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Synthesis, Microwave Spectrum, and Dipole Moment of Allenylisocyanide (H₂C═C═CHNC), a Compound of Potential Astrochemical Interest

Harald Møllendal,*,[†] Svein Samdal,[†] Abdellatif Matrane,[‡,§] and Jean-Claude Guillemin*,[‡]

[†]Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway

[‡]Sciences Chimique de Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France

[§]Laboratoire de Chimie Bio-Organique et Macromoléculaire, Faculté des Sciences et Techniques Marrakech, Université Cadi Ayyad, BP 549, Marrakech, Morocco

Ⓢ Supporting Information

ABSTRACT: An improved synthesis of a compound of potential astrochemical interest, allenylisocyanide (H₂C═C═CHNC), is reported together with its microwave spectrum, which has been investigated in the 8−120 GHz spectral range to facilitate a potential identification in interstellar space. The spectra of the ground vibrational state and of five vibrationally excited states belonging to three different vibrational modes have been assigned for the parent species. A total of 658 transitions with a maximum value of $J = 71$ were assigned for the ground state and accurate values obtained for the rotational and quartic centrifugal distortion constants. The spectra of five heavy-atom (^{13}C and ^{15}N) isotopologues were also assigned. The dipole moment was determined to be $\mu_a = 11.93(16) \times 10^{-30}$ C m, $\mu_b = 4.393(44) \times 10^{-30}$ C m, and $\mu_{tot} = 12.71(16) \times 10^{-30}$ C m. The spectroscopic work has been augmented by theoretical calculations at the CCSD/cc-pVTZ and B3LYP/cc-pVTZ levels of theory. The theoretical calculations are generally in good agreement with the experimental results.
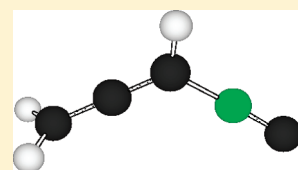
■ INTRODUCTION

Many nitriles (cyanides) have been detected in the interstellar medium (ISM), in comets or in the atmosphere of Titan.[1] Extensive recording of microwave, infrared, visible, and UV spectra of many compounds possessing this functional group has been performed to facilitate the detection of them in these environments, or to determine their partial pressures in planetary atmospheres.[2] We have recently reported the microwave (MW) spectra of two nitriles of potential astrochemical interest, namely, 3-aminoprop-2-enenitrile[3] and 3-mercaptoprop-2-enenitrile.[4] These two compounds are formally adducts of ammonia and cyanoacetylene,[3] and hydrogen sulfide and cyanoacetylene,[4] respectively.

Remarkably, isocyanides (isonitriles), which are 80−120 kJ/mol less stable than their nitriles isomers according to quantum chemical calculations,[5] are also of great interest in space science because several of them, such as hydrogen (HNC),[6] methyl (CH₃NC),[6] ethynyl (HC≡CNC),[7] magnesium (MgNC),[8] silicon (SiNC),[8] and aluminum isocyanide (AlNC),[8] have already been identified in the ISM by means of their MW spectra.

The existence in the ISM of the organic isocyanides CH₃NC[6] and HC≡CNC[7] is especially encouraging considering their high energies relative to their cyanide isomers and is also an indication that further isocyanides might be present in such environments. Interestingly, it has been demonstrated that UV photolysis in the solid state of cyanoacetylene or cyanobutadiyne leads to the formation of the corresponding isocyanides.[9,10] It is, therefore, possible that isocyanides might be formed in space by a similar mechanism. In fact, with the exception of the isomerization of hydrogen cyanide to hydrogen isocyanide,[11] very little is known about the ability of nitriles to isomerize to the corresponding isocyanides under UV irradiation and how this process is correlated to the nature of a substituent (and particularly to the presence of an unsaturated substituent in the α position), because such studies are very scarce.

However, the recent detection of allenylnitrile (H₂C═C═CHCN) in the ISM,[12] an α,β and β,γ-unsaturated compound, motivated the present synthetic work and first MW study of the corresponding isomer allenylisocyanide (H₂C═C═CHNC).

