

## Mass Spectra of Benzo-2,1,3-thiadiazoles

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The mass spectra of a number of benzo-2,1,3-thiadiazoles are reported and discussed. In most cases they exhibit molecular ions of very great abundance. The fragmentation of substituents is more important than fragmentation of the ring system, except for hydroxy- and alkoxy-substituted compounds.

As a continuation of our studies on the mass spectra of different types of organo-sulfur compounds<sup>1,2</sup> and to examine whether processes analogous to the benzyne formation postulated for benzo-2,1,3-selenodiazoles<sup>3</sup> were important, we have now investigated some benzo-2,1,3-thiadiazoles. Although the mass spectra of the isomeric 1,2,3-thiadiazoles<sup>4,5</sup> and the benzo-1,2,3-thiadiazole<sup>6</sup> have been reported and discussed, the mass spectrum of benzo-2,1,3-thiadiazole (*1*) has not been reported, except for the intensity of the  $M - 46$  ( $M - NS$ ) peak, which has been compared with the intensities of the analogous  $M - 30$  ( $M - NO$ ) and  $M - 28$  ( $M - N_2$ ) peaks from benzo-2,1,3-oxadiazole and benzo-1,2,3-triazole, respectively.<sup>6</sup> The abbreviated mass spectra of the benzo-2,1,3-thiadiazoles listed in Table 1 are given in Table 2.

### DISCUSSION

The mass spectrum (Fig. 1) of benzo-2,1,3-thiadiazole (*1*) displays the molecular ion as the base peak. The most important fragmentations are losses of H, HCN, and NS.

As expected, the halogen-substituted benzo-2,1,3-thiadiazoles (*2-8*) underwent stepwise loss of halogen atoms rather than fragmentation of the ring system, although peaks from  $M - NS$

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Table 1. Benzo-2,1,3-thiadiazoles (*1-35*).



No.	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>
1	H	H	H	H
2	Cl	H	H	H
3	H	Cl	H	H
4	Cl	H	H	Cl
5	Cl	Cl	H	Cl
6	Cl	Cl	Cl	Cl
7	F	Cl	H	Cl
8	Br	H	H	Br
9	CH <sub>2</sub> I	H	H	H
10	CH <sub>2</sub> Br	Cl	H	Cl
11	CH <sub>3</sub>	Cl	H	Cl
12	CH <sub>3</sub>	H	Cl	Cl
13	CH <sub>3</sub>	Cl	CH <sub>3</sub>	Cl
14	OH	H	H	H
15	H	OH	H	H
16	Cl	OH	H	H
17	OH	Cl	H	Cl
18	OCH <sub>3</sub>	H	H	H
19	H	OCH <sub>3</sub>	H	H
20	OCH <sub>3</sub>	H	H	Cl
21	Cl	OCH <sub>3</sub>	Cl	Cl
22	OCH <sub>2</sub> CH <sub>3</sub>	Cl	H	Cl
23	OC <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	H	Cl
24	NO <sub>2</sub>	H	H	H
25	H	NO <sub>2</sub>	H	H
26	NO <sub>2</sub>	Cl	H	H
27	NO <sub>2</sub>	Cl	H	Cl
28	NO <sub>2</sub>	Cl	Cl	NO <sub>2</sub>
29	NO <sub>2</sub>	Cl	NO <sub>2</sub>	Cl
30	NH <sub>2</sub>	NO <sub>2</sub>	H	Cl
31	NH <sub>2</sub>	NH <sub>2</sub>	H	H
32	H	SO <sub>2</sub> NH <sub>2</sub>	H	H
33	CHO	Cl	H	Cl

Table 2. Mass spectra of substituted benzo-2,1,3-thiadiazoles (1-36). Values of  $m/e$  are followed by intensity (%).

