Proton Magnetic Resonance Studies of Cyclic Compounds. Part VIII.[1] The Conformations of *cis*- and *trans*-Decahydroquinolines and their Acyl Derivatives

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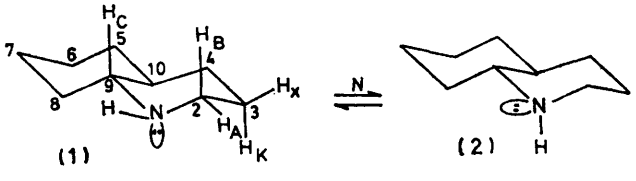
Proton magnetic resonance spectra are in accord with a twin-chair conformation for *trans*-decahydroquinoline and its acyl derivatives. *cis*-Decahydroquinoline prefers that twin-chair conformation which allows the nitrogen lone pair to occupy the hindered ' inside ' position. However, the *N*-benzoyl, *N*-benzenesulphonyl, *N*-carboxyanilide, and *N*-nitroso-derivatives of *cis*-decahydroquinoline adopt the alternative twin-chair conformation, thus avoiding the repulsive interaction between the *N*-substituent, and the C-8 methylene group.

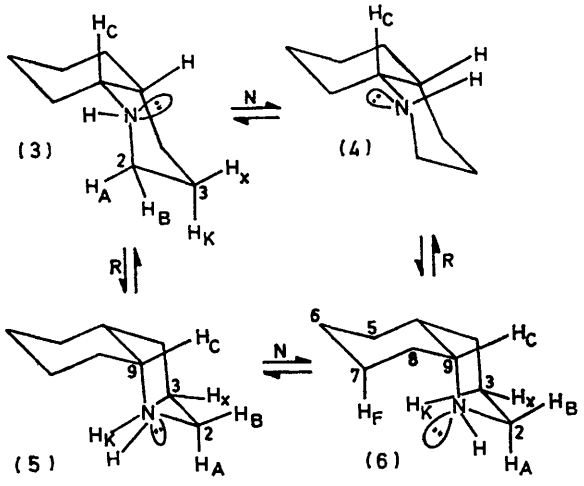
DECAHYDROQUINOLINE was first obtained in 1890 by Bamberger and his co-workers,[2,3] who reduced quinoline and tetrahydroquinoline with phosphorous and hydriodic acid, but did not recognise that their product was a mixture of *cis*- and *trans*-isomers. It was left to Hückel and Stepf, in 1927,[4] to isolate both a *solid* decahydroquinoline, m.p. 48° and a *liquid* decahydroquinoline b.p. 205°, after hydrogenation of quinoline over a platinum catalyst. The liquid base possessed the higher b.p., density, and refractive index; moreover, production of this isomer was favoured by increase in the acidity of the medium. For these reasons and by application of the well known Auwers–Skita rule, the liquid isomer was assigned the *cis*-configuration. Further work on the hydrogenation of quinoline was reported by Fujise,[5] and by Bailey and McElvain.[6] A synthesis of the solid base by ring closure was carried out by Clemo,[7] and subsequently, both isomers were independently synthesised from *cis*- and *trans*-2-substituted cyclohexylamines, these having been prepared by reductive methods of known stereospecificity.[8]

Our main purpose was to investigate the usefulness of ^{1}H n.m.r. spectroscopy in assessing both the configuration and the preferred conformations of decahydroquinoline and derivatives. During the work it was found that practically pure *cis*-decahydroquinoline (containing $\leqslant 3\%$ *trans*-isomer, by g.l.c. analysis) could be obtained by hydrogenation of quinoline in concentrated hydrochloric acid over platinum black (see Experimental section).

In *trans*-decahydroquinoline [(1) $\rightleftharpoons$ (2)],† the only conformational problem concerns the position of equilibrium with respect to nitrogen inversion (N). The



situation is more complicated for *cis*-decahydroquinoline where four possible conformations [(3)—(6)] are interconvertible, as shown, by ring inversion (R) and nitrogen inversion (N). Conformations (3) and (6) have N–H equatorial and lone-pair axial; (4) and (5) have N–H axial and lone-pair equatorial.



The 100 MHz spectrum of *trans*-decahydroquinoline in $CDCl_3$ containing $\sim 10\%$ C_6H_6 showed a broad, ill-defined envelope stretching from τ 8·0 to 9·2, and, at lower field, two well-separated signals which could be assigned confidently to the protons at position 2. Thus, the signal for the equatorial proton H_A at 7·15 was a doublet ($J \sim 12$ Hz), each component being a quartet (separations ~ 3 Hz). The signal for the axial proton H_B, at 7·55, was a triplet ($J \sim 12$ Hz), each component being a doublet (separations ~ 4 Hz). Irradiation at τ 8·44 where evidently both H_X and H_K are located, caused the low-field pattern for H_A and H_B to simplify to an AB-type quartet; in this quartet, the doublet for H_A ($J = 11{\cdot}8$ Hz) had sharp lines, but the doublet for H_B showed relatively broad lines, due probably to an incomplete decoupling of H_B from its large interaction with its axial neighbour H_K. These assignments, which were summarised in a preliminary note,[9] have been substantiated by analysis of the 220 MHz spectrum of (1) $\rightleftharpoons$

† Numbered to allow unambiguous use of *a* to indicate axial.