There is only one reported preparation of the title compound, and this involves a quite difficult synthesis of the propargyl derivative HC≡CCH₂NC, followed by a basic rearrangement of this compound to allenylisocyanide.[13] The spectroscopic characterization of allenylisocyanide is limited to the ¹H and ¹³C NMR spectrum and the most significant IR data.[14] We report here an improved synthesis of the title compound.

Scheme 1
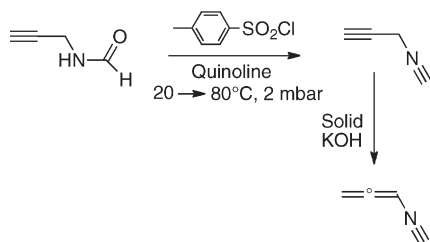
The experimental work has been augmented by high-level quantum chemical calculations, which were undertaken with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

■ EXPERIMENTAL SECTION

Synthesis of Allenylisocyanide. The experimental procedure of Zwikker and Stephany[13] has been modified to give a reproducible preparation of this compound (Scheme 1).

In a 100 mL one-necked, round-bottom flask equipped with a stirring bar were introduced propargylformamide (2.05 g, 25 mmol), *p*-toluensulfonylchloride (6.67 g, 35 mmol), and quinoline (6.46 g, 50 mmol). The flask was attached to a vacuum line equipped with three traps with stopcocks. The first and second trap each contained 2 g of KOH powder. The first trap was immersed in a liquid nitrogen bath and the apparatus was then evacuated to 2 mbar. The mixture was slowly heated to 80 °C for about 1 h. Propargylisocyanide was evacuated from the reaction mixture as it was formed, and condensed. At the end of the reaction, this first trap was isolated with stopcocks from the vacuum line and allowed to warm to room temperature for about 2 min. The mixture turned black quite rapidly. The low boiling compounds were then revaporized in vacuo and condensed in the second trap cooled at −80 °C. The stopcocks of this trap were closed, and the heterogeneous mixture was allowed to warm to room temperature and maintained at this temperature for 2 min. The mixture again turned black quite rapidly. The revaporization and condensation in the third trap cooled at −80 °C gave the expected product in a 35% yield. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.42 (dt, 2H, $^4J_{HH}$ = 6.6 Hz, $^4J_{NH}$ = 1.8 Hz (quadrupolar coupling), CH$_2$), 5.93 (t, 1H, $^4J_{HH}$ = 6.6 Hz, CH); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 85.7 ($^1J_{CH}$ = 171.6 Hz (t), CH$_2$), 86.1 ($^1J_{CH}$ = 198.1 Hz (t), $^1J_{CN}$ = 14.5 Hz (t, quadrupolar coupling), CH), 166.2 ($^1J_{NC}$ = 5.5 Hz (t, quadrupolar coupling), NC), 210.4 (s, C=$\underline{C}$=C).

Microwave Experiment. The spectrum of allenylisocyanide was studied in the 8−120 GHz frequency interval by Stark-modulation spectroscopy using the microwave spectrometer of the University of Oslo. Details of the construction and operation of this device have been given elsewhere.[15−17] This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of ≈0.10 MHz. Radio-frequency microwave double-resonance experiments (RFMWDR), similar to those performed by Wodarczyk and Wilson,[18] were also conducted to unambiguously assign particular transitions, using the equipment described elsewhere.[15] The spectra were measured at about −30 °C, or at room temperature at a pressure of roughly 10 Pa.
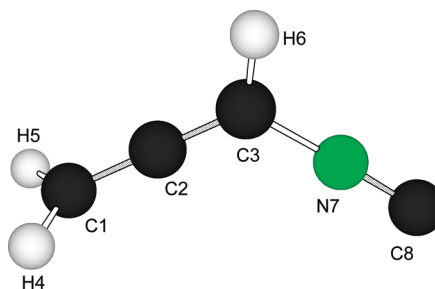

Figure 1. Model of allenylisocyanide with atom numbering.

