

## Photoelectron, Infrared, and Theoretical Study of the Thermolysis of 4-Azahepta-1,6-diyne: Spectra of Prop-2-ynylideneamine, $\text{H}-\text{C}\equiv\text{C}-\text{CH}=\text{NH}$ , and Penta-3,4-diene-1-yne, $\text{CH}_2=\text{C}=\text{CHC}\equiv\text{CH}$

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The conditions for and products of thermolysis of 4-azahepta-1,6-diyne,  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$ , have been investigated by microwave, photoelectron, i.r., and mass spectrometric techniques. Prop-2-ynylideneamine,  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ , is produced in good yield as well as penta-3,4-diene-1-yne,  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$ , from  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$ . Ionisation potential and vibrational data for  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ ,  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$ , and the precursors have been obtained. The ionisation energies have been assigned with the aid of theoretical calculations. Photoelectron data on 3-aminopropyne,  $\text{HC}\equiv\text{CCH}_2\text{NH}_2$ , have also been obtained.

The spectroscopy of small, unsaturated molecules containing doubly bonded nitrogen has been of interest since the report of the microwave spectrum of the simplest species, methyleneimine,  $\text{CH}_2=\text{NH}$ , in 1972.<sup>1</sup> Since this time the i.r.<sup>2,3</sup> and photoelectron spectra of  $\text{CH}_2=\text{NH}$ <sup>4-6</sup> have been reported. Several substituted imines, including the molecules  $\text{CH}_2=\text{NC}\equiv\text{N}$ ,<sup>7</sup>  $\text{MeCH}=\text{NH}$ ,<sup>8</sup>  $(\text{CF}_3)_2\text{C}=\text{NH}$ ,<sup>9</sup>  $\text{C}_6\text{H}_5\text{CH}=\text{NMe}$ ,<sup>10</sup> and  $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}$ <sup>11</sup> have been studied by various spectroscopic techniques. Further interest in this group of compounds has been stimulated by the observation of  $\text{CH}_2=\text{NH}$  in interstellar molecular clouds.<sup>12</sup>

In the present work a detailed study of the conditions under which prop-2-ynylideneamine (propargylimine),  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ , is produced by gas-phase thermolysis has been carried out. The thermolysis products and conditions have been followed using a combination of microwave, Fourier transform i.r. (f.t.i.r.) and photoelectron (p.e.) spectroscopy together with mass spectrometry.

$\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$  was originally produced by a two-step process involving *N*-chlorination of 3-aminopropyne,  $\text{HC}\equiv\text{C}-\text{CH}_2\text{NH}_2$ , with *N*-chlorosuccinimide followed by the removal of  $\text{HCl}$  using potassium *t*-butoxide.<sup>13</sup> The species was simultaneously detected by Hamada *et al.*<sup>14</sup> who obtained it directly by thermolysis of 4-azahepta-1,6-diyne  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$ . In the present study the direct thermolysis method proved to be the most suitable mainly because of its simplicity. The original direct thermolysis experiments used a temperature of 1050 °C,<sup>14</sup> however under these conditions the present p.e. measurements indicated that significant quantities of ethyne and hydrogen chloride were formed. Microwave experiments are sometimes not well suited to determining the optimum conditions due to the difficulties of deriving reliable quantitative information from intensities. In addition, many products such as ethyne do not possess a permanent dipole moment or are too light and thus are not, in general, observable by rotational spectroscopy.

The conditions and products of thermolysis were studied in detail using f.t.i.r. and mass spectrometric techniques, which indicated that appreciable amounts of  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$  were produced in addition to  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ . Several isotopic variants of  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$  have been studied by microwave spectroscopy,<sup>15</sup> yielding reliable structural data. To aid the assignment of the p.e. spectra, *ab initio* SCF MO calculations have been carried out on the neutral molecules and, because of a possible breakdown of Koopmans' theorem,<sup>16</sup> also on some cations. All the calculations used the GAUSSIAN 82 program<sup>17</sup> with the minimal STO-3G and split-valence 4-31G basis sets available in this package.

