<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Crystalline boron-linked tetraaminoethylene radical cations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Su, Yuanting; Li, Yongxin; Ganguly, Rakesh; Kinjo, Rei</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Su, Y., Li, Y., Ganguly, R., &amp; Kinjo, R. (2017). Crystalline boron-linked tetraaminoethylene radical cations. Chemical Science, 8(11), 7419-7423.</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2017</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/44257">http://hdl.handle.net/10220/44257</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2017 The Author(s) (published by Royal Society of Chemistry). This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.</td>
</tr>
</tbody>
</table>
Crystalline boron-linked tetraaminoethylene radical cations†

Yuanting Su, Yongxin Li, Rakesh Ganguly and Rei Kinjo

Single-electron oxidation of neutral boryl-linked tetraaminoethylene derivatives led to the formation of radical cations, which have been isolated and fully characterized. X-ray diffraction analysis, EPR spectroscopy, and computational studies revealed that the unpaired electron is delocalized over the B₂N₄C₂ skeleton and the spin density mainly resides on the carbon and boron atoms.

Introduction

Boron-containing radicals have been extensively studied due to their importance in fundamental chemistry and promising applications in various organic syntheses involving radical reactions. Thus far, a number of stable anionic and neutral boron radicals have been reported. By stark contrast, isolable boron radical cations are extremely rare probably due to the intrinsic electron deficient nature of boron. Indeed, only a handful of boron radical cations supported by the strong electron donors L have been isolated and structurally characterized by the Bertrand (I), Braunschweig (II), Xie (III), Himmel (IV), and Harman (V) groups (Fig. 1a). While two boron-containing radical cations (VI and VII) without Lewis base stabilization have also been reported, the unpaired electron was most likely localized in the substituents rather than the boron atoms.

Owing to their peculiar ability to serve as powerful organic reducing reagents, electron-rich olefins (EROs) have received a surging interest more than two decades. During the redox reactions with EROs, the corresponding oxidized forms of EROs, especially the radical cations are concomitantly generated and therefore have been considered as key species (Fig. 1b). Among them, the radical cation of tetrathiafulvalene (TTF) VIII has been extensively studied owing to its diverse utilities in various applications. Compared to TTF, tetraazafulvalenes (TAFs) IX feature more negative potentials which makes them attractive organic super-electron donors and organocatalysts. However, their corresponding radical cations IX⁺ have never been isolated thus far, mainly due to the facility of two-electron oxidation process attributed to the small electronic coupling. Recently, the Bertrand group reported two isolable triazaolefin radical cations (X⁺ and XI⁺) and demonstrated the methylene-tethered XI⁺ exhibits a larger electronic coupling.

Similarly, it has been reported that aliphatic tetraaminoethylene (TAEs) XII linked by (poly)methylene chains increases

---

Fig. 1 (a) Structurally characterized boron-containing radical cations. (b) Examples of radical cations of electron-rich olefins (Dipp = 2,6-diisopropylphenyl). (c) Present work.
the electronic coupling, which is, however, still not large enough to isolate the cation radical species \( \text{XII}^+ \), and indeed no structural authentication of such species has been done to date.\(^{11d,19} \) Because of the isoelectronic and isosteric relationships between the C–C and B–N units, boron atoms binding to nitrogen atoms have readily been incorporated into \( \pi \)-conjugation system.\(^{21,22} \) Accordingly, we envisaged that linking the nitrogen atoms of tetraaminoethylene by two boryl groups may effectively increase the electron coupling, and the corresponding radical cation could be stabilized through delocalization of both the positive charge and the unpaired electron over the \( \text{B}_2\text{C}_2\text{N}_4 \) framework as it should mitigate the electron deficiency of the boron centers. Consequently, synthetically challenging Lewis bases-free boron radical cations would be accessible. Herein, we show that in fact radical cations \( \text{XIII} \) involving a tetraaminoalkene unit (Fig. 1c) can be isolated. Their spectroscopic properties and structures are also presented.

