*J. Phys. Chem. A* **2007,** *111,* 1259−1264

# Synthesis and Characterization of (*E*)- and (*Z*)-3-Mercapto-2-propenenitrile. Microwave Spectrum of the *Z*-Isomer

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*Received: November 3, 2006; In Final Form: December 18, 2006*

The kinetically unstable compound 3-mercapto-2-propenenitrile (HS−CH═CH−C≡N) has been prepared for the first time by flash vacuum pyrolysis at 800 °C of 3-(*tert*-butylthio)-2-propenenitrile with a yield of 77% and a *Z*:*E* ratio of 8:1. Several deuterium and $^{15}N$ isotopologues were also prepared using isotopically enriched compounds. Quantum chemical calculations of the structural and conformational properties of the *Z*- and *E*-isomers were undertaken at the B3LYP/6-311++G(3df,2pd), MP2/6-311++G(3df,2pd), MP2/aug-cc-pVTZ, and G3 levels of theory. These methods all predict that the *Z*- and the *E*-forms each have two "stable" planar rotameric forms with the H−S−C═C link of atoms in either a synperiplanar or an antiperiplanar conformation, with the synperiplanar form of the *Z*-isomer as the global minimum. The *Z*-isomer has been investigated by means of Stark-modulation microwave spectroscopy. Spectra attributable to the parent and three deuterium-substituted isotopologues of a single conformer were recorded and assigned. Additionally, the spectrum belonging to the first excited state of the lowest bending vibration was assigned. The ground-state rotational constants obtained by the least-squares analysis of these transitions were found to be in excellent agreement with the corresponding approximate equilibrium values generated by the MP2/aug-cc-pVTZ calculations. The preferred conformer of this molecule was found to have a synperiplanar arrangement of the H−S−C═C chain of atoms and a planar or nearly planar geometry, with a stabilizing intramolecular hydrogen bond formed between the H atom of the thiol group and $\pi$-electron density associated with the C≡N triple bond. The possible astrochemical/astrobiological significance of this compound is discussed.

## Introduction

It has been suggested that the adducts of amines, alcohols, and thiols to cyanoacetylene (H−C≡C−C≡N) could have played a determining role as precursors of life in prebiotic chemistry and could be components of the interstellar medium or of planetary atmospheres.[1−3] Recently, the physical properties of the ammonia ($NH_3$) adducts to cyanoacetylene, (*E*)- and (*Z*)-3-amino-2-propenenitrile ($H_2NCH{=}CHC{\equiv}N$), have been investigated in our laboratories.[4,5] In our experiment, the *Z*- and *E*-isomers were obtained in a 95:5 ratio, the *Z*-isomer being more stable than the *E*-isomer. The infrared spectra of the *E*- and *Z*-isomers were assigned,[5] whereas the microwave (MW) spectrum of only the *Z*-form was identified.[4] The spectroscopic works were augmented by quantum chemical calculations.[4,5]

The subject of this study, 3-mercapto-2-propenenitrile (HS−CH═CH−C≡N, henceforth called MPN) is formally an adduct of dihydrogen sulfide ($H_2S$) to cyanoacetylene. The fact that several compounds containing sulfur have already been identified in interstellar space and in comets[6] makes the extraterrestrial existence of MPN a possibility that we thought deserved further investigation.

There have been attempts to synthesize and characterize MPN. Hartke and Günther[7] reported that they were able to obtain MPN in solution, but the compound decomposed readily and could not be isolated or characterized. The major aim of this work has therefore been to develop an effective preparation procedure for this kinetically unstable compound and to study its physical properties by means of mass spectrometry, NMR, infrared (IR), and microwave (MW) spectroscopies and high-level quantum chemical calculations. Much of this work is focused on the MW study because this method is useful for identifying molecules in interstellar space, in comets, and in the atmosphere of planets.[6] In addition, accurate structural information is obtained by the use of this method. Advanced quantum chemical calculations have now become a reliable and useful method for the investigation of properties of relatively small molecules, such as MPN. Such calculations were undertaken to augment the experimental work.

3-Mercapto-2-propenenitrile exists in the *Z*- and *E*-configurations, henceforth abbreviated Z-MPN and E-MPN, respectively. Rotation about the S−C bond allows rotational isomerism to exist for each of these forms. Typical examples of rotational isomerism are shown in Figure 1, where the four rotameric forms found as minima on the energy hypersurface in the quantum chemical calculations are depicted. The interesting structural and conformational properties and energy differences between the various forms of MPN are another focal point of this investigation.

