A quantum-chemical study of 1,2,3,4,5,6,7,8-octaazanaphthalene and its *N*-oxides

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Calculations of hypothetical molecules of octaazanaphthalene and its *N*-oxides were performed by the MNDO method with full geometry optimization. Probable decomposition reactions of these compounds were considered. Compounds with more pronounced alternation of charges on adjacent atoms were shown to be more thermodynamically favorable and thermally stable.

Key words: quantum-chemical calculations, MNDO method, 1,2,3,4,5,6,7,8-octaazanaphthalene, octaazanaphthalene *N*-oxides, stability.

Currently, considerable attention is given to the problem of the stability of compounds whose molecules contain chains of sp^2-hybridized N atoms.[1] This is due to the fact that this type of systems, in particular, cyclic systems, can be considered as inorganic analogs of classical conjugated molecules and as highly dense and highly energetic chemical compounds. Of undeniable interest is the search for stabilization mechanisms of this type of systems.

It was concluded in a theoretical study[2] of the nature of conjugation in this type of systems (in particular, in hexazine) performed using the *ab initio* method with the STO-3G basis set that the strongest reason for weakening of the bonds between nitrogen atoms is the interaction between the lone electron pairs and the N—N bond. A procedure was proposed for stabilization of the chains of conjugated N atoms, consisting of the involvement of the lone electron pairs in semipolar bonds. MNDO calculations of 1,3-substituted tetrazetes[3] and 1,3,5-substituted hexazines[4] showed that corresponding *N*-ylides, *N*-imines, and *N*-oxides are more stable than tetrazete and hexazine, respectively. Using MNDO calculations of 1,2,3,4,5,6-hexaazapentalene di-*N*-oxides, we have established[5] that the 2,5-di-*N*-oxide is the most stable of these compounds. The aim of this work was to find the most stable compounds in the series of octaazanaphthalene oxides.

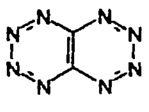
Calculation procedure

Calculations of 1,2,3,4,5,6,7,8-octaazanaphthalene (**1**) and its oxides (**2**—**9**) were performed by the MNDO method with full geometry optimization using the MNDO program (QCPE353).[6] The calculated enthalpies of formation and enthalpies of decomposition reactions of compounds **1** and **2**—**9** are listed in Table 1 and the energies of frontier orbitals and charges on the atoms are listed in Table 2.

Results and Discussion

Thermodynamic stability. It is impossible to make quantitative estimates of the contribution from the mutual "repulsion" of the lone electron pairs of N atoms when calculating the enthalpies of formation of oxides **2**—**9**. In this connection, we chose for comparison pairs of isomeric octaazanaphthalene dioxides **2** and **3**, **4** and **5**, and **6** and **7** with the same number and identical mutual arrangement of adjacent N atoms with the lone electron pairs. The relative thermodynamic stability of the isomers was evaluated directly from their enthalpies of formation (ΔH_f°, see Table 1).

Octaazanaphthalene 1,8-dioxide **2** is only slightly more stable than isomeric 1,5-dioxide **3** ($\Delta(\Delta H_f^\circ)$ =



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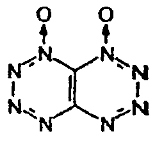

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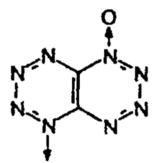

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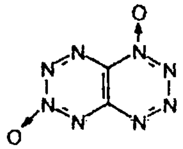

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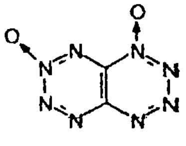

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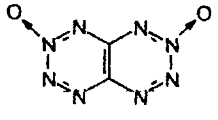

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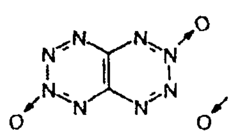

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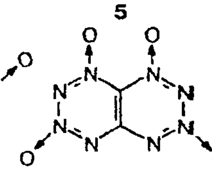

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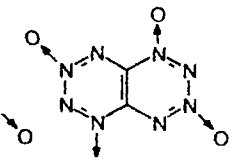

O **9**

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 879—881, May, 1999.

