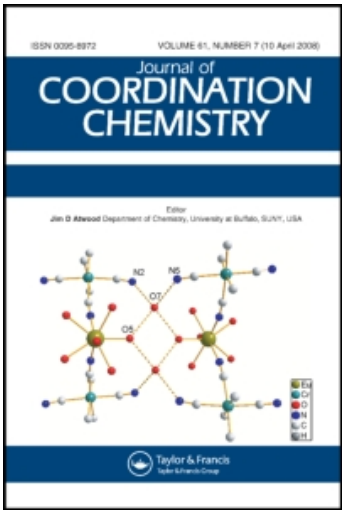

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N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine as ligands; spectroscopic and DFT studies of complexes with ZnX_2 (X=Cl, Br)

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N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine as ligands; spectroscopic and DFT studies of complexes with ZnX_2 (X = Cl, Br)

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Six new ZnX_2 (X=Cl, Br) complexes with N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine as ligands have been synthesized and characterized by MS, IR, NMR and DFT methods. All complexes have 1 : 1 stoichiometry. Complexation with N16-oxides involves inversion of the configuration at N16, converting ring C from a boat into a chair with the oxygen engaged in coordination. All complexes investigated are of composition $[(L–H)^+(ZnX_3)^-]$ (where L is N-oxide). The structures of the complexes obtained have been compared with those of the monoperchlorate salts of the N-oxides.

Keywords: *Bis*-quinolizidine N-oxides; Zinc(II) complexes; NMR spectroscopy; IR spectroscopy; DFT calculations

1. Introduction

Bis-quinolizidine alkaloids with the sparteine skeleton are an important group of compounds due to their biological applications. Since its discovery, sparteine has had a long history of use in medicine as antiarrhythmic substances and now it is used to investigate the activity of cytochrome P450 (CYP2D6) in patients with allergies and depression [1]. As early as 1929 there were indications that biological activity of sparteine may result from interaction with calcium ions *in vivo* [2, 3]. More recently Zn(II) complexes of bis-quinolizidine have been recognized as magnetic diluting agents for modelling type 1 blue copper proteins [4–7]. Such a wide scope of applications can be attributed to the flexible structure of bis-quinolizidine compounds. The most frequent type of conformation changes in this class of compounds involves inversion of the lone pair on the N16. If the lone pair is blocked, the conformational transition is almost impossible. The simplest way to block it is by reaction of the alkaloid base to afford its N-oxide.

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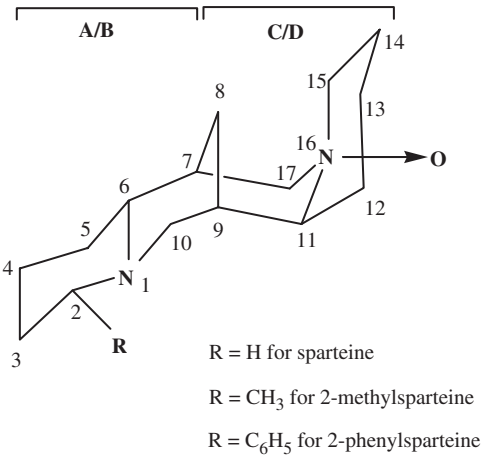


Figure 1. Conformation and atom numbering for N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine.

Low-volume substituents e.g. the methyl group, introduced at C2 α to the nitrogen involved in complexation, have some effect on the course of the reaction, by diminishing its yield when compared with sparteine [8]. In contrast to 2-methylsparteine, 2-phenylsparteine does not undergo complexation at all. In N-oxides the situation is different. As the metal is coordinated by the oxygen atom from the N-oxide, the presence of a substituent in ring A (even a phenyl group) has practically no influence on the course of complexation. Moreover, the N16-oxides **1**–**3** previously thought to adopt the all-chair conformation have been found recently to have ring C in a boat conformation [9], which is sterically more beneficial for complexation (see figure 1).

The present work is a continuation of investigation into the complexation ability of bis-quinolizidine N16-oxides, where coordination of lithium salts in the above compounds is realized through the oxygen atom of the $N \rightarrow O$ group with formation of stable complexes of 1 : 1 stoichiometry [10]. In this article we show possibility for complexes of bis-quinolizidine N-oxides not only with small cations, but also with zinc, which has been achieved for the first time for this group of compounds.

The formation of zinc(II) complexes with N16-oxides of sparteine (**1**), 2-methylsparteine (**2**) and 2-phenylsparteine (**3**), in which complexation causes a change in ring C conformation from boat to chair despite the presence of an N-oxide group, is studied using spectroscopic and DFT methods. The structure of the complexes obtained is compared with that of monoperchlorate salts of **1**–**3**.

