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Theoretical Study of the Tautomeric Reactions of Dinitromethane and Its Radical Cation

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Reactions of aci-form and diaci-form formation in dinitromethane and its radical cation have been theoretically studied at DFT B3LYP level of theory with 6-31G(d) basis set. The lowest energy structures of the dinitromethane aci-form and diaci-form were optimized. Analogous theoretical study was carried out for dinitromethane radical cation. In connection with observed conformation transitions in aci- and diaci-form, B3LYP level of theory with the 6-31G(d) basis set was used to investigate the relevant parts of dinitromethane and its radical cation ground state potential energy surfaces.

Keywords: B3LYP, dinitromethane, dinitromethane radical cation

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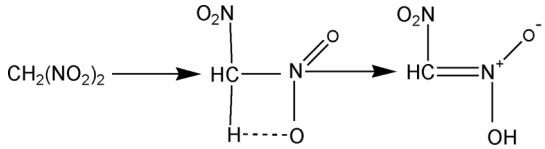
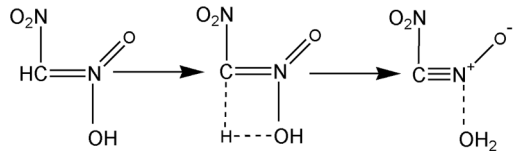
Introduction

Tautomeric transformations of nitroalkanes involving intramolecular migrations of hydrogen atom are of great interest for the elucidation of general trends in the reactivity of aliphatic nitro compounds [1,2]. For example, the reaction of aci-form (nitronic acid) formation in nitroalkanes is one of the possible pathways of nitroalkanes liquid-phase decomposition. These reactions were widely studied with different theoretical and experimental methods [3,4]. In spite of this, the reactions of nitroalkanes decomposition have not been fully explored [5]. Dinitromethane (DNM) has a low thermal stability in the gas phase [6], but mono-, tri-, and tetranitroalkanes are thermal stable compounds, which requires some explanation. In Khrapkovskii et al. [6], a mechanism that included elimination of water from the aci-form of DNM and accounted for the low thermal stability and for the specific position of DNM in the series of nitroalkanes was supposed. This mechanism involves the hydrogen transfer and isomerization to aci-form and further H_2O elimination from the latter.



(1)



(2)

A specific feature of this process is that it can occur in nitro-compounds with two or three hydrogen atoms at the α-position with respect to the nitro group and cannot occur in tri- or tetranitromethane.

It was found that aci-form formation reaction is the limiting step of this process. The activation barrier of DNM aci-form

formation is lower than for the nitromethane aci-form formation.

Further studies using nonempiric and DFT methods [7] make it possible to calculate accurately energetic values of these two stages. So it was proved that mechanism (1–2) could be realized. However, in Khrapkovskii et al. [6,7], less attention was paid to the reaction of aci-form formation and conformation transitions.

There are currently a lot of theoretical studies concern radical cations. Calculated data could be used for an accurate interpretation and analysis of the experimental, very popular mass spectroscopic data [4,5]. Activation enthalpies for the gas-phase unimolecular reactions of alkane radical-cations decomposition are lower than for similar reactions with neutral molecules [8].

In Nikolaeva et al. [9], the monomolecular decomposition of nitromethane and its radical cation was theoretically studied. Reaction of aci-form formation in nitromethane is endothermic and in nitromethane radical-cation it is exothermic.

The purpose of the present work is to study theoretically the mechanism of DNM and dinitromethane radical cation (DNM RC) aci-form and diaci-form formation. Therefore, we investigated the DNM and DNM RC aci-form and diaci-form ground-state potential energy surfaces (PES) by means of B3LYP level of theory with 6-31G(d) basis set. In particular, we address the questions related to the geometrical structure of aci-forms and diaci-forms, as well as the mechanism of conformation transitions.

Methods

DFT B3LYP level of theory with 6-31G(d) basis set was employed in this theoretical study. In Garivzianova et al. [8] it was shown that the values of the formation enthalpy of the nitro-compounds and activation enthalpies according to this method are in best agreement with experimental results.

The availability of the transition states was proved by the one negative eigenvalue of the Hessian matrix and also by the

intrinsic reaction coordinate (IRC) pathways from this transition state to reagents and to the products of the reaction.

The geometric structure was optimized using B3LYP with 6-31G(d), 6-311++G(d,p), 6-311++G(df,p) basis sets, HF/6-31G(d) and MP2 level of theory with 6-31G(d) basis set. All calculations were carried out using the Gaussian 98 W suite of programs [10].

Results and Discussions

Dinitromethane

In agreement with previous calculations [11], the lowest energy minimum on the ground-state PES concerning DNM does not correspond to C_s, C_2, and C_{2v} point groups of symmetry (local minimums). Global minimum is lower in energy than local minimums by 2–3 kJ/mol.

The optimized geometry of this minimum (B3LYP/6–31G(d)) shows a two-C-N bond distance of 151.4 and 149.9 pm (Table 1).

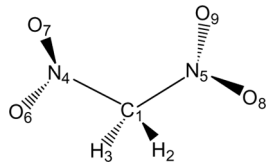
Unfortunately, the experimental data concerning geometric parameters are not available in spite of numerous experimental studies. However, this fact can be explained by the low thermical stability of this molecule.

The computation of the minimum reaction path for DNM aci-form formation was initially attempted by elongation of the C_1-H_2 bond. Starting at the equilibrium structure **1** (DNM, Fig. 1), the energy being minimized with respect to all other geometrical variables without imposing any geometrical restriction. The resulting stationary point **2** (Fig. 2) was characterized as a true transition structure by checking that it had only one imaginary harmonic vibrational frequency. This one imaginary harmonic vibrational frequency corresponded to an intramolecular hydrogen atom shift from carbon to oxygen. The IRC pathway to the product leads to the DNM aci-form (**3**, Fig. 2).

The energy of the DNM aci-form **3** is calculated to be 81.1 kJ/mol higher than DNM. It is worth noting that structure **3** is not unique and it does not correspond to the lowest energy

Table 1

Geometric parameters of dinitromethane (bond lengths in pm and angles in degrees)



	B3LYP				
Parameter	3-21G(d)	6-31G(d)	6-311++G(d,p)	6-311++G(df,p)	6-311++G(2d,p)
C_1H_2	108.4	108.7	108.5	108.0	108.4
C_1N_4	152.9	151.4	151.7	151.5	151.4
C_1N_5	149.9	149.9	150.5	150.0	149.9
N_4O_6	127.3	122.2	121.5	121.3	121.7
N_4O_7	126.6	121.8	121.1	120.7	121.7
N_5O_8	127.7	122.4	121.5	121.4	121.8
N_5O_9	127.7	122.4	121.6	121.4	121.8
O_8H_2	247.8	247.0	244.9	253.7	245.0
O_6H_3	261.5	260.1	255.8	271.5	256.7

(*Continued*)

