

## Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part VII 2,2'-Dithiodipyridine

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The mass spectral fragmentation of 2,2'-dithiodipyridine involves loss of the elements S, SH and S<sub>2</sub> from the molecular ion in addition to rupture of the central bonds. Molecular rearrangements accompany the disintegration.

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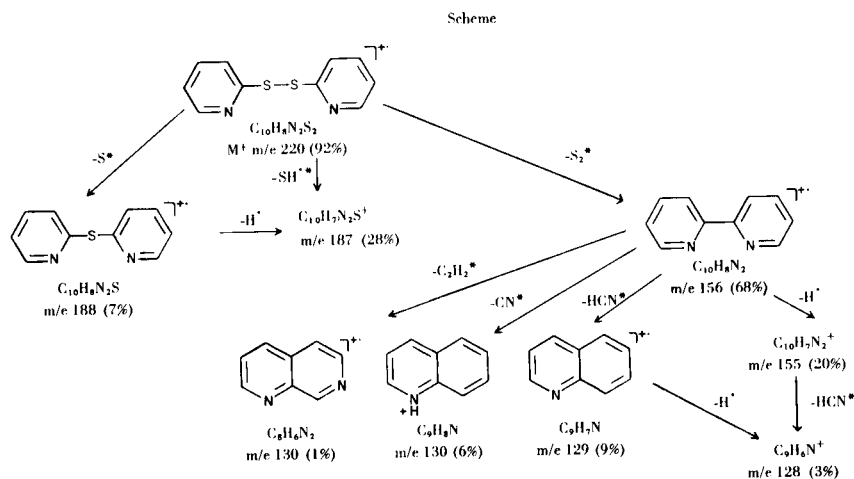
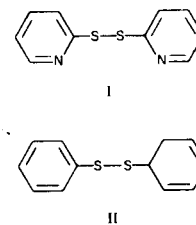
We have recently been interested in the molecular rearrangements which accompany the fragmentation on electron impact of relatives of 2,2'-bipyridyl containing an atom or group placed between the pyridine rings. So far we have reported the fragmentation patterns of di-2-pyridyl ketone (1), 2,2'-oxydipyridine (2) and 2,2'-thiodipyridine (3). The disintegration pathways in these cases show considerable differences from those of the diaryl analogues, benzophenone, diphenyl ether and diphenyl sulphide. We now report the mass spectrum of 2,2'-dithiodipyridine (1).

The mass spectrum of diphenyl disulphide (II) has been the subject of some interest (4-9). The base peak in the spectrum of (II) (5) is due to the molecular ion at mass 218. Peaks (less than 20%) at mass 186, 185 and 154 are due to loss of the elements S, HS and S<sub>2</sub> respectively from the molecular ion while the peak at mass 109 (60%), due to the C<sub>6</sub>H<sub>5</sub>S<sup>+</sup> ion, and those at lower mass originate

mainly from the rupture of the central bonds with the formation of two fragments.

Unlike the spectrum of diphenyl disulphide (II) (5) the base peak in the spectrum of 2,2'-dithiodipyridine (I) is not that due to the molecular ion. The base peak is at mass 78 and is due to the species of empirical formula C<sub>5</sub>H<sub>4</sub>N.

The molecular ion at mass 220 gives rise to a peak of about 92% of the intensity of the base peak. Unlike the spectrum of 2,2'-thiodipyridine (3), where the base peak



