

# Deprotonation of Benzoxazolium Salt: Trapping of a Radical-Cation Intermediate

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**S** Supporting Information

**ABSTRACT:** The deprotonation of N-2,6-diisopropylphenyl-substituted benzoxazolium tetrafluoroborate 1 with NaH results in the formation of electron-rich diaminodioxaethylene 2. The radical cation salt  $2^+BF_4^-$  is found to be an intermediate product in the redox reaction leading from 1 to 2.



C ince the late 1960s, an epoch of coordination compounds with N-heterocyclic carbenes (NHCs) as ligands initiated by the pioneering works of Wanzlick<sup>1</sup> and Ofele<sup>2</sup> and carried on with the subsequent studies of Lappert<sup>3</sup> has been continuing. The surge of interest in this field was caused by the first synthesis and X-ray-determined structural characterization of stable NHCs by Arduengo in the early 1990s.<sup>4</sup> Since then, use of manifold NHCs in coordination and organometallic chemistry has afforded numerous metal complexes whose applications have spread from homogeneous catalysis<sup>5</sup> to functional materials.<sup>6</sup> Among other different types of singlet carbenes are carbenes in which one or both heteroatoms are different from nitrogen,<sup>7-10</sup> monoheteroatom-substituted carbenes,<sup>8–11</sup> and even carbocyclic stable carbenes.<sup>8–12</sup> The replacement of nitrogen in NHCs by either sulfur or oxygen is recognized to be one of the most efficient tools for tuning of electronic properties and bulkiness of such compounds. A stable thiazol-2-ylidene as well as dimer dithiadiazafulvalene have been isolated and structurally characterized by means of single-crystal X-ray diffraction.<sup>13</sup> Meanwhile, N,O-heterocyclic carbenes (NOHCs) remain transient species, and even metal complexes with oxazol-2-ylidene ligands are quite rarer being mostly prepared by indirect methods via isocyanide derivatives.<sup>14</sup> Recently, a convenient straightforward synthetic route to such complexes based on the reaction of oxazolium salt with a metal precursor and an external base has been developed.<sup>12</sup>

Although stable sterically demanding acyclic aminooxycarbenes are known,<sup>16</sup> neither free NOHC nor its dimer has been isolated so far, in spite of the fact that the existence of NOHCs was theoretically predicted.<sup>17</sup> Taking into account a vast variety of stable carbenes and considering as a challenge the task to synthesize noncoordinated oxazol-2-ylidene derivatives, we have prepared benzoxazolium salt 1 and attempted its deprotonation. As a result, we have isolated the corresponding olefinic dimer of dioxadiazafulvalene 2 and surprisingly faced a nonpresumable paramagnetic species  $2^{\bullet+} \cdot BF_4^{-}$ .

For the synthesis of 1 we have chosen a high-yielding and easy to perform synthetic pathway<sup>15a,18</sup> based on the treatment of 4,6-di-tert-butyl-N-(2,6-diisopropylphenyl)-o-aminophenol with triethyl orthoformate under acidic conditions<sup>19</sup> (Scheme 1). Benzoxazolium salt 1 was obtained as a white solid in 89% yield. It is readily soluble in polar solvents such as CH<sub>3</sub>CN, THF, and CHCl<sub>3</sub>, moderately soluble in diethyl ether, and nearly insoluble in hydrocarbons. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 1 revealed the characteristic oxazolium proton (OCHN) resonance at 10.54 ppm and the corresponding carbon resonance at 193.2 ppm (see the SI).

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Scheme 1. Synthesis and Deprotonation of Benzoxazolium Salt 1



The molecular structure of 1 in the crystal was determined by single-crystal X-ray diffraction analysis. All structural parameters are very similar to the *N*-phenyl-substituted analogue reported previously<sup>15a</sup> (Table S2). The oxazole ring in 1 is essentially planar with the largest deviation from the mean plane of 0.004 Å. The arene ring of the 2,6diisopropylphenyl substituent is almost perpendicularly oriented to this plane with a dihedral angle of 88.0°. The nitrogen atom N1 is also in a nearly planar environment and lies only 0.006 Å above the plane formed by carbon atoms C2, C3, and C4.

