¹H N.M.R. Spectroscopic Studies of Rotational Isomers of Several 1,2-Diarylacenaphthylenes: Conformational Barriers and Buttressing Effects

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The conformational behaviour of 1,2-di-*o*-tolylacenaphthylene and seven of its 3′,3″-disubstituted derivatives has been investigated. The existence of the *syn* and *anti* isomers is evident from the resolution of the two respective pairs of methyl groups in their ¹H n.m.r. spectra at room temperature. Dynamic ¹H n.m.r. studies indicate that the rotational barriers, in the range 76–85 kJ mol⁻¹, are dependent on the nature of the 3′,3″-substituents. The buttressing effect of these substituents is found to follow the order: H < CN < CH_3 < Cl < CH_2OH < CHO ≈ CH_2Br. Interestingly, one of the precursors (a pinacol) to 1,2-di-*o*-tolylacenaphthylene shows both a propelling process and free rotation of the aryl rings. The corresponding pinacolone also exhibits a possible propelling interconversion of the two tolyl rings.

The possibility that the two benzene rings in biphenyl and its derivatives might be non-coplanar was realized some 80 years ago.[1] The theory of restricted rotation about the single bond joining the two benzene rings was, however, advanced only 20 years later.[2] Atropisomerism in numerous substituted biphenyls, readily evident from the optical resolution of enantiomers, was then extensively investigated.[3] Such restricted rotation is also expected to be observed in polyphenyl systems,[3] *e.g.* the *o*-

(1; X = CH₃)

	X	Y
(2)	CH₃	H
(3)	H	CH₃
(4)	CH₃	CH₃

syn-(5a)

anti-(5b) *anti*-(5b′)

terphenyls or in general 1,2-diarylbenzenoids, leading to the existence of rotational isomers when appropriate substituents are present in the benzene rings. This phenomenon has been clearly demonstrated in the conformational studies of 1,2-di-*o*-tolylbenzene (1),[4] and the 9,10-ditolylphenanthrenes (2) and (3).[5] Variable-temperature ¹H n.m.r. studies have also readily provided an estimation of the rotational barriers of the aryl rings between the *syn* and *anti* isomers of (1)[4] and (3).[5] 1,2-Di-*o*-tolylacenaphthylene (5), although it is not a 1,2-diarylbenzoid, is expected to behave similarly. In addition, results from conformational studies of sterically hindered tetrasubstituted ethylenes [(5) could be considered as a hindered tetra-aryl ethylene] by dynamic ¹H n.m.r. spectroscopy[6] would further suggest that discrete rotational isomers of (5), namely *syn*-(5a) and *anti*-(5b) and (5b′), could be observed by spectroscopic studies. This paper thus reports the existence of rotational isomers in 1,2-di-*o*-tolylacenaphthylene (5) and a series of its 3′,3″-substituted derivatives, and the estimation of their respective barriers to rotation by variable-temperature ¹H n.m.r. spectroscopy.
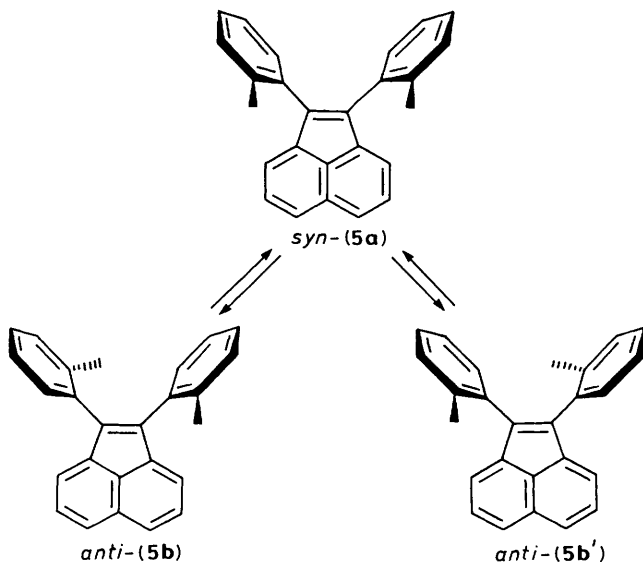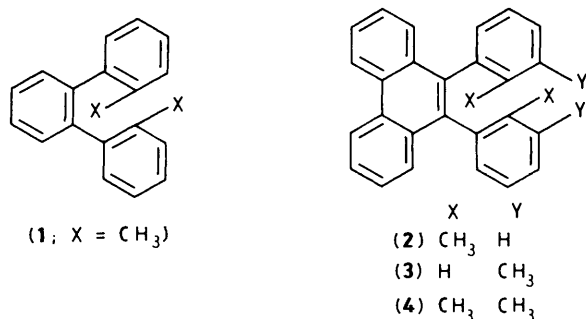
Results and Discussion

