Bromocyanocarbene and Bromoisocyanocarbene: A Combined Matrix-Spectroscopic and Density Functional Theory Study

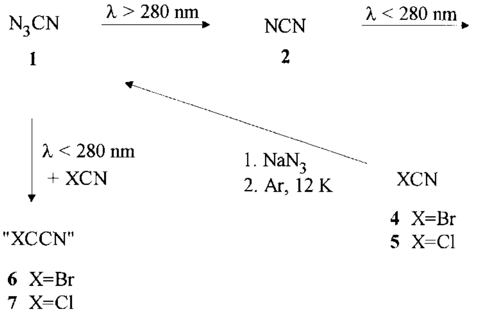
Günther Maier,* Axel Bothur, Jürgen Eckwert, and Hans Peter Reisenauer

Abstract: The C_2BrN potential-energy surface was explored by means of density functional calculations (B3LYP/6-311++G*). Six open-chain and three cyclic structures were found as minima. Photolysis of matrix-isolated (Ar, 12 K) cyanogen azide N_3CN (**1**) in the presence of BrCN (**4**) led, in addition to the expected nitrenes NCN (**2**) and CNN (**3**), to the bromine-containing singlet isocyanocarbene BrCNC (**11s**). The formerly unknown **11s** was identified and characterized by comparison of the experimental and calculated IR absorptions. Our findings were substantiated by isotopic substitution experiments. Only a tentative assignment could be made for the questionable singlet bromocyanocarbene BrCCN (**6s**). In similar matrix-isolation experiments with cocondensed **1** and ClCN (**5**), the chlorine analogue singlet chloroisocyanocarbene ClCNC (**7s**) was also identified by IR spectroscopy.

Keywords: carbenes · density functional calculations · matrix isolation · photochemistry

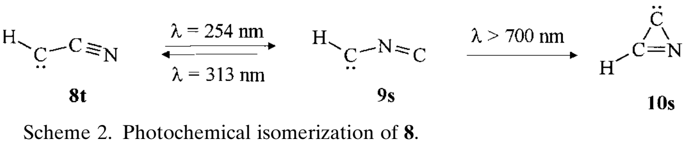
Introduction

In the mid-1960s Milligan et al. studied the photochemistry of matrix-isolated cyanogen azide N_3CN (**1**), a suitable precursor for the free nitrenes NCN (**2**) and CNN (**3**) (Scheme 1).[1, 2] Due to its explosive nature **1** was only synthesized in situ, by passing a gaseous mixture of BrCN (**4**) or ClCN (**5**) over NaN_3. Photolysis of **1** led to the expected products **2** ($\lambda >$ 280 nm) and **3** ($\lambda <$ 280 nm). An additional group of IR bands was observed by Jacox et al.,[1] who used cocondensed cyanogen halides ($\tilde{\nu} = 984$, 1035, 1923, and 2102 cm^{-1} for **4**, and 996, 1025, 1945, 2113, and 2118 cm^{-1} for **5**). Whereas in the original work neither composition nor structures were proposed for these halogen-containing compounds, Jacox later attributed[3] these IR bands to BrCCN (**6**) and ClCCN (**7**), respectively, but the electronic nature of these molecules (i.e., singlet or triplet) remained unknown. As far as we know no further report on this subject has appeared in the literature.



Scheme 1. Reaction scheme for the photolysis of **1**.

Earlier we showed that matrix-isolated triplet cyanocarbene HCCN (**8t**), which is formed by irradiation of diazoacetonitrile, isomerizes photochemically to isocyanocarbene HCNC (**9s**) and azacyclopropenylidene (**10s**), both of which are singlet species (Scheme 2).[4] In our studies on the spectroscopic properties of **3** and possible isomers, we observed the IR absorptions of BrCCN and ClCCN on irradiation of **1** in the presence of **4** or **5**.[5] Since these species are simply substituted analogues of **8**, we decided to explore the systems C_2BrN and C_2ClN with state-of-the-art theoretical methods to explain the experimental observations made by Jacox,[3] Milligan et al.,[1, 2] and us.



Scheme 2. Photochemical isomerization of **8**.

