sites and responsive chromophores or fluorophores constitute a feasible approach to measurement of bis(benzamidine) drugs, such as pentamidine. Sensors and reagents based on this approach could prove superior to conventional chromatographic methods for analysis of therapeutic drugs.[4a,16]

Acknowledgment. We gratefully acknowledge research support from the National Institutes of Health (Grant 5 RO3 AI30945-02).

Supplementary Material Available: UV-visible data presented as tables and graphs of absorbance vs guest:host ratio for titration of **1** and **2** with benzamidine hydrochloride and experimental procedures and characterization data for compounds **1**, **2**, **5**, **6**, **9** and complexes of **1** and **2** with benzamidine hydrochloride (8 pages). Ordering information is given on any current masthead page.

---

(15) Hamilton, A. D.; Pant, N.; Muehldorf, A. *Pure Appl. Chem.* **1988**, *60*, 533–538.

(16) (a) Kulinski, R. F. *LC-GC* **1990**, *8*, 370–376. (b) Lin, J. M.-H.; Shi, R. J.; Lin, E. T. *J. Liq. Chromatogr.* **1986**, *9*, 2035–2046. (c) Dickinson, C. M.; Navin, T. R.; Churchill, F. C. *J. Chromatogr.* **1985**, *345*, 91–97. (d) Aliu, Y. O.; Ødegaard, S. *J. Chromatogr.* **1983**, *276*, 218–223.

Hydrogen Pentazole: Does It Exist?

Kim F. Ferris† and Rodney J. Bartlett*,‡

Materials Science Department, Pacific Northwest Laboratory, Richland, Washington 99352
Quantum Theory Project, University of Florida Gainesville, Florida 32611

Received May 29, 1992

Pentazoles (RN_5) present a long history of controversy regarding their stability and isolation dating back to 1915 when Lipschitz reported the synthesis of the silver salt, AgN_5.[1] This was promptly refuted by Curtius et al.[2] who stated: "A repetition of Lipschitz's experiments has shown that all his observations ... are erroneous and that there is no formation of pentazoles." Further attempted syntheses were not successful until 1957, when Huisgen and Uzi reported the synthesis of the phenylpentazole derivative in a paper entitled, "Pentazoles I. The Solution of the Classical Problem of Organic Nitrogen Chemistry".[3] X-ray crystal structures for this species have also been determined;[4] however, no synthesis of the HN_5 pentazole prototype has ever been reported. Pentazoles are directly analogous to the cyclopentadienyl systems, and theoretical work has examined the nature of the anion (N_5^-)[5] and metal–ring complexes.[6] As part of a continuing investigation of nitrogen-based metastable species, Bartlett and co-workers have investigated the properties of N_3H_3,[7] N_4, N_6, and N_8,[8] as have others.[9] Theory predicts that N_3H_3, tetrahedral N_4, and octahedral N_8 are stable minimia for their respective potential energy surfaces, but experimental observation will be difficult and none has been reported.

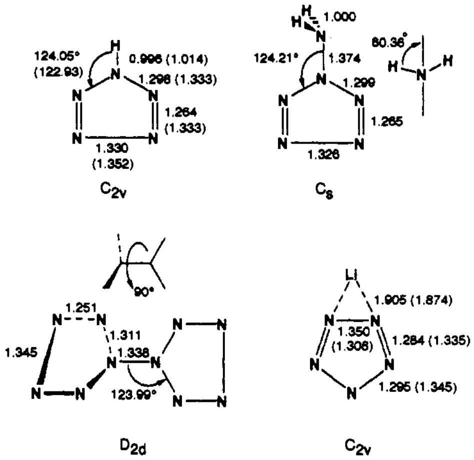

Figure 1. Molecular structure of pentazole and its derivatives determined at the SCF and MBPT(2) (in parentheses) levels. Values are given in angstroms and degrees. For hydrogen pentazole, CCSD results are 1.329, 1.304, and 1.360 Å for bonds, 1–2, 2–3, and 3–4 respectively. The NH bond is 1.010 Å.

