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A THEORETICAL STUDY OF THE THERMAL CURTIUS REARRANGEMENT OF SOME CINNAMOYL AZIDES USING THE DFT APPROACH

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The thermal Curtius rearrangement of cinnamoyl azide, 1-azido-3-phenylprop-2-ene-1-one, and the reactions of some of its derivatives is studied theoretically using the DFT (B3LYP-631G(*d,p*) approach. The potential energy surface profiles of the rearrangement are calculated. The transition state was located and confirmed. The Curtius rearrangement of the studied compounds is a one-stage, discrete reaction. A weak effect of substitution on the reaction rate is due to the unique, localized π system of the studied molecules; strong opposing dipoles span the whole molecule.

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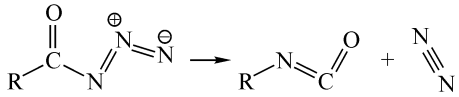
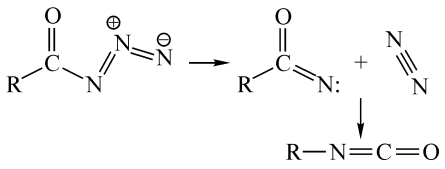
K e y w o r d s: Curtius rearrangement, cinnamoyl azides, DFT treatment, one stage mechanism.

Thermal transformations of carbonyl azides into isocyanates (Curtius rearrangement) provide a source for rich synthetic chemistry [1—4]. They have long been employed and the mechanism has been investigated experimentally for many years. The reaction proved to be typical of the mononuclear thermal decomposition of organic compounds [5].

The mechanism of the Curtius rearrangement has not been established for a long time. The main discussion was around two conceptions. In the first (Scheme 1), the reaction proceeds in one stage with a synchronous formation of isocyanate and N_2 evolution (a concerted mechanism). The second conception (Scheme 2) provides a two-stage mechanism. The first stage is the N_2 evolution with the formation of acyl nitrene and the second stage is the rearrangement of acyl nitrene into the product (Scheme 2).



Scheme 1



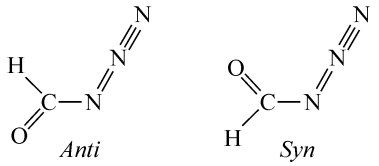
Scheme 2

In the photochemical Curtius rearrangement the formation of acyl nitrene was proved [2]. Thus, by analogy it was assumed that acyl nitrene participates in the thermal rearrangement of acyl azides. However, the experimental results indicated that acyl nitrenes as well as the by-products of their interaction with specific radical traps did not result from the thermal rearrangements of alkyl and aryl carbonyl azides [5]. The participation of acyl nitrene was found only in the thermal (and photochemical) decomposition of ethoxycarbonyl azide $EtOC(O)N_3$ [6] and it was the only case of the thermal reaction in which nitrene was experimentally identified by a chemical method [7].

The first systematic study of the thermal Curtius reaction of small azides provided by Rauk and Alewood [8] appointed out two degenerate states of formyl azide, one yielding carbonyl nitrene and another isocyanate. Abu-Eittah et al. [9] using MP2/6-31G* calculations concluded that while the Curtius rearrangement of formyl azide proceeds in one stage with a simultaneous formation of isocyanate and N_2 evolution (concerted mechanism), that of acetyl and benzoyl azides provides the two-stage mechanism. The first stage is the N_2 evolution with the formation of acyl nitrene and the second stage is the rearrangement of acyl nitrene into the corresponding isocyanate.

The electronic structure and pathways of the thermal isomerization of formyl nitrene and acetyl nitrene were studied by the B3LYP/6-311G(*d*,*p*) density functional method and *ab initio* G2(MP2,SVP) computational methods using the optimized geometries obtained from the B3LYP calculations. According to G2 calculations, both nitrenes have singlet ground states [10]. Based on the results of the calculations, the pathways of the transformation of nitrene formed in the thermal decomposition of acetyl azide were analyzed.

The PBE/TZ2P calculations performed by Zapalov and Tiger [11] suggest that the rearrangement of *syn* acyl azides is a one-stage process, in which the elimination of N_2 occurs synchronously with the rearrangement of atoms and bonds to form isocyanates, whereas the rearrangement of the *anti* conformer involves the formation of singlet acyl nitrene.



The same results were obtained by Kakker *et al.* [12].

The Curtius rearrangement of benzoyl azide in the presence of Lewis acids (BF_3, $AlCl_3$, $SbCl_5$) has been studied by DFT (PBE/TZ2P) methods [13a]. The complexation of Lewis acids (BF_3, $AlCl_3$, $SbCl_5$) with benzoyl azides leads to the formation of 1:1 and 1:2 stable complexes with the interaction of catalysts with O and N atoms of the carbonyl azide group. The potential energy surfaces of the catalytic rearrangement have been calculated for each complex and the transition states were established by the IRC calculation. The energy barriers of the transformation steps for the catalytic reactions are significantly lower in most cases in comparison with the uncatalyzed reaction. The activation energy decreases in the order $AlCl_3 > SbCl_5 > BF_3$ and correlates with a decrease in the Lewis acid strength. The interaction of Lewis acids with the carbonyl azide group causes a decrease in the $N_1{=}N_2$ bond strength and helps the thermal Curtius rearrangement to proceed to the products in one step.

In a recent study [13b], the results of experimental and theoretical studies on the thermal Curtius rearrangement of methyl 1-azidocarbonyl cycloprop-2-ene-1-carboxylate and methyl 1-azidocarbonyl cyclopropane-1-carboxylate have been reported. The kinetics of the Curtius rearrangement was studied by ^1H NMR spectroscopy and there is close agreement between the experimental and calculated enthalpies and entropies of activations.

It has been reported that cinnamoyl azides in refluxing *ortho*-dichlorobenzene could undergo the Curtius rearrangement to form the corresponding isocyanates and the subsequent $Hg(OAC)_2$ catalyzed cyclization affords isoquinolinones [14]. Cinnamic acid and cinnamoyl azides are unique, localized π electron systems. The electronic spectra and the electronic structure of these compounds have been studied [15]. It has been shown that the existence of opposing dipoles critically affects the electronic behavior of these compounds.

