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^{1}H and ^{13}C NMR spectral studies of some 2,4-diphenylquinoline derivatives

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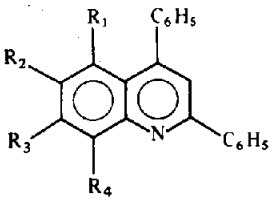
Abstract—The 400 MHz ^{1}H and 15 MHz ^{13}C NMR spectra of a series of 2,4-diphenylquinoline derivatives are presented. The characteristic H-3 and *ipso*-phenyl carbon signals are the most useful for the identification of these compounds. The effects of a *peri*-phenyl/methyl couple upon the ^{1}H and ^{13}C NMR spectra have been studied; these arise from the rotation and splaying out of the 4-phenyl ring.

1. INTRODUCTION

NMR spectroscopic studies of 2,4-diphenylquinoline derivatives are very scarce. The first report by REID and KOENIG [1] in 1972 of the 60 MHz NMR spectrum of 2,4-diphenylquinoline (1a) featured a very incomplete analysis which comprised a fourteen proton aromatic multiplet and a one proton olefinic singlet. MIYAJIMA *et al.* [2] later reported an aromatic multiplet only, extending from 7.1 to 8.4δ. NISHIO *et al.* [3] subsequently identified three separate multiplets representing ten, two and three protons, contrary to the earlier work [1] which noted a singlet resonance.

In view of this rather incomplete and contradictory situation, a 400 MHz ^{1}H NMR spectral study of several 1 derivatives has been undertaken, together with measurements of their ^{13}C chemical shifts, which have not been previously reported.



1

a: $R_1 = R_2 = R_3 = R_4 = H$,

b: $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$,

c: $R_1 = R_3 = H$, $R_2 = R_4 = CH_3$,

d: $R_2 = R_3 = H$, $R_1 = R_4 = CH_3$

2. EXPERIMENTAL

All samples were recorded as dilute solutions in $CDCl_3$, chemical shifts are reported as p.p.m. (δ) downfield from TMS. ^{1}H NMR spectra were recorded at 100 MHz (Jeol JNM-MH-100), 220 MHz (Perkin–Elmer R34 at P.C.M.U., Harwell), and 400 MHz (Bruker WH-400 at University of Sheffield). ^{13}C NMR spectra were obtained with a Jeol JNM-FX-60 spectrometer operating in the pulsed Fourier transform mode at 15 MHz, with broad band noise decoupling, pulse width 7 μs (45° pulse angle), pulse repetition rate 4 s, spectral width 1000 or 2500 Hz with 8K data points. For proton coupled spectra, the "Gated-1" alternatively pulsed sequence was used.

2,4-Diphenylquinoline (1a)

A mixture of freshly redistilled aniline (9.31 g, 0.10 mol) and dibenzoylmethane (24.67 g, 0.11 mol) was boiled under gentle reflux for 3 h. Water (50 ml) was added and the crude anil extracted with ether and dried ($MgSO_4$). The warmed crude anil was added dropwise to cold concentrated sulphuric acid (60 ml), keeping the temperature below 10°. When all the anil had been added, the solution was then heated on the water bath for one hour. The mixture was cooled, poured into ice water (500 ml) and made alkaline with solid sodium hydroxide. The crude product was filtered off, it was obtained as a yellow powder (9.6 g, 34%). Recrystallisation from an ethanol–water solvent pair afforded 1a as pale yellow prisms, m.p. 113–4°, [4] m.p. 114°. The picrate crystallised from ethanol as yellow needles, m.p. 201–2°, [5] m.p. 198°. By a similar procedure, 1b, 1c and 1d were also synthesised, the results obtained are shown in Table 1.

2-Phenylquinoline (m.p. 83–4°, [6] m.p. 83°) and 4-phenylquinoline (m.p. 59°, [7] m.p. 61°) were synthesised by established procedures. 2-Phenylpyridine and 4-phenylpyridine were commercially available.

3. RESULTS AND DISCUSSION

The analysis of the 400 MHz ^{1}H NMR spectrum of 1a is given in Table 2. The spectrum may conveniently be divided into three spectral regions as previously denoted by NISHIO *et al.* [3], however, these regions actually comprise 3H, 3H and 9H and *not* 3H, 2H and 10H as previously proposed [3]. The 10H multiplet could readily have been mistaken as that for the ten phenyl protons, which is clearly not the case. The three spectral regions overlap at 100 MHz, are partially resolved at 220 MHz, but are well separated at 400 MHz as shown in Fig. 1.

