Tetrahedron Vol 34, pp 769 to 777 Pergamon Press 1978 Printed in Great Britain

CHIRALITY AND CONFORMATIONAL CHANGES IN 4-PHENYLPHENANTHRENES AND 1-PHENYLBENZO[c]PHENANTHRENE DERIVATIVES

W. H. LAARHOVEN,* W. H. M. PETERS and A. H. A. TINNEMANS
Department of Organic Chemistry, Catholic University, Nijmegen, The Netherlands

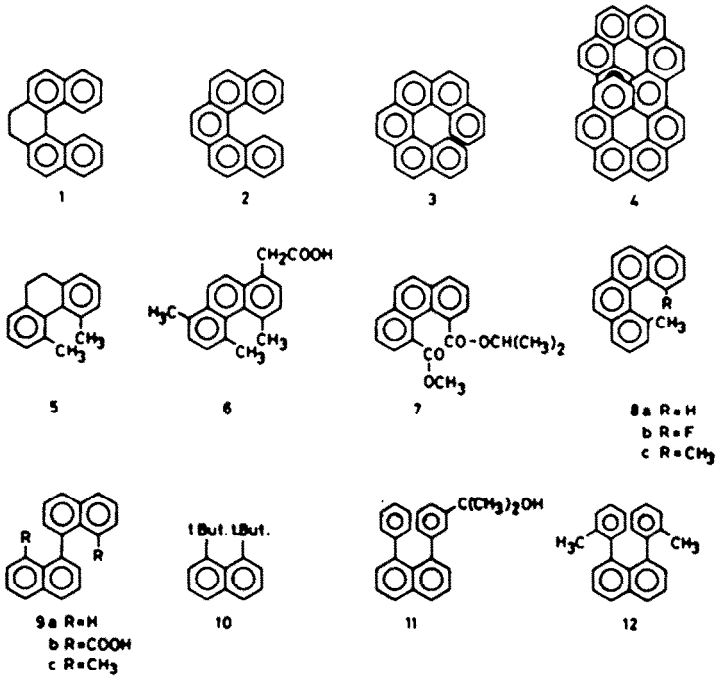
(*Received in UK 15 July 1977; Accepted for publication 30 August 1977*)

Abstract—NMR data of several 4-phenylphenanthrenes (**15**, **16**) have revealed that the crowding in these compounds does not lead to chirality at temperatures as low as −90°. The easy rotation of the phenyl substituent observed by NMR implies that notwithstanding the phenanthrene moiety in average behaves as a planar part the phenyl group does not experience steric hindrance.

The analysis of temperature-dependent NMR spectra of several derivatives of 1-phenylbenzo[c]phenanthrenes (**17**–**20**) indicated that in these compounds exchange processes do occur. By calculations of the free energies of activation from the NMR data two processes could be distinguished: *rotation* of the phenyl substituent at one side of the helical benzo[c]phenanthrene moiety, for which $\Delta G^{\ddagger}_{rot}$ is *ca.* 13.0 kcal/mol or slightly larger when bulky substituents are present at C_2, and *racemisation* by a rotation of the phenyl group around the opposite end of the benzo[c]phenanthrene skeleton with simultaneous inversion of the helical conformation. For this process $\Delta G^{\ddagger}_{rac}$ is *ca.* 16 kcal/mol. The results have been compared with comparable data of related compounds like 1,8-diphenylnaphthalene, hexahelicene, and 4-methylbenzo[c] phenanthrenes, and gave evidence for the remarkably small, space-demanding properties of the phenyl substituent in these compounds.

In the last two decades several aromatic molecules have been found which normally should be expected to be planar but which have groups interfering with that geometry. Such compounds (Scheme 1) possess chirality, and can essentially be resolved when the activation energy between the enantiomeric forms is sufficiently high.

Extensive investigations into the conformational[1] and chiral[2] properties of the helicenes (**2**, **3** and higher benzologues) have revealed that the benzene ring is surprisingly soft against twist; no great strain seems to be present in this type of compounds, and all of them racemize rather easily at *ca.* 200° (**2** even at room temperature). Martin *et al.* demonstrated[3] that the racemisation process does not involve breaking of any C–C bonds, and determined the free energy of activation for racemisation ($\Delta G^{\ddagger}_{rac}$) of several helicenes (Table 1). Obviously, the flexibility of the helical conformation increases with the number of benzo-groups ordered in circular fashion; stronger interference between the opposite ends in the larger helicenes does not lead to a proportional increase in $\Delta G^{\ddagger}_{rac}$. Accordingly, the double helicene **4** has a relatively low $\Delta G^{\ddagger}_{rac}$-value.[4] The flexibility of such aromatic systems has also been observed by Wijnberg[5] and Allinger.[6]



Scheme 1.

Table 1. Free energy of activation for racemisation ($\Delta G^{\ddagger}_{rac}$) of chiral aromatic compounds

