Nitrile Ylides: Allenic and Propargylic Structures from Pyrazinylnitrenes.

Experimental and Theoretical Characterization

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13   **15 Allenic**   **15 Propargylic**
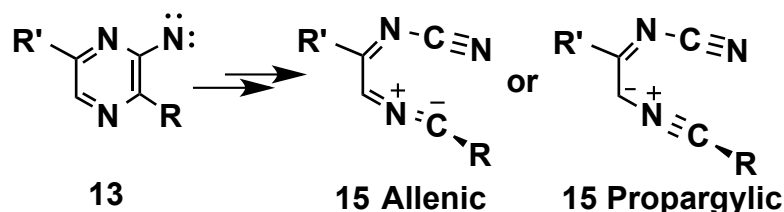
Abstract: Matrix photolysis of 2-pyrazinyl azides/tetrazolo[1,5-*a*]pyrazines generates nitrile

ylides **15** via pyrazinylnitrenes **13** and triazacycloheptatetraenes **14**. The nitrile ylides **15** are

characterized by IR spectroscopy in conjunctions with harmonic and anharmonic vibrational

frequency calculations. The nitrile ylides exist in the matrices in the *Z,Z*-conformations in which

they are born. Substitution on the nitrile carbon of nitrile ylides has a profound effect on their

structure. Even different conformers of the same molecule can have differences up to 200 cm^{-1} in

the IR absorptions of the ylide moieties. Nitrile ylides **15a** and **15b** (R = H or Cl, R' = H) have

allenic structures (**15** Allenic). Nitrile ylide **15c** (R = R' = CH$_3$) has a distinctly propargylic

structure (**15** Propargylic) in the experimentally observed *Z,Z*-conformation.

Introduction

Computational work by Caramella and Houk[1] demonstrated that nitrilium betaines, in particular

nitrile imines R-CNN-R'**1** and nitrile ylides R-CNCR$_2$' **2** are "floppy" molecules which can exist

in either propargylic (P) or allenic (A) structures (Chart 1). Meanwhile, many nitrile imines have

been isolated and investigated by X-ray crystallography, which has confirmed a variety of

structures ranging from propargylic to allenic.[2] Infrared spectroscopy is a valuable tool for

distinguishing the two forms, propargylic nitrile imines absorbing in the nitrile region, 2200-

2300 cm^{-1}, and allenic nitrile imines absorbing at lower frequencies, ca. 2000-2100 cm^{-1}. This

allows the experimental characterization of unstable nitrile imines under matrix-isolation

conditions aided by calculations of structures and infrared absorption frequencies.[3] A third class

of carbenic nitrilium betaines[4] (**1C**, **2C** Chart 1) is predicted to exist. The carbenic nitrile imines

are predicted not to show any characteristic absorptions in the cumulene region and only weak

absorptions in the 1600-1900 cm^{-1} region.[5]

Chart 1. Limiting Structures of Nitrile Imines and Nitrile Ylide
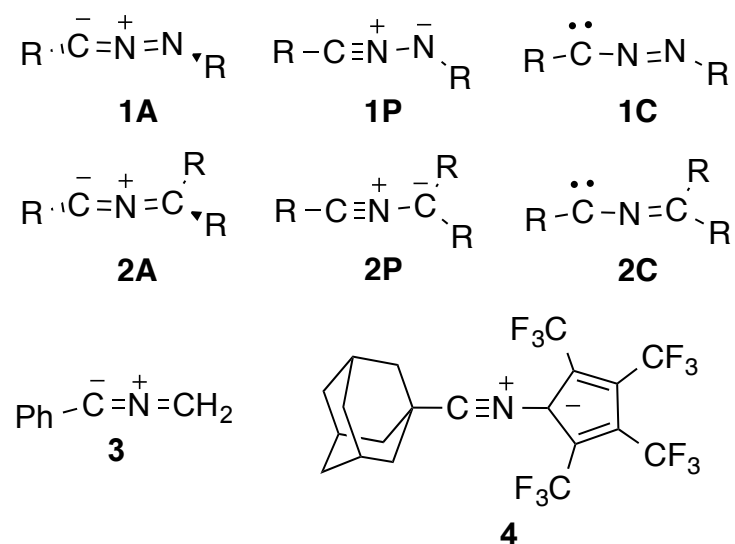
Similar behaviour can be expected of nitrile ylides **2** (Chart 1), and a wide range of IR

absorptions, from ca. 1900 to ca. 2300 cm^{-1} has been observed.[2] Thus, formonitrile methylide H-

C(-)=N(+)=CH$_2$,[6] benzonitrile methylide,[7] Ph-C(-)=N(+)=CH$_2$ **3** and acetonitrile *N*-(1-naphthyl)methylide[8] Me-C(-)=N(+)=CH-Np absorb at 1915, 1926 and 1946 cm^{-1}, respectively, in argon matrices, and all are assigned allenic structures (**2A**). In contrast, the stable nitrile ylide **4**, which has been characterized by X-ray crystallography absorbs at 2210 and 2323 cm^{-1} and is assigned a propargylic structure (**2P**).[9] It is emplasized that all nitrile betaines always have resonance structures that correspond to each of the three forms, allenic, propargylic, and carbenic. But one of these forms may dominate in the ground state structure, and the molecule may then exist in either a single-well potential with predominant allenic, propargylic, or carbenic structure, or it may exist in a double-well potential with a (small) barrier separating two geometrically distinguishable forms.

Generally, it is assumed that electronegative substituents on the trigonal carbon atom will favour a propargylic structure by encouraging a higher electron density on that carbon. This is also seen in the bis-trifluoromethyl nitrile ylide **7**, which is formed by either flash vacuum thermolysis (FVT) of the oxazaphosphole **5** or by photolysis of the azirene **6** in argon matrix and absorbs in the nitrile region at 2250 cm^{-1} (Eq. 1).[10] Our calculations at the B3LYP/6-31G* level reveal that there are two stable minima for this compound, an allenic form absorbing at 2021/2022 cm^{-1} (different conformers) and a propargylic form absorbing at 2321 cm^{-1}, and a very small energy barrier separates the two. Clearly, the propargylic form **7** is stable and observed in the matrix isolation experiment.
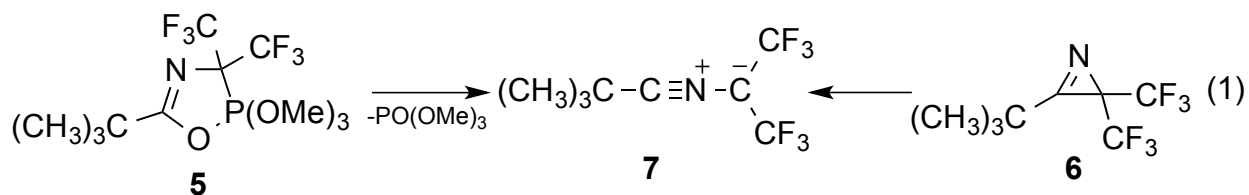
We have developed a unique method for generating nitrile ylides by ring opening of nitrenes or carbenes under matrix photolysis conditions (Scheme 1).[11] This reaction can take place whenever there is a *meta*-relationship between a ring nitrogen atom and the carbene or nitrene center. Thus, 3-pyridylcarbene **8a** and 3-pyridylnitrene **8b** undergo ring opening to the nitrile ylides **9**,[12] and 2-quinoxalinylnitrenes **10** afford nitrile ylides **11**[13] (for simplicity the seven-membered aza-, diaza-, and triazacycloheptatetraenes also involved in these reactions are omitted in Scheme 1).

