1,5-Diazabicyclo[3.1.0]hexanes and 1,6-diazabicyclo[4.1.0]heptanes: a new method for the synthesis, quantum-chemical calculations, and X-ray diffraction study*[1,*2]

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A new method was developed for the synthesis of 6-substituted 1,5-diazabicyclo[3.1.0]hexanes and 7-substituted 1,6-diazabicyclo[4.1.0]heptanes by condensation of *N*-monohalotrimethylene- and *N*-monohalotetramethylenediamines with carbonyl compounds in the presence of bases. X-ray diffraction studies and quantum-chemical B3LYP/6-31G* calculations demonstrated that the conformations of the resulting bicyclic systems are stabilized by stereoelectronic interactions. As a result, a boat conformation prevails in 1,5-diazabicyclo[3.1.0]hexanes, whereas the energies of chair, half-chair, and boat conformations of 1,6-diazabicyclo[4.1.0]heptanes are equalized.

Key words: 1,5-diazabicyclo[3.1.0]hexanes, 1,6-diazabicyclo[4.1.0]heptanes, synthesis, X-ray diffraction analysis, stereoelectronic effects, conformation.

It is known that diaziridine derivatives exhibit neurotropic activity[1,2] associated with inhibition of monoamine oxidase.[2,3] In this connection, a search for new simple general procedures for the synthesis of compounds of this class, including bicyclic diaziridines, is an urgent problem. 1,5-Diazabicyclo[3.1.0]hexanes **1** are among rather readily accessible and well-studied compounds. Earlier,[4,5a,6] these compounds have been synthesized by halogenation of 1,3-diazacyclohexanes **2** with NaOCl in water followed by intramolecular cyclization of monohalo derivatives **3**. Recently,[7] we have modified a procedure for the synthesis of compounds **1** by performing the process in aprotic organic solvents with the use of Bu^{t}OCl as the halogenating reagent and K_2CO_3 as the basic and dehydrating reagent. This made it possible to substantially simplify the isolation of the final products and perform the reactions with water-insoluble carbonyl compounds. Earlier,[5a] the simplest representative of 1,6-diazabicyclo[4.1.0]heptanes **4**, *viz.*, compound **4a**, has been synthesized through 1,3-diazacycloheptane **5a** and monochloro derivative **6a**. The starting diazacyclanes **2** and **5** were prepared by condensation of the carbonyl compound with the corresponding diaminoalkanes and then used in the subsequent reactions without isolation (Scheme 1).

However, known procedures for the synthesis of compounds **1** and **4** appeared to be unsuitable for these reactions, if substituents in carbonyl compounds are sensitive to strong halogenating reagents, such as NaOCl or Bu^{t}OCl. To overcome this limitation, we examined the possibility of performing pre-halogenation of 1,3- and 1,4-diaminoalkanes to form monochloro derivatives **7** and **8**, respectively, followed by condensation with the carbonyl compound to produce 1,3- or 1,4-diaza-1-chlorocycloalkanes **3** and **6** and the subsequent transformation into bicyclic compounds **1** and **4**, respectively, under the action of bases (Scheme 2). Diaminoalkanes were halogenated to monochloro derivatives **7** and **8** with an equimolar amount of Bu^{t}OCl in methanol or chloroform depending on the solubility of the starting carbonyl compound. Then the corresponding carbonyl compound and base (B) were added and the reaction mixture was kept at 0—20 °C,

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*[2] Preliminary results were published in the Abstracts of Papers of the I All-Russian Conference on Chemistry of Heterocycles Dedicated to the Memory of A. N. Kosta (V. V. Kuznetsov, S. A. Kutepov, and N. N. Makhova, Suzdal´, September 19—23, 2000, p. 243 (in Russian)) and in the Abstracts of Papers of the I International Conference "Nitrogen Heterocycles and Alkaloids" (V. V. Kuznetsov, S. A. Kutepov, N. N. Makhova, and K. A. Lyssenko, Moscow, October 9—12, 2001, **2**, p. 173 (in Russian)).

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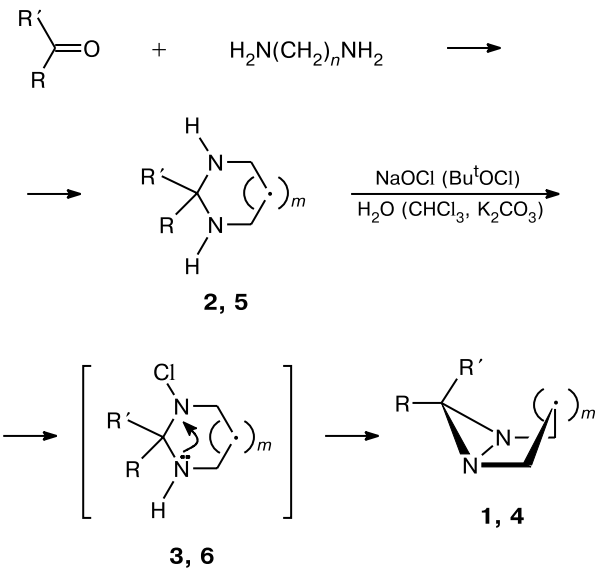
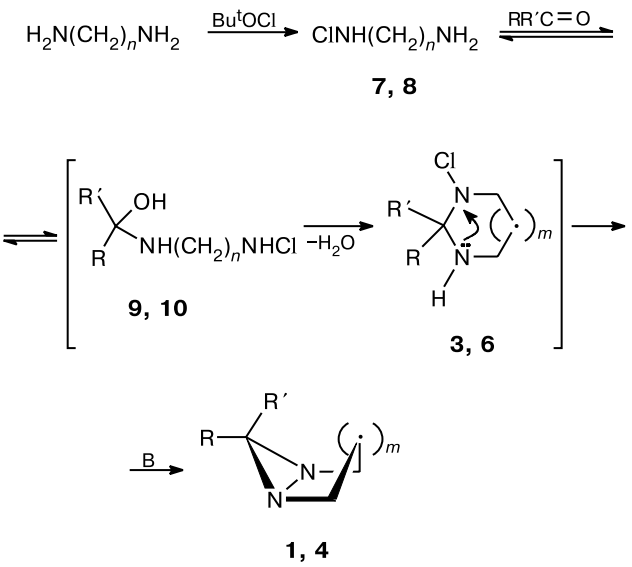
Scheme 1



1, 2, 3: n = 3, m = 1; **4, 5, 6:** n = 4, m = 2;
4a, 5a, 6a: R = R′ = H

after which the target bicyclic compound was isolated. The formation of compounds **3** and **6** can be represented as the result of intramolecular α-aminoalkylation of intermediate amino alcohols **9** and **10**, respectively (see Scheme 2).

