Comparable study of the structure of 1,2bis(2-acetamidoethyl) diaziridine and 3,3diethyldiaziridine with structures of related compounds by X-ray diffraction analysis and quantum chemical calculations Vladimir V. Kuznetsov, Ilya I. Marochkin, Alexander S. Goloveshkin, Nina N. Makhova, et al.

# **Structural Chemistry**

Computational and Experimental Studies of Chemical and Biological Systems

ISSN 1040-0400 Volume 28 Number 4

Struct Chem (2017) 28:1211-1221 DOI 10.1007/s11224-016-0908-5





Your article is protected by copyright and all rights are held exclusively by Springer Science +Business Media New York. This e-offprint is for personal use only and shall not be selfarchived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



**REVIEW ARTICLE** 



# Comparable study of the structure of 1,2-bis(2-acetamidoethyl) diaziridine and 3,3-diethyldiaziridine with structures of related compounds by X-ray diffraction analysis and quantum chemical calculations

Vladimir V. Kuznetsov<sup>1</sup> • Ilya I. Marochkin<sup>2</sup> • Alexander S. Goloveshkin<sup>3</sup> • Nina N. Makhova<sup>1</sup> • Igor F. Shishkov<sup>2</sup>

Received: 21 October 2016 / Accepted: 26 December 2016 / Published online: 20 February 2017 © Springer Science+Business Media New York 2017

Abstract The crystal structures of 1,2-bis(2acetamidoethyl)diaziridine and 3,3-diethyldiaziridine have been determined by single-crystal X-ray diffraction study. The studied diaziridine molecules have C<sub>2</sub> total group symmetry. The conformation of the studied molecules is similar to those of other diaziridines. A topological study within the framework of Bader's atoms in molecule (AIM) theory was performed for these molecules, their analogs and related compounds. From AIM and natural bond orbital (NBO) analysis data, an influence of the intramolecular interaction on chemical bonds was described and quantified. It was found that the N-N bond length increases on going from acyclic to cyclic molecules in accordance with increasing *p*-character of  $\sigma_{N-N}$ bonding orbitals. The lengthening of N-N bond lengths in diaziridine molecules in most cases is accompanied with increasing of the bond ellipticities demonstrating the  $\pi$ component contribution to these bonds.

**Keywords** X-ray diffraction study · Diaziridine structures · Natural bond orbital analysis · Atoms in molecule theory

Ilya I. Marochkin marochkin@phys.chem.msu.ru

- <sup>2</sup> Chemistry Department, Lomonosov Moscow State University, Leninsky Gory 1, Moscow, Russian Federation 119991
- <sup>3</sup> Russian Academy of Sciences, A. N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilova Str, Moscow, Russian Federation 119991

#### Introduction

For many years, study of molecular structure of diaziridines (1,2-diazacyclopropanes 1) has been a field of our scientific interest [1-8], which is caused by high theoretical and practical significance of this class of compounds. The diaziridine derivatives are capable of direct action on the central nervous system, revealing various types of neurotropic activity [9]. Under normal conditions, nitrogen atoms in the diaziridine ring are chiral, and, therefore, these compounds are convenient subjects for studying the stereochemistry of nitrogencontaining molecules [10]. In the last decades, diaziridines have been widely used in the ring-expansion reactions under the action of electrophilic reagents such as ketenes, isocyanates, isothiocyanates [11–15] or dipolarophiles in ionic liquids [16-22]. On the other hand, diaziridines are of interest as heterocyclic analogs of cyclopropanes 2, possessing a series of structural and electronic anomalies. In particular, the intramolecular C-C bond length in cyclopropane is abnormally short for cycloalkanes [23]. A known attempt to correlate the structural behavior of cyclopropane with the existing concept of cycloalkane structure was the Walsh diagram applying  $sp^2$ - rather than  $sp^3$ -hybridized orbitals of carbon to construct the molecular model of diaziridines 1. Further development of the Walsh diagram required considering  $sp^{2.5}$ - and  $sp^{5}$ -hybridized orbitals [24]. Adding nitrogen atoms with atomic radius, orbital size, and hybridization behavior similar to those of carbon does not violate the Walsh model and should not bring about significant differences between diaziridine and cyclopropane rings in terms of stereochemical behavior; hence, a certain structural analogy between these molecules should be expected. Thus, some decrease in the bond lengths between the diaziridine ring atoms relative to acyclic analogs can be possible.

<sup>&</sup>lt;sup>1</sup> N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp, Moscow, Russian Federation 119991

In particular it was shown [1-8] (Table 1) that endocyclic C-N bond length in the diaziridine 1a-h molecules varied from 1.442(2) Å in 1b to 1.455(2) Å in 1c with an average value of C-N bond length of 1.448 Å. These bond lengths are noticeably shorter than those in 1,2-dimethyl-1,2-diazetidine 3  $(1.481(8) \text{ Å } [25] \Delta r = 0.033 \text{ Å})$  or in 1,2-dimethylhydrazine 4 (1.463(5) Å [26],  $\Delta r = 0.015$  Å). These data may be compared with the C-C bond lengths in cyclopropane 2 (1.510(1) Å [23]), cyclobutane (1.552 Å [27],  $\Delta r = 0.042$  Å), and *n*-butane (1.531(2) Å [28],  $\Delta r = 0.021$  Å) (Table 1). Meanwhile, the N-N bond length of diaziridines [1-8] can vary from 1.503(2) Å in 1f to 1.545(7) Å in 1d with an average value of 1.517 Å, r(N-N)parameters are significantly greater than similar ones in 1,2dimethyl-1,2-diazetidine 3 (1.427(7) Å,  $\Delta r = 0.090$  Å) and in 1,2-dimethylhydrazine **4** (1.419(11) Å,  $\Delta r = 0.098$  Å). The more significant decrease of the C-C bond length, 1.454 Å [27], in the molecule of bicyclohexane 7 compared with cyclopropane 2 (1.510(1) Å,  $\Delta r = 0.056$  Å) was not observed for N-N bond length in diaziridines 1b (1.506(13) Å) and 1a  $(1.514(6) \text{ Å}, \Delta r = 0.008 \text{ Å})$ . The C-N and N-N bond lengths from the most published experimental studies are summarized in Table 1.

Earlier, X-ray diffraction studies of diaziridine structures were performed only in a few cases (e.g., for compounds 1e, f, g, h, Table 1), because most of the diaziridine derivatives are liquids. For experimental determination of the structures of several liquid diaziridines (e.g., compounds 1a-d, Table 1), electron diffraction was applied. Therefore, gaining new experimental data about structure of diaziridines is important for deeper insight into the previously elucidated features of diaziridine ring structure, in particular, increasing the N-N bond length and decreasing the C-N bond length in comparison with related structures.

