# Carbon-13 Spectra of Saturated Heterocycles. 10. Effect of Lone Electron Pairs on Nitrogen on the Chemical Shift of Antiperiplanar Vicinal Methyl Carbons[1†]

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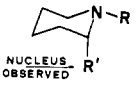
The $^{13}C$ spectra of the four diastereomeric 2,8-dimethyl-*trans*-decahydroquinolines as well as those of two of the cis isomers, of the eight diastereomeric 2-methyl-8-*tert*-butyl-*cis*- and -*trans*-decahydroquinolines, and of the *N*-methyl derivatives of the trans compounds have been examined. An antiperiplanar lone pair on nitrogen has a palpable upfield shifting effect on the carbon signal of an axial methyl group at C-2 in the *N*-methyl compounds, but no such effect is seen in the NH compounds.

In 1964, Hamlow et al.[2,3] showed that the lone pair on nitrogen in quinolizidine produces an upfield NMR shift of the axial protons in the position $\alpha$ to the nitrogen. In the following 15 years there was a great deal of controversy[4] as to whether the upfield shift of the protons antiperiplanar to a lone pair, e.g., in methylpiperidines (A), was

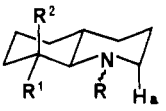



A, R = $CH_3$; R' = H
B, R = R' = H
C, R = R' = $CH_3$
D, R = H; R' = $CH_3$

due to the lone pair, the *N*-alkyl group, or both. The controversy logically extended to the question whether or not there were corresponding upfield shifts in piperidines (NH) (B) where they would be due solely to the antiperiplanar lone pair. Over the years it has become clear[5-8] that the shift in *N*-alkylpiperidines is real and is due *in part* to the effect of the lone pair (believed[3] to be a n–$\sigma^*$ interaction) and *in part* to the *N*-alkyl substituent. Surprisingly, however, experiment shows[9] that there is *no* upfield shifting effect at all due to the antiperiplanar lone pair in NH compounds such as piperidine itself.

It seemed of interest to explore the corresponding effects of gauche alkyl groups and antiperiplanar lone pairs on the $^{13}C$ chemical shift of an axial methyl substituent $\alpha$ to the nitrogen (C, D). Preliminary studies[10] indicated an upfield shifting effect on the $^{13}C$ signal in the *N*-methyl compounds (prototype C) similar to the effect on the proton shift. We now report additional data which confirm this shift and strongly suggest that it is caused *both* by the gauche *N*-methyl substituent *and* by the antiperiplanar lone pair. At the same time we adduce evidence that *no* corresponding shift is seen in the NH compounds (prototype D). The situation with respect to $^{13}C$ shifts is thus completely parallel to that with $^1H$ shifts.

Our previous approach[11] to the determination of the effect of antiperiplanar lone pairs on the shift of axial protons in *N*-alkylpiperidine systems (A) involved *N*-methyl-*trans*-decahydroquinoline (**1m**) as the model system. The *N*-methyl group may be forced entirely into the axial position by an equatorial ($\alpha$) methyl group at C-8




| R = H | R = $CH_3$ | $R^1$ | $R^2$ |
|---|---|---|---|
| 1 | 1m | H | H |
| 2 | 2m | $CH_3$ | H |
| 3 | 3m | H | $CH_3$ |
| 4 | 4m | $C(CH_3)_3$ | H |
| 5 | 5m | H | $C(CH_3)_3$ |

(**2m**) or it may be forced into an equatorial position by an axial ($\beta$) group at C-8 (**3m**). Similar effects are produced by *tert*-butyl substituents at C-8 (**4m** and **5m**; see also below).[9] In all cases, the axial proton at C-2 (H-$2_a$) moves upfield by about 0.8 ppm when the lone pair on the adjacent nitrogen is antiperiplanar as in **3m** and **5m**.

In contrast, no corresponding upfield shift of H-$2_a$ is seen in the homologous NH compounds (**3** compared to **2**).[12a] Even equatorial (**4**) and axial (**5**) 8-*tert*-butyl substituents do not produce palpable changes in the H-$2_a$ shift, though it is quite clear from observation of Bohlmann bands[13] in the infrared spectrum that the nitrogen H is indeed predominantly equatorial (and thus the lone pair axial) in **5** whereas it is predominantly axial (lone pair equatorial) in **4**[9] and though it is evident from both $^{13}C$ spectra[9] and from an X-ray structural study[14] that **5** in fact exists as a double

† Dedicated to Professor Harry S. Mosher on the occasion of his 65th birthday.

(1) Paper 9: Eliel, E. L.; Kandasamy, D.; Yen, Chen-yu; Hargrave, K. D. *J. Am. Chem. Soc.* **1980**, *102*, 3698.
(2) Hamlow, H. P.; Okuda, S.; Nakagawa, N. *Tetrahedron Lett.* **1964**, 2553.
(3) See also: Bohlmann, F.; Schumann, D.; Schulz, H. *Tetrahedron Lett.* **1965**, 173.
(4) E.g., see: Blackburne, I. D.; Katritzky, A. R.; Takeuchi, Y. *Acc. Chem. Res.* **1975**, *8*, 300.
(5) Booth, H.; Little, J. H. *Tetrahedron* **1967**, *23*, 291.
(6) Robinson, M. J. T. *Tetrahedron Lett.* **1968**, 1153.
(7) Ridell, F. G.; Lehn, J.-M. *J. Chem. Soc. B* **1968**, 1224.
(8) Lambert, J. B.; Keske, R. G. *Tetrahedron Lett.* **1969**, 2023.
(9) Vierhapper, F. W.; Eliel, E. L. *J. Org. Chem.* **1979**, *44*, 1081.
(10) Eliel, E. L.; Rao, V. S.; Vierhapper, F. W.; Zúñiga Juaristi, G. *Tetrahedron Lett.* **1975**, 4339.
(11) Eliel, E. L.; Vierhapper, F. W. *J. Am. Chem. Soc.* **1975**, *97*, 2424.
(12) (a) Vierhapper, F. W.; Eliel, E. L. *J. Org. Chem.* **1975**, *40*, 2734. (b) Eliel, E. L.; Vierhapper, F. W. *Ibid.* **1976**, *41*, 199.
(13) A recent collection of literature on Bohlmann bands is found in: M. Golfier In "Stereochemistry, Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 1, p 7.
(14) Hargrave, K. D.; Eliel, E. L. *Tetrahedron Lett.* **1979**, 1987; *Isr. J. Chem.* **1980**, *20*, 127.

0022-3263/80/1945-4844$01.00/0 

Table I. $^{13}C$ Chemical Shifts of 2-Methyl-*trans*-decahydroquinolines[a,b]

