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Investigations on Doubly Nitrogen-15 Labeled Isocyanogen (CNCN)

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Abstract: The doubly nitrogen-15 labeled isotopomer $C^{15}NC^{15}N$ of isocyanogen (CNCN) has been prepared by a known route in three steps from $[^{15}N_2]$hydrazine sulfate and quadricyclanone. The chemical reactivity of $C^{15}NC^{15}N$ has been explored. Most of the typical isonitrile reactions are too slow to compete with the polymerization of isocyanogen which starts as low as −80 °C; defined products were only obtained on bromination to Br_2CNCN (**7**) and on FVT at 750 °C to give partial conversion to cyanogen (NCCN). The ^{15}N and ^{13}C NMR spectra of **1**, **4**, $C^{15}NC^{15}N$, $^{15}NCC^{15}N$, and $[^{15}N_2]$**7** are discussed; important aspects are the previously "missing" cyano group in CN*CN* which has now been identified and an unusually large $^{13}C-^{15}N$ coupling (^1J = 48.9 Hz) in the central bond of isocyanogen.

Introduction

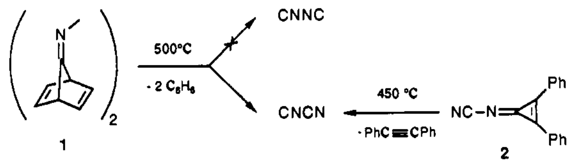
Until recently, cyanogen (NCCN), first prepared by Gay-Lussac in 1815,[1] was the only known isomer of the C_2N_2 family of molecules. In 1988, we reported another isomer which was obtained in high yield by flash vacuum thermolysis (FVT) of norbornadienone azine (**1**)[2] (Scheme I). From the mode of generation and from high resolution mass spectroscopy, ^{13}C and ^{14}N NMR spectroscopy,[2] as well as from the photoelectron spectrum[3] it was initially concluded that the new isomer was diisocyanogen, CNNC. However, in the meantime, it has been unambiguously shown by several methods (first by gas-phase microwave and high-resolution infrared spectroscopy,[4] later by matrix infrared spectroscopy,[5] by gas-phase electron diffraction,[6] by low-temperature X-ray crystal structure determination,[7] and by reinterpretation of the photoelectron spectrum based on high level theoretical calculation[8]) that the new isomer was in fact isocyanogen (CNCN); apparently, at some stage of the thermolysis of **1**, a rearrangement must have taken place.[5]

A rearrangement is not required for the independent synthesis of CNCN from **2** by Vogel, Altenbach et al. (Scheme I).[9] The products of both syntheses were identical, which gives additional support to the structure assignment. However, both groups[2,9] reported an apparent anomaly which was not in line with the proposed structure of CNCN: only one set of signals was observed for carbon ($\delta(^{13}C)$ = 172 ppm) and nitrogen ($\delta(^{14}N)$ = −233 ppm); both are typical values for isonitrile.[10]

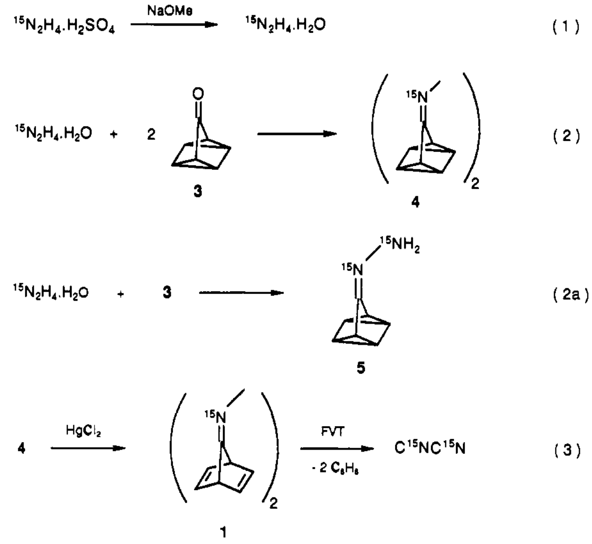
It was the main purpose of the present investigation to clarify this anomaly by preparing and studying $C^{15}NC^{15}N$; in addition, some properties of CNCN will be reported. The ^{15}N NMR spectra of labeled precursors will also be briefly discussed.

