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MOLECULAR MODELING OF THE MECHANISMS OF THERMOLYSIS OF NITRAMINO-1,2,4-TRIAZOLES

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Modeling of the probable mechanisms of the thermolysis of C- and N-nitramino-1,2,4-triazoles has been carried out by methods of mathematical chemistry. It was established that the formation is possible of a more diverse spectrum of products in their destruction than was previously recorded by different experimental methods. Subsequent assessment of the thermochemical preference for pathways of decomposition of the compounds was carried out by the density functional method in the B3LYP/6-31G approach. It was determined that the thermal destruction of C- and N-nitramino-substituted polynitrogen heterocycles, capable of tautomeric conversion, was most probably through the thermochemically least stable nitramine form. Thermal decomposition of the considered tautomers is preferred at the NNO_2 fragment and not at the triazole ring. The direction of the structural stabilization of the investigated compounds has been clarified by comparison of the geometric, electronic, and thermochemical characteristics of $C–NNO_2$- and $N–NNO_2$-substituted 1,2,4-triazoles.*

Keywords: nitramino-1,2,4-triazoles, structure–property interconnections, quantum-chemical calculations, density functional method, modeling of thermolysis mechanisms.

To assess the promise of the practical use of energy-rich materials (EM) information is necessary on their thermal stability, connected with the mechanisms of the thermal decomposition of substances [1-3]. The destruction of organic compounds is a multistage process. However, experimental investigations of the mechanisms of thermal decomposition of EM are limited, as a rule, by the initial step and/or analysis of the final thermolysis products (often incomplete), which clearly is insufficient for a complete and objective description of these processes [2, 3].

More attention has been paid in recent years to the design of various calculation methods enabling the properties of EM to be predicted [4-9]. Progress in modeling some properties of energy-rich compounds is not uniform. The theoretical description of the mechanisms of thermal decomposition of EM today is a complex problem, difficult to formalize [2], similar investigations are scarce. Consequently the design of effective approaches to the solution of this problem is extremely important. We have developed a methodology for computer modeling of the mechanisms of thermal decomposition of organic substances (mainly nitro compounds [10-18]).

Structures comprising the combination of an NNO_2 fragment with various polynitrogen heterocycles are well known among energy-rich compounds [19-22]. In particular, derivatives of 1,2,4-triazole [19, 23-25], some of which are shown in Fig. 1, are of undoubted interest as EM.

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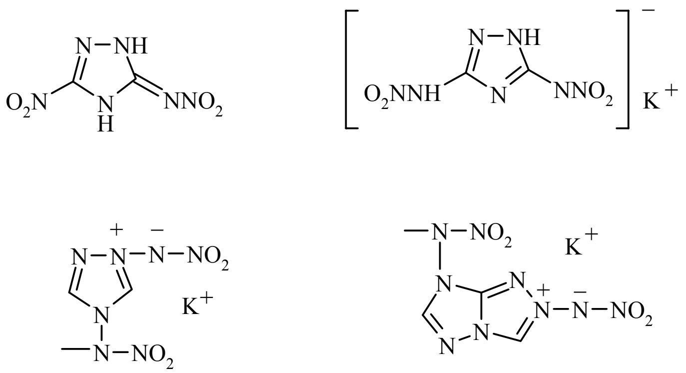
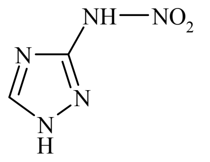


Fig. 1. Energy-rich nitraminotriazoles.

Generally available information on experimental and theoretical investigations of mechanisms of the thermal decomposition of this series of compounds is scarce [26-30]. Computer modeling of the mechanisms of thermal decomposition of similar compounds (**1** and **2**) has therefore been carried out in the present work.



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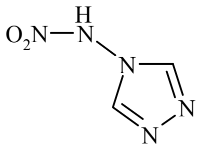

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The selection of precisely these structures was determined by the fact that, on the one hand, they are simple subjects to model, and on the other, there are experimental data for them on the composition of decomposition products and some analysis of the mechanism of the primary stage of thermal decomposition [26-30], which has enabled assessment of the quality of the results obtained by us.

The approach proposed by us to the mathematical modeling of the mechanisms of the thermal destruction of organic compounds has been described previously [10-18] . Empirical rules were developed in the approach based on the correlation of experimental data on the mechanism of thermal decomposition of nitro compounds of various classes. These rules enabled modeling of possible routes of destruction of these compounds. Collected into generators of conversions these rules are a system of expert formulations, in the structure of which criteria are laid down for the selection of reactions characteristic for compounds of this or any other class. These rules are used to generate Recombination Reaction Networks (RRN), which are a definite excess of the combinations of structures of intermediates and initial substances [11, 18, 31-33] involved in the thermolysis process.

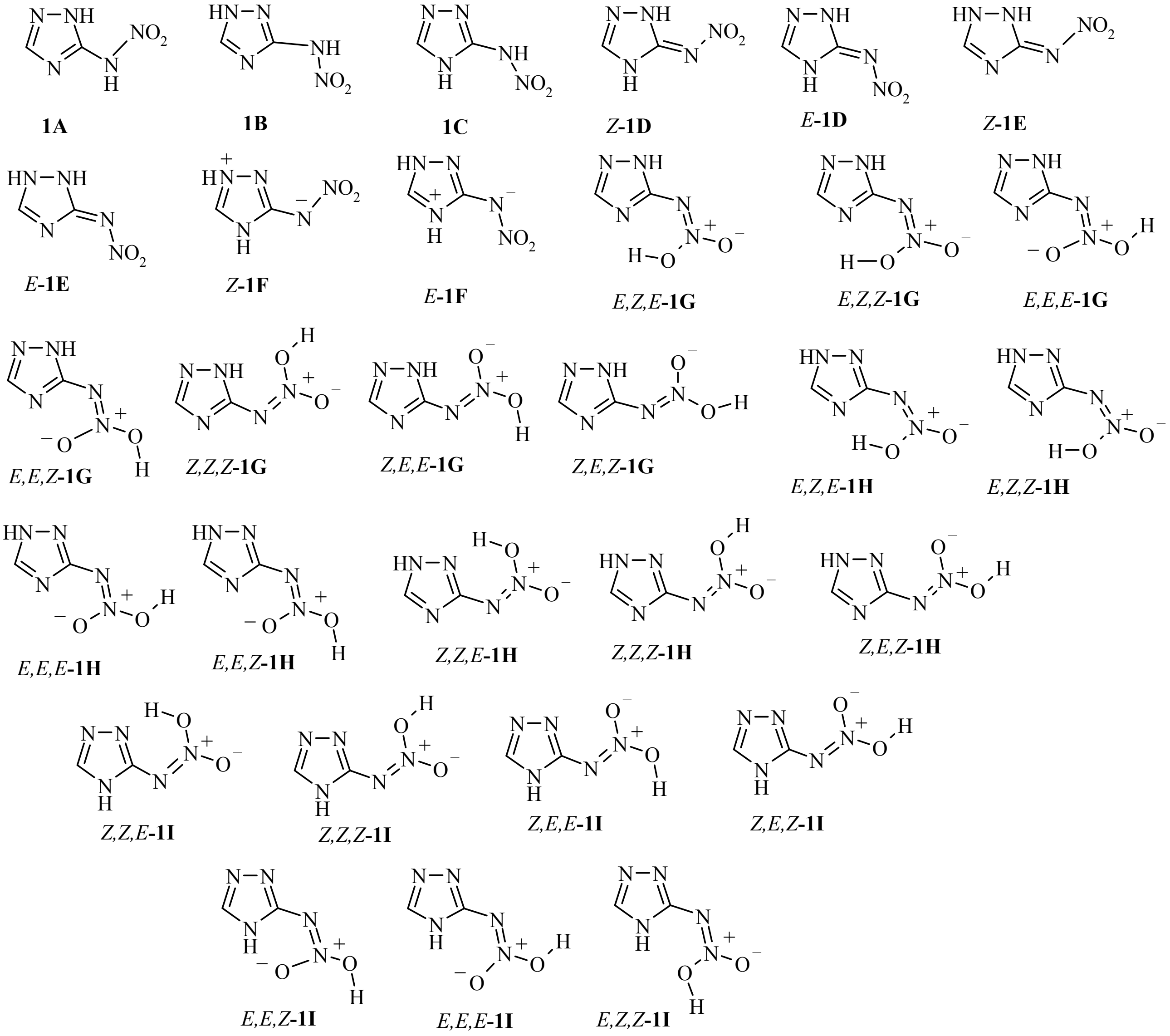
After the generation of possible mechanisms for the thermal decomposition of compounds, the energies of activation (E_{act}) [1] were then calculated for reactions occurring on thermolysis (to assess thermochemical preference for one or other channel of breakdown). Triplet spin states were considered for biradical structures. Calculations were carried out within the framework of density functional theory (DFT) with hybrid potential B3LYP [34] and the standard valence-split basis 6-31G* [35] when using the GAUSSIAN 98 set of programs [36] in the computer center of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

RESULTS AND DISCUSSION OF MODELING MECHANISMS OF THERMAL DECOMPOSITION OF COMPOUNDS

It is generally known that the directions of the thermal destruction of a compound depend on its structure. We attempted to assess this interconnection in the example of compounds **1** and **2**.

A characteristic feature of azoles having a monosubstituted or unsubstituted amino group as substituent is the capacity for tautomeric conversion caused by migration of proton (prototropic tautomerism). This process has been described in detail for azoles and azines in a series of reviews [37-40]. Nitramines **1** and **2** are typical compounds capable of this tautomerism. In addition it is necessary to consider one further form of tautomerism for compounds **1** and **2**, *viz*. formation of the *aci* form of the nitramino group [41-45].

In Fig. 2 are given the 30 tautomeric forms and rotational isomers possible for C-nitramino-1,2,4-triazole **1**.



1A **1B** **1C** *Z*-**1D** *E*-**1D** *Z*-**1E**

E-**1E** *Z*-**1F** *E*-**1F** *E,Z,E*-**1G** *E,Z,Z*-**1G** *E,E,E*-**1G**

E,E,Z-**1G** *Z,Z,Z*-**1G** *Z,E,E*-**1G** *Z,E,Z*-**1G** *E,Z,E*-**1H** *E,Z,Z*-**1H**

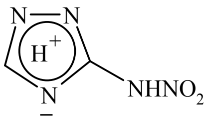
E,E,E-**1H** *E,E,Z*-**1H** *Z,Z,E*-**1H** *Z,Z,Z*-**1H** *Z,E,Z*-**1H**

Z,Z,E-**1I** *Z,Z,Z*-**1I** *Z,E,E*-**1I** *Z,E,Z*-**1I**

E,E,Z-**1I** *E,E,E*-**1I** *E,Z,Z*-**1I**

Fig. 2. Possible tautomers and rotational isomers of C-nitramino-1,2,4-triazole
(for tautomers **1D-I** the description of the isomeric forms begins with the exocyclic C–N bond).