To shed light upon the possible reasons of structural peculiarities of the diaziridine ring, in this article we determined the structures of two new diaziridines (1,2-bis(2-acetamidoethyl)diaziridine **1i** and 3,3-diethyldiaziridine **1j**) by X-ray diffraction analysis. Considering the obtained data, we performed a comparative study of the endocyclic bond lengths, hybridization of the N-N bonding orbital ( $\sigma_{N-N}$ ) and nitrogen lone pairs n(N), atomic charges, orbital interaction energy stabilization, and ellipticity of the N–N and C–N bonds by means of quantum chemical calculations for diaziridines **1a**-j and their structural analogs **3** and **4**.

## **Experimental section**

The commercially available reagents were purchased from ACROS catalog and were not further purified. IR spectra were recorded on a UR-20 spectrometer in KBr pellets, <sup>1</sup>H NMR

and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.47 MHz, respectively). Thin layer chromatography (TLC) was performed on Silufol-254-UV plates by spraying 3% solutions of diphenylamine in acetone, followed by heating the plate. The eluent (CHCl<sub>3</sub>) was washed twice with an equal volume of 25% aqueous NH<sub>3</sub> and dried over K<sub>2</sub>CO<sub>3</sub>. The melting point was determined on a GALLENKAMP device manufactured by Sanyo. Single crystal X-ray diffraction experiments were carried out on a Bruker APEX II CCD diffractometer. The crystals were kept at 100 K during data collection. The molecular structure was solved by charge flipping method with the *olex2.solve* structure solution program [30] incorporated in Olex2 [31] and refined from least-squares minimization with the XL refinement package [32]. Mass spectra were recorded on a Bruker micrOTOF II instrument using electrospray ionization (ESI). 1,2-(2-Acetamidoethyl)diaziridine 1i was synthesized according to known technique [33]. The physicochemical characteristics of compound 1i were close to those published previously [34]. 3,3-Diethyldiaziridine 1j was prepared by a method reported in [35-37].

*1,2-Bis(2-Acetamidoethyl)diaziridine* **1i**. A solution of *tert*-BuOCl (11.1 ml, 0.1 mol) in 20 ml of CHCl<sub>3</sub> was added dropwise at -5 to 0 °C with vigorous stirring to 2-acetamidoethylamine (17.6 g, 0.2 mol) in 100 ml of CHCl<sub>3</sub>, and finely ground potassium carbonate (27.6 g 0.2 mol) was added to the reaction mixture. Then paraformaldehyde (3.0 g, 0.1 mol) was added with stirring at 5-10 °C. Stirring was continued for 12 h at 20-22 °C. The inorganic precipitate was filtered off and washed with CHCl<sub>3</sub> (3 × 50 ml) and the solvent was removed on a rotary evaporator. Diaziridine **1i** was isolated by column chromatography on silica gel, L = 40–100 mm with CHCl<sub>3</sub> as the eluent, washed with an equal volume of 25% aqueous NH<sub>3</sub>, and dried with potassium carbonate.

3,3-Diethyldiaziridine **1j**. Ammonia (17 g, 1.0 mol) as a 25% aqueous solution and 3-pentanone (diethyl ketone) (8.6 g, 0.1 mol) were added to 100 ml of methanol at -15 °C with vigorous stirring. Then 96% hydroxylamine-O-sulfonic acid (HASA) (11.8 g, 0.1 mol) was added in small portions (about 0.05 g) at -20 to -15 °C over a period of 30 min and the reaction mixture was stirred under the same conditions for 2 h. The precipitate was separated and washed with methanol (3 × 20 ml), the solvent was removed on a rotary evaporator, diaziridine **1j** was extracted from the residue with hot ether (3 × 50 ml), the solvent was evaporated, and the final residue was recrystallized from acetone.

#### **Computational Methods**

Quantum chemical calculations were based on the B3LYP hybrid potential of the density functional theory (DFT) and

|    | Molecule  | <i>r</i> (N <b>-</b> N), Å                                   | <i>r</i> (C <b>-</b> N), Å                                   | Method       |
|----|---|--|--|--------------|
| 1a | $<^{N-Me}_{N-Me}$   | 1.514(6)   | 1.448(2)   | GED, [5]     |
| 1b | $<^{N}_{N}$   | 1.506(13)  | 1.442(2)   | GED, [7]     |
| 1c |   | 1.522(7)   | 1.455(7)   | GED, [8]     |
| 1d |   | 1.512(7) <sup><i>a</i></sup><br>1.545(7) <sup><i>b</i></sup> | 1.444(7) <sup><i>a</i></sup><br>1.443(7) <sup><i>b</i></sup> | GED, [8]     |
| 1e | $\underset{Me-N}{\overset{H-N}{\underset{N}{\rightarrow}}} \xrightarrow{\overset{N-H}{\underset{N-Me}{\rightarrow}}} \xrightarrow{N-H}$ | 1.512(2)   | 1.445(2)   | X-Ray, [2]   |
| 1f | Me = N<br>Me = N $Me = N$ $Me$  | 1.503(2)   | 1.454(2)   | X-Ray, [6]   |
|    |   | 1.517(2)   | 1.449(2)   | X-Ray, [1]   |
| Ig |   | 1.511(2)   | 1.452(2)   | GED, [4]     |
| 1h |   | 1.528(2)   | 1.452(2)   | X-Ray, [3]   |
| 3  | $\Box_{N-Me}^{N-Me}$  | 1.427(7)   | 1.481(8)   | MW+GED, [25] |
| 4  | MeHN-NHMe   | 1.419(11)  | 1.463(5)   | X-Ray, [26]  |
|    |   |  | <i>r</i> (C <b>-</b> C), Å                                   |              |
| 2  | $\square$   |  | 1.510(1)   | GED, [23]    |
| 7  | $3 \xrightarrow{1}{2}$  |  | 1.454 <sup>c</sup> 1.515 <sup>d</sup>                        | MW+GED, [27] |
| 5  |   |  | 1.552(1)   | GED, [28]    |
| 6  | ( <i>n</i> -butane)   |  | 1.531(2)   | GED, [29]    |

 Table 1
 The C-N and N-N endocycle bond lengths experimentally determined for diaziridine derivatives molecules and structurally related compounds

<sup>a</sup> Bond lengths of boat

<sup>b</sup> char-conformer

<sup>*c*</sup> The values of  $r(C_1-C_2)$  bond length

 $^{d}r(C_{1}-C_{3})$  and  $r(C_{2}-C_{3})$  bond lengths. Me-group corresponds to methyl group CH<sub>3</sub>

the second-order perturbation MP2 theory with the 6-311+G(2df,p) split-valence basis sets and Dunning's cc-pVTZ basis set. The geometry of the molecules was calculated for the most predominant conformation. Geometry optimizations, vibrational frequency calculations and natural bond orbital (NBO) analysis were carried out with the Gaussian 03 program [38]. The geometry optimizations were performed at the

MP2/cc-pVTZ level and the DFT/B3LYP/6-311+G(2df,p) approach. Vibrational frequencies at the B3LYP/6-311+G(2df,p) level of theory were used to characterize the stationary points as minima. Atomic charges at the B3LYP/6-311+G(2df,p) level were obtained using natural bond orbital analysis. The QTAIM computations were done with the AIMAII program package [39].