Table I. SCF and Correlated Vibrational Analysis for Pentazole (HN_5)

	SCF/DZP			MBPT(2)/DZP		
mode	sym	freq (cm^{-1})	IR intensity (km/mol)	sym	freq (cm^{-1})	IR intensity (km/mol)
1	b_1	666	(81.1)	b_1	636	(43.3)
2	b_1	817	(42.8)	b_1	743	(67.1)
3	a_2	841	(0.0)	a_2	745	(0.0)
4	a_1	1132	(14.8)	b_2	1026	(13.8)
5	b_2	1177	(20.8)	a_1	1050	(4.2)
6	a_1	1239	(0.3)	a_1	1083	(0.6)
7	b_2	1273	(17.1)	a_1	1148	(0.1)
8	a_1	1399	(7.6)	b_2	1160	(22.6)
9	a_1	1485	(3.9)	a_1	1193	(3.2)
10	b_2	1516	(14.5)	b_2	1252	(3.9)
11	b_2	1719	(1.4)	b_2	1465	(13.7)
12	a_1	3922	(193.1)	a_1	3700	(149.6)

In this paper, we present the structural and vibrational properties of the synthetic target and several novel pentazole derivatives calculated using coupled-cluster (CC) and many-body perturbation theory (MBPT) theory.[10] We use the ACES II program system[11] and DZP basis sets.[12] Our goal is to provide accurate structural, energetic, and spectral information as a prelude to potential experimental observation.

In Figure 1, we present the structural parameters for hydrogen pentazole (HN_5) and several potential derivatives, including the unusually interesting N_5–N_5 bipentazole molecule. Electron correlation effects lengthen most bonds and diminish the degree of bond alternation, suggesting greater aromaticity. The CCSD N–N bond lengths average 1.33 Å, being intermediate between ordinary N–N single, 1.40–1.47 Å, and double bonds, 1.20–1.24

---

† Pacific Northwest Laboratory.

‡ University of Florida.

(1) Lipschitz, J. *Ber.* **1915**, *48*, 410.

(2) Curtius, T.; Darapsky, A.; Müller, E. *Ber.* **1915**, *48*, 1614.

(3) Huisgen, R.; Uzi, I. *Chem. Ber.* **1957**, *90*, 2914.

(4) Witanowski, M.; Stefaniak, L.; Januszewski, H.; Bahadur, K.; Webb, G. A. *J. Cryst. Mol. Struct.* **1975**, *5*, 137. Wallis, J. D.; Dunitz, J. D. *J. Chem. Soc., Chem. Commun.* **1983**, *16*, 910.

(5) Sana, M.; Leroy, G.; Nguyen, M. T.; Elguero, J. *Nouv. J. Chim.* **1979**, *3*, 607. Nguyen, M. T.; Sana, M.; Leroy, G.; Elguero, J. *Can. J. Chem.* **1983**, *61*, 1435.

(6) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F.; Elguero, J. *Polyhedron* **1985**, *4*, 1721.

(7) Magers, D. H.; Salter, E. A.; Bartlett, R. J.; Salter, C.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 3435.

(8) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173.

(9) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 2070. Venanzi, T. J.; Schulman, J. M. *Mol. Phys.* **1975**, *30*, 281. Francl, M. M.; Cheswick, J. P. *J. Phys. Chem.* **1990**, *94*, 526. Blahous, C. P.; Schaefer, H. F., III *J. Mol. Struct.* (*THEOCHEM*) **1989**, *59*, 591. Huber, H.; Ha, T. K.; Tho, N. M. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *14*, 351. Huber, H. *Angew. Chem.* **1982**, *94*, 71. Saxe, P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 1761. Engelke, R. *J. Phys. Chem.* **1990**, *94*, 6924.

(10) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.

(11) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *ACES II* (*Advanced Concepts in Electronic Structure*), *A new ab initio program system for performing CC/MBPT calculations*; Quantum Theory Project, University of Florida: Gainesville, FL, 1992; ACES II uses the VMOL integral program of J. Almlöf and P. Taylor and the ABACUS integral derivative program of T. Helgaker, P. Jørgensen, H. J. Aa. Jensen, J. Olson and P. Taylor.