## Experimental Section

Caution: Low molecular weight thiols are often powerfully malodorous. All reactions and handling should be carried out in a well-ventilated hood.

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10.1021/jp0672508 CCC: $37.00

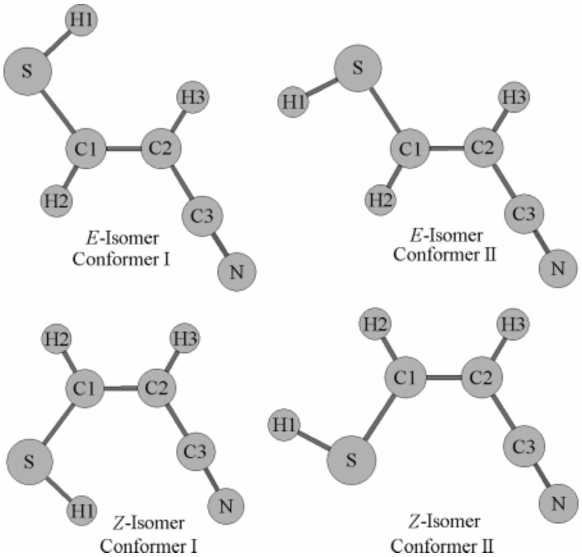
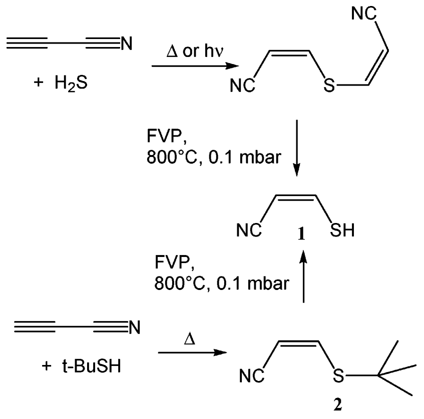


**Figure 1.** Models of two conformers of (*E*)-3-mercapto-2-propenenitrile and two conformers of (*Z*)-3-mercapto-2-propenenitrile. The H1−S−C1−C2 chain of atoms is synperiplanar in the conformers denoted I and antiperiplanar in the conformers denoted II.

**SCHEME 1**



**Synthesis of 3-Mercapto-2-propenenitrile and Its Isotopologues**. The thermal or photochemical reaction of $H_2S$ with cyanoacetylene led only to a bisadduct, the 3,3′-thiodi-2-propenenitrile,[8] (mainly the *Z*,*Z*-stereoisomer, >90%). We found that MPN can be prepared by flash vacuum pyrolysis (FVP) at 800 °C of 3-(*tert*-butylthio)-2-propenenitrile[9] (yield 77%) (Scheme 1). Pyrolysis of 3,3′-thiodi-2-propenenitrile also led to 3-mercapto-2-propenenitrile, but in a low yield (13%), in the presence of acrylonitrile and some other products. In both approaches, 3-mercapto-2-propenenitrile was obtained in an 8:1 (*Z*:*E*) ratio. The high kinetic stability observed for 3-amino-2-propenenitrile ($H_2NCH{=}CHCN$) by comparison with ethenylamine ($H_2C{=}CHNH_2$)[5] was not observed for the sulfur derivatives; the half-life of 3-mercapto-2-propenenitrile diluted in a solvent was about 1 day at room temperature, which is comparable with the half-life of ethenethiol.[10]

