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Natural-Abundance ^{15}N Nuclear Magnetic Resonance Spectroscopy. Chemical Shifts of Methyl-Substituted *trans*-Decahydroquinolines

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Abstract: ^{15}N chemical shifts of *trans*-decahydroquinoline, *N*-methyl-*trans*-decahydroquinoline, and 35 alkyl-substituted NH- and NCH_3-*trans*-decahydroquinolines are reported. Shift parameters for methyl substitution at the α, β, and γ positions, as well as parameters for mutual vicinal interactions between substituents ($\alpha\beta$), were calculated by linear regression analysis. The α-substitution parameters for the decahydroquinolines, which depend markedly on configuration, are consistent with those reported for piperidine when corrected for mutual vicinal interactions with C-8. An equatorial β-methyl group deshields the nitrogen more than does an axial group; a γ-axial methyl group in the nitrogen-containing ring is substantially shielding, while an equatorial one has essentially no effect. Different γ_a parameters are required for the secondary and tertiary piperidines. The conformation of the lone electron pair at nitrogen has no effect on the ^{15}N chemical shifts of the secondary amines, but has substantial influence on the shifts of the tertiary amines. Possible sources for these effects are discussed.

With the introduction of powerful and sophisticated FT NMR instrumentation, natural-abundance ^{15}N spectroscopy is gradually becoming a useful addition to the routine techniques of ^1H and ^{13}C NMR.[2] Establishment of accurate substitution parameters for ^{15}N, as has been done for ^{13}C, is desirable both for the practical purpose of structural assignments in unknown compounds and for the theoretical rationalization of shift effects. A set of empirical increments for methyl-substituted piperidines has recently been reported,[3] and a comparison with ^{13}C NMR parameters for the analogous methylcyclohexanes[4] has been made.[3a] Correlation between cyclohexanes and secondary piperidines gave a single line, whereas two different correlation coefficients were found for *N*-methylpiperidines, depending on the equatorial or axial orientation of the *N*-methyl group.[3]

The *trans*-decahydroquinoline system, because of its rigidity, and because the position of the substituent on N-1 can be influenced by bulky groups at C-8, C-3, and C-4a,[5,7] is very well suited as a model for investigation of conformational problems by spectroscopic methods[5] and for the determination of shift increments.[6] In this sequel to earlier ^1H and ^{13}C studies[5,6,7a] we report the ^{15}N spectra of a number of substituted *trans*-decahydroquinolines and *N*-methyl-*trans*-decahydroquinolines, and an interpretation of substituent effects on chemical shifts. The compounds investigated are shown in Scheme I; the chemical shifts and shift effects observed are collected in Table I.

The configuration of the decahydroquinolines has been determined by ^{13}C and ^1H NMR spectroscopy, and the conformational equilibria **e** $\rightleftarrows$ **a** (Scheme I) have been established both for the NH (**1** - **20**) and the NCH_3 derivatives (**1m** - **17m**).[5,7a] The stereochemistry of the compounds investigated, which is pivotal in the following discussion, may thus be considered known. Briefly, in the *N*-methyl series, compounds without substituents at C-8 in the decahydroquinoline ring exist with the N-CH_3 substituent ≥95% in the equatorial position. An axial substituent at C-3, C-8, or C-4a (as in **5m**, **6m**, **9m**, **11m**, **14m**, and **15m**) forces