| compd | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9[c] | C-10[c] | 2-$CH_3$ | C-q[d] | $CH_3$[e] | $NCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6[a] | 52.37 | 34.98 | 32.41 | 32.24 | 26.21 | 25.47 | 33.79 | 61.85 | 42.37 | 22.95 | | | |
| 7[a] | 47.53 | 31.33 | 26.79 | 32.47 | 26.29 | 25.74 | 34.31 | 53.96 | 43.92 | 18.62 | | | |
| 8 | 52.69 | 34.54 | 32.58 | 32.71 | 25.83 | 34.75 | 37.18 | 67.90 | 41.27 | 23.04 | | 18.49 | |
| 9 | 47.63 | 30.77 | 26.87 | 32.90 | 25.88 | 34.93 | 37.62 | 59.89 | 42.63 | 18.78 | | 18.52 | |
| 10 | 52.90 | 35.35 | 32.82 | 33.07 | 20.28 | 32.95 | 33.26 | 64.36 | 34.93 | 23.01 | | 12.62 | |
| 11 | 47.74 | 31.55 | 27.26 | 33.08 | 20.30 | 33.08 | 33.23 | 55.98 | 36.24 | 18.22 | | 12.29 | |
| 12 | 52.61 | 34.89 | 33.50 | 33.12 | 26.38 | 28.18 | 50.57 | 65.18 | 42.63 | 23.25 | 33.12 | 30.01 | |
| 13 | 47.55 | 31.30 | 27.81 | 33.38 | 26.40 | 28.37 | 50.92 | 57.14 | 44.16 | 17.98 | 33.09 | 29.91 | |
| 14 | 53.72 | 35.02 | 34.39 | 33.49 | 22.07 | 29.82 | 46.50 | 67.63 | 35.23 | 23.34 | 34.39 | 32.70 | |
| 15 | 47.90 | 31.21 | 28.62 | 33.57 | 22.18 | 29.84 | 46.61 | 59.43 | 36.62 | 18.04 | 34.43 | 32.71 | |
| 6m[a] | 59.72 | 34.65 | 32.75 | 33.52 | 25.77 | 26.07 | 30.86 | 69.19 | 41.51 | 21.93 | | | 37.14 |
| 7m[a] | 55.97 | 31.62 | 26.92 | 32.94 | 26.21 | 26.03 | 30.94 | 60.03 | 42.51 | 9.08 | | | 39.53 |
| 8m | 57.77 | 25.89 | 34.02 | 34.22 | 25.89 | 35.75 | 34.47 | 72.52 | 30.79 | 20.67 | | 18.77 | 25.56 |
| 9m | 56.03 | 23.05 | 27.87 | 34.21 | 25.82 | 35.95 | 34.02 | 62.94 | 31.59 | 18.18 | | 18.87 | 35.81 |
| 10m | 59.84 | 35.04 | 33.20 | 34.10 | 19.93 | 32.74 | 29.58 | 71.77 | 34.52 | 22.18 | | 12.05 | 37.12 |
| 11m | 56.04 | 31.67 | 26.88 | 33.51 | 20.28 | 32.78 | 29.24 | 62.70 | 34.76 | 8.75 | | 11.81 | 38.98 |
| 12m | 57.83 | 25.24 | 34.92 | 34.08 | 25.94 | 28.32 | 45.41 | 69.31 | 30.70 | 20.68 | 33.64 | 29.06 | 26.62 |
| 13m | 55.66 | 22.82 | 29.77 | 34.20 | 25.91 | 28.52 | 45.08 | 58.93 | 31.96 | 18.10 | 33.80 | 28.97 | 36.03 |
| 14m | 61.05 | 35.23 | 33.28 | 35.23 | 22.18 | 30.15 | 41.83 | 74.74 | 34.41 | 22.78 | 35.14 | 32.89 | 41.62 |
| 15m | 54.95 | 31.24 | 27.12 | 35.08 | 22.48 | 29.62 | 41.63 | 68.34 | 33.84 | 9.65 | 35.08 | 32.81 | 40.79 |

[a] The data for **6**, **7**, **6m**, and **7m** are repeated from ref 12b, which should be referred to for the method of assignment. [b] Solvent $CDCl_3$. In parts per million from internal $Me_4Si$. [c] C-9 and C-10 are used instead of C-8a and C-4a to reserve the use of "a" for axial. [d] Quaternary carbon of *tert*-butyl group. [e] $CH_3$ either at C-8 or of *tert*-butyl group.

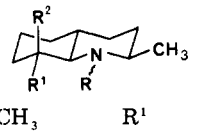
Table II. $^{13}C$ Chemical Shifts of 2-Methyl-*trans*-decahydroquinolinium Chlorides[a,b]

| compd | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | 2-$CH_3$ | C-q[c] | $CH_3$[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6·$H^+Cl^-$[a] | 54.26 | 30.78 | 30.46 | 32.00 | 24.87 | 24.87 | 29.59 | 61.71 | 38.36 | 19.31 | | |
| 7·$H^+Cl^-$[a] | 48.43 | 27.50 | 24.75 | 32.01 | 24.94 | 24.94 | 29.72 | 54.44 | 39.44 | 14.51 | | |
| 8·$H^+Cl^-$ | 54.74 | 30.44 | 30.44 | 32.63 | 24.77 | (35.26) | (34.87) | 66.72 | 38.14 | 19.60 | | 19.60 |
| 9·$H^+Cl^-$ | 49.04 | 27.28 | (24.59) | 32.34 | (25.04) | 34.77 | 34.77 | 60.65 | 39.10 | 14.76 | | 19.33 |
| 10·$H^+Cl^-$[e] | 55.82 | (31.39) | (31.39) | (33.03) | (18.96) | (32.48) | (30.90) | 65.42 | (32.62) | (19.55) | | 12.77 |
| 11·$H^+Cl^-$ | 48.88 | 27.52 | 25.44 | 32.84 | 19.23 | 32.08 | 30.21 | 56.94 | 33.08 | 14.71 | | 13.02 |
| 12·$H^+Cl^-$ | 55.51 | 29.37 | 31.08 | 33.15 | 25.15 | 28.06 | 49.62 | 64.65 | 38.76 | 20.22 | 33.73 | 30.05 |
| 13·$H^+Cl^-$ | 50.26 | (26.48) | (26.19) | 32.59 | 24.59 | 27.74 | 47.65 | 58.03 | 38.84 | 14.81 | 32.60 | 29.98 |
| 14·$H^+Cl^-$ | 57.84 | (29.41) | (32.08) | 33.78 | 20.74 | (29.01) | 43.95 | 67.99 | 33.16 | 19.13 | 34.45 | 32.63 |
| 15·$H^+Cl^-$ | 50.38 | 27.27 | 26.41 | 33.69 | 20.80 | 29.67 | 43.82 | 58.99 | 33.39 | 13.67 | 33.78 | 32.94 |

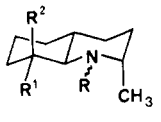
[a] The data for 6·$H^+Cl^-$ and 7·$H^+Cl^-$ are repeated from ref 12b. [b] Solvent $CDCl_3$ unless indicated; in parts per million from internal $Me_4Si$. [c] Quaternary carbon of *tert*-butyl group. [d] $CH_3$ either at C-8 or of *tert*-butyl group. [e] Solvent 1:3 $CDCl_3$-$CH_3OH$.

chair (only slightly distorted) with an axial *tert*-butyl group.

In order to explore corresponding effects in $^{13}C$ chemical shifts, we synthesized the equatorial (2β-$CH_3$) and axial (2α-$CH_3$) 2-methyl homologues **6–15**. To shift the *N*-

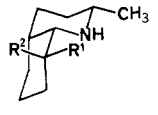


| R = H | R = $CH_3$ | R¹ | R² |
|---|---|---|---|
| 6 | 6m | H | H |
| 8 | 8m | $CH_3$ | H |
| 10 | 10m | H | $CH_3$ |
| 12 | 12m | $C(CH_3)_3$ | H |
| 14 | 14m | H | $C(CH_3)_3$ |

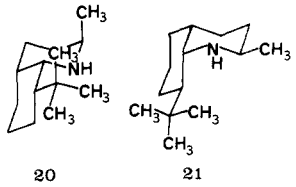


| R = H | R = $CH_3$ | R¹ | R² |
|---|---|---|---|
| 7 | 7m | H | H |
| 9 | 9m | $CH_3$ | H |
| 11 | 11m | H | $CH_3$ |
| 13 | 13m | $C(CH_3)_3$ | H |
| 15 | 15m | H | $C(CH_3)_3$ |

methyl groups to the equatorial and axial positions, respectively, we used 8-methyl (**8m–11m**) or 8-*tert*-butyl (**12m–15m**) levering groups as explained above. Equatorial 8-*tert*-butyl levering groups (**12**, **13**) were needed to produce a partial shift of the NH substituent from predominantly equatorial to predominantly axial. We did investigate the $^{13}C$ NMR spectra of the entire set of compounds mentioned above (**6–15**) as well as those of the 8-substituted *cis*-decahydroquinolines **16–21**.



