5.99 (s, CH), 6.77-8.05 (m, ArH); IR (Nujol) 1668 cm^{-1} (C=O); MS (*m/z*) 167 (7, Ph$_2$CH$^+$), 165 (11), 149 (100, EtOC$_6$H$_4$CO$^+$), 135 (11), 121 (34). Anal. Calcd for C$_{22}$H$_{20}$O$_2$: C, 83.52; H, 6.37. Found: C, 83.79; H, 6.37.

1-Bromo-1-(*p*-ethoxyphenyl)-2,2-diphenylethene (**1Ab**) was identified by comparison with an authentic sample: mp 94-96 °C (EtOH) (lit.[19] mp 95 °C); ^{1}H NMR (CDCl$_3$) δ 1.36 (t, *J* = 7 Hz, Me), 3.95 (q, *J* = 7 Hz, CH$_2$), 6.58-7.33 (m, ArH).

4'-Methoxy-2,2-diphenylacetophenone (**7Aa**)[18] was identified by comparison with an authentic sample.

4'-Ethoxy-2,2-bis(*p*-methoxyphenyl)acetophenone (**7Bb**) oil; ^{1}H NMR (CDCl$_3$) δ 1.34 (t, *J* = 7 Hz, Me), 3.67 (s, Me), 3.96 (q, *J* = 7 Hz, CH$_2$), 5.79 (s, CH), 6.68-7.96 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 14.20, 54.66, 56.89, 63.29, 113.67, 113.83, 129.25, 129.72, 130.83, 131.64, 158.17, 162.40, 196.79; IR (Nujol) 1678 cm^{-1} (C=O); MS (*m/z*) 227 (100 An$_2$CH$^+$), 149 (41, EtOC$_6$H$_4$CO$^+$), 121 (18).

9-(*p*-Ethoxybenzoyl)xanthene (**7Cb**): mp 131-133 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.37 (t, *J* = 7 Hz, Me), 4.01 (q, *J* = 7 Hz, CH$_2$), 5.74 (s, CH), 6.74-8.00 (m, ArH); IR (Nujol) 1666 cm^{-1} (C=O). MS (*m/z*) 181 (100, xanthylium), 149 (94, EtOC$_6$H$_4$CO$^+$), 121 (34). Anal. Calcd for C$_{22}$H$_{18}$O$_3$: C, 79.98; H, 5.49. Found: C, 80.19; H, 5.44.

1-Bromo-1-(*p*-ethoxyphenyl)-2,2-bis(*p*-methoxyphenyl)ethene (**1Bb**) was identified by comparison with an authentic sample: mp 77-80 °C (EtOH) (lit.[19] mp 76 °C); ^{1}H NMR (CDCl$_3$) δ 1.36 (t, *J* = 7 Hz, Me), 3.68 (s, Me), 3.80 (s, Me), 3.96 (q, *J* = 7 Hz, CH$_2$), 6.49-7.35 (m, ArH); MS (*m/z*) 440 (28, M$^+$ + 2), 438 (28, M$^+$), 359 (100, M$^+$ − Br).

9-[Bromo(*p*-ethoxyphenyl)methylene]xanthene (**1Cb**): mp 120-122 °C (benzene-EtOH); ^{1}H NMR (CDCl$_3$) δ 1.41 (t, *J* = 7 Hz, Me), 4.02 (q, *J* = 7 Hz, CH$_2$), 6.69-8.37 (m, ArH); MS (*m/z*) 394 (37, M$^+$ + 2), 392 (37, M$^+$), 313 (100, M$^+$ − Br). Anal. Calcd for C$_{22}$H$_{17}$O$_2$Br: C, 67.19; H, 4.36. Found: C, 67.24; H, 4.32.

4'-Methoxy-2,2-bis(*p*-methoxyphenyl)acetophenone (**7Ba**)[18] and 9-(*p*-anisoyl)xanthene (**7Ca**)[21] were identified by comparison with authentic samples.

Solvolysis of 1-Bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (1Aa) in 80% EtOH with NaOH. A mixture of triarylbromoethene **1Aa** (438 mg, 1 mmol) and 80% EtOH (v/v) (60 mL) containing NaOH (12 mmol) was heated at 120 °C for 65 h in a pressure bottle. After evaporation of the solvent the crude products were hydrolyzed with a solution of 6 M HCl (5 mL) and ethanol (50 mL). After reflux for 2 h, the

solvent was evaporated, and the products were extracted three times with ether. The organic layer was washed with water and saturated NaCl and dried. The solvent was removed, and the residue was analyzed by ^{1}H NMR (400 MHz). Then, the residue was dissolved in a mixture of ether and benzene. The organic layer was extracted with aqueous NaOH, and the alkaline extract was acidified and again extracted with ether. The ethereal layer was washed with water and saturated NaCl and dried. Evaporation of the ether yielded a crystalline 4'-hydroxy-2,2-diphenylacetophenone (**7Ac**) (43 mg): mp 179-181 °C (lit.[22] mp 180-182 °C); ^{1}H NMR (CDCl$_3$) δ 4.80 (br s, OH), 5.97 (s, CH), 6.76 (d, *J* = 9 Hz, ArH), 7.26 (s, ArH), 7.93 (d, *J* = 9 Hz, ArH).

The former organic layer was washed with water and saturated NaCl and dried. After evaporation of the solvent, the residue was submitted to column chromatography on silica gel. Gradient elution with dichloromethane and hexane gave **1Ab**, **1Aa**, **7Ab**, and **7Aa**, in turn.

Solvolysis of 1-Bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (1Aa) in Ethanol with 2,6-Lutidine. A mixture of triarylbromoethene **1Aa** (438 mg, 1.2 mmol), 2,6-lutidine (1.4 mL, 12 mmol), and ethanol (60 mL) was heated at 130 °C for 48 h in a pressure bottle. After evaporation of the solvent, the products were extracted with ether, and the organic layer was washed with water and saturated NaCl and dried. The solvent was evaporated, and the products were analyzed by ^{1}H NMR (400 MHz) by using hexamethylbenzene as an internal standard.

Registry No. 1Aa, 25354-48-7; **1Ab**, 121410-90-0; **1Ac**, 133776-70-2; **1Ad**, 135043-32-2; **1Ba**, 25354-46-5; **1Bb**, 135043-37-7; **1Ca**, 87712-58-1; **1Cb**, 135043-38-8; **2Aaa**, 122127-41-7; **2Aab**, 122127-42-8; **2Aac**, 122127-43-9; **2Aad**, 122127-48-4; **2Aba**, 121410-92-2; **2Abb**, 121410-93-3; **2Acc**, 122127-49-5; **2Add**, 122127-50-8; **2Aeb**, 135043-33-3; **2Afb**, 135043-34-4; **3Aaa**, 122127-44-0; **3Aab**, 122127-45-1; **3Aac**, 122127-46-2; **3Aad**, 122127-47-3; **3Abb**, 121410-91-1; **4a**, 41038-34-0; **4b**, 60883-74-1; (*E*)-**5a**, 128421-76-1; (*Z*)-**5a**, 128421-77-2; (*E*)-**5b**, 128421-73-8; (*Z*)-**5b**, 128421-74-9; **6a**, 122127-54-2; **6b**, 128421-72-7; **7Aa**, 1889-74-3; **7Ab**, 128191-31-1; **7Ba**, 61161-13-5; **7Bb**, 135043-35-5; **7Ca**, 87712-61-6; **7Cb**, 135043-36-6; TEA, 121-44-8; NaOMe, 124-41-4; NaOEt, 141-52-6; NaOPr, 6819-41-6; NaO-*i*-Pr, 683-60-3; KO-*t*-Bu, 865-47-4; *t*-BuOH, 75-65-0; K$_2$CO$_3$, 584-08-7; NaHCO$_3$, 144-55-8; NaOH, 1310-73-2; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *i*-PrOH, 67-63-0; 2,6-lutidine, 108-48-5; pyridine, 110-86-1; 1-(*p*-(methylthio)phenyl)-2,2-diphenylethene, 133776-80-4.

HCN Dimers: Iminoacetonitrile and *N*-Cyanomethanimine

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Abstract: Iminoacetonitrile (**1**) has been prepared by two methods: (i) thermal decomposition of the tosylhydrazone salts **13** at 200 °C and (ii) Ar matrix photolysis of azidoacetonitrile (**15**). Ab initio calculations indicate that **1Z** is of slightly lower energy than **1E**, and this is confirmed by the IR spectra with use of the thermal methods. **1E/1Z** undergo photochemical interconversion, giving a ca. 3:1 photostationary *E:Z* ratio. **1E** and **1Z** are fully characterized by their gas-phase, matrix, and thin-film IR spectra, which are in excellent agreement with ab initio calculations, by ^{1}H and ^{13}C NMR spectroscopy in solution, and by mass spectrometry. **1** polymerizes in solution above −40 °C; pyrolysis produces HCN, and matrix photolysis produces HNC and van der Waals complexes containing HNC. *N-tert*-Butyliminoacetonitrile thermally fragments to *tert*-butyl isocyanide and HCN. *N*-Cyanomethanimine (**3**) has also been prepared by two methods: (i) pyrolysis of trimethylenetetrazole (**20**) at 500-800 °C and (ii) pyrolysis of ditetrazolopyrazine **22** at 600-850 °C. Both methods are extremely clean. **3** is fully characterized by its IR spectrum in agreement with ab initio calculations and, in conjunction with other work, by its mass and millimeter-wave spectra. **3** is thermodynamically stable in the gas phase up to ca. 800 °C at low pressure and short contact times but polymerizes in the solid state above −100 °C.

Introduction

The covalent dimers of HCN are of considerable interest as potential interstellar and prebiotic molecules. Both HCN and HNC are widely distributed in interstellar clouds.[2] HCN, (CN)$_2$,

and cyanoacetylene have been detected in the atmosphere of Titan[3] and HCN and the CN radical on comets.[4] HCN is widely

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theorized to have played a crucial role in the prebiotic synthesis of amino acids, purines, and pyrimidines[5] on the primitive Earth, although the source of the HCN and the composition of the primordial atmosphere on Earth are still under debate.[6]

Mechanisms proposed for the tetramerization (to diaminomaleonitrile) and polymerization of HCN,[7,8] as well as the pentamerization to adenine[9] and the prebiotic syntheses of other purines and pyrimidines,[5] usually involve initial dimerization of HCN to iminoacetonitrile, HN=CHCN.[10] The problem with all these studies is that iminoacetonitrile has never been detected, and there is a long history of abortive syntheses of this compound.

Claisen and Mathews[13] in 1883 described the "sesquihydrochloride" of HCN, formulated as 2HCN·3HCl. On heating of this material in quinoline, Nef[14] isolated a small amount of a substance, mp 87 °C, that on the basis of a preliminary molecular weight determination (64 amu) was identified as "iminoformyl cyanide" (HN=CHCN). Willstätter and Wirth[15] "confirmed" this report, generating the same compound by thermal elimination of H_2S from thioformamide. However, Hinkel and Dunn[16]

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Table 1. Calculated Energies[a]

	HF/6-31G*		MP2/6-31G*	MP2/6-31G**	
	total energy	relative energy	total energy	total energy	relative energy
1Z	-185.758 16	-4.88	-186.339 79	-186.357 35	-5.41
1E	-185.757 99	-4.77	-186.339 09	-186.356 65	-4.97
2	-185.757 82	-4.66		-186.357 39	-5.43
3	-185.751 06	-0.42	-186.330 21	-186.346 01	1.71
2HCN	-185.750 39	0		-186.348 73	0
4Z	-185.738 82	7.26	-186.305 02	-186.322 66	16.36
4E	-185.737 50	8.09	-186.303 82	-186.321 52	17.07
H₂ + NCCN	-185.718 04	20.30		-186.332 29	10.32
5	-185.716 53	21.25			
2HN≡C	-185.710 66	24.93		-186.284 64	40.21
6	-185.699 61	31.86			
7	-185.691 90	36.70			
8Z	-185.687 98	39.16			
8E	-185.687 00	39.78			
9E	-185.674 95	47.34		-186.280 41	42.87
10	-185.655 32	59.65			
11	-185.645 28	65.95			
12	-185.624 30	79.12			

[a] Calculated[36] total energies in atomic units; relative energies in kilocalories/mole.

Table II. Relative Energies of 1Z and 1E[a]

level of theory	1Z (au)	1E (au)	ΔE (1E − 1Z) (kcal/mol)
HF/6-31G*	-185.758 06	-185.757 99	0.11
MP2/6-31G*	-186.323 27	-186.322 60	0.43
MP3/6-31G*	-186.326 78	-186.326 50	0.18
MP4(SDTQ)/6-31G*	-186.368 85	-186.367 95	0.56
MP2/6-31G**// MP2/6-31G*	-186.340 46	-186.339 79	0.42
MP3/6-31G**// MP2/6-31G*	-186.344 69	-186.344 42	0.17
MP4(SDTQ)/6-31G**// MP2/6-31G*	-186.386 76	-186.385 90	0.54
MP2/6-31G**	-186.340 49	-186.339 81	0.43
MP3/6-31G**	-186.344 78	-186.344 52	0.16
MP4(SDTQ)/6-31G**	-186.386 75	-186.385 90	0.53
ZPE[b]	24.82	24.77	-0.05

[a] MP3 and MP4(SDTQ) calculations were performed by using the GAUSSIAN 88 program package.[36] Total energies in atomic units (au). [b] Zero point energy in kilocalories/mole.

concluded that the compound obtained from the sesquihydrochloride in quinoline was not iminoacetonitrile but instead "iminoformyl isocyanide" (HN=CHNC). It was only in 1954 that Grundmann and Kreutzberger[17] determined that this so-called "HCN dimer" was neither a nitrile nor an isocyanide, but in fact a trimer, 1,3,5-triazine.

Boyer, Dunn, and Kooi[18] irradiated neat azidoacetonitrile (N_3CH_2CN) at -196 °C and observed IR bands at 3250, 3155, and 1605 cm⁻¹ ascribed to iminoacetonitrile (HN=CHCN). The bands for this compound were also reported to appear at 2210 and 1603 cm⁻¹.[19] Further irradiation at -196 °C caused the formation of new bands at 3250 (sh), 3135 (s), 2101 (s), 1618 (s), and 830 (s) cm⁻¹, which were assigned to the corresponding isocyanide (HN=CHNC).[18] In a subsequent paper, Boyer and Kooi[20] claimed the detection of the short-lived iminoacetonitrile (HN=CHCN) in the reaction of aminoacetonitrile with calcium hypochlorite, and it now absorbed at 3270, 2960, 2205, 1605, 1405, and 1320 cm⁻¹.

It will become obvious from the results presented in this paper that the above data compare unfavorably with the true values for

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HN=CHCN, even though this compound is in fact produced on photolysis of azidoacetonitrile in an Ar matrix at 308 nm.[21] As for the iminoformyl isocyanide (HN=CHNC) claimed by Boyer, Dunn, and Kooi,[18] we have shown[21] that the compound obtained was in fact the HCN monomer.