Results and Discussion

Scheme I



Scheme II



Initially, we tried to resolve the NMR problem by reinvestigating the ^{13}C and ^{14}N NMR spectra of the thermally very unstable CNCN at high concentration in Et_2O-d_{10} at −100 °C. Indeed, in addition to the "isonitrile" signals mentioned above, broad signals of low intensity were detected at approximately $\delta(^{13}C)$ = 92 ppm ($\nu_{1/2}$ = 25 Hz) and $\delta(^{14}N)$ = −165 ppm ($\nu_{1/2}$ = 900 Hz) which may be assigned to a cyano group.[10] It thus could no longer be excluded that the signals of the cyano part of the molecule had previously escaped detection due to ^{14}N quadrupole induced broadening. Nitrogen-15 labeling was the method of choice to overcome this problem.

Synthesis and Reactions. The synthesis of labeled CNCN followed essentially the sequence described previously (Scheme II).[2] Labeled hydrazine hydrate was obtained from labeled hydrazine sulfate with sodium methoxide in methanol (Scheme II, eq 1).

The reaction of $^{15}N_2H_4 \cdot H_2O$ with quadricyclanone (**3**) yielded, besides the desired azine **4** (eq 2), a small amount (about 10% of **4**) of the simple hydrazone **5** (eq 2a) which was detected and tentatively identified by its ^{15}N NMR data (δ = −85 ppm (=*N*—), δ = −276 ppm (-*NH*$_2$), $^1J(NN)$ = 11.1 Hz). The conversion of **4** to **1** and further to $C^{15}NC^{15}N$ proceeded as in the unlabeled series.[2] Side products in this thermolysis are $^{15}NCC^{15}N$ (8%) and $HC^{15}N$ (2%) (both identified by their ^{15}N NMR spectrum (Table I); yields were determined from the relative intensities of the ^{15}N

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signals) and acetylene (^{13}C NMR). Together with benzonitrile, these products had also been observed by matrix IR spectroscopy;[5] benzonitrile and hydrogen cyanide have been found to be the main products in the thermolysis of **4**.[11]

Still unresolved is the interesting question whether diisocyanogen, the most unstable[8,12] of the three C_2N_2 isomers, is also present in minute amounts (1–2%) in this reaction mixture. Both CNNC[5] and $C^{15}N^{15}NC$[13] have been tentatively identified as minor products by matrix infrared spectroscopy. In line with these observations, we found 1% tetrabromoformaldazine (**6**; identified by comparison of the GCMS with that of an authentic sample[14]) when reacting the pyrolysate from **1** after sublimation at about −100 °C with bromine; apparently the conditions for minute quantities of CNNC to survive are very critical and not yet well understood. While the formation of **6** according to eq 4 would strongly support the presence of CNNC, the evidence is inconclusive as **6** was not observed in subsequent experiments. Thus, the formation and existence of this elusive and long searched for isomer[14,15] still need confirmation.

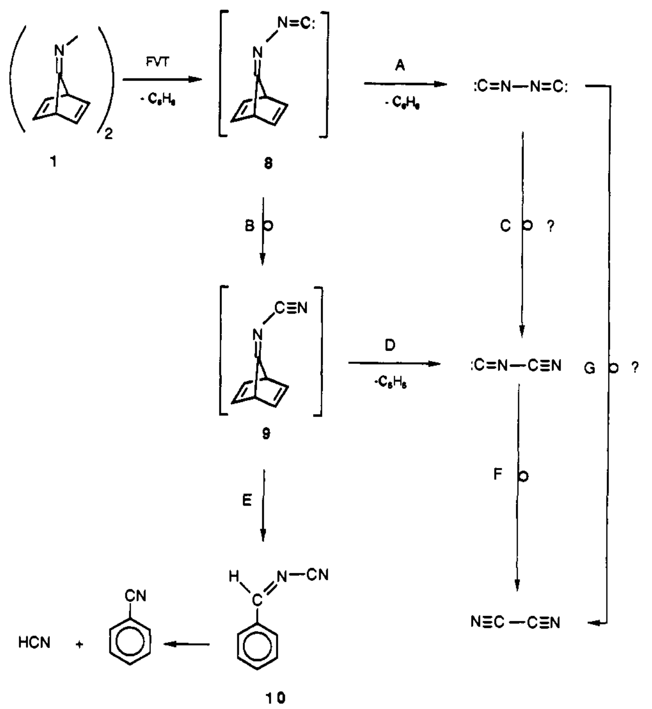
$$:C{=}N{-}N{=}C: + 2Br_2 \rightarrow Br_2C{=}N{-}N{=}CBr_2 \qquad (4)$$