Table 1. Theoretical Structures and Dipole Moments of H₂C=C=CHNC

	method	
	CCSD/cc-pVTZ[a]	B3LYP/cc-pVTZ[b]
	bond length (pm)	
C1−C2	130.4	129.5
C2−C3	131.1	130.8
C3−N7	138.9	138.0
N7−C8	117.2	116.9
C1−H4,5	108.2	108.4
C3−H6	107.9	108.3
	angle (deg)	
C1−C2−C3	178.5[c]	178.4[c]
C2−C3−N7	122.5	123.3
C3−N7−C8	177.4[c]	176.8[c]
C2−C3−H6	122.0	121.4
H4,5−C1−C2	120.9	121.3
	dipole moment (10^{-30} C m)	
μ_a	11.47	12.50
μ_b	4.61	4.91
μ_{tot}	12.37	13.43

[a] CCSD electronic energy: −547 266.02 kJ/mol. [b] B3LYP electronic energy: −548 564.72 kJ/mol. [c] Bent toward H6.

Quantum Chemical Methods. The present ab initio calculations were performed employing the Gaussian 03 suite of programs,[19] running on the Titan cluster in Oslo. Becke's three-parameter hybrid functional[20] employing the Lee, Yang, and Parr correlation functional (B3LYP)[21] was employed in the density functional theory (DFT) calculations. Coupled-cluster calculations with singlet and doublet excitations (CCSD)[22,23] were also performed. The CCSD calculations are very costly and were speeded up by making use of a B3LYP force field that was calculated prior to the CCSD calculations. Peterson and Dunning's[24] correlation-consistent cc-pVTZ basis set, which is of triple-ζ quality, was used in the calculations.

Quantum Chemical Calculations. CCSD/cc-pVTZ calculations of the optimized structure without symmetry restrictions, dipole moment, and electronic energies were first performed for allenylisocyanide employing the default convergence criteria of Gaussian 03. The calculations predicted that this molecule has a symmetry plane with two out-of-plane hydrogen atoms, as expected. A model of the allenylisocyanide with atom numbering

Table 2. Spectroscopic Constants[a,b,c] **of H₂C=C=CHNC**

	experimental		theoretical
vib state	ground	$\nu_{18} = 1$	ground
A (MHz)	28069.7626(61)	28369.270(16)	28030.6
B (MHz)	2813.63039(49)	2826.08291(90)	2807.3
C (MHz)	2599.00326(52)	2604.70603(87)	2597.4
Δ^d (10^{-20} u m²)	−3.17143(2)	−2.61563(3)	−3.48
D_J (kHz)	1.25301(41)	1.25730(98)	1.10
D_{JK} (kHz)	−94.8248(68)	−93.427(13)	−88.3
D_K (kHz)	2531.29(27)	2578.6(20)	2521
d_1 (kHz)	−0.314288(93)	−0.32201(18)	−0.266
d_2 (kHz)	−0.009573(44)	−0.013831(72)	−0.00656
H_J (Hz)	0.005861(96)	0.005861[e]	0.00373
H_{JK} (Hz)	−0.2099(37)	−0.245(14)	−0.338
H_K (Hz)	−13.873(19)	−13.027(32)	−13.4
H_{KJ} (Hz)	593.0(28)	842(59)	290
h_1 (Hz)	0.001718(39)	0.001718[e]	0.00141
h_2 (Hz)	0.000253(32)	0.000253[e]	0.000381
h_3 (Hz)	0.0000299(57)	0.0000299[e]	0.000208
rms[f]	1.281	1.570	
no. trans[g]	658	458	