There is one more $C_2H_2N_2$ isomer predicted by theory to be more stable than two molecules of HCN, viz. N-cyanomethanimine, H_2C=NCN. This compound was first prepared by Wentrup by thermolysis of 1,5-trimethylenetetrazole,[22] which remains the method of choice. It was identified by its high-resolution mass spectrum,[22] and subsequently by millimeter-wave[23,24] and photoelectron spectroscopy.[25,26] A far less efficient method of production is the pyrolysis of N,N-dimethylcyanamide,[27a] but the microwave spectrum of CH_2=NCN was first obtained in this way.[27b] The mechanism of pyrolysis of N,N-dimethylcyanamide is obscure, and the reaction is very sensitive to surface effects and reaction conditions:[27b,24,28] under certain conditions, no CH_2=NCN but instead HN=CHCN is obtained.[28-31]

In this paper we report full details of our preparations and characterization of HN=CHCN and CH_2=NCN. Some of the results have been published previously in preliminary form.[1b,21,25,28,32] Since reliable calculations of vibrational frequencies were required for definitive assignment of the IR spectra, a computational section is included.

Results and Discussion

1. Calculations.[36] The $C_2H_2N_2$ isomers **1–12** under consideration are shown on a qualitative energy scale relative to two molecules of HCN in Figure 1. The van der Waals dimer **2**, a known and linear molecule,[33] is also included. While not all the $C_2H_2N_2$ molecules are true HCN dimers in the sense that they are not expected to be formed by dimerization of HCN, they are nevertheless of relevance as precursors (e.g., aminocyanocarbene (**5**; see section 2)) or as possible photoisomerization products (e.g., isocyanides **4Z** and **4E**, and HNC (section 2h)), as postulated[10] dimers of HCN (**8E**, **8Z**), and in relation to structure determination of $C_2H_2N_2$ ions in mass spectrometry.[34,35] Further ex-

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(32) Wentrup, C. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: Orlando, FL, 1984; pp 395–432 (in particular p 403).

(33) Legon, A. C.; Millen, D. J. *Chem. Rev.* **1986**, *86*, 635–657 and references therein. Higher clusters, (HCN)ₙ are known: Anex, D. S.; Davidson, E. R.; Douketis, C.; Ewing, G. E. *Ibid.* **1988**, *92*, 2913–2925. Further discussion is given below and in refs 42–45.

(34) Nenner, I.; Dutuit, O.; Richard-Viard, M.; Morin, P.; Zewail, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1093–1098.
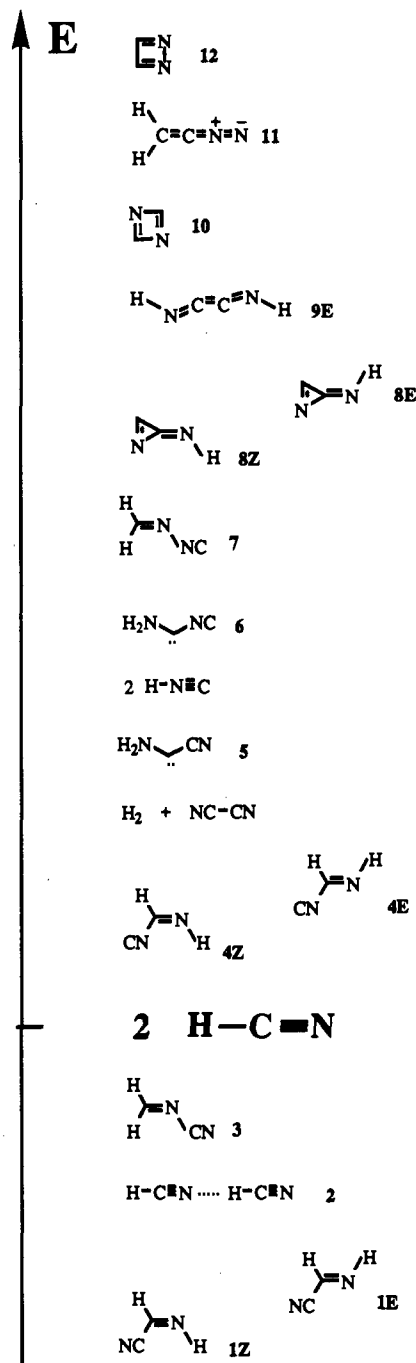

Figure 1. Structures of $C_2H_2N_2$ isomers, arranged according to energy based on HF/6-31G* calculations. For energy values see Tables I and II.

perimental and theoretical work on the molecular ions[34,35] and ionization potentials[25,26] will be published.

Absolute and relative enthalpies of formation calculated at the HF/6-31G* level of theory are given in Table I, and the full geometries optimized at this level for all of the molecules (**1–12**), and at the MP2/6-31G* level for **1Z**, **1E**, **3**, and **9E**, are published in the supplementary material.

Energy calculations were also performed at the MP2/6-31G** level of theory for the more important molecules (Table I). While

(35) Maquestiau, A.; Flammang, R.; Plisnier, M.; Schwarz, H.; Weiske, T.; Terlouw, J. K.; Wentrup, C. Abstract, 7th Congrès National de Spectrométrie de Masse Fondamental et Appliquée, Rennes, France, Sept 25–27, 1989; *Spectra Biol.* **1989**, *17*, 46.

(36) Ab initio calculations: Amos, R. D.; Rice, J. E. CADPAC: The Cambridge Analytic Derivatives Package, Issue 4.0, Cambridge, England, 1987. For Møller–Plesset (MP) 3 and MP4 calculations, GAUSSIAN 88 was used: Gaussian, Inc., Pittsburgh, PA.

Scheme I

a: M = Na
b: M = Li

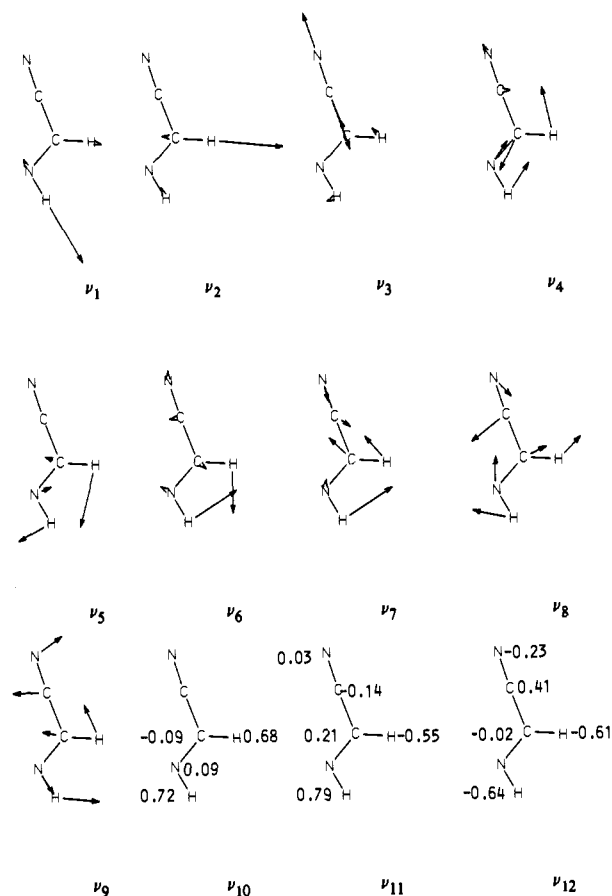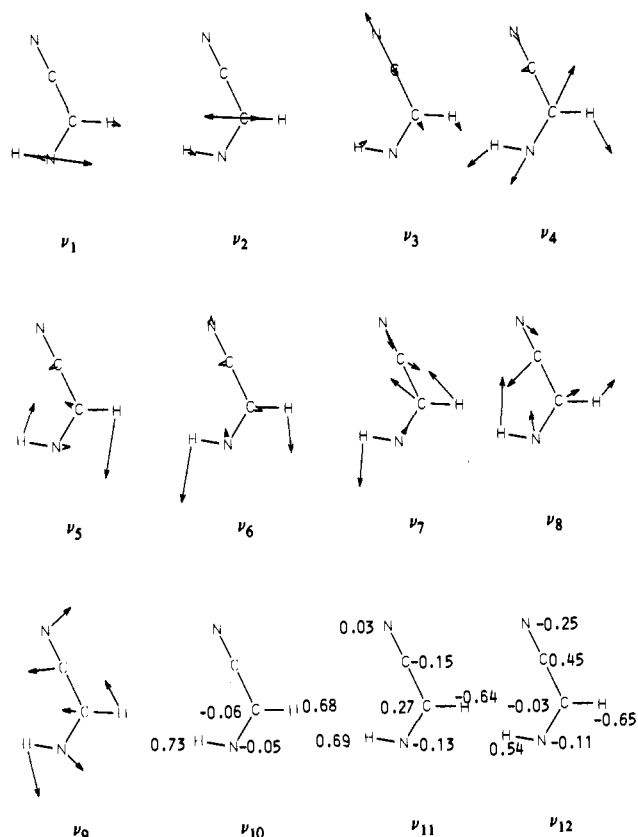**Chart I.** Normal Vibrations of 1E (MP2/6-31G* Calculations)
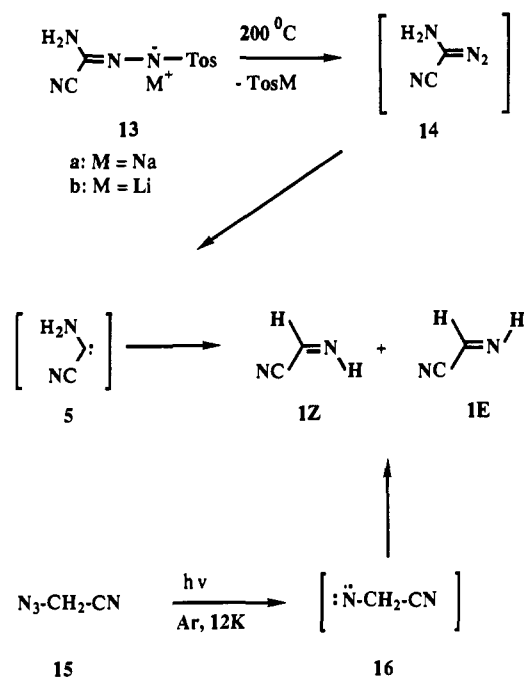
there are obvious changes in relative energies as a function of the basis set, these are of little consequence in the present study, except for the relative energies of **1Z** and **1E**, which are treated in detail below (Table II). The energy ordering used in Figure 1 pertains to the HF/6-31G* calculations, and these data are in qualitative agreement with earlier work on a more limited set of molecules at the DZ+P/SCEP level of theory.[12] The enthalpy of formation of the HCN···HCN van der Waals dimer (**2**) may be artificially low in our MP2/6-31G** calculations, which predict it to be the most stable of all the dimers. Further calculations of the energies and IR spectra of HNC···HCN, and HCN···HNC, and HN-C···HNC have been carried out and will be published separately. The energies increase in the following order: HCN···HCN (0), HCN···HNC (17.5), HNC···HCN (19.46), HNC···HNC (36.56 kcal/mol) (MP2/6-31G** level). These species are of importance as photofragmentation products of **1** (section 2h).

From the relative energies (Figure 1 and Table I) is may be safely concluded that **5**, **8**, and **9** (and the other high-lying species) are unlikely prebiotic HCN dimers. Apart from van der Waals dimers, only iminoacetonitrile (**1**) and *N*-cyanomethanimine (**3**) are found to be more stable than, or nearly equienergetic with, 2HCN. The energies of the isocyanomethanimines (**4**) are, however, low enough to merit further experimental work, and as will be shown below, the relatively low-lying aminocyanocarbene (**5**) is an excellent precursor of **1**. We have not calculated cyanomethylnitrene (**16**, Scheme I), but we can predict that it will lie ca. 80 kcal/mol above **1**.[37] **16**, too, is a useful precursor of **1**.

The relative energies of (*E*)- and (*Z*)-iminoacetonitrile (**1E** and **1Z**) are of importance for the assignment of infrared spectra. They are the only isomers close enough in energy to require an examination of the influence of the basis set on the energy ordering. Data are given in Table II. At the STO-3G level,[21] **1Z** was found to be lower than **1E** by 0.37 kcal/mol, but the order was reversed at the 4-31G (**1E** lower than **1Z** by 0.10 kcal/mol)[21] and 6-31G

Chart II. Normal Vibrations of 1Z (MP2/6-31G* Calculations)

(**1E** lower than **1Z** by 0.24 kcal/mol) levels. However, at still higher levels, **1Z** consistently becomes the lowest energy isomer,

(37) (a) Singlet methylnitrene is found not to be an energy minimum computationally.[37b] The transition state for decomposition of methyl azide to methanimine and N₂ can be estimated to lie ca. 81 kcal/mol above ground state methanimine.[37c] Accordingly, the transition state for the thermal reaction **15 → 1 + N₂** is expected to lie some 80 kcal/mol above **1**. (b) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270–284. (c) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; pp 204–205 and 227–228. Wentrup, C. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; pp 395–432.

HCN Dimers

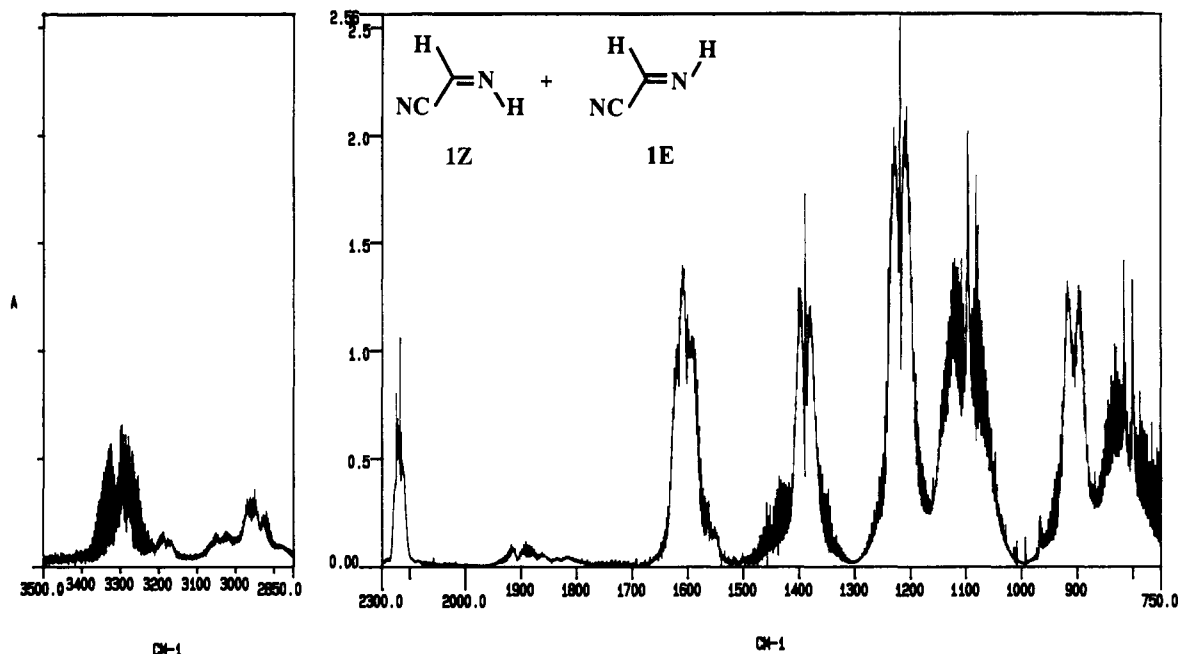J. Am. Chem. Soc., Vol. 113, No. 19, 1991   7265

Figure 2. Gas-phase IR spectrum of **1** produced from **13a** at 200 °C. Spectrum recorded at room temperature (1 mbar).