Table 1
Continued

	B3LYP				
Parameter	3-21G(d)	6-31G(d)	6-311++G(d,p)	6-311++G(df,p)	6-311++G(2d,p)
$N_4C_1N_5$	109.1	110.15	110.3	110.4	110.5
$C_1N_4O_6$	112.3	113.6	114.1	113.5	113.4
$C_1N_4O_7$	118.5	118.5	118.3	118.9	118.9
$C_1N_5O_8$	115.7	116.2	115.9	116.4	116.4
$C_1N_5O_9$	116.0	116.4	116.8	116.4	116.4
$O_7N_4C_1N_5$	1.69	4.08	21.1	−0.7	0.0
$O_8N_5C_1N_4$	85.6	85.3	70.5	90.7	90.0

	B3LYP				
Parameter	6-311G(d,p)	6-311++G(df,pd)	6-31 + G(d,p)	HF/6-31G(d)	MP2/6-31G(d)
C_1H_2	108.5	108.3	108.7	107.5	108.8
C_1N_4	151.9	151.5	151.6	147.9	150.0

C_1N_5	150.3	150.0	150.2	147.9	148.2
N_4O_6	121.5	121.3	122.4	118.7	123.7
N_4O_7	121.0	120.7	121.8	118.7	123.6
N_5O_8	121.7	121.4	122.5	118.7	124.0
N_5O_9	121.7	121.4	122.5	118.7	124.1
O_8H_2	245.6	244.7	245.8	263.9	250.8
O_6H_3	257.7	256.1	257.6	286.4	268.8
$N_4C_1N_5$	110.1	110.4	110.4	109.9	109.0
$C_1N_4O_6$	113.5	113.4	113.4	115.9	114.1
$C_1N_4O_7$	118.6	118.8	119.0	116.5	118.2
$C_1N_5O_8$	116.2	116.4	116.4	116.5	115.8
$C_1N_5O_9$	116.3	116.3	116.4	115.9	117.0
$O_7N_4C_1N_5$	0.7	−0.6	0.0	47.4	15.5
$O_8N_5C_1N_4$	89.0	90.6	90.0	47.2	74.8

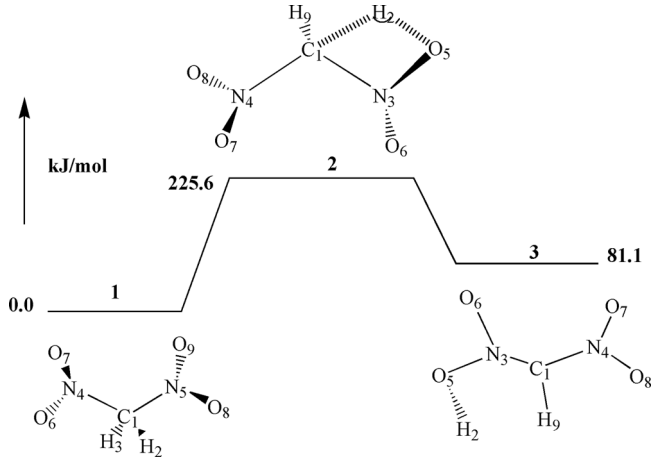


Figure 1. Potential energy diagram for reaction of aci-form formation in DNM. The geometric structure of the transition state (TS) **2** is represented in Fig. 2.

minimum calculated on the ground-state PES concerning **3**. Geometrical structures computed for the stationary points located on the DNM aci-form ground-state PES are given in Fig. 3.

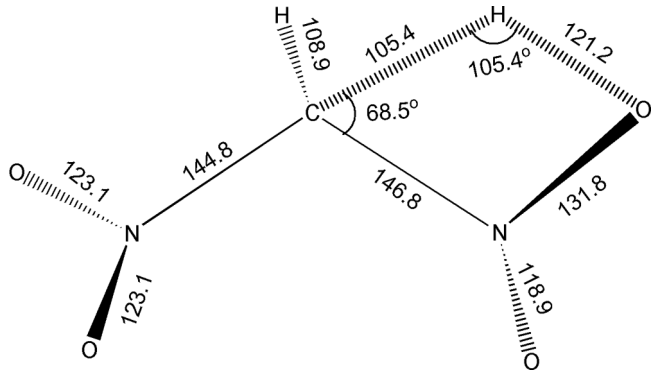


Figure 2. Optimized structures of the transition state for reaction of DNM aci-form formation (bond lengths in pm and angles in degrees).

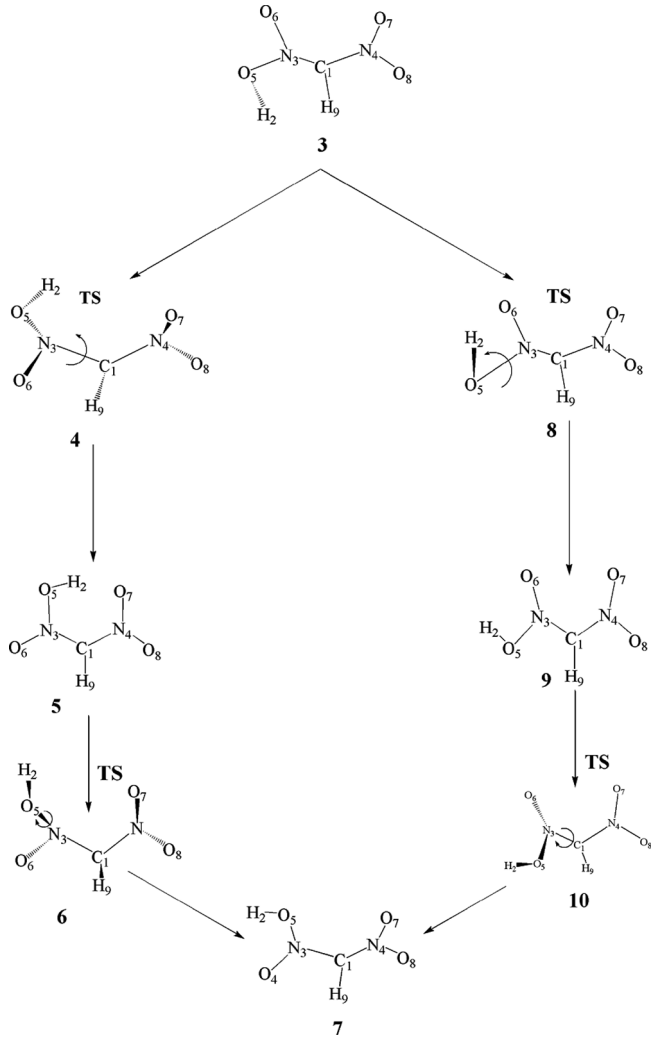


Figure 3. The conformation transition pathways in DNM aci-form.

Enthalpies of activations and enthalpies of reactions for the reactions of aci-form formation and of different conformation transitions in DNM and DNM RC are collected in Table 2.

