Mass Spectral Fragmentation Pattern of trans-1,2-Di-(3-pyridyl)ethylene and trans-1,2-Di(4-pyridyl)ethylene

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Mass Spectra, trans-1,2-Di(3-pyridyl)ethylene, trans-1,2-Di-(4-pyridyl)ethylene

The mass spectral fragmentation patterns of trans-1,2-di-(3-pyridyl)ethylene and trans-1,2-di-(4-pyridyl)ethylene obtained on electron impact have been elucidated. They are more complex than the disintegration pathway observed with trans-1,2-di-(2-pyridyl)ethylene.

The mass spectrum of stilbene (1) has attracted considerable interest. It is dominated by the peaks due to the molecular ion at mass 180, which is the base peak and the dehydrogenated species M-1 (85%) and M-2 (50%). The principal initial fragmentation routes involve the unusual loss of CH$_3^+$ from the molecular ion to give a peak at mass 165 (40%) and loss of C$_2$H$_2$ from the M-2 species to give a peak at mass 152 (10%).

We recently reported the mass spectral fragmentation pattern of trans-1,2-di-(2-pyridyl)ethylene (2). In this case the base peak was due to the (M-1)$^+$ ion, the M$^+$ ion giving rise to a peak of 36% of the intensity of the base peak. The principal fragmentation routes involved loss of HCN from the M-1 ion to afford a C$_8$H$_8$N$^+$ ion at mass 154 (9%) and rupture of one of the pyridyl-CH bonds to afford peaks at mass 104 due to the C$_7$H$_6$N$^+$ ion (10%) and at mass 78 due to the C$_5$H$_4$N$^+$ ion (14%). The loss of CH$_3^+$ was not a significant disintegration pathway. We have now extended this study to an analysis of the fragmentation pathways of trans-1,2-di-(3-pyridyl)ethylene (3) and trans-1,2-di-(4-pyridyl)ethylene (4). The mass spectrum of 4 has been briefly recorded but no high resolution mass measurements were reported.

The mass spectrum of trans-1,2-di-(3-pyridyl)ethylene (3) (Fig. 1) is quite different from that of trans-1,2-di-(2-pyridyl)ethylene (2)$^{13}$ and is more complex. Unlike 2, the base peak in the spectrum of 3 is due to the molecular ion at mass 182. The M-1 ion at mass 181 gives rise to a peak of 52% of the intensity of the base peak. Like 2, however, and in contrast to the fragmentation of stilbene, the loss of CH$_3^+$ from the molecular ion of 3 is a very minor fragmentation pathway. It produces a small peak (1%) at mass 167 due to a C$_{11}$H$_7$N$_2^+$ ion.

Another minor fragmentation route (Scheme 1) from the molecular ion of 3 involves loss of the elements C$_2$H$_2$ to afford a species of formula

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C_{10}H_{7}N_{2}® at mass 155 (4%) presumably a bipyridyl molecular ion less one hydrogen. This species is also formed by the loss of C_{2}H_{2} from the M-1 ion of 3 at mass 181. Metastable transitions for the fragmentations 182 → 155 and 181 → 155 were present. The analogous losses of C_{2}H_{2} and C_{3}H_{2} were not observed to any significant extent in the disintegration of 1,2-di-(2-pyridyl)ethylene (2)\textsuperscript{15}. The subsequent fragmentation of the C_{10}H_{7}N_{2}® ion at mass 155 involves loss of HCN. This accounts in part for the peak at mass 128 (4%) due to a C_{6}H_{4}N® ion considered to be the isoquinoline molecular ion less one hydrogen. A metastable peak for the transition 155 → 128 was observed. The C_{10}H_{7}N_{2}® ion may also lose C_{4}H_{3}® and this fragmentation route might account for the major component of the peak at mass 154 (5%) due to a C_{6}H_{4}N®- species. No metastable corresponding to the transition 155 → 104 was however observed.

The principal fragmentation route from the molecular ion of 3 involves loss of HCN from the M-1 ion at mass 181. This gives rise to a strong peak (40%) at mass 154 due to a C_{11}H_{8}N® ion probably the 3-phenylpyridine molecular ion less one hydrogen. Loss of hydrogen from the C_{11}H_{8}N® ion accounts for the small peaks at mass 153 (3%; C_{11}H_{7}N®), and 152 (1%; C_{11}H_{6}N®). A strong metastable peak is present corresponding to the 181 → 154 transition. The loss of HCN from the C_{11}H_{6}N® ion, for which a metastable is observed, accounts for the major component of the peak at mass 127 (5%; C_{10}H_{5}®) and further loss of H® for the peak at mass 126 (3%; C_{10}H_{4}®). The C_{11}H_{6}N® ion also loses C_{2}H_{2} and this disintegration provides another source of the C_{9}H_{4}N® ion at mass 128.

The small peak at mass 130 (2%) is due to a C_{9}H_{5}N® ion probably formed from the molecular ion of 3 by loss of \(\text{CH} = \text{CH-CN}\) although no metastable for the transition 182 → 130 was observed. The C_{9}H_{5}N® ion is depicted as the isoquinolinium ion. Likewise the C_{9}H_{5}N® species at mass 129 (4%), considered to be the isoquinoline molecular ion, may be formed by loss of the same elements (C_{9}H_{2}N) from the M-1 ion of 3 at mass 181.