Table III. Calculated IR Spectral Data and Rotational Constants of **4E**, **4Z**, and **9E**[a]

symmetry	vibration	assignment	frequency (intensity)
4E (62.772 181 7, 5.405 200 4, 4.976 668 4)[b]			
A'	ν_1	ν_{N-H}	3507 (6.9)
A'	ν_2	ν_{C-H}	3190 (16.0)
A'	ν_3	$\nu_{C=N}$	2159 (188.5)
A'	ν_4	$\nu_{C=N}$	1694 (72.2)
A'	ν_5	δ_{C-H}	1445 (18.2)
A'	ν_6	δ_{N-H}	1273 (58.9)
A''	ν_{10}	$\tau_{C=N}$	1089 (8.6)
A'	ν_7	ν_{C-NC}, δ_{NH}	966 (111.8)
A''	ν_{11}	CH, NH o.o.p. sym	863 (35.9)
A'	ν_8	δ_{NCN}	621 (6.2)
A''	ν_{12}	$\gamma_{NH,CH,NC}$	256 (9.2)
A'	ν_9	γ_{NCNC}	200 (2.5)
4Z (55.786 855 4, 5.446 885 7, 4.962 372 4)[b]			
A'	ν_1	ν_{N-H}	3487 (6.2)
A'	ν_2	ν_{C-H}	3260 (5.4)
A'	ν_3	$\nu_{C=N}$	2138 (165.6)
A'	ν_4	$\nu_{C=N}$	1688 (61.3)
A'	ν_5	δ_{C-H}	1437 (21.5)
A'	ν_6	δ_{N-N}	1252 (126.0)
A''	ν_{10}	CH, NH o.o.p. sym	1120 (84.7)
A'	ν_7	ν_{C-NC}, δ_{NH}	958 (47.4)
A''	ν_{11}	τ_{C-N}	860 (26.8)
A'	ν_8	δ_{HNCN}	588 (31.4)
A''	ν_{12}	$\tau_{C=N}$, $\gamma_{N=C}$	251 (6.1)
A'	ν_9	δ_{HNCNC}	195 (5.9)
9E (23.6130, 4.250, 4.175)[b]			
B_u	ν_1	$\nu_{a N-H}$	3489 (7.4)
A_g	ν_2	$\nu_{s N-H}$	3489 (0.0)
A_g	ν_3	$\nu_{C=C}$	2080 (0.0)
B_u	ν_4	$\nu_{C=N}$	1730 (81.5)
A_g	ν_5	$\delta_s HN$	1178 (0.0)
B_u	ν_6	$\delta_a HN$	1123 (435.9)
A_u	ν_7	τ_{N-H}	965 (135.6)
A_g	ν_8	δ_{HNC}	932 (0.0)
B_g	ν_9	skel tors	716 (0.0)
A_g	ν_{10}	skel tors	345 (0.0)
B_u	ν_{11}	skel tors	286 (6.1)
A_u	ν_{12}	skel tors	250 (0.01)

[a] MP2/6-31G* calculations for **4E** and **4Z**; MP2/6-31G** calculation for **9E** (**9Z** is not a minimum). Frequencies in reciprocal centimeters; intensities in km/mole; o.o.p. = out-of-plane. [b] Rotational constants A, B, and C in gigahertz.

0.54 kcal/mol below **1E** at the MP4/6-31G**//MP2/6-31G* level (Table II). This is in agreement with the results of Clemmons et al.[12] (**1Z** below **1E** by 0.31 kcal/mol at the DZ+P/SCEP level).

Vibrational frequencies and intensities for **1Z**, **1E**, **3**, **4Z**, **4E**, and **9E** were calculated at the MP2/6-31G* level. For **1E**, **1Z**, and **3**, these data are in Tables IV and V along with the experimental results. The calculated IR data for **4E**, **4Z**, and **9E** is given in Table III, as are the rotational constants. Note that the planar, trans-bent ethenediimine (**9E**) represents the only minimum found for this molecule at the MP2/6-31G** level. The corresponding Z form had been predicted as well by STO-3G and 4-31G calculations.[21]

The MP2/6-31G* geometries and normal vibrational modes of **1E**, **1Z**, and **3** are illustrated in Charts I–III. Approximate descriptions of the modes are given in Tables IV and V; refer to the charts for a full description.

2. Iminoacetonitrile (1). We have used two methods to generate this compound (Scheme I). One is the thermal decomposition of the sodium salt of 1-cyanoformamide tosylhydrazone (**13a**) at 200 °C. The lithium salt **13b** can be used equally well, but it is more hygroscopic and therefore less convenient. The reaction is believed to proceed via 2-amino-2-diazoacetonitrile (**14**), but this compound is unstable at 200 °C, which is the optimal temperature for the generation of **1**. The diazo compound **14** and aminocyanocarbene (**5**) are presumably formed in rapid succession, the latter isomerizing to **1**. Slow decomposition of **13a** at 150 °C with product isolation at 13 K gave rise to a weak signal at 2040 cm⁻¹ in the IR; if this is due to **14**, very little survives the experiment, for mass spectrometric monitoring of the process did not give any evidence for a m/z 82 species being formed. Instead, **1** is formed immediately, as described below.

The other method of producing **1** is the photochemical decomposition of azidoacetonitrile (**15**), formally via the nitrene **16**.[37] Both methods have advantages. The tosylhydrazone route from **13** allows the thermal generation of **1** under mild conditions. The azide route can only be used photochemically since a temperature above 500 °C is required to decompose **15** in a flash vacuum pyrolysis (FVP) system. Under these conditions, **1** decomposes almost completely to HCN. The two methods complement each other, and this was crucial for the unambiguous assignment of the infrared bands belonging to **1**.

(a) Gas-Phase IR Spectrum. The gas-phase IR spectrum (Figure 2) was obtained by passing the vapors from the decomposition of **13a** through a 6-m path length gas cell, initially at 6

Table IV. Infrared Spectroscopy Data of Iminoacetonitrile (1E and 1Z)

symmetry	vibration	assignment[a]	ω calcd (cm⁻¹)[b] (intensity (km/mol))	obsd gas phase (cm⁻¹)[a]	Ar matrix[c] ex 13a
			E Isomer (1E)		
A'	ν_1	ν_{N-H}	3473 (1.6)	3288 (w)	
A'	ν_2	ν_{C-H}	3164 (14.7)	(3050–2930)[l] (vw)	
A'	ν_3	$\nu_{C\equiv N}$	2205 (24.7)	2246.5 (w)	2240 (w)
A'	ν_4	$\nu_{C=N}$	1667 (24.1)	1609 (m)	1611 (s)
A'	ν_5	$\delta_{CH}\ \delta_{NH}$ as.	1443 (28.6)	1386 (m)	1375 (m)
A'	ν_6	$\delta_{NH}\ \delta_{CH}$ sym	1272 (48.9)	1218 (s)	1219 (m)
A''	ν_{10}	$\tau_{C=N}$	1125 (10.2)		1075 (vw)
A'	ν_7	$\nu_{CC},\ \delta_{NH}$	937 (46.3)	908 (m)	895 (s)
A''	ν_{11}	NH, CH o.o.p. sym	843 (52.8)	800 (m)	800 (m)
A'	ν_8	δ_{NCC}	621 (5.4)		
A''	ν_{12}	$\gamma_{NH,CH,CN}$	337 (4.9)		
A'	ν_9	$\delta_{C-N},\ \delta_{C\equiv N}$	243 (5.4)		
			Z Isomer (1Z)		
A'	ν_1	ν_{N-H}	3460 (1.8)	3288 (w)	
A'	ν_2	ν_{C-H}	3230 (5.2)	(3050–2930)[l] (vw)	
A'	ν_3	$\nu_{C\equiv N}$	2185 (18.7)	2239.5 (w)	2227 (w)
A'	ν_4	$\nu_{C=N}$	1646 (23.2)	1609 (m)	1600 (s)
A'	ν_5	$\delta_{CH},\ \delta_{NH}$ as.	1447 (17.1)	1387 (m)	1388 (m)
A'	ν_6	$\delta_{NH},\ \delta_{CH}$ sym	1265 (90.5)	1217 (s)	1221 (s)[m] 1216 (vs)[m]
A''	ν_{10}	NH, CH, o.o.p. sym	1150 (76.3)	1095 (s)	1096 (s)[m] 1093 (vs)[m]
A'	ν_7	$\nu_{CC},\ \delta_{NH}$	940 (22.0)	908 (m)	902 (s)
A''	ν_{11}	$\tau_{C=N}$	834 (13.9)	815 (m)	817 (w)[m] 816 (m)[m]
A'	ν_8	δ_{NCC}	607 (7.1)		
A''	ν_{12}	$\tau_{C=N},\ \gamma_{C\equiv N}$	330 (21.4)		
A'	ν_9	$\delta_{C-N},\ \delta_{C\equiv N}$	221 (14.2)		

	Ar matrix ex 15		$\Delta\nu(^{14}N-^{15}N)$[g]			$\Delta\nu(^1H_2-^2H_2)$[i]		
	308 nm[d,e]	254 nm[e,f]	obsd	calcd	thin-film ex 13a[h]	obsd	calcd[j]	calcd[k]
			E Isomer (1E)					
ν_1				8	3190 (free) (s), 3174, 3159 (AS) (s)	821	994	946
ν_2	2928° (vw)	2928 (vw)°		0	3017 (w)	724	734	775
ν_3	2240 (0.10)	2240 (0.25)	0	0	2241 (w)	10	118	101
ν_4	1610 (0.50)	1611 (0.6)	17	20	1604 (s)	24	48	30
ν_5	1375 (0.45)	1375 (0.53)	10	11	1406 (s)	254	276	179
ν_6	1219 (0.40)	1219 (0.5)	p	3	1268 (m)	233	308	329
ν_{10}	1075 (0.12)	1075 (0.1)	2	4	1132 (m)	131	264	194
ν_7	895 (0.28)	894 (0.5)	1	0.3	900 (m-s)		128	179
ν_{11}	800 (0.64)	800 (0.7)	1	0.1	855 (m-s)		153	155
ν_8	ca. 606ⁿ (0.02)	ca. 606ⁿ (vw)		6				
			Z Isomer (1Z)					
ν_1				8	3190 (free) (s), 3174, 3159 (AS) (s)	821	987	945
ν_2	2944° (vw)	2944 (vw)°		0	3017 (vw)	751	811	795
ν_3	2227 (0.03)	2227 (0.07)	0	0	2227		53	87
ν_4	1600 (0.15)	1600 (0.25)	18	22	1597	26	39	25
ν_5	1388 (0.08)	1388 (0.1)	4	4	1420	292	343	248
ν_6	1221 (0.30)	(1221) (s)ᵖ	p	7	1282	230	287	282
	1216 (0.42)	1217 (0.7)						
ν_{10}	1096 (0.36)	1096 (0.35)	1	2	1147	124	331	144
	1093 (0.15)	1093 (0.25)	1					
ν_7	902 (0.11)	902 (0.25)	1	2	907		71	221
ν_{11}	817 (0.06)		2	4			102	139
		816 (0.1)						
ν_8	ca. 606ⁿ (0.03)	ca. 606ⁿ (vw)		5				

[a] Gas-phase values at room temperature (1 mbar), 0.5-cm⁻¹ resolution: w, weak; m, medium; s, strong; v, very; AS, associated; o.o.p., out-of-plane; sym, symmetric; as., antisymmetric. [b] Calculated frequencies and intensities (MP2/6-31G*). [c] 13a thermolyzed at 200 °C. Ar matrix deposition at 20 K (8 × 10⁻⁶ mbar). Spectrum recorded at 20 K. [d] 15 deposited in Ar matrix at 30 K (10⁻⁵ mbar) and photolyzed at 308 nm (Lambda Physik excimer laser) at 11 K for 40 min. Spectrum recorded at 11 K. [e] Absorbance values (in parentheses) are variable and are given only as an indicative measure as integrated intensities were not recorded. They vary strongly depending on the quality of the matrix and the spectral resolution used. [f] 15 deposited in Ar matrix at 30 K (10⁻⁵ mbar) and photolyzed at 254 nm (low-pressure Hg lamp) at 12 K for 30 min. Spectrum recorded at 12 K. [g] Frequency shift (cm⁻¹) between bands for H¹⁴N=CHCN and H¹⁵N=CHCN. Observed values as in *d* at 308 nm. Calculated values (cm⁻¹) at 6-31G level only. [h] 13a thermolyzed at 200 °C and deposited neat on NaCl at 77 K and then warmed to 208 K. Data for Z isomer at 208 K. Data for *E* isomer at 0 °C. [i] Frequency shift (cm⁻¹) between bands for HN=CHCN and DN=CDCN in thin film as in *h*. [j] Calculated shifts (cm⁻¹) at 6-31G level. [k] MNDO calculated values (cm⁻¹). [l] Assignment uncertain; see text. [m] Two matrix sites. [n] Very weak bands present at 608, 606, and 604 cm⁻¹. Assignment uncertain. [o] Very weak C-H stretching bands. Attribution to individual isomers (1E and 1Z, or 1Z and 1E) uncertain. [p] Residual azide 15 interfering.