**Preparation of 3-Mercapto-2-propenenitrile (1)**. 3-(*tert*-Butylthio)-2-propenenitrile[9,11] (423 mg, 3 mmol) was vaporized in a vacuum line ($10^{-1}$ mbar) equipped with a short oven (15 cm) heated to 800 °C. The vacuum line was equipped with two traps. The first trap was held at room temperature and removed the oligomeric products, while thiol **1** was selectively condensed in the second trap, which was cooled to −100 °C. This temperature was chosen to trap 3-mercapto-2-propenenitrile, which is kinetically stable at this temperature, without the condensation of the isobutene byproduct. To record the NMR spectra, the cell was attached to a vacuum line and MPN and an NMR solvent ($CD_3CN$ or $CDCl_3$) were condensed on a cold finger (77 K) equipped at the bottom with an NMR tube. The solution was then transferred to the NMR tube and kept at low temperature (−50 °C) before analysis. MPN was obtained in a 77% yield and in an 8:1 *Z*:*E* ratio, according to the NMR spectrum. Attempts to condense and then vaporize MPN in vacuo led to a significant loss of product. To record the mass spectra of thiol **1**, the cooled cell was connected directly to the ionization chamber of the spectrometer. $^1$H NMR ($CDCl_3$) (*Z*-isomer): $\delta$ 4.17 (d, 1H, $^3J_{HH} = 12.8$ Hz, SH); 5.44 (d, 1H, $^3J_{HH} = 10.4$ Hz, CHCN); 7.06 (dd, 1H, $^3J_{HH} = 12.8$ Hz, $^3J_{HH} = 10.4$ Hz, CHS). $^{13}$C NMR ($CDCl_3$) (*Z*-isomer): $\delta$ 95.3 (d, $^1J_{CH} = 180.7$ Hz, CHCN); 115.3 (CN); 143.2 (d, $^1J_{CH} = 175.9$ Hz, CHS). $^1$H NMR ($CDCl_3$) (*E*-isomer): $\delta$ 3.67 (d, 1H, $^3J_{HH} = 11.3$ Hz, SH); 5.48 (d, 1H, $^3J_{HH} = 15.9$ Hz, CHCN); 7.28 (dd, 1H, $^3J_{HH} = 15.9$ Hz, $^3J_{HH} = 11.3$ Hz, CHS). $^{13}$C NMR ($CDCl_3$) (*E*-isomer): $\delta$ 96.5 (d, $^1J_{CH} = 179.9$ Hz, CHCN); 116.4 (CN); 144.3 (d, $^1J_{CH} = 176.7$ Hz, CHS). IR (film, 77 K): $\nu$ (cm$^{-1}$) 3063 ($\nu_{C=C-H}$), 2546 ($\nu_{S-H}$), 2214 ($\nu_{CN}$), 1633 ($\nu_{C=C}$). HRMS: calcd for $C_3H_3NS$, 84.99862; found, 84.9993. The half-life of compound **1** (5% diluted in $CDCl_3$) is on the order of about 1 day at room temperature in the presence of small amounts of duroquinone, a radical inhibitor.

**2- and 3-Deuterio-3-mercapto-2-propenenitrile (1a,b)**. A mixture of compounds **1a** and **1b** was obtained by thermolysis of a mixture of 2- and 3-deuterio-3-(*tert*-butylthio)-2-propenenitrile (**2a**,**b**), previously prepared by addition of 2-methyl-2-propanethiol-*d* to cyanoacetylene (or of 2-methyl-2-propanethiol to deuteriocyanoacetylene).[4,11] Similarly, FVP of 3-(*tert*-butylthio)-2-propenenitrile-$^{15}N$ (**2c**) (10% isotopic purity) gave 3-mercapto-2-propenenitrile-$^{15}N$ (**1c**). $^{13}$C NMR ($CDCl_3$): $\delta$ 115.2 ($^1J_{CN} = 18.2$ Hz, CN). $^{15}$N NMR ($CDCl_3$, 30.4 MHz): $\delta$ −109.9.

Further experimental data for compounds **1a**,**b** and **2a**−**c** are found in the Supporting Information.

**3-(Mercapto-*d*)-2-propenenitrile (1d) (DSCH═CHCN)**. The cell was first conditioned with heavy water. Fumes of MPN were then introduced. The spectra observed for DSCH═CHCN were observed to have roughly 50% of the intensity of those of the pure parent species.

**Microwave Experiment**. The spectrum of Z-MPN was recorded in the 50.0−80.0 GHz frequency region with the microwave spectrometer at the University of Oslo. Details of the construction and operation of this device, which has a 2 m Hewlett-Packard Stark cell, have been given elsewhere.[12,13] Although it is usual to cool the Stark cell while recording the spectra to increase spectral intensity, this was not possible during the present investigation, because of the low volatility of Z-MPN.

The quantum chemical calculations performed below at the MP2/aug-cc-pVTZ level predict that Z-MPN should have a dipole moment component along the *a* principal inertial axis of about $8.7 \times 10^{-30}$ C m (2.7 D). This should result in a comparatively strong MW spectrum. However, it turned out that it was problematic to obtain its Stark spectrum for several reasons. The samples used in our experiments were synthesized in Rennes and were transported to Oslo dissolved in dichloromethane. Purification was performed by distillation in vacuo and selective trapping of MPN at −78 °C. Unfortunately, it was not possible to remove the last remains of dichloromethane completely this way. This was essential because dichloromethane has a strong and rich MW spectrum. Pumping on the sample by simply using a diffusion pump was not sufficient. It was necessary to heat the sample vigorously with a heat gun while evacuating with a diffusion pump to remove the last dichloromethane completely. Much of the sample was destroyed or lost during this process.