2. Experimental

2.1. *General techniques*

The ^{1}H NMR and ^{13}C NMR spectra (including ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and DEPT) were measured on a Varian 300 Mercury spectrometer at 300.13 and

Table 1. Physico-chemical data of **4**–**9**.

Complex	M.p. [°C]	Yield [%]	Elemental analysis					
			Calculated			Found		
			%C	%H	%N	%C	%H	%N
[(Sparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$] (**4**)	189–192	87.3	42.60	6.39	6.63	42.64	6.08	6.44
[(Sparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$] (**5**)	175–180	83.3	33.33	5.00	5.19	32.51	4.23	5.16
[(2-Methylsparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$] (**6**)	155–160	77.5	43.99	6.64	6.41	42.74	6.38	6.40
[(2-Methylsparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$] (**7**)	203–208	74.4	34.66	5.23	5.05	35.12	5.02	5.00
[(2-Phenylsparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$] (**8**)	140–145	68.5	50.55	6.22	5.62	50.82	5.98	5.70
[(2-Phenylsparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$] (**9**)	162–166	67.8	40.91	5.03	4.55	40.04	4.91	4.52

75.462 MHz, respectively, and at ambient temperature using ~0.5 M solutions in DMSO with TMS as internal reference. The conditions of recording the spectra: ^{13}C NMR: acquisition time 1.5 s, spectral width 23 000 Hz, number of points 69 000; ^{1}H NMR: acquisition time 3.0 s, spectral width 9000 Hz, number of points 54 000; ^{1}H–^{1}H Cosy 90–90: relax. delay 1.0 s, acquisition time 0.17 s, spectral width 2 950 Hz, 2D width 2 950 Hz, 16 repetitions, 256 increments; ^{13}C–^{1}H COSY: relax. delay 0.9 s, acquisition time 0.18 s, spectral width 3 260 Hz, 2D width 22 630 Hz, 32 repetitions, 2×256 increments.

IR spectra were recorded on an FT-IR Bruker 113v spectrometer (KBr pellets). ESI mass spectra were obtained on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer.

The sample solutions were prepared in methanol. Elemental analysis was carried out by means of a Perkin-Elmer 2400 CHN automatic device.

2.2. *DFT calculations*

Information on the geometry of monoprotonated N-oxides **1**-H$^+$, **2**-H$^+$, **3**-H$^+$ and new complexes **4**–**9** was obtained from quantum-chemical calculations carried out by density functional theory method (DFT) at the B3LYP/6-311+G level implemented in the Gaussian 03 program package [11].

2.3. *Preparation of complexes*

Ligands **1**–**3** and their monoperchlorate salts were synthesized using methods previously described [9, 12, 13]. [*Caution*: The perchlorate salts described here are potentially explosive. However, we have not experienced any problems with the synthesis and manipulation.] $ZnCl_2$ and $ZnBr_2$ were commercial products of Aldrich. Complexes **4**–**9** were obtained by addition of a zinc salt dissolved in methanol in excess, to a methanol solution of a given N-oxide. The crystalline products were obtained by slow evaporation of the solvent. The physico-chemical data of the complexes are given in table 1.

3. Results and discussion

Given that the conformations of sparteine and 2-methylsparteine in zinc(II) complexes are almost identical to the conformations in monoprotonated sparteines [14], the structures of complexes **4**–**9** were compared to that of the initial monoperchlorate N-oxides.

In the positive-ion ESI mass spectra of **4**–**9**, the peaks of the protonated N-oxides are observed at $m/z = 251$ for **4** and **5**, $m/z = 265$ for **6** and **7** and $m/z = 327$ for **8** and **9**. Their presence shows loss of the sparteine ligand in solution samples of the complexes.

The negative mode ESI mass spectra of **4**–**9** show the presence of $ZnCl_3^-$ and $ZnBr_3^-$ anions situated at $m/z = 171$ and 305, respectively.