In this work, we report the results of a theoretical study on the thermal Curtius rearrangement of some cinnamoyl azides using the DFT(B3LYP/6-31G(*d*,*p*) procedures. The potential energy surfaces of the rearrangements have been calculated and the positions of the transition states have been located and confirmed. For all the studied compounds, the transformations of the studied azides to the corresponding isocyanates with N_2 evolution proved to be a one-stage reaction. The transition state is a specific configuration of the reactant.

The Curtius rearrangement of cinnamoyl azide or cinnamic acid has not been reported before. Both cinnamic acid and cinnamoyl azide proved to be unique, localized π systems. Each of the molecules contains from 3 to 4 electric dipoles, whereby each one opposes another. This feature has a remarkable effect on the electronic structure and the electronic spectra of the molecules. This structure has an apparent effect on the thermodynamic functions of the formation of cinnamic acid and its derivatives which are characterized as small, highly comparable and relatively independent of the substituent.

COMPUTATIONAL DETAILS

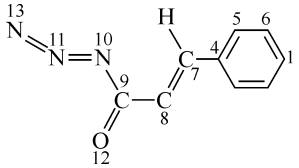
The DFT-B3LYP/6-31G(*d*,*p*) approach was used for the calculations using the Gamess 6.4 [16a], version 1998 and the Gaussian 09 program packages [16b]. In this work, the widely employed hybrid method denoted as B3LYP [17, 18], which includes a mixture of HF and DFT exchange terms and the gradient-corrected correlation functional of Lee, Yang and Parr [19, 20] as proposed and parameterized by Becke [21, 22], were used along with the 6-31G(*d*,*p*) double-zeta split basis sets [23].

In this work, the Curtius rearrangement of cinnamoyl azides, 2-phenylpropenoyl azides, starts with the geometry optimization of the reactant molecule, the elongation of the N10—N11 bond in a step-wise process, and the calculation of the total energy for the optimized geometry of the molecule at each specific value of the N10—N11 bond; the PES profiles of the process are calculated. The point of the maximum energy was subjected to a ″transition state search″, using the Gussian 0.9 package, whereby the transition state is located. Further calculations with IRC key word were performed to confirm that the transition state (TS) connects the proposed reactants and products.

The thermodynamic functions for the studied transformations were calculated in vacuum by computing the differences in electronic energies ΔE and enthalpies ΔH at 298 K upon the inclusion of zero-point energy and thermal corrections. All these terms were determined with a harmonic oscillator (rigid rotator approximations) [24] using the standard procedure in the Gaussian 09 program package [16b].

RESULTS AND DISCUSSION

Curtius rearrangement of cinnamoyl azide, 1-azido-3-phenylprop-2-ene-1-one. The Curtius rearrangement of cinnamoyl azide to the corresponding isocyanate, 2-phenyletheneisocyanate, and molecular nitrogen has not previously been studied. In this work, an attempt is made to investigate theoretically the reaction by stretching the N10—N11 bond of the azide group. The optimized geometry of the starting reactant (cinnamoyl azide) as obtained by B3LYP/6-31G(*d*,*p*) calculations is shown in Fig. 1 and the numerical values of the equilibrium structural parameters are given in Table 1. The variation of the structural parameters during the stretching of the N10—N11 bond is also given.



The results given in Table 1 indicate some important facts. The molecule is planar as evidenced by the values of the dihedral angles: C7—C4—C5—C6 (180°), C8—C7—C4—C3 (0°), C9—C8—C7—C4 (–180°), O12—C9—C8—C7 (0°), N10C9C8C7 (–180°), N11—N10—C9—C8 (180°), and

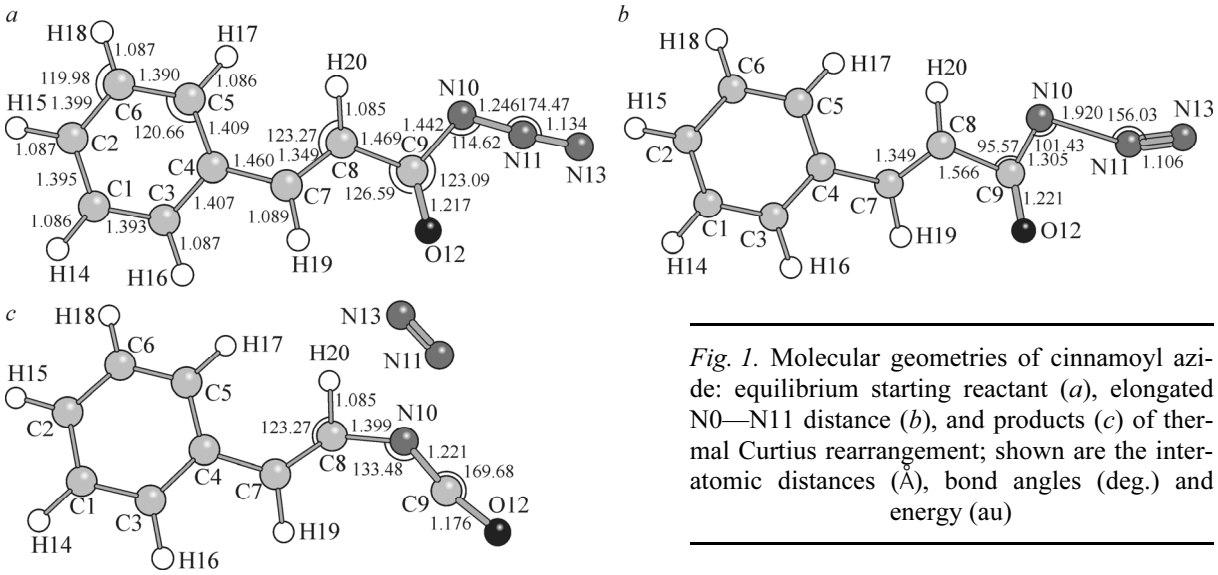


Fig. 1. Molecular geometries of cinnamoyl azide: equilibrium starting reactant (*a*), elongated N0—N11 distance (*b*), and products (*c*) of thermal Curtius rearrangement; shown are the interatomic distances (Å), bond angles (deg.) and energy (au)

