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Microwave Spectra and Molecular Structures of (*Z*)-Pent-2-en-4-ynenitrile and Maleonitrile

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Abstract: Accurate equilibrium structures have been determined for (*Z*)-pent-2-en-4-ynenitrile (**8**) and maleonitrile (**9**) by combining microwave spectroscopy data and ab initio quantum chemistry calculations. The microwave spectra of 10 isotopomers of **8** and 5 isotopomers of **9** were obtained using a pulsed nozzle Fourier transform microwave spectrometer. The ground-state rotational constants were adjusted for vibration−rotation interaction effects calculated from force fields obtained from ab initio calculations. The resultant equilibrium rotational constants were used to determine structures that are in very good agreement with those obtained from high-level ab initio calculations (CCSD(T)/cc-pVTZ). The geometric parameters in **8** and **9** are very similar; they also do not differ significantly from the all-carbon analogue, (*Z*)-hex-3-ene-1,5-diyne (**7**), the parent molecule for the Bergman cyclization. A small deviation from linearity about the alkyne and cyano linkages is observed for **7**−**9** and several related species where accurate equilibrium parameters are available. The data on **7**−**9** should be of interest to radioastronomy and may provide insights on the formation and interstellar chemistry of unsaturated species such as the cyanopolyynes.

Introduction

The sustained interest in the microwave spectra of nitriles derives from their relevance to the chemistry of the interstellar medium (ISM).[1−7] Over 100 molecules have been detected in the interstellar medium.[8] Although many of these molecules are simple di- or triatomic species, organic molecules with up to 13 atoms have been identified by radioastronomy. Among the larger species, including the largest ISM molecule yet detected ($HC_{11}N$), are the cyanopolyynes.[6−8] The cyanopolyynes, $H{-}(C{\equiv}C)_n{-}CN$ ($n = 0{-}5$), constitute a prominent, homologous series of interstellar molecules (Chart 1). With large dipole moments and correspondingly intense microwave rotational transitions, these species are readily amenable to radioastronomical detection. The corresponding symmetric analogues—in both the hydrocarbon $H{-}(C{\equiv}C)_n{-}H$ and dinitrile $NC{-}(C{\equiv}C)_n{-}CN$ series—are generally assumed to exist in interstellar clouds, although these species cannot be detected by radioastronomy because they lack a permanent dipole moment.

Chart 1

$H{-}(C{\equiv}C)_n{-}H$

$H{-}(C{\equiv}C)_n{-}C{\equiv}N$

$N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$

$H{-}C{\equiv}C{-}C{\equiv}N$

$H_2C{=}CH{-}C{\equiv}N$

$H_3C{-}CH_2{-}C{\equiv}N$

The chemistry of the ISM is not restricted to the maximally unsaturated species represented by the cyanopolyynes series. Observational data unequivocally establish that interstellar molecules exist in varying degrees of unsaturation in the hydrogen-rich ISM.[9,10] In the H_nC_3N series, $H{-}C{\equiv}C{-}CN$ (cyanoacetylene), $H_2C{=}CH{-}CN$ (acrylonitrile), and $H_3C{-}CH_2{-}CN$ (propionitrile; ethyl cyanide) have each been detected by radioastronomy (Chart 1).[2,4,11] In the H_nC_5N and higher series, only the maximally unsaturated linear cyanopolyynes have been detected in interstellar clouds.[3,5,12,13] The search for partially hydrogenated members of these series has been hindered by a lack of laboratory data. Although rotational constants have been estimated for all 18 hydrogenated derivatives of cyanodiacetylene (HC_5N),[10] experimental data are

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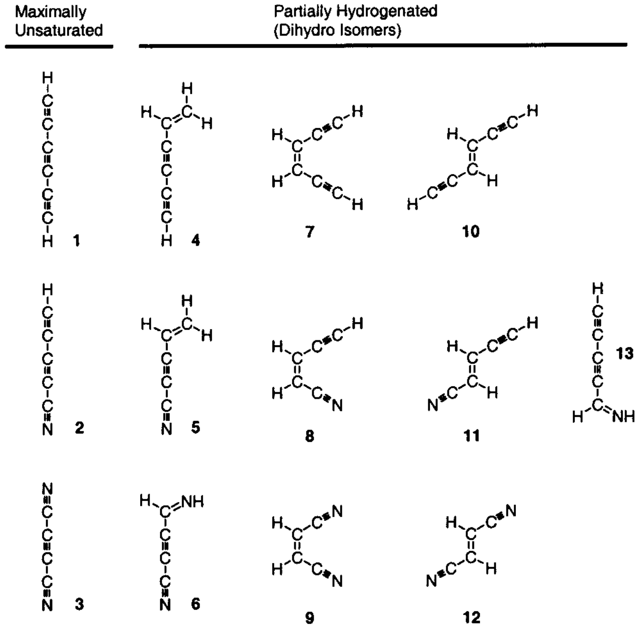
Chart 2

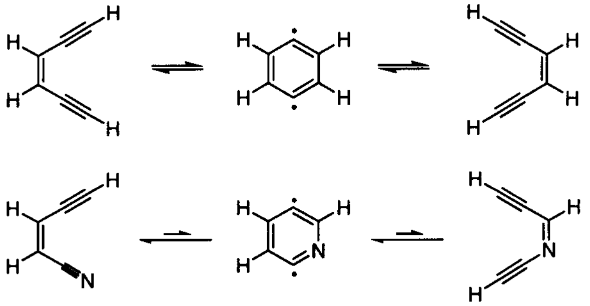


available only for 1-cyanobut-3-en-1-yne (**5**) and (*E*)-pent-2-en-4-ynenitrile (**11**) (Chart 2). An unsuccessful search for **11** in the ISM has been reported.[14,15]

In the homologous series HC≡C—C≡C—C≡CH (**1**), HC≡C—C≡C—C≡N (**2**), and N≡C—C≡C—C≡N (**3**) (Chart 2), the detection of partially hydrogenated derivatives would provide persuasive evidence for the existence of the undetectable, symmetric isomers **1** and **3**. Similarly, detection of the more polar isomers (nitrile **8** or dinitrile **9**) would provide evidence for the existence of the less polar structural analogue (enediyne **7**). In a different context, these partially hydrogenated derivatives display a key structural feature—a "kinked" carbon chain in the form of an enediyne or an enynenitrile—that, mechanistically and structurally, represents a logical link between the open-chain hydrocarbons that are known to exist in interstellar clouds and the aromatic compounds that are thought to exist in these clouds. Enediynes or enynenitriles may represent precursors for the formation of aromatic species or products of their degradation (Scheme 1). The presence of cyanopolyynes, their partially hydrogenated derivatives, long carbon chain radicals (HC_n, $n = 1-8$), and methylated polyynes in the ISM has ramifications for various reaction schemes theorized to account for the buildup of interstellar molecules and could have a bearing on the species that are responsible for the diffuse interstellar bands.[9,15,16]

We therefore find compelling reasons to study the chemistry and spectroscopy of the partially hydrogenated species depicted in Chart 2. We recently reported the laboratory rotational spectrum of enediyne **7**,[17] a partially hydrogenated derivative of polyyne **1**. Unless **7** is unusually abundant in interstellar clouds, it will be difficult to detect because of its small dipole moment (0.18 D). The nitrile analogues **8** and **9**, however, represent realistic targets for radioastronomical detection (dipole moments 3.53 and 5.25 D, respectively). We now describe the synthesis, rotational spectroscopy, and equilibrium structures for the partially hydrogenated cyanocarbons (*Z*)-pent-2-en-4-ynenitrile (**8**) and maleonitrile (**9**). The rotational constants reported here will enable astronomical searches for these nitriles.

Scheme 1



The detailed structures of unsaturated nitriles **8** and **9** are interesting in their own right. Recently, equilibrium or near-equilibrium structures of several related species such as malononitrile,[18] dicyanoethene,[18] acrylonitrile,[19] and crotononitrile[20] were described. We recently employed methodology that combines experimental spectral data and computed vibration–rotation parameters to obtain an accurate equilibrium structure for enediyne **7**.[17] It was of interest to extend this methodology to determine the equilibrium parameters for **8** and **9**, to make comparisons among these closely related systems and place any systematic changes on a firm basis. Finally, several recent experimental[21−25] and computational[25−34] studies probed the thermal cycloaromatization reaction of nitrile **8** and its simple derivatives (aza-Bergman cyclization; Scheme 1).