Syntheses.—In our attempt to synthesize the acenaphthylene-annelated dimethyldihydropyrene (6),[7] a series of 3′,3″-disubstituted 1,2-di-*o*-tolylacenaphthylenes were required as precursors. Although the addition[8,9] of aryl Grignard reagents to acenaphthenequinone and the subsequent pinacol rearrangements[9] of the diols have been extensively studied, we were interested in further converting the pinacolones to daryl acenaphthylenes. Thus, treatment of acenaphthenequinone with *o*-tolylmagnesium chloride resulted in a 40% yield of the diol (7). Only one isomer, m.p. 172–174 °C, was isolated. This is believed to be the *trans*-isomer similar to other reported examples.[8,9] Rearrangement of (7) in acetic acid in the presence of a catalytic amount of concentrated sulphuric acid yielded the ketone (8) which could be readily reduced to (9) with lithium aluminium hydride. Treatment of (9) in an acetic acid solution of iodine readily afforded di-*o*-tolylacenaphthylene (5) in 86% yield. A similar synthetic sequence starting with the mono-Grignard reagent from 2,6-dichlorotoluene[10] led to the diarylacenaphthylene (10). The series of derivatives (11)–(15) were then obtained following a similar route reported[11] earlier for a series of 9,10-diarylphenanthrenes. In order to compare these results with results obtained from the conformational
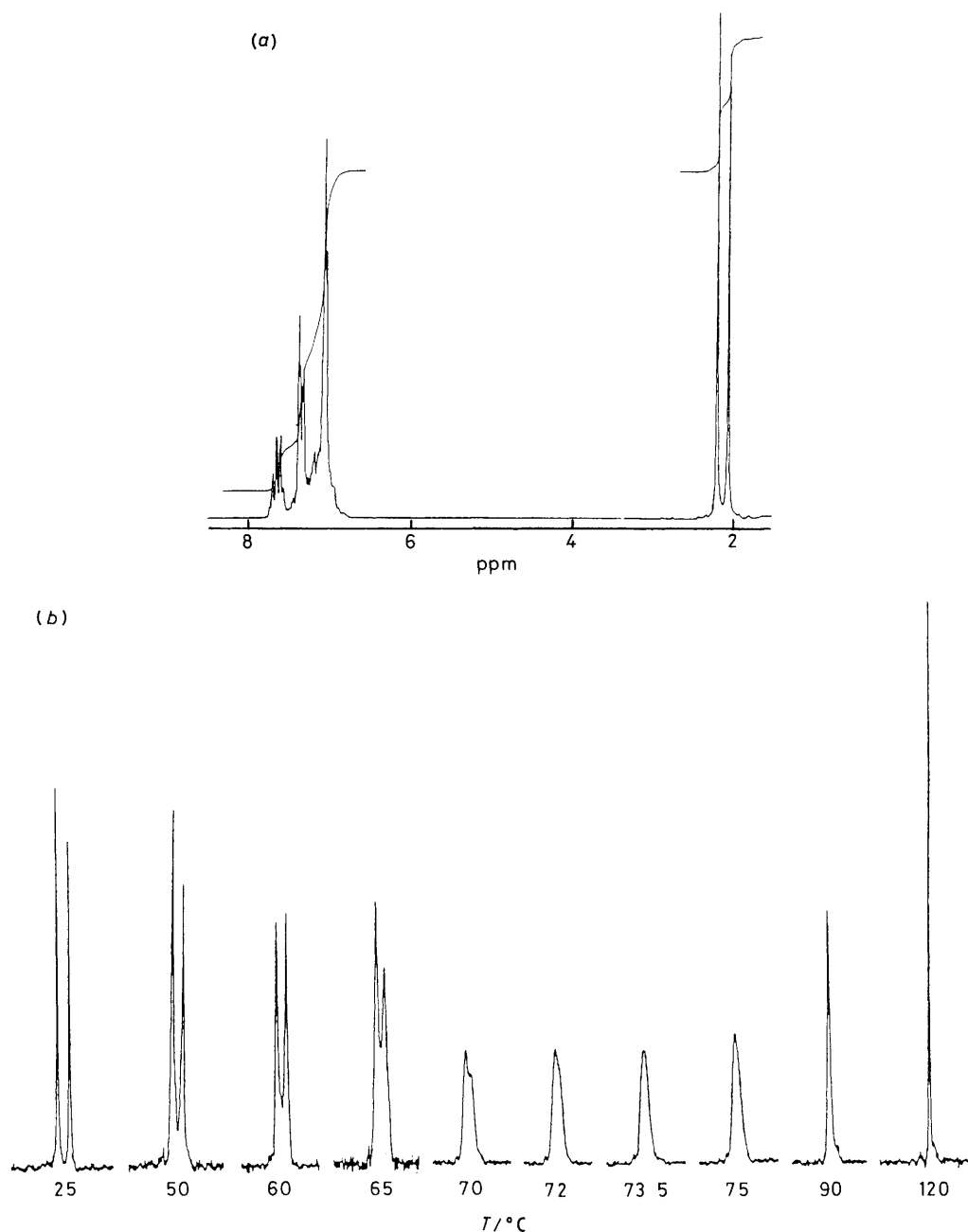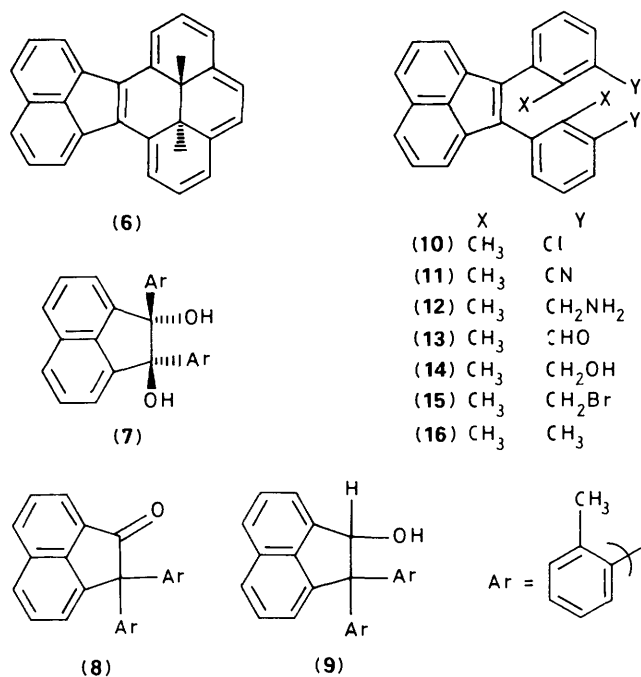
Figure 1. (a) ^{1}H N.m.r. spectrum of 1,2-di-o-tolylacenaphthylene (5) ([^{2}H]chloroform; 90 MHz). (b) ^{1}H N.m.r. spectra of the methyl protons of (5) at different temperatures ([^{2}H$_5$]nitrobenzene; 90 MHz).

