# Geometrical Isomerism in Benzyl Carbanions α-Substituted by 2- or 4-Pyridyl or Quinolyl Groups[1]

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$^1$H and $^{13}$C n.m.r. spectra of the sodium salt of the carbanion of 4-benzylpyridine in $Me_2SO$ show that the anion is non-symmetric at room temperature, because of slow rotation around the bond linking the carbanionic carbon with C(4) of the heterocycle. To establish unambiguously the stereochemistry of the parent system, a model in which rotation was prevented, the sodium salt of the anion of 3-methyl-4-benzylpyridine was studied. An analogous approach was followed for the anion of 2-benzylpyridine. The stereochemistry in these systems was assessed by measuring three stereodependent parameters: (i) $^3J_{C,H}$ between the appropriate carbon atom of the heterocycle and the proton bonded to the carbanionic carbon; (ii) nuclear Overhauser effects; and (iii) the effect on the $^{13}$C shifts of the heterocycle of a further phenyl group, as in the anions of diphenylmethylpyridines. The study was extended to 2- and 4-benzylquinoline. The data obtained suggest that in the anions of the 2-benzylheteroaromatic compounds the geometry with the phenyl ring *cis* to nitrogen is preferred; interference with the nitrogen lone pair is preferred to that with the aromatic =C–H bond.

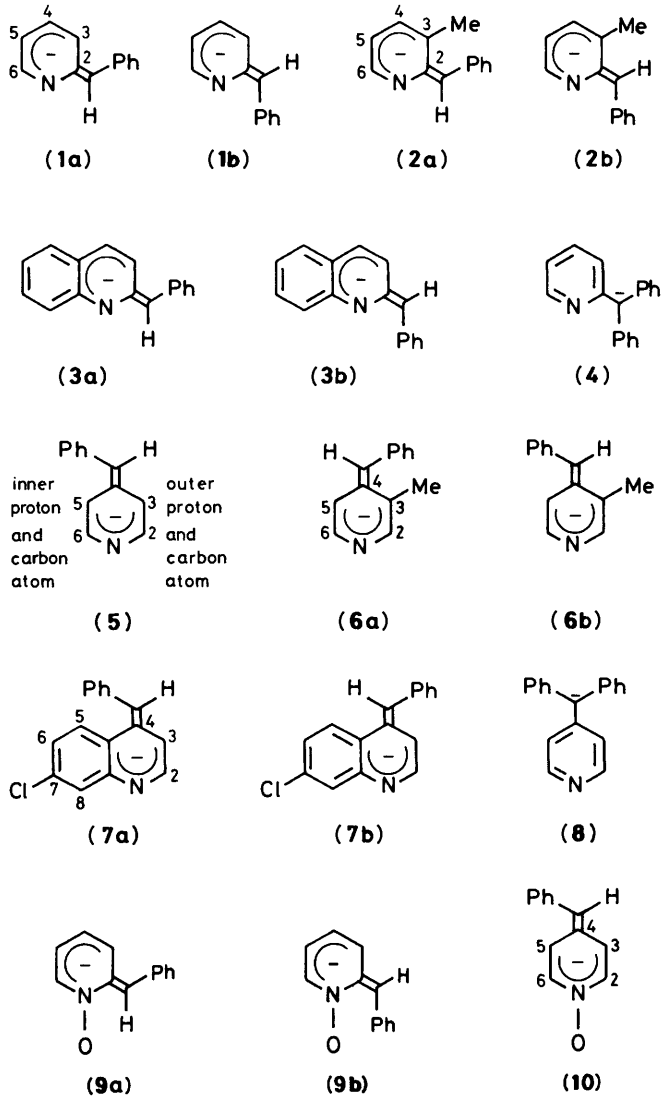
In the context of a study of effects exerted by primary organic functionalities,[2] substituted aryl rings,[3a] and heterocycles[2-4] on a contiguous 'reacting' or involved electron-rich group, one of us reported recently an investigation of α-substituted benzyl carbanions $PhCH^-X$:[2d] it was observed that the anion of 4-benzylpyridine exhibits non-equivalence of carbon atoms and protons at positions 3 and 5, and at positions 2 and 6 of the pyridyl ring. Slow rotation about the bond linking the carbanionic carbon atom and the C(4) of the heterocycle was inferred, resulting from the high π-bond character: a substantial π charge transfer from the carbanionic carbon to the heterocycle was documented,[2d] in line with the requirements of the valence bond formalism. According to the popular but qualitative classification of heterocycles into π-excessive and π-deficient systems,[5] heterocycles containing pyridyl-type nitrogen (*e.g.* azines and azoles) possess greater electron deficiency than their carbocyclic analogues. This idea suggested that the observations made on the anion of 4-benzylpyridine might be extended to other aza-heterocyclic systems. In order to elucidate the structural requirements for bond fixation between the carbanionic centre and the heterocycle, we undertook an extensive study of the n.m.r. behaviour of benzyl carbanions α-substituted with electron-poor aza-heterocycles. Here we report the results for carbanions obtained from 2-benzylpyridine, 2-benzylquinoline, 4-benzylpyridine, and 7-chloro-4-benzylquinoline. In addition, we report some results concerning the anions of 2- and 4-benzylpyridine 1-oxide.