	Compound	$\Delta G^{\ddagger}_{rac}$ (kcal/mol)	mechanism	method	ref.
1.	7,8-dihydro-dibenzo[c,g]phenanthrene	30.4	ring inversion	polarimetry	a
2.	dibenzo[c,g]phenanthrene (pentahelicene)	24.1	skeleton inversion	polarimetry	b
3.	hexahelicene	36.2	skeleton inversion	polarimetry	c
	heptahelicene	41.7	skeleton inversion	polarimetry	c
	octohelicene	42.4	skeleton inversion	polarimetry	c
	nonahelicene	43.5	skeleton inversion	polarimetry	c
4.	diphenanthro[4,3-a;3',4'-o]picene	ca. 36	skeleton inversion	polarimetry	d
5.	4,5-dimethyl-9,10-dihydro-phenanthrene	23.5	ring inversion	polarimetry	e
6.	1,4,5-trimethylphenanthryl-8 acetic acid	23.4	skeleton inversion	polarimetry	f
7.	4-carbomethoxy-5-carboisopropoxyphenanthrene	14.3	skeleton inversion	nmr	g
8a.	1-methylbenzo[c]phenanthrene	ca. 22*	skeleton inversion	polarimetry	h
8b.	1-fluoro-12-methylbenzo[c]phenanthrene	31.5	skeleton inversion	polarimetry	i
8c.	1,12-dimethylbenzo[c]phenanthrene	stable	skeleton inversion	polarimetry	j
9a.	1,1-binaphthyl	23.5	rotation	polarimetry	k
9b.	1,1'-binaphthyl-3,8'-dicarboxylic acid	23.5	rotation	polarimetry	k
9c.	8-methyl-1,1'-binaphthyl	27.2	rotation	polarimetry	k
10.	1,8-di-tert.butylnaphthalene	>24	skeleton inversion	nmr	l
11.	1-phenyl-8-m(2-hydroxy-2-propyl)phenylnaphthalene	16	rotation	nmr	m
12.	1,8-bis(*o*-tolyl)naphthalene	ca. 24	rotation	nmr	n

* This value is estimated from the data given in ref. 13 and comparison with the value from 6.

a. D.M. Hall and E.E. Turner, J. Chem. Soc. 1242 (1955). D.M. Hall, J. Chem. Soc. 3674 (1956);
b. ref. 2;
c. ref. 3;
d. ref. 4;
e. K. Mislow, R. Graeve, A.J. Gordon and G.H. Wahl, J. Amer. Chem. Soc. 86, 1733 (1964);
f. M.S. Newman and A.S. Hussey, J. Amer. Chem. Soc., 69, 3023 (1947);
g. R. Munday and I.O. Sutherland, J. Chem. Soc. B 80 (1968);
h. ref. 13;
i. M.S. Newman, R.G. Mentzer and G. Slomp, J. Amer. Chem. Soc. 85, 4018 (1963);
j. ref. 16;
k. M.M. Harris, R.Z. Mazengo and A.S. Cooke, J. Chem. Soc. C, 2575 (1967) and references cited therein;
l. ref. 8;
m. ref. 9;
n. ref. 10.

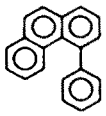
In most of the other examples given in Scheme 1 the non-planar structure is not casued by crowding of parts of the aromatic system itself but by steric interference of atoms or groups bound to the aromatic skeleton. In that case deformation of the polynuclear frame-work can be accompanied by bending of the relevant substituents out of the "plane" of the aromatic moiety. Sometimes $\Delta G^{\ddagger}_{rac}$-values strongly depend on the nature of the substituents in the overcrowded region as is illustrated by the data of **6** and **7**, and of the binaphthyl derivatives† **9a**, **b** and **c**.

The naphthyl derivatives **10–12** show that differences in the nature of the racemisation process depend on the substituents. In chiral **10** containing spherical substituents racemisation occurs by inversion of the deformation in the naphthalene moiety; $\Delta G^{\ddagger}_{rac}$ is at least 24 kcal/mol, much higher than the energy barrier for rotation of the t-Bu groups which is only 6 kcal.[8] In **11** and **12**, containing planar substituents,[9,10] however, the planes of the phenyl groups are at right angles to the naphthalene moiety; racemisation proceeds via rotation of the phenyl substituents which requires more energy than the conformational change by "flipping" of the naphthalene residue (24 and less than 9 kcal, respectively, for **12**).

We have extended these results with investigations on two other, possibly chiral systems, viz. compounds derived from 4-phenylphenanthrene (**13**), distinct from known, non-planar phenanthrenes by the presence of

†Recently an analysis of the inversion of **9a** by molecular mechanics has been published.[7]

only one, relatively large but planar substituent in the overcrowded area, and substitution products of 1-phenylbenzo[c]phenanthrene (**14**) which are structurally intermediate between **3** and **11** or **12**. They differ from **11** and **12** by fixation of one of the phenyl substituents, and reversely from hexahelicene by the possibility of, probably restricted, rotation of one of the helix ends. In both cases analysis of NMR spectra was used to establish the occurrence of chirality, and to investigate whether racemisation when occurring, proceeds through rotation or inversion.



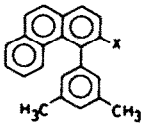
13

14

4-Phenylphenanthrenes

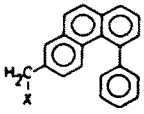
Two kinds of 4-phenylphenanthrene derivatives were investigated:

(1) Compounds containing a variable substituent at C_3 and in addition *meta*-methyl substituents in the phenyl-group in order to simplify the analysis of the NMR spectra **15a–c**. It appeared that in all three compounds the chemical shift of the singlet for the methyl groups at room temperature (δ = 2.32, 2.18 and 2.36 respectively) did not change on lowering the temperature to −90°. Apparently free rotation of the phenyl groups remains possible at this temperature.



15 a X = H
b X = C_6H_5
c X = I

(2) Compounds having a methylene group at C_7 which should lead to diastereotopic protons when chiral forms do exist (**16a,b**). Also in this case the singlet of the methylene group at room temperature (δ = 4.42 and 4.49, respectively) remained unchanged at −90°.

