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Energetic Materials **Very Important Paper**

Nitryl Cyanide, $NCNO_2$**

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In memory of Marilyn E. Jacox

Abstract: *The elusive nitryl cyanide, $NCNO_2$, has been synthesized and characterized. It was prepared in good yield, isolated by fractional condensation, characterized by NMR and vibrational spectroscopy, and studied by theoretical calculations. Nitryl cyanide holds promise as a high energy density material (HEDM) and might also prove useful as a HEDM building block. The simplicity and inherent stability of nitryl cyanide, together with the known multitude of nitriles in interstellar space, suggest that the compound might also be a potential candidate for observations in atmospheric and interstellar chemistry.*

As an intriguing example of a compound containing a strong oxidizer (NO_2 group) adjacent to an excellent fuel (CN group),[1] nitryl cyanide, $NCNO_2$ (**1**), is a very promising high energy density material (HEDM) by itself and might also be a suitable building block for other energetic compounds. Furthermore, nitryl cyanide might play an important role in atmospheric and interstellar chemistry in view of its simplicity and the known multitude of nitriles in interstellar space.[2] Surprisingly, $NCNO_2$ has not been prepared to date. Herein, the successful synthesis and the spectroscopic and computational characterization of nitryl cyanide are reported, and its potential as a promising reagent in HEDM chemistry is explored.

To the best of our knowledge, Klapötke et al. were the first to report an attempt towards the synthesis of $NCNO_2$.[3] In 1996, they explored the nitration of hydrogen cyanide with nitronium tetrafluoroborate, and observed signals of an unstable compound at −62.2 and −171.4 ppm in the low-temperature ^{14}N NMR spectrum. These signals were attributed to the nitrile isocyanide isomer $CNNO_2$ (**2**), in spite of the fact that this isomer was calculated to lie 37 kcal mol^{-1} higher than $NCNO_2$ at the MP2/6-31G(d) level of theory. This report was followed by computational studies by Bartlett and co-workers, who investigated a number of CN_2O_2 isomers using coupled-cluster CCSD(T)/TZ2P calculations,[4] and by Zhang et al., who studied reaction pathways of nitrogen dioxide with the cyanogen radical.[5] Nitryl cyanide was proposed to be kinetically stable with respect to unimolecular decomposition,[4] which was predicted to proceed through a single transition state that lies 53.6–53.9 kcal mol^{-1} above the ground state. Herein, the homolytic bond dissociation into neutral CN and NO_2 radical fragments was predicted to correspond to an enthalpy change of 62.0 kcal mol^{-1} at the CBS-QB3 (basis set extrapolated CCSD(T)) level of theory [Eq. (2)]. Thus, assuming that intermolecular decomposition pathways can be neglected, it appears that nitryl cyanide might indeed possess significant kinetic stability under ambient conditions and represent an attractive target for synthesis.

For the synthesis of $NCNO_2$, a range of experimental approaches were investigated, most of which are discussed in the Supporting Information. The high reactivity of $NCNO_2$ and the separation of reaction by-products required extensive method and solvent screening as well as careful control of the reaction conditions. Ultimately, the best reaction system for the isolation of $NCNO_2$ in substantial amounts proved to be that of $t\mathrm{BuMe_2SiCN}$ with NO_2BF_4 in nitromethane at −30 °C [Eq. (1)].

$$\mathrm{NO_2BF_4} + t\mathrm{BuMe_2SiCN} \rightarrow \mathrm{NCNO_2} + t\mathrm{BuMe_2SiF} + \mathrm{BF_3} \qquad (1)$$

The conversion was determined to be approximately 50 %, by in situ IR and NMR spectroscopic estimates, and is strongly dependent upon the reaction conditions. When an excess of the silyl cyanide was used, the yields dropped dramatically, and side products such as cyanogen were formed as the major species, apparently from the reaction of $NCNO_2$ with the silyl cyanide starting material. To decrease the amount of cyanogen formed, the silyl cyanide needs to be condensed at −196 °C above a frozen mixture of NO_2BF_4 in $MeNO_2$. This mixture must then be carefully thawed, and only small portions of the silyl cyanide must be dissolved at a time.