Table 2
Enthalpies of activations and enthalpies of reaction for the reactions of aci-form formation and of different conformation transitions in DNM and DNM RC

	$\Delta H(\mathbf{1})$-ΔH_i, kJ/mol		$\Delta H(\mathbf{1}+\bullet)$-$\Delta H_i$, kJ/mol
Structure	DNM	Structure	DNM+●
1	0	**1**+●	0
2	225.6	**2**+●	140.1
3	81.1	**3**+●	−19.5
4	220.9	**4**+●	29.5
5	24.8	**5**+●	−47.6
6	76.5	**6**+●	−25.5
7	57.8	**7**+●	−57.2
8	82.0	**8**+●	−18.7
9	51.2	**9**+●	−56.3
10	232.3	**10**+●	6.9
11	272.4	**11**+●	152.7
12	219.4	**12**+●	67.0
13	261.3	**13**+●	156.4
14	209.5	**14**+●	85.9
15	270.0	**15**+●	137.8
16	226.1	**16**+●	55.4
17	264.9	**17**●+	135.1
18	223.2	**18**+●	47.3
19	261.5	**19**+●	83.5
20	249.1	**20**+●	80.2
21	255.8	**21**+●	91.1
22	254.9	**22**+●	59.0
23	238.1	**23**+●	85.9
24	217.9	**24**+●	56.2
25	252.2	**25**+●	69.8
26	225.6	**26**+●	38.9
27	252.9	**27**+●	73.8
28	249.3	**28**+●	69.3
29	—	**29**+●	98.2
30	—	**30**+●	81.4

Geometric parameters of DNM aci-forms **3, 5, 7, 9** and TS structures **4, 6, 8, 10** are provided in Tables 3 and 4.

Structure **5** is predicted to be the lowest in energy because the planar six-membered cycle is realized in this structure. Structure **5** corresponds to the product of the reaction **3-4-5** (Fig. 3). The rotation of the $H_2O_5N_3O_6$ around the C_1-N_3 bond takes place in this conformation transition. Enthalpy of activation for this reaction is 220.9 kJ/mol and the enthalpy of reaction is −56.3 kJ/mol. The elongation of the C_1-N_3 bond occurs in TS **4**. The difference between bond lengths in **3** and **4** is 15.5 pm. That is why the activation barrier of the conformation

Table 3
Geometric parameters of DNM aci-forms (bond lengths in pm and angles in degrees)

	Structure			
Parameter	**3**	**5**	**7**	**9**
C_1H_9	107.6	107.5	107.6	107.5
C_1N_3	132.3	134.3	131.9	131.7
C_1N_4	143.1	140.2	143.1	142.8
N_3O_5	143.5	135.9	138.5	141.6
N_3O_6	120.8	121.9	123.5	122.2
N_4O_7	122.7	126.5	122.8	122.8
N_4O_8	123.7	122.6	123.6	123.7
O_5H_2	97.6	101.8	98.1	97.9
$N_3C_1N_4$	122.5	123.6	126.3	122.2
$C_1N_3O_5$	114.1	120.4	124.8	110.7
$C_1N_3O_6$	131.5	123.0	118.6	132.3
$C_1N_4O_7$	120.2	119.9	121.0	120.1
$C_1N_4O_8$	113.5	116.8	113.2	113.6
$N_3O_5H_2$	106.2	103.9	100.2	100.8
$O_6N_3C_1N_4$	5.14	180.0	180.0	0.0
$O_8N_4C_1N_3$	−177.9	−180.0	−180.0	−180.0
$O_6C_1N_3H_2$	−147.7	179.9	0.0	0.0

Table 4
Geometric parameters of TS for conformation transitions in DNM aci-forms (bond lengths in pm and angles in degrees)

	Structure			
Parameter	**4**	**6**	**8**	**10**
C_1H_9	108.5	107.7	107.5	107.9
C_1N_3	147.7	131.5	132.1	144.9
C_1N_4	141.6	143.7	143.2	135.9
N_3O_5	134.5	141.7	144.6	138.0
N_3O_6	118.5	122.5	120.8	119.6
N_4O_7	125.1	123.0	122.7	129.3
N_4O_8	123.0	123.3	123.7	122.6
O_5H_2	99.3	97.7	97.6	98.3
$N_3C_1N_4$	107.1	124.6	122.4	103.9
$C_1N_3O_5$	112.4	116.2	112.7	114.8
$C_1N_3O_6$	130.7	126.2	132.0	126.5
$C_1N_4O_7$	116.8	120.3	120.1	111.9
$C_1N_4O_8$	118.1	113.8	113.6	125.1
$N_3O_5H_2$	100.0	104.8	105.0	104.6
$O_6N_3C_1N_4$	66.3	−171.8	5.2	−111.8
$O_8N_4C_1N_3$	−161.1	−159.51	−178.1	−170.3
$O_6N_3O_5H_2$	−178.9	85.1	−128.5	12.9

transition **3-4-5** is 139.8 kJ/mol. This energy corresponds to the energy of the double bond rupture.

Besides the **3-4-5** reaction pathway there is another alternative conformation transition—**3-8-9** (Fig. 3). The rotation of the O_5-H_2 group around the N_3-O_5 bond takes place in structure **3** in this reaction. The rotational angle is 150°. As a result we have structure **9**. The planar cycle $H_2O_5N_3O_6$ is realized in this structure. The rotation barrier is predicted to be nearly 1 kJ/mol. Structure **9** is higher in energy than **5** at 26.4 kJ/mol mol in spite of the small value of the enthalpy of activation (Table 2).

Structure **6** was characterized as a transition state for the reaction **5** → **7**. Rotation of the O_5-H_2 group by 180° about the C_1-N_3 bond takes place in **5** → **7** conformation transition. The rotation about the N_3-O_5 bond caused a simultaneous elongation of this bond from 135.9 pm (**5**, Table 3) to 141.7 pm (**6**, Table 4). The enthalpy of activation for this reaction is 51.7 kJ/mol.

Structure **9** is predicted to lie 6.6 kJ/mol below structure **7**. The transition **9** → **7** is realized by the rotation of the $H_2O_5N_3O_6$ group about the C_1-N_3 bond by 180°. Structure **10** corresponds to the TS of this conformation transition. The C_1-N_3 bond is elongated from 131.7 (**9**, Table 3) pm to 144.9 pm (**10**, Table 4). The activation barrier for this conformation transition **9-10-7** is 181.1 kJ/mol.

The difference in energy between conformers of DNM aci-form can be explained by the analysis of the atomic charges and the intramolecular distances. The presence of an intramolecular hydrogen bond in DNM aci-form can also be associated with sufficient decreasing of the formation enthalpies. Such an intramolecular hydrogen bond is realized in **5**. A positively charged hydrogen atom H_2 is located between two negatively

Table 5
Charge distribution in DNM aci-forms, a.u

	Structure			
Atom	**3**	**5**	**7**	**9**
C_1	0.137	0.163	0.186	0.185
H_2	0.426	0.464	0.431	0.430
N_3	0.352	0.362	0.341	0.339
N_4	0.436	0.436	0.427	0.430
O_5	−0.470	−0.461	−0.431	−0.473
O_6	−0.335	−0.370	−0.426	−0.385
O_7	−0.369	−0.460	−0.377	−0.371
O_8	−0.393	−0.370	−0.386	−0.391
H_9	0.216	0.236	0.235	0.236

charged oxygen atoms O_5 and O_7 (Fig. 3, Table 3). Charge distribution data are represented in Table 5.