The major problem to be solved was the assignment of stereochemistry around the C=C bond between the carbanionic carbon and the heterocycle. We sought n.m.r. parameters that, once established in systems of known imposed stereochemistry, could be used as discriminating tests when applied to substrates of unknown stereochemistry. To construct models of imposed stereochemistry we used methyl substitution: thus, to decide the preferred configurations of the anions (**1**), (**3**), and (**5**), we studied the n.m.r. behaviour of the anions (**2**), (**6**), and (**7**), expecting that the isomers (**2b**), (**6b**), and (**7b**) would be preferred for steric reasons.

Once we had verified by nuclear Overhauser effect (n.O.e.) experiments our predictions for the anions (**2**), (**6**), and (**7**), we investigated (a) whether *cis*- and *trans*-$^3J_{C,H}$ between the proton of the carbanionic centre and the appropriate carbon atom of the heterocycle discriminate between the two opposite stereochemical situations; (b) whether n.O.e. experiments performed by irradiating at the frequency of the proton on the carbanionic centre ($H_\alpha$) would provide dependable responses for proximate protons; and (c) the effect on the $^{13}$C chemical shifts of the heterocycle of further phenyl substitution at the carbanionic carbon, as in the carbanions (**4**) and (**8**).

While this manuscript was in preparation, Bank and Dorr published the $^1$H and $^{13}$C n.m.r. analysis of the anions of 2-, 3-, and 4-benzylpyridines.[6] Although some of their results overlap with ours, their major attention was focused on anions prepared in tetrahydrofuran: as for many other benzyl carbanions, we have preferred $Me_2SO$ as solvent since in this medium ion pairing or aggregation of salts is minimized, as shown by the weak effect exerted on the $^{13}$C shifts by [2.2.1]cryptand.[2d] Bank's analysis and peak assignment were based on a reported[7] compression effect of the phenyl ring which would cause a low-field shift of the heterocyclic 'inner' protons facing the phenyl group [see formula (**5**)], in turn associated[8] with a high-field shift of the attached carbon signals. The limitation of this approach is that, in order to make the assignments, both geometrical isomers must be observed, so that one can see which resonance is low-field shifted: in the case of rapidly interconverting isomers low-temperature spectra are needed. These experimental conditions are not compatible with $Me_2SO$ solutions of the anions, and in low-freezing solvents the lowering of temperature may have profound effects on ion pairing or aggregation of carbanions.

We believe instead that our approach based on obtaining discriminative parameters in systems of imposed stereochemistry provides a methodology of wider scope, applicable also to systems where the single isomer present in solution has only one heterocyclic proton *ortho* to the carbanionic carbon (as in the anion of 4-benzylquinoline).




## Results

*Preparation of the Carbanion Sodium Salts; N.m.r. Data and Assignments.—General.* The carbanion sodium salts were prepared by deprotonation of the phenyl(heteroaryl)methanes by sodium methylsulphonylmethanide in $Me_2SO$ (obtained from powdered sodium amide and $Me_2SO$). The $^1H$ and $^{13}C$ shifts of the pyridylbenzyl carbanions are reported in Tables 1 and 3; those for the quinolylbenzyl systems are in Tables 2 and 4. Table 5 reports the C,H-coupling constants for the pyridyl-substituted carbanions; Table 6 reports those for the quinolyl-substituted systems.

*Systems Substituted at Position* 4.—Evidence that in the anion of 4-benzylpyridine no rotation occurs on the n.m.r. timescale between the carbanionic carbon and C(4) of the heterocycle is provided by the shift non-equivalence of H(3) and H(5), and of C(3) and C(5). The assignment of the $^{13}C$ spectrum is based on the observation that the C(5) signal of the methyl derivative (**6**) at 105.15 p.p.m exhibits $^3J_{C,H(\alpha)}$ 8.1 Hz; similarly the analogous high-field CH carbon signal at 106.03 p.p.m. for (**5**) has $^3J_{C,H(\alpha)}$ 8.5 Hz. Conversely, the signal for the quaternary carbon C(3) in (**6**) at 145.39 p.p.m, showing $^3J_{C,H(\alpha)}$ 5.5 Hz, is related to that of the CH carbon in (**5**), 114.75 p.p.m., with $^3J_{C,H(\alpha)}$ 7.0 Hz. Interpretation of the $^1H$ spectrum of (**6**) is straightforward: analogies of proton shifts of (**5**) and (**6**) provided the assignment for (**5**). 2D $^1H$, $^{13}C$ HETCOR experiments showed which protons are bonded to which carbon atoms in the anion (**6**), and thus also in (**5**).

