

Novel High-Energy Density Materials. Synthesis and Characterization of Triazidocarbenium Dinitramide, -Perchlorate, and -Tetrafluoroborate

Mark A. Petrie,^{*,†} Jeffrey A. Sheehy,[†] Jerry A. Boatz,[†] Golam Rasul,[‡]
G. K. Surya Prakash,[‡] George A. Olah,[‡] and Karl O. Christe^{*,†,‡}

Contribution from Hughes STX and Rocket Propulsion Directorate, Edwards Air Force Base, California 93524, and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089

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Abstract: The triazidocarbenium cation, $C(N_3)_3^+$, was successfully combined with the energetic $N(NO_2)_2^-$ and ClO_4^- anions in the form of highly energetic salts. The new $C(N_3)_3^+BF_4^-$ salt was also prepared, and all compounds were characterized by their material balances and vibrational spectroscopy. Electronic structure calculations were carried out for $C(N_3)_3^+$ at the B3LYP/6-31G*, B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, and HF/cc-pVDZ levels of theory. At all levels, the energy minimum is the planar C_{3h} structure, and the vibrational spectra were assigned and analyzed for this structure. The heats of formation of $C(N_3)_3^+N(NO_2)_2^-$ and $C(N_3)_3^+ClO_4^-$ were estimated to be endothermic by 252 and 218 kcal mol⁻¹ and explain the high explosive power of these salts.

Introduction

High-energy density materials (HEDM) are of great interest for energy storage and as propellants and explosives. Their performance strongly depends on the stoichiometry, i.e., a good oxidizer/fuel balance and highly negative heats of formation of the combustion products, the density, the amounts of gas or working fluid generated, the burning rates, and, very importantly, the heat of formation of the HEDM. The energy release is given by the difference between the heats of formation of the HEDM compound and of the combustion products and, therefore, increases with increasing endothermicity of the HEDM. Unfortunately, the stability of a compound generally decreases with increasing endothermicity. The goal of this study was to synthesize novel HEDM compounds at the limits of endothermicity and to examine their stabilities.

Since the azido group is a highly energetic ligand which adds about 87 kcal mol⁻¹ of endothermicity to a hydrocarbon compound,¹ the triazidocarbenium cation, $C(N_3)_3^+$, is ideally suited for HEDM applications. This cation was first prepared in 1966 by Müller and Dehnicke as its $SbCl_6^-$ salt² and was characterized in 1970 and 1975 by crystal structure determination³ and vibrational spectroscopy,⁴ respectively. Except for Schmidt's duplication⁵ of the original $C(N_3)_3^+SbCl_6^-$ synthesis² and a paper on the preparation of the analogous $C(N_3)_3^+UCl_6^-$ salt by Kolitsch and Müller,⁶ no further reports on these interesting compounds were found in the literature. Since the previously used counterions, i.e., $SbCl_6^-$ and UCl_6^- , are heavy nonenergetic anions, it was interesting to replace them by lighter and more energetic anions and to examine the stability of the resulting HEDM compounds.

Experimental Section

Caution! The azido compounds described in this study are highly shock sensitive and powerful explosives. These compounds should be handled only on a millimolar scale using appropriate safety precautions, i.e., face shields, gloves, protective jackets, and safety shields.

General. Commercially available Me_3SiN_3 , $SbCl_5$, $n-Bu_4N^+BF_4^-$, $n-Bu_4N^+ClO_4^-$, CCl_4 , $ClCH_2CH_2Cl$, $MeNO_2$, and $MeCN$ (Aldrich) were used as received. All solvents were dried by refluxing over CaH_2 and distillation from P_2O_5 . N_3SbCl_4 was prepared by a literature method.⁷ $K^+N(NO_2)_2^-$ was obtained from J. Bottaro (SRI). All air- and moisture-sensitive materials were handled either on a flamed out Pyrex vacuum line, equipped with grease-free Teflon valves, using Schlenck techniques or in the dry nitrogen atmosphere of a glovebox. Infrared spectra were recorded in the range of 4000–200 cm⁻¹ on a Mattson Galaxy 5030 FTIR spectrometer. Solid samples were prepared as KBr pellets. Raman spectra were recorded at variable temperature⁸ on a Cary model 83 spectrometer using the 488 nm exciting line of an Ar ion laser. The impact sensitivities of N_3SbCl_4 and $[C(N_3)_3^+][SbCl_6^-]$ were measured on an Olin Mathieson drop weight tester standardized with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine, 30 kg cm, 50%).

$[C(N_3)_3^+][SbCl_6^-]$. This compound was prepared according to the literature method² with minor modifications. N_3SbCl_4 (0.4956 g, 1.62 mmol) was prepared in situ or weighed into a 100 mL O-ring flask connected to a medium porosity frit and 100 mL filtrate receiving flask equipped with a magnetic Teflon stir bar. After the flask was connected to a glass vacuum line, predried $ClCH_2CH_2Cl$ (25 mL) and CCl_4 (5 mL) were condensed at -196 °C onto the solid. The mixture was warmed to ambient temperature, and the N_3SbCl_4 was dissolved. The yellow solution was warmed slowly to 90 °C and stirred for 4 h at this temperature. The solution was cooled to 0 °C, and a yellow crystalline solid deposited. The solid was filtered off by inversion of the glass filter assembly. After drying under vacuum, the solid was weighed: 0.2036 g; yield, 80% based on N_3SbCl_4 . The infrared and Raman spectra of the solid agreed well with those reported in the literature.^{2,4,5} The impact sensitivities of $[C(N_3)_3^+][SbCl_6^-]$ (20 kg cm) and its precursor N_3SbCl_4 (10 kg cm) were found to be greater than that of RDX (30 kg cm).