Table 1. Synthesis of 2,4-diphenylquinoline derivatives

Compound	Yield (%)*	M.p.	Molecular formula	Elemental-analysis Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
1b	20	†	$C_{22}H_{17}N$	89.3	5.9	4.9	89.5	5.8	4.7
1b picrate		208–9°	$C_{28}H_{20}N_4O_7$	64.2	3.9	10.6	64.1	3.8	10.7
1c	33	129–30°	$C_{23}H_{19}N$	89.4	6.3	4.6	89.3	6.2	4.5
1c picrate		173–4°	$C_{29}H_{22}N_4O_7$	64.4	4.1	10.3	64.7	4.1	10.4
1d	27	125–6°	$C_{23}H_{19}N$	89.0	6.2	4.8	89.3	6.2	4.5
1d picrate		158–9°	$C_{29}H_{22}N_4O_7$	64.8	4.0	10.3	64.7	4.1	10.4

*Crude yield based on aniline derivative.
†Sample could not be induced to crystallise (see also [7]).

Table 2. ^{1}H NMR spectra of 1a

δ	400 MHz (present work) Multiplicity	Integral	Assignment	Couplings	Literature assignment [3]
8.25	ddd	1 H	H-8	J_{78} 8.6 Hz J_{68} 1.2 Hz J_{58} 0.6 Hz	8.14–8.39 m 3 H
8.19	m	2 H	*o*-C_6H_5[2]		
7.91	ddd	1 H	H-5	J_{56} 8.2 Hz J_{57} 1.6 Hz J_{58} 0.6 Hz	7.72–7.95 m 2 H
7.82	s	1 H	H-3		
7.73	ddd	1 H	H-7	J_{78} 8.5 Hz J_{67} 6.9 Hz J_{57} 1.5 Hz	
7.54–7.58	m	5 H	C_6H_5[4]		7.35–7.65 m 10 H
7.52	m	2 H	*m*-C_6H_5[2]		
7.47	ddd	1 H	H-6	J_{56} 8.3 Hz J_{67} 6.9 Hz J_{68} 1.2 Hz	
7.46	m	1 H	*p*-C_6H_5[2]		

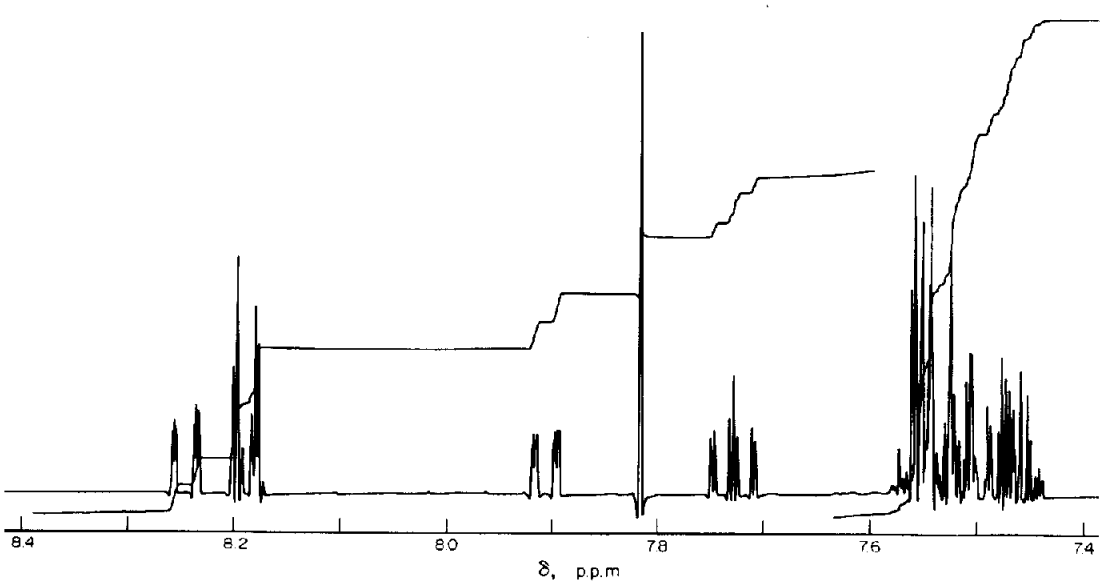
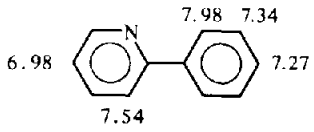


