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Electron Ionization-induced Loss of SO_2 from 2-Nitrodiaryl Sulfides

P.-H. Lambert,[1] S. Bertin,[1] J.-M. Lacoste,[1] J.-P. Volland,[1] A. Krick,[2] E. Furet,[3] A. Botrel[3] and P. Guenot[4]

[1] Institut de Recherches SERVIER, Division de Physico-Chimie Analytique, 11 rue des Moulineaux, 92150 Suresnes, France
[2] Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex, France
[3] Laboratoire de Physicochimie, Ecole Nationale Supérieure de Chimie de Rennes, avenue du Général Leclerc, 35700 Rennes, France
[4] Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

Electron ionization-induced loss of SO_2 from 2-nitrodiphenyl sulfide leads to the same ionic structure, or mixture of structures, as loss of N_2 from the molecular ion of N^1-phenylbenzotriazole. *Ab initio* calculations are in favor of the $[C_6H_4—N—C_6H_5]^{+\cdot}$ distonic nitrenium radical cation instead of the *N*-phenylbenzo-Δ^2-azirinium structure for the product ion. Collisionally activated dissociation mass-analyzed ion kinetic energy (CAD-MIKE) spectra of the four chloro isomers $[$3- or 4-$Cl—C_6H_3—N—C_6H_5]^{+\cdot}$ and $[C_6H_4—N—C_6H_4$-3 or 4-$Cl]^{+\cdot}$ show that these ions are non-interconverting structures and eliminate regioselectively their nitrene moiety. Comparison with the CAD-MIKE spectra of the product ions of the elimination of N_2 from N^1–3(or 4)-chlorophenylbenzotriazoles demonstrates that the loss of SO_2 from 2-nitrophenyl aryl sulfides occurs in the gas phase via an *ipso* rearrangement involving a [1,4] migration of the aryl group. © 1998 John Wiley & Sons, Ltd.

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KEYWORDS: 2-nitrodiaryl sulfides; N^1-arylbenzotriazoles; collisionally activated dissociation mass-analyzed ion kinetic energy spectroscopy; SO_2 elimination; aryl migration

INTRODUCTION

In solution, photochemical intramolecular oxygen transfer from a nitro group to an acceptor site has long been known.[1] In electron ionization (EI) mass spectrometry of aromatic compounds, *ortho*-oxygen transfer from a nitro group to carbon,[2,3] nitrogen or sulfur atoms,[4–9] carbon–carbon multiple bonds,[8,10–19] carbon–nitrogen double bonds,[11,19–22] cyclopropyl rings[19,23] and aromatic rings[19,24] has been extensively studied. However, for the particular case of the unexpected elimination of SO_2 from molecular ions of 2-nitrodiphenyl sulfides,[25,26] which are key intermediates in the synthesis of dibenzothiazepines, no mechanism or proof of structure of the product ions has been proposed. In this paper, we report some new experimental features which allow a better understanding of this reaction. In particular, we demonstrate that the loss of SO_2 occurs with an *ipso* rearrangement of the aryl group that was not originally carrying the nitro group to the nitrogen atom.

EXPERIMENTAL

The compounds investigated are shown in Scheme 1. Mass spectra were measured on a Finnigan MAT 95 Q BEqQ mass spectrometer under the following conditions: electron energy, 70 eV; emission current, 0.4 mA; source temperature, 160 °C; and direct insertion probe temperature, 25–35 °C. Helium was used as the collision gas in the second field-free region (FFR 2) for collisionally activated dissociation mass-analyzed ion kinetic energy (CAD-MIKE) experiments and the pressure was adjusted in order to achieve a reduction of 30% of the precursor ion beam intensity. Elemental compositions of all ions were checked by high-resolution measurements.

Compounds **1a–c** were synthesized by condensation of chlorobenzene with 2-nitro- (for **1a**), 2-nitro-4-chloro- (for **1b**) or 2-nitro-5-chloro- (for **1c**) thiophenolates (concentrated NaOH–EtOH, reflux). The isomers **1d** and **e** were obtained using the same conditions and starting from 2-chloronitrobenzene and 1,3- (for **1d**) or 1,4- (for **1e**) chlorothiophenolates. Compounds **2b** and **c** were synthesized by reaction of 1,3- or 1,4-chlorofluorobenzene with the anion of benzotriazole (K_2CO_3–DMF, reflux). Compound **2a** was prepared according to a procedure described elsewhere.[27] All these compounds were purified by recrystallization and their structures were confirmed by ^1H NMR spectroscopy. The other compounds were commercially available and were used without further purification.

Computational method

All calculations were performed with the Gaussian 94 suit of programs.[28] The geometries of the two radical

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* *Correspondence to*: P.-H. Lambert, Institut de Recherches SERVIER, Division de Physico-Chimie Analytique, 11 rue des Moulineaux, 92150 Suresnes, France.