We note that usually compound **1** is arbitrarily assigned the structure of one tautomer, for example **1A-C** [19, 26, 46-54], nitramine **1D** [28, 55], or zwitterion **1K** [26].



1K

There is no experimental proof of the dominant presence (or absence) of any tautomeric form on thermolysis of compound **1**. It is evident that the possibility of the existence of nitramine **1** in the form of any tautomer or mixture of tautomers may be determined by the actual conditions. This set of problems therefore remains open.

For example, is it possible for all of the tautomers represented in Fig. 2 to exist? Is the form of the initial tautomer reflected in the mechanism and composition of the products of thermolysis? On attempting to answer these problems we calculated the thermodynamic characteristics of tautomers **1A-I** and carried out modeling of the mechanisms of their thermolysis.

The total energies with correction for the zero vibrational energies (*E* + *ZPE*) of derivatives of 1,2,4-triazole **1A-I** and the energies for their tautomerization found by the method of [56] were calculated (Table 1). As is evident from Table 1 tautomer **1A** is thermodynamically the most stable in the gas phase. The closest to it in stability were tautomers **1B**, *E*-**1D** and *Z*-**1D**, for which (*E* + *ZPE*) was greater by 0.00042, 0.00140, and 0.00224 a.u. respectively compared with tautomer **1A**. The energies of tautomerization of compound **1A** were 0.3 (to **1B**), 0.9 (to *E*-**1D**), and 1.4 kcal/mol (to *Z*-**1D**).

TABLE 1. Energy Characteristics of Tautomers and Rotational Isomers of C-Nitramino-1,2,4-triazole **1A-I** in the Gas Phase

Compound	(*E* + *ZPE*), a.u.	E_{taut}*, kcal/mol	Compound	(*E* + *ZPE*), a.u.	E_{taut}*, kcal/mol
1A	-502.00630	0.0	*Z,E,Z*-**1G**	-501.99202	9.0
1B	-502.00588	0.3	*E,Z,E*-**1H**	-501.99117	9.5
1C	-501.99581	6.6	*E,Z,Z*-**1H**	-501.98139	15.6
Z-**1D**	-502.00406	1.4	*E,E,E*-**1H**	-501.98536	13.1
E-**1D**	-502.00490	0.9	*E,E,Z*-**1H**	-501.98507	13.3
Z-**1E**	-501.97946	16.8	*Z,Z,E*-**1H**	-501.98776	11.6
E-**1E**	-501.96841	23.8	*Z,Z,Z*-**1H**	-501.98101	15.9
Z-**1F**	-501.96726	24.5	*Z,E,Z*-**1H**	-501.98561	13.0
E-**1F**	-501.98159	15.5	*Z,Z,E*-**1I**	-501.98945	10.6
E,Z,E-**1G**	-501.99828	5.0	*Z,Z,Z*-**1I**	-501.97494	19.7
E,Z,Z-**1G**	-501.98509	13.3	*Z,E,E*-**1I**	-501.97616	18.9
E,E,E-**1G**	-501.98700	12.1	*Z,E,Z*-**1I**	-501.97798	17.8
E,E,Z-**1G**	-501.98837	11.3	*E,E,Z*-**1I**	-501.98224	15.1
Z,Z,Z-**1G**	-501.98513	13.3	*E,E,E*-**1I**	-501.98284	14.7
Z,E,E-**1G**	-501.99253	8.7	*E,Z,Z*-**1I**	-501.97481	19.8

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* Tautomerization energy (E_{taut}) of compound **1A** into the corresponding tautomer was calculated as $[(E + ZPE)_x - (E + ZPE)_y].627.5$ kcal/mol [56] (*E* is the total energy, *ZPE* is the correction for zero vibration energy, *x* is for data of compound **1A**, *y* for data of all other compounds).

The *aci* forms of nitramines **1G-I** are less stable than tautomer **1A** by 0.00802-0.03149 a.u. The tautomerization energy of compound **1A** into *aci* forms **1G-I** is in the range 5.0-19.8 kcal/mol. Tautomers *Z*-**1E** and *E*-**1E** are the least stable, and the most unprofitable in the gas phase are the zwitterions *Z*-**1F**.

We have modeled complete cycles of decomposition of all the possible tautomers. We have decided however to consider only individual examples which are the most characteristic. When considering the mechanisms for the thermal destruction of tautomers **1A-C** it is possible to isolate the three most probable directions for their homolytic decomposition, *viz*. fission of the nitro group (pathway I), breaking a N–N bond of the heterocycle (pathway II), and breaking of the exocyclic C–N bond (pathway III). It was shown previously in [18] that breaking a C–N bond of the ring in nitro-1,2,4-triazoles consumes 23.7-34.3 kcal/mol more than breaking the ring N–N bond (pathway II), consequently we have not considered the generation of pathways for thermal decomposition with breaking an intracyclic C–N bond (pathway IV).The thermochemically unprofitable nitro–nitrite rearrangement for nitro derivatives [1] has also not received attention.

When determining the preference of thermal decomposition of tautomers **1A-C** for one or other route of thermolysis, the energy af activation (E_{act}) of reactions taking place in the first step of decomposition were considered. As is evident from Table 2, the radical fission of the nitro group (pathway 1) is the most profitable,

TABLE 2. Activation Energies (E_{act}) of Reactions Occurring in the First Step of the Decomposition of Tautomers **1A-I**

Tautomer	E_{act}, kcal/mol			
	Pathway I	Pathway II	Pathway III	Pathway IV*
1A	27.9	68.1	87.1	
1B	30.1	69.8	84.1	
1C	26.6	69.8	87.2	
Z-**1D**	52.5	73.4	90.8	90.5
E-**1D**	53.1	73.1	91.3	91.1
Z-**1E**	46.8	62.6	69.9	89.4
E-**1E**	39.7	51.4	62.9	83.6
Z-**1F**	38.4	52.3	57.6	
E-**1F**	47.4	61.3	61.7	
E,Z,E-**1G**	50.9	70.7	82.3	
E,Z,Z-**1G**	42.3	68.9	73.7	
E,E,E-**1G**	47.5	69.7	74.9	
E,E,Z-**1G**	48.4	70.9	75.8	
Z,Z,Z-**1G**	44.5	70.7	73.8	
Z,E,E-**1G**	47.1	73.8	78.5	
Z,E,Z-**1G**	46.8	73.3	78,2	
E,Z,E-**1H**	46.5	72.5	78.4	
E,Z,Z-**1H**	40.1	71.7	72.0	
E,E,E-**1H**	47.6	72.7	74.5	
E,E,Z-**1H**	47.4	72.8	74.3	
Z,Z,E-**1H**	45.3	74.6	76.2	
Z,Z,Z-**1H**	40.9	71.1	71.8	
Z,E,Z-**1H**	48.3	71.6	74.7	
Z,Z,E-**1I**	51.9	73.7	83.5	
Z,Z,Z-**1I**	42.5	68.4	74.1	
Z,E,E-**1I**	47.3	67.7	74.8	
Z,E,Z-**1I**	48.5	71.7	76.0	
E,E,Z-**1I**	52.8	73.7	78.8	
E,E,E-**1I**	53.2	68.3	79.2	
E,Z,Z-**1I**	44.4	68.3	74.0	

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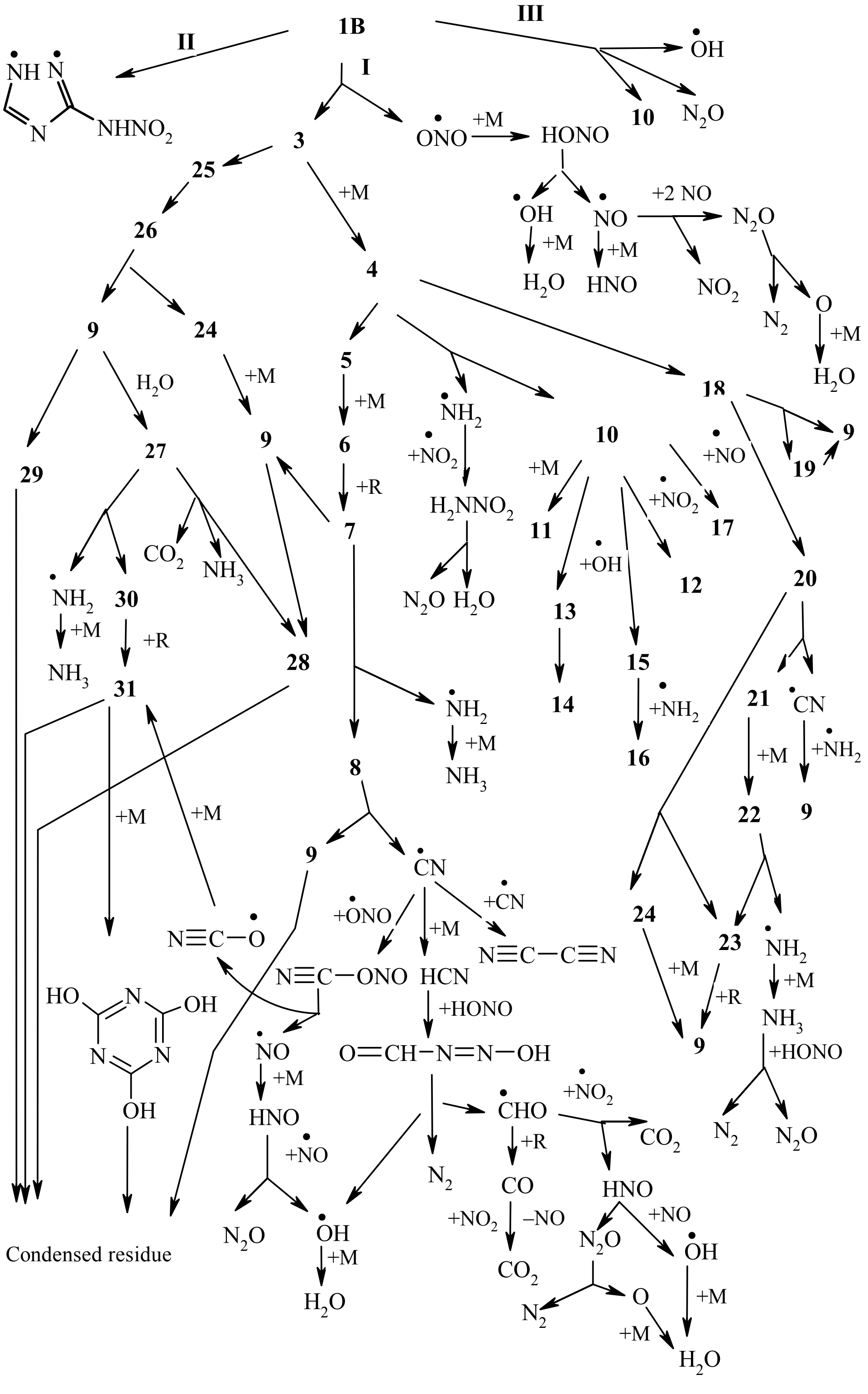
* Pathway IV was considered only for compounds **1D-E.**

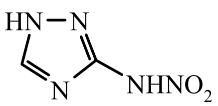
Scheme 1



Here and subsequently: M is molecule, R is radical. The enthalpies of reactions forming compounds not numbered in the scheme and obtained by the thermochemically preferred pathway for extensive destruction are given in [18].

for which the activation energy amounts to 26.6 to 30.1 kcal/mol. Processes going along pathways II and III require an energy consumption more than twice that of the process along pathway I.