Scheme 1. Ring Opening Reactions
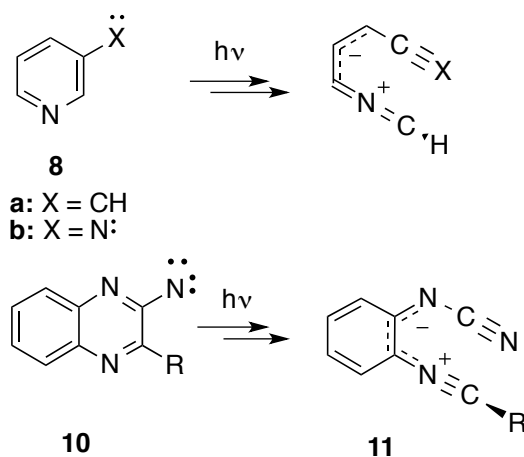
In this paper we wish to investigate the possibility of existence of closely related, and distinguishable, allenic and propargylic nitrile ylides, where substituent effects cause the predominance of one or the other structure. We report examples of both allenic and propargylic structures **15** formed by ring opening of pyrazinylnitrenes **13** and investigated by matrix isolation IR spectroscopy as well as calculations of their structures and harmonic and anharmonic vibrational frequencies.

Results and Discussion

1. The Unsubstituted Cyanimino Nitrile Ylide 15a. Pyrazinylnitrenes **13** undergo ring expansion to triazacycloheptatetraenes **14** when photolytically generated from the corresponding

tetrazoles **12T** or azides **12A** in low temperature argon matrices (Scheme 2). In the unsubstituted

parent compound, calculations at the G3(MP2) and CASPT2 levels indicate a modest barrier of

ca. 7 kcal/mol toward ring opening of **14a** to the delocalized nitrile ylide **15a**.[14] Accordingly,

14a was only observable during the first few minutes of photolysis. The nitrile ylide **15a** is

predicted to undergo very facile ring closure to 1-cyanoimidazole **16a** (2.5 kcal/mol barrier) as

well as a 1,7-hydrogen shift to isocyanovinylcarbodiimide **17a** (9.9 kcal/mol barrier), which

make it difficult to observe this ylide.[14]

**Scheme 2**. Triazacycloheptatetraenes and Nitrile Ylides from Pyrazinylnitrenes
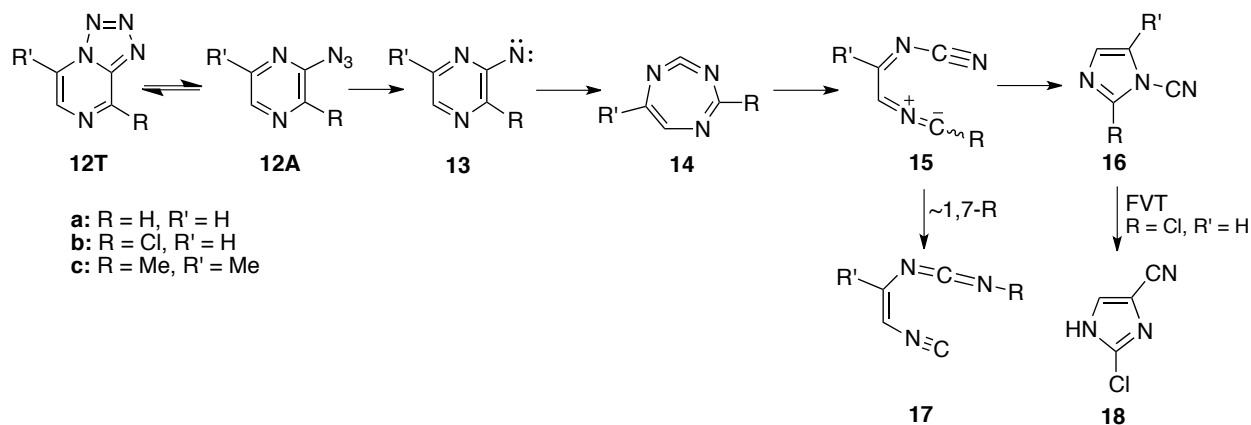
All the nitrile ylides described in this paper can exist as several different conformers, but

the *Z,Z*-conformers shown in Scheme 2 are predicted to be formed first in the matrix photolyses

of the pyrazinylnitrenes. Therefore, we present the structures of the *Z,Z*-conformers of **15a,b,c** in

Figure 1. The structures of the *Z,Z*-, *Z,E*-, and *E,E*-conformers are defined in Chart 2, and their

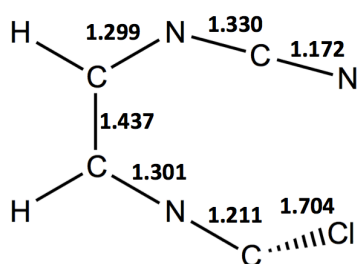relative energies are reported in the Supporting Information.

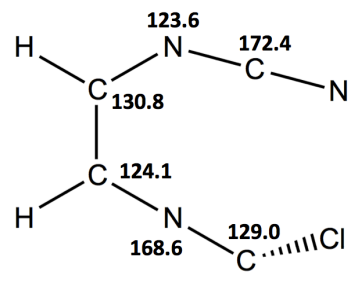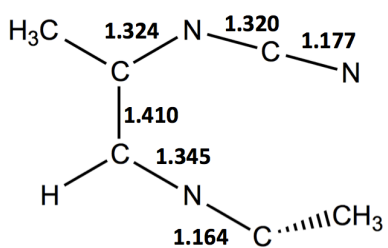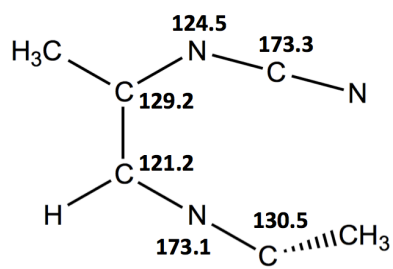**Chart 2**. Principal conformers of nitrile ylides **15**.
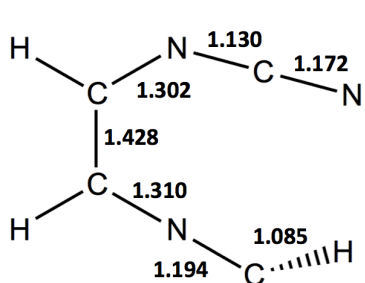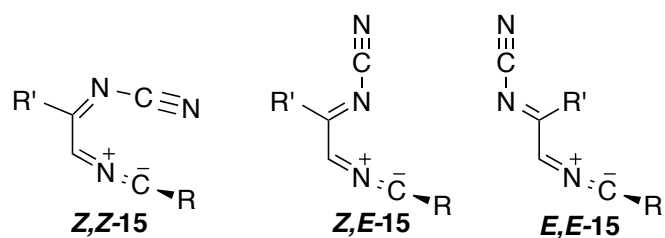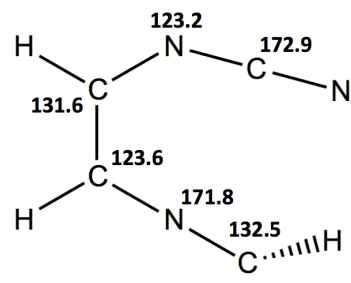
Figure 1. Calculated structures of the *Z,Z*-conformers of **15a,b,c** (B3LYP/6-31G*)

