Borylaminyl Radicals. *N*-(9-Borabicyclo[3.3.1]nonan-9-yl)-*N*-t-butylaminyl: a σ-Aminyl Radical

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The e.s.r. spectrum of the title dialkylborylaminyl radical indicates that the unpaired electron occupies an orbital located in the $C_2B\dot{N}C$ plane.

A wide variety of nitrogen-centred radicals are known and their structures and electronic configurations have attracted considerable interest over many years.[1—4] Recently, much controversy has surrounded the succinimidyl radical, in particular as to whether two electronic states (σ- and π-radicals) are necessary to explain the results of thermal chain brominations effected by *N*-bromosuccinimide.[5—7]

Although all known dialkylaminyl radicals have π-SOMOs, as shown in (**1**), we have argued[4] that replacement of the *N*-alkyl groups with metalloidal σ-donor–π-acceptor substituents will result in stabilisation of (**2**) relative to (**1**). However, a single trialkylsilyl ligand is insufficient to reverse the ordering of molecular orbitals and *N*-alkyl-*N*-trialkylsilylaminyls are still π-radicals.[4] The R_2B group is expected to be a more powerful π-acceptor than R_3Si and here we report an e.s.r. study of the *N*-alkyl-*N*-dialkylborylaminyl radical (**3**) which shows that the unpaired electron now occupies a σ-orbital.

The aminophosphine (**5**)† was prepared from *N*-lithio-*N*-t-butyl-9-amino-9-borabicyclo[3.3.1]nonane and diethyl chlorophosphite, as outlined in Scheme 1. The e.s.r. spectrum shown in Figure 1 and assigned to the transient borylaminyl radical

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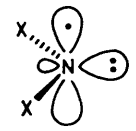
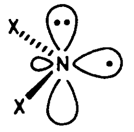
† Aminoboranes with an *N*-phosphino substituent have not been reported previously; satisfactory elemental analysis, n.m.r., and mass spectrometric data were obtained for new compounds.



(1)



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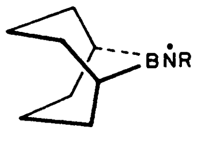
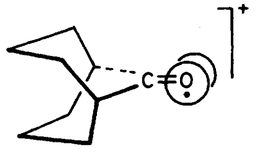


(3) R = Bu^t
(4) R = Me



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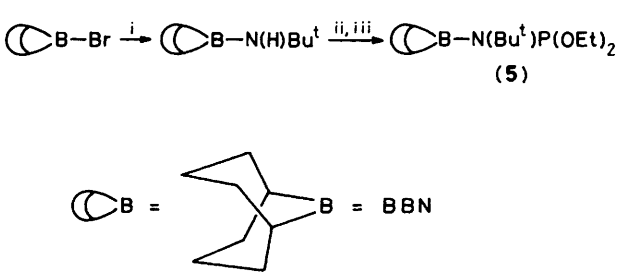

Scheme 1. i, excess Bu^{t}NH$_2$ in CH$_2$Cl$_2$–pentane, ii, Bu^{n}Li in hexane–Et$_2$O; iii, (EtO)$_2$PCl in hexane–Et$_2$O.

(3) was observed during continuous u.v. photolysis of a cyclopropane solution containing (5) and diethyl peroxide (both *ca.* 15% v/v) whilst the sample was in the microwave cavity of the spectrometer [see equation (1)]. The same spectrum was detected when Bu^{t}OOBu^t replaced the EtOOEt, although the spectrum of the t-butyl radical, formed as a secondary reaction product, often became obtrusive. The e.s.r. spectrum of the intermediate phosphoranyl radical (6) [a(P) 940.2 and a(N) 28.8 G at 147 K (1 G = 10^{-4} T)], α-scission of which gives rise to (3), was also detectable at temperatures below *ca.* 160 K.

$$\text{EtO}\cdot + \textbf{(5)} \rightarrow \underset{\textbf{(6)}}{(\text{BBN})\text{N}(\text{Bu}^t)\dot{\text{P}}(\text{OEt})_3} \rightarrow \textbf{(3)} + (\text{EtO})_3\text{P} \quad (1)$$

The spectrum of (3) at 224 K (g 2.0037) could be computer simulated on the basis of equal splittings of 16.2 G from ^{14}N (I 1) and from ^{11}B (I 3/2), along with a splitting of 4.0 G from six protons. The contribution from the radical containing ^{10}B [I 3, natural abundance 19.8%, $\gamma(^{10}\text{B})/\gamma(^{11}\text{B})$ 0.335] is not obvious in the experimental spectrum or its simulation (see Figure 1). The e.s.r. parameters are reasonable for a σ-borylaminyl radical which is close to linear at nitrogen and are not in accord with qualitative expectation for a π-radical.

In order to put these conclusions onto a more quantitative basis we have carried out semi-empirical MNDO–UHF molecular orbital calculations[8] for (4), the *N*-methyl analogue of (3). The BNC group was constrained to be linear, the C$_2$BNC skeleton was kept planar, and C_{2v} symmetry was imposed on the 9-borabicyclo[3.3.1]nonanyl group. The remaining geometrical variables were optimised and an INDO calculation[9] on the resulting structure yielded the splitting constants given in Figure 2. The major contributor to the SOMO is the N-2p$_\sigma$ orbital, as indicated, and the BN bond order is 1.6. Diagonalisation of the force constant matrix (MNDO) gave one negative eigenvalue, the magnitude of which corresponds to a very low normal frequency of 55 cm^{-1} associated principally with in-plane bending at nitrogen. Full structural optimisation for Me$_2$B$\dot{\text{N}}$Me gave a true energy minimum corresponding to a σ-radical in which the BNC angle was 165°. However, the structure with a linear BNC unit was less stable by only 0.4 kJ mol^{-1} and thus it is not possible to decide between linear and bent geometries for dialkylboryl-