[1] Part VII, H. Booth and P. R. Thornburrow, *J. Chem. Soc.* (*B*), 1971, 1051.
[2] E. Bamberger and F. Lengfeld, *Ber.*, 1890, **23**, 1143.
[3] E. Bamberger and S. Williamson, *Ber.*, 1894, **27**, 1458.
[4] W. Hückel and F. Stepf, *Annalen*, 1927, **453**, 163.
[5] S. Fujise, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **8**, 185.
[6] C. F. Bailey and S. M. McElvain, *J. Amer. Chem. Soc.*, 1930, **52**, 4013.
[7] G. R. Clemo, J. G. Cook, and R. Raper, *J. Chem. Soc.*, 1938, 1183.
[8] F. E. King, T. Henshall, and R. L. St. D. Whitehead, *J. Chem. Soc.*, 1948, 1373.
[9] H. Booth and A. H. Bostock, *Chem. Comm.*, 1967, 177.

(2) in $CDCl_3$. In addition to the signals for the 2-equatorial proton, at τ 6·95 (doublet, J = 12 Hz, each part a multiplet) and the 2-axial proton, at τ 7·35 (triplet, J = 11·7 Hz, each part a doublet, J = 3·2 Hz), a one-proton signal was now seen clearly at τ 7·91. This latter signal was triplet in character, but was only poorly resolved, the half-intensity width being *ca.* 21 Hz. Assignment of this resonance to H_C, the angular proton at position 9, follows from its relatively low-field shift and from its appearance, which is consistent with its being axial, and coupled to 2 axial and 1 equatorial neighbours. It is worth noting that the first-order type spectrum of a *trans*-twin-chair conformation [(1) or (2)] should give only two signals of triplet character, one from H_{2a} and one from H_9.

Unfortunately, these findings give us no clues to the position of the conformational equilibrium (1) ⇌ (2). Thus, comparisons of spectral parameters of (1) ⇌ (2) with those of piperidine, for which the most recent evidence [10] suggests a preference for the N–H equatorial conformation of ~ 0·4 kcal, are not meaningful. The chemical shifts of the 2,6-equatorial and 2,6-axial protons of 4-t-butylpiperidine, at τ 6·87 and 7·43 respectively ($CDCl_3$) are somewhat different from the shifts, reported above, for the 2*e* and 2*a* protons of (1) ⇌ (2). However, it is unreasonable to attribute these differences solely to a changed position in the conformational equilibrium, as the fused cyclohexane ring may itself cause movements in the shifts of H_{2e} and H_{2a}, either through long-range anisotropic effects, or indirectly, by inducing changes in the shape of the piperidine ring.

The 100 MHz spectrum of *cis*-decahydroquinoline in benzene (*cf.* ref. 9) showed a broad resonance stretching from τ 7·9 to 9·1, but well-separated from this envelope were *three* closely-spaced signals due to the 2-equatorial proton (H_A), the 2-axial proton (H_B), and the angular proton (H_C). The signal for H_A at τ 7·16 was a doublet (J_{gem} ~ 11·5 Hz), each component a multiplet, whilst the H_B signal at τ 7·56 was a triplet (J ~ 11·5 Hz), each component a multiplet. The third signal, at τ 7·42 slightly overlapped the H_B resonance, and was a narrow partly resolved signal with a half-intensity width of only 8 Hz; this was assigned to the angular proton H_C. Support for this interpretation came from the 220 MHz spectra for solutions in C_6D_6 and $CDCl_3$. The solution in $CDCl_3$ showed well-shifted signals for H_A at τ 6·96 (doublet, J = 12 Hz, each component showing further splitting), for H_B at τ 7·34 (triplet, J ~ 11 Hz, each component showing further splitting) and for H_C at τ 7·16 (narrow signal, half-intensity width 8·5 Hz).

Of great importance is the fact that the signal for the angular proton $H_C(H_9)$ was narrow, with a half-intensity width of only 8—8·5 Hz, a situation consistent only with conformations (5) and (6), in which the three couplings affecting H_C are all expected to be less than 4 Hz (J_{ea}, J_{ee}). The angular proton H_9 in conformations (3) and (4) is subject to one relatively large coupling (J_{aa}), in addition to two small couplings (J_{ae}). The 220 MHz spectrum of the *cis*-base in C_6D_6 confirmed the assignments previously made from the 100 MHz spectrum.

TABLE 1

Chemical shifts (τ values) of protons in decahydroquinoline

Isomer	Formula	Solvent	H_{2e}	H_{2a}	H_9	H_{3e}	H_{3a}	H_{7a}
trans-	(1) (2)	$CDCl_3$	6·95	7·35	7·91	*a*	*a*	*a*
trans-	(1) (2)	$CDCl_3/C_6D_6$	7·15	7·55	*a*	8·44 [b]	8·44 [b]	*a*
cis-	(5) (6)	$CDCl_3$	6·96	7·34	7·16	*a*	*a*	*a*
cis-	(5) (6)	C_6D_6	7·16	7·56	7·42	8·74 [b]	8·32 [b]	8·05 [c]

[a] Not seen. [b] By spin decoupling (100 MHz). [c] Tentative (from 220 MHz spectrum).