$$:C{=}^{15}N{-}C{\equiv}^{15}N + Br_2 \rightarrow Br_2C{=}^{15}N{-}C{\equiv}^{15}N \qquad (5)$$

Consisting mainly of CNCN, the just mentioned sublimate from the pyrolysis of **1** gave on reaction with bromine at −80 °C *N*-cyanodibromoformaldimine (**7**) as the major product (eq 5). It is a novel compound, and the only defined reaction product obtained so far from CNCN (both labeled and unlabeled) apart from its thermal conversion to NCCN (vide infra). Compound **7** is unstable and decomposes slowly on standing at room temperature; it was characterized by high-resolution mass spectroscopy and by its ^{13}C and ^{15}N NMR spectrum (see Experimental Section). The formation of **7** constitutes a chemical corroboration of the structure of CNCN, as the addition of bromine to the terminal carbon is a typical reaction of isonitriles.[16] Other attempted reactions were unsuccessful, because in solution CNCN tends to polymerize to a brownish-black polymer[2] at −80 °C to −50 °C; at such a low temperature, typical isonitrile reactions,[16] in particular that with *n*-butyllithium, do not have competitive rate. In the gas phase, however, CNCN turned out to be surprisingly stable.[17] When a purified sample of CNCN in a sealed high vacuum system at a pressure of 73 mmHg was kept at room temperature, the pressure fell to 45 mmHg in a period of 21 h. A brownish-black polymer was deposited on the glass wall; it will be subjected to further investigations. The residual gas was shown to be unchanged CNCN by its condensation with liquid nitrogen and measurement of the ^{13}C NMR signals at −60 °C in [D$_8$]toluene (δ = 172 ppm). Complexation with Cr(CO)$_5$·THF to give Cr(CO)$_5$·CNCN has recently been reported;[18] this complex had previously been obtained by a completely different synthesis and characterized by X-ray crystal structure determination.[19]

The genesis of CNCN as the unexpected thermolysis product from **1** is still not quite clear. Possible pathways are presented in Scheme III.

Scheme III



It is reasonable to assume that the fragmentation of **1** to C_2N_2 and benzene is a stepwise process, even though intermediates have never been observed. The straightforward first fragmentation product from **1** is **8**. The transformation of **8** to CNCN may in principle occur via two routes: A–C or B–D. The former involves a second fragmentation (route A) to give CNNC which, however, has not yet been unambiguously identified (vide supra); subsequent rearrangement of CNNC (route C) would give CNCN. Alternatively, **8** might rearrange to **9** by the isonitrile–nitrile rearrangement (route B)[16a] and then fragment (route D) to yield CNCN. We favor the route B–D because theoretical calculations predict the barrier for the process F to be approximately equal (37 kcal/mol,[12c] 41 kcal/mol[12d]) to that of process C (42 kcal/mol), whereas the barrier for the direct isomerization of CNNC to NCCN (route G) via a square intermediate was calculated to be much lower (17 kcal/mol)[12d] than those of routes C and F. Thus, if CNNC were formed in an early stage of the reaction it would isomerize to NCCN and not to CNCN.

It should be pointed out that NCCN by necessity is a rearrangement product of either CNNC or CNCN. In order to verify this aspect, we have subjected CNCN, which had been purified by sublimation at −100 °C, to FVT. At 500 °C (the reaction condition of the pyrolysis of **1**) the ratio of CNCN/NCCN (which was 90:8) remained constant within the experimental error. The thermal stability of CNCN is thus surprisingly high for the isolated molecule in the gas phase, especially if contrasted with its high reactivity in the condensed phase (i.e., polymerization at −80 °C). At 750 °C, the ratio CNCN/NCCN was found to be 1:1. It is tempting and in line with the calculations[12d] to ascribe the formation of NCCN during pyrolysis of **1** to the rearrangement of intermediate CNNC; this would imply that the ratio of CNCN/NCCN (which was 90:8) from **1** reflects the competition between the two possible modes of reaction of **8**: fragmentation (route A) and rearrangement (route B). However, as a referee pointed out, it cannot be excluded that the NCCN obtained in the direct pyrolysis of **1** stems from chemically activated CNCN.

