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MEMORANDUM FOR PRS (In-House Contractor Publication)

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29 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-2002-089
Jerry Boatz (PRSP) and Karl Christe (ERC), "New Polynitrogen Molecules - Energetic 'Air' as a Next-
Generation Propellant?"

DoD HPC Success Story Booklet

(Statement A)

Title: New Polynitrogen Molecules -- Energetic "Air" as a Next-Generation Propellant?

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HPC Resource Environments: IBM SP/P3 at ASC, SGI Origin 3800 at AFFTC

The identification, development, and formulation of new energetic materials for advanced rocket propulsion applications is an area of long standing interest to the Air Force. The performance limits of currently used propellants have been reached, so new energetic compounds are required to significantly improve the ability of the warfighter to access and control space.

Polynitrogen species such as the recently discovered N_5^+ cation are of interest as potential energetic ingredients in new propellant formulations. The recent successful synthesis of N_5^+ in macroscopic quantities has prompted the search for additional polynitrogen compounds. Computational chemistry plays a central role in determining the stabilities, potential synthetic pathways, and key spectroscopic "fingerprints" of new polynitrogen species.

Conventional techniques for characterizing new materials such as polynitrogens have relied heavily on costly and time-consuming experimental synthesis and characterization. However, the availability of HPC resources has significantly lessened the need for these more empirical approaches by enabling the application of reliable high-level quantum chemical calculations to reliably predict important properties such as heats of formation, stabilities, mechanisms of formation and decomposition, and spectroscopic constants. A key advantage of using HPC in

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this regard is the ability to efficiently "screen" a large number of potential polynitrogen molecules and focus subsequent experimental efforts on the subset of only the promising candidates.

The structures, stabilities, vibrational frequencies, and infrared intensities of several potential synthetic precursors to new polynitrogen species have been computed using ab initio electronic structure theory, at the second order perturbation theory level (MP2, also known as MBPT(2)), using the 6-31G(d) valence double-zeta polarized basis set. Shown in the accompanying figure is the predicted structure of triphenylmethyldiazonium cation, also known as trityldiazonium, which is a possible precursor to new polynitrogen compounds such as pentazole, a 5-membered ring system. The calculated structure shows that this cation is unstable with respect to dissociation of N_2 . Therefore, these calculations predict that this cation is not a viable polynitrogen precursor.

Although this is a negative result in the sense that it indicates that trityldiazonium is not a stable precursor, it is nonetheless a highly useful result in multiple ways. First, it saves significant time and effort by eliminating from consideration for subsequent attempts at synthesis a compound which is not likely to be stable. Furthermore, it suggests ways in which the trityldiazonium cation may be chemically modified in order to overcome its instability (e.g., by judicious placement of electron-withdrawing groups on the trityl moiety.) Future work in this area will examine such derivatives of the trityldiazonium cation, as well as other classes of promising polynitrogen precursors.

Primary CTA: CCM

Scientific visualization: WebLabViewerLite for visualization of optimized geometries.

References: (1) K.O. Christe, W.W. Wilson, J.A. Sheehy, and J.A. Boatz, "A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material", *Angew. Chem. Int. Ed.* 38, 2004-2009(1999).

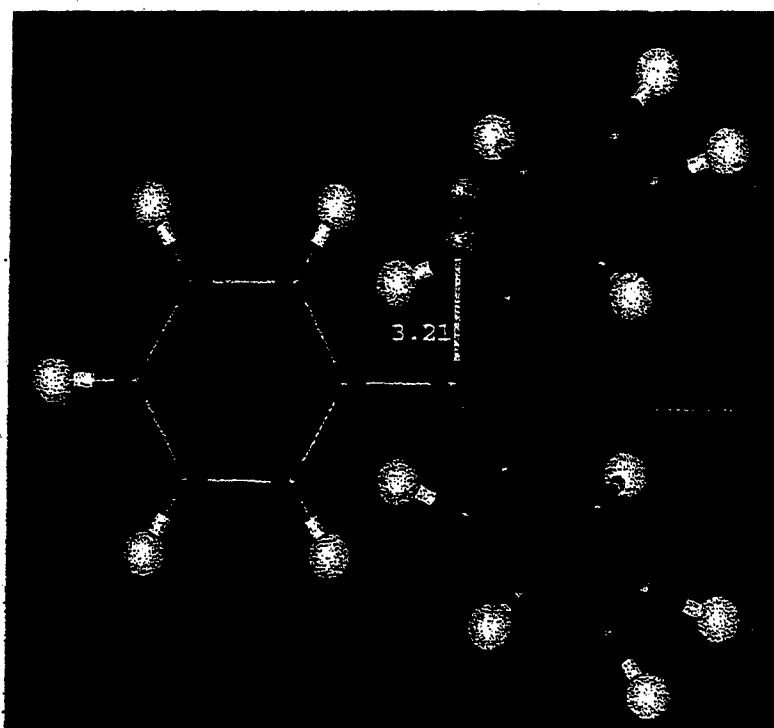


Figure Caption: MP2/6-31G(d) optimized structure of triphenylmethyldiazonium cation, $[\text{C}_{19}\text{N}_2\text{H}_{15}]^+$. The predicted C-N internuclear distance of 3.21 angstroms indicates that this cation is unstable with respect to dissociation to triphenylmethyl cation and N_2 .

Acronyms:

MP2	Moller-Plesset perturbation theory (second order)
MBPT(2)	Many-body perturbation theory (second order).