Results

Synthesis. A conventional, stereospecific synthesis of **8** has not been reported previously, although **8** has been generated upon photolysis of 2,3-pyridinedicarboxylic anhydride in an Ar matrix.[22,23] (Pyrolysis of the anhydride afforded only the isomeric **11**.[14]) We employed Pd-catalyzed coupling reactions to effect the stereospecific synthesis of **8**.[35,36] Commercially available methyl propiolate was converted to amide **14** using

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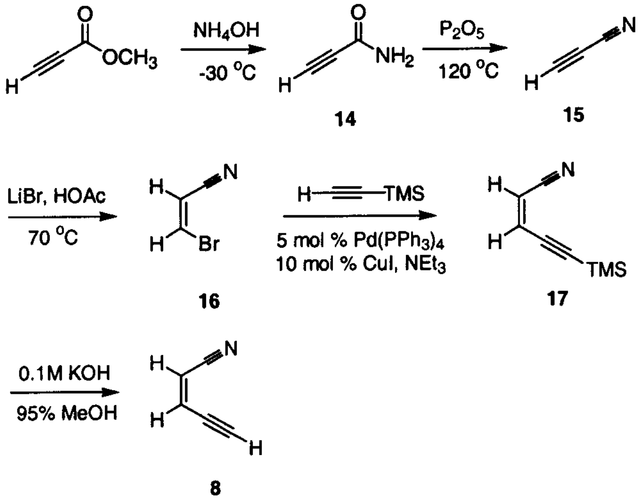
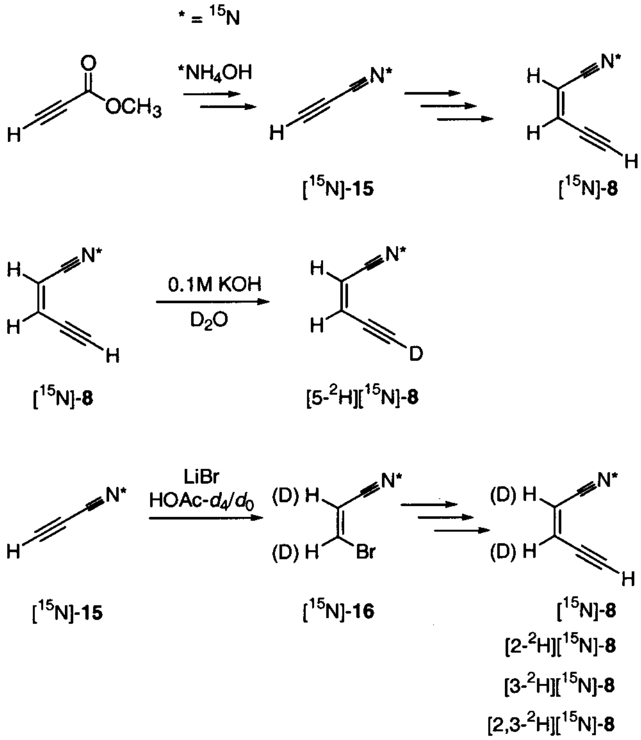
Scheme 2

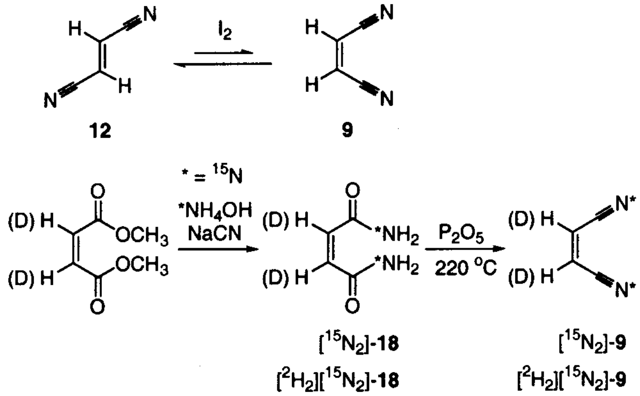


NH$_4$OH [37] and subsequently dehydrated with P$_2$O$_5$ (Scheme 2).[38] The resulting ynenitrile **15** was stereospecifically converted to (*Z*)-vinyl bromide (**16**) using LiBr in acetic acid.[39] Coupling **16** and TMS-acetylene with Pd(PPh$_3$)$_4$, CuI, and NEt$_3$ afforded the TMS-protected enynenitrile **17**. As is commonly observed for reactions of this type, the coupling reaction was sensitive to the choice of both the Pd catalyst and the amine.[35,36] Enynenitrile **17** was deprotected with KOH in MeOH. Neat enynenitrile **8** polymerizes rapidly at room temperature and is also fairly volatile; hence, special care was taken during the workup procedure. Following solvent removal at −41 °C under vacuum, nitrile **8** was distilled at room temperature and collected in a liquid nitrogen-cooled trap.

Scheme 3



Scheme 4



Microwave transitions for all five of the singly substituted ^{13}C isotopomers of enynenitrile **8** were assigned in natural abundance. The ^{15}N isotopomer, however, could not be observed in natural abundance (0.37%). An isotopically enriched sample of [^{15}N]-**8** was therefore prepared using 6 N ^{15}NH$_4$OH (Scheme 3). It was also necessary to synthesize the deuterated isomers due to the low natural abundance and quadrupolar nature of ^{2}H. [5-^{2}H][^{15}N]-(*Z*)-Pent-2-en-4-ynenitrile ([5-^{2}H][^{15}N]-**8**) was easily prepared via a base-catalyzed exchange of the acetylenic proton in D$_2$O using the previously prepared sample of [^{15}N]-**8**. In theory, these eight isotopomers should have been sufficient for an accurate structure determination, but problems still existed in determining the coordinates for the hydrogens at the double bond (vide infra). To resolve this difficulty, the remaining two singly substituted [^{2}H] isotopomers were synthesized. To avoid having two quadrupolar nuclei (^{2}H, ^{14}N) in the same sample, deuterium was introduced in a ^{15}N-enriched sample of nitrile **15** (Scheme 3). Cost considerations dictated a ^{15}N enrichment level of 50%, rather than 100%. Thus, a 1:1 mixture of nitriles, [^{15}N]-**15** and [^{14}N]-**15**, was treated with a 1:1 mixture of acetic acid-d_0 and -d_4 to afford a mixture of eight isotopomers of bromonitrile **16** (Scheme 3). Subsequent conversion of bromonitrile **16** afforded a mixture of eight isotopomers of enynenitrile **8**: [^{15}N]-**8**, [2-^{2}H][^{15}N]-**8**, [3-^{2}H][^{15}N]-**8**, and [2,3-^{2}H$_2$][^{15}N]-**8**, along with the corresponding series of [^{14}N] isotopomers. (The [^{14}N] isotopomers are not shown in Scheme 3.) This complex mixture was suitable for microwave analysis because the desired isotopomers [2-^{2}H][^{15}N]-**8** and [3-^{2}H][^{15}N]-**8** were the most abundant species and because they display the most intense transitions (they lack the quadrupole splitting of the corresponding [^{14}N] isotopomers).

The synthesis of maleonitrile (**9**) followed published procedures. The normal isotopomer was obtained from an iodine-catalyzed isomerization of the commercially available fumaronitrile (**12**),[40] resulting in a 1.7:1 mixture of **12**/**9** (Scheme 4). The quadrupole splitting arising from the two ^{14}N nuclei prevented the microwave spectra of the ^{13}C isotopomers of **9** from being observed in natural abundance, so the doubly labeled [^{15}N$_2$]-**9** was prepared (Scheme 4). Dimethyl maleate was converted to diamide **18** using ^{15}NH$_4$OH with a catalytic amount of NaCN[41] and then dehydrated with P$_2$O$_5$ to give the doubly labeled dinitrile [^{15}N$_2$]-**9** in poor overall yield. This sample

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afforded the spectrum of [$^{15}N_2$]-**9**, along with the spectra of the mono-^{13}C isotopomers [1-^{13}C][$^{15}N_2$]-**9** and [2-^{13}C][$^{15}N_2$]-**9** detected in natural abundance. As with enynenitrile **8**, the positions of the hydrogen atoms were poorly determined (vide infra) and therefore a dideuterated sample was prepared. [2,3-$^2H_2$]-Maleic anhydride was easily converted to [2,3-$^2H_2$]-dimethyl maleate using Fisher esterification conditions.[42] The deuterated ester was converted to the diamide [$^2H_2$][$^{15}N_2$]-**18** and then to the dinitrile [$^2H_2$][$^{15}N_2$]-**9** (Scheme 4), giving a suitable series of isotopomers for a structure determination.

Microwave Spectrum of (*Z*)-Pent-2-en-4-ynenitrile (8). The normal isotopic species of **8** exhibited both a- and b-type rotational transitions with the b-type transitions slightly more intense. The most intense of the transitions could be observed in 100 gas pulses with a signal-to-noise ratio in excess of 50. The transitions were split into as many as eight observable components from coupling of the ^{14}N nuclear electric quadrupole moment with the rotational motion. Assignments were relatively straightforward upon inspection of the characteristic hyperfine splitting. The transitions were fit with the Pickett global fit program[43] to two quadrupole hyperfine constants and the usual three rotational and five distortion constants. The coupling scheme was $I + J = F$. Table 1 lists a selection of the measured frequencies for the normal isotopic species and the residuals that result from a least-squares fit of these frequencies to a Watson *A*-reduced Hamiltonian in the I^r representation.[44] The complete set of transitions is available as Supporting Information.

As noted above, the five possible singly substituted [^{13}C] species, the [^{15}N] isotopomer, and the three [^2H][^{15}N] species were studied in natural abundance or enriched samples. The deuterium hyperfine splitting was minimal, although some b-type transitions were perceptibly split or broadened, leading to a significant reduction in intensity compared to the a-dipole transitions. In these cases, the line center or strongest feature was chosen as the unsplit center frequency. The observed transitions for these isotopomers are available as Supporting Information. These transitions were fit using the same procedure as the normal isotopomer (minus quadrupole coupling and with some distortion constants fixed at the normal species values, as appropriate). The derived spectral parameters for the 10 species are given in Table 2.

The absence of quadrupole hyperfine splittings in the spectrum of the [^{15}N]-substituted isotopomer facilitated the measurement of the dipole moment. A total of 14 components selected from 7 rotational transitions were least-squares fit to calculated Stark coefficients generated from perturbation theory to obtain dipole components: $\mu_a = 2.382(8)$ D and $\mu_b = 2.600(8)$ D giving a total dipole moment $\mu_{total} = 3.527$ D. The observed and calculated Stark coefficients are available as Supporting Information. The ab initio calculated dipole moment of 3.619 D is in good agreement (CCSD(T)/cc-pVTZ, vide infra).