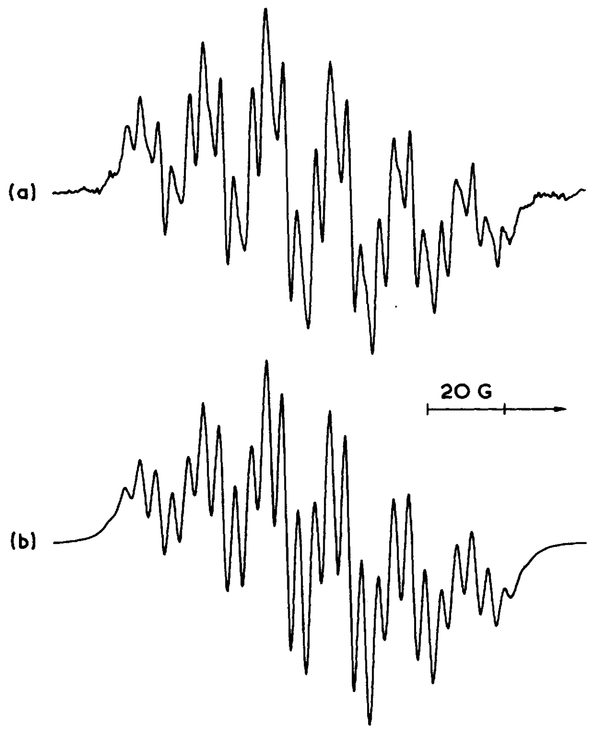

Figure 1. (a) E.s.r. spectrum of the *N*-t-butyl-*N*-dialkylborylaminyl radical (3) in cyclopropane at 224 K. (b) Computer simulation of the spectrum of (3) as a mixture of the ^{11}B- and ^{10}B-containing species present in natural abundance. The coupling constants are given in the text and the peak-to-peak linewidth is 3.3 G.

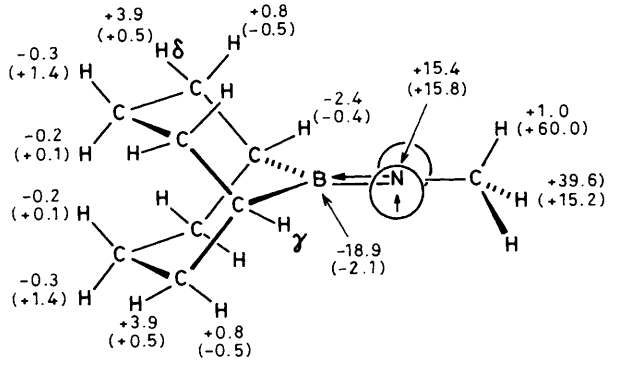

Figure 2. Splitting constants (G) for the radical (4) calculated using the INDO I method (see ref. 9). Unbracketed values refer to the MNDO-optimised C_s geometry of the σ-radical; those in parentheses refer to the π-radical which maintains the geometry of the σ-radical apart from the B–N distance which was optimised using INDO. ^{11}B-2s spin populations were converted to hyperfine splittings by multiplication by 720.8 G.

aminyl radicals on the basis of MNDO calculations. If these radicals are bent at nitrogen, inversion through a linear transition state probably requires very little energy. The differences in a(N) and $a(^{11}B)$ calculated using INDO for the linear (+16.2 and −15.9 G, respectively) and bent (+18.8 and −15.1 G) structures of $Me_2B\dot{N}Me$ were small.

For the MNDO-optimised linear structure of (**4**), interchange of the SOMO and HOMO after the initial Hückel calculation caused the INDO–SCF calculation to converge to an electronic configuration in which the unpaired electron occupies a BN π-orbital. Optimisation of the BN distance for this configuration led, as expected, to a longer, weaker bond and the calculated coupling constants for this π-radical are shown in parentheses in Figure 2. Similar nitrogen splittings are predicted for σ- and π-configurations, but the calculated boron and proton splittings are very different for the two states of (**4**) and comparison with the experimental values for (**3**) provides compelling evidence for a σ-SOMO. The small value of $a(^{11}B)$ for the π-radical suggests that the positive contribution arising from spin density on boron is similar in magnitude to the negative contribution arising from spin density on nitrogen *via* polarisation of the BN σ-bonding electrons.

We attribute the septet splitting of 4.0 G observed in the spectrum of (**3**) to equal (within the linewidth) coupling with two γ- and four δ-protons in the bicyclic system (see Figure 2). The long-range proton splittings accord well with expectation[10] for the σ-radical, since the four equatorial δ-protons are related to the N-2p$_\sigma$ orbital through a 'zig-zag' arrangement of σ-bonds. Large long-range splittings from the corresponding δ-protons have been reported for the radical cation of bicyclo[3.3.1]nonan-9-one (**7**) which is isoelectronic with the NH analogue of (**3**) and in which the SOMO is basically an O-2p$_\sigma$ orbital.[11]

The switch in electronic configuration between $R_2\dot{N}$ and $R\dot{N}BR_2$ is very reasonable since the latter is isoelectronic with the vinyl radical $R\dot{C}{=}CR_2$, the SOMO of which is well known to be a σ-orbital.[12]‡ Furthermore, the e.s.r. spectrum of $H_2BO^{\bullet}$ (isoelectronic with the borylaminyl $H_2B\dot{N}H$) trapped in an argon matrix at 4 K is also as expected for a σ-radical.[13]

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‡ Vinyls are generally bent at C_α; an exception is provided by $Me_3Si\dot{C}{=}C(SiMe_3)_2$ in which the $Si\dot{C}{=}C$ group appears to be effectively linear.[12]