Table 1. Key Harmonic and Anharmonic Wavenumbers for **Z,Z-15a**,**b**,**c**

Z,Z-15a		
Mode Description[a]	ω (ν) cm$^{-1\,b}$	I (km/mol) [b]
$\nu8$: δ_{CH}	1391 (1388)	26 (20)
$\nu7$: δ_{CH} + ν_{CC}	1420 (1410)	73 (55)
$\nu6$: $\nu_{s,\,CN}$ + δ_{CH}	1579 (1573)	245 (124)
$\nu5$: $\nu_{as,\,CN\,(CNC)}$	2010 (2001)	298 (281)
$\nu4$: $\nu_{as,\,CN\,(NCN)}$	2192 (2197)	70 (66)
Overtone and combination bands		
$2\nu10$	(2051)	(12)
$\nu14$ + $\nu9$	(2067)	(15)
$\nu15$ + $\nu8$	(2037)	(10)
$\nu16$ + $\nu7$	(2053)	(11)
$\nu16$ + $\nu8$	(2033)	(20)
$\nu9$ + $\nu20$	(1618)	(31)

Z,Z-15b		
$\nu8$: δ_{CH}	1226 (1222)	36 (33)
$\nu6$: δ_{CH} + ν_{CC}	1425 (1418)	149 (129)
$\nu5$: $\nu_{s,\,CN}$ + δ_{CH}	1574 (1567)	152 (149)
$\nu4$: $\nu_{as,\,CN\,(CNC)}$	1932 (1918)	135 (123)
$\nu3$: $\nu_{as,\,CN\,(NCN)}$	2188 (2194)	30 (27)
Combination band		
$\nu17$ + $\nu6$	(1947)	(15)

Z,Z-15c		
$\nu18$: δ_{CH}	1239 (1243)	80 (66)
$\nu17$: δ_{Me}	1353 (1344)	43 (35)
$\nu16$: δ_{Me}	1378 (1395)	10 (8)
$\nu15$: δ_{CH} + ν_{CC}	1409 (1402)	242 (209)
$\nu14$: δ_{Me}	1425 (1440)	13 (10)
$\nu11$: δ_{Me} + ν_{CC+CN}	1480 (1480)	42 (41)
$\nu10$: $\nu_{s,\,CN}$ + δ_{Me}	1537 (1536)	374 (366)
$\nu9$: $\nu_{as,\,CN\,(NCN)}$	2169 (2175)	183 (166)

$\nu 8: \nu_{as, CN (CNC)}$	2279 (2216)	172 (127)
Combination bands		
$\nu 25 + \nu 15$	(2314)	(11)
$\nu 24 + \nu 19$	(2221)	(10)

[a] δ = rocking, ν = stretching. [b] The values in parentheses are the anharmonic wavenumbers (ν) or intensities (I).
See Supporting Information for a full set of data for all conformers.

Key harmonic and anharmonic vibrational frequencies for **Z,Z-15a**,**b**,**c** and their spectroscopic assignments are presented in Table 1. The full vibrational data for all the conformers (Chart 2) are collected in the Supporting Information. From the calculated structure of the *Z,Z*-conformer of **15a** (Figure 1a), and the nature of the vibrational frequencies in Table 1, it is concluded that compound **15a** has a typically allenic structure of the CNC ylide moiety, with C=N and N=C bond lengths of 1.31 and 1.19 Å indicating double-bond character, and the calculated harmonic vibrational frequency of the CNC moiety is 2010 cm^{-1}. This is the strongest vibrator in the cumulene region (298 km/mol). The stretching of the nitrile group of the N-CN moiety is predicted at 2192 cm^{-1} as a much weaker vibrator (70 km/mol). The corresponding anharmonic frequencies are 2001 (NCN) and 2197 (NCN) cm^{-1}. CCSD(T) calculations lower the frequencies by ca. 5% (Table 1). Experimental absorptions seen during the first few minutes of photolysis at 222 nm at 2043 and 2139 cm^{-1} are in agreement, but, as reported previously, the 1,7-H shift plus cyclization cause rapid isomerization to the carbodiimide **17a** and 1-cyanoimidazole **16a**.

2. The *C*-Chloro Nitrile Ylide 15b. 8-Chloro-tetrazolo[1,5-*a*]pyrazine **12bT** was prepared according to the method of Stanovnik et al., who reported that this compound exists exclusively in the tetrazole form in chloroform solution.[15] When **12bT** is sublimed and co-deposited with Ar at 28 K, the resulting IR spectrum recorded at 10 K shows the presence of both tetrazole (**12bT**) and azide (**12bA**). Sublimation of **12bT** through an oven at 270 ^{o}C

afforded pure azide **12bA**, which featured strong absorptions at 1391 and 2139 cm^{-1} in the Ar

matrix at 10 K. This allows a differentiation of the bands due to azide and tetrazole as shown in

Figure S1 (Supporting Information). Irradiation of the Ar matrix at 222 nm for 6 minutes caused

the decomposition of **12bA** and development of new, strong bands at 638, 648, 1011, 1423,

1558, 1968 and 2269 cm^{-1} and weaker bands at 2180 and 2269 cm^{-1} (Figure 2).
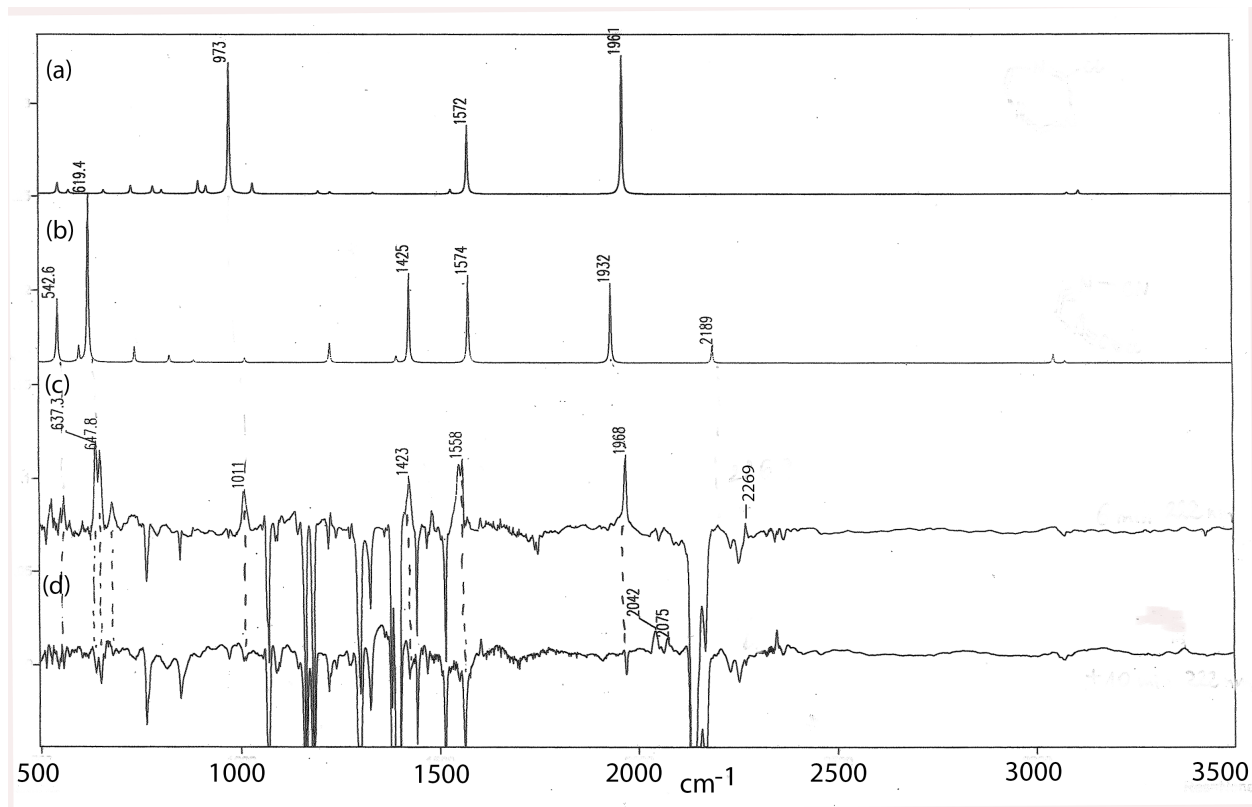
Figure 2. (a) Calculated IR spectrum of chloro-azacycloheptatetraene **14b**; (b) calculated