The hypothesis that the anion (**6**) of 4-benzyl-3-methylpyridine would prefer the structure (**6b**) to (**6a**) was confirmed by n.O.e. experiments: irradiation at the frequency of the methyl group produces a positive n.O.e. increment in the signals both of H(2) and H(α) (16%). Conversely, irradiation at the frequency of H(5) causes a positive n.O.e. only on H(6) (30%). Analogously, irradiating at the frequency of H(α) in the anion (**5**) gave positive n.O.e. increments of the signals due to the high-field H(3) (7.3%) and H(*ortho*) (6.3%) of the phenyl group. All these data unambiguously assign (i) the high-field carbon shift to the heterocyclic carbon atom facing the phenyl group; and (ii) a lower value to *cis*-$^3J_{C,H}$ [between C(3) and H(α)] than to *trans*-$^3J_{C,H}$ [between C(5) and H(α)].

The high-field displacement of the signals due to C(3) and C(5) in (**8**) relative to C(3) in (**5**) (4—5 p.p.m.) is smaller than that of C(5) relative to C(3) (8.72 p.p.m.) in (**5**). This fact can be rationalized by considering that in anion (**8**) two major effects are operative: (*a*) the aryl rings are more twisted than in (**5**) and the compression should be less effective; and (*b*) the presence of the second phenyl group will withdraw some negative charge from the heterocycle. Indications at hand[9] from another investigation predict that the amount of negative charge withdrawn from the carbanionic carbon atom by two phenyl rings in α-substituted diphenylmethyl anions is only *slightly* greater than that withdrawn from the carbanionic carbon by one phenyl in α-substituted benzyl anions: because of this, the low-field shift that the C(3) and C(5) experience as a result of less charge is only minor.

Two-dimensional HETCOR experiments provided the way to identify which protons are bonded to which carbon atoms in the anion (**9**) of 7-chloro-4-benzylquinoline. The protons H(2) and H(3) are easily differentiated from all the others because of the smaller $^3J$(H) values of the pyridine ring: the $^{13}C$ assignment of CH carbon signals thus becomes straightforward. The fact that the signal of C(3) in (**7**) occurs at fields similar to C(5) in (**5**) and (**6**) suggests that this carbon atom is affected by the phenyl ring of the benzyl moiety arranged as in the configuration depicted for (**7b**). This hypothesis is strengthened by the fact that $^3J_{C,H}$ is of *trans*-type (8.3 Hz), and is finally confirmed by the positive n.O.e. response of H(5) (17%) and H(*ortho*) (12%) on irradiating at the frequency of H(α). Finally the C(10) signal is distinguished from that of C(9) by its coupling with H(α) [$^3J_{C,H(\alpha)}$ 5.7 Hz].

The bond fixation between the carbanionic carbon atom and C(4) of the heterocycle in the anion of 4-benzylpyridine (**5**) is also evidenced in the anion of 4-benzylpyridine 1-oxide (**10**): in fact, in this case also, different $^1H$ and $^{13}C$ chemical shifts are found at room temperature for positions 3 and 5, and 2 and 6. Unfortunately, fewer data are available for (**10**) than for (**5**), due to the fact that the former sodium salt is considerably less soluble (0.08M) and undergoes a slow but irreversible degradation to an unknown species. The obtainment of $^{13}C$-coupled spectra was thus prevented. The reported $^{13}C$ assignments are based on analogy with effects observed with the anion (**5**), modified by the presence of the *N*-oxide functionality which causes[3] a *ca.* 10 p.p.m. high-field displacement of the signals of C(2), C(4), and C(6) relative to the analogous carbon atoms of (**5**).

*Systems Substituted at Position* 2.—The study of these systems takes advantage of the results obtained for the 4-isomers. The structure (**2b**) (*Z*) is supported by n.O.e. experiments that indicate a signal increase for H(4) (8%) and H(α) (20%) on irradiating at the frequency of the methyl group, and by the value of the coupling constant $^3J_{C(3),H(\alpha)}$ = 6 Hz.

