Physical Chemistry

Theoretical analysis of competitive directions of electrocyclization of 3,4,6-triazaocta-1,3,5,7-tetraene. Investigation of the structure and electrocyclization of 1,2,4-triazahexa-1,3,5-triene

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Theoretical analysis of competing directions of electrocyclization of triazatetraene $H_2C=CH-N=N-CH=N-CH=CH_2$, triazatrienes $H_2C=CH-N=N-CH=NH$ and $HN=N-CH=N-CH=CH_2$, and 1,4-diphenyl-1,2,4-triazabuta-1,3-diene Ph—N=N—C(R)=N—Ph was carried out. Specific features of cyclization of these compounds were explained by differences in the energies of π-orbitals of C=C, C=N, and N=N bonds and in bond orders of atoms forming a new bond in the reaction. The activation barrier and the structure of the transition state of the electrocyclization of 1,2,4-triazahexa-1,3,5-triene were studied by AM1, MNDO, and MINDO/3 methods. The electrocyclization of triazatriene is an asymmetric disrotatory process. The rotation angle of the terminal CH_2 group around the C=C bonds is twice as large as that of the NH group around the N=N bond. The 1,3-prototropic shift in dihydro-1,2,4-triazines is discussed.

Key words: 3,4,6-triazaocta-1,3,5,7-tetraene, 1,2,4- and 1,3,4-triazahexa-1,3,5-trienes, 1,4-diphenyl-1,2,4-triazabuta-1,3-diene, electrocyclization; 1,4- and 1,6-dihydro-1,2,4-triazines; quantum chemical calculation, semiempirical NDO methods.

Electrocyclization reactions were studied by many researchers both by semiempirical and nonempirical quantum chemical methods. Factors affected the relative stability of reagents and transition states were discussed, and the energies of disrotatory and conrotatory reaction routes were compared.[1—9] The aim of this work is the theoretical analysis of competing directions of the cyclization of 1,4-diphenyl-1,2,4-triazabuta-1,3-diene (**1**) and more detailed study of the main route of its cyclization by semiempirical AM1, MNDO, and MINDO/3 quantum chemical methods.

It is known that compound **1** (see Refs. 10—13), similarly to 1-phenyl- and 1-(2-pyridyl)buta-1,3-diene[1,2] as well as 4-phenyl-1-aza- or 1-phenyl-2-aza-[3,4] and 1-phenyl-1,3-diazabuta-1,3-dienes,[14,15] is able to undergo the 1,6-electrocyclization, in which the phenyl ring participates as the π-fragment of the hexa-1,3,5-triene system. Like in the acid-catalyzed[10,11] and thermal[11—13] processes, the 1,6-cyclization involving the N(1) atom of the azo group and the phenyl ring at the imine group (Scheme 1, direction *a*), which occurs *via* 1,8a-dihydrobenzo-1,2,4-triazine **2a** to form 1-phenyl-

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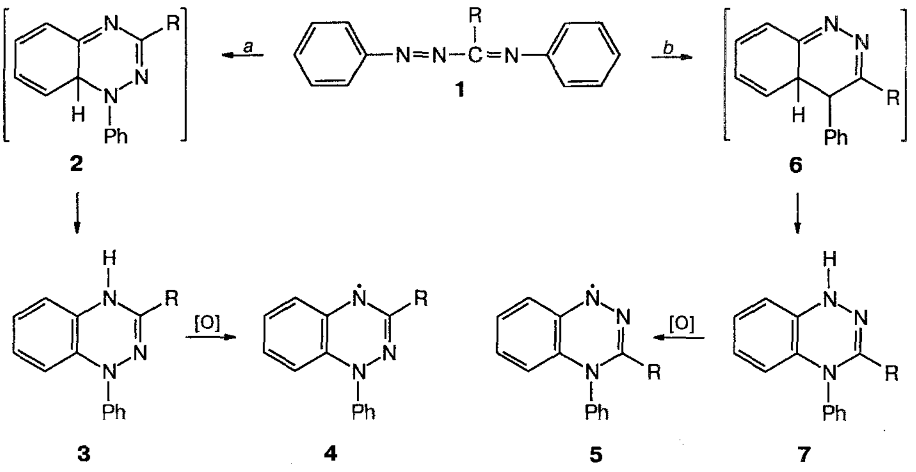
Scheme 1

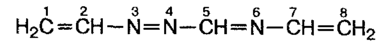


3-R-1,4-dihydrobenzo-1,2,4-triazines (**3**) easily oxidized to stable radicals (**4**), is the only[10,11,13] or predominant[12] direction of the reaction.