Even under the optimized conditions, reaction by-products ($t\mathrm{BuMe_2SiF}$, BF_3) and side products (NO_2, N_2O, CO_2, cyanogen) need to be removed by fractional condensation. The initial separation of BF_3 is critical, as BF_3 reacts with $NCNO_2$ in the liquid phase to form a yet to be identified white solid, which significantly lowers the yields. Pumping the volatile compounds through a succession of traps at −80, −96,

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−112, −126, and −196 °C allows the collection of relatively pure $NCNO_2$ at −112 °C. $NCNO_2$ could be obtained in good purity (> 95 % by IR spectroscopy) after three fractional condensation runs and isolated in approximately 40 % yield. Small amounts of NO_2 and traces of BF_3 and tBuMe$_2$SiF may remain after the purification steps.

$NCNO_2$ is colorless in the solid state. It melts to a colorless liquid at -85 ± 1 °C. Small amounts of nitrogen oxides can give it a pale yellow or bluish color. A density of $1.24 \pm 0.08\ \mathrm{g\,mL^{-1}}$ was measured for the liquid at −79 °C, which is comparable to that of $ClNO_2$ ($1.37\ \mathrm{g\,mL^{-1}}$ at 0 °C).[6] $NCNO_2$ is colorless in the gas phase. The vapor pressure of $NCNO_2$ was measured between −96 and 0 °C, giving an extrapolated boiling point of 7 °C and an enthalpy of evaporation of $6.8 \pm 0.2\ \mathrm{kcal\,mol^{-1}}$, which is in excellent agreement with our theoretically predicted value of $6.4\ \mathrm{kcal\,mol^{-1}}$ (see the Supporting Information). Gas-density measurements gave a molecular weight of $70 \pm 2\ \mathrm{g\,mol^{-1}}$ for $NCNO_2$ (calculated: $72.00\ \mathrm{g\,mol^{-1}}$). Its relatively high melting point of −85 °C, compared to −145 °C for $ClNO_2$,[6] suggests somewhat increased association in the liquid phase. This is also reflected by their Trouton constants (molar heat of evaporation divided by absolute boiling point), $24.3\ \mathrm{kcal\,K^{-1}\,mol^{-1}}$ for $NCNO_2$ and $23.9\ \mathrm{kcal\,K^{-1}\,mol^{-1}}$ for $ClNO_2$.[7]

Pure $NCNO_2$ is stable at room temperature. In the gas phase, it could be kept at low pressures in a glass vessel for several days with only trace amounts of CO_2 detectable by IR spectroscopy. In the liquid phase, color changes to greenish blue could be observed after several hours even at −80 °C because of trace amounts of impurities. Given the predicted high stability of monomeric $NCNO_2$, it appears that in the condensed phase, it might undergo more facile decomposition through intermolecular pathways. Our calculations suggest that trace amounts of NO_2 radicals can significantly lower the activation barrier for $NCNO_2$ decomposition ($\Delta G^{\neq}$: 54→ 28 $\mathrm{kcal\,mol^{-1}}$). A reaction with NO_2 could result in the formation of an unstable radical intermediate, NCN(O)O−NO_2, which presumably could decompose into NCNO, a well-known species of blue color.[8] We have observed NCNO by IR spectroscopy under certain reaction conditions (see the Supporting Information).

