Physical Chemistry

Conformational stability of peroxynitric acid molecule and the barriers to internal rotation about the O—O and N—O bonds

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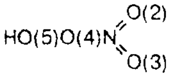
The structure of conformers and potential curves of the internal rotation (PCR) about the O—O and N—O bonds in peroxynitric acid (PNA) were calculated by the unrestricted Hartree—Fock—Roothaan method. The standard valence-split 6-31G and 6-31G* basis sets were used. The presence of two maxima on every curve has been shown. To refine the values of barriers to the internal rotation in the regions of minima and maxima of PCR, calculations taking into account the electron correlation energy have been carried out at the second- and fourth-order Møller-Plesset level of perturbation theory (MP2 and MP4, respectively). At the MP4/6-61G* level of approximation, the barriers to the rotation about the O—O bond are equal to 8.6 kJ mol^{-1} and 14.7 kJ mol^{-1}, and both barriers to the rotation about the N—O bond are equal to 33.5 kJ mol^{-1}. The results are compared with those published for PCR in hydrogen peroxide and peroxynitric acid.

Key words: peroxynitric acid, *ab initio* calculations, conformational analysis, barriers to internal rotation.

Peroxynitric acid  $HO(5)O(4)N\begin{smallmatrix}O(2)\\O(3)\end{smallmatrix}$ (PNA) is an inorganic peroxy acid, which can be considered as a mixed anhydride of two acids, HOOH and $HONO_2$, or as the first member of the homologous series of peroxy nitrates $ROONO_2$ (R = H).[1] The possibility of the formation of PNA as a long-lived complex $HO_2^{\cdot} \cdot NO_2^{\cdot}$ in the atmosphere and the importance of this complex as a source of $HO_2^{\cdot}$ and $NO_2^{\cdot}$ radicals have been considered previously.[2] The formation of PNA in the gas phase upon the photolysis of a mixture of H_2, O_2, and NO_2 was confirmed by the chemiluminescent method,[2,3] whereas its direct identification in the products of mixing Cl_2, H_2, and NO_2 with the air irradiated by UV light was achieved by IR spectroscopy.[4] Regardless of its importance from the viewpoint of the chemistry of atmosphere, PNA is an interesting molecule for its structural chemistry. Along with the conformational mobility due to the rotation about the O(5)—O(4) bond, the rotation about the

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N—O(4) bond as well as additional nonvalent interactions due to substitution of the nitro group for one H atom are also possible in HOOH. The rotation about the O—NO_2 bond also occurs in various esters of nitric acid. Thus, the resulting data allow one to make an estimate of the conformational mobilities of the molecules of these esters and those of other compounds containing the O—NO_2 groups. Because of the high instability of PNA, its geometric parameters were not studied experimentally. A theoretical study of the structure of PNA was first performed by the semiempirical MINDO/3 method[5] as well as by the *ab initio* method using the minimum STO-3G basis set. The *ab initio* quantum-chemical calculations of PNA in the 6-31G basis set as well as determination of the geometry of its ground state and spectra of excited states have also been carried out.[6] No conformational analysis of PNA was performed previously, except for attempts to estimate changes in its full energy[5,6] at four dihedral interplane HOON angles multiple of 90°. However, one can estimate neither position nor height of the barriers to rotation without tracing the potential curves of internal rotation (PCR). The rotation about the N—O(4) bond as well as values of the geometric parameters in the case of rotation about the O(5)—O(4) and N—O(4) bonds in PNA have never been investigated. The relationship between the barriers in the case of rotation about both these bonds is still unclarified.

These values allows one to make a quantitative estimate of the conformational stability of the PNA molecule and, hence, the equilibrium ratio of the conformers, and their plausible contribution to spectral characteristics and reactivity. The conformational analysis of H_2O_2 and several of the simplest organic peroxides was performed by *ab initio* methods.[7–9]

In this work, a theoretical study of the structure and reactivity of PNA have been performed. The *ab initio* calculations of PCR about the O(5)—O(4) and N—O(4) bonds have also been carried out and changes in the geometric parameters due to internal rotation have been analyzed.