With the aid of the generator of reactions the possibility emerged of predicting the complete (stepwise) spectrum of reactions occurring on thermal destruction of the compounds, and also the obtaining of the whole selection of final products of decomposition. We note that on rapid thermolysis of compound **1** [26] only NO, NO_2, HCN, CO, and N_2O were successfully confirmed experimentally. It is shown in Scheme 1 that on thermolysis the formation is possible of a whole series of other substances, not detectable experimentally due to the limitation of the method, including gaseous (H_2O, N_2, O_2, CO_2, HNCO, ammonia, cyanogen) and condensed substances [cyanamide, dicyandiamide, urea, cyanuric acid, melamine, 3(5)-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 1,2,4-triazole, 1,2,4-triazolone, 3(5)-nitro-1,2,4-triazole, 3(5)-nitroso-1,2,4-triazole). There are no experimental data on the composition of the condensed residue formed on thermolysis of nitramino-1,2,4-triazoles. It is known only [26, 57-59] that on thermal decomposition of various polynitrogen organic compounds condensed products of the triazine type are formed, which we have taken into consideration. The probability of forming analogous residues on thermolysis of nitramino-1,2,4-triazole is high.



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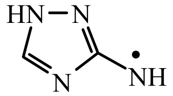

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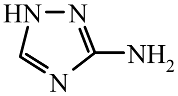

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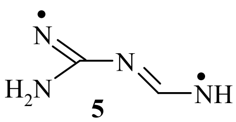

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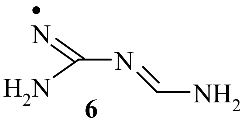

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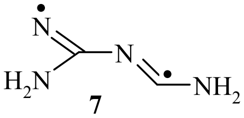

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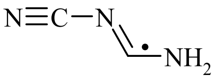

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$N{\equiv}C{-}NH_2$

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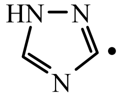

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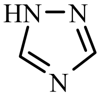

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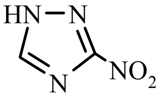

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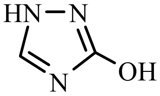

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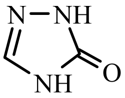

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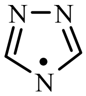

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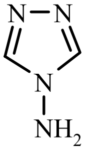

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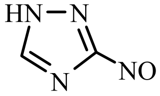

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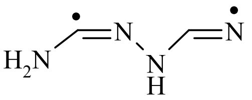

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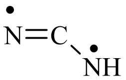

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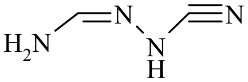

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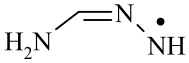

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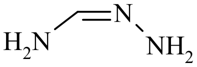

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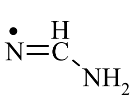

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$N{\equiv}C{-}\dot{N}H$

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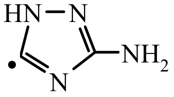

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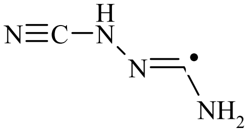

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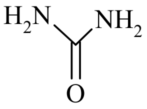

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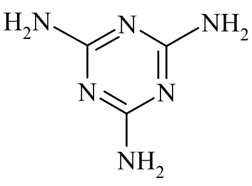

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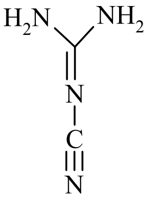

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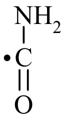


30

HN=C=O

31

To assess the thermochemical preference of these or any pathway for the thermolysis of compound **1B** (Table 3, [18]) we calculated the enthalpies of all the reactions obtained on generation.

According to Table 3 the thermochemically most advantageous variant of the stabilization of radical **3** is the formation of 3-amino-1,2,4-triazole **4**. Energy consumptions in this process vary from -18.1 to 20.1 kcal/mol (Nos. 1-3). Compound **4** is fairly stable, its subsequent destruction with fission of the exocylic C–N bond (to radical **10**) and endocyclic N–N and C–N bonds (to biradicals **5** and **18**) is accompanied by significant energy consumption (from 64.1 to 109.8 kcal/mol, Nos 4, 9, 17). Of the considered variants of decomposition of triazole **4,** the thermochemically most preferred is homolytic fission of the endocyclic N–N bond with an energy

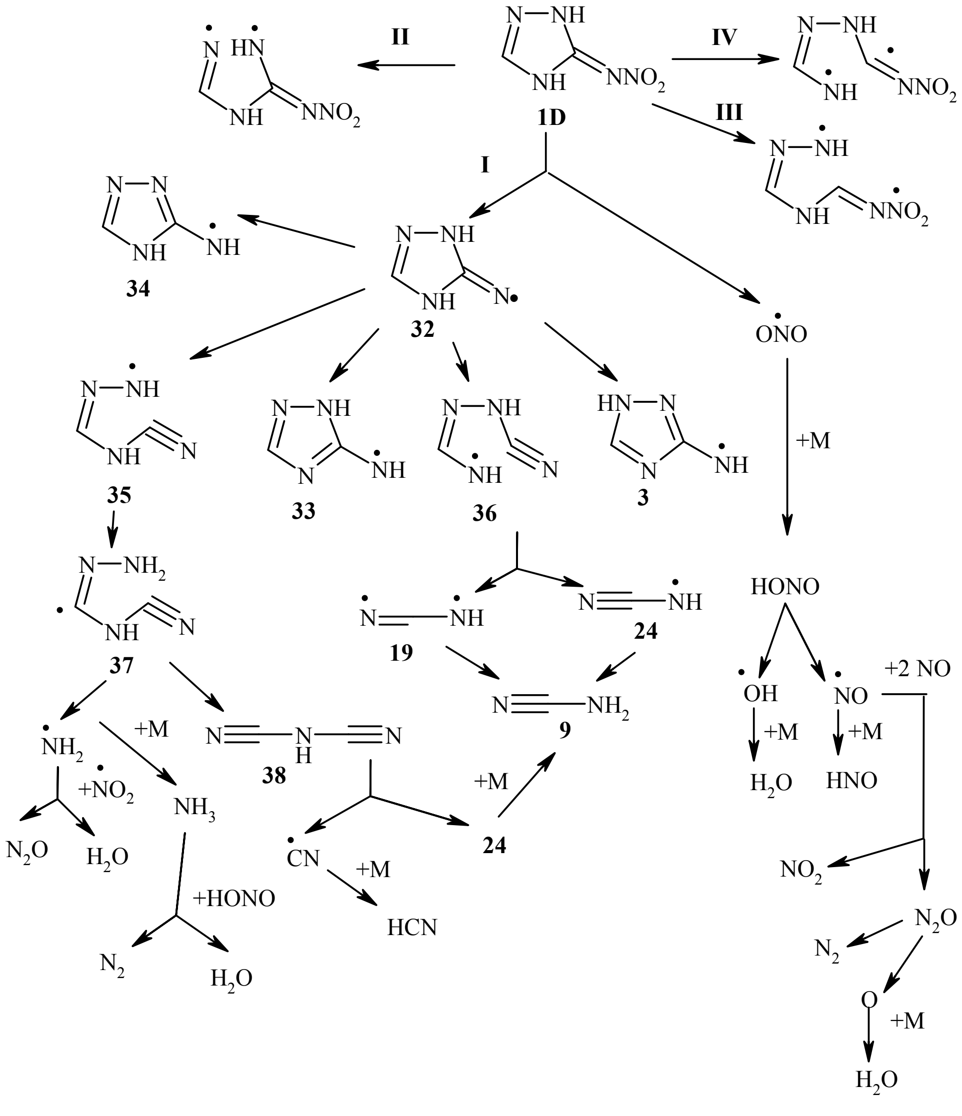
TABLE 3. Reactions Possible on Thermal Decomposition of Nitramino-1,2,4-triazoles **1** and **2** and Their Enthalpies