In addition, a quartet, centred on τ 8·05, was now visible and this was tentatively assigned to $H_F(H_{7a})$, a proton which is expected to be deshielded, in (5) or (6), as a result of its proximity to N–H or N-lone pair, respectively.[11,12]

Further information was deduced from spin decoupling experiments at 100 MHz on the solution of the *cis*-amine in C_6D_6. First, irradiation at τ 8·32 caused loss of a *small* coupling (3 Hz) from H_A and loss of a *large* coupling (11 Hz) from H_B. It was concluded that τ 8·32 represented the shift of the *axial* proton at position 3. Second, irradiation at τ 8·74 caused loss of a small coupling (3 Hz) from both H_A and H_B signals, demonstrating that τ 8·74 is the shift of the *equatorial* proton at position 3. The unusual deshielding of the 3-axial proton, relative to the 3-equatorial proton, is consistent with conformation (5) or (6), where it can be ascribed to steric compression (*cf.* ref. 12) by the axial proton at position 5. The fact that the chemical shifts of the 2-equatorial and 2-axial protons are almost identical to those of the corresponding protons in the *trans*-amine (1) ⇌ (2) also points to a preponderance of (5) and/or (6), since in (3) and (4) the axial proton at position 2 is expected to be deshielded, also as a result of steric compression. It must be emphasised that the arguments based on chemical shifts are not in themselves convincing, since they have ignored effects due to differing orientations of the nitrogen lone-pair in *cis*- and *trans*-bases. However, when the evidence is taken in conjunction with the appearance of the angular proton H_C, it is seen to be strongly in favour of conformation (5) and/or (6). Now since (4) and (5) are equivalent, or nearly equivalent, energetically, the exclusion of (4) implies the exclusion of (5). *Consequently under the conditions employed in this work, cis*-decahydroquinoline exists largely, or completely, in conformation

[10] R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *J. Chem. Soc.* (*B*), 1970, 127.

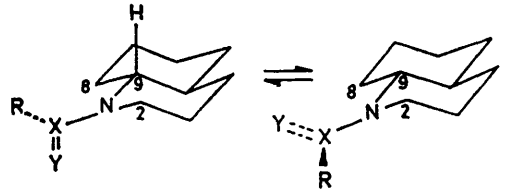
[11] H. Booth, *Progr. N.M.R. Spectroscopy*, 1969, **5**, 149.

[12] H. Booth, *Tetrahedron*, 1966, **22**, 615.

(6). However, the presence of small proportions of the remaining conformations cannot be excluded. In theory, the presence of *appreciable* proportions of conformations (3), (4), and/or (5), in equilibrium with (6), could be demonstrated from low-temperature spectra, provided one or both of the rate processes is sufficiently slow at the lowest temperature attainable. In the event, temperatures down to −83° caused no significant alteration in the spectrum of the amine in $CFCl_3$ apart from some general line-broadening, probably viscosity-promoted, at −70° to −83°.

Finally, it is notable that conformation (6) has the nitrogen lone-pair in a hindered ' inside ' position in the molecule. It seems, therefore, that for *cis*-decahydroquinoline, in the solvents used, the ' steric requirements ' of the nitrogen lone-pair are substantially less than those of the nitrogen-attached hydrogen atom.

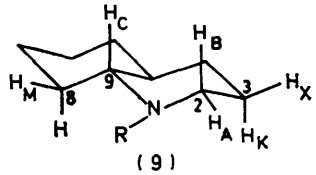
A number of *N*-acyl, and similar, derivatives of decahydroquinolines gave spectra which were interpretable in terms of twin-chair conformations. In these compounds the partial double-bond character of the N–X= bond induces planarity, or near planarity, of the three bonds to the nitrogen atom. The spectra of such compounds are influenced by the rate of interconversion of rotamers such as (7) and (8), and this in turn will depend on temperature. Further, chemical shifts in (7), particularly for protons at positions 2, 8, and 9, are expected to be considerably different from those in (8).



(7) (8)

