Heteroatom Chemistry
Volume 10, Number 7, 1999

# Nitrophenyl Azides: A Combined Experimental and Theoretical Study*

David Adam,[1] Gerhard Holl,[2] and Thomas M. Klapötke[1]

*Institute of Inorganic Chemistry, University of Munich (LMU), Butenandtstrasse 5-13 (Haus D), D-81377 Munich, Germany*

*Wehrwissenschaftliches Institut für Werk-, Explosiv- und Betriebsstoffe (WIWEB), Grßes Cent, D-53913 Swisttal, Germany*

*Received 17 February 1999; revised 27 April 1999*

ABSTRACT: *The thermal decomposition of three nitrophenyl azides, 1,3-5-*$(NO_2)_3$*-2,4,6-*$(N_3)_3$*-*$C_6$ *(TNTA,* **1***), 1,3-*$(NO_2)_2$*-2,4,6-*$(N_3)_3$ *-*$C_6H$ *(DNTA,* **2***), and 1,3,5-*$(NO_2)_3$*-2-*$(N_3)$*-*$C_6H_2$ *(TNMA,* **3***), were studied experimentally, and the reaction energies were calculated quantum-chemically [B3LYP/6-31G(d)//PM3/VSTO-3G(d)]. The compound that was most promising as a potential high energy density material (HEDM) was found to be 1,3-5-*$(NO_2)_3$*-2,4,6-*$(N_3)_3$*-*$C_6$ *(TNTA,* **1***), because the thermal decomposition led to gaseous products only (CO and* $N_2$*). The combustion of mixtures of with* $O_2$ *and* **1** *with* $NH_4NO_3$ *was also studied and calculated. The solid mixture of* **1** *and* $NH_4NO_3$ *in a 1:6 molar ratio was studied and discussed as a potential new HEDM.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 548–553, 1999

## *INTRODUCTION*

During the last eight years, significant advances have been made in the area of covalently bound azides, as indicated by the number of recent reviews covering various aspects of this subject [1a–c]. Recently, we and others reported on the convenient preparation of $N_2O_5$ and other nitrating agents as well as the nitration of covalent nonmetal compounds [2a–f].

Since highly toxic lead azide is still widely used as the initiator in ammunition [3], there is a great demand to find suitable nontoxic, heavy-metal-free substitutes that can be used as detonators [4]. Equally important, most solid rocket fuels are still based on mixtures of ammonium perchlorate, aluminum, and epoxy resins, which therefore generate exhaust plumes that contain large amounts of HCl and aluminum oxides [3]. The presence of these compounds is both environmentally not desirable, and more importantly, the trace of such rockets can easily be detected by radar [4].

The goal of our work is to find new metal and halogen-free high energy density materials (HEDM) that can be used either as initiators or solid rocket propellants. In the search for such new compounds, we combined azide and nitro groups in covalent molecules to provide both a fuel and oxidizer in one compound. These compounds are metal-free and combust ideally to give only gaseous products (i.e., $CO_2$ and $N_2$). Often, if the oxygen value is not balanced, mixtures with oxygen rich materials (i.e., nitrates) can be used to guarantee a complete reaction.

## *METHODS*

### *Experimental*

The three nitrophenyl azides, 1,3,5-$(NO_2)_3$-2,4,6-$(N_3)_3$-$C_6$ (TNTA, **1**), 1,3-$(NO_2)_2$-2,4,6-$(N_3)_3$-$C_6H$ (DNTA, **2**), and 1,3,5-$(NO_2)_3$-2-$(N_3)$-$C_6H_2$ (TNMA, **3**) were prepared by standard procedures according to