$[C(N_3)_3^+][BF_4^-]$. $[C(N_3)_3^+][SbCl_6^-]$ (0.5812 g, 1.23 mmol) and $n-Bu_4N^+BF_4^-$ (0.4361 g, 1.32 mmol) were weighed into a 100 mL

[†] Edwards Air Force Base.

[‡] University of Southern California.

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(1) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805.

(2) Müller, U.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 841.

(3) Müller, U.; Bärmighausen, H. *Acta Crystallogr.* **1970**, *B26*, 1671.

(4) Müller, U.; Kolitsch, W. *Spectrochim. Acta.* **1975**, *31A*, 1455.

(5) Schmidt, A. *Chem. Ber.* **1967**, *100*, 3725.

(6) Kolitsch, W.; Müller, U. *Z. Anorg. Allg. Chem.* **1974**, *410*, 21.

(7) Wiberg, N.; Schmid, K. H. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 444.

(8) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, *23*, 8.

O-ring flask connected to a medium porosity frit and 100 mL filtrate receiving flask equipped with a Teflon stir bar. After the flask was connected to a glass vacuum line, predried $\text{ClCH}_2\text{CH}_2\text{Cl}$ (25 mL) was vacuum transferred onto the solids. After the mixture was warmed to ambient temperature, the slurry of microcrystalline solids was stirred for 1 h. The insoluble $\text{C}(\text{N}_3)_3\text{BF}_4$ was isolated by vacuum filtration and dried at 10^{-2} Torr for 2 h (0.2058 g, 74% yield based on $\text{C}(\text{N}_3)_3\text{-SbCl}_6$). The white solid residue (0.8117 g), obtained after evaporating the filtrate to dryness consisted of mainly $n\text{-Bu}_4\text{N}^+\text{SbCl}_6^-$, some unreacted $[\text{C}(\text{N}_3)_3^+][\text{SbCl}_6^-]$ and $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$, and slightly soluble $[\text{C}(\text{N}_3)_3^+][\text{BF}_4^-]$. Cooling to 0°C prior to filtration increased the yield of the product to greater than 95%. The off-white product is very sensitive to impact and friction. For further use in other reactions, this compound was prepared *in situ* to avoid sensitivity problems.

$[\text{C}(\text{N}_3)_3^+][\text{ClO}_4^-]$. This salt was prepared in the same manner as $[\text{C}(\text{N}_3)_3^+][\text{BF}_4^-]$. $[\text{C}(\text{N}_3)_3^+][\text{SbCl}_6^-]$ (0.1761 g, 0.373 mmol) and $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$ (0.1551 g, 0.454 mmol) in predried $\text{ClCH}_2\text{CH}_2\text{Cl}$ (50 mL) were stirred for 1 h at room temperature. After filtration of the solution and drying of the solid under vacuum, the crystalline solid was weighed (62.5 mg, 71% yield based on $\text{C}(\text{N}_3)_3\text{SbCl}_6$). Immediately after weighing, the solid detonated sharply destroying the glass apparatus. The solids dissolved in the filtrate were not isolated. Subsequent syntheses were performed on a smaller scale (<15 mg) in an NMR tube fitted with a J. Young valve. Although five synthetic runs consistently resulted in the destruction of the apparatus, the identity of the salt was verified in one case by low-temperature Raman spectroscopy of a few isolated crystals remaining in the upper part of the tube after an explosion.

$[\text{C}(\text{N}_3)_3^+][\text{N}(\text{NO}_2)_2^-]$. $[\text{C}(\text{N}_3)_3^+][\text{BF}_4^-]$ (91.3 mg, 0.406 mmol) was prepared and isolated in a filter tube. $\text{K}^+\text{N}(\text{NO}_2)_2^-$ (61.8 mg, 0.426 mmol) was weighed into the attached 100 mL O-ring reaction vessel. Predried nitromethane (25 mL) was vacuum distilled onto the solids, and the mixture warmed to 0°C and stirred for 1 h. The solution was then warmed to ambient temperature and stirred for 20 min. The solution was filtered, and the volatiles were removed from the filtrate. The microcrystalline solid residue was weighed (100 mg, quantitative yield of $\text{C}(\text{N}_3)_3\text{N}(\text{NO}_2)_2$ based on $\text{C}(\text{N}_3)_3\text{BF}_4$) and taken into the drybox. Its Raman spectrum established that only the $[\text{C}(\text{N}_3)_3^+]$ and $[\text{N}(\text{NO}_2)_2^-]$ ions were present. This solid was found to be very sensitive to friction and impact. The identity of the filter cake (49.9 mg) was confirmed by Raman spectroscopy as KBF_4 . This reaction was also carried out successfully in acetonitrile solution. The $\text{C}(\text{N}_3)_3\text{N}(\text{NO}_2)_2$ salt was only marginally stable at room temperature and slowly decomposed in the course of 1 week.

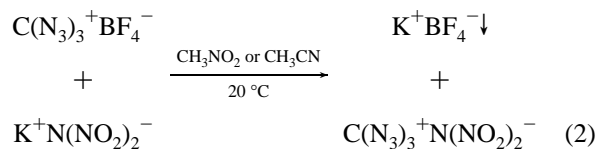
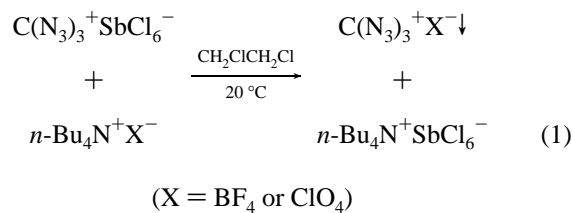
Computational Methods