**Table 1.** $^1$H N.m.r. shifts of pyridyl carbanions[a]

| Carbanion | H(2) | H(3) | H(4) | H(5) | H(6) | H(*ortho*) | H(*meta*) | H(*para*) | H(α) |
|---|---|---|---|---|---|---|---|---|---|
| (**1**) | | 5.29 | 6.36 | 5.28 | 7.49 | 7.30[b] | 6.67 | 5.98 | 4.28 |
| (**2**) | | 1.73[c] | 6.38 | 5.38 | 7.52 | 7.50 | 6.70 | 6.03 | 4.18 |
| (**5**) | 7.02 | 5.71 | | 6.32 | 7.19 | 6.69 | 6.79 | 6.13 | 4.29 |
| (**6**) | 7.09 | 1.68[c] | | 6.53 | 7.20 | 6.75 | 6.90 | 6.16 | 4.18 |
| (**9**) | | 6.83 | 6.32 | 5.27 | 7.38 | 6.90 | | 6.36 | 5.27 |
| (**10**) | 6.50 | 5.39 | | 6.40 | 6.88 | 6.60 | 6.78 | 6.70 | 4.52 |

[a] In $Me_2SO$ relative to $Me_4Si$. [b] Broad peak. [c] Methyl group.

**Table 2.** $^1$H N.m.r. shifts of quinolyl carbanions[a]

| Carbanion | H(2) | H(3) | H(4) | H(5) | H(6) | H(7) | H(8) | H(*ortho*) | H(*meta*) | H(*para*) | H(α) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (**3**) | | 6.12 | 6.55 | 6.62 | 6.22 | 6.60 | 6.84 | 7.72 | 6.82 | 6.26 | 4.47 |
| (**7**) | 7.04 | 6.3 | | 7.58 | 6.61 | | 6.90 | 7.12 | 6.96 | 6.50 | 5.32 |

[a] In $Me_2SO$ relative to $Me_4Si$.

**Table 3.** $^{13}$C Shifts of pyridyl carbanions[a]

| Carbanion | C(2) | C(3) | C(4) | C(5) | C(6) | $CH^-$(α) | C(*ortho*) | C(*meta*) | C(*para*) | C(*ipso*) | Me |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (**1**) | 158.76 | 116.17 | 130.14 | 100.19 | 148.32 | 83.98 | 119.81 | 126.89 | 110.48 | 145.05 | |
| (**2**) | 157.46 | 118.23 | 130.51 | 100.07 | 145.88 | 81.13 | 120.75 | 126.84 | 111.03 | 145.22 | 20.94 |
| (**4**) | 157.73 | 113.19 | 130.87 | 102.04 | 157.73 | 93.88 | 127.18 | 127.39 | 116.84 | *b* | |
| (**5**) | 145.22 | 114.75 | 145.09 | 106.03 | 147.68 | 83.65 | 120.06 | 127.63 | 112.41 | 144.11 | |
| (**6**) | 145.57 | 145.39 | 145.26 | 105.15 | 145.39 | 80.92 | 120.92 | 127.62 | 112.88 | 143.24 | 18.32 |
| (**8**) | 146.68 | 109.75 | 143.46 | 109.75 | 146.68 | 92.52 | 127.58 | 127.58 | 118.40 | 147.78 | |
| (**9**) | 146.60 | 110.56 | 123.87 | 97.60 | 137.41 | 77.80 | 121.67 | 129.05 | 115.02 | 143.73 | |
| (**10**) | 134.59 | 113.93 | 137.22 | 103.26 | 136.10 | 86.96 | 120.83 | 127.77 | 114.76 | 143.53 | |

[a] In $Me_2SO$ relative to $Me_4Si$. [b] Not detectable.

**Table 4.** $^{13}$C Shifts of quinolyl carbanions[a]

| Carbanion | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) | C(*ipso*) | C(*ortho*) | C(*meta*) | C(*para*) | $CH^-$(α) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (**3**) | 155.32 | 112.94 | 127.71 | 125.43 | 121.58 | 127.29 | 125.67 | 152.99 | 122.14 | 144.30 | 122.02 | 126.86 | 113.99 | 89.34 |
| (**7**) | 147.38 | 99.39 | 137.92 | 124.11 | 117.49 | 130.24 | 124.19 | 152.43 | 123.63 | 143.22 | 123.48 | 127.69 | 117.38 | 87.06 |

[a] In $Me_2SO$ relative to $Me_4Si$.