studies of the 9,10-dixylylphenanthrene (4),[12] the 1,2-dixylyl-acenaphthylene (16) was also prepared by reduction of the dibromide (15). Thus treatment of (15) with lithium aluminium hydride in refluxing tetrahydrofuran readily afforded the desired hydrocarbon (16) in 60% yield.

Rotational Isomers.—The two types of methyl protons in *syn*-isomer (5a) and *anti*-isomers (5b) and (5b') are in different magnetic environments and thus would be expected to appear at different chemical shifts. In fact the presence of such *syn* and *anti* rotational isomers was clearly evident when two well-resolved singlets for the methyl groups at the 2',2"-positions were observed in the respective ^{1}H n.m.r. spectra (90 MHz) of (5) and (10)–(16) in [^{2}H]chloroform at room temperature. The spectrum of (5) is shown in Figure 1(a). Even the respective reference protons at the 3',3"-positions, namely the formyl

protons in (13), the methylene protons in (14) and (15), and the 3',3"-methyl protons in (16), also appeared as two separate singlets, although the methylene protons in (14) and (15) are diastereotopic and should theoretically further resolve into AB systems.

The two tolyl rings in (5) are expected to tilt at an angle to the acenaphthylene moiety, similar to biphenyl systems.[13] Flipping processes [14] of the tolyl rings could then occur as shown in Figure 2. The presence of a mixture of these conformers would, in principle, result in several methyl signals in the ^{1}H n.m.r. spectrum. It is, however, believed that there are no substantial barriers [15] to these processes and thus the equilibria should be fast within the n.m.r. time scale. The rapid interconversions will then result in two averaged singlets for the methyl groups of the *syn*- and *anti*-isomers of (5), respectively. These methyl signals (δ 2.14, 2.01) are observed at ca. 0.2—0.4 ppm upfield from the

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(6)

	X	Y
(10)	CH$_3$	Cl
(11)	CH$_3$	CN
(12)	CH$_3$	CH$_2$NH$_2$
(13)	CH$_3$	CHO
(14)	CH$_3$	CH$_2$OH
(15)	CH$_3$	CH$_2$Br
(16)	CH$_3$	CH$_3$

(7)

(8)   (9)   Ar =

Table 1. Solvent shifts/Hz on the resolution of methyl protons at the 2',2''-positions in (10) and (11).