No.	Reaction	ΔH_f^0, kcal/mol	No.	Reaction	ΔH_f^0, kcal/mol
1	**3** + HNO_2 → **4** + ·ONO	-18.1	40	**32** → **35**	12.2
2	**3** + NH_3 → **4** + $\cdot NH_2$	12.4	41	**32** → **36**	12.7
3	**3** + H_2O → **4** + ·OH	20.1	42	**32** → **37**	27.5
4	**4** → **5**	64.1	43	**36** → **19** + **24**	50.5
5	**5** + HNO_2 → **6** + ·ONO	-16.4	44	**37** → **38** + $\cdot NH_2$	-9.5
6	**6** + ·ONO → **7** + HNO_2	24.7	45	**38** → **24** + ·CN	92.9
7	**7** → **8** + $\cdot NH_2$	22.8	46	**39** → **33**	-30.0
8	**8** → **9** + ·CN	49.5	47	**39** → **3**	-24.2
9	**4** → **10** + $\cdot NH_2$	109.8	48	**39** → **34**	-24.7
10	**10** + HNO_2 → **11** + ·ONO	-46.0	49	**40** → **10** + N_2O	31.9
11	**10** + $\cdot NO_2$ → **12**	-67.2	50	**41** + HNO_2 → **16** + ·ONO	-11.4
12	**10** + ·OH → **13**	-117.4	51	**41** + NH_3 → **16** + $\cdot NH_2$	19.1
13	**13** → **1b12**	-11.2	52	**41** + H_2O → **16** + ·OH	26.8
14	**10** → **15**	-11.9	53	**41** → **42**	61.8
15	**15** + $\cdot NH_2$ → **16**	-64.0	54	**16** → **15** + $\cdot NH_2$	64.0
16	**10** + ·NO → **17**	-54.7	55	**16** → **43**	64.2
17	**4** → **18**	101.5	56	**15** + HNO_2 → **44** + ·ONO	-27.7
18	**18** → **9** + **19**	-74.9	57	**44** → **11**	-6.8
19	**19** → **9**	-58.0	58	**43** → **45** + HCN	-9.2
20	**18** → **20**	-67.4	59	**45** → **46**	-33.8
21	**20** → **21** + ·CN	92.7	60	**46** + ·ONO → **47** + HNO_2	-1.1
22	**21** + HNO_2 → **22** + ·ONO	-6.2	61	**47** + ·ONO → **48** + HNO_2	-8.4
23	**22** → **23** + $\cdot NH_2$	61.4	62	**48** + ·ONO → **49** + HNO_2	-4.1
24	**23** + ·ONO → **9** + HNO_2	-37.4	63	**49** → N_2 + ·CN	2.4
25	**20** → **23** + **24**	46.7	64	**48** → **50** + ·CN	69.8
26	**3** → **25**	26.8	65	**50** + ·ONO → N_2 + HNO_2	-71.5
27	**25** → **26**	19.4	66	**46** → **24** + $\cdot NH_2$	51.0
28	**26** → **9** + **24**	-20.9	67	**46** → **51** + ·CN	95.0
29	**24** + HNO_2 → **9** + ·ONO	-16.8	68	**51** + HNO_2 → N_2H_4 + ·ONO	-3.3
30	**9** + H_2O → **27**	-40.2	69	$2N_2H_4$ + 2 ·ONO → → $3N_2$ + $4H_2O$	-232.4
31	**7** → **9**	-45.7	70	**42** → **54**	-46.9
32	6(**27**)→**28** + $6NH_3$+$3CO_2$	7.4	71	**54** → **55** + N_2	-9.3
33	**9** + **9** → **29**	-30.2	72	**55** → **56** + HCN	24.0
34	**27** → **30** + $\cdot NH_2$	91.0	73	**56** + ·ONO → HCN + HNO_2	-38.1
35	**30** + ·OH → **31** + H_2O	-81.4	74	N_2O_2 → N_2O + O	-8.8
36	**32** → **33**	-25.4	75	N_2O_2 → N_2 + O_2	-47.0
37	·CN + ·CN → $(CN)_2$	-142.4	76	N_2O_2 → ·ONO + $1/2N_2$	-79.3
38	**32** → **3**	-20.1	77	**48** → HCN + N_2	-56.9
39	**32** → **34**	-20.6			

of activation of 64.1 kcal/mol (No. 4) forming biradical **5**. In the subsequent decomposition of biradical **5** (along the chain **5** → **6** → **7** → **8** → **9**) the energy consumption in each step did not exceed 49.5 kcal/mol. Possible transformations of the radicals NH_2, CN, and cyanamide **9** formed in this way, and also the enthalpies of the reactions corresponding to them were considered in [18].

Another direction of conversion of radical **3** (rearrangement into radical **25**) is accompanied by an insignificant absorption of energy (26.8 kcal/mol, No. 26). The probability of this process occurring compared with the **3** → **4** transition is somewhat less. However low energy consumption in the formation of radical **26** from radical **25** (19.4 kcal/mol, No. 27), and also the exothermal nature of the subsequent reactions in the stepwise decomposition of **26** to **9**, enables this direction for the destruction of compound **1B** to be considered entirely probable. The presence may therefore be suggested of a set of competing processes in the multipathway decomposition of **1B**, occurring with various consumptions of energy. It is evident there is a preference for those pathways of compound destruction for which energy consumption is minimal.

Scheme 2



The thermal decomposition of tautomers **1D**,**E** may include homolytic removal of the nitro group (pathway 1), and fission of the endocyclic N–N (pathway II) and C–N (pathways III, IV) bonds. An example illustrating these processes is the decomposition of tautomer **1D** in Scheme 2. Tautomers **1D** and **1E** contain a dihydro-1,2,4-triazole ring. Analysis of the strength of C–N bonds in a similar series of structures has not been carried out previously. We therefore assessed the thermochemical preference for the thermal decomposition processes by pathways III and IV.

Calculation of the activation energies of the reactions occurring in the first stage of the decomposition of compound **1** (Table 2) indicates that, as in the case considered above, for tautomers **1D** and **1E** removal of the nitro group (pathway I) is the most advantageous. For the thermodynamically most stable tautomer *E*-**1D** the energy consumption is 53.1 kcal/mol, which is in good agreement with the experimental value for the activation energy for thermal decomposition of compound **1** in the solid phase (E_{act} = 53.0 kcal/mol) [28]. There is no proof in favor of a nitrimine structure for compound **1**, i.e. its existence in the form of tautomer **1D** in the crystalline state. However a nitrimine structure has been demonstrated by X-ray structural analysis for a series of its structural analogs [55].

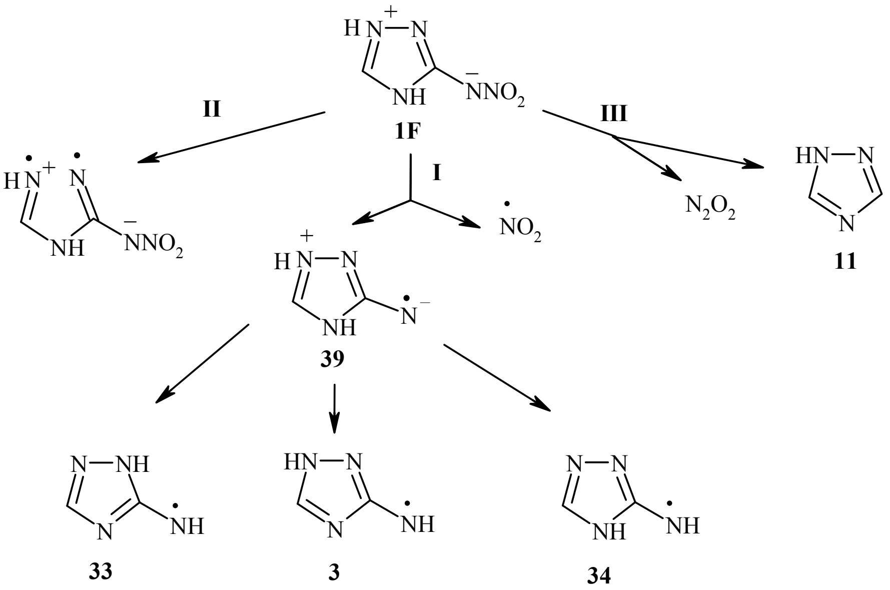
Further conversion of the primary intermediates obtained in the decomposition of nitrimine **1D** by pathway I has been studied in more detail. A fragment of the generated chains of intermediates and the possible sequences of their conversions is represented in Scheme 2. It should be mentioned that as a result of the generation of the whole spectrum of thermolysis reactions of isomer **1D**, the same set of final products was obtained as on decomposition of tautomer **1B** (the sole difference is the formation of dicyanamine **38**). However the sequence of reactions leading to the formation of final products was different. Probably the latter circumstance must be reflected in the quantitative ratio of thermolysis products.

To assess the thermochemical preference for the generated reactions on thermochemical decomposition of nitrimine **1D** we calculated their enthalpies (Table 3 [18]). As is seen from Scheme 2 radical **32** formed from compound **1D** may be rearranged into radicals **3**, **33**, **34**, **35**, and/or **36**. The data of Table 3 indicate that isomerization into radicals **3**, **33**, and **34** is thermochemically most advantageous, accompanied by the liberation of energy (see Nos. 36, 38, and 39 in Table 3). Subsequent decomposition of the intermediates formed is considered above in the example of radical **3**. In addition, fission of the endocyclic C–N bonds in radical **32** is accompanied by insignificant energy consumption (12.2, 12.7 kcal/mol, Nos. 40, 41 in Table 3), which under the thermolysis conditions permits the suggestion that the formation of radicals **35** and **36** is entirely probable. Conversion of radical **35** (Table 3) along the chain **35** → **37** (27.5 kcal/mol, No. 42) → **38** (-9.5 kcal/mol, No. 44) leads to dicyanamine **38**, the decomposition of which to radicals **24** and CN requires consumption of 92.9 kcal/mol (No. 45). Somewhat less advantageous in energy consumption (in comparison with the **35** → **37** transition) is the decomposition of radical **36** to radicals **19** and **24** (50.5 kcal/mol, Table 3, No. 43). Transformation of the latter radicals is considered above.

The thermochemical calculations carried out therefore confirm the correctness of considering additional (in comparison with nitramine **1B**) pathways for the destruction of nitrimine **1D** to the final decomposition products. In addition, it is necessary to mention that the energy consumption at the first stage of nitrimine **1D** decomposition is on average 24.6 kcal/mol greater (Table 2) than for nitramines **1A**-**C**. It therefore follows that thermolysis of compound **1** is thermochemically more preferred through the nitramine forms **1A**-**C** if carrying out the corresponding tautomeric transitions is possible.

The next tautomers of compound **1** considered by us were the zwitterions **1F**. On the basis of the arguments given above for nitramines **1A**-**C**, we restricted the analysis to three directions of thermolysis (Scheme 3): removal of the nitro group (pathway I), fission of the N–N bond in the hetero ring (pathway II), and fission of the exocyclic C–N bond (pathway III). Calculation of the activation energies (Table 2) of the reactions accompanying decomposition of the **1F** molecule indicates a preference for fission of the N–NO_2 bond (in accordance with pathway I) in comparison with other pathways of destruction. The values of E_{act} of the first stage of decomposition of zwitterions **1F** in this direction are found in the range 38.4 (for *Z*-**1F**) to 47.4 kcal/mol (for *E*-**1F**) (Table 2).