**16**, $R^1 = CH_3$; $R^2 = H$
**17**, $R^1 = H$; $R^2 = CH_3$
**18**, $R^1 = C(CH_3)_3$; $R^2 = H$
**19**, $R^1 = H$; $R^2 = C(CH_3)_3$



**20** **21**

**$^{13}C$ NMR Spectra.** Table I displays the chemical shifts for amines **6–15** and **6m–15m**; the shifts of their hydrochlorides are collected in Tables II and III. Assignment of the signals of the 8-methyl- or 8-*tert*-butyl-substituted compounds was achieved by comparison with the 8-methyl-*trans*-decahydroquinolines[12b] and 8-*tert*-butyl-*trans*-decahydroquinolines[9] and with **6** and **7** (or **6m** and

Table III. $^{13}C$ Chemical Shifts of *N*,2-Dimethyl-*trans*-decahydroquinolinium Chlorides[a,b]

| compd | C—2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | 2-$CH_3$ | C-q[c] | $CH_3$[d] | $NCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $6m_e \cdot H^+Cl^-$ | 63.0$_6$ | 32.8$_4$ | 30.7$_7$ | 32.9$_4$ | 24.1$_7$ | 25.4$_1$ | 27.4$_7$ | 70.6$_5$ | 38.9$_0$ | 18.6$_8$ | | | 35.9$_7$ |
| $6m_a \cdot H^+Cl^-$ | 59.7$_2$ | 25.6$_0$ | *e* | *e* | 25.0$_3$? | 25.0$_3$? | 28.1$_5$ | 67.5$_1$ | 31.6$_0$ | 17.7$_4$ | | | 25.8$_1$ |
| $7m_e \cdot H^+Cl^-$ | 58.8$_1$ | 28.8$_5$ | 24.7$_6$ | 32.3$_8$ | 24.6$_5$ | 25.2$_9$ | 27.2$_1$ | 62.5$_5$ | 39.8$_6$ | 11.0$_4$ | | | 38.5$_9$ |
| $7m_a \cdot H^+Cl^-$ | 59.3$_0$ | 23.3$_0$ | *e* | 32.8$_2$ | 25.0$_4$? | 25.0$_4$? | 28.0$_7$ | 59.3$_0$ | 33.6$_9$ | 15.5$_2$ | | | 35.7$_0$ |
| $8m_a \cdot H^+Cl^-$ | 61.4$_8$ | 25.8$_0$ | 30.5$_2$ | 32.9$_5$ | 24.6$_0$ | 34.7$_8$ | (33.7$_0$) | 73.2$_4$ | (33.1$_5$) | 18.0$_0$ | | 18.8$_9$ | 26.4$_9$ |
| $9m_a \cdot H^+Cl^-$ | 59.7$_1$ | 22.7$_5$ | (24.7$_9$) | (32.8$_9$) | (24.4$_4$) | 34.8$_7$ | (32.8$_9$) | 65.0$_3$ | (33.5$_3$) | 15.7$_5$ | | 18.9$_2$ | 35.3$_2$ |
| $10m_e \cdot H^+Cl^-$ | 64.1$_7$ | 32.3$_1$ | 30.9$_7$ | 33.5$_2$ | 18.4$_1$ | 31.3$_2$ | 28.4$_9$ | 72.9$_9$ | 32.6$_0$ | 18.2$_6$ | | 13.1$_8$ | 34.9$_0$ |
| $11m_e \cdot H^+Cl^-$ | 59.3$_8$ | 28.4$_2$ | 25.1$_4$ | (33.2$_0$) | 18.9$_4$ | 32.2$_5$ | 28.0$_2$ | 64.9$_3$ | (33.2$_8$) | 10.9$_3$ | | 18.6$_2$ | 38.0$_0$ |
| $12m_a \cdot H^+Cl^-$ | 62.2$_3$ | 21.2$_6$ | 28.7$_6$ | 31.2$_0$ | 24.0$_5$ | 26.4$_7$ | 45.3$_0$ | 70.3$_1$ | 30.7$_2$ | 18.5$_3$ | 34.1$_8$ | 29.3$_7$ | 28.3$_2$ |
| $13m_a \cdot H^+Cl^-$ | 60.5$_6$ | 22.5$_3$ | 26.3$_2$ | 31.6$_6$ | 23.3$_1$ | 26.8$_2$ | 44.8$_9$ | 62.4$_4$ | 32.8$_9$ | 16.4$_9$ | 33.2$_8$ | 29.5$_1$ | 35.5$_7$ |
| $14m_e \cdot H^+Cl^-$ | 68.0$_6$ | 32.6$_7$ | 30.3$_5$ | 34.7$_7$ | 20.0$_2$ | 31.5$_9$ | 42.0$_3$ | 76.6$_2$ | 33.2$_2$ | 18.5$_2$ | 34.5$_3$ | 33.2$_2$ | 38.2$_0$ |
| $15m_e \cdot H^+Cl^-$ | 60.6$_1$ | 28.7$_1$ | 25.1$_1$ | 34.4$_1$ | 20.7$_3$ | 31.3$_5$ | 41.0$_2$ | 68.3$_3$ | 33.6$_0$ | 11.0$_2$ | 34.4$_1$ | 33.4$_2$ | 40.0$_4$ |

[a] The data of $6m_e \cdot H^+Cl^-$, $6m_a \cdot H^+Cl^-$, $7m_e \cdot H^+Cl^-$, and $7m_a \cdot H^+Cl^-$ are repeated from ref 12b. [b] Solvent $CDCl_3$, in parts per million from internal $Me_4Si$. [c] Quaternary carbon of *tert*-butyl group. [d] $CH_3$ either at C-8 or of *tert*-butyl group. [e] Not seen.

Table IV. $^{13}C$ Chemical Shifts of 2-Methyl-*cis*-decahydroquinolines[a]

| compd | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | 2-$CH_3$ | C-q[b] | $CH_3$[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 53.6$_6$ | 30.0$_6$ | 31.1$_3$ | 24.8$_3$ | 26.7$_1$ | 28.4$_1$ | 36.6$_6$ | 60.6$_0$ | 36.8$_0$ | 23.0$_4$ | | 18.6$_7$ |
| 17 | 53.4$_4$ | 30.0$_1$ | 30.9$_3$ | 26.6$_2$ | 20.8$_0$ | 25.4$_3$ | 34.8$_6$ | 60.9$_6$ | 30.0$_1$ | 23.1$_1$ | | 17.8$_5$ |
| 18 | 53.2$_6$ | 29.8$_8$ | 31.3$_8$ | 25.2$_9$ | 27.2$_3$ | 21.7$_3$ | 51.4$_8$ | 58.1$_4$ | 37.0$_7$ | 23.3$_5$ | 34.4$_2$ | 29.1$_2$ |
| 19 | 53.3$_7$ | 29.5$_5$ | 30.2$_0$ | 22.2$_7$ | 21.5$_6$ | 20.9$_7$ | 52.2$_2$ | 56.9$_9$ | 30.5$_1$ | 23.3$_1$ | 33.5$_4$ | 28.5$_2$ |
| 20 | 47.6$_8$ | 24.7$_3$ | (25.8$_6$) | (25.5$_1$) | 17.1$_4$ | 21.5$_5$ | 51.4$_0$ | 49.0$_0$ | 37.6$_8$ | 18.0$_4$ | 32.7$_0$ | 29.0$_2$ |
| 21 | 44.5$_2$ | 35.3$_3$ | 25.9$_8$ | 31.8$_8$ | 21.7$_0$ | 27.9$_7$ | 41.6$_3$ | 57.6$_7$ | 38.1$_6$ | 22.5$_5$ | 33.4$_9$ | 29.1$_2$ |

[a] Solvent $CDCl_3$; in parts per million from internal $Me_4Si$. [b] Quaternary carbon of *tert*-butyl group. [c] $CH_3$ either at C-8 or of *tert*-butyl group.

**7m**, respectively), for which assignments had been aided by the preparation[12a] of partially deuterated analogues. Reported in Table IV are the chemical shifts of two of the four possible 2,8-dimethyl-*cis*-decahydroquinolines (**16, 17**) and of the four 2-methyl-8-*tert*-butyl-*cis*-decahydroquinolines (**18–21**) prepared in the course of the synthesis of **8–11** and **12–15**.