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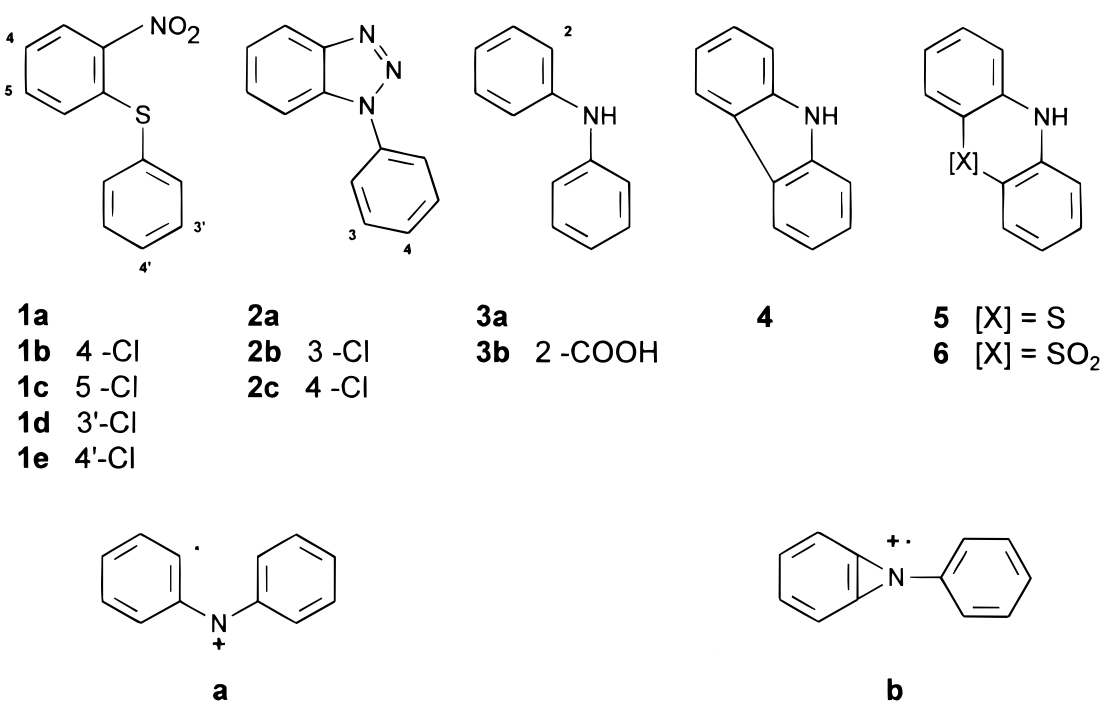


1a
1b 4-Cl
1c 5-Cl
1d 3'-Cl
1e 4'-Cl

2a
2b 3-Cl
2c 4-Cl

3a
3b 2-COOH

4

5 [X] = S
6 [X] = SO$_2$

a

b

Scheme 1

cations, namely the distonic structure **a** and the *N*-phenylbenzo-Δ^2-azirinium structure **b**, were fully optimized at the B3LYP level of Density Functional Theory[29] (DFT) using the 6–31 + G(d) basis set.

RESULTS AND DISCUSSION

El mass spectra of 2-nitrodiphenyl sulfides 1a–e

El (70 eV) mass spectra of compounds **1a–e** are listed in Table 1. They all show two major competitive fragmentation pathways: cyclization in dibenzothiophene by loss of HNO$_2$ and the unexpected loss of SO$_2$ which leads to the base peak directly for **1a** or after a consecutive loss of $^\cdot$Cl for **1b–e**.

At lower internal energies, the loss of SO$_2$ remains the only observable reaction and is, by far, the main fragmentation in the MIKE spectra of the molecular ions. This last point suggests that an intensive rearrangement occurs in the source with a very low activation energy. Compound **1a** has been compared with the possible candidate phenothiazine sulfone **6**. This hypothesis has been discarded with regard to the different CAD-MIKE spectra of their molecular ions. The loss of SO$_2$ from the molecular ion of the phenothiazine sulfone **6** occurs to a much smaller extent than for **1a** (data not shown).

Structure of [M – SO$_2$]$^{+\cdot}$ ions

The [M – SO$_2$]$^{+\cdot}$ ion from **1a** was compared with other [C$_{12}$H$_9$N]$^{+\cdot}$ ions with CAD-MIKE spectra methodology (see Fig. 1). Among the possible candidates investigated here, only the [M – N$_2$]$^{+\cdot}$ ion from *N*^{1}-phenylbenzotriazole (**2a**) shows a very similar CAD-MIKE spectrum and differs from the other carbazole-like structures ([**3a**]$^{+\cdot}$, [**3b** – H$_2$O – CO]$^{+\cdot}$, [**4**]$^{+\cdot}$, [**5** – S]$^{+\cdot}$ and [**6** – SO$_2$]$^{+\cdot}$) by, mainly, the presence of a narrow peak at *m*/*z* 77 ([C$_6$H$_5$]$^+$).

