Quantum chemistry study of the triplet nitrocompounds isomerization

Sergei D. Plechovitch, Alexandre D. Plechovitch, Sergei V. Zelentsov

Nizhnii Novgorod State University

Gagarin Ave., 23, Nizhnii Novgorod, 603950, Russia

Phone: +7 8314 659912

E-mail: zelentsov@chem.unn.ru

Summary. Isomerization reactions between nitroso oxide and nitrocompounds in both triplet and singlet states were studied with quantum chemistry methods. Calculated activation parameters for different paths of the isomerization reactions. It was shown that both in the singlet and triplet states the said reaction proceeds to the nitrocompound formation direction.

Keywords: isomerization, triplet state, singlet state, quantum chemical calculation, activation energy, uB3Lyp, CASSCF

Introduction

The idea about nitroso oxide existence has appeared for the first time in paper [1] where the reaction between molecular oxygen and nitrene in low-temperature glass-like matrices has been studied. Their decay gives nitro and nitroso compounds [1,2].However the mechanism of the reaction was not clear that time. It was only known the flash photolysis investigation of arylnitroso oxide reactions. It was shown that the kinetics of its delay could be described as the second order reaction that had the value close to diffusion limit. [10,11] The situation is only little changed up now: the mehanisms of the reactions are poorly studied. It is assumed [1,2] that nitroso oxides decay *via* bimolecular mode giving diperoxides as intermediates. For example, interaction of benzoyloxynitrene $PhCH_2ON$ with molecular oxygen proceeds via the 1,2,4,5-tetraoxo-3,6-diazinane [3] that according to the authors is the nitroso oxides (RONOO) recombination prouduct. However, according to kinetics studies (flash photolysis) consumption

of aromatic nitroso oxides obeys to the first order kinetics law and seems not to agree with the nitroso oxide dimerization [4,5]. Proposal about monomolecular isomerization of nitroso oxide into three-member cycle – dioxaziridine seems not to be true because of unsuccessful attempts to isolute the intermediate and high calculated activation barrier (about 150 –170 kJ/mol) for the cycle formation [6]. On the other hand it was proposed several times an idea of the nitroso oxides isomerization into nitrocompounds [7].

Investigation of the triplet nitrocompound – nitroso oxide mutual interconvertions is of great interest so as only the singlet state reaction systems have been studied [4,5,7,8,9] up to now. The reactions with involvement of the triplet species were very seldom studied. Quantum chemical calculations are the most appropriate methods for the situation.

The investigation of the said isomerization splits into solving of several concrete problems. At the first one has to be sure of the proper adequacy of the method used and of strategy chosen. At the second, it is desirable to find out geometries of both nitrocompounds and its isomerical nitroso oxide in the ground and excited states of different multiplicity. At the third, it is necessary to find geometries of the transitional states appropriate for the isomerization. And at last, one has to recover the reaction coordinate path to be sure of correctness of the calculated transitional state structure.

The calculation method selection

Table 1 shows the results of calculations of trans- HNOO molecule obtained with different methods and with different kinds of basis used. It was used CCSD(T)-3(Qf)/ccpVTZ, MP2/aug-cc-pVDZ, CASSCF(8,7)/aug-cc-pVDZ, B3LYP/6-311G, CASPT2(8,7)/aug-cc-pVDZ, and CASSCF(8,8)/6-31+g(d). As it was proper to proposed the CASSCF(8,8)/6-31+g(d) method was the best due to results obtained.