The deprotonation of benzoxazolium salt 1 was performed with NaH using a conventional synthetic protocol (Scheme 1). The reaction mixture turned bright fuchsia-pink immediately by mixing of oil-free sodium hydride with a solution of 1 in THF. An intensive evolution of hydrogen and simultaneous precipitation of sodium tetrafluoroborate was observed. The solution was losing color gradually while stirring and eventually became pale yellow-greenish. Instead of a stable oxazol-2ylidene, we have succeeded in the isolation of dimer dioxadiazafulvalene 2 as pale yellow crystals in 67% yield<sup>20</sup> (Scheme 1).

According to the single-crystal X-ray diffraction analysis, the observed bond lengths and valence angles in compound 2 (Table S2) are very similar to the corresponding structural parameters of analogues carbene dimer with benzothiazole rings.<sup>13</sup> The central double C2=C2' bond of 1.312(6) Å corresponds to a normal olefin.<sup>21</sup> The solid-state geometry of dimer 2 is close to planar, and there is a  $3.0^{\circ}$  twist about the central double bond. One oxazole ring is essentially planar within 0.004 Å. In addition, the arene ring of 2,6diisopropylphenyl substituent and the oxazole mean plane form an approximately right angle (89.4°). The nitrogen atom N1 in the planar oxazole ring is 0.010 Å outside the plane of its attached carbon atoms C2, C3, and C4. The largest deviation from the mean plane of the more distorted oxazole ring is equal to 0.033 Å. The 2,6-diisopropylphenyl substituent is twisted by 81.6° with respect to the corresponding oxazole mean plane. The nitrogen atom N1' in the distorted oxazol ring is 0.152 Å above the plane of its attached carbon atoms C2', C3', and C4'. The steric repulsion of two bulky 2,6diisopropylphenyl groups leads to the expected elongation of N1-C2 and O1-C2 (as well as N1'-C2' and O1'-C2') bonds by about 0.1 Å relative to benzoxazolium salt 1 and decrease of N1-C2-O1 and N1'-C2'-O1" angles up to

 $107.5^{\circ}$  and  $108.0^{\circ}$ , respectively. The C1–C3 and C1'–C3' bonds in 2 slightly lengthen in comparison to 1.

But what was a mysterious fuchsia-pink color which arose instantlyupon contact of benzoxazolium salt 1 with deprotonation agent? It should be noted that when the basic agent (NaH) was used, we were able to observe a fuchsia-pink color on a time scale of weeks. Unfortunately, all of our attempts to isolate this bright colored substance failed. The evaporation of solvents in vacuo as well as replacement of the polar medium by a less polar (diethyl ether) or nonpolar one (aromatic or saturated hydrocarbons) led to oily products and a change in color to tints of brown or even bleaching. At last, we succeeded in obtaining a radical cation salt  $2^{\bullet+}BF_4^-$  (Scheme 2) by means of heterogeneous reaction.<sup>22</sup>



Fuchsia-pink single crystals of 2<sup>+</sup>·BF<sub>4</sub><sup>-</sup> suitable for X-ray diffraction were obtained by deprotonation of a benzoxazolium salt 1 in toluene. A slow heterogeneous deprotonation of poorly soluble salt 1 probably afforded crystals of ionic product  $2^{\bullet+}BF_4^{-}$ , which also possesses a scanty solubility in nonpolar aromatic hydrocarbons. Radical cation  $2^{\bullet+}$  corresponds to a centrosymmetrical dimer with a central carbon-carbon bond of 1.371(4) Å in length. This bond is elongated in comparison with the double carbon-carbon bond in the neutral dimer 2 and normal double C=C bond in organic substances<sup>21</sup> (1.33) Å). On the other hand, it is substantially shorter than the normal single C-C bond<sup>21</sup> (1.54 Å). Noteworthy, the observed value is typical, for example, for a tetrathiafulvalene radical-cation<sup>23</sup> and dithiadiazafulvalene radical-cation<sup>24</sup> as well as for boron-linked tetraaminoethylene radical cations<sup>25</sup> and thus confirms the positive charge +1 on the dioxadiazafulvalene core of the species  $2^{\bullet+}$ . Both benzoxazole moieties are twisted by 5.1° about such a sesquilateral central carboncarbon bond. The increase of the distance between two oxazole parts of radical cation in  $2^{\bullet+}$  with respect to the neutral dimer 2 leads to a decrease of steric repulsion and results in the intermediate geometric parameters of the corresponding oxazole rings. The N1-C2 and O1-C2 bonds as well as valence angle N1-C2-O1 in 2<sup>•+</sup> reveal intermediate values