The 220 MHz spectrum of 1-benzoyl-*trans*-decahydroquinoline, in $CDCl_3$ at 13°, proved impossible to interpret. A well resolved multiplet at τ 6·45 to 6·90, representing three protons, was too complex for analysis. The remainder of the spectrum comprised a 1-proton multiplet at τ 7·75 (half-intensity width ~ 16 Hz) and the usual complex and extensive resonance stretching from τ 8·1 to 9·2. Fortunately, the 1-benzenesulphonyl derivative (9; R = SO_2Ph) of the *trans*-amine gave spectra at 100 and 220 MHz in which many features were interpretable. The 2-equatorial proton, H_A, appears at τ 5·91 as a doublet (J_{gem} ~ 13 Hz), each component being a multiplet. Well-shifted one-proton signals also appeared at 7·25 (quintet, separations ~ 7 Hz), 7·54 (triplet), and 7·80 (doublet). Of these signals, only the quintet at 7·25 was affected by simultaneous irradiation at 5·91, and this signal was therefore assigned to the *axial* proton at position 2. Confirmation of this interpretation came from a second decoupling experiment: irradiation at τ 8·45 caused the removal of small couplings from H_A, leaving a clean doublet (J = 13 Hz) and the simplification of H_B to a clean doublet (J = 13 Hz). In this way the AB-type quartet for the geminal protons H_A and H_B was exposed. Further, this decoupling experiment showed that H_X and H_K have identical, or nearly identical chemical shifts. An explanation of the observed quintet (J ~ 7 Hz) for H_B was now possible: the chemical shift equivalence of H_X and H_K produces for H_B a ' deceptively simple ' spectrum consisting of a triplet (separations = mean of J_{BK} and J_{BX} = 7 Hz), each component, a doublet, due to J_{BA} (J ~ 13 Hz). Owing to the overlapping of the two central lines, the result is a quintet, with separations of about 7 Hz, exactly as observed. The angular proton H_C, which is axial, and is coupled to two axial and one equatorial neighbours, gives rise to the signal at τ 7·54, appearing as a triplet (J_{aa} ~ 10·5 Hz), each part a doublet (J_{ae} ~ 3·5 Hz). Finally, the signal at τ 7·80 is a doublet (J ~ 12·5 Hz) each component being broadened by further couplings. The assignment of this resonance to H_M, the 8-equatorial proton, follows from the expectation that this proton will be influenced markedly by the proximity of the benzenesulphonyl substituent. Summarising, the ^1H n.m.r. spectrum is entirely consistent with the conformation (9; R = SO_2Ph).

It is notable that the chemical shifts of the 2,6-equatorial (τ 6·26) and 2.6-axial (τ 7·74) protons of 1-phenylsulphonyl-4-methylpiperidine (10) are considerably different from the shifts reported above for the 2-equatorial (τ 5·91) and 2-axial (τ 7·25) protons of the *trans*-decahydroquinoline derivative (9). In explanation, we suppose that, in (9), the precise conformation



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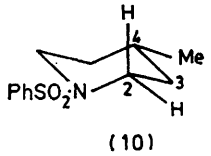


(10)

adopted by the benzenesulphonyl substituent is that which allows some relief of the $A^{(1,3)}$-type strain [13,14] between itself and the 8-methylene group. In contrast, the relief of the $A^{(1,3)}$-type strain between the benzenesulphonyl substituent and the 2-methyl group in 1-phenylsulphonyl-2-methylpiperidine is achieved by the molecule adopting a conformation in which the methyl group is *axial* (see later).

Spectral details for *trans*-decahydroquinoline *N*-carboxyanilide are given in Table 2, the multiplicity of signals being in good agreement with conformation (9; R = CONHPh). Thus, $H_A(H_{2e})$ was a doublet (J_{2e2a} ~ 14·0 Hz), each part showing four closely-spaced lines due to the couplings J_{AX} and J_{AK}. The 8-line signal for $H_B(H_{2a})$ contained two large separations (J_{AB} ~ 14 Hz; J_{BK} ~ 11·3 Hz) and one small separation (J_{BX} ~ 4·5 Hz). The angular proton $H_9(H_c)$ was a triplet (separations

[13] F. Johnson and S. K. Malhotra, *J. Amer. Chem. Soc.*, 1965, **87**, 5492.

[14] Y. L. Chow, C. J. Colon, and J. N. S. Tam, *Canad. J. Chem.*, 1968, **46**, 2821.

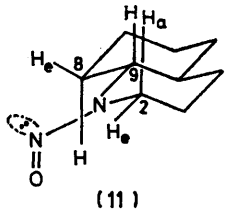
$\sim$ 10·5 Hz), each line being a doublet. The doublet (separation $\sim$ 10 Hz) at τ 7·88 was assigned to the equatorial proton at position 8.

TABLE 2

Chemical shifts (τ values) of protons in 1-substituted *trans*-decahydroquinolines (220 MHz, $CDCl_3$)

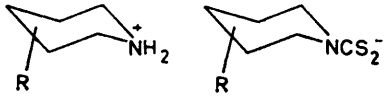
Substituent	Formula	H_{2e}	H_{2a}	H_9	H_{8e}
SO_2Ph	(9)	5·91	7·25	7·54	7·80
CONHPh	(9)	6·26	6·82	6·97	7·88
NO	(11)	4·83	7·64	6·64	7·55
CS_2^-	(18)	4·38	6·81	5·61	7·38

The 100 MHz spectrum of *N*-nitroso-*trans*-decahydroquinoline has already been interpreted in terms of conformation (11) [15,16] in which the N=O bond lies *anti* to the 8-methylene group. Our work (Table 2) confirms the assignments made by Chow and Colon [16] for the 2*e*, 2*a*, and 9 (angular) protons. In addition, the multiplet observed by Chow and Colon at τ 7·63 is resolved in the 220 MHz spectrum into a triplet ($J \sim 13$ Hz) at τ 7·64 due to the 2-axial proton, and a doublet ($J \sim 12$ Hz) at τ 7·55. The latter signal is almost certainly due to the 8-equatorial proton, which lies in the deshielding zone of the π-electron system.