The appearance of a single set of resonances for the anion (**1**) of 2-benzylpyridine obviously is no guarantee of the presence of a single isomer at room temperature. Evidence that the sodium salt of the anion (**1**) is present exclusively as a non-interconverting species in the form (**1b**) (*Z*), or that the same isomer contributes almost exclusively to a dynamic equilibrium population of (**1a**) and (**1b**), is based on the following observations: (i) n.O.e. experiments indicate a signal increase of H(3) (6%) on irradiating at the frequency of H(α); (ii) $^3J_{C(3),H(\alpha)}$ = 5.4 Hz; (iii) C(3) in (**1**) suffers a high-field shift of *ca.* 3 p.p.m. on going to the anion of 2-diphenylmethylpyridine (**4**), in analogy with that found for the 4-substituted series: this supports the view that the phenyl group in (**1**) is *trans* to C(3).

We expected that in the sodium salt of the anion of 2-benzylquinoline (**3**) the preferred configuration would be (**3b**), in analogy with (**1b**): however in this case the evidence is not so clear. The proton spectrum of (**3**) was interpreted on the basis of a 2D $^1$H COSY-90 experiment. The value of 8.3 Hz for $^3J_{C,H}$ between C(3) and H(α) is higher than expected for the *cis*-coupling of the arrangement (**3b**). Nonetheless, on irradiating at the frequency of H(α), a small positive n.O.e. was found for H(3) (3%) of the heterocycle. It is possible that the strong, or exclusive, preference for the *Z*-configuration in the anion of 2-benzylpyridine (**1**) no longer applies to the anion of 2-benzylquinoline (**3**). One interesting feature common to the anions (**1**)—(**3**) is associated with the *ortho*-protons of the phenyl ring of the benzyl moiety: in every case these signals are present at lower field than in their 4-isomer analogues, and appear broad and unresolved. A moderate, reversible line sharpening occurs on increasing the temperature of the sample from 22 to 50 °C, without appearance of a fine structure, however; higher recording temperatures were prevented by the possibility of decomposition of the methylsulphonylmethanide anion. This phenomenon may be interpreted as due to partial hindrance to rotation of the phenyl ring, the *ortho* carbon atoms of which might be involved in a six-membered ring arising from the co-ordination of the metal ion with one of these carbon atoms and the heterocyclic nitrogen.

The $^1$H n.m.r. spectrum of the sodium salt of the anion of 2-benzylpyridine 1-oxide has been interpreted on the basis of a two-dimensional COSY experiment. The value of $^3J_{C,H}$ between C(3) and H(α) is substantially higher than in the case of the anion of 2-benzylpyridine. An n.O.e. experiment performed by irradiating at the frequency of H(α) gave no increment for H(3) but a small increase for the *ortho*-protons of the phenyl group (*ca.* 6%). The shift of C(3) is 5.61 p.p.m. to higher field than in the corresponding deoxy anion (**1**). Since the *N*-oxide functionality affects only C(2), C(4), and C(6) displacing their resonances to high field, but not C(3) and C(5), this result should be interpreted as due, at least in part, to a compression effect of the phenyl group facing C(3). All these results point to the conclusion that the preferred geometrical arrangement for the anion of 2-benzylpyridine 1-oxide is (**9a**).