Bartlett et al. have predicted the heat of formation ($\Delta H^0_{f(\mathbf{1},gas)}$) of $NCNO_2$ as $60\ \mathrm{kcal\,mol^{-1}}$, using MBPT(2) calculations of the isodesmic reaction shown in [Eq. (3)]. We have used the most recent ΔH^0_f-NIST data (NIST = National Institute of Standards and Technology) for the compounds in [Eq. (2)–(4)], combined with reliable CBS–QB3 reaction enthalpies, and estimated a more accurate value of $\Delta H^0_{f(\mathbf{1},gas)} = 50.7 \pm 2\ \mathrm{kcal\,mol^{-1}}$ for $NCNO_2$. This is an extraordinarily high value for such a small molecule, almost rivaling that of HN_3 ($70\ \mathrm{kcal\,mol^{-1}}$[9]). Below, the ΔH^0_f values of the individual compounds that were used for our calculations are given in $\mathrm{kcal\,mol^{-1}}$ in parentheses.

$$\begin{gathered}\mathrm{NCNO_2}\ (\mathbf{1}) \rightarrow {}^{\bullet}\mathrm{CN}\ (+104.0) + {}^{\bullet}\mathrm{NO_2}\ (+7.9) \\ (\Delta H^0_{r,CBS-QB3} = +62.0\ \mathrm{kcal\,mol^{-1}},\ \Delta H^0_{f,\mathbf{1}} = +49.9\ \mathrm{kcal\,mol^{-1}})\end{gathered} \tag{2}$$

$$\begin{gathered}\mathrm{NCNO_2}\ (\mathbf{1}) + \mathrm{C_2H_6}\ (-20.0) \rightarrow \mathrm{CH_3CN}\ (+17.7) + \mathrm{CH_3NO_2}\ (-19.4) \\ (\Delta H^0_{r,CBS-QB3} = -32.4\ \mathrm{kcal\,mol^{-1}},\ \Delta H^0_{f,\mathbf{1}} = +50.8\ \mathrm{kcal\,mol^{-1}})\end{gathered} \tag{3}$$

$$\begin{gathered}\mathrm{NCNO_2}\ (\mathbf{1}) \rightarrow \mathrm{CO_2}\ (-94.1) + \mathrm{N_2}\ (0.0) \\ (\Delta H^0_{r,CBS-QB3} = -145.6\ \mathrm{kcal\,mol^{-1}},\ \Delta H^0_{f,\mathbf{1}} = +51.5\ \mathrm{kcal\,mol^{-1}})\end{gathered} \tag{4}$$

The predicted heat of formation for $NCNO_2$ in the liquid phase was obtained by subtracting $\Delta H_{\mathbf{1},vap(exp)}$ from $\Delta H^0_{f(\mathbf{1},gas)}$, that is, $\Delta H^0_{f(\mathbf{1},l)} = 50.7 - 6.8 = 43.9 \pm 2\ \mathrm{kcal\,mol^{-1}}$. EOM-CCSD/Def2-TZVPP calculations suggest that $NCNO_2$ does not have any spin-allowed electronic transitions in the visible spectrum, but two significant transitions in the UV region at 185 nm ($^1A_1 \rightarrow {}^1B_2$) and 161 nm ($^1A_1 \rightarrow {}^1A_1$). Geometry optimizations of the excited states at the td-ωB97X-D/aug-cc-pVTZ level of theory showed neither excited state to be dissociative. Consequently, we do not expect the compound to be light-sensitive. We have estimated the adiabatic ionization potential of **1** to be 12.7 eV at the CBS-QB3 level of theory. The adiabatic electron affinity of **1** was calculated to be 2.0 eV, which in comparison to 2.7 eV for the much larger C_{60} fullerene exemplifies a high electrophilicity.

$NCNO_2$ is very reactive. In the presence of BF_4^-, it was found to react with nitriles to form the corresponding acyl fluorides. As these compounds were difficult to separate, this hampered the use of acetonitrile for the synthesis of $NCNO_2$. It also appeared to react with the silyl cyanide starting materials to form cyanogen. It hydrolyzes slowly below 0 °C to ammonium nitrate, which was identified by ^{14}N NMR spectroscopy. The mechanism of hydrolysis is best described by the hydrolysis of $NCNO_2$ to HCN and HNO_3, followed by the well-known acidic hydrolysis of HCN to NH_3 and formic acid or CO, and NH_3 reacting with HNO_3 to give NH_4NO_3 [Eqs. (5)–(8)].

