specifically tritium-labelled isomers, and measurement of their rates of protiodetritiation in trifluoroacetic acid (TFA)–chloroform (9 : 1 v/v) at 100°. Comparison with rates of detritiation of [9-^{3}H]-phenanthrene in this medium and in TFA at both 100 and 70° leads to the following partial rate factors for detritiation in TFA at 70° (positions in parentheses): 10 250(1); 4 400(2); 905 (3); 8 770 (4); 25 000 (5); 6 530 (6); 21 600 (7); 18 200 (8); the corresponding σ^+-values are: −0.46; −0.415; −0.34; −0.45; −0.505; −0.435; −0.495; −0.485. The positional reactivity order: 5 > 7 > 8 > 1 > 4 > 6 > 2 > 3 is in very good agreement with that predicted by Hückel localization energies *viz.*: 5 > 7 > 4 > 8 > 6 > 1 > 2 > 3; as in the case of tetra- and penta-helicene, and chrysene, the calculations underestimate the reactivity of the most central positions of the molecule. With the exception of the 3- and 6-positions, all positions are 2—3 times more reactive than the corresponding positions in pentahelicene, whereas the calculations predict they should be the same [the average localization energy per position is predicted to be precisely constant (−2.366β) for tetra-, penta-, and hexa-helicene]. The contrasting and regular increase in reactivity along this series demonstrates the effect of the increased distortion of the aromatic rings so that the reaction ground states are destabilized. The increased reactivity does not arise from desolvation of the ground states for reaction of the (less soluble) higher homologues because: (i) coronene, which is planar, shows normal reactivity even though it is much less soluble than hexahelicene and (ii) the 1-, 3-, 4-, and 5-positions at the planar end of benzo[*a*]naphtho[1,2-*h*]anthracene (which is less soluble than the isomeric hexahelicene) are much less reactive (f_1 3 810; f_3 270; f_4 1 190; f_5 11 100; σ^+_1 −0.41; σ^+_3 −0.28; σ^+_4 −0.35; σ^+_5 0.46) than the corresponding positions in hexahelicene in contrast to localization energy predictions. The 1- and 2-positions of hexahelicene do not appear to be sterically hindered towards exchange (similar results were obtained for the 1-positions of tetra- and penta-helicene) reflecting the molecular distortion which maintains a minimum of 3 Å between C-1 and -16; if anything, the 1-position is rather *more* reactive relative to the other positions than might have been expected though no clear reason for this is evident. The hydrogen exchange data show that the 7-isomer should accompany formation of the 5-isomer in nitration, bromination, and acetylation of hexahelicene, rather than the 8-isomer recently reported. A number of annelation rules for electrophilic aromatic substitution are formulated.

IN this series, partial rate factors for detritiation of a range of polynuclear aromatic hydrocarbons have been reported, including data for helicenes up to and including pentahelicene. These latter are of particular interest because they give quantitative information regarding the effect of distortion of the aromatic ring upon electrophilic reactivity, an area where there has been no other information. In general it has been shown that, starting with planar phenanthrene, each additional benzene ring produces a 2—3-fold increase in positional reactivity, in contrast to theoretical predictions, and this we have attributed to loss of aromatic stabilization of the ground state molecule. In this paper we report data for hexahelicene, the last member of the helicene series in which there is no overlap of the terminal rings. A recent report of nitration, acetylation, and bromination of hexahelicene noted that the major product of substitution was the 5-isomer, with the 8-isomer probably being the next most abundant.[2] However this latter was not unambiguously proven, and our results will show that the 7- rather than the 8-isomer should be the main side-product.

As in the case of the other helicenes, the attractiveness of the unambiguous results from hydrogen exchange of specifically labelled compounds is moderated by the preparative difficulties involved, and for hexahelicene an additional complication has been the very low solubility combined with the low specific activity arising from the multistep synthesis. In consequence it proved advantageous to use chloroform–trifluoroacetic acid (TFA) (1 : 9 v/v) at 100° as the exchanging medium, and relate the rates obtained in this *via* a standard compound ([9-^{3}H]phenanthrene) to those obtained in TFA at 70° (the standard condition for detritiation) and thus obtain the partial rate factors. A byproduct of the syntheses was benzo[*a*]naphtho[1,2-*h*]anthracene, and some data for this molecule (which is planar at one end and distorted at the other) are also reported.

RESULTS AND DISCUSSION

In Table 1 are listed the rates of exchange relative to that of [9-^{3}H]phenanthrene, obtained as described above, together with the derived partial rate factors which were obtained as follows. The $k_{\text{rel.}}$ values were multiplied by 1 215, the partial rate factor for exchange of [9-^{3}H]phenanthrene in TFA at 100°. These gave partial rate factors under the latter conditions which were corrected to those at 70° in the usual way, *i.e.* the logarithms of the partial rate factors (p.r.f.s) were multiplied by 1.043, the ratios of the ρ factors for exchange at 70 and 100° (determined from the p.r.f.s for [9-^{3}H]phenanthrene under both conditions) and the antilog of the value obtained gives the partial rate factor, considered to be accurate to ±5%. From the partial