Results and Discussion

Potential-energy surface (PES) of the system C_2BrN: The structures, energies, and IR spectra of the C_2BrN isomers were calculated with the density functional method B3LYP/6-

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311++G*, since DFT methods are highly reliable even for molecules containing electron-rich bromine atoms.[6] Nine of the ten possible isomers were minima on the potential-energy surface (no imaginary frequencies), namely, three open-chain structures **6**, **11**, and **12** and two cyclic structures **13** and **14**, each in singlet (**s**) and triplet (**t**) state (Figure 1). Only triplet azacyclopropyne (**14t**) was confirmed as a transition state. Since the results for the potential-energy surfaces of C_2BrN and C_2ClN are very similar, only the former will be discussed in detail.

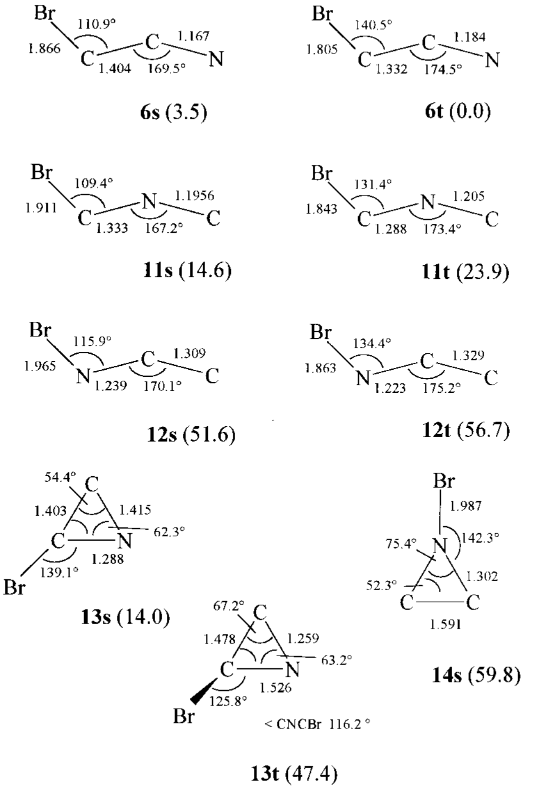


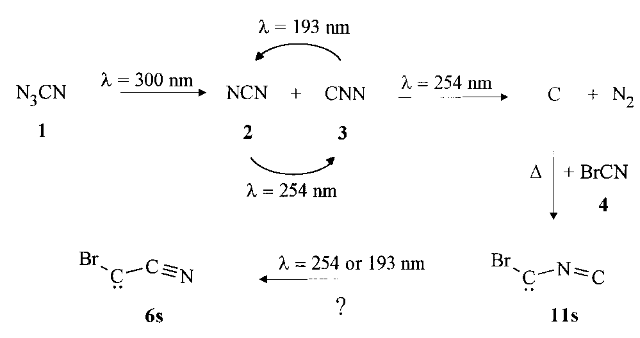
Figure 1. Calculated (B3LYP/6-311++G*) structures of C_2BrN isomers with bond lengths [Å]. Relative energies [kcal mol^{-1}] (including zero-point correction) are given in parentheses.

Relative energies of minima on the C_2BrN potential energy surface are given in Figure 1. Compared to the theoretical studies (B3LYP/6-311+G**) on C_2HN isomers,[7] substitution by bromine atoms leads to a stabilization of the singlet relative to the triplet species, and the strongest effect occurs in the case of an open-chain skeleton. As expected, the global mininum is triplet bromocyanocarbene BrCCN (**6t**) followed by its singlet counterpart **6s**, which lies only 3.5 kcal mol^{-1} higher in energy. The corresponding singlet/triplet gap of 16 kcal mol^{-1} in the parent compound HCCN (**8**) is much higher.[7] A more dramatic effect upon halogen substitution is observed for isocyanocarbene. Whereas singlet HCNC (**9s**) lies 3 kcal mol^{-1} above **9t** (B3LYP/6-311+G**;[7] in contrast to the experimental data[4]), the order is reversed in the case of BrCNC (**11s**), which is about 9 kcal mol^{-1} energetically more favorable than **11t**. With the exception of singlet bromoazacyclopropenylidene (**13s**), the remaining isomers are clearly higher in energy. Therefore, isolation of these compounds is less conceivable.