---

*Correspondence to:* Thomas M. Klapötke

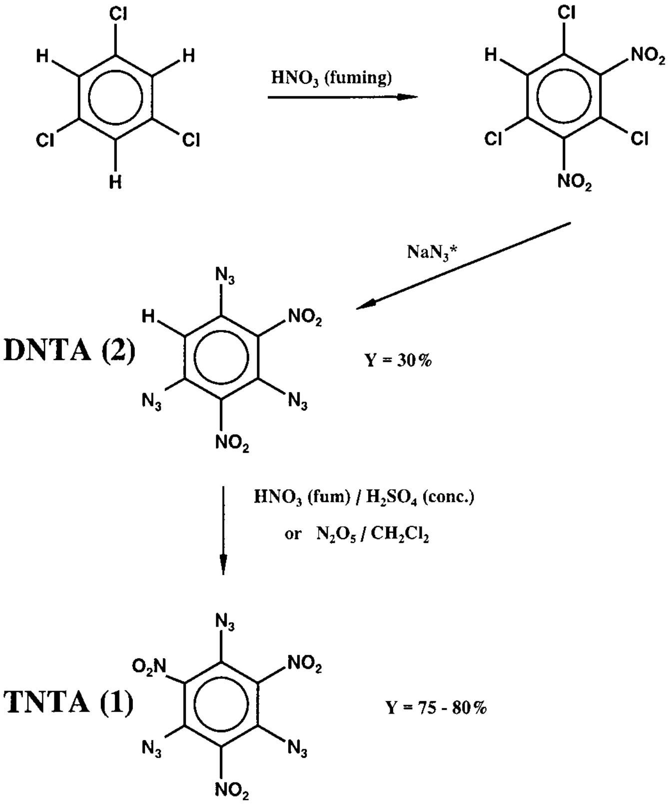
Contract Grant Sponsor: University of Munich.
Contract Grant Sponsor: Fonds der Chemischen Industrie.

Schemes 1 and 2 from 1,3,5-trichlorobenzene and 2-nitroaniline, respectively [5a, b]. All compounds were recrystallized three times. The identity of all compounds was checked by IR and Raman spectroscopy and $^{1}$H, $^{13}$C, and $^{14/15}$N NMR spectroscopy. The purity of all nitrophenyl azides was checked by C/H/N chemical analysis; all compounds showed satisfactory microanalytical data consistent with a purity of greater than 99.5%.

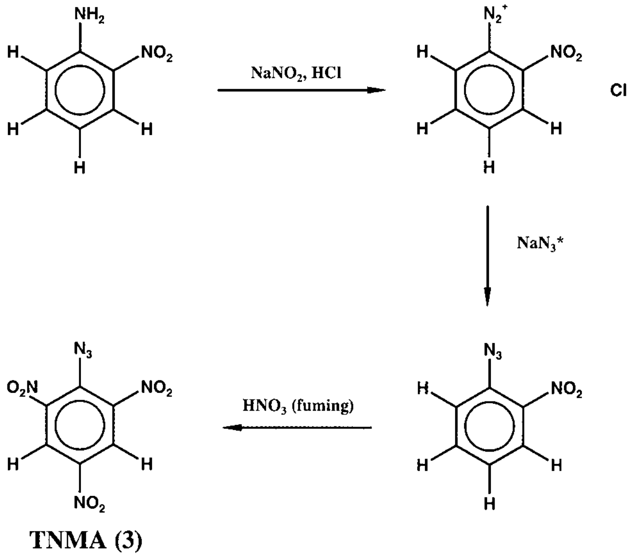
$^{14}$N NMR (20°C, $CH_2Cl_2$, $MeNO_2$, 28 MHz): **1**: $-27.6$ ($NO_2$); $-144.5$, $-153.0$ br, and $-290$ br ($N_3$); **2**: $-22.5$ br ($NO_2$); $-146.8$, $-151.0$, and $-290$ br ($N_3$); **3**: $-20.0$ br ($NO_2$); $-146$, $-153$, and $-290$ br ($N_3$). The IR spectra were recorded using a Perkin Elmer 983 high-resolution spectrophotometer and a 10 cm gas cell ($p$ = 2 torr) fitted with KBr plates. We recently determined the single crystal X-ray structure of **3**: orthorhombic, $P_{bca}$, $a$ = 10.34(5), $b$ = 12.52(5), and $c$ = 14.72(5) Å [5c].