#### **Results and Discussion**

First X-ray diffraction study of compounds 1i and 1j was performed.

Crystals of **1i** (C<sub>9</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>, M = 214.27) are monoclinic: space group C2/c (no. 15), a = 7.2491(6) Å, b = 6.6460(5) Å, c = 23.106(2) Å,  $\beta = 90.317(2)^\circ$ , V = 1113.19(16) Å<sup>3</sup>, Z = 4, T = 100 K,  $\mu$ (MoK $\alpha$ ) = 0.093 mm<sup>-1</sup>,  $D_{calc} = 1.279$  g/cm<sup>3</sup>, 3840 reflections measured ( $3.52^\circ \le 2\Theta \le 60.06^\circ$ ), 1603 unique ( $R_{int} = 0.0220$ ,  $R_{sigma} = 0.0301$ ) which were used in all calculations. The final  $R_1$  was 0.0399 (>2  $\sigma$ (I)) and  $wR_2$ was 0.1074 (all data).

Crystals of **1j** (C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>, M = 100.17 g/mol) are tetragonal: space group P4<sub>2</sub>bc (no. 106), a = 8.1506(6) Å, c = 18.726(2) Å, V = 1244.01(19) Å<sup>3</sup>, Z = 8, T = 100 K,  $\mu$ (MoK $\alpha$ ) = 0.067 mm<sup>-1</sup>,  $D_{calc} = 1.070$  g/cm<sup>3</sup>, 11,801 reflections measured (4.36°  $\leq 2\Theta \leq 57.98°$ ), 1654 unique ( $R_{int} = 0.0302$ ,  $R_{sigma} = 0.0204$ ) which were used in all calculations. The final  $R_1$  was 0.0467 (>2  $\sigma$ (I)) and  $wR_2$  was 0.1257 (all data). The crystal structures of **1i** and **1j** were deposited in Cambridge Crystallographic Data Centre (CCDC numbers are 1509186 and 1509187, respectively).

Figures 1 and 2 show a general view of molecules 1i and 1j in a crystal phase investigated by X-ray diffraction. The molecules have a second order rotational symmetry axis ( $C_2$  total symmetry group) passing through the middle of the N-N bond and ring carbon atom. It is known for diaziridine compounds that the alkyl substituents at the nitrogen atom occupy the *trans*-position relative to the ring plane.

The N-N bond length in 1,2-bis(2-acetamidoethyl)diaziridine molecule **1i** was found to be 0.089(7) and 0.097(11) Å larger than that in 1,2-dimethyl-1,2-diazetidine **3** and 1,2-dimethylhydrazine **4**, respectively. The endocyclic C-N bond length in **1i** is 0.023(8) Å shorter than that in molecule **3**, and in comparison with molecule **4** it seems to be unchanged within experimental accuracy (Table 2). The N–N bond length in compound **1j** is



**Fig. 1** General view of 1,2-bis(2-acetamidoethyl)diaziridine molecule **1i** in crystal. Atoms are represented by thermal displacement ellipsoids ( $\rho = 50\%$ ). The symmetry independent part is marked by labeled atoms



Fig. 2 General view of molecule 1j in crystal. Atoms are represented by thermal displacement ellipsoids ( $\rho = 50\%$ ). The symmetry independent part is marked by labeled atoms

0.097(7) Å longer than that in 1,2-dimethyl-1,2-diazetidine **3** and 0.105(11) Å longer than N-N bond length in 1,2-dimethylhydrazine **4**. The endocyclic C-N bond length in **1j** is shortened with respect to this bond length in the molecules of 1,2-dimethyl-1,2-diazetidine **3** ( $\Delta = 0.027(8)$  Å) and 1,2-dimethylhydrazine **4** ( $\Delta = 0.009(5)$  Å). Thus, the endocyclic bond lengths in **1i** and **1j** show the same trend that was observed in the previous studies (see Table 1).

The crystals of 1,2-bis(2-acetamidoethyl)diaziridine 1i and 3,3-diethyldiaziridine 1j were found to have layered structure in the 001 direction (Fig. 3). The molecules are held in the layers by means of hydrogen bonds between the nitrogen (1j) or oxygen (1i) lone pair of one molecule and the NH-group hydrogen atom of the second molecule (the N···O distance is 2.868(1) Å in 1i, and the N···N distance is 3.148(1) Å in 1j, Fig. 4). In 1i, the crystal layers are connected to each other by CH···O intermolecular interactions between the CH<sub>3</sub> groups and oxygen atoms of the acetyl groups (the C···O distance is 3.654(2) Å). In the crystals of 3,3-diethyldiaziridine 1j, there are weak H···H interactions.

The theoretical N-N and C-N bond lengths of 1a-j, 3 and 4 molecules were determined by quantum chemical calculations. The results are given in Table 3 and supplemented with experimental data for same values. Experimental endocyclic bond lengths in diaziridines 1a-j were found to be close to the calculated values. The MP2/cc-pVTZ approach appears to be slightly better in predicting the endocyclic N-N and C-N bond lengths. According to the MP2/cc-pVTZ results, the N-N bond lengths change from 1.488 to 1.522 Å (except for 1d), and the C-N bond lengths vary in the 1.441 ÷ 1.460 Å range. For 1,2-dimethyl-1,2-diazetidine 3, the N-N and C-N bond lengths are similar, 1.488 and 1.481 Å, respectively, but the calculated N-N bond length proved to be considerably longer than the experimental one.