between cation in 1 and neutral dimer 2 (Table S2). The oxazole rings in  $2^{\circ+}$  are planar within 0.011 Å. The arene rings of the 2,6-diisopropylphenyl substituents are twisted by 85.1° with respect to their oxazole mean planes. The nitrogen atoms deviate from the planes of their attached carbon atoms by 0.132 Å.

It is noteworthy that the structural parameters of compounds 2 and  $2^{\bullet+}$  are very close to the quite rare examples of NHC-cyclic (alkyl)(amino) carbene (CAAC) heterodimers and their very recently reported radical cations.<sup>26</sup>

A radical-cation  $2^{\bullet+}$  demonstrates an isotropic EPR spectrum at  $g_i = 2.0036$  with a complicated hyperfine structure (Figure 1) which was reliably simulated using the program



**Figure 1.** Spin densities as predicted by the Mulliken population analysis (a) and representation of SOMO for  $2^{\bullet+}$  (b) according to the DFT UB3LYP/6-31g(d,p) calculations. Experimental and simulated isotropic EPR spectrum of radical cation  $2^{\bullet+}$  in THF (c).

WinEPR Simfonia 1.25. The observed hyperfine structure of the spectrum is caused by hyperfine splitting of signal from the unpaired electron on two equivalent nuclei of nitrogen (<sup>14</sup>N, I = 1, 99.63%) with HFC constant  $a_i$ <sup>(14</sup>N) = 4.44 G, two pairs of protons in the third and fifth positions of both six-membered aromatic rings with constants  $a_i(2 {}^{1}H^5) = 1.25$  G and  $a_i(2 {}^{1}H^3)$ = 0.77 G, and four equivalent protons of methine fragment of isopropyl groups with  $a_i(4 \, {}^{1}\text{H}^{\text{CH of iPr}}) = 0.29 \text{ G}$  (Scheme 2). The HFS of the spectrum points out the  $\pi$ -character of the radical cation  $2^{\bullet+}$  with the delocalization of spin density throughout the  $\pi$ -systems of both benzoxazole moieties confirmed by the DFT UB3LYP/6-31g(d,p) calculations (for details, see the SI). The spin density distribution is in good agreement with the shape of SOMO radical cation  $2^{\bullet+}$ . The Mulliken population analysis confirms the ratio of the found HFCs with a larger one on the nitrogen atoms (Figure 1). The observance of HFC with methine protons that are located above and below the  $\pi$ -system can be rationalized by their conjunction with a  $\pi$ -molecular orbital of an unpaired electron.

Dioxadiazafulvalene 2 shows absorption only in the UV region (330-400 nm), whereas the THF solution of compound  $2^{\bullet+}\cdot\text{BF}_4^-$  features two broad absorbance bands in the range of 360-410 and 450-600 nm in the UV-vis spectrum. The second one sets conditions for fuchsia-pink coloration (for details, see the SI). The TD-DFT UB3LYP/6-31g(d,p) calculations show that the greatest contribution to the long-wave absorption comes from the SOMO-LUMO transition in  $2^{\bullet+}$  (97%).