### *Computations*

The structures of all compounds considered were fully optimized, and the vibrational frequencies and zero point energies (zpe) were computed using semiempirical calculations. All semiempirical calculations were carried out with the program package HyperChem [6] at the semiempirical PM3 [7] level of theory (PM3 is a re-parametrization of the semiempirical MNDO (see below) method introduced by Stewart) using a VSTO-3G* basis set (VSTO-3G* stands for a valence Slater-type orbital basis set where each Slater-type orbital is represented by a combination of three primitive Gaussian functions; the * denotes the inclusion of polarized functions). The PM3 method, which differs from AM1 (AM1 = Austin model) [8] only in the values of the parameters, was chosen because the parameters for PM3 were derived by comparing a much larger number and wider variety of experimental molecular properties with computed molecular properties. The PM3 is a reparametrization of MNDO (MNDO = modified neglect of diatomic overlap, introduced by Dewar and Thiel), which is based on the neglect of diatomic differential overlap (NDDO) approximation. The NDDO retains all one-center differential overlap terms when Coulomb and exchange integrals are computed. The PM3 method is within the restricted Hartree–Fock formalism. Finally, more accurate total energies were computed at the fully optimized PM3 structures using the hybrid density functional method at the B3LYP level of theory [9] and a 6-31G(d) basis set with the program package Gaussian 98 [10]. A “6-31G(d)” basis set is a split-valence basis, which means that the inner (core) and outer orbitals are described by different basis sets. In this case six Gaussian functions per basis function



**SCHEME 1** Preparation of **1** and **2**; $NaN_3^*$ indicated activated $NaN_3$, i.e., $NaN_3$ that contains ca. 1% $N_2H_5^+N_3^-$.



**SCHEME 2** Preparation of **1** and **3**; $NaN_3^*$ indicated activated $NaN_3$, i.e., $NaN_3$ that contains ca. 1% $N_2H_5^+N_3^-$.

are used for the core orbitals whereas the valence orbitals are represented by a double-zeta basis in which the one basis function is constructed from three Gaussian-type orbitals (GTO) and the second basis function from one GTO which is more diffuse. The (d) (equivalent to *) indicates the use of d-type Gaussian functions (polarization functions to account for higher angular momenta) for the second period elements (C, N, O). The hybrid computations were carried out at the HF-density (HF = Hartree-Fock) functional B3LYP level with the local Slater [11] exchange function extended by the nonlocal exchange function of Becke (B3) [9d]. "B3" denotes Becke's three parameter functional, where the non-local correlation is provided by the LYP (correlation functional of Lee, Yang and Parr) expression, and VWN (Vosko, Wilk and Nusair correlation functional) is the Local Spin Density correlation functional. Correlation was accounted for by using the nonlocal correlation functional of Lee–Young–Parr (LYP) [9a, c].

## *RESULTS AND DISCUSSION*

### *Experimental*

The thermal decomposition of three nitrophenyl azides, (compounds **1**, **2**, and **3**) was studied experimentally using gas-phase IR spectroscopy. For the experiments, a dry 120 mL stainless steel (T 316 SS) bomb was loaded with 100 mg of compound **1**, **2**, or **3** and evaluated. Then the steel bomb was heated for 20 minutes to 300°C, and the reaction products were detected by gas-phase IR spectroscopy. Dinitrogen, $N_2$, was detected by its characteristic purple gas-phase discharge color using a high-frequency brush electrode (Tesla coil). The thermal decomposition products shown in Reactions 1–3 were unambiguously identified by gas-phase IR spectroscopy and gas discharge ($N_2$). Whereas Reaction 1 yielded only CO and $N_2$, Reaction 2 produced HCN and traces of carbon soot, in addition to CO and $N_2$. In Reaction 3, we found HCN, $CO_2$, $NO_2$, $N_2$, and carbon soot.

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6 \rightarrow 6\ CO + 6\ N_2 \quad (1)$$

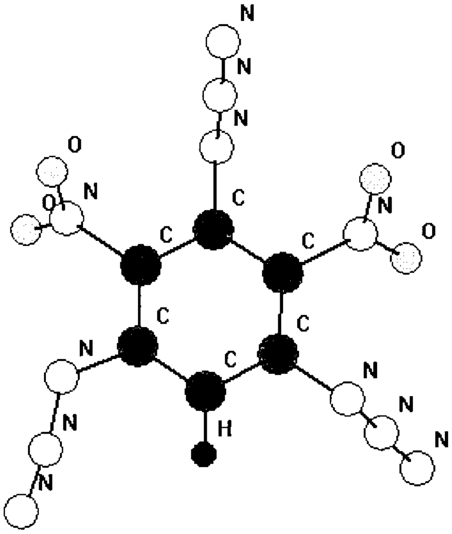


**FIGURE 2** Molecular structure of 1,3-$(NO_2)_2$-2,4,6-$(N_3)_3$-$C_6H$ **(2)**, fully optimized at the PM3/VSTO-3G(d) level of theory.