| Bond lengths         | $d/{ m \AA}$         | Bond angles            | w°         | Torsion angles                             | $\phi^{\circ}$ |
|----------------------|----------------------|------------------------|------------|--|----------------|
| 1,2-bis(2-acetamido  | ethyl)diaziridine 1i |                        |            |  |                |
| N1-N1 <sup>a</sup>   | 1.5161(18)           | C2-N1-N1 <sup>a</sup>  | 109.38(9)  | N1 <sup>1</sup> -N1-C2-C3                  | -99.90(8)      |
| N1-C1                | 1.4581(15)           | C1-N1-N1 <sup>a</sup>  | 58.67(5)   | N1-C2-C3-N2                                | -177.73(8)     |
| N1-C2                | 1.4642(13)           | C1-N1-C2               | 113.34(7)  | C4-N2-C3-C2                                | 162.58(9)      |
| O2-C4                | 1.2397(13)           | C4-N2-C3               | 121.66(9)  | C2-N1-C1-N1 <sup>a</sup>                   | 99.24(10)      |
| N2-C4                | 1.3399(14)           | O2-C4-N2               | 122.47(10) | C1-N1-C2-C3                                | -163.26(8)     |
| N2-C3                | 1.4511(13)           | O2-C4-C5               | 121.02(10) | C3-N2-C4-O2                                | -3.05(16)      |
| C4-C5                | 1.5013(14)           | N2-C4-C5               | 116.51(9)  | C3-N2-C4-C5                                | 177.63(9)      |
| C2-C3                | 1.5181(15)           | N1-C2-C3               | 108.39(8)  |  |                |
| C1-N1 <sup>a</sup>   | 1.4581(15)           | N1-C1-N1 <sup>a</sup>  | 62.65(9)   |  |                |
|                      |                      | N2-C3-C2               | 110.43(8)  |  |                |
| 3,3-diethyldiaziridi | ne 1j                |                        |            |  |                |
| N1-N1 <sup>b</sup>   | 1.522(2)             | C1-N1-N <sup>b</sup>   | 58.40(6)   | N1 <sup>b</sup> -N1-C1-C2                  | 104.08(10)     |
| N1-C1                | 1.452(2)             | N1-C1-N1 <sup>b</sup>  | 63.20(11)  | N1 <sup>b</sup> -N1-C1-C2 <sup>b</sup>     | -110.61(9)     |
| C1-N <sup>b</sup>    | 1.452(2)             | N1-C1-C2               | 118.00(6)  | N1 <sup>b</sup> -C1-C2-C3                  | -86.59(12)     |
| C1-C2                | 1.5134(14)           | N1 <sup>b</sup> -C1-C2 | 113.79(6)  | N1-C1-C2-C3                                | -157.71(10)    |
| C2-C3                | 1.5206(16)           | C2-C1-C2 <sup>b</sup>  | 118.36(13) | C2 <sup>b</sup> -C1-C2-C3                  | 58.58(8)       |
| N1A-N1A <sup>c</sup> | 1.523(2)             | C1-C2-C3               | 113.19(8)  | N1A <sup>c</sup> -N1A-C1A-C2A <sup>c</sup> | 110.65(9)      |
| N1A-C1A              | 1.455(2)             |                        |            | N1A <sup>c</sup> -N1A-C1A-C2A              | -104.04(9)     |
|                      |                      |                        |            | N1A-C1A-C2A-C3A                            | -80.32(13)     |
|                      |                      |                        |            | N1A <sup>c</sup> -C1A-C2A-C3A              | -151.38(9)     |
|                      |                      |                        |            | C2A <sup>c</sup> -C1A-C2A-C3A              | 65.35(11)      |
|                      |                      |                        |            |  |                |

**Table 2** The main bond lengths (d/Å), bond angles  $(\omega^\circ)$  and torsion angles  $(\phi^\circ)$  in 1,2-bis(2-acetamidoethyl)diaziridine **1i** and 3,3-diethyldiaziridine **1j** molecules

<sup>a</sup> 1-X,+Y,3/2-Z

<sup>b</sup>-X,1-Y,+Z

<sup>c</sup> 1-X,1-Y,+Z

### **Electronic property calculations**

The overall electronic picture of the diaziridine derivatives was evaluated by analysis from NBO method and AIM theory. The numerical results obtained by the B3LYP/6-311+G(2df,p)

**Fig. 3** Layered structure in **1i** (left) and **1j** (right) crystals, view along *b* axis. Atoms are represented by spheres

approximation are presented in Tables 4–7. The resulting NBO Lewis structure showed that the bonding  $\sigma_{N-N}$  orbital of the endocyclic bond was composed of *p*-rich nitrogen hybrids. As can be seen from Table 4, the highest value of sp<sup>8.81</sup> was computed in the case of most abundant *chair*-conformer



Fig. 4 Hydrogen bonds in 1i (left) and 1j (right) crystals. Atoms are represented by thermal displacement ellipsoids ( $\rho = 50\%$ ). Only NH hydrogen atoms are represented



of 3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane **1d**, the same compound was found to contain the longest experimental N–N bond length. Since the nitrogen atoms in 1,2-dimethyl-hydrazine **4** do not form a diaziridine ring, the NBO analysis determined the  $\sigma$ (N-N) bonding orbital to consist of nitrogen with nearly  $sp^3$  hybridization. The calculated hybridization of the lone pairs n(N) for diaziridines **1a-j** was in the range of  $sp^{1.35} \div sp^{2.00}$ ,  $sp^{3.03}$  for 1,2-dimethyl-1,2-diazetidine **3** and

the maximum value of  $sp^{4.44}$  was found for acyclic 1,2–dimethylhydrazine 4.

Like other cyclic compounds with high angle strain, for example, cyclopropane or aziridine, the studied diaziridines retain bond angles of about  $60^{\circ}$ , which is possible due to rehybridization resulting in increasing *p*-character of the bond. Indeed, for diaziridines compared with acyclic N-N compounds, NBO analysis confirms the decrease in the *p*-

Table 3 Calculated and experimental endocyclic N–N and C–N bond lengths (Å) of the diaziridines molecules 1a-j and of structural analogs 3, 4

