# Brief Communications

## Negative-ion mass spectra of some *N*-mesyl derivatives of *o*-(cycloalk-2-enyl)-, *o*-(cycloalk-1-enyl)-, *o*-(pent-2-enyl)-, *o*-dibromopentylanilines and ($\alpha$-bromoalkyl)indolines

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The formation and fragmentation of negative ions of some *N*-(methylsulfonyl)anilines upon resonance electron capture have been studied. The formation of long-living molecular ions is due to the presence of the mesyl groups in the molecules. The difference in negative-ion mass spectra of isomeric *N*-(methylsulfonyl)anilines has been revealed.

**Key words:** negative molecular ion, resonance electron capture, alkenylanilines, indolines.

The behavior of sulfoxides, sulfides,[1] and cyclic sulfones[2] upon resonance electron capture has previously been studied. It was found that negative molecular ions (NMI) can be generated only in the case of cyclic sulfones that contain double bonds or electron-withdrawing substituents.

Here we report the results of the investigation of some *N*-(methylsulfonyl)anilines to ascertain the influence of the Ms group and other substituents on processes of negative ion (NI) formation. To date, no common explanation has been found for the relation between average NMI lifetime relative to electron expulsion $\tau_e$ and properties of the molecule. One of the main factors that affect $\tau_e$ is the nature of LUMO, which usually bears an additional electron. Naturally, there are other factors that influence $\tau_e$ (*e.g.*, the number of degrees of freedom of the molecule,[3,4] changes in the NMI geometry,[5,6] *etc.*). The search for such factors is a topical problem that can be solved only in studies of compounds that form long-living NMI.

### Experimental

The mass spectra and effective negative ion yield curves were recorded on an MI-1201 spectrometer adopted to record negative ions. The electron energy scale was calibrated relative to the yield of $SF_6^{-\cdot}$ from $SF_6$. Half-height electron energy distribution was 0.3—0.4 eV, electron current, 0.5 μA; measuring inaccuracy of maxima, ± 0.1 eV. Determination of the life-

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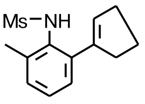
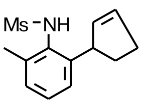
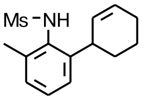
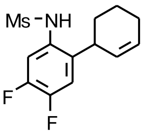
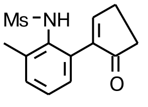
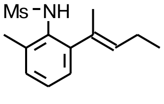
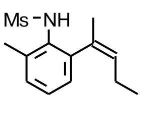
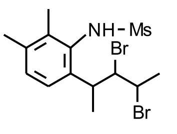
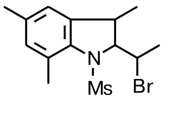
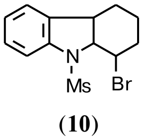
time $\tau_e$ relative to electron expulsion was carried out according to the known method.[7]

Quantum-chemical calculations were carried out by semi-empirical MNDO/d method, geometry optimization was carried out using the HyperChem program package.

*N*-(Methylsulfonyl)anilines **1**—**4** were synthesized by the reaction of 6-methyl-2-(cyclopent-1-enyl)aniline,[8] 6-methyl-2-(cyclopent-2-enyl)aniline, 6-methyl-2-(cyclohex-2-enyl)aniline[9] and 2-(cyclohex-2-enyl)-4,5-difluoroaniline[10] with methanesulfonyl chloride (MsCl). The synthesis of compounds **5**—**7** will be published elsewhere. Compounds **8** and **9** were obtained by bromination of *N*-methylsulfonyl-4,6-dimethyl-2-(1-methylbut-2-enyl)aniline in $CH_2Cl_2$. Hexahydrocarbazole **10** was prepared by bromination of *N*-methylsulfonyl-2-(cyclohex-2-enyl)aniline[11] in $CH_2Cl_2$. The purity and structures of the methanesulfonates obtained were proved by TLC, data from elemental analysis and $^1H$ and $^{13}C$ NMR spectroscopy, the spectra being recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz for $^1H$ and $^{13}C$, respectively).