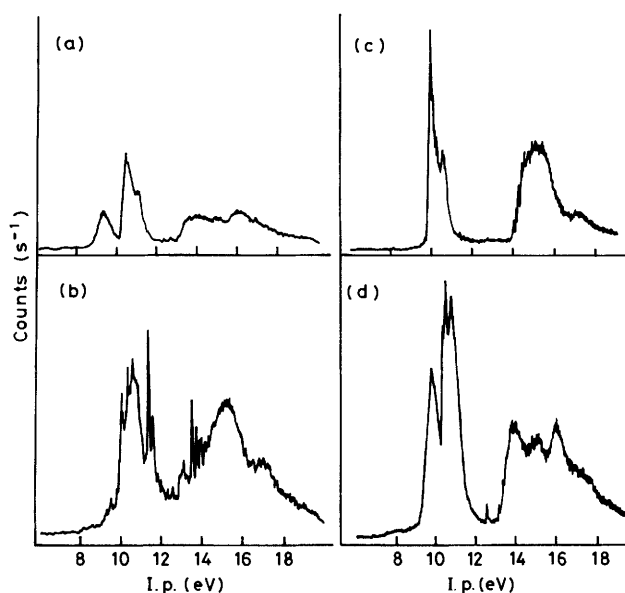


Figure 1. The photoelectron spectra of: (a) 4-azahepta-1,6-diyne,  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$ , (b) the thermolysis products of 4-azahepta-1,6-diyne, at 1050 °C, (c) the result of passing the products of thermolysis at 1050 °C through a -126 °C cold trap, and (d) of 3-aminopropyne  $(\text{HC}\equiv\text{C}-\text{CH}_2\text{NH}_2)$

The effect of introducing yne and ene groups adjacent to the imine function has been investigated by correlating the ionisation potentials with isoelectronic systems.

### Experimental and Results

The molecule prop-2-ynylideneamine was originally identified by microwave spectroscopy<sup>13</sup> which indicated the *Z* species to be the predominant isomer. This isomer has the two hydrogen atoms on opposite sides of the  $\text{C}=\text{N}$  bond whereas in the *E*-isomer they are on the same side. The *Z*:*E* ratio appears to be of the order of 4:1.<sup>14</sup> The microwave data have enabled structural and dipole moment information to be determined and the detailed results will be published separately.<sup>15</sup>

Experiments were carried out using 4-azahepta-1,6-diyne  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$  as a precursor to study the p.e. spectrum of  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ . When the parent, whose spectrum is shown in Figure 1(a), was thermolysed at 1050 °C a multicomponent

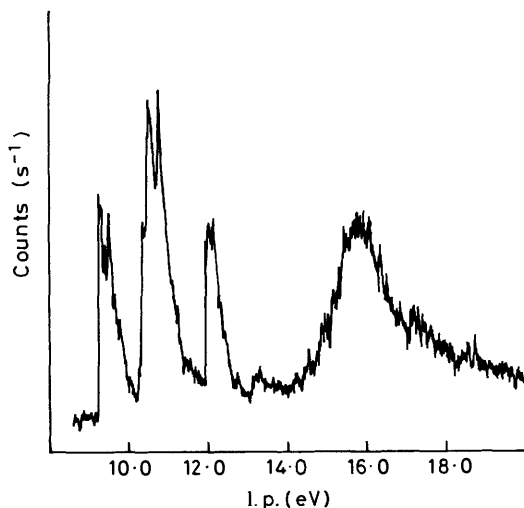


Figure 2. The photoelectron spectrum of penta-3,4-dien-1-yne,  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$

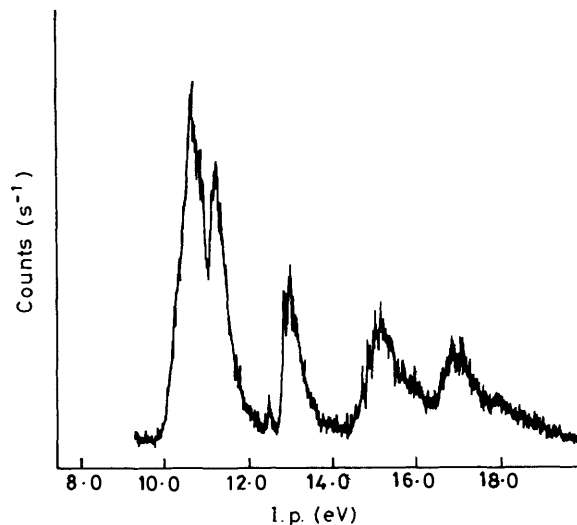


Figure 4. The photoelectron spectrum of (*Z*)-prop-2-ynylideneamine,  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$