1.	138(2), 137(20), 136(100)[M] <sup>+</sup> , 135(8), 110(6), 109(15), 108(2), 104(2), 103(5), 96(3), 92(7), 90(15), 84(2), 83(5), 82(4), 78(6), 77(9), 76(4), 71(3), 70(8), 69(3), 68(11), 64(10), 63(5), 58(5), 52(10), 51(15), 50(10), 46(19), 45(37).	14.	154(5), 153(9), 152(100)[M] <sup>+</sup> , 125(13), 124(17), 97(10), 93(8), 91(3), 65(5), 64(5).
2.	172(39), 170(100)[M] <sup>+</sup> , 143(4), 135(22), 126(6), 124(17), 108(50), 103(39), 85(45), 76(6).	15.	154(6), 153(9), 152(100)[M] <sup>+</sup> , 125(5), 124(37), 120(4), 106(4), 97(18), 91(6), 81(6), 80(25), 71(9), 70(11), 68(8), 64(10), 53(9), 52(27), 51(12).
3.	172(37), 170(100)[M] <sup>+</sup> , 143(5), 135(18), 126(6), 124(18), 108(5), 103(4), 85(5), 76(6).	16.	190(8), 189(30), 188(43), 187(76), 186(100)-[M] <sup>+</sup> , 185(18), 184(8), 183(40), 182(8), 181(22), 166(8), 164(14), 160(12), 158(26), 155(12), 152(38), 150(8), 149(18), 145(6), 143(16), 136(12), 134(12), 123(18).
4.	208(16), 207(5), 206(69), 205(9), 204(100)-[M] <sup>+</sup> , 179(2), 177(2), 171(14), 169(31), 160(7), 158(12), 142(3), 134(5), 110(9), 104(4), 103(5), 98(2), 83(2), 77(2), 76(3).	17.	224(12), 223(5), 222(57), 221(7), 220(83)-[M] <sup>+</sup> , 218(16), 208(6), 206(19), 204(26), 194(8), 192(9), 183(15), 181(7), 168(9), 156(8), 136(10), 135(6), 120(6), 119(6), 110(6), 98(11), 78(56), 77(11), 74(38), 59(67), 52(9), 51(9), 50(7), 45(38), 41(9).
5.	244(5), 242(35), 241(9), 240(100), 239(8), 238(100)[M] <sup>+</sup> , 207(5), 205(22), 203(35), 196(3), 194(6), 192(7), 170(5), 168(11), 144(4), 142(5), 120(5), 119(6), 100(3), 98(3), 75(3), 74(5), 59(6).	18.	168(4), 167(9), 166(69) [M] <sup>+</sup> , 165(19), 161(5), 139(5), 138(6), 137(100), 136(19), 135(21), 125(2), 123(20), 109(5), 97(3), 96(4), 93(12), 83(2), 79(2), 77(2), 76(7), 75(2).
6.	280(2), 278(14), 276(51), 274(100), 272(72)-[M] <sup>+</sup> , 241(11), 239(30), 237(31), 230(4), 228(8), 226(6), 207(9), 205(11), 204(18), 202(27), 195(9), 193(8), 181(4), 179(5), 178(5), 176(7), 172(6), 170(7), 167(5), 158(6), 155(10), 146(8), 144(12), 135(9), 134(8), 132(15), 123(8), 121(9), 109(20), 100(24), 86(12), 85(12), 79(9), 74(15), 70(11), 62(11), 47(11), 46(13).	19.	168(10), 167(14), 166(100)[M] <sup>+</sup> , 151(17), 137(10), 136(33), 123(25), 109(4), 80(9).
7.	226(12), 225(6), 224(67), 223(8), 222(100)-[M] <sup>+</sup> , 189(10), 187(24), 178(3), 176(5), 166(3), 164(5), 155(4), 153(10), 143(6), 113(4), 111(4).	20.	202(29), 201(11), 200(75)[M] <sup>+</sup> , 199(11), 197(7), 187(32), 185(29), 183(16), 181(9), 173(34), 172(12), 171(100), 170(12), 159(12), 157(32), 152(11), 143(6), 137(8), 136(7), 135(10), 127(7), 111(6), 100(5), 98(4), 83(5), 76(8), 75(7), 73(6), 70(9), 64(16), 52(5), 51(13), 46(11), 45(10).