Procedure of Calculation

The calculations were carried out on a CONVEX-C210 computer using the GAUSSIAN-82 program. The standard valence-split 6-31G and 6-31G* basis sets were used. The calculations of both PCR were carried out in the framework of the unrestricted Hartree—Fock—Roothaan (UHF) method in the 6-31G basis set. The potential curves of internal rotation about the O(5)—O(4) bond were calculated at fixed values of dihedral angle Q (HO(5)O(4)N), which varied from 0 to 360° with an increment of 10°, using optimized values of the rest of geometric parameters of PNA. The values of angle Q corresponding to minima and maxima of the total energy (E_{tot}) for a given PCR were refined by parabolic approximation using three points in the vicinity of each minimum and maximum. Optimization of the rest of structural parameters of PNA was repeatedly performed in the same (UHF/6-31G) approximation at a fixed value of the angle Q. The potential curves of internal rotation about the N—O(4) bond were calculated analogously as functions of the dihedral angle τ (O(5)O(4)NO(3)), which varied from 0 to 360° with an increment of 10°. The electron density distribution at the minima and maxima of both PCR were investigated in the framework of the Mulliken analysis of populations. Then the calculations of E_{tot} for the values of Q and τ corresponding to minima and maxima of E_{tot} on the PCR were carried out in the UHF/6-31G*, MP2/6-31G*, and MP4/6-31G* approximations using fixed values of the parameters optimized in the UHF/6-31G approximation. The results of the calculations of the PCR are presented in Table 1 and in Fig. 1, and the refined values of E_{tot} at the minima and maxima are listed in Table 2.

Results and Discussion

It has been shown previously[6] that the geometric parameters of the ground state of PNA, optimized in the UHF/6-31G, UHF/6-31G*, and MP2/6-31G approximations, are in qualitative agreement with each other. Taking into account the correlation energy in the MP2/6-31G approximation, the bond lengths in this molecule are increased by ~3% as compared to those calculated in the UHF/6-31G approximation, except for the N—O(4) bond, where the discrepancy amounts to ~20%. It was noted[6] that the experimental value of

Table 1. Geometric parameters and total energies E_{tot} for the HO_2NO_2 molecule optimized in the UHF/6-31G approximation for the fixed values of angle Q (HO(5)O(4)N) in the case of rotation about the O(5)—O(4) bond and those for the fixed values of angle τ (O(5)O(4)NO(3)) in the case of rotation about the N—O(4) bond

Q/	d/Å					φ/deg					τ/deg	E_{tot} + 353
deg	NO(2)	NO(3)	O(4)N	O(5)O(4)	HO(5)	O(3)NO(2)	O(4)NO(3)	O(5)O(4)N	HO(5)O(4)	O(4)NO(3)O(2)		(au)
						Rotation about the O(5)—O(4) bond						
0.0	1.222	1.192	1.399	1.449	0.969	129.3	113.6	112.6	105.7	180.0	180.0	−0.990022*
87.5	1.206	1.199	1.418	1.426	0.960	130.0	112.4	110.3	104.8	177.1	157.3	−0.994077**
180.0	1.200	1.208	1.396	1.451	0.961	129.7	111.3	109.4	99.1	180.0	180.0	−0.990112*
272.5	1.206	1.199	1.418	1.426	0.960	130.0	112.4	110.3	104.8	182.9	202.7	−0.994077**
						Rotation about the N—O(4) bond						
115.3	1.207	1.199	1.419	1.451	0.961	129.7	115.9	106.0	101.9	177.8	73.9	−0.986766*
87.8	1.206	1.199	1.418	1.426	0.960	130.0	112.4	110.3	104.8	177.1	157.4	−0.994077**
114.6	1.119	1.207	1.419	1.451	0.961	129.7	114.3	106.0	102.0	182.2	252.0	−0.986767*
87.6	1.199	1.206	1.418	1.426	0.960	130.0	117.5	110.3	104.8	183.0	334.9	−0.994077**

*Maximum. **Minimum.