$$\mathrm{NCNO_2} + \mathrm{H_2O} \rightarrow \mathrm{HCN} + \mathrm{HNO_3} \tag{5}$$

$$\mathrm{HCN} + 2\,\mathrm{H_2O} \rightarrow \mathrm{NH_3} + \mathrm{HCOOH} \tag{6}$$

$$\mathrm{HCOOH} \rightarrow \mathrm{CO} + \mathrm{H_2O} \tag{7}$$

$$\mathrm{NH_3} + \mathrm{HNO_3} \rightarrow \mathrm{NH_4NO_3} \tag{8}$$

The thermal decomposition of $NCNO_2$ was studied by heating the compound in a stainless steel cylinder, separating the products by fractional condensation, and analyzing them by IR spectroscopy. Heating for one hour to 50 and 100 °C, respectively, resulted only in little decomposition with most of the $NCNO_2$ being recovered unchanged, and heating to 140 °C for several hours was required to achieve complete decomposition. The major decomposition products were CO_2 (80 mol % based on carbon) and N_2 [Eq. (4)], but smaller amounts of NO and some NO_2 and N_2O were also observed, suggesting the possible involvement of a radical mechanism with the breakage of the C−N bond as the first step [Eq. (2)]. $NCNO_2$ was also found to be incompatible with fluorides, Lewis acids [BF_3 and $B(C_6F_5)_3$], elemental mercury, amines, and K_3PO_4.

Our observed vibrational spectra of $NCNO_2$ are in excellent agreement with the predicted ones (Table 1), and disagree with the alternative isocyanide isomer, $CNNO_2$ (see the Supporting Information), thus removing any doubt regarding the identity of the observed compound. The gas-phase IR spectrum exhibits one C≡N stretching band at 2238 cm^{-1}, which is close to that of Cl−CN (2219 cm^{-1}; Figure 1).[10] The symmetric and antisymmetric ONO stretching modes at 1300 and 1580 cm^{-1}, respectively, are comparable to those of NO_2 (1325, 1610 cm^{-1}).[10] In addition to the bands observed in the IR spectrum, the Raman spectra (Figure 2) show two bands at 216 and 267 cm^{-1}, which lie outside the range that was used for the IR measurements. Also, the band at 1575 cm^{-1} is relatively broad for the liquid-phase compound, but separated into two sharper bands in the solid state (Figure 2), indicating some interaction in the condensed phase.

Table 1: Fundamental vibrational modes of nitryl cyanide.

Vibrational assign. in C_{2v} symmetry	calcd. freq.[a] (IR) [Ra] int.	obsd.[b] IR freq. (gas)	obsd.[c] Ra freq. (liquid)
ν C≡N (A_1)	2227 (15) [10.0]	2238 w	2242 [10.0]
ν asym NO_2 (B_2)	1586 (100) [1.0]	1580 s	1577 [1.2]*
ν sym NO_2 (A_1)	1300 (33) [2.7]	1300 m	1304 [4.9]
ν C-N (A_1)	891 (10) [0.7]	890 m	896 [4.1]
δ wag NO_2 (B_1)	739 (2) [0.1]	720 w	721 [1.4]
δ rock NO_2 (B_2)	600 (0) [0.0]	(ca. 590)[d]	–
δ scissor NO_2 (A_1)	572 (1) [0.3]	576 vw	583 [1.4]
δ oop NCN (B_1)	278 (5) [0.1]	x	272 [1.0]*
δ ip NCN (B_2)	209 (2) [0.4]	x	216 [4.7]

