NOVEL MODIFICATIONS OF ELEMENTAL NITROGEN AND THEIR MOLECULAR STRUCTURES – A QUANTUM-CHEMICAL CALCULATION

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Using the quantum-chemical calculation methods QCISD and G3, the possibility of the existence of nitrogen molecules with the composition N_4, N_6, N_8 and N_{10} has been discussed. On the basis of the data obtained, the conclusion about possibility of existence of three novel polymorphic modifications of elemental nitrogen with an even number of atoms in molecules, namely N_4 with rectangular and regular tetrahedron shapes, and N_6 in a form remotely resembling an "open book", has been made. The values of bond lengths, valence and torsion angles, and oscillations frequencies in each of the above-mentioned forms of elemental nitrogen have been presented.

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INTRODUCTION

Molecule of elemental nitrogen is known to consist of two atoms with a triple bond between them.[1] The length of this bond is only 109.5 pm, and, owing to this, the N_2 molecule (dinitrogen) is characterized by a very high dissociation energy (941.64 kJ mol^{-1}) and by very less chemical activity.

Three crystalline modifications of N_2 are known. In the temperature range 36.61-63.29 K, β-N_2 phase having a hexagonal dense packing, a space P6_3 mmc^{-2} group, lattice parameters a = 3.93 Å and c = 6.50 Å, exists. At a temperature lower than 36.61 K, a stable α-N_2 phase having cubic lattice, a space P$2_1$3 group and a period of a = 5.660 Å, occurs. At a pressure of more than 3500 atmospheres and a temperature below 83.0 K, a hexagonal phase of dinitrogen, namely γ-N_2, is formed.

There are some theoretical indications that other nitrogen oligomers and polymers may be possible. These nitrogen modifications may have potential applications as materials with a very high energy density and as powerful propellants or explosives.[1] For most neutral polynitrogens are not expected to have a large barrier towards decomposition, and that the few exceptions would be even more challenging to synthesize than the tetranitrogen N_4 which is an analogue of tetrahedrane C_4, and has potential as a high-performance energetic material.[2] Nevertheless, cationic and anionic polynitrogens, namely cations of triazenium (N_3^+), tetrazenium (N_4^+), pentazenium (N_5^+), and azide-anione (N_3^-), pentazolide-anione (cyclic aromatic N_5^-) have been characterized.[1,3-9] However, all these nitrogen compounds have a positive or negative charge. Up to now, however, there is no information in the literature on the existence of other neutral simple substances consisting solely of nitrogen atoms.[10-12] In this connection, in the this article the possibility of the existence of polyatomic molecules of nitrogen with an even number of atoms, namely nitrogen molecules of N_4, N_6, N_8 and N_{10} compositions will be discussed.

CALCULATION METHOD

The calculation of molecular structures of polyatomic nitrogen molecules of N_4, N_6, N_8 and N_{10} compositions was carried out using the QCISD(T)/TZVP method, as described in detail earlier,[13] in combination with the Gaussian09 software package.[14] The initial structures of the N_4, N_6, N_8 and N_{10} molecules for carrying out quantum-chemical calculations are shown in figure 1.

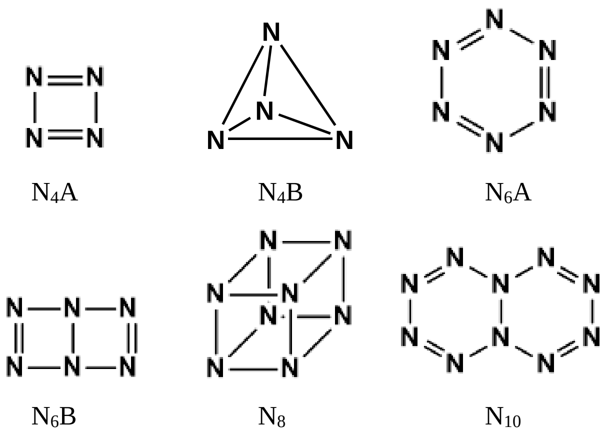

Figure 1. The assumed initial structures of nitrogen molecules.