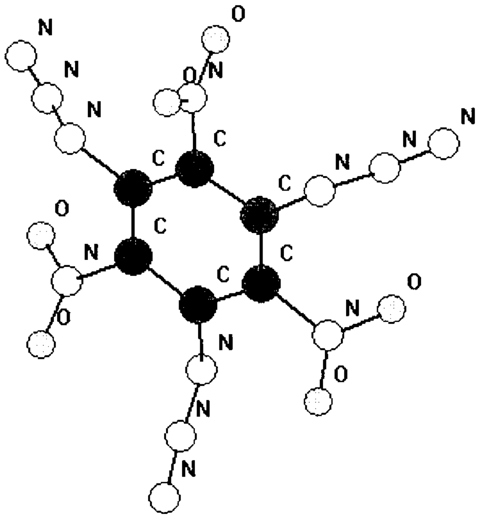


**FIGURE 1** Molecular structure of 1,3,5-$(NO_2)_3$-2,4,6-$(N_3)_3$-$C_6$ **(1)**, fully optimized at the PM3/VSTO-3G(d) level of theory.

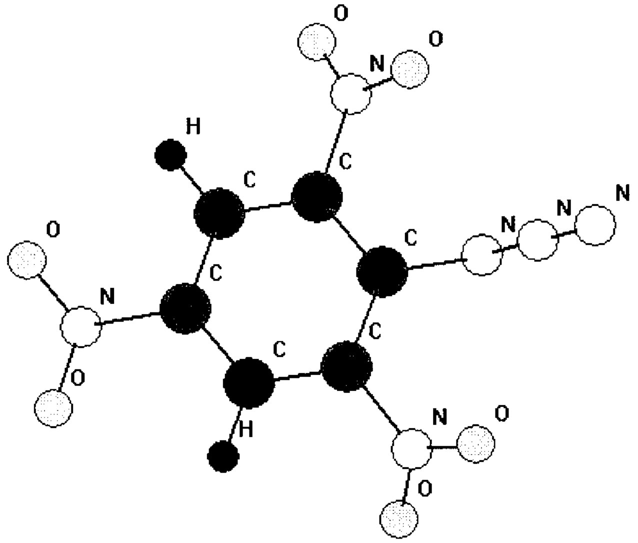


**FIGURE 3** Molecular structure of 1,3,5-$(NO_2)_3$-2-$(N_3)_3$-$C_6H_2$ **(3)**, fully optimized at PM3/VSTO-3G(d) level of theory.

$$1,3\text{-}(NO_2)_2\text{-}2,4,6\text{-}(N_3)_3C_6H \rightarrow HCN + 4\ CO + 5\ N_2 + C \qquad (2)$$

$$1,3,5\text{-}(NO_2)_3\text{-}2\text{-}(N_3)\text{-}C_6H_2 \rightarrow 2\ HCN + 2\ CO_2 + NO_2 + 3/2N_2 + 2\ C \qquad (3)$$

The combustion of **1** in an $O_2$ atmosphere (two fold excess) yielded $CO_2$, $N_2$, very small amounts of $NO_2$, and traces of $N_2O$ (Reaction 4). (Note: The stoichiometries implied in Reactions 1–4 are unverified.)

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6 + 3\ O_2 \rightarrow 6\ CO_2 + 6\ N_2 \qquad (4)$$

In a further experiment exploring the potential of **1** as a solid fuel, we mixed the material with the stoichiometric amount (cf. Reaction 5) of $NH_4NO_3$ and heated the mixture under a vacuum for 20 minutes to 300°C. The reaction products identified by gas-phase IR spectroscopy and gas discharge were $CO_2$, $N_2$, $H_2O$, and small amounts of $N_2O$ and $NO_2$ (Reaction 5). No carbon soot was left after the reaction in the steel bomb was complete. The formation of some $NO_2$ and $N_2O$ in the reaction of **1** with $NH_4NO_3$ indicates a relatively high combustion temperature; otherwise the formation of endothermic nitrogen oxides would not be expected.