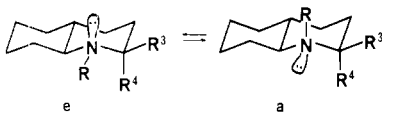
A comparison of the shift values leaves no doubt as to the correctness of the configurational assignments. Compounds **6, 8, 10, 12**, and **14** have an equatorially orientated methyl group at C-2; the chemical shifts occur at 23.1 ± 0.2 ppm. Compounds **7, 9, 11, 13**, and **15** with an axial methyl at C-2 show this signal at 18.3 ± 0.4 ppm; differentiation between these two groups of compounds is therefore trivial. Compounds **16–19** also have equatorial C-2 methyl groups (with similar shift values); their correct configurations and conformations can be assigned by comparison with the published data[15] of 2$\alpha$- and 2$\beta$-methyl-*cis*-decahydroquinolines, corrected by the substituent effects[9,12b,16] for axial or equatorial methyl or *tert*-butyl groups at C-8. Compound **20** is readily identified by the upfield signal of its axial methyl group at C-2, whose shift in the $^{13}C$ spectrum is superimposed on the framework of 8$\alpha$-*tert*-butyl-*cis*-decahydroquinoline.[9] The fourth stereoisomer in the 8-*tert*-butyl-*cis* series, **21**, exists in the alternate chair–chair conformation; thus its signal assignments are derived from those of 2$\beta$-methyl-*cis*-decahydroquinoline by addition of the shifts caused by an equatorial 8-*tert*-butyl group.[9]

The shift values of individual carbon atoms of **6–15** show the expected effects of axial and equatorial methyl groups at C-2[12b] and of axial or equatorial methyl or *tert*-butyl groups at C-8.[9,12b] Chemical shifts of carbon atoms remote from the substituents are similar throughout (e.g., C-3 or C-4 for **6, 8, 10, 12**, and **14** and **7, 9, 11, 13**, and **15**, respectively), although some long-range substituent effects do occur. A remarkably large one is seen at C-4 upon introduction of either an equatorial (1.09, 1.02 ppm) or an axial (1.83, 1.98 ppm) *tert*-butyl group at C-8. As in the case of compounds **4** and **5**[9,14] there is no indication that any of the compounds is in other than the double-chair conformation.

Comparing **8** and **10**, **12** and **14**, **9** and **11**, and **13** and **15**, one sees that any changes in the position of the proton–lone electron pair equilibrium on nitrogen caused by the biasing axial or equatorial methyl or *tert*-butyl groups at C-8 have no influence on the 2-$CH_3$ $^{13}C$ shifts. Evaluation of the Bohlmann region in the infrared spectrum had shown that methyl groups at C-8 cause only minor changes in the NH/lone pair equilibrium in *trans*-decahydroquinolines **2** and **3**;[9] similar results are now found in the 2-methyl homologues **8–11** by this technique (see below). In contrast, *tert*-butyl substituents at C-8 do cause a tangible change in the H/lone pair equilibrium on N (see ref 9 and below). While the equatorial methyl groups at C-2 in **12** and **14** are gauche to both the proton and the lone pair regardless of the position of the latter, there is a substantially greater proportion of lone pair anti to 2-$CH_3$ in **15** than in **13**. The observed shift difference of only 0.06 ppm must, however, be considered insignificant, especially since the less shielded carbon is actually the one with the higher proportion of the anti lone-pair arrangement.

We turn now to the *N*-methyl series. Compounds **10m, 11m, 14m**, and **15m** must have the *N*-methyl group completely in the equatorial position, whereas **8m, 9m, 12m**, and **13m** have entirely axial *N*-methyl groups. The conformational equilibrium $NCH_3(e) \rightleftarrows NCH_3(a)$ in **6m** and **7m** might be expected to be slightly less one-sided than in **1m** (≥95% equatorial):[11] in $\mathbf{6m_e}$ the *N*-methyl group encounters two vicinal gauche interactions with equatorial substituents, and there is evidence[1,17] that such a situation is less favorable than the corresponding one between an axial *N*-methyl and the equatorial $\alpha$ substituents. In $\mathbf{7m_e}$

(15) Booth, H.; Griffiths, D. V.; Jozefowicz, M. L. *J. Chem. Soc., Perkin Trans. 2* **1976**, 751.
(16) Vierhapper, F. W.; Eliel, E. L. *J.* Org. Chem. **1977**, *42*, 51.
(17) Crowley, P. J.; Robinson, M. J. T.; Ward, M. G. *Tetrahedron* **1977**, *35*, 915.



e a

| R = H | R = $CH_3$ | $R^3$ | $R^4$ |
|---|---|---|---|
| 1 | 1m | H | H |
| 6 | 6m | $CH_3$ | H |
| 7 | 7m | H | $CH_3$ |

a vicinal gauche interaction between *N*- and 2-methyl groups occurs, which is avoided in the *N*-methyl axial form **7m**$_a$. A combination of the effects found in **6m**$_e$ and **7m**$_e$ had resulted in a $\Delta G°_{293}$ (for the *N*-Me$_e$ ⇄ *N*-Me$_a$ equilibrium) of 1.95 kcal/mol in *N*,2,2,6-tetramethylpiperidine,[18] compared to the 2.7 kcal/mol found for *N*-methylpiperidine;[17] however, the proportion of *N*-methyl axial conformer is still very small. The slight upfield chemical shift of carbon atom 3 in **6m** (34.65 ppm) relative to corresponding shifts in **10m** (35.04 ppm) and **14m** (35.23 ppm) indeed gives a tenuous indication of a measurable proportion of **6m**$_a$.

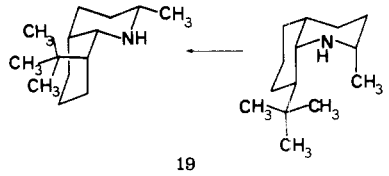
The chemical shifts of the equatorial 2-$CH_3$ groups of **6m**, **10m**, and **14m** and of **8m** and **12m** reflect only the small differences between the *N*-$CH_3$(e) and 2-$CH_3$(e) and the *N*-$CH_3$(a) and 2-$CH_3$(e) vicinal gauche interactions. The *N*-$CH_3$(a) shifts in **8m** and **12m** are also quite similar. The equatorial *N*-$CH_3$ in **14m**, on the other hand, shows a large deshielding effect (4.5 ppm) due to the *tert*-butyl holding group; a similar but smaller effect was seen for **5m**.[9] This is probably the result of steric compression which the *N*-$CH_3$ in **14m** can avoid even less than that in **5m**. In the 2-methyl axial series, the effect of the axial *tert*-butyl group (in **15m**) is again shielding, but only by less than 2 ppm.

The 2-$CH_3$ shifts for **7m**, **11m**, and **15m** and for **9m** and **13m** are the most interesting. Unlike in the corresponding secondary amines, the equatorial or axial position of the substituent on nitrogen has a very pronounced effect on the Me-2$_a$ shifts. Part of the large shielding (−9.5, −9.5, −8.4 ppm) in the *N*-$CH_3$ equatorially substituted compounds is, of course, due to the vicinal gauche interaction between 2-$CH_3$ and $NCH_3$; in cyclohexanes, such an interaction (correcting for the influence of holding groups) is ca. −6 ppm.[19] The probable cause for the additional upfield shift in the tertiary amines is the position of the lone electron pair on the nitrogen anti to the 2-$CH_3$. In support of this contention we note that the analogous effect of an equatorial C-2 methyl on an axial *N*-$CH_3$ is more "normal" (**2m**$^9$ → **8m**, −7.7 ppm; **4m**$^9$ → **12m**, −6.4 ppm). Moreover, in the hydrochlorides, where lone-pair effects cannot play a part, the effects of equatorial *N*-methyl groups on Me-2$_a$ are quite small (−3.5, −3.8, −2.7 ppm). Thus it seems that the anti orientation of the lone electron pair on nitrogen of a tertiary amine is the cause of an important part of the shielding effect in $^{13}C$ as it has already been shown to be in $^1H$ NMR spectra.[9]

We also recorded the $^{13}C$ spectra of the hydrochlorides of **6**–**15** (**6**·$H^+Cl^-$–**15**·$H^+Cl^-$) and of **6m**–**15m**. The tertiary amines with biasing groups at C-8 each give rise to one hydrochloride, whereas **6m** and **7m** each form two hydrochlorides with either axial or equatorial *N*-methyl groups (**6m**$_e$·$H^+Cl^-$, **6m**$_a$·$H^+Cl^-$, **7m**$_e$·$H^+Cl^-$, **7m**$_a$·$H^+Cl^-$). As in the cases of *N*,2-dimethyl- and *N*,2,6-trimethylpiperidinium chlorides, the proportion of axially *N*-methyl-substituted configurations is substantially greater in the salts than in the free amines. The ratio of **6m**$_e$·$H^+Cl^-$ to **6m**$_a$·$H^+Cl^-$ was found to be 60:40 by integration of the $^{13}C$ signals of corresponding C atoms in the two isomers; the ratio for **7m**$_e$·$H^+Cl^-$ and **7m**$_a$·$H^+Cl^-$ was 84:16.[20] This may be compared to the results for **1m**, where the ratio of **1m**$_e$·$H^+Cl^-$ to **1m**$_a$·$H^+Cl^-$ was 92:8.[20] This confirms once again[21] that the difference between vicinal gauche interactions of 2-$CH_3$ with axial *N*-$CH_3$ groups on one hand and equatorial ones on the other in the hydrochlorides is much more pronounced than the corresponding difference in the free bases. Similarly, the vicinal gauche interaction between $NCH_3$ and 2-$CH_3$ in **7m**$_e$·$H^+Cl^-$ must be larger than that in **7m**$_e$.