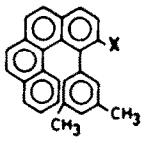


16 a X = Br
b X = OH

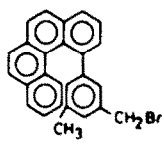
It must be concluded that 4-phenylphenanthrenes, even when a relatively large substituent is present at C_3 (**15b** and **c**), are not chiral at temperatures as low as −90°. The energy barrier between imaginable enantiomers will be in the order of 6 kcal/mol, a value based on NMR data found for the methylene protons in the comparable compound **20b** (see below: $\Delta\delta$ = 12 Hz, J_{AB} = 12 Hz), and on a rough estimation of the coalescence temperature (T_c) of **16** (far below −100°). The low barrier sharply contrasts with that found for **5**, **6** and **7**, in which crowding in the overlapping area seems at first sight of comparable magnitude. Free rotation of the phenyl group in **15** and **16** must therefore imply that notwithstanding the phenanthrene moiety in average behaves as a planar part the phenyl group does not experience steric hindrance.

1-Phenylbenzo[c]phenanthrenes

A similar study as described in the previous section was done with the compounds **17–20**.

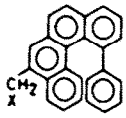


17 a X = H
b X = CH_3
c X = C_6H_5
d X = I



18

19a X = Br
b X = OH
c X = $OCH_2CH_2OCH_3$



20a X = OH
b X = $OCOCH_3$

The NMR spectrum of **17c** in tetrachloroethylene (TCE) above 58° shows a sharp singlet for the Me groups at δ 1.76 ppm. The singlet at 6.20 for the ortho protons in the phenyl ring is broadened by *meta* coupling. At −24° both signals have been split up in two signals of equal intensity. The coalescence temperature (T_c) for the CH_3 signals is 6°; for the ortho protons *ca.* 25°. Qualitatively similar results were obtained with compounds **17a**, **b** and **d**, but T_c is higher for **17b** and **d** (Table 2). In all compounds rather large differences between the δ-values of individual Me groups as well as ortho protons are

Table 2. NMR data of methyl groups and phenyl protons of some 1-(3,5-dimethylphenyl)benzo[c]phenanthrenes (**17a–d**) in CS_2 and tetrachloroethylene (TCE) at measuring temperature (T_m) indicated

Compound	solvent	δCH_3		δH_{ortho}		δH_{para}	T_m (°C)	T_c (CH_3)
17a	CS_2	2.39	1.50	7.47	5.55	6.42	−21	+3
	TCE	2.41	1.57	a	5.67	6.47	−21	+13
17b	TCE	2.36	1.57	a	5.48	6.38	+12	+53
17c	CS_2	1.93	1.55	a	5.56	6.21	−30	+2
	TCE	1.96	1.56	6.82	5.64	6.24	−24	+6
17d	CS_2	2.35	1.57	7.69	5.29	6.21	+13	
	TCE	2.37	1.57	7.79	5.30	6.39	+30	+66

[a] These absorptions are overlapped by other protons.

found at lower temperatures; those lying opposite to the terminal ring of the benzo[c]phenanthrene moiety experience strong shielding and give rise to signals at higher field. It is remarkable that these signals (δ *ca.* 1.55 and 5.5 ppm) measured in the same solvent are nearly independent of the substituent at C_2. For most compounds the position of the signal for the Me group at the other side of the phenyl ring is also rather constant; only with **17c** a substantial upfield shift is observed which can be ascribed to a shielding effect of the 2-phenyl group (a similar but smaller effect is found on the *para* proton). The signal of the ortho proton which is in the very neighbourhood of the C_2-substituent is more variable; in **17c** it is shifted upfield over 0.65 ppm in comparison with **17a** by shielding of the phenyl substituent; in **17d** the large iodine atom causes a downfield shift.

In contrast to these large shift differences of the protons of the phenyl groups the δ-values of the protons of the benzo[c]phenanthrene moiety remain nearly temperature independent. The chemical shifts for H_9 and H_{10} are nearly constant in the whole series of compounds investigated (**17–20**); those for H_{11} and H_{12} lying in the inner core of the helix exhibit only small differences (Table 3). The values do also not deviate much from those of the parent compound **14**. Apparently, **14** is already in such a helical conformation that the introduction of substituents at C_2 (in **17**) or C_{11} (in **19**) and of Me or even larger groups at the *meta* positions of the phenyl substituent (in **17** and **18**) do not lead to further deformation of the polycyclic framework.

The temperature dependence of the NMR spectra of the compounds **17a–d** points to a fast exchange process at high temperatures. Three different modes of conformational change can be considered:

(1) The 1-phenyl substituent rotates around its bond to the benzo[c]phenanthrene system at one and the same side of the plane of the polycyclic moiety (Scheme 2: I ⇄ II, III ⇄ IV). This motion does not lead to racemisation.

(2) The deformation of the benzo[c]phenanthrene moiety inverts, one end flipping up and the other end down, where the phenyl ring rotates in an independent motion as described under *i*. (I ⇄ III + IV; II ⇄ IV + III). This leads to racemisation.

(3) The 1-phenyl substituent rotates and slips at higher temperatures along the benzo[c]phenanthrene moiety via a transition state (V) in which the planes of both parts are perpendicular. This motion leads also to racemisation.