Fig. 1. 400 MHz ^{1}H NMR spectrum of 2,4-diphenylquinoline

The low field region comprised two signals, assigned to H-8 and the 2-phenyl *ortho* protons. The H-8 signal, which was absent in the spectra of 1c and 1d was a ddd, with couplings to H-7, H-6 and H-5. It formed part of an ABCD spin system which has been analysed by a first order treatment at 400 MHz. The remaining 2H signal approximated to a doublet, but contained considerable second order character, due to the minimal separation between the *meta*- and *para*- 2-phenyl chemical shifts. The *ortho* protons appeared so far downfield due to the diamagnetic anisotropy of the neighbouring aromatic ring, and the electrostatic field effect of the nitrogen lone pair. Similar downfield shifts have also been observed by GÜNTHER and CASTELLANO [8] for the H-3 proton in 2-phenylpyridine (2), likewise by SPOTSWOOD and TAIZER [9] in 2,2′-bipyridyl (3) and very recently by DRAKE and JONES [10] for 2,2′-biquinolyl.



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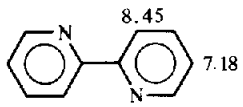


3

The central spectral region was regarded by NISHIO *et al.* [3] as a 2H multiplet. At 220 MHz and 400 MHz *three* well resolved signals were apparent. Although these signals were not completely separated at 100 MHz, they were nevertheless independently discernible. The signals were a "doublet", "singlet" and "triplet" respectively. The "doublet" (actually a ddd) represented H-5, part of the ABCD system. It appeared slightly downfield, compared with 2-phenylquinoline (see Table 3) due to a *peri*-deshielding effect [11a]. The singlet was readily assigned to H-3, since both positions 2- and 4- were occupied, resulting in a lack of splitting, any ^{5}J couplings to the *ortho*-phenyl protons should be very small. It was deshielded by two adjacent phenyl groups and appeared at a very similar chemical shift to that of H-5 in 2-chloro-3-benzyl-2,4-diphenylpyridine as recently reported by KATRITZKY *et al.* [12]. For the identification of 1 derivatives by ^{1}H NMR spectroscopy, this characteristic H-3 singlet is of the greatest value. The signal is readily discernible, even at 60 MHz, as noted by REID and KOENIG [1] for the "olefinic" proton. In the methylated derivatives 1b–1d it is well separated, since the remaining protons are shifted upfield leaving this region clearer. The "triplet" was due to H-7, another constituent of the ABCD spin system. The assignment was confirmed by spin decoupling experiments, irradiation of H-8 collapsed the signal, whilst irradiation of H-5 removed the fine *meta* coupling to leave a clear doublet of doublets, for the two remaining dissimilar *ortho* couplings. Further confirmation was obtained by selective removal of benzylic couplings [11b] to the well separated methyl groups in 1d.

The high field spectral region was particularly complex, and was only partially resolved at 400 MHz, at lower frequencies the signals overlapped considerably. In this region the signals for H-6 and for the remaining phenyl protons were present; total integration 9H. The 10H as previously suggested by NISHIO *et al.* [3] is therefore in error.

The 4-phenyl protons appeared as a complex multiplet which extended over just 0.04 p.p.m. at 400 MHz. At lower frequencies a singlet resonance only was observed, as previously found by HOUSE *et al.* [13] for the phenylnaphthalenes. The chemical shift of the 4-phenyl protons in 1a was very similar to those previously determined for 4-phenylpyridine (14) and 2-methyl-4-phenylquinoline [15].

The *meta*- and *para*- 2-phenyl protons appeared as two multiplets, with the *para* signal 0.06 p.p.m. upfield

Table 3. 400 MHz ^{1}H NMR spectra

	Chemical shift (δ)†									
							2-C_6H_5			4-C_6H_5
Compound*	H-2/H-4	H-3	H-5	H-6	H-7	H-8	*o*	*m*	*p*	
2-PQ	8.19	7.85	7.81	7.51	7.72	8.18	8.16	7.52	7.45	
4-PQ	9.00	7.53	8.02	7.63	7.86	8.47				7.53–7.59
1a		7.82	7.91	7.47	7.73	8.25	8.19	7.52	7.46	7.54–7.58
1b		7.80	7.85	7.26	(2.58)	8.17	8.24	7.50	7.44	7.51–7.54
1c		7.79	7.42	(2.42)	7.47	(2.92)	8.27	7.50	7.42	7.51–7.54
1d		7.70	(1.96)	7.11	7.45	(2.90)	8.27	7.49	7.42	7.36 (*o*) 7.41–7.44 (*m*/*p*)

*PQ: phenylquinoline.
†Values in parentheses are for the appropriate methyl group.

of that for the *meta* protons, which closely resembled the shieldings of 2 [8]. The remaining quinoline proton, H-6, also appeared in this region, the last constituent of the ABCD spin system.