Solvent	$\Delta\delta^a$ for (10)	$\Delta\delta^a$ for (11)
[^{2}H]Chloroform	2.7	7.2
Carbon tetrachloride	2.4	—^{b}
Hexachlorobutadiene	unresolved	unresolved
[^{2}H$_8$]Toluene	unresolved	2.4
[^{2}H$_5$]Nitrobenzene	5.1	6.4

^{a} Difference in chemical shifts for the methyl protons at the 2',2''-positions. ^{b} Low solubility.

methyl signal of toluene (δ 2.37),[16] presumably due to a small shielding effect of the opposite tolyl ring and/or the acenaphthylene ring. An unambiguous assignment of the two singlets to the *syn* and *anti*-isomers of (5) based on the chemical shift difference would, however, be impossible.

In the search for a suitable solvent which would allow dynamic n.m.r. studies at higher temperatures, it was found that the resolution of the methyl protons at the 2',2''-positions is dependent on the solvent shifts. The results observed for (10) and (11) are summarised in Table 1. [^{2}H$_8$]Toluene, a solvent which would in principle allow variable-temperature studies over a relatively wide range of temperature was found to be unsuitable for (10). On the other hand, the resolution of the methyl signals was consistently good in [^{2}H$_5$]nitrobenzene (Table 2). A representative dynamic n.m.r. experiment [Figure 1(*b*)] showed that the two methyl signals broadened as the temperature was raised, coalesced at a particular temperature, and reappeared as a sharp singlet at the averaged chemical shift at still higher temperatures. This phenomenon is typical of a dynamic uncoupled AB system.[17] When the sample was cooled, the original spectrum at room temperature was again observed. This is consistent with a true conformational interconversion between the *syn* and *anti* rotational isomers.

Conformational Barriers.—An estimation of the energy barrier for the *syn* $\rightleftharpoons$ *anti* interconversion process described above could be obtained from the coalescence temperature (T_c)

method.[4,5,17,18] An appreciable dependence of the frequency separation (Δv) of the methyl peaks on temperature was, however, observed. Thus the chemical shift difference (Δv) at T_c was calculated by extrapolating a linear plot of the chemical shift differences observed at *ca.* 25–60 °C where the rate of the site exchange is expected to be slow within the n.m.r. time scale. The transition state free energy at coalescence, $\Delta G_c^{\ddagger}$, could then be calculated from the following equation: $\Delta G_c^{\ddagger} = 0.019T_c(9.972 + \log T_c/\Delta v)$ kJ mol^{-1}.[17,19] This equation ideally applies only to equally intense exchanging sites; deviations from unity in the examples examined (Table 2) are not very significant and thus errors derived from this aspect are likely to be small. The $\Delta S^{\ddagger}$ value for rotational isomerism in the closely related compounds (5) and (10)–(16) is also expected to be approximately constant and thus the $\Delta G_c^{\ddagger}$ values obtained could be reasonably compared in order to indicate the relative energy barriers for the *syn* $\rightleftharpoons$ *anti* interconversion processes. On a 90 MHz spectrometer, the Δv values at 25 °C for (10) (5.1 Hz), (11) (6.4 Hz), and (13) (3.4 Hz) relative to the line-width of the signals did not seem to be sufficiently large to meet the requirement for this method of analysis. The small Δv values resulted in difficulty in acquiring an accurate T_c value and a temperature-dependent plot. The corresponding data were thus redetermined on a 250 MHz spectrometer (Table 2). The dynamic n.m.r. results for the systems under study in this work are summarized in Table 2. The barriers to rotation of the aryl rings in the series of 1,2-diarylacenaphthylenes were observed to be in the range 76–85 kJ mol^{-1}.

The *syn* $\rightleftharpoons$ *anti* isomerism in (5) and (10)–(16) should involve the rotation of at least one of the aryl rings. A similar rotational process is also expected to occur in (1)–(4). The energy barrier for isomerism reported for (1) (61.9 kJ mol^{-1})[4] is *ca.* 14 kJ mol^{-1} lower than that found for (5). A comparison of the energy barriers of (10), (11), and (13) with those of the corresponding 3',3''-disubstituted derivatives[4] of (1) also shows an average increase of about 11–12 kJ mol^{-1} in the former series. On the other hand, the similar rotational interconversion in (2) (*ca.* 130 kJ mol^{-1})[20] and (4) (*ca.* 140 kJ mol^{-1})[12] involves rotational barriers *ca.* 55 kJ mol^{-1} higher than those observed in (5) and (16), respectively. As the transition states in the rotational isomerism in (1)–(5) and (10)–(16) would be expected to involve near-planar aryl rings (see below), the above relative barriers are qualitatively consistent with an expected increase in the relative measures of 'steric effects' observed in triphenylene (17), dibenzofluoranthene (18), and dibenzochrysene (19).

