Polyatomic organic molecules can be synthesized in a mixture of simple gases containing H, C, N and O when this mixture is subject to external sources of energy such as electrical discharges. Starting materials for these syntheses are gases such as hydrogen, methane, ammonia, water and others. Since the early experiments by Miller [1] in 1953 and Miller and Urey [2], who produced amino acids in trying to simulate the primordial Earth's atmosphere by subjecting a constantly circulating mixture of CH\textsubscript{4}, NH\textsubscript{3}, H\textsubscript{2}O and H\textsubscript{2} at pressures near 1 atmosphere to an electrical discharge, it is now well established by means of many other experiments that under similar conditions amino acids and other organic compounds are synthesized. However, at considerably reduced pressures (near 10\textsuperscript{-2} Torr) the synthesis of organic molecules starting from simple gases is less well investigated and to our knowledge only very simple molecules have been generated this way. Thus the production of molecules at low pressure containing five and more atoms in the plasma of an electrical discharge is of interest in the context both of possible prebiotic synthesis of organic matter and of recent interstellar molecular detections. Both aspects can be studied by using the members in the series HCN, HC\textsubscript{3}N, HC\textsubscript{4}N, ..., as interstellar and laboratory probes. Although the low temperature, low density environment of interstellar clouds cannot be simulated easily.

In interstellar space HCN and HC\textsubscript{3}N are distributed throughout a wide variety of different molecular clouds, whereas HC\textsubscript{4}N has been discovered so far only in Sgr B2 [3, 4], in the envelope of the carbon star IRC +10216 [5] and in cold, dark dust clouds in the Taurus region [6, 7]. This latter region contains several small molecular clouds, one of which is located near the south eastern edge of Heiles' cloud 2, and we shall refer to it as TMC 1 (Taurus Molecular Cloud 1). TMC 1 is the only interstellar source presently known in which HC\textsubscript{4}N, HC\textsubscript{5}N, HC\textsubscript{6}N, and HC\textsubscript{7}N have been discovered to be present simultaneously [6, 7, 8, 9]. Interestingly all four chain molecules show similar concentrations which indicates that the chemistry in this source must be special in regard to producing long chain molecules. Churchwell et al. 1978 [5] suggest that one single reaction involving C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} or C\textsubscript{2}H\textsubscript{3}\textsuperscript{+} may convert the lower cyanoacetylenes HC\textsubscript{3}N into HC\textsubscript{4}N, HC\textsubscript{5}N and HC\textsubscript{6}N. Presently however, it is not clear by which reaction scheme larger molecules are created in interstellar space. Gas phase reactions, surface mechanisms or a combination of both are all conceivable possibilities.

In support of gas phase reactions as being capable of producing long carbon chain molecules, we would like to report the formation of HC\textsubscript{5}N in laboratory gas discharges. Since it was possible to produce cyanoacetylene, HC\textsubscript{3}N, by a radiofrequency discharge in a mixture of acetylene, HC\textsubscript{2}H\textsubscript{2}, and hydrogen cyanide, HCN [10] it was our aim to establish whether cyanoacetylene, HC\textsubscript{4}N, can be synthesized in a similar manner by the same method.

Although cyanoacetylene proves to be the major nitrogen containing product under the action of an electric discharge on mixtures of different simple gases, such as methane and nitrogen [11] or acetylene and hydrogen cyanide [10], it is the first time that HC\textsubscript{5}N has been observed in the latter mixture although HC\textsubscript{4}N has been prepared earlier.
by chemical methods [12]. The reaction scheme used in our experiment consists of an approximately 2:1 mixture of HCCN and HCN, which is subjected to a 4.5 MHz radio frequency discharge, under continuous flow conditions at a pressure of $10^{-2}$ to $10^{-1}$ Torr. Aside from HC$_5$N, which is made profusely, HC$_3$N is produced in small amounts. Other molecules such as H$_2$C$_2$HCN are detectable only in traces, whereas CH$_3$CN and H$_2$C$_2$HNC were not found. HC$_5$N was isolated by trapping the discharge products and then subjecting them to a low temperature distillation. Fig. 1a shows a medium resolution scan of such a purified HC$_5$N sample with the characteristic pattern of transitions arising from the excited vibrational levels belonging to the manifold $v_{11}$ of the lowest lying bending mode $v_{11}$ extending to the high frequency side of the ground state transition. The ground state $J=4 \leftrightarrow 3$ transitions of HC$_5$N and HC$_3$N under high resolution are presented in Figure 1b. For both molecules the two weak outer $A^F = 0$ hyperfine components could also be resolved, and from their measured separations a value of the $^{14}$N nuclear quadrupole coupling constant $eqQ$ was derived for each molecule. Transition frequencies and molecular parameters of HC$_5$N are collected in Table 1 and are compared with those of HC$_3$N and the interstellar values. HC$_5$N was first detected by its $J=4 \rightarrow 3$ transition in Sgr B2 by Avery et al. [3] and later Broten et al. [4] could derive from the observed separation of the three hyperfine components of the $J=1 \rightarrow 0$ transition a value of $eqQ = -4.12$ (7) MHz, which is barely in agreement with our value of $eqQ = -4.242$ (30) MHz. To aid our estimate of the error in the determination of the $eqQ$ value of HC$_5$N, we analysed the hyperfine components of the $J=4 \leftrightarrow 3$ transition of HC$_3$N only and compared the $eqQ$ value thus derived with the value obtained earlier by Creswell et al. from a least squares analysis of a more extended data set. The two values agree to within their quoted error limits.

