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UNUSUAL DESHIELDING OF ^{15}N IN BICYCLIC AMINES AND HYDRAZINES

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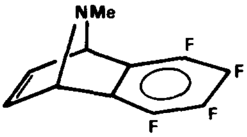
Summary: The bridging nitrogen in 7-aza- and 1,7-diazabicyclo[2.2.1]heptanes and unsaturated derivatives shows unusually large deshielding in the ^{15}N NMR.

The bridging nitrogen in 7-azabicyclo[2.2.1]heptanes and derivatives is unusual, showing remarkably high barriers to inversion at nitrogen[1] and some intriguing chemistry.[2] We have measured ^{15}N NMR spectra for a variety of N-bridged systems and find that these amines display the lowest-field ^{15}N signals yet recorded for secondary and tertiary amines (Table).

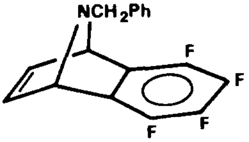
TABLE ^{15}N Chemical Shifts (relative to CH_3NO_2)

(1)



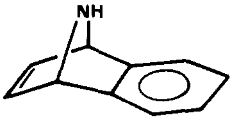
$-251{\cdot}5^{a,e}$

(2)



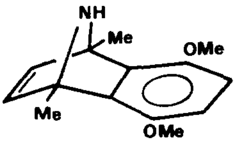
$-243{\cdot}2^{a,e,f}$

(3)



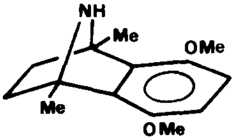
$-239{\cdot}6^{a,g}$

(4)



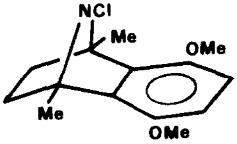
$-214{\cdot}4^{b}$

(5)



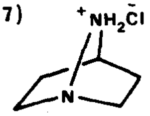
$-251{\cdot}7^{b}$

(6)



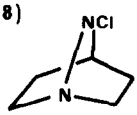
$-200{\cdot}1^{b,e,g}$ (major, syn-)^{i}
$-218{\cdot}3$ (minor, anti-)

(7)



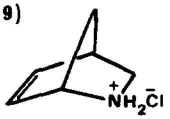
$-257{\cdot}2^{c,h}$ (N-7)
$-276{\cdot}0$ (N-1)

(8)



$-198{\cdot}0^{a,e}$ (N-7)
$-241{\cdot}5$ (N-1)

(9)



$-332{\cdot}7^{d,f}$

(a) CD_2Cl_2 (b) CD_2Cl_2/CH_2Cl_2 (c) D_2O (d) H_2O/D_2O (e) with added $Cr(acac)_3$ (f) with gated decoupling (g) with no decoupling (h) with inverse gating, no NOE (i) Cl syn- to dimethoxybenzo- ring. [Natural abundance ^{15}N spectra measured at 40.55 MHz.]

Thus nitrogen falls into line with oxygen,[3] phosphorus,[4] and silicon[5] which all show unusual deshielding in the 7-position of bicyclo[2.2.1]heptane, heptene or heptadiene skeleta.

The ^{15}N shifts for the tertiary amines (1) and (2) are over 70 ppm downfield of the most deshielded amine nitrogen previously recorded.[6] The secondary amines (3), (4), and (5) also show large downfield shifts and the downfield increment of *ca*. 37 ppm on replacing an ethano-bridge with an etheno- bridge [(5)→(4)] parallels a similar trend in C,[3] P,[4b] and O[3] systems. The N-chloroamine (6) is interesting for two reasons: firstly, it provides the lowest-field resonance for an amine nitrogen in this study[7] and secondly, it constitutes the first example of a system showing separate signals for the two invertomers at a single nitrogen.[8] Integration of the ^{15}N spectrum gave a ratio of 65:35 which corresponds closely with the (more reliable) ratio of 71:29 which was measured by ^{1}H nmr and assigned to the invertomers having the chlorine *syn*- and *anti*- to the aryl ring, respectively.

In the bicyclic hydrazine (7), N-1 is just within the 'normal' range for hydrazines (-270 to -330 ppm[6]); N-7 is deshielded. The N-chloro- analogue (8) shows significant deshielding of both nitrogens which suggests that the inductive effect of Cl is a factor. The bicyclic amine (9) is included as a point of reference and appears at an unexceptional chemical shift, emphasising the special nature of N-7 in this ring system.

It is unlikely that angle strain is the major factor since the CNC bond angle in these systems is less than that in azetidines[1] and, in any event, nitrogen in strained rings is normally highly shielded (e.g. aziridine, δ -393.3[6]). The deshielding of nitrogen in these bridged amines is consistent with increased delocalisation of the nitrogen lone pair when compared with normal amines.[9] We intend to extend the range of bridged amines and investigate possible empirical correlations of ^{15}N chemical shifts with (i) specific structural features, (ii) chemical shifts of other bridging atoms in similar systems and (iii) inversion barriers at nitrogen.

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1. J.W. Davies, J.R. Malpass and R.E. Moss, preceding paper and references therein.
2. M.L. Durrant and J.R. Malpass, *J. Chem. Soc. Chem. Commun.*, 1981, 1028; J. Davies, M.L. Durrant, J.R. Malpass, R.E. Moss and M.P. Walker, to be published.
3. T.T-T. Nguyen, C. Delseth, J-P. Kintzinger, P-A. Carrupt and P. Vogel, *Tetrahedron*, 1980, *36*, 2793.

4a. L.D. Quin and K.A. Mesch, *J. Chem. Soc. Chem. Commun.*, 1980, 959; F. Mathey and F. Mercier, *Tetrahedron Lett.*, 1981, 319.

b. L.D. Quin, K.C. Caster, J.C. Kisalus and K.A. Mesch, *J. Amer. Chem. Soc.*, 1984, *106*, 7021. After our work was completed, we found in this paper on bridged phosphines a reference to the independent observation of deshielded nitrogen in tertiary 7-azanorbornenes. No details of the compounds or chemical shifts were recorded.

5. H. Sakurai, Y. Nakadaira, T. Koyama and H. Sakaba, *Chem. Lett.*, 1983, 213.
6. G.J. Martin, M.L. Martin and J-P. Gouesnard, ^{15}N-NMR Spectroscopy, Springer-Verlag, Berlin 1981.
7. We have, as yet, no data on the N-chloro-derivative of (4) which might have been expected to show even more deshielding of the nitrogen due to the presence of chlorine and the etheno-bridge; such N-chloroamines are highly reactive.
8. Previously reported examples have involved double inversion in bicyclic hydrazines; Y. Nomura and Y. Takeuchi, *J. Chem. Soc. Chem. Comm.*, 1979, 295.
9. Theoretical approaches are being pursued, T.A. Claxton, University of Leicester.

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