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Mono- and Bis-Imidazolidinium Ethynyl Cations and the Reduction of the Latter to give an Extended Bis-1,4-([3]Cumulene)-*p*-Carbo-Quinoid System†

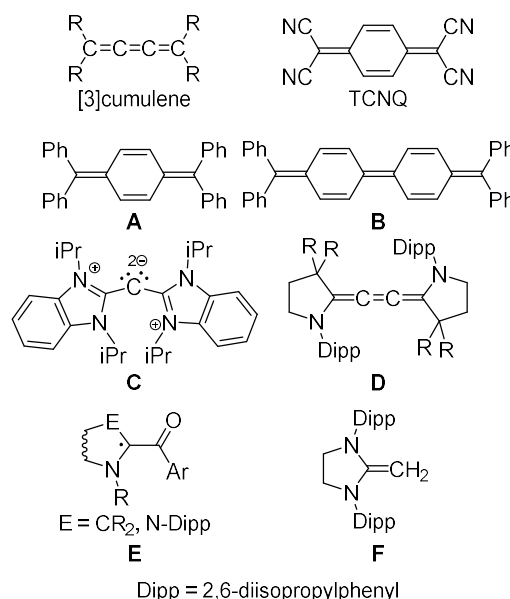
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Abstract: An extended π -system containing two [3]cumulene fragments separated by a *p*-carbo-quinoid and stabilized by two capping *N*-heterocyclic carbenes (NHCs) has been prepared. Mono- and bis-imidazolidinium ethynyl cations have also been synthesized from the reaction of an NHC with phenylethynyl bromide or 1,4-bis(bromoethynyl)benzene. Cyclic voltammetry coupled with synthetic and structural studies showed that the dication is readily reduced to a neutral, singlet bis-1,4-([3]cumulene)-*p*-carbo-quinoid due to the π -accepting properties of the capping NHCs.

Extended cumulenes and polyynes have received much recent attention. For example, Tykwinski^[1,2] and others^[3] have used them as molecular wires and as linkers between the end caps of rotaxanes.^[4] These extended linear carbon atom chains are conjugated π -systems, which allows for communication across their length.^[2] Shorter cumulenes, such as [3]cumulenes, were first reported by Brand in the early 1920's.^[5, 6] More recently, Diederich has looked at the synthesis and reactivity of these systems^[7, 8] as well as those of a number of push-pull/donor-

acceptor [3]cumulenes.^[9, 10] In addition, Ueta has reported the [2+2] cycloaddition of a [3]cumulene with tetracyanoethene.^[11]

Para-carbo-quinoids are conjugated molecules with extended π -systems and, as such, are also of interest. However, stable *para*-carbo-quinoids are uncommon. A well-known exception is tetracyanoquinodimethane (TCNQ)^[12], which is commonly used in charge transfer salts and was influential in the development of organic electronics; the TTF-TCNQ complex^[13-15] (TTF = tetrathiafulvalene) is considered to be the first organic metal. Also included in the category of *para*-carbo-quinoids are Thiele's **A**^[16] and Tschitschibabin's^[17] (Chichibabin's^[18]) **B** hydrocarbons, both initially reported in the early 1900's. The stability of **A** and **B** is largely attributable to their four phenyl substituents (*cf.* cyano groups in TCNQ),^[18] though compound **B** is highly oxygen sensitive as a consequence of its biradicaloid ground state.^[19]



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Supporting information for this article is given via a link at the end of the document.

Unique main group functionalities can be stabilized using singlet carbenes of which *N*-heterocyclic carbenes (NHCs)^[20] and cyclic alkyl amino carbenes (CAACs) are the most often employed.^[21, 22] In terms of carbon-based functional groups, these singlet carbenes have been used to isolate bent allenes **C**^[23], (also formulated as NHC→C←NHC carbones)^[24] and CAAC-functionalized [3]cumulenes **D**, including their dication and radical mono cations in which much of the spin density is carbon-based.^[25-28] A [3]cumulene stabilized by two capping 4-pyridylidene units has also been reported.^[29] In a similar vein, though carbene-centered radicals stabilized via the so-called captodative effect have been known for quite some time^[30, 31], stable NHC- and CAAC-based derivatives **E** have only recently been reported by Bertrand^[32, 33] and Hudnall.^[34] Finally, it would be remiss to not mention the recent work of Rivard on *N*-