(11)

Preliminary results arising from the spectra of some cyclic amine salts (12) of amine-*N*-carbodithioic acids have been reported.[17] In particular, it was noted that the 2,6-equatorial protons of the anion occurred at particularly low field (τ 3·5—4·5). Unfortunately, the precise bonding and stereochemistry of the NCS_2 moiety of the *N*-carbodithioate anion is not certain. The negative charge in the anion is expected to be



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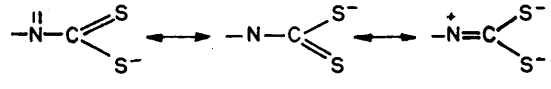
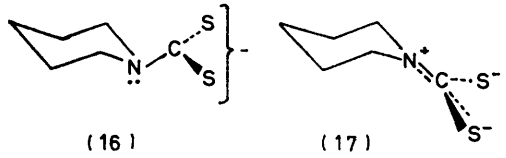
delocalised (13) $\leftrightarrow$ (14) over the system S–C–S, providing a charge distribution symmetrical with respect to the



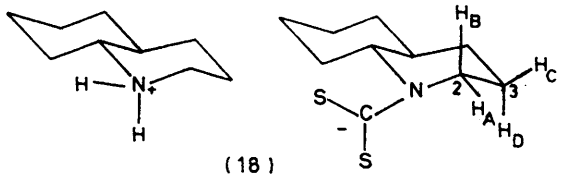
(13) (14) (15)

N–C bond. The extent to which the nitrogen lone-pair is delocalised (*cf.* ref. 15) is not known. It is expected that there will be some orbital overlap between the lone pair and the π-electron system. Indeed, the marked and preferential deshielding of the 2,6-equatorial protons in the anion of (12) is a strong pointer to conformation (17) rather than (16). In (17) the nitrogen is trigonal, and the 2,6-equatorial protons should be deshielded both as a result of lying in the plane of the π-system, and also because of steric compression by sulphur. Moreover, we [18] and others [19] have shown that the *N*-carbodithioate anions derived from 2-methylpiperidine and *cis*-2,6-dimethylpiperidine contain methyl groups in *axial* orientations, presumably to avoid the severe repulsive interactions between equatorial methyl groups and sulphur



(16) (17)

atoms. We conclude that the cyclic amine *N*-carbodithioate anions have the nitrogen atom essentially trigonal, as in (17). Now we consider *trans*-decahydroquinolinium *trans*-decahydroquinoline-*N*-carbodithioate (18), prepared from the free base and carbon disulphide. Here, relief of the $A^{(1,3)}$-type strain between the CS_2^- substituent and the 8-methylene group is only possible by a rotation about the exocyclic N–C bond. If the energy of the $A^{(1,3)}$ interaction is appreciably greater



(18)

than the delocalisation energy associated with orbital overlap of the nitrogen lone-pair and the CS_2^- π-system, the molecule would prefer a conformation with the plane of the CS_2 group parallel to the axial C–H bonds of the ring system. However, this possibility is not supported by the following arguments, based on the observed spectrum. The 220 MHz spectrum of (18) is complicated, but shows no less than eight well-shifted one-proton signals at low field, in addition to the NH_2^+ resonance. The 2-equatorial proton of the anion (H_A) gave a signal at τ 4·38 consisting of a 1,1,1,1-quartet, with separations of 13·0 and 7·1 Hz. These separations are unchanged in spectra recorded at 60, 100, and 220 MHz, and hence must equal the coupling constants involved, *i.e.* J_{AB} (13·0 Hz) and, probably, J_{AD} (7·1 Hz). Thus J_{AD} is unusually high for a vicinal J_{ea} coupling whilst J_{AC} must be $\sim$ 0. It is not possible to decide for certain whether these unusual J values reflect electronic effects, or changes in dihedral angles (ring-flattening). However, it does seem from models that the molecule would not benefit,

[15] Y. L. Chow, *Angew. Chem. Internat. Edn.*, 1967, **6**, 75.
[16] Y. L. Chow and C. J. Colon, *Canad. J. Chem.*, 1968, **46**, 2827.
[17] H. Booth and A. H. Bostock, *Chem. Comm.*, 1967, 637.
[18] A. H. Bostock, Ph.D. Thesis (Nottingham), April 1970; H. Booth and A. H. Bostock, to be published.
[19] T. P. Forrest and S. Ray, *Chem. Comm.*, 1970, 1537.

in energy terms, from a ring-flattening of the nitrogen-containing ring. Irradiation of the signal at τ 6·81 (see Table 3) caused loss of the 13 Hz coupling in the quartet at τ 4·38. Hence H_B is at τ 6·81 and its appearance as a triplet ($J_{AB} \sim J_{BD} \sim 12{\cdot}5$ Hz), each part being a doublet ($J_{BC} \sim 3$ Hz) lends support to the assignment. Had the plane of the CS_2^- group been *parallel* to the axial C–H bonds, one would have expected the *axial* proton H_B to be responsible for the quartet at 4·38. In this case, however, the signal at 6·81 would have to be assigned to the equatorial proton H_A, a most unlikely possibility in view of the observed multiplicity for this signal. The assignments of the remaining signals (Table 3) follow directly from their splittings and the process was facilitated by observation of the spectrum of the derived sodium salt, which lacks the signals due to the organic cation. The J values of Table 3 were obtained by direct

