

Startling bonds: revisiting C N+, via the helium bond in N≡C-He+.

Henry Rzepa 

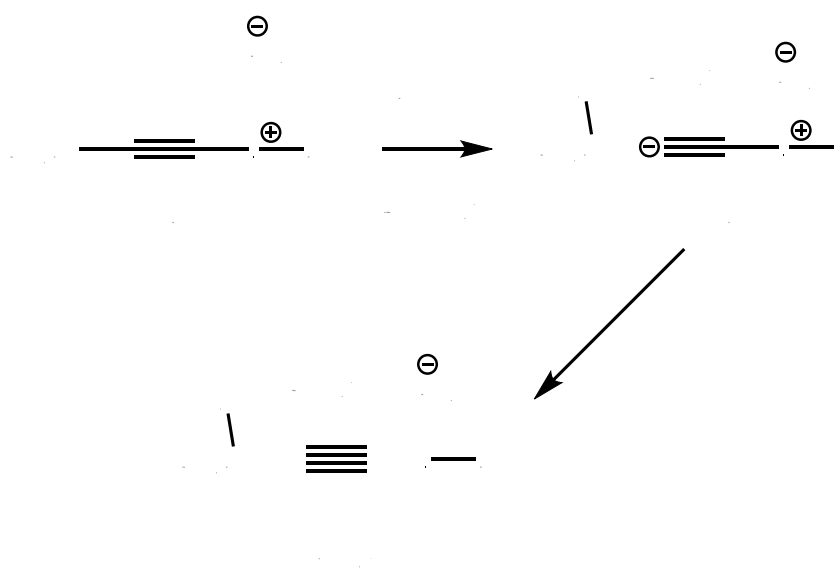
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Keywords

Interesting Chemistry

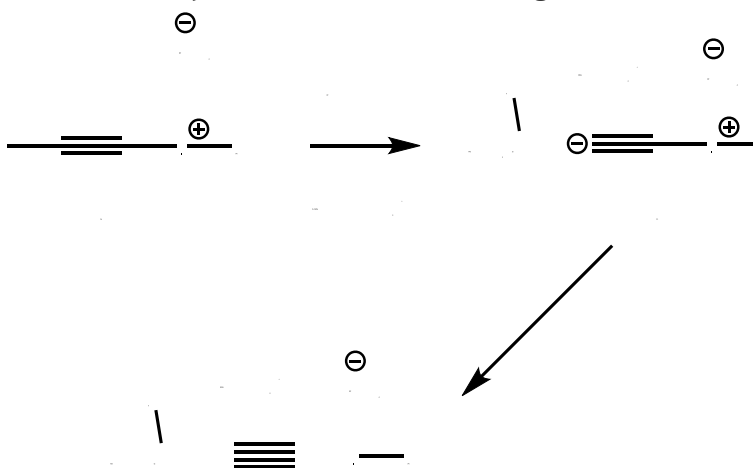


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Henry Rzepa's Blog

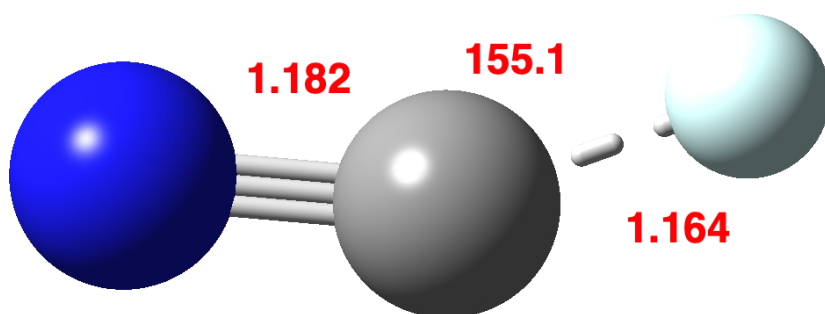
Although the small diatomic molecule known as dicarbon or C_2 has been known for a long time, its properties and reactivity have really only been determined via its very high temperature generation. My interest started in 2010, when I [speculatively proposed here](#) that the related isoelectronic species $C N^+$ might sustain a quadruple bond. Shortly thereafter, a torrent of theoretical articles started to appear in which the idea of a quadruple bond to carbon was either supported or rejected. Clearly more experimental evidence was needed. The recent appearance of a Chemrxiv pre-print entitled "*Room-temperature chemical synthesis of C_2* ". [cite]10.26434/chemrxiv.8009633.v1[/cite] claims to provide just this! Using the synthetic scheme outlined below, they trapped " C_2 " with a variety of reagents (see Figure 2A in their article), concluding that the observed reactivity best matched that of singlet "biradicaloid" C_2 sustaining



a quadruple bond.