Microwave Spectrum of Maleonitrile (9). The normal isotopic species of **9** exhibited only b-type rotational transitions due to the C_2 symmetry axis. The transitions in the normal isotopomer were split into numerous components (as many as 21 were observed in an optimal case) due to the nuclear quadrupole hyperfine interaction from the two $I = 1$, ^{14}N nuclei, resulting in a considerably weaker spectrum. Typically the strongest hyperfine components had signal-to-noise ratios of 15 after 1000 gas pulses.

Table 1. Selected Rotational Transition Frequencies for the Normal Isotopomer of (*Z*)-Pent-2-en-4-ynenitrile (**8**)

J_{KaKc}'	←	J_{KaKc}''	F'	←	F''	ν_{obs} (MHz)	$\Delta\nu^a$ (kHz)
1_{10}	←	1_{01}	0		1	5153.4986	−1.1
			2		1	5154.4806	2.1
			2		2	5154.5535	0.4
			1		1	5155.1309	−0.1
			1		2	5155.2044	−1.2
			1		0	5155.3178	0.3
1_{11}	←	0_{00}	1		1	9041.1281	−0.4
			2		1	9041.8566	1.0
			0		1	9042.9459	−0.5
2_{12}	←	1_{11}	1		0	8512.5760	1.3
			3		2	8513.2772	0.3
			2		1	8513.3073	2.4
			1		1	8514.3903	−2.3
2_{02}	←	1_{01}	2		1	9166.8522	−0.9
			3		2	9166.9609	−0.7
			1		0	9167.0929	0.6
2_{11}	←	1_{10}	1		1	9990.1033	−0.5
			3		2	9991.1896	0.5
			2		1	9991.3172	1.6
			1		0	9991.7365	1.4
			2		2	9991.9675	−0.7
3_{03}	←	2_{12}	2		1	9782.1375	0.7
			3		3	9782.2551	3.0
			4		3	9782.4547	0.2
			3		2	9782.9508	−0.5
			2		2	9783.2255	1.0
3_{13}	←	2_{12}	2		1	12719.1336	−2.6
			3		2	12719.2242	−2.7
			4		3	12719.2643	−1.9
4_{04}	←	3_{13}	4		4	14775.0512	−6.7
			3		2	14775.3086	1.4
			5		4	14775.4641	2.2
			4		3	14775.7982	1.8
			3		3	14776.3011	−3.1
5_{14}	←	5_{05}	4		4	12292.5839	0.0
			6		6	12292.8407	−1.0
			5		5	12294.1064	0.4
5_{14}	←	4_{23}	4		3	13693.9858	0.9
			6		5	13694.1193	0.8
			5		4	13694.7754	0.1

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$, where ν_{calc} is obtained from the spectroscopic parameters in Table 2.

Assignments were made based upon spectra predicted from ab initio calculations of the structure and by the characteristic hyperfine splitting patterns. The Pickett global fitting program[43] was employed in a manner analogous to enynenitrile **8**. In this case, the rotational and nuclear spin angular momentum were coupled according to the scheme, $I = I_{N1} + I_{N2}$, $F = I + J$, so that the energy levels can be characterized by *I* and *F* quantum numbers. A selection of the transitions that were fit is given in Table 3, with the complete set available as Supporting Information. The other four isotopomers (the [$^{15}N_2$] species, the two [^{13}C][$^{15}N_2$] isotopomers, and the [$^2H_2$][$^{15}N_2$] species) were observed in enriched samples, eliminating the complication from quadrupole splitting. The assigned transitions are available as Supporting Information. The spectral constants obtained from least-squares fitting the transitions for the five isotopomers are given in Table 4.

The [$^{15}N_2$] species was used to measure the dipole moment to avoid complications from hyperfine splitting. A total of five components were least-squares fit to obtain the value $\mu_b = \mu_{total} = 5.32(6)$ D. The observed and calculated Stark coefficients are available as Supporting Information. The ab initio calculated dipole moment of 5.25 D is in good agreement (CCSD(T)/cc-pVTZ, vide infra).

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Table 2. Spectroscopic Parameters (Watson *A*-Reduction, I^r Representation) for the Isotopomers of (*Z*)-Pent-2-en-4-ynenitrile (**8**)

	normal	[5-^{13}C]^g	[4-^{13}C]	[3-^{13}C]	[2-^{13}C]	[1-^{13}C]
$A_0^{(A)}$ (MHz)	7098.1999(10)	6999.3718(6)	7097.7278(6)	6975.4172(6)	6979.2761(7)	7096.8873(6)
$B_0^{(A)}$ (MHz)	2682.5976(5)	2617.4393(4)	2652.5151(3)	2676.3791(4)	2676.0393(4)	2653.9929(3)
$C_0^{(A)}$ (MHz)	1943.5372(7)	1901.8446(3)	1927.6665(3)	1930.9545(3)	1931.0753(3)	1928.3835(3)
Δ_J (kHz)	3.426(9)	3.426^a	3.426^a	3.426^a	3.426^a	3.426^a
Δ_{JK} (kHz)	−22.02(11)	−22.02	−22.02	−22.02	−22.02	−22.02
Δ_K (kHz)	45.23(26)	45.23	45.23	45.23	45.23	45.23
δ_J (kHz)	1.280(4)	1.280	1.280	1.280	1.280	1.280
δ_K (kHz)	3.50(26)	3.50	3.50	3.50	3.50	3.50
χ_{aa} (MHz)	0.248(2)	0.360(10)	0.234(7)	0.224(7)	0.264(15)	0.251(7)
$\chi_{bb} - \chi_{cc}$ (MHz)	−4.599(4)	−4.692(13)	−4.598(8)	−4.554(10)	−4.674(23)	−4.591(8)
$\Delta\nu_{rms}$ (kHz)^b	2.01	3.59	4.21	2.98	3.51	3.51
N^c	96	18	21	18	17	22
Δ (amu Å^2)^d	0.441	0.446	0.440	0.444	0.444	0.440
P_{aa} (amu Å^2)	188.612	193.304	190.748	189.051	189.075	190.642
P_{bb} (amu Å^2)	71.419	72.427	71.423	72.674	72.633	71.432
P_{cc} (amu Å^2)	−0.220	−0.223	−0.220	−0.222	−0.222	−0.220
A_0'' (MHz)^e	7098.2068	6999.3787	7097.7347	6975.4241	6979.2830	7096.8942
B_0'' (MHz)^e	2682.5729	2617.4146	2652.4904	2676.3544	2676.0146	2653.9682
C_0'' (MHz)^e	1943.5316	1901.8390	1927.6609	1930.9489	1931.0697	1928.3779

	[^{15}N]	[5-^{2}H][^{15}N]	[3-^{2}H][^{15}N]	[2-^{2}H][^{15}N]
$A_0^{(A)}$ (MHz)	6990.6039(19)	6668.3042(21)	6605.5701(34)	6608.9034(34)
$B_0^{(A)}$ (MHz)	2623.4805(6)	2521.8452(6)	2601.1504(17)	2602.5743(17)
$C_0^{(A)}$ (MHz)	1904.3839(7)	1826.7637(8)	1863.1939(15)	1864.1979(15)
Δ_J (kHz)	3.323(15)	3.146(16)	3.22(7)	3.21(7)
Δ_{JK} (kHz)	−21.35(13)	−20.40(13)	−19.46(23)	−19.61(23)
Δ_K (kHz)	44.0(4)	40.98(46)	37.7(7)	37.9(7)
δ_J (kHz)	1.232(4)	1.186(4)	1.28(5)	1.26(5)
δ_K (kHz)	3.47(18)	3.34(18)	3.34^f	3.34^f
χ_{aa} (MHz)				
$\chi_{bb} - \chi_{cc}$ (MHz)				
$\Delta\nu_{rms}$ (kHz)^b	1.49	1.88	1.27	1.45
N^c	28	27	13	13
Δ (amu Å^2)^d	0.446	0.464	0.445	0.444
P_{aa} (amu Å^2)	192.860	200.632	194.513	194.406
P_{bb} (amu Å^2)	72.517	76.020	76.730	76.691
P_{cc} (amu Å^2)	−0.223	−0.232	−0.222	−0.222
A_0'' (MHz)^e	6990.6105	6668.3105	6605.5765	6608.9098
B_0'' (MHz)^e	2623.4564	2521.8220	2601.1281	2602.5519
C_0'' (MHz)^e	1904.3786	1826.7586	1863.1901	1864.1939

[a] Distortion constants were fixed at the values for the normal species for analysis of the singly substituted ^{13}C isotopomers. [b] $\Delta\nu_{rms} = (\sum(\nu_{obs} - \nu_{calc})^2/N)^{1/2}$. [c] N is the number of fitted components. [d] Inertial defect $\Delta = I_c - I_a - I_b$. [e] Watson determinable rotational constants. [f] Fixed at the fitted value determined for the [5-^{2}H][^{15}N] species. [g] The atom numbering assigns 1-C to the cyanocarbon sequentially to 5-C, 5-H at the terminal acetylenic C−H atoms.

Structures. The spectral data are consistent with the gross geometric features expected for **8** and **9**. The rotational constants, or, interchangeably, the moments of inertia (I_a (amu Å^2) = 5.053 79 × 10^5/A (MHz)) are consistent with C_s and C_{2v} symmetry, respectively, for the two species. The enynenitrile **8** possesses 15 independent structural parameters (8 distances, 7 angles) while the more symmetric maleonitrile **9** has 7 parameters (4 distances, 3 angles). In both cases, there are sufficient isotopic data to determine a complete structure without assuming any parameters. There actually are fewer independent moments of inertia than determined, since only two of the three moments are independent for a rigid planar species. Still, there are 20 independent I's for **8** and 10 for **9**, which represents an overdetermined set in each case.

