Effect of *N*-Alkylation on the Position of Conformational Equilibrium in *cis*-Decahydroquinoline

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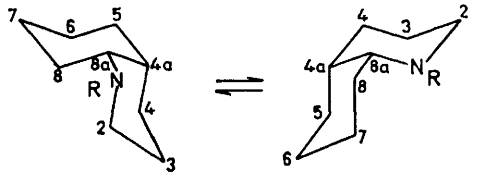
Summary ^{1}H, ^{13}C, and ^{19}F Magnetic resonance studies of *N*-substituted *cis*-decahydroquinolines show that the type (**2**) conformation is preferred for substituents H and CH_3, but that type (**1**) is preferred for CD_2CH_3 and CD_2CF_3.

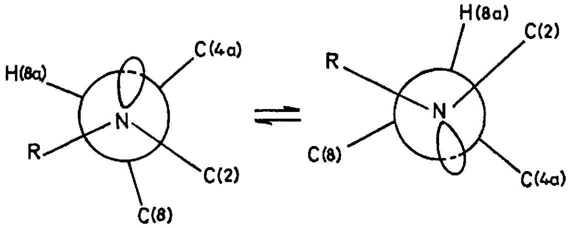
LOW-TEMPERATURE n.m.r. studies of several *N*-substituted *cis*-decahydroquinolines (**1**) $\rightleftharpoons$ (**2**) have given the proportions of conformations listed in Table 1. Carbon-13 shifts of (**1**) $\rightleftharpoons$ (**2**) are given in Table 2 or have been reported[1] (R = H); assignments were based on off-resonance experiments and shift calculations. That the processes being slowed at low temperatures are ring inversion processes is confirmed by the insensitivity to temperature variation of the spectra of the related *trans*-fused systems. Moreover, a full line-shape analysis on a series of ^{19}F spectra of ($\mathbf{1} \rightleftharpoons \mathbf{2}$; R = CH_2CF_3) recorded between −23 and +39 °C, gives $E_{\text{act.}}$ as 63·5 kJ mol^{-1}, a value similar to published values for *cis*-decalin derivatives.[2,3]

TABLE 1

R	%(1)	%(2)	Temp. (t/°C)	Spectrum
H	(Minor)	(Major)	+25	^{1}H(CW)
H	7	93	−40	^{13}C (FT)
CH_3	30	70	−50	^{13}C (FT)
CD_2CH_3	80	20	−63	^{1}H (CW)
CD_2CH_3	86	14	−55	^{13}C (FT)
CD_2CF_3	(Major)	(Minor)	+25	^{1}H (CW)
CH_2CF_3	84	16	−65	^{13}C (FT)
CH_2CF_3	83	17	−60	^{19}F (CW)



(1) (2)



(3) (4)

The results show an increasing preference for conformation of type (**1**) on proceeding along the series R = H, CH_3, CD_2CH_3 (≡ CD_2CF_3). This is possibly due to ring puckering around the nitrogen, itself a consequence of the smaller C–N bond distance relative to the C–C bond distance. The resulting Newman projections, for views along the N–C(8a) bond, are (**3**) and (**4**), for conformations (**1**) and (**2**) respectively. Thus, with R = H, the repulsive interaction which dominates the situation is C(2)–C(8) in (**3**), leading to a preference for (**4**). As R increases in size, the interaction R–C(8) in (**4**) eventually becomes dominant, leading to a preference for (**3**). However, the change in position of equilibrium, which accompanies the replacement of R = CH_3 by R = CD_2CH_3 is unexpectedly abrupt.

TABLE 2

Carbon-13 shifts (p.p.m. from Me_4Si) for ring carbons in *cis*-decahydroquinolines (**1**) ⇌ (**2**) ($CDCl_3$).

	Conformation (1) R			Conformation (2) R		
Carbon	CH_3	CD_2CH_3	CH_2CF_3	CH_3	CD_2CH_3	CH_2CF_3
2	47·4	46·2	47·1	58·3	52·8	56·3
3	25·3	25·9	25·4	21·6	21·9	21·7
4	22·8	23·9	22·8	30·8	29·1	29·3
5	31·6	31·9	31·4	26·3	*	*
6	20·9	21·1	20·6	26·1	26·6	23·2
7	25·7	25·7	25·2	19·6	20·9	19·5
8	15·6	16·0	18·5	29·3	31·3	*
8a	60·6	57·9	61·9	63·4	57·2	57·9
4a	36·0	36·0	35·1	36·3	36·8	36·7

* Masked by other signals.

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[1] H. Booth and (in part) D. V. Griffiths, *J.C.S. Perkin II*, 1973, 842.

[2] J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 2791.

[3] D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 3678.