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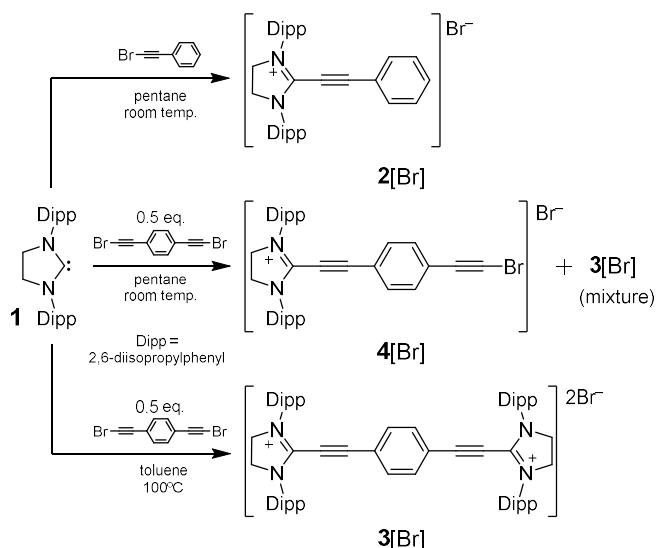
heterocyclic olefins **F**^[35] which are isolable molecules prepared from the reaction of an NHC and (Me₃Si)CH₂Cl.^[36]

Here we report the chemistry of the NHC, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene **1**, with ethynyl halides, further expanding the reactivity of NHCs with carbon-based functional groups. Specifically, we describe the synthesis of mono- and bis-imidazolidinium ethynyl cation-based salts **2**[Br] and **3**[Br], both propargyl cations, which have been characterized by a variety of structural methods, including spectroscopy, X-ray diffraction, and comparative computational studies. The redox chemistry of the cations **2** and **3** has also been explored and in the case of **3**, a double reduction was found to give a neutral, singlet bis-1,4-([3]cumulene)-*p*-carbo-quinoid **5**. The isolation of **5** can be attributed to the π -accepting properties of the NHC working in conjunction with the ability of the 1,4-ethynyl benzene group to readily reorganize to form the bis-1,4-([3]cumulene)-*p*-carbo-quinoid containing a total of 24 π -electrons (including the *N*-based lone pairs). This is in contrast to a recent computational study where derivatives that lack substantial π -accepting properties (e.g. carbene, R₂C, R = alkyl, aryl, nitrile, acetylene), form biradical species that maintain the non-quinoidial, -C \equiv C-C₆H₄-C \equiv C- bonding pattern.^[37]

NHC **1** readily reacts with phenylethynyl bromide at room temperature in pentane to give the salt **2**[Br] in reasonable yield (57%) as a tan colored powder (Scheme 1). However, the reaction of NHC **1** with 1,4-bis(bromoethynyl)benzene did not go to completion at room temperature (Scheme 1). Even with extended stirring, mixtures of **3**[Br] were contaminated with compound **4**[Br] (1:0.6 ratio by ¹H NMR spectroscopy), most likely due to the insolubility of **4**[Br] in pentane preventing further reaction with NHC **1**. Alternatively, reacting **1** with 1,4-bis(bromoethynyl)benzene in hot (100 °C) toluene overnight gave **3**[Br] as the only product in high isolated yield (89%). Compounds **2**[Br] and **3**[Br] were characterized by elemental analysis, IR, ¹H, and ¹³C NMR spectroscopies, and single crystal X-ray diffraction (Figure 1), whereas the impurity **4** was characterized (as its BPh₄ salt) by X-ray crystallography (see Supporting Information).