### Results and discussion

Treatment of tetaaryloxalaminide 1 (ref. 23) with one equivalent of dibromophenylborane in the presence of two equivalents of diisopropylethylamine in toluene afforded 2a as a yellow powder in 78% yield. A subsequent reaction between 2a and a stoichiometric amount of dibromophenylborane in toluene immediately afforded a brown precipitate, which was collected by filtration and then washed with hexane to give 3a as a white solid in 75% yield. A toluene solution of 3a with two equivalents of potassium graphite (KC\(_8\)) was stirred overnight under ambient condition, and a subsequent reaction between 3a and dibromophenylborane in the presence of two equivalents of potassium graphite (KC\(_8\)) afforded 4a as a yellowish green powder in 75% yield. A toluene solution of 4a immediately afforded a yellow powder in 78% yield. A subsequent reaction between 4a and dibromophenylborane afforded 4b as a yellowish green powder in 78% yield. A subsequent reaction between 4b and dibromophenylborane afforded 4c as a yellowish green powder in 69% yield. A subsequent reaction between 4c and dibromophenylborane afforded 4d as a yellowish green powder in 69% yield. A subsequent reaction between 4d and dibromophenylborane afforded 4e as a yellowish green powder in 69% yield.

![Scheme 1: Synthesis of compound 4](image)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{N} \text{H} )</td>
<td>2a (78%)</td>
</tr>
<tr>
<td>2. ( \text{B} \text{N} )</td>
<td>2b (74%)</td>
</tr>
<tr>
<td>3. ( \text{N} \text{H} )</td>
<td>2c (69%)</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>3a (75%)</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>3b (69%)</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>3c (69%)</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>4a (54%, ( \text{Ar} = \text{C}_6\text{H}_5 ))</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>4b (76%, ( \text{Ar} = 4\text{-F-C}_6\text{H}_4 ))</td>
</tr>
<tr>
<td>( \text{N} \text{H} )</td>
<td>4c (64%, ( \text{Ar} = 4\text{-Bu-C}_6\text{H}_4 ))</td>
</tr>
</tbody>
</table>

A toluene solution of 4a immediately afforded a yellow powder in 78% yield. A subsequent reaction between 4a and dibromophenylborane afforded 4b as a yellowish green powder in 78% yield. A subsequent reaction between 4b and dibromophenylborane afforded 4c as a yellowish green powder in 69% yield. A subsequent reaction between 4c and dibromophenylborane afforded 4d as a yellowish green powder in 69% yield. A subsequent reaction between 4d and dibromophenylborane afforded 4e as a yellowish green powder in 69% yield.

![Fig. 2](image)

(a) Solid-state structures of 4a (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: 1B–C1 1.460(5), 1B–N1 1.396(3), 1C6–N1 1.396(3), 1C7–N2 1.397(4), 1C6–1C7 1.323(7), 1C1–B1–N1 127.1(4), 1C1–B1–N2 127.1(4), 1N1–B1–N2 105.8(4). (b) The plot of the HOMO of 4a.
The first oxidation potentials of 4a–c are less negative than those of tetraazafuvalenes IX (around −1.00 V vs. SCE, Fe/Fe⁺: $E_{1/2} = 0.46$ V vs. SCE). Thus, upon incorporation of the boryl groups, the reducing power of compounds 4a–c becomes weaker than that of tetraazafuvalenes IX.

It has been reported that tetraaminethylen derivative typically undergoes the addition reaction with an electrophile at the central C=C moiety. To investigate the chemical behavior of 4, we performed their reactions with electrophiles. Treatment of a toluene solution of 4a with an equimolar amount of trifluoromethane sulfonic acid (HOTf) at room temperature afforded the corresponding conjugated acid 5a as a white powder in 85% yield (Scheme 2). The $^{11}$B NMR spectrum displays a broad singlet at 38.1 ppm which is shifted downfield with respect to that (25.4 ppm) of 4a. In the $^1$H and $^{13}$C NMR spectra, a singlet at 7.71 ppm for NCH$_n$ proton and 82.2 ppm and 187.4 ppm for the corresponding NCHN and NCN carbons were observed, respectively. Under the same conditions, 4b and 4c underwent protonation with HOTf to afford the respective products 5b and 5c in good yields. An X-ray diffraction studies of 5a revealed that both boron centers feature the trigonal-planar geometry. One of the central carbon atoms in the B$_2$N$_4$C$_2$N$_4$ ring is in the tetragonal configuration with a hydrogen atom whereas its adjacent caticonic carbon exhibits the trigonal-planar geometry with a normal C-C bond (Fig. 3a). The distance of the C25–C26 (1.490(5) Å) bond is significantly longer than the corresponding bond (1.323(7) Å) in 4a, and comparable to typical single C–C bond length. This results demonstrate the tetraaminethylen-type nature of 4.