TABLE 3

Spectral data for protons in *trans*-decahydroquinolinium *trans*-decahydroquinoline-1-carbodithioate (18)

Chemical shifts (τ)

	H_{2e}	H_{2a}	H_9	H_{8e}	H_{3a}	$\overset{+}{N}H_2$
Anion	4·38	6·81	5·61	7·38	8·04	—
Cation	6·40	7·20	7·54	7·85	—	2·4

Approximate coupling constants (Hz)

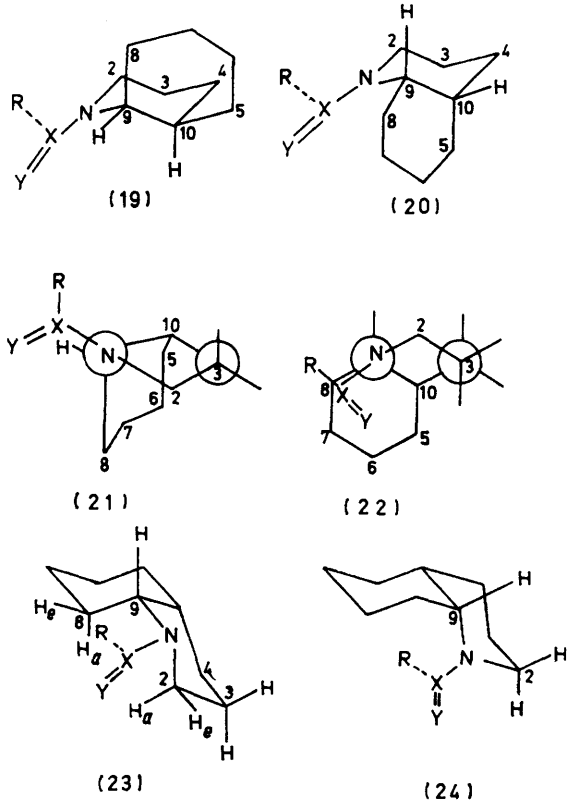
	J_{2e2a}	J_{2e3a}	J_{2a3a}	J_{2a3e}
Anion	13·0	7·1	12·5	5·5
Cation	12		13	3

	J_{8e8a}	$J_{9,8e}$	$\frac{1}{2}(J_{9,10} + J_{9,8a})$
Anion	11		10
Cation	11·5	3	10·5

measurement of the separations within the well-shifted one-proton signals; a more rigorous analysis was not possible because no assignment could be made within the broad, ill-defined resonance occurring at high field.

The conformation adopted by *N*-acyl- (and similar) derivatives of *cis*-decahydroquinoline are of considerable interest owing to the several possibilities involved. The two possible twin-chair conformations (19) [alternative viewings (21) and (23)] and (20) [alternative viewings (22) and (24)] are theoretically interconvertible by ring inversion; in addition, each conformation may have the *N*-substituent in one of two conformations with respect to rotation about the N–X bond, again with the possibility of mutual interconversion. Whereas conformation (6), similar to (20), was preferred for *cis*-decahydroquinoline itself, derivatives such as (19) ⇌ (20), where the nitrogen valencies are coplanar, might be expected to prefer conformation (19), owing to the $A^{(1,3)}$-type strain between the *N*-substituent and the 8-methylene group in conformation (20). This is especially clear in the drawings (21) and (22), which are alternative viewings of (19) and (20) respectively. Thus, in (22) the N–X and C-9–C-8 bonds are very nearly eclipsed, whereas in (21) it is the N–X and C_9–H bonds which are so disposed.

The room-temperature spectrum of 1-benzoyl-*cis*-decahydroquinoline gave a spectrum which included at low field (τ 5 to 8) several very broad signals, suggesting interconversion between conformations at a rate comparable with chemical-shift differences between corresponding protons in the conformations. At 100 °C, the spectrum showed three well-resolved signals at low field,



assigned to the protons on carbons adjacent to nitrogen. The triplet ($J \sim 11$ Hz), each part a doublet ($J \sim 4$ Hz), at τ 7·07, was due to the axial proton H_{2a}. The doublet ($J \sim 12$ Hz) at τ 5·75 showed fine structure due to further couplings and was assigned to the equatorial proton H_{2e}. Overlapping the H_{2a} signal was the signal of H_9, comprising a doublet ($J \sim 12$—13 Hz), with further unresolved small couplings, thus implicating conformation (23; R = Bz), and excluding (24; R = Bz). Conformation (23) was also clearly preferred for the *N*-benzenesulphonyl and *N*-carboxyanilide derivatives of *cis*-decahydroquinoline; spectral details are summarised in Table 4. Confirmation of the assign-

TABLE 4

Spectral data for protons in 1-substituted *cis*-decahydroquinolines (220 MHz, $CDCl_3$)

Chemical shifts (τ)

Substituent R	Conformation	H_{2e}	H_{2a}	H_9
Bz *	(23)	5·75	7·07	6·03
SO_2Ph	(23)	6·32	7·09	6·03
CONHPh	(23)	6·15	7·11	5·94