T a b l e 1

Variation of the total energy (au) *and geometric parameters of cinnamoyl azide with* N10—N11 *bond distance, in Curtius rearrangement as obtained from* DFT-B3LYP/631G(*d*,*p*) *calculation*

N10—N11	1.25[a]	1.92	1.923	1.924	1.925[b]	1.926	1.927	1.93
				Parameter (–)Energy				
	586.59497	586.53386	586.53385	586.53385	586.533847	586.53385	586.61956	586.6199
				Bond order. (Bondlength)				
C8—C9	1.051	0.793	0.782	0.775	0.770	0.755	0.00	0.00
(1.469)	(1.566)	(1.571)	(1.574)	(1.577)	(1.584)	(2.408)	(2.408)	
C9—O12	1.843	1.722	1.725	1.726	1.727	1.731	1.947	1.947
(1.217)	(1.221)	(1.220)	(1.219)	(1.219)	(1.218)	(1.176)	(1.176)	
N11—N13	2.276	2.690	2.691	2.691	2.691	2.690	2.609	2.610
(1.134)	(1.106)	(1.106)	(1.106)	(1.106)	(1.106)	(1.117)	(1.117)	
C9—N10	0.862	1.227	1.235	1.239	1.243	1.253	1.750	1.751
(1.469)	(1.305)	(1.302)	(1.301)	(1.300)	(1.297)	(1.221)	(1.221)	
N10—N11	1.332	0.309	0.301	0.298	0.294	0.287	0.080	0.070
(1.250)	(1.920)	(1.923)	(1.924)	(1.925)	(1.926)	(1.927)	(1.93)	
N10—O12	0.000	0.182	0.184	0.185	0.185	0.188	0.224	0.224
C8—O10	0.000	0.182	0.192	0.197	0.202	0.214	0.938	0.938
				Bond angle, θ°				
O12C9C8	126.6	124.4	124.4	124.39	124.38	124.36	165.39	165.4
N10C9C8	110.3	95.5	94.9	94.55	94.24	93.40	25.0	24.9
N11N10C9	114.6	101.43	102.0	102.14	102.68	102.68	115.6	115.6
N13N11N10	174.5	156.0	155.1	154.56	154.02	152.48	114.1	114.2

[a] Equilibrium geometry.
[b] Max. of PES for the starting reactant.

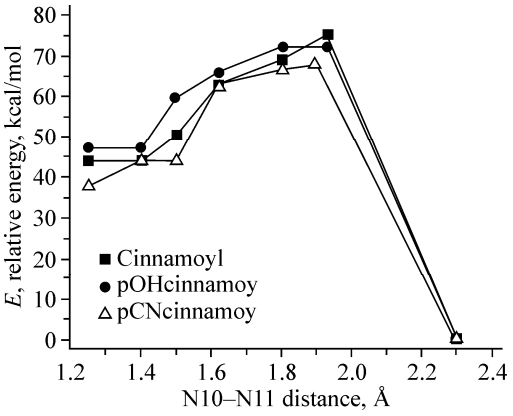


Fig. 2. Potential energy surface diagram (PES) of the Curtius rearrangement of cinnamoyl azides to the corresponding isocyanates and N_2

N13—N11—N10—C9 (–180°). The starting reactant is the *syn*-conformer. These results agree with the results reported for formyl and benzoyl azides [12, 13b], which means that one can rely upon the accuracy of the calculation method used in this work. The C8—C9 bond length (1.469 Å) is a real C—C single bond reflecting the sp^2 hybridization on both C8 and C9 atoms. The C9—O12 bond length (1.217 Å) is a typical C=O double bond. The electron repulsion between the lone pairs of electrons on O12 and N10 lead to an increase in the O12—C9—N10 bond angle to 123.1° and a decrease in the C8C9N10 bond angle to 110.3°. The N10—N11—N13 bond angle is 174.5°, which indicates that the azide group is slightly bent.

The Curtius rearrangement of cinnamoyl azide is started by a stepwise elongation of the N10—N11 bond distance, starting from the equilibrium bond length of 1.25 Å. At a distance of 1.92 Å significant changes are observed in the calculated geometric parameters of the molecule (Table 1, Fig. 1). The C8—C9—C10 bond angle has drastically decreased from about 110° to about 95° and the C8—C9 bond length has increased from 1.469 Å to 1.566 Å.

An increase in the N10—N11 distance to 1.925 Å gives the maximum point of the PES profiles (Fig. 2), the highest energy configuration of –586.53385 au, as compared to the energy of the starting equilibrium geometry of –586.58479 au. An increase in the N10—N11 distance to 1.927 Å causes three events to occur simultaneously:

1) break down of the C8—C9 bond; the bond order is now 0.00;

2) break down of the N10—N11 bond;

3) formation of THE C8—C10 bond; the transfer process.

The plot of PES is completed to N10—N11 = 2.300 Å.

Transition state. The transition state was located by carrying out a separate run, (″transition state search run″) on the configuration of the maximum point of the PES profile. The results obtained were:

1) the optimized geometry of the transition state;

2) the vibrational frequencies of the transition state geometry;

3) the thermodynamic functions of the transition state formation.

The results are given in Table 2 and Fig. 3.