The distance of the intramolecular hydrogen bond $H_2 \cdots O_7$ is 157.5 pm in **5**. Surprisingly large difference in energies between **3** and **9** can be explained by the Coulomb repulsion between hydrogen atoms $H_2 \cdots H_9$ in **3** (Fig. 3). The

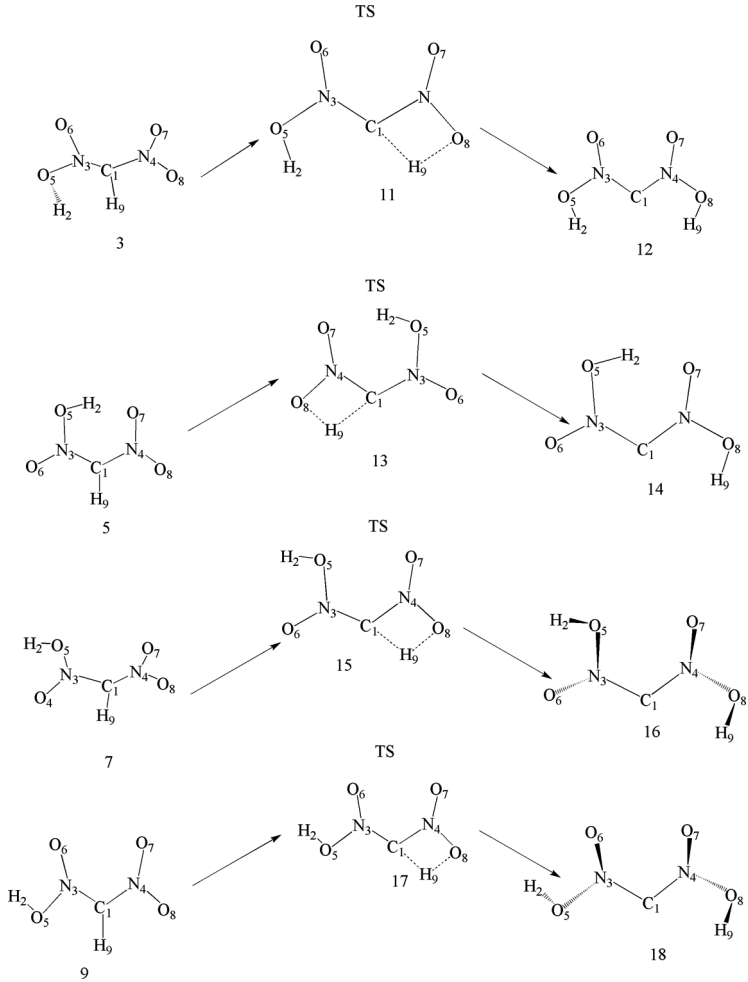


Figure 4. Pathways for DNM diaci-form formation.

distance between positively charged hydrogen atoms $H_2 \cdots H_9$ (Table 5) is 218.8 pm (Fig. 3, Table 3). Owing to this repulsion, the dihedral angle $O_6N_3O_5H_2$ in **3** is not planar (Fig. 3, Table 3). The value of this dihedral angle is −147.7°. As a result, the activation barrier of the conformation transition **3** → **9** is predicted to be very low (∼1 kJ/mol). Structure **3** transits to structure **9** and thereby the Coulomb repulsion seeks to zero.

The optimized conformers **7** and **9** have $H_2 \cdots O_6$ distances of 211.6 and 215.8 pm, respectively. Atomic charges of the oxygen atoms O_6 (Table 5, Fig. 3) concerning **7** and **9** are lower than

Table 6
Geometric parameters of TS for reaction of DNM diaci-forms formation (bond lengths in pm and angles in degrees)

	Structure			
Parameter	**11**	**13**	**15**	**17**
C_1N_3	133.4	135.4	132.6	132.8
C_1N_4	140.8	138.1	141.6	141.6
N_3O_5	140.4	138.9	141.0	139.9
N_3O_6	121.6	121.3	123.0	123.3
N_4O_7	120.4	123.4	120.5	120.4
N_4O_8	132.9	132.0	133.1	132.9
O_5H_2	97.9	99.7	98.0	97.9
C_1H_9	142.1	145.4	144.4	144.3
H_9O_8	125.2	124.1	122.1	122.8
$N_3C_1N_4$	117.1	117.5	119.6	115.5
$C_1N_3O_5$	113.7	121.6	118.3	111.7
$C_1N_3O_6$	131.4	123.7	125.8	131.5
$C_1N_4O_7$	134.6	133.9	136.2	135.1
$C_1N_4O_8$	101.2	103.2	100.7	101.0
$N_3O_5H_2$	103.9	106.1	100.4	101.2
$C_1H_9O_8$	104.4	103.3	104.8	101.0
$H_9O_8N_4$	81.3	81.3	82.3	82.1