× 10⁻² mbar. After all solvent remaining in the salt was removed, the gas cell was closed and allowed to fill with iminoacetonitrile.
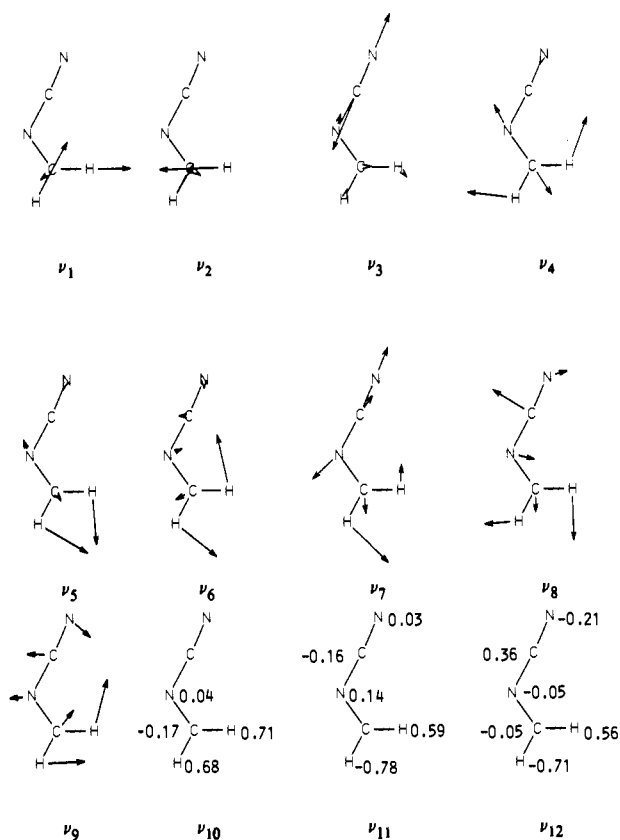
Spectra were measured at total pressures of 0.2–1 mbar. At 1 mbar, intense spectra due to 1 were obtained, with absorbance

HCN Dimers

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Table V. Infrared Spectrum of *N*-Cyanomethanimine (3)

symmetry	vibration	assignment	calcd (cm^{-1})[a] (intensity (km/mol))	obsd[b] (cm^{-1})	obsd[c] (cm^{-1})
A′	ν_1	ν_a CH$_2$	3291 (6.3)	3144 (w)	3137 (w)
A′	ν_2	ν_s CH$_2$	3163 (11.3)	3097 (m)	d
A′	ν_3	$\nu_{C\equiv N}$	2201 (5.9)	2211 (vs)	2208 (vs)
A′	ν_4	$\nu_{C=N}$	1696 (13.9)	1619, 1614 (s)	1621 (s)
A′	ν_5	δ_{CH_2}	1534 (9.4)	1463, 1456 (m-s)	1456 (m-s)
A′	ν_6	ρ_{CH_2}	1255 (6.7)	1219 (m)	1215 (m)
A″	ν_{10}	ω_{CH_2}	1098 (22.4)	1101, 1097 (m-s)	1090 (m)
A′	ν_7	ν_{C-N}	949 (6.1)	939 (w)	d
A″	ν_{11}	τ_{C-N}	784 (0.73)	754 (vw)	
A′	ν_8	δ_{HCNC}	613 (2.8)	636 (w)	
A″	ν_{12}	τ_{C-N}, $\gamma_{C\equiv N}$	358 (9.8)		
A′	ν_9	δ_{HCNCN}	241 (6.3)		

[a] MP2/6-31G* calculations. [b] Neat, 77 K. [c] In the presence of C$_2$H$_4$ and Ar, at 12 K. C$_2$H$_4$ absorbs at 3094, 2977, 1438, and 955 cm^{-1}. [d] Obscured by C$_2$H$_4$.

Chart III. Normal Vibrations of **3** (MP2/6-31G* Calculations)
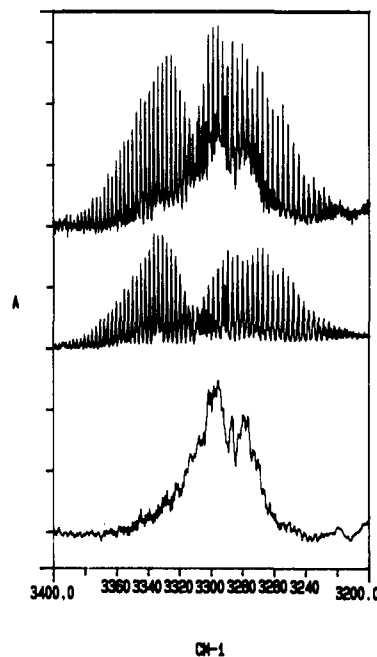

Figure 3. ν_{NH} region of the gas-phase IR spectrum of **1** (top), HCN (middle), and the spectrum of **1** after subtraction of HCN (bottom).

units up to 2.5 for the strongest peaks.

The dimers **1Z** and **1E** are reasonably long-lived under these conditions (half-life 40 min at ca. 0.4 mbar), easily permitting the measurement of the full IR spectrum at a resolution of 0.5 cm^{-1} in 17.2 min. HCN is invariably produced as a byproduct, but this can be minimized by ensuring that the temperature used for decomposing the salt **13** does not exceed 200 °C. HCN is *not* a product of the room temperature gas-phase decomposition of **1**; the spectrum of **1** gradually disappears as higher molecular weight, involatile compounds are formed, but the HCN concentration does not increase. The bands due to **1Z** and **1E** disappeared at the same rate under these conditions, and no new bands grew in.

The assignment of the experimental spectrum (Table IV) is made on the basis of the ab initio calculations (Table IV and Charts I and II). Not only the absolute frequency values but also the relative positions and intensities of bands due to the individual isomers (**1Z** and **1E**) are in excellent agreement with calculations. The only discrepancy is the out-of-plane deformation near 800 cm^{-1}, where theory predicts $\nu(E) > \nu(Z)$ (by 9 cm^{-1}). From the matrix spectra, to be described below, we know that **1Z** is the

major isomer (in agreement with the energy calculations (Table II)) and that **1Z** can be photolytically converted into **1E**. From thin-film experiments at −20 to 0 °C, we also know that the *Z* isomer disappears more rapidly on warmup. The assignment of bands to the individual geometrical isomers is therefore well secured.

The ν_{NH} stretching vibration (ν_1) gave rise to a very weak band of B type with the Q branch centered at 3288 cm^{-1}. This band occurs under the ν_{CH} band of HCN at 3311 cm^{-1}. Because HCN could never be completely eliminated, the ν_{NH} band of **1** was best observed by subtraction of the HCN spectrum (Figure 3). The value of 3288 cm^{-1} is in good agreement with expectations for an imine NH; in methanimine this band is observed at 3264 cm^{-1} in the gas phase,[38] and in ethylideneimine[39] in Ar matrix at 3264 (*E*; vvw) and 3247 cm^{-1} (*Z*, vvw), whereby another very weak band at 3288 cm^{-1} was ascribed to $2\nu_{C-N}$ ($\nu_{C-N} = 1660$ cm^{-1}). Our lower value of ν_{C-N} (1609 cm^{-1}) makes it impossible that our 3288-cm^{-1} band could be due to $2\nu_{C-N}$. However, the weaker band at 3180 cm^{-1} (Figure 2) is by shape and position very likely due to $2\nu_{C-N}$ ($2\nu_4$).

The ν_{CH} vibration (ν_2) expected between 3100 and 2900 cm^{-1} was very weak, weaker than the ν_{NH} band, and we do not claim its definitive identification in the gas-phase spectra, although very

(38) Hamada, Y.; Hashiguchi, K.; Tsuboi, M.; Koga, Y.; Kondo, S. *J. Mol. Spectrosc.* **1984**, *105*, 70-80.
(39) Stolkin, I.; Ha, T.-K.; Günthard, H. H. *Chem. Phys.* **1977**, *21*, 327-347.
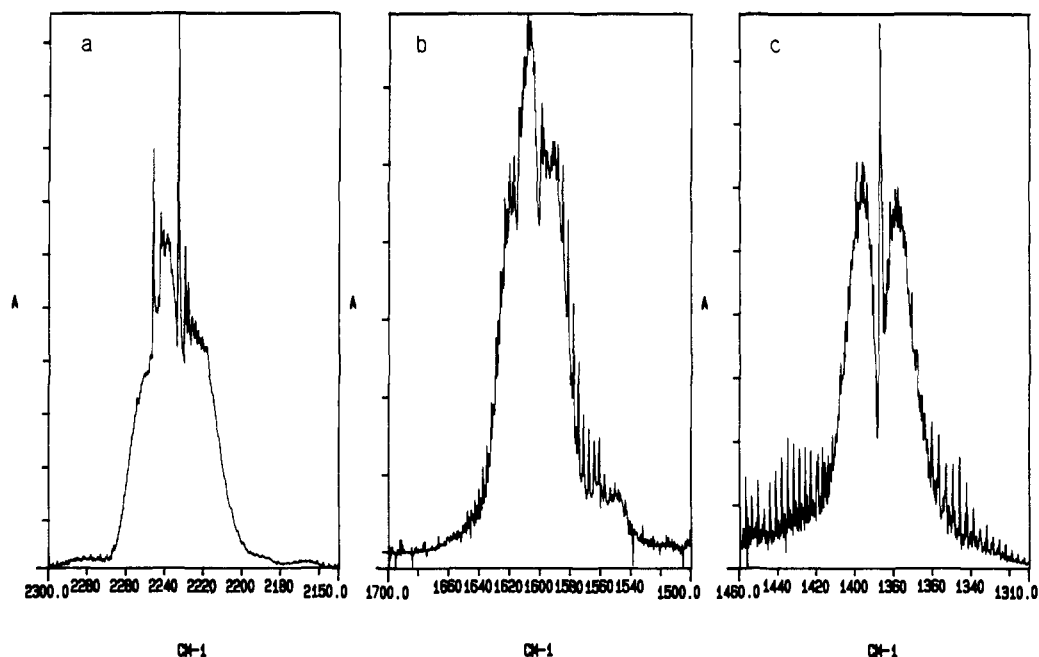
Figure 4. (a) $\nu_{C\equiv N}$ region of the gas-phase IR spectrum of **1**; **1E** at 2246.5 cm^{-1}, **1Z** at 2233.5 cm^{-1}. (b) $\nu_{C\equiv N}$ region centered at 1609 cm^{-1}. (c) C–H bending region (ν_5); **1Z** at 1387 cm^{-1}, **1E** at 1386 cm^{-1} for the Q branches.
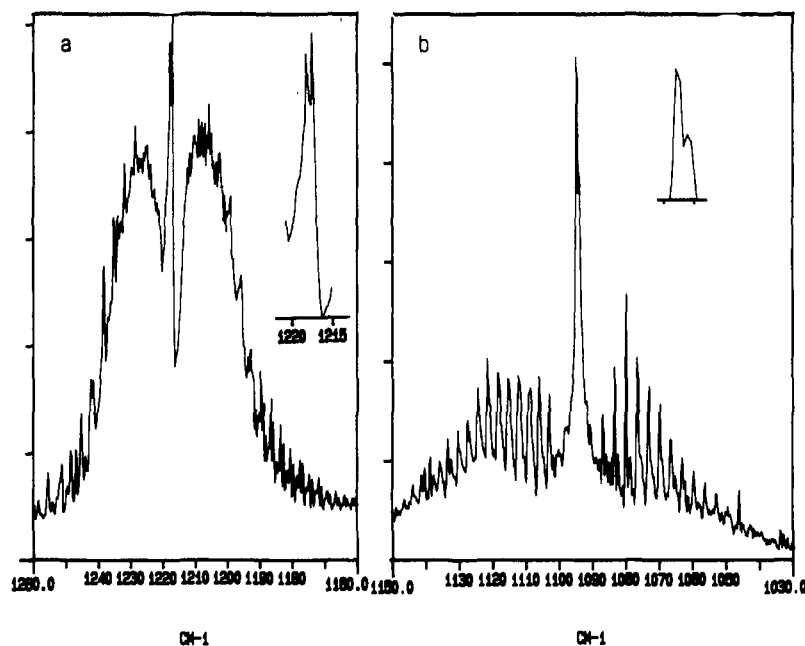

Figure 5. (a) N–H bending region (ν_6) of the gas-phase IR spectrum of **1**. Inset: **1E** at 1218 cm^{-1}, **1Z** at 1217 cm^{-1}. (b) Torsional mode ν_{10}, maximum (**1Z**) at 1095 cm^{-1}, shoulder at 1094 cm^{-1} (inset).

weak bands were present at 2930–3050 cm^{-1} (Figure 2). In the thin-film spectrum (vide infra), this band is located at 3017 (w) cm^{-1}, and in the matrix, at 2944–2928 (vw) cm^{-1}. In the thoroughly studied ethylideneimine,[39] these bands appear at 2954–2920 cm^{-1} in Ar matrix.

The $\nu_{C\equiv N}$ modes (ν_3) were observable as medium-intensity overlapping envelopes with sharp central bands at 2246.5 and 2233.5 cm^{-1} (Figure 4a), assigned to **1E** and **1Z**, respectively, on the basis of calculations and relative intensities (vide supra). The peak reported by Hamada et al.[30] (2250 cm^{-1} for **1Z**) could not be confirmed. Hamada's spectrum was of poorer quality and contained at least seven other species arising from the 1000 °C decomposition of N,N-dimethylcyanamide.[27a] Our assignments of the bands due to **1E** and **1Z** are in complete agreement with the matrix and thin-film spectra (vide infra).

ν_4, the C≡N stretching mode, is observed at 1609 cm^{-1} as two overlapping and unresolved bands due to the Z and E isomers

(Figure 4b). The value compares well with those for methanimine (1638 cm^{-1} in the gas phase[38] and 1641 cm$^-$ in Ar matrix[40]) and (Z)-1-propyn-3-imine (1591 cm^{-1});[41] the shape of the band is virtually identical with that reported for (Z)-1-propyn-3-imine in the gas phase.[41a]

ν_5, the C–H bending mode, gives rise to an A-type band at 1387 cm^{-1} (Q branch of the Z isomer). There is a weaker peak on the low-frequency side at 1386 cm^{-1}; ascribed to the Q branch of the E isomer (Figure 4c).

ν_6, the N–H bending mode, appears as an intense A-type band with partially resolved rotational fine structure of the P and R

(40) Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1975**, *56*, 333–356.

(41) (a) Hamada, Y.; Tsuboi, M.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1984**, *106*, 175–185. (b) Osman, O. I.; McNaughton, D.; Suffolk, R. J.; Watts, J. D.; Kroto, H. W. *J. Chem. Soc., Perkin Trans. 2* **1987**, 683–688. Kroto, H. W. Personal communication pertaining to the IR spectrum of **1Z**, 1989.
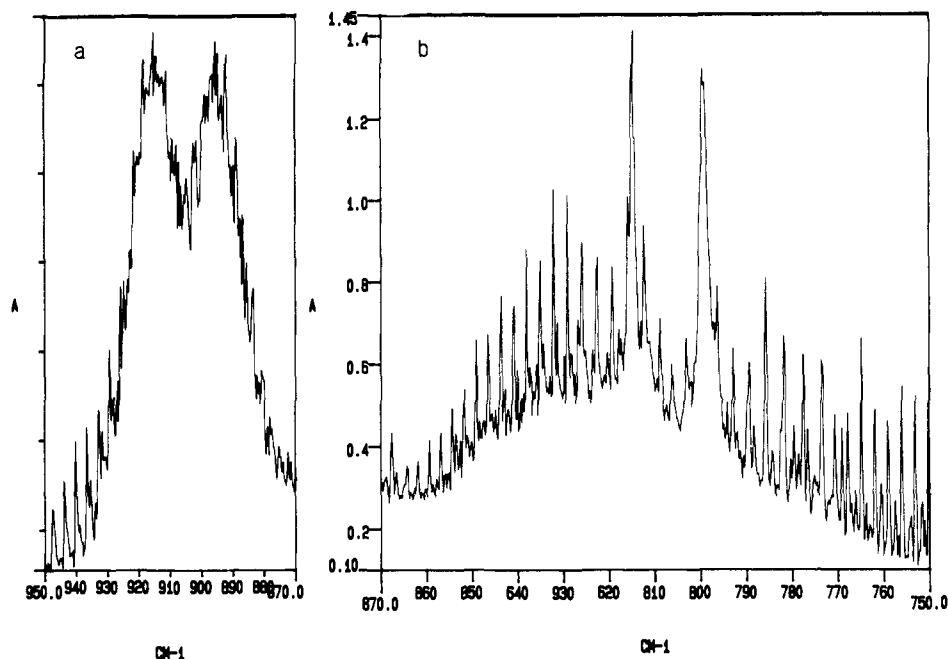
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Figure 6. (a) ν_7 region of the gas-phase IR spectrum of **1**. (b) ν_{11} region. Q branches, **1Z** at 815 cm^{-1}, **1E** at 800 cm^{-1}.

branches (Figure 5a). Two distinct Q branches are observed at 1218 and 1217 cm^{-1} and assigned to **1E** and **1Z**, respectively, on the basis of the calculations and in agreement with the matrix values. Again, the overall shape, position, and intensity of this band are very similar to those found for (Z)-1-propyn-3-imine[41] (1223 cm^{-1}).