Scheme 2



1, 3, 7, 9: n = 3, m = 1; **4, 6, 8, 10:** n = 4, m = 2

The effect of the nature of the base (Et_3N, K_2CO_3, or starting diaminoalkane), whose addition is necessary to neutralize the acid liberated in the course of the reaction,

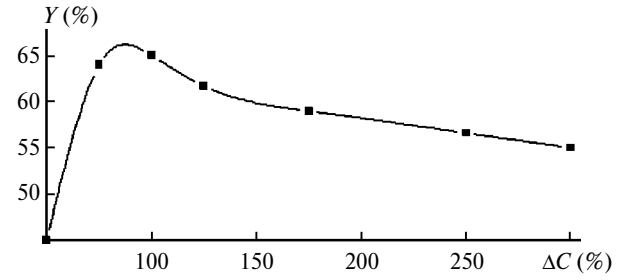
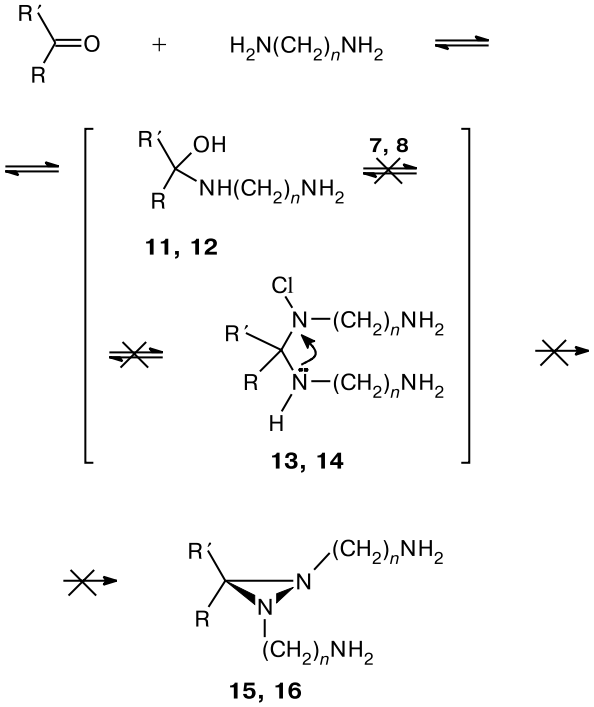


Fig. 1. Yield (Y) of 6-(3-nitrophenyl)-1,5-diazabicyclo[3.1.0]hexane (**1c**) in the presence of an excess (ΔC) of 1,3-diaminopropane.

on the yield of the final product was studied using the synthesis of 6-phenyl- and 6-(3-nitrophenyl)-1,5-diazabicyclo[3.1.0]hexanes (**1b** and **1c**), respectively, as examples. It was demonstrated that all the above-mentioned bases are suitable for this purpose, but the best results were obtained when an equimolar excess of the starting 1,3-diaminopropane was used (Fig. 1). Apparently, intramolecular α-aminoalkylation of amino alcohols **9** and **10** giving rise to 1-chlorodiazacycloalkanes **3** and **6**, respectively, is a more favorable process than the intermolecular reaction. The reactions of aminocarbinols **11** and **12** with the corresponding *N*-chlorodiaminoalkanes **7** and **8** through intermediate *N*-chloroaminals **13** and **14** would afford diaziridines **15** and **16**, respectively (Scheme 3).

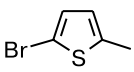
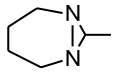
Scheme 3



The new procedure developed by us for the synthesis of bicyclic compounds **1** and **4** consists in keeping the reaction mixture without stirring in MeOH at 0—5 °C or in $CHCl_3$ at 5—20 °C. The reactions were carried out with a broad spectrum of various aldehydes, including those containing substituents sensitive to NaOCl and Bu^tOCl (for example, the cyclopropyl, thiophene, or furan groups). As a result, we prepared a series of not only known[8,9] but also of new 6-substituted 1,5-diazabicyclo[3.1.0]hexanes **1** and previously unknown 7-substituted 1,6-diazabicyclo[4.1.0]heptanes **4**, including those based on glyoxal (Table 1).

Earlier, analysis of ^1H and ^{13}C NMR spectra,[5a—d] semiempirical quantum-chemical calculations, and X-ray diffraction study[10] have demonstrated that 1,5-diazabicyclo[3.1.0]hexanes **1** adopt predominantly a boat conformation. By contrast, no unambiguous conclusion about the conformation of 1,6-diazabicyclo[4.1.0]heptane **4a** can be made due to a rapid interconversion between two twist conformations, which persists even at −80 °C.[5a]

Table 1. Yields and melting (boiling) points of 6-R-1,5-diazabicyclo[3.1.0]hexanes **1** and 7-R-1,6-diazabicyclo[4.1.0]heptanes **4**

Compound	R	Yield (%)	M.p. (b.p.)/°C [*p*/Torr]
1a	*cyclo*-C_3H_5	73	(110—111) [25]
1b	Ph	89	93—94 (*cf.* lit. data[8]: 93—94)
1c	3-$NO_2C_6H_4$	63	106, with decomp. (*cf.* lit. data[9]: 105, with decomp.)
1d	4-ClC_6H_4	59	103—105, with decomp. (*cf.* lit. data[9]: 104—105, with decomp.)
1e	2-Cl-5$NO_2C_6H_3$	85	134
1f		63	85.0—85.5
1g		69	214—215, with decomp. (*cf.* lit. data[10]: 215, with decomp.)
4b	Ph	59	90.0—91.5
4c	4-ClC_6H_4	60	65
4d	4-BrC_6H_4	95	95—96
4e		87	92—93
4f		47	Oil unstable under standard conditions
4g		31	Oil unstable under standard conditions
4h		51	204—206

Hence, in the present study we performed X-ray diffraction analysis of one of the compounds synthesized, *viz.*, of compound **4b** (and of **1d** compound for comparison purposes), and carried out quantum-chemical calculations of the energetically most favorable conformations of the simplest representatives of compounds of both types.

X-ray diffraction study demonstrated that both molecules **1d** and **4b** in the crystals have the approximate symmetry C_s, *i.e.*, the pseudoplane *m* passing through the C(6) and C(3) atoms in **1d** and through the C(7) atom and the midpoint of the C(3)—C(4) bond in **4b** (Fig. 2; Tables 2 and 3).

In the crystal of diaziridine **1d**, like in the crystal of 6,6′-bis(1,5-diazabicyclo[3.1.0]hexane) **1g**,[10] the pyrazolidine ring adopts an envelope conformation (dihedral angle (α) between the C(2)—C(3)—C(4) and N(1)—N(5)—C(2)—C(4) planes is 26.5°). In compound **1d**, the angle of the bend of the diaziridine ring from the base of the envelope (β) is 74.9°. Therefore, the overall conformation of the six-membered ring in the crystal of **1d** can be described as a flattened boat. In such a conformation, the lone electron pairs (n) of the N atoms are antiperiplanar to the C(2)—C(3) and C(3)—C(4) bonds of the ring, which can give rise to the n(N)—σ*(C—C) interaction and, according to the earlier data,[5a—c] to stabilization of this conformation.