IR and ¹³C NMR spectroscopies clearly identified the ethyne groups in **2** and **3** (**2**: ν = 2223 cm⁻¹, δ = 72.4 and 110.4 ppm; **3**: ν = 2227 cm⁻¹, δ = 75.0 and 109.8 ppm). In the solid state (Figure 1), both **2** and **3** feature typical C_{NHC}-C_{alkynyl} (**2**: 1.423(4) and 1.424(4) Å; **3**: 1.417(4) Å)^[38] and C \equiv C bond lengths (**2**: 1.196(4) and 1.203(4) Å; **3**: 1.197(4) Å). In addition, the C_{NHC}-C \equiv C angle is nearly linear in one of the two crystallographically inequivalent cations in **2**[Br] (171.3(3)°), slightly more bent in the second (167.3(3)°), and considerably bent (163.9(3)°) in the dication **3**. Density Functional Theory (DFT) calculations (PBE1PBE^[39-42]/(def2-)TZVP^[43,44]) on the cations **2** and **3** showed that a linear C_{NHC}-C \equiv C-C arrangement is preferred, implying that the observed bending is most likely a crystal packing effect due to a shallow potential for angle bending (see Supporting Information). This was confirmed by synthesizing a number of other mono-cation compounds similar to **2**, which were characterized using X-ray diffraction (**2**[PF₆], *para*-F-**2**[PF₆], *para*-Ph-**2**[Br]; see Supporting Information). An analysis of bond lengths and angles for the C_{NHC}-C \equiv C-Ar portion of the cations gave significant variation in the C_{NHC}-C \equiv C bond angle (from 163.9(3)° to 180.0°), showing that this is indeed the one position in each compound where flexibility can be induced during packing for crystallization. Finally, it should be noted that the C-C bond distances in the aryl ring attached to

the acetylene are consistent with those in a normal aromatic ring (**2**: 1.348(9)–1.415(6) Å; **3**: 1.386(4)–1.399(5) Å).



Scheme 1. Synthetic route to compounds **2**[Br], **3**[Br], and **4**[Br], from NHC **1** and ethynyl bromides.

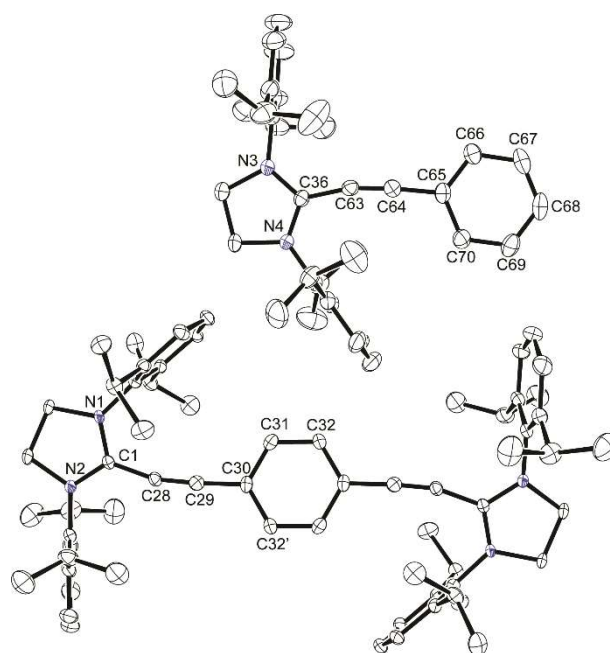


Figure 1. Solid state structure of the cation **2** (top, one of two cations in the asymmetric unit) and the dication **3** (bottom). Hydrogen atoms, anions, and co-crystallized solvent molecules have been omitted for clarity.

Compounds **2**[Br] and **3**[Br] were analyzed by cyclic voltammetry. The reduction of **2**[Br] was found to be a scan-rate dependent process, whereby the anodic peak current increased upon faster scanning (ν = 0.2–20 V s⁻¹) (E_m = -1.63V vs Fc^{0/+}). No processes were observed upon initial scanning in the anodic direction to 0 V. However, upon scanning first in the cathodic direction an induced process was observed at E = -0.73 V vs Fc^{0/+} (see Supporting Information). The peak current for this process was small and *decreased* with increasing scan rate (such a peak was not observed in scans greater than 10 V s⁻¹; see Supporting

Information). Attempts to chemically reduce the cation (KC_8) resulted in a dark red colored intractable material that gave a weak EPR signal. Multiple attempts to obtain pure material were unsuccessful and attempts to further identify this product were abandoned. DFT calculations showed that the unpaired electron in the purported neutral radical is highly delocalized. This does not, however, preclude the possibility for C-C bond formation via the terminal phenyl group.