Scheme 3



A fragment of the generated mechanism of thermolysis of compound *Z*-**1F** along pathway I is shown in Scheme 3 as an example. It is seen that radical **39** formed from zwitterion *Z*-**1F** may then be rearranged into radicals **3**, **33**, and **34** according to three independent directions, and all three rearrangement processes are accompanied by the release of energy (Table 3) -24.2 (No. 47), -30.0 (No. 46), and -24.7 kcal/mol (No. 48) respectively. Since only these intermediates **3**, **33**, and **34** are formed by the thermochemically preferred direction of decomposition of nitroamines **1A**, **1B**, and **1C,** it is correct to draw the conclusion as to the identity of the qualitative composition of the products of their decomposition and the decomposition products of compound *Z*-**1F**.

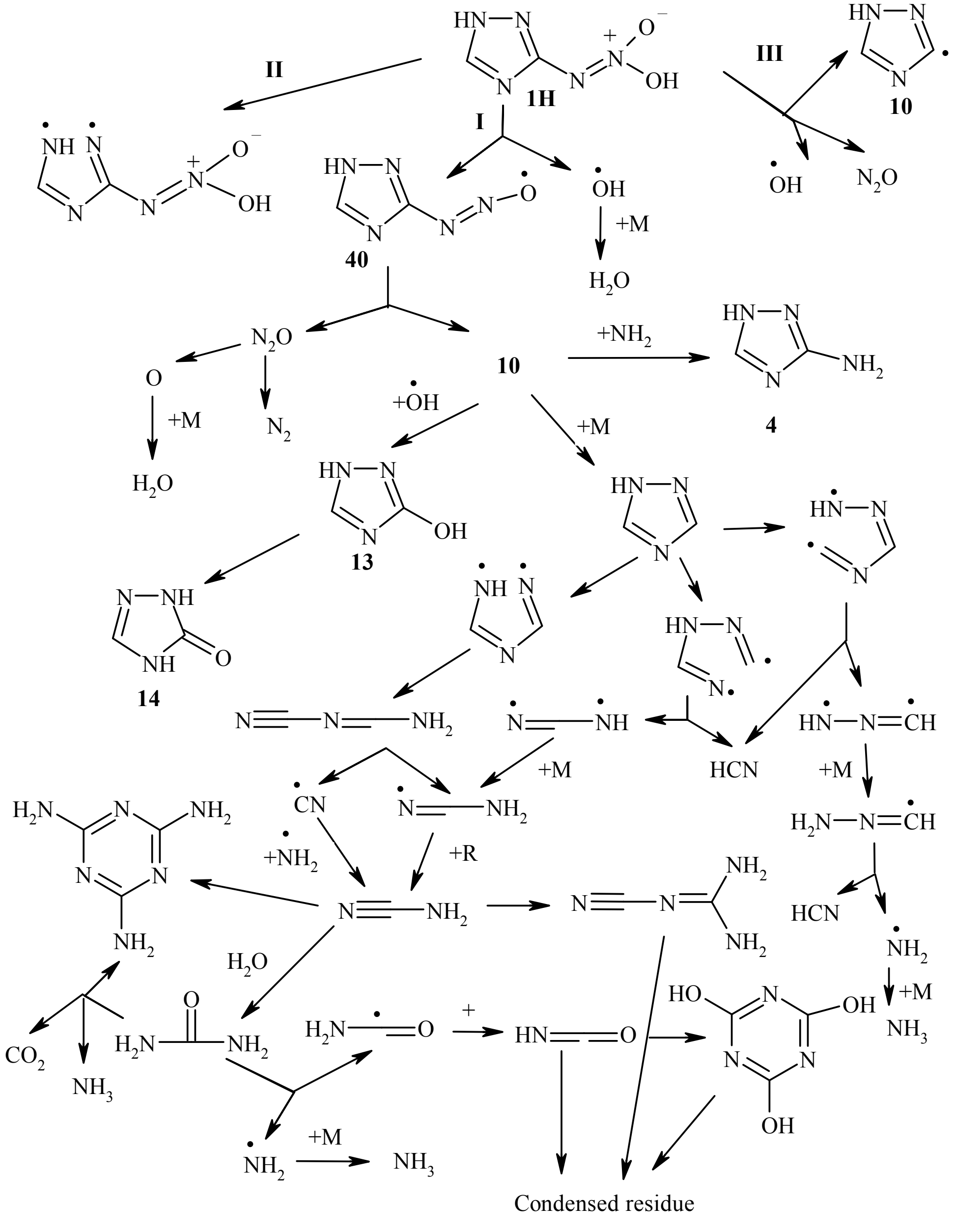
However the energy consumptions at the first stage of the decomposition of zwitterions **1F** are 14.7 kcal/mol greater (Table 2) than in the case of nitramines **1A-C**. It therefore follows that the destruction of compound **1** through the zwitterionic forms **1F** is thermochemically disadvantageous in comparison with decomposition through nitramine forms **1A-C**.

Next, the probable directions of decomposition of tautomers **1G-I** are removal of hydroxyl radical (pathway I), fission of the endocyclic N–N bond (pathway II), and fission of the exocyclic C–N bond with ejection of nitrous oxide (pathway III). The decomposition of form **1H** is given in Scheme 4 as an example of the decomposition of tautomers of group **1G-I**.

Thermochemically the most advantageous direction for the thermolysis of tautomers **1G-I** is the homolytic removal of hydroxyl (pathway I, Table 2). The activation energy for this process varies from 40.1 to 53.2 kcal/mol depending on the structure of the tautomer. Fission of the endocyclic N–N bond (pathway II) in tautomers **1G-I** consumes from 67.7 to 74.6 kcal/mol. Even higher energy consumption (71.8-83.5 kcal/mol) is necessary for fission of the exocyclic C–N bond (pathway III).

It should be mentioned that the activation barrier of the thermochemically most advantageous direction of decomposition of the tautomers of group **1G-I** (pathway I) with the minimal value of E_{act} = 40.1 kcal/mol for *E,Z,Z*-**1H** (Table 2) was significantly greater than in the case of breakdown of tautomers of group **1A-C** by pathway I (26.6-30.1 kcal/mol). Furthermore the absence from the decomposition products of such compounds as NO and NO$_2$, recorded experimentally in [26], is a characteristic feature of the mechanisms modeled as an example of the deeper destruction of tautomers **1H** (Scheme 4). The enthalpies of the elementary reactions

Scheme 4



accompanying the breakdown of **1H** are given in Table 3 and in [18]. On the basis of the given results it is correct to infer that the probability of homolytic decomposition of compound **1** through the *aci*-nitramine forms **1G-H** is small, since it consumes more energy in comparison with nitramine forms **1A-C**.

On the whole, analysis of the results of modeling the thermal destruction of the tautomers of C-nitramino-1,2,4-triazole **1,** and the quantum-chemical assessments of the energy consumption on carrying out the processes, indicate that in the presence of prototropic tautomerism thermal decomposition through the nitramine forms **1A-C** is the most probable.

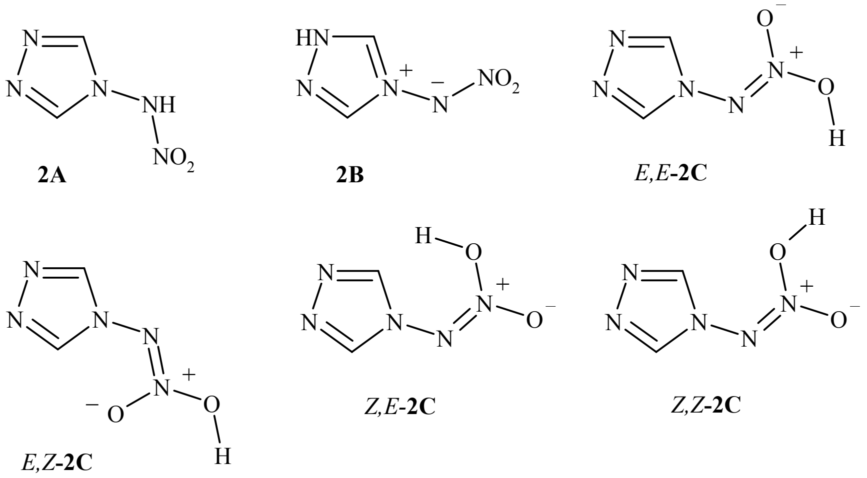


Fig. 3. Possible tautomers and rotational isomers of N-nitramino-1,2,4-triazole [description of the isomerism of the *aci*-nitro forms (**2C**) begins with the exocyclic N=N bond].

The existence of six tautomeric and rotational isomers is possible for N-nitramino-1,2,4-triazole **2** (Fig. 3).

Tautomer **2A** is the thermodynamically most stable isomer in the gas phase (Table 4). The total energy with correction for zero vibration energy ($E + ZPE$) of the less stable tautomer **2B** is greater than for nitramine **2A** (by 0.00599 a.u.). The tautomerization energy of nitramine **2A** into the onium nitrimide **2B** was 3.8 kcal/mol. We note however that the existence of N-nitramino-1,2,4-triazole as tautomer **2B** in solution is confirmed by ^{1}H NMR [46], and in the solid phase by X-ray structural analysis [60].

The *aci*-nitramino forms **2C** are thermodynamically even less stable than nitramine **2A**. The value of ($E + ZPE$) for them was greater by 0.00984 (*E,Z*-**2C**) to 0.02170 a.u. (*Z,E*-**2C**). The tautomerization energies for nitramine **2A** into *aci*-nitramines **2C** were in the range 6.2 (*E,Z*-**2C**) to 13.6 kcal/mol (*Z,E*-**2C**).

There are no data in the literature on the thermochemical stability of the tautomers of compound **2** under thermolysis conditions, consequently generation of the possible reactions of thermal decomposition was carried out for all the tautomers **2A-C**.

The modeling results showed that the thermal decomposition of nitramine **2A** is most probably in three directions: homolytic removal of the nitro group (pathway I). fission of the exocyclic N–N bond between the ring nitrogen atom and the nitramine fragment with ejection of nitrous oxide (pathway II), and fission of the

TABLE 4. Energy Characteristics of Tautomers and Rotational Isomers **2A-C** in the Gas Phase

Compound	($E + ZPE$), a.u.	E_{taut}*, kcal/mol
2A	-501.95040	0.0
2B	-501.94441	3.8
E,E-**2C**	-501.93869	7.4
E,Z-**2C**	-501.94056	6.2
Z,E-**2C**	-501.92870	13.6
Z,Z-**2C**	-501.93356	10.6

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* Tautomerization energy of nitramine **2A** into the corresponding tautomer was calculated in the same way as for the compounds given in Table 1.