(17)   (18)   (19)

R = H or CH$_3$
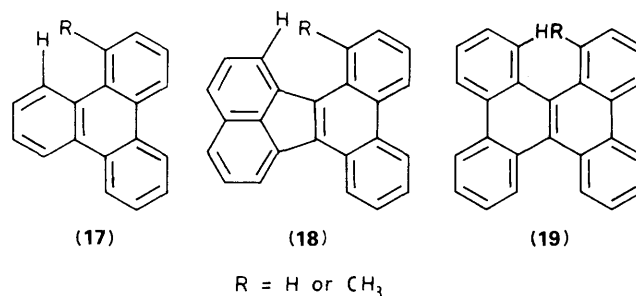
The conformational behaviour of (7) and (8) also deserve some mention. Although (7) is believed to be a *trans*-diol,[8,9] its ^{1}H n.m.r. spectrum in [^{2}H]chloroform showed three methyl singlets at δ 1.35, 1.56, and 2.33, respectively, in a ratio of *ca.* 1:2:1. This observation would suggest that (7) exists as the two rotamers (7a) [or (7a')] and (7b). The former showed a 'normal' toluene methyl signal (δ 2.33) and a methyl group (δ 1.35) shielded by the naphthalene moiety. The latter, with both methyl groups projecting over the naphthalene moiety (δ 1.56),
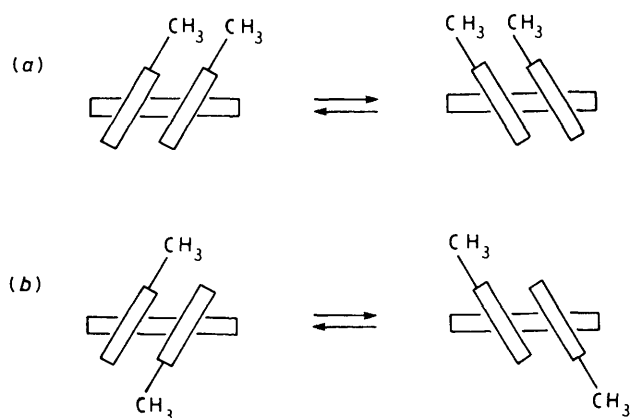
Figure 2. Simplified diagrams to illustrate the flipping processes of (a) syn and (b) anti 1,2-di-o-tolylacenaphthylene (5).

Table 2. Dynamic n.m.r. data for the barrier to rotation in 1,2-diaryl-acenaphthylenes.

Compound	Y	Ratio[a]	$\Delta v/Hz$ (ca. 25 °C)	$\Delta v/Hz$[b] (at T_c)	$T_c/°C$	$\Delta G_c^{\ddagger}/$ kJ mol^{-1}
(5)	H	1.0:1.1	12.5[c]	8.3[c]	72[c]	76.0
(10)	Cl	1.0:1.3	15.2[d]	8.2[d]	108[d]	84.3
(11)	CN	1.0:1.2	18.6[d]	10.7[d]	98[d]	81.1
(12)	CH_2NH_2	1.0:1.4	13.4[c]	—[e]	—[e]	—[e]
(13)	CHO	1.0:1.2	12.9[d]	5.1[d]	106[d]	85.3
(14)	CH_2OH	1.0:1.2	14.2[c]	6.6[c]	107[c]	84.7
(15)	CH_2Br	1.0:1.1	26.1[c]	11.4[c]	117[c]	85.3
(16)	CH_3	1.0:1.1	11.2[c]	8.1[c]	100[c]	82.5

[a] Ratio of rotational isomers determined by relative peak heights of the 2',2''-methyl signals. [b] Calculated by linear extrapolation to T_c of the chemical shift differences observed at 25–60 °C. [c] Data obtained from spectra determined using ca. 25–30 mg of sample in 0.5 cm^3 [$^2H_5$]nitrobenzene on a JEOL FX90Q (90 Mz) spectrometer. [d] Data obtained from spectra determined using ca. 20 mg of sample in 0.5 cm^3 [$^2H_5$]nitrobenzene on a Bruker WM250 (250 MHz) spectrometer. [e] No data available due to decomposition of sample.

has C_2 symmetry making the methyl groups equivalent. The conformation (7c) is believed to be least favourable due to two pairs of interaction between the methyl and hydroxy groups. Similar observation has been reported for other sterically crowded systems.[21] In the dynamic ^1H n.m.r. study of (7) in [$^2H_5$]nitrobenzene, all three methyl signals (shifted slightly to δ 1.60, 1.78, and 2.42 respectively) broadened as the temperature was raised. Although peak overlapping occurred as the peaks broadened, signals at δ 1.60 and 2.42 were observed to collapse first (with the relatively sharper signal at δ 1.78 still clearly visible) at about 102 °C ($T_c = 375$ K, $\Delta v = 73.7$ Hz, $\Delta G_c^{\ddagger} = 76.1$ kJ mol^{-1}). We believe that this phenomenon would in principle further result in an averaged signal at δ 2.01 at a higher temperature, corresponding to the propelling interconversion (7a) $\rightleftharpoons$ (7a'). This averaged signal and that at δ 1.78 then further collapsed at about 110 °C, resulting eventually in a singlet observed at δ 1.92 at 170 °C ($T_c = 383$ K, $\Delta v = 20.3$ Hz, $\Delta G_c^{\ddagger} = 81.8$ kJ mol^{-1}). This would correspond to the free rotation of the two tolyl rings.