**Table 5.** C,H-Coupling constants ($J$/Hz) of pyridyl carbanions

| Carbanion | Carbon | $^1J$ | $^2J$ | $^3J$ |
|---|---|---|---|---|
| (1) | 2 | | $J_{C,H(\alpha)}$ 3.3<br>$J_{C,H(3)}$ 3 | $J_{C,H(4)}$ 6<br>$J_{C,H(6)}$ 12<br>$J_{C,H(\alpha)} = J_{C,H(5)} = 5.4$ |
| | 3 | 153.6 | | $J_{C,H(6)}$ 7.2 |
| | 4 | 152.8 | | $J_{C,H(3)}$ 7.7 |
| | 5 | 160.3 | $J_{C,H(6)}$ 7.7 | $J_{C,H(4)}$ 4.8 |
| | 6 | 164.9 | $J_{C,H(5)}$ 4.9 | $J_{C,H(o)} = J_{C,H(3)} = 3.4$ |
| | α | 144.7 | | |
| (2) | 2 | | $J_{C,H(\alpha)}$ 3.3 | $J_{C,H(4)}$ 6; $J_{C,H(6)}$ 12<br>$J_{C,Me}$ 3 |
| | 3 | | | $J_{C,H(5)}$ 5, 4; $J_{C,H(\alpha)}$ 6 |
| | 4 | 152.4 | | $J_{C,H(6)} = J_{C,Me} = 7$ |
| | 5 | 160.2 | $J_{C,H(6)}$ 9.8 | |
| | 6 | 165.6 | | $J_{C,H(4)}$ 9.8 |
| | α | 145.5 | | $J_{C,H(o)}$ 3.9 |
| (5) | 2 | 164.5 | $J_{C,H(3)}$ 3 | $J_{C,H(6)}$ 12.2 |
| | 3 | 152.5 | $J_{C,H(2)}$ 7 | $J_{C,H(5)} = J_{C,H(\alpha)} = 7$ |
| | 4 | | | $J_{C,H(2)} = J_{C,H(6)} = 6.6$ |
| | 5 | 153.8 | $J_{C,H(6)}$ 5.1 | $J_{C,H(3)} = J_{C,H(\alpha)} = 8.5$ |
| | 6 | 163.8 | $J_{C,H(5)}$ 2 | $J_{C,H(2)}$ 10.9 |
| | α | 146.4 | | $J_{C,H(o)} = J_{C,H(3)} = 3.6$ |
| (6) | 2 | 163.4 | | $J_{C,H(6)}$ 10 |
| | 3 | | $J_{C,H(2)}$ 6.5 | $J_{C,H(5)} = J_{C,H(\alpha)} = 5.5$ |
| | 4 | | | |
| | 5 | 152.7 | $J_{C,H(6)}$ 8.1 | $J_{C,H(\alpha)}$ 8.1 |
| | 6 | 163.45 | | $J_{C,H(2)}$ 10 |
| | α | 147.4 | | |
| (9) | 2 | | $J_{C,H(3)}$ 4 | $J_{C,H(4)}$ 8; $J_{C,H(2)} = 12$ |
| | 3 | 158.1 | | $J_{C,H(\alpha)} = J_{C,H(5)} = 7$ |
| | 4 | 158.5 | | $J_{C,H(6)}$ 7.9 |
| | 5 | 166.2 | $J_{C,H(6)}$ 2 | $J_{C,H(3)}$ 7.2 |
| | 6 | 174.8 | $J_{C,H(5)}$ 3 | $J_{C,H(4)}$ 8 |
| | α | 152.8 | | |

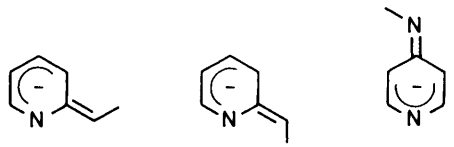
**Table 6.** C,H-Coupling constants ($J$/Hz) of quinolyl carbanions

| Carbanion | Carbon | $^1J$ | $^2J$ | $^3J$ |
|---|---|---|---|---|
| (3) | 2 | | $J_{C,H(3)}$ 3.3<br>$J_{C,H(\alpha)}$ 3.3 | $J_{C,H(4)}$ 7.2 |
| | 3 | 157.6 | | $J_{C,H(\alpha)}$ 8.3 |
| | 4 | 154.4 | | $J_{C,H(5)}$ 4.5 |
| | 5 | 155.3 | | $J_{C,H(7)}$ 8; $J_{C,H(4)}$ 4.4 |
| | 6 | 155.7 | | $J_{C,H(8)}$ 7.1 |
| | 7 | 154.9 | | $J_{C,H(5)}$ 8.6 |
| | 8 | 154.5 | | $J_{C,H(6)}$ 6.4 |
| | 9 | | | $J_{C,H(7)} = J_{C,H(5)} = 7$ |
| | 10 | | | $J_{C,H(4)}$ 5.5 |
| | α | 148.0 | | $J_{C,H(6)} = J_{C,H(8)} = J_{C,H(3)} = 6.7$<br>$J_{C,H(o)} = J_{C,H(3)} = 3.9$ |
| (7) | 2 | 162.6 | | |
| | 3 | 156.0 | $J_{C,H(2)}$ 8.3 | $J_{C,H(\alpha)}$ 8.3 |
| | 4 | | | *a* |
| | 5 | 154.8 | | |
| | 6 | 165.6 | | $J_{C,H(8)}$ 5.9 |
| | 7 | | $J_{C,H(8)} = J_{C,H(6)}$ 3.3 | $J_{C,H(5)}$ 13 |
| | 8 | 162.2 | | $J_{C,H(6)}$ 4.9 |
| | 9 | | | $J_{C,H(2)}$ 12.1; $J_{C,H(5)}$ 7.3 |
| | 10 | | | $J_{C,H(3)} = J_{C,H(6)} = J_{C,H(8)} =$<br>$J_{C,H(\alpha)} = 5.7$ |
| | α | 158.5 | | |

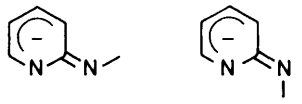
[a] Broad singlet.