(12) Dunning/Hay (9s,5p) contraction of the Huzinaga basis set, augmented with diffuse polarization functions on Li ($\zeta_d = 0.20$), N ($\zeta_d = 0.80$), O ($\zeta_d = 0.85$), and H ($\zeta_d = 1.00$). Dunning, T. H., Jr.; Hay, P. J. *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 23. Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

0002-7863/92/1514-8302$03.00/0

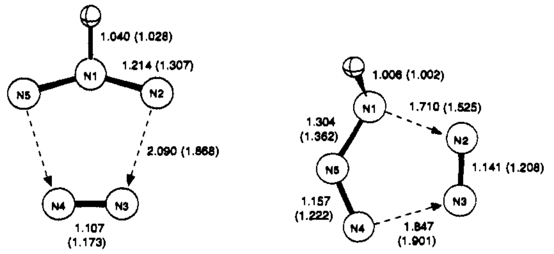

Figure 2. SCF transition-state structures for symmetric and nonsymmetric decomposition pathways of hydrogen pentazole. MBPT(2) structures are given in parentheses. Bond lengths are given in angstroms.

Å.[13] Experimental structural determination of the 4-(dimethylamino)phenyl derivative has found that the N–N bond distances are 1.30–135 Å. The N–N bond lengths for the pentazole anion are 1.298 Å at SCF, 1.350 Å at the MBPT(2) level, and 1,333 Å for CCSD.

Vibrational analyses performed at the SCF and MBPT(2) levels demonstrate that HN_5 is a minimum on its energy surface. It would be expected that the out-of-plane modes (b_2) would be particularly sensitive to electron correlation as these interactions involve the nitrogen lone pairs. Accordingly, the infrared intensities of the normal modes change, and the b_2 modes are reordered at the MBPT(2) level (Table I). Such qualitative changes with correlation were previously observed for the N_3H_3 isomer, and they differ from the agreement usually expected between scaled SCF frequencies and MBPT(2) predictions.

The stability of these molecules, and whether they can be successfully synthesized, depends on the activation energy for decomposition, among other factors.[14] To investigate possible unimolecular decomposition pathways we use "eigenvector following"[15] to locate two possible transition states (TS). Starting from the ground-state geometry, we determine a symmetric and a nonsymmetric pathway (Figure 2). The resulting reaction pathways are characterized as TSs by the presence of a single negative eigenvalue (620 cm^{-1} in both cases) and feature vastly different energetics. The MBPT(2) barriers are 48.0 and 22.8 kcal/mol for the symmetric and nonsymmetric processes, becoming 53.7 and 19.8 kcal/mol after estimation of the zero-point and internal energy corrections. The height of the barrier would suggest that hydrogen pentazole could be potentially isolated under gas-phase conditions. The asymmetric TS cleaves bonds heterolytically, enabling MBPT(2) to offer a good barrier approximation that should only be reduced by a few kilocalories/mole at higher levels of correlation. The homolytic barrier cleavage in the symmetric TS is poorly described by MBPT(2), but the barrier would still be expected to be too great to offer a competitive path.

Substitution by the electropositive atom Li or the electron-donating NH_2 group lowers the activation energy by 3.6 and 7.9 kcal/mol, respectively. As such, pentazoles with electron-withdrawing substituents, such as the known (dimethylamino)phenyl derivative, are more likely to be isolated. This particularly recommends a possible synthesis of the bipentazole molecule shown in Figure 1. Its potential aromaticity poses interesting questions.

Acknowledgment. K.F.F. acknowledges support from the Office of Basic Energy Sciences and R.J.B. from the Air Force Office of Scientific Research under Grant No. F49620-92-J-0141. The Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06 76RLO 1830.

---

(13) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L. E., Ed.; The Chemical Society: London, 1958.

(14) Questions of stability should also consider the potential for low-lying triplet electronic states that could provide a spin-forbidden decomposition path and fast bimolecular reactions of transients.

(15) Cerjan, C. J.; Miller, W. H. *J. Chem. Phys.* **1981**, *75*, 2800. Simons, J.; Jørgensen, P.; Taylor, H.; Ozment, J. *J. Phys. Chem.* **1983**, *87*, 2745.