Experimentally deduced enthalpies of formation of the [M – N$_2$]$^{+\cdot}$ ion from *N*^{1}-phenylbenzotriazole (**2a**)

Table 1 El (70 eV) mass spectra of 2-nitrodiaryl sulfides 1a–e

Ion	1a	1b	1c	1d	1e
	m/*z* [relative abundances of most significant ions (%)]				
M$^{+\cdot}$	231 (35)	265 (36)	265 (21)	265 (26)	265 (26)
[M – HNO$_2$]$^{+\cdot}$	184 (38)	218 (22)	218 (12)	218 (16)	218 (13)
[M – $^\cdot$NO$_2$ – $^\cdot$Cl]$^+$	—	184 (20)	184 (13)	184 (16)	184 (15)
[M – HNO$_2$ – $^\cdot$Cl]$^+$	—	183 (13)	183 (9)	183 (11)	183 (9)
[M – SO$_2$]$^{+\cdot}$	167 (100)	201 (47)	201 (41)	201 (38)	201 (38)
[M – SO$_2$ – $^\cdot$H]$^+$	166 (21)	—	—	—	—
[M – SO$_2$ – $^\cdot$Cl]$^+$	—	166 (100)	166 (100)	166 (100)	166 (100)
[M – SO$_2$ – $^\cdot$H – HCN]$^+$	139 (12)	—	—	—	—
[M – SO$_2$ – $^\cdot$Cl – HCN]$^+$	—	139 (28)	139 (25)	139 (29)	139 (35)
[C$_6$H$_5$]$^+$	77 (11)	77 (19)	77 (19)	—	—
[C$_6$H$_4$Cl]$^+$	—	—	—	111 (6)	111 (12)

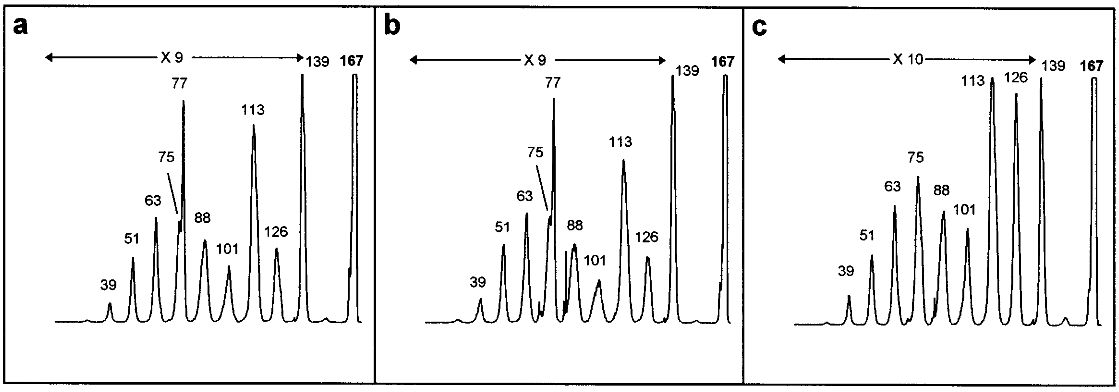


Figure 1. CAD-MIKE spectra of some $[C_{12}H_9N]^{+\cdot}$ resulting from loss of SO_2 from 2-nitrodiphenyl sulfide (a), loss of N_2 from N^1-phenyl benzotriazole (**b**) and molecular ion of carbazole (**c**).