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(2) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience: New York, 1979.
(3) (a) Duthaler, R. O.; Williamson, K. L.; Giannini, D. D.; Bearden, W. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8406-12. (b) Duthaler, R. O.; Roberts, J. D. Ibid. **1978**, *100*, 3882-89.
(4) (a) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612-22. (b) *Ibid.* **1972**, *94*, 5318-24. (c) Dalling, D. K.; Grant, D. M.; Paul, E. G. *Ibid.* **1973**, *95*, 3718-24.
(5) Eliel, E. L.; Vierhapper, F. W. *J. Am. Chem. Soc.* **1975**, *97*, 2424-28.
(6) (a) Eliel, E. L.; Vierhapper, F. W. *J. Org. Chem.* **1976**, *41*, 199-208. (b) Vierhapper, F. W.; Eliel, E. L. *Ibid.* **1977**, *42*, 51-62. (c) Booth, H.; Griffiths, D. V.; Jozefowicz, M. L. *J. Chem. Soc., Perkin Trans. 2* **1976**, 751-60.
(7) (a) Vierhapper, F. W.; Eliel, E. L. *J. Org. Chem.* **1979**, *44*, 1081-87. (b) Furst, G. T.; Lichter, R. L.; Vierhapper, F. W. *Ibid.* **1980**, *45*, 1521-2.
(8) Vierhapper, F. W.; Willer, R. L. *Org. Magn. Reson.* **1977**, *9*, 13-5.
(9) The signs of the shift effects in ref 3 have been reversed throughout this paper to correspond to the different reference system used (see also ref 2).

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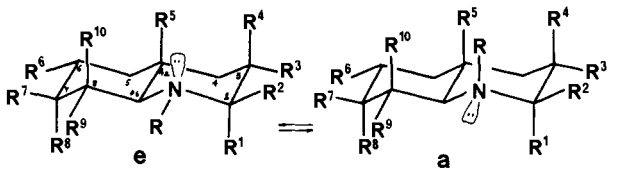
Scheme I



all R's = H except where indicated

	R = H	R = CH_3
R^1–R^{10} = H	1	1m
R^1 = CH_3	2	2m
R^2 = CH_3	3	3m
R^3 = CH_3	4	4m
R^4 = CH_3	5	5m
R^5 = CH_3	6	6m
R^6 = CH_3	7	7m
R^9 = CH_3	8	8m
R^{10} = CH_3	9	9m
R^9 = $C(CH_3)_3$	10	10m
R^{10} = $C(CH_3)_3$	11	11m
R^1 = R^9 = CH_3	12	12m
R^2 = R^9 = CH_3	13	13m
R^1 = R^{10} = CH_3	14	14m
R^2 = R^{10} = CH_3	15	15m
R^3 = R^5 = CH_3	16	16m
R^5 = R^9 = CH_3	17	17m
R^7–R^9 = $(CH_2)_4$	18	
R^8–R^9 = $(CH_2)_4$	19	
R^7–R^{10} = $(CH_2)_4$	20	

the N–CH_3 totally into conformation **e** while an equatorial substituent at C-8 (as in **8m**, **10m**, **12m**, and **13m**) leads to a quantitative shift to conformation **a**.[5] In the N–H series the equilibrium in C-8-unsubstituted compounds is ~70% **e**, ~30% **a**. Syn-axial methyl groups have little effect on this equilibrium (**8**, ~65% **e**; **9**, ~75% **e**), whereas a syn-axial *tert*-butyl group has a pronounced effect, and conformation **a** predominates (~80%) in **10**.[7] The equilibria in the secondary *trans*-decahydroquinolines were established by an investigation of the infrared Bohlmann bands,[7a] since ^1H and ^{13}C chemical shifts[7a] as well as ^{15}N chemical shifts[7b] are insensitive to these conformational changes.[6]

Results and Discussion

Because of the complexity of steric interactions in substituted organic molecules, NMR substituent parameters (for ^{13}C as well as ^{15}N) either show rather large standard deviations, or require large numbers of parameters to take care of the various subtle structural aspects.[8] The ^{13}C shifts of methylcyclohexanes were described by Grant and co-workers by 16 additive parameters for the ring carbon and an additional 6 for the methyl carbon atoms.[4b] Because of the still more complex stereochemical situation in the methyldecalins, a simpler set of parameters with correspondingly larger standard deviations was used.[4c]