The measured vapor pressure of Z-MPN at room temperature was roughly on the order of 10−25 Pa. The observed spectrum was much weaker than expected for a molecule with a dipole moment of roughly $9 \times 10^{-30}$ C m. It was therefore assumed that a major part of the vapor belongs to gaseous impurities. Several of these lines were checked against libraries of compounds whose MW spectra have been assigned, but no identifications of these impurity lines could be made. It was also observed that the intensity of the spectrum diminished rather rapidly with time in the Stark experiment. It is assumed that this is due to the kinetic instability of the compound. The cell therefore had to be refilled frequently with fresh sample.

## Quantum Chemical Calculations and Microwave Study

**Quantum Chemical Calculations**. The use of quantum chemical calculations provides two principal benefits to the study of a molecule by MW spectroscopy. First, the calculation of rotational constants and centrifugal distortion constants for the possible conformers of the molecule, along with the relative energies of these conformers, is of great assistance in assigning rotational spectra. Second, the quantum chemical calculations may provide additional information about the properties of the molecule that may not be readily available by experimental methods, such as predictions of the approximate equilibrium geometries of the conformers.

In the current investigation, ab initio geometry optimizations were performed for Z- and E-MPN using the Gaussian 03 electronic structure package[14] in conjunction with the University of Oslo's 64-processor HP "superdome" computer.[15] Second-order Møller−Plesset perturbation theory (MP2)[16] was used to incorporate the effects of electron correlation. These optimizations were undertaken using both the 6-311++G(3df,2pd) basis set[17,18] and Dunning's extensive aug-cc-pVTZ basis set,[19] which includes polarized functions for valence electrons and is augmented by extra diffuse functions. In addition, density functional theory (DFT) geometry optimizations were performed by use of the B3LYP hybrid functional (Becke's three-parameter hybrid functional,[20] employing the Lee, Yang, and Parr correlational functional[21]) in conjunction with the 6-311++G(3df,2pd) basis set.

Structure refinements were performed for the *Z*- and the *E*-isomers. No symmetry restrictions were imposed on the starting geometries, which were fully optimized. The MP2/6-311++G(3df,2pd), MP2/aug-cc-pVTZ, and B3LYP/6-311++G(3df,2pd) calculations all predict the same two minima on the potential energy hypersurface of each of the *Z*- and *E*-isomers. These minima all have a symmetry plane ($C_s$ symmetry). They are depicted in Figure 1, where it is seen that the H1−S−C1−C2 dihedral angle is either synperiplanar or antiperiplanar in these forms. The MP2/aug-cc-pVTZ structures and rotational constants of these four isomers are given in the Supporting Information, Table 6S. The MP2/aug-cc-pVTZ and B3LYP rotational constants of *Z*-isomer conformer I (assigned in this work) from these optimizations are presented in Table 1.

Calculations of the vibrational frequencies were performed by use of the B3LYP procedure. Positive values were predicted for all the normal vibrational frequencies of the four forms shown in Figure 1, as expected for minima of the potential energy hypersurface. The force field obtained in this connection was employed to calculate Watson's *A*-reduction quartic centrifugal distortion constants,[22] which are listed in the same table.

**TABLE 1: Spectroscopic Constants Obtained for the Lowest Energy Conformer of (*Z*)-3-Mercapto-2-propenenitrile from Quantum Chemical Calculations and Experiment**

| spectroscopic constant | B3LYP/ 6-311++G(3df,2pd) | MP2/ aug-cc-pVTZ | experiment |
|---|---|---|---|
| $A$/MHz | 9267.1 | 8751.1 | 8878.579(20) |
| $B$/MHz | 2535.4 | 2679.4 | 2640.8911(24) |
| $C$/MHz | 1990.9 | 2051.3 | 2033.2968(24) |
| $\Delta_J$/kHz | 1.98 | | 2.139(5) |
| $\Delta_{JK}$/kHz | −16.4 | | −15.462(12) |
| $\Delta_K$/kHz | 49.2 | | 41.2(3) |
| $\delta_J$/kHz | 0.610 | | 0.6851(10) |
| $\delta_K$/kHz | 3.17 | | 3.24(4) |

**TABLE 2: A Comparison of the Relative Energies[a] of the Stable Conformers of (*Z*)- and (*E*)-3-Mercapto-2-Propenenitrile Obtained from Quantum Chemical Calculations**

| | *Z*-isomer | | *E*-isomer | |
|---|---|---|---|---|
| method | conformer I | conformer II | conformer I | conformer II |
| B3LYP/6-311++G(3df,2pd) | 0.0 | 6.46 | 6.28 | 5.55 |
| MP2/6-311++G(3df,2pd) | 0.0 | 7.66 | 10.57 | 9.48 |
| MP2/aug-cc-pVTZ | 0.0 | 8.06 | 11.40 | 10.41 |
| G3 | 0.0 | 6.63 | 8.07 | 7.47 |

[a] Energy differences are quoted in kJ mol$^{-1}$.