By contrast, the bicyclic moiety in the crystal of compound **4b** adopts a chair-like conformation. This is

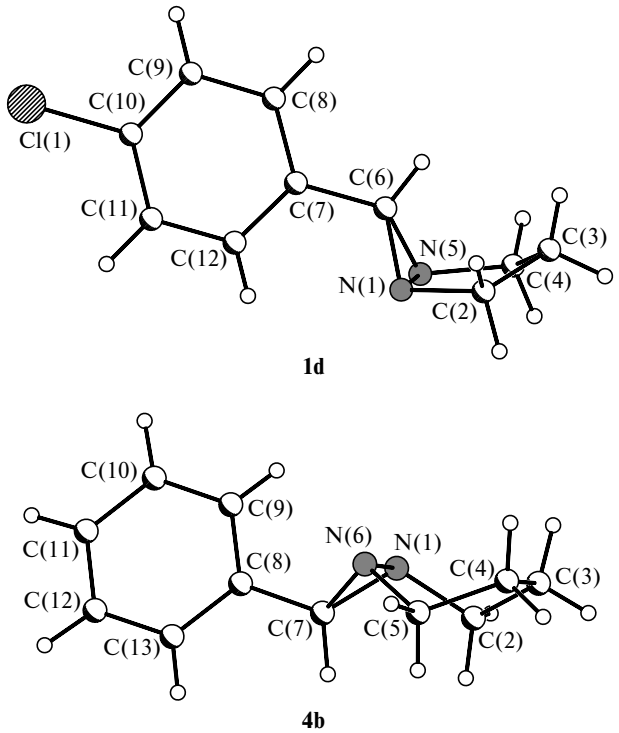


Fig. 2. Overall views of molecules **1d** and **4b** according to the results of X-ray diffraction analysis.

Table 2. Principal bond lengths (*d*) and bond angles (ω) in 1,5-diazabicyclo[3.1.0]hexanes according to the results of X-ray diffraction study of compound **1d** and quantum-chemical (B3LYP/6-31G*) calculations of molecule **1h**

Parameter	**1d**	**1h (boat)***	**1h (chair)***
Bond		*d*/Å	
N(1)—N(5)	1.517(2)	1.509	1.527
N(1)—C(2)	1.488(2)	1.482	1.488
N(1)—C(6)	1.456(2)	1.449	1.447
N(5)—C(4)	1.485(2)	—	—
N(5)—C(6)	1.458(2)	—	—
C(2)—C(3)	1.533(2)	1.542	1.538
C(3)—C(4)	1.531(2)	1.542	1.538
Angle		ω/deg	
N(5)—N(1)—C(2)	107.1(1)	107.5	107.3
N(5)—N(1)—C(6)	58.71(9)	58.6	58.1
N(1)—N(5)—C(4)	107.0(1)	—	—
N(1)—N(5)—C(6)	58.56(9)	—	—
C(2)—N(1)—C(6)	111.7(1)	112.5	112.6
C(6)—N(5)—C(4)	111.2(1)	—	—
N(1)—C(2)—C(3)	107.7(1)	108.1	105.9
C(4)—C(3)—C(2)	102.4(1)	102.1	103.3
N(5)—C(4)—C(3)	108.0(1)	—	—
N(1)—C(6)—N(5)	62.73(9)	62.7	63.7

* The geometry of the molecule was optimized within the symmetry C_s.

Table 3. Principal bond lengths (*d*) and bond angles (ω) in 1,6-diazabicyclo[4.1.0]heptanes according to the results of X-ray diffraction study of compound **4b** and quantum-chemical (B3LYP/6-31G*) calculations of molecule **4a**

Parameter	**4b**	**4a**		
		(chair)*	**(boat)***	**(h-chair)****
Bond		*d*/Å		
N(1)—N(6)	1.528(2)	1.521	1.501	1.515
N(1)—C(2)	1.478(2)	1.476	1.477	1.474
N(6)—C(5)	1.477(2)	—	—	1.490
N(1)—C(7)	1.452(2)	1.445	1.448	1.438
N(6)—C(7)	1.461(2)	—	—	1.450
C(2)—C(3)	1.516(2)	1.536	1.539	1.534
C(3)—C(4)	1.539(2)	1.554	1.554	1.529
C(4)—C(5)	1.518(2)	—	—	1.531
Angle		ω/deg		
N(6)—N(1)—C(7)	58.7(1)	58.2	58.8	58.7
C(2)—N(1)—C(7)	116.2(1)	116.2	117.2	117.7
N(1)—N(6)—C(7)	58.1(1)	—	—	58.0
C(5)—N(6)—C(7)	115.0(1)	—	115.2	—
N(1)—C(2)—C(3)	108.8(1)	109.0	117.8	117.3
N(6)—C(5)—C(4)	109.3(1)	—	—	115.3
C(2)—C(3)—C(4)	111.5(1)	111.3	112.6	108.5
C(3)—C(4)—C(5)	111.1(1)	—	—	110.0
N(1)—C(7)—N(6)	63.2(1)	63.5	62.4	63.3

* The geometry of the molecule was optimized within the symmetry C_s.

** The geometry of the molecule was optimized within the symmetry C_1.

the only of all possible conformations, in which the n(N)—σ*(C—C) interaction cannot occur (see Fig. 2). The six-membered ring in molecule **4b** adopts a boat conformation (C(2) and C(5) atoms deviate from the N(1)—N(6)—C(3)—C(4) plane by 0.67 Å) instead of the expected twist conformation,[5a] and the diaziridine ring forms an angle (γ) of 72.7° with the N(1)—N(6)—C(2)—C(5) plane (see Fig. 2). Apparently, the observed elongation of the N(1)—N(6) bond (1.528(2) Å) in molecule **4b** compared to the N(1)—N(5) bond (1.517(2) Å) in the structure of **1d** is attributable to an increase in the contribution of the p orbital of the N atom, because there is no n(N)—σ*(C—C) interaction in compound **4b**.

Since the N atoms in compound **4b** are involved in the intermolecular N(1)...H(12′)—C(12′) contacts ($1/2 - x$, $2 - y$, $-0.5 + y$) (N(1)...H(12′), 2.47 Å; N(1)...C(12′), 3.488(3) Å; N(1)—H(12′)—C(12′), 160°), the conformation of the bicyclic moiety (chair) observed in molecule **4b** may be attributed to the crystal packing effect.

With the aim of determining the energetically most favorable conformation and estimating the influence of the stereoelectronic effects on the preferable conformations of 1,5-diazabicyclo[3.1.0]hexanes **1** and 1,6-diazabicyclo[4.1.0]heptanes **4**, quantum-chemical calculations (B3LYP/6-31G*)[11] were carried out for model compounds **1h** (Fig. 3) and **4a** (Fig. 4) with R = R′ = H.