[a] B2PLYP/Def2-TZVPP frequencies (cm^{-1}) scaled by 0.989. ip = in plane, oop = out of plane. B_1 modes are perpendicular to the plane of the molecule, and B_2 modes are in the plane of the molecule. IR intensity (km mol^{-1}) and Raman activity ($Å^4 amu^{-1}$) are denoted as a fraction of the strongest band, which was assigned an intensity of 100 for the IR and an activity of 10 for the Ra spectrum. Raman activities were calculated at the B3LYP/aug-cc-pVTZ level of theory. [b] +25 °C, ca. 5 torr. "x" denotes out of the range of the instrument. Intensity: s = strong, m = medium, w = weak, vw = very weak. [c] −90 °C, Raman intensities within brackets are expressed relative to the most intense band. * indicates broad or complex bands. [d] Estimated from the observed combination band of 216 + ca. 590 at 802 cm^{-1} in the IR spectrum of the gas (see the Supporting Information).

The ^{13}C NMR spectrum shows one signal at 106.6 ppm, which is similar to those observed for a range of compounds, such as Cl−CN (95.5) and HCN (111.5 ppm),[11] and features the expected 1:1:1 triplet pattern, which is due to coupling with ^{14}N ($I = 1$) with $J(^{13}C–^{14}N) = 25$ Hz (Figure 3). In the ^{14}N NMR spectrum (Figure 3), however, this coupling could not be observed, as the quadrupole moment of ^{14}N leads to signal broadening. Both ^{14}N signals at −62.6 (NC*N*O_2) and −175 (*N*CNO_2) ppm are in good agreement with the calculated values (−55 and −168 ppm, respectively). The chemical shift for the nitro group (−62.6 ppm) is close to that in $ClNO_2$ (−70 ppm in CD_3CN at −33 °C). The chemical shift for the cyanide group (−175 ppm) is relatively close to that of the *N*CNH_2 moiety (−188 ppm in CD_3CN).[11]

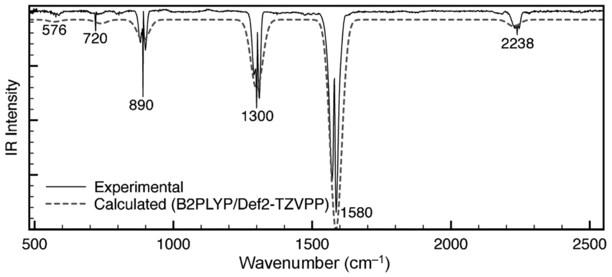


Figure 1. Calculated and observed infrared spectra of $NCNO_2$ in the gas phase.

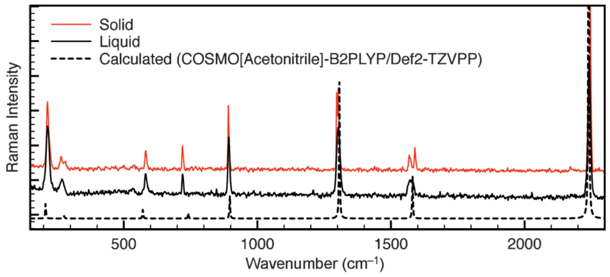


Figure 2. Observed Raman spectra of $NCNO_2$ in the solid state and in the liquid phase, together with the calculated spectrum.

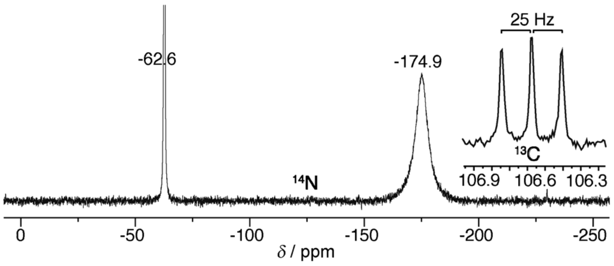
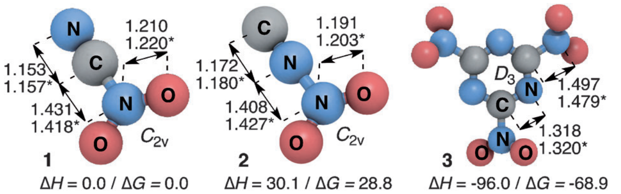


Figure 3. ^{14}N (230 K) and ^{13}C (238 K) NMR spectra of nitryl cyanide in SO_2 solution.