TABLE 1

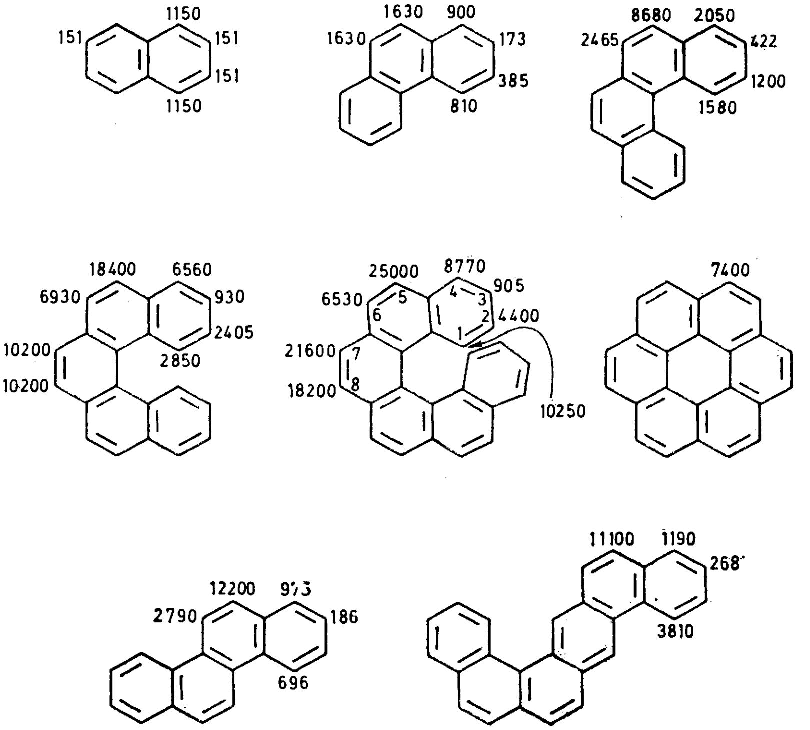
Relative rates of detritiation of [X-^{3}H]Ar in $CHCl_3$–TFA (1 : 9 v/v) at 100°, partial rate factors, σ^+ constants, and Hückel localization energies

X	Ar	k_{rel}	f [a]	σ^+	$-L_r^+/\beta$
9	Phenanthrene	1.0	1 630	−0.365	2.299
1	Hexahelicene	5.76	10 250	−0.460	2.338
2	Hexahelicene	2.56	4 400	−0.415	2.456
3	Hexahelicene	0.563	905	−0.340	2.479
4	Hexahelicene	4.965	8 770	−0.450	2.311
5	Hexahelicene	13.55	25 000	−0.505	2.2875
6	Hexahelicene	3.74	6 525	−0.435	2.315
7	Hexahelicene	11.75	21 600	−0.495	2.3065
8	Hexahelicene	10.0	18 200	−0.485	2.314
1	Benzo[*a*]naphtho[1,2-*h*]anthracene	0.175	268	−0.280	2.487
3	Benzo[*a*]naphtho[1,2-*h*]anthracene	2.23	3 810	−0.410	2.367
4	Benzo[*a*]naphtho[1,2-*h*]anthracene	0.73	1 190	−0.350	2.313
5	Benzo[*a*]naphtho[1,2-*h*]anthracene	6.24	11 100	−0.460	2.259

[a] For detritiation in anhydrous TFA at 70°.

rate factors the σ^+ constants were determined, and are also given in Table 1 along with the localization energies determined by the Hückel method. The partial rate factors are shown in Scheme 1 along with those previously obtained for lower members of the helicene series,[3-6] and other related compounds.[1] The main features of the results are as follows.

(i) The observed reactivity order, *viz.* 5 > 7 > 8 > 1 > 4 > 6 > 2 > 3 is in very good agreement with the predicted order, *viz.* 5 > 7 > 4 > 8 > 6 > 1 > 2 > 3, particularly when one considers the closeness of the reactivities predicted for all except the 2- and 3-positions. Previously we found the positional reactivity orders for tetra- and penta-helicene to also be in excellent agreement with prediction, there being only a single and minor discrepancy for each molecule.[5,6] These discrepancies arose from the most central position in each molecule being rather more reactive than predicted, and we suggested that this could be the region of maximum distortion (and therefore minimum ground state stabilization) of the molecules.[6] However, we have since observed the same discrepancy with chrysene [1] (which is essentially planar) and this suggests a more fundamental defect in the calculations. In hexahelicene too, the most central (8-) position is more reactive than predicted.



SCHEME 1

(ii) With tri-, tetra-, and penta-helicenes the 1-position is consistently less reactive than the 4-position [these are the 4- and 1-positions respectively in trihelicene (phenanthrene) the numbering in which is inconsistent with the higher homologues] and as predicted. However, the 1-

position of hexahelicene is *more* reactive than the 4-position, contrary to prediction. These facts together suggests that the reactivity of the 1-position of hexahelicene is somewhat enhanced, and various reasons could be postulated. The geometry of the molecule may be of prime importance and it should be noted that the molecule distorts in order to maintain a minimum of 3 Å between C-1 and -16,[7] *i.e.* the same distance as in pentahelicene. To achieve this the bond distances and angles are substantially different from normal, and it may be that formation of the transition state for 1-substitution affords particular relief of the molecular strain. Thus for example, the sum of the adjacent bond lengths is 2.792 Å for the 1-position compared to 2.756 Å for the 4-position,[7] so that less structural reorganisation may be needed on going to the sp^3-hybridised transition state for reaction at the former position.

(iii) The regular increase in reactivity with ring size noted for the lower helicenes [6] is on the whole maintained through to hexahelicenes, each position (except the 3- and 6-positions) being 2—3 times more reactive than those in pentahelicene. (The reason that the 3- and 6-positions do not follow the general trend is unclear; both are β-naphthalene-like with respect to the terminal ring.) The increase in reactivity is contrary to prediction and we attribute it, as in the case of the lower helicenes, to distortion of the molecule leading to loss of ground-state stability. Thus each position in hexahelicene is at least 10 times more reactive than Hückel calculations predict. The effect of ring size upon reactivity is most easily appreciated by comparison of Figures 1 and 2,* which show the predicted and observed variations in reactivity with ring size, respectively. The marked increase in observed reactivity with size contrasts with the constant reactivity (apart from some oscillation for the 1-position) that is predicted.