In the isolated molecule, the energy of the boat conformation (**1h** (**boat**)) with consideration for the zero-point energy (ZPE) is 3.4 kcal mol^{-1} lower than the energy of the chair conformation (**1h** (**chair**)). The geometry of **1h** (**boat**) rather adequately reproduces the corresponding experimental values for **1d**, except for a slight shortening of the N(1)—N(5) bond to 1.509 Å (see Table 2). The transformation from the boat conformation to the chair conformation in **1h** is accompanied by an increase in the N(1)—N(5) bond length to 1.527 Å, an increase in the C(2)—C(3)—C(4) bond angle from 102.1° to 105.9°, and an increase in the α angle from 24.9° to 31.3°. These changes are consistent with the presence of the n(N)—σ*(C—C) interaction in **1h** (**boat**). To estimate the contribution of the n(N)—σ*(C—C) interaction to stabilization of **1h** (**boat**), we carried out the NBO analysis,[12] which has earlier been successfully applied to the investigation of anomeric and related interactions (see, for example, Refs. 13a,b). In line with the published data[5a–d] and the observed variations in the geometric parameters, the NBO analysis demonstrated that the n-electrons of the N(1) and N(5) atoms in **1h** (**boat**) interact with the σ* orbitals of the C(2)—C(3) and C(3)—C(4) bonds. The contribution of these interactions to the charge delocalization is 4 kcal mol^{-1}. Both conformations of **1h**

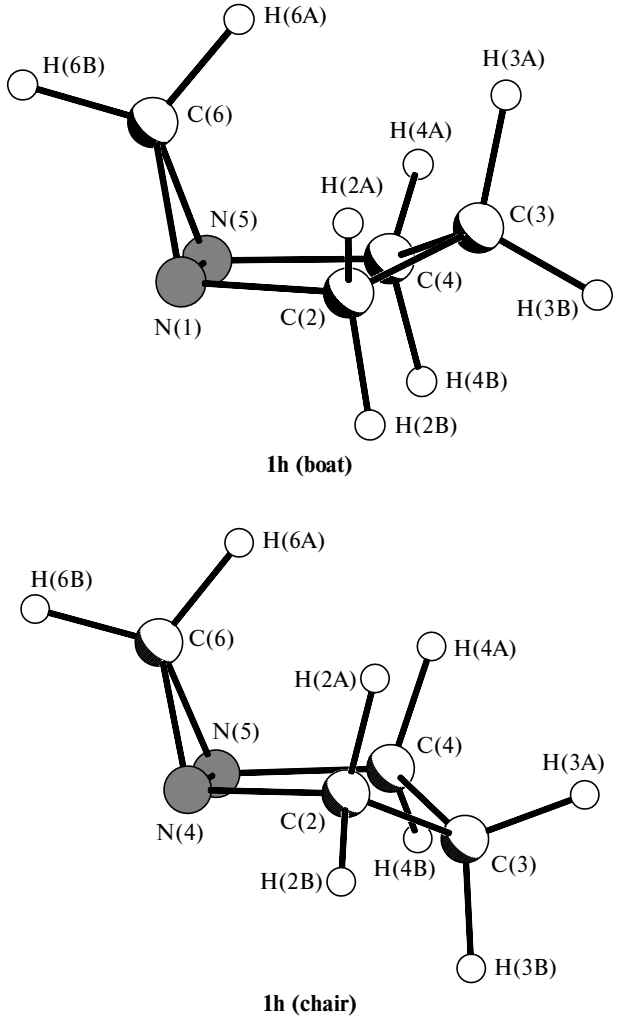


Fig. 3. Overall views of conformations **1h** (**boat**) and **1h** (**chair**) (calculated data).

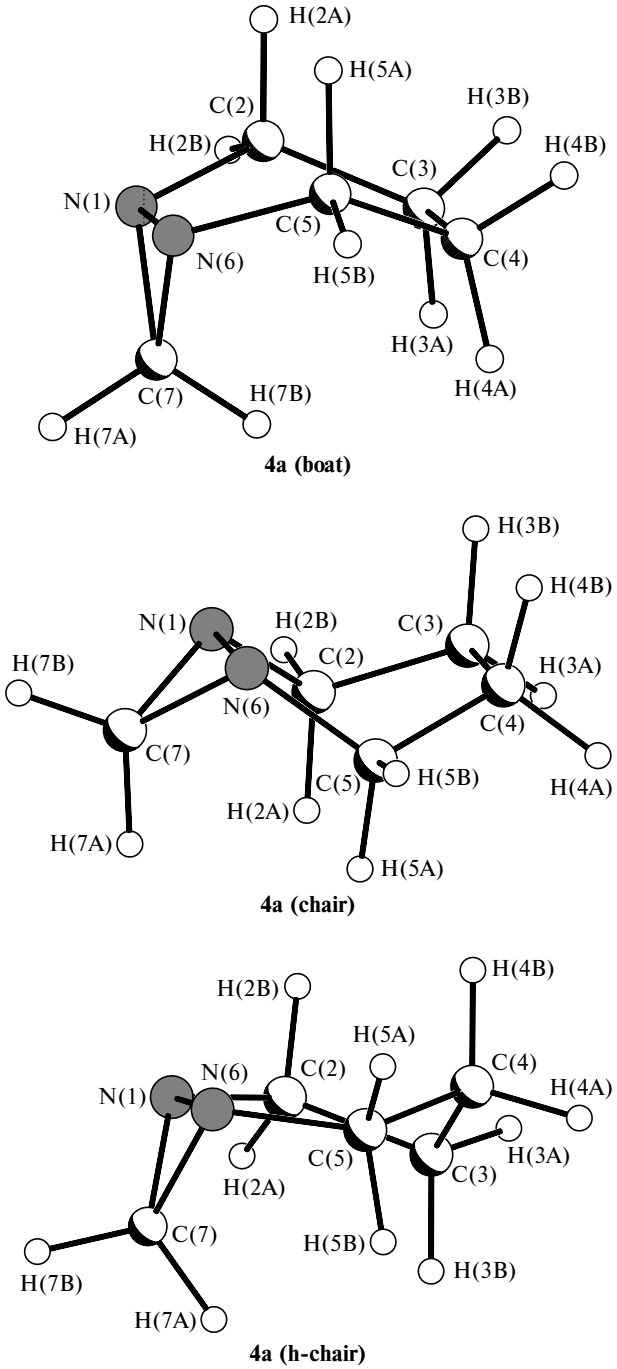


Fig. 4. Overall views of conformations **4a** (**boat**), **4a** (**chair**), and **4a** (**h-chair**) (calculated data).

are characterized by the presence of not only the n(N)—σ*(C—C) interactions but also of the n(N)—σ*(C(6)—H(6A)) interactions comparable in energy (3.5 kcal mol^{-1}) to the former interactions (see Fig. 3). Apparently, the latter interactions are responsible for the constancy of the dihedral angle β (73.7 and 73.9° in **1h** (**boat**) and **1h** (**chair**), respectively).