In contrast to the amines where substituent effects of the holding groups were small for carbon atoms distant from C-8, considerable shift changes are observed in the hydrochlorides upon introduction of the *tert*-butyl group (e.g., 1–5 ppm for C-2 in the **m**·$H^+Cl^-$ series). The largest differences are seen for **12m**$_a$·$H^+Cl^-$. Here the additional proton on nitrogen apparently causes sizable deformations of the molecule, since both the shift values of the piperidine moiety are changed compared to those of the 8-methyl analogue **8m**$_a$·$H^+Cl^-$, and even the carbocyclic part is palpably changed compared to **13m**$_a$·$H^+Cl^-$.

Of the six cis-ring-fused compounds investigated, 2$\alpha$-methyl-8$\beta$-*tert*-butyl-*cis*-decahydroquinoline (**19**) is the most interesting. Both the $^{13}C$ shift values and the $^1H$ NMR spectrum show clearly that the compound exists practically exclusively in the conformation with axial *tert*-butyl and equatorial 2-methyl groups. An attempt to freeze the equilibrium (at −70 °C, a temperature where ring inversion of *cis*-decahydroquinolines is slow on the NMR time scale[16]) showed no measurable proportion of another conformation. In the proton NMR spectrum, the signal due to the proton at C-9 shows the same sharp resonance (coupled only to two gauche protons at C-10 and C-8) as that in the conformationally identical compounds **16**–**18** and **20**. Evidently, the syn-axial interaction between C-8 and 2-$CH_3$ in the alternate conformation together with the preference of the parent *cis*-decahydroquinoline ring system for the conformation shown on the left for **19** (0.9



19

kcal/mol[16]) is sufficient to compensate for the unfavorable interaction of the axial *tert*-butyl group.

**$^1H$ NMR Spectra.** The 100-MHz proton NMR spectral data of **6**–**21** and of **6m**–**15m** are collected in Table V. As in the case of **1**–**5**,[9] the chemical shifts of H-2$_e$ or H-2$_a$ in the secondary amines only reflect substituent effects of the biasing groups at C-8 but give no indication of the change in conformational equilibrium on nitrogen. In contrast, in the series of tertiary amines the axial protons in **6m**, **10m**, and **14m** (where the *N*-methyl group is equatorial) are shifted so strongly upfield that they are no longer resolved from the envelope of the remaining protons.

(18) Anet, F. A. L.; Yavari, I.; Ferguson, I. J.; Katritzky, A. R.; Moreno-Mañas, M.; Robinson, M. J. T. *J. Chem. Soc., Chem. Commun.* **1976**, 399.

(19) (a) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612; **1972**, *94*, 5318. (b) Vierhapper, F. W.; Willer, R. L. *Org. Magn. Reson.* **1977**, *9*, 13.

(20) The ratios are tentative. Unlike in ref 1 we did not here take elaborate precautions to assure that the hydrochlorides were at equilibrium.

(21) See ref 1 and footnotes 42–44 in ref 1.

Table V. Melting Points of Picrates and $^1$H NMR Chemical Shifts of 2-Methyldecahydroquinolines

| compd | mp[b] | chemical shift[a] H-2$_e$ | H-2$_a$ | 2-CH$_3$ | NCH$_3$ | others |
|---|---|---|---|---|---|---|
| 6 | *b* | | 2.70 | 1.07 (d, 6.3) | | H-9, 2.17 |
| 7 | *b* | 3.32$_5$ | | 1.19$_5$ (d, 7) | | H-9, 2.43$_5$ |
| 8 | 163-165 | | 2.64 | 1.10 (d, 6.3) | | 8-CH$_3$, 0.91$_5$ (d, 6) |
| 9 | 172-173 | 3.38 | | 1.18 (d, 7) | | 8-CH$_3$, 0.87 (d, 6); H-9, 2.07 |
| 10 | 154-156 | | 2.61 | 1.07 (d, 6.3) | | 8-CH$_3$, 0.94 (d, 7); H-9, 2.29 (d, 9, of d, 4) |
| 11 | 186-188 | 3.35$_5$ | | 1.19$_5$ (d, 7) | | 8-CH$_3$, 0.91$_5$ (d, 7); H-9, 2.59 (d, 8, of d, 4) |
| 12 | 191-193 | | 2.57$_5$ | 1.06 (d, 6.3) | | CH$_3$ (Bu), 1.00$_5$; H-9, 2.13 |
| 13 | 173-175 | 3.32 | | 1.18 (d, 7) | | CH$_3$ (Bu), 0.98; H-9, 2.39$_5$ |
| 14 | 205-207 | | 2.56[c] | 1.06 (d, 6.3) | | CH$_3$ (Bu), 1.11$_5$; H-9, 2.61 (d, 10, of d,5);[c] H-7$_e$, 2.07 (d, 12, of m) |
| 15 | 170-172 | 3.39 | | 1.17$_5$ (d, 7) | | CH$_3$ (Bu), 1.11$_5$; H-9, 2.93$_5$ (d, 10, of d, 5.5) |
| 16 | 195-197 | | 2.59 | 1.06$_5$ (d, 6.3) | | 8-CH$_3$, 0.91$_5$ (d, 6.5); H-9, 2.71 (s, $w_{1/2}$ = 6) |
| 17 | 173-177 | | 2.65 | 1.07 (d, 6.3) | | 8-CH$_3$, 1.02 (d, 7); H-9, 2.60 (s, $w_{1/2}$ = 5) |
| 18 | 189-190 | | 2.58 | 1.04$_5$ (d, 6.3) | | CH$_3$ (Bu), 0.94$_5$; H-9, 3.03$_5$ (s, $w_{1/2}$ = 6) |
| 19 | 151-152 | | 2.61 | 1.04 (d, 6.3) | | CH$_3$ (Bu), 0.92; H-9, 2.83 (s, $w_{1/2}$ = 5.5) |
| 20 | 165-167 | 3.31[d] | | 1.20 (d, 7) | | CH$_3$ (Bu), 0.95; H-9, 3.31 (s, $w_{1/2}$ = 8)[d] |
| 21 | 169-171 | | 2.83[c] | 0.95 (d, 6) | | CH$_3$ (Bu), 0.99; H-9, 2.83[c] |
| 6m | *b* | | *e* | 1.12 (d, 6) | 2.23 | |
| 7m | *b* | 3.07 | | 0.98 (d, 7) | 2.29 | |
| 8m | 114-116 | | 2.78$_5$ | 1.09 (d, 6.8) | 2.07 | 8-CH$_3$, 0.95 (d, 6) |
| 9m | 189-191 | 3.00 | | 1.20$_5$ (d, 7) | 2.36 | 8-CH$_3$, 0.90 (d, 6) |
| 10m | 173-175 | | *e* | 1.10 (d, 6) | 2.13$_5$ | 8-CH$_3$, 0.93 (d, 7) |
| 11m | 155-157 | 3.13$_5$ | | 0.96$_5$ (d, 7) | 2.21$_5$ | 8-CH$_3$, 0.93 (d, 7) |
| 12m | 124-127 | | 2.80 | 1.02[f] | 2.04 | CH$_3$ (Bu), 0.98$_5$ |
| 13m | 169-173 | 2.92 | | 1.22$_5$ (d, 7) | 2.32$_5$ | CH$_3$ (Bu), 0.99 |
| 14m | 149-151 | | *e* | 1.08$_5$ (d, 6) | 2.18$_5$ | CH$_3$ (Bu), 1.14 |
| 15m | 163-165 | 3.10 | | 0.92 (d, 7) | 2.21 | CH$_3$ (Bu), 1.13 |

[a] In parts per million from Me$_4$Si. Solvent CDCl$_3$; ~10% solutions. Reported values are centers of signals in the spectra. Parenthesized values are coupling constants (in hertz); $w_{1/2}$ is the width at half-height in hertz. Only clearly resolved signals and couplings are reported. [b] In °C; recrystallized from EtOH. Compounds **6**, **7**, **6m**, and **7m** have been previously characterized.[12] [c] H-2$_a$ and H-9 overlaid. [d] H-2$_e$ and H-9 overlaid. [e] Overlaid by other signals and not resolved. [f] Partly overlaid by the butyl CH$_3$ signal.