In order to differentiate between these possibilities the NMR spectra of the compounds **18–20** containing diastereotopic protons were measured at various temperatures (Table 4). The NMR spectrum of **18** at low

Table 3. Chemical shifts in ppm of substituted 1 - phenylbenzo[c]phenanthrenes at 50°

Compound	solvent	H_9	H_{10}	H_{11}	H_{12}	H_{ortho}	CH_3	CH_2
14	CS_2	7.55	7.08	6.79	7.72		-	-
17a	TCE		7.10	6.81	7.74	6.61	1.97	-
17b	TCE		7.08	6.88	7.91		1.97	-
17c	TCE	7.52	7.04	6.77	7.83	6.20	1.74	-
17d	TCE	7.51	7.11	6.94	7.81	6.56	1.96	-
18	CS_2		7.11	6.88			1.95	4.13
19a	CS_2 + $CDCl_3$		7.21	-		6.94	-	4.37
19b	CS_2		7.09	-		6.85	-	4.28
19c	CS_2		7.06	-		6.80	-	4.23
20a	$CDCl_3$		7.10	6.86		6.88	-	5.01
20b	CS_2		7.10	6.80		6.84	-	5.58

Table 4. NMR data of the diastereotopic methylene protons and some other protons at low temperature (T_m) of the compounds **18–20**

compound	solvent	T_m (°C)	δ_{CH_2} (ppm)	J_{AB} (Hz)	$T_c(CH_2)$	other protons	T_c (°C)
18	CS_2	-52	4.54; 4.45 3.63; 3.62	9.5 9.5	+15	CH_3: 2.44; 1.57	+15
19a	CS_2+$CDCl_3$	-43	4.39; 4.37	9.5	+65	H_{meta}: 7.48; 6.54	+5
19b	CS_2	-40	4.34; 4.32	12.0			
	CCl_4	-10	4.34; 4.32	12.0	+48	H_{meta}: 7.04; 6.28	+14
19c	CS_2	-60	4.22; 4.13	12.5	+48	H_{meta}: 7.30; 6.31	+4
20b	CS_2	-82	5.52; 5.41	12.0	+55	H_{meta}: 7.33; 6.40	-4

temperature (−52°) shows two signals for the Me group and two AB patterns for the methylene residue. The intensity ratio between the Me-signals as well as the CH_2-signals is about 5:4, pointing to an unequal population of diastereomeric forms (e.g. I and II, or I and IV). The higher intensity is found for the Me signal at higher field (δ = 1.57 ppm) and the methylene signal at lower field (δ = 4.54 and 4.45) suggesting that the bromomethyl group is preferably at the outside of the helical structure (e.g. position B in I). The shift difference between the methylene protons in the less intense signal (δ = 3.63 and 3.62) is very small. Probably the Br atom is turned away form the benzophenanthrene moiety when the bromomethyl group comes into the overcrowded region (position A in I). The methylene protons are then at nearly equal distance from the opposite ring, thus experiencing nearly equal shielding effects. The other AB pattern is better resolved as the bromomethyl group can rotate more freely when being at the outside of the helix.

At higher temperatures (> 50°)both the Me as well as the methylene signal appear as sharp signals. Evidently **18** racemizes at higher temperature and the observed exchange process is not only rotation of the phenyl substituent. The coalescence temperature for both groups of protons is about 15°. Due to the small shift differences within the AB patterns it could not be observed whether conversion of two AB patterns to one (rotation) and conversion of an AB pattern to a singlet (racemisation) occur at the same temperature or have to be considered as separate processes. Unfortunately the NMR data of most of the other compounds (**19a,b**, **20a**) did not answer this question. The shift difference in the AB pattern of **19a** is very small, probably for a similar reason as given for the high field CH_2-signal in **18**. The CH_2-signal of the alcohol **19b** is badly resolved, even in the presence of a shift reagent as a consequence of broadening by H-bonding. The CH_2-signal of **20a** remains even completely unresolved. Only **19c** and **20b** gave AB patterns with differences large enough to determine T_c rather accurately.

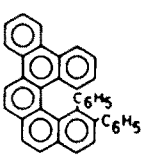
Notwithstanding the small values of **19a** and **19b** all compounds have been used for calculations of the free energies of activation for the exchange processes observed. To that aim exchange rates (k_c) were determined with the equations: $k_c = \pi(\delta\Delta)/\sqrt{2}$; (1) (for uncoupled protons: Me in **17** and **18**),[11] and $k_c = \pi[(\delta\Delta)^2 + 6J_{AB}^2]^{1/2}/\sqrt{2}$; (2) (for coupled protons: CH_2, in **18–20**, H_{meta} in **19** and **20**). $\Delta G^{\neq}$-values were then obtained from the Eyring eqn (3) taking the transmission coefficient as unity because the occurrence of an intermediate is improbable:

$$\Delta G^{\neq} = 4.57\, T_c(10.32 + \log T_c/k_c). \qquad (3)$$

For the compounds **17a–d** $\Delta G^{\neq}$-values were also determined by simulation of the Me-signals which are broadened by the exchange reaction. With the NMRTW2 program the spectra were calculated and pictured on a screen by a POP-11/45 computer, Vector General Display, General Purpose Graphic System Software, using $(T_{2,0})^{-1}$ = 2.5 Hz. The life time τ was found by trial and error until form and position of the singulets were identical with the experimental data. From these τ-values (10 values for each compound) the activation parameters were calculated with the eqn (3).

The $\Delta G^{\neq}$-values obtained by the two methods appeared to be equal within the accuracy of the methods used (Table 5). For the compounds **19–20** the values based on the diastereotopic methylene protons, which concern an exchange process leading to racemisation, are significantly larger than those based on phenyl protons, which concern rotation of the phenyl substituent. On the whole, the latter are rather equal to those found for the exchange process in **17–18** which must also be a rotation of the substituted phenyl group. The higher $\Delta G^{\neq}_{rot}$-values for **17b** and **d** can be ascribed to the additional steric hindrance of the rotation caused by the 2-methyl- or 2-iodo substituent in these compounds. It deserves attention that the 2-phenyl substituent in **17c** does not lead to such an increase of $\Delta G^{\neq}_{rot}$. This may be ascribed to the disc-like shape or a more flexible character of the phenyl group.