TABLE 5. Activation Energies (E_{act}, kcal/mol) of Reactions Occurring at the First Stage of Decomposition of Tautomers **2A-C**

Tautomer	E_{act}		
	Pathway I	Pathway II	Pathway III
2A	25.8	40.7	65.3
2B	59.2	38.3	49.3
E,E-**2C**	48.2	33.3	68.4
E,Z-**2C**	49.4	34.4	68.8
Z,E-**2C**	39.0	27.0	65.0
Z,Z-**2C**	42.1	30.4	67.1

endocyclic N–N bond (pathway III). Calculations of the activation energy of the reactions at the first stage of the thermal destruction of compound **2A** (Table 5) indicate a significant thermochemical preference for the homolytic fission of the N–NO_2 bond (pathway I), E_{act} = 25.8 kcal/mol) compared with other decomposition pathways. A fragment of the generated mechanism of the stepwise destruction of compound **2A** along pathway I is given in Scheme 5. As in the case of the destruction of compound **1**, the decomposition products of nitramine **2A** include, apart from those recorded experimentally (N_2O, NO_2, CO_2, HCN [26]), a series of other substances (H_2O, N_2, O_2, CO, HNCO, ammonia, cyanamide, dicyandiamide, cyanogen, urea, cyanuric acid, melamine, 4-amino-1,2,4-triazole, 1,2,4-triazole, 3-amino-, 3-nitro-, 3-nitroso-1,2,4-triazoles, and 1,2,4-triazol-3-one).

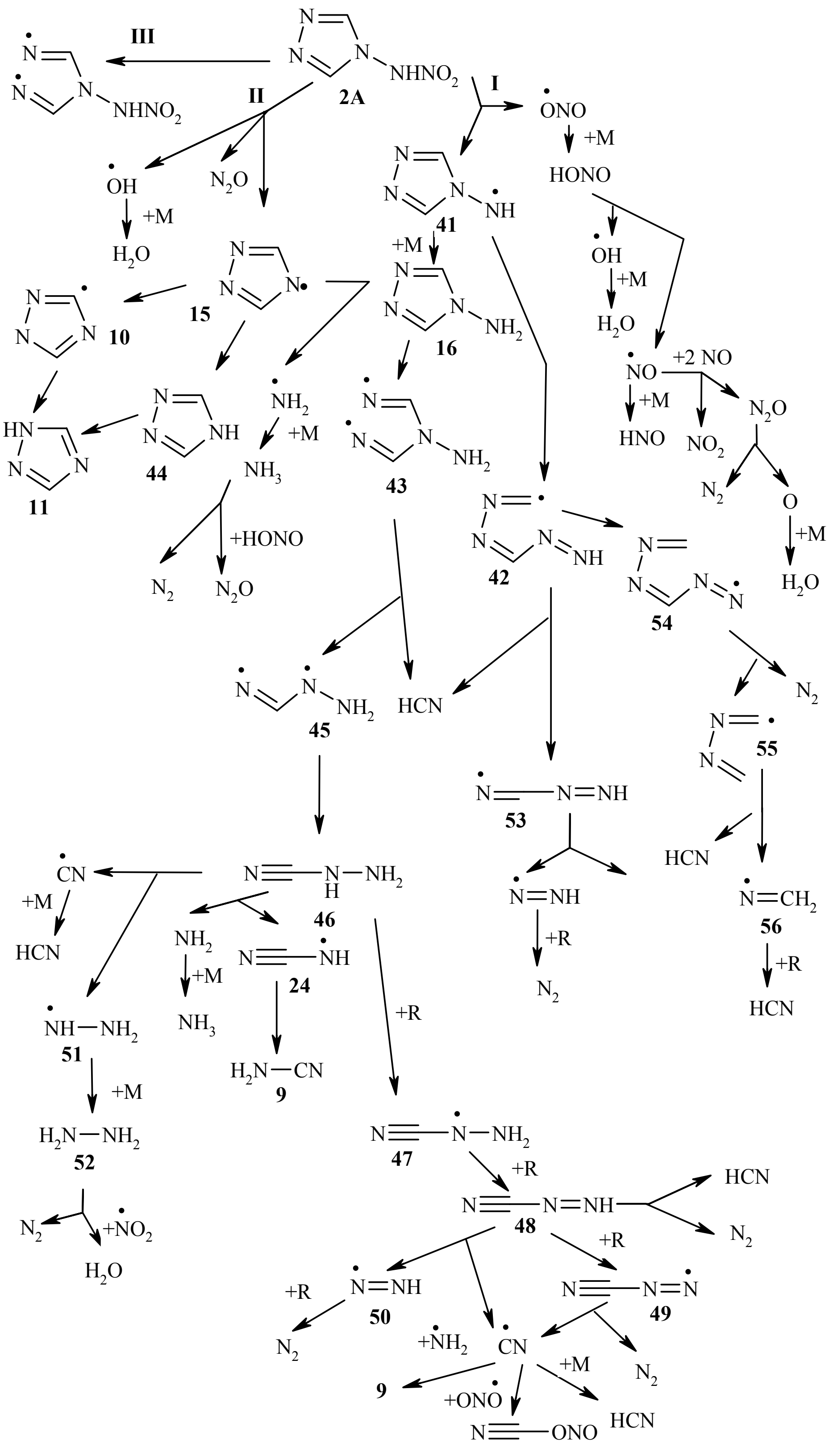
Calculations were carried out of the enthalpies of the individual reactions (Table 3) of the thermolysis process to assess the probable directions of the stepwise destruction of tautomer **2A** along pathway I. For intermediate **41**, obtained from compound **2A** in accordance with Scheme 5, two routes of conversion are possible: the formation of 4-amino-1,2,4-triazole **16** and rearrangement into radical **42** accompanied by fission of the endocyclic C–N bond.

It follows from Table 3 that the formation of triazole **16** (No. 50-52) is thermochemically more advantageous (by 46.4-73.2 kcal/mol) than radical **42** (No. 53). Subsequent destruction of compound **16** with fission of the endocyclic (64.2, No. 55) and exocyclic (64.0 kcal/mol, No. 54) N–N bonds, leading to the formation of radicals **15** and **43** respectively are equally probable according to energy consumption. Radical **15** emerging exothermally in this way (-27.7 kcal/mol, No. 56) may be transformed into 4H-1,2,4-triazole **44**, and subsequently, also with release of energy (-6.8 kcal/mol, No. 57) into 1H-1,2,4-triazole **11**. Rearrangement of radical **15** into radical **10** is accompanied by a somewhat larger energy consumption compared with the **15** → **44** → **11** conversion (11.9 kcal/mol, No. 14) and consequently is thermochemically less probable. The possible subsequent conversions of intermediate **10** and compound **11** are described above.

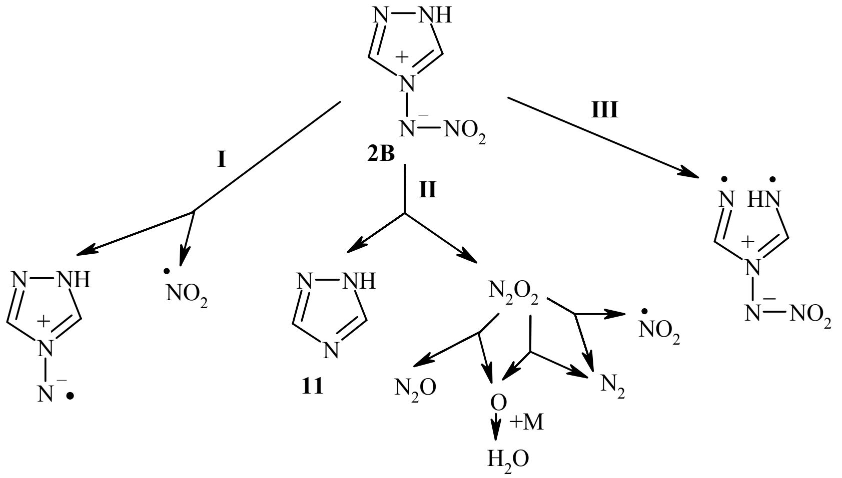
On decomposing 4-amino-1,2,4-triazole **16** to radical **43** futher conversions occur (Table 3) along the chain **43** → **45** (-9.2, No. 58) → **46** (-33.8, No. 59) → **47** (-1.1, No. 60) → **48** (-8.4, No. 61) → **49** (-4.1, No. 62) → N_2 + ·CN (2.4 kcal/mol, No. 63). The first five steps of this process are accompanied by marked liberation of energy and the last only by an insignificant energy consumption (2.4 kcal/mol). All the considered chain of conversions must be recognized as advantageous energetically, and consequently extremely probable thermochemically.

We now consider the possible mechanisms of thermal destruction of the other tautomer of compound **2**, the 4-nitrimide of 1,2,4-triazole **2B**. Probable directions of its decomposition are the following: homolytic removal of NO_2 (pathway I), fission of the semipolar N^+–N^- bond (pathway II), and splitting of the endocyclic N–N bond (pathway III) (Scheme 6). The distinctive feature of the destruction of this tautomer, in contrast to nitramine **2A**, is the thermochemical preference for fission of the N^+–N^- bond (pathway II). The activation energy for the process of splitting this semipolar bond is 38.3 kcal/mol (Table 5).

Scheme 5


2A
I
II
III
NHNO2
ONO
+M
HONO
OH
H2O
N2O
NO
+2 NO
HNO
NO2
N2
O
NH2
NH3
+HONO
41
16
15
10
11
44
43
42
54
55
56
45
HCN
53
+R
46
NH
24
9
H2N—CN
47
48
49
50
51
52
H2N—NH2
CN
+NH2
+ONO
N≡ONO
+NO2

Scheme 6



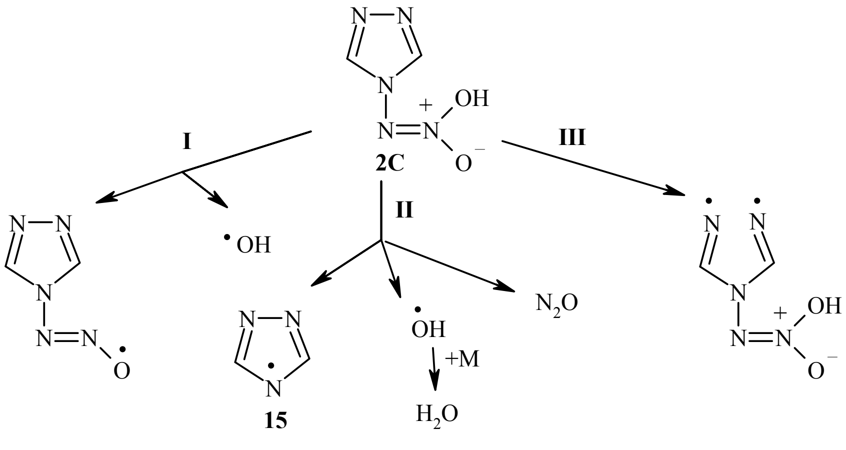
The product N_2O_2 formed in the first stage of destruction of compound **2B** (by pathway II) may be decomposed to O_2, N_2, N_2O, or NO_2 by three independent directions with the liberation of energy (Nos 74-76, Table 3). The second product of the first decomposition of nitrimide **2B** is 1,2,4-triazole **11**, probable pathways for the destruction of which have been discussed above.