[a] The experimental constants are Watson's S-reduction, I^r representation.[27] The theoretical rotational constants are calculated from the CCSD structure, whereas the theoretical centrifugal distortion constants were obtained in the B3LYP calculations. The B3LYP rotational constants were A = 29154.2 MHz, B = 2804.6 MHz, and C = 2604.0 MHz. [b] Uncertainties represent one standard deviation. [c] Spectra in Tables 3S (ground state) and 4S (Supporting Information) (ν_{18}, lowest in-plane bending vibration). [d] Defined by $\Delta = I_c - I_a - I_b$, where I_a, I_b, and I_c are the principal moments of inertia. Conversion factor: 505379.05 × 10^{-20} MHz u m². [e] Fixed in the least-squares fit. [f] Root-mean-square of a weighted fit. [g] Number of transitions used in the fit.

is shown in Figure 1. The CCSD structure and dipole moment are listed in Table 1. The dipole moment components have been transferred from the standard orientation system of Gaussian 03 to the principal inertial axis system using Bailey's program.[25] The rotational constants calculated from this structure are shown in Table 2 together with experimental results. The CCSD electronic field gradients were also computed, and Bailey's program[25] was used to calculate the principal-axes nuclear quadrupole coupling constants of the nitrogen nucleus from them as χ_{aa} = 0.030 MHz, χ_{bb} = −0.175 MHz, and χ_{ab} = −0.307 MHz.

The calculations of the structure, dipole moment, vibrational frequencies, quartic and sextic Watson S-reduction centrifugal distortion constants, and vibration−rotation constants (the α's) were calculated at the B3LYP/cc-pVTZ level, which is much less costly than CCSD/cc-pVTZ calculations of the same parameters. The B3LYP structure and dipole moment is listed in Table 1 together with the corresponding CCSD parameters. The centrifugal distortion constants are listed in Table 2, and the B3LYP rotational constants calculated from the structure in Table 1 are given in the footnote of Table 2. The vibrational fundamental frequencies and the vibration−rotation constants are shown in Table 1S in the Supporting Information.

It is noted that the B3LYP bond lengths are generally shorter by roughly 1 pm than the corresponding CCSD bond lengths, whereas the angles agree to within better than 1° (Table 1). The

C1=C2=C3 and the C3N7≡C8 groups are bent away from one another toward H6 by roughly 1.5° in both calculation methods.

The present isocyanide, H₂C=C=CHNC, might have a relevance to its interstellar cyanide isomer, H₂C=C=CHCN, as remarked above. A comparison of the electronic energies of these two molecules is, therefore, of interest, and CCSD/cc-pVTZ calculations were performed for H₂C=C=CHCN as well. The optimized structure of the cyanide is listed in Table 2S in the Supporting Information. The electronic energy difference was found to be 105.8 kJ/mol favoring H₂C=C=CHCN. This value is similar to previous calculations of this isomerization energy of some other systems (see above).[5]

Microwave Spectrum and Assignment. The CCSD calculations (Table 2) predict that H₂C=C=CHNC has a large dipole moment with its major component of about 11.5 × 10^{-30} C m along the a-inertial axis. Allenylisocyanide is a near-prolate asymmetric rotor with the Ray's asymmetry parameter[26] of $\kappa \approx -0.98$. The strongest transitions of this spectrum will, therefore, be the a-type R-branch transitions. The rotational and quartic centrifugal distortion constants in Table 2 were used to predict the approximate frequencies of these transitions, which were found to be close to the predictions. Their assignments were confirmed by their Stark effects, RFMWDR patterns, and fit to Watson's S-reduced Hamiltonian.[27]

The preliminary spectroscopic constants obtained from the ^aR-transitions were used to predict the frequencies of the less intense b-type lines, which were readily assigned. The perpendicular b-type transitions have generally much larger quadrupole splittings than the parallel a-type transitions. However, no b-type lines were seen to be split by more than 0.5 MHz, which is the resolution of this spectrometer. The negligible quadrupole splittings are presumably the result of comparatively small quadrupole coupling constants of the nitrogen nucleus, which is in accord with the results of the CCSD calculations above (χ_{aa} = 0.030 MHz, χ_{bb} = −0.175 MHz, and χ_{ab} = −0.307 MHz).