The choice of these initial structures was determined by two factors. First, the valence possibilities of the nitrogen atom (which capable to bind with one, two or three neighboring atoms by means of three chemical bonds according to the exchange mechanism) and secondly, with the greatest typicality of these structures compared with other structures with a corresponding number of atoms. In this connection, the regular octahedron in the case of N_6, the hexagonal bipyramid and the dodecahedron in the case of N_8, the two-capped cube or the two-capped dodecahedron in the case of N_{10} were not included in the number of initial structures. The correspondence of the found stationary points to energy minima was proved in all cases by the calculation of the second derivatives of energy with respect to the atom coordinates All equilibrium structures corresponding to the minima on the potential energy surfaces has only positive frequencies. The values of the standard thermodynamic characteristics of the nitrogen-containing compounds under examination were calculated using the G3 method described in earlier in detail.[15] All quantum-chemical calculations were carried out in the Joint Supercomputer Center, Kazan Branch of RAS – Branch of Federal Scientific Center "Research Institute for System Studies of the Russian Academy of Sciences" (http://www.jscc.ru).

RESULTS AND DISCUSSION

According to the results of our calculations, only three of the six structures of polyatomic nitrogen molecules mentioned above are stable, namely the N_4A structure in the form of a rectangle, N_4B in the form of a regular tetrahedron, and the N_6B structure in the form of an "open book". All these modifications have been shown in figure 2.

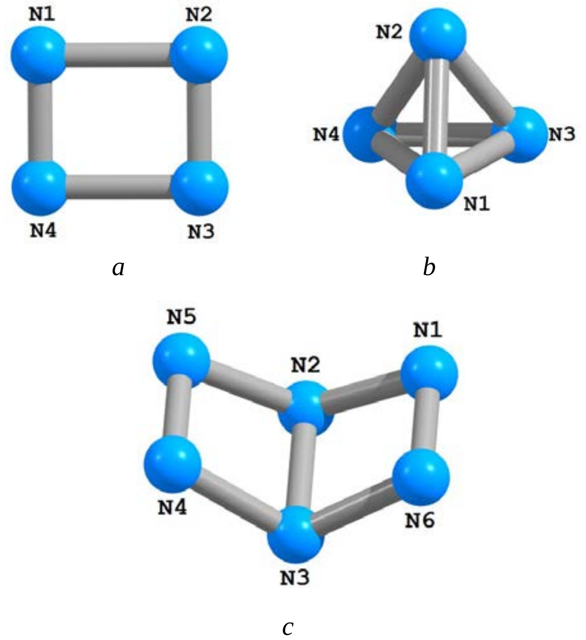

Figure 2. Molecular structures of three theoretically possible polymorphic modifications of elemental nitrogen.

The geometric parameters of these above-mentioned stable structures (bond lengths, valence and torsion angles) have been presented in the Table 1. As can be seen from these data, in the polyatomic nitrogen molecules under examination, the nitrogen–nitrogen bond lengths are much larger than those in the N_2 molecule; it is quite natural, because the theoretically expected multiplicity of bonds in them should be lesser than one in a dinitrogen molecule. It should be noted in this connection that for the N_2 molecule itself, according to the QCISD(T)/TZVP method, the bond length (N1N2) is 110.3 pm that is very close to the experimental value of (109.5-110.0) pm.[1] It is interesting that, according to our calculations, for a "planar" version of the tetranitrogen molecule N_4A, not a square or orthorhombic structure is realized, as might be expected, but a rectangular structure, with rather considerably different "longitudinal" and "transverse" bond lengths (154.6 and 127.1 pm, respectively) (Figure 2). At the same time, for the "tetrahedral" variant N_4B, the structure of the regular tetrahedron, where all the lengths of nitrogen-nitrogen bonds are exactly the same and have an intermediate values between the nitrogen- nitrogen bond lengths in the structure of N_4A.

Table 1. Parameters of the molecular structure of four- and six-atom nitrogen molecules.