Comparison of the decomposition products of tautomers **2B** and **2A** shows that their qualitative compositions are close, however the quantitative ratio of products may differ significantly. In addition since the routes for the formation of the final products are different, it is evident that the overall energy consumption (from all the chains of conversions) in these processes will also be different. A detailed assessment of them is the subject of our further investigations.

It is necessary to note that the energy consumption (Table 5) in the most preferred first stage of decomposition (pathway I, Scheme 5) of nitramine **2A** is 12.5 kcal/mol less than the energy consumption on decomposition by the most preferred direction for nitrimide **2B** (pathway II, Scheme 6). These data indicate a thermochemical preference for decomposition of compound **2** through the nitramine form **2A**.

Possible directions for the thermal decomposition of tautomer **2C** are removal of hydroxyl radical (pathway 1, Scheme 7), fission of the exocyclic N–N bond between the nitrogen atom of the heterocycle and the NNO_2 fragment with ejection of nitrous oxide (pathway II, Scheme 7), and fission of the endocyclic N–N bond

Scheme 7



(pathway III, Scheme 7). Calculations showed (Table 5) that thermochemically the most advantageous is the homolytic splitting of the exocyclic N–N bond (pathway II). Depending on the structure of tautomer **2C**, the energy consumption in its decomposition is from 27.0 to 34.4 kcal/mol.

Further destruction of the 1,2,4-triazole radical **15** formed from tautomer **2C** occurs according to reactions given above (see Schemes 1, 4, 5). Its recombination with NH_2 radical is shown in Scheme 1, leading to the formation of 4-amino-1,2,4-triazole **16**. Rearrangement of intermediate **15** into radical **10** and then into 1,2,4-triazole **11** is shown in Scheme 5. The stepwise destruction of compound **11** to the simplest final decomposition products is shown in Scheme 4.

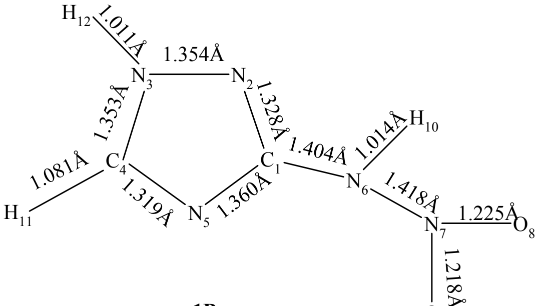
The difference of the modeled mechanisms of thermolysis of tautomer **2C** from the decomposition mechanisms of tautomers **2A** and **2B** is the absence from the decomposition products of the first tautomer of nitrogen dioxide, recorded experimentally in [26]. This circumstance indicates the low probability of destruction (under the experimental conditions of [26]) of compound **2** as tautomer **2C**. The first stage of the destruction of *aci*-nitramino form **2C** in the preferred direction (pathway II, Scheme 7) is at an energy consumption (Table 5) comparable with the decomposition of the nitramine form **2A** by the most advantageous pathway (pathway 1, Scheme 5): the difference is from 1.2 (for *Z,E*-**2C**) to 8.6 kcal/mol (for *E,Z*-**2C**). Together these data indicate a low probability for the presence of tautomer **2C** on thermolysis of compound **2**.

There are no experimental data on the activation energy of the thermal decomposition reaction of compound **2** in the gas and solid phases. In the liquid phase for nitramine **2** E_{act} is 40.05 (in water), 29.22 (in phenyl benzoate), and 19.63 kcal/mol (in isopropyl alcohol) [26]. Such significant differences of E_{act} may probably be explained by differences in the decomposition mechanisms of compound **2** in the different solvents. We note however, that the experimental values of E_{act} are close to the E_{act} calculated by us for reactions proceeding along the preferred pathway of decomposition of tautomers **2A-C** (Table 5), viz. 38.3 for **2B** (pathway II), 27.0-34.4 for **2C** (pathway II), and 25.8 kcal/mol for **2A** (pathway I).

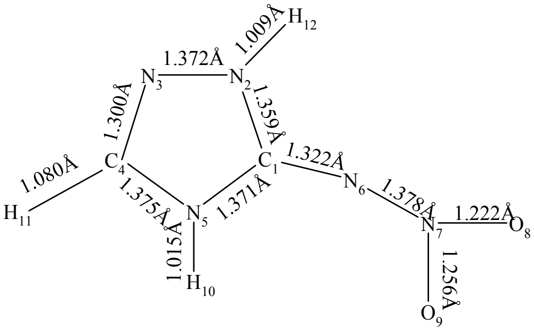
Analysis of the mechanisms of thermolysis of compounds **1** and **2** provides a basis for supposing that, independent of the tautomerism, the primary stage of the thermal decomposition does not affect the 1,2,4-triazole ring but is initiated by destruction of the NNO_2 fragment. However the energy consumption on decomposition of tautomers **1A-I** and **2A-C** varies over a wide range (from 25.8 to 53.2 kcal/mol; Tables 2, 5). The differences in thermochemical stability of compounds **1A-I** and **2A-C** is caused both by the position of the NNO_2 fragment on the heterocycle (on the carbon atom or the nitrogen atom) and by the differences in structure.

Calculations of geometric parameters have been carried out and chemical bond orders have been estimated [35] (Fig. 4*a,b*, 5*a,b*) with the aim of clarifying the connection between the activation barriers of the decomposition reactions of the various forms of the tautomers of compounds **1** and **2** and their structure.

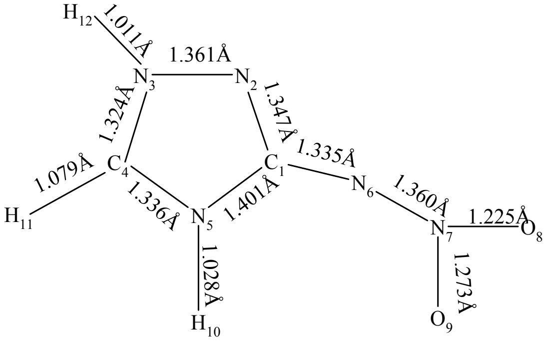
As follows from the calculation results, the transition from 3-nitramino-1,2,4-triazole **1B** to nitrimine *E*-**1D**, zwitterions *E*-**1F**, and *aci*-nitramine *E,Z,Z*-**1H** is accompanied by a reduction in the $N_{(6)}$–$N_{(7)}$ bond length of 0.040, 0.058, and 0.159 Å respectively. An increase was thereby observed in the order of this bond of 0.120, 0.183, and 0.555. For tautomers *E*-**1D** and *E*-**1F** the data obtained correlate with the increase in energy consumption (of 23.0 and 17 kcal/mol, Table 2), occurring on homolytic fission of this bond (in comparison with compound **1B**). Destruction of tautomers **1B**, *E*-**1D**, and *E*-**1F** begins with fission of the N-NO_2 bond (Table 2). *aci*-Nitramine *E,Z,Z*-**1H**, in difference to compounds **1B**, *E*-**1D**, and *E*-**1F**, was characterized by the significant nonequivalence of the NO bonds. The $N_{(7)}$–$O_{(9)}$(H) bond was lengthened compared with the $N_{(7)}$–$O_{(8)}$ bond by 0.193 Å (Fig. 4) and as a consequence its order was significantly reduced (by 0.565). As a result, just the $N_{(7)}$–$O_{(9)}$ fragment of the *E,Z,Z*-**1H** molecule (and not the $N_{(6)}$–$N_{(7)}$ bond as in tautomers **1B**, *E*-**1D**, and *E*-**1F**) proved to be a weak link under the conditions of thermal decomposition (Table 2). However for that compound, the thermochemically most unstable of the *aci*-nitramines, the energy consumption on homolytic fission of the $N_{(7)}$–$O_{(9)}$ bond proved to be 10.0 kcal/mol greater than in the case of nitramine **1B** (Table 2). The tautomer, obtained by combination of the 1,2,4-triazole ring with a C-nitramine substituent, is thermochemically the least advantageous. Molecular systems, in which the C-nitramine group is transformed into nitrimine, zwitterionic nitramine, and hydroxydiazenoxide groupings are more stable.



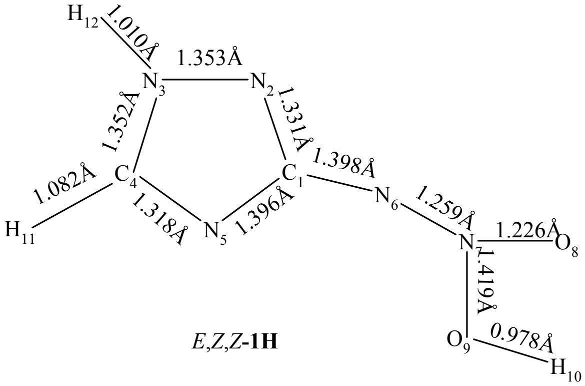
1B



E-**1D**

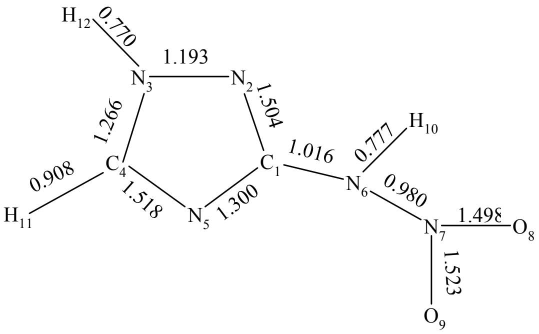


E-**1F**

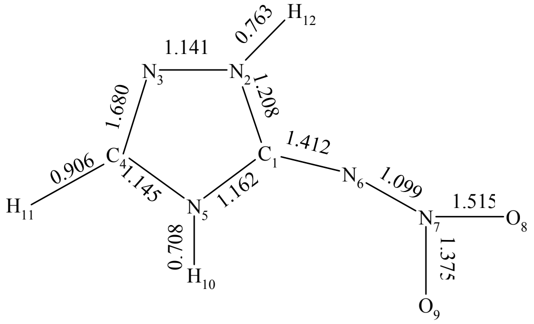


E,*Z*,*Z*-**1H**

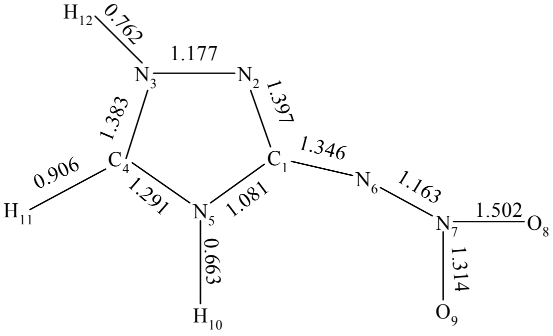
Fig. 4*a*. Calculated chemical bond lengths for the tautomers of compound **1**.



