Intramolecular Aromatic Substitution Reactions in Substituted *N,N*-Dimethylthiobenzamide Ions[†]

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The molecular ions of *N,N*-dimethylthiobenzamide and its *ortho* substituted derivatives (substituents CH_3, Cl, Br, I) lose a hydrogen atom and/or the *ortho* substituent. The mechanism of this process has been studied by measurements of the ionization energies, appearance energies of the product ions *m/z* 164 and the kinetic energy release during this process. The structure of the product ions *m/z* 164 and relevant reference ions have been investigated by mass analysed ion kinetic energy spectra, *B/E* linked scan spectra and collision induced decompositions. The results show clearly the formation of two different kinds of product ions *m/z* 164 depending on the substituent lost. Type a ions are formed by loss of a H atom or the CH_3 substituent and correspond to protonated 3,4-benzo-*N*-methylpyroline-2-thione. The formation of these ions occurs by a hydrogen rearrangement followed by an intramolecular substitution via a 5-membered cyclic intermediate and is associated with a large release of kinetic energy. In contrast, the loss of the halogeno substituents to give type b ions probably occurs via a direct displacement reaction by the sulfur atom of the thioamide group giving rise to Gaussian shaped peaks mass analysed ion kinetic energy spectra.

Recently we investigated the energetics and the kinetic energy release during intramolecular aromatic substitution reactions of molecular ions[1–5] and the influence of the leaving groups on these reactions. One important result was the observation of a correlation between the position of the transition state of the reaction on the reaction coordinate and the partitioning of the transition state energy between internal energy and kinetic energy of the reaction products according to the Hammond postulate. In the model reactions studied 5- and 6-membered rings are formed in the critical configurations of the substitution reactions. This variation of the ring size of the transition states had no clear effect on the energy partitioning and on the kinetic energy release. In each of the four reaction series most of the excess energy is released as kinetic energy if a strongly bonded leaving group is lost by an endothermic reaction with a 'late' transition state, while loss of a weakly bonded substituent by an exothermic reaction with an 'early' transition state results only in the release of a small portion of the excess energy as kinetic energy.[5] However, it has been shown that the kinetic energy release during a mass spectrometric fragmentation may depend on the ring size of a cyclic transition state; smaller rings corresponding to 'tight' transition states are expected to favour the release of a larger amount of the excess energy as kinetic energy of the products.[6] Hence, it was of interest to study an intramolecular aromatic substitution reaction via a 4-membered ring in the critical configuration of the molecular ions.

ortho Substituted *N,N*-dimethylbenzamides appeared at first to be suitable model compounds. Schwarz *et al.* have shown[7] that the *N,N*-dimethylbenzamide ions lose a hydrogen atom from the *ortho* position of the phenyl group and they postulated a 4-membered transition state for this reaction. However, although a Cl substituent is lost from the molecular ions of the corresponding *o*-chlorbenzamide the abundance of the $[M-Cl]^+$ ions is much less than that of the $[M-H]^+$ ions from the parent compound. Recently a more careful investigation of the formation of $[M-H]^+$ ions from the molecular ions of *N,N*-dimethylbenzamides and related compounds[9] revealed a more complicated multistep mechanism for this reaction, including a 5-membered transition state for the substitution step. These observations excluded the *N,N*-dimethylbenzamides as model compounds from this study.

Similarly to *N,N*-dimethylbenzamide a very large $[M-H]^+$ ion peak is observed in the 70 eV mass spectrum of *N,N*-dimethylthiobenzamide, which persists in the 15 eV spectrum. The hydrogen atom lost stems from the phenyl group and the mass spectra of *ortho* substituted derivatives (see below) show an abundant loss of this substituent from the molecular ions in contrast to the corresponding *N,N*-dimethylbenzamides. Hence, we expected that the loss of a hydrogen atom or of an *ortho* substituent, respectively, from the molecular ions of substituted *N,N*-dimethylthiobenzamides occurred via an intramolecular aromatic substitution reaction with a 4-membered cyclic transition state, the mechanism originally proposed for the analogous fragmentation of the benzamides.[7] In the course of our detailed study of the intramolecular substitution reactions of *ortho* substituted *N,N*-dimethylthiobenzamide ions reported in this paper however, (see below), it became obvious that the ion beam

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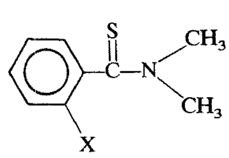
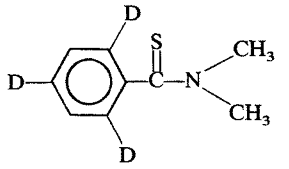
chemistry of these compounds is more complicated than expected and that although fragment ions of the *m*/*z* value expected for the products of the intramolecular aromatic substitution are formed with high abundances from all compounds, the course of the reaction and the structure of the product ions show an interesting dependence on the type of substituent lost.



X	
H	**1a**
CH_3	**1b**
Cl	**1c**
Br	**1d**
I	**1e**



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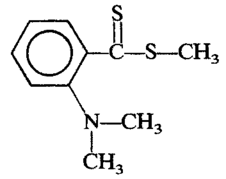

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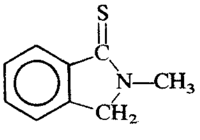

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RESULTS

Mass spectra

The 70 eV mass spectra of *N*,*N*-dimethylthiobenzamide (**1a**) and its *ortho* substituted derivatives **1b–1e** are given in Table 1. It has been shown previously[9] that the parent compound **1a** fragments by electron impact via two routes: (i) formation of a thiobenzoyl ion, *m*/*z* 121, by loss of the dimethylamino group, followed by elimination of a CS molecule to give *m*/*z* 77 ions, and (ii) formation of *m*/*z* 164 by loss of a H atom from the phenyl ring. The *m*/*z* 164 ions decompose further by loss of a ˙SH radical (ions *m*/*z* 131) and to some extent by loss of a molecule $CH_2{=}N{-}CH_3$ (ions *m*/*z* 121). The 15 eV mass spectrum of **1a** contains only a small peak at *m*/*z* 121 (4%) and a large peak at *m*/*z* 164 (65%) the base peak corresponding to the molecular ions. Hence from the two fragmentation routes of the molecular ions the loss of a H atom is energetically favoured.

N,*N*-dimethyl-2,4,6-trideuterobenzamide ions $[\mathbf{2}]^{+\cdot}$ generated by 70 eV electron impact lose 78% D and 22% H, the loss of D rising slightly to *c*. 82% at 15 eV. At the same time an isotope effect k_H/k_D of about 2 is observed. It is not clear whether there is a small contribution from loss of a H atom by one of the *N*-methyl groups to *m*/*z* 164 ions or whether the H and D atoms at the trideuterophenyl group lose their positional identity to some extent before the fragmentation. Nevertheless, no exchange occurs between H atoms in the phenyl ring and in the *N*-methyl groups because the $[C_6H_5]^+$ ion peak *m*/*z* 77 is completely shifted to *m*/*z* 80 in the mass spectrum of the trideutero compound.