The spectra of 1b, 1c and of 1d are given in Table 3. Those of 1b and 1c were very similar to that of 1a, introduction of the methyl groups facilitated certain assignments either by elimination of a particular proton signal, by introduction of additional long range benzylic coupling effects [11b], or through upfield shifts which left the singlet for H-3 further resolved.

The spectrum of 1d exhibited several interesting features. Whilst the CH_3(6) and CH_3(8) signals of 1c and 1d were unremarkable, the CH_3(5) peak in the *peri*-substituted compound 1d appeared at 1.98 δ, an upfield shift of 0.56 p.p.m. from CH_3(5) in 5-methylquinoline [16]. Similar upfield shifts of *peri*-methyl protons have also been experienced in the phenylnaphthalene [17] and phenylanthracene series [18, 19] as shown in Table 4.

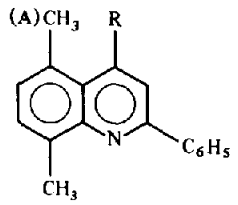
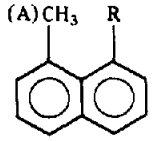
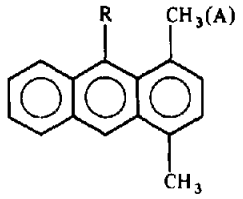
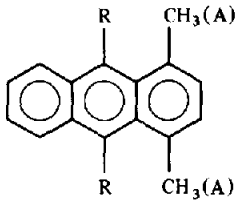
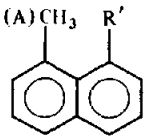
These effects have been explained [13] by the rotation of the phenyl group out of the plane of the naphthalene ring, such that the methyl protons become positioned in the anisotropic region of the aromatic ring. HARRIS *et al.* [20] have suggested, in accordance with the ring current shielding effect model of JOHNSON and BOVEY [21], that a dihedral angle of the order of 55° would correspond to the observed upfield methyl proton chemical shift. Substituent effects upon the phenyl proton shieldings have not been observed by the earlier workers, since the phenyl signal was either regarded as a singlet [18] or the phenyl shifts were not specifically analysed at all [17, 19, 20] due to the complexity of the spectra when determined at a lower magnetic field.

LE FÈVRE *et al.* [22] have estimated from a study of molar Kerr constants that liquid 1-phenylnaphthalene dissolved in non-polar media has a dihedral angle, between the aromatic ring planes, of 50°. The *peri*-proton alone being sufficient to prevent attainment of a uniplanar structure. No information is available, however, concerning the degree of splaying outwards of the phenyl group, such that the C(2)–C(1)–C(*ipso*) bond angle is increased beyond 120°. In the ^{1}H NMR spectrum of 1-phenylnaphthalene [13], the phenyl protons appeared as a singlet, but the precise shielding of the H-2 proton was not elucidated. In the present work, the closely similar compound 4-phenylquinoline has been examined (see Table 3). The phenyl protons are not quite equivalent and occur as a multiplet extending over only 0.06 p.p.m. at 400 MHz. The H-3 singlet is readily identified and absorbs at 7.53 δ, deshielded by 0.27 p.p.m, with respect to quinoline [23]. A similar situation is evident in the reported spectrum for 4-phenylpyridine [14]. The conformation of this compound is still a matter of debate, although a non-coplanar twisted form is preferred [24], certain experimental evidence favours the planar version [25]. The ^{1}H NMR spectra suggest that when a *peri*-phenyl/hydrogen couple is present, the relief of strain is accomplished by out-of-plane rotation of the phenyl group, but that it does not splay outwards. As a consequence the phenyl protons are essentially equivalent, and there is no anisotropic shielding effect upon the adjacent *ortho* proton on the naphthalene or quinoline ring.