The IR spectra of N-oxides **1**–**3** show very strong bands assigned to the stretching vibrations characteristic of the N → O group at 935 cm^{-1} [15]. However, in the spectra of their complexes with zinc salts these bands are reduced in intensity or disappear, and new bands (characteristic of N-oxide group) appear at 1175–1210 cm^{-1} due to the formation of a donor-acceptor oxygen-metal band. The band *trans* characteristic of N-oxides (2800 cm^{-1}, 2760 cm^{-1}) disappears as a result of protonation of the nitrogen

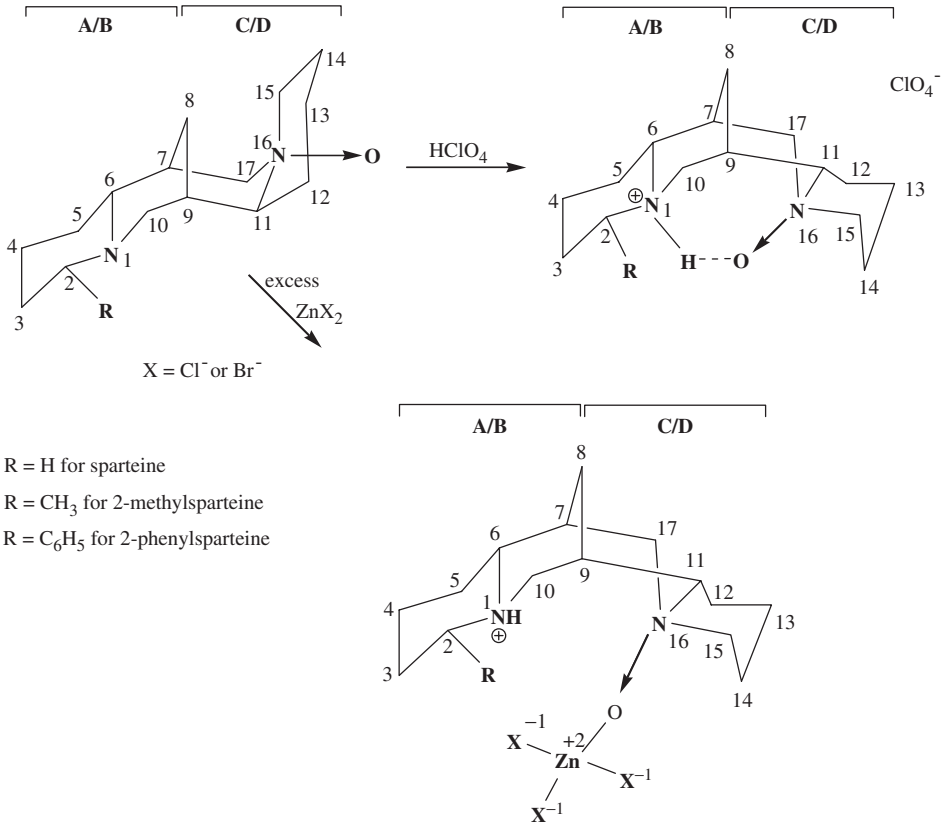


Figure 2. The configurational-conformational change that occurs in the N-oxide skeleton upon protonation or complexation.

atom N1. In addition, a few absorption bands arise at 300–350 cm^{-1} assigned to the metal-halogen bond. On the basis of a comparison of these results with those earlier obtained for the complex of N1 sparteine with $ZnCl_2$ of the known structure [16], the general formula of $[(\text{N-oxide-H})^+(ZnX_3)^-]$ (see figure 2) was assigned to complexes **4**–**9**.

The NMR data for N-oxides **1**–**3**, their monoperchlorate salts and zinc complexes **4**–**9** are collected in tables 2 and 3. Analysis of the chemical shifts given in tables 2 and 3 reveals the conformational changes in the bis-quinolizidine skeleton in N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine, on passing from the free bases to the monoperchlorate salts and zinc complexes. Both perchlorate salts and complexes occur in the cisoidal form with ring C in the chair conformation.

Analysis of the ^{13}C chemical shifts of C2, C3, C4, C5, C7, C8 and C9 carbon atoms of the perchlorate salts and the complexes reveals that the δ_C values are close to those of their analogues in the relevant N-oxides (protonation and complexation effects range from −2.7 to +0.6 ppm). This result corroborates the presence of chemically unchanged A and B rings preserving the *trans* quinolizidine form in the salts and complexes. Most indicative of the all-chair sparteine skeleton in monosalts and complexes of **1**–**3** are the large upfield shifts observed for C12, C14 and C17 which in the *cis*-quinolizidine fragment C/D are subjected to γ-gauche interaction. This produces a diamagnetic shift of the signals assigned to these carbon atoms relative to their positions in the spectra of the free bases. However, they correspond to the transition from the boat-chair *trans* quinolizidine C/D into all-chair *cis*-quinolizidine C/D. In the N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine, the C/D rings are in the boat-chair conformation, but with a junction *cis*. The greatest changes in the chemical shifts are observed at C17 (over 10 ppm). The complexation shifts of the other carbon atoms at the α position with respect to the N-oxide group (C15 and C11) have a positive sign and range from 3.4 to 4.5 ppm (see table 4).