Table 1 Comparison of different methods usage for the *trans*-HNOO calculation

Method	r(O—O), nm	r(N—O), nm	r(N—O)—r(O—O), nm
CCSD(T)-3(Q_f)/ccpVTZ**	0.1286	0.1306	0.0200
MP2/aug-cc-pVDZ***	0.1263	0.1382	0.1190
CASSCF(8,7)/aug-cc-pVDZ ***	*0.1300*	*0.1310*	*0.0010*
UB3LYP/6-311G*	*0.1348*	*0.1315*	*-0.0033*
CASPT2(8,7)/aug-cc-pVDZ ***	*0.1303*	*0.1319*	*0.0016*
CASSCF(8,8)/6-31g +(d)*	*0.1315*	*0.1322*	*0.0007*
CASSCF(8,7)/aug-cc-pVDZ ***	*0.1300*	*0.1310*	*0.0010*
CASSCF(8,7)/aug-cc-pVTZ***	*0.1297*	*0.1306*	*0.0009*

* This work.
** *DeKock, R.L.; McGuire, M.J.; Piecuch, W.D.; et al.* // J. Phys. Chem. A. 2004. V. **108**. P. 2893 – 2903.
*** Talipov M.R.; Ryzhkov A.B.; Khursan, S.L; Safiullin, R.L.; et.al.// J.Struct. Chem. A. 2006. V. **47** .6. P.1062-1069.

Results and their discussion

Isomerizations in the system of nitromethane – its isomeric nitroso oxides. We have studied niromethane family reactions both in the singlet and triplet states using CASSCF(8,8)/6-31+g (d). The results obtained are gathered in Tables 2-4.

Investigation of the reaction for the singlet state molecules has revealed an increase of the N – O length from 0.1261 up to 0.1314 nm for *trans* – isomer and from 0.1261 up to 0.1300 nm - for the *cis*- isomer. For the triplet state molecules the corresponding value are from 0.1358 up to 0.1530 nm in the case of *trans*-isomer and from 0.1358 up to 0.1514 nm – in the case of *cis*-

isomer. There has place a decrease of electronic densities on the oxygen atoms and its increase on the nitrogen atom of the nitroso oxide. Such a behavior could be traced for both the singlet and triplet state both *cis*- and *trans*-isomers that should produce increase of reactivity in the electrophilic attacks.

Due to the data shown in the table there observes a symmetrical deformation vibration at $1129.1i$ cm^{-1} being the critical one for the reaction of nitromethane $\rightarrow$ its *trans*-isomeric nitroso oxide. It is the only vibration having an imaginary frequency. In the case of the same reaction for the triplet state molecules there has place a deformational vibration with the only imaginary frequency at $93.691i$ cm^{-1}. In the case of the nitromethane $\rightarrow$ nitroso oxide reaction proceeding with the singlet state molecules involvement the critical deformational vibration is at $817.001i$ cm^{-1} for *trans*-nitroso oxide and the critical torsion vibration at $173.00i$ cm^{-1}. The main participants of the vibrations are methyl and nitroso groups. From the images shown on the Figs. 1 and 2 it is evident that the critical vibrations are directed to the transition states geometries. In addition, successful recovery of the reaction path points out to correctness of the calculations made. From the Figs. 1 and 2 it is evident that in the case of the triplet state the reaction can proceed to both forward and backward direction (the activation energies are of 1.54 and 6.43 kcal/mol respectfully). However it is hardly possible in both directions for the singlet state molecules (it could be realized at elevated temperatures) because of high values of activation barriers (being of 31.15 and 39.87 kcal/mol for forward and backward directions respectfully). From the data mentioned one can jump to the conclusion that the isomerization reactions have the only direction – from nitroso oxide into nitrocompound [8].

Table 2. Nitromethane, corresponding N-nitroso oxide and their transition state

Property[*]	Nitroso oxide isomer	Nitrocompound	Nitroso oxide	Transition state
Singlet state S_0				
E, a.u.	*Trans*	-243.79756157	-243.72178555	-243.67210967
μ, D		3.8916	3.7101	2.9582
E, a.u.	*Cis*	-244.79756157	-243.72603435	-243.66245958
μ, D		3.8916	2.5580	2.3327
Triplet state T_1				
E, a.u.	*Trans*	-243.71964371	-243.69128428	-243.68881503
μ, D		3.0567	2.9696	2.9533
E, a.u.	*Cis*	-243.71964371	-243.68544003	-243.67518027
μ, D		3.0567	2.6800	2.6367

[*] - E – electronic energy of a molecule (a.u.) and μ – its dipole moment (in D).