Table 1. Partial 70 eV electron impact mass spectra of substituted *N*,*N*-dimethylthiobenzamides

m/z	1a	1b	1c	1d	1e
$[M]^{+\cdot}$	79	99	131[a]	38[a]	24
$[M-H]^+$	100	62	80[a]	5[a]	1
$[M-H_2S]^{+\cdot}$	40	25	12[a]	—	—
$[M-N(CH_3)_2]^+$	100	100	137[a]	29[a]	8
165	(M)	6	12	12	11
164	[b]	47	87	100	100
150	2	1	1	1	2
149	1	2	8	11	18
148	1	3	5	4	7
136	—	12	—	—	—
135	3	[d]	3	—	—
134	2	59	2	3	5
132	7	12	3	1	—
131	[c]	50	31	9	5
123	5	3	2	1	1
122	10	1	—	3	5
121	[d]	7	17	17	31
120	2	1	19	17	18
118	7	5	—	—	—
117	3	7	2	2	5
116	4	14	4	3	4
108	4	4	5	3	3
104	8	4	1	1	1
103	4	6	1	2	2
102	1	5	9	4	2
93	3	3	7	3	5
92	3	6	1	—	—
91	13	63	10	3	3
90	3	15	4	3	5
89	6	24	7	3	3
78	8	4	2	4	10
77	55	15	12	8	16
76	5	4	9	7	9
75	4	4	24	7	7
74	12	16	51	11	3
69	10	9	14	6	9
63	6	14	7	4	5
52	3	3	—	16	55
51	27	12	10	11	31
50	10	6	10	10	26
49	2	1	1	1	5
47	5	4	8	3	2
45	8	13	11	4	6
44	26	13	19	5	3
43	2	2	4	1	1
42	12	11	22	8	8
41	2	4	2	1	1
40	1	1	1	1	1
39	10	18	8	7	13
38	3	3	2	2	5
37	2	1	2	1	6

[a] Sum of isotope peaks $^{35}Cl/^{37}Cl$ or $^{79}Br/^{81}Br$.
[b] $[M-H]^+$.
[c] $[M-H_2S]^{+\cdot}$.
[d] $[M-N(CH_3)_2]^+$.

The two fragmentation routes are also observed for the decomposition of the molecular ions of **1b–1e**.[10] The *ortho* substituted thiobenzoyl ions (and their fragmentation products) still carry a large fraction of the total ion current in the mass spectra of the methyl and chloro substituted derivatives **1b** and **1c**, but are of much lower abundance for the bromo and iodo derivatives **1d** and **1e**, respectively. The other fragmentation route gives rise to $[M-H]^+$ ions *and* $[M-CH_3]^+$ or $[M-Cl]^+$ ions, respectively, in the mass spectra of **1b** and **1c** with comparable abundances. Obviously the elimination of a H atom and of the *ortho* substituent can compete with each other during the fragmentation of **1b** and **1c** ions. In contrast the molecular ions of **1d** and **1e** greatly favour the elimination of the *ortho* substituents Br and I, respectively, with the peaks of the resulting m/z 164 ions dominating the spectra. Interestingly, one observes also a variation in the intensity distribution between the product ions m/z 149, m/z 131, m/z 121 and m/z 120 from the further fragmentation of m/z 164 ions in the series **1a**–**1e**. The loss of a methyl group to give m/z 149 ions (see below) is not important for m/z 164 ions formed from **1a** and **1b**, but increases steadily for **1c**, **1d** and **1e**. Similarly, the formation of m/z 121 ions and m/z 120 ions corresponding to the thiobenzoyl ion $[C_7H_5S]^+$ and an ion $[C_7H_4S]^{+\cdot}$, respectively, is only observed for m/z 164 ions from **1c**–**1e**. On the other hand, the elimination of a SH radical from m/z 164 ions to give m/z 131 ions occurs with a large intensity only for m/z 164 ions from **1a**–**1c**, and the intensity of the m/z 131 peak decreases in the mass spectra of **1d** and **1e** in spite of an increase in the intensity of the m/z 164 ions. This hints at different reaction mechanisms for the formation of m/z 164 ions in the series **1a**–**1e**, which results in m/z 164 ions of different internal energies or of different structures.

Energy data for the formation of *m/z* 164 ions

The ionization energies (I(M)) of **1a**–**1e** and the appearance energies ($A(m/z$ 164)) of m/z 164 ions in the mass spectra of these compounds are listed in Table 2, together with relevant thermochemical data. I(M) and $A(m/z$ 166) from the trideuterated derivative **2** are also included. The I(M) of **1a** (and **2**) is only influenced slightly by the substituents in **1b**–**1e**, as expected. The appearance energies for the $[M-H]^+$ ions (m/z 164) from **1a** and the $[M-D]^+$ ions (m/z 166) from **2**, respectively, are not significantly different. Therefore, if the $[M-H]^+$ ions in the mass spectrum of **2** are formed by a process competing with the elimination of a D atom, this process probably has a higher appearance energy. The value of $A(m/z$ 164) for **1b** is slightly lower than for **1a** and **2**, but the activation energy $\varepsilon_{f\neq}$ for the formation of m/z 164 ions from the molecular ions is the same for the compounds **1a** and **1b**, and corresponds to the activation energy of $[M-D]^+$ ions m/z 166 from **2**. In the case of the three halogeno derivatives $A(m/z$ 164) and $\varepsilon_{f\neq}$ are larger for the chloro compound **1e**, while $\varepsilon_f^{\neq}$ for the bromo compound **1d** is slightly smaller and $\varepsilon_f^{\neq}$ for the iodo compound **1e** distinctly smaller than for **1a**, due to a decrease in $A(m/z$ 164). Thus, in contrast to intramolecular aromatic substitution reactions with 5- and 6-membered transition states, which show either constant values[1,4,11] for $\varepsilon_{f\neq}$ or a linear decrease[2,3] with the dissociation energy of the bond to the leaving group, no simple correlation is observed in the case of **1a**–**1e**.