8.	297(5), 296(50), 295(8), 294(100), 292(50)[M] <sup>+</sup> , 250(1), 248(2), 246(1), 220(5), 218(7), 215(28), 213(27), 184(7), 148(5), 134(22), 108(3), 84(5), 51(9).	21.	274(9), 272(25), 271(6), 270(57), 269(13), 268(57)[M] <sup>+</sup> , 257(11), 255(33), 253(33), 229(11), 227(30), 225(30), 222(20), 221(12), 220(71), 219(24), 218(71), 217(21), 185(43), 184(17), 183(100), 182(7), 181(26), 166(18), 158(6), 157(7), 151(12), 149(11), 148(13), 137(6), 136(30), 135(13), 132(8), 124(8), 123(11), 110(9), 109(11), 108(7), 79(6), 76(8), 74(71), 70(13), 64(8), 59(100), 52(7), 51(100), 50(7), 46(14), 45(71), 44(14), 43(13), 41(29).
9.	276(5) [M] <sup>+</sup> , 151(6), 150(16), 149(100), 128(6), 127(12), 122(17), 105(7), 90(5), 64(8), 63(9), 55(6), 52(6), 51(5), 50(5), 46(7), 45(8).	22.	252(3), 250(14), 248(22)[M] <sup>+</sup> , 224(14), 223(6), 222(72), 221(9), 220(100), 206(7), 204(11), 169(5), 155(5), 98(5).
10.	296(-)[M] <sup>+</sup> , 221(20), 219(72), 218(14), 217(59), 216(13), 185(8), 184(45), 183(16), 182(100), 180(13), 166(15), 158(8), 156(8), 151(13), 149(13), 148(15), 147(8), 136(33), 135(12), 124(9), 123(12), 110(7), 109(10), 108(8), 88(7), 83(6), 78(7), 77(7), 76(12), 75(9), 70(7), 64(13), 51(12), 50(10), 46(11), 45(17), 44(10).	23.	309(8), 307(20)[M] <sup>+</sup> , 292(8), 290(10), 262(10), 260(6), 216(7), 214(16), 206(5), 204(8), 186(9), 170(5), 119(9), 118(6), 94(6), 93(100), 86(8), 77(40), 70(5), 65(49), 51(34).
11.	222(14), 221(8), 220(69), 219(14), 218(100)-[M] <sup>+</sup> , 217(17), 185(55), 184(14), 183(97), 182(7), 158(3), 156(6), 149(8), 148(8), 147(5), 124(5), 120(2), 109(5), 94(8).	24.	183(7), 182(9), 181(100)[M] <sup>+</sup> , 151(30), 136(5), 135(50), 123(24), 109(7), 108(23), 104(14), 91(7), 83(5), 82(5), 76(13), 75(5), 70(5), 64(20), 52(6), 51(6), 50(5), 46(5), 45(29).
12.	222(14), 221(8), 220(67), 219(17), 218(100)-[M] <sup>+</sup> , 217(11), 185(30), 184(10), 183(90), 182(5), 151(8), 148(10), 147(4), 124(5), 109(5).	25.	183(6), 182(6), 181(100) [M] <sup>+</sup> , 151(11), 136(4), 135(42), 123(22), 109(5), 108(22), 91(5), 83(5), 77(5), 76(8), 64(16), 50(6).
13.	236(13), 235(8), 234(75), 233(15), 232(100)-[M] <sup>+</sup> , 231(8), 199(32), 197(100), 187(12), 183(8), 162(8), 161(12), 152(8).	26.	220(6), 218(8), 217(35), 216(9), 215(100)[M] <sup>+</sup> , 204(5), 187(17), 185(50), 183(5), 181(7), 172(5), 171(7), 170(13), 169(20), 159(17), 142(10), 135(8), 134(25), 133(9), 125(5), 108(12), 107(6), 98(7), 89(5), 83(12), 76(10), 75(10), 70(17), 69(8), 64(9), 52(5), 51(7), 46(7), 45(7).
		27.	253(15), 252(11), 251(73), 250(10), 249(100)-[M] <sup>+</sup> , 233(5), 223(15), 222(13), 221(76),