The torsional mode ν_{10} gives rise to a distinct C-type band centered at 1095 cm^{-1} and dominated by the Z isomer, which has a far higher calculated intensity than the E. The small spike seen at 1094 cm^{-1} (Figure 5b) may or may not be due to the Q branch of **1E**; in the matrix this band is very weak and appears at 1075 cm^{-1}. The average rotational spacing of the P and R branches is 3.1 cm^{-1}, and the band shape and position are very similar to those for (Z)-1-propyn-3-imine[41a] (1094 cm^{-1}). The pure C-type structure of the band demonstrates the planarity of the molecule being observed.

ν_7 is composed of both C–C stretching and N–H bending. It gives rise to a weak- to medium-intensity, unresolved band centered at 908 cm^{-1} for **1Z** and **1E** (Figure 6a). A band of similar shape was observed at 925 cm^{-1} in (Z)-1-propyn-3-imine and ascribed to C–C stretching.[41a]

The out-of-plane distortion, ν_{11}, appears as two distinct C-type bands with Q branches at 815 cm^{-1} (**1Z**) and 800 cm^{-1} (**1E**) (Figure 6b). The R branch of **1Z** shows an average spacing of 3.3 cm^{-1} and the P branch of **1E** an average spacing of 4.1 cm^{-1}. The assignment of $\nu_Z > \nu_E$ for this band is opposite to the calculation but in agreement with the much larger calculated intensity for **1E**. All the other bands and the thermochemistry (Table II) indicate that more **1Z** and **1E** is present, and it is only due to the higher intensity of ν_{11} for **1E** that this band reaches virtually the same intensity as that for **1Z**. The matrix spectrum implies that the high-frequency band (815 cm^{-1}) is due to **1Z**. The tentative assignment[30] of a weak band at 800 cm^{-1} to **1Z** seems to be in error.

Some minor bands that are not due to iminoacetonitrile as their relative intensities varied in different experiments were observed at 2803 and 2598 cm^{-1} (C type, average spacing of 3 cm^{-1} in the P and R branches). If the precursor **13** was decomposed too rapidly, additional bands due to NH_3 appeared (930, 965 cm^{-1}). Careful heating of **13** eliminated the production of these bands.

(b) Matrix IR Spectrum of 1 from 13a. Iminoacetonitrile (**1**) from the decomposition of the sodium salt **13a** at 200 °C was deposited in an Ar matrix at 22 K (8 × 10^{-5} mbar). The IR spectrum, measured at 10 K, is shown in Figure 7, and the bands
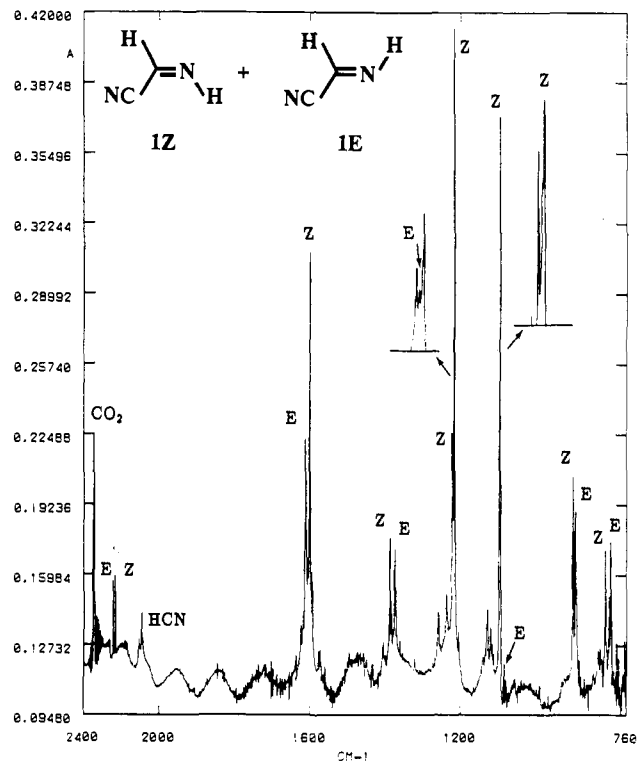
Figure 7. Ar matrix IR spectrum of **1E/1Z** from **13a**, deposited at 10 K. Inset: ν_6 band showing **1Z** at 1221, 1216 cm^{-1} and **1E** at 1219 cm^{-1}; ν_{10} band showing **1Z** at 1096, 1093 cm^{-1} (see text). Band at 2340 cm^{-1} due to extraneous CO_2; band near 2100 cm^{-1} due to HCN. Impurity peaks at 1260, 1238, 1168, 1118 cm^{-1} do not appear in other spectra. Other impurities occasionally appear at 2260 cm^{-1} due to "dusting" of the salt **13a** onto the matrix.

are listed in Table IV. There is some difficulty in obtaining good matrices because the salts **13** tend to decompose in an uneven manner, with occasional bursts of dust being carried with the Ar stream to the matrix. Some peaks indicate the presence of two sites (Table IV). Nevertheless, good matrices and highly reproducible spectra were obtained. Since **1** decomposes thermally to HCN, the matrices invariably contain small amounts of matrix-isolated HCN.[42] Since the bands due to HCN vary in

Figure 8. Difference IR spectrum resulting from 5-min photolysis of Ar-matrix isolated **1** (high-pressure Hg–Xe lamp). Positive bands are due to **1E** and negative bands to **1Z**. The ν_6 band o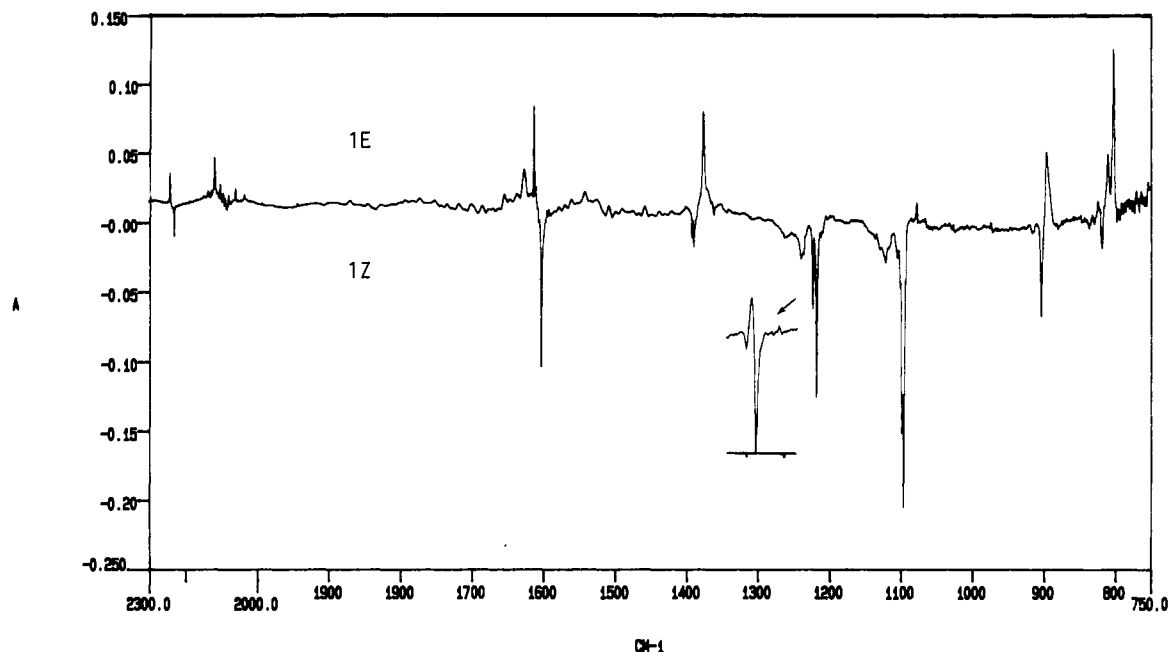f **1E** at 1219 cm^{-1} does not appear in this subtraction, but only after further destruction of **1Z** (1221, 1216 cm^{-1}) for 10 min as seen in the inset.

intensity in different spectra, and they are not obtained initially when using **15** as a photochemical precursor (see section 2c), their presence does not cause any difficulty in assigning the peaks due to **1E** and **1Z**.

As expected, band positions and $Z{:}E$ ratios for **1** agree well with the gas-phase data. The assignment of bands to **1Z** and **1E** was made by photolysis of the matrix with the unfiltered light from a high-pressure mercury–xenon lamp, which caused initial conversion of the Z to the E isomer as well as the slow destruction of both to give HNC and a mixture of HNC···HCN van der Waals dimers as described in section 2h. The initial $E{:}Z$ ratio was approximately 1:1 as measured by the relative intensities of the C≡N stretching vibrations at 2240 and 2227 cm^{-1} (actually, there was a little more **1Z** than **1E** as expected from the relative energies; see Figure 7 and the calculated intensities in Table IV). Photolysis rapidly converted this to a ca. 4:1 $E{:}Z$ ratio. A difference spectrum showing partial conversion of **1Z** to **1E** is shown in Figure 8. Further irradiation with the light of the high-pressure Hg–Xe lamp did not significantly alter the ratio of **1E** to **1Z**, but slowly destroyed both. Irradiation at 254 nm for 20 min rapidly destroyed both **1E** and **1Z**. The photoproducts are described in section 2h.

From the above observations, the assignment of bands to the individual isomers is clearcut. The frequencies and intensities are also in excellent agreement with calculations (see Table IV). Of note is the very weak ν_{10} (C≡N torsion) of **1E** at 1075 cm^{-1}, drastically weaker than the two sites of the ν_{10} for **1Z** at 1093, 1096 cm^{-1}. In ethylideneimine, both of the torsional modes are very weak, with E weaker than Z.[39] Also ν_6 of **1E** is weaker than and often hidden between the strong ν_6 bands of **1Z** at 1221, 1216 cm^{-1}. That the two bands for ν_{10} (**1Z**) at 1096, 1093 cm^{-1} are due to different sites is seen from the fact that a different ratio of these two peak intensities is obtained from the azide **15** (see Table IV). Bands due to N–H stretching (ν_1) could not be assigned in the matrix spectra. This band was very weak in the gas phase, and the failure to observe it in the matrices is not unexpected, particularly since HCN and/or van der Waals complexes (vide infra) are invariably present.

(c) Matrix IR Spectrum of 1 from Azidoacetonitrile (15). Iminoacetonitrile (**1**) was also generated by Ar matrix photolysis of **15**. Complete photolysis of a very concentrated matrix or neat

15 with a low-pressure mercury lamp (254 nm) at 12 K for 8 h gave essentially solid HCN (consisting of linear hydrogen-bonded (HCN)$_n$), together with smaller amounts of HNC[42–46] (see section 2h for further details).

Photolysis of a thick but well-isolated Ar matrix at 254 nm (12 K) caused development of new bands due to **1E** and **1Z** in a ratio of ca. 4:1 (relative intensities of the C≡N stretching vibrations at 2240 and 2227 cm^{-1}). All the bands obtained from **13a** and described above were observed (together with very weak bands near 600 cm^{-1}, which are likely to be due to ν_8, but the intensities of these last bands are so low that a definitive assignment would be hazardous). All the bands are listed in Table IV. Under these conditions (254 nm), iminoacetonitrile (**1**) can only be observed as long as unreacted azide is still present replenishing **1**, which is being continuously destroyed by the 254-nm radiation. In this experiment, azide was still present after 170 min, but once the azide was consumed, **1** disappeared within 20 min, as was also observed in the case of short-wavelength irradiation of **1E/1Z** from **13a** (vide supra) and of **1** produced from **15** at 308 nm (vide infra). The maximum intensity of bands due to **1** was obtained after 70 min. After 170 min, the intensities had decreased to the same level as at 30 min. The ca. 4:1 $E{:}Z$ ratio maintained for 170 min is presumably the photostationary state at 254 nm.

Since **1** is destroyed by 254-nm light, it cannot be prepared in pure form at this wavelength. The UV spectrum of a matrix containing **1** shows a maximum at ca. 225 nm, tailing off toward 335 nm. **1** is therefore more stable at longer wavelengths, and it proved to be possible to generate it by photolysis of the azide **15** at 308 nm with complete conversion of the azide (40 min).[21] The same IR spectrum of **1E/1Z** was obtained (Table IV), and

(42) For a thorough discussion of the vibrational spectra of HCN in the gas, liquid, solid, and matrix states, see: Chadwick, B. M.; Edwards, H. G. M. *Mol. Spectrosc. (Chem. Soc., London)* **1973**, *1*, 446–522.

(43) For HCN van der Waals multimers in matrices and solid (HCN)$_n$, see also: (a) King, C. M.; Nixon, E. R. *J. Chem. Phys.* **1968**, *48*, 1685–1695. (b) Walsh, B.; Barnes, A. J.; Suzuki, S.; Orville-Thomas, W. J. *J. Mol. Spectrosc.* **1978**, *72*, 44–56.

(44) For HCN monomer and van der Waals dimer in Ar matrix, see also: Pacansky, J. *J. Phys. Chem.* **1977**, *81*, 2240–2243.

(45) For ab initio calculations of IR spectra of HCN clusters, see: Kofranek, M.; Karpfen, A.; Lischka, H. *Chem. Phys.* **1987**, *113*, 53–64.

(46) For matrix IR spectroscopy of HNC, see: (a) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1967**, *47*, 278–285. (b) Milligan, D. E.; Jacox, M. E. *Ibid.* **1963**, *39*, 712.

(47) IR spectra of solid HCN at 10 and 77 K are available as supplementary material. The spectrum does not change appreciably between 10 and 77 K: 3140 (ν_3), 2099 (ν_1), 1615 ($2\nu_2$), 824 (ν_2) cm^{-1}.