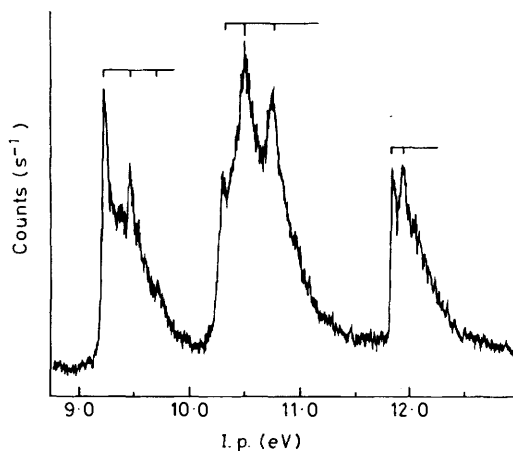


Figure 3. Expansion of the region 9–13 eV in the photoelectron spectrum of penta-3,4-dien-1-yne,  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$

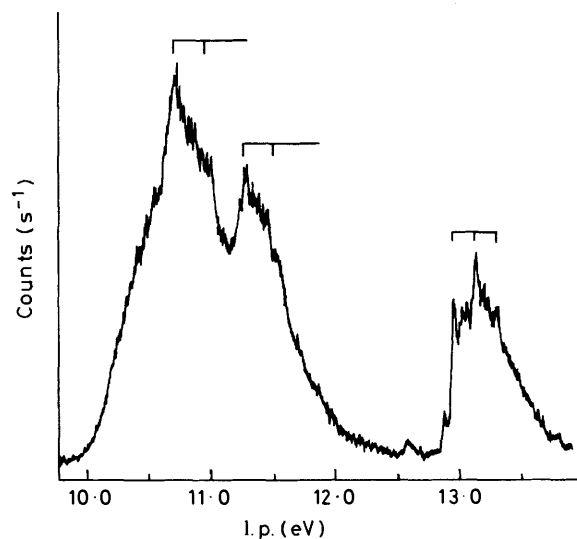
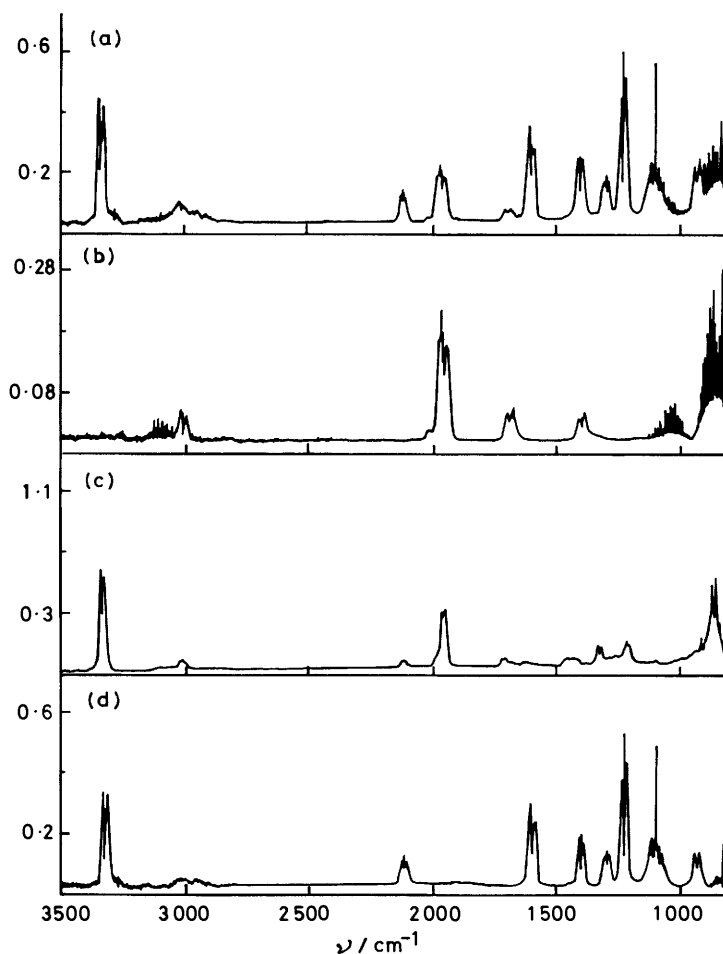