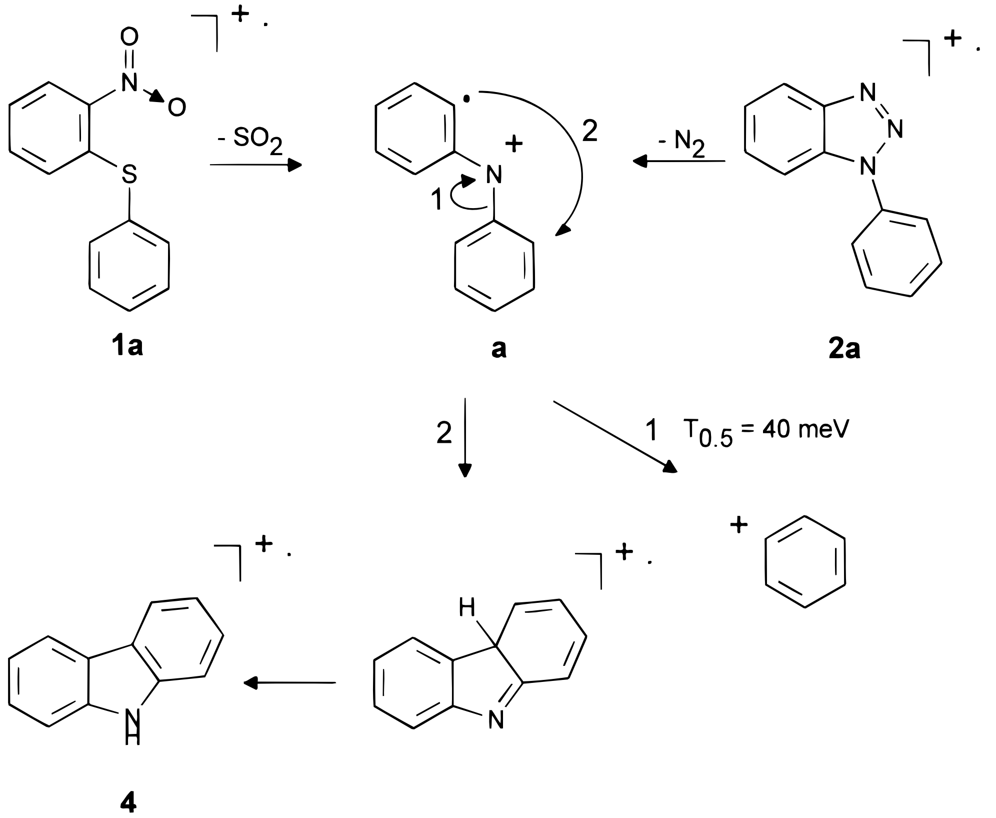
clearly distinguishes this ion from the ionized carbazole **4** (1636.5 and 1001.1 kJ mol^{-1}, respectively[30]). The distonic radical cation structure **a** (see Scheme 2) has previously been suggested for the $[M - N_2]^{+\cdot}$ product ion from *N*-phenylbenzotriazoles.[31] This non-cyclic structure can easily explain the formation of $[C_6H_5]^+$. The measured value of 40 meV for the kinetic energy release during the metastable transition $[\mathbf{1a} - SO_2]^{+\cdot} \rightarrow [C_6H_5]^+$ is in agreement with a simple bond cleavage such as that proposed in Scheme 2.

For the chloro compounds **1b–e**, the comparison of the CAD-MIKE spectra of their $[M - SO_2]^{+\cdot}$ ions (*m*/*z* 201) leads to the following conclusions.

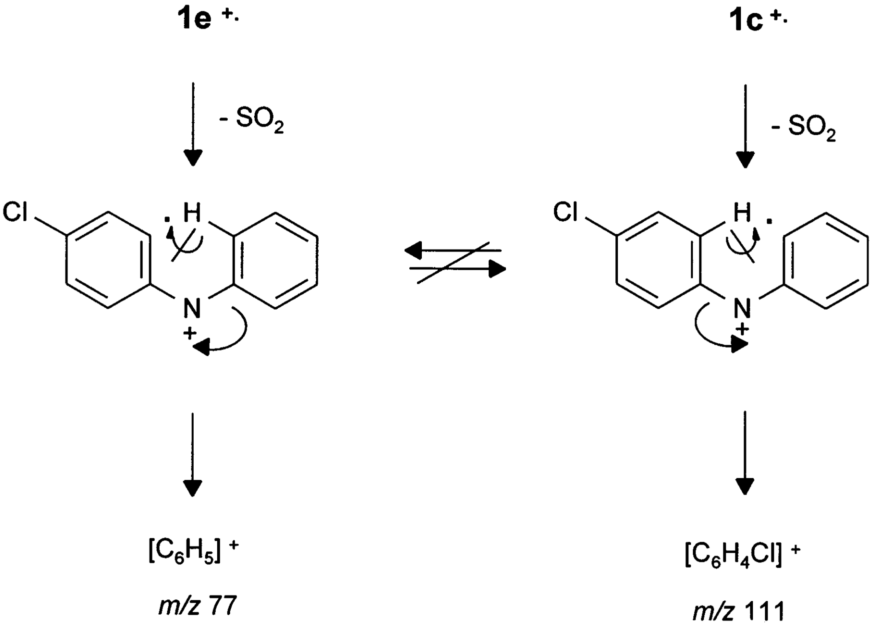
(i) The arylium ions (*m*/*z* 77, $[C_6H_5]^+$, or *m*/*z* 111, $[C_6H_4Cl]^+$) are produced with very high regioselectivity. The only detectable arylium ion is the one which was not primarily substituted by the nitro group. This implies that there is no migration of one hydrogen atom from a phenyl group to the other which should give equivalent aromatic rings (Scheme 3).

(ii) The hypothetical *N*-phenylbenzo-Δ^2-azirinium structure **b** (Scheme 1) has been eliminated for experimental and thermodynamic reasons. First, the CAD-MIKE spectra of $[M - SO_2]^{+\cdot}$ ions from isomers **1b** and **c** (see Fig. 2) show differences in the relative abundances of the $[C_6H_5]^+$ ion (*m*/*z* 77). This is proof that there is no established equilibration in the source between $[\mathbf{1b} - SO_2]^{+\cdot}$ and $[\mathbf{1c} - SO_2]^{+\cdot}$ via a common symmetrical structure like *N*-phenylbenzo-Δ^2-azirines **b**′ and **b**″, which should give equivalent *meta* and *para* positions for the chloro atoms (Scheme 4). Analoguous features are observed for isomers **1d** and **e**.