The equilibrium geometry of the free triazidocarbenium cation was calculated employing Hartree–Fock self-consistent-field (SCF) and density-functional theory (DFT) methods in 6-31G*⁹ and cc-pVDZ¹⁰ atomic basis sets. The so-called B3LYP functional^{11,12} was employed in all DFT calculations. Harmonic force constants, vibrational frequencies, and infrared intensities were computed on the basis of analytic second derivatives of the molecular energy and first derivatives for the dipole moment with respect to nuclear coordinates at all levels of calculation. Additionally, Raman scattering activities were calculated for SCF wave functions by differentiation of the polarizability with respect to normal coordinates. All electronic structure calculations were performed using the Gaussian program system.¹³ The calculated Hessian matrices (second derivatives of the energy with respect to Cartesian coordinates) were converted to symmetry-adapted internal coordinates for further analysis using the program systems GAMESS¹⁴ and Bmtrx.¹⁵

Results and Discussion

Syntheses and Properties of $\text{C}(\text{N}_3)_3^+$ Salts. The conversion of the previously known² $\text{C}(\text{N}_3)_3^+\text{SbCl}_6^-$ salt into salts contain-

ing more energetic anions was achieved by the following metathetical reactions (eqs 1 and 2). As is generally the case



with metathetical reactions, the combination of the smallest cation and anion results in the highest lattice energy and the least soluble product. Thus, the triazidocarbenium perchlorate and tetrafluoroborate salts precipitated in high yields from $\text{ClCH}_2\text{CH}_2\text{Cl}$ solutions, with the larger $n\text{-Bu}_4\text{N}^+$ and SbCl_6^- ions remaining in solution. For the $\text{N}(\text{NO}_2)_2^-$ salt, the use of $\text{K}^+\text{N}(\text{NO}_2)_2^-$ as a starting material required the reverse approach, i.e., the use of a $\text{C}(\text{N}_3)_3^+$ salt with a small anion, such as BF_4^- . This allowed K^+BF_4^- to precipitate while keeping $\text{C}(\text{N}_3)_3^+\text{N}(\text{NO}_2)_2^-$ in solution. Also, the use of different solvents, i.e., CH_3NO_2 or CH_3CN , was required.

All of these $\text{C}(\text{N}_3)_3^+$ salts are highly energetic and very shock-sensitive materials which must be handled with great care. Even the previously reported SbCl_6^- salt is significantly more shock-sensitive than the high-performance explosive RDX (cyclonite or 1,3,5-trinitroaminocyclohexane). The shock-sensitivity of these $\text{C}(\text{N}_3)_3^+$ salts increases in the following anion order: $\text{SbCl}_6^- < \text{BF}_4^- < \text{N}(\text{NO}_2)_2^- < \text{ClO}_4^-$. The ClO_4^- salt is so sensitive that during six preparations the compound exploded each time, and in four cases, it exploded even before the $\text{ClCH}_2\text{-CH}_2\text{Cl}$ solvent could be removed. In spite of these challenges, a material balance and its low-temperature Raman spectrum were obtained, and its composition was confirmed. All compounds were characterized by vibrational spectroscopy.

Vibrational Spectra and Computational Results. The observed vibrational spectra and their assignments are given in Figures 1–3 and Table 1. The assignments for the ClO_4^- ,¹⁶ $\text{N}(\text{NO}_2)_2^-$,¹⁷ and BF_4^- ¹⁶ anions are well established and require no further discussion. Since the previously reported⁴ vibrational analysis of $\text{C}(\text{N}_3)_3^+$ was carried out without the help of electronic structure calculations, its geometry and vibrational spectra were calculated at different levels of theory. As can be seen from Table 2, the calculated geometries are in reasonable

(13) Gaussian 94, Revision D.4; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(14) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(15) Bmtrx version 2.0. Komornicki, A.; Polyatomics Research Institute: Palo Alto, CA, 1996.

(16) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie, Anorganische und Allgemeine Chemie in Einzeldarstellungen VII*; Springer-Verlag, Heidelberg, New York, 1966.

(17) Christe, K. O.; Wilson, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. *Inorg. Chem.* **1996**, *35*, 5068.

(9) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(10) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

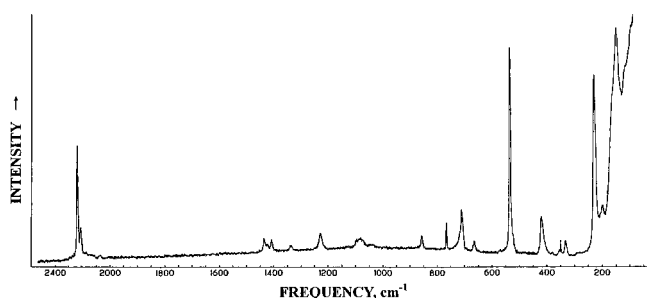
(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *7*, 785.

(12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

Table 1. Vibrational Spectra of $C(N_3)_3^+ClO_4^-$, $C(N_3)_3^+N(NO_2)_2^-$, and $C(N_3)_3^+BF_4^-$