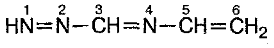
Thermolysis of triazadiene **1** in boiling anisole results in the formation (in addition to radical **4** in a yield of 70 %) of the radical product.[12] The parameters of the ESR spectrum of this product are very similar to those of radical **4**. These were the only grounds for assuming[12] that this product had the structure of isomeric 3-R-4-phenyl-1,4-dihydrobenzo-1,2,4-triazin-1-yl (**5**). Thus, the possibility of cyclization of triazadiene **1** was also assumed to occur *via* direction *b* through intermediate **6** to form dihydrobenzotriazine **7** (see Scheme 1), *i.e.*, with involvement of the imine N atom and the phenyl ring at the azo group, which was not observed for other related systems.[7—10] For example, 1-phenyl-1,2-diazabuta-1,3-dienes (phenylazoethylenes) containing phenyl substituents at azo groups exhibit no tendency for 1,6-electrocyclization. The so-called "dimerization" according to the Diels—Alder scheme (one molecule acts as a C=C-dienophile and another molecule acts as a heterodiene) is typical of them.[16,17]

Triazadiene **1** contains two phenyl rings, which can submit their π-electronic systems for electrocyclization reactions. In essence, it is the 3,4,6-triazaocta-1,3,5,7-tetraene system, for which the possibility of several competing directions of the reaction should be considered: the 1,8-electrocyclization similar to the cyclization of octa-1,3,5,7-tetraene,[11] two 1,6- (see above), and several 1,5- and 1,4-cyclizations.

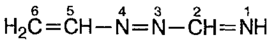
To simplify the analysis of the reactivity of the triazaoctatetraene system of compound **1**, the results of the calculation of electronic structures of 3,4,6-triazaocta-1,3,5,7-tetraene (**8**), 1,2,4-triaza-, and 1,3,4-triazahexa-1,3,5-trienes (**9** and **10**, respectively) are discussed in this work. Triazatrienes **9** and **10** are used for considering possible competing directions of the electrocyclization of triazaoctatetraene **8** to form heterocycles **11** and **12**. Various isomers of triazatriene **9** and the route of its 1,6-electrocyclization are considered in more detail.


$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{N}=\overset{4}{N}-\overset{5}{CH}=\overset{6}{N}-\overset{7}{CH}=\overset{8}{CH_2}$

8


$\overset{1}{HN}=\overset{2}{N}-\overset{3}{CH}=\overset{4}{N}-\overset{5}{CH}=\overset{6}{CH_2}$

9


$\overset{6}{H_2C}=\overset{5}{CH}-\overset{4}{N}=\overset{3}{N}-\overset{2}{CH}=\overset{1}{NH}$

10

Methods of calculation

Quantum chemical calculations of electronic and spatial structures of polyenes **8**—**10** and cyclization products **13**—**17** were performed by the MINDO/3,[18] MNDO,[19] and AM1[20] methods using the AMPAC program with complete optimization of geometric parameters. The "reaction coordinate" method[21] was used for calculating the cyclization of triazatriene **9**. The distance between the N(1) and C(6) atoms of the forming (breaking) N(1)—C(6) bond was chosen as the reaction coordinate. The transition state T (the saddle point) was found in the SADLE regime and was confirmed by the analysis of first and second derivatives at the saddle point.[21] Parameters of intermediate forms I^1 and I^2 were obtained by the "reaction coordinate" method at fixed distances $d_{1,6}$ equal to 2.40 and 2.00 Å, respectively.