IR spectrum of chloro-nitrile ylide **15b**, both at the B3LYP/6-31G* level (wavenumbers scaled

by 0.9613). (c) Experimental spectrum, (Ar, 10 K) after photolysis of **12bT/12bA** at 222 nm for

6 min. The negative bands are due to **12bT/12bA**. (d) Bleaching of the primary photoproducts on

further irradiation at 222 nm for 10 min; formation of new bands at 2042 and 2075 cm^{-1}.

The 2269 cm^{-1} band is assigned to the nitrile group 2-chloro-1-cyanoimidazole **16b**. When **12bT/12bA** is photolysed with brodband irradiation from the high-pressure Hg/Xe lamp from the beginning, **16b** is obtained quantitatively (Figure S2). The calculated infrared spectrum of **16b** at the B3LYP/6-31+G* level is in excellent agreement with experiment (Figure S2). Furthermore, proof of structure is given by the isolation of 2-chloro-4-cyanoimidazole **18** following FVT of **12b** at 500 $^{\circ}$C; **18** can be formed exothermically in a series of 1,5-shifts of CN and H with an overall calculated activation barrier of ca. 46 kcal/mol (Figure 3). Such barriers are readily accessible by FVT at 500 $^{\circ}$C.
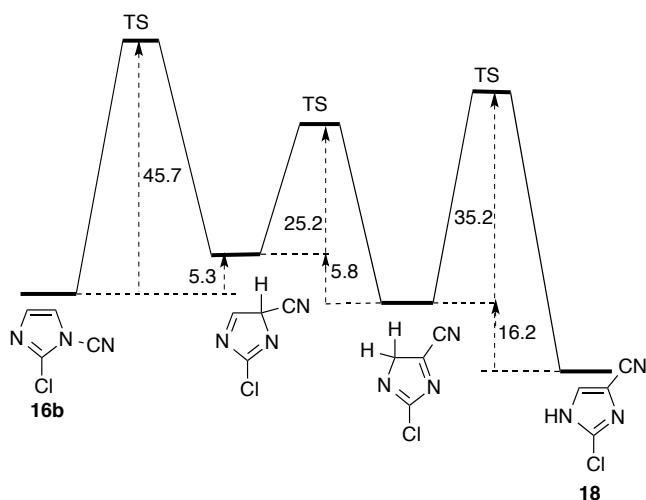
Figure 3. Calculated thermal activation barriers (kcal/mol) for 1,5-CN and 1,5-H shifts in 2-chlorocyanoimidazoles (B3LYP/6-31+G*).

The calculated energy profiles for the rearrangements of **14b** to **15b**, of **15b** to **16b**, and of **15b** to *N*-chloro-*N'*-(isocyanovinyl)carbodiimide **17b** are presented in the Supporting Information (Figures S4-S6).

Comparison with the calculated IR spectra of **14b** and **15b** indicates that both of these compounds are present in the matrix after brief photolysis at 222 nm (Figure 1c). Bands at 1011,

1558 (doublet band) and 1968 cm^{-1} correlate well with predictions for **14b**, and the bands at 550, 637/648, 1423, 1558 (doublet band), 1968 and 2190 correspond to the nitrile ylide **15b**. These values are in excellent agreement with calculations (Table 1) and are discussed below. Close inspection reveals that the peak at 1968 cm^{-1} is in fact a doublet at 1968-1970 cm^{-1} (Figure 3). Even after 20 annealing cycles to 35 K, the two peaks at 1968-1970 cm^{-1} did not merge into a single one at 1968 cm^{-1}. The loss of resolution after many annealing cycles is normal. In contrast, FVT of **13b** resulted in a single well-defined peak at 1968 cm^{-1}, which is ascribed to **14b** (Figure 3d). Therefore, we can conclude that the triazacycloheptatetraene **14b** and the chloro-nitrile ylide **15b** give rise to the two peaks at 1968 and 1970 cm^{-1} in the photolysis spectrum.
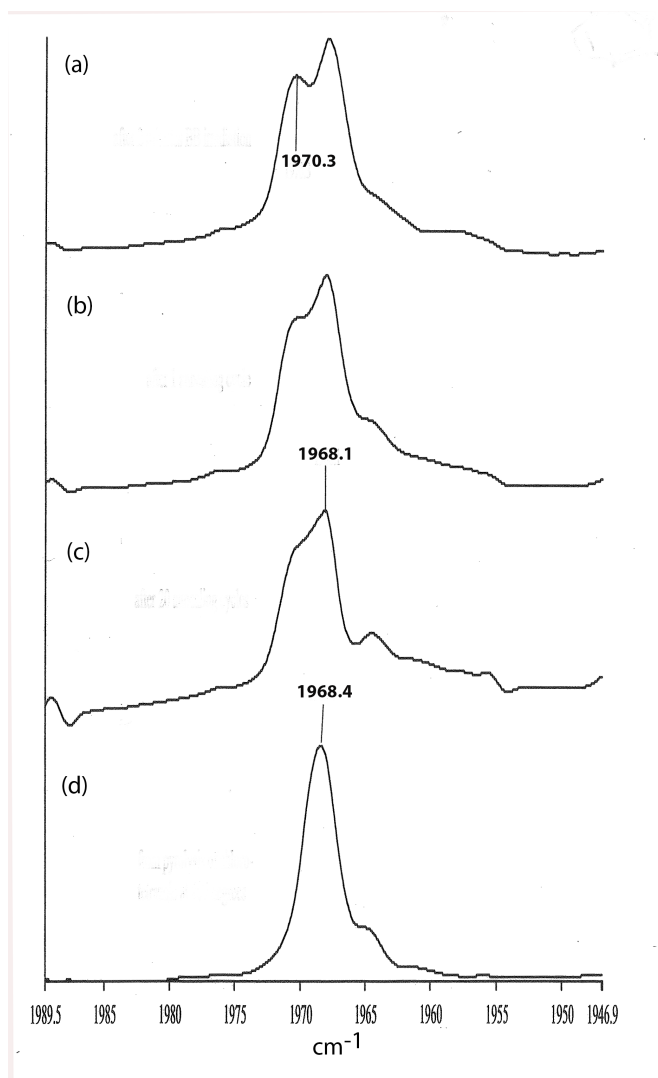
Figure 4. (a)-(c) The 1968-1970 cm^{-1} band from the photolysis of **13bT/13bA** in Ar matrix at 10 K (from Figure 1). (a) As obtained in Figure 1. (b) After 1 cycle of annealing to 30 K. (c) After 20 cycles of annealing to 30 K. (d) The 1968 cm^{-1} band obtained after FVT of **13bT/13bA** at 400 ^{o}C and isolation of the product in Ar matrix at 10 K.

