

2-Pyrazinylnitrene and 4-Pyrimidylnitrene. Ring Expansion to 1,3,5-Triazacyclohepta-1,2,4,6-tetraene and Ring Opening to (2-Isocyanovinyl)carbodiimide

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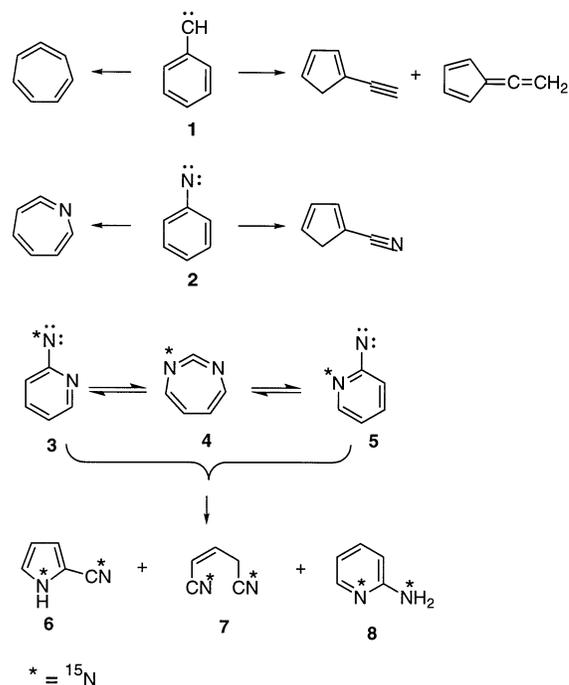
Received March 8, 2002

Tetrazolo[1,5-*a*]pyrazine/2-azidopyrazine **9T/9A** undergo photolysis in Ar matrix at cryogenic temperatures to yield 1,3,5-triazacyclohepta-1,2,4,6-tetraene **21** as the first observable intermediate, and 1-cyanoimidazole **11** and (2-isocyanovinyl)carbodiimide **22** as the final products. The latter tautomerizes to 2-(isocyanovinyl)cyanamide **23** on warming to 40 K. The same intermediate **21** and the same final products are obtained on matrix photolysis of the isomeric tetrazolo[1,5-*c*]pyrimidine/4-azidopyrimidine **24T/24A**. These photolysis results as well as those of the previously reported thermal ring contraction of ¹⁵N-labeled 2-pyrazinyl- and 4-pyrimidylnitrenes to 1-cyanoimidazoles can all be rationalized in terms of selective ring opening of **21** or nitrine **10** to a nitrile ylide zwitterion **28** prior to formation of the final products, **11** and **22**. The results are supported by high-level ab initio and DFT calculations (CASPT2-CASSCF(6,6), G3(MP2), and B3LYP/6-31+G*) of the energies and IR spectra of the intermediates and products.

Introduction

The ring expansion and ring contraction of arylcarbenes and arylnitrenes, exemplified by phenylcarbene **1** and phenylnitrene **2** in the diagram below, is a subject of ongoing interest.¹

The interconversion of 2-pyridylnitrenes **3** and **5** via 1,3-diazacyclohepta-1,2,4,6-tetraenes **4** under conditions of flash vacuum thermolysis (FVT) has been established by ¹⁵N and substituent labeling.² Several seven-membered-ring carbodiimide intermediates of type **4** have been characterized by IR spectroscopy,^{3,4,5} and the dibenzo derivative of **4** was observed to dimerize at -40 °C to afford a diazete derivative, which was characterized by X-ray crystallography.³ Formation of the triplet nitrene **3** under both FVT and photolysis conditions has been ascertained by ESR spectroscopy.⁶ The ring expansion of **3** to **4** under Ar matrix photolysis conditions has also been established, and the reaction is of synthetic value



as a means of preparation of diazepine derivatives by solution photolysis.⁷ In contrast, the end products of FVT of **3** are cyanopyrroles **6** (2- and 3-cyanopyrroles interconvert thermally via a series of 1,5-shifts of H and CN), glutacononitrile **7**, and 2-aminopyridine **8**.^{2,3,4}

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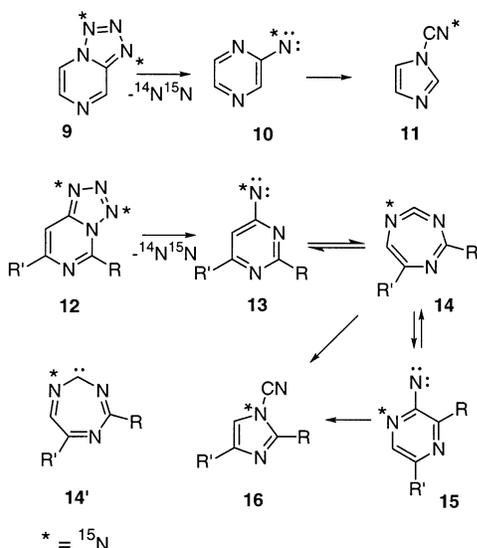
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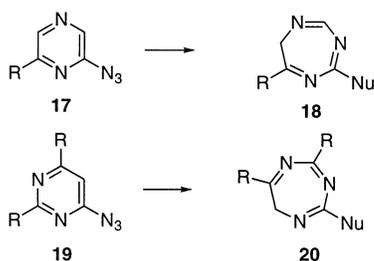
SCHEME 1



Flash vacuum thermolysis (FVT) of both tetrazolo[1,5-*a*]pyrazine **9T** and 5,7-disubstituted tetrazolo[1,5-*c*]pyrimidines **12T** ($R = \text{CH}_3$; $R' = \text{CH}_3, \text{OCH}_3, \text{or SCH}_3$) affords 1-cyanoimidazoles **11** and **16** in high yields⁸ (Scheme 1). The reaction also takes place on thermolysis of **9T** in solution or as a neat solid.^{8,9}

¹⁵N labeling experiments revealed that 2-pyrazinylnitrene **10** contracts directly to **11** with the ¹⁵N label exclusively on the exocyclic CN group, whereas 4-pyrimidylnitrene **13** undergoes complete migration of the ¹⁵N label, which can be explained by initial ring expansion to 1,3,5-triazacyclohepta-1,2,4,6-tetraene **14** (and/or the isomeric carbene, 2,4,6-triazacycloheptatrienylidene **14'**). Subsequent ring contraction of **14**, either directly or via the pyrazinylnitrene **15**, yields the ring-labeled 1-cyanoimidazole **16**.⁸

Photolysis of **9** in benzene or chloroform solution yields small amounts of the ring contraction product **11** together with much polymeric material.⁹ A higher yield is obtained in ethanol solution,¹⁰ and in acetic acid 1-acetylimidazole is formed,¹¹ a reaction that is attributed to initial formation of **11**.⁹ Triazepines **18** and **20** have been isolated from the photolysis of azides/tetrazoles **17** and **19** in the presence of sodium methoxide and diethylamine.¹²



In this paper we report the results of a detailed investigation of the Ar matrix photolysis of tetrazolopyrazine **9** and tetrazolo[1,5-*c*]pyrimidine **24**.