In line with the oxidation potentials, chemical single-electron oxidations of 4a and 4b were readily accomplished by using of [Ph$_3$C][B(C$_6$F$_5$)$_3$I] as an oxidizing agent. Reactions of 4a to 4c, with [Ph$_3$C][B(C$_6$F$_5$)$_3$I] in CH$_2$Cl$_2$ at ambient temperature smoothly generated 4a$^{++}$ and 4b$^{++}$ as NMR-silent red (4a$^{++}$: 84%) and reddish brown powder (4b$^{++}$: 87%), respectively (Scheme 2). Crystals suitable for X-ray crystallographic studies were obtained by recrystallization from CH$_2$Cl$_2$ and toluene solution. Like the neutral 4a and 4b, 4a$^{++}$ and 4b$^{++}$ bearing the 9π-system retain the planar B$_2$N$_3$C$_2$ skeletons with trigonal planar sp$^3$ boron atoms (Fig. 3b and S73†). Upon oxidation of 4a to 4a$^{++}$, the B–N bonds (1.458(3)–1.474(3) Å) and the C=C (1.414(3) Å) bond are very slightly lengthened, while the endocyclic C–N bonds (1.352(2)–1.365(2) Å) are shortened, which is in good agreement with the electronic structure of 4. Thus, upon removal of one electron from the HOMO of 4 (Fig. 2b), the electron density in the C=C and N–B–N π-bonding orbitals decreases, leading to the elongation of the C=C and B–N distances, while the repulsion between the bonding (N–B–N and C=C) electron pairs decreases resulting in the shortening of the C–N bond distances. Note that $^*$ corresponds to the first example of radical cations derived from BN heterocycles featuring some aromatic nature (Fig. S84, Table S2). Moreover, $^{++}$ corresponds to the anion radical of organic pentalone, among which only the derivatives featuring thermodynamically highly stabilizing benzo substituents have been structurally characterized.

The EPR spectrum of 4a$^{++}$ measured in fluorobenzene at room temperature displays a complex system (g = 2.0050) arising from couplings with two boron ($^1$B$^{\text{I}}=1.16$ G, $^1$B$^{\text{II}}=0.63$ G), four nitrogen ($^4$N = 1.53 G), and four hydrogen atoms ($^2$H = 1.32 G) at the ortho-positions of phenyl groups (Fig. 4a). The $^{11}$B hyperfine coupling constant is smaller than those of I (6.43 G) and isolable boron radical anions, but comparable to those of II ($\leq 1.18$ G) and reported stable neutral boron radicals (0.96–8.5 G). The moderate $^{13}$B$^{\text{II}}$ coupling constant together with relative small $^{14}$N values suggests delocalization of the unpaired electron over the B$_2$N$_3$C$_2$ core. To gain more insight into the electronic structure of 4a$^{++}$, unrestricted DFT calculations were performed at the UMO62X/6-31G(d,p) level. NBO method confirmed that the spin density is entirely delocalized over the B$_2$N$_3$C$_2$ framework with some extension to the two Ph groups on the B atoms (Fig. 4b). The spin density is estimated to be present mainly on the carbon (0.26e × 2) and the boron (0.19e × 2) atoms with a relatively small contribution of the nitrogen atoms (0.02e × 4). While the several resonance forms including $^1$4$^+$, $^2$4$^+$, $^4$4$^+$ can be drawn for 4$^+$ (Fig. 4c), the X-ray diffraction analysis, ESR spectra in

![Scheme 2 Synthesis of 4$^{++}$ and 5.](image-url)
Fig. 4 (a) Experimental (red) and simulated (black) EPR spectra of 4a⁺⁺ in fluorobenzene at room temperature. (b) The plot of the spin density of 4a⁺⁺. (c) The selected resonance forms of 4⁺⁺.

Combination with DFT results indicate that compared with the N-centered radical form 4⁺⁺⁺, contribution of others including the tetraminoalkene radical cation 4⁺⁺⁺ and boron radical cation 4⁺⁺⁺⁺ is more significant to the actual electronic structure of 4⁺⁺⁺.

Conclusions

In summary, we have shown that boryl-tethered tetraminoalkene derivatives 4 can be readily synthesized and they undergo protonation reaction and one-electron oxidation reaction. The former afforded the corresponding salts 5 whereas the latter led to the formation of isolable radical cations 4⁺⁺⁺. X-ray diffraction analysis, EPR spectra as well as computational studies of 4⁺⁺⁺ revealed the unpaired electron delocalized over the B₂N₄C₂ framework mainly resides on the carbon and boron atoms.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to Nanyang Technological University (NTU) and the Singapore Ministry of Education (MOE2015-T2-2-032) for financial support. We also sincerely appreciate Prof. Richard Webster for the EPR characterizations.

Notes and references