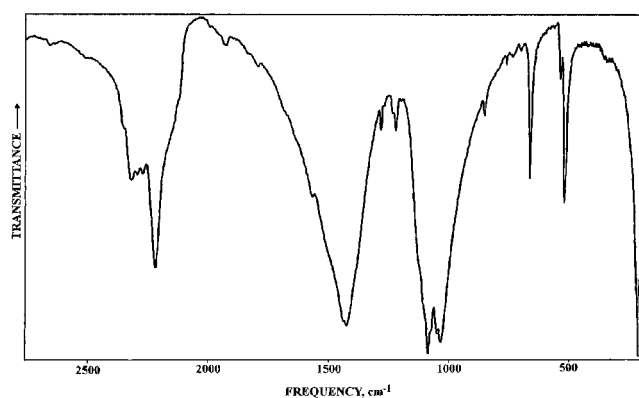
		obsd freq, cm^{-1} (rel int)		assignments (point group)			
$C(N_3)_3^+ClO_4^-$ Raman ($-110\text{ }^\circ C$)	$C(N_3)_3^+N(NO_2)_2^-$ Raman	$C(N_3)_3^+BF_4^-$		$C(N_3)_3^+(C_{3h})$	$ClO_4^-(T_d)^c$	$N(NO_2)_2^-(C_2)^d$	$BF_4^-(T_d)^c$
		IR	Raman				
2220(6.6)	2227(1.7)		2218(4.6)	$\nu_1(A')$			
2208(1.6)	2205(0.6)	2222s 1573w	2207(1.2)	$\nu_9(E')$			
	1578(0+), 1513(1.7) 1497(0.3)					$\nu_1(A)$	
	<i>a</i>					$\nu_9(B)$	
1435(1.0)	1435(0.8)	1434vs	1435(0.7), 1408(0.4)	$\nu_{10}(E')$		$\nu_2(A)$	
	1339(9.7)					$\nu_{10}(B)$	
1230(1.4)	1225(0+)	1226w	1227(0.8)	$\nu_2(A')$			
	1195(0.6)						
	1162(1.1)						
		<i>b</i>	1089(0.4)	$\nu_{11}(E')$			$\nu_3(F_2)$
	1010(1.7)	1032–1085vs,br				$\nu_{11}(B)$	
	955(0.8)					$\nu_3(A)$	
948(3.6)					$\nu_1(A1)$		
858(1.2)	860(0.6)	857vw	857(0.7)	$\nu_3(A')$		$\nu_4(A)$	
	828(10)						$\nu_1(A1)$
	760(0.3)	768w	765(1.1)			$\nu_{12}(B)$	
	<i>a</i>					$\nu_{13}(B)$	
	748(1.4)					$\nu_5(A)$	
710(2.9)	708(0.8)	705vw, 737vw 667m	710(1.6) 664(0.5)	$\nu_{12}(E')$ $\nu_6(A'')$			
628(1.1)					$\nu_4(F_2)$		
533(10)	527(5.3)	533w 519m	533(10) 520(0.8)	$\left\{ \begin{array}{l} \nu_4(A') \\ \nu_7(A'') \\ \nu_{15}(E'') \end{array} \right.$			$\nu_4(F_2)$
	488(1.4)					$\nu_6(A)$ $\nu_{14}(B)$	
465(0.1)							
418(1.6)	415(1.1)		418(1.5) 348(0.2), 355(0.4)	$\nu_{13}(E')$	$\nu_2(E)$		$\nu_2(E)$
	328(6.1)					$\nu_7(A)$	
228(7.1)	220(8.6)		228(7.2)	$\nu_5(A')$			
155(3.4)			162sh 147(2.6) 115sh 90sh	lattice vibrations $\nu_{16}(E'')$ $\nu_{14}(E')$ $\nu_8(A'')$			

^a Obscured by $C(N_3)_3^+$. ^b Obscured by BF_4^- . ^c Assignments from ref 9. ^d Assignments from ref 10.

**Figure 1.** Raman spectrum of solid $C(N_3)_3^+BF_4^-$.

agreement with the experimental one,³ which suffers from relatively large uncertainties arising from the three azido ligands not being identical in the crystal structure of $C(N_3)_3^+SbCl_6^-$. We emphasize that, at all levels of our calculations, the minimum-energy structure was always planar (C_{3h}). Therefore, the slight out-of-plane distortion, observed for $C(N_3)_3^+$ in its $SbCl_6^-$ salt, is probably caused by the previously discussed crystal field effects,³ which would also explain why all three azido ligands are distorted out of the plane in the same direction and not alternatingly up and down as expected from repulsion arguments.

The observed and calculated vibrational frequencies for $C(N_3)_3^+$ are summarized in Table 3. As can be seen, the density

**Figure 2.** Infrared spectrum of solid $C(N_3)_3^+BF_4^-$ recorded in a KBr disk.

functional theory (DFT) calculations duplicate the observed frequencies very well, particularly after scaling of the N_3 stretching modes. In the previous study,⁴ all six stretching modes, but only three of the ten deformation modes, had been correctly identified. As demonstrated by the present analysis (Tables 3 and 4), the electronic structure calculations allow unambiguous assignments for all of the deformation modes and also show that, as expected for a strongly coupled system of

Table 2. Observed and Calculated Geometries of the $C(N_3)_3^+$ Cation

	obsd ^a	B3LYP/6-21G*	B3LYP/cc-pVDZ	B3LYP/cc-pVTZ	HF/cc-pVDZ
C–N _α	1.312–1.358(18)	1.352	1.353	1.347	1.336
N _α –N _β	1.411–1.361(19)	1.275	1.275	1.268	1.290
N _β –N _γ	1.022–1.069(17)	1.122	1.122	1.110	1.080
N _α –C–N _α	119.2–120.6(1.7)	120.0	120.0	120.0	120.0
N _α –N _β –N _γ	160.0–167.1(2.5)	170.4	170.4	171.0	172.4
C–N _α –N _β	107.3–108.0(1.7)	116.9	116.7	117.2	114.3
E–N _α –N _β ^b	2.3–7.8(1.3)	0	0	0	0

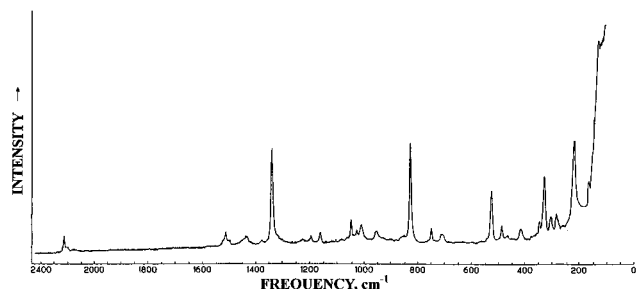
^a Data from ref 3. ^b Tilt of the N₃ groups out of the CN₃ plane.