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Results and Discussion

Matrix Isolation and Photolysis of Tetrazolo[1,5-*a*]pyrazine 9T. Compound **9** exists in the tetrazole form (**9T**) in the solid form in KBr as evidenced by the absence of IR absorptions due to the azido group in the region of 2100 cm^{-1} (Figure S1a), but in CHCl_3 solution it exists as a mixture of azide (**9A**) (2126 cm^{-1}) and tetrazole. Sublimation of **9T** and co-deposition with Ar at 25 K also affords a mixture of azide and tetrazole, **9A/9T** (Figure S1b). Sublimation of **9T** through an oven at 325 °C and co-deposition with Ar at 25 K affords the almost pure azide **9A**, thereby permitting a clear assignment of bands to the tetrazole and azide forms (Figure S1c). The azide group gives rise to major absorptions at 2129 (vs), 2152 (m), and 2165 (m) cm^{-1} . Weaker combination or overtone bands are present at 2209 and 2311 cm^{-1} .

Photolysis of an Ar matrix of **9A/9T** in the cavity of an ESR spectrometer afforded a triplet nitrene ESR spectrum characterized by the zero-field splitting parameters $D/hc = 1.014(2)$ and $E = 0.000 \text{ cm}^{-1}$.⁶ Infrared spectroscopic monitoring of the photolysis at 7 K revealed that when using $\lambda > 310 \text{ nm}$, only the azide was photolyzed. When using $\lambda > 260 \text{ nm}$, both tetrazole and azide were photolyzed. After 45 min of irradiation with $\lambda > 260 \text{ nm}$, **9T/9A** had completely disappeared from the IR spectrum (Figure 1b). Important new absorptions appeared at 2118 (shoulder), 2135, and 2268 cm^{-1} together with an unsymmetrical doublet at 3420 and 3430 cm^{-1} and indicate that two photoproducts, **11** and **22**, are formed (Scheme 2). The most intense band at 2135 cm^{-1} (Figure 1b) is assigned to the carbodiimide stretch of structure **22**. There is also an isocyanide band at slightly lower frequency (shoulder at 2118 cm^{-1}). The unsymmetrical doublet at 3420 and 3430 cm^{-1} is ascribed to the N–H bonds. 1-Cyanoimidazole **11** exhibits a sharp and moderately intense absorption at 2268 cm^{-1} . This compound is clearly identified by comparison with the IR spectrum of an authentic sample (Figure 1a).

Density functional theory (DFT) calculations at the B3LYP/6-31+G* level supported the infrared spectral assignments (Figure 1c,d). Compound **22** can exist in *cis* and *trans* forms, and both of these can exist in *s-Z* and *s-E* forms. The calculated infrared spectra of all the configurations of **22** are very similar (Figure S2). Each exhibits a strong carbodiimide band around 2140 cm^{-1} , an N–H stretch at ca. 3450 cm^{-1} , and an isocyanide stretch at ca. 2105 cm^{-1} . The predicted values are in good agreement with the experimental ones, and this is also true for the absorptions in the fingerprint region (Figure S2).

Peaks ascribed to the cyclic carbodiimide **21** were observed at the early stages of the photolysis of **9**. A weak band at 1973 cm^{-1} , ascribed to the stretching of the carbodiimide function, appears and then disappears upon further irradiation. Changing the wavelength of irradiation did not cause any significant improvement in the intensities of the bands ascribed to this species. The calculated (B3LYP/6-31+G*) infrared spectrum of **21** is tabulated in the Supporting Information and shows a

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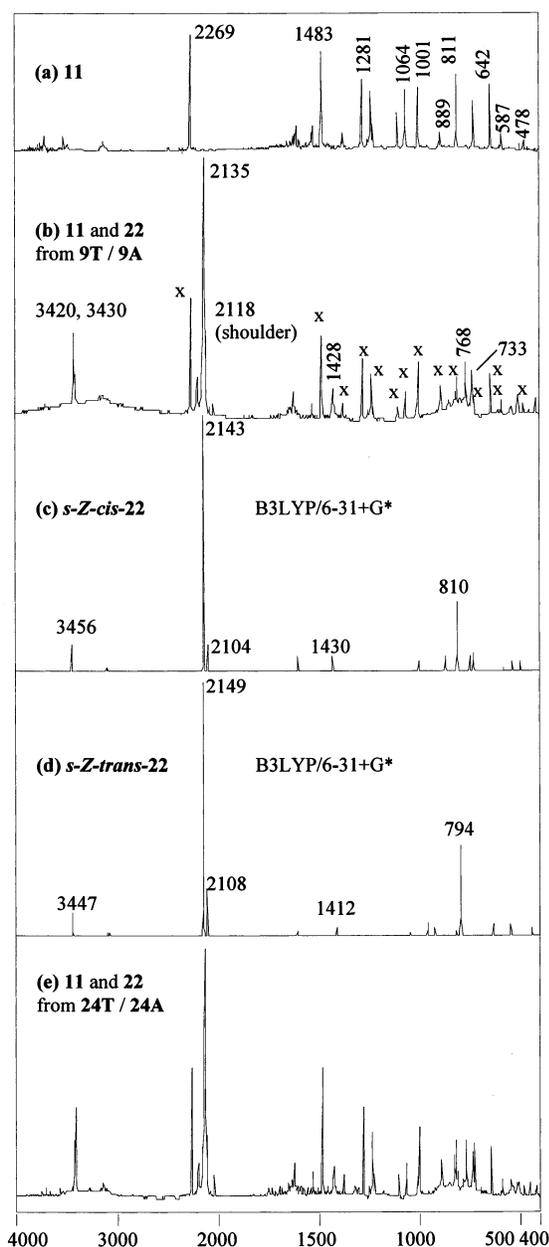
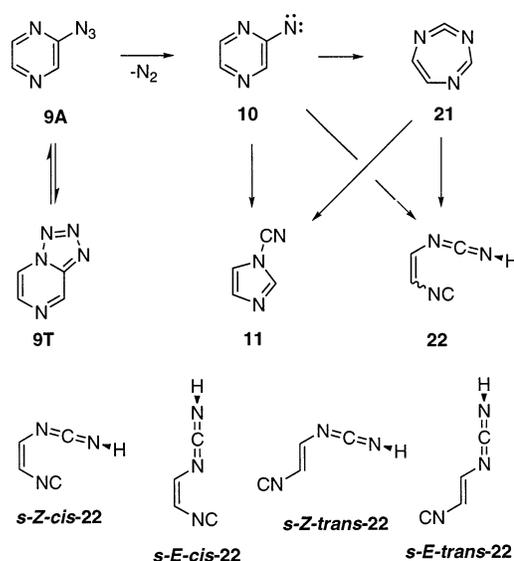


FIGURE 1. (a) Authentic 1-cyanoimidazole **11** in Ar matrix at 7 K; (b) **11** and **22** in Ar matrix as obtained after 45-min photolysis of **9T/9A**; bands labeled "X" belong to **11**; (c) B3LYP/6-31+G* calculated IR spectrum of *s-Z-cis-22*; (d) calculated IR spectrum of *s-Z-trans-22*; (e) **11** and **22** in Ar matrix as obtained after 40-min photolysis of **24T/24A**.