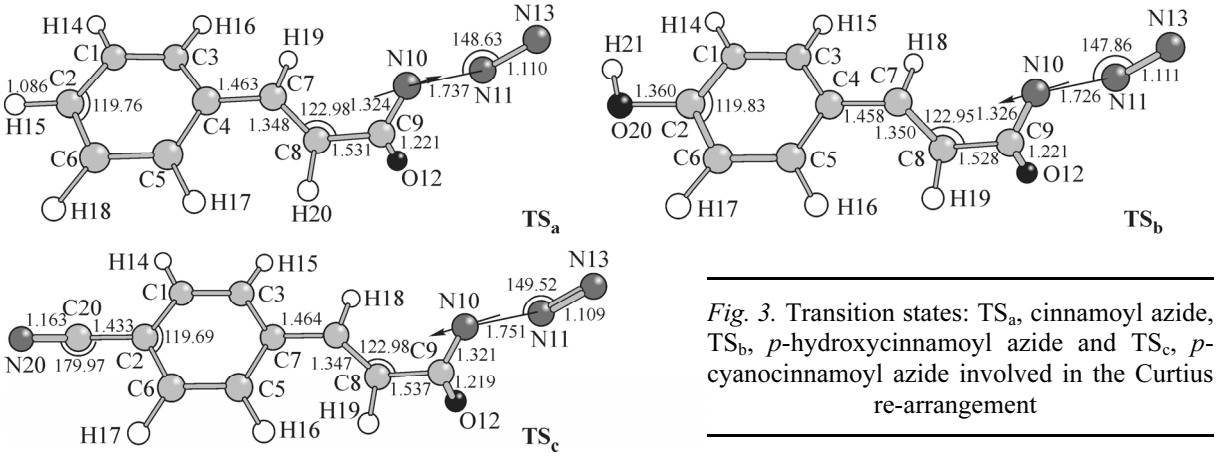


Fig. 3. Transition states: TS_a, cinnamoyl azide, TS_b, *p*-hydroxycinnamoyl azide and TS_c, *p*-cyanocinnamoyl azide involved in the Curtius re-arrangement

Table 2

Geometry optimized parameters of the transition states obtained in the transformation of the studied substituted cinnamoyl azides to the corresponding isocynates and molecular N_2

Parameter	Cinnamoyl azide	*p*-Hydroxy-	*p*-Cyano-
Total *E*, au	–586.539851	–661.761839	–678.779543
Imag. freq., cm^{-1}	–581.64	–589.46	–570.66
Zero P. E., kcal/mol	89.58	92.27	88.58
t_c to *E*, kcal/mol	96.99	100.39	97.17
Bond length, Å (Bond order)			
C4—C7	1.463 (1.111)	1.458 (1.124)	1.464 (1.109)
C7—C8	1.348 (1.739)	1.350 (1.722)	1.347 (1.748)
C8—C9	1.531 (0.865)	1.528 (0.873)	1.537 (0.854)
C9—O12	1.221 (1.64)	1.221 (1.647)	1.219 (1.650)
C8—O10	2.124 (0.189)	2.125 (0.189)	2.121 (0.190)
C9—N10	1.221 (1.64)	1.326 (1.374)	1.321 (1.395)
N10—N11	1.737 (0.581)	1.726 (0.595)	1.751 (0.563)
N11—N13	1.11 (2.862)	1.111 (2.851)	1.109 (2.875)
Bond angle, deg.			
C7C8C9	122.89	122.95	122.98
C8C9O12	126.54	126.83	125.98
N10C9O12	137.51	137.05	138.37
C8C9N10	95.83	95.99	95.54
C9N10N11	105.53	105.84	105.24
N10N11N13	148.63	147.86	149.52
Dihedral angle, deg.			
C8C9N10N11	179.89	179.94	179.59
C9N10N11N13	172.53	171.78	173.20
C4C7C8C9	172.77	173.32	171.96
C4C5C7C8	177.35	177.25	178.34
C7C8C9N10	70.06	69.41	71.21

The position of the transition state was confirmed by carrying out additional IRC calculations where the transition state optimized configuration is subjected to the IRC-key-word calculations. The calculations step towards the reactant and products (Fig. 4). The calculations are valuable for verifying that the transition state obtained is the one which is related to correct products. The results for cinnamoyl azide are shown in Fig. 4. The total energies resulted from IRC-calculations are exactly of the right reactant (cinnamoyl azide) and the product (2-phenylpropenyl isocyanate plus molecular nitrogen).

The optimized structural parameters of the transition state TS_a (Table 2) are illustrative. The

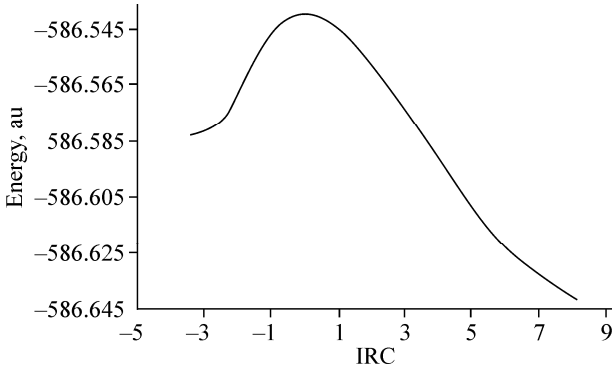


Fig. 4. The intrinsic reaction path (IRC) for the transformation of cinnamoyl azide to isocyanate and nitrogen

N10—N11 distance is 1.737 Å and the total energy is –586.53985 au. TS_a, has the following characterristic features:

1) the C4C7C8C9 dihedral angle is 172.8°, which means that the TS_a geometry is not planar and there is a distinct bent between the propenyl group and the benzene ring. The azide group is not linear but distinctly bent; the N10N11N12 bond angle is 149.5°. TS_a is a singlet configuration of the reactant with an energy barrier of the transformation reaction $\Delta E = E_{TS} - E_R = 34.28$ kcal/mol. The energy of the $^3A^*$ triplet transition state is slightly lower than that of the singlet state, $\Delta_{st} = 4.26$ kcal/mol.

2) an imaginary vibrational frequency of 581.64i cm^{-1}.

The optimized structural parameters of TS_a (transition state of cinnamoyl azide) are given in Table 2 and Fig. 3. The N10—N11 distance (the parameter of migration) is 1.737 Å whereas its value is 1.25 Å in the reactant. The N11—N12 bond length changes from 1.340 Å to 1.110 Å and approaches the bond length in the N_2 molecule of 1.103 Å. The C9—N10 bond length is shortened from 1.440 Å (in the starting molecule) to 1.300 Å (in TS) and becomes similar to that in the isocyanate molecule. In TS the C8—C9—N10 angle drastically decreases to about 94° vs. about 110° in cinnamoyl azide, and as a result, N10 approaches C8.