1066-5285/99/4805-0870 $22.00

Table 1. Enthalpies of formation[a] ($\Delta H_f°$) and enthalpies of decomposition reactions (ΔH_r) of octaazanaphthalene and its oxides calculated by the MNDO method

Compound	$\Delta H_f°$ /kcal mol^{-1}	Reaction route[b]	ΔH_r /kcal mol^{-1}
1	148.9	*A*	−59.0
2	171.8	*B*	−43.2
3	172.4	*B*	−43.8
		C	−90.7
4	168.4	*B*	−39.8
		D	−32.7
5	174.4	*B*	−45.8
		D	−38.7
		C	−92.7
6	168.1	*D*	−32.4
7	176.7	*D*	−41.0
		C	−95.0
8	201.3	*E*	−26.9
9	212.3	*F*	−84.4
		E	−37.9

[a] The calculated $\Delta H_f°$ values for N_2, N_2O, NO, C_2N_2, and C_2N_2O are 8.0, 30.9, −0.1, 65.9, and 81.7 kcal mol^{-1}, respectively.

[b] The composition of the products of the decomposition reaction (depending on the reaction route) is: *A*, $C_2N_2 + 3\ N_2$; *B*, $C_2N_2O + 2\ N_2 + N_2O$; *C*, $C_2N_2 + 2\ N_2 + 2\ NO$; *D*, $C_2N_2 + N_2 + 2\ N_2O$; *E*, $C_2N_2O + 3\ N_2O$; and *F*, $C_2N_2 + 2\ N_2O + 2\ NO$.

0.6 kcal mol^{-1}). The difference in stability for isomers **4**, **5** ($\Delta(\Delta H_f°)$ = 6.0 kcal mol^{-1}) and **6**, **7** ($\Delta(\Delta H_f°)$ = 8.6 kcal mol^{-1}) is substantially higher. A pronounced alternation of charges on the atoms in the molecules of the more stable isomers **2**, **4**, and **6** is observed. In the case of the less stable isomers **3**, **5**, and **7** this alternation is violated (see Table 2).

It seems likely that alternation of charges is one of the reasons for the increasing thermodynamic stability of the molecule, since for such a charge distribution the difference in the orbital electronegativity[*] of adjacent atoms is maximum, which results in maximum "sagging"[7] of the HOMO. The HOMO energies of isomers **2**, **4**, and **6** are considerably lower that those of the **3**, **5**, and **7** isomers (see Table 2). The most pronounced alternation of charges is observed for octaazanaphthalene 1,3,6,8-tetraoxide (**8**), *viz.*, charges on the atoms in molecule **8** vary to the greatest extent. In fact, this compound is much more stable than its isomer **9** ($\Delta(\Delta H_f°)$ = 11.0 kcal mol^{-1}).

Thermal stability. To estimate the thermal stability of compounds under study, we calculated the enthalpies of their decomposition reactions, ΔH_r (see Table 1), related to the activation energies of decomposition in accordance with the Bell—Evans—Polanyi principles.[7] Only the most probable reactions occurring without rearrangements and only primary decomposition products were considered. Needless to say this is a rather approximate approach suitable only for performing rough estimates of stability.

Most likely, compound **1** will decompose into three nitrogen molecules and one dicyanogen molecule (route *A*, see Table 1). Judging by the large ΔH_r value (−59 kcal mol^{-1}) of the decomposition reaction, compound **1** must not possess high thermal stability. On the one hand, this is due to the destabilizing interaction between the lone electron pairs of adjacent N atoms, resulting in the increase in $\Delta H_f°$ values, and, on the other hand,

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[*] For comparison it should be noted that the charges on the N atoms in molecule **1** are close to zero; however, it is impossible to compare the thermodynamic stability of this molecule with that of dioxides on the basis of the ΔH_f value, since these compounds have different elemental compositions.