Further photolysis at 222 nm for 10 min caused all the absorptions of **14b** and **15b** to disappear. Minor new peaks at 2042 and 2075 cm^{-1} (Figure 2) may be ascribed to the *N*-chloro-*N'*-(isocyanovinyl)carbodiimide **17b**, which has a predicted N=C=N vibration at 2059 cm^{-1} and

an isonitrile group absorption at 2097 cm^{-1}; this process is calculated to have a thermal activation barrier of 44 kcal/mol, but the reaction is predicted to be endothermic by ca. 12 kcal/mol (Figure S6, Supporting Information). Accordingly, only a minor amount of **17b** is formed.

The structure of the chloro-nitrile ylide **15b** is predicted to be allenic like the parent compound **15a** with C=N and N=C bond lengths of 1.30 and 1.21 Å for the initially-formed *Z,Z*-conformer (Figure 1b); the vibrational frequency at 1970 cm^{-1} is assigned to the CNC nitrile ylide moiety (calculated intensity 135 km/mol). The weak band at 2190 cm^{-1} assigned to the NCN moiety has a much lower calculated intensity of 30 km/mol (Table 1). The calculated anharmonic frequencies of these two moieties in the *Z,Z*-conformer are 1918 and 2194 cm^{-1}, respectively (Table 1). The other two conformers of **15b** have ylidic CNC absorptions at 1919-1882 cm^{-1} and nitrile NCN absorptions at 2194-2217 (Supporting Information). Thus, all the considered conformers of **15b** are predicted to have allenic structures of the nitrile ylide moieties.

3. The *C*-Methyl Nitrile Ylide 15c. A mixture of 2-azido-3,6-dimethylpyrazine **13cA** and 5,8-dimethyltetrazolo[1,5-*a*]pyrazine **13cT** was obtained by mild FVT (180-200 $^{\circ}$C) of the tetrazole and deposited in an Ar matrix at 20 K. Photolysis of this matrix at 254 nm for 3 min caused disappearance of the azide (2134, 1357, 1292 cm^{-1}) and development of new bands at 1251, 1420, 1521, 2156 and 2270 cm^{-1} in excellent agreement with calculations for the nitrile ylide **15c** (Figure 5). An additional peak at 1988 is assigned to the triazacycloheptatetraene **14c** The bands of both species were bleached on further irradiation at 310-390 nm for 7 min, when new signals due to 2,5-dimethyl-1-cyanoimidazole **16c** developed at 2261 and 1366 cm^{-1} (Figure 6). Compound **16c**[16] was also prepared by FVT of **13c**, and a matrix deposition of this material confirmed its identity with the product of photolysis at 310-390 nm (Figure S9).

Figure 5. (a) IR difference spectrum arising from the photolysis of **12cT/12cA** in Ar matrix at 254 nm for 10 min. Peaks at 2156 and 274 cm^{-1} are assigned to nitrile ylide **15c** in the Z.Z-conformation (**Z,Z-15c**). The small peak at 1988 cm^{-1} is ascribed to the triazacycloheptatetraene **14c**. Negative peaks are due largely to the azide **12cA**. (b) Calculated IR spectrum of nitrile ylide **Z,Z-15c** (B3LYP/6-31G*, wavenumbers scaled by 0.9613).
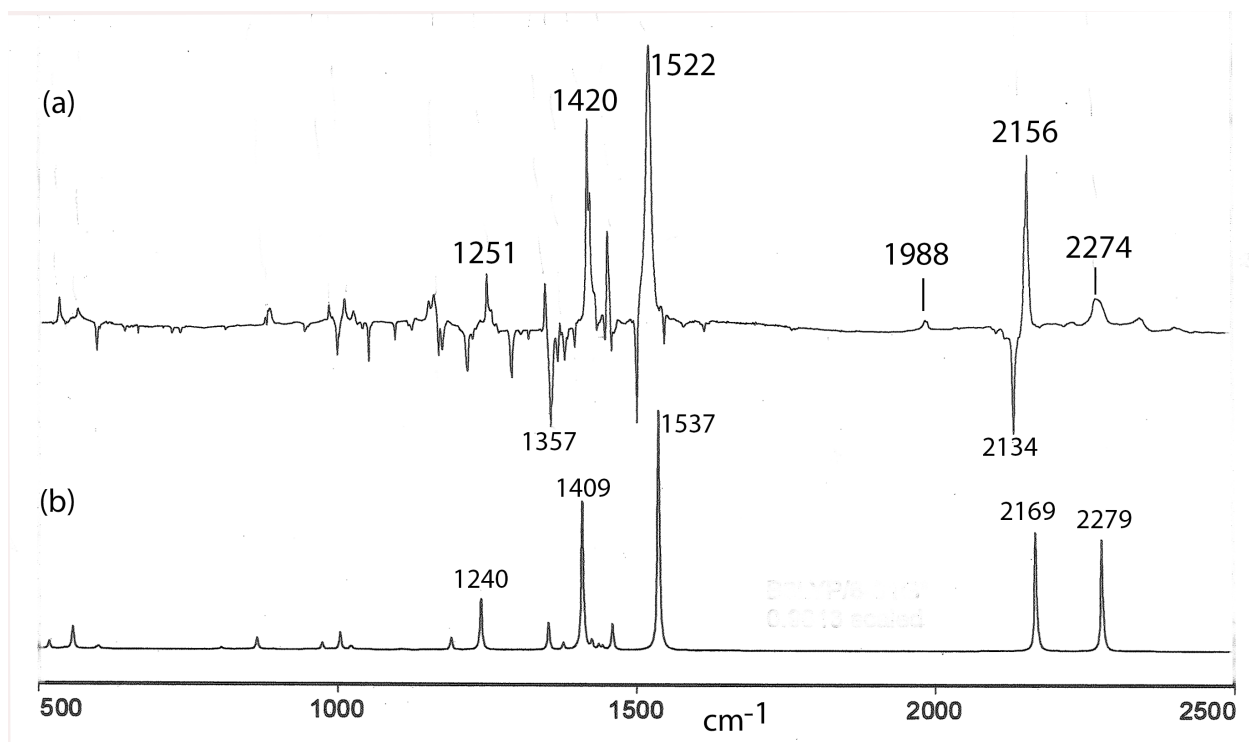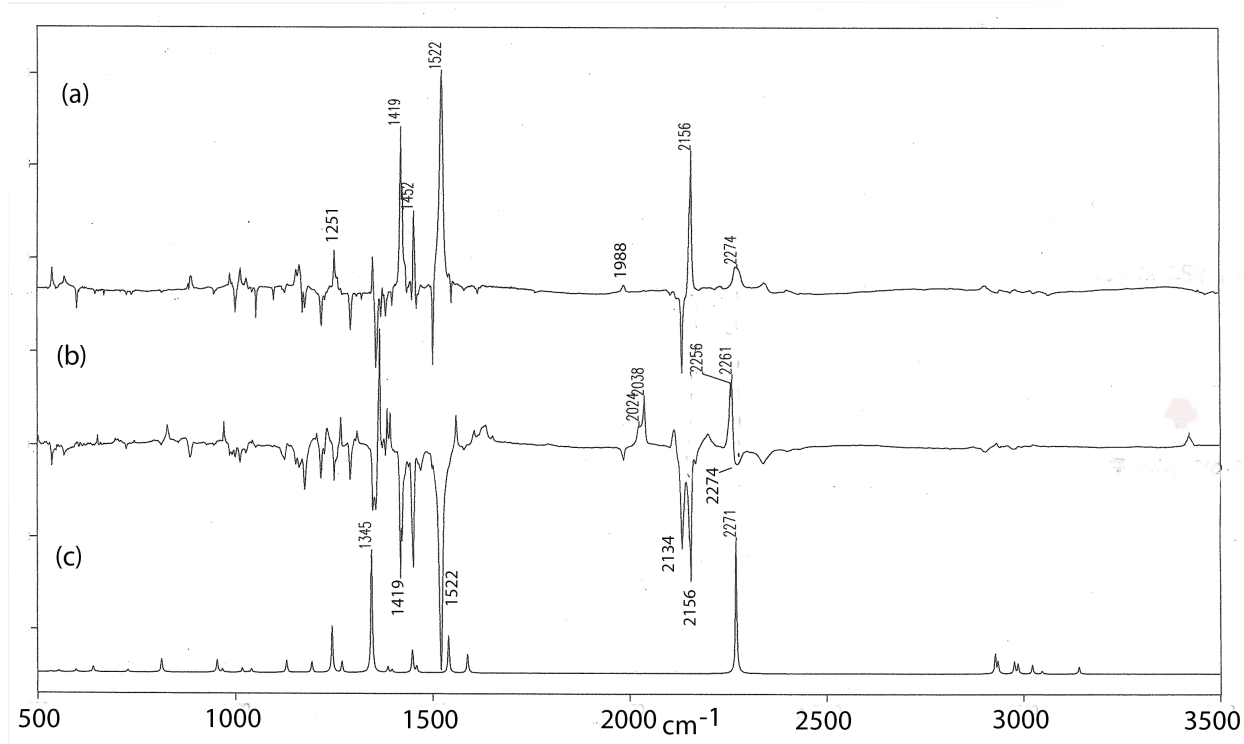
Figure 6. (a) IR difference spectrum arising from the photolysis of **12cT/12cA** in Ar matrix at 254 nm for 10 min; negative peaks are due to azide **12cA.** (b) Further photolysis at 310-390 nm for 7 min; the products **14c** and **15c** formed in (a) as well as the azide **12cA** are bleached. (c) Calculated IR spectrum of 2,5-dimethyl-1-cyanoimidazole **16c** (B3LYP/6-31G*, wavenumbers scaled by 0.9613).