Relative energy calculations were performed for conformers I and II of both the *Z*- and *E*-isomers. The relative energies were obtained from geometry optimizations at the B3LYP/6-311++G(3df,2pd), MP2/6-311++G(3df,2pd), and MP2/aug-cc-pVTZ levels and from G3 calculations.[23] The results of these calculations are presented in Table 2.

It can be seen from this table that Z-MPN conformer I is the global minimum favored by 5.6−11.4 kJ/mol relative to the other conformers, depending on the computational procedure. This energy difference is quite consistent with the experimental finding above that *Z*- and the *E*-isomers are formed in an 8:1 ratio. It is therefore possible that the formation of MPN is thermodynamically controlled.

An interaction between the hydrogen atom of the thiol group and the nitrile group seems to be possible in the most "stable" form (*Z*-isomer conformer I). This rotamer is predicted to be 6.5−8 kJ/mol more stable (Table 2) than the *Z*-isomer conformer II, in which this interaction is not possible.

Interestingly, the energy difference between conformers I and II of E-MPN is calculated to be much less (roughly 1 kJ/mol). No interaction of this kind is of course possible in the *E*-isomers of MPN. The small energy difference calculated for the last-mentioned conformers is reminiscent of the energy difference found for the corresponding two rotameric forms of a similar molecule, ethenethiol (0.6 kJ/mol).[24−26]

**Assignment of the Microwave Spectrum of Conformer I**. The fact that the quantum chemical calculations indicate that Z-MPN conformer I would be lower in energy made us search first for this rotamer. A prediction of the MW spectrum of this conformer was therefore made using the predicted MP2 rotational and B3LYP centrifugal distortion constants shown in Table 1.

The components of the molecular electric dipole moment along the principal inertial axes, obtained from the B3LYP calculation, were $\mu_a = 8.7 \times 10^{-30}$ C m (2.6 D), $\mu_b = 8.3 \times 10^{-30}$ (2.5 D), and $\mu_c = 0.0 \times 10^{-30}$ C m (for symmetry reasons). The *a*-type, R-branch transitions were sought first,

**TABLE 3: Experimental Spectroscopic Constants for the Parent and Three Deuterium-Substituted Isotopologues of (*Z*)-3-Mercapto-2-propenenitrile**

| spectroscopic constant | HSCH═CHCN | DSCH═CHCN | HSCD═CHCN | HSCH═CDCN | HSCH═CHCN, excited state |
|---|---|---|---|---|---|
| $A$/MHz | 8878.579(20) | 8617.4[a] | 8383.9[a] | 8230.1[a] | 8878.579[b] |
| $B$/MHz | 2640.8911(24) | 2639.533(74) | 2615.666(86) | 2622.79(11) | 2635.23(13) |
| $C$/MHz | 2033.2968(24) | 2018.487(85) | 1991.60(10) | 1986.87(13) | 2031.19(16) |
| $\Delta_J$/kHz | 2.139(5) | 2.092(15) | 2.040(17) | 2.039(20) | 2.058(27) |
| $\Delta_{JK}$/kHz | −15.462(12) | −14.34(4) | −13.87(6) | −13.79(9) | −15.14(10) |
| $\Delta_K$/kHz | 41.2(3) | 41.2[b] | 41.2[b] | 41.2[b] | 41.2[b] |
| $\delta_J$/kHz | 0.6851(10) | 0.6851[b] | 0.6851[b] | 0.6851[b] | 0.6851[b] |
| $\delta_K$/kHz | 3.24(4) | 3.24[b] | 3.24[b] | 3.24[b] | 3.24[b] |
| $\sigma$/kHz | 0.10 | 0.15 | 0.15 | 0.15 | 0.23 |
| $N$[c] | 123 | 54 | 50 | 42 | 52 |

[a] See the text for the method used to evaluate the *A* rotational constants for deuterium-substituted isotopologues. The accuracy of the *A* rotational constant of the deuterated species is estimated to be within ±5 MHz. [b] Constant fixed at the value obtained from the ground-state spectrum of the parent isotopologue.

because of the large dipole moment component along the *a* axis and the characteristic pattern displayed by these transitions. Identifying these transitions was not, however, a trivial matter, owing to the low volatility and instability of Z-MPN and problem of removing dichloromethane, as described in the Experimental Section.

