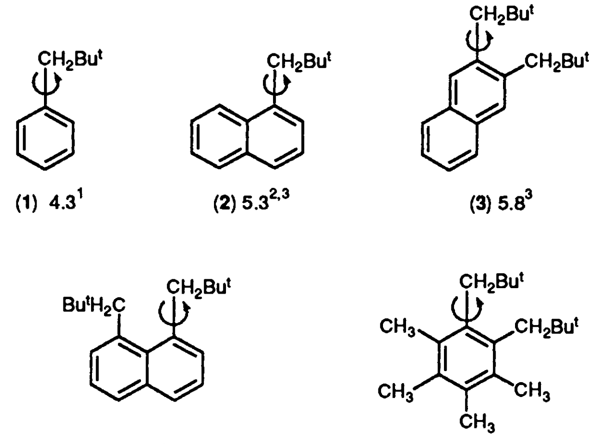
Synthesis of 13,14-Dialkylpicenes and Hindered Rotation of the Alkyl Groups as Studied by Dynamic NMR spectroscopy and Molecular Mechanics Calculations

J. Edgar Anderson* and Bernt R. Bettels
Chemistry Department, University College, Gower Street, London WC1E 6BT

The synthesis of four 13,14-dialkylpicenes is reported. NMR spectra at various temperatures and molecular mechanics calculations indicate that while the α-carbon atoms are near the aromatic plane, the remaining carbon atoms are above or below the plane, the two substituents being *trans* in that way. There is a barrier to rotation of alkyl groups through the plane of the ring to interconvert up–down and down–up conformations of 11–12 kcal mol^{-1}, which is dependent on the substituent.

The most significant feature of the conformational analysis of substituted alkyl benzenes, which occur widely in organic chemistry, is likely to be the steric interaction between the phenyl group and the alkyl sidechain. For a primary alkyl group CH_2X, if X is large, analysis seems simple—the ground state will have the CH_2–X bond near to perpendicular to the aromatic plane, and there will be a barrier to rotation about the phenyl–CH_2 bond to move X from one side of the plane to the other. Even when X = t-butyl,[1] the barrier to rotation of the CH_2X group is only about 4.3 kcal mol^{-1}.† Simple substitution raises the barrier slightly as the series (1)–(4) indicates (see the Figure), but the effect is small, since a single substitution leaves one *ortho*-position unhindered, so rotation can take place. Substitution of both *ortho*-positions[4,5] is required before high barriers to CH_2X rotation are found; compound (5) is an example.[3,4]

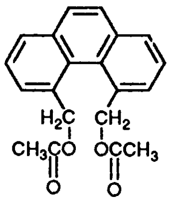


(1) 4.3[1] (2) 5.3[2,3] (3) 5.8[3]

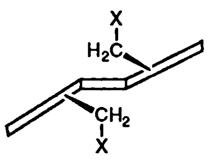
(4) 7.4[3] (5) 16.2[3,4]

Figure. Rotational barriers/kcal mol^{-1}.

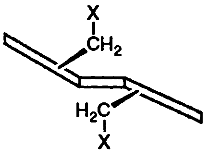
Conformational analysis of aromatic systems is complicated by the fact that as congestion increases, abandonment of aromatic planarity may be more attractive energetically than the more usual distortions of simpler molecules. Phenanthrenes with CH_2X substituents in the 4 and/or 5-positions reflect a delicate conformational balance. 4-Methylphenanthrene appears to be planar while the 4,5-dimethyl compound has these groups twisted 33° on either side of the plane.[6] In the former case, with the methyl group in the plane, the methyl rotational barrier in the solid state[7] is 5.1 kcal mol^{-1}, much higher than in the latter case, 2.3 or 2.7 kcal mol^{-1}. In the compound (6), substituents are displaced on either side of the mean plane of the aromatic system[8–10] and there is a high barrier of 18.1 kcal mol^{-1} to interconversion of enantiomeric structures which can be represented diagramatically as (7) and (8).