Studies of the severely hindered *peri*-phenyl/phenyl couple have attracted much interest. The crystal structure [26] of 1,4,5,8-tetraphenylnaphthalene 4 indicates that the maximum angle between the mean planes of the phenyl groups and the central naphthalene is 58°. Furthermore, the phenyl groups are splayed apart such that the C(2)–C(1)–C(*ipso*) angle is increased to 123.4°, whilst the C(9)–C(1)–C(*ipso*) is reduced to 116.8°. The C(1)–C(8) distance is 2.510 Å, which increases to 2.945 Å between the *ipso*-phenyl carbons and to 4.820 Å between the *para* carbons. The ^{1}H NMR spectrum of 4 has been studied by RABINOVITZ, AGRANAT and BERGMANN [27]. The phenyl protons exhibited significant upfield shifts (0.61 p.p.m. for *ortho/meta*; 0.38 p.p.m. for *para*) accounted for by a mutual shielding effect of the two almost parallel phenyl groups. The smaller effect at the *para*-phenyl protons is consistent with their greater separation, as shown by the subsequent crystallographic study [26]. However, the chemical shifts must also include another, much smaller shielding component which arises from a second anisotropic effect originating from the naphthalene ring. This effect is only operative when the phenyl groups are splayed outwards thereby reducing the distance involved. In the reported ^{1}H NMR spectrum of 4 the four equivalent naphthalene protons absorb at 7.20 δ, an *upfield* shift of 0.26 p.p.m. compared with the parent hydrocarbon [11c], whilst in 4-phenylquinoline (and by analogy in 1-phenylnaphthalene) a *downfield* shift of 0.27 p.p.m. occurred, clear evidence for the second anisotropic shielding effect. The results obtained for 4 are also supported by studies upon 1,8-diphenylnaphthalene 5. The crystal structure [28] indicates a dihedral angle of 70° again with a significant splaying of the phenyl groups. In the reported ^{1}H NMR spectrum [13] the phenyl protons appeared as a broadened singlet shifted upfield by 0.53 p.p.m., detection of potential different effects at the *ortho/meta/para* positions is therefore not feasible. The naphthalene ring proton ABC spin system was not specifically assigned [13]. The signals may now be interpreted as 7.26 δ (H-2/H-7), 7.44 δ (H-3/H-6) and 7.83 δ (H-4/H-5), such that H-2/H-7 are shielded by 0.20 p.p.m. whilst the remaining protons are little affected. These effects closely parallel those observed for 4 and are consistent with the present proposal that the splaying outwards of the phenyl groups renders the second anisotropic shielding effect operative.

Crystallographic studies of compounds containing a *peri*-phenyl/methyl couple are not yet available. However, from the previous discussion it may be postulated that the phenyl group should rotate out of the plane of the naphthalene ring, with a dihedral angle

Table 4. *Peri*-substituent effects in aromatic and heteroaromatic compounds

Compound	Chemical shift (δ) of CH_3 (A) R = H	R = C_6H_5 or R′	*Peri*-effect (p.p.m.)*	Ref.
	2.54	1.98	0.56	†
	2.57	2.00	0.57	17
	2.68	1.85	0.83	18
	2.73	1.92	0.81	19
	2.53	1.75	0.78	20

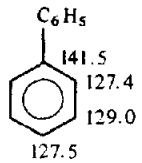
*δ(R = H) − δ(R = C_6H_5).
†This work.
R′ = 8-methyl-1-naphthyl.

in the region of 50°. Furthermore, since it has been shown that the 1,8-dimethylnaphthalene molecule suffers distortion [29] such that the methyl groups are splayed outwards; then it is to be expected that a similar bending effect would occur for the *peri*-phenyl/methyl couple to ease the steric repulsion. These effects should then give rise to certain distinctive features in the ^{1}H NMR spectrum of 1d (see Table 3). First, the CH_3(5) signal would become positioned in the anisotropic shielding region of the 4-phenyl group and be subject to a significant upfield shift (compare Table 4) as already discussed. Second, the H-3 proton should experience a net upfield shift due to the anisotropic effect of the splayed 4-phenyl group. The observed upfield shift (0.12 p.p.m.) is smaller than that for the *peri*-phenyl/phenyl couple (0.20–0.26 p.p.m.)