The minor component of the peak at mass 104, due to a C_{7}H_{4}N® ion (1%), is presumably formed by rupture of one of the CH-pyridyl bonds of 3. This fragmentation route from 3 is very much less pronounced than the similar bond rupture observed
with trans-1,2-di-(2-pyridyl)ethylene (2). The other component of the central bond rupture of 3, the C₅H₄N²⁺ ion at mass 78, is also present only in small amounts (2%). In contrast the C₅H₄N⁺ ion gave rise to a prominent peak in the spectrum of 2.

The peaks at mass 103 (2%; C₅H₃N⁺), 102 (5%; C₅H₄N⁺), 102 (2%; C₅H₂N⁺) and 101 (3%; C₅H₂⁺) in the spectrum of 3 are typical of those observed from the fragmentation of isoquinoline derivatives. Likewise the peaks below a mass of 100 are largely those to be expected from pyridine and benzene derivatives and require no comment.

The empirical formulae of the ions obtained by high resolution mass measurements are given in Table I. Fragmentation pathways where the appropriate metastable transitions were observed are denoted in the Schemes by an asterisk.

The spectrum of trans-1,2-di-(4-pyridyl)ethylene (4) (Fig. 2) is very similar to that of trans-1,2-di-(3-pyridyl)ethylene (3) but is quite different from that of trans-1,2-di-(2-pyridyl)ethylene (2). There are, however, a few differences between the fragmentation patterns of 3 and 4 (Scheme 2). The most striking difference is that the base peak in the spectrum of 4 is due to the M-1 ion at mass 181. The M⁺ ion at mass 182 gives rise to a peak of 90% of the intensity of the base peak. There is also significant loss of CH₃⁺ from the molecular ion of 4. The peak at mass 155 is much more pronounced in 4 than in 3. In the spectrum of 4 it is made up of contributions from a C₁₁H₉N⁺ ion (12%), presumably the 4-phenylpyridine molecular ion as well as the C₁₀H₇N⁺ (3%) ion observed in the spectrum of 3. There is a cluster of small peaks (1-2%) at mass 142, 141 and 140 in the spectrum of 4. These arise from the loss of C₈H₇⁻ from the molecular ion of 4 giving a C₁₀H₈N⁺ ion at mass 142 followed by loss of hydrogen. This disintegration route is known to occur in both pyridine and 4,4'-bipyridine but is scarcely present in the case of 3. Another minor difference between the spectra of 3 and 4 is in the composition of the peak at mass 128. In 4 a substantial contribution to this peak comes from a C₁₀H₈N⁺ species (4%), depicted as the naphthalene molecular ion, formed by loss of HCN from the C₁₁H₉N⁺ species at mass 155. The major component of this peak is, however, due to the C₅H₄N⁺ ion (7%) as in the spectrum of 3.

### Experimental

The spectra were determined with an A. E. I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was 100 °C. Elemental compositions were obtained by the peak matching method.

trans-1,2-Di-(3-pyridyl)ethylene and trans-1,2-di-(4-pyridyl)ethylene were analytically pure.

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Table I. Empirical formula of fragment ions*.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (formula)</th>
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<tbody>
<tr>
<td>3</td>
<td>167 (C₁₀H₇N₂); 155 (C₁₀H₇N₂); 154 (C₁₀H₇N); 152 (C₁₀H₈N); 130 (C₁₀H₈N); 129 (C₁₀H₈N); 128 (C₁₀H₇N); 127 (5%; C₁₀H₇N); 126 (C₁₀H₆N); 104 (1%; C₅H₄N); 102 (5%; C₈H₇N); 91 (M⁺); 90 (C₅H₄N); 89 (C₇H₅); 88 (C₇H₆); 87 (C₇H₇).</td>
</tr>
<tr>
<td>4</td>
<td>155 (12%; C₁₁H₉N); 155 (3%; C₁₀H₇N₂); 154 (C₁₀H₈N); 153 (C₁₀H₇N); 152 (C₁₀H₆N); 142 (C₁₀H₆N); 141 (C₁₀H₇N); 140 (C₁₀H₆N); 129 (C₁₀H₆N); 128 (7%; C₈H₇N); 128 (4%; C₁₀H₈); 127 (11%; C₁₀H₇); 127 (1%; C₈H₇N); 126 (C₁₀H₆); 104 (2%; C₅H₄N); 104 (2%; C₅H₄N); 103 (C₅H₄N); 102 (4%; C₅H₄); 102 (1%; C₅H₄N); 101 (C₅H₄); 100 (1%; C₅H₄); 100 (1%; C₅H₄N); 99 (1%; C₅H₄); 99 (1%; C₅H₄N); 91 (M⁺); 90 (C₅H₄N); 89 (C₇H₅); 88 (C₇H₆); 87 (C₇H₇).</td>
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* Only peaks above mass 80 and ≥ 1% of base peak in intensity are recorded.
Scheme 2