The close agreement between our NMR data for $NCNO_2$ and those previously attributed to $CNNO_2$[3] prompted our reinvestigation of the alleged synthesis of the latter. The nitration of HCN with NO_2BF_4 was thus performed in Freon-11 at 0 °C. Aside from the signal of unreacted HCN at −118.8 ppm, a sharp signal at −64.2 ppm and a broad signal at −171.9 ppm were observed, in agreement with the values reported by Klapötke et al. (−62.2, −120.0, and −171.4 ppm).[3] However, the chemical shifts of these signals are in poor agreement with the predicted values for $CNNO_2$ [−80 ppm (*N*O_2) and −164 ppm (C*N*)] suggesting that it had not been generated in the previously reported experiment, and that only the thermodynamically favored compound $NCNO_2$ had been produced. The Raman spectrum of the $CFCl_3$ solution at −60 °C and a gas phase IR spectrum of the purified reaction mixture revealed spectral features that are identical to those observed for isolated $NCNO_2$.

As $NCNO_2$ has an excellent oxygen balance [Eq. (4)] and a large positive heat of formation, it might be of interest as a high energy density material (HEDM). We have estimated the specific impulse (I_{sp}, rocket propellant performance) of $NCNO_2$ in vacuum, and predicted a value of 343 s. This value can be compared to 240 s for hydrazine. It even exceeds that of a standard $(NO_2)_2$/hydrazine bipropellant by 10 s. There are many potential applications of $NCNO_2$ in synthesis, and these include homo- and co-polymerization resulting in energetic polymers, azide to nitrotetrazole transformations, and modification of various dienes through 1,3- and 1,4-dipolar cycloaddition reactions. Politzer and co-workers have considered the cyclo-oligomerization of $NCNO_2$ as a pathway to cubane-like HEDMs.[12] The trimer of $NCNO_2$, 2,4,6-trinitro-1,3,5-triazine (**3**), is particularly interesting (Scheme 1). The first literature reference to the latter compound is over 106 years old;[13] however, to the best of our knowledge, it has never been prepared. It is possible that **3** could be formed from $NCNO_2$ in a manner analogous to the known trimerization of other nitriles.[14] Compound **3** has previously been predicted to be a powerful HEDM with a density of 1.99 $g\,cm^{-3}$.[15] Using the same approach as for $NCNO_2$, we have estimated values of $\Delta H^0_{f(\mathbf{3},gas)} = 62.6 \pm 2$ $kcal\,mol^{-1}$, $\Delta H_{\mathbf{3},vap} \approx 13.7$ $kcal\,mol^{-1}$, $\Delta H_{\mathbf{3},sub} \approx 18.0$ $kcal\,mol^{-1}$, and $\Delta H^0_{f(\mathbf{3},s)} = 44.6 \pm 5$ $kcal\,mol^{-1}$ for 2,4,6-trinitro-1,3,5-triazine. Using the latter value, we predicted a detonation pressure of 42.1 GPa and a detonation velocity of 9770 $km\,s^{-1}$ for 2,4,6-trinitro-1,3,5-triazine, which implies that in terms of these properties, this compound outperforms the standard high-explosive material HMX by 13 and 6 %, respectively. Because of the high oxygen content of 2,4,6-trinitro-1,3,5-triazine, this compound might also have potential as an ingredient in rocket propellants. Several other higher oligomeric structures, such as the boat- and adamantane-type tetramers, are thermodynamically viable relative to **1**, whereas more strained ones, such as the cubane analogues, are not (e.g., **4**–**7**; Supporting Information, Scheme S1).