Chemical shift changes of 6 ppm are noted for C6 and C10 which are in the γ position with respect to the N-oxide group. These changes follow mainly from the arrangement of the N–O group which is different from that in the initial N-oxide in which this group is at a considerable distance from both C6 and C10. The chemical shift changes at the carbon atoms are accompanied by those on the protons linked to these carbon atoms; the changes are the greatest at H6, H10 and H15. Changes in the chemical shifts have also been observed for the protons at C2 (the signal above 2.60 ppm) in the α position towards the protonated N1. The signal assigned to the methyl group, appearing at about 18.6 ppm for perchlorate salt and complexes of **2**, indicates that this group is in an equatorial position as in the free base (21.07 ppm). Apart from the data listed in tables 2 and 3, the spectra of the monoperchlorate salt and the complexes of 2-phenylsparteine N-oxide also show 127.09, 127.05 and 126.9 ppm; C values (for **3**-$HClO_4$) and 139.66, 128.21 and 120.16 ppm; C values (for complexes **8** and **9**) belonging to the phenyl substituent. The signal at 7 ppm is assigned to the aromatic protons. In the NMR spectra of the perchlorate salts and complexes the signal of the "acidic" proton is shifted very strongly downfield. The acidic proton is located on N1 and the signal assigned to it appears at about 18 ppm.

Taking into account the experimental findings, the binding energies for **4**–**9** were calculated and collected in table 5. The most stable 1 : 1 complexes in the gas phase are

Table 2. ^{13}C and ^{1}H NMR chemical shifts of N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine and their perchlorate salts (in DMSO).

	Sparteine N16-oxide		Sparteine N16-oxide × $HClO_4$		2-Methylsparteine N16-oxide		2-Methylsparteine N16-oxide × $HClO_4$		2-Phenylsparteine N16-oxide		2-Phenylsparteine N16-oxide × $HClO_4$	
C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H ($CDCl_3$)	δ_C	δ_H
2	54.96	2.08ax 2.70eq	52.35	2.54ax 3.00eq	57.13	2.06ax	57.06	2.60ax	68.03	3.07	67.32	3.75ax
3	25.28	1.54 1.54	23.90	1.36 1.70	34.83	1.20 1.58	33.26	1.30 1.75	36.52	1.52 1.70	33.87	1.50 1.65
4	23.87	1.18 1.68	22.69	1.36 1.60	23.77	1.19 1.62	22.57	1.19 1.62	23.84	1.78 1.42	23.04	1.19 1.62
5	28.76	1.26 1.26	28.11	1.72 2.04	29.73	1.22 1.22	28.16	1.78 2.02	29.43	1.48 1.58	28.12	1.46 1.52
6	66.41	1.80	60.77	2.68	66.44	1.90	61.15	2.71	66.52	2.14	61.00	2.90
7	33.06	1.84	33.44	2.10	33.02	1.90	33.68	2.12	33.13	2.03	33.65	2.00
8	27.44	1.30ax 2.31eq	27.23	1.60ax 1.70eq	27.57	1.30ax 2.30eq	27.91	1.52ax 1.60eq	27.74	1.49 2.32	27.86	2.10 2.00eq
9	32.48	1.84	33.13	2.10	33.27	1.90	33.68	2.12	33.32	1.77	33.46	2.38
10	62.18	1.98ax 2.50eq	55.72	2.62ax 3.02eq	57.68	1.75ax 2.90eq	51.79	2.60ax 3.42eq	58.74	1.76 2.50	51.00	2.50ax 3.40eq
11	72.20	3.28	75.55	3.56	72.33	3.22	75.67	3.57	72.31	3.51	75.90	3.47
12	27.24	1.40 2.70	24.78	1.54 2.13	27.35	2.40ax 1.28eq	24.81	2.18ax 1.60eq	27.32	2.59 1.20	25.02	2.18ax 1.75eq
13	16.88	1.24 1.46	21.63	1.47 1.70	16.93	1.23 1.50	21.63	1.45 1.70	16.94	1.53 1.21	21.44	
14	20.90	2.12ax 1.44eq	22.31	1.77ax 1.36eq	20.95	2.18ax 1.50eq	22.36	1.70ax 1.40eq	20.93	2.42 1.56	22.29	2.40ax 1.80eq
15	64.52	3.60ax 2.82eq	69.05	3.72ax 3.34eq	64.59	3.60ax, 2.82eq	68.98	3.66ax, 3.42eq	64.72	3.65 3.20	68.00	3.78ax 3.60eq
17	69.04	3.62ax 3.36eq	58.00	4.08ax 3.34eq	68.98	3.34ax 3.21eq	58.27	3.38ax 4.10eq	69.14	3.89 3.48	58.00	3.50ax 4.10eq
CH_3	–	–	–	–	21.07	1.04	18.67	1.10		–	–	–

δ_H values are mainly extracted from the HET-COR spectrum.