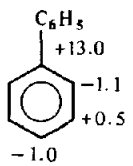
[13, 28] which would be consistent with an anticipated lesser degree of molecular distortion. Third, the phenyl protons should, in turn, experience an anisotropic effect from the quinoline ring current. It will be noted from Table 3 that for each of 1a–1c a very close multiplet was observed for the 4-phenyl protons, whilst for 1d two separated multiplets appeared, the *meta/para* protons being shielded by *ca.* 0.13 p.p.m. and the *ortho* protons by 0.22 p.p.m. when compared with 1a. These assignments were substantiated by irradiation of the 2-phenyl *ortho*-protons which produced no effect. The greatest shielding occurred at the *ortho* protons, in closest proximity to the heterocyclic ring. Earlier investigations [17–20] of compounds with *peri*-phenyl/methyl couples failed to detect such *ortho*-phenyl/β ring proton interactions since in these studies, performed at lower field strengths, the phenyl protons were regarded as a simple singlet and detailed analyses of the polycyclic ring systems were not attempted. However, one isolated report is of interest, since a shielding effect of 0.18 p.p.m. is evident at the *peri* H-5/H-8 protons in the spectrum of 1,4-dimethyl-9,10-diphenylanthracene [19], consistent with the splaying of the phenyl rings in their direction. Usually such *peri* protons experience deshielding effects [11a].

The present study of the *peri*-phenyl/methyl couple has afforded an opportunity for the extent of the second anisotropic effect in the *peri*-phenyl/phenyl case to be assessed independently.

There are no literature reports of ^{13}C NMR spectral studies of phenylquinolines or of phenylpyridines. The spectrum of biphenyl has been reported [30] from which phenyl Substituent Chemical Shifts (S.C.S.) are available as shown below.



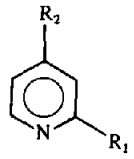
Chemical shifts (δ)



Phenyl S.C.S. (p.p.m.)

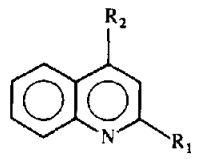
GOBERT *et al.* [31] have studied the spectra of a range of phenyl substituted polycyclic aromatic compounds and have established some useful rules for the assignment of the phenyl carbons. For phenyls which occupy an unhindered site (e.g., biphenyl, 2-phenylnaphthalene), $\delta_o - \delta_m$ is negative, but if the phenyl group is adjacent to one *peri*-hydrogen (e.g. 1,4-diphenylnaphthalene) then $\delta_o - \delta_m$ was positive and in the range +1.7–1.9 p.p.m. If two *peri*-protons surrounded the phenyl group (e.g., 9.10-diphenylanthracene) then $\delta_o - \delta_m$ was in the range +2.3–2.9 p.p.m. For all of the compounds studied the shieldings of the *meta* and *para* phenyl carbons were largely unaffected by the number of *peri*-substitutions and absorbed in the narrow ranges of 128.2–128.8δ and 126.8–127.4δ respectively.

Before an analysis of the ^{13}C NMR spectrum of 1a was attempted, the spectra of certain model compounds 6–9 were first examined to establish the phenyl carbon shieldings. The results obtained are shown in Tables 5 and 6. The *ipso* carbons absorbed at *ca.* 139–140δ (2-phenyl series) and at *ca.* 138–139δ (4-phenyl series). These differences, although small, appear to be characteristic for each series.



6 $R_1 = C_6H_5$, $R_2 = H$

7 $R_1 = H$, $R_2 = C_6H_5$



8 $R_1 = C_6H_5$, $R_2 = H$

9 $R_1 = H$, $R_2 = C_6H_5$

Furthermore, since the signals appeared in a region which was devoid of quinoline carbon signals [32], then such resonances present a simple diagnostic test to indicate the degree of phenyl substitution present.

The *ortho/meta* phenyl carbon shieldings of 6 and 8 were quite similar and were assigned such that $\delta_o - \delta_m$ was negative for these unhindered compounds. Conversely, in the 4-phenyl series, the *ortho*-phenyl carbons of 9 were at significantly lower field than those of 7. This is consistent with the previously established

Table 5. Assignments of phenyl carbons

Compound	^{13}C Chemical shift (δ)				
	2-phenyl carbons				
	ipso	ortho	meta	para	$\delta_o-\delta_m$(p.p.m.)
6	139.6	127.1	128.9	129.1	−1.8
8	139.9	127.8	129.0	129.5	−1.2
1a	140.0	127.9	129.1	129.6	−1.2
	4-phenyl carbons				
7	138.4	127.2	129.4	129.3	−2.2
9	138.3	129.8	128.8	128.7	+1.0
1a	138.8	129.8	128.9	128.7	+0.9

Table 6. ^{13}C NMR spectra of phenyl- pyridines and quinolines (heterocyclic ring carbons only)*