The inertial data in Tables 2 and 4 allow R_0 and R_s structures to be determined. The R_0 structural parameters were obtained by least-squares fitting the I_a and I_b moments of inertia to obtain the effective structure in the ground vibrational state.[44] The R_s parameters were obtained by calculating the atom coordinates from differences in the moments of inertia upon isotopic substitution to obtain the substitution structure.[44,45] These structural parameters are given in Tables 5 (enynenitrile **8**) and 6 (maleonitrile **9**). The derived principal axes Cartesian coordinates are provided as Supporting Information.

Small but significant differences between the two sets of parameters can make interpretation difficult, especially when seeking high accuracy or making comparisons with related species. The situation is further complicated since the parameter values vary depending on which sets of I's are used to derive the two structures. This complication arises because of zero-point vibrational effects, which contribute vibration−rotation interaction and centrifugal distortion effects to the spectrally derived moments of inertia. Although $I_a + I_b = I_c$ for a rigid planar molecule, zero-point effects in a nonrigid planar molecule give rise to an inertial defect, ($\Delta = I_c - I_b - I_a$), where Δ is a small positive number for both enynenitrile **8** and maleonitrile **9** (Tables 2 and 4). Hence, if one chooses to fit the I_a and I_c moments, the I_b and I_c moments, or all the I's in the least-squares fitting procedure, slightly different R_0 parameters will result.

This complication motivated us to correct the ground-state rotational constants for zero-point vibrational effects, to obtain an equilibrium structure. We used the relationship

$$A_0 = A_e - \sum_i \alpha_i^A/2$$

where A_0 is the ground-state rotational constant, A_e is the

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Table 3. Selected Rotational Transition Frequencies for the Normal Isotopomer of Maleonitrile (**9**)

$J_{KaKc}' \leftarrow J_{KaKc}''$	I'	F' ←	I''	F''	ν_{obs} (MHz)	$\Delta\nu^a$ (kHz)
$1_{10} \leftarrow 1_{01}$	1	0	1	1	5431.1415	−2.5
	2	2	2	1	5430.8194	−0.7
	2	2	2	3	5430.7871	−0.9
	0	1	2	1	5430.7164	0.0
	0	1	2	2	5430.6578	−0.5
	1	2	1	2	5430.0839	−1.0
	2	3	2	3	5429.7473	1.0
	2	3	2	2	5429.7201	−0.2
	1	1	1	2	5429.3903	−0.1
	2	1	0	1	5428.4366	−1.1
	2	1	2	2	5428.4366	1.5
$1_{11} \leftarrow 0_{00}$	2	1	0	0	9350.5860	3.8
	2	1	2	2	9350.5860	3.8
	1	1	1	1	9349.6211	0.5
	2	3	2	2	9349.2680	3.3
	1	2	1	1	9348.9114	2.6
	0	1	0	0	9348.3001	−3.1
	0	1	2	2	9348.3001	−3.1
	2	2	2	2	9348.1975	0.5
	1	0	1	1	9347.8413	0.2
$2_{12} \leftarrow 1_{01}$	2	2	2	2	13267.0933	1.9
	2	2	0	1	13267.0933	−0.8
	2	3	2	2	13267.4369	−0.9
	2	3	2	3	13267.4692	5.4
	1	1	1	0	13267.4997	−12.0
	1	1	1	1	13267.5547	−0.5
	1	3	1	2	13267.9528	1.7
	2	4	2	3	13268.4581	2.3
	2	1	2	2	13268.6772	−0.8
	2	1	0	1	13268.6772	−3.4
	2	1	2	1	13268.7387	2.6
	0	2	2	2	13268.8643	5.4
	0	2	0	1	13268.8643	2.8
	0	2	2	1	13268.9161	−0.9
	2	0	0	1	13269.2616	2.4
	2	0	2	1	13269.3109	−3.8
$5_{14} \leftarrow 5_{05}$	2	3	2	3	12194.7616	−1.6
	0	5	0	5	12195.0212	−0.8
	2	7	2	7	12195.2819	−0.9
	2	3	2	4	12195.3783	3.0
	2	4	2	3	12195.3783	1.2
	0	5	2	6	12195.8940	−0.5
	2	6	0	5	12195.8940	−2.0
	2	4	2	4	12195.9877	−1.5
	1	6	1	6	12196.3434	−1.1
	1	4	1	4	12196.6083	4.8
	2	6	2	6	12196.7667	−1.8
	2	4	2	5	12196.8909	4.4
	2	5	2	4	12196.8909	4.1
	2	6	2	5	12197.2756	−0.5
	2	5	2	6	12197.2756	−0.9
	2	5	2	5	12197.7833	−0.8
$5_{14} \leftarrow 4_{23}$	2	3	2	2	12746.4673	−4.8
	0	5	0	4	12746.6032	−3.2
	2	7	2	6	12746.7437	1.9
	2	4	2	3	12747.1067	2.9
	1	6	1	5	12747.2869	−0.5
	1	4	1	3	12747.4245	2.8
	2	6	2	5	12747.5086	0.9
	2	5	2	4	12748.0303	0.6

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$, where ν_{calc} is obtained from the spectroscopic parameters in Table 4.

equilibrium value and α_i^A are the vibration−rotation interaction constants which are completely determined by the quadratic and cubic force fields. Analogous equations hold for B_0 and C_0. The summation is over the $3N - 6$ vibrations.

Calculation of the vibration−rotation interaction constants, α_i, requires computation of harmonic and anharmonic force constants. Pioneering studies of the computation of α_i [46,47] and the determination of equilibrium structures[48−50] have been described recently. The vibrational contributions can be evaluated relatively accurately, even at somewhat low levels of theory (often at the SCF level), to provide good corrections to the ground-state moments. In this work, we have closely followed our analysis of enediyne **7**.[17] Two approaches were used to determine these vibrational corrections and obtain "experimental" equilibrium rotational constants. In the first approach (force field I), both the quadratic and cubic force constants and corresponding equilibrium structure were calculated at the SCF level using the DZP basis set.[51] The second approach (force field II) is based on these quadratic force constants and equilibrium structure, but with inclusion of electron correlation approximated by partial fourth-order many-body perturbation theory (SDQ-MBPT(4)). The cubic force constants were then determined at the SCF level at the same geometry and transformed into the normal coordinate representation defined by the SDQ-MBPT(4) force field.

The ab initio force fields obtained from approaches I and II were used to compute corrections to the rotational constants for all isotopomers of both **8** and **9**. Using the equation above, and the Watson determinable constants[44] in Tables 2 and 4 (A_0'', etc.), a set of equilibrium rotational constants (A_e, etc.) were obtained. These corrections (α's) and the equilibrium constants are given in Supporting Information. The resultant equilibrium I_a^e and I_b^e rotational constants were then least-squares fit to provide the two "experimental" or "empirical" equilibrium structures in Tables 5 and 6 and illustrated in Figures 1 and 2. We also list for comparison the equilibrium structure calculated at the CCSD(T)/cc-pVTZ level of theory. This method has been shown to give very accurate equilibrium parameters for the enediyne **7**.[17] It is gratifying that the three equilibrium structures in Tables 5 and 6 agree to much better than 0.01 Å and 0.5° in nearly all cases.

It is difficult to rigorously estimate the accuracy of the R_e structures in Tables 5 and 6. One auspicious indicator in the "experimental structures" is the reduction in the inertial defect (Δ) close to the theoretical "perfect value" of zero. For enynenitrile **8**, this quantity is 0.083 amu Å^2 for force field I, and it further reduces to 0.014 amu Å^2 for force field II. In the case of **9**, force field I gives 0.0639 amu Å^2 and force field II gives 0.0209 amu Å^2. The small nonzero values for force field II are of the magnitude expected from electronic contributions to the moment of inertia,[44,52,53] which were not included in our calculations. Judging from the small variation between the structures from force fields I and II, the small inertial defect for force field II, and the close agreement with our highest level ab initio structure, we conservatively estimate that the bond distances and angles from force field II have uncertainties no greater than 0.005 Å and 0.5°. These parameters are considered the best estimates of the equilibrium values from this work.

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Table 4. Spectroscopic Parameters (Watson *A*-Reduction, I^r Representation) for the Isotopomers of Maleonitrile (**9**)

	normal	$[^{15}N_2]$	$[1-^{13}C][^{15}N_2]$	$[2-^{13}C][^{15}N_2]$	$[^2H_2][^{15}N_2]$
$A_0^{(A)}$ (MHz)	7389.5090(7)	7171.7463(22)	7171.1519(25)	7043.4849(23)	6406.4225(26)
$B_0^{(A)}$ (MHz)	2672.5944(7)	2552.7297(9)	2526.1919(8)	2546.9872(8)	2512.4622(9)
$C_0^{(A)}$ (MHz)	1959.5221(12)	1879.6055(11)	1865.1385(7)	1867.5652(7)	1801.9498(10)
Δ_J (kHz)	3.258(7)	3.048(20)	2.980(21)	2.985(21)	2.743(21)
Δ_{JK} (kHz)	−21.51(23)	−20.54(22)	−20.02(8)	−20.11(9)	−16.7(2)
Δ_K (kHz)	45.7(4)	44.1(6)	43.2(6)	42.4(5)	34.7(5)
δ_J (kHz)	1.190(3)	1.102(9)	1.102[a]	1.102[a]	1.097(10)
δ_K (kHz)	3.7(5)	3.8(4)	3.8[a]	3.8[a]	1.98(24)
χ_{aa} (MHz)	0.0579(15)				
χ_{bb}- χ_{cc} (MHz)	−4.688(2)				
$\Delta\nu_{rms}$ (kHz)[b]	2.82	2.20	1.91	2.53	2.68
N[c]	152	16	12	12	14
Δ (amu Å^2)[d]	0.421	0.431	0.431	0.435	0.427
P_{aa} (amu Å^2)	189.307	198.192	200.271	198.640	201.362
P_{bb} (amu Å^2)	68.602	70.684	70.689	71.969	79.100
P_{cc} (amu Å^2)	−0.211	−0.216	−0.216	−0.218	−0.214
A_0'' (MHz)[e]	7389.5155	7171.7524	7171.1579	7043.4909	6406.4280
B_0'' (MHz)[e]	2672.5696	2552.7055	2526.1680	2546.9633	2512.4448
C_0'' (MHz)[e]	1959.5169	1879.6009	1865.1342	1867.5609	1801.9447

[a] Fixed at the value for the $[^{15}N_2]$ species. [b] $\Delta\nu_{rms} = (\sum(\nu_{obs} - \nu_{calc})^2/N)^{1/2}$. [c] N is the number of fitted rotational transitions (= number of hyperfine components in the normal isotopomer). [d] Inertial defect $\Delta = I_c - I_a - I_b$. [e] Watson determinable rotational constants.