Molecule N_4A			
N-N bond lengths, pm		**Valence angles, deg**	
(N1N2)	154.6	(N1N2N3)	90.0
(N2N3)	127.1	(N2N3N4)	90.0
(N3N4)	154.6	(N3N4N1)	90.0
(N4N1)	127.1	(N4N1N2)	90.0
Torsion (dihedral) angles, deg			
(N1N2N3N4)	0.0	(N2N3N4N1)	0.0
(N3N4N1N2)	0.0	(N4N1N2N3)	0.0
Molecule N_4(B)			
N-N bond lengths, pm		**Valence angles, deg**	
(N1N2)	146.7	(N1N2N3)	60.0
(N1N3)	146.7	(N1N2N4)	60.0
(N1N4)	146.7	(N1N3N2)	60.0
(N2N3)	146.7	(N1N3N4)	60.0
(N2N4)	146.7	(N1N4N2)	60.0
(N3N4)	146.7	(N1N4N3)	60.0
Torsion (dihedral) angles, deg			
(N1N2N3N4)	70.6	(N2N3N4N1)	–70.5
(N3N4N1N2)	–70.6	(N4N1N2N3)	–70.5
Molecule N_6(B)			
N-N bond lengths, pm		**Valence angles, deg**	
(N1N2)	147.8	(N1N2N5)	109.1
(N2N3)	153.0	(N2N5N4)	95.3
(N3N6)	147.7	(N5N4N3)	95.3
(N6N1)	125.8	(N4N3N6)	109.1
(N2N5)	147.7	(N3N6N1)	95.3
(N5N4)	125.8	(N6N1N2)	95.3
(N4N3)	147.7	(N2N3N4)	84.7
		(N2N3N6)	84.7
		(N3N2N1)	84.7
		(N3N2N5)	84.7
Torsion (dihedral) angles, deg			
(N1N2N5N4)	–82.5	(N6N3N4N5)	82.5
(N1N6N3N4)	–82.6	(N6N1N2N5)	82.5
(N1N2N3N6)	0.0	(N5N2N3N4)	0.0
(N2N3N6N1)	0.0	(N2N3N4N5)	0.0
(N3N6N1N2)	0.0	(N3N4N5N2)	0.0
(N6N1N2N3)	0.0	(N4N5N2N3)	0.0
(N5N2N3N6)	–109.8	(N1N2N3N4)	109.8

The structure of N_6B, as it should be expected, is non-coplanar. There are three different kinds of nitrogen-nitrogen bonds having different lengths in it. Two of them are relatively short (125.8 pm) and correspond to the double N=N bond; the other five in own length correspond to a single N-N bond, but one of them forming sui generis "binding" of this "open book" itself, is noticeably longer than the other four, 153.0 and 147.7 pm, respectively.

Table 2. The oscillation frequencies in the N_4A, N_4B and N_6B.

Oscillation frequency, cm^{-1}	Assignment of oscillation frequency
Molecule N_4(A)	
402	Wagging
493	Stretching (*asym.*) with participation of atoms (N1N2) and (N3N4)
904	Stretching (*sym.*) with participation of atoms (N1N2) and (N3N4)
998	Scissoring
1296	Stretching (*asym.*) with participation of atoms (N1N4) and (N2N3)
1526	Stretching (*sym.*) with participation of atoms (N1N4) and (N2N3)
Molecule N_4(B)	
695	Scissoring with change of all valence angles
695	Scissoring with participation of atoms (N1N4) and (N2N3), concerning (N2N4) bond
915	Stretching (*asym.*) with change of (N1N4), (N1N3) and (N2N3) bond lengths
915	Stretching with change of (N1N3), (N1N4), (N2N3) and (N2N4) bond lengths
917	Scissoring with change of angles (N3N1N4) and (N3N2N4)
1288	Stretching (*sym.*) with participation of all participation of all N atoms
Molecule N_6(B)	
383	Conjugation of two rocking oscillations of (N4N3N6) and (N1N2N5)
447	Scissoring with participation of atom groupings (N3N4N6) and (N1N2N5)
468	Scissoring with participation of atom grouping (N3N4N6)
578	Stretching (*sym.*) with change of bond lengths in pairs (N2N5), (N1N2) and (N4N3), (N3N6)
716	Stretching (*asym.*) with change of bond lengths in pairs (N2N5), (N1N2) and (N4N3), (N3N6)
749	Stretching (*sym.*) with change of bond lengths in pairs(N1N2), (N2N5), and (N4N3), (N3N6), and (N2N3), too
841	Scissoring with participation of atom groupings (N1N2N5) and (N3N4N6)
917	Rocking with participation of atom groupings (N1N2N5) and (N3N4N6)
946	Scissoring with change of bond length (N2N3)
1030	Conjugation of several scissoring oscillations
1447	Stretching (*asym.*) with change of bond lengths (N1N6) and (N4N5)
1510	Stretching (*sym.*) with change of bond lengths (N1N6) and (N4N5)

As a result of the above differences, both sides of the "cover" of this "open book" are in fact not rectangles, as might be expected at first glance, but are identical isosceles trapezoids. The sum of the valence angles (N3N6N1) + (N6N1N2) + (N1N2N3) + (N2N3N6) and (N4N3N2) + (N3N2N5) + (N2N5N4) + (N5N4N3) are the same and are equal to exactly 360.0°. What is remarkable, the values of the valence angles (N1N2N5) and (N4N3N6) are much closer to 90° than to 180°, so the degree of non-coplanarity of the molecular structure of N_6B should be considered as very significant.