Thermal Decomposition of Solid RDX Begins with N–N Bond Scission

Charles A. Wight*,† and Tod R. Botcher

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Received June 15, 1992

Cyclic nitramine propellants such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) have found wide application as explosives and propellants. Although a great deal of empirical data are available concerning the explosive properties of these materials,[1,2] surprisingly little is known about the detailed mechanism of their combustion.[3,4]

Several recent studies have attempted to identify the *initial* step in the thermal decomposition mechanism. One of the obvious choices for this is scission of one of the N–N bonds. Thermodynamic studies identify this as the weakest bond in the molecule,[5] and results from thermogravimetric mass spectrometry experiments on HMX are consistent with this homolysis mechanism,[6] though these authors also propose that competing bimolecular pathways are required to explain deuterium kinetic isotope effects.[7] Indirect evidence supporting the importance of the N–N bond scission mechanism can be found from thermal decomposition studies of other closely related nitramines.[8,9] Also, ultraviolet photolysis experiments on crystalline RDX have shown that N–N homolysis is a primary reaction pathway,[10] though thermal pyrolysis might not follow the same mechanism.

Zhao et al. proposed an alternative mechanism in which gas-phase RDX molecules each decompose by concerted depolymerization that initially forms three molecules of methylenenitramine,[11] CH_2NNO_2. Under these conditions, the N–N bond scission channel accounts for only about one-third of the product yield. Sewell and Thompson have recently published a classical dynamics study of RDX decomposition[12] that supports the experimental findings of Zhao et al. Also, some of the early thermal pyrolysis work on isotopically substituted RDX supports a mechanism in which the N–N bond is preserved in the decomposition reaction.[13,14]

Our experiment is designed to rapidly quench and trap the initial pyrolysis products following rapid IR laser heating of solid RDX. To do this, we form a thin film (approximately 20 mm in diameter by 5–20 μm thick) of the pure solid material by vapor deposition from a Knudsen oven at 120 °C onto an infrared-transparent window (CaF_2 or CsI) at 77 K inside a vacuum Dewar vessel. The film is warmed to room temperature in order to convert the amorphous solid to a crystalline form of RDX. A second CsI window is then used to cover the sample, and this "sandwich" arrangement is remounted in the vacuum Dewar vessel and recooled to 77 K. The sample is irradiated with a CO_2 laser tuned to the P(20) line at 944 cm^{-1}, which rapidly heats it from 77 K

[†] Alfred P. Sloan Research Fellow, 1990–1994.

(1) Meyer, R. *Explosives*; Verlag Chemie: Weinheim, 1977.

(2) Federoff, B. T.; Sheffield, O. E. *Encyclopedia of Explosives and Related Items*; Picatinny Arsenal: Dover, NJ, 1966; Report No. PATR-2700, Vol. III.

(3) Adams, G. F.; Shaw, R. W., Jr. *Annu. Rev. Phys. Chem.*, in press.

(4) Alexander, M. H.; Dagdigian, P. J.; Jacox, M. E.; Kolb, C. E.; Melius, C. F.; et al. *Prog. Energy Combust. Sci.* **1991**, *54*, 203.

(5) Melius, C. F. In *Chemistry and Physics of Energetic Materials*; Bulusu, S. N., Ed.; Kluwer: London, 1990.

(6) Behrens, R., Jr.; Bulusu, S. *J. Phys. Chem.* **1991**, *95*, 5838.

(7) Rodgers, S. L.; Coolidge, M. B.; Lauderdale, W. J.; Shackelford, S. A. *Thermochim. Acta* **1991**, *177*, 151.

(8) Brill, T. B.; Brush, P. J. *Philos. Trans. R. Soc. London, A* **1992**, *339*, 377.

(9) Oxley, J. C.; Hiskey, M.; Naud, D.; Szekeres, R. *J. Phys. Chem.* **1992**, *96*, 2505.

(10) Pace, M. D. *J. Energ. Mater.* **1985**, *3*, 279.

(11) Zhao, X.; Hintsa, E. J.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 801.

(12) Sewell, T. D.; Thompson, D. L. *J. Phys. Chem.* **1991**, *95*, 6228.

(13) Suryanarayana, B.; Graybush, R. J.; Autera, J. R. *Chem. Ind. (London)* **1967**, 2177.

(14) Suryanarayanan, K.; Bulusu, S. *J. Phys. Chem.* **1972**, *76*, 496.

0002-7863/92/1514-8303$03.00/0