**Table 1.** NI mass spectra of compounds **1**—**10**

| Compound | τ/ms | *m*/*z* (*I* (%))/*E** |
|---|---|---|
| <br>(**1**) | 182 | 251 $[M]^-$ (38.5)/0.2; 250 $[M - H]^-$ (1.4)/7.5; 172 $[M - MeSO_2]^-$ (0.1) 0.2, (0.1)/3.5, (0.2)/7.6; 79 $[MeSO_2]^-$ (100)/0.3, (3.2)/4.4, (1.3) 7.4; 64 $[SO_2]^-$ (2)/0.2, (0.2)/3.6, (0.5)/7.4; 48 $[SO]^-$ (<0.1)/0.2, (0.2)/4.5 |
| <br>(**2**) | 140 | 251 $[M]^-$ (97)/0.2; 250 $[M - H]^-$ (2.7)/7.5; 210 $[M - C_3H_4 - H]^-$ (11)/1.5, (0.7)/4.7; 184 $[M - C_5H_7]^-$ (0.1)/8; 172 $[M - MeSO_2]^-$ (1.3)/0.3, (<0.1)/4, (<0.1)/8.2; 79 $[MeSO_2]^-$ (100)/0.3, (1)/4.4, (1.3)/8; 64 $[SO_2]^-$ (1.3)/0.1, (2.3)/3.9, (1.6)/7.6; 48 $[SO]^-$ (3.6)/0.2; (0.5)/3.4 |
| <br>(**3**) | 167 | 265 $[M]^-$ (100)/0.1; 264 $[M - H]^-$ (4.4)/7.1; 210 $[M - C_4H_6 - H]^-$ (2.6)/1.4, (1)/4.6; 186 $[M - MeSO_2]^-$ (0.5)/0.1, (<0.1)/2.9, (0.1)/7.5; 184 $[M - C_6H_9]^-$ (<0.1)/7.7; 81 $[C_6H_9]^-$ (0.6)/4; 79 $[MeSO_2]^-$ (27.8)/0.2, (0.8)/4.2, (0.4)/7.9; 64 $[SO_2]^-$ (0.1) 0.1, (0.1)/3.6, (0.1)/7.5; 48 $[SO]^-$ (<0.1)/0.2, (0.2)/4.4 |
| <br>(**4**) | 237 | 287 $[M]^-$ (100)/0.1; 268 $[M - H]^-$ (0.4)/0.3, (<0.1)/7.8; 232 $[M - C_4H_6 - H]^-$ (<0.1)/4.3; 208 $[M - MeSO_2]^-$ (0.2)/0.2, (<0.1) 3.7, (<0.1)/8; 206 $[M - C_6H_8]^-$ (<0.1)/7.7; 81 $[C_6H_8]^-$ (<0.1)/8; 79 $[MeSO_2]^-$ (5.7)/0.2, (0.2)/4.5, (<0.1) 8; 64 $[SO_2]^-$ (<0.1)/0.2, (<0.1)/3.4, (<0.1)/7.7; 48 $[SO]^-$ (<0.1)/0.2, (<0.1)/4.5 |
| <br>(**5**) | 236 | 265 $[M]^-$ (26.3)/0.2; 264 $[M - H]^-$ (0.2)/7.4; 236 $[M - CO - H]^-$ (0.1) 7.9; 186 $[M - MeSO_2]^-$ (0.2)/0.2, (0.1)/4, (0.1)/8; 184 $[M - C_5H_5O]^-$ (2.4)/0.3, (0.6)/4.2, (0.5)/8.5; 159 $[M - C_2HC_5H_5O]^-$ (0.5)/3.1; 79 $[MeSO_2]^-$ (100)/0.2, (0.2)/4.2, (<0.1) 7; 64 $[SO_2]^-$ (0.4)/0.2, (9)/3.7; 48 $[SO]^-$ (1.7)/0.4, (0.1)/4.5 |