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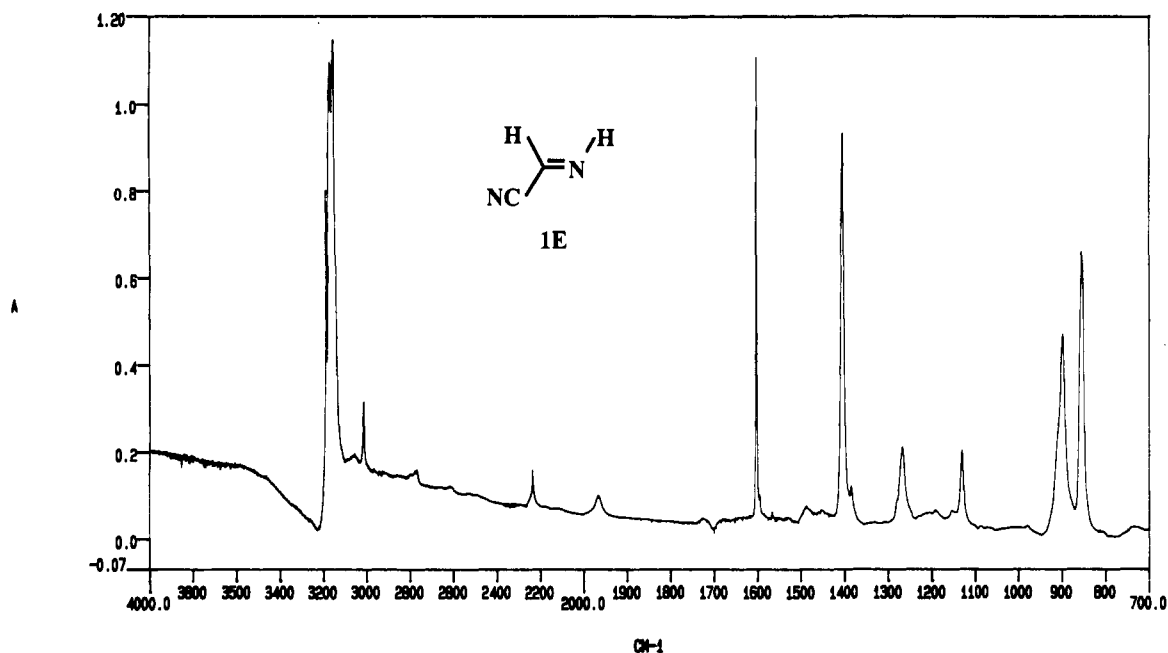*J. Am. Chem. Soc., Vol. 113, No. 19, 1991* 7271

Figure 9. Thin-film IR spectrum of 1E at 0 °C.

again these compounds were totally destroyed on irrradiation at 254 nm for 20 min (Ar, 12 K). The initial $E:Z$ ratio was ca. 3:1 at 308 nm. Since all the bands due to 1E and 1Z are now known from the studies described above, a much more secure assignment can be made (Table IV) than was possible in the preliminary report.[21] Nevertheless, the 308-nm photolysis is complicated by the fact that a third photoproduct, C (A and B being 1E and 1Z), is also formed. Product C, which may be more than one compound, absorbs at 2100 and 1626 cm^{-1}, and other weaker bands may be due to this product also. We now know that product C is a secondary product of the photolysis of 1, and further discussion is deferred until section 2h.

The assignment of the C=N stretching vibrations (ν_4) was confirmed by analogous photolysis of ^{15}N-labeled 15 (46:46:8 mixture of $NCCH_2{}^{15}N^{14}N^{14}N$, $NCCH_2{}^{14}N^{14}N^{15}N$, and $NCCH_2{}^{14}N_3$), which gave rise to red shifts of 17–18 cm^{-1} for the ν_4 bands and small or zero shifts for the other bands, in good agreement with calculations (Table IV).[21]

(d) Thin-Film IR Spectrum of 1 from 13. This was obtained by collecting the pyrolyzate from either 13a or 13b (200 °C) on a KBr disk at 18 or 30 K (different experiments, neat, no Ar, 10^{-4} mbar). The IR spectrum so obtained is very different from the matrix or gas-phase spectra, as can be expected from the occurrence of extensive hydrogen bonding. The initial spectrum at 18–30 K showed little resolution of the bands due to 1E and 1Z. $\nu_{C=N}$ appeared at 2239 (vw) and 2227 (vvw) cm^{-1}, and $\nu_{C=N}$ was strong and sharp at 1606 cm^{-1}. The remaining bands due to 1 showed no splitting and occurred at 1379, 1261, 1100, and 908 cm^{-1}. However, the most conspicuous features were strong bands at 3242, 3166, and 3020 cm^{-1} and medium–strong bands at 2080, 2088, and 840 cm^{-1}. These features look very much like the fundamental bands of HCN, but they are not due to pure solid HCN.[42–44] In particular, the frequency of the C=N stretch is too low and the C—H bend too high. They are not due to the $(HCN)_2$ van der Waals dimer or any of the known HCN multimers[43,44] either, particularly because the bands near 2114 cm^{-1} are missing. The situation is very similar to that observed for HCN in the presence of methanimine $(CH_2=NH)$ in nitrogen matrix[48] (3018, 2076, 862.5 cm^{-1}) and ascribed to the acid–base complex $HCN/HN=CH_2$. We believe, therefore, that the species being observed here is in fact the complex $HCN/HN=CHCN$. This is corroborated by the fact that a very similar spectrum is

produced on photolysis of the azide 15 at 12 K (254 nm, section 2h). Furthermore, this complex decomposes to HCN and 1 on warming to 77 K. With HCN being partially removed by constant pumping, small residual signals due to ordinary, solid HCN remained at 2099 and 824 cm^{-1} at 77 K, and the bands due to 1E and 1Z now started splitting into doublets. When the complex was further warmed to 208 K (10^{-4} mbar), the spectrum of neat 1E and 1Z with well-resolved bands was obtained. At 247 K (10^{-4} mbar), both isomers were evaporating from the film, the Z isomer evaporating faster. As a result, the IR spectrum of pure 1E was obtained at –20 to 0 °C. The spectrum is shown in Figure 9, and the data for both 1E and 1Z are listed in Table IV.

It will be seen from Table IV that several bands are blue-shifted in the thin film relative to the matrix values. In particular, the NH bending (ν_6) shows a ca. 62-cm[-1] blue shift in the Z isomer and ca. 50-cm[-1] shift in the E isomer. The C=N torsion (ν_{10}) likewise shows blue shifts of 57 and 51 cm^{-1} in the E and Z isomers, respectively, whereas the N—H stretch (ν_1) exhibits a red shift of ca. 100 cm^{-1} compared with the gas-phase values. These are precisely the vibrations expected to be the most strongly influenced by hydrogen bonding. Indeed, Jacox and Milligan[40] have observed such blue shifts of up to 24 cm^{-1} for methanimine $(CH_2=NH)$ when going from Ar to more polar N_2 and CO_2 matrices; here, ν_6 (NH bending), ν_7 (containing ca. 40% NH deformation), and ν_8 (C=N torsion) were most affected. Thus, our thin-film data for 1Z and 1E are in excellent agreement with expected shifts from the gas-phase and matrix values and therefore confirm that the compound observed is iminoacetonitrile (1).

For further confirmation of the IR assignments, dideuterio-iminoacetonitrile was analogously generated from $13a-d_2$ and examined in thin film. The shifts observed (Table IV) are in good agreement with calculations and leave no doubt that the compound is iminoacetonitrile.

It could have been thought that 1 would react with HCN on warmup, giving aminomalononitrile (17), especially since other imines are said to undergo such reactions, even at low temperature.[49] This reaction may occur in the presence of HCN, but

$$HN=CHCH + HCN \rightarrow H_2NCH(CN)_2$$
$$\quad\quad \mathbf{1} \quad\quad\quad\quad\quad\quad\quad\quad \mathbf{17}$$

by constant pumping during warmup it can be completely suppressed. 17, which is itself an unstable compound, was liberated

(48) Moore, C. B.; Pimentel, G. C.; Goldfarb, T. D. *J. Chem. Phys.* **1965**, *43*, 63–70.

(49) Guillemin, J. C.; Denis, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 951.
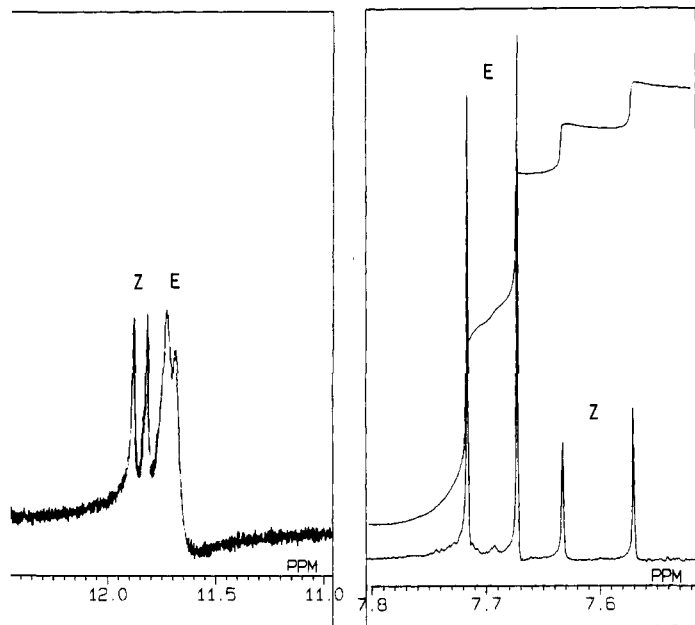
Figure 10. ^{1}H NMR spectrum of 1Z/1E (CD$_2$Cl$_2$, -40 °C). $E:Z$ = 2.9:1.

from its tosylate and examined by IR and NMR (see the Experimental Section). It was present neither in the thin-film IR spectra of pure **1** nor in the NMR spectra to be described below.

(e) NMR Spectra of 1. Having established a method for preparing neat iminoacetonitrile (**1**), we found it proved possible to record its proton (Figure 10) and ^{13}C NMR spectra in CD$_2$Cl$_2$ solution at -40 °C. The spectra were fully assigned through selective (^{1}H NMR) and uniform (^{13}C NMR) proton decoupling sequences and corroborate the earlier and less complete data of Xiang[50] for the product of the reaction between aminoacetonitrile and *tert*-butyl hypochlorite at -40 °C. The NMR evidence, taken together with the IR evidence presented above, proves that Xiang's method indeed does produce **1**, and hence the similar treatment of aminoacetonitrile with calcium hypochlorite[20] probably also produces **1**, even though the infrared data reported[20] disagree rather seriously with the true values given in Table IV.

The $E:Z$ ratio of **1** in CD$_2$Cl$_2$ solution at -40 °C was 2.9:1 as determined by ^{1}H NMR on the basis that $^3J_{HH}$ is larger for the Z than for the E isomer, as has been established for other imines (RCH=NH) in solution at -100 °C (ca. 25 and 16 Hz, respectively).[51] Z/E isomerization did not take place at -100 °C,[51] and the $E:Z$ ratio of alkylamines[51] was close to 3:1, just as observed for **1E/1Z** in the present work. The significance of these $E:Z$ ratios is not clear at present, but they are unlikely to be thermodynamic equilibrium ratios. The barriers to internal rotation and inversion of the C=NH group in ethylideneimine are calculated as 70.6 and 20.8 kcal/mol, respectively,[39] and in *N*-methylmethanimine these barriers were determined to be 58.1 and 23.8 kcal/mol, respectively.[52] The preponderance of **1E** in the solid and liquid thin films and in solution may be preconditioned by the liberation of **1** from the complex HCN/HN=CHCN (section 2d). The gas-phase and matrix ratios of $Z:E > 1$ is more likely to reflect the thermodynamic equilibrium ratio (Figures 4a and 7).

(f) Mass Spectrum of 1. We have previously reported the collision–activation mass spectrum (CAMS) of **1** produced from **13a**, **13b**, and **15**, and differentiated it from that of H$_2$C=NCN (**3**) by MS/MS and neutralization–reionization mass spectrom-

etry.[28,35] In the present work, we confirmed that the species whose IR and NMR spectra are described above has, in fact, a molecular mass of 54. Gentle heating of the salt **13a** in the direct-insertion probe of the mass spectrometer gave rise to a strong peak at m/z 54 (100% at 8 eV). There were no signals at higher m/z values (see the Experimental Section for details).

(g) Thermal Decomposition of 1. The inevitable formation of HCN as a byproduct of the generation of **1** at 200 °C was described above. **1** is stable at -40 °C but starts to polymerize to a red-brown-black material immediately above -40 °C. In its neat state, **1** is, however, observable for brief periods of time even at 0 °C.

FVP of **1** at 500 °C with isolation of the product at 77 K gave pure solid HCN, identified by its IR spectrum[42] (3140 (ν_3), 2099 (ν_1), 1615 (2ν_2), 824 (ν_2) cm^{-1}), which was identical with that of authentic HCN at 77 K.[47] FVP of azidoacetonitrile (**15**) at temperatures between 500 °C (required for the commencement of pyrolysis) and 1000 °C gave virtually pure HCN with only minute amounts of **1** surviving at the lower pyrolysis temperature. The identity of HCN was established by IR (10, 77, 298 K), millimeter-wave, and mass spectrometry. The IR spectrum at 10 K is available as supplementary material. The identity of **1** was established by CAMS.[28]

Because of this quantitative dissociation of **1** to HCN at elevated temperatures, such methods are preparatively of little use, even if **1** may be detected spectroscopically. The mild decomposition of **13** at 200 °C remains the only synthetically useful method of generating **1**. The attempted pyrolytic procedure of Hoffmann and Barth[11b] gave only HCN. The 1000 °C pyrolysis of *N,N*-dimethylcyanamide is very inefficient and gives minute amounts of **1**.[27-31] The proposition[27b] that **1** decomposes thermally to dicyanogen (NCCN) is erroneous: no dicyanogen is observed under either thermal or photochemical conditions.

(h) Photochemistry of 1. Depending on conditions, several different products can be generated by the photolysis of **1**. Irradiation of a concentrated Ar matrix of **15** at 254 nm (low-pressure Hg lamp, 12 K) gave, besides **1Z** and **1E**, strong bands at 2080, 2088 cm^{-1}, frequencies too low to be due to HCN.[42-45] They show great similarity with the species generated thermally from **13a** and ascribed to the complex HCN/HN=CHCN (section 2d). Strong, broad bands at ca. 800 and 3100–3300 cm^{-1}, assignable to this complex, were also present. Medium–strong bands due to HNC were formed as well (508, 517, 2033, 3598, 3604 cm^{-1}).[46] Similar irradiation of neat solid **15** at 12 K gave, eventually, solid HCN and small amounts of HNC.

The IR spectrum of solid HCN[47] is identical within experimental error with that reported by Boyer, Dunn, and Kooi[18] and ascribed to isocyanomethanimine (**4**), allegedly formed by photoinduced isomerization of **1**. We therefore conclude that Boyer's photoproduct was HCN and not **4**. The reason for the misassignment[18] is easily found: Boyer et al. asserted that no HCN was formed. However, the comparison was made with the IR values for HCN in liquid solution, which are very different from those pertaining to the neat solid at 77 K.[42] It is not so surprising, then, that HCN polymer, including traces of adenine, was formed upon warmup to room temperature.