(6)



(7)



(8)

We now report a new series of compounds, the 13,14-dialkylpicenes (9), which appear to be planar, and which by combining aspects of *ortho*-substitution and of the phenanthrene framework, have a particularly high barrier to Ar–CH_2X rotation.

Results and Discussion

Synthesis.—13,14-Dialkylpicenes (9) have not to our knowledge been previously reported, but are readily prepared by oxidative photocyclisation of bis-(1-naphthyl)dialkylethylenes (10) which are synthesised by titanium-mediated dimerisation of 1-alkanoylnaphthalenes. By this means, (**9a–d**) have been obtained as sharply melting solids, see the Experimental section.

Dynamic NMR Spectroscopy.—The proton NMR spectrum of the α-CH_2-group of (**9b–d**) is temperature-dependent, see Table 1. For the ethyl compound (**9b**), this signal appears as a spin-coupled quartet at 50 °C. Broadening of the CH_2 signal occurs as the temperature is lowered until about −27 °C, when the signal splits. It appears as two multiplets at −55 °C, the AB part of an ABX_3 spectrum. Irradiation of the methyl-group frequency at this temperature reduces the methylene-group spectrum to an AB system (δ_{AB} = 287 Hz at 400 MHz, J_{AB} =

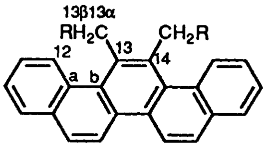
---

† 1 cal = 4.182 J.

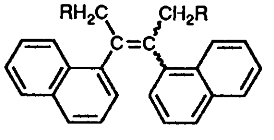
Table 1. NMR data for 13,14-dialkylpicenes (**9a–d**).

Nucleus	Picene	Substituent	Signal	Chemical shift (ppm)	$T_{coalesc.}$/K	k_{rotn} at $T_{coalesc.}$/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
^1H	(**9a**)	methyl	α-CH_2				
			-CH_3	3.04			
			aromatic[a]	7.26–8.66			
	(**9b**)	ethyl	α-CH_2	3.59	246	637	11.1
			-CH_3	1.31			
			aromatic	7.57–8.68			
	(**9c**)	n-hexyl	α-CH_2	3.49	260	654	11.8
			β-CH_2 *etc.*	1.26–1.68			
			-CH_3	0.86			
			aromatic	7.45–8.61			
	(**9d**)	n-decyl	α-CH_2	3.49	262	658	11.9
			β-CH_2 *etc.*	1.25–1.67			
			-CH_3	0.89			
			aromatic	7.45–8.62			
^{13}C	(**9a**)	methyl	-CH_3	28.75			
			aromatic[a]	as (**9b**)[b]			
	(**9b**)	ethyl	α-CH_2	32.93			
			-CH_3	14.51			
			aromatic quaternary	136.6, 133.1, 130.8, 129.9, 128.8			
			other aromatic	128.2, 128.0, 126.6, 125.8, 124.7, 121.0			
	(**9c**)	n-hexyl	α-CH_2	32.88			
			other-CH_2	31.82, 31.48, 29.73, 22.83			
			-CH_3	14.07			
			aromatic	as (**9b**)			
	(**9d**)	n-decyl	α-CH_2	32.86			
			other-CH_2	31.94, 31.81, 30.02, 29.61 29.59, 29.36, 29.26, 22.72			
			-CH_3	14.15			
			aromatic	as (**9b**)			

[a] Aromatic proton and carbon-13 signals may be assigned by referring to the spectrum of the parent picene.[22] [b] For each of (**9a–d**), values of aromatic chemical shifts were identical to within 0.1 ppm, except that for (**9a**), where a signal at δ 132.2 replaces that at δ 136.6.