Table 5. Structural Parameters for (*Z*)-Pent-2-en-4-ynenitrile (**8**)

				structures[a]				
parameter[b]	B3LYP/ 6-31G*[c]	BPW91/ cc-pVDZ[d]	CASSCF(6,6)/ 3-21G[e]	1 R_0	2 R_s	3 R_e	4 R_e	CCSD(T)/ cc-pVTZ
$N\equiv C_1$ (Å)	1.164	1.178	1.151	1.161	1.151	1.159	1.158	1.161
C_1-C_2 (Å)	1.425	1.425	1.424	1.428	1.437	1.426	1.427	1.426
$C_2=C_3$ (Å)	1.352	1.366	1.335	1.343	1.343	1.348	1.345	1.345
C_3-C_4 (Å)	1.416	1.416	1.424	1.418	1.442	1.418	1.420	1.419
$C_4\equiv C_5$ (Å)	1.211	1.226	1.199	1.212	1.188	1.208	1.207	1.209
C_2-H (Å)	1.086	1.099	1.071	1.101	1.101	1.078	1.072	1.077
C_3-H (Å)	1.088	1.102	1.072	1.097	1.097	1.079	1.079	1.078
C_5-H (Å)	1.066	1.078	1.051	1.054	1.057	1.059	1.062	1.059
$N\equiv C_1-C_2$ (deg)	178.1	178.0	179.4	178.6	178.0	178.6	178.7	178.6
$C_1-C_2=C_3$ (deg)	123.9	124.3	123.7	122.6	122.3	122.6	122.6	123.0
$C_2=C_3-C_4$ (deg)	125.4	125.7	124.2	123.9	123.2	123.9	123.9	124.3
$C_3-C_4\equiv C_5$ (deg)	178.0	177.8	179.4	179.5	178.0	179.4	179.5	179.0
$H-C_2=C_3$ (deg)	119.8	119.4	119.9	122.9	122.8	120.1	119.5	120.2
$H-C_3-C_4$ (deg)	116.8	116.7	116.9	115.8	116.5	118.0	117.9	117.2
$C_4\equiv C_5-H$ (deg)	178.5	178.6	179.1	179.3	178.4	179.1	179.2	178.9
$N\equiv C_1-C_2=C_3$ (deg)	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
$C_2=C_3-C_4\equiv C_5$ (deg)	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
$C_3-C_4\equiv C_5-H$ (deg)	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0

[a] R_0 effective structure 1 was obtained by a least-squares fitting of the 20 I_a, I_b effective moments (Table 2). R_s substitution structure 2 was obtained from Kraitchman's equations, which determine atom coordinates from differences in moments of inertia upon isotopic substitution using the effective constants (Table 2). R_e equilibrium structures 3 and 4 were obtained by least-squares fitting the 20 I_a, I_b empirical equilibrium rotational constants (Table S13) obtained using force fields I and II, respectively. R_e structure 4 has uncertainties of 0.005 Å in distances and 0.5° in angles (see ref 17). [b] Atom numbering. See footnote *a*, Table 2. [c] References 33 and 32. [d] Reference 30. [e] Reference 25.

Discussion

Interstellar Chemistry. As noted earlier, cyanopolyynes as large as $HC_{11}N$, along with two partially hydrogenated members of the H_nC_3N series (acrylonitrile and ethyl cyanide), have been detected in the interstellar medium. Our current study provides experimental rotational spectra for nitrile **8**, a member of the H_nC_5N series, and dinitrile **9**, a structural analogue of **8** with greater polarity. These data provide the basis for subsequent efforts to detect these species in laboratory experiments involving discharges or combustion processes and in the interstellar medium. Detection in well-designed laboratory experiments and observation by radioastronomers would have important implications concerning the mechanism of formation of complex organic molecules in interstellar clouds.

Nitrile **8** appears to be a more likely candidate for detection in the ISM than dinitrile **9**. While **8** has the smaller dipole moment (3.53 vs 5.32 D), its rotational transitions are more intense since each level is split into fewer states by nitrogen quadrupole coupling. Furthermore, although approximately 44 interstellar species containing one nitrogen atom have been observed in the ISM, only 3 species containing two nitrogen atoms have been detected.[8] The intensity of an interstellar transition, however, depends on abundance as well as inherent line strength. Even species such as CO or NO, with small dipole moments (<0.1 D), have been observed in interstellar clouds. The mechanisms of formation and destruction will govern the interstellar abundance. These mechanisms remain unknown at the current time.

Structure Determination. It is worth noting that several heavy-atom parameters in the substitution structures (R_s parameters in Tables 5 and 6) disagree markedly with the equilibrium values. This difference is readily traced to small coordinate values, which are well known to be troublesome in this analysis.[44,54,55] (See Supporting Information for atom

Table 6. Structural Parameters for Maleonitrile (**9**)

			structure[a]				
parameter	HF/ STO-3G[b]	HF/ 3-21G[c]	1 R_0	2 R_s	3 R_e	4 R_e	CCSD(T)/ cc-pVTZ
H−C (Å)	1.086	1.072	1.099	1.099	1.078	1.075	1.076
C═C (Å)	1.324	1.322	1.340	1.338	1.344	1.341	1.342
C−C (Å)	1.457	1.423	1.428	1.446	1.427	1.429	1.426
C≡N (Å)	1.157	1.139	1.160	1.143	1.158	1.157	1.161
H−C═C (deg)	120.2	119.8	122.2	122.2	119.7	119.4	119.8
C−C═C (deg)	123.9	124.1	123.1	122.6	123.1	123.2	123.5
N≡C−C (deg)		179.5[d]	178.4	177.2	178.4	178.4	178.4
N≡C−C═C (deg)		0.0	180.0	180.0	180.0	180.0	180.0

[a] See footnote *a*, Table 5. Here, the 10 I_a and I_b effective moments of inertia were used from Table 4 (1-R_0, 2-R_s) and the 10 empirical equilibrium values from Table S21, (3-R_e, force field I and 4-R_e, force field II, respectively). R_e structure 4 has uncertainties of 0.005 Å in distances and 0.5° in angles (see ref 17). [b] Reference 87. [c] Reference 88. [d] Distortion in the direction opposite that observed experimentally.

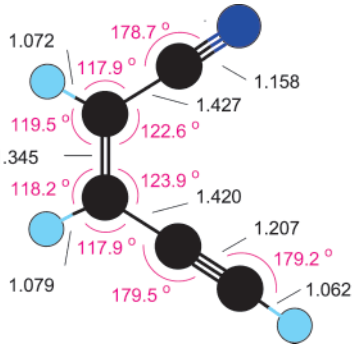

Figure 1. Equilibrium structure (R_e) of (*Z*)-pent-2-en-4-ynenitrile (**8**).

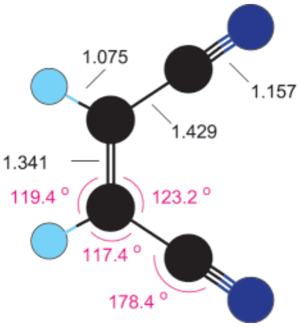

Figure 2. Equilibrium structure (R_e) of maleonitrile (**9**).

coordinates.) By contrast, the heavy-atom parameters for the R_0 structure are considerably closer to the equilibrium values, although the light-atom (H-containing) parameters are still poorly determined. Of course, the literature contains other examples where both heavy- and light-atom parameters derived from R_0 structures display poor agreement with equilibrium values.[56] Nevertheless, the R_0 analysis is probably the preferable methodology to minimize complications from vibrational effects in structure determinations for situations such as encountered in our examples.

Of course, the ideal is to obtain equilibrium parameters. This is not practical, from experiment alone, for molecules as large as **8** and **9** because the complete set of accurate α's is rarely measurable.[57] Consequently, spectroscopists have pursued a number of ways to analyze a set of ground-state rotational constants, making various approximations to reduce or cancel vibrational isotope effects and obtain near-equilibrium structures.[58] Another approach combines spectral or diffraction data, along with ab initio calculations using empirically derived structure offset values, to arrive at near-equilibrium parameters.[58,59] The procedure used here of calculating the ground-state vibration−rotation interaction constants is attractive because it is still more rigorous. Its accuracy principally depends on the approximations made in the ab initio calculation (basis set, level of theory, etc.). It appears that quite accurate equilibrium structures may be obtained by these methods, even when the rotation−vibration interaction effects are determined at the SCF level.[60] This matter needs further investigation and testing before a general assessment of the accuracy and reliability of the method can be made.