## Discussion

*Stereochemical Assignments.*—Our approach to assigning the stereochemistry of the exocyclic C=C bond appears soundly based and dependable: all the three stereodependent probes chosen, $^3J_{C,H}$, the n.O.e. response, and the shielding effect of a further phenyl group at the carbanionic carbon in diphenylmethyl derivatives, provide internally consistent answers. Small $^3J_{C,H}$ values are accompanied by positive n.O.e. between proximate protons attached to positions involved in the $^3J$ coupling: larger $^3J_{C,H}$ values are accompanied by absence of n.O.e. between protons attached to positions involved in the pertinent $^3J$ coupling.



(*E*)-(**11**) (*Z*)-(**11**) (**13**)



(*E*)-(**12**) (*Z*)-(**12**)

Once it is ascertained that a phenyl ring causes a high-field shift of the signal due to the heterocyclic carbon atom facing it, the effect of a further substitution with a phenyl ring at the carbanionic carbon atom would be expected to move upfield the signal of the heterocyclic carbon atom *trans* to the first phenyl group: this prediction is experimentally verified.

Comparison of the $^1H$ and $^{13}C$ chemical shifts reported in Table 7 for the configurationally fixed anions of 2-ethylpyridine (**11**),[10] 2-methylaminopyridine (**12**), and of 4-methylaminopyridine (**13**),[11,12] indicates that there is an upfield shift of the signals both of the carbon atom and of the attached proton *ortho* to the anionic centre and proximate to the substituent, relative to those in the arrangement of opposite stereochemistry. In contrast, for the configurationally frozen diphenylmethyl carbanion [7,8] a different trend is found, analogous to that with the anion (**5**).

It appears therefore that an inner proton is sensitive to ring current effects while an inner carbon signal is shifted to high-field by 'compression' effects, whatever the anisotropic influence of the substituent facing it. Furthermore, while *ortho*-carbon signals of the time-averaged diphenylmethyl carbanion are low-field shifted in the triphenylmethyl carbanion (122.8 p.p.m.),[13] the isochronous C(3) and C(5) (109.75 p.p.m.) in the diphenylmethyl anion (**8**) are slightly high-field shifted relative to the mean shift (110.39 p.p.m.) of C(3) and C(5) of the benzylic anion (**5**). This phenomenon may be interpreted as circumstantial evidence that, analogously to (**5**), in the anion (**8**) a high double-bond character between the carbanionic carbon atom and C(4) of the heterocycle is retained, forcing the π cloud of the pyridyl ring to be co-aligned with the $p_\pi$ orbital of the carbanionic carbon atom, perhaps at the expense of a larger mutual twisting of the two phenyl rings.

An analogous situation may pertain to the case of the 2-pyridyl(diphenyl)methyl carbanion (**4**): evidence that indeed most of the charge initially present on the heterocycle in the benzyl anion (**1**) is retained also on the pyridyl ring of the anion (**4**) is provided by the fact that the C(5) signal of (**4**) moves only 1.85 p.p.m. to low field relative to (**1**), while the C(*para*) signal of the triphenylmethyl carbanion is displaced to low field by 7 p.p.m. relative to the diphenylmethyl carbanion.[13]

*Charge Demands and Bond Fixation.*—The tendency of an organic functionality to withdraw mesomerically a negative charge is best described by the mesomeric charge demand $q_x$, defined [2d] as the fraction of π charge transferred to the functionality from a charged site (carbanion or nitranion): so far we have obtained $q_x$ values for a number of organic primary functionalities in benzyl carbanions [2d] $PhCH^-X$ and in diactivated methane carbanions $XYCH^-$:[9] 2- and 4-pyridyl groups ($q_x = 0.41$)[2d] are ranked high in this quantitative, although empirical, scale, being similar to a methoxycarbonyl group ($q_x = 0.404$).[2d]

The remarkable propensity of aza-heterocycles to delocalize negative charge is certainly responsible for the double-bond fixation of the exocyclic C=C bond in the anions of 2- and 4-methylpyridine [14] and of 2-ethylpyridine,[10] and of the exocyclic C=N bond in the anions of 2- and 4-amino-[11,12,15] and methylamino-pyridines.[11,12] In the anions of 2- and 4-aminopyridines [11,12,15] substitution of a hydrogen atom with a phenyl group affords the anions of 2- and 4-anilinopyridines and double-bond fixation between the nitranionic centre and the carbon atom of the heterocycle is no longer evidenced at room temperature.[1f] This phenomenon is not restricted to the pyridine ring: in fact, while geometric isomerism is present in the anion of 2-methylaminopyrimidine,[16] it has vanished in the anion of 2-anilinopyrimidine.[16] The present results support instead the idea that substitution with a phenyl ring in carbanions stabilized by 2- or 4-pyridyl systems does not interfere with the observation of bond fixation at room temperature. Since the C=C and C=N bonds have almost the same stability, the reason for the different behaviour of the anions of anilinopyridines and benzylpyridines should be sought in the different electronegativities of carbon and nitrogen: whereas in the anions of anilinopyridines the charge is competitively delocalized by the two nitrogen atoms, in pyridyl(benzyl) carbanions the charge is preferentially transferred onto the more electronegative pyridyl nitrogen, thus allowing the formation of a more complete exocyclic double bond.