The geometry optimization of **4a** revealed three conformations of this bicyclic compound with close energies. In two of these conformations, the six-membered ring adopts a boat conformation, but the overall conformation of the bicyclic moiety in these two cases can be described as a boat-like conformation (**4a** (**boat**)), in which the diaziridine ring and the C(3)—C(4) bond are on the same side of the N(1)—N(6)—C(2)—C(5) plane, and a chair-like conformation (**4a** (**chair**)), in which the diaziridine ring and the C(3)—C(4) bond, on the contrary, deviate in opposite directions. In another chair-like conformation of bicyclic compound **4a**, the six-membered ring adopts a half-chair conformation (**4a** (**h-chair**)) with the C(3) and C(4) atoms deviating from the N(1)—N(6)—C(2)—C(5) plane by 0.36 and −0.41 Å, respectively (see Fig. 4). Although **4a** (**boat**) is characterized by the lowest energy, this conformation is only 0.45 kcal mol^{-1} more stable than **4a** (**h-chair**) taking account of ZPE. The energy of

the latter conformation is, in turn, only 1.35 kcal mol^{-1} lower than the energy of **4a** (**chair**). Such insignificant differences in the energy of the conformations of molecule **4a** agree well with the efficient flattening of the six-membered ring observed from the NMR spectra.[5a]

In spite of the fact that three conformations of **4a** are close in energy, their geometric parameters and, primarily, the N(1)—N(6) bond lengths are substantially different and (like those in molecule **1h**) are determined by the presence and strength of the n(N)—σ*(C—C) interactions (see Table 3). Thus, the shortest N—N bond (1.501 Å) is observed in conformation **4a** (**boat**), in which the contribution of the n(N)—σ*(C—C) interaction to the charge delocalization is 6.8 kcal mol^{-1} (according to the results of the NBO analysis). To the contrary, **4a** (**chair**), in which this interaction is *a priori* absent, has the longest N—N bond (1.521 Å). Conformation **4a** (**h-chair**) is, in turn, characterized by the intermediate value of the N—N bond length (1.515 Å) as well as by the differences in the bond angles at the C(2) and C(5) atoms, which is associated with the fact that only one N atom in this conformation is involved in the n(N(6))—σ*(C(5)—C(4)) interaction with the energy of 6.4 kcal mol^{-1}.

Since the remaining bond lengths in both molecules **1h** and **4a** depend only slightly on the conformation, the observed correlation between the N—N bond length and the strength of the n(N)—σ*(C—C) interaction can serve as a reliable criterion in studies of stereoelectronic interactions in such systems. For example, the N—N bond in *trans-exo*-2,4,6-trimethyl-1,3,5-triazabicyclo[3.1.0]hexane, in which the n(N)—σ*(C—N) interaction has a higher energy, is shortened to 1.511 Å.[14]

Apparently, the observed variations in the angle of the bend (γ) of the diaziridine ring (71.9—75.2°) in compound **4a**, in contrast to the constancy of the corresponding dihedral angle β in molecule **1h**, result from the difference in the energy (3.8—4.8 kcal mol^{-1}) of the n(N)—σ*(C(7)—H(7A)) interactions.

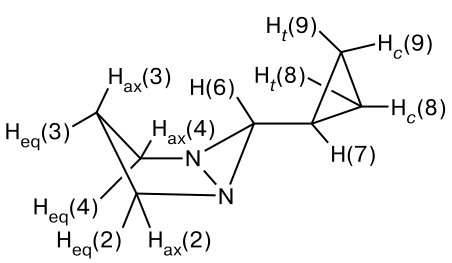
The character of the ^{1}H NMR spectra of compounds **1** and **4** is consistent with the data from X-ray diffraction analysis and quantum-chemical calculations. For example, the NMR spectra of compounds **1** at 20 °C have multiplets with fine splitting patterns, which indicates that the molecules in solution occur predominantly in a single conformation stable within the NMR time scale. By contrast, the spectra of compounds **4** both at 20 and −80 °C have broadened poorly resolved multiplets, which indicates that several conformations with close energies occur in dynamic equilibrium in solution.

To summarize, X-ray diffraction analysis, NMR spectroscopic studies, and quantum-chemical calculations demonstrated that the stereoelectronic interactions play the main role in stabilization of the conformations of the nitrogen-containing bicyclic compounds under consideration. As a result, a boat conformation prevails in 1,5-diazabicyclo[3.1.0]hexanes **1** and, which is more unusual, the energies of chair, half-chair, and boat conformations in 1,6-diazabicyclo[4.1.0]heptanes are equalized.

Experimental

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets. The ^{1}H NMR spectra of compounds **1a,c—e,g** and **4b—d,g** were measured on a Bruker DRX-500 spectrometer (500 MHz). The ^{1}H NMR spectra of compounds **1b,f** and **4e,f,h** were recorded on a Bruker AM-300 spectrometer (300 MHz). The assignment of the signals in the spectrum of compound **1a** was made based on the COSY 2D homonuclear correlation spectrum. The spin system of compound **1a** was analyzed with the use of the CALM program for iterative analysis. This program allowed us to calculate the ^{1}H NMR spectra of this compound based on the spin-spin coupling constants, which were roughly determined from the experimental spectrum, as the initial approximation and then to perform an iterative search for the parameters of the spin system (proton chemical shifts and spin-spin coupling constants) to achieve the best fit of the calculated spectrum to the experimental data. For the remaining compounds **1** and **4**, the spin-spin coupling constants were calculated manually. The ^{13}C NMR spectrum of compound **4h** was recorded on a Bruker DRX-500 spectrometer (125.8 MHz). The ^{13}C NMR spectra of compounds **1a** and **4c,e** were measured on a Bruker AM-300 spectrometer (75.5 MHz). The ^{13}C NMR spectra of compounds **1b,f** and **4b,d** were recorded on a Bruker WM-250 spectrometer (62.9 MHz). The chemical shifts are given in the δ scale with respect to the residual signals of the protons of the deuterated solvent. The mass spectra were obtained on an MS-30 spectrometer. The TLC analysis was carried out on Silufol UV-254 plates; visualization was carried out with iodine vapor and independently by spraying with a solution of diphenylamine in acetone followed by heating of the plates ($CHCl_3$—MeOH, 10 : 1, as the eluent).

6-Cyclopropyl-1,5-diazabicyclo[3.1.0]hexane (1a). A solution of Bu^{t}OCl (2.2 mL, 16.5 mmol) in MeOH (3 mL) was added dropwise to a solution of 1,3-diaminopropane (2.4 g, 33 mmol) in MeOH (15 mL) at 0 °C and then formylcyclopropane (1.2 g, 16.6 mmol) was added. The reaction mixture was kept at this temperature for 1 h and then at 20 °C for 1 h. The precipitate that formed was filtered off and the yield of compound **1a** (73%) was determined by iodometric titration. The solvent was evaporated *in vacuo*, the residue was distilled off, and the fraction with b.p. 110—111 °C (25 Torr) was collected. Compound **1a** was obtained in a yield of 1.4 g (68%), d_4^{20} 1.02, n_D^{20} 1.490, R_f 0.56. Found (%): C, 67.5; H, 9.7; N, 22.5. $C_7H_{12}N_2$. Calculated (%): C, 67.7; H, 9.7; N, 22.6.