Compound **3** was found to undergo two sequential, reversible redox processes (*i.e.* an $E_{\text{rev}}E_{\text{rev}}$ mechanism^[45]) with E_m of -1.18 V and -1.48 V vs $\text{Fc}^{0/+}$ (Figure 2). The first process is likely a one electron reduction to form a radical cation, followed by a second reduction to give the neutral species.^[46] These redox processes are much lower in potential than those of TCNQ (-0.30 V and -0.88 V vs $\text{Fc}^{0/+}$).^[47] Chemical reduction of **3**[Br] with two equivalents of KC_8 in THF resulted in rapid formation of an intensely blue colored solution with black precipitate (graphite). Upon workup, a blue-black material was obtained in low isolated yield (33%) due to its extreme solubility in compatible solvents (pentane, toluene, or THF). IR spectroscopy showed the introduction of a new signal at 2082 cm^{-1} , and the concomitant loss of the $\text{C}\equiv\text{C}$ stretch ($\nu = 2227\text{ cm}^{-1}$ in **3**[Br]), which is consistent with the presence of a cumulene functional group and the formation of **5** (Scheme 2).

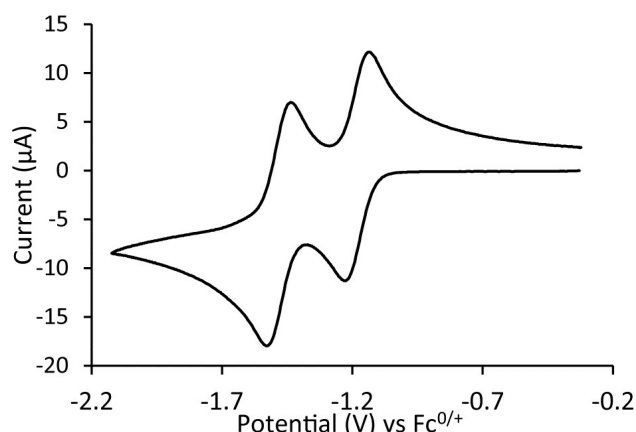
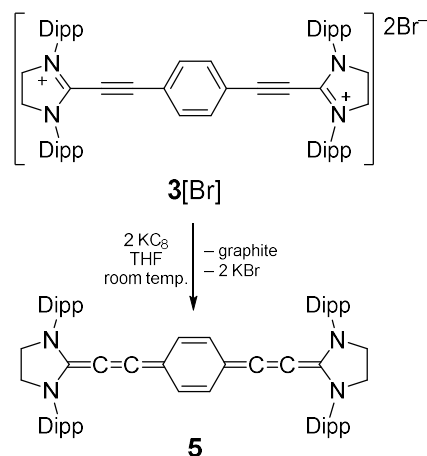


Figure 2. Cyclic voltammogram of compound **3**[Br] in CH_2Cl_2 containing 0.4M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at a Pt electrode at room temperature; sweep rate 0.2 V s^{-1} with the potential starting at -0.3 V and sweeping in the anodic direction first.

The neutral reduction product **5** could conceivably exist in any of three possible forms: a neutral open shell biradical (singlet or triplet) or as a neutral closed shell singlet cumulene.^[18] DFT calculations indicated that the closed shell singlet form is the global energy minimum and lies *ca.* 60 kJ mol^{-1} below the open shell triplet biradical state; there was no indication of a low-energy open shell singlet state. Magnetic susceptibility measurements on the solid confirmed that **5** is diamagnetic and carefully prepared samples were EPR silent. Although a clean solution state ^1H NMR spectrum of **5** could not be obtained, most likely due to the presence of very minor amounts of paramagnetic impurities, a clean solid state ^{13}C NMR spectrum was recorded and showed good correlation with the calculated chemical shifts (see Supporting Information). The solution UV-Vis spectrum for **5** showed one main absorption at 595 nm (pentane, $\epsilon = 23970\text{ L mol}^{-1}\text{ cm}^{-1}$), which matches with the observed blue color of the solution. The calculated λ_{max} of **5** is *ca.* 550 nm in *n*-pentane (525

nm in gas phase), which is reasonably close to the observed main absorption and corresponds to a HOMO to LUMO transition with no charge transfer character (see Supporting Information).