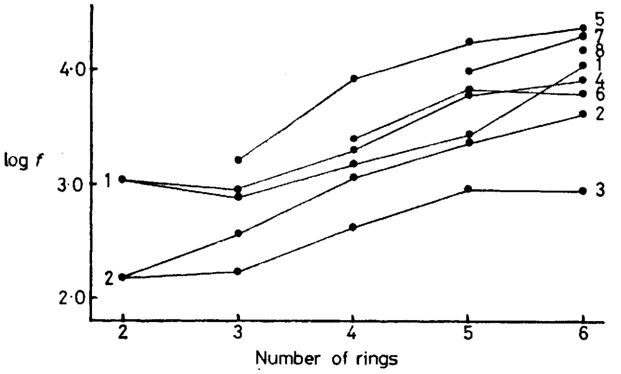


FIGURE 1 Variation in logarithm of partial rate factor with number of rings in helicenes. 1,2, *etc.* = positions in each helicene

(iv) It could be argued that the reactivity increase is a consequence of the decreased solubility of the helicenes along the series, leading to desolvation of the ground state. However, this argument can be discounted for two reasons.

(a) Coronene is significantly less soluble than hexahelicene yet its partial rate factor (7 400) [7] is significantly *less* than the average value per position for hexahelicene (11 950) even though the localization energy (—2.306β) [8] predicts it to be *more* reactive than hexahelicene (for which the average value is —2.366β).

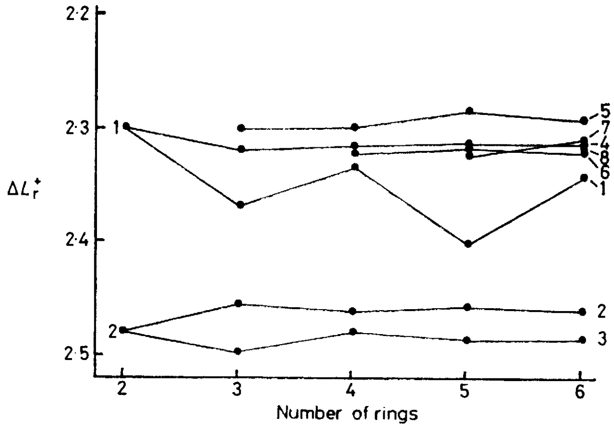


FIGURE 2 Variation in Hückel localization energy with number of rings in helicenes. 1,2, *etc.* = positions in each helicene

(b) Benzo[*a*]naphtho[1,2-*h*]anthracene is less soluble than hexahelicene, yet the partial rate factors for the 1-, 3-, 4-, and 5-positions (which are at the virtually planar end of the molecule) are 3 810, 270, 1 190, and 11 100, respectively (see Scheme 1), substantially lower than the values for the corresponding positions in hexahelicene; again localization energy calculations (Table 1) predict a converse reactivity order. This is most clearly evident in Figure 3, which shows a plot of log partial rate factors *versus* localization energies for the corresponding positions in phenanthrene, benzo[*a*]naphtho[1,2-*h*]-anthracene, and hexahelicene; the hexahelicene values

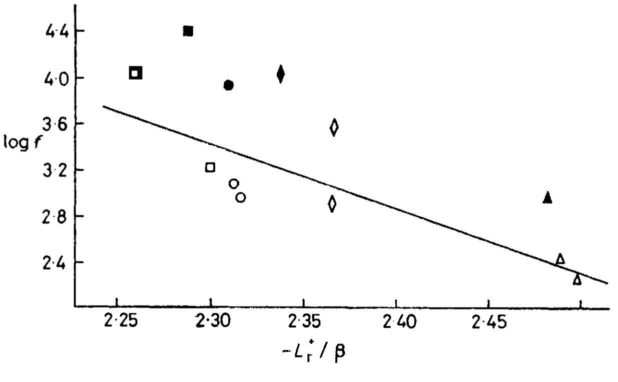


FIGURE 3 Correlation of logarithms of partial rate factors *versus* Hückel localization energies for corresponding positions in phenanthrene, benzo[*a*]naphtho[1,2-*h*]anthracene, and hexahelicene. □, 9-Phenanthrene-like positions; ○, 1-phenanthrene-like positions; △, 2-phenanthrene-like positions; ◇, 4-phenanthrene-like positions. Filled points are hexahelicene positions. Correlation line drawn for non-hexahelicene positions

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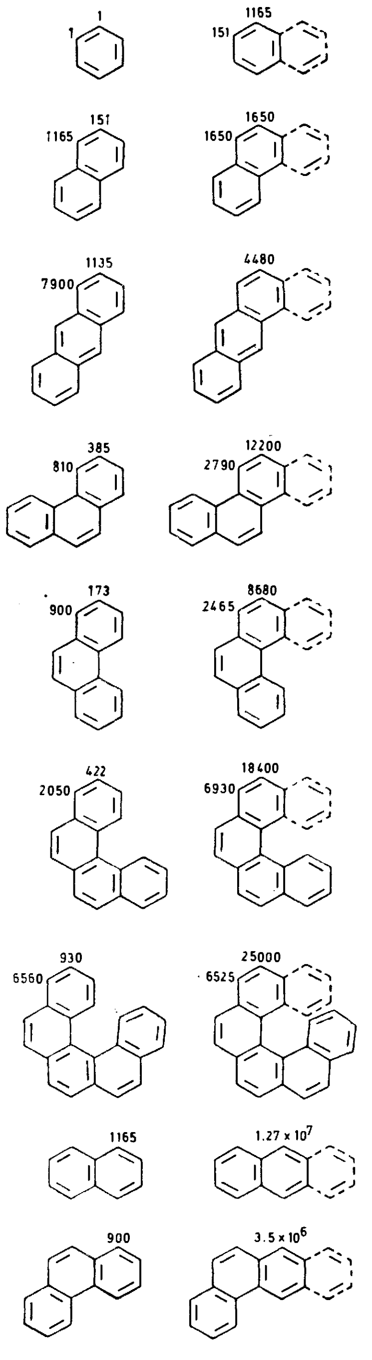
* For consistency, phenanthrene is numbered in these Figures in the same way as for the other helicenes, *i.e.* positions 1—4 become 4—1, respectively.