Table 2. Relative energies (kJ mol^{-1}) of conformers of $HOONO_2$ corresponding to the maxima and minima on the curves of potential energy of internal rotation about the O—O (angle Q) and O(4)—N (the angle τ) bonds calculated in different approximations (the geometric parameters were taken from Table 1)

Method of calculation	Maxima		Minima	
	Q/deg			
	0.0	180.0	87.5	272.5
UHF/6-31G	10.6	10.6	0	0
UHF/6-31G*	10.2	13.8	0	0
MP2/6-31G*	7.9	14.3	0	0
MP4/6-31G*	8.6	14.7	0	0
	τ/deg			
	73.9	252.0	157.4	334.9
UHF/6-31G	19.2	19.2	0	0
UHF/6-31G*	30.8	30.7	0	0
MP2/6-31G*	36.1	36.0	0	0
MP4/6-31G*	33.5	33.4	0	0

the N—O(4) bond length found from the microwave spectra (1.50—1.53 Å) is much closer to the value calculated in the UHF/6-31G (1.418 Å) approximation than to that calculated in the MP2/6-31G approximation (1.714 Å). For this reason, the UHF/6-31G approximation used in the present work to optimize the geometry of PNA in calculating the PCR can be considered as reasonably correct and allows one to obtain reliable results with moderate expenditure of computing time.

As can be seen from Fig. 1, the PCR about each of the O(5)—O(4) and N—O(4) bonds have two maxima.

The maxima and minima on the PCR corresponding to the rotation about the O(5)—O(4) bond correspond to a symmetric spatial arrangement of the HO_2 and NO_2 groups. This leads to a quasidegeneration of the E_{tot} for two minima. Both maxima correspond to the value of the angle Q, which virtually is equal to 0 and 180°, *i.e.*, to the *cis*- and *trans*-positions of the H atom relative to the N atom. In both maxima, all atoms of the PNA molecule are in the same plane: the dihedral angles O(4)NO(3)O(2) and O(5)O(4)NO(3) are equal to 180°.

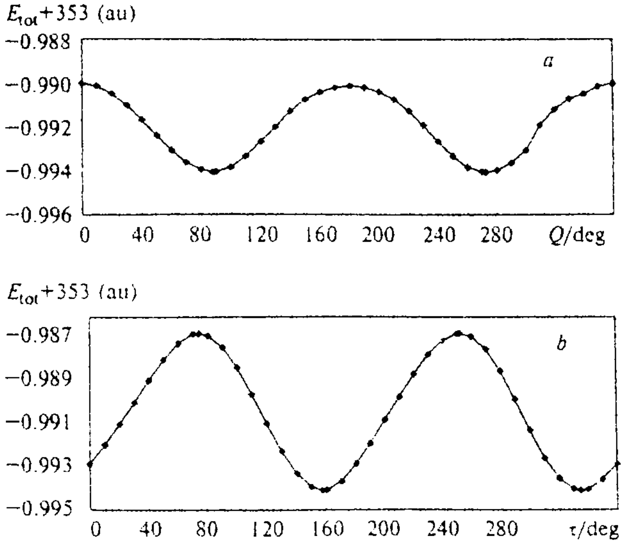


Fig. 1. Potential curves (PCR) corresponding to the internal rotation about the O(5)—O(4) (*a*) and N—O(4) (*b*) bonds calculated in the UHF/6-31G approximation.