Table 2. Continued.

	220(20), 219(83), 206(16), 205(11), 204(22), 203(19), 195(8), 193(43), 192(5), 171(10), 170(24), 169(12), 168(43), 161(13), 159(17), 158(5), 142(18), 133(12), 117(9), 101(12), 100(12), 98(16), 83(10), 75(15), 74(14), 70(20), 59(19), 46(14), 45(15), 44(12).
28.	298(14), 297(7), 296(63), 295(9), 294(100) [M] <sup>+</sup> , 248(5), 222(5), 220(8), 219(5), 206(9), 204(13), 202(9), 200(13), 186(5), 184(6), 172(8), 170(13), 169(6), 155(8), 136(7), 135(10), 134(8), 132(27), 123(9), 117(16), 109(10), 100(14), 99(16), 85(12), 83(11), 70(9), 46(11), 44(17).
29.	298(12), 297(5), 296(19), 295(7), 294(80) [M] <sup>+</sup> , 265(12), 263(17), 250(9), 248(13), 240(7), 238(7), 222(41), 221(7), 220(69), 218(11), 208(12), 206(40), 205(7), 204(51), 202(11), 201(28), 200(9), 199(78), 171(25), 169(21), 167(16), 155(13), 132(31), 117(11), 109(13), 79(20), 52(13), 44(39), 30(100).
30.	232(34), 231(10), 230(100) [M] <sup>+</sup> , 212(13), 202(14), 200(41), 186(27), 185(10), 184(70), 172(43), 171(9), 170(80), 152(14), 151(24), 150(40), 135(21), 124(16), 108(10), 103(10), 98(13), 94(11), 78(9), 77(19), 76(9), 70(11), 64(13), 63(11), 52(20), 51(14).
31.	166(100) [M] <sup>+</sup> , 165(16), 151(9), 149(9), 148(7), 139(6), 138(7), 136(27), 135(15), 134(9), 79(13), 64(9), 53(7), 52(11), 51(9), 50(6), 46(7), 45(9), 44(7).
32.	217(5), 216(5), 215(45) [M] <sup>+</sup> , 199(12), 153(6), 152(20), 151(100), 137(5), 136(7), 135(72), 124(13), 123(6), 109(9), 108(27), 103(15), 91(10), 83(11), 80(7), 77(10), 76(12), 75(11), 70(10), 69(9), 64(35), 52(13), 51(12), 50(17), 46(11), 45(12).
33.	234(18), 233(11), 232(29) [M] <sup>+</sup> , 231(12), 208(17), 207(8), 206(64), 205(16), 204(100), 203(10), 179(7), 177(11), 171(17), 170(11), 169(33), 168(20), 160(6), 158(7), 142(12), 110(11), 101(17), 100(12), 98(10), 75(21), 70(11).
34.	266(100), 264(100) [M] <sup>+</sup> , 222(5), 220(16), 218(16), 186(10), 185(67), 183(10), 158(13), 141(10), 133(7), 132(7), 114(13), 77(5), 76(7), 69(7), 51(5), 50(5).
35.	224(5), 223(13), 222(93), 221(34), 220(100) [M] <sup>+</sup> , 219(5), 193(4), 187(5), 186(9), 185(56), 184(7), 176(11), 174(20), 158(11), 153(11), 141(9), 128(5), 127(10), 114(10), 111(8), 110(20), 100(5), 75(5), 51(5), 50(5).

are present in all of the spectra with M-HCN and M-halogen-HCN often occurring.

The halomethyl compounds (9,10) have low molecular ion abundances with significant tropylium type ion peaks at M-halogen.<sup>7</sup> For the iodo compound the only other significant feature is the loss of HCN from this ion while for the

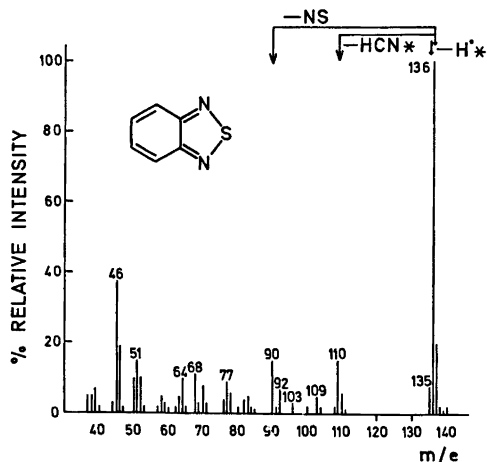


Fig. 1. Mass spectrum of benzo-2,1,3-thiadiazole (I).

bromo derivative Cl loss and Cl+NS loss from this tropylium type ion are significant.

The isomeric methyl benzo-2,1,3-thiadiazoles (11,12) yield virtually identical spectra which have high abundance molecular ions and M-Cl ion with small but significant M-Cl<sub>2</sub> ions. The methyl benzo-2,1,3-thiadiazole (13) with one more chlorine has identical characteristics.

The hydroxy isomers (14,15) have similar spectra with the loss of HCN, CO, and HCN+CO being significant.<sup>8</sup> The expulsion of carbon monoxide is more important when the hydroxyl is in the 5- than in the 4-position. Expulsion of carbon monoxide is important for the chlorinated hydroxy derivatives (16,17).