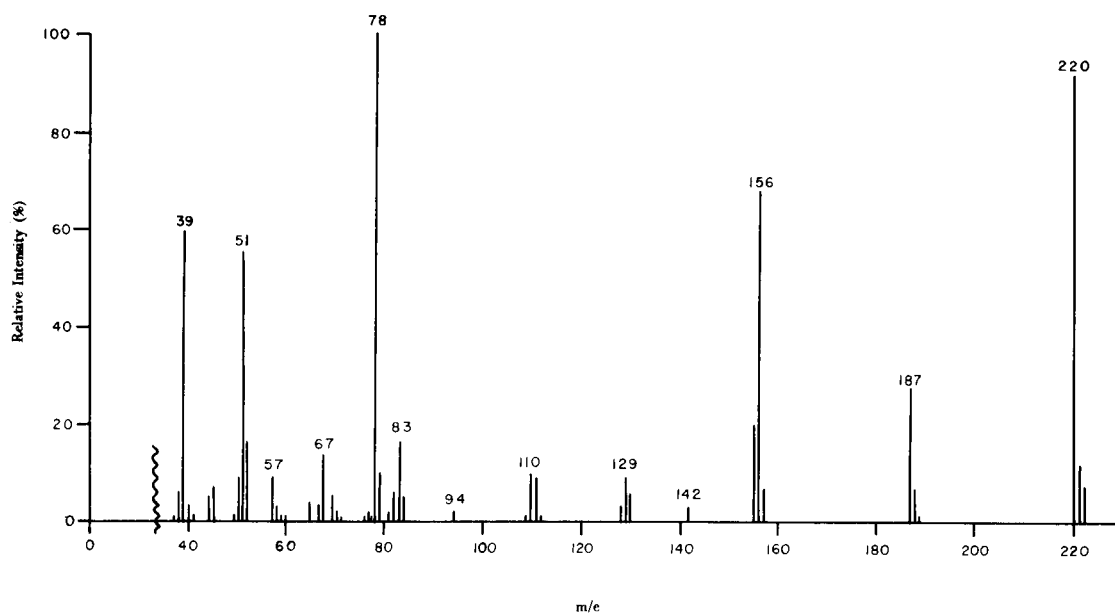


Figure: Mass Spectrum of 2,2'-Dithiodipyridine.

is due to the M-1 ion, there is no prominent peak in the spectrum of 2,2'-dithiodipyridine corresponding to the M-1 ion.

Table I  
High Resolution Data for 2,2'-Dithiodipyridine

m/e	Elemental Composition	Observed Mass	Calculated Mass
188	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S	188.0407	188.0408
187	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> S	187.0331	187.0330
156	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	156.0687	156.0687
155	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	155.0611	155.0609
142	C <sub>5</sub> H <sub>4</sub> NS <sub>2</sub>	141.9786	141.9785
130	C <sub>9</sub> H <sub>8</sub> N (6%)	130.0655	130.0657
130	C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> (1%)	130.0532	130.0531
129	C <sub>9</sub> H <sub>7</sub> N	129.0578	129.0578
128	C <sub>9</sub> H <sub>6</sub> N	128.0500	128.0500
111	C <sub>5</sub> H <sub>5</sub> NS	111.0143	111.0143
110	C <sub>5</sub> H <sub>4</sub> NS	110.0065	110.0064
109	C <sub>5</sub> H <sub>3</sub> NS	108.9987	108.9986
84	C <sub>4</sub> H <sub>4</sub> S (2%)	84.0034	84.0034
84	C <sub>3</sub> H <sub>2</sub> NS (5%)	84.9908	84.9908
83	C <sub>4</sub> H <sub>3</sub> S (16%)	82.9956	82.9955
83	C <sub>3</sub> HNS (2%)	82.9827	82.9830
82	C <sub>4</sub> H <sub>2</sub> S	81.9880	81.9877
81	C <sub>4</sub> HS	80.9799	80.9799
79	C <sub>5</sub> H <sub>5</sub> N	79.0422	79.0422
78	C <sub>5</sub> H <sub>4</sub> N	78.0343	78.0344
77	C <sub>5</sub> H <sub>3</sub> N	77.0265	77.0265
69	C <sub>3</sub> HS	68.9799	68.9799

The initial fragmentation of the molecular ion of 2,2'-dithiodipyridine follows four different pathways. One route involves loss of S to form a species of empirical formula C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>S at mass 188 (7%) almost certainly due to the 2,2'-thiodipyridine molecular ion (*cf.* 3). This species may lose H<sup>+</sup> to form the C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>S<sup>+</sup> ion at mass 187 (28%). A second fragmentation route from the molecular ion of 2,2'-dithiodipyridine involves the loss of SH<sup>+</sup>. This gives rise to the same species, namely the C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>S<sup>+</sup> ion at mass 187 depicted as the M-1 ion of 2,2'-thiodipyridine. Two metastable transitions corresponding to the loss of 32 (S) and 33 (SH) mass units from the molecular ion of 2,2'-dithiodipyridine at mass 220 were observed.