The photolysis of matrix-isolated **1** is more complicated, and further work will be required for a more full understanding of the processes. During the photochemical generation of **1** from **15** (308 nm, Ar, 12 K), additional bands not assignable to **1** appeared at 2117 (m), 2100 (s), and 1626 (m) cm^{-1}, together with several other, weaker bands. The 1626-cm^{-1} band is due to an imine since in the ^{15}N-labeled run, a shift of 20 cm^{-1} to lower wavenumbers was observed. These signals also developed, together with others, on irradiation of matrix-isolated **1** generated thermally from **13a** (high-pressure Hg–Xe lamp, Ar, 15 K) and are therefore ascribed to photoproducts of **1**. We have speculated that this product ("product C"), which may be composed of more than one compound, could be ethenediimine (**9**).[21] However, this could not explain the bands in the 2100-cm^{-1} region, which, according to calculations (Table III), are IR-inactive for **9E**. Only one minimum (**9E**) was located computationally. The trans form (**9Z**)

(50) Xiang, Y.-B. Dissertation, ETH Zurich, Switzerland, 1986. Eschenmoser, A. Private Communication, ETH Zurich, Switzerland, 1988.

(51) Guillemin, J.-C.; Denis, J.-M. *Angew. Chem.* **1982**, *94*, 715; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 690. *Angew. Chem. Suppl.* **1982**, 1515–1525. Braillon, B.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Nouv. J. Chem.* **1982**, *6*, 121–122.

(52) Merenyi, G.; Wettermark, G.; Ross, B. *Chem. Phys.* **1973**, *1*, 340.

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Figure 11. IR spectrum of neat *N*-cyanomethanimine (3) at 77 K.

was found not to be stable. Further work on the identity of "product C" and on the specific generation of isocyanomethanimines **4** will be carried out.

Short-wavelength (254 nm) irradiation of matrices containing **1E** and **1Z** rapidly destroyed both isomers as well as product C (for *Z/E* isomerization, see section 2b). The same ultimate products were formed from thermally produced **1** (from **13a**) and photochemically produced **1** (from **15**). Very prominent peaks due to HNC developed immediately upon photolysis and appeared at 3616 (w), 3612 (w), 3604 (s), 3598 (s), 2033 (w), 518 (s), and 514 (s) cm^{-1}. The frequencies of HNC are known to be sensitive to and split by the matrix environment.[46] Our data are in good agreement with the values of HNC in nitrogen-containing Ar matrices.[46] The very high frequency of the stretching vibration near 3600 cm^{-1} and the very low one for the bending near 518 cm^{-1} leave little scope for any other possibility. Since these features are very weak in the photolysis of *neat* **1** at 12 K and absent at 77 K where they are replaced by those of HCN, there can be no doubt that HNC is an important initial photoproduct of **1**. HCN itself is only isomerized to HNC in the vacuum UV[46] region and does not undergo photoreaction at the wavelengths used here.

Since HNC is formed from **1**, one more molecule of HNC or HCN must be formed as well. In the matrix photolysis, this must give rise to van der Waals dimers. There was very little evidence for monomeric HCN in good matrices.[42-44] There were relatively weak features that might be ascribed to the well-characterized HCN···HCN van der Waals dimer;[44] these occurred at 3206, 2090, 1560, 1450, 794, and 731 cm^{-1}. However, the possible occurrence of this dimer is totally insignificant in comparison with the strong signals that do not correspond to any known compound that we are aware of. One set of signals was 3330 (s, broad), 3298 (vs), 3237 (s), 2125 (w–m), 2077 (m), 1350 (w), 736 (vs), and 706 (s) cm^{-1}. Another set occurred at 3240 (s), 3166 (s), 2115 (s), 2058 (s), 1024 (w), and 808 (m) cm^{-1}. The sets do not necessarily correspond to only one compound each, but since the starting material is $C_2H_2N_2$, the end product is HCN under both thermal and photochemical conditions and these products are not formed without matrix isolation, the only reasonable interpretation is that they are van der Waals complexes of the types HN≡C···HC≡N, HC≡N···HN≡C, and HN≡C···HN≡C. Note in particular that the strong band at 3330 cm^{-1} is at far higher frequency than is known for any of the (HCN)$_n$ dimers and multimers[43] (3306 cm^{-1} is the highest reported value[44]).[53]

The corollary is that iminoacetonitrile (**1**) fragments initially to HNC and HCN. This is confirmed by the observation that *N*-alkyliminoacetonitriles photochemically decompose to alkyl isocyanides and HCN[18] (and they do not photoisomerize to isocyano-*N*-alkylmethanimines[18]). We find that *N-tert*-butyliminoacetonitrile (**18**) also decomposes to *tert*-butyl isocyanide (**19**) and HCN on FVP at 500 °C.

$$(CH_3)_3CN{=}CHCN \xrightarrow{\text{FVP}} (CH_3)_3CN{\equiv}C + HCN$$
$$\textbf{18} \qquad\qquad\qquad \textbf{19}$$

3. *N*-Cyanomethanimine (3) was generated from two different precursors, 1,5-trimethylenetetrazole (**20**)[22] and the ditetrazolopyrazine **22**[28] (Scheme II). Gentle FVP of **20** at 300–450 °C with product isolation at 77 K gave rise to a new band of medium strength at ~2130 cm^{-1}, assigned to the azide **21**. On the reaction being warmed to room temperature, this band disappeared and the spectrum became identical with that of **20**, demonstrating that **20** is the stable form in the crystalline state at room temperature but the azide form **21** is populated in the gas phase. This phenomenon is even more pronounced in the case of tetrazolo[1,5-*a*]pyridine/2-azidopyridine.[57]

FVP of **20** at temperatures between 500 and 800 °C caused loss of N$_2$ and ethylene (presumably via **21**) and quantitative formation of *N*-cyanomethanimine (**3**). Ethylene was identified by its IR spectrum at 12 K. When the product was condensed

(53) CN radicals were not formed on matrix photolysis of **1**. There is some uncertainty in the literature concerning the IR frequency of CN. Milligan and Jacox[46a] reported 2046 cm^{-1} for CN produced by vacuum-UV photolysis of HCN, NC–CN, FCN, ClCN, and BrCN. Another signal at 2056 was ascribed, less securely, to "an isomeric form of cyanogen". It is not due to CN–CN, which is now known,[54] for the $\nu_{C{\equiv}N}$ band at 2294 cm^{-1} was missing. There is no CN–CN formed in our photolyses either, but the 2056-cm^{-1} band of Milligan and Jacox could in principle correspond to our band at 2058 cm^{-1}. Easley and Weltner[55] were unable to produce the 2046-cm^{-1} band of Milligan and Jacox in the matrix photolysis of ICN, where they did observe the ESR spectrum of CN. Instead, they observed an IR signal at 2057 cm^{-1}. In our investigation[56] of this chemistry, we find that the CN radical absorbs in Ar matrix at 2049 cm^{-1}. The 2057 cm^{-1} signal of Easley and Weltner is due to I–NC.

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Scheme II

at 77 K, the IR spectrum of pure **3** was obtained (Figure 11). Strong signals at 2211 cm⁻¹ (C≡N) and 1619, 1614 cm⁻¹ (C=N) (two sites) are particularly characteristic. All the observed vibrational frequencies are in very good agreement with calculations (Table V). (See Chart III for the normal modes.)

Warming of the sample of **3** above −100 °C caused polymerization to a colorless polymer,[22] whereby the C≡N absorption shifts to 2230 cm⁻¹ and the C=N absorption at 1614, 1619 cm⁻¹ vanishes. The polymerization was complete at −55 °C.

It is quite difficult to obtain the IR spectrum of pure **3** (Figure 11; the original spectrum, without any subtraction is shown). It requires rapid sublimation of the starting material (**20**) (1 min at a pyrolysis temperature of 500 °C). When slower sublimation is used, **3** polymerizes in part before or during deposition and a spectrum containing **3**, polymer, and azide **21** or azide **21** trapped in the polymer is obtained. The azide absorbs at 2135 cm⁻¹ in the polymer matrix at 77 K and disappears completely on very slow warmup between −50 °C and room temperature. If warmup is not slow, the azide is trapped in part in the solid polymer and remains at room temperature. This explains the observation[22] that the polymer is sometimes explosive on rapid heating to 200 °C.

Because of the requirement of rapid sublimation of **20** and deposition of **3**, it is not possible to obtain a good Ar matrix of **3**. However, attempted Ar matrix isolation of **3** at 12 K gives a spectrum qualitatively identical with that shown in Figure 11 (2208, 1621, 1456, 1215, 1090 cm⁻¹) together with bands due to ethylene (3094, 2977, 1438, 955 cm⁻¹). The bands were broader, and there was no splitting of bands due to sites in this sample.

FVP of the ditetrazole **22** at 600–850 °C with product deposition at 77 K gave the IR spectrum of **3**, identical in all respects with that obtained from **20** and shown in Figure 11. In the lower temperature regime, **22** also gives rise to the ring-opened azide absorbing at 2133 cm⁻¹ (77 K), which disappears on slow warmup to room temperature but is otherwise trapped in the polymer of **3** as described above. The IR spectra of the pure polymer of **3** obtained from **20** and **22** were identical. Thus, after ring opening (possibly stepwise) and double N₂ elimination, **22** cleaves into two molecules of **3** and is therefore an excellent source of **3** for spectroscopic purposes. No ethylene or other compounds were formed.

Obviously, **3** is much more prone to polymerization than is **1**. We find it hard to believe a claim[27b] that **3** was present in a 1–2-year-old sample of gaseous HCN in equilibrium with liquid HCN at 277 K. In our numerous depositions of HCN we have

not seen any evidence of **3** being formed.

3 is much more stable than **1** toward unimolecular fragmentation into HCN. Whereas **1** is cleaved rapidly above 500 °C (this is at least in part due to chemical activation when generated from azide or diazo precursors[37c]), significant peaks due to HCN start appearing only around 800 °C in the pyrolyses of **20** and **22**, with **3** still being by far the major product even at 850 °C.

The high-resolution mass spectrum of **3** produced from **20** has been reported by one of us previously.[22] The CAMS of **3** from **20** and **22** are identical and distinguishable from that of **1**.[28] In the present study, we have confirmed that the product of FVP of **20** has a molecular mass of 54. The molecular ion of **20** (m/z 110) disappeared at temperatures above 500 °C, being replaced by m/z 54 (50), 53 (58), 28 (100), and 27 (40).

The millimeter-wave (MMW) spectrum of **3** produced from **20** completely confirmed the structure of **3**.[23] However, one question remained: two sets of quadrupole coupling constants for the C=N and C≡N nitrogen atoms were compatible with the experimental data. The correct choice was made on the basis of ab initio calculations,[23] and this was subsequently confirmed experimentally from the measurement of low-J rotational transitions.[24]

The fact that two molecules of **3** are produced from one molecule of **22** made it possible to observe the well-resolved transitions of **3** at low pressure (1.3 × 10⁻² mbar) in the 2-m flow-through microwave absorption cell. Previously observed[23] transitions due to **3** were observed, and only traces of HCN and NH₃ were present as impurities. The rotational transitions, $J_{KaKc} = 3_{12} \leftarrow 2_{11}$ (32035.303 MHz) and $J_{KaKc} = 3_{13} \leftarrow 2_{12}$ (30716.052 MHz), are most characteristic as regards the nitrogen quadrupole hyperfine splittings. The measurement of these splittings confirmed that solution one[23] is the correct one, giving quadrupole coupling constants in agreement with the results[24] of the low-J measurements.[58]

Conclusion

Iminoacetonitrile (**1**) is obtained by thermal decomposition of the tosylhydrazone salts **13** and by photochemical decomposition of azidoacetonitrile (**15**), particularly in an Ar matrix and at wavelengths above 300 nm. **1Z** is thermodynamically more stable than **1E**, but **1Z** is photochemically converted to **1E**, giving a ca. 3:1 $E:Z$ ratio. **1E** and **1Z** are completely characterized by their IR spectra in the gas phase, in Ar matrix, and in thin film, as well as by mass spectrometer and ¹H and ¹³C NMR spectroscopy in solution. **1** rapidly polymerizes above −40 °C but can be observed in the neat state for brief periods of time up to 0 °C and in the gas phase at room temperature. Pyrolysis of **1** produces HCN. Photolysis of **1** produces HNC and van der Waals complexes of the types HNC⋯HCN, HCN⋯HNC, or HNC⋯HN⋅.

N-Cyanomethanimine (**3**), an isomer of **1**, is obtained in virtually quantitative yield on pyrolysis of trimethylenetetrazole (**20**) and bistetrazolopyrazine **22** and is fully characterized by its IR, mass, and millimeter-wave spectra. **3** polymerizes above −100 °C in the neat state but can be observed at room temperature at ca. 10⁻² mbar (MMW spectroscopy). **3** is quite stable thermodynamically, surviving FVP at 850 °C with only minor decomposition to HCN.

The methods reported should be the methods of choice for the preparations of **1** and **3**. Further work will focus on the chemistry of iminoacetonitrile, the HNC complexes, the HCN/HN= CHCN complex, and attempts to generate 1-isocyanomethanimine (**4**), aminocyanocarbene (**5**), and derivatives of ethenediimine (**9**). The successful generation[59] of S=C=C=S gives hope that **9** may be accessible.

(58) The observed MMW spectra of **3** and those simulated for solution 1 and solution 2[23] are given in the thesis of P. Lorenčak.[1b] The measurements were carried out in the laboratory of Prof. M. Winnewisser, University of Giessen (Germany). We thank Dr. B. P. Winnewisser (Giessen) for the computational work and for stimulating discussions.

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Experimental Section

Apparatus. The FVP apparatus employed 10-cm-length (0.8-cm-i.d.) quartz tubes in housings flanged to Leybold–Heraeus closed-cycle liquid He cryostats (for matrix isolation; 10–30 K) or Air Products liquid N_2 cryostats (for isolation at 77 K). Pressures were 10^{-3}–10^{-5} mbar. Further details were as published.[60]

The same type of pyrolysis oven was flanged directly to the ion source housing of a Kratos MS25RFA mass spectrometer for direct monitoring of FVP products. The pyrolysis tube extended to within 1 cm of the ion source.

IR spectra were recorded on a Mattson Sirius 100 or Perkin-Elmer 1700X FTIR spectrometer at a resolution of 0.5 or 1 cm^{-1}; UV spectra were recorded on a Varian Cary 1, and NMR spectra on a JEOL GX 400 spectrometer (400 MHz for ^{1}H, 100.6 MHz for ^{13}C).

Irradiations were carried out with low-pressure Hg lamps (75 W; 254-nm maximum output), a high-pressure Xe–Hg lamp (1000 W, Hanovia), or a Lambda Physik EMG53-MSC excimer laser operating at 308 nm.