Table 3. ^{13}C and ^{1}H NMR chemical shifts of sparteine N16-oxide, 2-methylsparteine N16-oxide and 2-phenylsparteine N16-oxide complexes with zinc(II) salts (in DMSO).

	[(Sparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$]		[(Sparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$]		[(2-Methylsparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$]		[(2-Methylsparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$]		[(2-Phenylsparteine N16-oxide-H)$^+$($ZnCl_3$)$^-$]		[(2-Phenylsparteine N16-oxide-H)$^+$($ZnBr_3$)$^-$]	
C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
2	52.3	2.6ax 3.0eq	52.3	2.6ax 3.0eq	56.9	2.7ax	57.0	2.7ax	67.5	3.7	67.4	3.8
3	23.9	1.4 1.7	23.8	1.4 1.7	33.2	1.2 1.8	33.2	1.2 1.8	33.9	1.6 1.8	33.8	1.7 1.8
4	22.6	1.4–2.0	22.6	1.3–2.1	22.5	1.4–2.1	22.5	1.4–2.1	23.0	1.6–2.0	22.9	1.5–2.1
5	28.1	1.7 2.1	28.1	1.7 2.0	28.1	1.7 2.1	28.1	1.7 2.1	28.1	1.9–2.1	28.1	1.6–2.2
6	60.7	2.7	60.7	2.7	61.0	2.7	61.0	2.7	61.8	2.9	61.8	2.9
7	33.4	2.1	33.4	2.1	33.5	2.2	33.5	2.3	33.5	2.3	33.4	2.2
8	27.2	1.5 2.2ax	27.2	1.5 2.0ax	27.9	1.6ax 2.1eq	27.9	1.7ax 2.1eq	27.9	1.9–2.1	27.8	1.6–2.2
9	33.1	2.1	33.1	2.1	33.6	2.15	33.6	2.15	33.6	2.0	33.6	2.0
10	55.7	3.0 2.8eq	55.7	3.0 2.8eq	51.8	3.4ax 2.6eq	51.7	3.35ax 2.6eq	53.2	2.5 2.6	53.1	2.5 2.6
11	75.7	3.6	75.7	3.6	75.7	3.6	75.6	3.6	75.9	3.4	75.8	3.4
12	24.7	1.5 2.2	24.7	1.5 1.8	24.8	2.2ax 1.6eq	24.8	2.15ax 1.55eq	25.0	1.6 2.2	25.0	1.6 2.2
13	21.6	1.4–2.0	21.6	1.3–2.1	21.6		21.6	1.4–2.0	21.4	1.6–2.0	21.4	1.5–2.1
14	22.3	1.44–2.0	22.2	1.3–2.1	22.3	2.1–1.5	22.3	2.1–1.4	22.3	1.6–2.0	22.2	1.5–2.1
15	69.0	3.7ax 3.4eq	69.0	3.7ax 3.4eq	69.0	3.7ax 3.4eq	68.9	3.7ax 3.4eq	68.8	3.5 3.8	68.7	3.5 3.8
17	58.1	3.4ax 4.1eq	58.0	3.4ax 4.1eq	58.3	4.1ax 3.4eq	58.3	4.1ax 3.35eq	58.4	3.5 4.2	58.3	3.5 4.2
CH_3	–	–	–	–	18.6	1.1	18.7	1.1	–	–	–	–

δ_H values are mainly extracted from the HET-COR spectrum.

Table 4. ^{13}C complexation effect in sparteine N16-oxide, 2-methylsparteine N16-oxide and 2-phenylsparteine N16-oxide complexes with zinc(II) salts.