The *apparent* heat of formation $\Delta H_f'(m/z$ 164) including any excess energy $(\varepsilon^* + T_B)$ of the reaction products can be calculated from $A(m/z$ 164), and the heats of formation of the parent molecules M and neutral fragments X according to Eqn (1).

$$\begin{aligned}\Delta H_f'(m/z\ 164) &= \Delta H_f(m/z\ 164) + \varepsilon^* + T_B\\ &= A(m/z\ 164) + \Delta H_f(\mathrm{M}) - \Delta H_f(\mathrm{X})\end{aligned}$$

No experimental ΔH_f(M) values are available for compounds **1a**–**1e** and the ΔH_f(M)s have been calculated by Benson's group equivalent method,[12] using a value of +80.3 kJ mol^{-1} for the contribution of the CS group of a thioamide.[13] The values used for ΔH_f(M) and ΔH_f(X) and the resulting values of $\Delta H_f'(m/z$ 164) are listed in Table 2. In the series **1a**–**1e** $\Delta H_f'$ (m/z 164) is not constant, but values ranging from 817 to 952 kJ mol^{-1} are obtained. $\varepsilon_{f\neq}$ is neither constant nor linearly correlated to the dissociation energy of the leaving group X in the series **1a**–**1e** nor is any linear correlation observed between $\Delta H_f'(m/z$ 164) and the dissociation energy.[5] The mass analysed ion kinetic energy (MIKE) spectra of the molecular ions **1a**–**1e** all contain a large signal for the fragmentation to m/z 164 ions. The peak shapes of these signals are clearly different for $[\mathbf{1a}]^{+\cdot}$, $[\mathbf{1b}]^{+\cdot}$ and $[\mathbf{1c}]^{+\cdot}$, $[\mathbf{1d}]^{+\cdot}$, $[\mathbf{1e}]^{+\cdot}$, respectively. In the MIKE spectra of the former two molecular ions, broad and flat-topped or dish-topped signals are observed, while in the MIKE spectra of the other three molecular ions the formation of m/z 164 ions is associated with broad Gaussian shaped peaks (Fig. 1). It is obvious from these results, that the

Table 2. Ionization energies (*I*(M)), appearance energies of *m/z* 164 ions (*A*(*m/z* 164)) and thermochemical data of the fragmentation of substituted *N,N*-dimethylthiobenzamide ions

		1a	**1b**	**1c**	**1d**	**1e**	**2**
I(M)	(eV)	8.0	7.8	8.0	7.8	7.8	8.0
$A(m/z$ 164)	(eV)	9.4	9.3	9.7	9.1	8.8	9.5
$\varepsilon_{f\neq}$	(eV)	1.4	1.5	1.7	1.3	1.0	1.5
ΔH_f(M)	(kJ mol^{-1})	128	95	97	152	210	—
ΔH_f(X)	(kJ mol^{-1})	218	142	132	112	107	—
$\Delta H_f'(m/z$ 164)	(kJ mol^{-1})	817	850	911	918	952	—
T_B	(meV)	430	545	90	185	345	—
T_{22}/T_{50}	—	1.86	1.33	2.53	2.39	2.26	—
$\Delta H_f'(m/z\ 164)_{corr}$	(kJ mol^{-1})	776	797	902	900	918	—
ΔH_R^+	(kJ mol^{-1})	+68	+44	+153	+107	+44	—
$\varepsilon_{r\neq}$	(kJ mol^{-1})	+67	+100	+9	+18	+52	—

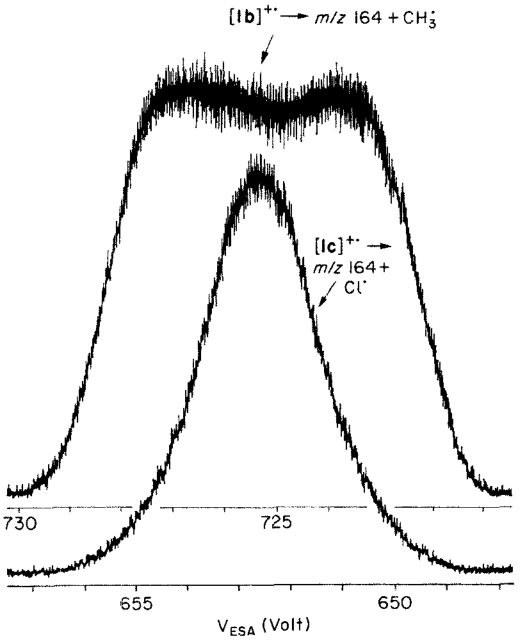


Figure 1. MIKE spectra of m/z 164 ion formation from **1b** and **1c**.

m/z 164 ions are formed by at least two different processes in the series **1a**–**1e**, which may either differ in the structure of the reaction products or exhibit a very different behaviour for partitioning of the transition state excess energy.

The maximum amount of kinetic energy, T_B, released during the fragmentation can be calculated[14] from the peak width at the base of the signals.[15] These values of T_B are used to correct the apparent heat of formation, $\Delta H_f'(m/z\ 164)$, and to approach the true heat of formation of the ion m/z 164. The values of $\Delta H_f'(m/z\ 164)_{corr}$ are listed in Table 2 and it appears that two limiting values are obtained in this series of compounds at $\Delta H_f(m/z\ 164) \leq 776\ \text{kJ mol}^{-1}$ and at $\Delta H_f(m/z\ 164) \leq 900\ \text{kJ mol}^{-1}$, respectively. Thus, either m/z 164 ions of the same structure are formed throughout the series **1a**–**1e**, but a large amount in excess of $100\ \text{kJ mol}^{-1}$ remains as internal excess energy in the product ions during the loss of halogen substituents from **1c**, **1d** and **1e**, contrasting the loss of H and CH_3 from **1a** and **1b**, or more likely m/z 164 ions of different structures are formed by loss of the substituents from **1a**, **1b** and **1c**, **1d**, **1e** respectively.

Metastable ion spectra of the *m/z* 164 ions

The *metastable ion* (MI) spectra of m/z 164 ions from **1a**–**1e** listed in Tables 3 and 4, respectively, have been obtained by the linked scan B/E technique[16] from decompositions in the first field free region preceding the magnetic field and by the direct analysis of daughter ion (DADI) technique[17] from decompositions in the second field free region preceding the electrostatic analyser of a VG ZAB-2F mass spectrometer. It is clearly seen that two different m/z 164 species are generated from **1a**–**1e** by loss of the *ortho* substituent.

Table 3. Linked scan *B/E* spectra of *m/z* 164 ions from *N,N*-dimethylthiobenzamides (70 eV)

m/z	**1a** X=H	**1b** CH_3	**1c** Cl	**1d** Br	**1e** I	**2**[a]	e	c
163	2	5	4	1	1	5	—	8
149	2	2	39	100	100	1	1	5
135	3	4	3	1	1	3	6	—
131	100	100	100	21	7	100[b]	100	100
123	1	4	1	1	1	—	—	4
121	1	1	5	10	10	—	2	—
118	—	—	—	—	—	—	—	12
91	1	1	1	1	1	1	1	—

[a] m/z 166 (≙$[M-D]^+$), all m/z values are shifted by 2 u.
[b] m/z 132 6%.