Compared to route D, rearrangement of **9** to **10** (route E) and subsequent cleavage to benzonitrile and hydrogen cyanide is only a minor pathway. This is in contrast to the high yield of benzonitrile and hydrogen cyanide on thermolysis of **4**;[11] obviously, the latter does not proceed via **9**.

In passing we want to mention briefly an unsuccessful attempt for an alternative approach to CNNC. It is based on the concept of Thiele[14] who treated **6** with Zn, expecting to obtain CNNC in a formal reversal of eq 4; he noticed a strong "isonitrile odor"

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Table I. NMR Data of CNCN, NCCN, and HCN (δ in ppm, J in Hz)

	^{14,15}N NMR[a]		^{13}C NMR[a]		
compd	$\delta(^{14,15}\mathrm{N})$[b]	$^2J(^{15}\mathrm{N}^{15}\mathrm{N})$	$\delta(^{13}\mathrm{C})$[c]	multiplicity	$^nJ(^{13}\mathrm{C}^{15}\mathrm{N})$
$C^{15}N\mathrm{C}^{15}\mathrm{N}$	−233	4.6	171.1	dd	5.8 (n = 1) 5.8 (n = 3)
$C^{14}N\mathrm{C}^{14}\mathrm{N}$[d]	−233		172.0		
$\mathrm{C}^{15}\mathrm{N}C^{15}N$	−169	4.6	92.8	dd	17.4 (n = 1) 48.9 (n = 1)
$\mathrm{C}^{14}\mathrm{N}C^{14}N$	−165[e]		92.0[f]		
$^{15}NCC^{15}N$	−133		96.3	dd	20.2 (n = 1) 4.9 (n = 2)
$^{14}NCC^{14}N$[g]	−134		93		
$\mathrm{H}C^{15}N$	−120		111.9[h]	d	17.4 (n = 1)
$\mathrm{H}C^{14}N$	−130[i]		110.9[j]		

[a] The data refer to the nuclei indicated in italics. [b] Relative to $\mathrm{Me^{15}NO_2}$. [c] Relative to TMS. [d] Reference 2. [e] $\Delta\nu(1/2)$ = 900 Hz. [f] $\Delta\nu(1/2)$ = 25 Hz. [g] Reference 22. [h] Other couplings: $^1J(^{13}\mathrm{CH})$ = 260.6 Hz, $^2J(^{15}\mathrm{NH})$ = 8.6 Hz. [i] Reference 23. [j] Reference 29.

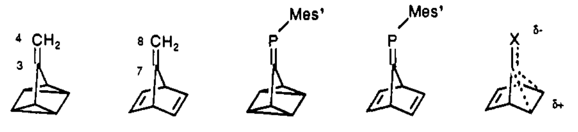
which he considered to be an indication for the possible formation of CNNC. Being aware of the extreme instability of this compound, we attempted the reduction of **6** by passing it in vacuum over a column of triphenylphosphine.[20] The triphenylphosphine was immediately covered with a brownish-black layer ($(\mathrm{CNNC})_n$?); volatile products were trapped in liquid nitrogen; the mass spectrum and the photoelectron spectrum showed a superposition of the known signals of HCN and NCCN.[21]

NMR Spectroscopy. One of our major goals was the clarification of the NMR data of isocyanogen. This has been fully achieved by the measurements performed on $\mathrm{C^{15}NC^{15}N}$.

The $\mathrm{C^{15}NC^{15}N}$, purified by sublimation below −100 °C at 10^6 mbar, was dissolved in $\mathrm{Et_2O}$-d_{10}, and the NMR spectra were measured at −100 °C to prevent polymerization. According to the spectra, $\mathrm{C^{15}NC^{15}N}$ was the major component; $\mathrm{^{15}NCC^{15}N}$, $\mathrm{HC^{15}N}$, and acetylene were minor products. The NMR data of the nitrogen-containing products are collected in Table I.