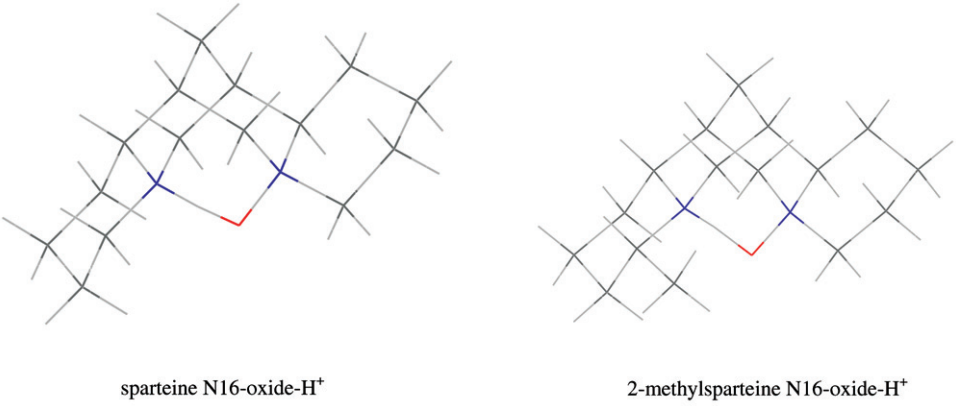
C	[(Sparteine N16-oxide-H)$^+$ $(ZnCl_3)^-$] $\Delta = \delta_4 - \delta_1$	[(2-Methylsparteine N16-oxide-H)$^+$ $(ZnCl_3)^-$] $\Delta = \delta_6 - \delta_2$	[(2-Phenylsparteine N16-oxide-H)$^+$ $(ZnCl_3)^-$] $\Delta = \delta_8 - \delta_3$
2	−2.7	−0.2	−0.5
3	−1.4	−1.6	−2.6
4	−1.3	−1.3	−0.8
5	−0.7	−1.6	−1.3
6	−5.7	−5.4	−4.7
7	+0.3	+0.5	+0.4
8	−0.2	+0.3	+0.2
9	+0.6	+0.3	+0.3
10	−6.5	−5.9	−5.5
11	+3.5	+3.4	+3.6
12	−2.6	−2.6	−2.3
13	+4.7	+4.7	+4.5
14	+1.4	+1.3	+1.4
15	+4.5	+4.4	+4.1
17	−10.9	−10.7	−10.7
CH_3	–	−2.5	–

Table 5. Calculated energies of bis-quinolizidine N16-oxide complexes. Total energies are given in Hartrees (H = 627.5 kcal mol^{-1}).

Compound	*E*
Sparteine N16-oxide (**1**)	−771.21
Sparteine N16-oxide-H^+	−772.16
Sparteine N16-oxide + $ZnCl_3$ (uncomplexed)	−3932.15
Sparteine N16-oxide−$ZnCl_3$ (complexed)	−3932.80
Sparteine N16-oxide−$ZnCl_3$*	−3932.45
Sparteine N16-oxide + $ZnBr_3$ (uncomplexed)	−10273.80
Sparteine N16-oxide−$ZnBr_3$ (complexed)	−10275.40
2-MethylSparteine N16-oxide (**2**)	−810.01
2-MethylSparteine N16-oxide−H^+	−811.46
2-MethylSparteine N16-oxide + $ZnCl_3$ (uncomplexed)	−3970.99
2-MethylSparteine N16-oxide−$ZnCl_3$ (complexed)	−3971.80
2-MethylSparteine N16-oxide−$ZnCl_3$*	−3971.01
2-MethylSparteine N16-oxide + $ZnBr_3$ (uncomplexed)	−10313.10
2-MethylSparteine N16-oxide−$ZnBr_3$ (complexed)	−10314.08
2-PhenylSparteine N16-oxide (**3**)	−1002.24
2-PhenylSparteine N16-oxide−H^+	−1003.24
2-PhenylSparteine N16-oxide + $ZnCl_3$ (uncomplexed)	−4163.22
2-PhenylSparteine N16-oxide−$ZnCl_3$ (complexed)	−4164.63
2-PhenylSparteine N16-oxide−$ZnCl_3$*	−4164.34
2-PhenylSparteine N16-oxide + $ZnBr_3$ (uncomplexed)	−10504.88
2-PhenylSparteine N16-oxide−$ZnBr_3$ (complexed)	−10506.27

*Complexes formed with unchanged initial N-oxide.

formed with bromide salts. The binding energy values calculated for sparteine N16-oxide with zinc chloride show that the structures in which a change in ring C conformation takes place (complexes **4**, **6**, **8**) are energetically more favorable than those in which bis-quinolizidine skeleton of the initial N-oxide is unchanged



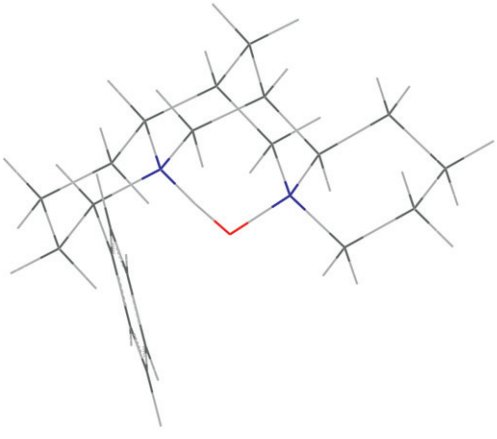


Figure 3. The optimized structure of protonated sparteine, 2-methylsparteine and 2-phenylsparteine N16-oxides.