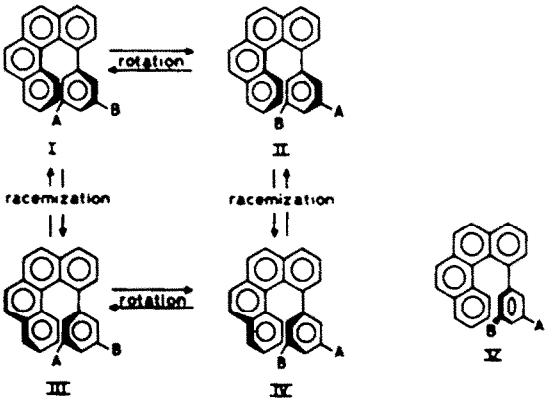
The $\Delta G^{\neq}_{rot}$-values of the compounds **17a** and **c**, **18–20** are much lower than those found for **11** and **12** (Table 1). An explanation may be that in the benzo[c]phenanthrene derivatives the helical form of the molecular framework allows more space to the phenyl substituent than the less deformed structure of the naphthalene derivatives. In previous work[12] we found that even in phenyl-substituted pentahelicenes like **21** relatively low $\Delta G^{\neq}_{rot}$-values are found: 16 kcal/mol for C_{14}-phenyl rotattion; 10 kcal/mol for C_{13}-phenyl rotation.



21

The racemisation process

$\Delta G^{\neq}_{rac}$ of **19–20** is very much lower than $\Delta G^{\neq}_{rac}$ of hexahelicene (**3**) which racmises according to Martin *et al.* via a non-planar but achiral, intermediate state.[3b] The absence of a fixating bridge at one end of the helix in 1-phenylbenzo[c]phenanthrenes (**14**) provides these compounds with another pathway of lower energy to reach their enantiomeric forms. The energy barriers found are of the same order as that of **11** which should racemise by rotation of the phenyl groups in a cog-wheel-like movement.[9] Applied to 1-phenylbenzo[c]phenanthrenes the mechanism might be described by the transformation I→[V]→IV (see Scheme 2). Apparently, the 1-phenyl-substituent has



Scheme 2.

Table 5. Free energies of activation for exchange processes (rotation and racemisation) in the compounds 17–20

compound	solvent	protons used	$\Delta\delta$ (ppm)	J_{AB} (Hz)	T_c (°C) [a]	k_e	$\Delta G^{\ddagger}_{rac}$ [b]	$\Delta G^{\ddagger}_{rot}$ [b]	$\Delta G^{\ddagger}_{rot}$ [c]
17a	CS_2	CH_3	0.89	-	276	197.7		13.2±0.3	12.9±0.4
	TCE	CH_3	0.84	-	286	186.6		13.7±0.3	13.1±0.4
17b	TCE	CH_3	0.79	-	326	175.4		15.8±0.4	15.0±0.5
17c	CS_2	CH_3	0.38	-	275	84.4		13.6±0.3	13.1±0.4
	TCE	CH_3	0.40	-	279	88.9		13.8±0.3	13.6±0.4
17d	TCE	CH_3	0.80	-	339	177.7		16.4±0.5	16.0±0.5
18	CS_2	CH_3	0.87	-	286	193.3		13.7±0.3	
	CS_2	CH_2	0.86	-	288	189.9		13.7±0.3	
19a	CS_2	CH_2	0.02	12	337	51.9	17.0±1.1		
	CS_2	H_{meta}	0.94	3	287	209.5		13.3±0.3	
19b	CCl_4	CH_2	0.01[5]	12	321	65.4	16.2±1.1		
	CCl_4	H_{meta}	0.76	3	287	169.6		13.8±0.3	
19c	CS_2	CH_2	0.09[5]	12.5	321	71.2	16.1±0.5		
	CS_2	H_{meta}	0.99	3	277	216.6		13.2±0.3	
20b	CS_2	CH_2	0.11[5]	12	328	70.1	16.5±0.5		
	CS_2	H_{meta}	0.97	3	269	207.2		12.8±0.3	

[a] The accuracy of the coalescence temperatures T_c is 1°C for the compounds 17 and 18, about 20°C for the methylene groups of the compounds 19a and b and about 5°C for those of the compounds 19c and 20b.

[b] Calculated with the formula 1 (or 2) and 3.

[c] Calculated from the computed τ-values ($= 1/k_e$) and formula 3.

special properties which contribute to a relatively low energy barrier in this process: for 1-methylbenzo[c]phenanthrene (8a) $\Delta G^{\ddagger}_{rac}$ = *ca.* 22 kcal/mol.[13] In the foregoing it has been suggested that these special properties concern a larger flexibility in comparison with Me (and other) substituents.

Another explanation of the low $\Delta G^{\ddagger}_{rac}$-values of derivatives of 14 might be that the ground-state energy of the benzo[c]phenanthrene moiety in 14 is higher than in 8. This could be excluded, however, by calculations using the Warshell programme,[14] in which the ground-state conformations are found by minimising the energy. The results are given in Table 6. The reliability of the programme was checked with 4,5- and 2,7-dimethylphenanthrene, the energy difference of which (13.6 kcal/mol) is in good accordance with that from heats of combustion[15] (12.5 ± 1 kcal/mol); and with 1,12- and 5,8-dimethylbenzo[c]phenanthrene, for which the same is true (10.4 and 11.0 ± 1.5 kcal/mol, respectively). The calculations revealed that the benzo[c]phenanthrene moiety in 8c and 14 have nearly the same ground-state energy. The small difference found (1.9 kcal/mol) cannot explain that 8c does not racemise at all below its decomposition temperature[16] (280°) whereas $\Delta G^{\ddagger}_{rac}$ for 14 is only *ca.* 16 kcal/mol.