Figure 5. Expansion of the region 10–14 eV in the photoelectron spectrum of (*Z*)-prop-2-ynylideneamine,  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$

spectrum, Figure 1(b), was obtained in which only the sharp features due to  $\text{HC}\equiv\text{CH}$  and  $\text{HC}\equiv\text{N}$  could be unequivocally identified. This indicated that lower thermolysis temperatures were desirable. In fact, based on precursor loss it appeared that thermolysis began at *ca.* 500 °C, and it was found that 740 °C was an optimum temperature for detection, taking into account the decomposition of the parent together with the production of minimal  $\text{HC}\equiv\text{CH}$  and  $\text{HC}\equiv\text{N}$ . When the products were passed into a  $-126$  °C trap it was found that a volatile component passed through whose spectrum is shown in Figure 1(c). This species was readily identified as propadiene<sup>18</sup> essentially uncontaminated by any other compound. This thermolysis-trapping procedure was continued for 3 h during which time *ca.* 200 mg of parent were consumed. When the contents of the trap were warmed to  $-75$  °C the component which evolved gave rise to the spectrum shown in Figure 2, the first three bands of which are shown in more detail in Figure 3. This component was subsequently shown to be mainly  $\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$  (see below). After pumping at  $-75$  °C for 1 h and slowly warming to  $-60$  °C, essentially pure prop-2-ynylideneamine,  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ , whose spectrum is shown in Figure 4, was obtained. A more detailed scan of the region between 10 and 14 eV is shown

in Figure 5. Thermolysis experiments were also carried out on 3-aminopropyne ( $\text{HC}\equiv\text{C}-\text{CH}_2\text{NH}_2$ ) whose p.e. spectrum is shown in Figure 1(d). It cracked in a more complex manner than 4-azahepta-1,6-diyne and its breakdown products were not investigated in further detail.

The spectra resulting from a low, resolution f.t.i.r. study of the system using a roughly parallel procedure are shown in the sequence Figures 6(a)–(d). Figure 6(a) shows the spectrum obtained on flowing the products of the thermolysis of  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$  at 740 °C directly through the multiple-traversal cell of the spectrometer. The f.t.i.r. spectrum of the species which passed through a  $-126$  °C trap downstream from the thermolysis zone is shown in Figure 6(b) and, as discussed above, this species is propadiene.<sup>19</sup> The component which volatilises from the  $-75$  °C trap gave the f.t.i.r. spectrum shown in Figure 6(c) and was identified by mass spectrometry, having the formula  $\text{C}_5\text{H}_4$ . As discussed later we concluded that this component is penta-3,4-dien-1-yne and the gas-phase f.t.i.r. spectrum shown in Figure 6(c) is in excellent agreement with the



**Figure 6.** The f.t.i.r. spectra of: (a) the thermolysis of 4-azahepta-1,6-diyne at 740 °C, (b) using -126 °C trap on (a) allowing the passage of propadiene only, (c) the contents of the -126 °C trap when warmed to -75 °C, and (d) the contents of the -126 °C when pumped at -75 °C and then warmed to -60 °C

report of solution measurements.<sup>20</sup> A very weak band observed at 2119  $\text{cm}^{-1}$  has been assigned to the  $\text{-C}\equiv\text{C-}$  stretching frequency. In general these vibrations have an intensity <10% that of the  $\text{C}\equiv\text{H}$  stretching frequency,<sup>21</sup> which is here measured as 3333  $\text{cm}^{-1}$ . After pumping the trap contents at -75 °C for 1 h, almost all the  $\text{C}_5\text{H}_4$  is removed and by warming the trap to -60 °C an almost pure sample of  $\text{HC}\equiv\text{C-CH=CH}$  is obtained which yields the f.t.i.r. spectrum shown in Figure 6(d).

To confirm the identification of the various components produced by thermolysis, the system was connected to the volatile inlet of a mass spectrometer. With the trap held at -126 °C, peaks due to the parent molecule,  $m/e$  93,  $\text{HC}\equiv\text{C-CH=NH}$  ( $\text{C}_3\text{H}_3\text{N}$ ),  $m/e$  53, and a group at  $m/e$  62–66 were obtained. On warming the trap to -75 °C the peaks at  $m/e$  62–66 increased in intensity compared with the others. The most intense peak in this group was  $m/e$  64, indicating a species with formula  $\text{C}_5\text{H}_4$ . After pumping on this trap for 1 h at -75 °C, it was warmed to -60 °C, whereupon the  $\text{C}_5\text{H}_4$  component decreased significantly and the peak at  $m/e$  53,  $\text{HC}\equiv\text{C-CH=NH}$ , became the most intense. These results agree well with those obtained from the p.e. and f.t.i.r. measurements.

