The 1-Azabicyclo[4.4.4]tetradec-6-yl Radical: Evidence that Three-electron C· : N Bonding in a Neutral Radical is Very Weak

Martyn C. R. Symons,[*a] **Harish Chandra,**[a] **and Roger W. Alder**[*b]

[a] *Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, U.K.*
[b] *School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, U.K.*

The title radical has been generated by γ-radiolysis of 1-azoniatricyclo[4.4.4.0^{1,6}]tetradecane tetrafluoroborate and shows hyperfine coupling to three hydrogens, A = 24 G (G = 10^{-4} T), but A_N is small, <8 G; this shows that the spin density on nitrogen is no more than 5% and indicates very weak three-electron bonding.

Three-electron σ-bonding continues to excite interest, extending to the use of species containing such bonds as reagents in organic synthesis.[1] There is now extensive experimental data on homonuclear three-electron σ-bonding involving first and second row elements.[2—4] Most well characterised[5] heteronuclear three-electron σ-bonds are found between atoms or groups of similar electronegativity.

Three-electron σ-bonding has also been the subject of high-level (MP2/6-31G* or better) *ab initio* calculations.[6] For heteronuclear three-electron bonds involving the simple hydrides of first and second row elements, Clark[6b] finds a good correlation between the calculated dissociation energies and the difference in the ionisation energies of the partners. While the calculated bond dissociation energy of $[\text{H}_3\text{N}\cdots\text{NH}_3]^+$ is 150 kJ mol^{-1}, Clark finds that $[\text{H}_3\text{C}\cdots\text{NH}_3]$ is not a bound species at UHF/6-31G. A simple valence bond explanation is the effectiveness of the no-bond resonance (a), compared with the ineffectiveness of resonance (b).

$$\text{H}_3\text{N}^{+\cdot}\,\text{:NH}_3 \longleftrightarrow \text{H}_3\text{N:}\,{}^{\cdot}\text{NH}_3^{+} \qquad \text{(a)}$$

$$\text{H}_3\text{C}^{\cdot}\,\text{:NH}_3 \longleftrightarrow \text{H}_3\text{C:}^{-}\,{}^{\cdot}\text{NH}_3^{+} \qquad \text{(b)}$$

We sought experimental evidence for the strength of interaction between a carbon radical and an amino nitrogen in the bicyclo[4.4.4]tetradecane system† by generating radical (**1**) which may be compared with the stable radical cation (**2**), the *X*-ray structure of whose perchlorate salt is known.[4a] The bicyclo[4.4.4]tetradecane system has a strong tendency to adopt structures with the bridgehead atoms directed inwards.[3] Thus 1,6-diazabicyclo[4.4.4]tetradecane has inwardly-directed nitrogen lone pairs, despite the unfavourable four electron interaction between them.[10] Intrabridgehead interactions are also known to be through-space rather than through-bond.[11] Thus radical (**1**) should have an *in,in* structure ideal for three-electron bond formation.

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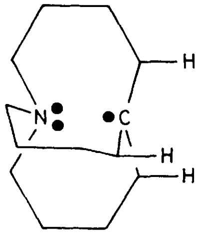
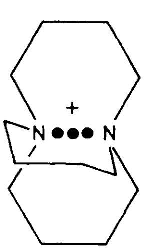
† One previous experimental result which might be thought to address the formation of a three-electron C···N bond in a neutral radical is the e.s.r. spectrum of the 1-azabicyclo[2.2.2]oct-4-yl (quinuclidin-4-yl) radical.[7] A_N was indeed found to be notably small (1.80 G) when compared with A_N = 16.96 G for the 1,4-diazabicyclo[2.2.2]octane (DABCO) radical cation.[8] However it is now generally accepted that the major interaction in the DABCO radical cation is through-bond rather than through-space[9] and this should also be true of any similar interaction in the quinuclidin-4-yl radical.



(1)



(2)

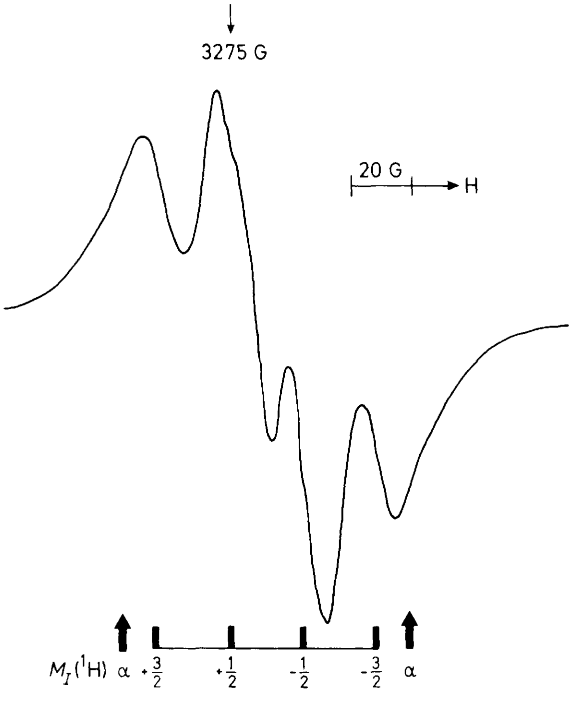


Figure 1. First derivative *X*-band e.s.r. spectrum for 1-azoniatricyclo[4.4.4.$0^{1,6}$]tetradecane tetrafluoroborate after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the neutral radical. Lines α represent our outer limit for any ^{14}N splitting.

Attempts to generate radical (**1**) in solution have been unsuccessful so far. However, radical (**1**) is formed by exposure of 1-azoniatricyclo[4.4.4.$0^{1,6}$]tetradecane tetrafluoroborate[12] to ^{60}Co γ-rays at 77 K, either as the pure salt or in dilute frozen CD_3OD solution. The e.s.r. spectrum obtained from the pure salt is shown in Figure 1. In both media, a quartet of broad lines [A = 24 G (G = 10^{-4} T), *ca.* 1 : 3 : 3 : 1] resulted which is assigned to hyperfine coupling to the three pseudo-equatorial equivalent protons shown in structure (**2**). Shoulders appeared on the ± 3/2 features, possibly due to ^{14}N hyperfine coupling; however $A_{\parallel}$ is <8 G, and $A_{\perp}$ <6 G. In contrast, the nitrogen hyperfine coupling in (**2**) is very large (35.9 G for two equivalent nitrogens).[13] If, as we expect, the nitrogen in (**1**) is strongly pyramidalised inward, the best estimate of the nitrogen spin density is obtained from the upper limit for $A_{\perp}$. The usual procedures[14] give a 2s population of *ca.* 1% and a 2p population of *ca.* 4%, *i.e.* a total spin density of *ca.* 5% on nitrogen.

We conclude that three-electron σ-bonding is quite unimportant in this sterically very favourable situation, in agreement with Clark's calculations and the simple resonance picture described above. Further efforts to generate radical (**1**) in solution in order to obtain a better resolved e.s.r. spectrum will be made.

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