Scheme 1. Nitryl cyanide (**1**), nitryl isocyanide (**2**), and 2,4,6-trinitro-1,3,5-triazine (**3**). Relative enthalpies and Gibbs free energies were calculated at the M06-2X/cc-pVTZ level of theory ($kcal\,mol^{-1}$, 1 atm, 298 K). Geometries [Å] were determined by M06-2X/cc-pVTZ and RI-B2PLYP/def2-TZVPP (*) optimizations.

In conclusion, the elusive nitryl cyanide, $NCNO_2$, has been synthesized and characterized. It was prepared in good yield, isolated by fractional condensation, and characterized by NMR and vibrational spectroscopy and theoretical calculations. Nitryl cyanide holds promise as a high energy density material and might also prove useful as a HEDM building block. The simplicity and inherent stability of nitryl cyanide, together with the known multitude of nitriles in interstellar space,[2] suggest that this compound might also be a potential candidate for observation in atmospheric and interstellar chemistry.

Experimental Section

Caution! Many of the materials described in this work are toxic, as well as energetic and likely to be explosive, especially in the condensed phase. They should only be handled on a small scale while taking appropriate safety measures, such as wearing ear plugs, face shield, leather gloves, and protective clothing, and working in a well-ventilated environment. Also, care should be exercised when using nitromethane as a solvent, particularly in a closed system, because it can result in violent explosions when ignited by a suitable initiator. All manipulations were performed using standard vacuum-line and dry-box techniques. Nitromethane was pre-dried with $MgSO_4$, and then dried over 3 Å molecular sieves. Dry solvents were stored over 3 Å molecular sieves in flasks sealed with Teflon valves. Commercially available NO_2BF_4 (Sigma–Aldrich) was exposed to a dynamic vacuum overnight to remove any adventitious volatile impurities. Commercially available tBuMe$_2$SiCN (Aldrich) was purified by trapping it at −20 °C under a high dynamic vacuum to remove the more volatile Me_3SiCN impurity.

Apparatus: NMR spectra were recorded on a Bruker AMX 500 (^{14}N, $\nu_0 = 36.13$ MHz) and on a Varian NMRS-600 (^{13}C, $\nu_0 = 150.9$ MHz) spectrometer. Spectra were externally referenced to neat CH_3NO_2 ($\delta_0 = 0.00$ ppm) for ^{14}N NMR spectra and to neat tetramethylsilane for ^{1}H and ^{13}C spectra. Raman spectra were recorded in J. Young tubes on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd:YAG laser at 1064 nm. IR spectra were recorded on a Midac, M series, FT-IR spectrometer, using a Pyrex glass cell equipped with AgCl windows.

Preparation of $NCNO_2$: NO_2BF_4 (404 mg, 3.0 mmol) was placed into a glass vessel equipped with a Teflon valve. Nitromethane (2–5 mL) was condensed into the reactor at −196 °C; the mixture was thawed and stirred and then frozen at −196 °C. tBuMe$_2$SiCN (217 mg, 1.5 mmol) was then condensed above the frozen mixture at −196 °C. The frozen mixture was thawed at approximately −30 °C. Once the thawing had been completed, the cold liquid was swirled to dissolve small portions of tBuMe$_2$SiCN frozen on the walls of the reactor. This was repeated until all of the tBuMe$_2$SiCN had reacted. This ensures that the silicon compound is always in the presence of an excess of oxidizer and typically prevents the appearance of a green–blue color, usually indicative of decomposition. Effervescence followed each silyl cyanide addition. The complete dissolution of the cyanide starting material was carried out within approximately five minutes; afterwards, the yellow mixture was frozen at −196 °C and separated by fractional condensation through traps at −80 and −196 °C in a dynamic vacuum. The contents of the −196 °C trap were then similarly separated through −96, −112, and −196 °C traps with $NCNO_2$ accumulating mostly in the −112 °C trap (0.19 mmol, ca. 30 mol %, estimated total yield; 12 mol % yield of isolated material based on tBuMe$_2$SiCN). The yields were estimated by measuring the pressure of the different gaseous fractions in calibrated volumes on the glass vacuum line. The purity of the isolated materials was estimated by a combination of IR and NMR measurements. The only major impurity found was a few mol % of N_2O_4. $NCNO_2$: ^{14}N NMR (500 MHz, SO_2, unlocked, −33 °C): $\delta = -62.6$ (s, sharp, NC*N*O$_2$), −175 ppm (s, broad, *N*CNO$_2$). ^{13}C NMR (600 MHz, SO_2, unlocked, −30 °C): $\delta = 106.6$ ppm (1:1:1 t, $^1J(^{13}C{-}^{14}N) = 25$ Hz, N*C*NO$_2$). IR (11 torr): $\tilde{\nu} = 2869$ (vw), 2593 (vw), 2463 (vw), 2238 (w), 2186 (vw), 1580 (s), 1300 (m), 890 (m), 802 (vw), 720 (w), 576 (vw) cm^{-1}. Raman (−90 °C): $\tilde{\nu} = 2242$ (10), 1577 (broad, 1.2), 1304 (4.9), 896 (4.1), 721 (1.4), 583 (1.4), 272 (broad, 1.0), 216 (4.7) cm^{-1}.