The numerical values of the optimized geometric structural parameters of TS (Table 2 and Fig. 3) support the suggested mechanism of the rearrangement. The C8—C9 bond length is elongated to 1.537 in TS from 1.469 Å in the starting molecule. This behavior precedes the complete rupture of the bond. It is interesting to find out that the C9—O12 bond length has almost the same value of 1.221 Å in TS as well as in the starting molecule. However, the N10—N11 bond length decreased from 1.134 Å in the starting compound to 1.110 Å in TS, which is typical of the bond length in the N_2 molecule.

Variations of bond angles in TS as compared to those in the starting reactant are illustrative. The O12—C9—C8 bond angle is not significantly changed from 126.6° in starting cinnamoyl azide to 124.38° in TS. The N10—C9—C8 bond angle decreases in TS to 95.5° from 110.3° in the starting reactant. This substantial decrease is a strong evidence for the next rupture of the C8—C9 bond and the formation of the C8—N10 bond. The decrease in C9—N10—N11 and N10—N11—N13 bond angles from 114.6° and 174.5° in the geometrically optimized reactant to 102.7° and 154.0° in TS is a strong evidence for the subsequent break down of the N10—N11 bond and the separation of the N2 molecule.

The TS formation is accompanied by a substantial charge redistribution, resulting in large differrences between their dipole moments and the dipole moments of the starting *syn*-cinnamoyl azides. The NBO charge densities given in Table 3 indicate a rather high charge density on N10 and a low

Table 3

Atomic charge (*q*) *distribution*, NBO, *and diploe moments* (μ) *in cinnamoylazides and the corresponding transition states*

Compound	*q* (on selected atoms)						μ, D
	R	C8	O12	N10	N11	N13	
$R(CO)N_3$ / *syn*-Cinnamoyl azide	1.028	–0.317	–0.560	–0.406	0.247	0.008	4.50
TS_a	0.982	–0.250	–0.594	–0.356	0.105	0.113	3.71
syn-p-Hydroxy Cinnamoylazide	1.051	–0.329	–0.564	–0.407	0.247	0.002	5.86
TS_b	1.007	–0.260	–0.598	–0.364	0.106	0.109	5.03
syn-p-Cyano Cinnamoylazide	0.990	–0.298	–0.553	–0.408	0.248	0.021	1.66
TS_c	0.943	–0.233	–0.586	–0.347	0.102	0.121	2.66

TS_a — transition state of cinnamoyl azide; TS_b — trans. state of *p*-hydroxycinnamoyl azide; TS_c — trans. state of *p*-cyanocinnamoyl azide.

density on C8 in all the studied species, starting molecules, and TSs. This is an illustration that the electron transfer takes place from N10 to C8, i.e., from the azide group to the ethane group during the rearrangement of azide to isocyanate.

Increasing the N10—N11 distance from 1.926 to 1.927 Å and repeating the calculations, we observed significant changes occurring synchronously:

1) complete rupture of the N10—N11 bond with the extrusion of the N_2 molecule;

2) rupture of the C8—C9 bond and the rearrangement of bonds and atoms to give the corresponding isocyanate (2phenyletheneisocyanate) (Fig. 1).

In the separated N_2 molecule the N—N bond length is 1.117 Å, which agrees nicely with the experimental bond length of 1.16 Å in the N_2 molecule. The N—C bond in the product (isocyanate) is 1.221 Å as compared with 1.199 Å in CH_3NCO [10], and the C—O bond is 1.176 Å as compared to 1.173 Å [10].

The results of this work predict that the conversion of cinnamoyl azide to isocyanate and nitrogen is a one-stage reaction that goes through TS that is a specific configuration of the reactant which goes directly to the products; no nitrene intermediate is obtained

$$Ph—C=C—CO—N—N \equiv N \rightarrow [TS] \rightarrow Ph—C=C—NCO + N_2.$$

At the N10—N11 distance of 1.93 Å an additional run was carried out with full geometry optimization, and the energy of the product was calculated to be –586.6950 au, and the distance between the isocyanate molecule and the N_2 molecule is 4.000 Å.

The thermodynamic parameters of the formation of different species involved in the Curtius rearrangement of the studied azides are given in Table 6.

***p*-Hydroxycinnamoyl azide, 1-azido-3-(4-hydroxypheny)prop-2-ene-1-one.** Table 4 and Fig. 5 give the variation of the geometry of the optimized parameters of *p*-hyroxycinnamoyl azide with the elongation of the NIO—N11 distance and the atom numbering system of the molecule.

The optimized geometry of *p*-hydroxycinnamoyl azide when the N10—N11 bond length is increased to 1.920 Å is shown in Fig. 5 and Table 4 and is significantly different from those of the equilibrium configuration. At the N10—N11 distance of 1.920 Å the optimized geometric parameters are as follows: the C8—C9—N10 bond angle (θ) has decreased from 110.3° to 95.5°; the single C8—C9 bond length has increased from 1.465 Å to 1.588 Å, proceeding to be ruptured, and the triple bond character increases between N11—N13; the bond order changes from 2.27 to 2.69.

Table 4 shows the variation of the optimized geometric parameters of *p*-hydroxycinnamoyl azide with the variation of N10—N11 from 1.920 Å to 1.931 Å. The configuration with the N10—N11 distance of 1.93 Å was subjected to TS search calculations that give

1) the optimized parameters of TS_b;

2) the vibrational frequencies of the TS_b configuration;

3) the thermodynamic functions of TS_b formations.

TS_b has an imaginary vibrational frequency at 661.76i cm^{-1}. The position of this TS is confirmed by carrying out an additional run for IRC calculations.

The optimized geometry of TS_b is given in Table 2 and Fig. 3. TS_b is a specific configuration of *p*-hydroxycinnamoyl azide with an activation barrier of 34.27 kcal/mol.