| Compound               |   | ſ   | N-N bond length (                                      | Å)                               | C-N endo  | cyclic bond length (                           | (Å)                              |
|------------------------|---|---|--|----------------------------------|---|--|----------------------------------|
| (Symmetry)             | Chemical formula  | B3LYP/6-<br>311+G(2df,p)  | MP2/cc-pVTZ  | Exp. (Table 1)                   | B3LYP/6-311+G(2df,p)  | MP2/cc-pVTZ                                    | Exp. (Table 1)                   |
| 1a (C2)                | < <sup>N-Me</sup><br>N-Me   | 1.480   | 1.488  | 1.514(6)                         | 1.440   | 1.445  | 1.448(2)                         |
| 1b (Cs)                | $<^{N}_{N}$   | 1.505   | 1.513  | 1.506(13)                        | 1.444   | 1.448  | 1.442(2)                         |
| 1c (Cs)                |   | 1.508   | 1.522  | 1.522(7)                         | 1.455   | 1.456  | 1.455(7)                         |
| 1d (Cs)                | $<^{N}_{N}$   | 1.504   | 1.516 <sup><i>a</i></sup><br>1.548 <sup><i>b</i></sup> | $1.512(7)^{a}$<br>$1.545(7)^{b}$ | 1.445   | $1.447^{\ a}$<br>$1.446^{\ b}$                 | $1.444(7)^{a}$<br>$1.443(7)^{b}$ |
| 1e (C1)                | $\stackrel{\mathrm{H-N}}{\underset{\mathrm{Me-N}}{\overset{\mathrm{I}}{\rightarrow}}} \rightarrow \stackrel{\mathrm{N-H}}{\underset{\mathrm{N-Me}}{\overset{\mathrm{N-H}}{\rightarrow}}}$ | 1.486<br>1.496  | 1.493<br>1.504   | 1.512(2)                         | 1.437<br>1.440<br>1.457*<br>1.446*  | 1.441<br>1.460<br>1.449*<br>1.443*             | 1.445(2)                         |
| 1f(C1)                 | $Me = N \longrightarrow N = Me$<br>$Me = N \longrightarrow N = Me$  | 1.496<br>1.500  | 1.502<br>1.509   | 1.503(2)                         | 1.443<br>1.436<br>1.446*<br>1.452*  | 1.461<br>1.462<br>1.464*<br>1.464*             | 1.454(2)                         |
| 1g (Cs)                |   | 1.521<br>1.506  | 1.544<br>1.518   | 1.517(2)<br>1.511(2)             | 1.443<br>1.445*   | 1.446<br>1.448*                                | 1.449(2)<br>1.452(2)             |
| <b>1h</b> (Cs, Cs, C1) |   | 1.488 <sup><i>a</i></sup><br>1.506 <sup><i>b</i></sup><br>1.499 <sup><i>c</i></sup> | 1.521 <sup><i>b</i></sup><br>1.513 <sup><i>c</i></sup> | 1.528(2)                         | 1.452 <sup><i>a</i></sup><br>1.449 <sup><i>b</i></sup><br>1.441/1.454 <sup><i>c</i></sup> | 1.453 <sup>b</sup><br>1.444/1.460 <sup>c</sup> | 1.452(2)                         |
| 1i (C1)                | $<^{\mathrm{N-(CH_2)_2NHAc}}_{\mathrm{N-(CH_2)_2NHAc}}$   | 1.489   | 1.498  | 1.5161(18)                       | 1.439   | 1.445  | 1.4581(15)                       |
| 1j (C2)                | ${}_{Et}^{Et} \times {}_{N-H}^{N-H}$  | 1.503   | 1.517  | 1.524(2)                         | 1.450   | 1.450  | 1.454(2)                         |
| <b>3</b> (C2)          | $\Box_{N-Me}^{N-Me}$  | 1.485   | 1.488  | 1.427(7)                         | 1.481   | 1.481  | 1.481(8)/1.471(7)                |
| <b>4</b> (C1)          | MeHN-NHMe   | 1.423   | 1.427  | 1.419(11)                        | 1.457   | 1.456  | 1.463(5)                         |

In compounds with different endocyclic C-N bonds, all C-N bond lengths were shown

\*The values for the second diaziridine cycle

<sup>*a*</sup> Bond lengths of *boat* 

<sup>b</sup> char

<sup>c</sup> h-chair conformer, respectively

| Table 4     | Hybridization of the N-N bond   | ing orbital $(\sigma_{N-N})$ | and lone e  | electronic pair | of nitrogen | atom $n(N)$ | in diaziridines | 1a-j, | 1,2-dimethyl-1,2- |
|-------------|---------------------------------|------------------------------|-------------|-----------------|-------------|-------------|-----------------|-------|-------------------|
| diazetidine | 3 and 1,2-dimethylhydrazine 4 c | computed from B3             | 3LYP/6-311- | +G(2df,p) app   | broach      |             |                 |       |                   |

| Compound/<br>Symmetry | Molecule  | σ(N-N)  | <i>n</i> (N)   |
|-----------------------|---|---|--|
| 1a (C2)               | < <sup>N-Me</sup><br><sup>I</sup> N-Me  | $0.707(sp^{7.19})$ N+ $0.707(sp^{7.19})$ N  | $n(\mathbf{N})=(sp^{1.78})\mathbf{N}$  |
| 1b (Cs)               | $<^{\rm N}_{\rm N}$   | $0.707(sp^{7.59})$ N+ $0.707(sp^{7.59})$ N  | $n(\mathbf{N})=(sp^{1.64})\mathbf{N}$  |
| 1c (Cs)               |   | $0.707(sp^{7.77})$ N+ $0.707(sp^{7.77})$ N  | $n(\mathbf{N})=(sp^{1.81})\mathbf{N}$  |
| 1d (Cs)               | $<_{\rm N}^{\rm N}$   | $0.707(sp^{8.81})$ N +0.707( $sp^{8.81}$ )N   | $n(N)=(sp^{1.62})N$  |
| 1e (C1)               | $\underset{Me-N}{\overset{H-N}{\longrightarrow}} \xrightarrow{\overset{N-H}{\underset{N-Me}{\longrightarrow}}}$   | $0.708(sp^{6.55})N + 0.707(sp^{6.96})N$<br>$0.702(sp^{6.99})N + 0.712(sp^{7.04})N*$   | $n(N) = (sp^{1.29})N$<br>$n(N) = (sp^{1.30})N$<br>$n(N) = (sp^{1.30})N*$<br>$n(N) = (sp^{1.95})N*$ |
| 1f (C1)               | $\frac{Me-N}{Me-N} \rightarrow \frac{N-Me}{N-Me}$   | $0.709(sp^{6.71})N + 0.705(sp^{6.76})N$<br>$0.705(sp^{6.93})N + 0.710(sp^{6.79})N*$   | $n(N) = (sp^{1.94})N$<br>$n(N) = (sp^{1.94})N$<br>$n(N) = (sp^{2.12})N*$<br>$n(N) = (sp^{1.90})N*$ |
| 1g (Cs)               | $ \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ N \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ I \\ I \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ I \\ I \\ I \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \end{array} }^{N} \underbrace{ \begin{array}{c} N \\ I \\$ | $\begin{array}{l} 0.707(sp^{7.33})\mathrm{N} + 0.707(sp^{7.33})\mathrm{N} \\ 0.707(sp^{7.88})\mathrm{N} + 0.707(sp^{7.88})\mathrm{N} \end{array} *$ | $n(N)=(sp^{1.54})N$<br>$n(N)=(sp^{1.50})N*$  |
| 1h (Cs)               |   | $0.707(sp^{7.62})N + 0.707(sp^{7.62})N$   | $n(\mathbf{N})=(sp^{1.80})\mathbf{N}$  |
| 1i (C1)               | $<^{\mathrm{N-(CH}_2)_2\mathrm{NHAc}}_{\mathrm{N-(CH}_2)_2\mathrm{NHAc}}$   | $0.707(sp^{7.62})$ N + $0.707(sp^{7.62})$ N   | $n(N) = (sp^{1.77})N$  |
| 1j (C2)               | ${}^{\text{Et}}_{\text{Et}} \times {}^{\text{N-H}}_{\text{N-H}}$  | $0.707(sp^{8.43})$ N + $0.707(sp^{8.43})$ N   | $n(\mathbf{N})=(sp^{1.35})\mathbf{N}$  |
| <b>3</b> (C2)         | $\Box_{\rm N-Me}^{\rm N-Me}$  | $0.707(sp^{4.57})$ N+ $0.707(sp^{4.57})$ N  | $n(N) = (sp^{3.03})N$  |
| <b>4</b> (C1)         | MeHN–NHMe   | 0.819( <i>sp</i> <sup>3.22</sup> )N+0.708( <i>sp</i> <sup>2.99</sup> )N   | $n(N) = (sp^{4.44})N$<br>$n(N) = (sp^{4.24})N$   |