The relative heats of formation and the geometric parameters of compounds studied calculated by the MINDO/3, MNDO, and AM1 methods turned out to be similar. In this connection, in discussion of results we will predominantly consider data of the AM1 method and compare values obtained by different methods only if necessary (Tables 1—5).

Results and Discussion

3,4,6-Triazaocta-1,3,5,7-tetraene (8). It is common practice to consider electrocyclization reactions (including 1,8-electrocyclization) as processes allowed or forbidden by symmetry.[5—9] For example, the transformation of *Z,Z*-octa-1,3,5,7-tetraene (which is the isoelectronic analog of tetraene **8**) to cycloocta-1,3,5-triene is a conrotatory process.[8] However, as in other heteropolyenes,[3,4,6,9] the MO (Fig. 1) and transition states (see below) of triazapolyenes **8**—**10** are asymmetric.

Table 1. Vertical ionization potentials (*IP*/eV)[25] and calculated energies of the π-MO (ε/eV) for ethylene, methylenimine, and diazene

Compound	IP_π	AM1		MNDO		MINDO/3	
		ε_π	ε_{π^*}	ε_π	ε_{π^*}	ε_π	ε_{π^*}
$H_2C{=}CH_2$	10.51	−10.55	1.43	−10.17	1.32	−10.34	2.19
$H_2C{=}NH$	12.43	−12.34	1.32	−12.13	1.17	−11.49	2.18
$HN{=}NH$	14.34	−14.10	0.85	−14.09	0.00	−12.20	1.96

Table 2. Relative total energies (*E*) for compounds **9a,f**, **10**, and **13—15**

Compound	*E*/kcal mol^{-1}		
	MNDO	MINDO/3	AM1
9a	24.7	23.0	22.9
9f	23.5	18.0	13.8
10	23.5	17.9	27.9
13	0.0	0.0	0.0
14	−5.4	−15.6	−4.8
15	3.3	−2.9	1.0

Let us consider the question of the preferableness of one or another direction of the cyclization of tetraene **8**, analyzing the energy of the initial stage of the process. Let $\Delta\beta_{ab}$ be the perturbation (the integral of the interaction between 2pπ-AO of atoms a and b, which form a new a—b bond at the beginning of an approach). The change in the energy caused by the $\Delta\beta_{ab}$ perturbation is estimated by the equation[22]

$$\Delta E_{ab} = 2\Delta\beta_{ab}p_{ab}, \qquad p_{ab} = 2\sum_j C_{aj}C_{jb},$$

where p_{ab} is the bonding order of the a and b atoms. The latter are attracted at $p_{ab} > 0$ and repulsed at $p_{ab} < 0$.

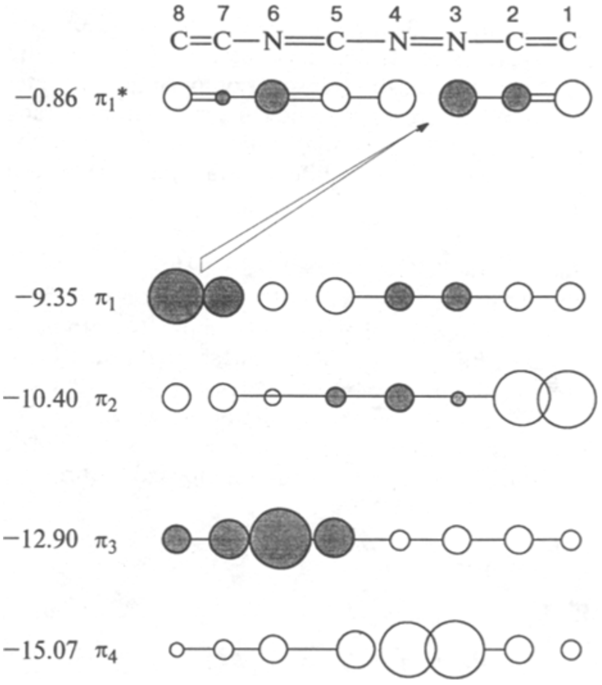


Fig. 1. Energy and composition of the π-MO of triazatetraene **8** (the MNDO method).