Table 3. Observed and Calculated Frequencies of $C(N_3)_3^+$

assignment in point group C _{3h}	approx mode description	obsd freq, cm ⁻¹ (IR int) [Ra int] ^a	calcd freq, cm ⁻¹ (IR int) [Ra int (pol)]					
			B3LYP/ 6-31G*		B3LYP/ cc-pVDZ		B3LYP/ cc-pVTZ	HF/cc-pVDZ
			scaled ^c	unscaled	scaled ^c	unscaled	unscaled	unscaled
A' (–Ra) ν ₁	νN≡N in phase	2218 [4.6]	2211	2345 (2)	2207	2340 (0)	2334 (0)	2707 (0) [458(0.12)]
ν ₂	νN–N in phase	1227w [0.8]	1242	1317 (0)	1242	1317 (0)	1306 (0)	1313 (0) [27(0.16)]
ν ₃	mix of CNN and N ₃ bending and ν _{sym} CN ₃	857vw [0.7]		861 (0)		866 (0)	859 (0)	918 (0) [1.8(0.18)]
ν ₄	δN ₃ in phase	533w [10]		530 (0)		529 (0)	542 (0)	589 (0) [3.2(0.10)]
ν ₅	mix of δN ₃ and δCNN in phase	224vw [7]		220 (0)		220 (0)	223 (0)	246 (0) [5.2(0.11)]
A'' (IR–) ν ₆	γCN ₃	667m [0.5]		671 (19)		674 (19)	680 (19)	781 (51) [0]
ν ₇	γN ₃ in phase	503 m		520 (20)		522 (20)	541 (17)	590 (31) [0]
ν ₈	mix of γN ₃ and τNNCN, in phase	90 [sh] ^b		85 (1)		86 (1.1)	88 (0.8)	94 (5.1) [0]
E' (IR, Ra) ν ₉	νN≡N out of phase	2207ms [1.2]	2207	2340 (386)	2203	2336 (377)	2330 (386)	2701 (239) [123(0.75)]
ν ₁₀	ν _{as} CN ₃ and δCN ₃	1435vs [0.7]	1424	1510 (1011)	1429	1514 (998)	1490 (1017)	1615 (1184) [18(0.75)]
ν ₁₁	mix of δN ₃ , νN–N out of phase, and δCNN	1076m [0+]	1075	1140 (84)	1077	1142 (88)	1130 (96)	1114 (190) [3.7(0.75)]
ν ₁₂	mix of δN ₃ + δNNC	710vw [1]		709 (1)		710 (0.6)	719 (0.6)	793 (7.0) [1.5(0.75)]
ν ₁₃	mix of δN ₃ + δCN ₃	418 [1.5]		424 (0)		424 (0.1)	431 (0.1)	455 (0.3) [4.7(0.75)]
ν ₁₄	mix of δCNN and δN ₃	115 [sh] ^b		114 (0)		114 (0.3)	116 (0.3)	134 (0.5) [5.8(0.75)]
E'' (–Ra) ν ₁₅	γN ₃ out of phase	533w [10]		543 (0)		544 (0)	562 (0)	615 (0) [3.9(0.75)]
ν ₁₆	mix of γN ₃ and τNNCN	162 [sh] ^b		176 (0)		176 (0)	178 (0)	196 (0) [1.7(0.75)]

^a The observed frequencies were mainly taken from either this study or the solution data from ref 4 in the case of interference from the anions.

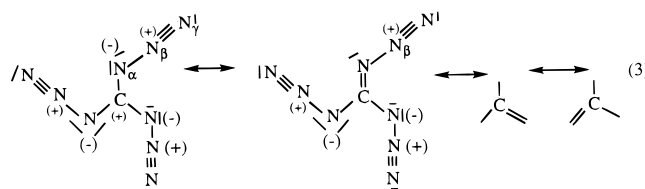
^b These assignments are tentative due to interference from lattice vibrations. ^c The frequencies involving mainly stretching motions of the N₃ groups were scaled by an empirical factor of 0.943 to maximize their agreement with the observed values.

**Figure 3.** Raman spectrum of solid $C(N_3)_3^+N(NO_2)_2^-$.

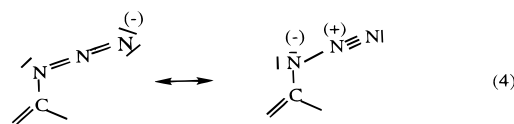
similar masses, most of the fundamental vibrations are highly mixed.

The internal force constants of greatest interest are the C–N_α, the N_α–N_β, and the N_β–N_γ stretching constants. Our values of $f_{C-N} = 5.59$, $f_{N_{\alpha}-N_{\beta}} = 6.47$, and $f_{N_{\beta}-N_{\gamma}} = 18.35$ mdyne/Å, which were obtained by an intrinsic frequency analysis^{18,19} and scaled by a factor of $0.943^2 = 0.89$ (see Table 3), are in good agreement with the previously reported⁴ values of 5.5–6.0, 6.30, and 20.38 mdyne/Å, respectively, which were obtained with the Fadini approximation.²⁰ The f_{C-N} value of 5.59 mdyne/Å is significantly larger than the value for the C–N single bond of 4.26 mdyne/Å²¹ and corresponds to a bond order of 1.31, which is in very good agreement with the Löwdin bond order²² of 1.38 calculated at the B3LYP/6-31G* level (eq 3), demonstrating that the carbocationic center of $C(N_3)_3^+$ is highly resonance

stabilized by the three azido groups. The large difference



between the values of $f_{N_{\alpha}-N_{\beta}}$ (6.47 mdyne/Å) and $f_{N_{\beta}-N_{\gamma}}$ (18.35 mdyne/Å), as well as that between the observed and calculated bond distances (see Table 2), confirms that these bonds are better described as a single and a triple bond, respectively, rather than as two double bonds.⁴ This bonding picture generally holds for covalent azides and, therefore, does not require any further discussion (eq 4).