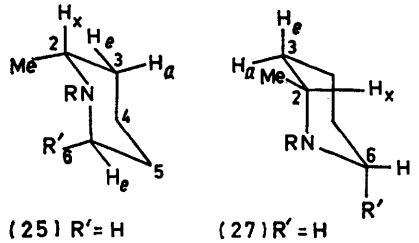
Approximate coupling constants (Hz)

Substituent R	J_{2e2a}	J_{2a3a}	J_{2a3e}	$J_{9,8a}$
Bz *	12	12	4	12·5
SO_2Ph	13	13	2·5	13
CONHPh	13	13	2·5	12

* Measured at 60 MHz and +100°.

ments was provided by spectra recorded at higher field strength and by double-irradiation experiments. Thus, the low-field doublets due to $H_{2e}(H_A)$ and $H_9(H_C)$, which overlapped in spectra at 60 MHz, were separated in spectra recorded at 100 and 220 MHz. Irradiation of the triplet at τ 7·10 (H_B) in the spectrum of the *N*-benzenesulphonyl derivative caused collapse of the doublet at τ 6·30, the doublet at τ 6·03 remaining unaffected, thus allowing assignment of the former doublet to the equatorial proton $H_{2e}(H_A)$.

The preference shown by *N*-acyl derivatives of *cis*-decahydroquinoline for conformation (23) finds an exact parallel in the preference shown by similar derivatives of 2-methylpiperidine and of *cis*-2,6-dimethylpiperidine for conformations (25) and (26) respectively, with methyl groups *axial*. This situation was first established by



(25) R' = H (27) R' = H
(26) R' = Me (28) R' = Me

Chow, Colon, and Tam,[14] largely from chemical-shift arguments. We support the findings of Chow *et al.* by measurements of the band-widths (= separation of outer lines) of the signal for the methine proton H_X in the spectra of the acyl derivatives (Table 5). For example,

TABLE 5

Spectral data for acyl derivatives of 2-methylpiperidine and of *cis*-2,6-dimethylpiperidine (60 MHz, $CDCl_3$)

Chemical shifts (τ)

Compd.	Substnt. R	H_{2e}	H_{6e}	H_{6a}	CH_3
(25)	CONHPh	5·55	6·10	7·10	8·87
(25)	SO_2Ph	5·80	6·35	7·05	9·05
(26)	CONHPh	5·65	5·65		8·75

Coupling constants and band-widths (Hz)

Compd.	Substnt. R	$J_{CH_3\text{-}CH}$	H_{2e} band-width
(25)	CONHPh	6·8	25·0
(25)	SO_2Ph	6·8	26·0
(26)	CONHPh	6·8	26·0

in the spectrum of 1-phenylsulphonyl-2-methylpiperidine (25; R = $PhSO_2$), the H_X signal (τ 5·80) has a band width of 26·0 Hz, a value expected for (25) (band-width = $J_{ea} + J_{ee} + 3\ J_{CH_3\text{-}CH}$), rather than (27) (band-width = $J_{aa} + J_{ae} + 3J_{CH_3\text{-}CH}$). Although there are four possible conformations (29), (30), (31), and (32) for *N*-nitroso-*cis*-decahydroquinoline, the spectra in $CDCl_3$ and benzene showed the presence of only two conformations (29) and (30) in equal proportions. The evidence is convincing and is summarised below.

(*a*) Conformers (31) and (32) are at once excluded because no narrow resonances, to be expected of the angular proton H_C, were observed at low field.

(*b*) The assignments of Table 6 were made on the basis of the observed separations within multiplets (which

TABLE 6

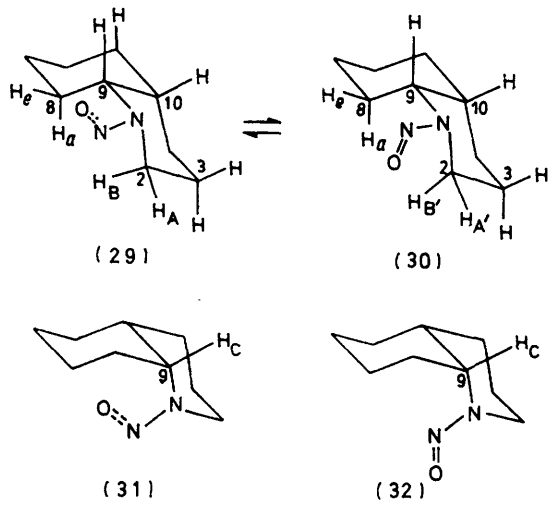
Spectral data for protons in 1-nitroso-*cis*-decahydroquinoline (29) ⇌ (30) (220 MHz)

Conformation	Solvent	H_{2e}	H_{2a}	H_9
(29)	$CDCl_3$	5·45	6·33	4·90
(29)	C_6D_6	5·68	6·90	4·90
(30)	$CDCl_3$	5·25	7·31	5·30
(30)	C_6D_6	5·32	7·75	5·52

Approximate coupling constants (Hz)

Conformation	Solvent	J_{2e2a}	J_{2a3a}	J_{2a3e}	$J_{9,8a}$	$J_{9,8e}$	$J_{9,10}$
(29)	$CDCl_3$	13	12	3	12	4	4
(30)	$CDCl_3$	13·5	12	3	11	5	5

approximated to the coupling constants), and on the belief (*cf.* refs. 16, 20) that the chemical shift difference between geminal protons at C-2 is much greater for those lying *cis*- to the nitroso-function, as in (30), than for



those lying *trans*- to this function, as in (29). The τ 5·2 to 5·6 region of the spectrum in $CDCl_3$ includes *three* overlapping one-proton multiplets, but these signals were well-separated when benzene was the solvent.