$f_{2,3\text{-benzo}}$	$f_{3,4\text{-benzo}}$	$f_{2,3}/f_{3,4}$
1165	151	7.7
11	1.42	7.75
2.7	?	
31.7	3.44	9.2
50	2.74	18
44	3.4	13
26.9	1.0	26
10 900		
3 900		

Scheme 2

are all well above the line which correlates the other points.

(v) In ref. 6, we noted that the average localization energy per position was identical (—2.366β) for both tetra- and penta-helicene (with that for phenanthrene being only marginally different). Curiously the same value is also obtained for hexahelicene (and also for chrysene[1] which is an isomer of tetrahelicene). To see if this might be a general phenomenon for large polycycles, we have calculated the localization energies for 1,2,5,6-dibenzoanthracene and benzo[*a*]naphtho[1,2-*h*]-anthracene (Table 2). However, for these molecules (which are isomers of penta- and hexa-helicene respectively but contain an anthracene nucleus) the corresponding values are —2.325 and —2.314β, respectively, so it may be that the constant localization energy effect only applies to molecules which have a phenanthrene-like arrangement of any three adjacent benzene rings.

(vi) A recent report of nitration, bromination, and acetylation of hexahelicene showed that in each case the 5-derivative was the principle product as predicted by our data. However, the next most abundant isomer was

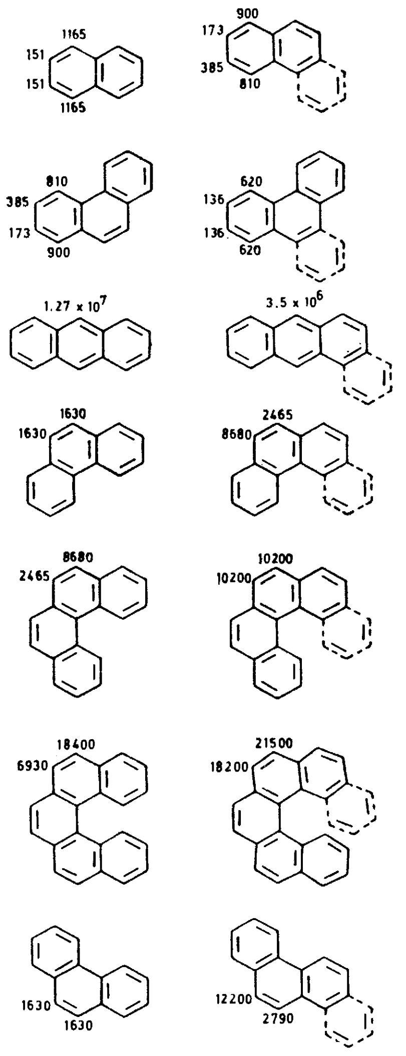
TABLE 2

Hückel localization energies

Position r	$-L_r^+/\beta$ 1,2,5,6-Dibenzoanthracene	 Benzo[*a*]naphtho-[1,2-*h*]anthracene
1	2.369	2.367
2	2.438	2.437
3	2.491	2.487
4	2.313	2.313
5	2.259	2.259
6	2.277	2.270
7	2.131	2.094
8	2.369	2.323
9	2.438	2.459
10	2.491	2.469
11	2.313	2.309
12	2.259	2.238
13	2.277	2.321
14	2.131	2.282
15		2.270
16		2.122
$\Sigma(-L_r^+/\beta)n$	2.325	2.314

identified (by n.m.r. analysis only) as the 8-isomer whereas our results predict that it should be the 7-isomer (though both should be formed in rather similar amounts). Since both the 7- and 8-positions are virtually equally hindered [from the *X*-ray data[7] one can calculate that the 8—9 *peri*-distance is actually very slightly less (2.483 Å) than the 6—7 *peri*-distance (2.489 Å)] and hydrogen exchange invariably predicts the correct reactivity sequence for unhindered (or equally hindered) positions, some doubt attaches to the validity of the n.m.r. analysis.

(vii) In Parts 24 and 27 of this series we introduced some annelation rules for electrophilic aromatic substitution and this approach is now analysed further using the extra data available from this and other[9,10] work. Consider first the effects of the 2,3- and 3,4-benzo-substituents (Scheme 2). Annelation gives either a phenanthrene-like or an anthracene-like system (last two molecules), and in general the 2,3-benzo-substituent produces activation, the effect being much greater when an anthracene-like structure is obtained. The effect of the 3,4-benzo-substituent is a relatively small activation in each case except for the 4-pentahelicene–6-hexahelicene relationship which is slightly anomalous



Ratio of partial rate factors for annelated molecule to original molecule

Interaction	1,2–5	1,2–6	1,2–7	1,2–8
	0.77	1.15	2.55	0.70
	0.76	0.35	0.79	0.69
	0.28			
	1.51	5.3		
	1.18	4.1		
	1.17	2.6		
			7.48	1.71

SCHEME 3

as noted under (iii) above. These results should permit reasonable prediction of some partial rate factors, *e.g.* we estimate the partial rate factor for the 6-position of 1,2-benzanthracene will be 9 000 ± 500.