The structural features (Figure 1) of the C_s-symmetric open-chain C_2BrN isomers can be summarized as follows: **6s** has a bent carbene-like structure with a C–C bond that is much longer than the C–N Bond. In contrast, **6t** has an allenic structure with a shortened C–C bond and a longer C–N bond. Analogous observations can be made for the isomers **11** and **12**. The triplet species are expected to behave like quasilinear molecules, as is known for HCCN.[8] Singlet bromoazacyclopropenylidene (**13s**) is a planar (C_s symmetry) molecule with very similar single-bond lengths in the ring. The situation changes for the triplet molecule **13t**, which loses its C_s symmetry by displacement of the bromine atom out of the plane of the ring. A very interesting molecule is the highly strained bromoazacyclopropyne (**14s**), which represents a minimum on the hypersurface. The C–C bond, formally written as a triple bond, is extremly long (1.591 Å) and should have diradical character, similar to the recently described silacyclopropyne.[9]

Matrix-isolation experiments with cocondensed N_3CN (1) and BrCN (4): The experimental results of Milligan et al.[1, 2] were confirmed, but some new aspects were uncovered. Irradiation ($\lambda = 300$ nm) of an argon matrix containing **1** cocondensed with **4** led to the formation of **2** and **3**. The IR absorptions of **2** and **3** were split due to a matrix effect. Upon subsequent photolysis at 254 nm, the bands of **2** and **3** decreased in intensity, while the group of IR absorptions, first observed by Milligan et al.[1, 2] and attributed to BrCCN (**6**), emerged at 2101.1, 1922.3, 1034.3, and 984.5 cm^{-1}. Another IR band at 672.4 cm^{-1} could be related to this group. The intensity of these IR absorptions was high provided those of unchanged **4** were also strong. This implies that the compound under discussion is produced by the reaction of a photolysis product of **2** and/or **3**, most probably a carbon atom,[1, 10] with **4** and maintains the empirical formula C_2BrN, in agreement with the suggestion of Jacox.[3]

On photolysis in argon with an ArF excimer laser ($\lambda = 193$ nm), three reactions were observed (Scheme 3): 1) **3** was transformed back into **2**; 2) the isocyanide BrNC was identified as a photoproduct of **4**;[11] 3) the IR bands of **11s**—the identification is discussed below—at 1922.3, 1034.3, and 672.4 cm^{-1} decreased in intensity, whereas the remaining bands, probably of **6s**, at 2101.1 and 984.5 cm^{-1} became more intense (Figure 2). The origin of the IR band which appeared at about 1831 cm^{-1} remains unknown.



Scheme 3. Reaction scheme for the photolysis of **1** cocondensed with **4**.

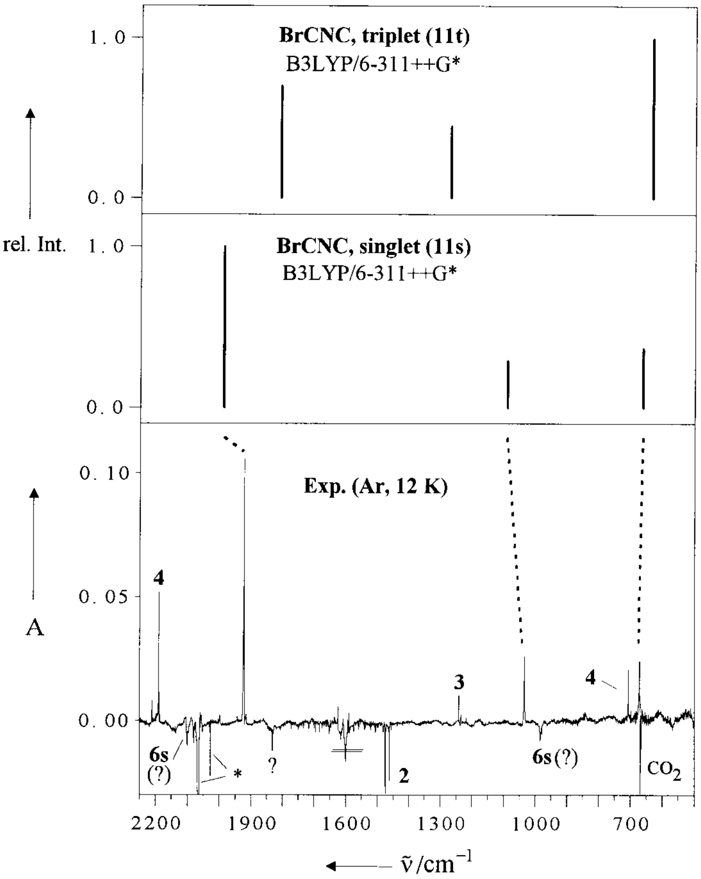


Figure 2. Comparison of the matrix IR spectrum (Ar, 12 K; bottom) of singlet BrCNC (**11s**) with the calculated (B3LYP/6-311++G*) IR bands of **11s** (middle) and **11t** (top). The experimental spectrum is a difference spectrum of the photolysis of cocondensed N_3CN (**1**) and BrCN (**4**), in which negative absorptions are bands that grew, and positive absorptions are bands that decreased on photolysis at $\lambda = 193$ nm. Bands of $BrN^{12}C$ (2067 cm^{-1}) and $BrN^{13}C$ (2028 cm^{-1}) are indicated by an asterisk.