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6 + 6\ NH_4NO_3 \rightarrow 6\ CO_2 + 12\ N_2 + 12\ H_2O \qquad (5)$$

All three nitrophenyl azides were also investigated in terms of their explosive properties. Compounds **1** and **2** were found to be impact-sensitive (by drop hammer testing), with **1** being slightly more sensitive than **2**. Compound **3** showed only very moderate impact sensitivity. Again, **1** and **2** detonate violently upon ignition, whereas **3** often deflagrates upon ignition; however, it was observed that explosions also occurred. Thermally, all three compounds are stable up to temperatures over 100°C and only show very moderate to low hygroscopy.

In addition to the combustion experiments of **1** with $NH_4NO_3$ in a steel bomb under a vacuum described previously, we ignited 1:6 molar ratio mixtures of these two components under atmospheric conditions and ambient pressure with a magnesium igniter. In all cases, the mixture detonated violently.

## *Computational Aspects*

The structures of all compounds considered were fully optimized, and the vibrational frequencies and zpe were computed using semiempirical calculations at the PM3 level of theory (Figures 1–3, Table 1). Finally, more accurate total energies were computed at the fully optimized PM3 structures using the hybrid method at the B3LYP level of theory (Table 1).

The calculated total energies (Table 1) can be used to theoretically predict the heat of the decomposition reaction of **1**. The heat of Reaction 6 was calculated ($\Delta U^{cl} = -368.6$ kcal mol$^{-1}$), and after correction [12] for zpe (Table 1; $\Delta U^{vib} = -33.1$ kcal mol$^{-1}$), differences in rotational ($\Delta U^{rot} = 21/2$ RT) and translational ($\Delta U^{tr} = 33/2$ RT) degrees of freedom, and the work term ($p\Delta V = 11$ RT) (R = 8.3143

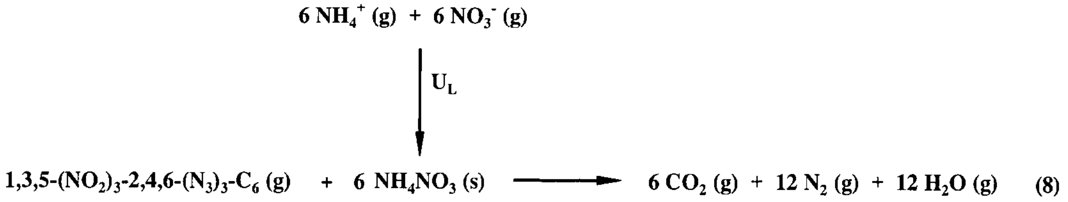
**TABLE 1** Computed Total Energies

| | *E*$^{PM3^a}$ (*au*) | *zpe*$^{PM3^a}$ (*kcal mol*$^{-1}$) | $-$ *E*$^{B3LYP^b}$ (*au*) | *Symmetry* | *NIMAG*$^c$ |
|---|---|---|---|---|---|
| $1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6$ (**1**) | 0.393316 | 75.7 | 1336.412619 | $C_1$ | 0 |
| $1,3\text{-}(NO_2)_2\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6H$ (**2**) | 0.392401 | 73.5 | 1131.945568 | $C_1$ | 0 |
| $1,3,5\text{-}(NO_2)_3\text{-}2\text{-}(N_3)\text{-}C_6H_2$ (**3**) | 0.137496 | 71.3 | 1009.285757 | $C_1$ | 0 |
| CO | −0.031502 | 3.3 | 113.309436 | $C_{\infty v}$ | 0 |
| $N_2$ | 0.027952 | 3.8 | 109.523966 | $D_{\infty h}$ | 0 |
| $CO_2$ | −0.135584 | 6.9 | 188.580425 | $D_{\infty h}$ | 0 |
| $NO_2$ | −0.003034 | 6.2 | 205.069992 | $C_{2v}$ | 0 |
| HCN | 0.052476 | 10.3 | 93.422622 | $C_{\infty v}$ | 0 |
| $NH_4^+$ | 0.244454 | 32.6 | 56.890763 | $T_d$ | 0 |
| $NO_3^-$ | −0.148786 | 9.7 | 280.333232 | $D_{3h}$ | 0 |
| $O_2$ | −0.006703 | 3.0 | 150.316546 | $D_{\infty h}$ | 0 |
| $H_2O$ | −0.085159 | 14.5 | 76.408066 | $C_{2v}$ | 0 |