The second group of annelation effects are those which operate through an intervening ring and are given in Scheme 3. In each case the annelating ring is added across the equivalent of a 1,2-position of naphthalene to produce an effect at a position x in the other ring of naphthalene or an annelated derivative; we refer to this as the 1,2-x annelation effect. For example, the first entry in Scheme 3 shows that the 1-position of naphthalene and the 1-position of phenanthrene are related *via* a 1,2-5-annelation factor (which actually reduces the reactivity by the factor of 0.77 shown). The factors in this group are less straightforward than those above.

1,2-5-*Annelation Factor.*—For planar molecules this produces a small deactivation, whereas in the non-planar helicenes a small activation is obtained. This latter almost certainly arises from superimposition of the rate enhancement arising from non-coplanarity, upon the deactivation which would otherwise apply (and is indeed predicted).

1,2-6-*Annelation Factor.*—Except in the phenanthrene–triphenylene transformation (which is also anomalous with regard to the 1,2-7-factor describing, through symmetry, the same position in triphenylene), this factor produces a moderate activation which is largest in the non-planar helicenes.

1,2-7-*Annelation Factor.*—If we regard the phenanthrene–triphenylene transformation as anomalous, then this factor produces the largest activation of the four interactions considered.

1,2-8-*Annelation Factor.*—This is similar to and slightly more deactivating than the 1,2-5-factor in the naphthalene–phenanthrene and phenanthrene–triphenylene transformations. However in the phenanthrene–chrysene transformation, activation is obtained and this is both anomalous and contrary to localization energy predictions.

EXPERIMENTAL

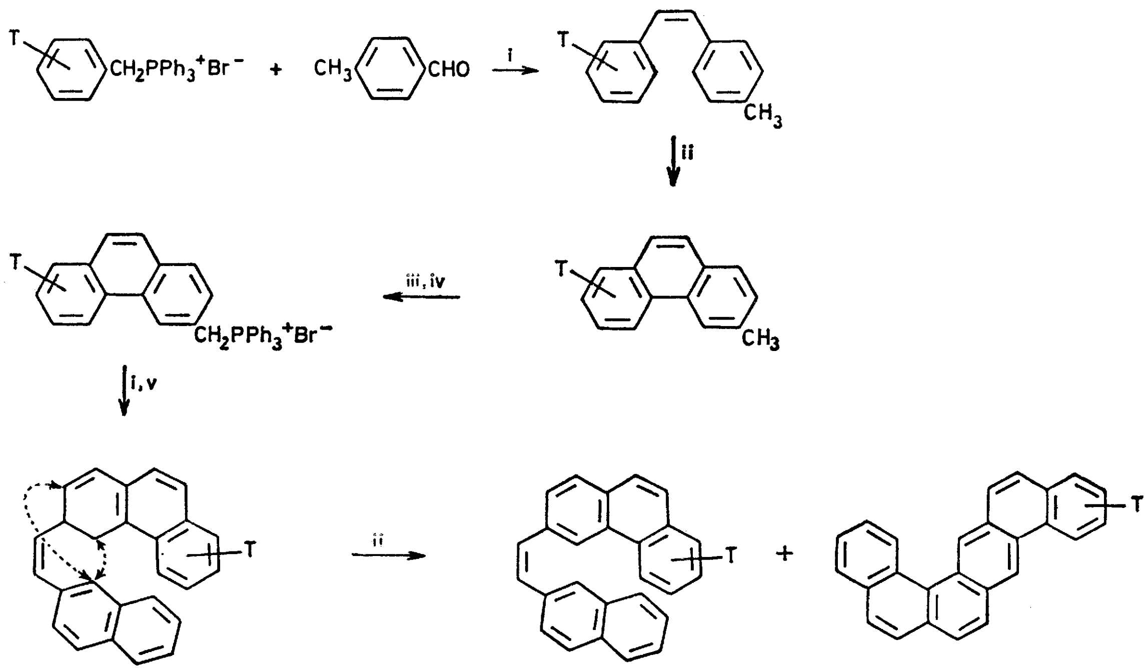
The methods of making each specifically labelled isomer are displayed in Schemes 4—9, and involved photocyclization of a specifically labelled precursor. In each case benzo[*a*]naphtho[1,2-*h*]anthracene was obtained as a byproduct, but is illustrated in Scheme 4 only. The technique involved substantial losses of specific activity along the route from initial to final compound, partly due to the increase in molecular weight, but also due to detritiation occurring under the acid conditions created in certain steps; in particular, side-chain bromination produced hydrogen bromide under anhydrous conditions. For example, the 1,3-detritiated compound had a specific activity of only 0.3 mCi g^{-1} compared to 50 mCi g^{-1} in the starting material, and the specific activities (calculated and found) at each stage of the preparation of this compound are given in order to indicate the problem. The combination of very low solubility and low specific activity resulted in satisfactory kinetic studies with benzo[*a*]naphtho[1,2-*h*]anthracene being obtained only with the 1-, 3-, 4-, and 5-labelled compounds.