A similar situation obtains in the *trans*-decahydroquinolines compared with the piperidines. Because of the additional factor of the relative position of the nitrogen, the necessary set of parameters for the ^{13}C NMR data in this class of compounds would have been very large; as a consequence, a calculation of additive parameters by multiple linear regression was not attempted and substituent effects were simply listed as a collection of empirical data.[5] For the ^{15}N NMR data of piperidines, Roberts[3] gives a list of nine substituent parameters. Clearly, the more complex substitution situation in the decahydroquinolines must lead to a larger set, if standard deviations are to be kept small. Consequently, a set of 14 parameters was calculated by linear regression analysis; their values are listed in Table II. Vicinal gauche interactions which do not inlude the nitrogen ($\beta\gamma$ effects in Grant's[4b] terminology) are omitted. The calculations are based on *trans*-decahydroquinoline as a constant term; to be used for piperidines the calculated values must be corrected by subtracting the appropriate additional interaction with C-8 (i.e., α_e(piperidine) = ($\alpha_e - \alpha_e\beta_e$)(*trans*-decahydroquinoline), and similarly for α_a). Agreement with the parameters for the methylpiperidines calculated by Roberts[3] is good. If more accurate chemical shifts for certain situations need to be estimated, they should be taken directly from Table I.

Table I. ^{15}N Chemical Shifts[a] and Shift Effects[b] of *trans*-Decahydroquinolines and *N*-Methyl-*trans*-decahydroquinolines

compd	chem shift	compd	chem shift	
1	54.3	1m	48.5	(−5.8)
2	63.1	2m	43.4	(−19.7)
	(+8.8)		(−5.1)	
3	72.2	3m	60.6	(−11.6)
	(+17.9)		(+12.1)	
4	55.1	4m	48.5	(−6.6)
	(+0.8)		(0.0)	
5	44.1	5m	40.8	(−3.3)
	(−10.2)		(−7.7)	
6	47.5	6m	43.5	(−4.0)
	(−6.8)		(−5.0)	
7	53.6	7m	48.6	(−5.0)
	(−0.7)		(+0.1)	
8	49.6	8m[c]	26.0	(−23.6)
	(−4.7)		(−22.5)[c]	
9	51.4	9m	45.8	(−5.6)
	(−2.9)		(−2.7)	
10	54.3	10m[c]	28.2	(−26.1)
	(0.0)		(−20.3)[c]	
11	55.7	11m	46.9	(−8.8)
	(+1.4)		(−1.6)	
12	58.9	12m[c]	34.2	(−24.7)
	(+4.6)		(−14.3)[c]	
13	66.8	13m[c]	35.8	(−31.0)
	(+12.5)		(−12.7)[c]	
14	60.2	14m	40.3	(−19.9)
	(+5.9)		(−8.2)	
15	70.0	15m	58.3	(−11.7)
	(+15.7)		(+9.8)	
16	47.2	16m	42.6	(−4.6)
	(−7.1)		(−5.9)	
17	41.3	17m[d]	26.5	(−14.8)
	(−13.0)		(−22.0)[d]	
18	48.3			
	(−6.0)			
19	48.1			
	(−6.2)			
20	50.3			
	(−4.0)			

[a] In ppm from liquid ammonia (see Experimental Section). [b] Parenthesized value below shift values = shift difference from parent compound 1 or 1m. Parenthesized values on right of *N*-methyl shifts = shift difference between NCH_3 and NH compound. A plus sign indicates deshielding caused by ring substitution or N-methylation. [c] Axial N–CH_3 group. [d] Predominantly axial N–CH_3 group (cf. ref 6a).

Table II. Substituent Parameters for Methyl Substitution in *trans*-Decahydroquinolines and *N*-Methyl-*trans*-decahydroquinolines[a]

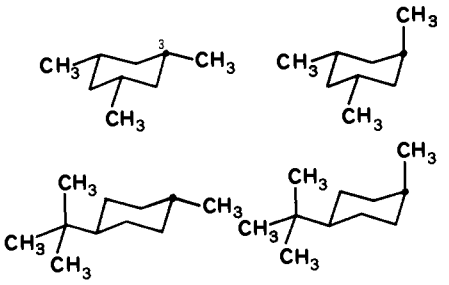
α_e	−6.2 ± 0.4	α_a	−23.5 ± 0.6
β_e	17.6 ± 0.4	β_a	8.7 ± 0.4
γ_e	-0.0_4 ± 0.3	γ_a	−10.4 ± 0.5 (−8.0 ± 0.5)[b]
G_γ	2.7 ± 0.4		
γ_{ge}[c]	−5.3 ± 0.3	γ_{ga}[c]	−2.9 ± 0.3
$\alpha_e\beta_e$	−5.3 ± 0.6	$\alpha_a\beta_a$	−0.5 ± 0.8
$\alpha_e\beta_a$	−14.1 ± 0.6	$\alpha_a\beta_e$	−7.8 ± 0.8
	r = 0.9991		std dev = 0.7 ppm