**IR Spectra.** Since neither $^1$H nor $^{13}$C NMR spectra permitted conclusions to be drawn as to the position of the conformational equilibrium on nitrogen in **6** and **15**, an investigation of the Bohlmann-band region in the infrared analogous to the one previously reported for **1**–**5**[9] was carried out. The integrated intensities of the relevant regions together with the percentage of Bohlmann bands in relation to the total area are reported in Table VI. Only one proton is axial on a ring carbon atom $\alpha$ to nitrogen in **7**, **9**, **11**, **13**, and **15** and in their *N*-methyl derivatives; the Bohlmann-band areas in these compounds are therefore much smaller, and the margin of error in their evaluation is correspondingly larger than those in **1**–**5**,[9] **6**, **8**, **10**, **12**, and **14** and their *N*-methyl derivatives.

The results are nevertheless unambiguous for both series, with equatorial and with axial 2-CH$_3$. Among the secondary amines, only compounds **12** and **13** (with an equatorial 8-*tert*-butyl group and thus a predominantly axial *N*-H and equatorial lone pair) show a strongly diminished percentage of the Bohlmann-band area, while the areas for **6**, **8**, **10**, and **14** and again those for **7**, **9**, **11**, and **15** are of the same order of magnitude.[22] Among the tertiary amines, the areas for both the compounds with equatorial 8-methyl (**8m**, **9m**) and those with equatorial 8-*tert*-butyl (**12m**, **13m**) groups are strongly reduced compared to those for **6m**, **10m**, and **14m** and **7m**, **11m**, and **15m**, respectively. The former are compounds with an axial *N*-methyl substituent and, hence, equatorial lone pairs whereas the latter have equatorial *N*-methyl groups and axial pairs. The absolute areas in the tertiary series are much larger because of the additional proton on the methyl group anti to the lone pair and because of additional *N*-methyl absorption in that region. Clearly the IR

Table VI. Integrated Intensities[a] of the IR Bands in the Region of 3100–2500 cm$^{-1}$

| compd | IR region 3100-2500 | 3100-2815 | 2815-2500[b] | 2815-2500[c] |
|---|---|---|---|---|
| 6 | 36.52 | 30.16 | 6.36 | 5.02 (13.7) |
| 8 | 39.13 | 32.54 | 6.59 | 5.25 (13.4) |
| 10 | 39.22 | 32.51 | 6.71 | 5.37 (13.7) |
| 12 | 41.68 | 39.36 | 2.32 | 0.98 (2.4) |
| 14 | 47.85 | 40.52 | 7.33 | 5.99 (12.5) |
| 7 | 34.61 | 31.62 | 2.99 | 1.65 (4.8) |
| 9 | 36.61 | 33.27 | 3.34 | 2.00 (5.5) |
| 11 | 36.92 | 33.43 | 3.49 | 2.15 (5.8) |
| 13 | 45.27 | 42.76 | 2.51 | 1.17 (2.6) |
| 15 | 43.96 | 40.33 | 3.63 | 2.29 (5.2) |
| 6m | 40.00 | 30.04 | 9.96 | 8.62 (21.6) |
| 8m | 42.48 | 38.42 | 4.06 | 2.72 (6.4) |
| 10m | 44.44 | 34.44 | 10.00 | 8.66 (19.5) |
| 12m | 47.08 | 44.91 | 2.17 | 0.83 (1.8) |
| 14m | 50.79 | 40.43 | 10.36 | 9.02 (17.8) |
| 7m | 39.13 | 32.93 | 6.20 | 4.86 (12.4) |
| 9m | 41.09 | 37.98 | 3.11 | 1.77 (4.3) |
| 11m | 40.47 | 34.54 | 5.93 | 4.59 (11.3) |
| 13m | 47.25 | 44.95 | 2.30 | 0.96 (2.0) |
| 15m | 48.81 | 41.55 | 7.26 | 5.92 (12.1) |

[a] Units of L cm$^{-2}$ mol$^{-1}$ × 10$^{-3}$. [b] Bohlmann band region. [c] Bohlmann band region, corrected for background by subtracting the area of 4-NCD$_3$.[9] Parenthesized values are the ratios of the values for the corrected 2815–2500-cm$^{-1}$ region to those for the 3100–2500-cm$^{-1}$ region multiplied by 100 (=percent of Bohlmann bands). The estimated error in the corrected integrated intensities is ±10%.

(22) Since additional C–H vibrations are introduced into the molecule by the different biasing groups, complete agreement cannot be expected (see Discussion in ref 9).

spectra (Bohlmann region) suggest that in the tertiary amines an equatorial 8-methyl or 8-*tert*-butyl group excludes conformations with an equatorial *N*-methyl, whereas in the secondary amines only the equatorial 8-*tert*-butyl group forces the proton on nitrogen largely (but not exclusively) into the axial position.

**Conclusions.** We conclude that in *N*-methylpiperidines (prototype C) the $^{13}C$ signal of an axial methyl group at C-2 is shifted upfield both as a result of the Me/Me gauche interaction and as a result of the presence of the antiperiplanar lone pair. In the corresponding hydrochlorides, where there is Me/Me gauche interaction but no antiperiplanar lone pair, the upfield shift is reduced to less than half the previous value; thus more than half the shielding is due to the lone pair. Yet, no upfield shift of the $2_a$-$CH_3$ signal due to the antiperiplanar lone pair is seen in the piperidine (NH) series (prototype D).

**Synthesis of 2-Methyldecahydroquinolines.** With the exception of **12**, **15**, **20**, and **21**, the *trans*-decahydroquinolines were prepared from the corresponding quinolines (**22**–**24**) via the 5,6,7,8-tetrahydro compounds (**25**–**27**)[23] as previously described.[12a]

Reduction of 2-methyl-8-*tert*-butyl-5,6,7,8-tetrahydroquinoline (**27**) with sodium–ethanol gave mixtures of two trans (**13**, **14**) and two cis isomers (**18**, **19**) in appreciable amounts besides traces of **12**. Hydrogenation of **24** over Raney nickel at high pressure and temperature gave **12** along with much **18**. No detectable amounts of the isomer with axial 2-methyl and 8-*tert*-butyl groups (**15**) were formed by either method. Equilibration of the *N*-nitroso derivative of **14** with base gave *N*-nitroso-2$\beta$-methyl-8$\beta$-*tert*-butyl-*cis*-decahydroquinoline, which was denitrosated to **21**.[24c] In an analogous way, **20** was prepared from *N*-nitroso-**18**.[24c] Finally, **15** was obtained by N-nitrosation of **5**, followed by $\alpha$-lithiation, methylation, and denitrosation.[24c]

## Experimental Section

The $^1H$ and $^{13}C$ NMR spectra and the IR spectra were recorded on the instruments and by the procedures described in ref 9. $^{13}C$ chemical shifts are estimated to be within ±0.05 ppm.

Melting points were determined on a Kofler hot stage. The melting points of the picrates of **8**–**21** and **8m**–**15m** are included in Table V. All new compounds gave satisfactory elemental (C, H) analyses, performed at the Institute of Physical Chemistry, University of Vienna.