[1,3-^{3}H$_{2}$]*Hexahelicene.*—This was prepared by the route shown in Scheme 4. [3-^{3}H]Toluene (specific activity 50 mCi g^{-1}) was prepared from 3-bromotoluene *via* hydrolysis of the Grignard reagent with tritiated water. Side-chain bromination with *N*-bromosuccinimide (NBS) gave [3-^{3}H]benzyl bromide, sp. act. 20 mCi g^{-1} (*cf.* 26.75 mCi g^{-1} calculated). Reaction of the benzyl bromide with triphenylphosphine in boiling xylene gave a quantitative yield of the corresponding phosphonium salt which was reacted with n-butyl-lithium and β-naphthaldehyde to give a *cis–trans*-mixture of [3-^{3}H]-4′-methylstilbene (59%), m.p. 117 °C (lit.,[11] 116.5—117 °C), sp. act. 17 mCi g^{-1}. This compound was photocyclized as described previously[6] to give [5,7-^{3}H$_{2}$]-3-methylphenanthrene (60%), m.p. 62 °C (lit.,[12] 61—62 °C), sp. act. 15 mCi g^{-1} (*cf.* 17 mCi g^{-1} calculated). Side-chain bromination with NBS gave [5,7-^{3}H$_{2}$]bromomethylphenanthrene, m.p. 114 °C (lit.,[13] 114 °C), sp. act. 2 mCi g^{-1} (*cf.* 10.7 mCi g^{-1} calculated) which was converted into the phosphonium salt as above and thence *via* reaction with n-butyl-lithium and 2-naphthaldehyde into a *cis–trans*-mixture of 1-(2-naphthyl)-2-(3-[5,7-^{3}H$_{2}$]phenanthryl)ethylene, sp. act. 0.5 mCi g^{-1} (*cf.* 1.64 mCi g^{-1} calculated). The *trans*-product was filtered from the reaction mixture, washed several times with 3 : 1 methanol–water, air dried, sublimed, and recrystallized from benzene–ethanol. The ethereal filtrate (containing *cis*-alkene with a small amount of *trans*-alkene) was concentrated, and the residue sublimed, then recrystallized from benzene–ethanol. This treatment gave the *cis*-isomer (23%), m.p. 128 °C (lit.,[14] 127—128 °C), and the *trans*-isomer (36%), m.p. 216 °C (lit.,[14] 216 °C). G.l.c. analysis of the mixture on a 300 mm × 3 mm i.d. column packed with 100—120 mesh Chromosorb G containing 1% OV17 as stationary phase and operated at 290 °C gave relative *cis* : *trans* retention times of 1 : 2.7.

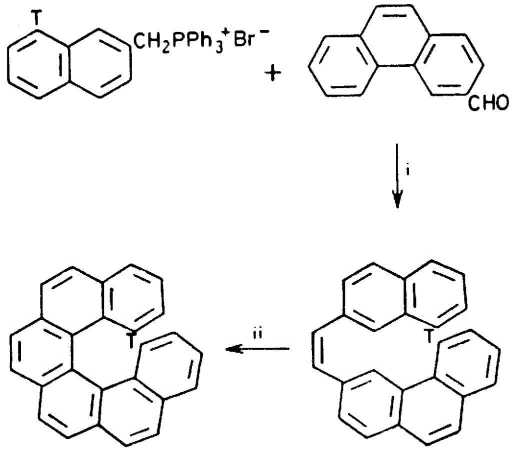
A solution of *trans*-1-(2-naphthyl)-2-(3-[5,7-^{3}H$_{2}$]phenanthryl)ethylene (0.33 g, 0.001 mol) in benzene (1 000 ml) with iodine (10 mg) was irradiated through a quartz vessel with a 124 W medium pressure mercury-vapour lamp. When reaction was complete (the time depended upon the state of the lamp and so was monitored by g.l.c. using the above conditions) the benzene solution was washed with sodium thiosulphate solution and water, and dried (Na_2SO_4). Concentration gave a yellow oil which was chromatographed on alumina (neutral, activity grade III) using pentane–benzene (60 : 40) as eluant. The first fraction was recrystallized from benzene–i.m.s. to give [1,3-^{3}H$_{2}$]hexahelicene (22%), m.p. 233 °C (lit.,[14,15] 231—233 °C), sp. act. 0.3 mCi g^{-1} (*cf.* 0.5 mCi g^{-1} calculated; the overall activity yield, even after allowing for molecular weight increase, was therefore only 2.25%). Further elution with benzene gave [1,3-^{3}H$_{2}$]benzo[*a*]naphtho[1,2-*h*]anthracene (50%), m.p. 125 °C (lit.,[15] 124 °C). The g.l.c. retention times of these products relative to the *cis*-alkene above were 1.08 and 3.27, respectively.

[1-^{3}H]*Hexahelicene.*—This was prepared by the route shown in Scheme 5. 7-[1-^{3}H]Naphthylmethyl(triphenyl)phosphonium bromide and 3-phenanthraldehyde were prepared as described previously[6] and were reacted in the presence of n-butyl-lithium to give a *cis–trans*-mixture of 1-(2-[7-^{3}H]naphthyl)-2-(3-phenanthryl)ethylene. This was resolved as described above, and the *trans*-isomer photocyclized as above to give [1-^{3}H]hexahelicene, m.p. 233 °C, with [1-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene being obtained as the byproduct.

[2-^{3}H]*Hexahelicene*.—This was prepared according to Scheme 4, the starting material being [4-^{3}H]toluene prepared from 4-bromotoluene in the usual way. The rest of the preparation followed exactly the route given for the 1,3-ditritiated isomer and led, *via cis-* and *trans*-1-(2-naphthyl)-2-(3-[6-^{3}H]phenanthryl)ethylene, to [2-^{3}H]hexahelicene, m.p. 233 °C, [2-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene being obtained as the byproduct.



SCHEME 4 Reagents: i, Bu^{n}Li; ii, I_2–u.v.; iii, NBS; iv, PPh_3; v, β-naphthaldehyde



SCHEME 5 Reagents: i, Bu^{n}Li; ii, I_2–u.v.