Table 1. Theoretical (B3LYP/6-311++G*) and experimental (Ar and N_2, 12 K) IR absorptions (cm^{-1}) of singlet BrCNC (**11s**). Relative intensities are given in parentheses.

	sym	calcd	exptl (Ar, 12 K)	exptl (N_2, 12 K)
ν_{NC}	a′	1987.3(1.00)[a]	1922.3(1.00)	1925.7
ν_{CN}	a′	1088.7(0.29)	1034.3(0.31)	1038.5
δ_{CNC}	a′	661.0(0.37)	672.4(0.16)	–
ν_{CBr}	a′	410.0(0.07)	–	–
δ_{CNC}	a″	252.9(0.02)	–	–
τ	a′	191.1(<0.01)	–	–

[a] Absolute intensity: 354.8 km mol^{-1}.

Bromoisocyanocarbene BrCNC (11s): The best agreement between the calculated (B3LYP/6-311++G*) IR spectra of the C_2BrN isomers **6**–**14** and the observed IR absorptions whose intensity decreases upon photolysis at 193 nm is found for singlet bromoisocyanocarbene BrCNC (**11s**). This is true of the band positions and of the relative intensities (Table 1). The calculated IR absorptions of **11t**, **6s**, **6t**, and of the remaining isomers do not match the observations sufficiently (Figure 2; calculated IR absorptions of the C_2BrN isomers are listed in Table 2). Of the six theoretically expected absorptions of **11s**, three are found in the experimental spectrum, whereas two of the remaining bands, a C-N-C-bending and a torsional vibration, are expected to lie below the experimental range of 300 cm^{-1} and have very low intensity. The most prominent band is the stretching vibration of the isocyano group at 1922 cm^{-1}, whose value is similar to the corresponding vibration of singlet HCNC (**9s**; 1860 cm^{-1} in an argon matrix[4]) and is rather low for an isonitrile. The C–N single-bond vibration is at 1034 cm^{-1} and has one-third of the intensity of the isocyano-stretching band. In addition a bending vibration of the CNC skeleton can be detected at 672 cm^{-1}. The C–Br stretching vibration is expected to have nearly the same position as an absorption of CNN (391.5 cm^{-1}) and therefore could not be unambiguously identified.

To substantiate our assignment, we calculated IR spectra of the isotopomers $Br^{13}C^{14}N^{12}C$, $Br^{12}C^{14}N^{13}C$, $Br^{13}C^{14}N^{13}C$, and $Br^{12}C^{15}N^{12}C$ and compared them with experimental observations, including the values for the isotopically substituted precursor $^{15}N_3CN$ (from ref. [2]) and $N_3{}^{13}CN$ (this work). The ν_{NC} and ν_{CN} bands of all four isotopomers were detected experimentally, and their isotopic shifts correlated well with the calculated values (Table 3). Deviations of calculated from observed shifts in the case of the C=N stretching vibration seemed to be caused by an anharmonic resonance of this vibration with the first overtone of ν_{CN}. The wavenumber difference $2\tilde{\nu}_{CN} - \tilde{\nu}_{NC}$ (Table 3) is changed dramatically by isotopic substitution. Small values of this difference, which are found for the isotopomers $Br^{13}C^{14}N^{12}C$ and $Br^{13}C^{14}N^{13}C$, lead to a relatively large deviation of the experimental value from the calculated value.

Bromocyanocarbene BrCCN (6s): To our surprise, the most satisfactory agreement between the experimental IR absorptions at 2101 and 985 cm^{-1} and theoretical IR wavenumbers is not found for triplet bromocyanocarbene BrCCN (**6t**), the global minimum on the theoretical energy hypersurface, but rather for singlet BrCCN (**6s**) (Table 2). This is in contrast to the unsubstituted cyanocarbene **8**, which exists in cryogenic matrices only in the triplet state,[4] and reflects the stabilizing

Table 2. Theoretical (B3LYP/6-311++G*) IR absorptions (cm^{-1}) of the C_2BrN isomers **6s**, **6t**, **11t**, **12s**, **12t**, **13s**, **13t**, and **14s**. Absolute intensities (km mol^{-1}) are given in parentheses.