(complexes **4***, **6***, **8***). The difference in binding energy varies from 182 kcal/mol (complexes **8** and **8***) to 496 kcal/mol (complexes **6** and **6***). The monodentate coordination of zinc(II) salts with the all-chair conformation of bis-quinolizidine skeleton has also been found for sparteine N1-oxide complex with $ZnCl_2$ where structure was confirmed by X-ray diffraction [16]. The structures of monoprotonated N-oxides and newly obtained complexes **4**–**9** fully optimized by using the Gaussian03 package at the B3LYP level are shown in figures 3–5. For monoperchlorate salts of compounds **1**–**3** the calculated N1 $\cdots$ O distance of 2.48 Å is almost the same as that obtained by X-ray methods: 2.492 Å for **1**-H^+ and 2.471 for **3**-H^+ Å [17, 18]. The N1 $\cdots$ O distance in salts is by about 0.3 Å shorter than the corresponding distance observed in the zinc complexes due to the intramolecular hydrogen bond N1–H $\cdots$ O and the cation size.

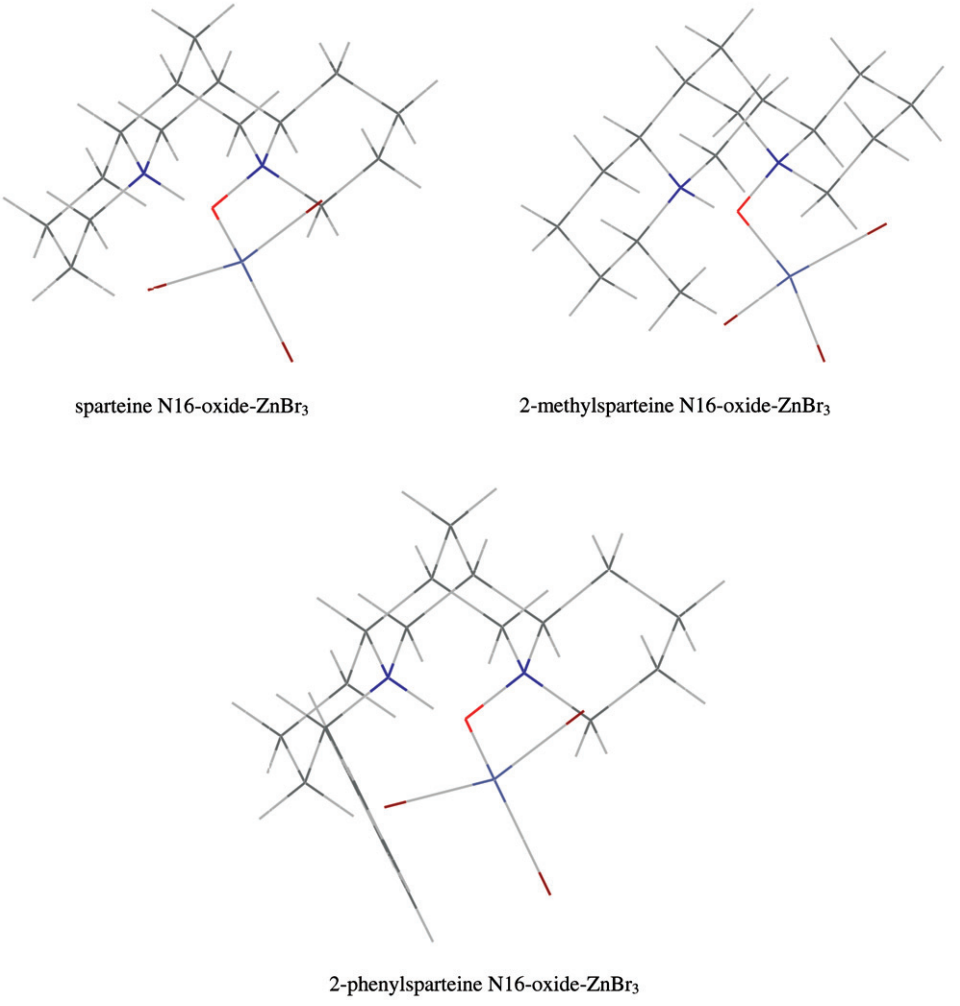


Figure 4. The optimized structure of sparteine N16-oxide, 2-methylsparteine N16-oxide and 2-phenylsparteine N16-oxide complexes with zinc bromide.

4. Conclusions

In this article it is shown that sparteine N16-oxides form complexes not only with small cations (lithium), but also with zinc.