As the N10—N11 bond is increased from 1.93 Å to 1.931 Å, both C8—C9 and N10—N11 bonds are simultaneously ruptured with the separation of the N_2 molecule and the rearrangement to the product (the corresponding isocyanate 2-(4-hydroxyphenyl) etheneisocyanate) (Fig. 5). At the N10—N11 distance of 1.931 Å, the C9—C8 bond order is 0.00 which means the complete rupture of the C8—C9 bond, whereas the C8—N10 bond order is now 0.934, declaring that the bond formation between C8 and O10 did take place (Table 4).

At the configuration with the N10—N11 distance of 1.93 Å an additional run was carried out with the fully optimized configuration, and the energy of the product was found to be –661.98012 au, and the distance between isocyanate and the N_2 molecule was 3.975 Å.

T a b l e 4

Variation of geometric parameters of p-hydroxycinnamoyl azide with N10—N11 *distance*, Å *in Curtius rearrangement as obtained from* DFT-B3LYP/6-31G(*d*,*p*) *calculation*

N10—N11 dist., Å*	1.25	1.920	1.928	1.929	1.930	1.931
	Parameter Bond order, (Bond length), Å					
C8—C9	1.061 (1.465)	0.810 (1.558)	0.785 (1.569)	0.780 (1.572)	0.773 (1.575)	0.000 (2.911)
C9—O12	1.380 (1.218)	1.715 (1.223)	1.720 (1.221)	1.721 (1.220)	1.723 (1.219)	1.942 (1.177)
N11—N13	2.274 (1.134)	2.690 (1.106)	2.691 (1.106)	2.691 (1.106)	2.691 (1.101)	2.610 (1.116)
C9—N10	0.855 (1.445)	1.217 (1.308)	1.235 (1.303)	1.238 (1.301)	1.244 (1.299)	1.755 (1.220)
N10—N11	1.336 (1.250)	0.315 (1.920)	0.297 (1.928)	0.294 (1.929)	0.290 (1.930)	0.081
N10—O12	0.000 0.000	0.000	0.184	0.185	0.186	0.225
C8—O10	0.000 0.000	0.000	0.182	0.196	0.202	0.934
	Bond angle, θ, deg.					
O12C9C8	126.8	124.5	124.4	124.4	124.4	165.4
N10C9C8	110.3	96.5	95.1	94.9	94.3	24.8
N11N10C9	114.6	100.9	101.6	101.7	102.0	115.5
N13N11N10	174.5	157.2	155.0	154.7	153.4	114.1

*Max. of PES.

The thermodynamic parameters of the transformation of *p*-hydroxycinnamoyl azide to the corresponding isocyanate and N_2 are given in Table 6.

***p*-Cyanocinnamoyl azide, 1-azido-3-(4-cyanophenyl)prop-2-ene-1-one.** The Curtius rearrangement of *p*-cyanocinnamoylazide has been studied similarly. At the N10—N11 bond distance of

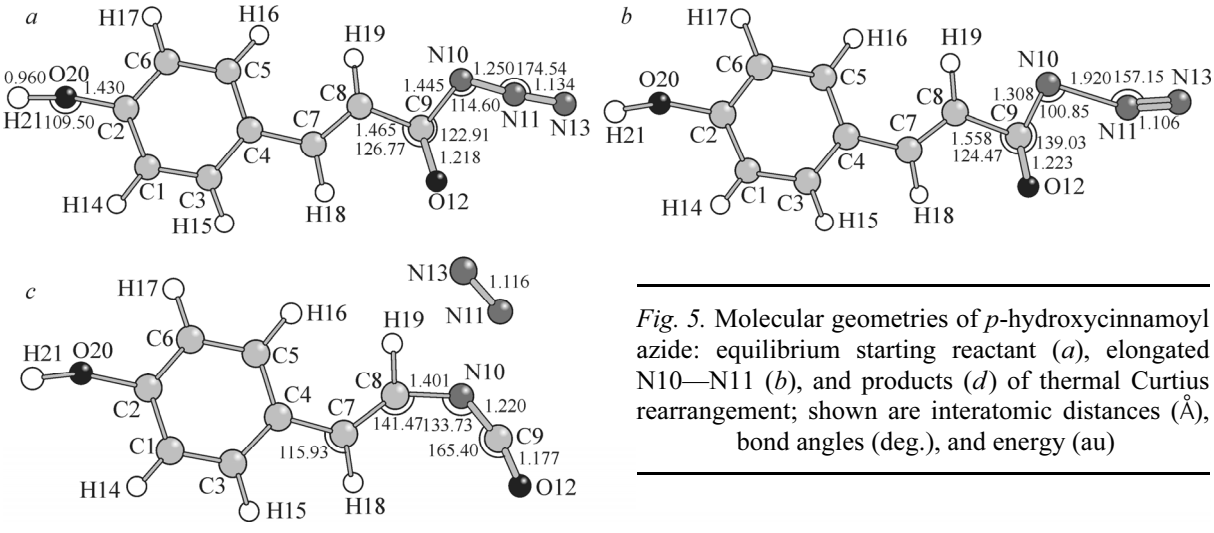


Fig. 5. Molecular geometries of *p*-hydroxycinnamoyl azide: equilibrium starting reactant (*a*), elongated N10—N11 (*b*), and products (*d*) of thermal Curtius rearrangement; shown are interatomic distances (Å), bond angles (deg.), and energy (au)

Table 5

Variation of geometric parameters of p-cyanocinnamoyl azide with N10—N11 *distance*, Å *in Curtius rearrangement as obtained from* DFT-B3LYP/6-31G(*d*,*p*) *calculations*