6s	6t	11t	12s	12t	13s	13t	14s
2177.7(18.4)	1931.3(15.6)	1809.0(44.7)	1952.4(519.1)	1849.4(51.4)	1683.9(80.2)	1659.7(29.2)	1547.8(71.3)
1034.4(69.2)	1302.3(59.8)	1269.8(28.7)	1208.5(5.0)	1190.3(20.3)	1326.3(34.2)	925.6(239.8)	1351.1(53.3)
671.3(53.5)	582.9(26.2)	633.0(64.3)	585.8(85.0)	484.6(73.2)	947.6(120.7)	553.7(39.3)	657.1(187.8)
484.9(19.2)	459.3(3.4)	398.5(1.7)	343.4(77.7)	380.3(17.9)	451.8(5.7)	461.8(42.7)	349.6(8.4)
327.2(22.0)	431.8(7.3)	378.4(1.3)	270.7(26.8)	375.6(17.0)	391.4(12.5)	365.2(1.0)	320.9(1.3)
178.7(3.4)	152.4(5.8)	173.6(3.9)	176.4(0.7)	142.3(17.1)	309.8(2.6)	297.0(0.6)	289.8(55.8)

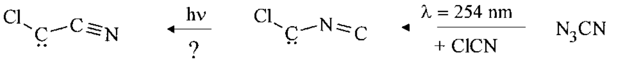
Table 3. Calculated (B3LYP/6-311++G*), corrected [$\tilde{\nu}_{cor} = \tilde{\nu}_{obsd}(Br^{12}C^{14}N^{12}C) \times \tilde{\nu}_{calcd}(isotopomer)/\tilde{\nu}_{calcd}(Br^{12}C^{14}N^{12}C)$], and observed IR absorptions (cm^{-1}) of BrCNC (**11s**) isotopomers.

Isotopomer	approx. description	calcd	cor	exptl (Ar, 12 K)
$Br^{12}C^{14}N^{12}C$	ν_{NC}	1987.3	–	1922.3
	ν_{CN}	1088.7	–	1034.3
	$2\nu_{CN} - \nu_{NC}$	190.1	–	146.3
$Br^{13}C^{14}N^{12}C$	ν_{NC}	1968.6	1921.6	1918.4
	ν_{CN}	1059.7	1006.7	1006.9
	$2\nu_{CN} - \nu_{NC}$	150.8	–	95.4
$Br^{12}C^{14}N^{13}C$	ν_{NC}	1952.4	1888.5	1889.4
	ν_{CN}	1079.7	1029.9	1030[a]
	$2\nu_{CN} - \nu_{NC}$	207.0	–	170.6
$Br^{13}C^{14}N^{13}C$	ν_{NC}	1951.6	1887.8	1885.6
	ν_{CN}	1050.6	998.1	999.3
	$2\nu_{CN} - \nu_{NC}$	149.6	–	113.0
$Br^{12}C^{15}N^{12}C$	ν_{NC}	1951.7	1891.2	1890[a]
	ν_{CN}	1084.4	1034.4	1035[a]
	$2\nu_{CN} - \nu_{NC}$	217.1	–	180.0

[a] N_2, 12 K. Value taken from ref. [2].

effect of the bromine substituent on the singlet state. No further experimental IR bands could be assigned without doubt. For example, a high-intensity bending vibration of **6s** is calculated to lie at 671.3 cm^{-1}, but apart from the δ_{CNC} band of **11s** (672.4 cm^{-1}) only an absorption of CO_2 (667.8 cm^{-1}) is found in this range of the experimental spectrum (Figure 1), which possibly overlaps with the sought-after vibration. Thus, the identification of **11s** remains tentative.