Table 3. Activation energies (E_a) of the nitromethane isomerization into the corresponding N – nitroso oxide

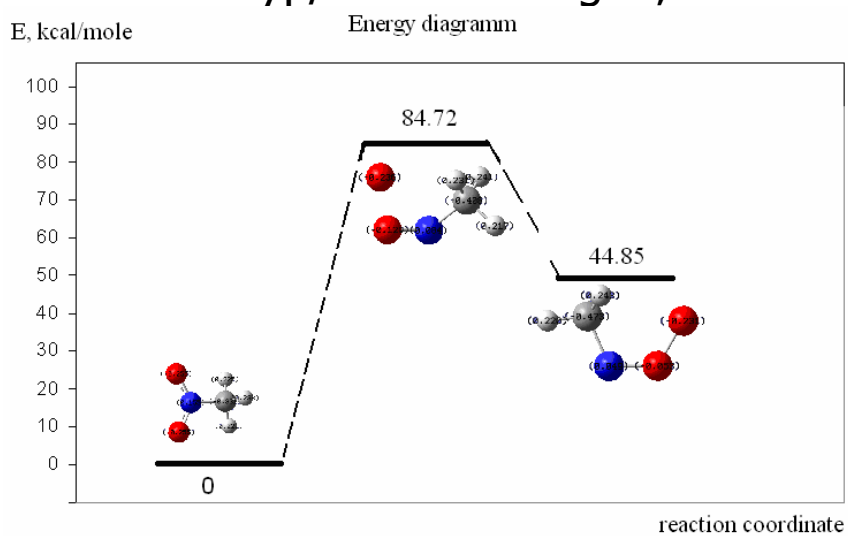| Nitroso oxide isomer	E_a, kcal/mol	
	The forward reaction	The backward reaction
The ground singlet state S_0		
Trans	78.66	31.15
Cis	84.72	39.87
The excited triplet state T_1		