The structure and IR spectrum of nitrile ylide **15c** is most interesting. The calculated C=N and N=C bond lengths are 1.35 and 1.16 Å, i.e. there is much more bond order alternation, and the NC bond has the character of a triple bond, although there is a N≡C-CH$_3$ angle of 130° (Figure 1c). The calculated harmonic vibrational frequencies of 2279 and 2169 cm^{-1} (anharmonic frequencies 2216 and 2175 cm^{-1}, respectively) are unusual in that it is the higher frequency that is due to the ylide moiety, NCN (Table 1). These data suggest that this nitrile ylide, **Z,Z-15c**, has a propargylic structure (Scheme 3). Notably, the ordering of the CNC and NCN frequencies is

inverted for the *Z,E*- and *E,E*-conformers, i.e. these conformers have allenic structures similar to those of **15a** and **15b** with IR frequencies of 2125 and 2024 cm^{-1}, respectively (see Supporting Infortmation). The lowest energy conformer of **15c** is the *Z,Z* form, **Z,Z-15c**, and this remains true at the CBS-QB3 computational level (see Supporting Information).

Scheme 3. Formation of the propargylic nitrile ylide *Z,Z*-**15c**

13c   14c   **Z,Z**-15c   16c
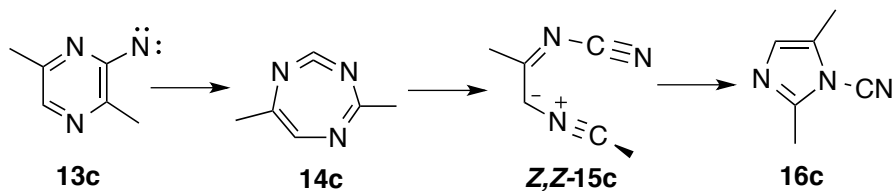
The clean IR spectrum of nitrile ylide **15c** (Figures 5 and 6) clearly demonstrates that this nitrile ylide retains the *Z,Z*-structure in which it was born from **14** or **15** (Scheme 3). By inference, this will also be the case for the other nitrile ylides **15a** and **15b**. The calculated energy barriers for interconversion of nitrile ylide conformers are 12-17 kcal/mol (Figure 7), which is high enough that individual conformers will be stable in the low-temperature matrices, but low enough that facile interconversion may take place at higher temperatures. In the cases of **15a** and **15b** the *Z,Z*-conformers are not the lowest energy, but in the case of **15c** it is. However, the energy differences are at most a couple of kcal/mol (Figure 7).
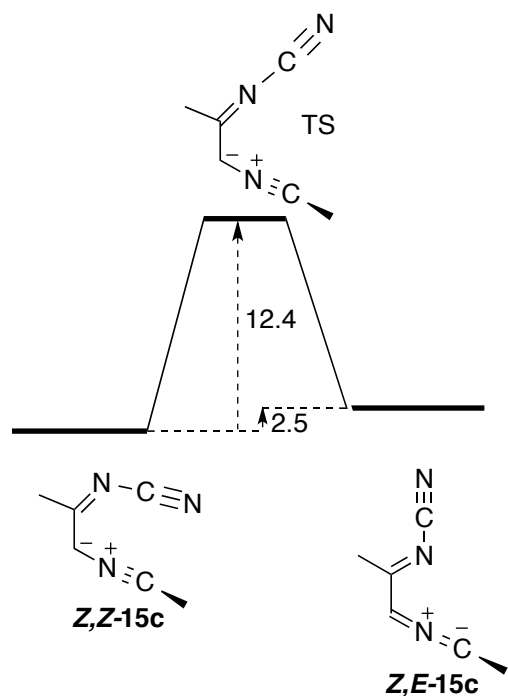
Figure 7. Interconversion of conformers of nitrile ylide **Z,Z-15c** and **Z,E-15c** at the CBS-QB3/6-31G* level (energies in kcal/mol). The corresponding barriers for **Z,Z-15a** and **Z,Z-15b** are 17.5 and 17.9 kcal/mol, respectively, and these reactions are exothermic by 0.6 and 0.7 kcal/mol, respectively (see Figure S7, Supporting Information).