Table 4. MIKE spectra of *m/z* 164 ions from *N,N*-dimethylthiobenzamides (70 eV)

m/z	**1a** X=H	**1b** CH_3	**1c** Cl	**1d** Br	**1e** I	**2**[a]	e	c
163	200[b]	2	13	7	1	58[b]	40[b]	8
149	1	1	20	100	100	1	—	4
135	4	4	4	2	1	8	8	—
131	100	100	100	40	12	100	100	100
123	1	3	1	2	2	1	—	4
121	1	1	8	36	36	1	2	—
118	—	—	—	—		—	—	12
91	2	2	3	3	2	3	4	—

[a] m/z 166 (≙$[M-D]^+$) all m/z values +2 u.
[b] Interference peak.

The first type of m/z 164 ions (**A**) is produced in the mass spectra of **1a** and **1b** and decomposes mainly by loss of an $^{\cdot}SH$ radical to m/z 131 ions. The same fragmentations, accompanied by minor loss of $^{\cdot}SD$ (or H_2S) are observed in the MI spectrum of the $[M-D]^+$ ions of **2**. Therefore, if some of the $[M-H]^+$ ions, m/z 164, of **1a** are formed by loss of a H atom from the *N*-methyl groups as discussed previously, these ions do not contribute to the MI spectrum of m/z 164 ions. It is much more likely, however, that the $[M-H]^+$ ions in the mass spectrum of **2** arise from some 'scrambling' of the H and D atoms at the phenyl group of the trideuterated derivative during the fragmentation to ions **A** and not from a separate process.

The presence of a second type of m/z 164 ions (**B**) is most clearly seen in the MI spectra of the m/z 164 ions from **1e**. These ions **B** are characterized by the loss of a methyl group and a fragment of mass 43, probably $CH_2{=}N{-}CH_3$. A small signal for the loss of $^{\cdot}SH$ is also observed. This last reaction appears to be due to the presence of a small amount of ions **A** because the intensity of the signal at m/z 131 rises by a factor of *c.* 2 if the m/z 164 ions from **1e** are generated at 15 eV. Similarly, the metastable m/z 164 ions in the 70 eV mass spectra of **1c** and **1d** are a mixture of ions **A** and **B** as is indicated by strong signals at m/z 149 and m/z 131 in the MI spectra, the relative abundance of the product ions m/z 131 again increasing with decreasing electron energy.

The formation of m/z 164 ions of different *structures* **A** and **B** within the series **1a**–**1e** is proven by their collisional activation (CA) spectra obtained by collisional activation with He in the second field free region (Table 5).

The CA spectra of the *m/z* 164 ions from **1a** and **1b** are identical within the limits of error, and consequently the *stable* and *metastable* *m/z* 164 ions from both compounds are an identical species **A**. The CA spectrum of *m/z* 164 ions from **1e** is distinctly different and in contrast to the MI spectrum obtained from metastable ions independent of the electron energy used to generate the *m/z* 164 ions. Thus, the *stable* *m/z* 164 ions in the mass spectrum of **1e** are most probably a single species **B** differing in structure from the isomeric ions **A**. The CA spectrum of *m/z* 164 ions from **1d** is identical with that obtained for **1e**. Therefore, in contrast to *metastable m/z* 164 ions from this compound which correspond to a mixture of ions **A** and **B** the *stable m/z* 164 ions are all of type **B**. In continuation of this trend the CA spectrum of *m/z* 164 ions generated by 70 eV electrons from **1c** is much more similar to the CA spectra obtained from **1d** and **1e** than the corresponding MI spectra of metastable *m/z* 164 ions. However, the intensities of the product ions *m/z* 134, *m/z* 130, *m/z* 116 and *m/z* 89 show clearly that the *stable m/z* 164 ions are also a mixture of ions **A** and **B**. However, contrary to the MI spectrum of the *metastable m/z* 164 ions, which changes drastically on lowering the electron energy towards an increasing amount of ions **A** in the mixture, the CA spectrum of the *stable m/z* 164 ions is not altered by lowering the electron energy down to (nominal) 12 eV. Summarizing, these results show that *m/z* 164 ions of different structures **A** and **B** arise from molecular ions of *ortho* substituted *N,N*-dimethylthiobenzamide, depending on the substituent lost. By loss of a H atom and a CH_3 substituent from **1a** and **1b**, respectively, only ions of type **A** are formed. The loss of Cl, Br and I from **1c**, **1d** and **1e**, respectively, gives ions of type **A** and **B**, the concentration of ions **A** decreasing in that order. The *stable m/z* 164 ions from **1c–1e** are predominantly or completely of structure **B** and the mixture of *metastable m/z* 164 ions is obviously depleted of type **B** ions by lowering the electron energy. Thus, the MI spectra of metastable ions generated by impact with low energy electrons indicate the presence of a larger fraction of ions **A**, which are formed in a process with a higher activation energy. Therefore the *A*(*m/z* 164) values obtained from **1c–1e** correspond to the formation of ions **B**, while the *A*(*m/z* 164) values obtained from **1a** and **1b** are associated with ions **A**.

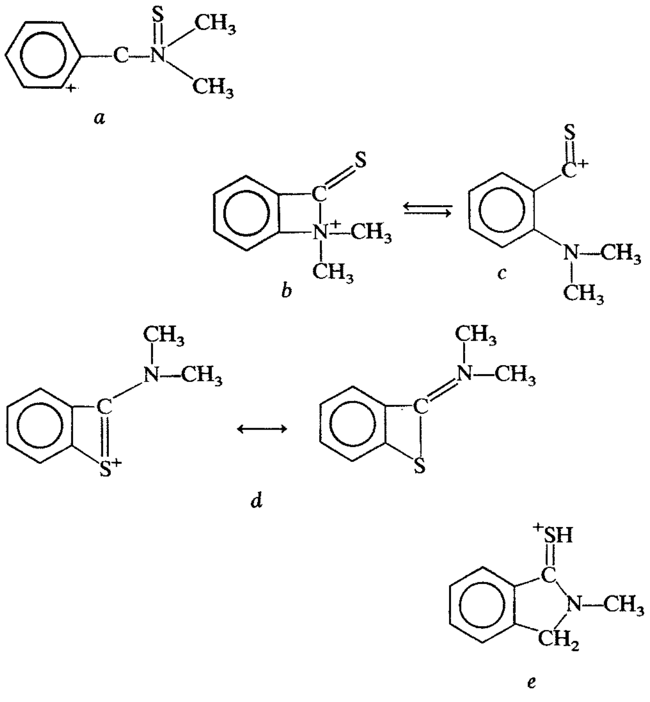
Table 5. Linked scan CA spectra of *m/z* 164 ions from *N,N*-dimethylthiobenzamides (70 eV)