Table 2. The HOMO and LUMO energies (*E*) and charges (*q*) on the N and C atoms in the molecules of octaazanaphthalene and its *N*-oxides calculated by the MNDO method

Compound	$-E_{HOMO}$	$-E_{LUMO}$	*q*/au									
	eV		N(1)	N(2)	N(3)	N(4)	C(4a)	N(5)	N(6)	N(7)	N(8)	C(8a)
1[*]	11.85	3.09	0.02	0.01	0.01	0.02	−0.06	0.02	0.01	0.01	0.02	−0.07
2	11.27	3.30	0.36	−0.12	0.10	−0.11	0.16	−0.11	0.10	−0.13	0.36	−0.28
3	10.77	3.34	0.33	−0.12	0.07	−0.07	−0.05	0.33	−0.12	0.07	−0.08	−0.05
4	11.27	3.09	0.37	−0.13	0.10	−0.13	0.18	−0.19	0.32	−0.02	0.08	−0.29
5	10.55	3.25	0.32	−0.12	0.05	−0.05	−0.07	0.06	0.03	0.30	−0.16	−0.16
6	11.05	2.87	−0.20	0.32	−0.03	0.09	−0.28	0.10	−0.03	0.32	−0.20	0.18
7	10.19	3.18	−0.14	0.30	0.03	0.05	−0.04	−0.14	0.29	0.03	0.04	−0.04
8	11.54	3.13	0.42	−0.23	0.40	−0.23	0.25	−0.23	0.40	−0.23	0.42	−0.37
9	10.18	3.45	0.37	−0.20	0.39	−0.20	−0.03	0.37	−0.20	0.39	−0.20	−0.03

[*] According to calculations, a planar structure with D_{2h} symmetry corresponds to a minimum on the potential energy surface of molecule **1**. As in the structure of naphthalene, in this structure the N(1)—N(2), N(3)—N(4), N(5)—N(6), and N(7)—N(8) bonds are shortened to 1.25 Å, whereas the remaining bonds are lengthened (d(N(2)—N(3)) = d(N(6)—N(7)) = 1.35 Å, d(N(1)—C(8a)) = d(N(4)—C(4a)) = d(N(5)—C(4a)) = d(N(8)—C(8a)) = 1.40 Å). The C(4a)—C(8a) bond length (1.41 Å) is close to those in aromatic compounds.[8]

to the fact that decomposition products, particularly, N_2 molecules, are more thermodynamically favorable.

It is unlikely that decomposition of octaazanaphthalene oxides will begin with elimination of an oxygen atom, since this reaction is very endothermic (ΔH_r values lie in the range 96 to 104 kcal mol^{-1}). Most likely, the decomposition will begin with cleavage of the N—N bonds followed by abstraction of N_2, N_2O, NO, and dicyanogen or dicyanogen oxide molecules. The decomposition route and the composition of reaction products are dependent on the mutual arrangement of the O atoms (see note "*b*" to Table 1, routes *B—F*). According to the Bell—Evans—Polanyi principles,[7] the route characterized by the largest heat of reaction should be realized most easily. It stands to reason that changes in the decomposition mechanisms can introduce some corrections; however, it is hardly probable that this would affect the overall decomposition pattern.

Analysis of the data listed in Table 1 shows that, in essence, the composition of decomposition products rather than the thermodynamic stability of compounds is the factor determining thermal stability, since the $\Delta(\Delta H_r)$ value is appreciably larger than $\Delta(\Delta H_f^\circ)$, which has a maximum value of only 11 kcal mol^{-1} for the pair of *N*-oxides **8** and **9**. At the same time, all thermodynamically more stable isomers are also more thermally stable, *i.e.*, the mutual arrangement of O atoms, resulting in the alternation of charges on the N atoms, simultaneously provides the "best" composition of decomposition products of the molecule. In addition, it should be noted that introduction of *N*-oxide oxygen atoms into a polynitrogen molecule in order to reduce the destabilizing effect of the lone electron pairs of adjacent N atoms does not necessarily lead to an increase in the thermal stability of the molecule. For instance, taking into account that the MNDO method appreciably underestimates the ΔH_f° value for the NO molecule (the difference between the experimental and calculated values is −21.7 kcal mol^{-1}), it is likely that tetraoxide **9** is close in stability to octaazanaphthalene.

Thus, our quantum-chemical study of the molecules of octaazanaphthalene and octaazanaphthalene oxides made it possible to establish that their thermodynamic and thermal stabilities are dependent on the mutual arrangement of O atoms in the molecule, as in the case of hexaazapentalene oxides. The molecules with the most pronounced alternation of charges on the ring atoms appeared to be the most stable.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33712a).

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Received June 9, 1998;
in revised form November 4, 1998