Materials. 1-Cyanoformamide tosylhydrazone and its sodium and lithium salts (13a and 13b) were prepared according to the literature.[11a] Tosylhydrazone: mp 203 °C; ^{13}C NMR (CD$_3$OD) δ 145.6, 136.9, 131.7, 130.6, 129.1, 113.9, 21.6. **13a:** mp 208 °C dec; UV λ$_{max}$ (H$_2$O) (ε) 228 (14 900), 223 (13 200 nm); IR (KBr) 3441 (s), 3327 (s), 2247 (s), 1601 (s, sh), 1219 (s), 1055 (s), 655 (s) cm^{-1}; molecular mass by MS 258 (see Iminoacetonitrile for a description of the procedure). **13b** (very hygroscopic; stored under Ar at 0 °C): mp 172 °C dec, λ$_{max}$ (H$_2$O) (ε) 288 (15 000), 225 (13 500) nm; IR (KBr), 3443 (s, br), 3340 (s, br), 2914 (m), 2235 (m), 1234 (m), 1082 (s, br), 659 (m) cm^{-1}. (1-Cyanoformamide tosylhydrazone)-d_3 was prepared by exchange of the undeuterated tosylhydrazone with D$_2$O (99.8% D; 10^4 molar excess) under Ar at room temperature. After the mixture was stirred for 3 days, the hydrazone was filtered and a new charge of D$_2$O added. This operation was repeated five times. The sodium salt was prepared as above.

Azidoacetonitrile (15) was prepared according to Freudenberg:[61] bp 65 °C (17 Torr); bp 53 °C (12 Torr); IR (CCl$_4$) 2130 (vs), 2108 (vs), 2080 (vs) cm^{-1}; IR (Ar, 12 K) 2237 (wv), 2219 (vw), 2210 (wv), 2145 (s), 2115 (vs), 2088 (s), 1440 (m), 1262 (m), 1255 (s), 925 (s), 872 (m), 697 (m), 685 (m), 561 (m), 552 (m) cm^{-1}; UV (CH$_3$OH) λ$_{max}$ 212 nm with a second, very weak maximum at 278 nm extending to 320 nm; UV (CH$_3$CN) λ$_{max}$ 228 nm with a weaker maximum at 284 nm extending to 340 nm (lit.[62] UV (CH$_3$CN) λ$_{max}$ 221 nm (log ε = 2.494)); ^{1}H NMR (CDCl$_3$) δ 4.20 (s); ^{13}C NMR (CDCl$_3$) δ 113.9 (CN), 37.1 (CH$_2$).

Azidoacetonitrile-^{15}N (NCCH$_2^{15}$N^{14}N$_2$:NCCH$_2^{14}$N$_2^{15}$N:NCCH$_2^{14}$N$_3$ = 46:46:8). Chloroacetonitrile (128 mg, 1.16 mmol) in 5 mL of dry DMSO was treated with 100 mg (1.54 mmol) of sodium azide (92 atom % terminal ^{15}N) and stirred under N$_2$ at 70 °C for 7 h. After the mixture was cooled to room temperature, the azidoacetonitrile-^{15}N was distilled bulb-to-bulb at room temperature into a receiver cooled in dry ice. IR (Ar, 12 K) 2122 (vs), 2106 (s), 2101 (s), 2072 (vs), 1240 (s), 1212 (m), 927 (m) cm^{-1}. The identity of the product was established by the successful preparation of unlabeled 15 using exactly the same procedure in several test runs.

6,7-Dihydro-5H-pyrrolotetrazole (1,5-trimethylenetetrazole) (20) was prepared according to the literature:[22] mp 109–110 °C; ^{1}H NMR (CDCl$_3$) δ 4.39–4.15 (m, 2 H, H-C(5)), 3.05–2.81 (m, 4 H, H-C(7) and H-C(6)); ^{13}C NMR (CDCl$_3$) δ 162.5 (br s, C(7a)), 44.18 (br t, ^1J = 148.5 Hz, C(5)), 27.21 (br t, ^1J = 136.3 Hz, C(7)), 18.26 (br t, ^1J = 138.4 Hz, C(6)); MS m/z (relative abundance) 110 (9.5), 67 (14.4), 55 (48), 54 (69), 53 (52), 52 (15), 51 (14), 42 (14), 41 (20), 40 (11), 39 (65), 28 (100), 27 (58), 26 (47).

5H,10H-Ditetrazolo[1,5-a:1',5'-d]pyrazine (22) was prepared by a modification of Boyers method.[18] Azidoacetonitrile (4.0 g, 0.05 mol) dissolved in 5 mL of benzene was heated for 3 days in a Parr bomb at 125 °C. After cooling and distillation of the solvent, the substance, which was covered by black dust, was sublimed at 195 °C (10^{-2} Torr) to give 1.84 g (46% the yield is not easily reproduced) of white crystals: mp >350 °C; ^{1}H NMR (DMSO-d_6) δ 6.10 (s); ^{13}C NMR (DMSO-d_6) δ 147.9 (br s, C=N), 42.83 (t, ^1J = 151.8 Hz, CH$_2$); MS m/z (relative abundance) 164 (8.2), 54 (100), 53 (29), 40 (17), 28 (31), 26 (23).

Aminomalononitrile[63] (17) was liberated from its p-toluenesulfonate (Aldrich Chemical Co.) (5 g in 30 mL of H$_2$O) by neutralization with 30 mL of a saturated aqueous solution of sodium hydrogen carbonate.

Extraction with ether (8 × 80 mL) followed by rapid evaporation in vacuo gave a yellow oil, which at room temperature polymerized within 1 h: IR (film) 2212 (s, sh), 2193 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.66 (br, 2 H), 4.86 (s, 1 H).

(N-tert-Butylimino)acetonitrile[20] (18): ^{13}C NMR (CDCl$_3$) δ 137.8 (d, ^1J = 181.8 Hz, CH), 114.7 (d, ^2J = 17.1 Hz, C≡N), 60.8 (decet, ^2J = 4.3 Hz, C(CH$_3$)$_3$), 27.8 (quartet of septets, ^1J = 127.0 Hz, ^3J = 4.3 Hz, C(CH_3)$_3$.

Iminoacetonitrile (1). (i) The salts **13** invariably contain a small amount of THF from the preparation. This is first removed by continuous pumping at 10^{-2}–10^{-6} mbar while slowly heating the salt to 200 °C. Usually, 10–15 min will suffice. For gas-phase spectroscopy, the THF is pumped through the gas cell. For matrix-isolation spectroscopy, the THF is condensed on the radiation shield of the cryostat before the cold-head and the shield are turned into position for matrix deposition. UV (Ar matrix, 15 K) λ$_{max}$ 225 nm, tailing off toward 335 nm.

The gas-phase IR spectrum was obtained in a 6-m path length multiple-reflection cell at room temperature. **13a** (200 mg) was placed in a Pyrex tube attached to the gas cell and slow heated to 200 °C. After 8 min at 10^{-2} mbar, no more THF was observed. (Z)- and (E)-iminoacetonitrile (1Z and 1E) were allowed to fill the cell to 1 mbar and had a half-life of ca. 40 min at 0.4 mbar. After the compounds were left in the gas cell for several half-lives, the IR spectrum of 1 vanished. The $Z:E$ ratio did not change appreciably during this time. No new volatile products were formed. The amount of HCN did not increase. The spectra are presented and discussed in the text.

The Ar matrix IR spectrum was obtained similarly by placing **13a** (100 mg) in a Pyrex sublimation tube provided with an Ar inlet. An initial layer of Ar was deposited at 10^{-4} mbar for 5 min. CsI, KBr, and NaCl targets and windows were used. 1 was cocondensed with Ar at 22 K (8 × 10^{-5} mbar) for 15 min, and the spectrum was recorded. Subsequent photolysis with the unfiltered light from the Hg–Xe lamp for 30 min changed the original $E:Z$ ratio of ca. 1:1 to ca. 4:1. Photodecomposition caused formation of HNC and HNC van der Waals complexes as described in the text. The same spectra were obtained from 13b.

The thin-film IR spectrum was similarly obtained by deposition at 77 K (10^{-4} mbar). HCN was removed by continuous pumping between 77 and 200 K. On further warming, the Z isomer evaporated. At 0 °C only the E isomer remained. After 1 min at 0 °C, the E isomer had vanished too. This experiment has been repeated several times, but the precise temperatures where changes happen naturally depend on the rates of heating and pumping. The spectra are described in the text.

The NMR spectra of 1 were obtained starting from 1 g of 13a placed in a 50-mL flask attached to one side of a cold-finger. The other side was attached to a vacuum line. The cold-finger was fitted with a rubber septum injection port and a 25-mL receiver flask. The system was evacuated to 10^{-3} mbar and the cold-finger was filled with liquid N$_2$. CD$_2$Cl$_2$ (0.5 mL) was sprayed onto the cold-finger with a syringe. The salt 13a was heated to 175 °C, when decomposition visibly began. The temperature was slowly increased to 200 °C. After 1 h, the heat was removed and liquid N$_2$ was removed from the cold-finger. The system was brought to atmospheric pressure with dry N$_2$, and a further 1 mL of CD$_2$Cl$_2$ (prechilled to −76 °C) was sprayed onto the cold-finger through the injection port. As the CD$_2$Cl$_2$ solution melted, it was collected at 77 K in the 25-mL flask beneath the cold-finger; from here it was transferred to an NMR tube cooled to −78 °C. The NMR spectrometer tube was precooled to −60 °C. At no time during the transfers did the sample temperature rise above −35 °C. The spectra were recorded at −40 °C.

1E: ^{1}H NMR (CD$_2$Cl$_2$) δ 11.65 (s, br, 1 H, NH), 7.69 (d, J = 17.4 Hz, 1 H, CH); ^{13}C NMR (CD$_2$Cl$_2$) δ 147.2 (dd, ^1J = 187.4 Hz, ^2J = 8.5 Hz, C=N), 115.0 (dd, ^2J = 16.5 Hz, ^3J = 23.8 Hz, C≡N).

1Z: ^{1}H NMR (CD$_2$Cl$_2$) δ 11.85 (d, J = 24.7 Hz, 1 H, NH); 7.60 (d, J = 24.7 Hz, 1 H, CH); ^{13}C NMR (CD$_2$Cl$_2$) δ 142.6 (dd, ^1J = 202.0 Hz, ^2J = 12.8 Hz, C=N), 111.2 (dd, ^2J = 18.5 Hz, ^3J = 15.9 Hz, C≡N). The $E:Z$ ratio was 2.9:1. The assignments were confirmed by sequential decoupling experiments.

HCN was invariably present (^{13}C NMR δ 109.6), but its intensity decreased on warming due to reaction with 1. The signals due to 1 started decreasing immediately on warming above −40 °C, with concomitant formation of brown strings of polymer in the NMR tube. This developed into a black solid after 1 h at room temperature.

The mass spectrum of 1 was obtained by heating 13a or 13b in the direct insertion probe of the mass spectrometer. If the salts are heated too rapidly, the gas evolution carries small particles of the salts to the ion source, so that the molecular ions of 13 can actually be observed (13a: m/z 258). With gentle heating from 150 to 200 °C, after small amounts of THF had disappeared (m/z 72), strong signals due to 1 appeared: MS (70 eV) m/z 54 (60.9), 53 (69.4), 28 (100), 27 (64.5), 26 (12.7); MS (8 eV) m/z 54 (100), 53 (81), 28 (39), 27 (12). In spite of a careful

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search, a peak due to aminodiazoacetonitrile (14) (m/z 82) was not observable.

(ii) Iminoacetonitrile (1) was also produced by matrix photolysis of azidoacetonitrile (15). The sample of 15 was maintained at -20 °C and deposited with Ar at 30 K (3 × 10⁻⁵ mbar). Spectra were recorded at 12 K. Photolyses at 254 and at 308 nm (12 K) are described in the text.

Pyrolysis of azidoacetonitrile (15) was carried out at temperatures between 500 and 1000 °C, and the products were examined by IR (77 K) and millimeter-wave spectroscopy. Only HCN was detected.[47] For the successful detection of 1 by FVP/CAMS, see ref 28.

Pyrolysis of N-tert-butyliminoacetonitrile (18) at 500 °C (10⁻⁴ mbar) gave a liquid product, which was examined by IR, GC (SE 52 column, 50–250 °C at 80 °C/min), and GC–MS. Only two compounds were detected under these conditions: pivalonitrile (retention time 52 s; IR 2238 cm⁻¹; m/z 83 (11), 82 (98)) and tert-butyl isocyanide (19) (retention time 74 s; IR 2135 cm⁻¹; m/z 83 (6), 82 (86)). In addition, HCN was detected by IR spectroscopy at 77 K. All three products were identified by comparison with authentic materials.[64]

N-Cyanomethanimine (3). (i) 1,5-Trimethylenetetrazole (20) (20 mg) was placed immediately behind the sublimation zone of the FVP apparatus attached to a liquid N₂ cryostat.[60] The system was evacuated to 5 × 10⁻⁴ mbar, the pyrolysis zone heated to the desired temperature (500–800 °C), and the cryostat cooled to 77 K. The sublimation zone was rapidly heated to 500 °C, and the product was collected on the salt disk for 1 min. The IR spectrum of 3 shown in Figure 11 was recorded.

Ethylene was detected in an analogous experiment with product isolation at 12 K. C₂H₄: IR 3094 (s), 2977 (s), 1438 (s), 955 (vs) cm⁻¹. 3: IR 2208 (vs), 1621, 1456, 1215, 1090 cm⁻¹.

On warmup, 3 started polymerizing above -100 °C. The polymerization was complete at -55 °C. The colorless polymer: IR (solid film), 2229 (s), 1410 (m), 1325 (w–m), 1160 (m, sh), 1135 (m), 1000 (w–m), 950 (m), 800 (w–m, br).

Slow FVP of 20 at 350–500 °C gave, in part, azide 21 (2128 cm⁻¹) trapped in the solid matrix composed largely of 20 and the polymer (2229 cm⁻¹), as described in the text.

At temperatures above 500 °C, azide 21 (2135 cm⁻¹) trapped in the polymer alone was obtained on slow pyrolysis. At temperatures of 700–800 °C, none of the azide 21 survived.

(ii) An IR spectrum of 3 identical with the one shown in Figure 11 was obtained by FVP of the ditetrazolopyrazine 22 at 600 °C. Warmup to room temperature gave the polymer, identical with the one described under (i). At temperatures below 600 °C, small amounts of the azide

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(64) 19 was prepared according to: Gokel, G. W.; Widera, R. P.; Weber, W. P. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, pp 232–235. Pivalonitrile was obtained from Aldrich Chemical Co.

corresponding to 22 (2133 cm⁻¹) were trapped in the solid polymer.

The pyrolyses of 20 and 22 were also monitored by mass spectrometry. The molecular ion of 20 had completely disappeared at 500 °C and that of 22 at 600 °C. MS of 3 from 20: m/z (relative abundance) 54 (50), 53 (58), 28 (100), 27 (40).

Millimeter-wave spectra[58] of 3 produced from 20[23] and 22[1b] were recorded in the frequency range 28.0–38.0 GHz and confirmed the previous assignments.[23,24]