m/z	**1a** X=H	**1b** CH_3	**1c** Cl	**1d** Br	**1e** I	**2**	*e*	*c*
163	(200)	(179)	(24)	(38)	(39)	(187)	(349)	(159)
162	87	84	16	10	11	91	66	40
161	—	—	—	—	—	16	—	—
149	(15)	(24)	(231)	(204)	(231)	11	(12)	(30)
148	48	65	100	100	100	65	31	32
147	—	—	—	—	—	11	—	—
146	11	15	5	3	3	11	6	3
135	(35)	(44)	(13)	(4)	(4)	(29)	(32)	3
134	100	100	45	36	32	100	100	11
133	—	—	14	21	20	24	—	—
131	(735)	(810)	(227)	(21)	(10)	(677)	(408)	(680)
130	67	78	18	6	4	(119)	44	100
128	13	13	4	2	1	10	14	8
123	1	10	1	1	1	1	1	(18)
122	4	7	7	12	11	6	5	3
121	(62)	(36)	(67)	(101)	(100)	(26)	(25)	13
120	9	9	9	19	17	15	6	4
119	4	6	1	6	5	5	3	3
118	17	10	1	3	2	10	12	(71)
117	13	14	13	21	19	22	16	13
116	93	87	29	21	19	101	72	8
109	3	1	1	1	1	—	2	2
108	4	6	8	18	16	—	3	2
107	—	—	4	8	7	—	—	—
104	11	8	5	9	7	10	12	8
103	14	16	7	10	9	14	15	21
102	7	11	4	5	4	13	8	13
93	4	4	4	10	8	—	4	1
91	(20)	(17)	(4)	(4)	(4)	(24)	(18)	19
90	15	17	7	13	12	13	13	11
89	35	36	8	7	8	37	28	23
77	14	11	4	8	7	7	12	24

[a] Values in parentheses were not used for normalization of spectra.

DISCUSSION

A priori the structures *a–e* (Scheme 1) can be assigned to *m/z* 164 ions arising from the molecular ions of *N,N*-dimethylthiobenzamides by loss of a substituent from the *ortho* position of the phenyl group.



Scheme 1

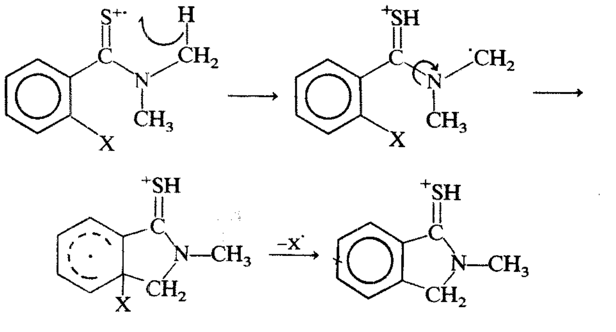
The ions *a* would be formed by a simple bond cleavage in the molecular ions without any assistance from the neighbouring thioamide group. This process can be excluded by the two following arguments. (i) Loss of a substituent from an aromatic ring by direct bond cleavage in the molecular ions is a high energy process at least for the loss of a H atom and a CH_3 radical from **1a** and **1b**, respectively, with critical energies >4.5 eV,[18] in contrast to the observed $\varepsilon_f^{\neq}$ of 1.5 eV for the reaction of **1a** and **1b** (Table 2). Even for **1e** the observed $\varepsilon_f^{\neq}$ of 1.0 eV is distinctly below the activation energy of 2.3 eV[18] for the loss of I from the molecular ion of iodobenzene.

(ii) In the mass spectrum of *N,N*-dimethyl-*p*-chlorothiobenzamide loss of the Cl substituent is not observed, but only the formation of $[M-H]^+$ ions with a comparable high intensity as in the mass spectrum of **1a**. This certainly shows the operation of an '*ortho* effect' during the fragmentation of the *ortho* isomer **1c**.

The ions *b* would arise from an intramolecular displacement of the *ortho* substituent in the molecular ion by the dimethylamino group via a 4-membered cyclic transition state. A complete transfer of the dimethylamino group to the *ortho* position during the displacement reaction gives rise to the *o*-dimethylaminothiobenzoyl ion *c*. Ion *c* is a valence tautomer of ion *b* and both species are probably in equilibrium with each other. It is not possible to estimate the heat of formation of *b*, but *c* is likely to be the more stable species because of the ring strain in ion *b*. Hence ion *c* would be favoured in the equilibrium.

An attack of the S atom of the thioamide group during the intramolecular aromatic substitution reaction in **1a**–**1e** via a 4-membered cyclic transition state would lead to ion *d*. Ion *d* is stabilized by a resonance distribution of the positive charge between the S and N atom, but destabilized by the ring strain in the 4-membered ring. However, the ring strain in *d* should be less than in *b*, considering the larger covalent bond length at a S atom.

The ion *e* would be the result of a multistep fragmentation pathway analogous to the formation of the $[M-H]^+$ ions from *N,N*-dimethylbenzamide[8] depicted in Scheme 2.

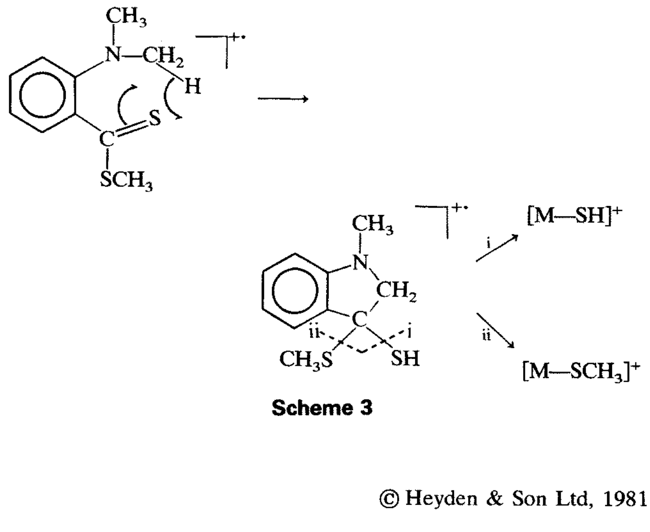


Scheme 2

The reaction starts with a hydrogen migration from one of the *N*-methyl groups to the S atom of the thioamide group and proceeds by an attack of the radical site on the phenyl group and displacement of the *ortho* substituent. This last reaction step corresponds to an intramolecular aromatic substitution in the molecular ions via a 5-membered cyclic transition state, which *a priori* should be more favourable than the reactions with 4-membered transition states giving rise to ions *b*, *c* or *d*.