DFT calculations show that for the two structures **a** and **b**, the spin contamination could be considered as



Scheme 2. Competitive evolution of the $[C_6H_4—N—C_6H_5]^{+\cdot}$ distonic ion **a** by single bond α-cleavage to give the phenylium ion (route 1) or cyclization to carbazole (route 2).[31]



Scheme 3. Regioselectivity of the collision-induced formation of arylium $[C_6H_5]^+$ and $[C_6H_4Cl]^+$ ions from $[\mathbf{1e}-SO_2]^{+\cdot}$ and $[\mathbf{1c}-SO_2]^{+\cdot}$. The arylium formed is the one which was not originally substituted by the nitro group in the precursor compounds **1e** and **c**.

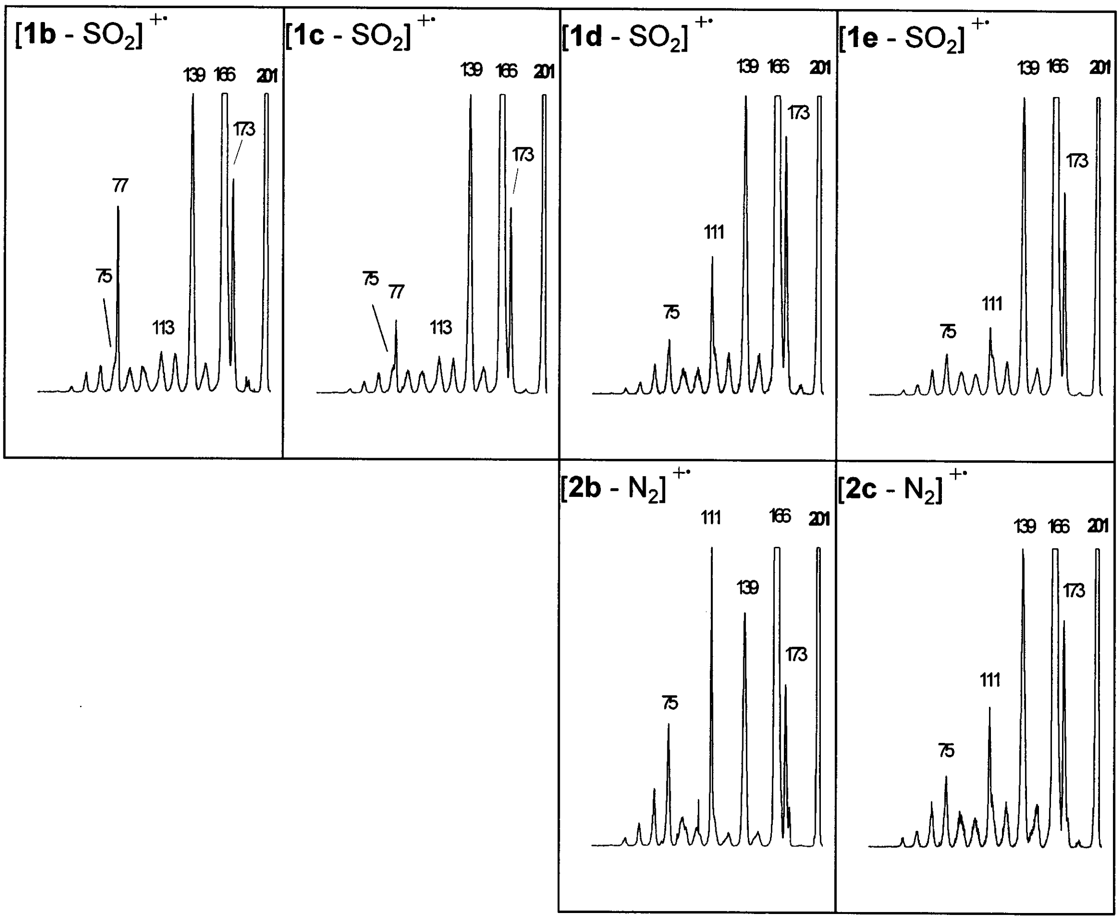
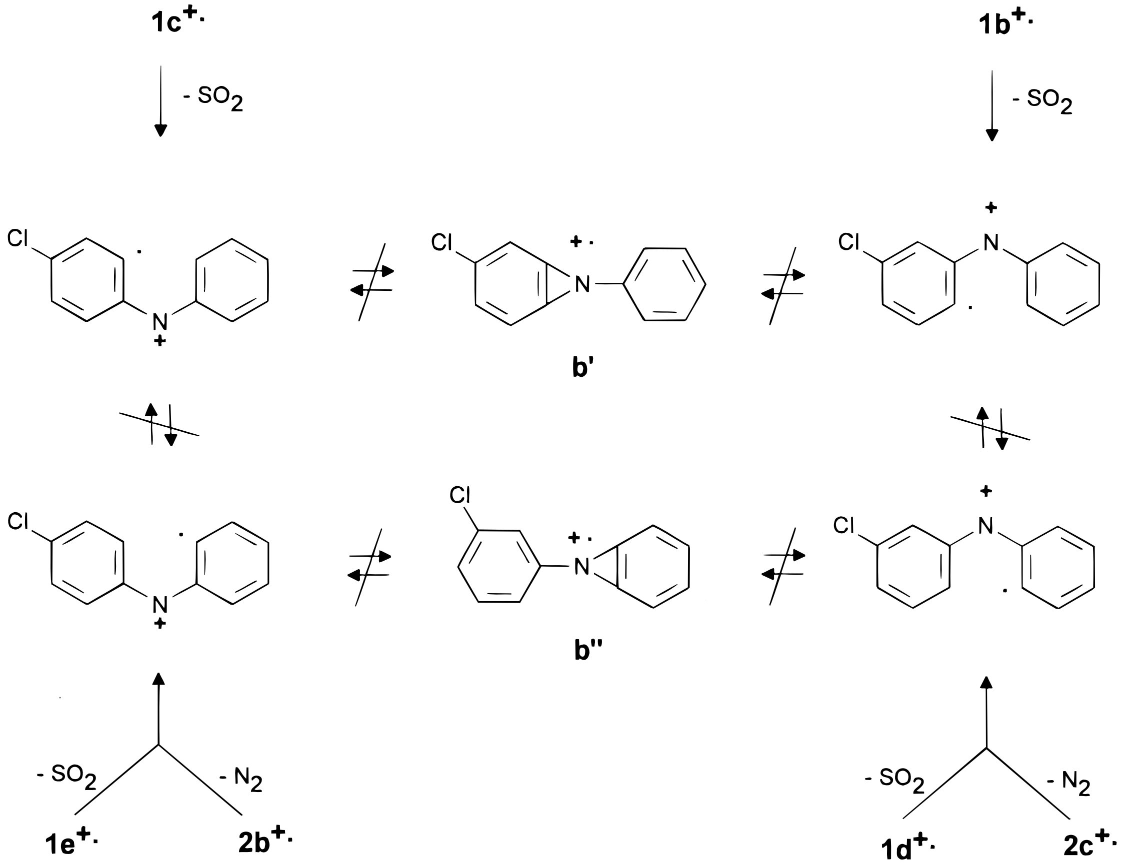
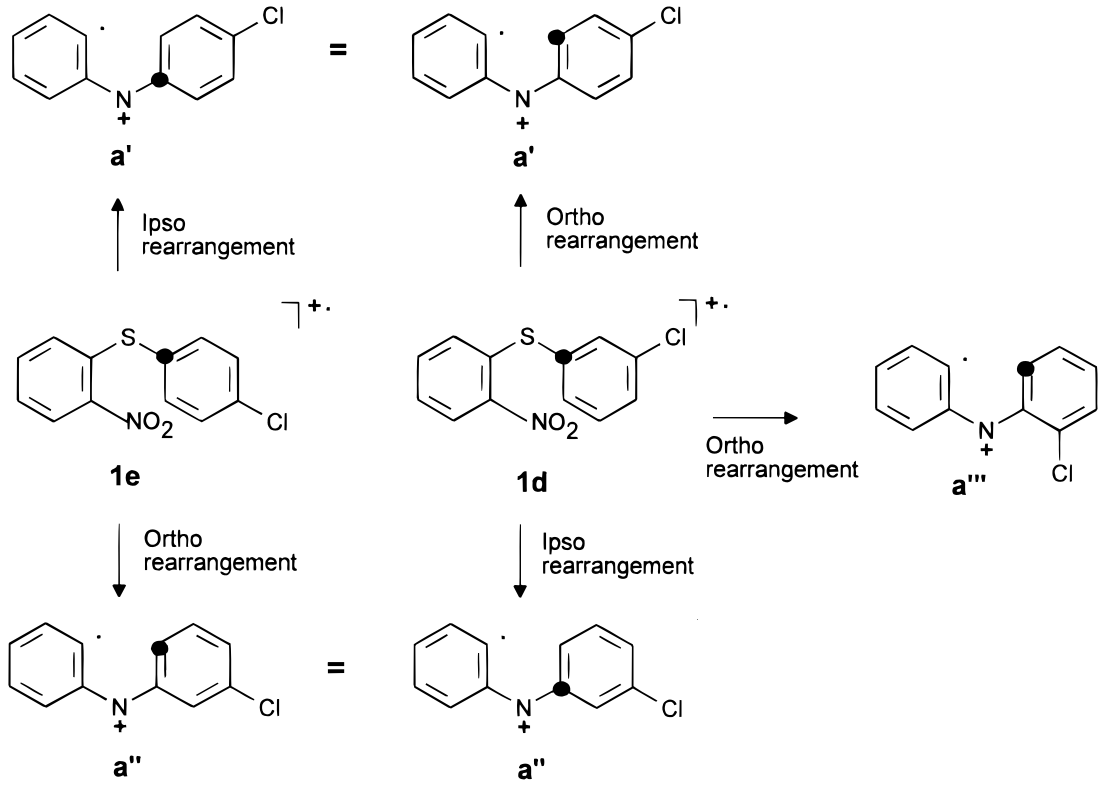