Table 3. Bond lengths (*d*) in the molecules of **9a,f**, **13**, and **15** and the transition states **T** and **I**^{2} optimized by the AM1 method

Compound	*d*/Å					
	N(1)—N(2)	C(2)—N(3)	N(3)—C(4)	C(4)—C(5)	C(5)—C(6)	N(1)—C(6)
9a	1.219	1.460	1.298	1.406	1.334	5.835
9f	1.217	1.454	1.283	1.396	1.341	3.163
T	1.254	1.386	1.346	1.349	1.406	2.017
I^2	1.292	1.359	1.394	1.303	1.459	2.000
13	1.338	1.319	1.426	1.296	1.518	1.475
15	1.358	1.313	1.430	1.422	1.359	1.436

Table 4. Changes in torsion angles (τ) in the electrocyclization of triazatriene **9** (the AM1 method)

Angle	τ/deg				
	9f	**I**^{1}	**T**	**I**^{2}	**13**
C(3)—N(2)—N(1)—H(7)	179	−176	−159	−137	−143
N(4)—C(5)—C(6)—H(10)	−173	173	159	132	127
N(4)—C(5)—C(6)—H(11)	5	−20	−52	−87	−116
H(8)—C(3)—N(2)—N(1)	−146	−153	−160	−166	−173
C(3)—N(2)—N(1)—C(6)	−21	−20	−18	−18	−10

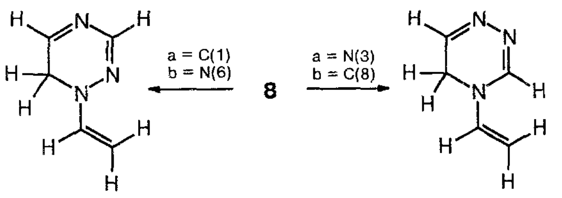
Table 5. Activation energy (E_a), torsion angles (τ), and distance ($d_{1,6}$) in the transition state **T** for the cyclization of triazatriene **9f**

Method	E_a /kcal mol^{-1}	$d_{1,6}$/Å	τ/deg	
			C(3)—N(2)—N(1)—H(7)	N(4)—C(5)—C(6)—H(11)
AM1	29	2.02	22	57
MNDO	25	2.03	17	52
MINDO/3	25	2.22	48	56

In the buta-1,3-diene molecule, the bond order of terminal atoms is smaller than zero, *i.e.*, they are repulsed, and, hence, the transoid conformation is preferable.[23] Bonding orders of some pairs of atoms of tetraene **8**, which reflect the potential ability to form eight-, six-, or five-membered cycles, differ substantially (the MNDO method):

a,b	1,8	1,6	3,7	3,8	4,8
p_{ab}	−0.024	0.060	0.020	0.093	−0.005

The bonding order of N(3) and C(8) atoms is the highest followed by that of C(1) and N(6) atoms. In both cases, the electrocyclization should result in the formation of six-membered cycles (**11** and **12**). It is likely that alternating the attraction between C(1) and N(6) atoms and the repulsion between C(1) and N(4) or C(8) atoms is a property of the topological nature.



11 **12**

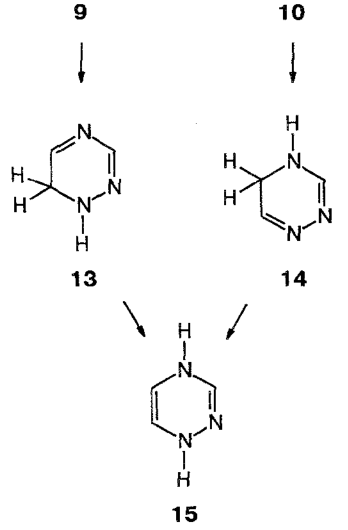
The formation of a five-membered cycle by binding N(4) and C(8) atoms and an eight-membered cycle due to binding terminal atoms in tetraene **8** is highly improbable. This conclusion is in accordance with the data of thermolysis of 1,4-diphenyltriazadiene **1** (the dibenzoannelated analog of triene **8**).[11–13] However, 1,6-electrocyclization to form a bond between the C(1) and N(6) atoms in both cases requires $E \rightarrow Z$-isomerization of the azo fragment, which usually does not occur for azobenzenes under conditions of thermal processes.[24]