(**9**) **a**; R = H
b; R = CH3
c; R = [CH2]5CH3
d; R = [CH2]9CH3



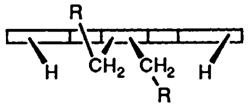
(**10**)

13 Hz). On the basis of a coalescence of the A and B parts of the decoupled signal at −27 °C, the rate of interconversion $k = \pi[(\delta^2 + 6J^2)/2]^{\frac{1}{2}}$ is 641 s^{-1} at that temperature, whence the free energy of activation for the process is 11.1 kcal mol^{-1}. All other proton NMR signals and all carbon-13 NMR signals for (**9b**) are essentially temperature independent.

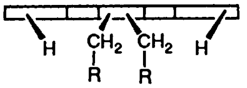
The *trans*-conformation appears to be less crowded than any *cis*-one and should thus be preferred. While nothing in the NMR spectrum proves this, molecular mechanics calculations reported below confirm this relative stability.

Similar behaviour is observed in the corresponding CH_2 signals of (**9c**) and (**9d**). This is summarised in Table 1, and barriers to the conformational process are derived. Changes in other methylene-group signals in these latter compounds should take place, but could not be clearly distinguished owing to signal overlap. In none of the three compounds was there any sign of a second set of signals at low temperature which might be attributable to a second, *cis* kind of conformation.

Molecular Mechanics Calculations.—We used Allinger's MMP2 program[11] to calculate stable conformations of compound (**9b**), and found the *trans*-planar aromatic system with one methyl group on either side of the plane, represented diagrammatically as (**11**), to be preferred. Rather less stable is



(**11**)



(**12**)

the *cis*-conformation (**12**), while conformations with one hydrogen and the methyl of either ethyl group on the same side of the plane are all at least a further 6 kcal mol^{-1} less stable. Table 2 summarises other relevant details of the two stable conformations. The differences in interaction of groups *cis* and *trans* lead to the characteristic differences in bond angles and bond lengths *etc.* shown in Table 2 and need not be referred to further in this text. Insofar as molecular mechanics calculations have satisfactorily predicted the non-planarity of 4,5-dimethylphenanthrenes,[7] we feel that the present prediction of an essentially planar system for the *trans*-conformation of diethylpicene, see Table 2, is credible.

Inspection of models of (**9b**) and non-optimised calculations suggests that interconversion of enantiomeric *trans*-conform-

Table 2. Selected molecular mechanics calculated parameters for *trans* and *cis* conformations of 13,14-diethylpicene[a].

	trans	*cis*	
Bond lengths/Å			
C_{13}–C_{14}	1.376	1.375	
C_{13}–$C_{13\alpha}$	1.531	1.531	
Bond Angles/°			
C_{14}–C_{13}–$C_{13\alpha}$	116.3	116.3	
C_{12b}–C_{13}–$C_{13\alpha}$	120.6	120.6	
Dihedral Angles/°			
C_{12a}–C_{12b}–C_{13}–$C_{13\alpha}$	−3.7	−8.5	−6.5
$C_{13\alpha}$–C_{13}–C_{14}–$C_{14\alpha}$	5.7	11.9	
C_{14}–C_{13}–$C_{13\alpha}$–$H_{13\beta}$	130.5	136.5	−115.2
C_{14}–C_{13}–$C_{13\alpha}$–$H_{13\beta}$	29.2	37.7	−5.8
C_{14}–C_{13}–$C_{13\alpha}$–$C_{13\beta}$	−95.8	−90.5	108.3
Conformational Energies/ kcal mol^{-1}			
Compression	3.8331	3.8256	
Bending	11.4439	11.3205	
Stretch-bend	0.4397	0.4280	
van der Waals (1,4)	17.8063	17.8585	
van der Waals (other)	8.3462	8.2383	
Torsional	−38.9117	−36.1511	
Dipole	0.1205	0.1183	
Total	3.0780	5.6381	
Relative steric energy	0.0	2.5601	
Aromatic non-planarity Δ,/°[b]			
Rings A–E	0.7,1.0,1.4,1.0,0.7	0.8,1.4,2.5,1.8,1.4	

[a] For numbering see diagram of (**9**). [b] The mean deviation from 0° for the six endocyclic C–C–C–C dihedral angles for each ring.