As a result of complexation with ZnX_2 (X=Cl, Br) the nitrogen atom N1 undergoes protonation and the conformations of ring C in the N16-oxides of sparteine, 2-methylsparteine and 2-phenylsparteine change from boat to chair. A structural comparison of the complexes obtained and those of N1-oxide of sparteine with $ZnCl_2$ has revealed that the position of the N-oxide group (N1 or N16) has no effect on the structure of the complexes obtained. The general formula of the complexes can be written as $[(\text{N-oxide-H})^{+}(ZnX_3)^{-}]$.

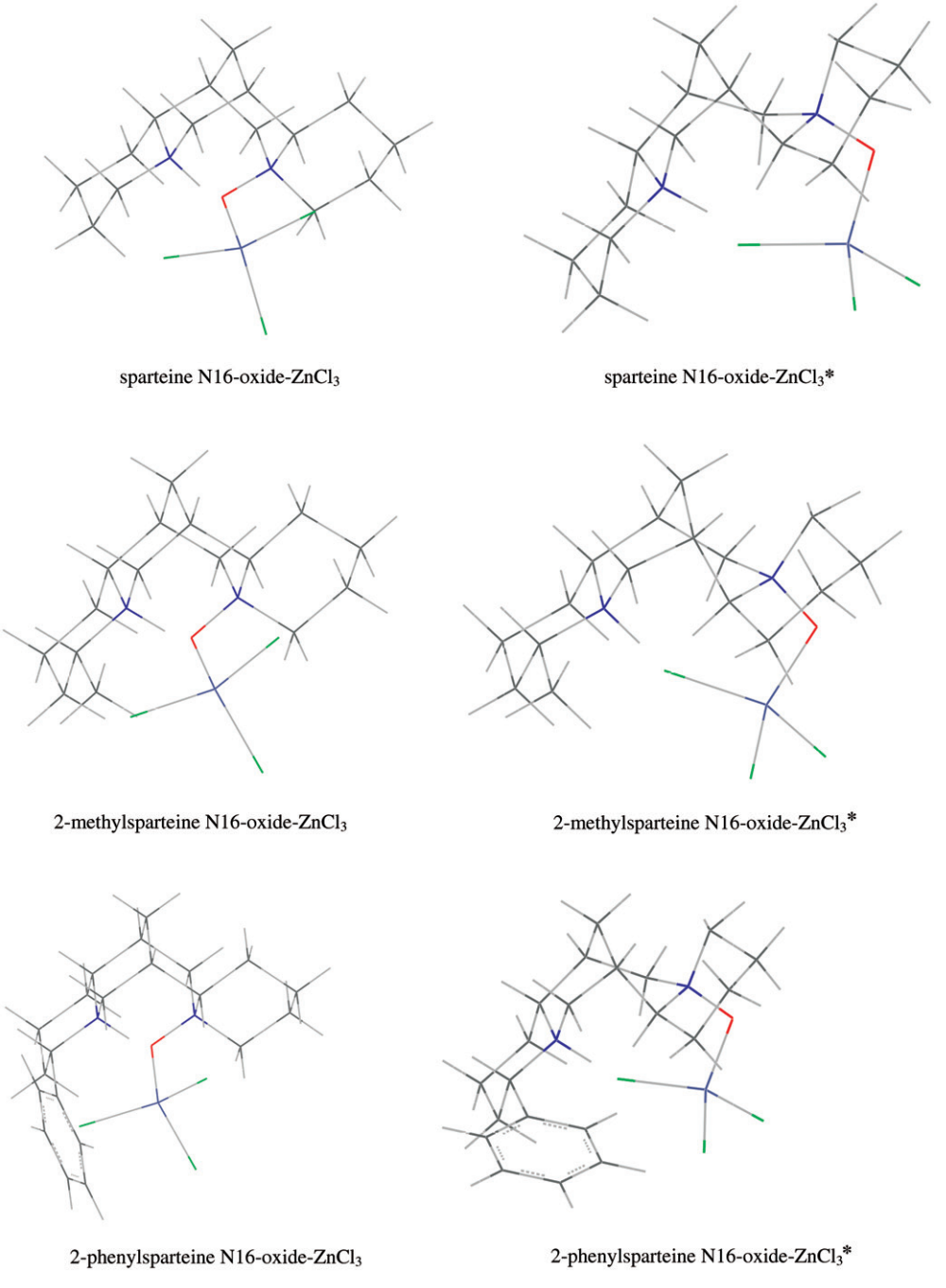


Figure 5. The optimized structure of sparteine N16-oxide, 2-methylsparteine N16-oxide and 2-phenylsparteine N16-oxide complexes with zinc chloride. *The complexes formed with unchanged initial N-oxide.

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