One more argument can be advanced in favor of the predominant 1,6-cyclization of tetraene **8** at N(3) and C(8) atoms. Triazapolyenes **8**—**10** studied contain C=C, C=N, and N=N bonds. It is noteworthy that ionization potentials of π-MO of ethylene ($H_2C=CH_2$), methyleneimine ($H_2C=NH$), and diazene (HN=NH) differ considerably,[25] and the semiempirical calculations reproduce well these differences (see Table 1): the energies of π-MO calculated by the AM1 and MNDO methods are close to the experimental ionization potentials.

The same considerable differences in energies of the π-orbitals predominantly localized on C=C, C=N, and N=N bonds determine several properties and peculiarities of the cyclization of tetraene **8**. The higher occupied π_1-MO (see Fig. 1) is mainly localized at the C(7)=C(8) bond, the second MO (π_2) is localized at the C(1)=C(2) bond, and the third (π_3) and fourth (π_4) MO are localized at the imino and azo groups, respectively.

In the skewed $Z^{3,4}$,$Z^{5,6}$-conformation (**9f**), which is "prestarting" for the cyclization, the localization of the π-MO at all multiple bonds increases. Of possible π—π*-interactions, the interaction between the π-MO localized at the C(7)=C(8) bond and the π*-MO at the N(3)=N(4) bond with coordination of the C(8) and N(3) atoms is the most efficient (see Fig. 1, Table 1). The interaction between the n*(N) MO of the N=N bond and the unoccupied π*-MO localized at the C(7)=C(8) bond can make a certain contribution to the energy of electrocyclization.

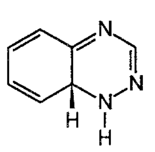
Triazahexa-1,3,5-trienes (9 and 10). Trienes **9** and **10** can be used as models for discussing two methods for cyclization of tetraene **8**, which results in the formation of vinyldihydrotriazines **11** and **12**. The interaction of terminal atoms of trienes **9** and **10** results in the formation of dihydrotriazines **13** and **14**, which do not contain vinyl groups. The 1,3-prototropic shift in dihydrotriazines **13** and **14** results in the formation of 1,4-dihydro-1,2,4-triazine (**15**).

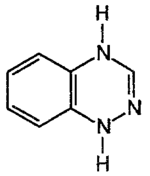


Relative total energies ΔE of compounds **9**, **10**, and **13**—**15** are compared in Table 2. Electronic and spatial parameters of acyclic (**9** and **10**) and cyclic (**13**—**15**) structures and the transition state for the **9** → **13** electrocyclization are presented in Tables 3 and 4. The energies of cyclic forms **13** and **14** are 24 to 30 kcal mol^{-1} lower than those of $E^{2,3}E^{3,4}E^{4,5}$-isomers (*tEt*-isomers)[+] of trienes **9** and **10**, *i.e.*, structures **13** and **14** are more stable.

According to the AM1 method, heterocycle **13** is more stable than the *tEt*-conformation of triene **9** (ΔE = 11.8 kcal mol^{-1}), which agrees well with the data on the cyclization of octa-1,3,5,7-tetraene **8**. For example, cycloocta-1,3,5-triene is more stable (by 20.7 kcal mol^{-1}) than the cisoid acyclic isomer according to the AM1 approximation, while in terms of the nonempirical MP/6-31G* + ZPE scheme this difference is 13.7 kcal mol^{-1} (see Ref. 8). Our calculations show that 1,4-dihydro-1,2,4-triazine **15** formed from isomers **13** and **14** by a 1,3-sigmatropic shift is less stable than these isomers (see Table 2).