[a] Substituent parameters for piperidine: α_e(piperidine) = $\alpha_e - \alpha_e\beta_e$; α_a(piperidine) = $\alpha_a - \alpha_a\beta_e$. [b] First value is for NH; parenthesized value is for NCH_3 compounds. [c] γ gauche effects (see text).

α Effects (NH → NCH_3)

The parenthesized values next to the chemical shifts of compounds **1m**–**17m** in Table I give the shift difference between corresponding tertiary and secondary amines. As is immediately evident, introduction of an axial N–CH_3 into a *trans*-decahydroquinoline (e.g., **8** → **8m**: −23.6) causes a shielding which

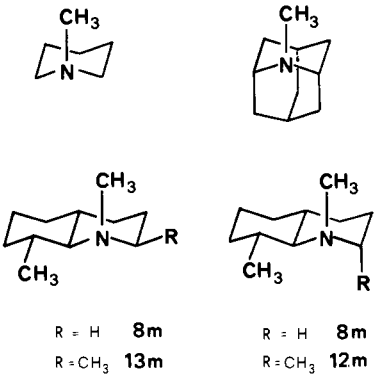
Scheme II



is roughly 18 ppm larger than an equatorial N–CH_3 (e.g., **9** → **9m**: −5.6). Based on his investigations of piperidines and related compounds, Roberts has calculated an $\alpha_{equatorial}$ parameter of +2.2 ppm and an α_{axial} parameter of −20.2 ppm.[3,9] Both values rest on assumptions. The α_e term has been derived from *N*-methylated dimethylpiperidines with biasing 3-axial-methyl groups (*trans*-3,5-dimethylpiperidine and 3,3-dimethylpiperidine) to avoid possible contributions from axial conformations in the nonbiased *N*-methylpiperidines. The calculation requires, however, that the γ_a effect of the biasing 3-methyl group be identical for both the N–H reference and N–CH_3 compound. In the *N*-methyl-*trans*-decahydroquinoline series a smaller shielding effect (compared with the secondary decahydroquinolines) is induced by γ_a substituents when the biasing substituents are in the piperidine part of the molecule (**5m**, **6m**). On the other hand, γ_a values similar to the parent (**1** and **1m**) are obtained if the equally biasing 8β-methyl group is used (**9** and **9m**). The results of Robinson et al.[10] offer strong evidence that *N*-methylpiperidine exists to ~99% in the *N*-methyl equatorial form. This indicates that an α_e effect for *N*-methylpiperidines should be closer to 0 (the value for piperidine) than +2, and that γ_a is larger (more shielding) for secondary than for tertiary compounds.