It is well-known that the deprotonation of imidazolium salts in basic medium afforded either stable NHCs<sup>4</sup> or tetraminoethylenes.<sup>27</sup> Noteworthy, the synthetic strategy of deprotonation of 1,3-thiazolium salts in the presence of base is one of the most employed pathways toward dithiadiazafulvalene and gives rise to a wide range of various substituted electron-rich ethylenes,<sup>13,28</sup> while only two cyclic thiazol-2-ylidenes have been described to date.<sup>13</sup>

Concerning NHCs electronic stabilization rather than steric demand was found to play a crucial role in the carbenes dimerization.<sup>29</sup> As for N,S-heterocyclic carbenes (NSHCs), the only N-2,6-diisopropylphenyl-substituted one is a stable crystalline solid at ambient temperature, while even the Nmesityl-substituted analogue is persistent in solution up to 0 °C.<sup>13</sup> Thus, the bulkiness of the substituents becomes the most important factor for kinetic stabilization of NSHCs and especially NOHCs. Indeed, we could not observe a free carbene 3 (Scheme 2), while we succeeded in the isolation of its dimer 2 and trapped radical cation salt  $2^{\bullet+} \cdot BF_4^-$ , though the formation and transformation of the latter is opened to question. Noteworthy, the energetic preference of the dioxadiazafulvalene 2 in comparison with a free carbene 3 was estimated by DFT UB3LYP/6-31g(d,p) calculations and amounts to 33.0 kcal/mol (see the SI for details). Generally, both for NHCs and NSHCs two mechanisms of dimerization and formation of the electron-rich olefins are discussed: either a direct reaction of two carbenes ("Wanzlick equilibrium") or an indirect reaction where the carbene reacts with the corresponding azolium salt followed by a deprotonation of the intermediate to yield the ethylenic dimer.<sup>28,30</sup> The indirect ionic mechanism is more preferable and has been supported experimentally by <sup>13</sup>C NMR investigations for some derivatives.<sup>30a,31</sup> Being not able to rule out the direct carbene coupling, we suppose, that dimerization of 3 most likely proceeds by the nucleophilic addition of the carbene 3 to its benzoxazolium precursor 1 leading to the protonated dimer intermediate 4 and followed by an acid-base reactionintramolecular proton transfer-to yield dioxadiazafulvalene 2 (Scheme 2). Thus, the radical cation  $2^{\bullet+}$  probably arises from some redox reaction of intermediate 4 resulting in the elimination of atomic hydrogen rather than proton. The following reduction of  $2^{\bullet+} \cdot BF_4^-$  with NaH gives dimer 2 as final product. Unfortunately, the conditions providing redox reactions in this system are unsure at this time. As a confirmation of the proposed mechanism, we have carried out the reaction of 2 with HBF<sub>4</sub> and observed the formation of radical cation salt  $2^{\bullet+} \cdot BF_4^-$  with the simultaneous hydrogen evolution (for details see the SI).

The cyclic voltammogram of **2** is well comparable with NHC-CAAC heterodimers previously reported<sup>26</sup> and shows two reversible one electron waves at  $E_{1/2}^1 = -0.48$  and  $E_{1/2}^2 = +0.22$  V vs Fc<sup>+</sup>/Fc. These redox processes correspond to the successive formation of radical cation **2**<sup>•+</sup> and dication **2**<sup>2+</sup> (Scheme 3), which were also generated in situ by both electrolysis and chemical oxidation using the treatment of **2** with 1 and 2 equiv of AgBF<sub>4</sub> (for details see the SI). In addition, the stoichiometric reaction between neutral dioxadiazafulvalene **2** and its dication **2**<sup>2+</sup> gave the radical cation **2**<sup>•+</sup>, indicating reversible electron transfer.

In conclusions, a novel NOHC precursor 1 has been synthesized using triethyl orthoformate for cyclization of 4,6di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-aminophenol under acidic conditions. Deprotonation of this bulky benzoxazolium salt 1 afforded dimer diaminodioxaethylene 2 as the final product, and the formation of the stable carbene instead. Along with dioxadiazafulvalene 2, radical-cation salt  $2^{\circ+}\cdot BF_4^-$  has

#### Scheme 3. Oxidation of 2



been trapped and structurally characterized. This paramagnetic compound  $2^{\bullet+} \cdot BF_4^-$  is thought to be an intermediate in the redox reaction leading from 1 to 2.

### ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b03928.

Experimental details, crystallographic data, computational details, copies of IR, <sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, and electronic absorption spectrum of  $2^{+} \cdot BF_{4}^{-}$ along with a photo of the colored solution (PDF)

#### **Accession Codes**

CCDC 1851514, 1852042, and 1883398 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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