Having recorded the spectrum of Z-MPN without transitions belonging to dichloromethane, it was possible to identify *a*-type, R-branch transitions, having relatively high values of $K_{-1}$. Fitting these transitions in a least-squares analysis, using the ROTFIT program due to Sørensen,[27] allowed the rotational constants *B* and *C* to be determined with a high degree of accuracy. Subsequently, a number of *b*-type, Q-branch transitions were identified and incorporated into the fit, which led to a reduction in the error associated with the value of the *A* rotational constant. The rotational and quartic centrifugal distortion constants (*A*-reduction $\mathrm{I^r}$ representation[22]) obtained from the least-squares fit are reported in Tables 1 and 3, while the transition frequencies and residual errors from the last cycle of the fit are given in the Supporting Information, Table 1S.

The inertial defect defined as $\Delta = I_c - I_a - I_b$, where $I_a$, $I_b$, and $I_c$ are the principal moments of inertia, was calculated from the rotational constants of the ground vibrational state of the parent species using a conversion factor of $505379.05 \times 10^{-20}$ u m$^2$ MHz and found to be $\Delta = 0.2635(4) \times 10^{-20}$ u m$^2$. This value should be compared to the inertial defect of vinyl cyanide ($H_2C{=}CHC{\equiv}N$), which is $0.163 \times 10^{-20}$ u m$^2$,[28] and to the inertial defect of the synperiplanar conformer of ethenethiol, which is $0.0312 \times 10^{-20}$ u m$^2$.[24−26] Both these compounds are known to be planar.[4,24−26] The fact that Z-MPN has the largest inertial defect of these three compounds was expected because it is larger with more low-frequency modes than found in either vinyl cyanide or ethenethiol. It is therefore concluded that the title molecule has a planar or nearly planar equilibrium geometry.

It was not possible to determine the dipole moment because the transitions were so weak that no quantitative measurements could be made.

In addition to the ground-state spectrum, a total of 52 transitions were observed that could be attributed to a vibrationally excited state of conformer I. The spectroscopic constants obtained by fitting this spectrum are given in Table 3, and the observed transition frequencies and residuals are in the Supporting Information, Table 2S. Only $^a$R transitions with relatively high $K_{-1}$ were assigned in this case, owing to insufficient spectral intensity. It was therefore not possible to determine an accurate value of the *A* rotational constants. This parameter was therefore held fixed at the value of the ground-state constant.

According to the above calculation of the vibrational frequencies of Z-MPN at the B3LYP/6-311++G(3df,2pd) level of theory, the vibrational mode having the lowest frequency will be an in-plane bending frequency at 127 cm$^{-1}$. It is considered probable that the observed excited-state spectrum corresponds to this vibrational mode.

**Spectra of Isotopologues**. The ground-state rotational spectra of three deuterium-substituted isotopologues, namely, DSCH═CHCN, HSCD═CHCN, and HSCH═CDCN, were recorded using isotopically enriched samples of Z-MPN produced according to the methods described above. For each of the deuterated isotopologues, a number of *a*-type, R-branch transitions were observed, and the rotational constants obtained from the least-squares analysis of these transitions can be found in Table 3. The measured transition frequencies and residual errors from the least-squares fit are given in the Supporting Information, Tables 3S−5S.

It was not possible to assign the spectrum of the HSCH═CHC$^{15}$N species, which was synthesized as described in the Supporting Information, because the 10% $^{15}$N enrichment used in this case apparently resulted in too weak intensities of the spectral lines.

Because only *a*-type transitions were assigned, the *A* rotational constant could not be accurately determined. The inertial defect varies little for various isotopologues of a planar compound. Therefore, the value of *A* for each deuterium isotopologue was varied systematically, but held fixed in the least-squares procedure, until a value of $0.264 \times 10^{-20}$ u m$^2$ was obtained for the inertial defect. The values of the $A_0$ constants estimated in this way are shown in Table 3. The fact that an approximate value of the inertial defect of these isotopologues is similar to that of the parent species for a planar compound makes it possible to estimate the accuracy of the $A_0$ rotational constants obtained in this manner. The $A_0$ rotational constants of the deuterated species shown in Table 3 are therefore estimated to be accurate to within ±5 MHz.