(*c*) Chemical shift differences ($\nu_A - \nu_B$) and ($\nu_{A'} - \nu_{B'}$) agree with published work on *N*-nitrosopiperidines,[16,20] bearing in mind the usual deshielding effect on H_{2a} caused by H_{8a}.

(*d*) The effects on chemical shifts of moving from $CDCl_3$ to benzene are closely similar to those recorded for *N*-nitrosopiperidines,[16] thus increasing confidence in the assignments made.

Finally, the disfavouring of conformations (31) and (32) is again attributed to steric interaction between the substituent on nitrogen, and the C-8 methylene group [see formula (22)]. The corresponding eclipsing effect in (29) and (30) involves the *N*-substituent and a hydrogen atom [see formula (21)].

[20] R. K. Harris and R. A. Spragg, *J. Mol. Spec.*, 1967, **23**, 158.

EXPERIMENTAL

M.p.s were obtained on a Kofler block. ^{1}H N.m.r. spectra were measured on a Perkin-Elmer R.10 (60 MHz), Varian HA-100 (100 MHz) and Varian HR-220 (220 MHz) spectrometers. Analytical g.l.c. of amines employed a Perkin-Elmer 800 Gas chromatograph; the 12 ft × ¼ in column was packed with Carbowax 20M (5%) on a support of alkali-treated Chromosorb W.

trans-*Decahydroquinoline*.—The commercial sample (Koch–Light Laboratories) was purified by sublimation at 100° and atmospheric pressure. The colourless needles produced had m.p. 48—48·5° and gave a single peak (retention time 19·7 min) on g.l c. analysis (column temperature 110°).

cis-*Decahydroquinoline*.—Quinoline (35 g) was heated in refluxing ethanol over Raney nickel (5—6 g) during 12 h. The mixture was filtered and distilled. The purified quinoline (25 g) was dissolved, with cooling, in concentrated hydrochloric acid (100 ml) and hydrogenated over platinum black (3 g) in an all-glass system at room temperature and a pressure of 2 atm. After nine days, 23 l (4·95 mol) of hydrogen had been absorbed. The mixture was filtered, basified (40% sodium hydroxide solution), and extracted several times with ether. Distillation of the dried (KOH) extracts gave *cis*-decahydroquinoline (stereochemical purity, by g.l.c., was ⩾97%) as a colourless liquid, b.p. 80—83°/13 mm. The retention time on g.l.c. examination was 22·1 min (column temperature 110°).

1-*Phenylsulphonyl*-trans-*decahydroquinoline*.— Treatment of *trans*-decahydroquinoline with an excess of benzenesulphonyl chloride, in the presence of aqueous sodium hydroxide (10%) produced a solid, crystallisation of which from ethanol gave the pure *amide*, m.p. 81—81·5° (Found: C, 64·3; H, 7·5; N, 4·8. $C_{15}H_{21}NO_2S$ requires C, 64·5; H, 7·5; N, 5·0%).

The following derivatives of *trans*-decahydroquinoline were prepared by published procedures: 1-benzoyl-*trans*-decahydroquinoline, m.p. 54—56° (lit.,[4] 56°); 1-nitroso-*trans*-decahydroquinoline, m.p. 30—32° (lit.,[21] 32—33°); *trans*-decahydroquinoline-1-carboxyanilide, m.p. 154° (lit.,[4] 153—155°); *trans*-decahydroquinoline picrate, m.p. 159° (lit.,[4] 158°); *trans*-decahydroquinolinium *trans*-decahydroquinoline-1-carbodithioate, m.p. 111° (from ethyl acetate) (lit.,[4] 120°).

1-*Phenylsulphonyl*-cis-*decahydroquinoline*.—The method was similar to that used for the *trans*-base and gave the *amide* as plates, m.p. 121·5° (Found: C, 63·9; H, 7·6; H, 4·9. $C_{15}H_{21}NO_2S$ requires C, 64·5; H, 7·5; N, 5·0%). The following derivatives of *cis*-decahydroquinoline were prepared by the published procedures: 1-benzoyl-*cis*-decahydroquinoline, m.p. 99·5° (lit.,[4] 96°); 1-nitroso-*cis*-decahydro quinoline, prepared by the method of Chow,[21] was a yellow liquid, b.p. 140—145°/1 mm; *cis*-decahydroquinoline-1-carboxyanilide, m.p. 177—178° (lit.,[4] 163—165°); *cis*-decahydroquinoline picrate, m.p. 144—144·5° (lit.,[4] 142—145°).

[1/1942 *Received*, 22*nd October*, 1971]

[21] Y. L. Chow, *Canad. J. Chem.*, 1967, **45**, 53.