<sup>\*</sup> The values for the second diaziridine cycle

hybridization for the lone pair of nitrogen and then increase in the *p*-component for the N–N bond. The dependence of the N-N bond lengths in diaziridines **1a-j** on the hybridization of N-N bonding orbital ( $\sigma_{N-N}$ ) in these molecules is presented in Fig. 5. As can be seen from Fig. 5, increasing the N-N bond lengths on going from acyclic to cyclic molecules is correlated with increasing the *p*-character of the  $\sigma_{N-N}$  bonding orbitals.

The atomic charges calculated by the NBO method for N and C atoms of diaziridines **1a-j** together with data for **3** and **4** are given in Table 5. Among diaziridines, the highest negative charge on the N atoms was found for **1j** in which the N–N bond is

somewhat longer than in other diaziridines. Another set of atomic charges was obtained from QTAIM analysis of the B3LYP/6-311+G(2df,p) molecular wave functions. For most of the atomic charges, the tendencies calculated using this approach show resemblance to NBO data. We noted that the scatter of NBO charge values of diaziridines was more pronounced than that determined by the AIM theory. The N atomic charge in diaziridine compounds changed insignificantly in contrast to the carbon atomic charge. In the case of 1,2-dimethyl-1,2-diazetidine **3** and 1,2–dimethylhydrazine **4**, the C atomic charge is calculated to be markedly different from those in diaziridines that we study.



Fig. 5 Hybridization of the  $\sigma_{N\text{-}N}$  bonding orbital depending on bond length for studied compounds

Detailed analysis of the orbital interactions derived from NBO theory did not show any obvious differences in the stabilization energies of diaziridines versus acyclic compounds containing the N-N bond. Anomeric effect observed due to n(N) and  $\sigma^*(C-H)$  and/or  $\sigma^*(C-C)$  interactions is still the dominant factor in stabilization of both 1,2-dimethyl-1,2-diazetidine **3**, 1,2-dimethylhydrazine **4**, and diaziridines **1a-j**. In compounds with diaziridine rings, along with the interactions related to the anomeric effect, large stabilization energy comes from interactions between orbitals of the diaziridine moiety, namely  $\sigma(C-N) \rightarrow \sigma^*(N-N)$  and  $\sigma(N-N) \rightarrow \sigma^*(C-N)$ . Their values are shown in Table 6. Owing to the presence of the amide bond in compound **1i**, the molecule is mainly stabilized by the strong  $n(N) \rightarrow \sigma^*(C = O)$  interaction, while the  $\sigma(N-N) \rightarrow \sigma^*(C-N)$  stabilization energy is about 4 kcal/ mol, like in other diaziridines. The  $\sigma(C = C) \rightarrow$  $\sigma^*(C = C)$  interaction is most pronounced in compound **1h** because of the aromatic phenyl group.

As follows from the AIM analysis, one characteristic that distinguishes the electronic structure of diaziridines from that of other compounds at the bond critical point

Table 5 Natural atomic charges (q) as obtained from NBO and atomic charges from QTAIM analysis

|    |   | N cl                                    | harge                                   | C cł             | narge           |
|----|---|---|---|------------------|-----------------|
|    | Substance   | NBO                                     | QTAIM                                   | NBO              | QTAIM           |
| 1a | $<^{ m N-Me}_{ m N-Me}$   | -0.375                                  | -0.630                                  | -0.024           | 0.466           |
| 1b | $<^{\mathrm{N}}_{\mathrm{N}}$   | -0.370                                  | -0.602                                  | -0.026           | 0.456           |
| 1c |   | -0.366                                  | -0.623                                  | 0.273            | 0.500           |
| 1d |   | -0.361                                  | -0.616                                  | -0.009           | 0.480           |
| 1e | $M = N \xrightarrow{H = N} M = M \xrightarrow{I}_{N = M e} M = M e$   | -0.351<br>-0.490<br>-0.357*<br>-0.463** | -0.600<br>-0.622<br>-0.609*<br>-0.618** | 0.093<br>0.106*  | 0.474<br>0.501* |
| 1f | Me - N<br>Me - N $N - MeN - Me$   | -0.354<br>-0.370<br>-0.347*<br>-0.355** | -0.615<br>-0.629<br>-0.615*<br>-0.627** | 0.116<br>0.129*  | 0.491<br>0.507* |
| 1g | $ \underbrace{ \overset{N}{\underset{N}{\longrightarrow}}}_{N} \underbrace{ \overset{N}{\underset{N}{\underset{N}{\longrightarrow}}}_{N} \underbrace{ \overset{N}{\underset{N}{\underset{N}{\longrightarrow}}}_{N} \underbrace{ \overset{N}{\underset{N}{\underset{N}{\longrightarrow}}}_{N} \underbrace{ \overset{N}{\underset{N}{\underset{N}{\underset{N}{\underset{N}{\longleftarrow}}}_{N} \underbrace{ \overset{N}{\underset{N}{\underset{N}{\underset{N}{\underset{N}{\underset{N}{\underset{N}{\underset{N}{$ | -0.354<br>-0.361*                       | -0.615<br>-0.618*                       | 0.104<br>0.125*  | 0.494<br>0.512* |
| 1h |   | -0.364                                  | -0.626                                  | 0.139            | 0.493           |
| 1i | $<^{\mathrm{N-(CH_2)_2NHAc}}_{\mathrm{N-(CH_2)_2NHAc}}$   | -0.382                                  | -0.643*                                 | -0.013           | 0.479           |
| 1j | $Et \xrightarrow{N-H} V_{N-H}$  | -0.500                                  | -0.645                                  | 0.263            | 0.497           |
| 3  | $\Box_{N-Me}^{N-Me}$  | -0.390                                  | -0.628                                  | -0.177           | 0.264           |
| 4  | MeHN-NHMe   | -0.506<br>-0.501                        | -0.639                                  | -0.359<br>-0.375 | 0.278<br>0.294  |