N10N11 dist., Å*	1.250	1.920	1.924	1.925	1.926	1.927	1.930
			Parameter Bond order, (Bond length), Å				
C8—C9	1.044 (1.473)	0.788 (1.569)	0.773 (1.576)	0.767 (1.579)	0.769 (1.583)	0.000 (2.403)	0.000 (2.403)
C9—O12	1.044 (0.473)	1.728 (1.219)	1.732 (1.219)	1.733 (1.218)	1.735 (1.217)	1.958 (1.174)	1.958 (1.174)
N11—N13	1.383 (1.216)	2.692 (1.106)	2.693 (1.106)	2.693 (1.106)	2.692 (1.106)	2.610 (1.116)	2.611 (1.116)
C9—N10	2.280 (1.133)	1.244 (1.305)	1.235 (1.302)	1.239 (1.300)	1.244 (1.299)	1.736 (1.283)	1.736 (1.223)
N10—N11	1.432 (0.874)	0.312 (1.920)	0.302 (1.924)	0.298 (1.925)	0.293 (1.926)	0.077 (1.927)	0.077 (1.930)
N10—O_{12}	0.000	0.183	0.186	0.187	0.188	0.222	0.222
C8—O10	0.000	0.184	0.187	0.203	0.209	0.952	0.952
			Bond angle, θ, deg.				
O12C9C8	126.4	124.3	124.2	124.2	124.2	165.0	165.3
N10C9C8	110.3	96.0	94.4	94.07	93.6	25.1	25.1
N11N10C9	114.5	101.6	102.0	102.22	102.5	116.0	116.0
N13N11N10	174.3	156.9	155.6	154.96	154.1	114.1	114.1

*Max. of PES.

1.920 Å the energy increases from –678.82609 au (source molecule) to –678.77437 au and the geometric parameters of this conformer change significantly from those of the starting reactant, as shown in Table 5 and Fig. 6. The C8—C9 bond length has increased from 1.473 Å to 1.53 Å, the C8—C9—N10 bond angle (θ) has significantly decreased from 110.3° to 95.5°, and this leads to an apparent approach of N10 to C8. Also, the N11—N13 bond order increased from 2.28 to 2.89; these events precede the rupture of the N10—N11 bond and the separation of the nitrogen molecule N11—N13.

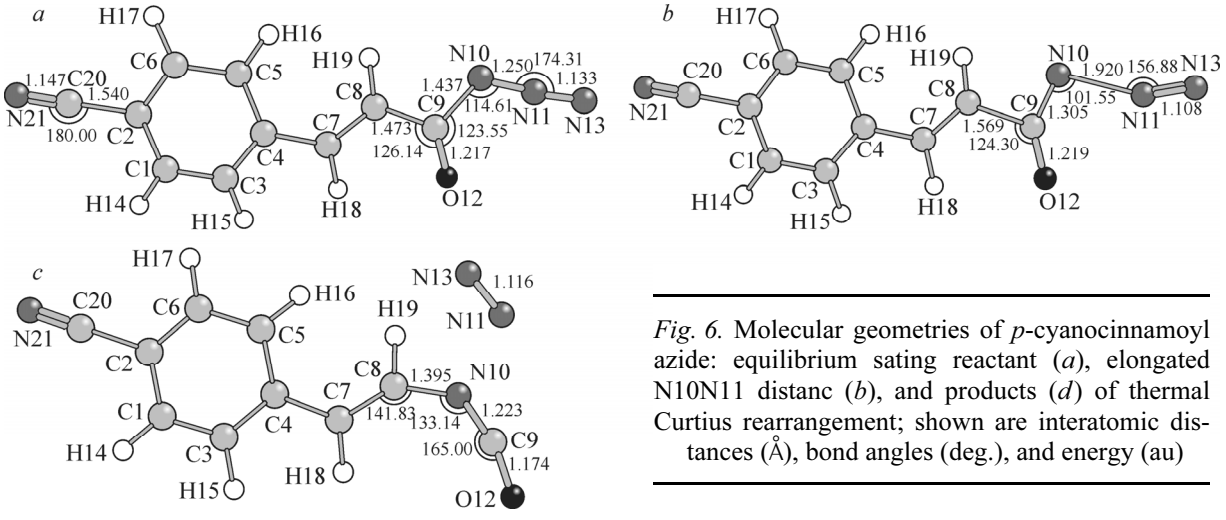


Fig. 6. Molecular geometries of *p*-cyanocinnamoyl azide: equilibrium sating reactant (*a*), elongated N10N11 distanc (*b*), and products (*d*) of thermal Curtius rearrangement; shown are interatomic distances (Å), bond angles (deg.), and energy (au)

Table 6

Thermodynamic functions of the transformation reactions of the Cinnamoyl azide derivatives to corresponding isocyanate and nitrogen molecule. Total energy is in au whereas other functions are in kcal/mol

Azide	Reactant	T.S.	Product	ΔE	ΔE^*	E_r	ΔH
Cinnamoyl	–586.59497	–586.53985	–586.66950	34.2	28.996	–47.08	–51.13
ZPE	92.44	89.58	89.87				
TC	99.41	96.99	98.64				
p-Hydroxy cinnamoyl	–661.81649	–661.76184	–661.89012	34.23	30.85	–46.20	–47.01
ZPE	95.09	100.93	92.49				
TC	102.79	100.39	101.99				
p-Cyano cinnamoyl	–678.83405	–678.77954	–678.91084	34.21	30.55	–48.19	–51.47
ZPE	91.473	88.579	88.939				
TC	99.608	97.172	98.274				

$\Delta E = E_{\text{transition state}} - E_{\text{reactants}}$ — energy barrier of transformation reaction.
$\Delta E^* = \Delta E + \Delta(\text{ZPE}) + \Delta(\text{TC})$ — activation energy of the reaction.
$E_r = E_{\text{product}} - E_{\text{reactants}}$ — reaction energy.
$\Delta H = E_r + \Delta(\text{TC}) + RT$ — enthalpy of the reaction.

Table 5 shows the variation of the optimized geometric parameters of *p*-cyanocinnamoyl azide as the N10—N11 distance varies from 1.92 Å to 1.93 Å. At a length of 1.926 Å a TS search is applied and one gets all the structural parameters of TS denoted as TS_c.

The characteristic features of the TS configuration (Table 2) compared to those of the starting molecule are: a decrease in the C9—O12 bond length from 1.847 Å to 1.735 Å, and in the C8—C9 bond length from 1.04 Å to 0.769 Å, a distinct decrease in C8—C9—N10 bond angle (θ) from 110.3° to 95.5°.