The NMR data of the ^{14}N- and ^{15}N-labeled compounds agree quite well; in view of the different conditions of the measurements, especially small temperature differences, it is not certain whether the occasional slight differences in chemical shifts are real, i.e., isotope shifts. The data are in good agreement with the structure of CNCN; in fact, both the isonitrile group and the nitrile group reveal their identity by rather typical values. The isonitrile group had already been identified for $\mathrm{C}^{14}N\mathrm{C}^{14}\mathrm{N}$;[2] this is now confirmed by the ^{15}N values ($\delta(^{15}\mathrm{N})$ = −233 ppm; $\delta(^{13}\mathrm{C})$ = 171.1 ppm). The nitrile group had previously been overlooked[2] due to the extremely broad signals (vide supra). In general, the nitrogen chemical shifts of nitriles are less shielded than those of isonitriles, the carbon chemical shifts however are more shielded;[10] $\mathrm{C^{15}NC^{15}N}$ fits into this picture. Compared to the shifts of NCCN, both nuclei of the *cyano* group of CNCN are more shielded. This might in part be a reflection of inductive substituent effects, since the *cyano* group (Hammet constant σ_m = 0.62) is substituted by another cyano group in NCCN but by a less electron-withdrawing *isocyano* group (σ_m = 0.48)[24] in CNCN. The nitrogen chemical shift of the *isocyanide* of $\mathrm{C}N\mathrm{CN}$ is more shielded than those of other isocyanides (δ = −181 to −218 ppm[25]). This can be due to the anisotropy effect of the cyano group. This effect is known to shield in particular nuclei which reside in the interior of di- and polyacetylenes;[29] it probably also contributes to the shielding of $\mathrm{NCC}N$ ($\delta(^{13}\mathrm{C})$ = 96.3 ppm) relative to that of $\mathrm{MeC}N$ ($\delta(^{13}\mathrm{C})$ = 117.7 ppm[29]).

Scheme IV



11 12 13 14 15

(Mes'= 2,4,6- tri-tert- butylphenyl)

Table II. Chemical Shift Values of the Exocyclic Double Bond Systems C═X in **1**, **4**, and **11–14**[a]

compd	X	$\delta(^{13}\mathrm{C})$	$\delta(^{15}\mathrm{N})$	$\delta(^{31}\mathrm{P})$	$\Delta\delta(\mathrm{X})$[b]
1	NR	181.5	−52.8		
4	NR	180.2	−121.8		−69.0
11[c]	$\mathrm{CH_2}$	156.6 [C(3)] 100.6 [(C4)]			
12[c]	$\mathrm{CH_2}$	177.1 [(C7)] 78.9 [(C8)]			−21.7[d]
13[e]	PMes*	193.7		189.9	
14[e]	PMes*	207.4		89.9	−100.0

[a] δ [ppm] relative to TMS (^{13}C), $\mathrm{MeNO_2}$ (^{15}N), 85% $\mathrm{H_3PO_4}$ (^{31}P). [b] $\Delta\delta(\mathrm{X}) = \delta(\mathrm{X}$, norbornadiene) − $\delta(\mathrm{X}$, quadricyclane). [c] Reference 30. [d] $\Delta\delta$ for the exocyclic carbons: $\delta(\mathrm{C(8)}) - \delta(\mathrm{C(4)})$. [e] Reference 31.

The coupling constants of $\mathrm{C^{15}NC^{15}N}$ are also informative. The isonitrile carbon has two identical couplings to nitrogen-15: $^1J = {}^3J$ = 5.8 Hz. The nitrile carbon, on the other hand, has two very different one-bond couplings: ^1J = 17.4 and ^1J = 48.9 Hz. Comparison of the smaller coupling with that of $\mathrm{^{15}NCC^{15}N}$ (^1J = 20.2 Hz) and $\mathrm{HC^{15}N}$ (^1J = 17.4 Hz) leads to its assignment to the nitrile bond; this is also in line with other nitrile couplings which normally fall into the range of 15–20 Hz.[26] This leaves the large coupling for the central C–N bond. We have at present no satisfactory explanation for this unusually large value. Formally, both carbon and nitrogen are sp-hybridized, but this holds for the terminal carbon–nitrogen bonds as well. According to a relation proposed by Binsch et al.[27] (eq 6) one calculates an *average* hybridization for both carbon and nitrogen in the central bond of $\mathrm{sp}^{0.6}$.