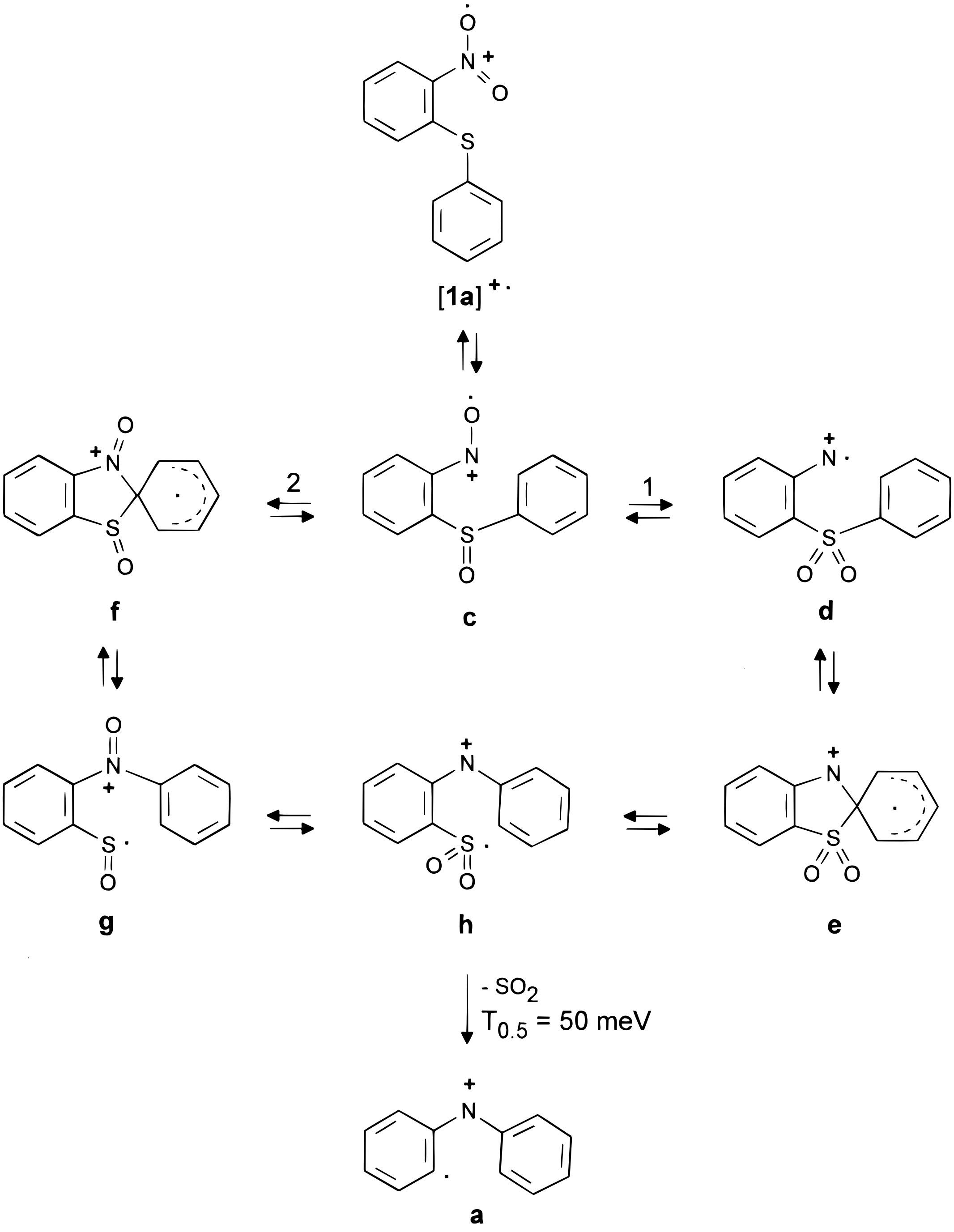
Figure 2. CAD-MIKE spectra of some $[C_{12}H_8ClN]^{+\cdot}$ ions resulting from loss of SO$_2$ from the isomers of the chloro substituted 2-nitrodiarylsulfides **1b**–**1e** (top) and from the loss of N$_2$ from the N^1-chlorophenylbenzotriazoles **2b** and **c** (bottom).



Scheme 4. The $[C_{12}H_8ClN]^{+\cdot}$ radical cations produced by SO_2 elimination from the four isomers **1b–e** give CAD-MIKE spectra which differ mainly in the nature and the relative abundances of the arylium fragment ion ($[C_6H_5]^+$ or $[C_6H_4Cl]^+$). There is no established equilibrium between these distonic structures and the hypothetical Δ^2-azirinium structure should be excluded.