**Table 6** Orbital interaction with the maximum value of the energy stabilization  $E^{(2)}$  in kcal/mol for the studied substances predicted from NBO analysis by B3LYP/6-311+G(2df,p) approach

|                | Molecule  | N-N   | E <sup>(2)</sup> , kcal/mol |
|----------------|---|---|-----------------------------|
| 1a (C2)        | $<^{N-Me}_{N-Me}$   | $n(N) \rightarrow \sigma^*(C-H)$                      | 4.59                        |
| 1b (Cs)        | $<^{N}_{N}$   | $\sigma(\text{N-N}){\rightarrow}\sigma^*(\text{C-N})$ | 3.87                        |
| 1c (Cs)        |   | $\sigma(\text{C-H}){\rightarrow}\sigma^*(\text{C-N})$ | 5.94                        |
| 1d(Cs)         | $<^{N}_{N}$   | $\sigma(N-N) \rightarrow \sigma^*(C-N)$               | 4.06                        |
| 1e (C1)        | H-N N-H   | $n(N) \rightarrow \sigma^*(C-H)$                      | 5.50                        |
| 10 (01)        | Me-N N-Me   |   | 5.22                        |
| 18(01)         | Me-N_N-Me   |   | 5.85                        |
| If (C1)        | Me-N N-Me   | $n(N) \rightarrow \sigma^*(C-H)$                      | 5.86                        |
| 1g (Cs)        | $\langle N \\ N $ | $\sigma(N-N){\rightarrow}\sigma^*(C-N)$               | 4.4                         |
| <b>1h</b> (Cs) |   | $\sigma(C=C){\rightarrow}\sigma^*(C=C)$               | 21.13                       |
| 1i (C2)        | $<^{\mathrm{N-(CH_2)_2NHAc}}_{\mathrm{N-(CH_2)_2NHAc}}$   | $n(N) \rightarrow \sigma^*(C=O)$                      | 65.33                       |
| 1j (C2)        | $Et \xrightarrow{H} N-H$                                  | $\sigma(N\text{-}N){\rightarrow}\sigma^*(C\text{-}N)$ | 4.82                        |
| <b>3</b> (C2)  | $\square_{N-Me}^{N-Me}$                                   | $n(N) \rightarrow \sigma^*(C-H)$                      | 6.28                        |
| <b>4</b> (C1)  | MeHN-NHMe   | $n(N) \rightarrow \sigma^*(C-H)$                      | 7.36                        |

is the bond ellipticity parameter. This value shows a significant difference between the diaziridine ring and acyclic compounds with N-N single bond. The bond ellipticity parameter  $\varepsilon$  values are presented in Table 7 for diaziridines **1a-j** including data for compounds **3** and **4**.

The bond ellipticity values calculated at the bond critical points show the  $\pi$ -component contribution to the selected bonds. There are some differences between the ellipticities of endo- and exocyclic C–N bonds. Diaziridines **1a-j** are affected by the electron delocalization. The 1,2-dimethyl-1,2-diazetidine **3** and 1,2-dimethylhydrazine **4** have a different type of N-N bond, which can be reflected in shortening of the N-N bond length.

It should be noted that in spite of the direct dependence of the hybridization degree of  $\sigma_{N-N}$  bonding orbital from the N-N bond length (Fig. 5), a strong

correlation between the N-N bond length and its ellipticity for the studied compound **1a-j**, **3** and **4** was not obtained (Table 7 and Fig. 6). Nevertheless, the lengthening of N-N bond on going from acyclic to cyclic molecules is accompanied with increasing bond ellipticity. Among diaziridines **1a-j**, there is also the trend to increasing bond ellipticity with elongation bond length excepting diaziridine **1d**, which shows the smallest value  $\varepsilon$  from all studied diaziridines **1a-j**, but is still significantly higher than for non-diaziridine compounds **3** and **4**.

#### Conclusion

In summary, experimental X-ray diffraction analysis of 1,2-bis(2-acetamidoethyl)diaziridine and 3,3-

|     | Substance   | N-N(cyclic)    | N-C(cyclic)                      | N-C(acyclic)                     |
|-----|---|----------------|----------------------------------|----------------------------------|
| 1a  | < <sup>N-Me</sup><br><sup>I</sup> N-Me  | 0.378          | 0.218                            | 0.019                            |
| 1b  | $<^{\mathrm{N}}_{\mathrm{N}}$   | 0.436          | 0.267                            | 0.017                            |
| 1 c | $>_{N}^{N}$   | 0.398          | 0.251                            | 0.027                            |
| ld  | $<^{\mathrm{N}}_{\mathrm{N}}$   | 0.237          | 0.274                            | 0.262                            |
| 1e  | $ \underset{Me-N}{\overset{H-N}{\underset{N-Me}{\rightarrow}}} \sim \underset{N-Me}{\overset{N-H}{\underset{N-Me}{\rightarrow}}} $  | 0.376<br>0.395 | 0.318<br>0.246<br>0.262<br>0.279 | 0.014<br>0.018                   |
| lf  | Me = N<br>Me = N $N = MeN = Me$   | 0.384<br>0.372 | 0.246<br>0.243<br>0.218<br>0.267 | 0.006<br>0.007<br>0.008<br>0.006 |
| g   | $ \underbrace{ \begin{array}{c} N \\ I \\ N \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ N \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ N \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ N \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ I \\ N \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\ I \\ I \\ I \\ I \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \end{array}}_{N} \underbrace{ \begin{array}{c} N \\ I \\$ | 0.434<br>0.501 | 0.264<br>0.255                   | 0.017<br>0.013                   |
| l h |   | 0.410          | 0.260                            | 0.012                            |
| li  | $<^{\mathrm{N-(CH_2)_2NHAc}}_{\mathrm{N-(CH_2)_2NHAc}}$   | 0.397          | 0.273                            | 0.013                            |
| ij  | $Et \sim N-H \\ Et \sim N-H$  | 0.439          | 0.283                            | -                                |
| 3   | $\begin{bmatrix} N-Me \\ N-Me \end{bmatrix}$  | 0.099          | 0.034                            | 0.038                            |
| 4   | MeHN-NHMe   | 0.006          | -                                | 0.060/0.062                      |

**Table 7** The bond ellipticities  $\varepsilon = [\lambda_1/\lambda_2-1]$  of N–N and C–N bonds in comparison with acyclic C–N bond ellipticities computed from AIM analysis

diethyldiaziridine was performed, and it was found that the C–N and N–N bond lengths in these compounds were close to the values previously found experimentally for other diaziridines. The N–N endocyclic bond lengths were longer than the N–N bond lengths in 1,2dimethyldiazetidine and 1,2-dimethylhydrazine, whereas C–N endocyclic bond lengths were shorter in comparison with these compounds.