$$|^1J(^{13}\mathrm{C}^{15}\mathrm{N})| = 0.0125(\%\mathrm{s_c})(\%\mathrm{s_n}) \qquad (6)$$

However, such a simple analysis relating coupling to s-character, appropriate for most C–N single bonds, is probably not correct for CNCN.[28] In the first place, even though the central N–C bond is usually formulated as a single bond in normal Kekulé structures, theoretical calculations indicate a higher bond order.[8,12] Secondly, lone pairs may contribute to the Fermi contact in a sense opposite to that of the normal one-bond effect.[29] Finally, in a molecule with the unusual bonding situation of CNCN, one cannot exclude that the normally dominant Fermi contact term is overruled by orbital and spin dipolar terms as is the case for C≡N bonds.[29] All these aspects are applicable to CNCN, so that an interpretation must wait for a detailed theoretical analysis. Nevertheless, in a qualitative sense, the large central N–C coupling reflects in all likelihood the high s-contribution to this bond. It may be relevant to point out that the large coupling in the central C–N bond (J = 48.9 Hz) is brought back to normal proportions on bromination of $\mathrm{C^{15}NC^{15}N}$ to **7** (J = 9.4 Hz).

Finally, an interesting correlation emerges from a comparison of the nitrogen-15 chemical shifts of **1** and **4** with NMR data of **11–14** (Scheme IV, Table II). While the *carbon* atoms of the exocyclic double bond (*C*═X) differ little between the quadricyclane/norbornadiene couples (**4**/**1**) or show a slight trend to become deshielded (**11**/**12**, **13**/**14**), there is a clear tendency of

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the exocyclic *atom X* (**4**, **1**, X = N; **11**, **12**, X = C; **13**, **14**, X = P) to be considerably more shielded in the norbornadiene systems **1**, **12**, and **14**. This can be rationalized by homoconjugative electron donation from the norbornadiene system to the exocyclic double bond as indicated in the resonance structure **15**. Unfortunately, it is not possible to draw quantitative conclusions from the magnitude of the chemical shift differences $\Delta\delta$ for two reasons: the effect of charge density on the chemical shift is not known for all the nuclei and variation in the paramagnetic contribution to δ may blur the picture. Nevertheless, the qualitative trend seems to be that homoconjugation increases for C=X in the direction C=C (apolar) < C=N (polar) < C=P (unstable double bond in **14** vs no double bond in **15**; double bond rule[31]).

Experimental Section

^1H and ^{14}N NMR spectra were recorded on a Bruker WM 250 spectrometer at 250.13 MHz for ^1H and at 18.07 MHz for ^{14}N; ^{13}C and ^{15}N NMR spectra and the ^{14}N NMR spectrum of **7** were recorded on a Bruker MSL 400 spectrometer at 100.63 MHz for ^{13}C, at 28.90 MHz for ^{14}N, and at 40.56 MHz for ^{15}N. Mass spectra were recorded on a Finnigan Mat 90 (HRMS) and on a 5970 Hewlett Packard mass selective detector connected to a Hewlett Packard 5890 gas chromatograph equipped with a 24-m Cp silica 19 capillary column (GC/MS). $[^{15}N_2]$Hydrazine sulfate was purchased from MSD Isotopes.