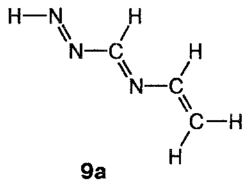
At first sight these results contradict the experimental data on the cyclization of 1,4-diphenyl-1,2,4-triazabuta-1,3-diene[10—13] and 1-phenyl-1,3-diazabuta-1,3-dienes,[14,15] for which structures of the **2** and **5** types and their analogs were not isolated and even were not observed due to the fast 1,3-sigmatropic shift. To eliminate this "contradiction", we calculated structures of heterocycles **16** and **17**, benzoannelated analogs of dihydrotriazines **13** and **15**.

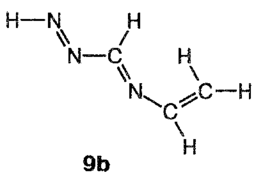

16

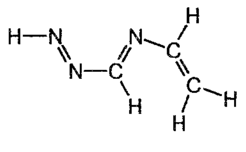

17

According to the AM1 method, the energy of the structure of **17** is 28.7 kcal mol^{-1} lower than that of **16**, *i.e.*, it is more stable than isomer **16**. Benzoannelation stabilizes the form with a shifted proton, which is observed in the cyclization of dienes of the **1** type.[10—13]

Geometry of 1,2,4-triazahexa-1,3,5-triene. The stability of various isomers is rarely discussed in theoretical works on electrocyclization of trienes and especially of their azo analogs (see, *e.g.*, Ref. 7). Only a starting structure with a cisoid conformation of the whole chain is usually considered.[1—4,8]


9a


9b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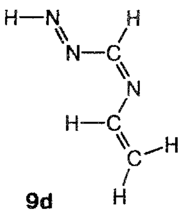
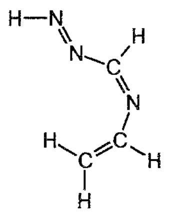
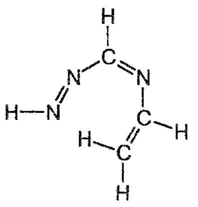
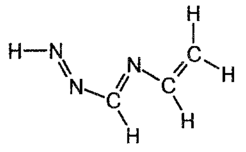
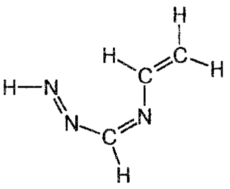

9d


9e


9f


9g


9h

We tried to study energies and structures of eight isomers of triene **9** (isomers **9a**—**9h**). Other eight isomers with the azo group in the *Z*-configuration ($Z^{1,2}$-isomers) were not considered, because the thermal $E \rightarrow Z$-isomerization is not typical of the azo group.[25] The series of the relative stability of isomers of triene **9** obtained by the AM1 and MNDO methods differ.

AM1 **f** > **h** > **e** > **d** > **c** > **g** > **b** > **a**
MNDO **d** > **g** > **f** > **h** > **a** > **c** > **e** > **b**

It is likely that data of semiempirical methods are not enough for solving the question concerning the relative stability of isomers of polyenes at a small difference in energies. The same situation relates to heterocycles **13** and **14** (see Table 2). However, geometric parameters of isomers (see Fig. 2) calculated by the AM1 and MNDO methods turned out to be close.

It should be mentioned that isomer **9f** is "pre-starting" for the **9** → **13** electrocyclization (Fig. 2). Three semiempirical methods show that the form of **9f** is the twice skewed *gZg*-configuration, which is more energetically favorable than the planar *cEc*-isomer. The fact that such a configuration is energetically favorable has already been mentioned for hexa-1,3,5-triene and the imine of cinnamic aldehyde (4-phenyl-1-azabuta-1,3-diene).[3,4] It can be assumed that one of the reasons for decreasing the total energy of the twisted isomer **9f** is

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[+] Here and hereinafter: *t*, *trans-*; *c*, *cis-*; and *g*, *gauche-* conformations.