Trans	19.33	1.54
Cis	27.88	6.43
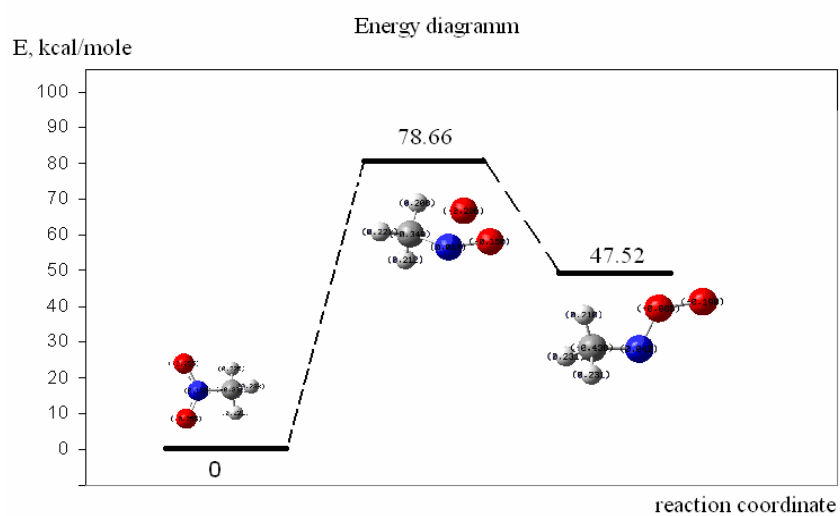
Fig. 1 Energy reaction diagram for transformation of nitromethane into nitroso oxide in the singlet state
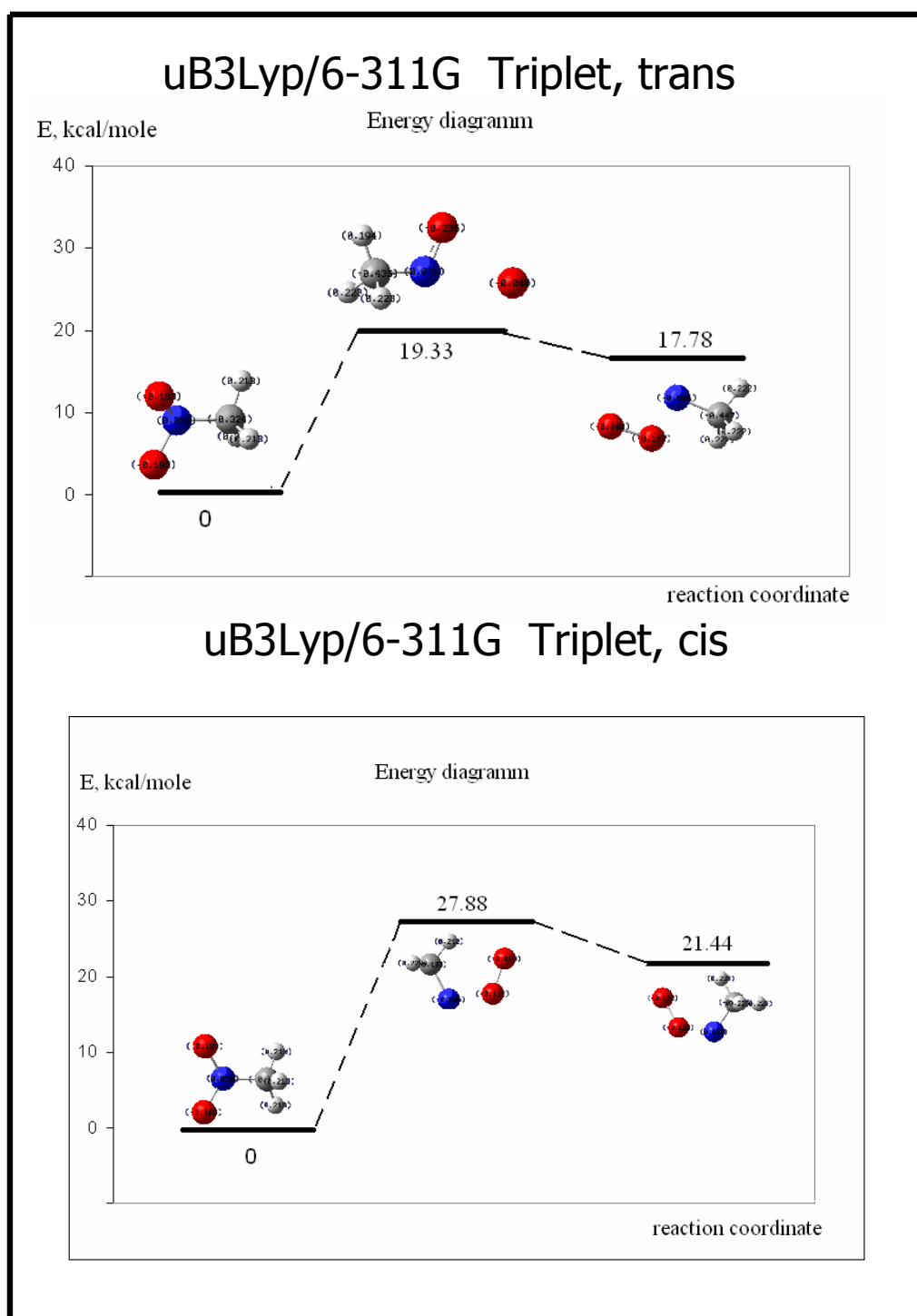
Fig. 2 Energy reaction diagram for transformation of nitromethane into nitroso oxide in the triplet state