Empirical Comparisons. There have recently been a number of careful studies reporting equilibrium (or near-equilibrium) structures, employing the various methods mentioned in the previous paragraph, for structurally related molecules of 3−6 carbons containing alkene, alkyne, and nitrile groups. The bond distances for these species (and several prototype species) are listed for comparison with the values for **7**−**9** in Table 7. These structures have uncertainties ranging from 0.001 to 0.005 Å. The lack of variation in the detailed bond distances and angles in **7**−**9** is striking. It is clear that any variation in the C≡N distances for several other species are also well within the uncertainty range, a trend noted in other examples as well.[61] The variation in C≡C distances is also very small with an indication of a slight lengthening in **7** and **8**. The C═C distances vary over a wider range, lengthening slightly when adjacent to another π system due to delocalization effects. The C−C bonds are most sensitive to their environment, showing considerable shortening from ethane (1.522 Å).[62] Thus, the triple bonds are relatively insensitive to multiple conjugation effects in these

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(55) In **8**, the b_0 coordinates of 1-C and 4-C are 0.103 and 0.038 Å, respectively, and the b_s values are 0.116 and 0.068 Å. In **9**, the b_0 coordinate of the cyano carbons is 0.055 Å and the b_s value is 0.077 Å

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(59) Recent examples: (a) Breidung, J.; Demaison, J.; Margulès, L.; Thiel, W. *Chem. Phys. Lett* **1999**, *313*, 713−717. (b) Margulès, L.; Demaison, J.; Boggs, J. E. *J. Phys. Chem. A* **1999**, *103*, 7632−7638. (c) Demaison, J.; Margulès, L.; Breidung, J.; Thiel, W.; Bürger, H. *Mol. Phys.* **1999**, *97*, 1053−1067. (d) Kochikov, I. V.; Tarasov, Y. I.; Spiridonov, V. P.; Kuramshina, G. M.; Saakjan, A. S.; Yagola, A. G. *J. Mol. Struct.* **2000**, *550*−*551*, 429−438.

(60) For several other examples of this approach, see: References 17, 48−50, and 59c.

(61) Le Guennec, M.; Woldarczak, G.; Burie, J.; Demaison, J. *J. Mol. Spectrosc.* **1992**, *154*, 305−323.

(62) Tam, H. S.; Choe, J.-I.; Harmony, M. D. *J. Phys. Chem.* **1991**, *95*, 9267−9272.

Table 7. Selected Values of Equilibrium Bond Distances (Å)[a]

species	formula	$C\equiv N$	$C\equiv C$	$C=C$	$C-C$	ref
enediyne **7**	$HCCCH=CHCCH$		1.208	1.347	1.421	*e*
enynenitrile **8**	$HCCCH=CHCN$	1.158	1.207	1.345	1.420,[b] 1.427[c]	*f*
enedinitrile **9**	$NCCH=CHCN$	1.155		1.345	1.429	*f*
1,1-dicyanoethene	$CH_2=C(CN)_2$	1.158		1.342	1.437	*g*
malononitrile	$CH_2(CN)_2$	1.155			1.464	*g*
acrylonitrile	$CH_2=CH(CN)$	1.157		1.337	1.432	*h*
(*Z*)-crotononitrile	$CH_3CH=CH(CN)$	1.158		1.341	1.431,[c] 1.490[d]	*i*
(*E*)-crotononitrile	$CH_3CH=CH(CN)$	1.158		1.339	1.430,[c] 1.491[d]	*i*
propene	$CH_3CH=CH_2$			1.333	1.496	*j*
acetonitrile	$CH_3C\equiv N$	1.156			1.457	*k*
methylacetylene	$CH_3C\equiv CH$		1.204		1.458	*l*
cyanoacetylene	$HC\equiv CC\equiv N$	1.161	1.206		1.376	*m*
acetylene	$HC\equiv CH$		1.203			*n*
ethylene	$H_2C=CH_2$			1.332		*n*

[a] The uncertainties are estimated to range from 0.001 to 0.005 Å. [b] $C-CCH$. [c] $C-CN$. [d] $C-CH_3$. [e] Reference 17. [f] This work. [g] Reference 18. [h] Reference 19. [i] Reference 20. [j] Reference 62. [k] Reference 61. [l] Reference 89. [m] Reference 90. [n] Reference 56a.

molecules, while small changes and somewhat larger effects are seen in the $C=C$ and $C-C$ linkages. Additional examples of these trends and variations are available.[17,61,63]

A small deviation from linearity about the $C-C\equiv C$, $C-C\equiv N$, and $C\equiv C-H$ linkages is evident in both enynenitrile **8** (Figure 1) and enedinitrile **9** (Figure 2). A similar distortion of the alkyne groups was observed in enediyne **7**, where the $C-C\equiv C$ angle is 178.8°.[17] Deviations from linearity about triple-bonded carbon were proposed years ago in other systems (e.g., vinylacetylene,[64] acrylonitrile,[65] 1,4-pentadiyne,[66] malononitrile,[67] and 3-butynenitrile[68]), although the interpretation of this effect was perhaps clouded by experimental uncertainties and the small magnitude of the effect. The issue of these subtle distortions regularly arises in other systems.[69] Recent studies determined accurate equilibrium parameters and established that effects of this magnitude (1−2°) clearly occur in dicyanoethene,[18] malononitrile,[18] and acrylonitrile,[19] as well as **7**−**9**. A much larger repulsion is observed in sulfur dicyanide, where the $S-C\equiv N$ angle is 175.2°.[18] The effect is smaller (~0.5°) in the crotononitrile isomers.[20] The significance of this subtle electronic effect is not clear.

Conclusions

Accurate gas-phase equilibrium structures have been determined for (*Z*)-pent-2-en-4-ynenitrile and maleonitrile through an integrated collaboration involving synthetic organic chemistry, Fourier transform microwave spectroscopy, and quantum chemistry. The experimental spectroscopic data provide the basis for subsequent efforts to detect these species in laboratory experiments involving discharges or combustion processes and in the interstellar medium.

Methods Section

Spectroscopy. The rotational microwave spectra were recorded with two Balle-Flygare FT microwave spectrometers[70,71] operating between 5 and 15 GHz, using a General Valve series 9 pulsed nozzle. For dipole moment measurements, a modified Bosch fuel injector was used as the nozzle source.[72] The FT spectrometers were recently automated using software and hardware modifications developed at the University of Kiel.[73] The gas expansion axis was perpendicular to the microwave cavity axis, providing average line widths of ~30 kHz full width at half-maximum. Peak frequencies were reproducible to within 4−5 kHz. Stark effect splittings of **8** were observed by applying dc voltages of up to 4.2 kV of opposite polarity to two parallel steel mesh plates (~30 cm apart)[74] producing shifts as large as 900 kHz. For **9**, voltages of up to ±3.8 kV were employed giving shifts as large as 1.5 MHz. The $J = 1 \leftarrow 0$ transition of OCS was used as a calibration standard (μ(OCS) = 0.715 20 D).[75]

One or two drops of enynenitrile **8** were placed in the liquid reservoir chamber of the General Valve nozzle, and "first run" He/Ne carrier gas (10% He, 90% Ne) at 1−2.9 atm total backing pressure was passed over the material before expansion into the evacuated spectrometer chamber. Some experiments employed a few drops of sample in a 1-L bulb pressurized to ~3 atm by the carrier gas; this gave transitions of similar intensity. The transitions from ^{14}N-containing species exhibited splittings due the nuclear hyperfine interaction, which spread them over about 1−2 MHz, allowing easy recognition and assignment of the three most intense components and often several of the weaker ones.

Maleonitrile **9** was observed by placing ~20−50 mg of the solid sample into the reservoirs attached to either nozzle. A small band heater was placed around the reservoirs and heated to 50−70 °C to observe the spectra. The normal isotopomer transitions were split into many components over about 1.0−2.5 MHz due to the splitting from two ^{14}N nuclei. In most cases, only the stronger components were measured and assigned due to the complexity arising from the splitting.

Ab Initio Calculations. All calculations reported in this work were performed with a local version of the ACES II program system.[76] Geometry optimizations were performed using the coupled-cluster

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approximation limited to single and double excitations (CCSD)[77] and CCSD(T) in which CCSD is augmented by a correction for triple-excitation effects.[78] Analytical gradient methods[79,80] were used to determine the equilibrium geometries and corresponding dipole moments. Basis sets used in the geometry optimizations were a triple-ζ plus double-polarization (TZ2P) basis[81] and the correlation consistent cc-pVTZ basis of Dunning.[82]

In addition, the quadratic and cubic force fields were determined at the self-consistent field level of theory by a procedure based on numerical differentiation of analytically computed second derivatives.[50,83,84] These force fields were then used to calculate vibrational corrections to the rotational constants according to the formulas described by Mills.[85] A (nearly negligible) correction for centrifugal distortion effects needed to convert rotational constants belonging to the set of Watson's determinable parameters to equilibrium rotational constants was calculated on the basis of the equations given by Kirchhoff.[86]

General Synthetic Methods. NEt_3 was stirred over CaH_2 overnight and then distilled under N_2. LiBr was oven dried for 24 h and stored in a desiccator. Iodine and fumaronitrile were sublimed under vacuum before use. Isotopically labeled $^{15}NH_4OH$ was purchased from Cambridge Isotope Laboratories. Other compounds from commercial sources were used without further purification. Unless otherwise noted, ^1H and ^{13}C NMR spectra (Bruker AC-300 spectrometer, Varian Unity-500) and ^2H NMR spectra (Bruker AC-250 spectrometer) were obtained in $CDCl_3$ or $CHCl_3$, respectively. ^1H and ^{13}C chemical shifts were referenced to residual solvent, while ^2H chemical shifts were referenced to CD_2Cl_2. All air- or moisture-sensitive reactions were carried out under an argon atmosphere under anhydrous conditions. Flash column chromatography was conducted on silica gel (E. Merck 60, 230−400 mesh).