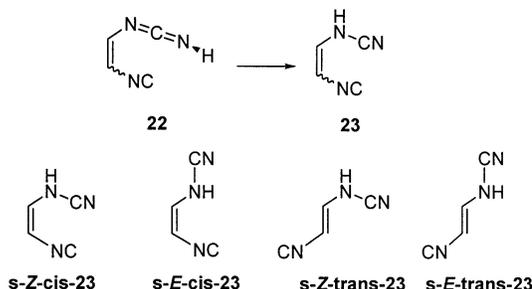
strong carbodiimide stretch at 1954 cm^{-1} and a medium intensity absorption at 866 cm^{-1} . The latter is matched by a band at 840 cm^{-1} in the experimental spectrum when the 1973 cm^{-1} band is present. All other calculated bands are relatively weak. Some of the experimental bands will be obscured by the much stronger bands of **9T/9A**, **11**, or **22**, or they are simply too weak to be observed.

Three weak, unassigned bands appear at 2034, 2048, and 2109 cm^{-1} at the same time as **21** on photolysis of **9**. They may be due to overtones or combination bands belonging to **21**, matrix effects, or, less likely, unknown intermediates.

SCHEME 2

**Isomerization of Carbodiimide **22** to Cyanamide **23****

23. Warmup of the matrix containing **22** and **11** was used to isomerize **22** to the cyanamide **23**. Argon begins to evaporate at approximately 36 K. The matrix was slowly warmed above this temperature (approximately 0.5 K every 10–15 min), which allowed the slow evaporation of Ar with minimal loss of solute. At 40–41 K a new band at 2241 cm^{-1} appeared in the IR spectrum, while ν_{NCN} (2135 cm^{-1}) and the N–H bands ($3420, 3430\text{ cm}^{-1}$) of **22** diminished in intensity (Figure S3). Concomitant broadening and weakening of the bands indicates extensive loss of Ar and some loss of solute. The band at 2268 cm^{-1} (CN group of **11**) is an example of these effects. After 15 min at 40 K the 2241 cm^{-1} band had increased significantly in intensity relative to the one at 2268 cm^{-1} and shifted slightly to 2240 cm^{-1} (Figure S3). Very little **22**



was left at this stage. Several minutes later the 2240 cm^{-1} band had reached its maximum intensity (now slightly shifted to 2238 cm^{-1}) (Figure S3). Also present were the band due to **11** (2268 cm^{-1}) and the isocyanide band at 2126 cm^{-1} . Further heating of this virtually neat mixture produced only slightly weaker spectra with increased water content.

The results indicate a thermal isomerization of **22** to **23**. The bands at 2238 and 2126 cm^{-1} are assigned as the nitrile and isocyanide absorptions of **23**, respectively. The bands due to **11** remained essentially unchanged during this process, as shown by comparison with an IR spectrum of neat **11** at 7 K (Figure S3). This spectrum did not change upon warming to 41 K.

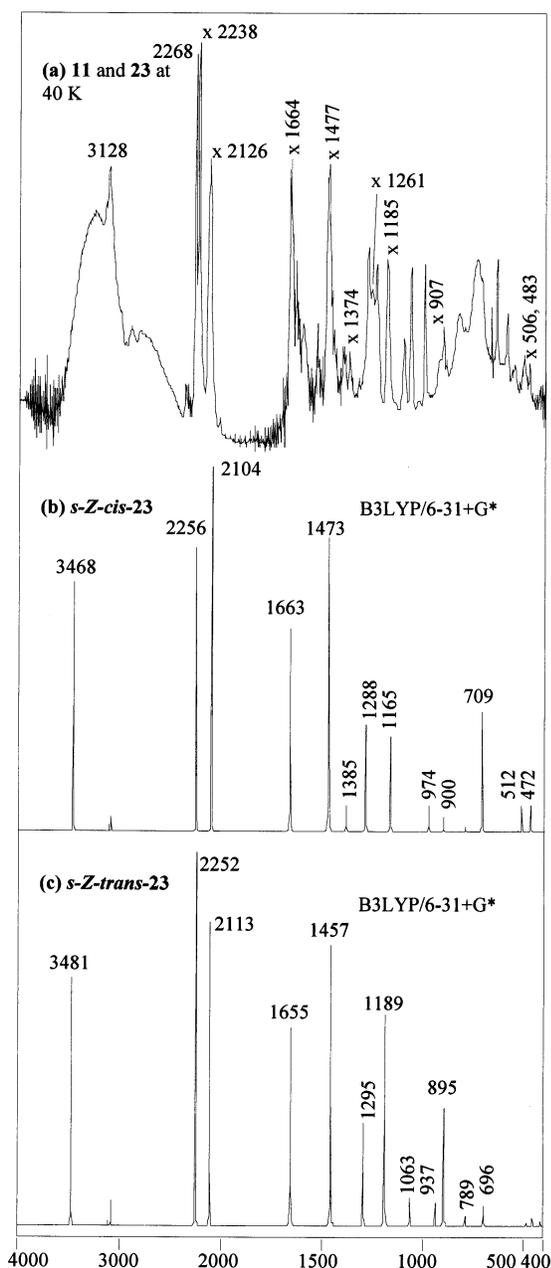
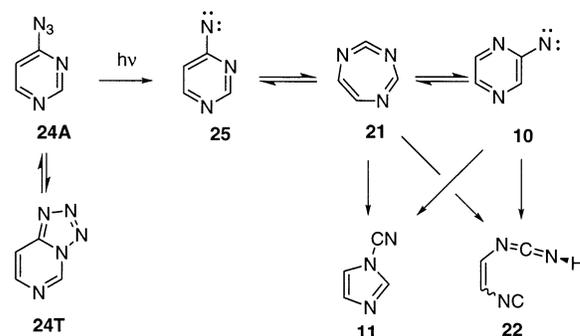


FIGURE 2. (a) Neat **11** and **23** at 40 K as obtained after evaporation of Ar from the matrix of **11** and **22** generated from **9T/9A**; bands labeled "X" are ascribed to **23**; (b) B3LYP/6-31+G* calculated IR spectra of (b) *s-Z-cis-23* and (c) *s-Z-trans-23*.