¹³C NMR Spectra. The ¹³C NMR chemical shifts of $C(N_3)_3^+BF_4^-$ and $C(N_3)_3^+SbCl_6^-$ in CH_3CN solution were measured at room temperature and consist of single peaks at δ 176.8 and 176.4, respectively. A sample of $C(N_3)_3^+SbCl_6^-$ in CF_3SO_3H solution was also recorded and showed a single peak at δ 175.5. The observed shifts are in good agreement with the value of δ 181.4 calculated by us with the IGLO method²³ using the B3LYP/6-31G* geometry. The protonation of the $C(N_3)_3^+$ cation was also studied at this level and suggests a proton affinity of 64.5 kcal mol⁻¹ for the free gaseous cation. As expected from the calculated charge distribution in $C(N_3)_3^+$

(18) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 1819.

(19) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 5774.

(20) Fadini, A. Z. *Naturforsch.* **1966**, *21a*, 426. Sawodny, W.; Fadini, A.; Ballein, K. *Spectrochim. Acta.* **1965**, *21*, 995. Becher, H. J.; Mattes, R. *Spectrochim. Acta.* **1967**, *32A*, 2449.

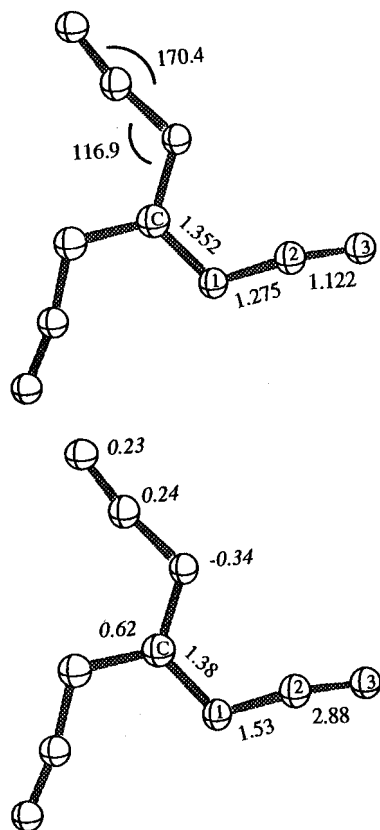
(21) Siebert, H. Z. *Anorg. Allg. Chem.* **1953**, *273*, 161.

(22) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.

Table 4. Unscaled B3LYP/cc-pVDZ Symmetry Force Constants and Potential Energy Distribution of C_{3h} $C(N_3)_3^+$

calcd freq, cm^{-1}	symmetry force constants ^a								PED ^b	
	F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	F_{66}	F_{77}	F_{88}		
A' ν_1	2340	F_{11}	21.286							72(1) + 28(2)
ν_2	1317	F_{22}	1.099	8.409						53(2) + 35(3) + 10(4) + 2(1)
ν_3	866	F_{33}	-0.285	0.248	8.979					46(5) + 35(4) + 10(3) + 9(2)
ν_4	529	F_{44}	0.148	0.313	0.030	0.495				86(4) + 13(5) + 1(3)
ν_5	220	F_{55}	-0.174	0.966	0.712	0.052	1.182			60(4) + 40(5)
			F_{66}	F_{77}	F_{88}					
A'' ν_6	674	F_{66}	0.533							61(6) + 23(8) + 16(7)
ν_7	522	F_{77}	0.005	0.015						99(7)
ν_8	86	F_{88}	-0.071	0.003	0.164					56(7) + 44(8)
			F_{99}	$F_{10,10}$	$F_{11,11}$	$F_{12,12}$	$F_{13,13}$	$F_{14,14}$		
E' ν_9	2335	F_{99}	21.192							73(9) + 26(11)
ν_{10}	1514	$F_{10,10}$	-0.472	6.695						44(10) + 34(13) + 14(14) + 4(11) + 3(12)
ν_{11}	1142	$F_{11,11}$	1.192	0.710	8.478					43(13) + 27(11) + 23(14) + 3(10) + 2(12) + 1(9)
ν_{12}	710	$F_{12,12}$	0.125	-0.017	0.302	0.504				54(12) + 34(14) + 11(13)
ν_{13}	423	$F_{13,13}$	0.024	0.586	0.165	-0.17	1.198			77(12) + 22(13)
ν_{14}	114	$F_{14,14}$	-0.160	0.677	1.010	0.044	0.097	1.188		44(14) + 35(12) + 20(13)
			$F_{15,15}$	$F_{16,16}$						
E'' ν_{15}	544	$F_{15,15}$	0.015							99(15) + 1(16)
ν_{16}	176	$F_{16,16}$	0.006	0.197						76(15) + 24(16)

^a Stretching force constants in $mdyn/\text{\AA}$, deformation constants in $(mdyn \text{\AA})/\text{rad}^2$, and stretch-bend interaction constants in $mdyn/\text{rad}$. ^b PED in percent. The symmetry coordinates are defined as: (1) $\nu N\beta-N\gamma$, in phase; (2) $\nu N\alpha-N\beta$, in phase; (3) $\nu_{sym} CN_3$; (4) δN_3 in plane, in phase; (5) δCNN , in plane, in phase; (6) γCN_3 , out of plane; (7) γN_3 , in phase; (8) $\tau NNCN$, in phase; (9) $\nu N\beta-N\gamma$, out of phase; (10) ν_{as} , CN_3 ; (11) $\nu N\alpha-N\beta$, out of phase; (12) δN_3 , in plane, out of phase; (13) δ_{sciss} , CN_3 ; (14) δCNN , in plane, out of phase; (15) γN_3 , out of phase; (16) $\tau NNCN$, out of phase.