The difference between the mass spectra of the isomeric methoxy compounds (18,19) is interesting (Fig. 2). For both isomers loss of a methyl radical followed by expulsion of carbon monoxide is important as in the mass spectra of anisoles.<sup>9</sup> However, although the 5-methoxy compound expels formaldehyde from the molecular ion to give an intense peak (33 %) with a less significant loss of formyl radical (10 %), the 4-methoxy derivative displays the loss of formyl radical as the base peak with formaldehyde expulsion being less important (19 %). Intense metastables support these transitions in both spectra. Significantly the mass spectrum of the chloro-substituted 4-methoxy derivative (20) displays the loss of formyl radical as the base peak. Loss of methyl radical and carbon

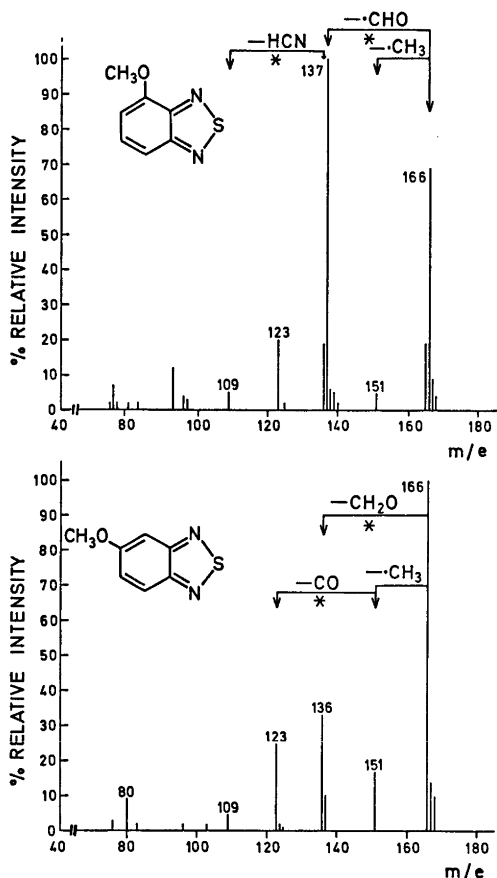


Fig. 2. Mass spectra of 4- and 5-methoxy benzo-2,1,3-thiadiazoles (18, 19).

monoxide is important for both chloro-substituted methoxy derivatives (20,21).

In the spectrum of 4-ethoxy-5,7-dichlorobenzo-2,1,3-thiadiazole (22), the ion giving rise to the base peak is found to be formed in the same way as in many phenetoles.<sup>10</sup> The fragmentation of the phenoxy ion dominates the spectrum of the phenoxy-substituted derivative (23).<sup>11</sup>

In the nitro-substituted benzo-2,1,3-thiadiazoles (24–29) a change in the position of the nitro group does not change the fragmentation pattern significantly. The spectra of the 4- and 5-nitro benzo-2,1,3-thiadiazoles (24,25) are practically identical. The only important fragmentations are of the nitro group.<sup>12</sup> In the amino-substituted compounds (30,31) the expected fragmentations of the amino group are found,<sup>13</sup>

although where a nitro group is present (30) its fragmentation dominates.

The fragmentation of the sulfonamide (32) is completely analogous to that of benzene sulfonamide.<sup>14</sup> That is, expulsion of the  $\text{NH}_2$  group gives a significant ion (12%) while further loss of SO affords the base peak. Expulsion of the  $\text{SO}_2\text{NH}_2$  from the molecular ion produces the second most abundant peak. Loss of carbon monoxide gives the base peak in the aldehyde (33) with further loss of chlorine radical producing a significant peak.<sup>15</sup>

The naphthalene derivatives (34,35) behave similarly. Loss of halogen and NS from the molecular ion base peaks produce the most significantly ions in the spectra.

## CONCLUSION

The dominating feature of the mass spectra of the benzo-2,1,3-thiadiazoles is that they almost all exhibit molecular ions of very great abundance (often the base peak as in the benzo-2,1,3-selenodiazoles<sup>3</sup>). The fragmentation of the ring system is far less important than fragmentation of the substituents. Thus it is often easy to deduce from the mass spectra the nature, but not the positions of the substituents except for the hydroxy- and alkoxy-benzo-2,1,3-thiadiazoles. Fragmentations analogous to the benzyne formation postulated for the benzo-2,1,3-selenodiazoles<sup>3</sup> are not found.

## EXPERIMENTAL

The benzo-2,1,3-thiadiazoles were synthesized in known ways.<sup>16,17</sup>

The mass spectra were determined on a GEC-AEI MS-902S double focusing mass spectrometer with ionizing potential of 70 eV and an accelerating potential of 8 kV. The compounds were introduced *via* the direct insertion probe at an inlet temperature of 150 °C.

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