Oscillation frequencies of polynitrogen molecules N_4A, N_4B and N_6B are depicted in Table 2. According to theoretical expectations, 6 oscillations must be active in the IR spectrum in the case of N_4A and N_4B, and 12, in the case of N_6B. Our calculated values match the theoretical expectations.(Table 2). As may be seen from these data, the sets of vibrational frequencies in polynitrogen molecules are quite different among themselves. At the same time, what is interesting, in N_4B, there are two pairs of oscillations of different nature with the almost identical in frequency, 695 and 915 cm^{-1} whereas in N_4B and N_6B, nothing like this occurs.

Table 3. Calculated standard thermodynamic parameters of formation of N_4A, N_4B and N_6B molecules from dinitrogen.

Compound	$\Delta_f H^0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}	$\Delta_f G^0$, kJ mol^{-1}
N_4A	771.6	248.6	810.8
N_4B	771.0	230.9	815.6
N_6B	1009.5	278.2	1096.7

The values of standard thermodynamic characteristics, namely $\Delta_f H^0$ (kJ mol^{-1}), S^0 (J mol^{-1} K^{-1}) and $\Delta_f G^0$ (kJ mol^{-1}), of the formation of N_4A, N_4B and N_6B were calculated with using of G3 method and are presented in the Table 3. As follows from the data given in it, they all have positive values. In this connection, this fact attracts its attention that the values of these standard parameters for compounds N_4A and N_4B despite the very significant difference in their molecular structures, are nevertheless extremely close to each other. It is easy may be shown with using of these data and well-known values of $\Delta_f H^0$ and S^0 for dinitrogen (0 kJ mol^{-1} and 191.6 J mol^{-1} K^{-1}, respectively,[16] they cannot be formed directly from N_2 within the framework of the isobar process by general eqns. (1-3)

$$2N_2\,(gas) \rightarrow N_4A\,(gas) \quad (1)$$

$$2N_2\,(gas) \rightarrow N_4B\,(gas) \quad (2)$$

$$3N_2\,(gas) \rightarrow N_6\,(gas) \quad (3)$$

Table 5. Calculated standard thermodynamic parameters of formation of N_4A, N_4B and N_6B molecules from atomic nitrogen.

Reaction	ΔH^0, kJ	S^0, J K^{-1}
4N (gas) → N_4A (gas)	–1119.6	–364.6
4N (gas) → N_4B (gas)	–1120.2	–382.3
6N (gas) → N_6 (gas)	–1827.3	–641.6

The point is that for each of these processes, the value of the standard enthalpy of the reaction (ΔH^0_{298}) is positive, and, on the contrary, the standard entropy (S^0_{298}) is negative (Table 4), and in accordance with the classical Gibbs-Helmholtz equation $\Delta G^0 = \Delta H^0 - T\Delta S^0$, their synthesis directly from the "ordinary" dinitrogen N_2 is thermodynamically forbidden process. However, from the thermodynamic point of view, the formation of N_4A, N_4B and N_6B from atomic nitrogen according to schemes (4-6) is perfectly permissible and, nevertheless, as can be shown using the values of $\Delta_f H^0$ and S^0 for atomic nitrogen (472.8 kJ mol^{-1} and 153.3 J mol^{-1} K^{-1}, respectively),[16] for each of reactions (4-6) ΔH^0 as well as ΔS^0 are *negative* (Table 5) so that in a certain temperature range each of them are thermodynamically resolved. It should be noted in this connection that according to our calculation using the G3 method, the standard enthalpy of the N_2(gas) → 2N (gas) process, in fact, the energy of N≡N bond in the dinitrogen molecule is 936.60 kJ mol^{-1}, which is in very good agreement with the experimental value of 941.64 kJ mol^{-1}. How to synthesize these novel polymorphic modifications of nitrogen is another problem, the discussion of which is beyond the scope of this paper, and further researches are needed for it.

$$4N \text{ (gas)} \rightarrow N_4(A) \text{ (gas)} \quad (4)$$

$$4N \text{ (gas)} \rightarrow N_4(B) \text{ (gas)} \quad (5)$$

$$6N \text{ (gas)} \rightarrow N_6 \text{ (gas)} \quad (6)$$

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest, financial or otherwise.

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