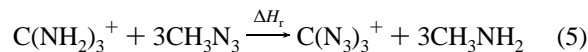
**Figure 4.** B3LYP/6-31G*-optimized structure, Löwdin bond orders, and NBO charges for the triazidocarbenium cation of symmetry C_{3h} .

(see Figure 4), protonation should occur at the N_α atom which carries a high negative charge of -0.34 electron. Protonation at N_β and N_γ , which carry positive charges, is less favored by 23.0 and 13.1 $kcal\ mol^{-1}$, respectively. On the basis of our IGLO calculations, the N_α -protonated triazidocarbenium cation (see Figure 5) should be shielded by 20.8 ppm in the ^{13}C NMR spectrum, relative to $C(N_3)_3^+$. On the basis of the very small

shielding of only 1 ppm observed for $C(N_3)_3^+$ solutions in CF_3SO_3H , it appears that $C(N_3)_3^+$ is not protonated in this system.

Thermochemical Properties. In view of the high sensitivity of most of the triazidocarbenium salts, direct calorimetric measurements were experimentally too difficult, and the heats of formation were evaluated using a combination of available experimental data and computational methods. Two approaches were considered. The first one involved the calculation by *ab initio* methods of the heat of formation of the free gaseous $C(N_3)_3^+$ ion, which when combined with the heat of formation of the free gaseous counterion and an estimate of the lattice energy, yields the heat of formation of the corresponding $C(N_3)_3^+$ salt. The second one involved the calculation of the energy difference between the closely related guanidinium and triazidocarbenium cations by *ab initio* methods, followed by a correction of the experimentally determined heats of formation of the corresponding guanidinium salts by this difference, and application of a lattice energy correction based on the estimated difference in their molecular volumes. The second approach was deemed to result in more reliable values and was used for this study.

The heat of formation of $C(N_3)_3^+$ was calculated to be 285.8 $kcal\ mol^{-1}$ more endothermic than that of the guanidinium ion using the isodesmic reaction (eq 5). The value of ΔH_f (56.3



$kcal\ mol^{-1}$) was obtained from the total energies of all four components of eq 5, calculated at the B3LYP/6-31G* level. The heats of formation of CH_3NH_2 ²⁴ and CH_3N_3 ²⁵ were taken from the literature as -5.5 and $71.0\ kcal\ mol^{-1}$, respectively.

(23) (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Princ. Prog.* **1991**, *23*, 165. (b) ^{13}C NMR chemical shifts were calculated by IGLO/II (Basis II: C or N, 9s 5p 1d contracted to [51111,2111,1]; d exponent, 1.0; H, 5s 1p contracted to [311,1]; p exponent, 0.70) methods using B3LYP/6-31G* geometries (i.e., at the IGLO/II/B3LYP/6-31G* level). ^{13}C NMR chemical shifts were referenced to tetramethylsilane (calculated absolute shift, i.e., $\sigma(C) = 218.13$).

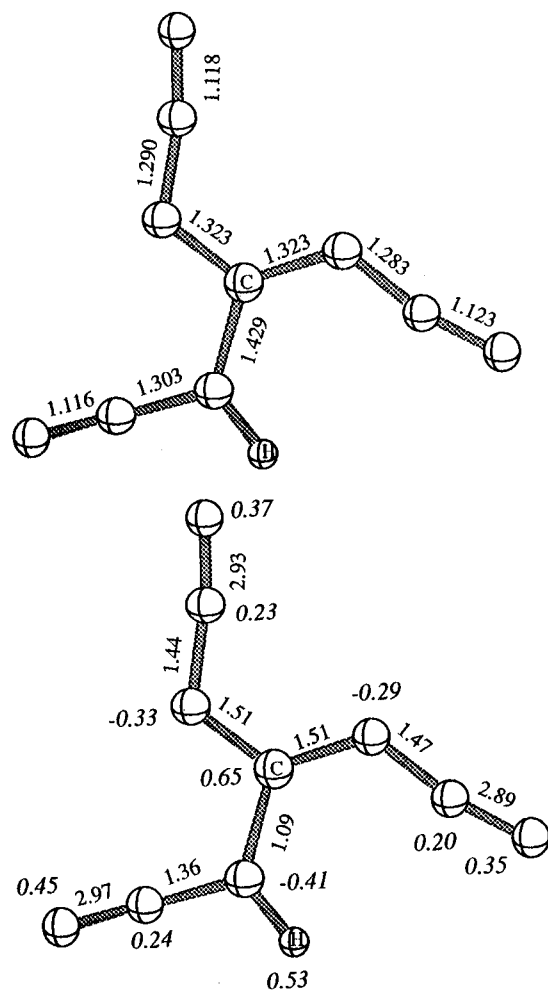


Figure 5. B3LYP/6-31G*-optimized structure, Löwdin bond orders, and NBO charges for the proto-triazidocarbenium dication of symmetry C_3 .

The experimentally known values for the heats of formation of the $C(NH_2)_3^+$ salts of $N(NO_2)_2^-$,²⁶ ClO_4^- ,²⁷ and NO_3^- ²⁷ (see Table 5) were taken as starting points, and the calculated energy difference of 285.8 kcal/mol⁻¹ between the $C(N_3)_3^+$ and $C(NH_2)_3^+$ cations was used to obtain the heats of formation of the $C(N_3)_3^+$ salts. These values were then corrected by 6.7 kcal/mol⁻¹ for the decrease in lattice energy estimated for going from the smaller $C(NH_2)_3^+$ to the larger $C(N_3)_3^+$ cation. The resulting values for the heats of formation of the $C(N_3)_3^+$ salts are summarized in Table 5.

