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Metastability

The Demise and Revival of Diazirinone**

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Dedicated to Professor Gernot Frenking on the occasion of his 65th birthday

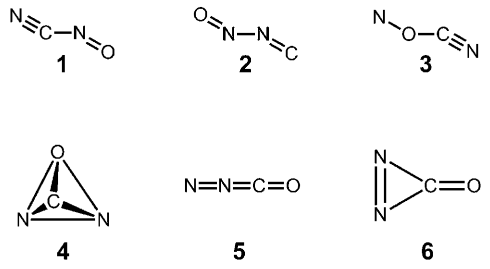
diazirinone · isoelectronics · mass spectrometry · matrix isolation · metastability

Much can be learned from the study of molecules that are at the precipice of destruction. Compounds in this realm must wage a constant battle for survival against dissociation, dimerization, polymerization, reduction/oxidation, and isomerization, and in the most extreme cases, human philosophy. These molecules challenge our beliefs on what it means to exist. Despite the numerous pitfalls, the scientific value and lessons provided by these compounds continue to proliferate.[1] As said recently by Frenking, "The successful synthesis of a molecule that was thought to be too unstable to be isolated is often published as a spectacular achievement of experimental chemistry."[2]

The development of new metastable species has benefited greatly in recent years thanks to significant gains in synthetic chemistry. As an illustrative example, the long-sought 1,2-dihydro-1,2-azaborine, which is isoelectronic to benzene, has recently been reported.[3] The synthesis of this compound was possible only because of advances in ring-closing metathesis. Similarly AsP_3, valence-shell isoelectronic to P_4, was only recently synthesized thanks to the development of new P_3 transfer reagents.[4] Complementing the advances in synthetic chemistry, the elaborate stabilization/observation methods of matrix isolation and mass spectrometry continue to provide the first experimental insights into even higher energy compounds.

Further demonstrating the impact of metastability is the open-chain molecule N_4. One would not expect this molecule to exist as it is the dimerization product of the second most stable diatomic molecule N_2. However, neutralization–reionization mass spectrometry (NRMS) experiments by Cacace et al. have provided sufficient evidence that the open-chain isomer of this molecule is metastable with a half-life as low as only 1 μs.[5] In contrast, the isoelectronic molecule OCCO is a conjugate of two molecules of CO, of which the latter coincidentally has the highest bond dissociation energy of all diatomic molecules. Owing to the appreciable stability of CO_2 as well as C_3O_2, OCCO has long been an experimental target, and was even once fraudulently marketed as a homeopathic drug. However, not all is so bright for OCCO, and although it may seem viable to a chemist or a snake oil salesman, a low barrier to decomposition through a singlet–triplet surface crossing prohibits any claim to metastability.[6]

Maintaining the N_4 isoelectronic theme, species of the type CN_2O have long been subject to much experimental and theoretical work.[7] Nitrosyl cyanide (**1**, NCNO; Scheme 1), despite its high energy, is remarkably well studied. Further, matrix isolation and photochemical treatment of nitrosyl cyanide has lead to the identification of nitrosyl isocyanide (**2**, ONNC) and isonitrosyl cyanide (**3**, NOCN).[8] More elusive are the three direct CO and N_2 conjugates: the strained tetrahedrane-like structure **4**, the triplet open-chain structure **5** (NNCO), and singlet diazirinone **6** (N_2CO). The two latter species are lower in energy than any of the nitrosyl cyanide species.



Scheme 1. Viable isomers of CN_2O.

In 2005, two independent experimental investigations of CO/N_2 conjugates were reported. By ionization of a CO/N_2 mixture, mass selection, and NRMS analysis of the resultant species, de Petris et al. convincingly identified a neutral species with NNCO connectivity.[9] They excluded formation of diazirinone because the cation precursor could not be found as a minimum on the N_2CO^+ potential energy surface. In accompaniment, diazirinone was declared the transient product of *p*-nitrophenoxychlorodiazirine when treated with a fluoride source.[10] Despite being the sole experimental method for the synthesis of diazirinone at that time, the characterization of diazirinone was dependent on the assignment of a single infrared band at 2150 cm^{-1}, which was proposed to decay rapidly upon decomposition of the transient species into carbon monoxide (and N_2). Recent investigations have refuted these claims for the existence of diazirinone, and the evanescent IR band has been reassigned to condensed-phase carbon monoxide which undergoes a change in spectroscopic principals as it moves into the gas

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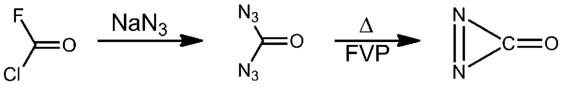
phase.[11] Despite these exhaustive efforts, diazirinone has thus remained an elusive molecule.

In reporting the first conclusive synthesis of diazirinone, Zeng et al. have now resolved the troubled history of diazirinone.[12] The synthesis was accomplished thanks to bravery in the isolation and characterization of the highly explosive carbonyl diazide ($OC(N_3)_2$).[13] The simplest route to diazirinone would be to isolate the carbonyl diazide species in a cryogenic matrix, photolyze the two azides, and generate the corresponding dinitrene which should form diazirinone. Interestingly, upon visible-light irradiation, carbonyl diazide photolyzes partially to generate the mononitrene $N_3C(O)N$, but before the second photolysis step can occur the carbonyl nitrene undergoes a Curtius rearrangement to give N_3–NCO.[14] Undeterred, Zeng et al. have exploited flash-vacuum pyrolysis (FVP) of $OC(N_3)_2$ to produce isolable amounts of diazirinone (Scheme 2), such that their recent paper also includes a photograph of the frozen sample isolated in a cold trap.



Scheme 2. Synthesis of diazirinone.

Of paramount importance is the agreement of the experimental IR spectrum with the anharmonic frequencies predicted previously. Most critical of these is the C=O fundamental stretch predicted at 2046 cm^{-1} and found experimentally at 2034 cm^{-1} (Ar matrix); this is in marked contrast to the questionable band at 2150 cm^{-1} referred to before.[10] The assignments made by Zeng et al.[12] are further supported by the identification of weaker fundamental frequencies, extensive isotopic labeling studies, and the observation of a strong peak at 1857 cm^{-1}, which is consistent with the prediction of a strong Fermi resonance with the 2034 cm^{-1} band.[11]

Quite surprising also is the significant stability of diazirinone in the gas phase (the experimental half-life amounts to 1.4 h at ambient temperature). As well as allowing for more rigorous future studies, this property suggests that this compound may in fact be a viable candidate for detection in interstellar space. These future studies may best be performed with rotational spectroscopy which may also provide valuable insight into the aromaticity of diazirinone. Diazirinone's candidacy as an interstellar molecule is significant as the detection of diazirinone would classify it as one of the few aromatic compounds to be detected in space. In these regard, the report by Zeng et al. is just a first step, but in light of the preceding difficulties in the synthesis and identification of diazirinone, the successful synthesis is a critical first step in understanding this molecule, its properties, and its reactivity.

More generally, it is worth recognizing that the existence of the elusive title molecule (though a different isomer) was first hinted at in mass spectrometric experiments.[9] A similar success story is associated with free carbonic acid (H_2CO_3), whose existence was first demonstrated by NRMS in 1987,[15] followed by isolation of the bulk substance[16,17] then observation first in aqueous solution[18] and now finally in the gas phase.[19] Accordingly, we may optimistically await the preparation of other elusive molecules implicated by mass spectrometry, such as N_4,[5] O_4,[20] water oxide H_2OO,[21] and *meta*-benzoquinone.[22]

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