| <br>(**6**) |  | 253 $[M]^-$ (70)/0.2; 252 $[M - H]^-$ (1.4)/7.8; 238 $[M - Me]^-$ (0.4)/4.4; 224 $[M - Et]^-$ (1.8)/4.3, (2.1)/1.4; 174 $[M - MeSO_2]^-$ (<0.1)/0.2, (0.1) 3.6, (0.2)/8.4; 79 $[MeSO_2]^-$ (100) 0.4, (1.6)/4.4, (<0.1)/8.3; 64 $[SO_2]^-$ (<0.1)/0.2, (0.1)/3.4, (0.1)/7.5; 48 $[SO]^-$ (<0.1)/0.2, (0.3)/4.6 |
| <br>(**7**) | 56 | 253 $[M]^-$ (12)/0.2; 252 $[M - H]^-$ (1.4)/7.6; 238 $[M - Me]^-$ (0.6)/3.7; 224 $[M - Et]^-$ (1.6)/0.9, (1.3)/3.7; 174 $[M - MeSO_2]^-$ (0.4)/0.2, (0.5) 2.7, (1.7)/7.2; 79 $[MeSO_2]^-$ (100) 0.2, (3.5)/4, (<0.1)/8; 64 $[SO_2]^-$ (0.1)/0.2, (0.7)/3.5, (0.9)/7.9; 48 $[SO]^-$ (<0.1)/0.2, (0.9)/4.2 |
| <br>(**8**) | 82 | 425, 427, 429 $[M]^-$ (0.7)/0.3, (1.3) 0.3, (0.6)/0.3; 345, 347 $[M - HBr]^-$ (50)/0.1, (48.9)/0.1; 226 $[M - C_3H_5Br_2]^-$ (0.2)/1.1; 198 $[M - C_5H_9Br_2]^-$ (8)/1.3; 158, 160, 162 $[Br_2]^-$ (33.4)/0.1, (65.3)/0.1, (31.9)/0.1; 79 $[MeSO_2]^-$ (73)/0.2, (<0.1)/4.3, (<0.1)/8.3; 79, 81 $[Br]^-$ (100)/0.1, (97.8)/0.1, 64 $[SO_2]^-$ (0.6) 0.2, (31.4)/3.7; 48 $[SO]^-$ (0.1)/4.4, (0.1)/0.4 |
| <br>(**9**) | 113 | 345, 347 $[M]^-$ (31.1)/0.1, (30.4)/0.1; 265 $[M - HBr]^-$ (7.3)/0.1; 79 $[MeSO_2]^-$ (42)/0.2, (1.5)/4.4, (0.2) 8.2; 79, 81 $[Br]^-$ (100)/0.1, (97.8) 0.1; 64 $[SO_2]^-$ (<0.1)/0.2, (40)/3.8, (9)/6.9; 48 $[SO]^-$ (0.2)/0.2, (0.1)/4.7 |
| <br>(**10**) | 292 | 329, 327 $[M]^-$ (2.4)/0.3, (2.3)/0.3; 249 $[M - HBr]^-$ (17.6)/0.1; 79 $[MeSO_2]^-$ (21.5)/0.2, (<0.1)/4.4, (<0.1)/8.1; 79, 81 $[Br]^-$ (100)/0.1, (97.8)/0.1; 64 $[SO_2]^-$ (0.1)/0.3, (0.6) 3.9, (0.2)/7.4; 48 $[SO]^-$ (<0.1)/0.3, (0.1)/4.7 |