The assignments of the spectral transitions were gradually extended to higher and higher values of the principal quantum number J and the pseudo quantum number K_{-1}. Ultimately, 658 transitions with a maximum J = 71 were assigned and included in a weighted least-squares fit of Watson's S-reduction Hamiltonian, including rotational, quartic, and sextic centrifugal distortion constants employing Sørensen's program Rotfit.[28] The spectrum is shown in Table 3S in the Supporting Information, and the spectroscopic constants are reported in Table 2. It should be possible to predict accurately the frequencies of ground-state transitions not listed in Table 3S (Supporting Information) using the spectroscopic constants in Table 2.

Comparison of the experimental and theoretical spectroscopic constants is in order. The ground-state experimental rotational constants A, B, and C (Table 2) are larger by 39.5, 6.3, and 1.6 MHz, respectively, than their CCSD counterparts. This is less than 0.3% in each case. The B3LYP quartic centrifugal distortion constants agree to within roughly 10%, with the exception of d_2, where a 3 times larger deviation is seen (Table 2). The sextic centrifugal distortion constants display an order-of-magnitude agreement.

Vibrationally Excited States. Allenylisocyanide has four fundamental vibrations with harmonic frequencies below 600 cm^{-1} according to the B3LYP calculations (Supporting Information, Table 1S). Two of these are in-plane bending vibrations, ν_{18} and ν_{16}, with harmonic frequencies of 140 and 303 cm^{-1}, respectively, whereas the fundamental with a frequency of 270 cm^{-1} (ν_{17}) can

Table 3. Spectroscopic Constants[a,b,c,d] of Vibrationally Excited States of H_2C=C=CHNC

	vibrational state			
	$\nu_{18} = 2$	$\nu_{18} = 3$	$\nu_{17} = 1$	$\nu_{16} = 1$
A (MHz)	28797.46(7)	29526(10)	27633.86(12)	30033.56(17)
B (MHz)	2738.3491(22)	2850.3931(76)	2805.1962(28)	2817.2119(33)
C (MHz)	2610.3839(24)	2616.0156(70)	2600.1849(23)	2604.6751(29)
Δ^e (10^{-20} u m²)	−2.0000(2)	−1.231(6)	−4.0839(1)	−2.1893(1)
D_J (kHz)	1.2542(40)	1.2513(96)	1.2544(32)	1.1757(35)
D_{JK} (kHz)	−84.420(41)	−93.81(50)	−102.07(18)	−118.32(17)
d_1 (kHz)	−0.3018(15)	−0.3032(82)	−0.29918(93)	−0.3164(12)
rms[f]	1.593	1.238	1.581	1.653
no. trans[g]	121	34	80	78

[a] S-reduction, I^r representation.[27] [b] The quartic centrifugal distortion constants D_K and d_2 of these excited states have been preset at the ground-state values of 2531.29, and −0.009573 kHz, respectively, in the least-squares fit. [c] Uncertainties represent one standard deviation. [d] Spectra are listed in Tables 4S—8S in the Supporting Information. ν_{18}, ν_{17}, and ν_{16} refer to the lowest in-plane bending, the lowest torsional, and the second-lowest in-plane bending vibrations, respectively; see text. [e] Defined by $\Delta = I_c − I_a − I_b$. [f] Root-mean-square deviation for a weighted fit. [g] Number of transitions used in the fit.

perhaps best be described to be a torsional vibration involving the two out-of-plane hydrogen atoms H4 and H5, while the 330 cm^{-1} vibration (ν_{15}) is an out-of-plane vibration. These fundamentals have significant Boltzmann populations at room temperature, and it should, therefore, be possible to assign the MW spectra of excited states of at least some of these modes. The ground-state transitions were, therefore, expected to be accompanied by several weaker lines belonging to the MW spectra of vibrationally excited states and with modulation patterns very similar to those of the ground-state lines. This was also observed, and a total of five vibrationally excited states MW spectra were assigned in the same manner as described for the ground state. Their spectroscopic constants are listed in Tables 2 and 3, whereas the spectra are found in Tables 4S—8S in the Supporting Information.