The instruments used were a Perkin-Elmer PS16/18 photoelectron spectrometer, a Hewlett-Packard 8460A microwave spectrometer, a Bomem DA3.002 Fourier transform i.r. spectrometer, and a Kratos MS80RF mass spectrometer. The precursor was held in a Rotaflo glass vessel and its vapour was passed through a quartz tube (length 25 cm, i.d. 0.8 cm) which

was heated over *ca.* 15 cm by an electrical furnace. The temperature was measured using a Pt-Rh thermocouple. The thermolysis products were passed through a -126 °C trap directly into the inlet system of the spectrometer. The contents of the -126 °C trap were warmed up slowly and examined. The i.r. spectra were obtained using a multiple-traversal cell set to give a path length of *ca.* 16 m with sample pressures of 0.05–0.1 Torr. Normally 50 scans were co-added and the resolution used was 1.0  $\text{cm}^{-1}$ .

**Photoelectron Analysis.**— $(\text{HC}\equiv\text{C-CH}_2)_2\text{NH}$ . The spectrum shown in Figure 1(a) exhibits two clear ionisation features centred at 9.31 and at 10.55 eV, with a pronounced shoulder at 11.06 eV, followed by a series of broad bands starting at 13 eV. The first band seems to have a broad simple Franck-Condon envelope suggesting that it belongs to a single ionisation potential (i.p.). The second band has a more complicated contour with maxima at 10.55 and 11.06 eV and an overall intensity of about three times that of the first band. Theoretical SCF MO calculations have been carried out on this molecule. For one calculation, a  $\text{C}_s$  structure, in which both  $\text{C}\equiv\text{C-H}$  groups are staggered relative to the N lone pair and the N-H bond, has been assumed. A second calculation has been carried out for the  $\text{C}_1$  structure which results by rotating one  $\text{C}\equiv\text{C-H}$  group by 180° about the C-N bond. Calculations for both conformers were carried out which indicated that they were of very similar energy; the  $\text{C}_1$  species lying <10 kJ below the  $\text{C}_s$

**Table 1.** Experimental and calculated i.p.s (eV) for 4-azahepta-1,6-diyne ( $\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{NH}$ 

Expt.	Calc. <sup>c</sup>		Assignments
	C <sub>s</sub>	C <sub>1</sub>	
9.31 <sup>a</sup>	10.01	10.02	A' lone pair
10.55 <sup>a</sup>	10.33	10.33	A' -C≡C-
	10.37	10.53	A' out-of-plane
11.06 <sup>a</sup>	10.76	10.67	A' and in-plane
	10.97	11.16	A' π orbitals
13.0—17.0 <sup>b</sup>	14.94	14.93	σ orbitals
	16.05	15.49	
	16.30	16.35	
	17.10	17.25	
	18.03	17.98	

<sup>a</sup> Error  $\pm 0.05$  eV. <sup>b</sup> Broad unresolved bands with maximum at 16.0 eV. <sup>c</sup> 4-31G SCF MO calculations.

**Table 2.** Experimental and calculated i.p.s (eV) of 3-aminopropyne,  $\text{HC}\equiv\text{CCH}_2\text{NH}_2$ 

Expt. <sup>a</sup>	Calc. <sup>b</sup>	Assignments
9.85	9.03	A' N lone pair
10.55 <sup>c</sup>	9.68	A' C≡C out-of-plane π orbitals
	11.16	A' C≡C in-plane π orbitals
13.80 <sup>d</sup>	14.46	A' C≡C, C-C, and C-N σ orbitals
15.10 <sup>d</sup>	17.38	A' C-H, N-H out-of-plane σ orbitals
16.00 <sup>d</sup>	17.98	A' C-C and C-N σ orbitals

<sup>a</sup> Error  $\pm 0.05$  eV. <sup>b</sup> 4-31G SCF MO calculations. <sup>c</sup> Strong feature centred at 10.70 eV with an apparent vibration progression of  $1910 \pm 50 \text{ cm}^{-1}$ . <sup>d</sup> Possible assignments.

species. This insensitivity to conformation indicates that the calculated i.p.s are reliable.