Introduction of an axial *N*-methyl group has a very strong shielding effect. The resulting deviation from the $^{15}N/^{13}C$ correlation line has been associated[3a] with a nitrogen lone pair oriented antiperiplanar to two carbon atoms. By contrast, the lone pair is oriented antiperiplanar to two hydrogen atoms when an equatorial *N*-methyl group is introduced. These results are analogous to ^{13}C results in the methyldecahydroquinoline series.[5] Thus, part of the shielding caused by the axial *N*-methyl group may be ascribed to the difference in n–σ^* interactions with C–C vs. C–H bonds. The ^{13}C shift difference between an axially or equatorially methyl-substituted cyclohexyl carbon is between 4.1 ppm (C-3 in *cis*-1,3,5-trimethylcyclohexane vs. 1-*trans*-3-*cis*-5-trimethylcyclohexane)[4a,8] and 5.4 ppm (C-4 in *trans*- vs. *cis*-4-methyl-*tert*-butylcyclohexane)[8] (Scheme II). The ^{15}N-shift differences for equatorially and axially methyl-substituted nitrogen in piperidine hydrochlorides is 4.7 ppm for the two *N*,*cis*-3,5-trimethylpiperidinium chlorides[3b] and 6.1 to 6.8 ppm (depending on the solvent) for the *N*-methyl-*trans*-decahydroquinolinium chlorides.[3b] This latter value can be compared with the *trans*-decahydroquinoline results in Table I. Assuming that the shift influence of the biasing C-8 methyl groups is equal for **8** and **8m**, and for **9** and **9m**,[11] the difference for equatorial and axial N–CH_3 can be taken directly as the difference between the effects of N-methylation: −23.6 − (−5.6) = −18 ppm. However, this value still contains the difference in vicinal gauche interactions for C-8 with the axial or equatorial *N*-methyl (see below). A possible way of taking these interactions into account is to assume that the vicinal gauche interaction between the additional methyl group at C-2 with the axial *N*-methyl in **13m** equals the corresponding one for C-8-methine in **8m** (cf. Scheme III). This interaction parameter may be computed by comparing effects of N-methylation in **13** and **8**: −31.0 (**13** → **13m**) − (−23.6) (**8** → **8m**) = −7.4. Subtracting this $\alpha_a\beta_e$ parameter (see below), one obtains −23.6 − (−7.4) = −16.2 ppm as the effect of an axial N–CH_3 on piperidine. The larger value reported by Roberts derives from the effect of N-methylation on the resonance position of azaadamantane (−20.2 ppm).[3,9] While the *N*-methyl group in this molecule must be axial with respect to one piperidine ring regardless of conformation, at the same time there must be two methylene groups anti to the N–CH_3. This might be compensated for in the following way: the effect of one such antiperiplanar methyl group is seen by comparison of the N-methylation effect in **8** (→ **8m**: −23.6) with that in **12** (→ **12m**: −24.7 ppm), which induces an additional shift of −1.1 ppm (cf. Scheme III). Thus the value of −20.2 should perhaps be reduced by 2 × −1.1 ppm (neglecting unlikely differences between anti methyl and methylene carbons), and the α_a effect then becomes ~−18 ppm. Considering the number of possible errors in these calculations, the agreement is very good and the effect of an axial N–CH_3 on an otherwise unsubstituted piperidine may thus be estimated at −17 ± 1 ppm.

Scheme III



β Effects (C_α–H → C_α–CH_3)

Replacement of an equatorial hydrogen at C-2 of **1** by a methyl group produces a deshielding of +17.9 ppm, very similar to the values reported for piperidines.[3] The slightly different values for the two other occurrences (**13** vs. **8**: +17.2; **15** vs. **9**: ±18.6) probably arise from slight geometric differences between these compounds rather than from a change in N–H/N-pair equilibrium.[7,12] An axial CH_3 at C-2 causes a deshielding of 9.0 ± 0.3 ppm, again identical with the value found for piperidines.[3] In this treatment β effects for the N–H and N–CH_3 compounds are arbitrarily assumed to be equal.

γ Effects (C_β–H → C_β–CH_3)

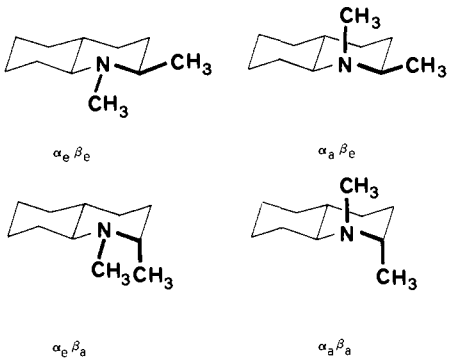
The effects on ^{13}C chemical shifts produced when a hydrogen three bonds removed from a carbon is replaced by a methyl group are known to cover a wide range of values,[4b] with anti effects generally small, and gauche effects quite large and shielding. The results in Table I afford five geometrically different γ interactions: a γ_e (from **4**), two different γ_a's (from **5** and **6**, for a methyl group on a tertiary and a quaternary carbon, respectively), and two γ_{gauche} interactions (γ_{ge}, γ_{ga}) arising from substitution at C-8 (**8** and **9**). The same γ_{gauche} effect for the axial methyl at C-8 can be used for secondary and tertiary nitrogens, but different values are required for intraannular γ_a substitution (see above for α effects). This can be seen as follows: assuming a ratio of >95% **e**: <5% **a** for **1m** and a shift of 30.7 [i.e., **1** + (**8m** − **8**)] for **1ma**, a shift of 48.5–49.4 ppm (depending on whether the percentage of **1ma** is assumed to be 0 or 5%) is calculated for **1me**. Use of the γ effect in the secondary amines **5**, **6**, and **9** with **5m**, **6m**, and **9m** results in values of 51.0, 50.3, and 48.7 ppm for **1me**, respectively. Considering that 49.4 ppm is the upper limit for the **1me** shift,[5] this variation shows the need for using different γ_a values in the N–H and N–CH_3 series.