**Failure To Detect Further Isomers**. The absence of transitions attributable to conformer II of Z-MPN or to conformers I and II of E-MPN is not unexpected, since the quantum chemical predictions (Table 2) of the relative energies of conformers I and II suggest that conformer II is at least 6 kJ mol$^{-1}$ higher in energy than conformer I. An energy difference of this magnitude would cause the spectrum of conformer II to be substantially weaker than that of conformer I. A number of weak transitions were observed that were not assigned to conformer I. It is

**TABLE 4: Principal Axes Coordinates (pm) of Some Atoms in (*Z*)-3-Mercapto-2-propenenitrile**

| atom | $r_s$ coordinates[a] | | | $r_e$ coordinates[b] | | |
|---|---|---|---|---|---|---|
| $i$ | $\|a_i\|$ | $\|b_i\|$ | $\|c_i\|$ | $a_i$ | $b_i$ | $c_i$ |
| H1 | 31.3 | 131.8 | 0.2 | 45.7 | −131.1 | 0.0 |
| H2 | 134.5 | 185.0 | 0.1 | 131.7 | 185.4 | 0.0 |
| H3 | 113.3 | 213.4 | 0.2 | −108.3 | 215.9 | 0.0 |

[a] See the text for the method used to determine $r_s$ coordinates. [b] From an ab initio geometry optimization at the MP2/aug-cc-pVTZ level of theory.

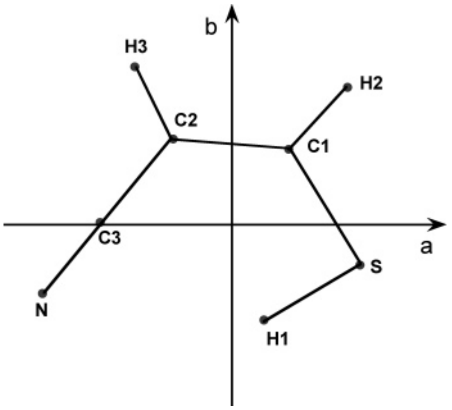


**Figure 2.** *Z*-Isomer conformer I in the $a-b$ principal inertial axis system.

believed that these transitions belong either to further vibrationally excited states of conformer I or to impurities in the sample.

Attempts to assign spectra of conformers I and II of the *E*-rotamer were also made, but without success. This is in accord with the quantum chemical predictions of the energy differences (Table 2) and the fact that 3-mercapto-2-propenenitrile is formed in an 8:1 *Z*:*E* ratio.

**Substitution Coordinates**. A method for determining the position of an atom in a molecule by considering the equilibrium moments of inertia of isotopically substituted species was developed by Kraitchman.[29] By solving Kraitchman's equations with the equilibrium moments of inertia of the parent and substituted isotopologues, the coordinates of the substituted atom can be calculated in the principal inertial axis system of the parent isotopologue. For the case of a nonplanar asymmetric rotor, Kraitchman's equations take the form

$$|\alpha_s| = \left(\frac{\Delta P_\alpha}{\mu}\right)\left\{1 + \frac{\Delta P_\beta}{(I_\alpha - I_\beta)}\right\}\left\{1 + \frac{\Delta P_\gamma}{(I_\alpha - I_\gamma)}\right\}$$

where $\alpha_s$ is the principal axis coordinate of the substituted atom, $\Delta P_\alpha = -\Delta I_\alpha + \Delta I_\beta + \Delta I_\gamma$, and $\Delta I_\alpha = I'_\alpha - I_\alpha$. The position of an atom relative to the three principal inertial axes can be calculated by cyclic permutation of $\alpha$, $\beta$, and $\gamma$ over $a$, $b$, and $c$. It should be noted that this method gives the modulus of the coordinates of an atom. Experimental values for the equilibrium moments of inertia were not determined during the course of the present investigation; however, solving Kraitchman's equations with ground-state moments of inertia will instead yield the substitution ($r_s$) coordinates[30] of the substituted atom.

This procedure was carried out using the ground-state moments of inertia obtained from the spectra of the parent and deuterated isotopologues of conformer I, giving the magnitudes of the principal axis coordinates of three H atoms, which are reported in Table 4. Also reported in Table 4 are the principal axis coordinates of these atoms, as predicted in the ab initio calculation at the MP2/aug-cc-pVTZ level of theory.

The agreement between the two sets of coordinates is good, especially when the small differences usually observed between $r_e$ and $r_s$ values are taken into account. It is concluded that the observed microwave spectra belong to conformer I of Z-MPN, because very different substitution coordinates would have been found for the other three forms. It is also concluded that the MP2/aug-cc-pVTZ geometry optimization is an accurate representation of this conformer. This is in accord with the finding that MP2 structures obtained using large basis sets are close to the equilibrium structures.[31] A model of conformer I of Z-MPN in the $a-b$ principal axes system, based on the MP2/aug-cc-pVTZ result, is shown in Figure 2.