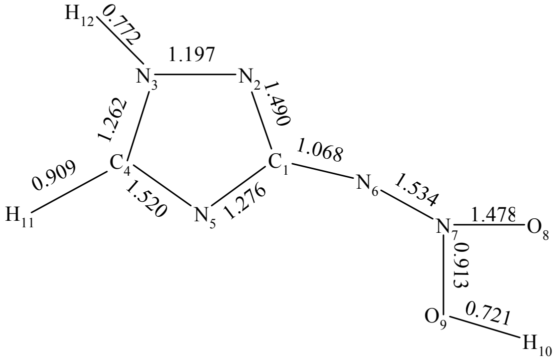
1B



E-**1D**



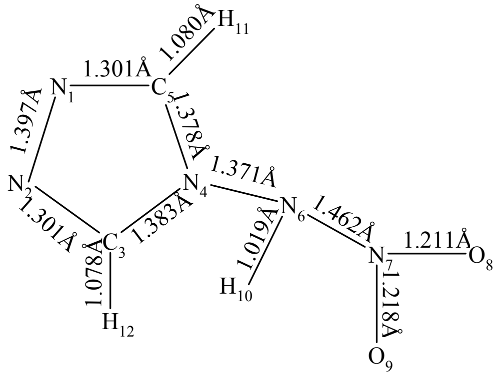
E-**1F**



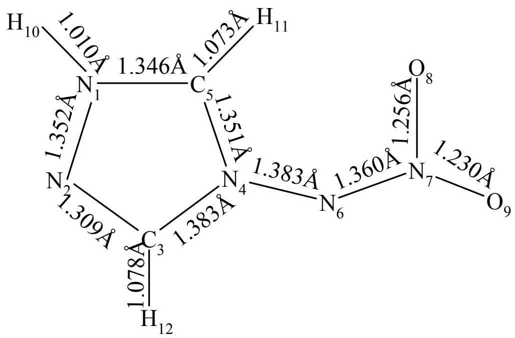
E,*Z*,*Z*-**1H**

Fig. 4*b*. Calculated chemical bond orders for the tautomers of compound **1**.

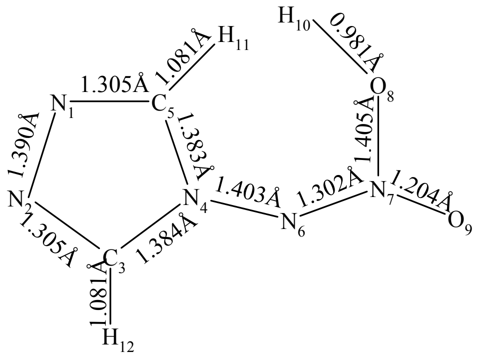
Concerning N-nitraminotriazole **2**, according to the result of the calculations given in Fig. 5, on going from 4-nitramino-1,2,4-triazole **2A** to the onium nitrimide **2B** and then to the *aci*-nitramine *Z,E*-**2C,** the length of the $N_{(6)}$–$N_{(7)}$ bond is reduced by 0.102 and 0.364 Å, and its order increased by 0.274 and 0.525 respectively. As a consequence, the energy consumption for tautomer **2B** occurring on homolytic fission of this bond grows by 33.4 kcal/mol (in comparison with nitramine **2A**, Table 3). Destruction of the *aci*-nitramine *Z,E*-**2C** with fission of the formal $N_{(6)}$–$N_{(7)}$ double bond is not very likely. Of the compounds of this series only for nitramine **2A** is the process of decomposition possible beginning with the homolytic fission of the $N_{(6)}$–$N_{(7)}$ bond (removal of the nitro group).



2A

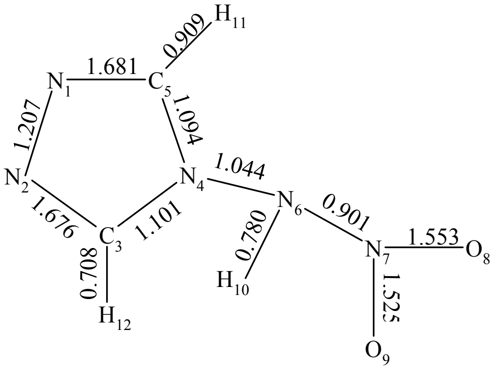


2B

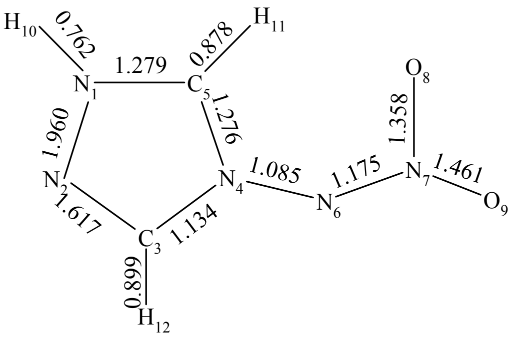


Z,E-**2C**

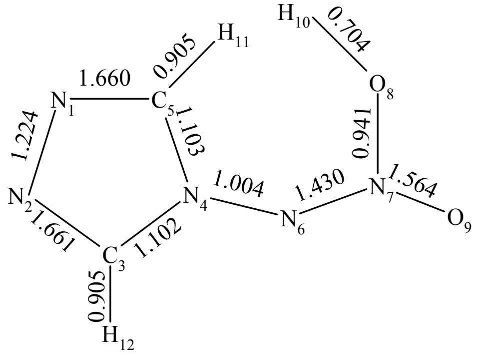
Fig. 5*a*. Calculated chemical bond lengths for the tautomers of compound **2**.



2A



2B



Z,E-**2C**

Fig. 5*b*. Calculated chemical bond orders for the tautomers of compound **2**.

The $N_{(4)}$–$N_{(6)}$ bond length on going from tautomer **2A** to **2B** and *Z,E*-**2C** is increased by 0.012 and 0.032 Å respectively. In spite of the lengthening, the order of this bond in the onium nitrimide **2B** remains greater only by 0.041 (in comparison with nitramine **2A**). The latter circumstance in all probability is caused by the semipolar character of the $N_{(4)}$–$N_{(6)}$ bond in tautomer **2B**. The order of this same bond in *aci*-nitramine *Z,E*-**2C** is reduced by 0.040 (in comparison with nitramine **2A**). The increase in length of the $N_{(4)}$–$N_{(6)}$ bond on going from nitramine **2A** to tautomer **2B** and *Z,E*-**2C** leads to a reduction in energy consumption occurring on homolytic fission (by 2.4 and 13.7 kcal/mol, respectively, Table 3).

The thermal destruction of the onium nitrimide **2B** and *aci*-nitramine *Z,E*-**2C** therefore begins with removal of the NNO_2 fragment from the heterocycle. The activation barrier of the decomposition reaction of tautomer **2B** proved to be 12.5 kcal/mol greater than the barrier for removal of the nitro group from nitramine **2A**. This difference is insignificant for *aci*-nitramine *Z,E*-**2C**, being 1,2 kcal/mol.

The N–O bonds in *aci*-nitramine *Z,E*-**2C**, in difference to nitramine **2A** and onium nitrimide **2B**, are significantly nonequivalent (Fig. 5). This is expressed by the fact that the $N_{(7)}$–$O_{(8)}$ bond is lengthened compared with the $N_{(7)}$–$O_{(9)}$ bond by 0.193 Å, and its order is reduced by 0.624. However homolytic fission of the $N_{(7)}$–$O_{(8)}$ bond has no advantage in energy consumption over destruction of the tautomer *Z,E*-**2C** with primary fission of the $N_{(4)}$–$N_{(6)}$ bond. The activation barrier in the latter case is less by 12.0 kcal/mol (Table 3).

Modeling the mechanisms of thermolysis of the tautomers of the C- and N-nitramino-1,2,4-triazoles has enabled a complete spectrum of the reactions occurring on decomposition of these compounds to final products to be obtained. Together with the experimentally recorded simplest products of destruction (N_2O, NO, NO_2, CO, CO_2, HCN) on thermolysis of nitraminotriazoles, the formation is possible of a whole series of other gaseous and condensed products including H_2O, N_2, O_2, CO_2, HNCO, ammonia, cyanamide, dicyandiamide, cyanogen, dicyanamine, urea, cyanuric acid, melamine, 3(5)-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 1,2,4-triazole, 1,2,4-triazolone, 3(5)-nitro-1,2,4-triazole, and 3(5)-nitroso-1,2,4-triazole. Comparison of the composition of the decomposition products according to the group of tautomers (separately for C- and N-nitramino-1,2,4-triazoles) indicates that their qualitative composition is close, however, owing to the differences in the routes of formation of the final products, their quantitative ratios may differ significantly.

It has been established that the primary decomposition of the tautomers of C- and N-nitramino-1,2,4-triazoles is preferably at the NNO_2 fragment and not at the triazole ring.

The assessment of the thermochemical preference among the decomposition pathways of the compounds, which has been carried out, permits the conclusion that the thermal destruction of C- and N-nitramino-substituted polynitrogen heterocycles, capable of tautomeric rearrangement, is most probably through the thermochemically least stable nitramine forms. In the C–NNO_2-1,2,4-triazole series the tautomers most stable towards thermal destruction are those in which the nitramine fragment is in the form of a nitrimine, a zwitterionic nitramine, or a hydroxydiazenoxide group. For the N–NNO_2 substituted 1,2,4-triazoles structural stabilization of the molecular system is provided by the junction of the NNO_2 fragment with the heterocycle at the tertiary nitrogen atom in the onium N-nitrimide form.

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