Table 4 Geometries and electronic density distribution in the compounds studied

Compound	Multiplicity	r(O—O),nm	r(N—O), nm	Q(N)	Q(O^1)	Q(O^2)	Q(C)	Spin density
Nitromethane								
RNO$_2$	1	0.2239	0.1262	0.156	-0.255	-0.255	-0.331	0
	3	0.2198	0.1358	0.500	-0.183	-0.183	-0.324	O(1) 1.008 O(2) 0.501 N(3) 0.493
RNOO	1	0.1363	0.1314	0.042	-0.086	-0.190	-0.438	0
	3	0.1.370	0.1530	-0.004	-0.167	-0.048	-0.447	O(1) 0.222 O(2) 0.827 N(3) 0.927

trans-RNOO-TS	1	0.1884	0.1352	0.063	-0.150	-0.206	-0.349	0
	3	0.2625	0.1242	0.711	-0.235	-0.040	-0.435	O(1) -0.085 O(2) 1.568 N(3) 0.479
cis-RNOO	1	0.1392	0.1306	0.049	-0.053	-0.231	-0.473	0
	3	0.1377	0.1514	0.013	-0.123	-0.112	-0.461	O(1) 0.155 O(2) 0.975 N(3) 0.854
cis- RNOO -TS	1	0.1543	0.1353	0.084	-0.129	-0.236	-0.408	0
	3	0.1350	0.1617	-0.006	-0.112	-0.093	-0.489	O(1) 0.153 O(2) 0.884 N(3) 0.923

Table 5. Critical vibrations in the reactions studied*.

Nitromethane		
	Cis – transition state	*Trans* – transition state
singlet		
triplet		

*) Arrows are displacement vectors for the vibrations

Isomerization of nitrobenzene into N-nitroso oxides

Tables 6-8 contain the results of the quantum chemical calculations of nitrobenzene and its isomeric N-nitroso oxides with CASSCF(8,8)/6-31 +g(d) method. It was found out that the N-O bond length in the singlet trans-isomers becomes larger and increases from 0.1260 up to 0.1320 nm in the case of *trans*-isomer and from 0.1260 up to 0.1310 nm – for *cis*- isomer. In the case of the triplet state molecules the corresponding changes are of from 0.1350 up to 0.1520 nm in the case of *trans* – isomer and from 0.1353 up to 0.1495 nm – for *cis*-isomer. In addition, there has place decrease of the electron density on oxygen atoms and its increase on the nitrogen atom. The latter can be traced in both multiplicity states for both *cis*- and *trans*-isomer.

Due to the data presented in Table 9 in the case of *trans* - phenylnitroso oxide we observe symmetrical deformation vibration at 795.06i cm^{-1}.In the case of the triplet *trans*-isomer there has place a torsian vibration at 63.10i cm^{-1}. For *cis*-isomer in the singlet state we observe a tortian vibration having an imaginary frequency of 99.60i cm^{-1} and at 63.06i cm^{-1} in the case of the triplet *trans*-isomer.

Activation energies of the nitrobenzene – phenyl-N-nitroso oxide isomerization are shown in the Table 7. Ub3lyp/311G method was used for energy optimization in the case. Having in mind data shown on Figs. 3 and 4 one can conclude that the reaction proceeds towards the nitrocompound formation. So, the activation energy for transformation of trans-nitroso oxide molecule into nitrobenzene state is 63.81 kcal/mol in the singlet and 22.35 kcal/mol – in the triplet state. For the *cis*-nitroso oxide – nitrobenzene reaction the corresponding values are 23.50 and 60.00 kcal/mol respectively.

Thus, comparison of the data presented leads us to conclusion that the isomerization of nitrocompound into nitroso oxide gives an increase of bond lengths and an increase of the electronic density at nitrogen atom.