(10) (a) Crowley, P. J.; Robinson, M. J. T.; Ward, M. G. *J. Chem. Soc. Chem. Commun.* **1974**, 825–6. (b) Robinson, M. J. T. *Ibid.* **1975**, 844–5. (c) Crowley, P. J.; Robinson, M. J. T.; Ward, M. G. *Tetrahedron* **1977**, *33*, 915–25.

(11) This assumption is based on comparison of the **1** → **9** shift difference with that for **1m** → **9m**, which are essentially identical (2.7 vs. 2.9 ppm).

(12) Vierhapper, F. W.; Eliel, E. L.; Zúñiga, G. *J. Org. Chem.* **1980**, *45*, 4844–50.

Scheme IV



In order to account for the shifts in **6**, **16**, and **17**, one must use an additional parameter ("G_γ") which is presumably due to the geminal substitution at C-4a. The same parameter will fit the *N*-methyl compounds **6m**, **16m**, and **17m**.

Vicinal Interactions

1,2-Disubstitution on cyclohexanes causes a number of vicinal interactions that can influence ^{13}C chemical shifts. Vicinal parameters ($\alpha\beta$, $\beta\gamma$) were calculated[4b] to permit prediction of chemical shifts in such compounds. For the methyldecalins a simplified approach using one V_g parameter was chosen.[4c]

Because of the more complex substitution pattern and especially because of the importance of the orientation of the lone pair on tertiary nitrogen shifts, such a simplification would give very high standard deviations in calculated ^{15}N parameters of decahydroquinolines. Four $\alpha\beta$ parameters are derived from the *N*-methyl-*trans*-decahydroquinolines (Scheme IV). The $\alpha_e\beta_e$ effect (−5.3 ppm) is identical with the value previously reported for the *N*-methylpiperidines.[3b,9] Comparison of the chemical shifts of *N*-methylpiperidine[3] with **1m**, and of **1m** with **3m**, shows that the size of a second $\alpha_e\beta_e$ effect (between $CH_3(2)$ and NCH_3 in **3m**) is nearly equal in size to the first one (between C-8 and NCH_3 in **1m**). It is unlikely that a substantial part of the shielding effect in **3m** can be ascribed to an increased proportion of **3ma**,[3a,10] since the shift difference between **15m** and **9m**, −12.5 ppm, in which the NCH_3 group must be completely equatorial, and that between **3m** and **1m**, −12.1 ppm, is practically identical.

On the assumption that the β effect in the N–H compounds may be applied to the N–CH_3 series, the $\alpha_e\beta_a$ effect (in **2m**) is strongly shielding. In analogy to axial N-methylation, this may be related to the positioning of a carbon atom anti to the lone pair of nitrogen in a tertiary amine. The fact that the effect is virtually the same in **14m**, where the *N*-methyl group is constrained to be equatorial,[12] allows the exclusion of a significant amount of **2ma** as a potential source of the high shielding in **2m**. The $\alpha_a\beta_e$ effect (in **13m**) is also shielding, but only to the extent of approximately 60% of $\alpha_e\beta_a$, presumably because the nitrogen lone pair is already anti to two carbon atoms (in **8m**) prior to the introduction of the β-methyl group. The $\alpha_a\beta_a$ effect has already been discussed in connection with the α_a parameter (see above).