$[^{15}N_2]$Quadricyclanone Azine (4). Sodium methoxide (5.2 mL of a 0.73 M solution in methanol) was slowly added to a refluxing suspension of $[^{15}N_2]$hydrazine sulfate (250 mg, 1.9 mmol) in methanol (95 mL). This suspension was stirred at 60 °C for 9 h. After filtration, to remove Na_2SO_4, quadricyclanone (430 mg, 4.05 mmol) was added, and the reaction mixture was stirred for 5 h at 50 °C. The reaction mixture was concentrated and recrystallized from methanol to yield **4** as white crystals (280 mg; 70% yield): ^1H NMR ($CDCl_3$) δ 2.34–2.29 (m, *E*-bridgehead C*H*, 1 H), 2.16–2.08 (m, C*H*, 4 H), 1.65–1.61 (m, *Z*-bridgehead C*H*, 1 H); ^{13}C NMR ($CDCl_3$) δ 181.5 (dd, *C*=^{15}N, $^1J(^{13}C^{15}N) = {}^2J(^{13}C^{15}N) = 4.5$ Hz), 22.5 (ddd, *E*-bridgehead *C*, $^2J(^{13}C^{15}N) = {}^3J(^{13}C^{15}N) = 6.8$ Hz, $^1J(^{13}CH) = 175$ Hz, 20.3 (d, *E*-*C*H, $^1J(^{13}CH) = 180$ Hz), 18.5 (d, *Z*-CH, $^1J(^{13}CH) = 180$ Hz), 17.7 (d, *Z*-bridgehead *C*, $^1J(^{13}CH) = 179$ Hz); ^{15}N NMR ($CDCl_3$) δ −121.8; HRMS calcd for $C_{14}H_{12}{}^{15}N_2$ 210.0914, found 210.0907.

$[^{15}N_2]$Norbornadienone Azine (1). The synthesis of (labeled) **1** was performed from **4** exactly as described for the unlabeled series in ref 2. **1**: ^1H NMR ($CDCl_3$) δ 6.89–6.86 (m, *E*-=C*H*, 2 H), 6.80–6.77 (m, *Z*-=C*H*, 2 H), 4.47 (br s, *E*-bridgehead C*H*, 1 H), 4.01 (br s, *Z*-bridgehead C*H*, 1 H); ^{13}C NMR ($CDCl_3$) δ 180.2 (dd, *C*=^{15}N, $^1J(^{13}C^{15}N) = {}^2J(^{13}C^{15}N) = 3.3$ Hz), 139.7 (d, *E*-=*C*H, $^1J(^{13}CH) = 178$ Hz), 138.5 (d, *Z*-=*C*H, $^1J(^{13}CH) = 179$ Hz), 51.6 (td, *E*-bridgehead *C*H, $^2J(^{13}C^{15}N) = {}^3J(^{13}C^{15}N) = 5.2$ Hz, $^1J(^{13}CH) = 153$ Hz), 47.6 (d, *Z*-bridgehead *C*H, $^1J(^{13}CH) = 156$ Hz); ^{15}N NMR ($CDCl_3$) δ −52.3; HRMS calcd for $C_{14}H_{12}{}^{15}N_2$ 210.0914, found 210.0915.

$[^{15}N_2]$Isocyanogen. Flash vacuum thermolysis experiments were performed in an aluminum oxide tube with a length of 25 cm and a diameter of 15 mm.[32] After the pyrolysis tube two U-tubes were placed after one another. It was connected to a high vacuum line described by Vreugdenhil and Blomberg.[33] The pressure (measured near the pump) was 10^{-6} mbar. In a typical run **1** (130 mg, 0.62 mmol) was sublimed into the hot zone during a period of ca. 36 h, with a sublimation furnace (Büchi GKR50) to heat the sample bulb (50 °C). The pyrolysate was trapped in the first U-tube which was cooled to −196 °C. When the pyrolysis was finished, the liquid nitrogen was replaced by a pentane bath which was held at −130 °C to −110 °C by addition of liquid nitrogen. The volatile products were distilled into the second U-tube which was kept at −196 °C. The yield was assumed to be 60%, the value reported in ref 2. The condensed $C^{15}NC^{15}N$ could be stored in liquid nitrogen: NMR spectra, see Table I; MS (70 eV) m/z (%) 54(100), 39(3), 27(13), 24(13); this pattern is practically identical[2] with that of $C^{14}NC^{14}N$ with the expected mass differences; HRMS calcd for $C_2{}^{15}N_2$ 54.0002, found 53.9972.