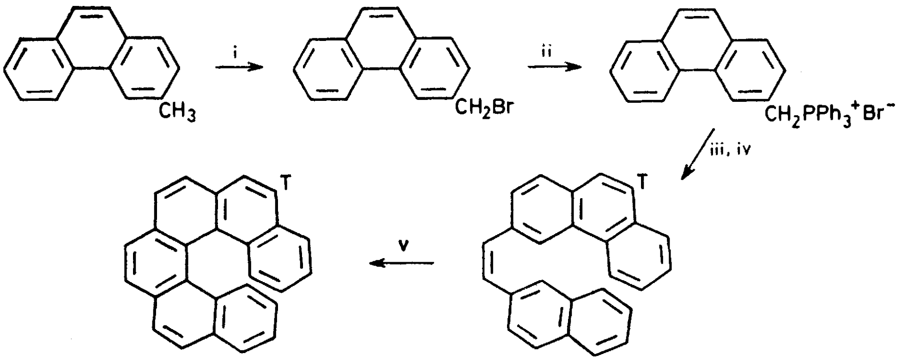
[4-^{3}H]*Hexahelicene*.—By using [2-^{3}H]toluene as starting material, the route outlined in Scheme 4 and details as for the 1,3-ditritiated isomer, led, *via cis-* and *trans*-1-(2-naphthyl)-2-(3-[8-^{3}H]phenanthryl)ethylene, to [4-^{3}H]-hexahelicene, m.p. 233 °C, [4-^{3}H]benzo[*a*]naphtho[1,2-h]anthracene being obtained as the byproduct.

[5-^{3}H]*Hexahelicene*.—This was prepared according to the route given in Scheme 6. The essential starting material was [9-^{3}H]-3-methylphenanthrene, prepared by the method described previously.[16] This was converted into the bromomethyl derivative and then reacted in identical steps to those described above for preparation of the 1,3-ditritiated isomer to give, *via cis-* and *trans*-1-(2-naphthyl)-2-(3-[9-^{3}H]-phenanthryl)ethylene, [5-^{3}H]hexahelicene, m.p. 233 °C, with [5-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene as the byproduct.

[6-^{3}H]*Hexahelicene*.—This was prepared according to the route given in Scheme 7. The essential starting material here was [10-^{3}H]-3-methylphenanthrene, prepared by the method previously described.[16] The bromomethyl derivative was then reacted according to the method given for the 1,3-ditritiated isomer to give, *via cis-* and *trans*-1-(2-naphthyl)-2-(3-[10-^{3}H]phenanthryl)ethylene, [6-^{3}H]hexahelicene, m.p. 233 °C, with [6-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene as the byproduct.

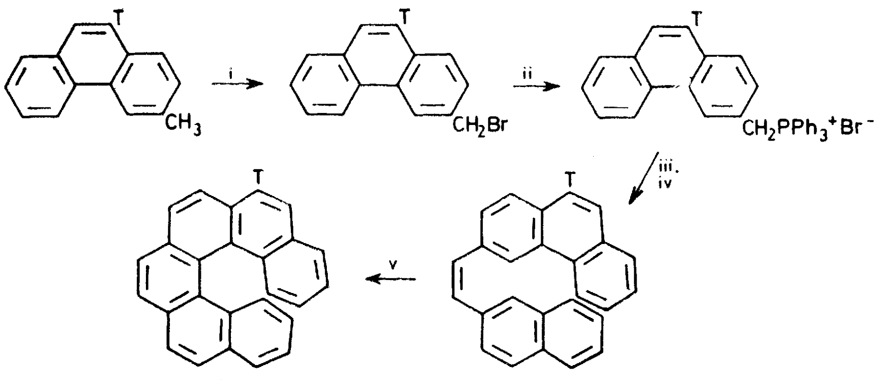
[7-^{3}H]*Hexahelicene*.—This was prepared according to the route given in Scheme 8. A mixture of potassium permanganate (100 g, 1.0 mol) in water (2 l) was heated to b.p. and allowed to cool to room temperature. Decolourizing carbon (50 g; Nuchar C-190N; Eastman) was added in small portions with stirring, and when this addition was complete the mixture was heated again until the colour of potassium permanganate had disappeared. The cooled mixture was filtered, the residue washed with water (2 l) and oven dried (100 °C) during 24 h. This product was used as described below.

[α-^{3}H]-2-*Naphthylmethyl alcohol*. 2-Naphthaldehyde (7.8 g, 0.05 mol), tritiated sodium borohydride (1 mg), and dry tetrahydrofuran (100 ml) were heated under reflux during 15 min and then allowed to cool. Sodium borohydride



+[5-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene.

Scheme 6 Reagents: i, NBS; ii, PPh_3; iii, Bu^nLi; iv, β-naphthaldehyde; v, I_2-u.v.

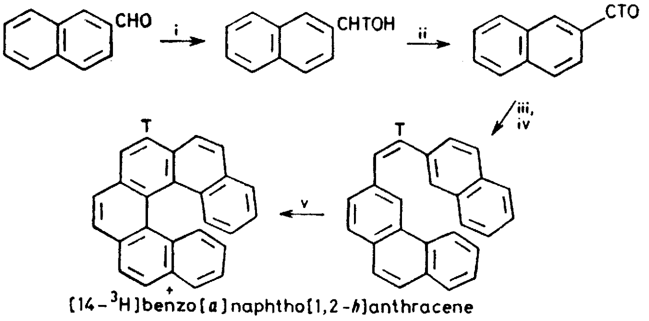


+ [6-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene

Scheme 7 Reagents: i, NBS; ii, PPh_3; iii, Bu^nLi; iv, β-naphthaldehyde; v, I_2–u. v.