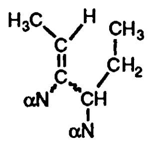
ations *i.e.*, up–down with down–up takes place *via* the *cis*-conformation reached by a rotation of one methyl group through the gap between the two ethyl groups, the 13–14 gap, rather than the 12–13 gap or the 14–1 gap. Simulation of this process by use of the drive option of molecular mechanics leads to energies much higher than are found experimentally. This suggests that successful simulation requires simultaneous management of the rotation of both ethyl groups, which was considered too laborious. The rotation of both methyl groups is probably much restricted in the transition state, which should lead to a negative entropy of activation, and thus, an experimental enthalpy of activation somewhat lower than the experimental free energy of activation of 11.1 kcal mol^{-1}.

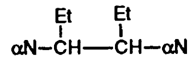
Our studies have been limited to a set of picenes with primary alkyl substituents. During rotation of a chain through the gap between the 13- and 14-positions, the β-atom is most involved in the hindrance to rotation. The fact that the barriers for the hexyl and decyl compounds (**9c**) and (**9a**) are not much greater than that of (**9b**) suggests that the γ-carbon is directed away from interaction with the second alkyl group. A second β-substituent should lead to marked reductions in the rate of interconversion, and perhaps to configurationally stable up–down and down–up enantiomers of the *trans* conformation.

Experimental

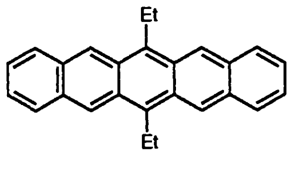
NMR spectra were recorded for *ca.* 0.05 mol dm^{-3} solutions in CF_2Cl_2–CD_2Cl_2 (4:1) on a Varian VXR400 spectrometer with an operating frequency of 400 MHz for protons. FIDs were unweighted, acquisition times were 2 s, and at least 8 data points per Hz were used.

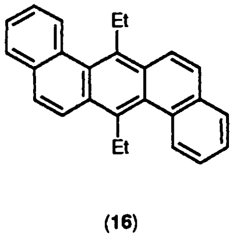
Picenes were obtained as components of the mixture of

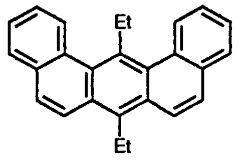

(13)


$\alpha N{-}\overset{\mathrm{Et}}{\overset{|}{\mathrm{C}}}\mathrm{H}{-\!-}\overset{\mathrm{Et}}{\overset{|}{\mathrm{C}}}\mathrm{H}{-}\alpha N$

(14)


(15)


(16)


(17)

αN = 1-naphthyl

products from the photolysis of mixtures of diasteroisomeric 1,2-dialkyl-1,2-bis-(1-naphthyl)ethylenes (**10**). Ethylenes in hexane or cyclohexane as solvent with added iodine were oxygenated[12] and irradiated for periods that varied from 20 min to 14 h.

The photoproduct is a mixture of compounds the composition of which varies unpredictably with reaction conditions. The ethyl compound will serve as an example. Preparative TLC or GLC leads to several fractions not all of which were pure.

Compounds (**13**) (mixture of stereoisomers) then (**14**) (apparently a single diastereoisomer) eluted, which follow the unchanged *trans*-isomer of the starting alkene (**10b**). The first polycyclic alkene to elute is (**15**), identified from the simplicity of its proton and carbon-13 NMR spectra, followed by the *cis*-alkene (**10b**). Then the picene (**9b**), and two structural isomers of (**9b**) follow, which both have only six kinds of aromatic proton, but which show one and two kinds of ethyl group, respectively, in the NMR spectrum and so may be compounds (**16**) and (**17**). Formation of anthracenes *i.e.* (**15**)–(**17**), as well as phenanthrenes *i.e.* (**9**) is not unprecedented,[13,14] nor is the migration of the naphthalene substituent from the α- to the β-position,[15] as implied by structures (**15**) and (**17**).