For the lattice energy correction, the molar volume difference (78 Å³) between $C(N_3)_3^+$ and $C(NH_2)_3^+$ was extrapolated from the known crystal structures of $C(N_3)_3^+SbCl_6^-$ ³ and $C(N_3)_2(NH_2)^+SbCl_6^-$,²⁸ and the empirical relationship, $U_L(\text{kcal mol}^{-1}) = 556.3 (\text{molar volume in Å}^3)^{-1/3} + 26.3$,²⁹ was used

(24) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. A.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd Ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(25) Rogers, D. W.; McLafferty, F. J. *J. Chem. Phys.* **1995**, *103*, 8302.

(26) Schmitt, R. J.; Bottaro, J. C.; Penwell, P. E. SRI International, Menlo Park, CA 94025, Final Report under contract no. N00014-88-C-0537 (Jan. 5, 1993).

(27) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(28) Choi, C. S. In *Energetic Materials, Vol. 1, Physics and Chemistry of the Inorganic Azides*; Fair, H. D., Walker, R. F., Eds.; Plenum Press: New York, 1977; p 120.

(29) Richardson, T. J.; Tanzella, F. L.; Bartlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937.

Table 5. Lattice Energy Corrected Heats of Formation^a of Triazidocarbenium Salts Derived from a Combination of Experimental and Computational Results

$C(N_3)_3^+N(NO_2)_2^-$	[251.8]
$C(N_3)_3^+ClO_4^-$	[218.4]
$C(N_3)_3^+NO_3^-$	[200.0]
$C(N_3)_3^+BF_4^-$	[-128.0]
$C(NH_2)_3^+N(NO_2)_2^-$	-40.7 ^b
$C(NH_2)_3^+ClO_4^-$	-74.1 ^c
$C(NH_2)_3^+NO_3^-$	-92.5 ^c
$C(NH_2)_3^+BF_4^-$	[-420.5]
$NH_4^+N(NO_2)_2^-$	-35.8 ^b
$NH_4^+ClO_4^-$	-70.7 ^c
$NH_4^+NO_3^-$	-87.4 ^c
$NH_4^+BF_4^-$	-415.4 ^d

^a All values in kcal mol⁻¹. Numbers in brackets have been calculated from the nonbracketed experimental values assuming $C(N_3)_3^+$ to be 285.8 kcal mol⁻¹ more endothermic than $C(NH_2)_3^+$ and the lattice energies of its salts being 6.7 kcal mol⁻¹ lower than those of the corresponding $C(NH_2)_3^+$ salts. ^b Data from ref 26. ^c Data from ref 27. ^d Data from ref 30.

Table 6. Endothermicity of $C(N_3)_3^+ClO_4^-$ and $C(N_3)_3^+N(NO_2)_2^-$ Compared to That of O_3 and HN_3

compound	ΔH_f°		ΔH_{dec} (kcal g ⁻¹)
	kcal mol ⁻¹	(kcal g ⁻¹)	
O_3	34.1 ^a	0.71	0.71
$C(N_3)_3^+ClO_4^-$	218.4 ^b	0.92	1.32
$C(N_3)_3^+N(NO_2)_2^-$	251.8 ^b	1.03	1.42
HN_3	70.3 ^c	1.63	1.63

^a Data from ref 24. ^b Data from this study. ^c Data from ref 27.

to estimate the lattice energy difference between $C(N_3)_3^+SbCl_6^-$ and $C(NH_2)_3^+SbCl_6^-$ as 6.7 kcal mol⁻¹.

No experimental value was available for the heat of formation of $C(NH_2)_3^+BF_4^-$. However, the heat of formation of $NH_4^+BF_4^-$ is known.³⁰ Since the heat of formation differences between the NH_4^+ salts of $N(NO_2)_2^-$,²⁶ ClO_4^- ,²⁷ and NO_3^- ²⁷ are practically identical to those found for the corresponding $C(NH_2)_3^+$ salts, the same should hold for the BF_4^- salts, and the heats of formation of $C(NH_2)_3^+BF_4^-$ and $C(N_3)_3^+BF_4^-$ were estimated (see Table 5) from those of the corresponding nitrates by subtracting the $NH_4NO_3 - NH_4BF_4$ difference from these values.

As can be seen from the data in Tables 5 and 6, triazidocarbenium dinitramide and -perchlorate are highly endothermic compounds. Their endothermicity per mole exceeds those of ozone and hydrazoic acid; however, their molecular weights are also higher. To obtain a better measure for their energy density, the molar endothermicities were divided by the molecular weights. As can be seen from Table 6, the energy densities in kcal g⁻¹ for the triazidocarbenium perchlorate and -dinitramide are remarkably high for ionic solids and fall between those of gaseous O_3 and HN_3 . Since these triazidocarbenium salts are highly overoxidized, they actually do not decompose to the elements but form CO_2 , and the heat of formation of CO_2 (-94.1 kcal mol⁻¹) must be added to obtain the actual heats of decomposition. This raises the decomposition energies of $C(N_3)_3^+ClO_4^-$ and $C(N_3)_3^+N(NO_2)_2^-$ to 1.32 and 1.42 kcal g⁻¹, which approach that of HN_3 . Since the triazidocarbenium salts are overoxidized, further energy could be gained by adding some fuel, such as powdered aluminum, to these compounds.

Conclusion

The triazidocarbenium cation, a highly endothermic species, has successfully been combined for the first time with energetic

(30) Johnson, D. A. *J. Chem. Soc., Dalton Trans.* **1988**, 445.

anions, such as perchlorate or dinitramide. The resulting salts are very powerful explosives. Although their sensitivity is too high for practical applications, these compounds represent a new class of high-energy density materials and demonstrate that endothermicities as high as 1 kcal g⁻¹ are achievable for ionic solids.

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KN(NO₂)₂. The work at the Phillips Laboratory was financially supported by the Propulsion Directorate of the US Air Force and that at USC by the National Science Foundation (K.O.C.) and the Office of Naval Research (G.R. and S.P.). This paper is dedicated to a pioneer of azide chemistry, Prof. Kurt Dehnicke, on the occasion of his 65th birthday.

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