**Starting 2-Methylquinolines. 2-Methylquinoline (22)** and **2,8-dimethylquinoline (23)** were prepared from aniline or *o*-toluidine as described.[25] **2-Methyl-8-*tert*-butyl-quinoline** was synthesized in an analogous way from 2-*tert*-butylaniline (**28**), which in turn was made from *tert*-butylbenzene via 2,4-dinitro-*tert*-butylbenzene,[26] 4-amino-2-nitro-*tert*-butylbenzene (**29**),[26] and 2-*tert*-butylnitrobenzene (**30**). The diazotized **29** was reduced with THF[27] instead of hypophosphorous acid;[26] **30** was reduced to **28** with hydrazine hydrate–Raney nickel.

**2-*tert*-Butylnitrobenzene (30).** 4-Amino-2-nitro-*tert*-butylbenzene hydrochloride[26] (230 g, washed with ether and dried) was suspended in 300 mL of concentrated HCl plus 360 mL of $H_2O$, and the suspension was stirred and cooled to ≤0 °C. A solution of 72 g of $NaNO_2$ in 480 mL of $H_2O$ was slowly added. When the addition was complete, the mixture was stirred for 1 h, and 950 mL of cold THF was slowly added. The mixture was cooled to ≤−5 °C, and a solution of 400 g of sodium acetate in $H_2O$ was added. The solution was stirred vigorously; when the addition was complete, the ice–sodium chloride bath was removed, and stirring was continued overnight. The mixture was steam distilled, and the product (**30**) was extracted from the distillate with $CH_2Cl_2$ and distilled to give 126 g (70%) of **30**, bp 121 °C (15 torr) [lit.[26b] bp 114–115 ° (10 torr)].

**2-*tert*-Butylaniline (28)** was prepared from 126 g of **30** and 126 g of hydrazine hydrate in 1 L of EtOH with Raney nickel[28] by the general procedure reported[28] in quantitative yield; bp 111 °C (13 torr) [lit.[26b] bp 102 °C (10 torr)].

**2-Methyl-8-*tert*-butylquinoline (24).** Concentrated HCl (145 mL) was gradually added to 59.6 g (0.4 mol) of **28**. The precipitate of the resulting hydrochloride was crushed, and the suspension was cooled to 0 °C and stirred magnetically. A mixture of 42.4 g of acetaldehyde plus 10.6 mL of $H_2O$ was added during 30 min. After another 30 min, 29 g of $ZnCl_2$ was added, the ice bath was removed, and the mixture was gradually brought to 140 °C (bath temperature) over a period of 4 h and was kept at that temperature for 24 h. The mixture was then poured onto 200 g of NaOH in 300 mL of $H_2O$ plus 800 g of ice and was steam distilled (~12 L of distillate). The distillate was extracted with $CH_2Cl_2$, and the extracts were dried over $Na_2SO_4$ and distilled to give 8 g of unreacted **28** [bp 105–110 °C (12 torr)], 5 g of *N*-ethyl-2-*tert*-butylaniline [bp 120 °C (12 torr)], and 17 g (21%) of **24** (bp 135–140 °C (12 torr)], which crystallized (mp 55 °C, from EtOH):[29] $^1H$ NMR ($CDCl_3$) $\delta$ 7.86, 7.08 (H-4, H-3, AB, $J$ = 8 Hz), 7.52 (m, H-5,6,7), 2.67 (s, 2-$CH_3$), 1.70 (s, $CH_3$ (Bu)); $^{13}C$ NMR 155.4$_7$ (C-2), 147.4$_3$ (C-8), 146.8$_8$ (C-9), 136.3$_5$ (C-4), 127.2$_1$ (C-10), 126.2$_2$, 125.7$_2$ (C-5,6), 124.9$_7$ (C-7), 36.5$_3$ (C-q), 31.0$_8$ ($CH_3$ (Bu)), 25.4$_5$ (2-$CH_3$) ppm. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.55; H. 8.39.

**2-Methyl-5,6,7,8-tetrahydroquinolines.** The synthesis of 2-methyl-5,6,7,8-tetrahydroquinoline (**25**) by hydrogenation of **22** over Pt in concentrated HCl at 50 psi pressure of $H_2$ has been described.[23] 2,8-Dimethyl-5,6,7,8-tetrahydroquinoline (**26**) and 2-methyl-8-*tert*-butyl-5,6,7,8-tetrahydroquinoline (**27**) were synthesized by the same method in 91% (**26**) and >95% (**27**) yields. Compound **26** was purified via acetylation of the side products as described.[23]

**2,8-Dimethyl-5,6,7,8-tetrahydroquinoline (26):** $^1H$ NMR ($CDCl_3$) $\delta$ 7.18, 6.82 (H-4, H-3, AB, $J$ = 8 Hz), 2.70 (H-5,8, m), 2.47 (s, 2-$CH_3$), 1.77 (m, H-6,7), 1.34 (d, 7 Hz, 8-$CH_3$); $^{13}C$ NMR 160.1$_9$ (C-9), 154.9$_7$ (C-2), 136.7$_4$ (C-4), 128.0$_7$ (C-10), 120.2$_3$ (C-3), 35.6$_2$ (C-8), 31.4$_5$ (C-7), 29.0$_3$ (C-5), 24.14 (2-$CH_3$), 21.5$_2$ (8-$CH_3$), 20.2$_0$ (C-6); picrate, mp 116–117 °C. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65. Found: C, 52.50; H, 4.65.

**2-Methyl-8-*tert*-butyl-5,6,7,8-tetrahydroquinoline (27):** $^1H$ NMR ($CDCl_3$) 7.18, 6.82 (H-4, H-3, AB, $J$ = 8 Hz), 2.58 (m, H-5,8), 2.48 (s, 2-$CH_3$), 1.80 (m, H-6,7), 1.00 (s, $CH_3$ (Bu)); $^{13}C$ NMR 158.8$_0$ (C-9), 153.8$_7$ (C-2), 136.1$_7$ (C-4), 130.9$_2$ (C-10), 119.8$_4$ (C-3), 49.2$_0$ (C-8), 35.7$_3$ (C-q), 29.3$_5$ (C-5), 28.8$_6$ ($CH_3$ (Bu)), 26.2$_7$ (C-7), 24.2$_0$ (2-$CH_3$), 22.2$_2$ (C-6); picrate, mp 145–147 °C. Calcd for $C_{20}H_2N_4O_7$: C, 55.55; H, 5.59. Found: C, 55.70; H, 5.40.

**2-Methyldecahydroquinolines. 2-Methyl-*trans*-decahydroquinolines 6 and 7** were prepared by reduction of **25** with sodium and ethanol and isolated by preparative gas chromatography as previously described.[12b] Alternatively, **6** was obtained as the major product of the hydrogenation of **22** at high pressure and temperature over Raney nickel[15] and purified via the *N*-benzoyl derivative.[24b] The 2$\alpha$ isomer **7** was prepared in pure form from the *N*-nitroso derivative.[24a,c]

**2,8-Dimethyl-*trans*-decahydroquinolines 8–11.** Reduction of **26** with sodium–ethanol gave an 80% yield of a mixture of 12% **8**, 21% **9**, 51% **10**, and 13% **11** besides minor amounts of **16** and **17**. Initially, **8**, a mixture of **9** and **10**, and **11** were separated by preparative gas chromatography on a 20% Carbowax 20M plus 10% KOH column[12] at 130 °C, followed by separation of **10** and

(23) Vierhapper, F. W.; Eliel, E. L. *J. Org. Chem.* **1975**, *40*, 2729.
(24) The results concerning *N*-nitrosodecahydroquinolines are reported elsewhere: (a) Vierhapper, F. W. *Monatsh. Chem.* **1980**, *111*, 551; (b) *J. Org. Chem.* **1980**, *45*, 3111; (c) manuscript in preparation.
(25) (a) Mills, W. H.; Harris, J. E. G.; Lambourne, H. *J. Chem. Soc.* **1921**, *119*, 1294. (b) Manske, R. H. F.; Marion, L.; Leger, F. *Can. J. Res., Sect. B* **1942**, *20*, 133.
(26) (a) Biekart, H. J. B., Dessens, H. B.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 321. (b) Shoesmith, J. B.; Mackie, A. *J. Chem. Soc.* **1928**, 2335.
(27) Meerwein, H.; Allendörfer, H.; Beckmann, P.; Kunert, F.; Morschel, H.; Pawellek, F.; Wunderlich, K. *Angew. Chem.* **1958**, *70*, 211.
(28) "Organicum"; Addison-Wesley: Reading, MA, 1973.
(29) Compound **24** can be extracted with ether from aqueous acidic solutions. This has to be watched if separation from secondary amines by acetylation of the latter is attempted.