The results of the calculations are listed in Table 1 which shows that the ionisation potential associated with the lone pair should be the lowest, closely followed by the four associated with the π orbitals of the C≡C groups which should span a range of ca. 0.5 eV. The calculation is consistent with the assignment of the first band to the N lone pair and the second band to the four acetylenic π orbitals. The calculation also indicates a gap of 4 eV before the onset of the five ionisations associated with the σ orbitals above 14.9 eV.

$\text{HC}\equiv\text{CCH}_2\text{NH}_2$ . Figure 1(d) shows the p.e. spectrum of 3-aminopropyne,  $\text{HC}\equiv\text{C}-\text{CH}_2\text{NH}_2$ . The first ionisation potential belongs to the lone pair on the N atom at 9.85 eV. The next band, centred at ca. 10.70 eV, which is roughly twice the intensity of the first, is expected to arise from the ionisation of the out-of-plane and in-plane π orbitals associated with the -C≡C- group. The calculation (Table 2) indicates that the two i.p.s are 1.48 eV apart; however as we have seen we do not expect Koopmans' theorem to be particularly good in these types of molecules. The two peaks are separated by  $1910 \pm 100 \text{ cm}^{-1}$  which is almost certainly a C≡C stretching frequency as expected. The next features in the spectrum, commencing at ca. 13.50 eV, are expected to be due to ionisations involving mainly σ-type orbitals. The ionisation data and the assignments are given in Table 2.

$\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ . The p.e. spectrum of  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ , (Z)-prop-2-ynylideneamine, is shown in Figure 4 and the measured i.p. data are given in Table 3 together with the results of the SCF MO calculations (details of which are given in the Table footnotes). Six i.p.s are expected in the region up to 21 eV and the four associated with the π and lone pair orbitals are predicted to lie below 14 eV. There are three distinct features

**Table 3.** Observed and calculated i.p.s (eV) of (Z)-prop-2-ynylideneamine,  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ 

Expt. <sup>a</sup>	Calc. <sup>b</sup>	Calc. <sup>c</sup>	Assignments
10.55 <sup>d</sup>	9.13	(11.85) <sup>e</sup>	A' N lone pair
10.76 <sup>f</sup>	9.71	(10.62) <sup>e</sup>	A' π(C≡C) orbitals
11.31 <sup>f</sup>	10.04	(11.34) <sup>e</sup>	A' π(C≡C) orbitals
13.13		13.77	A' π(C=N) orbital
15.3 <sup>g</sup>		17.43	A' σ(C=N) orbital
17.1 <sup>g</sup>		19.23	A' σ(H-C≡C-C) orbitals
18.1 <sup>g</sup>		20.72	A' σ(C≡C-C) orbitals

<sup>a</sup> Vertical i.p. error  $\pm 0.05$  eV unless indicated. <sup>b</sup> ΔSCF using 4-31G SCF MO calculations. <sup>c</sup> Koopmans' theorem using 4-31G SCF MO calculations. <sup>d</sup> Estimated  $\pm 0.1$  eV overlapped (see text). Adiabatic i.p.  $10.1 \pm 1$  eV. <sup>e</sup> Note that the Koopmans' calculation has this assignment reversed. <sup>f</sup> Vibrational component at ca.  $2000 \pm 100 \text{ cm}^{-1}$ . <sup>g</sup> Error  $\pm 0.1$  eV.

between 10 and 14 eV, a region which is shown in more detail in Figure 5. The intensity of the first, with a maximum at 10.76 eV, is roughly twice that at 11.31 eV, suggesting that there may be two i.p.s in the 10.7 eV region. This possibility is supported by the band contour which starts at ca. 10.0 eV, and curves smoothly up to 10.55 eV (shoulder) and then up to the maximum at 10.76 eV, the i.p. of the second band. The band observed at 13.13 eV is reliably assigned to the out-of-plane bonding combination of the π(>C=N') and π(-C≡C-) as the calculation suggests that it is well separated (at 13.77 eV) from the rest (see Table 3). The three most prominent features in this band (Figure 5) form a progression with a frequency of  $1320 \pm 100 \text{ cm}^{-1}$ . In the neutral molecule the C=N stretching frequency is  $1590 \text{ cm}^{-1}$ .<sup>14</sup>