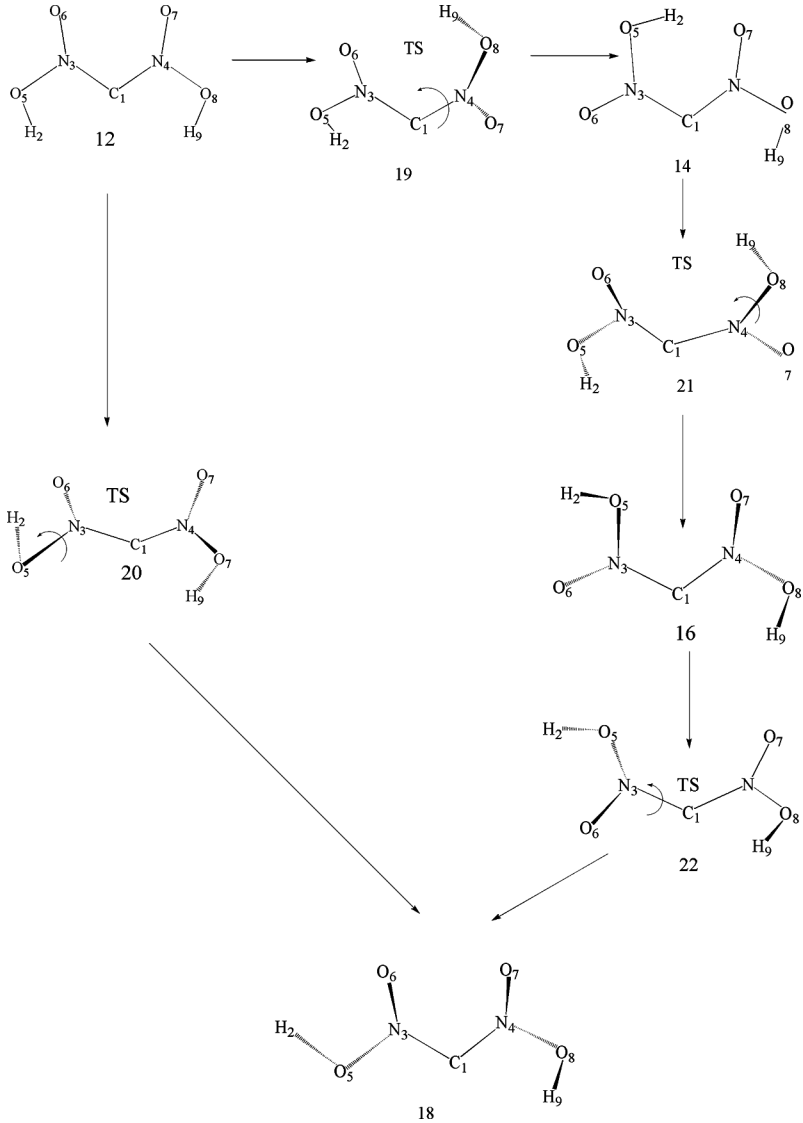


Figure 5. The conformation transition pathways in DNM diaci-form.

the atomic charge of O_7 in **5** (Table 5, Fig. 3). Therefore, there is no stabilizing intramolecular hydrogen bond in structures **7** and **9** as there was in **5.** As a result, structures **7** and **9** are predicted to be higher in energy than **5**.

We have also studied possible reaction pathways of DNM diaci-form formation form DNM aci-form (Fig. 4). Reactions of DNM diaci-form formation are realized by hydrogen atom

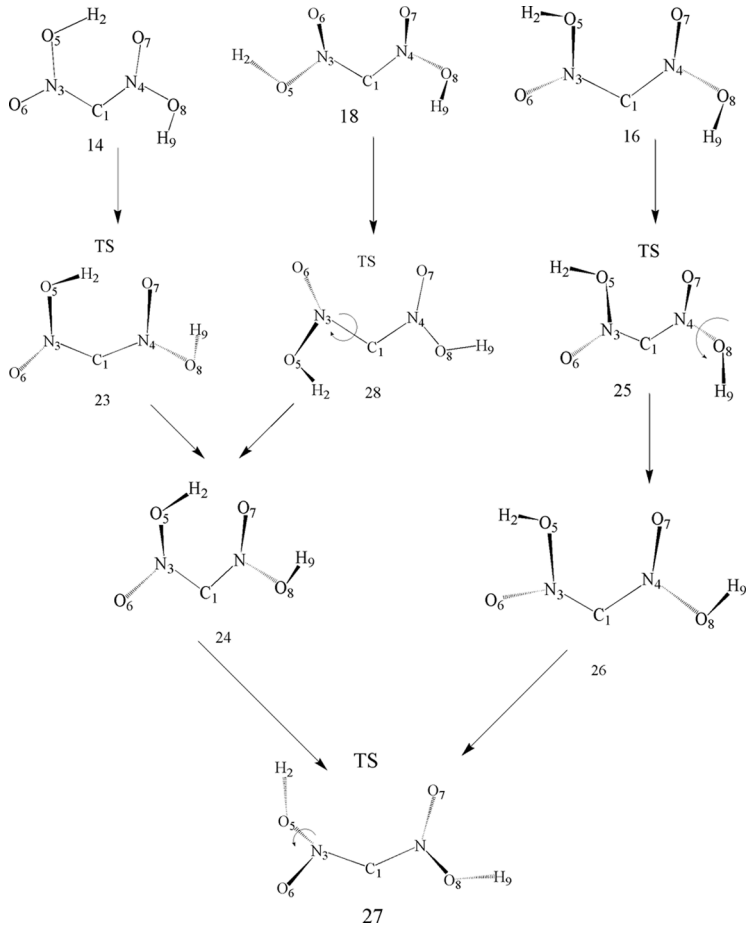


Figure 6. The conformation transition pathways in DNM diaci-form.

shift from carbon to oxygen in DNM aci-form conformations **3, 5, 7, 9**. As a result we have four different conformers of DNM diaci-form (Fig. 4).

Geometric parameters of TS optimized structures **11, 13, 15**, and **17** (Fig. 4) are given in Table 6.

Enthalpies of activation and enthalpies of reaction for the reactions of DNM diaci-form formation are represented in Table 2.

Activation barriers (Fig. 4) for these reactions do not differ much. The lowest activation barrier corresponds to the reaction

Table 7
Geometric parameters of DNM diaci-forms (bond lengths in pm and angles in degrees)

	Structure					
Parameters	**12**	**14**	**16**	**18**	**24**	**26**
C_1N_3	136.8	134.3	135.0	134.2	132.2	132.7
C_1N_4	136.8	140.0	133.2	136.0	138.9	132.5
N_3O_5	139.2	137.5	139.7	139.5	138.1	139.7
N_3O_6	121.3	125.7	121.6	123.1	127.4	123.4
N_4O_7	121.3	120.8	122.7	121.4	120.8	122.7
N_4O_8	139.2	137.2	141.7	139.3	138.2	142.1
O_5H_2	98.2	98.4	98.1	98.0	97.9	97.9
O_8H_9	98.2	101.1	97.9	98.2	100.4	97.9
$N_3C_1N_4$	110.4	111.5	116.3	111.9	112.0	117.9
$C_1N_3O_5$	111.0	113.2	112.3	111.3	113.4	112.1
$C_1N_3O_6$	134.2	134.4	132.9	132.5	132.5	131.4
$C_1N_4O_7$	134.3	120.9	126.2	133.0	122.2	127.3
$C_1N_4O_8$	111.0	124.7	118.2	112.0	122.8	116.6
$N_3O_5H_2$	101.6	101.5	102.5	101.5	101.8	101.4
$N_4O_8H_9$	101.1	104.4	100.9	102.0	103.3	100.9
$O_6N_3C_1N_4$	0	0	30.9	20.9	−8.9	33.6
$O_8N_4C_1N_3$	180.0	0	26.6	−161.3	−25.0	36.7
$H_2O_5N_3O_6$	−180.0	179.9	173.3	−1.6	−3.2	−0.7
$H_9O_8N_4O_7$	−180.0	179.9	0.5	174.0	160.1	1.4

5-13-14 (261.3 kJ/mol) and the highest to reaction **3-11-12** (272.4 kJ/mol). Reactions of DNM diaci-form formation are endothermic. These reactions can be realized only by heat consumption.

Structures **12, 14, 16, 18** can transit one to another. As it is easily seen in Figs. 5 and 6, the conformation transitions in DNM diaci-form are similar to conformation transitions in the DNM aci-form (rotation of O-N-O-H group about the C-N bond and rotation of O-H group about the N-O bond). A scheme of different possible transitions between structures **12, 14, 16, 18** is represented in Fig. 5.