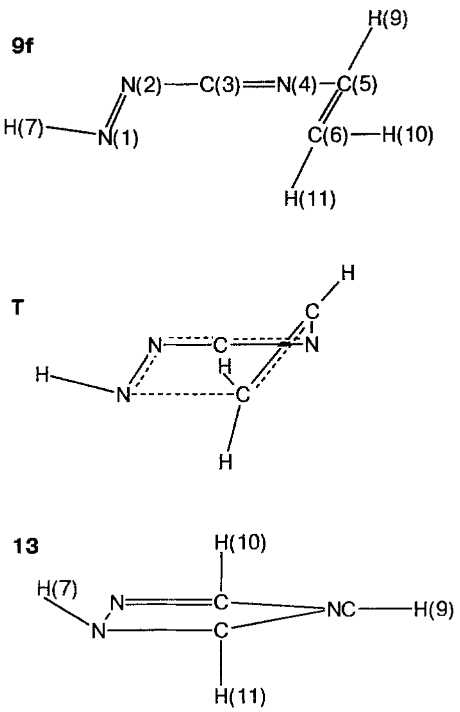

Fig. 2. Fragments of isomer **9f**, transition state **T**, and heterocycle **13** in the *yz* plane.

the positive bond order $p_{1,6}$ = 0.101: terminal atoms of triazatriene **9** are not repulsed, but attracted.

The structures of **9a—9e** differ considerably in values of stretching angles. For example, the N—C—N and C—N—C angles in isomer **9d** are 6 to 8° larger than those in **9a**. These data make it possible to exclude the possibility of invoking intramolecular H-bonds to explain the increased stability of skew configurations. The geometric structure of isomer **9f** is presented in Fig. 2.

Transition state of the 9f → 13 reaction. The energy profile of the electrocyclization of triazatriene **9** from the conformation **9f** to 1,6-dihydro-1,2,4-triazine (**13**) is shown in Fig. 3. The $d_{1,6}$ distance between N(1) and C(6) atoms, which form a new bond, is chosen as the reaction coordinate. The dependence of the energy *E* on $d_{1,6}$ is obtained at fixed values of $d_{1,6}$ and the complete optimization of other geometric parameters. The transition state **T** (the saddle point at $d_{1,6}$ = 2.017 Å) and the structure $\mathbf{I}^2$ with $d_{1,6}$ = 2.00 Å localized by the reaction coordinate method on the energy profile (see Fig. 3) differ considerably in bond lengths (see Table 3) and torsion angles (see Table 4).

The considerable rearrangement of the electronic structure of the cyclizing molecule of triene **9** occurs just at $d_{1,6} \approx 2.0$ Å. The transition state **T** is characterized by a noticeable alignment of bond orders. The electronic structure of conformation $\mathbf{I}^1$ with the fixed value $d_{1,6}$ = 2.4 Å is similar to that inherent in the initial form of **9f**.

The comparison of spatial parameters of the transition state **T**, the acyclic form **9f**, and cycle **13** shows that

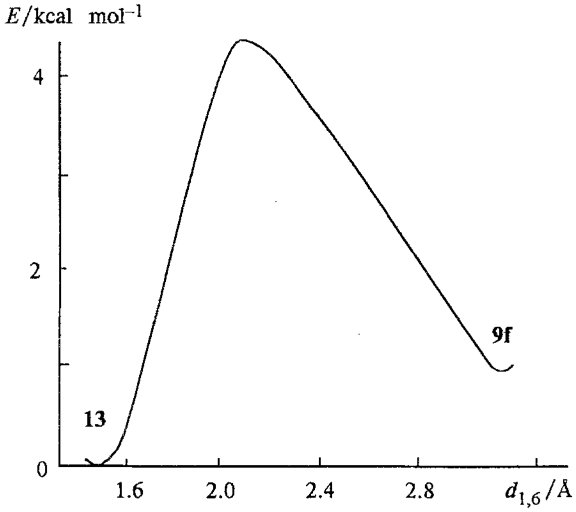

Fig. 3. Energy profile of the electrocyclization of triazatriene **9f**.

some of them are closer to initial values and other are closer to final values (see Tables 3 and 4). For example, the lengths of the C(5)—C(6) bonds in structure **T** and cycle **13** differ only by 0.012 Å, while the difference is 0.055 Å compared to the initial molecule. The opposite situation is observed for N(1)—N(2) and N(3)—C(4) bonds, but the differences are less pronounced. The bond orders are changed, on the average, by 0.30 to 0.50.