Which of the fragmentation pathways is actually followed during the decompositions of the molecular ions of **1a**–**1e** and which of the structures *b*–*e* corresponds to the product ions *m/z* 164 of type **A** and **B** can be determined by comparing the heats of formation of the reference ions and their MI and CA spectra with the corresponding data for **A** and **B**. The heat of formation of the *o*-dimethylaminothiobenzoyl ion *c* can be estimated from the $A(c) = 7.99$ eV of this ion in the mass spectrum of *o*-dimethylaminodithiobenzoic acid methyl ester (**3**). With $\Delta H_f(\mathbf{3}) =$ 201 kJ mol^{-1} calculated from increments[12] and ΔH_f $(CH_3S\cdot) = 142$ kJ mol^{-1} [19] $\Delta H_f(c) \leq 830$ kJ mol^{-1} is obtained. This value can be corrected to ≤ 803 kJ mol^{-1} by the maximum kinetic energy release associated with the loss of a CH_3S radical from $[\mathbf{3}]^{+\cdot}$ ions. Similarly, the heat of formation of the unsubstituted thiobenzoyl ion $[C_6H_5CS]^+$ has been estimated from the $A[C_6H_5CS]^+ = 9.49$ eV of this ion in the mass spectrum of dithiobenzoic acid methyl ester ($\Delta H_f =$ 192 kJ mol^{-1} [12]), leading to ΔH_f $[C_6H_5CS]^+ \leq$ 966 kJ mol^{-1}. As expected *c* is stabilized by the strongly electron-donating dimethylamino group, the effect being of the same order of magnitude as in the benzoyl ion.[20] $\Delta H_f(c) \leq 803$ kJ mol^{-1} is too large to identify the structure *c* as the type **A** *m/z* 164 ions from the *N,N*-dimethylthiobenzamides **1a** and **1b**, but *c* is still a candidate for the type **B** *m/z* 164 ions from **1c**–**1e**. This can be excluded, however, by a comparison of the MI and CA spectra (Tables 3 and 4). Metastable *c* ions mainly lose a SH radical to give *m/z* 131 ions and only to a small extent a CH_3 radical. This would be in accord with type **A** *m/z* 164 ions, but not with *m/z* 164 ions of type **B**. Furthermore, the CA spectrum of *c* ions is different from the CA spectra of *m/z* 164 ions of type **A** and **B**. These results show that neither *m/z* 164 ions of type **A** nor of type **B** are represented by ion *c*. Similarly, the structure *b* can be excluded because of the expected equilibrium between ions *b* and ions *c*.

It is possible, however, that contrary to expectation the ions *m/z* 164 in the mass spectrum of **3** have a structure different from *c*. The molecular ions of **3** lose a SH radical besides a SCH_3 radical with a similar appearance energy of 7.80 eV and similar intensity. A fragmentation mechanism which accounts for both reactions and which gives *m/z* 164 ions differing in structure from *c* is depicted in Scheme 3. In this case the $\Delta H_f \leq 803$ kJ mol^{-1} derived from the $A(m/z$ 164)



Scheme 3

in the mass spectrum of **3** does *not* correspond to $\Delta H_f(c)$. However, if the molecular ions of **3** avoid the formation of ions *c* by the mechanism of Scheme 3, $\Delta H_f(c)$ should be even larger than 803 kJ mol^{-1}, still excluding structure *c* for the *m/z* 164 ion of type **A**, but not for ions of type **B**.

Ion *e* corresponds to the S-protonated thiolactam 3,4-benzo-*N*-methylpyroline-2-thione (**4**). The gas phase basicity of some aromatic thioamides has been determined and it has been shown that these compounds are protonated at the thiocarbonyl group in the gas phase.[21] Hence ions *e* should be generated by chemical ionization of **4** using isobutane as reagent gas. A proton affinity of 958.8 kJ mol^{-1} (derived from the gas phase basicity 927.1 kJ mol^{-1} by correction for the free proton entropy) has been found for the closely related *N,N*-dimethylthiobenzamide.[21] If this value is accepted for the proton affinity of **4** and combined with $\Delta H_f(\mathbf{4}) = 182$ kJ mol^{-1} (from increments[12]) $\Delta H_f(e) = 750 \pm 30$ kJ mol^{-1} is obtained. This is close to the $\Delta H_f(m/z\ 164) = 776$ kJ mol^{-1} of the type **A** ions derived from the *A*(*m/z* 164) in the mass spectrum of **1a** and suggests structure *e* for these ions **A**. Indeed this assignment is corroborated by a comparison of the MI and CA spectra of ions *e* generated by chemical ionization (methane) of **4** with the corresponding spectra of ions **A** (Tables 3–5). The intensity of the MI spectra of ions *e* obtained from both field free regions is rather low, the only intense signal being due to formation of *m/z* 131 ions by loss of SH. A better proof is given by the CA spectrum of ions *e*, which is identical to that of *m/z* 164 ions of type **A** from *ortho* substituted *N,N*-dimethylthiobenzamides.

The correlation of *m/z* 164 ions of type **A** with structure *e* leaves structure *d* or less likely structures *b* and *c* (because of some ambiguity in the structure of the corresponding reference ion) for *m/z* 164 ions of type *b*. Unfortunately, no direct proof can be given for the structure *d*, because no suitable precursor for ions *d* is available. There is an indirect argument in favour of structure *d* for the type **B** ions, however. *N,N*-dimethylbenzamide ions fragment to the oxygen analogue of type **A** ions paralleling the behaviour of **1a**, but the tendency to form the oxygen analogue of type **B** ions from *ortho* substituted *N,N*-dimethylbenzamides is small or absent.[8] This is difficult to explain if the intramolecular substitution occurs by the dimethylamino group present in the benzamides *and* thiobenzamides. The different fragmentations in both series of compounds are much easier to rationalize if substitution has to occur by the oxygen atom and sulfur atom, respectively, of the amide groups, because the formation of a 4-membered ring in the product ions *d* with the rather long covalent bonds at a S atom is easier.[22]