* Electron energy values (eV) in the maxima of the resonance curve.

## Results and Discussion

Table 1 lists relative intensities of the NI lines and electron energies in the maxima of the resonance curves.

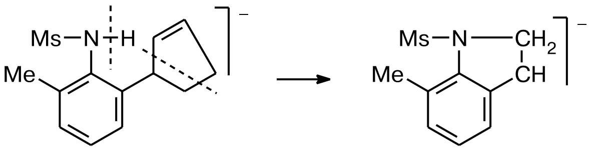
The NMI, $[MeSO_2]^-$, and $Br^-$ peaks are the most intense peaks in the region of thermal energies of electrons. The presence of NMI and $[MeSO_2]^-$ signals in the mass spectra of compounds studied suggests that the electron capture occurs on the vacant MO with the major contribution of the Ms group. Benzene and its derivatives (except for nitrobenzene) do not produce long-living NMI, which confirms indirectly this conclusion.[12,13] Moreover, quantum-chemical calculations of the molecules studied and their NMI showed that the orbital with the major contribution of $MeSO_2NH$ group (~80%) and the contribution of the benzene ring (~20%) is the LUMO in compounds **1**—**7**. The low yield of NMI in the case of compounds **8** and **10** is evidently related to the low σ*-MO of C—Br, so that the competitive formation of $Br^-$ leads to the reduction of peak intensities in the mass spectra. At the same time, the relative intensity of the NMI peak in the spectrum of compound **9**, which also contains σ*-MO of C—Br, is ~31%. Quantum-chemical calculation showed that the repulsion of atoms of the Ms group and Br atom in NMI of this compound takes place, in contrast to **8** and **10**. Probably, such intramolecular interaction stabilizes NMI with an additional electron on the vacant orbital with the major contribution of the Ms group.

An interesting tendency is observed as regards generation of $[MeSO_2]^-$ in the region of thermal energies of electrons. The preponderant formation of such ions for compounds **1**, **5**, **6**, and **7** where the substituent is conjugated with the benzene ring can be explained by the higher stability of the neutral radical due to the delocalization of the radical center. On the contrary, for compounds **2**—**4** where the substituent is not conjugated with the benzene ring relative yield of NMI is higher. The presence of F atoms in compound **4** favors the stabilization of NMI[14,15] and thus the formation of $[MeSO_2]^-$ becomes less probable.

Noteworthy is the sensitivity of mass spectra of NI to the structure of compounds studied. Thus the average lifetime $\tau_e$ of the *cis*-isomer **6** is more than twice as high as that for *trans*-isomer **7**. The probable reason for the enhanced stability of NMI is the intramolecular interaction of the Ms group and an alkenyl substituent. The similar effect was observed earlier in nitrotoluenes.[12] The quantum-chemical calculations of the geometry of these isomers and their NMI showed that the Ms group in compound **6** is turned in such a way that the O atom is arranged close to the alkenyl substituent, while in molecule **7** it is remote from the substituent.

The sensitivity to the structure of compounds is manifested in the upfield resonances (at 1.5—4.5 eV). Thus alkenylaniline **2** gives an additional ion with *m/z* 210, which is absent in the spectrum of compound **1**. The formation of this ion can be explained by the fragmentation of the cyclopentenyl group with subsequent intramolecular cyclization (Scheme 1).

**Scheme 1**



The similar process is also typical of cyclohexenyl derivatives **3** and **4**, but not of compound **1**. This is due to the conjugation of the double bond of the substituent with the π-electrons of the benzene ring, which inhibits such process. The conjugation also favors stabilization of NMI because the mean lifetime $\tau_e$ of compound **1** is larger than that of alkenylaniline **2**.

The presence of an O atom in the cyclopentenyl group of compound **5** favors the appearance of new states of NMI and hence the appearance of new pathways of fragmentation, which lead to ions $[M - H]^-$, $[M - HCO]^-$ and $[M - C_5H_5O]^-$ in the region of energies of 8 eV (see Table 1).

Thus, based on the results of this study and the literature data for the generation of NI in substituted benzenes, a conclusion can be made that the ability of this class of compound for thermal energy electron capture is governed by the presence of the $MeSO_2NH$ group, which interacts with the π-system of the benzene ring, though the nature of some other substituents has also noticeable effect.

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