The anharmonic frequency calculations predict overtones or combination bands in the range 1900-2300 cm^{-1} for all the nitrile ylides, but these bands are weak and cannot be confused with the strong, observed, CNC (ylide) and NCN (cyanamide) absorptions (see Table 1).

Conclusion and Outlook

Nitrile ylides **15a-c** are obtained by photolysis of 2-pyrazinyl azides/tetrazolo[1,5-*a*]pyrazines **12a-c** in Ar matrices. The ylides **15b-c** are characterized by their infrared spectra, which show excellent agreement with harmonic and anharmonic frequency calculations. The nitrile ylides

exist in the matrices in the *Z,Z*-conformations in which they are born. 1,3,5-Triazacyclohepta-1,2,4,6-tetraenes **14b-c** are formed and observed at the same time.

Substitution on the nitrile carbon of nitrile ylides has a profound effect on their structure. Even different conformers of the same molecule can have differences up to 200 cm^{-1} in the IR absorptions of the ylide moieties. The parent formonitrile cyanimidoylide **15a** and the cyanogen chloride analog **15b** have allenic structures. The acetonitrile cyanimidoylide **15c** has a propargylic structure in the *Z,Z*-conformation, whereas the corresponding *Z,E*- and *E,E*-conformers have allenic structures.[17] In an effort to understand the factors that influence nitrile ylide structures, we will report further calculations on a variety of substituted nitrile ylides to investigate how simple substitution on the nitrile-type carbon of nitrile ylides by methyl, *tert*-butyl, or phenyl groups may shift the preferred structure from allenic to propargylic. In several instances, both forms can coexist with small energy barriers separating them. We will also seek to determine the factors that may stabilize carbenic nitrile ylides.

Computational Method

B3LYP/6-31G* calculations were performed using the Gaussian 09 suite of programs.[18] The B3LYP method has been used extensively for calculations of species derived from carbene and nitrene rearrangements.[1,3,19] Transition state positions were checked with internal reaction coordinate calculations. In addition, energies of nitrile ylide conformers were also obtained at the CBS-QB3 level. Vibrational frequencies in the harmonic approximation were calculated at the B3LYP/6-31G* level. The anharmonic wavenumbers were obtained using the parallel variational multiple window configuration interaction software (P_VMWCI$_2$ algorithm).[20,21] These wavenumbers were obtained initially from a variational and perturbation-variation treatment

developed to solve the vibrational Schrödinger equation.[22] Scaling factors of 0.9613 and 0.9676 were used for harmonic and anharmonic wavenumbers, respectively.[3]

Experimental Section

Materials and General Methods. 2,3-Dichloropyrazine were purchased from Aldrich Chemical Company. 3-Chloro-2-hydrazinopyrazine,[23] 8-chlorotetrazolo[1,5-*a*]pyrazine[15] **12bT** (mp 107-107 $^{\circ}$C) and 5,8-dimethyltetrazolo[1,5-*a*]pyrazine[16] **12cT** were synthesized according to the literature. POCl$_3$ was distilled under vacuum before use. DMF was dried by stirring overnight with CaH$_2$, then distilling under vacuum from MgSO$_4$. Diethyl ether was dried from sodium benzophenone ketal. The apparatus used for matrix isolation, analytical and preparative thermolyses were as previously described.[24] Tetrazoles/azides **12T/12A** were sublimed into the apparatus in a flow of Ar. Photolysis used a 1000 W high-pressure Hg/Xe lamp, a 75 W low pressure Hg lamp (254 nm), or an excimer laser lamp operating at 222 nm (25 mW/cm^2).

Photolysis of 8-Chlorotetrazolo[1,5-a]pyrazine 12bT/2-azido-3-chloropyrazine 12bA in Ar Matrix at 10 K.

Compound **12bT/12bA** was co-sublimed with Ar at 75 $^{\circ}$C for 15 min and condensed on a KBr target at 28 K. The matrix was subsequently cooled to 10 K, and the infrared spectrum of the **12bT** (T)/**12bA** (A) mixture was recorded. IR (Ar, 10 K)/cm^{-1} 3570 w (T), 3544 w (A), 3111 w (T), 2256 w (A), 2250 w (A), 2173 w (A), 2169 w (A), 2152 w (A), 2139 m (A), 2133 m (A), 1855 w (T), 1594 w (T), 1573 w (A), 1561 w (A), 1540 w (T), 1516 w (A), 1506 m (T), 1479 m (T), 1474 m (T), 1469 s (T), 1443 w (A), 1425 w (A), 1420 w (A), 1401 w (A), 1398 w (A), 1395 m (A), 1391 m (A), 1379 w (A), 1363 m (T), 1356 w (T), 1327 w (A), 1321 w (T), 1316 w (T), 1309 w (T), 1301 m (A / T), 1295 w (A), 1293 w (A), 1288 w (A), 1241 w (T), 1223 w (A),

1196 w (T), 1186 w (A), 1182 w (A), 1165 w (A), 1162 w (A), 1149 w (A / T), 1145 w (T), 1142 w (T), 1107 w (T), 1098 s (T), 1087 w (A / T), 1081 w (T), 1077 w (T), 1073 w (A / T), 1071 w (A), 1064 m (A / T), 1054 w (T), 1049 w (T), 996 w (T), 988 w (T), 974 w (T), 971 s (T), 879 w (T), 851 w (A), 824 w (T), 793 w (T), 772 w (T), 768 w (A), 766 w (A), 764 w (A), 660 m (T), 659 w (T), 603 w (T), 472 w (A), 470 w (A), 468 w (A), 423 w (A). Identification of **12bA** was achieved in a separate experiment by passing **12bT** through an oven at 270 ^{o}C (See Figure S1).

Broadband UV irradiation of the mixture for 30 minutes resulted in the production of 2-chloro-1-cyanoimidazole **16b** as the predominant product. IR (Ar, 10 K)/cm^{-1} 3295 w, 3181 w, 3152 w, 2269 s, 2214 w, 2162 w, 2159 w, 2140 w, 2055 w, 1599 w, 1593 w, 1590 w, 1538 m, 1485 s, 1478 w, 1456 w, 1441 w, 1382 m, 1376 w, 1372 w, 1314 w, 1300 w, 1280 m, 1271 m, 1224 w, 1138 w, 1115 w, 1110 w, 1098 m, 1062 w, 1000 w, 993 w, 989 w, 979 w, 975 w, 968 w, 964 w, 944 w, 938 w, 922 w, 920 w, 903 w, 901 w, 898 w, 895 w, 869 w, 867 w, 863 w, 861 w, 791 w, 788 w, 785 w, 776 w, 774 w, 765 w, 760 w, 743 w, 741 w, 735 w, 731 w, 727 w, 726 w, 722 w, 650 w, 637 w, 588 w, 476 w.

See the text and Figures 2 and 3 for photolysis at 222 nm.

FVT of 8-Chlorotetrazolo[1,5-*a*]pyrazine 12bT/2-azido-3-chloropyrazine 12bA with Ar Matrix isolation at 10 K.