So, it seems that the resemblance in steric properties between a methyl substituent and a fused benzo group in polycyclic aromatics previously found by Newman[17] cannot be extended to a freely rotation phenyl substituent. In a way the latter behaves, at least in the systems investigated, as a less space-demanding group. With respect to the crystallographic dimensions of methyl and phenyl groups this could not be expected *a priori*.

EXPERIMENTAL

For the recording of spectral data the following apparatus was used: A Varian MAT SM2B mass spectrometer, a Beckman DK2A or a Cary 15 UV spectrophotometer, a Perkin-Elmer 254 IR instrument, and a Varian HA100 NMR instrument. M.ps were determined with a Leitz m.p. microscope, and are uncorrected.

The synthesis of the compounds 15a–c and 17a–d has been described previously.[18]

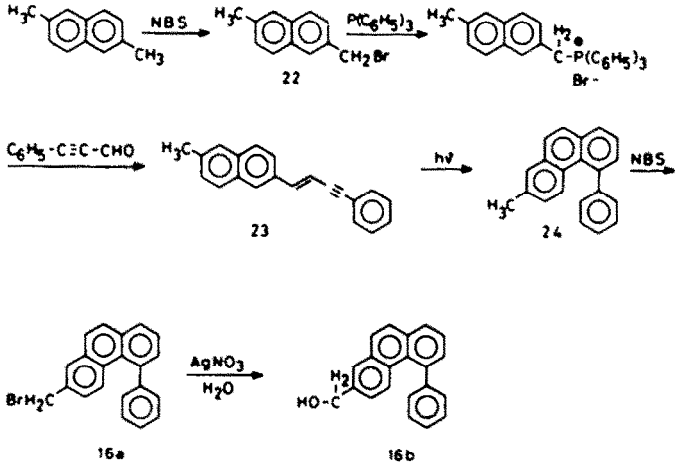
7 - *Bromomethyl* - *and* 7 - *hydroxymethyl* - 4 - *phenylphenanthrene.* (Scheme 3, 16a and 16b). 2,6 - Dimethylnaphthalene was treated with N-bromosuccinimide (NBS) in CCl_4. The monobromide 22 thus obtained (m.p. 90°) was converted into its triphenyl phosphonium–salt by reflux with an equimolar amount of $(C_6H_5)_3P$ in xylene for 4 hr. The salt (m.p. 272°; yield 60%) was used in a Wittig reaction with phenylpropargylaldehyde in MeOH as the solvent.[19] The resulting butenyne 23 was obtained in 67% (m.p. *cis* 23: 153°; *trans* 25: 159°).

Irradiation of 23 in hexane at 300 nm for 6 hr gave 24. It was purified by chromatography on Al_2O_3 with hexane/toluene (3:1) as the eluens and crystallisation from MeOH Yield: 50%; m.p. 144°; *m/e*: 268 (100%), 253 (63%); UV: λ_{max} (log ε) in MeOH, 297

Table 6. Energies calculated with the Warshell program

compound	total energy (kcal/mol)	energy of the benzo c phenanthrene moiety[a] (kcal/mol)
4,5-dimethylphenanthrene	-3529.4	
2,7-dimethylphenanthrene	-3543.0	
1,12-dimethylbenzo[c]phenanthrene (8c)	-4321.4	-3733.6
5,8-dimethylbenzo[c]phenanthrene	-4331.8	-3740.5
benzo[c]phenanthrene	-3741.6	-3741.6
1-phenylbenzo[c]phenanthrene (14)	-4974.9	-3731.7
3-phenylbenzo[c]phenanthrene	-4988.0	-3740.6

[a] These values are found by replacement of the substituents by hydrogen without changing the conformation and taking the C–H distance 1.08 Å.



Scheme 3.

(4.11): [277(4.39)], 256 (4.67), 223 (4.66), 204 (4.57); NMR (CS_2, TMS): δ 2.32 (3H, s, CH_3), 6.76 (1H, d, H_6), 7.28 (5H, s, C_6H_5), 7.17–7.53 (6H, m), 7.66 (1H, d, H_1).

Bromination of **24**, with NBS gave the product **16a** in 61% yield, m.p. 132–134°; UV: λ_{max} (log ϵ) in CH_3OH, [290 (4.22)], 264 (4.69), 227 (4.50), 204 (4.46); NMR (CS_2, TMS): δ 4.42 (2H, s, CH_2), 6.94 (1H, d, H_6), 7.21–7.64 (11 H, m), 7.70 (1H, d, H_1).

The bromide **16a** (90 mg) was dissolved in 5 ml ethylene glycol monoethyl ether. A soln of $AgNO_3$ (110 mg) in 10 ml water was added, and the mixture was refluxed for 30 min. After filtration and evaporation the residue was distilled with steam, extracted with ether, dried, and again evaporated. The resulting **16b** was purified over a silicagel column, yield: 33%; m.p. 106–108°; *m/e* 284 (M⁺,32%); NMR (C_2Cl_4, TMS): δ 1.97 (1H, s, OH), 4.29 (2H, s, CH_2), 6.89 (1H, d, H_6), 7.28 (5H, s, C_6H_5), 7.27–7.62 (6H, m), 7.69 (1H, d, H_1).