A third fragmentation pathway from the molecular ion of 2,2'-dithiodipyridine gives rise to a strong peak at mass 156 (68%) of empirical formula C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> by loss of S<sub>2</sub>. A strong metastable peak is present corresponding to the transition 220 → 156. The species at mass 156 is considered to be due to the 2,2'-bipyridyl molecular ion. It may lose H<sup>+</sup> to form the M-1 ion of 2,2'-bipyridyl (C<sub>10</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup>) at mass 155 (20%). The subsequent fragmentation of the C<sub>10</sub>H<sub>8</sub>N<sub>2</sub><sup>+</sup> and C<sub>10</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup> ions is the same as that already reported for the disintegration of 2,2'-bipyridyl and its M-1 ion (10). This fragmentation produces the peaks (3-9%) at mass 130 (C<sub>9</sub>H<sub>8</sub>N<sup>+</sup> and C<sub>8</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>), 129 (C<sub>9</sub>H<sub>7</sub>N<sup>+</sup>) and 128 (C<sub>9</sub>H<sub>6</sub>N<sup>+</sup>) by loss of CN<sup>+</sup>, C<sub>2</sub>H<sub>2</sub> and HCN as shown in the Scheme. Metastables were observed for most of these transitions.

Table II  
Metastable Ions

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S	220 → 188	160.7	160.7	S
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> S	220 → 187	158.9	158.9	SH
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	220 → 156	110.6	110.6	S
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>9</sub> H <sub>8</sub> N	156 → 130	108.4	108.3	CN
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>8</sub> H <sub>6</sub> N <sub>2</sub>	156 → 130	108.4	108.3	C <sub>2</sub> H <sub>2</sub>
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>9</sub> H <sub>7</sub> N	156 → 129	106.8	106.7	HCN
C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>9</sub> H <sub>6</sub> N	155 → 128	105.8	105.8	HCN

The fourth fragmentation pathway from the molecular ion of 2,2'-dithiodipyridine involves rupture of the central bonds. As in the disintegration routes already described for 2,2'-oxydipyridine (2) and 2,2'-thiodipyridine (3), hydrogen migrations sometimes accompany the rupture of the central bonds. These processes account, at least in part, for the peaks at mass 142 (3%; C<sub>5</sub>H<sub>4</sub>NS<sub>2</sub><sup>+</sup>), 111 (9%; C<sub>5</sub>H<sub>5</sub>NS<sup>+</sup>), 110 (10%; C<sub>5</sub>H<sub>4</sub>NS<sup>+</sup>), 109 (1%; C<sub>5</sub>H<sub>3</sub>NS<sup>+</sup>), 79 (10%; C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>), 78 (100%; C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>) and 77 (1%; C<sub>5</sub>H<sub>3</sub>N<sup>+</sup>). Contributions to the C<sub>5</sub>H<sub>5</sub>NS<sup>+</sup>, C<sub>5</sub>H<sub>4</sub>NS<sup>+</sup>, C<sub>5</sub>H<sub>3</sub>NS<sup>+</sup>, C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>, C<sub>5</sub>H<sub>4</sub>N<sup>+</sup> and C<sub>5</sub>H<sub>3</sub>N<sup>+</sup> ions also come from rupture of the central bond of 2,2'-thiodipyridine at mass 188 (3). Furthermore contributions to the base peak at mass 78 (C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>) will eventuate from the rupture of the central bond of 2,2'-bipyridyl at mass 156 (10) and from the M<sup>++</sup> ion of 2,2'-bipyridyl (10).

The peak at mass 94 is due to the M<sup>++</sup> ion of 2,2'-thiodipyridine (3). Contributions to the peak at mass 110 (C<sub>5</sub>H<sub>4</sub>NS<sup>+</sup>) come also from the M<sup>++</sup> ion of 2,2'-dithiodipyridine.

The peaks (2-16%) at mass 84 (C<sub>4</sub>H<sub>4</sub>S<sup>+</sup> and C<sub>3</sub>H<sub>2</sub>NS<sup>+</sup>), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup> and C<sub>3</sub>HNS<sup>+</sup>), 82 (C<sub>4</sub>H<sub>2</sub>S<sup>+</sup>) and 81 (C<sub>4</sub>HS<sup>+</sup>) are formed from higher mass species in a similar way to that already described for 2,2'-thiodipyridine (3).

Peaks below a mass of 75 require little comment. They are analogous to those reported in the spectrum of 2,2'-thiodipyridine (3) or are the fragments to be expected from the disintegration of pyridine derivatives. The peak at mass 69 is due to a C<sub>3</sub>HS<sup>+</sup> species.

The elemental composition of the ions from the fragmentation of 2,2'-dithiodipyridine are given in Table I and the metastable transitions of importance in elucidating the disintegration pathways in Table II.

#### EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionizing current of 70 eV. The ion source temperature was 60°. Elemental compositions were obtained by the peak matching method.

2,2'-Dithiodipyridine was analytically pure.

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