Chloroisocyanocarbene ClCNC (15s) and chlorocyanocarbene ClCCN (7s): When **1** was cocondensed with **5**, the experimental observations upon photolysis were similar to those with **4** as the partner molecule. A group of bands, originally assigned by Jacox et al. to ClCCN (**7**),[1–3] proved to result from a mixture of at least two compounds. By comparison with the calculated spectra (B3LYP/6-311++G*) and the corresponding bromine compound **6s**, one of those species was identified as singlet chloroisocyanocarbene ClCNC (**15s**) (Scheme 4, Table 4). The spectroscopic properties of **7s** resemble those of **6s**. Especially the shifts observed on going from the heavier bromine substituent to the lighter chlorine atom agree excellently with the calculated shifts and therefore substantiate our findings. The IR absorptions of the second species at 2114 and 995 cm^{-1} agree better with the calculated IR absorptions of singlet chlorocyanocarbene (**7s**) than with those of the other C_2ClN isomers (Table 5), but as in the case of **6s** this assignment must be regarded as tentative, since no further bands were found.



7s **15s** **5** **1**

Scheme 4. Reaction scheme for the photolysis of **1** cocondensed with **5**.

Table 4. Theoretical (B3LYP/6-311++G*) and experimental (Ar, 12 K) IR absorptions (cm^{-1}) of singlet ClCNC (**15s**). Relative intensities are given in parentheses.

	sym	calcd	exptl (Ar, 12 K)
ν_{NC}	a′	2008.4 (1.00)[a]	1943.6 (1.00)
ν_{CN}	a′	1074.2 (0.35)	1023.7 (0.46)
δ_{CNC}	a′	746.6 (0.50)	769.5 (0.10)
ν_{CCl}	a′	490.8 (0.03)	–
δ_{CNC}	a″	245.3 (0.02)	–
τ	a′	209.8 (<0.01)	–

[a] Absolute intensity: 351.5 km mol^{-1}.

Table 5. Calculated (B3LYP/6-311++G*) IR absorptions (cm^{-1}) of the C_2ClN isomers: singlet ClCCN (**7s**), triplet ClCCN (**7t**), and triplet ClCNC (**15t**). Absolute intensities (km mol^{-1}) are given in parentheses.

7s	7t	15t
2194.4(24.7)	1938.9(17.3)	1824. (40.4)
1039.3(111.2)	1341.7(88.8)	1290.5(43.2)
744.8(66.1)	667.3(34.3)	729.5(89.2)
546.4(7.3)	501.5(2.3)	458.6(0.4)
319.2(23.5)	427.5(6.9)	372.7(1.1)
202.6(5.7)	175.2(6.9)	189.0(4.4)

Conclusions

The bromine-containing species that appears upon photolysis of N_3CN (**1**) in presence of cocondensed BrCN (**4**) can be identified as the formerly unknown singlet bromoisocyanocarbene BrCNC (**11s**), a strongly bent molecule. The structural assignment is based on the agreement of the experimental IR absorptions with spectra calculated by the density functional method B3LYP/6-311++G* and substantiated by changes in the spectra upon isotopic substitution. Similar observations were made when **4** was replaced by ClCN (**5**), and the chlorine analogue ClCNC (**15s**) was observed. The identification of the cyanocarbenes singlet BrCCN (**6s**) and singlet ClCCN (**7s**) remains tentative, since for both species only two experimental bands were found.

Experimental Section

General: The equipment for matrix-isolation studies, photolyses, and pyrolyses is described in detail elsewhere.[4, 12] Commercially available argon, nitrogen (Messer Griesheim, 99.996%), $^{15}N_2$, and BrCN were used without further purification.

Br¹³CN ([^{13}C]**4**) was synthesized according to a procedure given in Brauer's handbook:[13] In a flask, Br_2 (2.95 g) was layered below water (30 mL) at 2 °C. Over 30 min an aqueous solution of $K^{13}CN$ (1.00 g) and $Na^{12}CN$ (0.161 g) in H_2O (18 mL) was added dropwise under stirring. In the next 2 h the mixture was warmed to 40 °C. The volatile product was removed by an argon stream, passed through $CaCl_2$, and trapped at −25 °C. The crude product was purified by passing it several times through a cold trap filled with sodium wire and stored under argon.

ClCN (**5**) was prepared by a method described by Brauer.[13] Into a cooled suspension (−10 °C) of NaCN (2.85 g) in CCl_4 (170 mL) and acetic acid (2 mL), gaseous Cl_2 was bubbled slowly enough to maintain total absorption. After 2 h the mixture was warmed to room temperature. Volatile ClCN was removed in a nitrogen stream, passed through a tube containing $CaCl_2$ and trapped at −40 °C.

Sodium azide NaN_3 was activated by the procedure of Nelles.[14]

Calculations: The calculations were performed with the Gaussian package of programs.[15]

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