By such means, compounds (**9a**–**d**) were obtained. 13,14-Dimethylpicene (**9a**), m.p. 274 °C (Found: C, 93.95; H, 5.9. $C_{24}H_{18}$ requires C, 94.08; H, 5.92%). 13,14-Diethylpicene (**9b**), m.p. 197 °C (Found: C, 93.35; H, 6.65. $C_{26}H_{22}$ requires C, 93.37; H, 6.63%). 13,14-Di-n-hexylpicene (**9c**), m.p. 232–233 °C (Found: C, 91.15; H, 8.6. $C_{34}H_{38}$ requires C, 91.43; H, 8.57%). 13,14-Di-n-decylpicene (**9d**), m.p. 250–255 °C (Found; C, 89.5; H, 10.0. $C_{42}H_{54}$ requires C, 90.26; H, 9.74%).

Ethylenes (**10**) were obtained from ketones (**11**) by use of titanium(0), obtained from titanium tetrachloride by reduction with lithium aluminium hydride[16,17] as a catalyst. Ketones were obtained from the corresponding alcohols by oxidation.[18] These alcohols were obtained from 1-bromonaphthalene and the appropriate aldehyde using n-butyl-lithium in solution.[19–21]

References

1 J. E. Anderson, H. Pearson, and D. I. Rawson. *J. Chem. Soc., Chem. Commun.*, 1973, 95; J. E. Anderson, D. Casarini, and L. Lunazzi, *J. Org. Chem.*, 1989, in the press.

2 J. E. Anderson and D. J. D. Barkel, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1053.

3 J. E. Anderson, D. J. D. Barkel, and F. S. Jorgensen, *J. Chem. Soc., Perkin Trans. 2*, 1988, 199.

4 D. T. Dix, G. Fraenkel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 1966, 517.

5 C. A. Cupas, J. M. Bollinger, and M. Haslanger, *J. Am. Chem. Soc.*, 1968, **90**, 5502.

6 F. Imashiro, A. Saika, and Z. Taira, *J. Org. Chem.*, 1987, **52**, 5727.

7 K. Takegishi, F. Imashiro, T. Terao, and H. Saika, *J. Chem. Phys.*, 1984, **80**, 1089.

8 R. Munday and I. O. Sutherland, *J. Chem. Soc. B*, 1968, 80.

9 R. N. Armstrong, H. L. Ammon, and J. N. Darnow, *J. Am. Chem. Soc.*, 1987, **109**, 2077.

10 A. Mannschreck, E. Gmahl, T. Burgmeister, F. Kastner, and V. Sinnwell, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 270.

11 N. L. Allinger and H. L. Flanagan, *J. Comput. Chem.*, 1983, **4**, 399.

12 F. B. Mallory and C. W. Mallory, *Org. React.*, 1984, **30**, 1.

13 S. D. Cohen, M. V. Mijovic, and G. A. Newman, *J. Chem. Soc., Chem. Commun.*, 1968, 722.

14 P. R. West, S. K. Chaudhury, J. M. Vernon, and R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 1984, 613.

15 J. E. Anderson, D. J. D. Barkel, and J. E. Parkin, *J. Chem Soc., Perkin Trans 2*, 1987, 955.

16 R. Dams, M. Malinowski, I. Westdorp, and H. Y. Geise, *J. Org. Chem.*, 1982, **47**, 248.

17 J. E. McMurry, M. P. Flemming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, 1978, **42**, 3255.

18 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.

19 P. D. Bartlett and E. B. Lefferts, *J. Am. Chem. Soc.*, 1955, **77**, 2804.

20 H. Gilman, C. G. Brammer, and R. U. Ingham, *J. Org. Chem.*, 1957, **22**, 685.

21 R. G. Jones and H. Gilman, *Org. Reactions*, 1951, **6**, 339.

22 'Spectral Atlas of Polycyclic Aromatic Compounds,' vol. 2, Kluwer, Dordrecht, 1988.

Paper 0/00454E
Received 31*st January* 1990
Accepted 7*th March* 1990