The Detection of the New Molecule Prop-2-ynylideneamine, H–C≡C–CH=NH, by Microwave Spectroscopy

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The new molecule prop-2-ynylideneamine, H–C≡C–CH=NH, has been produced by flowing propargylamine over *N*-chlorosuccinimide, and then over potassium t-butoxide; the molecule was detected by microwave spectroscopy and its rotational parameters determined as a necessary preliminary to a radioastronomical search.

It has become clear that an understanding of the origin of the long carbon chain molecules HC_nN (n = 1, 3, 5, 7, 9, 11), discovered in molecular clouds and circumstellar shells by radioastronomy, holds one of the keys to a better understanding of interstellar chemistry.[1] Ion-molecule reaction schemes have been proposed which have been able to explain some, though by no means all, of the observations. In such schemes, more saturated relatives of the cyanopolyynes play an integral role.[2] For instance CH_2=NH, related to HC≡N by the addition of two H atoms, is relatively abundant in the interstellar medium.[3] In a similar way the abundance of HC≡CCH=NH (HC≡C–C≡N plus two H atoms) should yield further critical information on the synthetic mechanism involved in the production of larger interstellar molecules. These interesting problems provided the main incentive for this study whose preliminary results are presented here.

The experimental system, which was similar to that of Guillemin and Denis,[4,5] consisted of an ampoule of propargylamine (HC≡C–CH_2NH_2, Aldrich) connected to two 0.8 cm i.d. reactor tubes, the first loosely filled with *ca.* 7 cm of finely powdered *N*-chlorosuccinimide (NCS) (Aldrich), the second filled with *ca.* 30 cm of potassium t-butoxide powder (Aldrich)

Table 1. Observed and calculated rotational constants for HC≡C–CH=NH.

	Observed	Calculated I	Calculated II	Calculated III
A	54959(300)	52944	52578	53828
B	4862.33(5)	4917.5	4903.5	4862.0
C	4458.27(5)	4499.5	4485.2	4459.3
B–C	404.06	418.0	418.3	402.7

and heated to 60 °C over the whole of its length. Propargylamine flowed slowly through the reactor zones and the resultant vapour passed *via* a −78 °C U-trap through the 1 m cell of a Hewlett Packard 8460A microwave spectrometer at *ca.* 40 10^{-3} mmHg pressure.

In a typical experiment the system was pumped overnight prior to the introduction of propargylamine. Initially strong spectra of cyanoethyne, vinyl cyanide, methyl cyanide, and ammonia were observed, but after *ca.* 1 h a new, relatively strong spectrum was detected, very close to that predicted for *trans*-prop-2-ynylideneamine (H atoms in *trans* configuration). No evidence for the *cis* isomer has been obtained so far. The rotational constants determined from a least squares fit of 11 R-branch transitions between 26.5—40.0 GHz, are presented in Table 1, together with the rotational constants (Set I) calculated using the structural parameters r(H–C≡) = 1.055, r(C≡C) = 1.209, r(C–C) = 1.444 Å, and <(C–C=N) = 123.9° taken from propynal[6] and r(C=N) = 1.273, r(N–H) = 1.023, r(C–H) = 1.081 Å, <(C=N–H) = 110.5, and <(H–C=N) = 119.7° taken from methanimine.[7]

Set II was calculated with the same parameters as in Set I but with an increase of 0.008 Å in r(C=N) over that in CH_2=NH, in line with that observed for r(C=O) between H_2C=O and HC≡C–CH=O.[8] Set III was calculated using the Set II parameters with the exception that the ∠ (C–C=N) has been opened up by 1.15°, the amount required to fit *B* exactly. Such an increase is to be expected if account is to be taken of the way in which the NH group tends to affect a neighbouring group.

As indicated in Table 1 there is excellent agreement between the predicted and observed constants, confirming the identity of the new species. All other feasible molecules give vastly poorer agreement between observed and calculated constants lending further support to the assignment.

$$H\text{–}C{\equiv}C\text{–}CH_2NH_2 \xrightarrow{NCS} HC{\equiv}C\text{–}CH_2NHCl \xrightarrow[KOBu^t]{60\ ^\circ C} HC{\equiv}C\text{–}CH{=}NH \quad (1)$$

The result of this study indicates that reaction (1) can be used to study the new species by spectroscopic methods. The resulting data is to be used as a basis for a search for this interesting species in interstellar molecular clouds which are known to contain cyanoethyne and cyanopolyynes. The abundances of this species and related ones are necessary pieces of information in the study of interstellar chemistry, in particular, in determining the importance of ion-molecule schemes in the origin of larger molecules such as the polyynes.

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