Sample Preparation and Handling. Samples of enynenitrile **8** were prepared by KOH-mediated deprotection of a trimethylsilyl-substituted precursor **17**. The deprotected enynenitrile was collected in a liquid nitrogen-cooled flask, thawed, transferred to a dry glass ampule via pipet, cooled in liquid nitrogen, and sealed under vacuum. In the case of the deuterated samples, the ampules were prewashed with D_2O in order to minimize loss of deuterium via isotopic exchange with the glass surface. Ampules were packaged in a Styrofoam container in dry ice and shipped to the University of Michigan for characterization by Fourier transform microwave spectroscopy. ^1H NMR spectroscopy of these samples often revealed Me_3SiF as an impurity, but this impurity did not interfere with accurate measurement of rotational spectra. The short warming to room temperature necessary for ampule preparation resulted in discoloration of the sample. The products causing this discoloration were not visible in the ^1H NMR spectra, nor did they interfere with measurement of rotational spectra. Samples of **9** were relatively stable solids and were shipped to Michigan in glass vials packed in dry ice. ^1H NMR spectra indicated that the dinitrile samples contained unknown impurities, but these impurities did not interfere with the microwave experiments.

Propiolamide (14). In a slight modification of the literature procedure,[37] 10 mL of NH_4OH was cooled to −30 °C and methyl propiolate (5.03 g, 59.8 mmol) added dropwise. The reaction was stirred for 20 min at −30 °C. Solvent was removed under vacuum (0.1 mmHg) overnight to yield 3.86 g (94%) of amide **14** as a yellow solid: ^1H NMR δ 6.2 (br s, 1H), 5.9 (br s, 1H), 2.85 (s, 1H); ^{13}C NMR δ 153.8, 117.6, 74.5.

Propiolonitrile (15). In a slight modification of the published procedure,[38] P_2O_5 (40 g, 280 mmol) and **14** (3.86 g, 55.9 mmol) were well mixed, as solids, under N_2 in the distillation pot of a dry, short-path distillation apparatus. The distillation pot was heated to 125 °C, and 1.74 g (61%) of nitrile **15** was collected as a white solid at −78 °C. *Caution: This product is a severe vesicant and great care should be taken when using it. It will penetrate gloves with ease and causes painful burns and blistering:* bp 44 °C; ^1H NMR δ 2.50.

(*Z*)-3-Bromoacrylonitrile (16). Synthesized according to the literature procedure[39] and purified by vacuum distillation (20 mmHg, 80 °C). *Caution: This product is a severe vesicant and great care should be taken when using it. It will penetrate gloves with ease and causes painful burns and blistering as well as redness of the eyes. It should be worked with only in a fume hood:* ^1H NMR δ 7.23 (d, $J = 8.1$ Hz, 1H), 6.28 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR δ 129.4, 114.8, 106.9.

(*Z*)-5-Trimethylsilylpent-2-en-4-ynenitrile (17). A dry flask charged with $Pd(PPh_3)_4$ (1.0 g, 0.87 mmol) and CuI (0.34 g, 1.8 mmol) was subjected to three pump/Ar flush cycles. NEt_3 (25 mL) was added and the solution turned black. **16** (2.27 g, 17.2 mmol) and trimethylsilylacetylene (5.5 mL, 39 mmol) were added. After stirring for 70 min, the solution was quenched by pouring into a mixture of H_2O (25 mL) and saturated aqueous NH_4Cl (25 mL). The aqueous solution was extracted with Et_2O (3 × 25 mL), and the organic layers were combined, washed with H_2O (25 mL) and brine (25 mL), dried over $MgSO_4$, and filtered, and solvent was removed by rotary evaporation. The resulting black oil was purified by flash column chromatography (SiO_2, 5% EtOAc/hexanes) to yield 1.62 g (63%) of the protected enynenitrile **17** as a clear oil: $R_f = 0.20$; ^1H NMR δ 6.28 (d, $J = 11.1$ Hz, 1H), 5.61 (d, $J = 11.1$ Hz, 1H), 0.23 (s, 9H); ^{13}C NMR δ 129.7, 115.6. 109.8, 108.5, 99.0, −0.53.

(*Z*)-Pent-2-en-4-ynenitrile (8). 17 (3.44 g, 23.0 mmol) was added to 40 mL of a 0.13 M KOH solution in MeOH and and the resultant mixture stirred for 30 min at −41 °C. After warming to room temperature, H_2O (40 mL) and CH_2Cl_2 (20 mL) were added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL), and the organic layers were combined, washed with H_2O (40 mL) and brine (40 mL), dried over $MgSO_4$, and filtered, and solvent was removed under vacuum (0.02 mmHg) at −41 °C. The nitrile **8** was collected at 77 K upon warming to room temperature: ^1H NMR δ 6.29 (dd, $J = 10.8$, 2.1 Hz, 1H), 5.73 (dd, $J = 11.1$, 0.9 Hz, 1H), 3.65 (dd, $J = 2.4$, 0.6 Hz, 1H); ^{13}C NMR δ 128.9, 115.3, 110.2, 90.0, 78.1.

[^{15}N]-Propiolamide ([^{15}N]-14). A 6 N $^{15}NH_4OH$ solution (5 mL) was cooled to −20 °C and methyl propiolate (2.18 g, 25.9 mmol) added dropwise. The reaction was stirred for 20 min at −20 °C. Solvent was removed under vacuum (0.1 mmHg) overnight to yield 1.20 g (66.7%) of the amide as a yellow solid: ^1H NMR δ 6.24 (dd, $J[^{15}N-^1H] = 89.9$ Hz, 2.7 Hz, 1H), 5.90 (dd, $J[^{15}N-^1H] = 90.6$ Hz, 2.7 Hz, 1H), 2.85 (s, 1H).

[^{15}N]-(*Z*)-3-Bromoacrylonitrile ([^{15}N]-16). [^{15}N]-Propiolamide (1.20 g, 17.1 mmol) and [^{14}N]-propiolamide (3.78 g, 54.7 mmol) were mixed to provide 24% ^{15}N enrichment. ^{15}N-enriched (*Z*)-3-bromoacrylonitrile was then synthesized as described above: ^1H NMR δ 7.23 (d, $J = 8.1$ Hz, 1H), 6.28 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR δ 129.3, 114.7 (d, $J[^{15}N-^{13}C] = 17.8$ Hz), 106.9, (d, $J[^{15}N-^{13}C] = 3.8$ Hz).

[^{15}N]-(*Z*)-5-Trimethylsilylpent-2-en-4-ynenitrile ([^{15}N]-17). The reaction was performed as described for the normal isotopomer using ^{15}N-enriched (*Z*)-3-bromoacrylonitrile [^{15}N]-**16**: ^1H NMR δ 6.28 (d, $J = 11.1$ Hz, 1H), 5.61 (d, $J = 11.1$ Hz, 1H), 0.23 (s, 9H); ^{13}C NMR δ 129.7, 115.6 (d, $J[^{15}N-^{13}C] = 18.4$ Hz), 109.8, 108.5 (d, $J[^{15}N-^{13}C] = 3.9$ Hz), 99.0, −0.53.

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[^{15}N]-(*Z*)-Pent-2-en-4-ynenitrile ([^{15}N]-8). The reaction was performed as described for the normal isotopomer using ^{15}N-enriched (*Z*)-5-trimethylsilylpent-2-en-4-ynenitrile [^{15}N]-**17**: ^{1}H NMR δ 6.29 (dd, $J = 10.8$, 2.1 Hz, 1H), 5.73 (dd, $J = 11.1$, 0.9 Hz, 1H), 3.65 (dd, $J =$ 2.4, 0.6 Hz, 1H); ^{13}C NMR δ 128.8, 115.3 (d, $J[^{15}N-^{13}C] = 17.8$ Hz), 110.1 (d, $J[^{15}N-^{13}C] = 3.2$ Hz), 90.0, 78.1.

[5-^{2}H][^{15}N]-(*Z*)-Pent-2-en-4-ynenitrile ([5-^{2}H][^{15}N]-8). [^{15}N]-**8** was added to 40 mL of a 0.1 M KOH solution in D_2O and the resultant mixture stirred for 30 min. The reaction mixture was extracted with CH_2Cl_2 (30 mL followed by 20 mL). The organic layers were combined, washed with D_2O (20 mL), dried over $MgSO_4$, and filtered. Solvent was removed under vacuum (0.02 mmHg) at −41 °C. The product was collected at 77 K upon warming to room temperature: ^{1}H NMR δ 6.30 (d, $J = 11.1$ Hz, 1H), 5.73 (d, $J = 11.1$, 1H); ^{2}H NMR δ 3.68 (s).