(0.9 g, 0.025 mol) was added and the mixture heated under reflux during 24 h. Work-up gave [α-^{3}H]-2-naphthylmethyl alcohol containing a small amount of unchanged aldehyde.

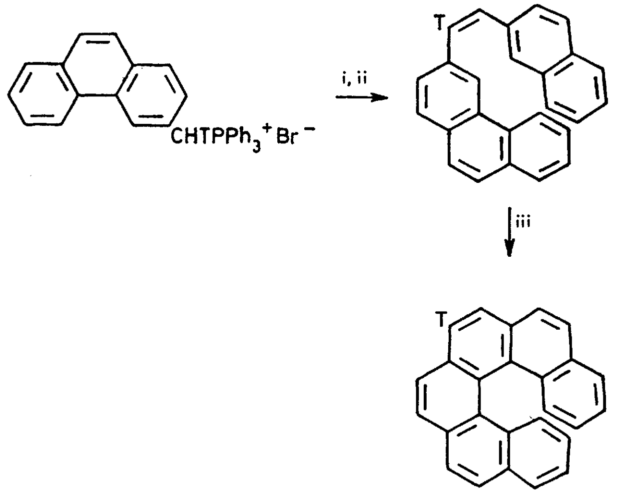
[α-^{3}H]-2-*Naphthaldehyde*. Oxidising carbon (44 g, 3.66 mol), prepared as above, [α-^{3}H]-2-naphthylmethyl alcohol (7.9 g, 0.05 mol), and dry benzene (300 ml) were heated under reflux during 3 h. The mixture was allowed to cool to room temperature, filtered, and the residue washed well with benzene. The combined filtrates were washed with water (3 × 10 ml) and 10% sodium chloride (10 ml) and dried (Na_2SO_4). Removal of benzene gave [α-^{3}H]-2-naphthaldehyde (7.6 g, 97%).



+ [14-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene

Scheme 8 Reagents: i, $NaBT_4$; ii, MnO_2–C; iii, 3-phenanthryl-(triphenyl)phosphonium bromide; iv, Bu^nLi; v, I_2–u.v.

[α-^{3}H]-2-Naphthaldehyde was reacted with 3-phenthrylmethyl(triphenyl)phosphonium bromide according to the general procedure described for preparation of the 1,3-ditritiated isomer to give, *via cis-* and *trans*-1-[^{3}H]-1-(2-naphthyl)-2-(3-phenanthryl)ethylene, [7-^{3}H]hexahelicene, m.p. 233 °C, with [14-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene as byproduct.



+ [15-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene

Scheme 9 Reagents: i, Bu^nLi; ii, β-naphthaldehyde; iii, I_2–u.v.

[8-^{3}H]*Hexahelicene*.—This was prepared by the route given in Scheme 9. [α-^{3}H]-3-Phenanthrylmethyl(triphenyl)phosphonium bromide was prepared as described previously [6] and then reacted with n-butyl-lithium and 2-naphthaldehyde according to the general method given for the 1,3-ditritiated isomer to give, *via cis*- and *trans*-1-(2-naphthyl)-2-[^{3}H]-2-(3-phenanthryl)ethylene, [8-^{3}H]hexahelicene, m.p. 233 °C, with [15-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracene as byproduct.

Kinetic Studies.—The general method for carrying out the kinetic studies has been described previously,[9,17] and was further modified in the present work in that chloroform–trifluoroacetic acid (*ca.* 1 : 9 v/v) was used as the exchanging medium. Various batches of acid mixture had to be employed in view of kinetic difficulties arising out of the very low solubility and (except for the 1,3-ditritiated compound) low specific activities. To ensure that no errors arose from failure to reproduce the acid mixtures, the rate of exchange of [9-^{3}H]phenanthrene was determined in each acid batch, and the partial rate factors calculated (as described in the Results and Discussion section) from the rate relative to that of phenanthrene; rates were measured at 100 °C. The rate coefficients obtained for each isomer, the rate coefficients for [9-^{3}H]phenanthrene in each batch, and the derived partial rate factors are given in Table 3. For the 1,3-ditritiated compounds first-order kinetic plots were, as expected, not obtained. Instead they gave curved plots, which were resolved in each case into two first-order components, the faster of which was attributed to exchange at the 1-position and was confirmed (in the case of hexahelicene) by measurement of the separately prepared 1-labelled isomer; the slow rate of exchange was therefore due to reaction at the 3-position. For benzo[*a*]naphtho[1,2-*h*]anthracene separate confirmation of the assignments was not obtained, but it seems inconceivable that these could be incorrect.

TABLE 3

Rate coefficients for exchange of [*X*-^{3}H]hexahelicenes, [*Y*-^{3}H]benzo[*a*]naphtho[1,2-*h*]anthracenes, and [9-^{3}H]-phenanthrene in various chloroform–trifluoroacetic acid media (1 : 9 v/v) at 100 °C

X	10^7k/s^{-1}	10^7k/s^{-1} (phenanthrene)	*f* [a]
1	5 790	1 007	10 200
	5 950	1 030	10 300
2	2 540	1 000	4 450
	2 540	1 007	4 430
1,3	6 460	1 120	10 250
	630		905
4	4 950	1 000	8 740
	5 300	1 065	8 790
5	14 000	1 000	25 900
	13 500	1 030	24 100
6	3 990	1 030	6 770
	3 480	1 065	6 280
7	12 600	1 000	23 200
	11 250	1 030	20 000
8	10 000	1 000	18 200
	10 650	1 065	18 200
Y			
1,3	2 500	1 120	3 810
	196		268
4	730	1 000	1 190
5	6 240	1 000	11 100

[a] For detritiation in anhydrous TFA at 70°.

[0/1512 *Received*, 3*rd October*, 1980]

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