Hogen-Esch's CNDO calculations [10] on the anion of 2-ethylpyridine predicted that the *Z*-isomer of (**11**) would be preferred: however, non-bonded interactions (ion pairing, aggregation) would favour the *E*-configuration. We always believed that non-bonded interactions of the anionic site(s) with the environment would be minimized in $Me_2SO$: indeed our results for the carbanion of the 2-benzylpyridine are in accord with the *Z*-configuration of the structure (**1b**) and thus agree with Hogen-Esch's predictions. Finally, whereas in the anions of 2-aminopyridines ($C_5H_4N-NH^-$) the 'in-plane' amine lone pair is 'larger' than the hydrogen atom,[12] it appears that in our 2-benzylpyridine and quinoline anions, the 'in-plane' pyridyl nitrogen lone pair is 'smaller' than the hydrogen atom of the CH bond at position 3. A substantially different situation appears to pertain to the anion of 2-benzylpyridine 1-oxide: the oxygen atom bonded to nitrogen forces the phenyl ring to face C(3).

## Experimental

N.m.r. spectra ($^1H$ and $^{13}C$) were recorded with a Varian XL-300 instrument (300 MHz for $^1H$). Carbanions were prepared according to a previously reported procedure.[2d,f,13]

*Materials.*—2- and 4-Benzylpyridine were commercial products (Fluka). For the preparation of 2-benzyl-3-methylpyridine,[17] 4-benzyl-3-methylpyridine,[18] 2-benzylquinoline,[19–21] and 7-chloro-4-benzylquinoline we treated the appropriate 2- and 4-halogenoazine with the sodium salt of the anion of phenylacetonitrile according to the procedure first devised by Cutler [22] for the preparation of 7-chloro-4-benzylquinoline, subsequently modified [17] for the preparation of 2-benzyl-3-methylpyridine (use of 2 mol equiv. of base instead of 1). The resulting α-(2-quinolyl)phenylacetonitrile (m.p. 93 °C; lit.,[23] 93 °C) was hydrolysed under Cutler conditions (60% $H_2SO_4$ at reflux for 1 h) to give 2-benzylquinoline. Analogously, 4-chloro-3-methylpyridine [24] gave α-(3-methylpyridyl)phenylacetonitrile [oil; purified by chromatography (Found: C, 80.9; H, 5.9; N, 13.2. $C_{13}H_{10}N_2$ requires C, 80.7; H, 5.8; N, 13.45%)], which under Cutler hydrolytic conditions gave 4-benzyl-3-methylpyridine.[18] 2-Bromo-3-methylpyridine [25] and 4-chloro-

**Table 7.** Chemical shifts of nuclei *ortho* to the anionic centre in carbanions and nitranions

| Compd. | Nuclei | Ref. | *Z* | *E* | *Z* − *E* |
|---|---|---|---|---|---|
| **(11)** | H(3) | 10 | 5.40 | 5.32 | 0.08 |
| | C(3) | | 126.8 | 109.2 | 17.6 |
| **(12)** | H(3) | 11 | 5.81 | 5.58 | 0.23 |
| | C(3) | | 114.5 | 102 | 12.5 |
| **(13)** | H(3),H(5) | 11 | 5.89 | 5.60 | 0.29 |
| | C(3),C(5) | | 115 | 102 | 13 |
| $Ph_2CH^-$ [a] | H(2),H(6) | 7, 8 | 6.17[b] | 6.63[c] | −0.46 |
| | C(2),C(6) | 8 | 121.6[d] | 112.6[e] | 9 |
| $Ph_2CH^-$ [f] | H(2),H(6) | 1 | 6.51 | | |
| | C(2),C(6) | 14 | 116.1 | | |
| $Ph_3C^-$ [f] | H(2),H(6) | *g* | 7.31 | | |
| | C(2),C(6) | 14 | 122.8 | | |

[a] THF–Li, −80 °C. [b] Outer *ortho*-proton. [c] Inner *ortho*-proton. [d] Outer *ortho*-carbon. [e] Inner *ortho*-carbon. [f] $Me_2SO$–Na, room temperature. [g] V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, 1963, **85**, 2328.

3-methylpyridine[24] were prepared as previously described. 2-Chloroquinoline and 4,7-dichloroquinoline were commercially available (Fluka).

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