[a] Fully optimized at the PM3 level of theory using a VSTO-3G(d) basis set, PM3/VSTO-3G(d).

[b] B3LYP single point calculation at the fully optimized PM3 structure using a 6-31G(d) basis set, (the notations "3G*" and "3G(d)" are equivalent, see above) B3LYP/6-31G(d)//PM3/VSTO-3G(d).

[c] NIMAG = number of imaginary frequencies.



**SCHEME 3** Energy cycle to estimate the heat of Reaction (8). The total electronic energies for 1,3,5-$(NO_2)_3$-2,4,6-$(N_3)_3$-$C_6$ **(1)**, $NH_4^+$, $NO_3^-$, $CO_2$, $N_2$, and $H_2O$ were taken from the B3LYP/6-31G(d)/PM3/VSTO-3G(d) computational results (Table 1). The lattice energy of $NH_4NO_3$ was calculated using the linear relationship $U_L$ (Kcal mol$^{-1}$) = 556.3 $V_M^{-0.33}$ (Å$^3$) + 26.3 [13]; $V_M(NH_4NO_3)$ was taken to be equal to 77 Å$^3$, which was estimated from the density in the solid state ($d$ $NH_4NO_3$ = 1.720 g cm$^{-3}$) [14].

J K$^{-1}$ mol$^{-1}$, T = 298 K), it was converted into the $\Delta H°$ value at room temperature (enthalpy value): $\Delta H°$ (6) = −379.2 kcal mol$^{-1}$.

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6\ (g) \rightarrow 6\ CO\ (g) + 6\ N_2\ (g) \qquad (6)$$

Because Reaction 6 represents the decomposition (and not combustion) of compound **1**, we looked at the combustion of **1** in oxygen according to Reaction 7:

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6\ (g) + 3\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ N_2\ (g) \qquad (7)$$

The calculated total energies (Table 1) can be used to predict theoretically the heat of the combustion reaction of **1** in an oxygen atmosphere. The heat of Reaction 7 was calculated ($\Delta U^{el}$ = −792.7 kcal mol$^{-1}$), and after correction [12] for zpe (Table 1; $\Delta U^{vib}$ = −20.5 kcal mol$^{-1}$), differences in rotational ($\Delta U^{rot}$ = 15/2 RT) and translational ($\Delta U^{tr}$ = 12 RT) degrees of freedom, and the work term ($p\Delta V$ = 8 RT), was converted into the $\Delta H°$ value at room temperature (enthalpy value): $\Delta H°$ (7) = −796.9 kcal mol$^{-1}$.

In order to estimate more reliably the energy release with a practically usable oxidizer, we decided to calculate the energy of Reaction 8 introducing $NH_4NO_3$ and using an energy cycle as shown in Scheme 3:

$$1,3,5\text{-}(NO_2)_3\text{-}2,4,6\text{-}(N_3)_3\text{-}C_6\ (g) + 6\ NH_4NO_3\ (s) \rightarrow 6CO_2\ (g) + 12\ N_2\ (g) + 12\ H_2O\ (g) \qquad (8)$$

$\Delta E°$ (8) = −883.6 kcal mol$^{-1}$.

The calculated energy value of −883.6 kcal mol$^{-1}$ makes the 1:6 molar mixture of **1** and $NH_4NO_3$ a very promising high energy density material (HEDM) [15], the potential of which we will explore in more detail in future studies.

## ACKNOWLEDGMENTS

We thank Dr. F. Geith and Mr. Martin Freytag for his help with the experimental work.