The tetrazole was co-sublimed with Ar through the FVT oven held at 400 ^{o}C, and the product was deposited on a KBr target at 27 K. The matrix was subsequently cooled to 10 K. The IR spectrum of the thermolysis products is shown in Figure S3. Four species were identified: azide **12bA**, nitriles **16b** and **18**, and the cyclic carbodiimde **14** (1968 cm^{-1}). When this experiment was repeated at 500 ^{o}C, only the nitriles **16b** and **18** survives (Figure S3). IR (FVT 500 ^{o}C, Ar, 10 K)/cm^{-1}: 3515 w, 3487 w, 3483 w, 3474 w, 3467 m, 3460 w, 3457 w, 3451 w, 3153 w, 3141 w,

2951 w, 2903 w, 2889 w, 2864 w, 2854 w, 2268 s, 2257 w, 2249 w, 2240 w, 1581 w, 1573 w,

1547 w, 1541 w, 1537 w, 1533 w, 1528 w, 1488 m, 1486 m, 1483 m, 1480 s, 1468 w, 1456 w,

1453 w, 1450 w, 1441 w, 1439 w, 1430 m, 1419 w, 1413 w, 1380 s, 1373 w, 1344 w, 1326 w,

1324 w, 1299 w, 1278 s, 1271 s, 1256 w, 1194 w, 1181 w, 1138 w, 1136 w, 1104 w, 1098 m,

1091 w, 1064 w, 1060 w, 1045 w, 1014 w, 989 w, 984 w, 966 w, 896 w, 894 w, 866 w, 863 w,

860 w, 852 w, 784 w, 780 w, 778 w, 776 w, 759 w, 731 w, 730 w, 727 w, 726 w, 722 m, 691 w,

651 m, 650 m, 641 w, 637 w, 591 w, 588 w, 579 w, 576 w, 563 w, 549 w, 476 w, 471 w, 444 w.

2-Chloro-4-cyanoimidazole 18.

The tetrazole/azide **12bT/12bA** (0.313 g, 2.04 mmol) was sublimed (60 $^{\circ}$C, 0.01 hPa) through

the FVT oven at 500 $^{\circ}$C in the course of 7 h. The light yellow material that collected at the oven

exit was removed and then sublimed (oil bath 115 $^{\circ}$C, 0.1 hPa) to give 2-chloro-4-

cyanoimidazole **18** as a white solid in an isolated yield of 69 mg (27 %). 2-Chloro-1-

cyanoimidazole **16b** could not be detected among the crude FVT products by ^{1}H NMR. Note that

the conditions used for reparative FVT are harsher than those for Ar matrix isolation (25 cm

pyrolysis tube vs 10 cm; 10^{-2} hPa vs 10^{-5} hPa). Consequently, much charring took place in the

preparative FVT tube, the yield was modest, and complete isomerization of **16b** to **18** took place.

Nitrile **18** was crystallized from hexane; m.p. 226 – 228 ^{0}C dec; ^{1}H NMR (acetone-d_6, 400MHz):

δ 8.01 (s 1H); ^{13}C NMR (acetone-d_6, 100MHz) δ 114.0 (s); 114.9 (s); 129.4 (d); 133.5 (s);

DEPT-135 NMR (acetone-d_6) δ129.4 (s) ppm (Figures S10-S12); MS: m/z 129, 127, 102, 100;

IR (KBr)/cm^{-1} 3129 s, 3056 s, 3010 m, 2944 s, 2900 s, 2871 s, 2847 s, 2819 s, 2760 s, 2723 s,

2662 s, 2627 s, 2568 m, 2508 m, 2470 m, 2438 m, 2376 w, 2271 w, 2243 w, 2193 w, 2127 w,

1771 w, 1683 w, 1563 m, 1547 m, 1512 m, 1496 m, 1436 s, 1377 w, 1334 s, 1296 w, 1274 s,

1236 m, 1191 w, 1177 w, 1138 m, 1098 w, 1008 s, 987 m, 896 m, 847 s, 689 w, 648 s, 631 m,

622 m, 578 w, 569 w, 563 w, 554 w, 492 m, 490 m, 457 w, 419 w. MS m/z 129 (M$^+$ (^{37}Cl), 27%), 127 (M$^+$ (^{35}Cl), 93), 102 (36), 100 (100), 75 (18), 66 (20), 53 (21) 47 (30). Anal. calc. for C$_4$H$_2$ClN$_3$: C, 37.67; H, 1.58; N, 32.95. Found: C, 37.66; H, 1.51; N, 33.23 %.

Deposition of 2-Chloro-4-cyanoimidazole 18 in Ar at 10 K.

Nitrile **18** was co-sublimed at 105 ^{o}C with Ar (120 hPa) for 12 min, and the material was deposited on a KBr target at 25 K. The matrix was cooled to 10 K, and the IR spectrum was recorded: IR (Ar, 10 K) cm^{-1} 3486 s, 3478 m, 3270 w, 3244 w, 3237 w, 3168 w, 2968 w, 2267 w, 2257 w, 2250 w, 2247 w, 2243 w, 2240 w, 1557 w, 1554 w, 1547 w, 1543 w, 1493 w, 1488 s, 1430 m, 1418 w, 1412 m, 1342 w, 1328 w, 1324 m, 1271 m, 1264 w, 1259 w, 1237 w, 1188 w, 1181 w, 1175 w, 1150 w, 1145 w, 1125 w, 1097 m, 1077 w, 995 w, 988 w, 968 w, 964 w, 960 w, 958 w, 953 w, 853 w, 850 w, 835 w, 787 w, 779 w, 778 w, 642 w, 638 w, 622 w, 620 w, 611 w, 609 w, 564 w, 560 w, 558 w, 549 m, 512 w, 500 m, 444 w.

Deposition of 5,8-Dimethyltetrazolo[1,5-*a*]pyrazine 12cT/2-azido-3,6-dimethylpyrazine 12cA

The tetrazole **12cT** was passed through the FVT apparatus with Ar at 180-200 ^{o}C in order to generate the azide **12cA**, and the mixture was condensed on a KBr target at 20 K. The matrix was subsequently cooled to 10 K, and the infrared spectrum of the **12cT** (T)/**12cA** (A) mixture was recorded. IR (Ar, 10 K)/cm^{-1} for tetrazole **12cT**: 1501, 1356, 1267, 1217, 1176, 1095, 1052, 1001, 599. IR (Ar, 10 K)/cm^{-1} for azide **12cA**: 2134, 1449, 1381, 1357, 1292, 1225, 1218, 1176, 1125, 1001, 723.

See the text and Figures 5 and 6 for the results of photolyses at 254 and 310-390 nm.

2,5-Dimethylimidazole-1-carbonitrile 16c was obtained by FVT of **12cT/12cA** at 450 ^{o}C and deposited in Ar matrix at 10 K. The IR spectrum is shown in Figure S9.

ASSOCIATED CONTENT

Supporting Material Available: Difference-IR spectrum showing bands due to **7T** and **7A**. Matrix-IR spectra relating to **16b**, **14b**, and **16c**, ^{1}H and ^{13}C NMR spectra of **18**, calculated structures of conformers of **15a-c,** and potential energy diagrams for the reactions **14→15**, **15→16**, **15→17, 16→18**, *Z,Z*-**15a** → *Z,E*-**15a** and *Z,Z*-**15b** → *Z,E*-**15b.** Cartesian coordinates, energies, harmonic and anharmonic vibrational data and imaginary frequencies of transition state structures. This material is available free of charge via the Internet at www.acs.pubs.org.

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Notes

The authors declare no competing financial interest.

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