The ^1H n.m.r. spectrum ([^2H]chloroform) of (8) was relatively simpler. The methyl groups appeared as two singlets at δ 2.27 and 1.90 respectively in a 1:1 ratio. This is consistent with conformer (8a'). The slightly less shielded 2''-methyl signal (δ 1.90) compared with those in (7a) (δ 1.35) and (7b) (δ 1.56) could be due to a tilting ring [see (8a')] to minimize the steric

(7a)

(7a')

(7b)

(7c)

(8a)

(8a')
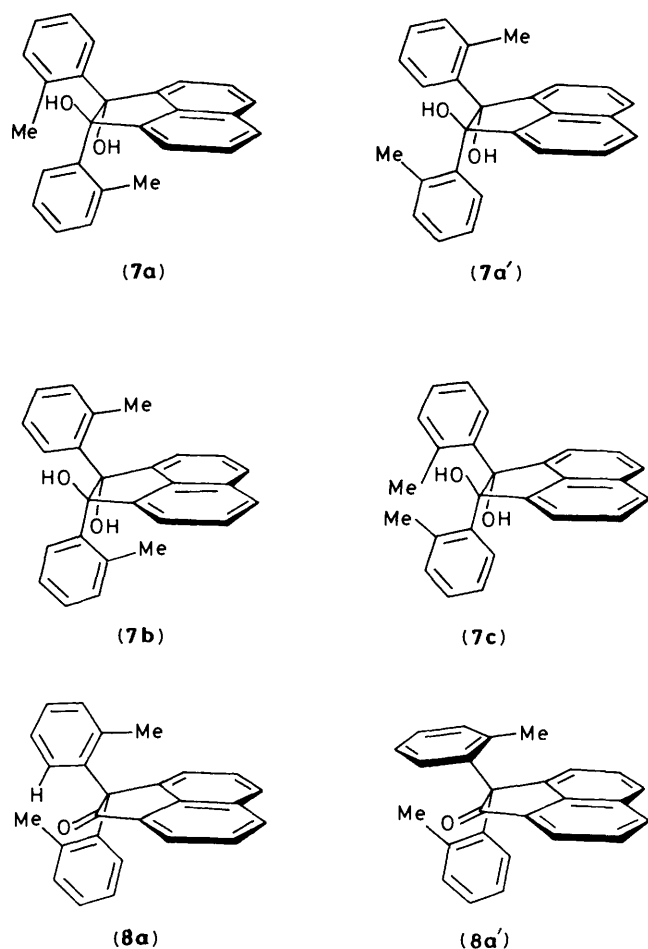
interaction between 6''-H and the 2'-methyl group [see (8a)]. The 6'-H was also clearly observed as a relatively shielded broad doublet ($J = 7.8$ Hz) at δ 6.59. Although a significant solvent shift in [$^2H_5$]nitrobenzene resulted in poorer resolution of the methyl signals (δ 2.07, 2.03), dynamic ^1H n.m.r. study of (8a') indicated a rotational barrier of ca. 75.5 kJ mol^{-1} ($T_c = 333$ K, $\Delta v = 3.6$ Hz) for the tolyl rings—a value comparable to that required for the propelling processes of the tolyl rings in (7a) $\rightleftharpoons$ (7a').

Buttressing Effects.—Two transition states, namely (I) and (II), are possible for the rotational isomerism in (5) and (10)–(16). In either transition state, one aryl ring is expected to be near perpendicular and another near planar to the acenaphthylene moiety. Unfavourable interactions in either case would

(I)

(II)
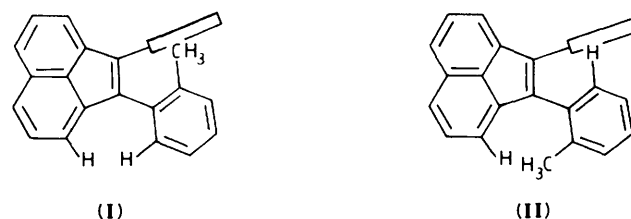
involve the 2'-methyl group. In (1) the 2'-methyl group is projecting into the π-cloud of the opposite aryl ring whereas steric interaction between the 2'-methyl group and 3-H occurs in (II). The substituent 3'-X, however, seems to alter the rotational barrier slightly. This, we believe, is due to the