The formation of *m/z* 164 ions **A** from the molecular ions of **1a** and **1b** as depicted in Scheme 2 corresponds to an intramolecular aromatic substitution reaction via a 5-membered cyclic transition state. Indeed, the loss of a H atom and a methyl group from $[\mathbf{1a}]^{+\cdot}$ and $[\mathbf{1b}]^{+\cdot}$, respectively, exhibit the characteristics of such a process.[5] The critical energy $\varepsilon_{f\neq}$ of the substitution reaction appears to be independent of the dissociation energy of the leaving group, indicating that a reaction step preceding the dissociation of the bond to the substituent determines the critical energy of the total process. The energy determining reaction step may be either the hydrogen rearrangement within the thioamide, group, or, in analogy to other intramolecular substitution reactions,[1–5] the formation of an intermediate with a tetracoordinated C atom at the *ortho* position of the phenyl group by attack of the radical site of the rearranged molecular ions. The intermediates are formed as chemically activated species, and the excess energy is distributed between internal energy and kinetic energy of the products during the further reaction. Both the loss of H$^\cdot$ and CH$_3^\cdot$ from $[\mathbf{1a}]^{+\cdot}$ and $[\mathbf{1b}]^{+\cdot}$ are endothermic reactions (Table 2) with late transition states according to the Hammond postulate, the positions of transition states X_0^* on the reaction coordinate[23] being calculated to be 0.64 and 0.55, respectively. Hence, a large fraction of the transition state energy is expected to be released as kinetic energy of the products. This is corroborated by the MIKE spectra of the molecular ions of **1a** and **1b**, which show broad dish-topped signals for the reaction leading to ions **A**, indicating a non-statistical distribution and a large amount of kinetic energy released. Indeed an energy partition quotient $q = 0.62$ and 0.53 is obtained for the intramolecular substitution reaction of $[\mathbf{1a}]^{+\cdot}$ and $[\mathbf{1b}]^{+\cdot}$, respectively, in agreement with *q*-values of other endothermic intramolecular substitution reactions.[5]

The intramolecular substitution reaction by loss of the halogen substituents in $[\mathbf{1c}]^{+\cdot}$–$[\mathbf{1e}]^{+\cdot}$ gives rise to signals with Gaussian peak shapes in the MIKE spectra, attributed to a statistical distribution of the kinetic energy released and the maximum amount of the kinetic energy is less than in the case of $[\mathbf{1a}]^{+\cdot}$ and $[\mathbf{1b}]^{+\cdot}$. A similar change in the peak shapes and the corresponding distribution of kinetic energies and in the value of T_B has also been observed for the dependence of other intramolecular aromatic substitution reactions[1–5] on the substituents lost and has been explained by a change in the transition state from a 'late' to an 'early' position on the reaction coordinate in each series of compounds, because the same product ions are formed throughout each series regardless of the type of substituent lost. In the case of *ortho* substituted *N,N*-dimethylthiobenzamides, however, the change in the kinetic energy distribution and in the T_B-values between **1a** and **1b** on the one hand and **1c**–**1e** on the other hand is certainly due to a change in the fragmentation mechanism. While $[\mathbf{1a}]^{+\cdot}$ and $[\mathbf{1b}]^{+\cdot}$ react by a substitution reaction via a 5-membered cyclic transition state, $[\mathbf{1c}]^{+\cdot}$–$[\mathbf{1e}]^{+\cdot}$ do so by a 4-membered cyclic transition state, the structure of the product ions **B** corresponding either to *d* or to *c*. The activation energy $\varepsilon_{f\neq}$ of this process depends clearly on the decreasing dissociation energy of the bond to the leaving group in the order Cl > Br > I and parallels the critical energy for the loss of the halogen substituent from the halogeno benzene ions.[18] Hence the bond to the halogeno substituents is partly cleaved in the transition state of the formation of ions **B** from $[\mathbf{1c}]^{+\cdot}$–$[\mathbf{1e}]^{+\cdot}$, which can be easily explained by a 'direct' substitution without the formation of a chemically activated intermediate. Probably this is also the reason for a statistical distribution of the kinetic energies released during the process giving rise to the Gaussian peak shapes of the corresponding signals in the MIKE spectra. One could surmise that the formation of ions **B** from [**1c**]$^{+\cdot}$–[**1e**]$^{+\cdot}$ is an endothermic reaction, but as the structure of ions **B** is not exactly known and as no reference ions are available, ΔH_f(**B**) cannot be determined independently. If ΔH_f(**B**) = 900 kJ mol^{-1}, as suggested by the limiting value of $\Delta H_f'$(**B**)$_{corr}$ in Table 2, the formation of ions **B** from [**1c**]$^{+\cdot}$, [**1d**]$^{+\cdot}$ and [**1e**]$^{+\cdot}$ is endothermic by 153, 107 and 44 kJ mol^{-1}, respectively. Consequently, the activation energies $\varepsilon_{r\neq}$ of the reverse reactions are small and more or less completely released as kinetic energy of the products.

The change in the mechanism of the intramolecular aromatic substitution reaction of *ortho* substituted *N*,*N*-dimethylthiobenzamides in dependence on the type of the substituent is an interesting feature of this reaction system. It is not completely clear why this happens and why the energetically more favoured reaction product of type **A** is not formed throughout the whole series of compounds. One reason may be the fact that intramolecular substitution to ion **A** via a 5-membered cyclic transition state requires a constant $\varepsilon_{f\neq}$ of 1.4 eV, while the values of $\varepsilon_f^{\neq}$ for the formation of product ions **B** via a direct substitution by a 4-membered transition state depend on the dissociation energy of the leaving group. Extrapolating $\varepsilon_{f\neq}$ for the formation of ions **B** from [**1a**]$^{+\cdot}$ by loss of a H atom gives $\varepsilon_{f\neq} \approx 2$ eV, which is well above $\varepsilon_f^{\neq}$ for the reaction to ions **A**. On the other hand $\varepsilon_f^{\neq}$ for the formation of ions **B** from [**1d**]$^{+\cdot}$ (1.3 eV) and [**1e**]$^{+\cdot}$ (1.0 eV) is below the (constant) $\varepsilon_{f\neq}$ of 1.4 eV for the reaction to ions **A**. Hence only a small amount of ions **A** are formed in competition with ions **B**. Furthermore, in contrast to the fragmentation of [**1b**]$^{+\cdot}$ and [**1c**]$^{+\cdot}$, which exhibit peaks for $[M-H]^+$ ions[24] besides peaks for $[M-CH_3]^+$ and $[M-Cl]^+$ ions, respectively, in their normal mass spectra and MI spectra, no $[M-H]^+$ ions are observed in the spectra of [**1d**]$^{+\cdot}$ and [**1e**]$^{+\cdot}$.