Table 6. Nitrobenzene, corresponding N-nitroso oxide and their transition state [*)]

Property[**)]	Nitroso oxide isomer	Nitrocompiound	Nitroso oxide	Transition state
Singlet state S$_0$				
E, a.u..	*Trans*	-436.73020785	-436.62844226	-436.5250090
μ, D		5.1289	6.0793	4.0394
E, a.u.	*Cis*	-436.73020785	-436.63454345	-436.71776024
μ, D		5.1289	5.4864	4.5372

Triplet state T_1				
E, a.e.	*Trans*	-434.20253810***	-434.16689130***	-434.18129500***
μ, D		2.9839	3.4999	3.4265
E, a.e.	*Cis*	-436.65343192	-436.61595046	-436.65166740
μ, D		3.8054	5.0417	4.2341

*) The data obtained with the ub3lyp/6-311g method.

**) - E – electronic energy of a molecule (a.u.) and μ – dipole moment of the particle (in D).

***) The data obtained with the CASSCF(8,8)/6-31g +(d) method

Table 7. Activation energies (E_a) of the nitrobenzene isomerization into the corresponding N – nitroso oxide

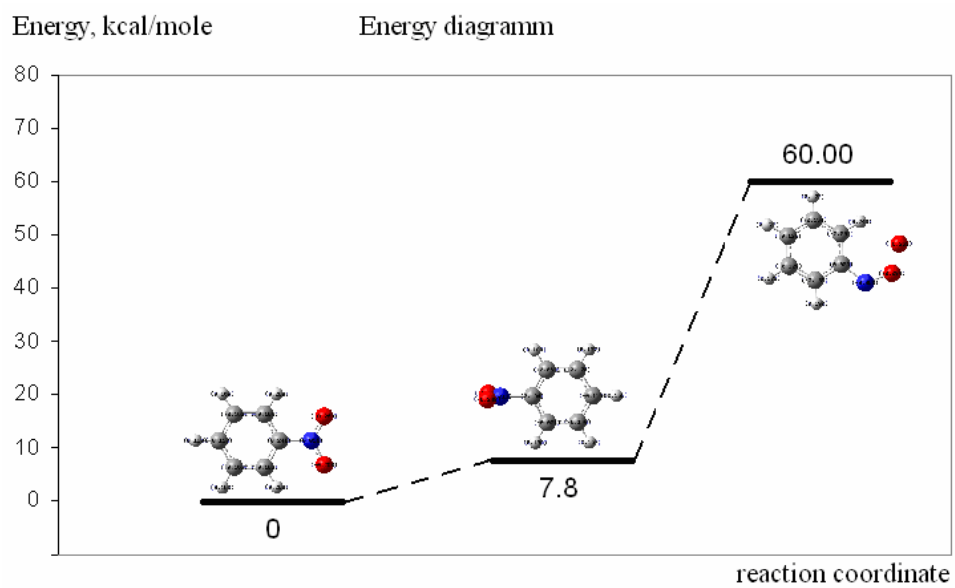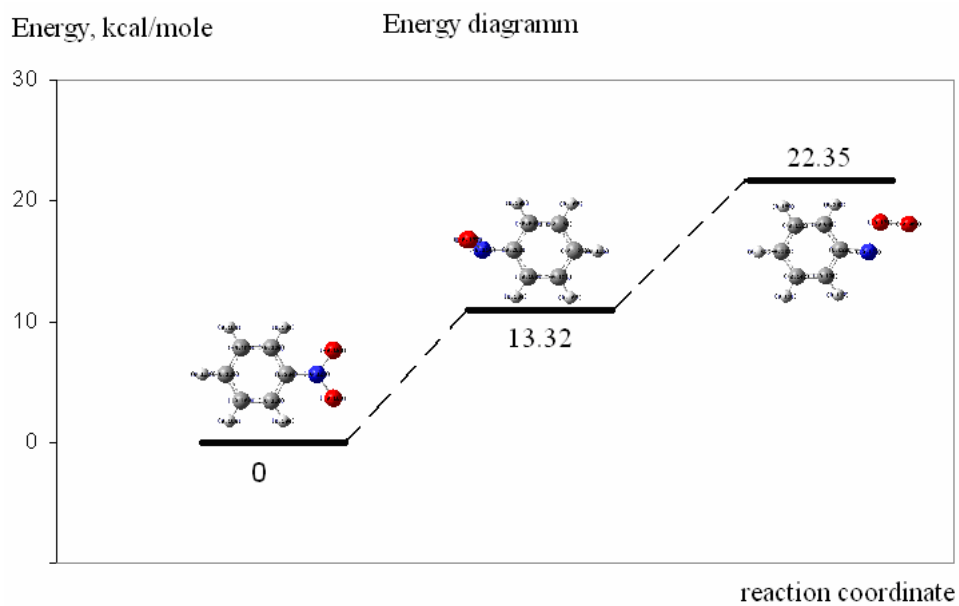| Nitroso oxide isomer	E_a, kcal/mol	
	The forward reaction	The backward reaction
The ground singlet state S_0		
Trans	128.67	63.81
Cis	72.00	60.00
The excited triplet state T_1		
Trans	0.00	22.35
Cis	67.46	23.50
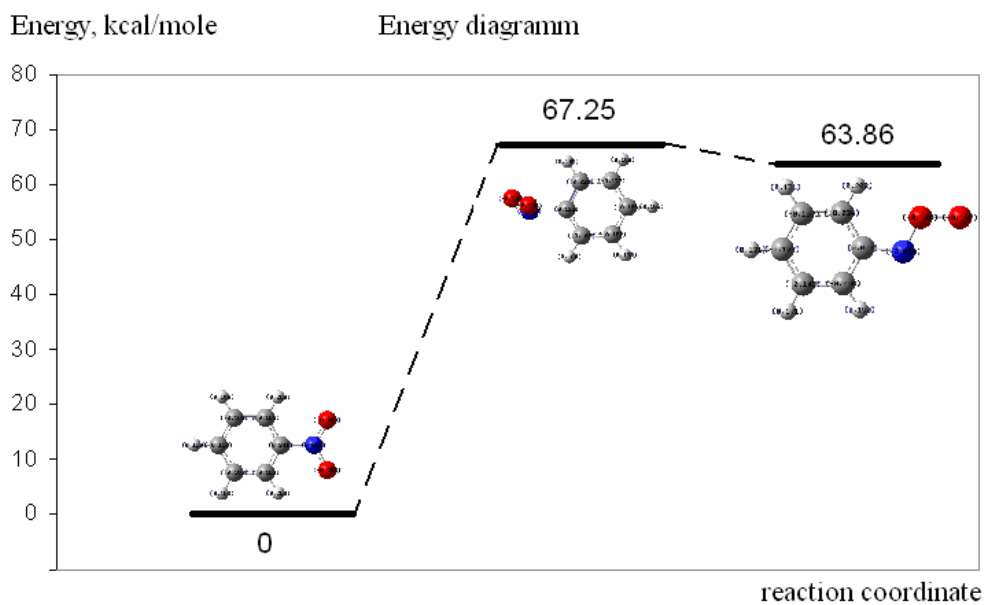
Fig. 3 Energy reaction diagram for transformation of nitrobenzen into nitroso oxide in the singlet state