Having identified the bands due to **11**, the remaining bands due to **23** can be assigned (Figure 2a). DFT calculations of the IR spectra of the *s-Z* and *s-E* forms of *cis-23* and *trans-23* at the B3LYP/6-31+G* level confirmed the assignment (Figure 2b,c and Figure S4). Due to the broadness of the bands in the neat spectra, it is not possible to extract detailed information on *cis/trans* and *s-Z/s-E* isomer ratios.

Matrix Isolation and Photolysis of Tetrazolo[1,5-*c*]pyrimidine **24T.** The IR spectrum of this compound in KBr is that of the tetrazole form **24T** only (Figure S5a). Sublimation and co-deposition with Ar at 25 K gives rise to a mixture of azide **24A** and tetrazole **24T**, and

SCHEME 3



sublimation through an oven at 325 °C gave essentially the azide **24A** (Scheme 3; Figure S6a). Thus, subtraction of the spectra allowed the generation of the individual spectra of azide and tetrazole (Figure S5b). Absorptions due to the azide appear at 2133 and 2166 cm^{-1} . A weaker combination or overtone band is present at 2295 cm^{-1} . In the fingerprint region the strongest absorptions due to the azide are at 1293, 1303, and 1576 cm^{-1} .

As in the case of the pyrazine analogue **9**, photolysis of **24A/24T** with $\lambda > 260$ nm caused the rapid development (within 1.5 min) of a weak band at 1973 cm^{-1} ascribed to the cyclic carbodiimide **21**. It reached its maximum intensity after 4 min and disappeared on further photolysis (vanishing completely after 34 min). After 40 min of irradiation at $\lambda > 260$ nm **24T/24A** had also completely disappeared (Figure S6). Comparison with the spectra described above demonstrates that the photoproduct was composed of **11** (2269 cm^{-1}) and **22** (2118, 2135, 3420, and 3430 cm^{-1}) (Figure 1e). The two N–H bands (3420, 3430 cm^{-1}) of **22** have different intensities when generated from **9** and **24**. From **9**, the 3430- cm^{-1} band was the strongest, while from **24** the 3420- cm^{-1} band was dominant. Either matrix site effects or different conformer populations may be responsible for this and other minor differences between the spectra. In the photoproduct from **24** a shoulder appeared at 2164 cm^{-1} , which was absent in the product from **9**.

A comparison of appropriate absorption band areas indicates that the same relative quantities of **11** and **22** are formed from the two precursors **9** and **24**. The matrix containing **11** and **22** obtained by photolysis of **24** was warmed to 40 K as above. As expected, **22** was converted to cyanamide **23** (Figure S7).

Molecular Orbital Calculations. (A) Computational Details. Standard ab initio and DFT calculations were performed using the Gaussian 98 suite of programs,¹³ and multiconfiguration SCF (MCSCF) calculations were carried out using the MOLPRO 2000 programs.¹⁴ The structures and energies of all species and

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TABLE 1. Calculated Relative Energies (kcal/mol) of the Three Lowest Electronic States of Nitrenes **10 and **25** Using Various Single-Determinant and Multiconfiguration Methods**

computational level ^a	10			25		
	¹ A''	¹ A'	³ A''	¹ A''	¹ A'	³ A''
UHF/6-31G*	0.0	61.5	-17.5	0.0	51.0	-17.9
UMP2/6-31G*	0.0	<i>b</i>	-11.9	0.0	<i>b</i>	-14.9
CASSCF(6,6)/6-31G*	0.0	9.2	-18.3	0.0	-7.7	-23.1
CASSCF(8,8)/6-31G*	0.0	9.9	-17.2	0.0	-10.7	-24.8
CASPT2/6-31G* ^c	0.0	41.2	-19.8	0.0	31.6	-23.9

^a Fully optimized at the level specified unless otherwise noted.

^b Does not exist on the MP2/6-31G* potential energy surface.

^c Based on CASSCF(6,6)/6-31G* optimized geometries.

related transition structures were investigated by the G3-(MP2) theory.¹⁵ This corresponds effectively to the QCISD-(T)/G3Large//MP2/6-31G* level of theory including zero-point energy (HF/6-31G*) and higher level corrections. For the nitrene systems and several related isomers, the energies were examined by multireference calculations. Vibrational spectra of all molecules were computed with a DFT method, B3LYP/6-31+G*. For zwitterionic or ylidic species, we have found that it is necessary to use basis sets incorporating diffuse functions in order to achieve good agreement with experimental infrared spectra.¹⁶ A scaling factor for the B3LYP/6-31+G* vibrational frequencies has not been established rigorously, but we have used the same scaling factor (0.9613) as for the B3LYP/6-31G* level.¹⁷ In our experience, this may slightly underestimate the vibrational frequencies. The correct location of the various transition states, which are characterized by having one imaginary frequency, was verified by means of internal reaction coordinate (IRC) calculations.

(B) Singlet and Triplet Nitrenes. Previous computational studies by Borden and co-workers have demonstrated that the open-shell singlet state (¹A₂) of phenylnitrene lies well below the closed-shell singlet,¹⁸ and it is necessary to use high-level ab initio methods for reliable computations of their energies. Moreover, it has been shown that DFT methods are not well suited for calculations of diradical-type (open-shell) molecules.¹⁹

First, we examine the energy difference of the three lowest states of nitrenes **10** and **25**, namely ³A'', ¹A'', and ¹A', using various single-determinant and multiconfiguration methods (Table 1). As expected, the triplet (³A'') is predicted to be the ground state for both nitrenes at all levels of theory (Table 1). However, the relative energies of the two singlet states are strongly dependent

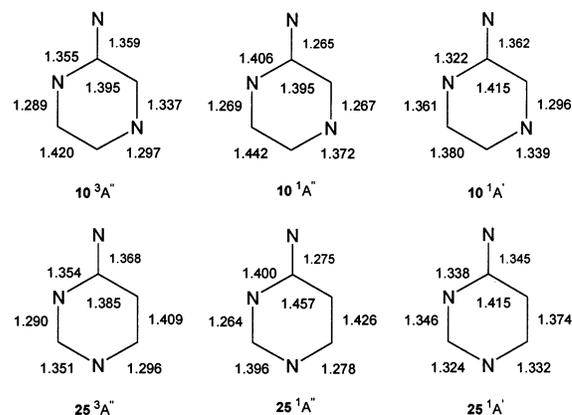


FIGURE 3. CASSCF(6,6) optimized bond lengths (Å) of different electronic states of nitrenes **10** and **25**.

on the level of theory considered. At the unrestricted Hartree–Fock (UHF) level, the open-shell singlet (¹A'') is substantially more stable than the closed-shell singlet (¹A'). Surprisingly, the closed-shell singlet is not a stable equilibrium structure at correlated levels of theory, such as MP2, B3LYP, and QCISD. Geometry optimization without symmetry constraint at these levels of theory causes direct collaps to the seven-membered-ring carbo-diimide **21**. It is important to note that the squared spin expectation values ($\langle S^2 \rangle$) of the UHF wave functions of the ³A'' (2.72 for **10** and 2.68 for **25**) and ¹A'' (1.64 for **10** and 1.62 for **25**) states are significantly different from those of the corresponding pure spin states. In particular, the ¹A'' state is severely spin contaminated by the triplet state. Thus, we would expect the stabilities of the ³A'' and ¹A'' states to be overestimated by the UHF-based methods.