**Evidence for Intramolecular Hydrogen Bonding**. It was found that the agreement between the experimentally determined ground-state rotational constants for conformer I and the approximate $r_e$ values from a geometry optimization at the MP2/aug-cc-pVTZ level (Table 1) was to within 1−2%. It is therefore considered likely that the structure predicted by this calculation represents a close approximation to the actual equilibrium structure of Z-MPN and that a closer examination of this structure will allow useful information regarding the interaction between the thiol and nitrile groups.

One parameter of particular interest in this respect is the distance between the H atom of the thiol group and the midpoint of the C≡N bond, which takes a value of 251 pm in this calculation. This represents a significant reduction from the value of 290 pm for the sum of the van der Waals radii[32] of the hydrogen atom (120 pm)[32] and the half-thickness of an aromatic molecule (170 pm)[32] involved in the interaction and suggests that these groups do form an intramolecular hydrogen bond. It is also noted that the C≡N and S−H bonds are 18° from being parallel. The corresponding bond moments[33] are therefore almost antiparallel, which is an ideal situation stabilizing conformer I.

Another interesting result is the similarity in the energies predicted for conformers I and II of E-MPN, which differ by approximately 1 kJ mol$^{-1}$ for a given level of theory (Table 2). Hydrogen bonding is of course not possible in the *E*-isomers. In contrast, the difference between conformers I and II of Z-MPN is greater than 6 kJ/mol according to the calculations, which is another indication that the observed conformer I is indeed stabilized by the formation of an intramolecular hydrogen bond.

The six-membered ring formed by the hydrogen bond should increase electron conjugation in conformer I as compared to conformer II. This electron delocalization should lead to slightly shorter S−C1 and C2−C3 bonds and longer S−H1, C1═C2, and C3≡N bonds in conformer I as compared to conformer II. This is exactly what the MP2/aug-cc-pVTZ calculations predict (Table 6S, Supporting Information).

Conformer I is not the first example of internal hydrogen bonding involving thiol and nitrile groups. Another example is 3-mercaptopropionitrile ($HSCH_2CH_2C{\equiv}N$),[34] in which its most stable conformer seems to be stabilized by this interaction. Another similar example where the thiol group interacts with a triple bond is seen in 3-butyne-1-thiol ($HSCH_2CH_2C{\equiv}CH$),[35] where a C≡C bond is the proton acceptor group.

In fact, a number of other molecules possessing a thiol group acting as proton donor in intramolecular hydrogen bonds have been studied to date, including cyclopropanemethanethiol ($C_3H_5CH_2SH$),[36] 2-furanmethanethiol ($C_4H_3OCH_2SH$),[37] 1,2-ethanedithiol ($HSCH_2CH_2SH$),[38] 2-propenethiol ($H_2C{=}CHCH_2SH$),[39] aminoethanethiol ($H_2NCH_2CH_2SH$),[40−42] methylthioglycolate ($HSCH_2COCH_3$),[43] thiiranemethanethiol ($C_2H_3$-

$SCH_2SH$),[44] and 3-butene-1-thiol ($HSCH_2CH_2CH{=}CH_2$).[45,46] It is also known that hydrogen bonds involving thiol groups are of importance in biological structures, owing to the presence of this functional group in the amino acid cysteine. Hydrogen bonding between the −SH group of cysteine and O and N atoms, along with aromatic rings, exerts an influence over the structure and activity of protein molecules.[47]

## Conclusions

We report the first successful synthesis of MPN in high yield and in an 8:1 *Z*:*E* ratio, and we have been able to characterize the *Z*- and *E*-isomers by several physical techniques. High-level quantum chemical calculations show that there are two stable planar forms of both Z- and E-MPN. The global minimum is found for Z-MPN conformer I. The MW spectra of the parent species of this form and three deuterated species have been assigned. These spectra may form the basis for a possible identification of this compound in interstellar space, in comets, and in the atmosphere of planets. Evidence is presented to show that the global minimum is stabilized by a weak internal hydrogen bond formed between the hydrogen atom of the thiol group and the $\pi$ electrons of the nitrile group.

**Acknowledgment.** The Research Council of Norway (Program for Supercomputing) is thanked for a grant of computer time. G.C.C. thanks the Research Council of Norway for financial assistance through Contract 160265/V30. J.-C.G. thanks PNP and PCMI (INSU-CNRS), the GDR CNRS “Exobiologie”, and the CNES for financial support.

**Supporting Information Available:** Preparation and NMR data of deuterated isotopologues and assigned microwave spectra and additional results from quantum chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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