1 - (3 - *Bromomethyl* - 5 - *methylphenyl*) - *benzo[c]phenanthrene* (**18**). Treatment of 1 - (3,5 - dimethylphenyl)-benzo[c]phenanthrene[18] with one equivalent of NBS gave the monobromination product **18** contaminated with some dibromo-product and starting material. By chromatography over a short column of silicagel and crystallisation from MeOH the contaminations could be eliminated for the greater part. Only a slight amount of the dibromo derivative has remained. M.p. 65–67°; *m/e*: 412, 410 (M⁺, 67%), 331 (M⁺–Br, 100%).

11 - *Substituted* 1 - *phenylbenzo[c]phenanthrenes*. (Scheme 4, **19a–c**). Irradiation of **25** in hexane in the presence of 4 mol% I_2 gave **16** in 70% yield. It was purified by columnchromatography over silicagel with hexane/toluene (8:1) as the eluens and crystallisation from MeOH (m.p. 146°).

Bromination of **26** with one equivalent of NBS in CCl_4 gave 56% of **27** which was converted into its triphenyl phosphonium salt (m.p. 290°) by treatment with $(C_6H_5)_3P$ in xylene under reflux. The Wittig reaction of the salt with phenylpropargylaldehyde resulted in **28**, m.p. (*trans* **28**) 141°; *m/e*: 318 (M⁺, 39%), 303 (M⁺–CH_3, 100%).

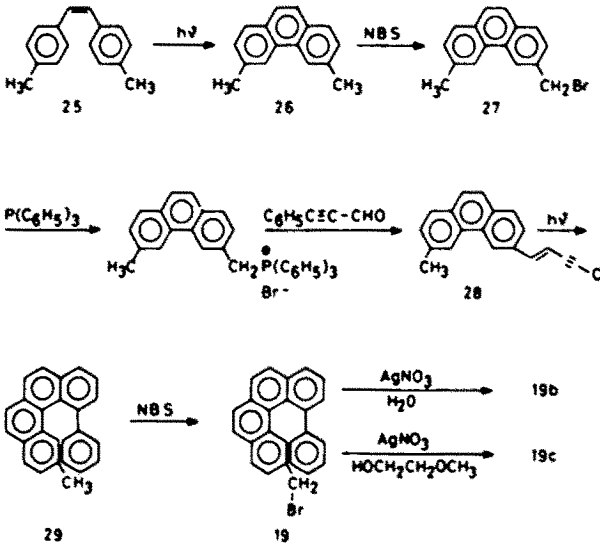
Irradiation of the isomer mixture of **28** in benzene at 300 nm for 10 hr gave **29**, m.p. 170°; *m/e*: 318 (100%); UV: λ_{max} (log ϵ) in CH_3OH, [310 (4.14)], 289 (4.59), 282 (4.58), [250 (4.29)], 229 (4.66), 205 (4.65); NMR (CCl_4, TMS): δ 2.10 (3H, s, CH_3), 6.85 (5H, broadened singlet, C_6H_5), 6.88 (1H, d, H_{10}), 7.40–7.85 (9H, m).

Bromination of **29** with NBS resulted in the product **19a**, which was purified by columnchromatography on silicagel using hexane/toluene (8:1) as the eluens and crystallisation from EtOH, m.p. 200–202°; *m/e*: 398, 396 (M⁺, 21%), 317 (100%) UV: λ_{max} (log ϵ) in CH_3OH, [325 (4.01)], 292 (4.67), [285 (4.64)], 232 (4.70); NMR (CS_2 + $CDCl_3$, TMS): δ 4.37 (2H, J_{AB} = 10 Hz, CH_2), 6.94 (5H, broadened singlet, C_6H_5), 7.21 (1H, d, H_{10}), 7.55–7.95 (9H, m).

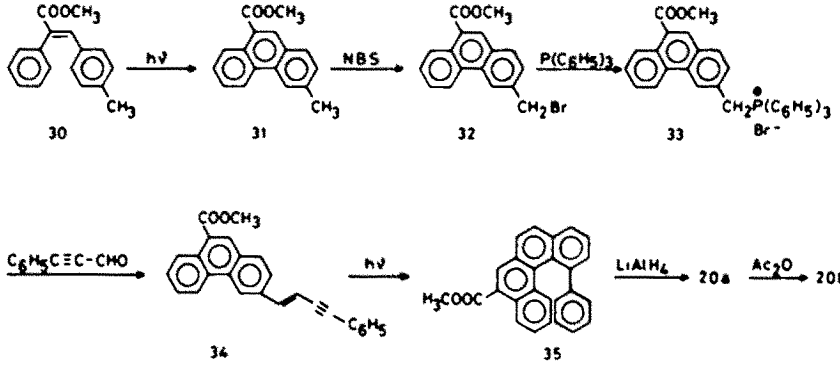
The second product **19b** was obtained from **19a** in a similar way as **16b** from **16a**, yield: 40%; oil; *m/e*: 334 (M⁺, 100%); NMR (CS_2, TMS): δ 4.28 (2H, J_{AB} = 12 Hz, CH_2), 6.85 (5H, broadened singlet, C_6H_5), 7.09 (1H, d, H_{10}), 7.51–7.90 (9H, m).

By a similar procedure, but using ethyleneglycol monomethyl ether and water in the ratio 10:1 **19a** could be converted in the product **19c**, yield: 42%; oil; *m/e*: 392 (M⁺, 10%), 391 (M⁺-1, 56%), 266 (100%); NMR (CS_2, TMS): δ 3.21 (3H, s, OCH_3), 3.35 (4H, m, CH_2–CH_2), 4.23 (2H, J_{AB} = 12.5 Hz, CH_2), 6.80 (5H, broadened singlet, C_6H_5), 7.06 (1H, d, H_{10}), 7.46–7.87 (9H, m).