Compound	^{13}C Chemical shift (δ)										
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3†	
6	157.7	120.7	136.9	122.3	149.9						
7	150.6	121.9	148.6	121.9	150.6						
8	157.6	119.1	136.9	127.7	126.5	129.8‡	130.0‡	148.6	127.4		
9	150.4	121.6	149.0	126.1	126.9	129.6	130.1	148.8	126.9		
1a	157.2	119.6	149.5	125.9	126.6	129.7	130.4	149.2	126.1		
1b	157.2	118.9	149.3	125.6	128.8	140.1	129.5	149.4	124.1	21.7	
1c	154.3	118.9	148.8	122.6	135.9	132.2	137.9	146.6	125.9	21.8 (6)	18.3 (8)
1d	153.6	120.7	149.9	133.2	129.1‡	129.1‡	136.5	148.9	125.4	24.4 (5)	18.8 (8)

*For chemical shifts of phenyl carbons see Table 7.
†Assignments shown in parentheses.
‡Assignments may be reversed (see also Table 7).

rules [31], since for 7, with an unhindered phenyl, $\delta_o-\delta_m$ should be negative, whilst for 9, which has one adjacent *peri*-hydrogen, $\delta_o-\delta_m$ should be positive. In the heterocyclic series although the precise values of $\delta_o-\delta_m$ were outside the ranges previously experienced for carbocyclic ring systems, nevertheless the general relationships were still valid. For all of the compounds studied the *meta* and *para* carbons absorbed in the narrow ranges of 128.8–129.4δ and 128.7–129.6δ respectively, and were found to be independent of the number of *peri*-interactions, as noted previously [31].

The proton coupled spectra of 6 and 7 were also consistent with the assignments made. In each case the *ortho* phenyls appeared as a doublet of distorted triplets ($^1J_{oo}$, $^3J_{oo'}$, $^3J_{op}$) whilst the *meta* phenyls were generally more intense and split into a doublet of doublets ($^1J_{mm}$, $^3J_{mm'}$). The proton coupled spectra of the phenylquinoline derivatives proved too complex to analyse with certainty.

The ^{13}C NMR spectrum of 1a should contain a total of 17 peaks, comprising 4 large methine peaks (*ortho*/*meta*-phenyl carbons); 7 smaller methine peaks (C-3, C-5, C-6, C-7, C-8 and *para*-phenyls) and 6 quaternary carbons (C-2, C-4, C-9, C-10 and *ipso*-phenyls). The 15 MHz spectrum (see Tables 6 and 7 and Figure 2) revealed that all the carbon signals were separated, a remarkable lack of overlap, considering the complexity of the ^{1}H NMR spectrum.

Assignment of the quaternary carbons was straightforward, the two *ipso*-phenyl carbons were readily identified through use of the empirical rules previously established. Since there were two signals in

Table 7. ^{13}C NMR spectra of 2,4-diphenylquinolines (phenyl ring carbons only)*

Compound	^{13}C Chemical shift (δ)							
	2-phenyl				4-phenyl			
	ipso	ortho	meta	para	ipso	ortho	meta	para
1a	140.0	127.9	129.1	129.6	138.8	129.8	128.9	128.7
1b	140.1	127.8	129.1	129.5	138.9	129.8	128.8	128.6
1c	140.2	127.6	128.9	129.3	139.5	129.8	128.7	128.3
1d	139.7	127.6	128.9†	129.5	143.5	129.4	128.1	127.8

*For chemical shifts of quinoline ring carbons see Table 6.
†Assignments may be reversed (see also Table 6).

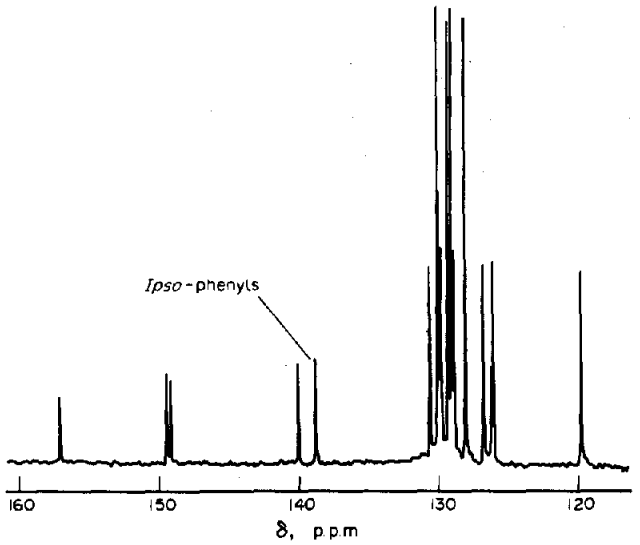


Fig. 2. 15 MHz ^{13}C NMR spectrum of 2,4-diphenylquinoline

the 138–140δ region, the presence of two substituted phenyl groups was immediately apparent. The two bridgehead and two substituted sites were then ascribed by comparison with the spectrum of quinoline [32] and through consideration of phenyl S.C.S. effects [30].