[^{2}H] Isotopomers of (*Z*)-3-Bromoacrylonitrile (16). [^{15}N]-Propiolamide (1.17 g, 17.7 mmol) and [^{14}N]-propiolamide (1.66, 24 mmol) were mixed to provide a sample of amide **14** with 41% enrichment in ^{15}N. The nitrile **15** was then synthesized as described above. The deuterated isotopomers of bromonitrile **16** were synthesized using a 1:1 mixture of acetic acid-d_0 and acetic acid-d_4 with otherwise the same procedure as for the normal isotopomers. A mixture of eight isotopomers was obtained. [^{15}N]-**16**, [2-^{2}H][^{15}N]-**16**, [3-^{2}H][^{15}N]-**16**, [$^2H_2$][^{15}N]-**16**, [^{14}N]-**16**, [2-^{2}H][^{14}N]-**16**, [3-^{2}H][^{14}N]-**16**, [$^2H_2$][^{14}N]-**16**: ^{1}H NMR δ 7.23 (d, $J = 8.1$ Hz; 1:1:1 t, $J[^2H-^1H] = 1.5$ Hz, 1H, ═C*H*CC), 6.28 (d, $J = 8.1$ Hz; m, 0.68 H, ═C*H*Br); ^{2}H NMR δ 7.28 (br s, 0.45 D, ═C*D*CN), 6.32 (d, $J[^2H-^1H] = 1.1$ Hz, 1.0 D, ═C*D*Br).

[^{2}H] Isotopomers of (*Z*)-5-Trimethylsilylpent-2-en-4-ynenitrile (17). The reaction was performed as described for the normal isotopomer using the mixture of [^{1}H/^{2}H][^{14}N/^{15}N] isotopomers of **16**. A mixture of eight isotopomers was obtained [^{15}N]-**17**, [2-^{2}H][^{15}N]-**17**, [3-^{2}H][^{15}N]-**17**, [$^2H_2$][^{15}N]-**17**, [^{14}N]-**17**, [2-^{2}H][^{14}N]-**17**, [3-^{2}H][^{14}N]-**17**, [$^2H_2$][^{14}N]-**17**: ^{1}H NMR δ 6.28 (d, $J = 11.1$ Hz; 1:1:1 t, J[^{2}H−^{1}H] = 1.5 Hz, 0.75 H, ═C*H*CN), 5.61 (d, $J = 11.1$ Hz; 1:1:1 t, J[^{2}H−^{1}H] = 1.5 Hz, 0.58 H, ═C*H*CC), 0.23 (s, 9 H, TMS); ^{2}H NMR: 6.31 (br s, 0.50 D, ═C*D*CN) 5.65 (br s, 1.0 D, ═C*D*CC).

[^{2}H] Isotopomers of (*Z*)-Pent-2-en-4-ynenitrile (8). The reaction was performed as described for the normal isotopomer using the mixture of [^{1}H/^{2}H][^{14}N/^{15}N] isotopomers of **17**. A mixture of eight isotopomers was obtained [^{15}N]-**8**, [2-^{2}H][^{15}N]-**8**, [3-^{2}H][^{15}N]-**8**, [$^2H_2$][^{15}N]-**8**, [^{14}N]-**8**, [2-^{2}H][^{14}N]-**8**, [3-^{2}H][^{14}N]-**8**, [$^2H_2$][^{14}N]-**8**: ^{1}H NMR δ 6.29 (dd, $J =$ 11.1, 2.4 Hz; 1:1:1 t, d, $J[^2H-^1H] = 1.5$ Hz, 0.6 Hz, 0.82 H, ═C*H*CN), 5.73 (dd, $J = 11.1$, 0.9 Hz; m, 0.63 H, C*H*CC), 3.64 (dd, $J = 2.4$, 0.9 Hz, 1.0 H, CC*H*); ^{2}H NMR δ 6.33 (br s, 0.57 D, C*D*CN), 5.77 (d, $J[^2H-^1H] = 1.9$ Hz, 1.0 D, C*D*CC).

Maleonitrile (9). Iodine (4 g, 51.2 mmol) and fumaronitrile (**12**; 0.6 g, 2.4 mmol) were heated to 177 °C for 7 h in a round-bottom flask. $CHCl_3$ and sodium thiosulfate were added, and the solution was allowed to stand overnight.[40] The solution was then filtered and the solvent removed via rotary evaporation to yield a brown solid. The brown solid was purified by sublimation (35 °C, 0.02 mmHg) to give a 1.7:1 mixture of **12**:**9** as white crystals. **9**: ^{1}H NMR δ 6.18 (s, 1.00 H); ^{13}C δ 118.4, 113.2. **12**: ^{1}H NMR δ 6.27 (s, 1.71 H).

[$^{15}N_2$]-Maleamide ([$^{15}N_2$]-18). A total of 10 g of 6 N $^{15}NH_4OH$ (60 mmol) was cooled to 0 °C and dimethyl maleate (2.18 g, 15.1 mmol) added. NaCN (0.05 g, 1.0 mmol) was added as a catalyst[41] and the reaction stirred for 6 h, during which time [$^{15}N_2$]-**18** precipitated from solution as a white solid. The precipitate was collected by vacuum filtration, dried under vacuum (0.1 mmHg), and recrystallized twice from MeOH to afford 750 mg (62%) of [$^{15}N_2$]-**18** as a pinkish-white solid: ^{1}H NMR (Me$_2$SO-d_6) δ 8.44 (dd, $J[^{15}N-^1H] = 88.2$, 2.1 Hz, 1.9 H), 7.39 (dd, $J[^{15}N-^1H] = 87.6$, 2.1 Hz, 1.9 H) 6.06 (s, 2.0 H); ^{13}C NMR (Me$_2$SO-d_6) δ 166.5 (d, $J[^{15}N-^{13}C] = 15.8$ Hz), 132.1 (d, $J[^{15}N-^{13}C]= 8.9$ Hz). Normal isotopomer [$^{14}N_2$]-**18**: ^{1}H NMR (Me$_2$SO-d_6) δ 8.44 (br s, 1.9 H), 7.39 (br s, 1.9 H), 6.07 (s, 2.0H); ^{13}C NMR (Me$_2$SO-d_6) δ 166.6, 132.1.

[$^{15}N_2$]-Maleonitrile ([$^{15}N_2$]-9). [$^{15}N_2$]-**18** (0.750 g, 6.46 mmol) was well mixed with P_2O_5 (4.12 g, 14.5 mmol) under N_2 in a water-cooled sublimator. The apparatus was heated to 220 °C under aspirator vacuum (30 mmHg) for 4 h. During this time, a white solid collected on the coldfinger but most of the solid condensed on the sides of the sublimator. To collect this material, the sublimation chamber was immersed in a 110 °C oil bath to the level of the coldfinger under aspirator vacuum (30 mmHg) until all of the solid sublimed. The coldfinger was rinsed with ether and solvent removed under via rotary evaporation to yield 110 mg (21%) of the expected dinitrile [$^{15}N_2$]-**9** as a white solid, along with impurities present in the ^{1}H NMR spectrum: ^{1}H NMR δ 6.22 (s); ^{13}C NMR δ 118.3 (d, $J[^{15}N-^{13}C] =$ 1.89 Hz), 113.1 (d, $J[^{15}N-^{13}C] = 113.1$ Hz).

[$^2H_2$]-Dimethyl Maleate.[42] [$^2H_2$]-Maleic anhydride (1.00 g, 9.93 mmol; Aldrich) was dissolved in MeOH (3 mL, 74.1 mmol) and 2 drops of concentrated sulfuric acid added. The reaction was covered with foil and stirred for 48 h. Et_2O (10 mL) and saturated aqueous Na_2CO_3 (10 mL) were added and the layers separated. The aqueous layer was extracted with Et_2O (3 × 10 mL), and the Et_2O layers were combined, washed with brine (10 mL), dried over $MgSO_4$, and filtered, and solvent was removed via rotary evaporation to yield 0.98 g (68%) of [$^2H_2$]-dimethyl maleate as a clear liquid: ^{1}H NMR δ 3.80 (s). ^{2}H NMR (referenced to $CDCl_3$) δ 6.30 (s); ^{13}C NMR δ 165.5 (s), 129.2 (1:1:1 t, $J = 25.4$ Hz), 52.0 (s).

[$^2H_2$][$^{15}N_2$]-Maleamide ([$^2H_2$][$^{15}N_2$]-18). [$^2H_2$][$^{15}N_2$]-**18** was obtained in 13% yield using the procedure described for the [$^{15}N_2$] isotopomer: ^{1}H NMR (Me$_2$SO-d_6) δ 8.48 (dd, $J[^{15}N-^1H] = 88.5$, $[^1H-^1H] = 2.4$ Hz, 2.0 H), 7.39 (dd, $J[^{15}N-^1H] = 87.6$, $[^1H-^1H] = 2.4$ Hz, 2.0 H); ^{2}H NMR (Me$_2$SO) 6.02 (s); ^{13}C NMR (Me$_2$SO-d_6) δ 166.9 (d, $J[^{15}N-^{13}C] = 15.9$ Hz), 131.9 (1:1:1 t, d, $J[^2H-^{13}C] = 26.1$ Hz, $J[^{15}N-^{13}C] = 8.3$ Hz).

[$^2H_2$][$^{15}N_2$]-Maleonitrile [$^2H_2$][$^{15}N_2$]-9). [$^2H_2$][$^{15}N_2$]-**9** was obtained in 48% yield using the procedure described for the [$^{15}N_2$] isotopomer: ^{2}H NMR δ 6.25 (s); ^{13}C NMR δ 118.6 (1:1:1 t, $J[^2H-^{13}C] = 28$ Hz), 113.7 (d, $J[^{15}N-^{13}C] = 17.9$ Hz).

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Supporting Information Available: Tables of rotational frequencies for all isotopomers; Stark effect data; R_0 and R_s Cartesian principal axis coordinates; vibration−rotation constants (α's) and equilibrium rotational constants. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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