8 - *Substituted* 1 - *phenylbenzo[c]phenanthrenes*. (Scheme 5,



Scheme 4.



Scheme 5.

28a and **b**). *Cis* α - phenyl - *p* - methylcinnamic acid was obtained from *p* - tolualdehyde and phenylacetic acid.[20] It was converted into its methyl ester (m.p. 91°),[20] and the ester was irradiated in hexane at 300 nm for 20 hr in the presence of 5 mol% I_2. The irradiation mixture contained in addition to the desired product **31**, some *trans*-**30** and an acid fraction. By repeated columnchromatography on silicagel, checked by NMR, the pure phenanthrene derivative **31** was obtained in 48% yield, m.p. 52–54°; *m/e*: 250 (M^+, 100%); UV: λ_{max} (log ε) in CH_3OH, 304.5 (4.12), 256 (4.65), 235 (4.42), 211 (4.41); NMR (CCl_4, TMS): δ 2.17 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 6.89–7.26 (2H, J_{AB} = 8 Hz, H_1, H_2), 7.37 (1H, t, H_6), 7.45 (1H, t, H_7), 7.85 (1H, s, H_4), 8.05 (1H, s, H_{10}), 8.20 (1H, d, H_5), 8.99 (1H, d, H_8).

The conversion of **31** into **32** (m.p. 112–114°), **33** (yield 81%, m.p. 253°) and **34** (yield 63%, m.p. *cis*-**33**: 93–95°; *trans*-**33**: 98–100°) was done in the same way as described for the synthetic sequence **26** → **28**.

Irradiation of **34** in benzene at 360 nm for 30 hr gave **35**. M.p. 206°; *m/e*: 362 (M^+, 100%); UV: λ_{max} (log ε) in CH_3OH, 292 (4.63), 231 (4.60); NMR ($CDCl_3$, TMS): δ 4.0 (3H, s, OCH_3), 6.88 (1H, t, H_{11}), 6.92 (5H, broadened singlet, C_6H_5), 7.23 (1H, t, H_{10}), 7.61–7.96 (6H, m), 8.50 (1H, s, H_7), 8.68 (1H, d, H_9).

The ester was saponified, the resulting acid (m.p. 265–266°) was dissolved in ether with a small amount of benzene, and reduced with LAH, giving the product **28a** in 90% yield. Without purification this was heated with Ac_2O and NaOAc on a boiling water bath for 4 hr. The mixture was treated several times with Na_2CO_3 to remove unreacted anhydride, extracted with ether, dried over $MgSO_4$, and evaporated. The residue was purified over silicagel giving the acetylated product **28b** as an oil in 45% yield. *m/e*: 376 (M^+, 100%); NMR (CS_2, TMS): δ2.04 (3H, s, CH_3), 5.55–5.61 (2H, J_{AB} = 12 Hz, CH_2), 6.80 (1H, t, H_{11}), 6.84 (5H, broadened singlet, C_6H_5), 7.10 (1H, t, H_{10}), 7.47–7.85 (8H, m).

Acknowledgement—The authors are indebted to Professor R. J. F. Nivard for his interest in this work, to Mr. H. H. K. Brinkhof for measuring the NMR spectra and to Drs. F. W. Pijpers and L. C. Caruthers for the NMR simulation experiments.

REFERENCES

[1]For a review see R. H. Martin, *Angewandte Chemie* Int. Ed. **13**, 649 (1974).
[2]Ch. Goedicke and H. Stegemeyer, *Tetrahedron Letters* **937** (1970).
[3a]R. H. Martin and M. J. Marchant, *Ibid.* 3707 (1970); [b]*Ibid.*, *Tetrahedron* **30**, 347 (1974).
[4]W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Ibid.* **30**, 3343 (1974).
[5]H. Wijnberg, W. C. Nieuwpoort and H. T. Jonkman, *Tetrahedron Letters* 4623 (1973).
[6]N. L. Allinger, J. T. Sprague and T. Liljefors, *J. Am. Chem. Soc.* **96**, 5100 (1974).
[7]R. E. Carter and T. Liljefors, *Tetrahedron* **32**, 2915 (1976).
[8]J. E. Anderson, R. W. Franck and W. L. Mandella, *J. Am. Chem. Soc.* **94**, 4608 (1972).
[9]H. O. House, W. J. Campbell and M. Gall, *J. Org. Chem.* **35**, 1815 (1970).
[10]R. L. Clough and J. D. Roberts, *J. Am. Chem. Soc.* **98**, 1018 (1976).
[11]H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 228 (1956).
[12]W. H. Laarhoven and P. G. F. Boumans, *Rec. Trav. Chim.* **94**, 114 (1974).
[13]M. S. Newman and W. B. Wheatley, *J. Am. Chem. Soc.* **70**, 1913 (1948).
[14]A. Warshel and S. Lifson, *J. Chem. Phys.* **53**, 582 (1970).
[15]M. A. Frisch, C. Barker, J. L. Margrave and M. S. Newman, *J. Am. Chem. Soc.* **85**, 2356 (1963).
[16]M. S. Newman and R. M. Wise, *Ibid.* **78**, 450 (1948).
[17]H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave and M. S. Newman, *Ibid.* **87**, 5557 (1965).
[18]A. H. A. Tinnemans and W. H. Laarhoven, *J. Chem. Soc.* Perkin II, 1114 (1976).
[19]A. H. A. Tinnemans and W. H. Laarhoven, *Ibid.* Perkin II, 1104 (1976).
[20]G. H. Jeffery and A. I. Vogel, *Ibid.* 658 (1948).