IR, ν/cm^{-1}: 630, 670, 840, 950, 1020, 1220, 1250, 1440, 2890, 2940, 2990, 3110. ^{1}H NMR ($CDCl_3$), δ: 0.17 (m, 2 H, H_t(8), H_t(9), $^3J_{H_t(8)-H_t(9)}$ = 9.23 Hz); 0.23 (m, 2 H, H_c(8), H_c(9), $^3J_{H_c(8)-H_c(9)}$ = −9.40 Hz, $^2J_{H_t(8(9))-H_c(8(9))}$ = −4.51 Hz, $^3J_{H_t(9)-H_c(9(8))}$ = 5.96 Hz, $^3J_{H_c(8)-H_c(9)}$ = 9.40 Hz); 0.68 (m, 1 H, H(7), $^3J_{H(7)-H_t(8(9))}$ = 4.82 Hz, $^3J_{H(7)-H_c(8(9))}$ = 8.56 Hz); 1.50 (m, 1 H, H_{eq}(3), $^3J_{Heq(3)-Hax(3)}$ = −13.16 Hz); 2.00 (d, 1 H, H(6), $^3J_{H(6)-H(7)}$ = 4.87 Hz); 2.72 (m, 2 H, H_{eq}(2), H_{eq}(4), $^3J_{Hax(2(4))-Heq(3)}$ = 8.18 Hz, $^3J_{Hax(2(4))-Hax(3)}$ = 11.03 Hz); 3.13 (m, 2 H, H_{eq}(2), $H_{eq}(4)_{eq}$, $^2J_{Hax(2(4))-Heq(2(4))}$ = −12.07 Hz, $^3J_{Heq(2(4))-Hax(3)}$ = 8.92 Hz). ^{13}C NMR ($CDCl_3$), δ: −0.2 (C(8), C(9)); 9.5 (C(7)); 20.6 (C(3)); 50.0 (C(2), C(4)); 56.3 (C(6)).

6-Aryl- and 6-heteroaryl-1,5-diazabicyclo[3.1.0]hexanes (1), 7-aryl- and 7-heteroaryl-1,6-diazabicyclo[4.1.0]heptanes (4) (general procedure). A solution of Bu^{t}OCl (0.022 mol) in MeOH or $CHCl_3$ (3 mL) was added dropwise with active stirring to a solution of diaminoalkane (0.04 mol) in MeOH (30 mL) for **1b,c,e—g** and **4b,e—h** or in $CHCl_3$ (30 mL) for **1d** and **4c,d** at −5—0 °C. Then a solution of aldehyde (0.02 mol) in the corresponding solvent (4—6 mL) was added. The reaction mixture was kept for 24 h at 0—5 °C (with the use of MeOH) or at 20—25 °C (with the use of $CHCl_3$) and filtered through a thin layer (1.5—2.0 cm) of silica gel. The solvent was evaporated *in vacuo* and water (50 mL) was added to the residue. The reaction mixture was saturated with NaCl, extracted with ether or CH_2Cl_2 (3×30 mL), and dried with K_2CO_3. The solvent was evaporated *in vacuo* and the residue was recrystallized from acetone or ether. The spectroscopic characteristics of the compounds are given in Table 2.

6-Phenyl-1,5-diazabicyclo[3.1.0]hexane (1b). The IR spectrum is identical with the published data.[9] ^{1}H NMR ($CDCl_3$), δ: 1.90 (m, 1 H, H_{ax}(3)); 1.95 (m, 1 H, H_{eq}(3), ^2J = −12.0 Hz); 3.18 (m, 2 H, H_{ax}(2), H_{ax}(4), $^3J_{Hax(2(4))-Heq(4)}$ = 8.5 Hz, $^3J_{Hax(2(4))-Hax(3)}$ = 11.3 Hz); 3.59 (m, 2 H, H_{eq}(2), H_{eq}(4), ^2J = −12.1 Hz, $^3J_{Heq(2(4))-Heq(3)}$ = 1.3 Hz, $^3J_{Heq(2(4))-Hax(3)}$ = 8.8 Hz); 3.59 (s, 1 H, HC_{ring}(6)); 7.33 (m, 5 H, HC_{Ar}). ^{13}C NMR ($CDCl_3$), δ: 21.6 (C_{ring}(3)); 52.2 (C_{ring}(2(4))); 56.6 (C_{ring}(6)); 127.2 (C_{Ar}(2(6))); 128.16 (C_{Ar}(3(5))); 128.4 (C_{Ar}(4)); 137.0 (C_{Ar}(1)). Partial mass spectrum (EI, 70 eV), *m/z* (I_{rel} (%)): 160 $[M]^+$ (24.8), 159 $[M - H]^+$ (100), 83 $[M - Ph]^+$ (15), 65 $[Ph]^+$ (28.8).

6-(3-Nitrophenyl)-1,5-diazabicyclo[3.1.0]hexane (1c). The IR spectrum is identical with the published data.[9] ^{1}H NMR (DMSO-d_6), δ: 1.85 (m, 1 H, H_{ax}(3)); 1.90 (m, 1 H, H_{eq}(3), ^2J = −12.2 Hz); 2.95 (m, 2 H, H_{ax}(2), H_{ax}(4), $^3J_{Hax(2(4))-Heq(3)}$ = 8.4 Hz, $^3J_{Hax(2(4))-Hax(3)}$ = 11.1 Hz); 3.51 (m, 2 H, H_{eq}(2), H_{eq}(4), $^2J_{Hax(2(4))-Heq(2(4))}$ = −12.3 Hz, $^3J_{Heq(2(4))-Heq(3)}$ = 1.4 Hz, $^3J_{Heq(2(4))-Hax(3)}$ = 8.8 Hz); 3.59 (s, 1 H, HC_{ring}(6)); 7.61 (t, 1 H, HC_{Ar}(5)); 7.75 (d, 1 H, HC_{Ar}(6), $^3J_{H(CAr(6))-H(CAr(5))}$ = 7.8 Hz); 8.11 (d, 1 H, HC_{Ar}(4), ^3J = 5.6 Hz); 8.15 (s, 1 H, HC_{Ar}(2)).

6-(4-Chlorophenyl)-1,5-diazabicyclo[3.1.0]hexane (1d). The IR spectrum is identical with the published data.[9] ^{1}H NMR (DMSO-d_6), δ: 1.85 (m, 2 H, H_{ax}(3), H_{eq}(3), ^2J = −12.0 Hz); 2.91 (m, 2 H, H_{ax}(2), H_{ax}(4), $^3J_{Hax(2(4))-Heq(3)}$ = 8.5 Hz); 3.47 (m, 2 H, H_{eq}(2), H_{eq}(4), ^2J = −12.1 Hz, $^3J_{Heq(2(4))-Hax(3)}$ = 8.7 Hz); 3.37 (s, 1 H, HC_{ring}(6)); 7.35 (q, 4 H, HC_{Ar}, AB system, Δν = 25, ^3J = 12.0 Hz).