Scheme 5. Possible isomeric structures for $[M - SO_2]^{+\cdot}$ ions starting from *meta* and *para* isomers **1d** and **e**. The carbon originally bonded to the sulfur atom is marked. The opposite mechanism from opposite isomers could lead to the same ion structure.



Scheme 6. Hypothetical mechanisms for the elimination of SO_2 from 2-nitrodiphenyl sulfide molecular ion. The aryl migration is effective before (route 1) or after (route 2) the transfer of the second oxygen atom.

weak, with $\langle S^2 \rangle = 0.77$. We could therefore adequately represent the pure doublet state of the molecules and we might expect to be able further to investigate quantitatively the reaction path leading from **a** to **b**. This result is not really surprising, as DFT wavefunctions on open-shell molecules are known to show little to no spin contamination.[32,33]

The comparison of the total energies of the two radical ions, $E(\mathbf{a}) = -517.090771$ au and $E(\mathbf{b}) = -517.078247$ au, leads to the conclusion that the distonic structure **a** is 33 kJ mol^{-1} more stable than **b**. This value can be considered to be small, but it is still significant at this DF level of theory. This result therefore corroborates the experimental findings. It should be pointed out that initial calculations, using the AM1 semi-empirical method, gave and energy advantage of nearly 88 kJ mol^{-1} in favor of structure **a**.

Mechanism of SO_2 elimination

As shown in Scheme 5, the problem is to elucidate which of the carbon atoms is bonded to the nitrogen atom after the loss of SO_2. For example, loss of SO_2 from **1e** could lead to **a**′ after a mechanism of direct migration of the chlorophenyl group (*ipso* rearrangement) in such a way that the carbon atom, which was first bonded to the sulfur atom, is bonded to the nitrogen atom in the final product, or to **a**″ after attack of the nitrogen on the *ortho*-carbon followed by 1,2-migration of a hydrogen atom (*ortho* rearrangement). For isomer **1d**, differing only in the relative position of the chlorine, we have a reverse situation and a third possibility with the formation of **a**‴ via the *ortho* mechanism.

For **a**′, depending on the *para* position of the chlorine atom, the positive charge is considered to be more delocalized by the mesomeric donor effect and, consequently, we expect more sp^2 character for the C—N bond, decreasing the relative abundance of the chlorophenylium ion in the CAD-MIKE spectrum by increasing the C—N bond strength. Experimentally, we observe this phenomenon: the $[C_6H_4Cl]^+$ fragment ion (*m/z* 111) is less abundant in the CAD-MIKE spectrum of $[\mathbf{1e} - SO_2]^{+\cdot}$ than for $[\mathbf{1d} - SO_2]^{+\cdot}$ (see Fig. 2). This is in favor of a direct transposition mechanism via an *ipso* rearrangement. This point has been unambiguously confirmed by comparison with the CAD-MIKE spectra of the $[M - N_2]^{+\cdot}$ ion from *N*-chlorophenylbenzotriazoles **2b** and **2c** where the relative positions of the chlorine atoms are not suspected to change during the N_2 elimination. Although these spectra are not exactly superimposable on those of $[\mathbf{1e} - SO_2]^{+\cdot}$ and $[\mathbf{1d} - SO_2]^{+\cdot}$, indicating mixtures of ions in different ratios, the same relationship is observed for the relative abundances of the $[C_6H_4Cl]^+$ fragment ions depending on the chlorine atom position.

As shown in Scheme 6, the most probable structure of the transition state could be a five-membered spiro structure such as **e** or **f**. Such intermediates have already been involved in some EI-induced Truce–Smiles-type rearrangements in gas phase.[34–36] After the probably reversible transfer of the first oxygen atom to the sulfur atom, leading to 2-nitrosophenyl phenylsulfoxide **c**, we can postulate two mechanisms: the transfer of the second oxygen atom is effective before (route 1) or after (route 2) the migration of the phenyl group. The loss of SO, observed in the MIKE spectrum of **1a**, can be explained by the intermediate **g** and is in favour of route 2.

The structure of the last intermediate, **h**, is supported by the range of the kinetic energy release values for the loss of SO_2 from compounds **1a**–**e** (44 meV $< T_{0.5} <$ 66 meV), which can be compared with the single bond dissociation $[C_6H_5SO_2]^+ \rightarrow [C_6H_5]^+ + SO_2$ (81 meV)[37] or to the loss of SO_2 (50 meV $< T_{0.5} <$ 80 meV) produced with a similar mechanism from *gem*-disulfones.[36]

CONCLUSION

All molecular ions of 2-nitrodiaryl sulfides described in this paper undergo an intensive loss of SO_2. This reaction is the first observable when the internal energy of the molecular ions is increasing. We have shown that the structure of the product ion is in agreement with the previously suggested distonic structure **a**, and that this intensive rearrangement takes place with a direct [1,4] transposition of the phenyl group to the nitrogen, although the structures of some intermediates were not well established.

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