In another synthesis, tBuMe$_2$SiCN (425 mg, 3.0 mmol) was reacted with NO_2BF_4 (835 mg, 6.3 mmol) in nitromethane (5 mL) as described above. The crude reaction mixture was separated by fractional condensation through traps at −80, −96, −126, and −196 °C in a dynamic vacuum, and the contents of the −126 trap were refractionated twice through −96, −112, and −196 °C traps, then once more through −112 and −196 °C traps. This afforded approximately 1.4 mmol of $NCNO_2$ (purity > 95 mol % by IR spectroscopy; 45 %

yield of isolated material based on *t*BuMe$_2$SiCN), demonstrating the sensitivity of the yield of NCNO$_2$ to the reaction conditions, both during the synthesis and separation steps.

See the Supporting Information for further characterization data and experimental details and for descriptions of most other synthetic approaches.

Computational details: Geometry optimization and frequency analysis of NCNO$_2$, CNNO$_2$, and 2,4,6-trinitro-1,3,5-triazine in the gas phase were performed using the second-order perturbation corrected "double hybrid" density functional B2PLYP of Grimme[16] together with the resolution of identity (RI) approximation, and Ahlrichs Def2-TZVPP[17] basis set, using ORCA 2.9.[18] All species (Scheme 1) were also calculated using the hybrid meta exchange-correlation density functional M06-2X and the cc-pVTZ basis set, using Gaussian 09, rev A02.[19] The B2PLYP and M06-2X DFT functionals have been extensively tested in large test sets and have reported mean absolute energy deviations of 2.5[20] and 2.2[21] kcal mol^{-1}, respectively. The CBS-QB3[22,23] composite method was employed to study various structures in the gas phase. CBS-QB3 is based on CCSD(T) energies extrapolated to the basis set limit using MP2 and MP4 calculations together with empirical corrections, and is expected to be highly accurate for thermochemistry. Its mean absolute deviation in the G2 test set is reported to be 0.87 kcal mol^{-1}.[22] ΔH_{vap} and ΔH_{sub} values were estimated from the electrostatic surface potential (ESP) calculated at the B3LYP/6-31G(d) level of theory, using a parameterized relationship[24] and the HS95-v9 program.[25] Nuclear magnetic shielding tensors for **1** were calculated in acetonitrile at the GIAO-PCM-B3LYP/6-311++(3df,3pd) level of theory and were empirically corrected according to a fit with experimental values (see the Supporting Information). Excited-state calculations at the EOM-CCSD[26] and TD-ωB97X-D[27] levels of theory were performed with Gaussian 09. The rocket propellant performance was estimated using the thermochemical code RPA v.1.2.8.0, assuming a combustion chamber pressure of 7 MPa, expansion to vacuum, and a nozzle expansion ratio of 70. The detonation pressure and velocity of **3** were estimated using Cheetah 7.[28]

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