We succeeded in optimizing two other structures of DNM diaci-forms **24** and **26** in addition to structures **12, 14, 16**, and **18** (Fig. 5). The scheme for these conformation transitions is shown in Fig. 6.

There are two possible channels for the reaction of DNM diaci-form **24** formation (**14-23-24** and **18-28-24**). Conformation transition **14-23-24** (Fig. 6) is realized by rotation of O_8-H_9 group about bond N_4-O_8 and **18-28-24** by rotation of the

Table 8
Charge distribution in DNM diaci-forms, a.u

	Structure					
Atom	**16**	**14**	**24**	**12**	**26**	**18**
C_1	0.120	0.093	0.171	0.043	0.211	0.118
H_2	0.427	0.431	0.429	0.424	0.423	0.422
N_3	0.341	0.308	0.284	0.329	0.311	0.302
N_4	0.317	0.329	0.333	0.329	0.324	0.338
O_5	−0.441	−0.427	−0.432	−0.441	−0.444	−0.442
O_6	−0.347	−0.449	−0.491	−0.334	−0.402	−0.387
O_7	−0.378	−0.293	−0.290	−0.334	−0.381	−0.338
O_8	−0.463	−0.459	−0.463	−0.441	−0.467	−0.441
H_9	0.425	0.465	0.457	0.424	0.424	0.428

Geometric parameters of TS structures for conformation transitions in DNM diaci-form (Figs. 5 and 6) are represented in Table 9.

Table 9
Geometric parameters of TS for conformation transitions in DNM diaci-forms (bond lengths in pm and angles in degrees)

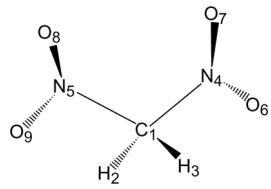
	Structure							
Parameters	**19**	**20**	**21**	**22**	**23**	**25**	**27**	**28**
C_1N_3	135.0	133.6	134.8	132.8	132.0	132.2	132.5	134.5
C_1N_4	130.5	136.4	132.9	129.8	139.9	132.9	132.2	129.7
N_3O_5	140.5	143.2	140.1	140.2	140.6	143.7	140.0	140.9
N_3O_6	120.5	122.4	121.5	122.2	126.6	122.4	123.4	120.6
N_4O_7	123.1	121.3	121.4	122.2	120.7	122.5	121.4	124.8
N_4O_8	141.9	139.3	146.3	142.0	137.4	142.2	146.7	141.0
O_5H_2	97.9	97.5	98.1	98.1	97.6	97.6	97.9	97.9

O_8H_9	97.8	98.1	97.6	97.8	101.0	97.9	97.5	97.8
$N_3C_1N_4$	121.1	112.9	117.5	125.6	112.0	118.9	119.3	121.0
$C_1N_3O_5$	116.8	111.7	112.5	114.1	131.9	112.2	112.4	116.7
$C_1N_3O_6$	128.6	132.5	132.7	128.9	122.3	131.5	131.1	128.7
$C_1N_4O_7$	132.1	132.2	126.9	131.7	122.2	127.7	128.3	131.8
$C_1N_4O_8$	114.1	112.4	118.7	114.5	121.9	115.9	116.8	112.6
$N_3O_5H_2$	104.3	104.2	102.6	102.2	104.6	103.3	101.4	104.5
$N_4O_8H_9$	103.7	102.2	104.0	103.9	102.8	101.1	103.7	100.3
$O_6N_3C_1N_4$	−100.4	−21.3	32.6	95.6	8.3	32.9	−35.2	−103.3
$O_8N_4C_1N_3$	179.8	158.7	27.9	−178.3	27.6	40.2	−38.6	−177.0
$H_2O_5N_3O_6$	−178.8	−90.8	171.0	−2.1	89.1	−99.4	−1.2	−176.7
$H_9O_8N_4O_7$	173.9	−172.3	−104.0	−179.9	158.8	1.82	104.9	2.6

O_6-N_3-O_5-H_2 group about the N_3-O_5 bond (Fig. 6). Activation barriers for these two conformation transitions are roughly similar.

Structure **25** is characterized as a true transition structure for the conformation transition **16-25-26** (Fig. 6). DNM diaci-form **24** can transit in **26** through TS **27** by O_5-H_2 group rotation about the C_1-N_3 bond (Fig. 6).

Table 10
Geometric parameters of DNM RC (bond lengths in pm and angles in degrees)



Parameter	B3LYP/6-31G(d)
C_1H_2	109.2
C_1N_4	156.1
C_1N_5	156.1
N_4O_6	123.3
N_4O_7	119.1
N_5O_8	119.1
N_5O_9	123.3
O_9H_2	274.5
O_6H_3	274.5
$N_4C_1N_5$	108.3
$C_1N_4O_6$	106.9
$C_1N_4O_7$	121.3
$C_1N_5O_8$	121.3
$C_1N_5O_9$	106.9
$O_7N_4C_1N_5$	32.3
$O_8N_5C_1N_4$	32.3

Geometric parameters of DNM diaci-forms **12, 14, 16, 18** (Fig. 5) and **24, 26** (Fig. 6) are represented in Table 7. Charge distribution is represented in Table 8.

Geometric parameters of TS structures for conformation transitions in DNM diaci-form (Figs. 5 and 6) are represented in Table 9. Activation enthalpies and enthalpies of reactions for these processes are collected in Table 2.

DNM diaci-form **14** and **24** are predicted to be lowest in energy. Six-membered cycles with the intramolecular hydrogen bond O_5-$H_2 \cdots O_7$ are realized in **14** and **24** analogous to **5**. But in **24** (Fig. 6) this cycle is not planar as it was in **5** and **14**.

Dinitromethane Radical Cation (DNM RC)

The stages for decomposition of DNM RC through aci-form formation are analogous to DNM. In further discussion we will use Figs. 1 and 3–6 and will add an index (+•). Activation enthalpies and enthalpies of reactions concerning aci-form and diaci-forms formations and different conformation transitions are represented in Table 2.

Table 11
Charge distribution in DNM RC diaci-forms, a.u

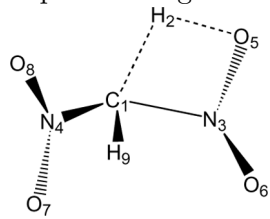
Atom	6-31G(d)
C_1	−0.110
H_2	0.338
H_3	0.338
N_4	0.518
N_5	0.518
O_6	−0.112
O_7	−0.189
O_8	−0.189
O_9	−0.112

The optimized structure of DNM RC (Tables 10 and 11) has both C-N bonds of 156.1 pm and corresponds to C_2 point group symmetry.

Optimized geometrical parameters of TS corresponding to the reaction of DNM RC aci-form formation are collected in Table 12.