Scheme 2. Reduction of **3**[Br] to form the cumulene **5**.

Dark blue/black crystals of **5** were grown from a cold (-35°C) pentane solution and were found to be suitable for analysis by X-ray crystallography (Figure 3, top). Compound **5** crystallizes in the space group $P2_1/c$ with the asymmetric unit containing one-half of the molecule. The metrical parameters for **5** are significantly different from **3** in each of the bond lengths between the two NHC fragments (Figure 3, middle). The $\text{C}_{\text{NHC}}\text{-C}$ bond is shorter by *ca.* 4% , while the central C-C bond has elongated by *ca.* 3.5% (*i.e.* no longer $\text{C}\equiv\text{C}$) and the $\text{C-C}_6\text{H}_4\text{-C}$ fragment has distinct quinoidal character with alternating double and single bonds. Fascinatingly, both the dication **3** and the cumulene **5** have nearly identical *overall* structures (see the overlay in Figure 3, bottom). Thus, the addition of two electrons to **3** to afford **5** causes no perceptible change in the separation of the $\text{NHC}\cdots\text{NHC}$ moieties in these species (**3** $10.733(6)\text{ \AA}$ and **5** $10.716(10)\text{ \AA}$) as a result of the offsetting C-C bond lengthening and shortening in the central $(\text{CC})\text{C}_6\text{H}_4(\text{CC})$ core.

Bond length alternation (BLA) in cumulenes was originally observed by Tykwinski^[48] using X-ray crystallographic data. It has been noted that BLA is greatest with [3]cumulenes and decreases as the cumulene chain lengthens. Cumulene **5** has a BLA of 0.085 .^[49] When compared to other [3]cumulenes, **5** has a BLA that is similar to a standard cumulene ($\text{R}_2\text{C}=\text{C}=\text{CR}_2$, $\text{R} = 3,5\text{-tBuPh}$; $\text{BLA} = 0.086$) and much different than that of a polarized [3]cumulene, $((\text{Ph}(\text{iPr})\text{N})(\text{Ph}(\text{Me})\text{N})\text{C}=\text{C}=\text{C}(\text{CN})_2)$; $\text{BLA} = 0.172$), which reflects the relatively symmetrical nature of each [3]cumulene in **5**. The $\text{C}_{\text{NHC}}=\text{C}=\text{C}$ angle ($167.0(5)^\circ$) is slightly less bent than that in the dicationic precursor ($163.9(3)^\circ$). However, a computational analysis of **5** showed that a linear $\text{C}_{\text{NHC}}\text{-C}\equiv\text{C}\text{-C}$ arrangement is again preferred in the gas phase with a shallow potential for angle bending (see Supporting Information).