## REFERENCES

[1] (a) Tornieporth-Oetting, I. C.; Klapötke, T. M. Angew Chem 1995, 107, 509; (b) Tornieporth-Oetting, I. C.; Klapötke, T. M. Angew Chem Int Ed Eng 1995, 34, 511; (c) Tornieporth-Oetting, I. C.; Klapötke, T. M. Covalent Inorganic Non-Metal Azides. In Combustion Efficiency and Air Quality, Hargittai, I., Vidoczy, T., Eds.; Plenum Press: New York, 1995, 51–62.
[2] (a) Millar, R. W.; Colclough, M. E.; Golding, P.; Honey, P. J.; Paul, N. C.; Sanderson, A. I.; Stewart, M. J. Phil Trans R Soc Lond A, 1992, 339, 305; (b) Harris, A. D.; Trebellas, J. C.; Jonassen, H. B. Inorg Synth 1967, 9, 83; (c) Trofimova, J.; Spieß, G.; Klapötke, T. M. Intl J of Vibrational Spectroscopy, 1998, 2 (1), (section 2c); (d) Paul, N. Modern Explosives and Nitration Techniques. In Explosives in the Service of Man; The Royal Society of Chemistry; Bookcraft: Bath, 1997; p 79; (e) Feuer, H.; Nielsen, A. T.; Eds.; Nitro Compounds; VCH Verlagsgesellschaft: Weinheim, 1990; (f) Nielsen, A. T.; Nitrocarbons; VCH Verlagsgesellschaft: Weinheim, 1995.
[3] Köhler, J.; Meyer, R. Explosivstoffe, 7th edn.; VCH Verlagsgesellschaft: Weinheim, 1991.
[4] Farnfield, R. Environmental Effects of Blasting: Recent Experiences. In Explosives in the Service of Man; The Royal Society of Chemistry, Bookcraft: Bath, 1997, p 153.
[5] (a) Bailey, A. S.; Case, J. R. Tetrahedron 1958, 3, 113; (b) Shea, K. J.; Kim, J. S. J Am Chem Soc 1992, 114, 4846; (c) Adam, D.; Klapötke, T. M.; Mallinson, P. Acta Cryst, in press.
[6] HyperChem 5.0, Molecular Visualization and Simulation Program Package, Hypercube: Gainesville, FL 1997.
[7] (a) Stewart, J. J. P.; J Comp Chem 1989, 10, 209; (b) Stewart, J. J. P. J Comp Chem 1989, 10, 221.
[8] (a) Dewar, M.; Thiel, W.; J Am Chem Soc 1977, 99, 4499; (b) Dewar, M. J. S.; McKee, M. L.; Rzepa, H. S. J Am Chem Soc 1978, 100, 3607; (c) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F. J Am Chem Soc 1985, 107, 3902; (d) Dewar, M. J. S.; Reynolds, C. H. J Comp Chem 1986, 2, 140.

[9] (a) Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785; (b) Becke, A. D.; Phys Rev A 1988, 38, 3098; (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Chem Phys Lett, 1989, 157, 200; (d) Becke, A. D. J Chem Phys 1993, 98, 5648.

[10] Gaussian 98 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98 (Revision A.3), Gaussian, Inc.: Pittsburgh, PA, 1998.

[11] Slater, F. C. Chem Phys Rev, 1951, 81, 285.

[12] (a) Klapötke, T. M.; Schulz, A. Quantenmechanische Methoden in der Hauptgruppenchemie; Spektrum: Heidelberg, 1996; p 92. (b) Klapötke, T. M.; Schulz, A.; Harcourt, R. D. Quantum Chemical Methods in Main-Group Chemistry; Wiley & Sons: New York, 1998, p 89.

[13] Mallouk, T. E.; Rosenthal, G. L.; Müller, G.; Brusasco, R.; Bartlett, N.; Inorg Chem 1984, 108, 4937. (b) Klapötke, T. M.; Tornieporth-Oetting, I. C. Nichtmetallchemie; VCH Verlagsgesellschaft: Weinheim, 1994, p 76.

[14] Sigma-Aldrich Chemie GmbH. Aldrich Catalogue, Steinheim, 1996–1997, p 114.

[15] Klapötke, T. M. Chem Ber 1997, 130, 443; and references therein.