To understand the reasons for the peculiarity of the diaziridine ring structure, an AIM/NBO analysis of the intramolecular interaction effects on the chemical bonds for diaziridines **1a-j** and related compounds **3** and **4** was carried out and quantified. A direct dependence of elongation of the N–N bond diaziridine **1a-j** molecules and the *p*-character of the  $\sigma_{N-N}$  bonding orbital was found. The similar direct dependence of the N-N bond ellipticity for diaziridines **1a-j** from the N–N bond length was not revealed, but the increasing of the N-N bond ellipticity had a tendency to occur with the increasing of N-N bond length.



Fig. 6 The N-N bond ellipticity depending on bond length for studied compounds

**Acknowledgements** This study has been supported by Russian Foundation for Basic Research (Project 16-33-00130 mol\_a), and structural studies have been supported by Russian Science Foundation (Project 14-13-00884).

#### References

- Kuznetsov VV, Makhova NN, Dekaprilevich MO (1999) RussChemBull,IntEd 48(3):617–619
- Petukhova VY, Kuznetsov VV, Shevtsov AV, Strelenko YA, Makhova NN, Lyssenko KA, Antipin MY (2001) RussChemBull, IntEd 50:440–444
- Kuznetsov VV, Kutepov SA, Makhova NN, Lyssenko KA, Dmitriev DE (2003) Russ Chem Bull, IntEd 52(3):665–673
- Atavin EG, Golubinsky AV, Popik MV, Kuznetsov VV, Makhova NN, Vilkov LV (2003) Zh Strukt Khim 44(5):851–854
- Atavin EG, Golubinsky AV, Popik MV, Kuznetsov VV, Makhova NN, Anikeeva AV, Vilkov LV (2003) Zh Strukt Khim 44(5):855– 859
- Petukhova VY, Makhova NN, Ananikov VP, Strelenko YA, Fedyanin IV (2004) Russ Chem Bull 3:612–617
- Vishnevskiy YV, Vogt N, Vogt J, Rykov AN, Kuznetsov VV, Makhova NN, Vilkov LV (2008) J Phys Chem A 112(23):5243– 5250
- Vishnevskiy YV, Schwabedissen J, Rykov AN, Kuznetsov VV, Makhova NN (2015) J. Phys. Chem. A 119(44):10871–10881
- 9. Paget CJ, Davis CS (1964) J Med Chem 7:626
- Shustov GV, Kadorkina GK, Varlamov SV, Kachanov AV, Kostyanovskii RG, Rauk A (1992) J Am Chem Soc 114:1616
- Shevtsov AV, Petukhova VY, Strelenko YA, Lyssenko KA, Fedyanin IV, Makhova NN (2003) Mendeleev Commun. 13(5): 221–223
- 12. Shevtsov AV, Petukhova VY, Strelenko YA, Makhova NN (2005) Mendeleev Commun. **15**(1):29–31
- Shevtsov AV, Kuznetsov VV, Lyssenko KA, Belyakov PA, Makhova NN (2006) Mendeleev Commun. 16(4):218–220
- Shevtsov AV, Kuznetsov VV, Kislukhin AA, Petukhova VY, Strelenko YA, Makhova NN (2006) J. Heterocyclic Chem. 43:881
- Shevtsov AV, Kislukhin AA, Kuznetsov VV, Petukhova VY, Maslennikov VA, Borissova AO, Lyssenko KA, Makhova NN (2007) Mendeleev Comm 17(2):119–121
- Syroeshkina YS, Kuznetsov VV, Lyssenko KA, Makhova NN (2008) Mendeleev Commun. 18(1):42–44
- Syroeshkina YS, Kuznetsov VV, Struchkova MI, Epishina MA, Makhova NN (2008) Mendeleev Commun. 18(4):207–208
- Syroeshkina YS, Ovchinnichov IV, Kuznetsov VV, Kachala VV, Nelyubina YV, Lyssenko KA, Makhova NN (2009) Mendeleev Commun. 19(5):276–278
- Syroeshkina YS, Kuznetsov VV, Kachala VV, Makhova NN (2009) J Heterocyclic Chem 46:1195

- Petukhova VY, Pleshchev MI, Fershtat LL, Kuznetsov VV, Kachala VV, Makhova NN (2012) Mendeleev Commun. 22(1):32–34
- Pleshchev MI, Petukhova YS, Kuznetsov VV, Khakimov DV, Pivina TS, Struchkova MI, Nelyubina YV, Makhova NN (2013) Mendeleev Commun 23(1):34–36
- Pleshchev MI, Das Gupta NV, Kuznetsov VV, Fedyanin IV, Kachala VV, Makhova NN (2015) Tetrahedron 71:9012–9021
- 23. Bastiansen O, Fritsch FN, Hedberg K (1964) Acta Cryst **17**(5):538– 543
- 24. March J (1987) Organic chemistry. Part 1. Moscow (Russ. Transl.)
- 25. Gebhardt KF, Oberhammer H, Zeil W (1980) J Chem Soc Farad Trans II **76**:1293–1303
- Chiu NS, Sellors HL, Schaefer L, Kohata K (1979) J Am Chem Soc 101:5883–5889
- Mastryukov VS, Osina EL, Vilkov LV, Hildebrandt RL (1977) J Amer Chem Soc 99:6855
- Egawa T, Fukuyama T, Yamamoto S, Takabayashi F, Kambara H, Ueda T, Kuchitsu K (1987) J Chem Phys 86(11):6018–6026
- Bradford WF, Fitzwater S, Bartell LS (1997) J Mol Struct 38:185– 194
- Bourhis LJ, Dolomanov OV, Gildea RJ, Howard JAK, Puschmann H (2015) Acta Cryst A 71:59–75
- Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H (2009) J Appl Crystallogr 42:339–341
- 32. Sheldrick GM (2008) Acta Cryst. A 64:112–122
- Makhova NN, Mikhailyuk AN, Kuznetsov VV, Kutepov SA, Belyakov PA (2000) Mendeleev Commun. 10(5):182–184
- Kuznetsov VV, Makhova NN, Strelenko YA, Khmel'nitskii LI (1991) The Role of pH in the Synthesis of Diaziridines. Bull Acad Sci USSR Div Chem Sci 40:2496–2503
- Schmitz E, Ohme R (1965) 3,3-Pentamethylenediazirine Org. Syntheses 45:83–86
- Paulsen SR, Huck G (1961) Beitrag zur Chemie der Diazacyclopropane. Ber 94:968–1961
- Takhistov VV, Klinduhova TK, Klinduhov VP, Yandovsky VNZ (1974) Zh Org Khim (Russian) 10(6):1140–1145
- 38. Frish MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann JR, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komazomi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PM, Johnson B, Chen W, Wong MW, Andres JL, Gonzales C, Head-Gordon M, Replogle ES, Pople JA (2003) Gaussian 03 (Revision D01). Gaussian Inc., Pittsburgh
- 39. Keith TA AIMAll v.15.09.12; http://aim.tkgristmill.com