The barrier for this reaction is 140.1 kJ/mol (Table 2), 85.5 kJ/mol lower than for the formation of DNM aci-form. The pathway for this reaction is **1**+●-**2**+●-**3**+●. DNM RC

Table 12
Geometric parameters of the transition state for reaction of DNM RC aci-form formation (bond lengths in pm and angles in degrees)



Parameter	B3LYP/6-31G(d)
C_1H_9	109.3
C_1H_2	141.7
H_2O_5	128.5
C_1N_3	148.6
C_1N_4	149.6
N_3O_5	131.3
N_3O_6	117.4
N_4O_7	119.8
N_4O_8	123.0
$N_3C_1N_4$	113.9
$C_1N_3O_5$	98.0
$C_1N_3O_6$	134.8
$C_1N_4O_7$	121.0
$C_1N_4O_8$	108.0

Table 13
Geometric parameters of DNM RC aci-forms (bond lengths in pm and angles in degrees)

	Structure							
Parameter	3+●	4+●	5+●	6+●	7+●	8+●	9+●	10+●
C_1H_9	108.4	108.7	108.5	108.6	108.4	108.5	108.4	108.6
C_1N_3	136.2	145.9	140.1	134.8	135.6	135.1	135.9	145.9
C_1N_4	144.9	147.2	144.8	144.5	144.7	144.9	144.5	145.3
N_3O_5	135.5	132.9	131.6	137.2	135.2	137.2	135.2	132.1
N_3O_6	121.2	117.9	120.9	122.6	121.8	122.1	121.6	118.3
N_4O_7	123.3	121.6	121.6	121.6	120.3	120.1	120.2	123.1
N_4O_8	120.1	121.9	124.4	122.0	123.2	123.3	123.3	121.3
O_5H_2	98.4	98.9	102.7	98.7	98.8	98.5	98.9	99.5
$N_3C_1N_4$	117.0	114.7	121.7	119.2	119.5	117.8	116.9	113.0
$C_1N_3O_5$	120.7	118.8	122.0	118.8	114.8	117.7	112.6	112.6
$C_1N_3O_6$	122.8	122.5	118.2	121.4	122.8	123.4	122.6	123.4
$C_1N_4O_7$	107.2	112.7	114.1	111.9	107.7	122.7	122.8	114.4
$C_1N_4O_8$	122.3	116.8	118.2	117.9	121.9	106.4	107.4	115.4
$N_3O_5H_2$	110.7	109.4	106.3	108.2	106.2	108.7	106.1	108.3
$O_6N_3C_1N_4$	2.6	75.9	−180	176.9	178.5	3.73	−2.2	−86.7
$O_7N_4C_1N_3$	101.1	162.2	180	−118.0	−97.0	79.7	80.6	−4.3
$O_6N_3O_5H_2$	−178.4	179.8	−179.9	107.2	−0.3	−121.3	−0.6	2.2

Table 14
Charge distribution in DNM RC aci-forms, a.u

	Structure							
Atom	3+●	4+●	5+●	6+●	7+●	8+●	9+●	10+●
C_1	0.248	0.916	0.319	0.317	0.299	0.275	0.290	0.247
H_2	0.485	0.0003	0.512	0.497	0.502	0.491	0.499	0.510
N_3	0.393	−0.028	0.393	0.335	0.392	0.352	0.390	0.412
N_4	0.459	−0.069	0.471	0.451	0.446	0.462	0.453	0.488
O_5	−0.362	0.008	−0.344	−0.393	−0.377	−0.391	−0.376	−0.307
O_6	−0.152	0.051	−0.134	−0.116	−0.203	−0.129	−0.199	−0.116
O_7	−0.192	0.085	−0.211	−0.251	−0.212	−0.214	−0.212	−0.309
O_8	−0.209	0.072	−0.360	−0.193	−0.194	−0.186	−0.192	−0.265
H_9	0.328	−0.036	0.354	0.353	0.347	0.340	0.346	0.340

aci-form formation is calculated to be exothermic. The energy of the DNM RC aci-forms **3**+●, **5**+●, **7**+●, and **9**+● (Table 13, Fig. 3) is calculated to be lower than DNM RC (1+●). Geometric parameters of transition states concerning conformation transitions are collected in Table 13.

DNM RC aci-forms **7**+● and **9**+● are calculated to be lower than **3**+● and **5**+● (Table 2). This can be explained by decreasing the positive charge of the carbon atom in **7**+● and **9**+● in comparison with structure **5**+● (Table 14). As a result, the repulsion between the carbon atom and two nitrogen atoms is decreased. In addition, intramolecular interaction $O_6 \cdots H_2$

Table 15
Geometric parameters of TS for reaction of DNM RC diaci-forms formation (bond lengths in pm and angles in degrees)

	Structure			
Parameter	11+●	13+●	15+●	17+●
C_1N_3	138.6	139.5	148.0	138.3
C_1N_4	147.5	147.0	137.8	146.3
N_3O_5	134.6	134.7	130.5	134.3
N_3O_6	120.9	120.8	118.4	121.3
N_4O_7	118.3	120.2	121.5	118.4
N_4O_8	130.4	128.5	135.3	130.9
O_5H_2	98.7	99.5	125.9	99.0
O_8H_9	128.0	126.5	140.9	126.6
H_9C_1	139.2	144.0	98.9	140.5
$N_3C_1N_4$	116.6	117.3	118.5	115.7
$C_1N_3O_5$	117.3	124.2	97.4	112.1
$C_1N_3O_6$	125.2	118.7	135.2	125.3
$C_1N_4O_7$	134.3	132.3	120.9	135.0
$C_1N_4O_8$	97.7	100.1	117.3	97.6
$N_3O_5H_2$	108.4	109.4	85.0	106.4
$N_4O_8H_9$	84.3	84.7	103.4	84.7
$O_8H_9C_1$	103.3	102.7	106.1	102.7

stabilizes structures **7**+● and **9**+●. Repulsion between hydrogen atoms H_2 and H_9 takes place in **3**+●.

Optimized geometric parameters of TS structures for reaction of DNM RC diaci-form formation of DNM RC diaci-form and TS structures concerning conformation transitions in DNM RC diaci-form are collected in Tables 15–17.

Charge distributions in DNM RC diaci-forms are represented in Table 18.