In the case of the *o*-chloro derivative **1c** the MI and CA spectra of the $[M-Cl]^+$ ions *m*/*z* 164 show the presence of a mixture of product ions of type **A** and **B**. Although most of the *stable* product ions correspond to ions **B**, which consequently should have a lower appearance energy than ions **A**, the appearance energy of ions **A** from this compound cannot be much larger. This is corroborated by the formation of $[M-H]^+$ ions from *metastable* and *unstable* molecular ions of **1c**, the $[M-H]^+$ ions being formed only via the 5-membered cyclic transition state reaction as indicated by a broad flat-topped signal for the corresponding reaction in the MIKE spectrum. Obviously, there are three intramolecular aromatic substitution reactions competing with each other in the molecular ions of the *o*-chloro compounds **1c**, two of them giving rise to product ions **A** and its chloro substituted analogue, respectively, by a 5-membered cyclic transition state, the third one producing product ions **B** probably via a 4-membered cyclic transition state. Hence the *o*-chloro derivative **1c** represents a 'crossing-point' in the series of *N*,*N*-dimethylthiobenzamides for the intramolecular aromatic substitution reactions with 5- and 4-membered cyclic transition states.

The $\varepsilon_{f\neq}$(**B**) = 1.7 eV of ions **B** in the mass spectrum of **1c** is somewhat larger than the $\varepsilon_f^{\neq}$(**A**) = 1.5 eV of ions **A** from **1a** and **1b**, and the arguments in the preceding paragraph suggest $\varepsilon_{f\neq}$(**A**) > 1.7 eV for ions **A** from **1c**, in contrast to the assumption of a constant value of $\varepsilon_{f\neq}$(**A**) = 1.5 eV for the substitution via a 5-membered cyclic transition state for all leaving groups. Therefore, the possibility that there is another effect operating in the series **1a**–**1e** *raising* the appearance energy of ions **A** in that order cannot be excluded. This effect may be due to a steric hindrance of the hydrogen migration within the thioamide group preceding the substitution reaction (see Scheme 2). From scale models of the molecules **1a**–**1e** it is seen that bulky *ortho* substituents hinder the *N*,*N*-dimethylthioamide group in adopting a configuration with a short distance between a H atom of the *N*-methyl group and the S atom. In line with this explanation for a change in the mechanism of the substitution reaction of [**1a**]$^{+\cdot}$–[**1e**]$^{+\cdot}$ is the observation that although *N*,*N*-dimethylbenzamide forms $[M-H]^+$ ions analogous to ions **A**, neither its *o*-chloro nor its *o*-bromo derivative[8] gives rise to a comparable large amount of $[M-Cl]^+$ and $[M-Br]^+$ ions, respectively. Obviously, an intramolecular aromatic substitution via a preceding H migration and a 5-membered cyclic transition state in the substitution step does not take place in these molecular ions, although no competition by the other 'direct' substitution reaction occurs. However, more experiments with suitable model compounds are needed to prove that the intramolecular aromatic substitution in the molecular ions of *N*,*N*-dimethylbenzamides and of the corresponding thioamides following the mechanism of Scheme 3 can be suppressed by a steric hindrance of the preceding hydrogen migration.

EXPERIMENTAL

The mass spectra were obtained with a Vacuum Generators ZAB-2F-mass spectrometer under the following conditions: electron energy: 70 eV or as indicated; trap current 200 μA, acceleration voltage: 8 kV; ion source temperature: *c*. 200 °C; mass resolution: 3000; direct insertion of the samples.

The MIKE spectra and CA spectra were measured on the same instrument using the same conditions. For measuring the CA spectra He was used as the collision gas and was introduced into the collision cell within the first and second field free region at such a rate that the intensity of the selected parent ion was reduced to *c*. 10% of its original value.

The kinetic energy *T* released during the fragmentations was determined with the ZAB-2F instrument under the conditions mentioned above and an energy resolution of *c*. 4000. The reproducibility of the *T*-values was better than ±5%. The measurements were also performed with a Varian MAT 311A mass spectrometer giving the same results within the error of measurement.

The ionization energies and appearance energies of the relevant ions were obtained with a Vacuum

Generators MM12B-mass spectrometer modified as described previously,[1] using the semi-log plot method[25] and CH_3I (I(M) = 9.5 eV[18]) as a reference introduced simultaneously with the sample.

Operation conditions: trap current 20 μA; acceleration voltage: 4 kV; ion source temperature: *c.* 200 °C; mass resolution: 800. The values given in Table 2 are the mean values of three independent measurements. The reproducibility of ionization energies *c* ±0.05 eV, of appearance energies *c* ±0.1 eV.

The (substituted) *N,N-dimethylthiobenzamides* **1a–1e** were synthesized from the corresponding benzamides, obtained by standard procedures from the (substituted) benzoic acids and dimethylamine, by reaction with P_4S_{10} in pyridine.[26]

N,N-dimethyl-2,4,6-*trideuterothiobenzamide* (**2**) was prepared by converting 2,4,6-trideuteroaniline (from exchange of aniline with D_2O) to 2,4,6-trideuterobenzoic acid via 2,4,6-trideuterobromobenzene by standard methods and following the usual route from benzoic acid to *N,N*-dimethylthiobenzamide. The D content of **2** was 97.7% and 93.3% d_3, 6.5% d_2, 0.2% d_1 derivative (by mass spectrometry, 10 eV).

Dithiobenzoic acid methyl ester and o-*dimethylaminodithiobenzoic acid methyl ester* (**3**) were obtained from the corresponding Grignard iodides and CS_2 in THF, followed by reaction with CH_3I after addition of some CuCl to the reaction mixture and by the usual isolation procedure[27] in 23% and 75% yield, respectively. The dithiobenzoic acid methyl ester contained a small amount of the free acid as an impurity even after repeated distillation; **3** was obtained in pure form after vacuum distillation.

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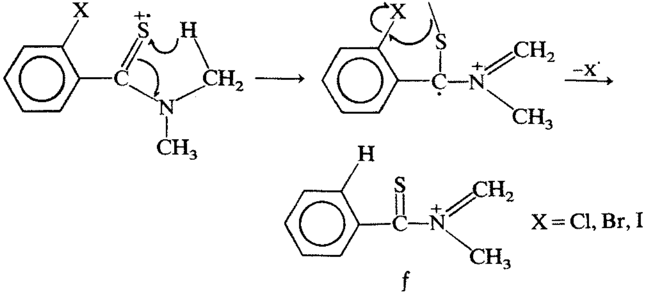

f

We did not succeed in preparing reference ions of structure *f* in an unequivocal manner, hence structure *f* cannot be completely ruled out for ions **b** on experimental evidence. However, thiobenzamide ions substituted at the *ortho* position by Cl, Br and I, but not by CH_3, lose their substituent in a reaction with similar characteristics to substituent loss from **1c–1d**. (H. F. Grützmacher, to be published in this journal). In the absence of the *N*-methyl groups, the substituent loss from the halogeno substituted thiobenzamides corroborates the conclusion, that in both series of compounds the fragmentation occurs by attack of the sulfur atom via a 4-membered transition state and that *d* is the structure of ions **B**.
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