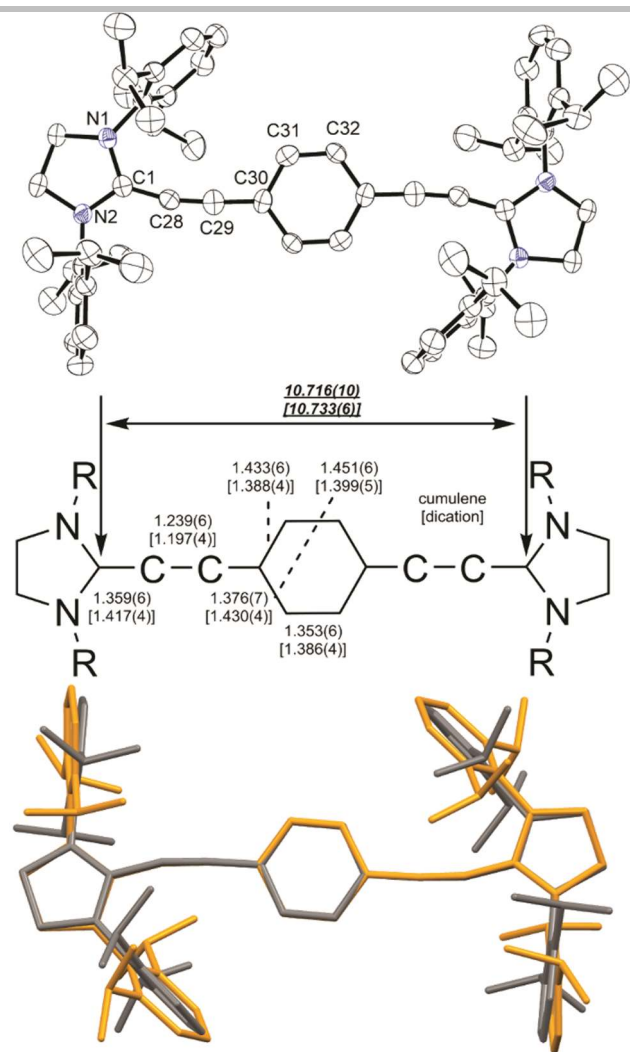


Figure 3. Solid state structure of cumulene **5** (top; 50% ellipsoids, hydrogen atoms removed), bond lengths (Å) of cumulene **5** and dication **3** [in brackets] (middle), and an overlay of both the dication **3** (grey) and cumulene **5** (orange) showing the similarity between the structures (bottom).

Nucleus Independent Chemical Shift (NICS) calculations were performed for **5** and the results were compared to values calculated for the dication **3** as well as to those of three model systems: benzene, *p*-benzoquinone, and a phenyl substituted [3]cumulene similar to **5**.^[50] The results (Table 1) show that the central ring in **3** has a NICS(1)_{zz} value quite similar to that of benzene (−24 ppm and −30 ppm, respectively), indicative of aromatic character, whereas the cumulene **5** has a NICS(1)_{zz} value very similar to that calculated for *p*-benzoquinone (2 ppm and 3 ppm, respectively), consistent with their antiaromatic nature. This data, along with the bond lengths from the crystal structures, reinforces the idea that there is a loss of aromaticity at the central C₆H₄ ring when the dication of **3** is converted to the cumulene **5**, and supports the quinoidal description of the central ring in **5**. The quinoidal description of **5** is also supported by the morphology of the HOMO (*i.e.* the LUMO of the dication **3**), which shows alternating bonding/anti-bonding character for the C-C bonds of the central ring (see Supporting Information).

Table 1. Calculated Nucleus Independent Chemical Shifts

Compound	NICS(1) _{zz} (ppm)
	−30
	3
	−6
	−24
	2

In conclusion, we have shown that NHCs react with ethynyl bromides to give mono- and bis-imidazolidinium ethynyl cations. Although the mono cation **2** produces intractable materials upon chemical reduction, the bis-substituted dication **3** can be reduced to give a novel bis-cumulene **5** that is quinoidal in character, as evidenced by X-ray crystallography and DFT calculations. We also discovered that there is very little change in the distance between the NHC moieties upon adding two electrons to the dication **3** to form **5**. This may prove to have useful applications in materials chemistry where disruption of the solid state structure is to be avoided, *e.g.* crystalline redox switches.

While reading this manuscript for submission, we discovered the recent pre-publication of the first crystalline monomeric allenyl/propargyl radical stabilized by CAAC ligands by the Bertrand group.^[51] This communication highlights the significance and currency of the results reported herein. Rapid advances in the chemistry of carbon species enabled and supported by singlet carbenes can be expected.

As recommended by a reviewer, we attempted the reaction of **5** dissolved in degassed C₆D₆ with one atmosphere of dihydrogen and noted no reaction at room temperature. Despite the small singlet-triplet energy gap of **5**, the morphologies of its frontier orbitals are not suitable for this type of reactivity. However, compound **5** is extremely reactive towards CH₂Cl₂ and CHCl₃, resulting in loss of its blue color in such solutions. The reaction products were not characterized.

Experimental Section

See Supporting Information for experimental, computational, and extended crystallographic details. CCDC 1549498-1549504 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Database Centre.

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Keywords: cumulenes • *N*-heterocyclic carbenes • alkynes • X-ray crystallography • propargyl cations

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