buttressing effect of the substituent. A greater steric demand of 3′-X would force the 2′-methyl group closer to the π-cloud of the opposite aryl ring in (I) or the 3-H in (II), thus increasing the energy barrier for isomerisation. Previous work on the buttressing effect in biphenyl systems[22] has shown that the steric demand of selected functional groups follows the decreasing order: NO_2 > Br > Cl > CH_3 > OCH_3; our systems would, however, supplement the series with more examples of varying nature in steric demand. A few comparisons on the buttressing effect of different substituents could be made based on the energy barriers observed for (5) and (10)–(16). Obviously (5) would experience the least buttressing effect due to the smallest steric demand of 3′-H. Replacement of the 3′-H with chlorine as in (10) increases the rotational barrier significantly by 8.3 kJ mol^{-1}. The increase in rotational barrier in going from (11), (16), to (10) is consistent with the increase in steric demand[23] of the cylindrical cyano group, the conical methyl group, and the spherical chlorine atom. With the 3′-methyl group as a reference, substitution of a proton at the 3′-methyl group also increases the buttressing effect as in (14) and (15). The relatively large spatial requirement of the bromine atom in (15) results in the highest rotational barrier among all the 3′,3″-disubstituted derivatives of (5) studied in this work. Another interesting observation is the higher rotational barrier observed for (13) compared with that of (14). In fact our results seem to show a similar steric demand for both the formyl (13) and the bromomethyl groups (15). Alkyl aryl ketones are known to prefer coplanarity between the ring and the carbonyl group in order to achieve maximum π-electron delocalization.[24] Such a preference in (13) would then be expected to increase appreciably the steric demand of the formyl group. Our results on the rotational barriers in the series of 9,10-diarylacenaphthylenes (5) and (10)–(16) have thus indicated that the buttressing effect (steric demand) of selected functional groups follows the order: H < CN < CH_3 < Cl < CH_2OH < CHO ≈ CH_2Br.

Experimental

M.p.s were determined on a Sybron/Thermolyne MP 12615 melting point apparatus and were uncorrected. [1]H N.m.r. spectra were determined in [2H]chloroform on a JEOL FX90Q (90 MHz) Fourier Transform spectrometer. Dynamic n.m.r. studies were carried out in [2H5]nitrobenzene on a JEOL FX90Q (90 MHz) or a Bruker WM250 (250 MHz) Fourier Transform spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard. The i.r. spectra were recorded on a Perkin-Elmer 1310 i.r. spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV, electron impact being used. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. All evaporation were carried out under reduced pressure on a rotary evaporator at ca. 40 °C, and all organic layers were washed with water and dried with anhydrous magnesium sulphate. Preparations of (10)–(15) will be published elsewhere.

1,2-Dihydroxy-1,2-bis(2-methylphenyl)acenaphthene (7). —The Grignard reagent was first prepared by reacting 2-chlorotoluene (8.33 g, 65 mmol) with magnesium (1.58 g, 65 mmol) in dry THF (50 cm³) with 1,2-dibromoethane as an initiator. The reaction mixture was heated under reflux for 8 h under nitrogen and cooled in an ice-bath. 9,10-Acenaphthenequinone (1.50 g, 8.23 mmol) was added and the reaction mixture was again heated at reflux for 15 h, cooled in an ice-bath, and hydrolysed with conc. HCl. Dichloromethane was added to extract the reaction mixture, then washed, dried, and evaporated. The crude product was filtered through a column of silica gel with hexane–dichloromethane (1:2) as eluant to give

the diol (7), 1.20 g (40%). Recrystallization from benzene–cyclohexane gave colourless crystals of (7), m.p. 172—174 °C (Found: C, 85.0; H, 6.0. $C_{26}H_{22}O_2$ requires C, 85.2; H, 6.1%); $v_{max.}$ 3 200 (OH), 3 040, 3 000, 2 900, 1 590, 1 470, 1 440, 1 275, 1 195, 1 140, 1 090, 1 020, 990, 900, 815, 780, 735, 660, and 640 cm^{-1}; δ_H(90 –Hz) 1.35, 1.56, 2.33 (ratio ca. 1:2:1, total 6 H, s, Me), 2.14, 2.59 (ratio 1:1, total 2 H, s, OH, exchanged with D_2O), and 6.6–8.2 (14 H, m, Ar); m/z 366 (M^+, 5%), 364 (55), 348 (40), 330 (35), 305 (25), 273 (20), 246 (84), 245 (50), 229 (23), 202 (33), and 119 (100).