DNM RC diaci-form **26**+● is predicted to be lowest in energy (Fig. 6, Table 2). The activation barrier for reaction

Table 16
Geometric parameters of DNM RC diaci-forms (bond lengths in pm and angles in degrees)

	Structure					
Parameter	12+●	14+●	16+●	18+●	24+●	26+●
C_1N_3	138.8	135.4	137.2	136.8	133.3	135.0
C_1N_4	138.8	139.2	137.4	137.1	137.3	135.1
N_3O_5	134.9	134.0	134.9	134.9	134.0	135.1
N_3O_6	119.7	122.1	120.3	120.5	123.2	120.9
N_4O_7	119.7	119.4	120.2	119.9	119.6	120.6
N_4O_8	134.9	134.7	135.2	135.0	135.1	135.9
O_5H_2	98.7	98.8	98.7	098.9	98.9	98.8
O_8H_9	98.7	99.4	99.0	98.7	99.4	98.9
$N_3C_1N_4$	115.8	119.9	120.8	119.0	124.5	126.9
$C_1N_3O_5$	115.2	118.3	115.6	110.8	113.7	110.9
$C_1N_3O_6$	127.2	125.0	127.1	127.0	125.1	127.1
$C_1N_4O_7$	127.2	119.7	121.9	126.7	120.6	122.3
$C_1N_4O_8$	115.2	122.4	116.1	115.7	121.7	116.2
$N_3O_5H_2$	108.0	108.5	108.0	105.8	105.8	105.6
$N_4O_8H_9$	108.0	108.6	105.5	108.2	108.7	104.7
$O_6N_3C_1N_4$	29.1	−30.1	24.3	30.9	−19.3	18.4
$O_8N_4C_1N_3$	155.7	32.5	−42.1	−23.12	18.5	−19.6
$H_2O_5N_3O_6$	170.9	−173.6	172.6	−0.4	0.0	0.4
$H_9O_8N_4O_7$	−170.9	172.6	0.77	−172.9	176.7	0.1

Table 17

Geometric parameters of TS for conformation transitions in DNM RC diaci-forms (bond lengths in pm and angles in degrees)

	Structure							
Parameter	19+●	20+●	21+●	22+●	23+●	25+●	27+●	28+●
C_1N_3	136.5	134.6	136.1	136.3	131.8	133.4	135.0	135.6
C_1N_4	141.3	137.6	136.1	140.5	138.1	135.8	133.9	140.4
N_3O_5	134.3	138.6	134.4	134.7	137.1	138.8	134.5	134.3
N_3O_6	121.0	118.9	120.0	121.4	121.5	119.2	120.1	121.7
N_4O_7	117.9	118.7	185.5	118.6	118.3	119.4	119.0	118.0
N_4O_8	134.3	134.5	138.9	133.6	134.8	135.4	139.3	134.6
O_5H_2	97.9	97.7	98.0	97.8	97.8	97.7	98.2	98.1
O_8H_9	97.9	98.0	97.9	98.3	98.8	98.2	97.7	97.9
$N_3C_1N_4$	114.7	121.1	122.4	114.2	125.5	127.9	128.1	115.5
$C_1N_3O_5$	116.8	111.3	116.3	116.3	114.4	111.2	110.9	112.3
$C_1N_3O_6$	126.1	129.1	126.6	127.1	126.5	129.4	127.1	126.2
$C_1N_4O_7$	121.9	126.1	123.8	123.3	121.3	122.9	123.3	122.0
$C_1N_4O_8$	120.4	116.1	115.3	113.0	120.6	115.3	117.7	119.6
$N_3O_5H_2$	108.2	108.4	108.7	107.8	108.7	108.2	106.7	106.7

(*Continued*)

Table 17
Continued

	Structure							
Parameter	19+●	20+●	21+●	22+●	23+●	25+●	27+●	28+●
$N_4O_8H_9$	110.3	108.9	108.1	107.8	109.3	106.2	108.6	110.0
$O_6N_3C_1N_4$	−23.6	25.2	−13.1	5.9	−15.2	16.4	26.4	24.9
$O_7N_4C_1N_3$	−110.9	−22.0	−141.0	102.4	−166.9	162.7	167.7	106.1
$H_2O_5N_3O_6$	−176.3	101.9	−172.0	178.0	−103.5	102.1	1.6	−2.9
$H_9O_8N_4O_7$	−177.6	−175.3	101.0	0.3	176.7	−0.1	105.8	172.1

Table 18
Charge distribution in DNM RC diaci-forms, a.u

	Structure					
Atom	16+●	14+●	24+●	26+●	12+●	18+●
C_1	0.378	0.381	0.501	0.508	0.299	0.394
H_2	0.488	0.494	0.496	0.489	0.485	0.491
N_3	0.383	0.382	0.358	0.357	0.382	0.360
N_4	0.371	0.374	0.368	0.360	0.382	0.385
O_5	−0.348	−0.340	−0.352	−0.359	−0.347	−0.360
O_6	−0.187	−0.271	−0.333	−0.242	−0.170	−0.219
O_7	−0.210	−0.155	−0.163	−0.223	−0.170	−0.351
O_8	−0.368	−0.358	−0.366	−0.380	−0.347	−0.187
H_9	0.492	0.493	0.491	0.490	0.485	0.487

3+●-**11**+●-**12**+● is 172.2 kJ/mol and for reaction **3**+●-**11**+●-**12**+● it is 191.4 kJ/mol (Fig. 4, Table 2).

There is one more possible channel for DNM RC diaci-form formation. Migration of hydrogen atom H_9 from O_8 to O_6 in **14**+● (Fig. 5) is realized in reaction **14**+●-**29**+●-**30**+●. Optimized geometric structures of TS **29**+● and DNM RC diaci-form **30**+● are represented in Fig. 7. It is worth noting that this channel is not possible in the case of the neutral molecule of DNM.

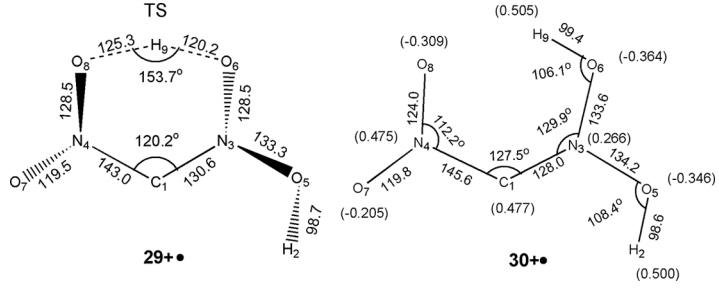


Figure 7. Optimized structure of TS **29**+● and diaci-form TS **30**+● (bond lengths in pm and angles in degrees).

The energy of TS **29**+● is calculated to be 12.3 kJ/mol higher than the energy of **14**+●. DNM RC diaci-form **30**+● is predicted to be lower at −4.5 kJ/mol than **14**+●.

Conclusion

Theoretical study of the tautomeric reactions in DNM and DNM RC was carried out with DFT B3LYP/6–31G(d) basis set. The activation barrier for the DNM aci-form formation is calculated to be 85.4 kJ/mol higher than for the DNM RC aci-form formation.

DNM RC aci-form formation is calculated to be exothermic. It is worth noting that for DNM this reaction is calculated to be endothermic.

According to calculated data, the structure of the aci-form with planar six-membered cycle is predicted to be lowest in energy in the case of a neutral molecule. The analogous structure corresponds to the energy minimum on the DNM diaci-form ground state.

For the DNM RC aci-form, the energy minimum on the PES corresponds to structures **7**+● and **9**+●.

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