The strongest spectrum of these excited states has an intensity of roughly 50% of the intensity of the ground-state spectrum. This spectrum presumably belongs to the first excited state of the lowest in-plane bending vibration. This assignment has been made because the absolute value of the pseudo inertial defect, $\Delta = I_c − I_a − I_b$, where I_a, I_b, and I_c are the principal moments of inertia, decreases (Table 2) from the ground state value, which is typical for an in-plane vibration.[29] Relative intensity measurements performed largely as described by Esbitt and Wilson yielded 122(25) cm^{-1} for this fundamental, in good agreement with the B3LYP value (141 cm^{-1}).

Two further excited states of this vibration were assigned. The spectroscopic constants are listed in Table 3. It is seen that the rotational constants vary in a rather regular fashion, which is typical for an essentially harmonic vibration.

The spectrum of the first excited state of the torsional vibration (ν_{17}) having an intensity of about 25% of the intensity of the ground-state spectrum, was also assigned. The spectroscopic constants of this state are shown in Table 3. It is seen that the absolute value of Δ increases compared to Δ of the ground vibrational state, which is typical for an out-of-plane vibration.[29] Relative intensity measurements yielded 256(30) cm^{-1} for this mode, which compares well with the calculations (270 cm^{-1}).

Finally, a spectrum about one-fifth as strong as the spectrum of the ground state was identified. This spectrum is assumed to belong to the first excited state of the second-lowest in-plane fundamental. The spectroscopic constants derived for this spectrum

Table 4. Experimental and B3LYP/ccpVTZ Vibration—Rotation Constants

	vib state[a]					
	$\nu_{18} = 1$		$\nu_{17} = 1$		$\nu_{16} = 1$	
	exptl	theoret	exptl	theoret	exptl	theoret
α_A (MHz)	−299.51	−307.9	435.90	164.9	−1963.80	1603.0
α_B (MHz)	−12.45	−11.8	8.43	8.0	−3.58	−12.5
α_C (MHz)	−5.71	−5.5	1.18	−0.2	−5.68	−4.9

[a] See text for definition.

are shown in Table 4. The relative-intensity frequency of this vibration is ca. 315 cm^{-1}, compared to the B3LYP value of 303 cm^{-1}.

Searches were also made in an attempt to assign the spectrum of the out-of-plane bending vibration calculated to have a frequency of 330 cm^{-1}, but this spectrum was not identified.

The vibration—rotation constants calculated from $\alpha_X = X_0 − X_1$, where X is a rotational constant (A, B, or C), X_0 is the rotational constant of the ground-vibrational state (Table 2), and X_1 is the rotational constant of the first excited state of a fundamental vibration, are listed in Table 4 for the three lowest vibrational modes. The same table contains the corresponding B3LYP parameters. It is seen from this table that the agreement between the observed and calculated α's are in fair agreement for the lowest bending vibration (ν_{18}), while much larger discrepancies are seen for the two other vibrations (ν_{17} and ν_{16}). This is to be expected because the α's depend critically on the third derivative of the energy with respect to the structure.

Spectra of Isotopologues. The spectra of isotopologues are useful for the determination of molecular structure and would be of interest in the case of an interstellar detection of the title compound. Efforts to assign the spectra of the four ^{13}C and one ^{15}N isotopologues in natural abundance (1.1 and 0.4%, respectively) were, therefore, undertaken.

The structure in Table 1 was used to predict the changes of the rotational constants caused by isotopic substitution. These changes were added to the experimental rotational constants (Table 2) and used to predict the spectra of the isotopologues. The MW