Our results show, that long carbon chain molecules can be formed by gas phase reactions under the action of electrical discharges, although the details of the reaction scheme are by no means established. Since only the stable end products of the gas discharge were monitored little can be said at present about the intermediates which must be involved in the reaction scheme. At a number density of about $5 \times 10^{14}$ molecules cm$^{-3}$ and with the large volume-to-surface ratio of our reaction cell, we believe that gas phase reactions are primarily responsible for the formation of HC$_3$N and HC$_5$N. Most likely, they are formed by binary collisions between ions such as C$_2$H$_3^+$, CH$_3^+$ with HCN, or HC$_3$N involving reactions of the type:

$$C_2H_x^+ + HCN \rightarrow HC_{x+2}N^+ + H_2$$

($n = 1, 3, \ldots; x = 2, 3$). Stable isotope tracers of the parent gases under different experimental conditions are now being employed in the hope of elucidating some details of the production mechanisms.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Relative intensity</th>
<th>Observed frequency</th>
<th>Calculated frequency</th>
<th>Observed frequency</th>
<th>Calculated frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 4 \rightarrow 3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F = 4 \rightarrow 4$</td>
<td>2.08</td>
<td>10649.244 (10)</td>
<td>10650.657 (12)</td>
<td>36392.326 (12)</td>
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</tr>
<tr>
<td>$3 \rightarrow 2$</td>
<td>23.81</td>
<td>10650.567</td>
<td>10650.657</td>
<td>36392.326</td>
<td></td>
</tr>
<tr>
<td>$4 \rightarrow 3$</td>
<td>31.25</td>
<td>10650.650 (100)</td>
<td>10650.650 (100)</td>
<td>36392.326 (100)</td>
<td>36392.326</td>
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<tr>
<td>$5 \rightarrow 4$</td>
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<td>10650.690</td>
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<tr>
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<td>10652.475 (10)</td>
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<td>36394.169 (10)</td>
<td>36394.169</td>
</tr>
<tr>
<td>$3 \rightarrow 3$</td>
<td>2.08</td>
<td>10652.475 (10)</td>
<td>10652.475 (10)</td>
<td>36394.169 (10)</td>
<td>36394.169</td>
</tr>
</tbody>
</table>

$B_0$ = 1331.323 (5) b, $D_0$ = 0.02826 (107)b, $eqQ$ = -4.242 (30), $eqQ$ = -4.12 (7) MHz.

a From Creswell, Winnewisser, Gerry (1976).
b Obtained from a least squares fit to the data of Ref. [12] and Ref. [5] and present data.
c From Alexander, Kroto, Walton (1976) Ref. [12].
d From Broten et al. (1976) Ref. [4].
Formation of Cyanopolyynes in Gas Discharges

Fig. 1. Recorder tracing of the $J = 4 \rightarrow 3$ transition of HC$_5$N produced by an electrical discharge.

(a) Medium resolution scan of the HC$_5$N near 10.6 GHz.
The vibrational satellite spectra arise mainly from the $v_{11}$ bending vibration.

(b) Comparison between the $J = 4 \rightarrow 3$ transitions of HC$_3$N and HC$_5$N in the vibrational ground state. The HC$_5$N spectrum was obtained by frequency doubling.

Recently, Vasile and Smolinsky [13] examined the basic ion chemistry of an acetylene discharge at slightly higher pressures (0.4 Torr) than ours using mass spectrometry. They conclude that the larger acetylene molecules are obtained by ionic condensation reactions which may be summarized by a reaction sequence of the form

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_4^+$$

followed by $C_4H_2^+ + C_2H_2 \rightarrow C_6H_y^+$ with $x, y = 2, 3, 4, \ldots$. These reactions are quite analogue to both the reactions held responsible for producing the longer cyanopolyynes in our laboratory experiment and to the reaction scheme put forward by Churchwell et al. for the interstellar formation of cyanopolyynes [5].

Thus it seems likely that C$_2$H$_2$ and HCN are principally involved in the interstellar formation of HC$_3$N and the cyanopolyynes. This is reinforced by the detection of circumstellar acetylene, HCCH and methane CH$_4$ in the expanding envelope of IRC +10216 through infrared techniques [14, 15]. It is interesting to note that C$_3$N and C$_4$H are also constituents of the same envelope [16, 17] in which HCN had been observed earlier and where HC$_5$N and HC$_7$N have been detected very recently.

Quite in contrast Turner and Zuckerman [18] did not detect HCN ($J = 1 \rightarrow 0$) in TMC 1, which indicates that in this source the cyanopolyynes are more abundant than HCN. Presumably HCN has been reacted into cyanopolyynes and other molecules.

Although our present laboratory experiments lend some support to the ion-molecule reaction scheme in producing interstellar cyanopolyynes, laboratory catalytic surface reactions by Anders et al. [19] show that straight hydrocarbon chains are produced efficiently on surfaces as well. In this context we may note that Haberkorn et al. [20] try to explain the varying $^{13}$C/$^{12}$C ratios in HC$_3$N [7] by surface formation of interstellar cyanoacetylene on dust grains.