To provide a proper description of the near-degeneracy problem involved, we have examined the relative energies of the three electronic states of **10** and **25** using a MCSCF approach. Complete-active-space SCF (CASSCF)²⁰ calculations were performed with six active electrons in six active orbitals (4 π orbitals and 2 nitrene in-plane p orbitals), i.e., (CASSCF(6,6)), in conjunction with the 6-31G* basis set. Further expansion of the active space to CASSCF(8,8) leads to small changes in the relative energies (Table 1). The CI coefficients of the CASSCF-(8,8) calculations indicate that the (6 \times 6) configuration space provides a sufficient and balanced description of all the states involved. At the CASSCF level, the ¹A'/¹A'' relative energies are substantially less than the corresponding HF values (Table 1). In fact, a reversal of the ¹A'/¹A'' preference is calculated for nitrene **25**.

Dynamic electron correlation effects were included by carrying out second-order multireference perturbation (CASPT2)²¹ single-point energy calculations at the CASSCF(6,6) optimized geometries. As evidenced in Table 1, inclusion of dynamic electron correlation stabilizes preferentially the open-shell over the closed-shell singlet. Thus, the lowest singlet state of **10** and **25** is confirmed to be open-shell as in the case of phenylnitrene.¹⁸ It is important to note that the CASPT2 theory tends to suffer from a systematic error proportional to the number of

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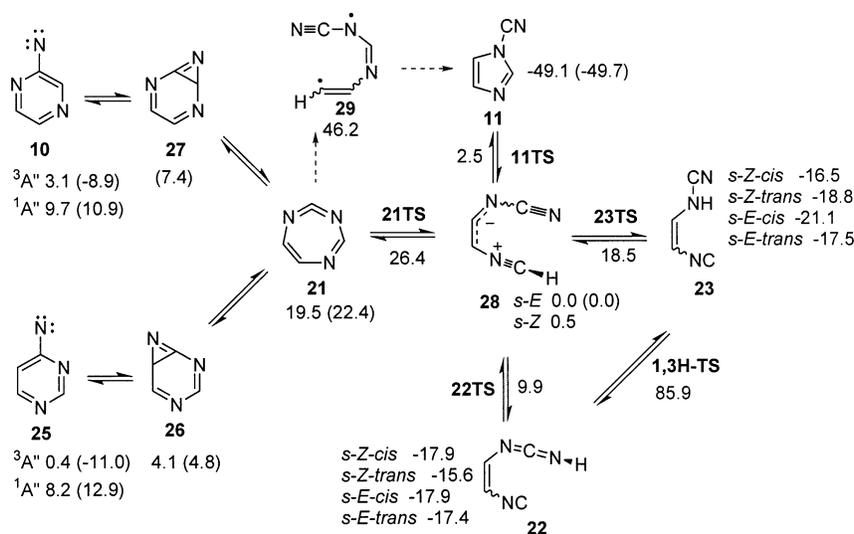
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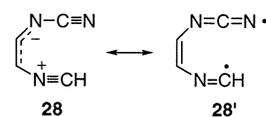
SCHEME 4. Schematic Energy Diagram Showing the Interconversions of the C₄H₃N₃ Isomers^a

^aG3(MP2) energy values (with CASPT2/6-31G*+ZPE values in parentheses) in kcal/mol.

unpaired electrons.²² A more definitive estimate of the ¹A'/¹A'' energy difference may require multireference configuration interaction (MRCI) calculations using a larger active space. Our best estimate of the singlet–triplet gap (Δ_{ST}) of **10** is 19.8 kcal mol⁻¹ (CASPT2), similar to that calculated for phenylnitrene (18 kcal mol⁻¹).¹⁸ A slightly larger Δ_{ST} value is predicted for nitrene **25** (23.9 kcal mol⁻¹). These Δ_{ST} values are only half that found for the unsubstituted parent system NH. For phenylnitrene, Borden and co-workers have attributed this mainly to the ability of the phenyl group to delocalize the unpaired π electron in the open-shell singlet state. A similar rationalization can be applied to the nitrenes examined in this paper. In particular, the delocalization of the unpaired π electron in the open-shell singlet states is readily shown in the CAS optimized geometries (Figure 3): the C–N bond length of the ¹A'' state is significantly shorter than those in the ³A'' and ¹A' states.

(C) Reaction Mechanism. It is reasonable to assume that the thermal rearrangement processes occur on the singlet state potential energy surface. In the case of matrix photochemistry we cannot be sure that the same electronic states and the same reaction mechanisms will apply, and it is computationally demanding to perform calculations of excited-state reactions of this complexity. Thus, the discussion of reaction mechanism here is focused on the singlet potential energy surface. A coherent schematic energy diagram involving all the relevant molecules and some transition states, calculated at the G3(MP2) and CASPT2-CASSCF(6,6) levels of theory, is presented in Scheme 4, and the relative energies are tabulated in Table 2. For molecules other than the nitrenes, it is reasonable to employ the single-determinant method to predict their energies. This is readily confirmed by the fact that the G3(MP2) and CASPT2 relative energies of **11**, **21**, **22**, and **28** are in close agreement (Table 2). Unless otherwise noted, the relative energies reported in the text correspond to the G3(MP2) values.