6-(2-Chloro-5-nitrophenyl)-1,5-diazabicyclo[3.1.0]hexane (1e). Found (%): N, 17.1. $C_{10}H_{10}ClN_3O_2$. Calculated (%): N, 17.5. IR, ν/cm^{-1}: 2926, 1538, 1354, 1076, 831, 747. ^{1}H NMR (DMSO-d_6), δ: 1.95 (m, 1 H, H_{ax}(3)); 2.00 (m, 1 H, H_{eq}(3), ^2J = −12.0 Hz); 3.10 (m, 2 H, H_{ax}(2(4)), $^3J_{Hax(2(4))-Heq(3)}$ = 8.5 Hz); 3.53 (s, 1 H, HC_{ring}(6)); 3.61 (m, 2 H, H_{eq}(2(4)), ^2J = −12.1 Hz, $^3J_{Heq(2(4))-Hax(3)}$ = 8.8 Hz); 7.61 (d, 1 H, HC_{Ar}(3)); 8.11 (d, 1 H, HC_{Ar}(4), ^3J = 7.8 Hz); 8.15 (s, 1 H, HC_{Ar}(6)).

6-(2-Pyridyl)-1,5-diazabicyclo[3.1.0]hexane (1f). Found (%): N, 25.8. $C_9H_{11}N_3$. Calculated (%): N, 26.1. IR, ν/cm^{-1}: 3025, 1672, 1204, 1067, 712. ^{1}H NMR (DMSO-d_6), δ: 1.80 (m, 2 H, H_{ax}(3), H_{eq}(3), ^2J = −11.8 Hz); 3.08 (m, 2 H, H_{ax}(2(4)), $^3J_{Hax(2(4))-Heq(3)}$ = 8.3 Hz, $^3J_{Hax(2(4))-Hax(3)}$ = 11.1 Hz); 3.30 (s, 1 H, HC_{Py}(6)); 3.56 (m, 2 H, H_{eq}(2(4)), $^3J_{Heq(2(4))-Hax(3)}$ = 8.9 Hz); 7.13 (t, 1 H, HC_{Py}(5), $^3J_{H(CPy(5))-H(CPy(4))}$ = 6.8 Hz, $^3J_{H(CPy(5))-H(CPy(6))}$ = 5.3 Hz); 7.26 (d, 1 H, HC_{Py}(3), $^3J_{H(CPy(3))-H(CPy(4))}$ = 7.8 Hz); 7.58 (t, 1 H, HC_{Py}(4)); 8.40 (d, 1 H, HC_{Py}(6)). ^{13}C NMR (DMSO-d_6), δ: 21.50 (C_{ring}(3)); 52.35 (C_{ring}(2(4)); 57.39 (C_{ring}(6)); 121.13 (C_{Py}(3)); 123.46 (C_{Py}(5)); 136.79 (C_{Py}(4)); 148.52 (C_{Py}(6)); 157.07 (C_{Py}(2)).

7-Phenyl-1,6-diazabicyclo[4.1.0]heptane (4b). Found (%): N, 15.6. $C_{11}H_{14}N_2$. Calculated (%): N, 16.1. IR, ν/cm^{-1}: 2938, 1568, 1325, 1052, 858, 745. ^{1}H NMR (DMSO-d_6), δ: 1.61 (m, 4 H, H_{ax}(3), H_{eq}(3), H_{ax}(4), H_{eq}(4)); 2.90 (m, 2 H, H_{ax}(2), H_{ax}(5)); 3.30 (m, 2 H, H_{eq}(2), H_{eq}(5), $^2J_{Heq(2(5))-Hax(2(5))}$ = −13.5 Hz); 3.79 (s, 1 H, HC_{ring}(7)); 7.30 (m, 5 H, HC_{Ar}). ^{13}C NMR (DMSO-d_6), δ: 7.41 (C_{ring}(3(5))); 37.04 (C_{ring}(2(4))); 57.71 (C_{ring}(7)); 118.34 (C_{Ar}(2(6))); 118.75 (C_{Ar}(3(5))); 124.03 (C_{Ar}(4)); 127.19 (C_{Ar}(1)).

7-(4-Chlorophenyl)-1,6-diazabicyclo[4.1.0]heptane (4c). Found (%): N, 13.0. $C_{11}H_{13}ClN_2$. Calculated (%): N, 13.4. IR, ν/cm^{-1}: 3084, 2953, 1594, 1336, 1070, 796, 762. ^{1}H NMR (DMSO-d_6), δ: 1.72 (m, 4 H, H_{ax}(3), H_{eq}(3), H_{ax}(4), H_{eq}(4)); 2.88 (m, 2 H, H_{ax}(2), H_{ax}(5)); 3.42 (m, 2 H, H_{eq}(2), H_{eq}(5), $^2J_{Heq(2(5))-Hax(2(5))}$ = −13.1 Hz); 3.49 (s, 1 H, HC_{ring}(7)); 7.28 (q, 4 H, HC_{Ar}, ^3J = 11.2 Hz). ^{13}C NMR (DMSO-d_6), δ: 7.41 (C_{ring}(3(5))); 37.04 (C_{ring}(2(4))); 57.71 (C_{ring}(7)); 118.34 (C_{Ar}(3(5))); 118.75 (C_{Ar}(2(6))); 124.03 (C_{Ar}(4)); 127.19 (C_{Ar}(1)).

7-(4-Bromophenyl)-1,6-diazabicyclo[4.1.0]heptane (4d). Found (%): N, 10.8. $C_{11}H_{13}BrN_2$. Calculated (%): N, 11.1. IR, ν/cm^{-1}: 2914, 1585, 1340, 1105, 858, 740. ^{1}H NMR ($CDCl_3$), δ: 1.71 (m, 4 H, H_{ax}(3), H_{eq}(3), H_{ax}(4), H_{eq}(4)); 2.85 (m, 2 H, H_{ax}(2), H_{ax}(5)); 3.40 (m, 2 H, H_{eq}(2), H_{eq}(5)); 3.49 (s, 1 H, HC_{ring}(7)); 7.30 (q, 4 H, HC_{Ar}, AB system, Δν = 80.0, ^3J = 8.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 17.63 (C_{ring}(3(4))); 47.31 (C_{ring}(2(5))); 67.97 (C_{ring}(7)); 122.45 (C_{Ar}(1)); 129.29 (C_{Ar}(3(5))); 131.49 (C_{Ar}(2(6))); 137.88 (C_{Ar}(4)).

7-(2-Pyridyl)-1,6-diazabicyclo[4.1.0]heptane (4e). Found (%): N, 23.5. $C_{10}H_{13}N_3$. Calculated (%): N, 24.0. IR, ν/cm^{-1}: 1658, 1186, 1032, 710. ^{1}H NMR ($CDCl_3$), δ: 1.69 (m, 4 H, H_{ax}(3), H_{eq}(3), H_{ax}(4), H_{eq}(4)); 2.92 (m, 2 H, H_{ax}(2), H_{ax}(5)); 3.45 (m, 2 H, H_{eq}(2), H_{eq}(5), $^2J_{Heq(2(5))-Hax(2(5))}$ = −13.0 Hz); 3.78 (s, 1 H, HC_{ring}(7)); 7.13 (d, 1 H, HC_{Py}(3), ^3J = 7.8 Hz); 7.25 (t, 1 H, HC_{Py}(5), $^3J_{H(CPy(5))-H(CPy(4))}$ = 6.9 Hz, $^3J_{H(CPy(5))-H(CPy(6))}$ = 5.0 Hz); 7.68 (t, 1 H, HC_{Py}(4)); 8.48 (d, 1 H, HC_{Py}(6)). ^{13}C NMR ($CDCl_3$), δ: 17.23 (C_{ring}(3(4))); 47.24 (C_{ring}(2(5))); 68.82 (C_{ring}(7)); 120.96 (C_{Py}(3)); 123.50 (C_{Py}(5)); 136.87 (C_{Py}(4)); 148.71 (C_{Py}(6)); 157.59 (C_{Py}(2)).