δ and More Remote Effects

Replacement of either hydrogen at C-8 in **1** by a *tert*-butyl group (**10**, **11**) introduces a deshielding δ-shift effect on nitrogen. (Comparison with the 8-methyl compounds **8** and **9** shows a cancellation or reversal of the characteristic shielding of the γ-gauche effects). The deshielding character of the "syn-axial" δ effect is analogous to that observed in ^{13}C spectra in these compounds[7a] and others of similar orientation.[6,13]

While syn-axial methyl groups have no substantial influence on the NH **a** ⇄ **e** conformational equilibrium (the assumption[3a] that **8** exists essentially in conformation **a** has been found incorrect[7a]), *tert*-butyl groups in an identical situation do shift the equilibrium measurably.[7a] Comparison of the chemical shifts of **1**, **8**, and **9** with **10** and **11** confirms that the position of the lone pair does not give rise to substantial shift effects in secondary amines (even though it does so in tertiary ones) and that ^{15}N NMR (like ^1H and ^{13}C NMR)[7] cannot be used for the determination of the N–H/N–lone pair equilibrium. Effects of N-methylation are slightly different for **10** and **11** compared to the 8-methyl compounds. Since the steric strain in these compounds is considerable, it is not surprising that the δ effects for NH and NCH_3 compounds should differ, as do the γ_a effects (see above).

In **17m** the "syn-axial" interaction between $CH_3(8)$ and NCH_3 in conformation **e** is opposed by the syn-axial interaction between $CH_3(4a)$ and NCH_3 in **a**. Proton and ^{13}C spectra had shown that the predominant form is likely to be **17ma**.[6a] The δ interaction between the two methyl groups results in a diminished shielding upon N-methylation. Completely analogous results, of the same order of magnitude, are seen in ^{13}C NMR (e.g., for C-4a in **17m**),[6a] and in the ^{15}N NMR spectra of *cis*-decahydroquinolines bearing methyl groups in similar conformations.[14]

The shift effect of a methyl group at C-6 (oriented "doubly ϵ" to N-1) in **7** and **7m** is small. Finally, fusion of a second cyclohexyl ring instead of the 8-methyl groups in **18**, **19**, and **20** has a noticeably different influence on the nitrogen chemical shift. This points to the importance of multiple long-range effects[8] and explains why simple addition of β_e and γ_e effects to the chemical shift of piperidine does not give the correct value for *trans*-decahydroquinoline.

In summary, comparison of the ^{15}N shifts of **1** and **1m** with *C*-methyl-substituted *trans*-decahydroquinolines allows calculation of substitution parameters for this class of compounds. As with ^1H and ^{13}C NMR, ^{15}N-spectroscopy is useful for the estimation of conformational equilibria in tertiary, but not in secondary amines.

Experimental Section

The preparation of the compounds used in this investigation has been described elsewhere.[6a,b,12,15]

Nitrogen chemical shifts were measured in the Fourier transform mode with broad-band proton decoupling by using a JEOL PFT-100 spectrometer equipped with the EC-100 data system and operating at 10.09 MHz. A sweep width of 5 kHz over 8K data points was used. For the N–H decahydroquinolines a pulse width corresponding to a tip angle of 30° and a repetition time of 2 s was employed; this was increased to 4 s for the methylated series. The N–H series required 5–10K transients, while the *N*-methyl compounds required 25K transients for an adequate signal-to-noise ratio. Samples were 2–4 M in C_6H_6/C_6D_6 solution. The reference signal was derived from a concentric capillary of ^{15}N-enriched nitromethane. Chemical shifts are reported in parts per million to lower shielding from anhydrous liquid ammonia by using the expression $\delta_{NH_3} = \delta_{CH_3NO_2} + 380.2$.[16]

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(14) (a) Vierhapper, F. W.; Furst, G. T.; Lichter, R. L. *Org. Magn. Reson.*, in press. (b) It should be noted, however, that the same finding—diminished shielding upon N-methylation—would result from enhancement of the proportion of **17me** to the **17ma**/**17me** equilibrium. This possibility seems unlikely in view of the ^{13}C NMR results.[6a]

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(16) Reference 2, pp 28ff.