Assignments of the high intensity peaks for the *ortho/meta*-phenyl carbons were made by direct comparison with the analyses of the model compounds 6 to 9 (see Table 5). The assignments were further confirmed by reference to the spectrum of 1d in which the 2-phenyl carbons absorbed at their expected shifts whilst the 4-phenyl carbons shieldings were modified by a *peri*-proximity effect (see later discussion).

For the assignments of the low intensity methine peaks, the *para*-phenyl carbons were initially allocated by comparison with the appropriate shifts for 6–9. The heterocyclic ring carbons were then assigned by comparison with the respective shieldings for quinoline [32] and also through the application of methyl S.C.S. effects to the derivatives 1b and 1c.

The C-3 signal, largely unaffected by the methyl substitutions, appeared at 119.6δ; in the proton coupled spectrum this well separated signal was a sharp doublet with no fine coupling present.

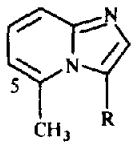
In the ^1H NMR spectrum of 1a, downfield shifts of the *ortho* 2-phenyl and of the quinoline ring H-3 proton occurred, however, such deshielding effects were not exhibited by the respective carbons in the ^{13}C NMR spectrum. The S.C.S. effects which occurred upon introduction of the phenyl group into the quinoline ring are listed in Table 8. Different effects occurred with the site of substitution; at the 4-position the result was similar to that (+13.0 p.p.m.) for biphenyl [30], whilst at the 2- position a much smaller effect resulted. Since parallel effects also occurred in the pyridine derivatives 6 and 7 (see Table 6), this smaller effect must presumably originate from the adjacent nitrogen atom. The *peri*-deshielding effect by a 4-methyl group is quite significant (−3.9 p.p.m.) [33], but for a 4-phenyl group it was much smaller (−1.5 p.p.m.). GOBERT *et al.* [19] have observed a similar smaller effect in 9,10-diphenylanthracene (−1.2 p.p.m.). A very curious substituent effect occurred with 1c and 1d. Introduction of an 8-methyl group resulted in a *ca.* 3 p.p.m. shielding effect at C-2, much larger than the normal 8-methyl S.C.S. effect at that carbon [33]. No explanation can be offered for this shift, other than that of a subtle steric effect.

Table 8. S.C.S. effects for phenyl substitution

	2-phenyl	4-phenyl
C-2	+7.4	+0.2
C-3	−1.8	+0.7
C-4	+1.2	+13.3
C-5	+0.1	−1.5
C-6	+0.1	+0.5
C-7	+0.6	+0.4
C-8	+0.6	+0.7
C-9	+0.3	+0.5
C-10	−0.8	−1.3

The ^{13}C NMR spectrum of 1d featured a number of interesting effects as a result of the *peri*-phenyl/methyl couple. The CH_3(5) signal absorbed at 24.4δ, compared to 18.1δ in 5,8-dimethylquinoline [34], a downfield shift of 6.3 p.p.m. This *peri*-proximity effect is comparable to those reported by GOBERT *et al.* [19] for 1,4-dimethyl-9,10-diphenylanthracene (+6.5 p.p.m.), and by WILSON and STOTHERS [35] for 1,8-dimethylnaphthalene (+6.7 p.p.m.) from which it would appear that the effect is mainly dependent upon the nature of the directly bonded atom (*viz* carbon) rather than upon the complete grouping. In this respect it is interesting to note that MAURY and PIGIÈRE [36] have observed

that the chemical shifts of CH_3(5) in each of 10a–10c were very similar.



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a R = CH_3,

b R = C_2H_5,

c R = $CH(CH_3)_2$.

A similar effect also took place at the 4-*ipso* phenyl carbon, in the form of a downfield shift of 4.7 p.p.m., compared with 3.4 p.p.m. for the 9,10-*ipso*-phenyl carbons of 1,4-dimethyl-9,10-diphenylanthracene [19]. The smaller effect observed in the anthracene series presumably results from the lesser degree of phenyl distortion due to the additional buttressing effect of the H-5 and H-8 *peri*-protons. Very small effects also occurred at the other 4-phenyl ring carbons, whilst the 2-phenyl shifts were unaffected. These small deviations proved valuable for confirmation of certain phenyl shieldings for 1a.

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