The results of ¹⁵N labeling described in the Introduction (Scheme 1) demand that it is either the pyrazinylnitrenes (**10**, **15**) or the seven-membered rings (**14**, **21**) that undergoes ring contraction to 1-cyanoimidazoles (**11**, **16**) under thermal conditions. In the case of the pyridylnitrenes, we know that the nitrenes **3** and **5** actually interconvert, because nitrogen-scrambled 2-aminopyridine **8** is formed.^{1a,2} In the present work, it is possible that the products could be formed directly from pyrazinylnitrene **10** via ring opening to zwitterion **28**. Both nitrenes can cyclize exothermally to azirines (**26** and **27**). The energy of the seven-membered-ring carbodiimide **21** is comparable to or lower than those of the singlet nitrenes. The calculated infrared stretching frequency of this molecule (1954 cm⁻¹) agrees well with the weak band at 1973 cm⁻¹ observed during the early stages of the photolysis of **9** and **24**. Carbodiimide **21** is predicted to have a modest barrier of 6.9 kcal/mol toward ring opening to zwitterion **28**, via transition state **21TS**. This barrier can be easily overcome under FVT conditions, and in the matrix it may be either a photochemical or a chemically activated process (using excess energy from the initial photolysis of the azides or tetrazoles). Zwitterion **28** is calculated to be substantially lower in energy than cumulene **21**, by 19.5 kcal/mol (Table 2). The ground state of **28** is singlet, and the triplet diradical (**28'**) lies

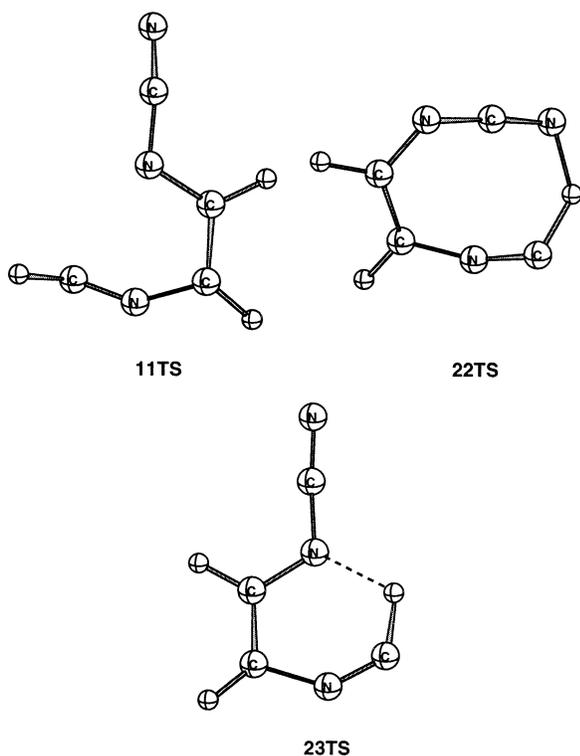


substantially higher in energy (35.7 kcal/mol). The cis-form of **28** (having a formal *cis*-C=C bond) can exist in *s-E* and *s-Z* conformations with respect to the N–CN group, with a slight preference for the *s-E* form (by 2.0 kcal/mol). The corresponding trans-forms (see Supporting Information) cannot lead to the observed products. Interconversion of the *s-E* and *s-Z* conformers requires a calculated barrier of 18.3 kcal/mol. Both conformations are characterized by large dipole moments, 7.40 and 5.79 D for *s-E* and *s-Z* forms, respectively. The calculated

(22) Andersson, K.; Roos, B. O. *Int. J. Quantum Chem.* **1993**, *45*, 591.

structure of **28** indicates that this molecule exists as a zwitterion with two CN triple bonds (HC–N = 1.19 Å; N–CH = 1.33 Å; CH–CH = 1.41 Å; CH–N = 1.31 Å; N–CN = 1.34 Å; CN = 1.19 Å, MP2/6-31G*). **28** may also be described as a nitrile ylide with a delocalized negative charge. The calculated atomic charges indicate that the negative charge is delocalized on the CH (nitrile ylide) and the two N atoms of the cyanamide moiety (MP2/6-31G* NBO charges on the heavy atoms along the chain HCNC(H)C(H)NCN in *s-Z-28*: 0.200, –0.226, –0.242, 0.065, –0.520, 0.369, –0.385).

Ring closure of *s-E-28*, via transition state **11TS**, would give 1-cyanoimidazole **11** with a very small barrier (2.5 kcal/mol; Scheme 4), and a 1,7-hydrogen shift, via **22TS**, would give the observed ring-opened carbodiimide **22** with a barrier of ca. 10 kcal/mol. Since **28** is expected to be generated initially in the *s-Z* conformation in the matrix, the requirement of *s-Z/s-E* isomerization may impede the formation of **11**, thereby making the formation of **22** competitive. A 1,5-hydrogen shift in **28**, via **23TS**, to give cyanamide **23** directly requires an activation barrier of 18.5 kcal/mol and is not observed. It is worth noting that the 1,7-shift in **28** involves the transfer of a hydrogen atom to the lone pair of a triple-bonded nitrogen atom; therefore it may be described as a pseudo-pericyclic reaction,²³ and it is not subject to the Woodward–Hoffmann rules of orbital symmetry.



The tautomerization of **22** to **23** only happens when Ar evaporates and the matrix softens. The intramolecular reaction would constitute a 1,3-hydrogen shift, and it has a very high calculated barrier of 103.8 kcal/mol, via the **1,3H-TS** (Scheme 4). It is, therefore, very likely to be an intermolecular proton transfer reaction. We have cursorily

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TABLE 2. Calculated Relative Energies (kcal/mol)^{a,b}

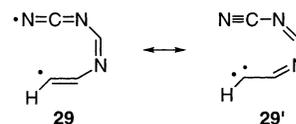
species	point group	B3LYP/6-31+G*	G3(MP2)	CASPT2 ^b
310 (³ A'')	C _s	–3.1	3.1	–8.9
110 (¹ A')	C _s	3.1	9.7	10.9
325 (³ A'')	C _s	–5.2	0.4	–11.0
125 (¹ A')	C _s	1.8	8.2	12.9
26 (¹ A)	C ₁	8.2	4.1	4.8
27 (¹ A)	C ₁	c	c	7.4
21 (¹ A)	C ₁	–5.6	19.5	22.4
<i>s-E-28</i> (¹ A)	C ₁	0.0	0.0	0.0
<i>s-Z-28</i> (¹ A)	C ₁	1.9	0.5	
11 (¹ A)	C _s	–41.8	–49.1	–49.7
<i>s-Z-cis-22</i> (¹ A)	C ₁	–13.0	–17.9	
<i>s-Z-trans-22</i> (¹ A)	C ₁	–11.7	–15.6	
<i>s-E-cis-22</i> (¹ A)	C ₁	–13.3	–17.9	–14.3
<i>s-E-trans-22</i> (¹ A)	C ₁	–13.8	–17.4	
<i>s-Z-cis-23</i> (¹ A)	C _s	–8.6	–16.5	
<i>s-Z-trans-23</i> (¹ A)	C _s	–11.2		–18.8
<i>s-E-cis-23</i> (¹ A)	C _s	–13.8	–21.1	
<i>s-E-trans-23</i> (¹ A)	C _s	–10.7	–17.5	
28' (³ A'')	C ₁	21.7	35.7	
29 (³ A'')	C _s	49.5	46.2	

^a The total energy of the reference molecule (*s-E-28*) at the B3LYP/6-31+G*, G3(MP2), and CASPT2/6-31G* levels is –318.376821, –317.89384, and –317.39919 hartrees, respectively.