2,2-Bis(2-methylphenyl)acenaphthen-1-one (8).—The diol (7) (0.80 g, 2.2 mmol) was dissolved in acetic acid (25 cm³) and conc. H_2SO_4 (0.7 cm³) was added. The mixture was heated at reflux for 45 min, cooled, and extracted with dichloromethane. The organic layer was washed with aqueous $NaHCO_3$ solution, dried, and evaporated. Filtration through a column of silica gel using hexane–dichloromethane (1:1) as eluant yielded the ketone (8), 0.66 g (87%). Recrystallization from methanol gave colourless crystals of (8), m.p. 132–133 °C (Found: C, 89.4; H, 5.7. $C_{26}H_{20}O$ requires C, 89.6; H, 5.8%); $v_{max.}$ 3 060, 2 920, 1 715 (CO), 1 590, 1 480, 1 455, 1 425, 1 375, 1 360, 1 335, 1 250, 1 215, 1 160, 1 120, 1 060, 1 030, 990, 970, 940, 925, 890, 830, 820, 780, 745, 720, 670, and 640 cm^{-1}; δ_H(90 MHz) 1.90, 2.27 (ratio 1:1, total 6 H, s, Me), 6.59 (1 H, br d, J = 7.8 Hz, 6′-H), and 6.8–8.2 (13 H, m, Ar); m/z 348 (M^+, 100%), 330 (97), 305 (84), 289 (67), 229 (60), 228 (37), and 144 (29).

2,2-Bis(2-methylphenyl)acenaphthen-1-ol (9).—A solution of (8) (0.50 g, 1.44 mmol) in dry THF (25 cm³) was added to $LiAlH_4$ (0.16 g, 4.31 mmol), suspended in dry THF (5 cm³) under nitrogen. The mixture was then heated at reflux for 45 min, decomposed (water followed by 1 mol dm^{-3} HCl) and extracted with dichloromethane. The organic layer was washed, dried, and evaporated to afford the crude product. Recrystallization from benzene–hexane gave colourless crystals of (9) (0.47 g, 94%), m.p. 164–165 °C (Found: C, 89.1; H, 6.2. $C_{26}H_{22}O$ requires C, 89.1; H, 6.3%); $v_{max.}$ 3 400 (OH), 3 040, 2 950, 1 590, 1 475, 1 440, 1 290, 1 165, 1 105, 1 075, 1 040, 900, 820, 775, 745, 730, 720, and 640 cm^{-1}; δ_H(90 MHz) 1.53 (1 H, br s, OH, exchanged with D_2O), 2.00 (6 H, br s, Me), 6.28 (1 H, br s, 1-H), and 6.9—7.8 (14 H, m, Ar); m/z 350 (M^+, 11%), 332 (100), 317 (15), 289 (11), 245 (36), 239 (46), 151 (17), and 119 (14).

1,2-Bis(2-methylphenyl)acenaphthylene (5).—The alcohol (9) (0.30 g, 0.86 mmol) and iodine (0.1 g) were added to acetic acid (30 cm³) and the mixture was heated at reflux for 1 h. The reaction mixture was cooled, decomposed with aqueous sodium thiosulphate solution until the brown colour was discharged, and then extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was chromatographed on silica gel using hexane as eluant to yield the desired hydrocarbon (5) (0.25 g, 86%) as a thick orange-red oil (Found: M, 332.1562. $C_{26}H_{20}$ requires M, 332.1565); $v_{max.}$ 3 020, 2 900, 1 470, 1 420, 1 090, 1 025, 900, 815, 760, 740, 720, and 630 cm^{-1}; δ_H 2.01, 2.14 (ratio 1.0:1.1, total 6 H, s, Me), and 7.0–7.8 (14 H, m, Ar); m/z 332 (M^+, 100), 302 (11), 239 (54), 192 (55), 160 (64), and 128 (36).

1,2-Bis(2,3-dimethylphenyl)acenaphthylene (16).—A solution of dibromide (15) (0.20 g, 0.386 mmol) in dry THF (20 cm³) was added dropwise to a suspension of $LiAlH_4$ (36 mg, 0.964 mmol) in dry THF (10 cm³). The reaction mixture was heated at reflux under nitrogen for 5 h, cooled, and decomposed with ethyl acetate. Dilute HCl was added until all solid materials dissolved. The mixture was then extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was filtered through a column of silica gel using hexane–dichloromethane (1:1) as eluant to yield the desired

hydrocarbon (16) (81 mg, 60%). Recrystallization from benzene–ethanol gave orange crystals of (16), m.p. 168–170 °C (Found: C, 93.3; H, 6.7. $C_{28}H_{24}$ requires C, 93.3; H, 6.7%); $v_{max.}$ 3 200, 2 925, 2 900, 1 575, 1 445, 1 420, 1 370, 1 205, 1 110, 1 075, 1 050, 1 000, 980, 900, 810, 775, 755, 740, and 720 cm^{-1}; δ_H(90 MHz) 1.98, 2.08 (ratio 1:1, total 6 H, s, 2′,2″-Me), 2.23, 2.25 (ratio 1:1, total 6 H, s, 3′,3″-Me), and 7.0–7.8 (12 H, m, Ar); m/z 360 (M^+, 100%), 345 (28), 330 (17), 254 (23), 253 (31), 239 (23), 165 (13), and 156 (11).

Acknowledgements

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