7-(2-Furyl)-1,6-diazabicyclo[4.1.0]heptane (4f). Found (%): N, 16.6. $C_9H_{12}N_2O$. Calculated (%): N, 17.1. ^{1}H NMR

($CDCl_3$), δ: 1.66 (m, 4 H, $H_{ax}(3)$, $H_{eq}(3)$, $H_{ax}(4)$, $H_{eq}(4)$); 3.46 (m, 2 H, $H_{ax}(2)$, $H_{ax}(4)$); 3.56 (m, 2 H, $H_{eq}(2)$, $H_{eq}(5)$); 3.59 (s, 1 H, $HC_{ring}(7)$); 6.30 (d, 1 H, $HC_{Het}(3)$, ^3J = 2.0 Hz); 6.36 (t, 1 H, $HC_{Het}(4)$, $^3J_{H(C_{Het}(4))-H(C_{Het}(5))}$ = 1.75 Hz); 7.45 (d, 1 H, $HC_{Het}(5)$).

7-(5-Bromo-2-thienyl)-1,6-diazabicyclo[4.1.0]heptane (4g). Found (%): N, 10.6. $C_9H_{11}BrN_2S$. Calculated (%): N, 10.8. ^{1}H NMR ($CDCl_3$), δ: 1.69 (m, 4 H, $H_{ax}(3)$, $H_{eq}(3)$, $H_{ax}(4)$, $H_{eq}(4)$); 2.85 (m, 2 H, $H_{ax}(2)$, $H_{ax}(5)$); 3.47 (m, 2 H, $H_{eq}(2)$, $H_{eq}(5)$, ^2J = −11.5 Hz); 3.75 (s, 1 H, $HC_{ring}(7)$); 6.91 (d, 1 H, $HC_{Het}(3)$); 7.19 (d, 1 H, $HC_{Het}(4)$, ^3J = 1.5 Hz).

7,7′-Bis(1,6-diazabicyclo[4.1.0]heptane) (4h). Found (%): S, 61.5; H, 9.1; N, 28.7. $C_{10}H_{18}N_4$. Calculated (%): S, 61.8; H, 9.3; N, 28.8. ^{1}H NMR ($CDCl_3$), δ: 1.59 (m, 4 H, $H_{ax}(3)$, $H_{ax}(3')$, $H_{ax}(4)$, $H_{ax}(4')$); 1.69 (m, 4 H, $H_{eq}(3)$, $H_{eq}(3')$, $H_{eq}(4)$, $H_{eq}(4')$, ^2J = −12.3 Hz); 2.41 (s, 2 H, $HC_{ring}(7)$, $HC_{ring}(7')$); 2.68 (m, 4 H, $H_{ax}(2)$, $H_{ax}(2')$, $H_{ax}(5)$, $H_{ax}(5')$); 3.39 (m, 4 H, $H_{eq}(2)$, $H_{eq}(2')$, $H_{eq}(5)$, $H_{eq}(5')$, ^2J = −12.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 17.04 ($C_{ring}(3)$, $C_{ring}(3')$ ($C_{ring}(4)$, $C_{ring}(4')$); 46.78 ($C_{ring}(2)$, $C_{ring}(2')$ ($C_{ring}(5)$, $C_{ring}(5')$); 68.48 ($C_{ring}(7)$, $C_{ring}(7')$).

6-Phenyl- (1b) and 6-trinitrophenyl-1,5-diazabicyclo[3.1.0]hexane (1c) in the presence of Et_3NH or K_2CO_3. A solution of Bu^tOCl (0.04 mol) in MeOH (6 mL) was added dropwise with stirring to a solution of 1,3-diaminopropane (0.04 mol) in MeOH (30 mL) at −5—0 °C. Then Et_3NH or K_2CO_3 (0.04 mol) and the corresponding aldehyde (0.02 mol) were added dropwise. The reaction mixture was stirred at 0—5 °C for 12 h and filtered through a thin layer (1.5—2.0 cm) of silica gel. The solvent was concentrated *in vacuo*. The residue was dissolved in water (50 mL), saturated with NaCl, extracted with ether or CH_2Cl_2 (3×30 mL), and dried with K_2CO_3. The solvent was concentrated *in vacuo* and the mixture was recrystallized from acetone or ether. The yields of compounds **1b** and **1c** prepared with the use of Et_3NH were 21 and 25%, respectively. The yields of these compounds obtained with the use of K_2CO_3 were 33 and 31%, respectively.

X-ray diffraction study. All X-ray data were collected on a SMART CCD-1000 diffractometer (ω scanning technique, frames were exposed for 10 s). The X-ray data were processed with the use of the SAINT PLUS program package. The empirical absorption correction was applied based on equivalent reflections with the use of the SADABS program. The principal crystallographic data and details of the refinement are given in Table 4. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic and isotropic thermal parameters. The H atoms were revealed from difference electron density syntheses and included in the final refinement with isotropic thermal parameters. All calculations were carried out on a personal computer with the use of the SHELXTL PLUS ver. 5.0 program package.

Table 4. Principal crystallographic parameters of compounds **1d** and **4b**

Parameter	$C_{10}H_{11}ClN_2$ (**1d**)	$C_{11}H_{14}N_2$ (**4b**)
M	194.66	174.24
$F(000)$	816	412
μ(Mo-Kα)/cm^{-1}	3.57	0.78
Space group	*Pbca*	$P2_12_12_1$
Diffractometer	«SMART CCD-1K»	
Scanning mode	ω Scan technique	
ω Scan step/deg	0.3	
Exposition time per frame/s	10	
T/K	110	
a/Å	14.255(5)	7.669(1)
b/Å	8.935(2)	10.350(2)
c/Å	14.779(4)	12.087(2)
V/Å^3	1882.3(8)	959.4(3)
Z	8	4
d_{calc}/g cm^{-3}	1.374	1.310
$2\theta_{max}$/deg	58	52
Number of measured reflections	6345	6189
Number of independent reflections	2463 (R_{int} = 0.0201)	1862 (R_{int} = 0.0320)
wR_2 based on F^2 for all reflections	0.1562	0.0935
R_1, based on F for reflections with $I > 2\sigma(I)$	0.0532 (1990 reflections)	0.0372 (1610 reflections)
GOF	1.075	1.042

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