7981

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Table 5. Spectroscopic Constants[a,b,c,d] of the Ground Vibrational State of Isotopologues of $H_2C\!=\!C\!=\!CHNC$

	species				
	$H_2{}^{13}C\!=\!C\!=\!CHNC$	$H_2C\!=\!{}^{13}C\!=\!CHNC$	$H_2C\!=\!C\!=\!{}^{13}CHNC$	$H_2C\!=\!C\!=\!CH^{15}NC$	$H_2C\!=\!C\!=\!CHN^{13}C$
A (MHz)	27819(9)	28184(10)	27283(10)	28260(30)[e]	27649(15)
B (MHz)	2735.4177(89)	2794.3144(95)	2813.7922(76)	2788.58(13)	2734.380(16)
C (MHz)	2529.9202(89)	2583.6348(91)	2591.9297(58)	2579.20(13)	2527.786(17)
Δ^e (10^{-20} u m^2)	−3.160(6)	−3.183(7)	−3.150(7)	−3.17(2)	−3.17(1)
D_J (kHz)	1.2024(26)	1.1923(23)	1.278(25)	1.1890(54)	1.2020(29)
D_{JK} (kHz)	−91.329(38)	−92.207(43)	−96.2(18)	−91.813(70)	−91.989(44)
rms[f]	1.426	1.344	1.112	1.700	1.641
no. trans[g]	99	112	19	70	90

[a] S-reduction, I^r representation.[27] [b] The quartic centrifugal distortion constants D_K, d_1, and d_2 of these isotopologues have been preset at the ground-state values of 2531.29, −0.314288, and −0.009573 kHz, respectively, in the least-squares fit. [c] Uncertainties represent one standard deviation. [d] Spectra are listed in Tables 9S−13S in the Supporting Information. [e] Defined by $\Delta = I_c - I_a - I_b$. [f] Root-mean-square deviation for a weighted fit. [g] Number of transitions used in the fit.

Table 6. Substitution Coordinates

	$|a|$/pm	$|b|$/pm
C1	228.00(4)	41.9(2)
C2	111.85(7)	im[a]
C3	2.4(33)	73.3(1)
N7	128.25(9)	im[a]
N8	229.32(4)	53.4(1)

[a] This coordinate is small, and an imaginary value is obtained using the Kraitchman equations[31] due to zero-point vibrations.

cell was cooled to −30 °C in order to enhance the intensities of the spectra of these minority species. The ^aR-type spectra of the isotopologues (Tables 9S−13S, Supporting Information) were found to be very close to the predictions. The assignments of several of these transitions were confirmed by MWRFDR experiments. No b-type lines were identified.

No definite assignments were obtained for the a-type low-K_{-1} transitions of the ^{15}N isotopologue. A relatively accurate value of the A rotational constant could, consequently, not be obtained experimentally. However, the existence of a symmetry plane in the molecule and two out-of-plane hydrogen atoms indicates that the pseudo inertial defect should be approximately -3.17×10^{-20} u m^2 obtained for the other species (Tables 2 and 5), and this was used to derive a value of 28260(30) MHz for the A rotational constant (Table 5) in a trial-and-error procedure.

Structure. The rotational constants of the parent and substituted species in Tables 2 and 5 allow the Costain substitution coordinates (r_s coordinates)[30] to be calculated employing Kraitchman's equations.[31] The result is displayed in Table 6. The uncertainties listed in this table have been calculated as recommended by van Eijck.[32] It is seen from this table that the $|b|$ coordinates of C2 and N7 obtained in this manner are found to have a small and imaginary value. This is caused by an unfortunate combination of a small coordinate and zero-point vibrations. Moreover, the $|a|$ coordinate of C3 is as small as 2.4 pm. Not surprisingly, an attempt to calculate an accurate substitution structure for the heavy atoms using the coordinates in Table 6 resulted in unrealistic bond lengths with large uncertainties, which is assumed to be due to the presence of these three small coordinates.