^b CASPT2/6-31G*/CASSCF(6,6)/6-31G*+ZPE (HF/6-31G*) level.
^c Does not exist on the B3LYP/6-31+G* and MP2/6-31G* potential energy surfaces.

ily examined the hydrogen transfer reaction HNCNH → H₂NCN via a hydrogen-bonded dimer (a primitive model for the solid state). The calculated barrier for hydrogen transfer in the (HNCNH)₂ dimer is substantially less than that for the unimolecular 1,3-H shift process. Thus, our calculations support the idea that tautomerization of **22** to **23** is an intermolecular process.

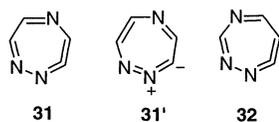
It could be argued that the seven-membered-ring **21** should have been able to undergo alternate ring opening to an isomeric vinyl diradical **29** (Scheme 4), which could also collapse to 1-cyanoimidazole **11**. If this reaction were involved in the thermal process, it would have given the wrong ¹⁵N labeling results, in contradiction with Scheme 1. In fact, our G3(MP2) calculations indicate that **28** is 46.2 kcal/mol more stable than **29**. The higher stability of zwitterion **28** compared to **29** is undoubtedly due to the resonance stabilization of the former, which is not available for the vinyl diradical **29**. The calculated structural parameters (e.g. ∠HCC = 136°) and the occupied molecular orbitals indicate that this diradical has a high degree of carbene character (**29'**).



On the basis of the CASPT2 results (Table 2), the singlet nitrenes **10** and **25** are comparable in energy to the seven-membered-ring **21**. Fused azirines **26** and **27** represent intermediates en route from nitrenes **25** and **10**, to carbodiimide **21** (Scheme 4). Both **26** and **27** are calculated to be stable equilibrium structures at the HF and CASSCF levels. However, azirine **27** is not a stable species at the B3LYP/6-31+G* and MP2 levels, collapsing directly to **21** upon geometry optimization. At the CASPT2 level, **26** and **27** are 8.1 and 3.5 kcal/mol lower in energy

than the corresponding singlet nitrenes, and they are significantly more stable than **21** (Table 2). Ring expansion of phenylnitrene to didehydroazepine has been shown to be a facile process.²⁴ We believe that similar ring expansion reactions of nitrenes **10** and **25** to **21** are also relatively straightforward processes.

We have cursorily considered the alternate seven-membered-ring cumulenes **31** and **32** that might have been formed by ring expansion of nitrenes **10** and **25**. At the B3LYP/6-31+G* level the bond lengths of the former indicate that it exists as an ylide (**31'**) with its major IR absorption at 1761 cm⁻¹; however, the MP2/6-31G* geometry is that of structure **31** with a long N–N single bond (1.49 Å). This observation has prompted us to undertake more extensive calculations on seven-membered-ring cumulenes in order to determine the reality of ylides of the type **31'**. The results will be published elsewhere. Compound **32** exists as a ketenimine with a major IR absorption at 1868 cm⁻¹ as expected at the B3LYP/6-31G* level. No experimental observations make it necessary to consider compounds **31**–**32** further in the present chemical context.²⁶



The relative energies of the cyanoimidazoles at the B3LYP/6-31+G* level are the following: 1-CN, 15.4 kcal/mol; 2-CN, 2.3 kcal/mol; 4-CN, 0.0 kcal/mol; 5-CN, 0.2 kcal/mol. High-temperature FVT causes sigmatropic 1,5-shifts of cyano groups in cyanocyclopentadienes, pyrroles, imidazoles, and their benzo analogues.²⁵ Such processes have not been observed under the conditions of the present paper but takes place very easily in 2-chloro-1-cyanoimidazole.²⁷

In summary, selective ring opening of the seven-membered-ring cyclic carbodiimide **21** to the nitrile ylide zwitterion **28** provides a mechanistic rationale for the formation of the final products, **11** and **22**. Further work in our laboratory indicates that ring opening of heteroarylnitrenes may be a rather common reaction under the conditions of matrix-isolation photolysis, and in several cases also on gas-phase thermolysis. Some heteroarylcarbenes undergo analogous ring opening reactions. The ring openings may take place in either the nitrene (carbene) itself or in the seven-membered-ring cumulene, depending on the nature of the system.

Experimental Section

Compounds **9T**,²⁸ **11**,²⁸ and **24T**²⁹ were prepared according to literature procedures.

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Photolysis of Tetrazolo[1,5-*a*]pyrazine **9T/2-Azidopyrazine **9A** in Ar Matrix at 7 K.** Tetrazole **9T** was sublimed at 70 °C in a stream of Ar and deposited on a CsI window at 25 K in the course of 20 min. The matrix was cooled to 7 K and the IR spectrum of **9T/9A** recorded: IR (Ar, 7K) 3091 w, 3018 w, 2311 w, 2209 w, 2165 m, 2152 m, 2129 s, 2119 w, 1852 w, 1583 m, 1579 m, 1523 m, 1518 m, 1477 s, 1474 s, 1467 m, 1462 m, 1446 w, 1436 w, 1403 s, 1369 w, 1356 m, 1345 s, 1307 w, 1301 w, 1291 s, 1232 w, 1205 w, 1187 w, 1174 w, 1168 w, 1157 w, 1151 w, 1140 w, 1128 w, 1086 w, 1080 m, 1030 w, 1025 w, 1020 m, 1018 w, 1016 w, 1011 s, 993 w, 913 w, 908 w, 842 w, 822 w, 798 m, 796 m, 794 s, 718 w, 646 w, 644 w, 597 m, 544 w, 430 w, 426 w, 416 w cm⁻¹. UV irradiation ($\lambda > 260$ nm; 45 min) using the unfiltered light from a 1000-W high-pressure Hg/Xe lamp resulted in complete conversion to 1-cyanoimidazole **11** and carbodiimide **22**: IR (Ar, 7K) 3430 m, 3420 m, 2282 w, 2268 m, 2204 w, 2135 s, 2118 m, 2084 w, 2044 w, 1642 w, 1625 w, 1532 w, 1485 m, 1428 w, 1378 w, 1281 m, 1252 w, 1240 w, 1234 m, 1226 w, 1105 w, 1103 w, 1070 w, 1067 w, 1065 w, 1015 w, 1011 w, 1008 w, 1001 m, 890 m, 851 w, 826 w, 819 w, 810 m, 794 w, 768 m, 761 w, 737 w, 733 m, 725 w, 645 w, 642 m, 608 w, 597 w, 593 w, 587 w, 544 w, 538 w, 507 w, 478 w, 418 w cm⁻¹.