Inspired by the report of this chemical synthesis, I thought I would revisit $C N^+$ to speculate how it too might be made. A colleague (thanks Ed!) had alerted me to a probably ultimate method for generating cations using tritium.[cite]10.1021/ja00212a052[/cite] Radioactive decay♥ loses an electron by β emission and forms He^+ , which is followed by expulsion of a helium atom to leave behind a cationic centre; in this example at the sp-carbon of an alkyne.

So on[^] to explore the energetics of generating cationic $C N^+$ by this synthetic/nuclear-decay method[†]. The thermochemistry of the reaction $(N \equiv C-T \rightarrow) N \equiv C-He^+ + e \rightarrow N \equiv C^+ + He \rightleftharpoons C N^+$ will be calculated using the CCSD(T)/Def2-TZVPP method.[‡] Firstly the geometry of $N \equiv C-He^+$, which is bent and not linear. This species sustains a short C-He bond, which has a calculated Wiberg bond order of **0.67**. [Recollect the excitement](#) when a report appeared of bonded helium, which has a computed bond order of just 0.15! The C-He stretch in $N \equiv C-He^+$ is 907 cm^{-1} with the bend being 193 cm^{-1} and the $C \equiv N$ stretch 2116 cm^{-1} .



Click image to view 3D animated model

A He atom is then lost, resulting in an exo-energetic $\Delta\Delta G_{298}$ of **-12.6** kcal/mol (see FAIR data DOI: [10.14469/hpc/5691](https://doi.org/10.14469/hpc/5691)). Despite all that energy injected by a nuclear decay process, together with the supercharged leaving group, the reaction is only moderately exo-energetic.

Is this experiment a viable method for generating **C N⁺** cations? Since the half-life of T, aka ³H, is ~11 years, any experiment must be run for months to generate detectable amounts of products (six months as reported here[cite]10.1021/ja00212a052[/cite]). The **C N⁺** must therefore be trapped as soon as it is formed. The selection of the chemical traps (avoiding HCN itself?) which could demonstrate the nature of this species will therefore be an interesting challenge, should anyone wish to try this experiment.

♥A similar procedure was used to generate the hitherto elusive [perbromic acid](#) by β decay of ⁸³Se into ⁸³Br. †The thermochemistry for the method reported here[cite]10.26434/chemrxiv.8009633.v1[/cite] will be explored separately. ‡The second of the two consecutive experimental C-H BDEs (bond dissociation energies) for the reaction H-C≡C-H → H-C≡C· and then H-C≡C· → C C is known experimentally to be about 20 kcal/mol lower than the first. This observation is most simply explained by the formation of a 4th bond, here represented by . If you are interested in how to invoke this and other chemically useful glyphs, [see here](#). Such thermochemistry was previously evaluated using correlated methods[cite]10.1002/chem.201400356[/cite] such as CCSD(T) and MRCI (multi-reference configuration interaction, used specifically for C₂); procedures which reproduced well these relative experimental BDEs. [cite]10.1002/chem.201400356[/cite] Here (see FAIR data DOI: [10.14469/hpc/5684](https://doi.org/10.14469/hpc/5684)) I found that using single reference CCSD(T)/Def2-TZVPP throughout also gives a similar result, the second BDE being ~22 kcal/mol less than the first. Accordingly, this method is here used to estimate the geometry and energy of N≡CHe⁺ and its carbon-helium bond-dissociation to give **C N⁺** + He. I recognise that ultimately, multi-reference methods should also be used to check these results.

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