uB3Lyp/6-311G Triplet, trans

Energy, kcal/mole Energy diagramm

30

22.35

20

13.32

10

0

0

reaction coordinate

uB3Lyp/6-311G Triplet, cis

Energy, kcal/mole Energy diagramm
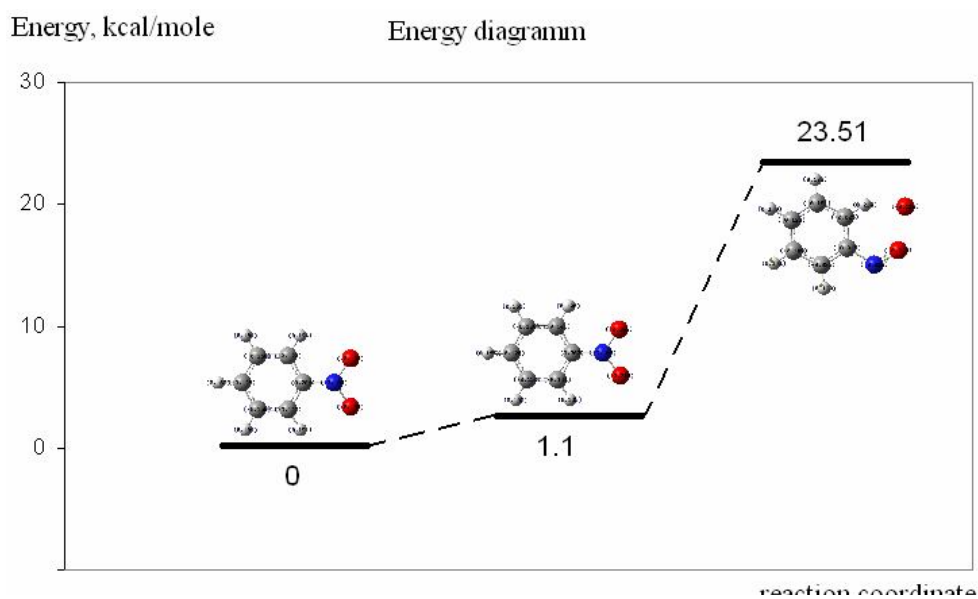
30

23.51

20

10

1.1

0

0

reaction coordinate

Fig. 4 Energy reaction diagram for transformation of nitrobenzene into nitroso oxide in the triplet state

Table 8 Geometries and electronic density distribution in the compounds studied

Compound	Multiplicity	r(O—O),nm	r(N—O), nm	Q(N)	Q(O^1)	Q(O^2)	Q(C)	Spin density
Nitrobenzene								
RNO$_2$	1	0.2232	0.1266	0.014	-0.268	-0.268	0.241	0
	3	0.2202	0.1353	-0.109	-0.183	-0.183	0.284	O(1) 0.769 O(2) 0.769 N(3) 0.350
trans- RNOO	1	0.1372	0.1326	-0.050	-0.120	-0.192	0.007	0
	3	0.1361	0.1523	-0.129	-0.171	-0.060	0.028	O(1) 0.243 O(2) 0.596 N(3) 1.066
trans-RNOO - TS	1	0.2240	0.1263	0.013	-0.248	-0.248	0.184	0

TS	3	0.2189	0.1360	-0.114	-0.177	-0.177	0.202	O(1) 0.624 O(2) 0.876 N(3) 0.384
cis- RNOO	1	0.1403	0.1315	-0.063	-0.084	-0.263	0.009	0
	3	0.1377	0.1495	-0.103	-0.131	-0.121	0.008	O(1) 0.341 O(2) 0.597 N(3) 0.571
cis- RNOO - TS	1	0.2240	0.1263	0.013	-0.248	-0.248	0.184	0
	3	0.2190	0.1360	-0.114	-0.177	-0.177	0.202	O(1) 0.754 O(2) 0.754 N(3) 0.370

[*)]- RNO_2 - nitrocompound, RNOO – nitroso oxide, RNOO – TS – the isomerization transition state

Table 9. Critical vibrations in the reactions studied[*]

Nitrobenzene		
	Cis- transition state	*Trans*- transition state
singlet		
triplet		

[*] Arrows are displacement vectors for the vibrations

Conclusion

Thus, we have performed modeling of isomerization of nitroso oxides into nitrocompounds and of its reversed reaction $R-NO_2 \leftrightarrow R-NOO$ in the both singlet and triplet states, with the CASSCF(8,8)/6-31+g(d) and uB3Lyp/6-311g methods. It was shown that both in the singlet and triplet states the said reaction proceeds to the nitrocompound formation direction. In the course of the isomerization from nitrocompounds into nitroso oxides there has place an increase of the bond length and of electronic density on the nitrogen atom.

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