The initial structure of the *gZg*-isomer of **9f** is nonplanar: the HN=N and H_2C=CH fragments are turned around the N(2)—C(3) and N(4)—C(5) single bonds approximately by 35°. On the contrary, heterocycle **13** is planar. Therefore, the **9f** → **13** cyclization is accompanied by unfolding both around double and single bonds and by decreasing stretching angles.

The description of the electrocyclization in the Cartesian coordinates gives a more complete notion about the motion of atoms in space. The fragments of structures **9f**, **T**, and **13** in the *yz* plane are presented in Fig. 2. The N and C atoms of heterocycle **13** are arranged in the *xy* plane, from which only the H(7), H(10), and H(11) atoms deviate by 0.43, 0.76, and −1.06 Å, respectively.

The consideration of rotation angles around double bonds makes it possible to draw a conclusion that the electrocyclization of **9f** is the disrotatory process. It should be emphasized that the H(10)C(6)H(11) terminal fragment undergoes unfolding, which is twice as large as that of the N(1)—H(7) fragment. Therefore, the movement of the H(7) atom is twofold smaller than those of H(10) and H(11). The rotation of the N(1)—H(7) fragment is caused by the change in the hybridization of the N(1) atom. In the initial molecule of **9f** the N(1) atom is sp^2-hybridized, the C(3)N(2)N(1)H(7) fragment is planar, and the unshared electron pair of the N(1) atom is directed toward the H(11)—C(6) bond. The distance between N(2) and H(11) is equal to 2.77 Å. In heterocycle **13** the configuration of bonds of the N(1) atom is pyramidal and, therefore, the H(7) atom is shifted from the plane of the cycle. The change in hybridization of the N(1) atom and unfolding the NH group around the N=N bond is the single and continuous process.

It is noteworthy that prior to cyclization **9f** is the twice skew *gEg*-conformer (see Fig. 2), in which n—π(C=C)- and π(N=N)—π(C=C)-interactions are realized in combination. The planar form (the *cZc*-isomer of triene **9**) is not stable (there is no local minimum of the total energy) and is less stable than the structure of *gZg*-**9f** (according to the calculations by the AM1 method, ΔE = 2.46 kcal mol^{-1}). In this form, the n—π(C=C)-interaction is excluded, because these orbitals are orthogonal, *i.e.*, only the π—π-interaction can appear. The combined occurrence of n—π- and π—π-interactions are more energetically favorable, and this is the reason for twisting of isomer **9f** and is realized at the initial stage of the electrocyclization. The π(C=C)—π*(N=N)-interaction is stronger than the n(N)—π*(C=C)-interaction, because the calculation suggests that the electron density (~0.02 e^-) is transferred from the C=C bond to the N=N bond.

There is an opinion in the literature[6,9] that the electrocyclization of 1-azadienes involves only the terminal N atom. Both orbitals of this atom (n- and p_π-AO) participate equally in the considered process of the electrocyclization of 1,2,4-triazahexa-1,3,5-triene (**9**). The rotation angle of the N—H fragment is two times smaller than that of the CH_2 fragment, because the axis of the N—H bond in heterocycle **13** is not orthogonal to its plane, and the unshared electron pair of the N(1) atom is conjugated with the N=C bond. The changes in energies of the higher occupied MOs Ψ_1 and Ψ_2 are small in the cyclization.

Structure	**9f**	**T**	**13**
Ψ_1/eV	−9.86	−8.92	−9.18
Ψ_2/eV	−9.92	−10.07	−10.70

A decrease in the activation energy for triazatriene **9** compared to that for hexa-1,3,5-triene is caused by the small unfolding of the N—H bond in the cyclization.

Thus, the electrocyclization of 1,2,4-triazahexa-1,3,5-triene is the asymmetric disrotatory thermally allowed process. The methods compared give the same description of the reaction route and similar values of parameters of the transition state and activation energies (see Table 5). However, more rigorous calculating methods are needed for discussion of the relative stability of isomers of triazatriene **9**, which are close in energy.

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