9 on a 20% QF-1 column at 110 °C. Alternatively, 8 could be obtained as the major product by hydrogenation of 23 at high pressure and temperature over Raney nickel.[24b]

**2,8-Dimethyl-*cis*-decahydroquinolines 16 and 17.** Hydrogenation of 23 in concentrated HCl at 50 psi of $H_2$ and 70 °C until no further hydrogen uptake was observed[16] gave a mixture of ~80% 16, 17, and 10 and 20% starting material. The mixture was separated by preparative GC on the Carbowax–KOH column at 150 °C. After the decahydro compounds were collected, the starting material was recovered at a 200 °C column temperature. The cis compounds 16 and 17 were obtained in a ratio of ~2:1.

**2-Methyl-8-*tert*-butyl-*trans*-decahydroquinolines.** Reduction of 27 with sodium–ethanol gave a mixture of 8% 18, 31% 19, 47% 14, and 9% 13 together with traces of 12 and some unidentified compounds. The mixture was separated by column chromatography on aluminum oxide 90 (Merck, 70–230 mesh) with *n*-hexane as solvent. Compounds 18 and then 14 were eluted; addition of increasing amounts of ether gave 19 and 13. The compounds were obtained completely pure by submitting the samples to preparative gas chromatography (Carbowax–KOH, 160 °C). Hydrogenation of 24 at high pressure and temperature as for 22[15] gave a mixture of mainly 18 and 12 (ratio ~3:1) besides small amounts of other isomers. Separation by column chromatography (aluminum oxide, *n*-hexane) gave both isomers GC pure.

Compound 15 was obtained from *N*-nitroso-8β-*tert*-butyl-*trans*-decahydroquinoline[24b] by α-lithiation, α-methylation, and denitrosation of the resulting *N*-nitroso-15.[24c] The cis isomers 20 and 21 were also prepared from their *N*-nitroso derivatives.[24c]

The *N*-methyl derivatives 6m–15m were prepared by the Eschweiler–Clarke procedure.[30] Hydrochlorides were precipitated by passing gaseous HCl into the solutions of the amines in ether. The picrates were made by addition of an ethereal solution of picric acid to the solutions of the amines in ether and recrystallization from ethanol.

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**Registry No.** 6, 18609-01-3; 6m, 18609-11-5; 7, 18610-37-2; 7m, 18609-07-9; 8, 73698-32-5; 8·HCl, 75031-04-8; 8m, 75031-05-9; 8m·HCl, 75031-06-0; 9, 75031-07-1; 9·HCl, 75031-08-2; 9m, 75031-09-3; 9m·HCl, 75031-10-6; 10, 75031-11-7; 10·HCl, 75031-12-8; 10m, 75031-13-9; 10m·HCl, 75031-14-0; 11, 75031-15-1; 11·HCl, 75031-16-2; 11m, 75031-17-3; 11m·HCl, 75031-18-4; 12, 75031-19-5; 12·HCl, 75031-20-8; 12m, 75031-21-9; 12m·HCl, 75031-22-0; 13, 75031-23-1; 13·HCl, 75031-24-2; 13m, 75031-25-3; 13m·HCl, 75031-26-4; 14, 75031-27-5; 14·HCl, 75031-28-6; 14m, 75031-29-7; 14m·HCl, 75031-30-0; 15, 75045-70-4; 15·HCl, 75031-31-1; 15m, 75031-32-2; 15m·HCl, 75031-33-3; 16, 75031-34-4; 17, 75031-35-5; 18, 75031-36-6; 19, 75031-37-7; 20, 75031-38-8; 21, 75031-39-9; 22, 91-63-4; 23, 1463-17-8; 24, 75031-40-2; 26, 75031-41-3; 26 picrate, 75031-42-4; 27, 75031-43-5; 27 picrate, 75031-44-6; 28, 769-92-6; 30, 1886-57-3; *N*-ethyl-2-*tert*-butylaniline, 75031-45-7.

(30) (a) Clarke, H. T.; Gillespie, H. B.; Weisshaus, S. Z. *J. Am. Chem. Soc.* **1933**, *55*, 4571. (b) Ehrenstein, M.; Bunge, W. *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 1728.

# Reaction of Mesoionic Thiazolones with *m*-Chloroperbenzoic Acid. Oxidative Dipole Extensions

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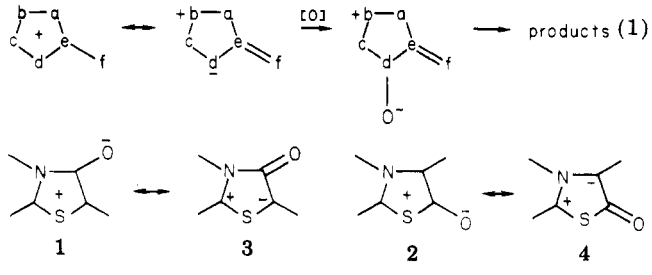
The oxidation of anhydro-4-hydroxy-2,3,5-triarylthiazolium hydroxides (1) with *m*-chloroperbenzoic acid gave (in primary alcohols) 2,5-dialkoxy-2,3,5-triarylthiazolidin-4-ones (5) and *N*-aroylthiobenzanilides (6). Oxidation of anhydro-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide (2) gave 3-methyl-2-phenylthiazolidine-4,5-dione (8) and *N*-formyl-*N*-methylthiobenzamide (9). The products arise from initial oxidations at the carbon atoms at position 5 of 1 and position 4 of 2, and transformation modes to the final products are discussed. These oxidations are the first examples of oxidative dipole extensions.

To date, no reactions of mesoionic systems or heteroaromatic betaines with peracids have been described.[1] The electrophilic nature of peracids is revealed in oxidations of amines,[2] sulfides,[3] and double bonds.[4] On this basis the peracid oxidation of dipolar species can be expected to occur at the nucleophilic terminus and to give oxidized intermediates which retain the dipolar character. We report the oxidation of two isomeric mesoionic systems (1[5,6] and 2[7]). Our expectation was that, according to eq 1,[8] the oxidation would occur specifically *on carbon* at position 5 of 1 and position 4 of 2, through the established[9,10] dipolar reactive forms 3 and 4, respectively.




(1) The oxidation of some pyridinium betaines by hydrogen peroxides was recently reported. Katritzky, A. R.; Ramsden, C. A.; Zakaria, Z.; Harlow, R. L.; Simonsen, S. H. *J. Chem. Soc., Chem. Commun.* **1979**, 363.
(2) Ibne-Rasa, K. M.; Edwards, J. O. *J. Am. Chem. Soc.* **1962**, *84*, 763.
(3) Overberger, C. G.; Cummins, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 4250.
(4) Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231 and references cited therein.
(5) Ohta, M.; Chosho, H.; Shin, G.; Ichimura, K. *Nippon Kagaku Zasshi* **1969**, *88*, 440; *Chem. Abstr.* **1964**, *61*, 14657.
(6) Potts, K. T.; Chen, S. J.; Kane, J.; Marshall, J. L. *J. Org. Chem.* **1977**, *42*, 1633.
(7) Ohta, M.; Shin, C. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 704.
(8) This general representation of mesoions was proposed by: Ollis, W. D.; Ramsden, C. A. *Adv. Heterocycl. Chem.* **1976**, *19*, 6.
(9) Potts, K. T.; Houghton, E.; Singh, U. P. *J. Org. Chem.* **1974**, *39*, 3627.
(10) Potts, K. T.; Baum, J.; Houghton, E.; Roy, D. M.; Singh, U. P. *J. Org. Chem.* **1974**, *39*, 3619.

0022-3263/80/1945-4850$01.00/0 