As the N10—N11 distance is increased from 1.926 Å to 1.927 Å, both C8—C9 and N10—N11 bonds are ruptured simultaneously in one-step, and both bonds and atoms rearrange to give 2-(4-cyanophenyl)etheneisocyanate and nitrogen molecule is separated (Fig. 6).

The geometric parameters of the resultant isocyanate are given in Fig. 6. The N10—C9 bond length is 1.22 Å as compared with 1.199 Å [10]; the C9—O12 bond length is 1.17 Å as compared to 1.173 Å [10]. The profile of the potential energy surface diagram for the transformation of *p*-cyano-cinnamoyl azide to the corresponding isocyanate is given in Fig. 2.

At a configuration with the N10—N11 distance of 1.93 Å an additional run was carried out with complete optimization of the geometric parameters; the total energy of the products is –678.91083 au. The distance between the isocyanate molecule and the N_2 molecule is 3.534 Å.

The thermodynamic functions of the *p*-cyanocinnamoyl transformation are given in Table 6.

Thermodynamic functions of the rearrangement of the studied azides. The calculations of the thermodynamic properties of a reaction are implemented using the different computation program packages.

According to Gaussian [25] procedures, the key thermochemical properties are.

E_{tot} is the total electronic energy as calculated by a given theoretical model and ZPVE is the zero point vibrational energy. The zero point corrected total energy E_0 is given by

$$E_0 = E_{\text{tot}} + \text{ZPVE},$$

whereas the thermal correction $E(0—298)$ is given by

$$E(0—298) = dE_{\text{el}} + dE_{\text{vib}} + dE_{\text{rot}} + dE_{\text{trans}}.$$

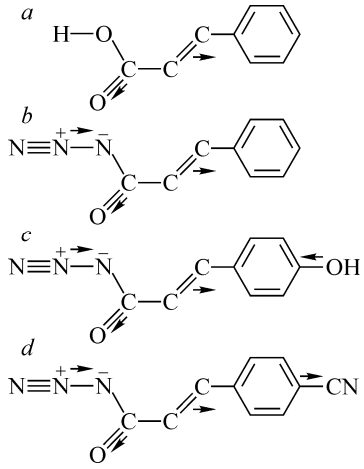


Fig. 7. Local opposing electric dipoles in the studied molecules: (*a*) cinnamic acid, (*b*) cinnamoyl azide, (*c*) *p*-hydroxycinnamoyl azide, and (*d*) *p*-cyanocinnamoyl azide

The energy at 298.15 K is

$$E_{298} = E_0 + E(0—298)$$

and

$$H_{298} = E_{298} + RT.$$

The calculated values of the thermodynamic functions of the dissociation of the studied azides are given in Table 6. The numerical values of the thermodynamic functions are characterized by that they are relatively small, highly comparable and are apparently independent on the nature of the substituent. The ΔH values for the different reactions vary between –47 kcal/mol and –52 kcal/mol. These features are correlated to the electronic structure of the studied compounds. The results of MO calculations of Mosquera [26] suggest that cinnamic acid behaves as if it consists of two independent fragments: the benzene ring and the propenoic acid fragment. On the other hand, the results of the spectral studies on cinnamic acid and cinnamoyl azides [15] predict that such compounds are distorted, have localized and unique π systems as a result of the existence of strong ″opposing″ electric dipoles (Fig. 7). Zapalove and Tiger [13a] found that the interaction of Lewis acids with the carbonyl azid group in benzoyl azide helps the thermal Curtius rearrangement of benzoyl azide into phenyl isocyanates to proceed. The activation energy decreases in the $AlCl_3 > SbCl_3 > BF_3$ ranges of Lewis acids and it correlates with the decrease of the Lewis acid strength. In this work, the —OH group (an electron donor) facilitates the thermal Curtius rearrangement in hydroxycinnamoyl azide more than the —CN group (an electron withdrawing group in *p*-cyanocinnamoyl azide). In the work of Zapalove, all the studied reactions proceeded as a one-stage discrete reaction without the nitrene intermediate.

CONCLUSIONS

In this work, the thermal Curtius rearrangement is theoretically studied for some cinnamoyl azides, 1-azido-3-phenylprop-2-ene-1-one, which has not been studied before. The mechanism of the rearrangement is investigated.

Geometry optimization, energy calculations, vibrational frequencies, and intrinsic reaction coordinate calculations were carried out using the DFT/B3LYP/6-31G(*d*,*p*) procedures and the results were confirmed by applying the same calculations to different systems and comparing the results with the appropriate ones found in the literature [12, 13a]. The results of this work suggest:

1) Cinnamoyl azides rearrange to the corresponding isocyanates with the expulsion of a nitrogen molecule. The rearrangement is a one-stage reaction that passes through TS that is a specific configuration of the reactant; the TS position was localized and confirmed. TSs are characterized by having imaginary vibrational frequencies. The parameters of the geometry optimized TSs were calculated and interpreted. Their values are different from the values of the starting molecules and their variations are in line, which supports the suggested mechanism. The transformation of the studied azides to the corresponding isocyanates and molecular nitrogen proved to be a one-stage reaction.

2) Both TS atoms and bonds rearrange in one step to the corresponding isocyanate with the expulsion of the nitrogen molecule. This mechanism is confirmed for cinnamoyl azide, *p*-hydroxycinnamoyl azide, and *p*-cyanocinnamoyl azide. Nitrene intermediate is not obtained.

3) TS is a singlet configuration of the reactant; calculations on an assumed triplet TS did not change the reaction mechanism. The energy gap $\Delta E = E_s - E_t$ is rather small (of the order of 4.0 kcal/mol), which means that state crossing is probable. Such a small energy difference between these terms means that singlet TS can convert to the triplet state, thus making the rearrangement to the

isocyanate energetically unfavourable. Experimentally, this is not the case since the Curtius rearrangement is characterized by a high yield of isocyanate [2].

4) The activation barrier of the TS formation is not apparently affected by the nature of the substituents: this feature has been interpreted to be related to the electronic structure of the studied molecules.

5) The thermodynamic functions of the studied transformations are of small and comparable values and are weakly dependent on the substituent. These results are due to the rigid and localized π system of the studied molecules.

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