Warmup of Matrix-Isolated **11 and **22**: Conversion of **22** to Cyanamide **23**.** The Ar matrix containing **11** and **22** was warmed to 36 K, at which temperature Ar started to evaporate as indicated by a slight pressure increase. The temperature was raised slowly by 0.5 K every 10–15 min in the course of several hours, until all Ar had evaporated. The temperature at this stage was 41–42 K. Broadened IR bands resulted for the neat **11** and **23**: IR (Ar, 41–42 K) 3128 m, 2268 s, 2238 s, 2126 m, 2030 w, 1534 w, 1480 m, 1401 w, 1374 w, 1328 w, 1282 m, 1261 m, 1240 m, 1185 m, 1102 m, 1068 m, 1026 w, 1001 m, 930 w, 907 m, 892 w, 832 m, 733 m, 642 m, 592 m, 553 w, 505 w, 484 w cm⁻¹.

Deposition of Authentic 1-Cyanoimidazole **11 at Cryogenic Temperatures. (a) With Ar.** A stoppered Pyrex vessel containing **11** was immersed in an ice–salt bath (–15 °C), the stopper was opened, and **11** was volatilized and co-deposited with a stream of Ar onto a CsI window at 25 K in the course of 16 min. The coolant was replaced with ice (–2 °C), and deposition continued for another 15 min, after which the ice bath was removed and the vessel allowed to warm to room temperature (5 min). The sample was stoppered and the matrix cooled to 7 K. Some absorptions of **11** were split into doublets: IR (Ar, 7 K) 3135 w, 2282 w, 2278 w, 2269 s, 2266 s, 1617 w, 1597 w, 1593 w, 1531 w, 1526 w, 1483 s, 1480 s, 1378 w, 1375 w, 1289 w, 1281 m, 1278 m, 1252 w, 1234 m, 1233 m, 1226 w, 1106 w, 1101 m, 1067 w, 1064 m, 1001 m, 894 w, 889 w, 888 w, 811 m, 727 w, 725 m, 723 m, 642 m, 595 w, 587 w, 586 w, 498 w, 478 w cm⁻¹.

(b) Without Ar. The stoppered vessel containing **11** was cooled with an ice–salt bath (as above), the stopper was opened, and **11** was sublimed onto the deposition window at 7 K for 20 min. The vessel was closed, and the IR spectrum recorded. All bands were broadened: IR (neat, 7 K) cm⁻¹ 3126 m, 2266 s, 1530 w, 1483 m, 1375 w, 1281 m, 1239 m, 1192 w, 1101 w, 1064 m, 999 m, 979 w, 894 w, 831 w, 752 w, 642 m, 589 w, 485 w. Warming of **11** to 55 K caused no changes in the IR spectrum.

Photolysis of Tetrazolo[1,5-*c*]pyrimidine **24T/4-Azidopyrimidine **24A** in Ar Matrix at 7 K.** Tetrazole **24T** was sublimed at 50–52 °C in a stream of Ar and co-deposited with Ar on a CsI window at 25 K in the course of 20 min. The matrix was cooled to 7 K, and the IR spectrum of **24T/24A** was recorded: IR (Ar, 7K) 3065 w, 3045 w, 2449 w, 2436 w, 2295 w, 2289 w, 2253 w, 2203 w, 2177 w, 2171 w, 2166 m, 2155 w, 2133 s, 2009 w, 1621 m, 1611 w, 1578 w, 1590 m, 1576 s, 1566 w, 1561 w, 1549 w, 1530 w, 1504 w, 1495 w, 1463 m, 1458 m, 1402 w, 1396 w, 1387 m, 1376 w, 1371 w, 1354 w, 1349 w, 1339 w, 1321 w, 1313 w, 1309 w, 1303 s, 1293 m, 1244 w, 1231 w, 1224 w, 1200 w, 1164 w, 1148 m, 1140 w, 1114 w, 1099 w,

1071 m, 1009 w, 989 m, 971 w, 968 w, 907 m, 864 m, 835 m, 822 m, 820 m, 769 w, 701 m, 667 m, 641 w, 590 m, 551 w, 536 w, 424 w, 418 w cm^{-1} . UV irradiation ($\lambda > 260 \text{ nm}$; 40 min) using the 1000-W high-pressure Hg/Xe lamp resulted in complete conversion to 1-cyanoimidazole **11** and carbodiimide **21**: IR (Ar, 7K) 3430 m, 3419 m, 2282 w, 2269 m, 2205 w, 2164 w, 2135 s, 2118 m, 2084 w, 2044 w, 1626 w, 1532 w, 1484 m, 1428 w, 1379 w, 1281 m, 1252 w, 1240 w, 1236 m, 1232 w, 1226 w, 1105 w, 1103 w, 1070 w, 1064 w, 1011 w, 1008 w, 1001 m, 889 m, 851 w, 826 w, 823 w, 819 w, 811 m, 768 m, 761 w, 739 w, 737 w, 734 m, 727 w, 725 w, 645 w, 642 m, 597 w, 593 w, 587 w, 545 w, 537 w, 516 w, 507 w, 478 w, 453 w, 419 w cm^{-1} . This spectrum was essentially identical with that obtained from photolysis of **9T/9A**.

Warmup of Matrix-Isolated 11 and 22 Generated from 24T/24A. The warm procedure described for the photoproduct from **9** above was used. Neat **11** and **23**: IR (Ar, 42.5–43.5 K) 3130 m, 2269 s, 2239 s, 2139 s, 2031 w, 1533 w, 1483 m, 1404 w, 1375 w, 1329 w, 1282 m, 1240 m, 1186 m, 1103 m, 1068 m, 1026 w, 1000 m, 907 m, 893 w, 835 m, 739 m, 642 m, 591 m, 508 w, 484 w cm^{-1} .

Acknowledgment. The support of this work by the Australian Research Council and the National University of Singapore is gratefully acknowledged.

Supporting Information Available: Figure S1a, the IR spectrum of **9T** in KBr; Figures S1b,c, the IR spectra of **9A** and **9T** in Ar matrix; Figure S2, the calculated IR spectra of the four conformers of **22** and comparison with experiment; Figure S3, the IR spectra during isomerization of **22** to **23**; Figure S4, the calculated (B3LYP/6-31+G*) IR spectra of the four conformers of **23** and comparison with experiment; Figure S5a, the IR spectrum of **24T** in KBr, and Figure S5b, the mixture of **24A** and **24T** in Ar matrix; Figure S6, the photolysis of **24A/24T** to **11** and **22**; Figure S7, the thermal isomerization of **22** (derived from **24**) to **23**; tables of Cartesian coordinates, absolute energies, and IR spectra of all calculated compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0256991