Table 7. Second-Order Stark Coefficients[a] and Dipole Moment of $H_2C\!=\!C\!=\!CHNC$

		$\Delta\nu$ E^{-2}/10^{-6} MHz V^{-2} cm^2	
transition		obs	calcd
$4_{1,4} \leftarrow 3_{1,3}$	$M = |1|$	−17.6(4)	−17.58
$5_{1,4} \leftarrow 4_{1,3}$	$M = |1|$	−3.92(10)	−4.22
$5_{1,4} \leftarrow 4_{1,3}$	$M = |2|$	−11.4(3)	−10.87
$5_{1,5} \leftarrow 4_{1,4}$	$M = |1|$	11.5(3)	11.88
$5_{1,5} \leftarrow 4_{1,4}$	$M = |2|$	21.0(5)	20.23
$6_{1,5} \leftarrow 5_{1,4}$	$M = |1|$	−1.70(4)	−1.82
$6_{1,6} \leftarrow 5_{1,5}$	$M = 0$	0.72(2)	0.0751
$6_{1,6} \leftarrow 5_{1,5}$	$M = |1|$	1.76(4)	1.65
$6_{1,6} \leftarrow 5_{1,5}$	$M = |2|$	4.52(8)	4.32

dipole moment (10^{-30} C m)

μ_a = 11.93(16) μ_b = 4.393(44) μ_c = 0.0[b] μ_{tot} = 12.71(16)[c]

[a] Uncertainties represent one standard deviation. [b] By symmetry; see text. [c] In debye units: 3.811(47) D. Conversion factor: 1D = 3.33564×10^{-30} C m.

Sometimes an accurate r_0 structure can be obtained even in cases where the calculation of an accurate r_s structure is impossible. Attempts to calculate an r_0 structure using Kisiel's program Strfit[33] were performed with results that were similar to those described above for the attempts to derive an accurate substitution structure. It is concluded that the present experimental data are insufficient to obtain an accurate structure of this compound. However, the good agreement between the CCSD and the experimental rotational constants of the ground state (Table 2) alluded to above is a strong indication that the CCSD structure is indeed accurate and close to the equilibrium structure.

Dipole Moment. The second-order Stark coefficients shown in Table 7 were used to determine the dipole moment of allenylisocyanide. The cell was calibrated using OCS, whose dipole moment was taken to be $2.38568(66) \times 10^{-30}$ C m.[34] The theoretical second-order Stark coefficients were calculated using the Golden and Wilson formalism,[35] which is implemented in the program MB04.[36] The result of the least-squares fit is shown in Table 7. The experimental dipole moment components, $\mu_a = 11.93(16) \times 10^{-30}$ C m, $\mu_b = 4.393(44) \times 10^{-30}$ C m,

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and $\mu_{tot} = 12.71(16) \times 10^{-30}$ C m, are in good agreement with the CCSD results (11.47×10^{-30}, 4.61×10^{-30}, and 12.34×10^{-30} C m; Table 1).

CONCLUSIONS

The microwave spectra of the ground and five vibrationally excited states of the parent species and of five heavy-atom (^{13}C and ^{15}N) isotopologues have been investigated and assigned for allenylisocyanide. Calculations of the structure and the dipole moment have been performed at the CCSD/cc-pVTZ level of theory, whereas a range of molecular parameters have been calculated for this compound at the B3LYP/cc-pVTZ level of theory.

A total of 658 transitions were used to determine the spectroscopic constants of the ground vibrational state of the parent molecule, and accurate rotational and quartic centrifugal distortion constants have been obtained. The experimental rotational constants are in excellent agreement with the CCSD counterparts. Good agreement was obtained for the quartic centrifugal distortion constants and the B3LYP counterparts. The experimental sextic centrifugal distortion constants are in order-of-magnitude agreement with the B3LYP predictions. CCSD calculations provide dipole moments that are in good agreement with experiments.

Attempts to calculate accurate r_s and r_0 structures of the heavy-atom skeleton failed presumably because of three very small principal-axis coordinates. CCSD/cc-pVTZ calculations of the cyanide isomer indicate that allenylisocyanide is about 105 kJ/mol less stable than its cyanide isomer $H_2C=C=CHCN$.

ASSOCIATED CONTENT

S **Supporting Information.** Results of the theoretical calculations and the microwave spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Tel: +47 2285 5674. Fax: +47 2285 5441. E-mail: harald.mollendal@kjemi.uio.no (H.M.), jean-claude.guillemin@ensc-rennes.fr (J.-C.G.).

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