It is difficult to assign the first three i.p.s unequivocally as the 4-31G calculations predict the order: 10.62 eV, out-of-plane combination of π(C≡C) and π(C=N); 11.34 eV, in-plane π(C≡C); and 11.85 eV, N lone pair, see Table 3. Intuition, however, suggests that the lone pair ionisation is likely to be the highest.<sup>22</sup>

To clarify the situation, calculations on the cations were carried out which indicated that these three orbitals were very close (within 1 eV, Table 3) and indicated that the N lone pair ionisation is the first rather than the third, as suggested by the 4-31G Koopmans' approximation calculation. This indicates that a correlated wavefunction study might be appropriate. However the proximity of the ionisation potentials, according to the calculations, and the overlapping observed in the spectrum suggest that it would be difficult to make a definitive assignment. A plausible explanation of the structure observed in Figures 4 and 5 is that the N lone pair ionisation, which is expected to give rise to a broad band, starts at ca. 10.0 eV (the adiabatic i.p.) and has a maximum at ca. 10.55 eV (the vertical i.p.). It thus underlies the sharp feature at 10.76 eV which has a prominent shoulder at 11.01 eV (separation 0.25 eV =  $2000 \text{ cm}^{-1}$ ). These features are thus assigned as the first two members of a progression in the C≡C stretching frequency associated with the π(A') ionisation. The second sharp peak, at 11.31 eV, which also has a similar shoulder is assigned to the π(A') ionisation. The strength of the 10.76 eV feature arises because of its close coincidence with the maximum of the N lone pair i.p. A similar situation appears to arise for  $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}$ .<sup>11</sup> The bands which remain (above 14 eV) belong mainly to ionisations which involve the σ framework (Table 3). We note that the LNDO/S and MNDO calculations using Koopmans' theorem and PERTCI ionic state calculations by Schulz and Schweig<sup>11</sup> predict that the N lone pair and π(A') ionisations of prop-2-ylideneamine are essentially degenerate.

$\text{CH}_2=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$ . The spectrum of this species, which may be vapourised from the trap at  $-75^\circ\text{C}$ , is shown in Figure 2.



species  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$  which is an isomer of the well known vinyl cyanide,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ , is found to be relatively stable and can be handled fairly easily using standard trapping techniques.

As  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$  has been detected in interstellar space, its isomer  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$  is of interest as it is also a feasible product of the interstellar processes that give rise to  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ . These molecules are important as the processes which produce them are likely to play an important role in the production of the long chain poly-yne.

The p.e. data indicate that the first two i.p.s are almost coincident and unresolved. They can not thus be separated experimentally. Theoretical calculations also do not yield an unequivocal assignment. The Koopmans' theory result indicates that the out-of-plane  $\pi$  orbital (which is antibonding between the acetylenic and imine groups) is the first i.p. and the N lone pair orbital is the third. The cation calculation however indicates that the latter is the first by 0.58 eV and that there is a significant breakdown in the Koopmans' approximation in this case, an observation which is consistent with results obtained previously for related molecules.<sup>25</sup> One reason is that there is a significant degree of interaction between the imino and yne group  $\pi$  system.

In Figure 7 a correlation diagram is presented for the highest occupied lone pair and  $\pi$ -type molecular orbital energies for molecules isoelectronic with  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$  and  $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}$ .<sup>11,26,27</sup> The diagram shows that the behaviour for the two sets (the substituted ynes and enes) are in excellent semiquantitative agreement as far as the trends are concerned. One sees, as expected, a general stabilisation of all the  $\pi$  orbitals as the end group changes from  $\text{CH}_2 \rightarrow \text{NH} \rightarrow \text{O}$ .

Other species are produced but they can be separated by careful control of the conditions and the use of trapping techniques. The i.r. data presented here are consistent with and complement those published previously by Hamada *et al.*<sup>14</sup> However using the present method we have been able to obtain the f.t.i.r. data of an essentially pure sample of  $\text{HC}\equiv\text{C}-\text{CH}=\text{NH}$ .

#### Acknowledgements

We thank Mr. A. Greenway for mass spectroscopic analysis. D. McN. and J. D. W. thank the S.E.R.C. for financial support. Maintenance support from the Sudanese Government and O.R.S. scheme for O. I. O. is gratefully acknowledged. The experiments were carried out on S.E.R.C. funded instruments.

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Received 24th March 1986; Paper 6/579