$[^{15}N_2]$*N*-Cyanodibromoformaldimine (7). Bromine (0.5 mmol, 25 μL) was added at −100 °C to a solution of $[^{15}N_2]$isocyanogen (0.35 mmol) in Et_2O-d_{10}. This solution was slowly warmed up to −20 °C to give a solution of **7**: ^{13}C NMR (Et_2O-d_{10}) δ 129.7 (dd, *C*=^{15}N, $^1J(^{13}C^{15}N) = 5.1$ Hz, $^3J(^{13}C^{15}N) = 2.1$ Hz), 109.0 (dd, *C*^{15}N, $^1J(^{13}C^{15}N) = 15.1$ Hz (cyano-*N*), $^1J(^{13}C^{15}N) = 9.4$ Hz (imino-*N*)); ^{15}N NMR (Et_2O-d_{10}) δ −95.3 (d, $^2J(^{15}N^{15}N) = 4.0$ Hz), −131.5 (d, $^2J(^{15}N^{15}N) = 4.0$ Hz). The solvent was evaporated in vacuo at −20 °C, resulting in a colorless crystalline product which melted just below room temperature HRMS (measured with a direct inlet system keeping the temperature of the sample at −20 °C) calcd for $C_2{}^{15}N_2{}^{79}Br^{81}Br$ 213.8348, found 213.8326. Both in crystalline form and in solution **7** polymerized slowly at room temperature to yield a colorless compound, insoluble in organic solvents (pentane, diethyl ether, chloroform).

Reaction of the Pyrolysate of (Unlabeled) 1 with Bromine. The pyrolysate obtained from unlabeled **1** (330 mg, 1.6 mmol), estimated to contain 1 mmol of CNCN (after sublimation; see $[^{15}N_2]$isocyanogen) Br_2 (160 mg, 1 mmol), and $CDCl_3$ (3.5 mL) were condensed in vacuo (10^{-3} mbar) to a flask which was cooled with liquid nitrogen. This mixture was warmed in an acetone/dry ice bath to −70 °C and stirred for several hours; then it was further warmed to −20 °C. **6**: GCMS (GC retention time 8.10 min) MS (70 eV) *m/z* (%) 372 (17, $M^{\bullet+}$), 291 (86), 186 (100), 105 (35). **6** (independently synthesized by the method described in ref 14): GCMS (GC retention time 8.07 min) MS (70 eV) *m/z* (%) 372 (17, $M^{\bullet+}$), 291 (65), 186 (68), 105 (43). **7**: GCMS (GC retention time 4.19 min) MS (70 eV) *m/z* (%) 212 (9, $M^{\bullet+}$), 131 (100), 105 (6).

Pyrolysis of Unlabeled CNCN. In a typical run, the sublimed pyrolysate from unlabeled **1** (330 mg; 1.6 mmol), estimated to contain 1 mmol CNCN (vide supra), was sublimed by "warming" with a pentane/liquid nitrogen bath (ca. −130 °C) into the hot zone (*T* = 500 °C or 750 °C) during a period of 3 h. The products were trapped in a U-tube cooled at −196 °C. After the pyrolysis, they were distilled as described earlier (see $[^{15}N_2]$isocyanogen); no residue remained after the sublimation. All products were dissolved in diethyl ether. The ratio of CNCN/NCCN was determined by ^{13}C NMR spectroscopy (the ^{13}C NMR spectra were calibrated by the ^{15}N NMR spectrum).

Reaction of 6 with Triphenylphosphine. At room temperature **6** was sublimed in vacuo over a vertical column of triphenylphosphine with a length of 20 cm and a diameter of 15 mm at room temperature. The triphenylphosphine at the top of the column was immediately covered with a brownish-black layer. The volatile products were trapped in a U-tube which was cooled at −196 °C. They were analyzed by mass and photoelectron spectroscopy and gave spectra as expected for a mixture of NCCN and HCN[21] (see supplementary material).

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Supplementary Material Available: ^{15}N NMR spectra of $[^{15}N_2]$isocyanogen and $[^{15}N_2]$-*N*-cyanodibromoformaldimine (**7**), GCMS of the products obtained from the reaction of the pyrolysate of unlabeled **1** with bromine and GCMS of **6**, ^{13}C NMR spectra of unlabeled CNCN and its pyrolysate at 500 °C and 750 °C, and mass spectrum and photoelectron spectrum of the products obtained from the reaction of **6** with triphenylphosphine (13 pages). Ordering information is given on any current masthead page.

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