As can be seen from Table 1 and Fig. 1, the N—O(2) bond length is the largest (1.222 Å) for the *cis*-conformer (Q = 0°) and the smallest (1.206 Å) for the *trans*-conformer (Q = 180°) in the case of rotation about the O(5)—O(4) bond. On the contrary, the N—O(3) bond length has its minimum and maximum value (1.192 Å and 1.208 Å) at Q = 0° and Q = 180°, respectively. Thus, in the case of the shortening of one of these bonds the synchronous lengthening of the other occurs, so that both bonds suffer the greatest changes at the top of the rotation barriers. The O(5)—O(4) and N—O(4) bond lengths reach their maximum and minimum values in the vicinity of the extrema on the PCR curve. In this case, the shortest O(5)—O(4) bond (1.426 Å) corresponds to the longest N—O(4) bond (1.418 Å) at both minima. On the contrary, the longest O(5)—O(4) bond (1.444—1.451 Å) corresponds to the shortest N—O(4) bond (1.396—1.399 Å) at the maxima. The length of the H—O(5) bond remains nearly the same in the case of rotation about the O(5)—O(4) bond.

The bond angles O(3)NO(2), O(4)NO(3), and O(5)O(4)N remain nearly unchanged as Q changes from 0 to 360°. The changes in the HO(5)O(4) angle (from ~99 to ~106°) in the case of rotation about the O(5)—O(4) bond are likely associated with plausible interaction of the H atom with the terminal O(3) and O(2) atoms.

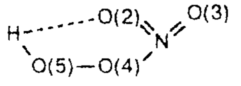
Regularities of changes in dihedral angles O(4)NO(3)O(2) and O(5)O(4)NO(3) are similar since the deviations of both angles are largest at the minima (for Q angles close to 87.5° and 272.5°). Both angles, O(4)NO(3)O(2) and O(5)O(4)NO(3), are equal to 180° at Q = 0° (or 180°). However, in this case the largest deviation of the O(4)NO(3)O(2) angle from 180° does not exceed 3°, whereas it is ~23° for the O(5)O(4)NO(3) angle. Hence, the O(4)NO(3)O(2) nitro group remains nearly planar all the time in the case of the internal rotation about the O(5)—O(4) bond, whereas the O(5) atom comes out of this plane by ~23°. In other words, the O(5) atom is virtually in the *trans*-position to the O(3) atom over the whole range of the changing Q angle. This is likely the reason for the higher sensitivity of the N—O(2) bond length towards a change in the position of the H atom upon the rotation (Δ(N—O(2)) = 0.02 Å) as compared to that of the N—O(3) bond length to such a rotation (Δ(N—O(3)) = 0.01 Å).

In the case of rotation about the N—O(4) bond (see Table 1, Fig. 1), the barriers are more than twice as high as those in the case of rotation about the O(5)—O(4) bond. The lengths of the N—O(2), N—O(3), N—O(4), and H—O(5) bonds change no more than by 0.01 Å, which is appreciably less than their changes with changing *Q* angle. Only the peroxide O(5)—O(4) bond at the tops of the barriers is lengthened by ~0.03 Å.

In the case of internal rotation about the N—O(4) bond, the bond angles and the dihedral angle O(4)NO(3)O(2) are not considerably changed, *i.e.*, the O(4)NO(3)O(2) fragment remains nearly planar as the angle τ changes from 0 to 360°. Changes in the dihedral angle HO(5)O(4)N are appreciably greater, the values of this angle along a given PCR vary in the range from 87.6 to 115.3° deviating to opposite sides from the right angle corresponding to the perpendicular position of the p-AOs of the peroxide oxygen atoms.

The necessity of allowing for the electron correlation energy in the calculations of the energies of peroxide compounds has been shown previously.[10,11] Therefore, to determine the barriers to the internal rotation about the O(5)—O(4) and N—O(4) bonds, the calculations of the energies of the conformers taking into account the correlation energy were performed at the second- and fourth-order Møller-Plesset level of perturbation theory (MP2 and MP4, respectively).

Table 2 gives the results of the calculations of relative energies of the $HOONO_2$ conformers in a number of approximations using the optimized geometric parameters corresponding to the maxima and minima in the case of internal rotation about the O(5)—O(4) and N—O(4) bonds listed in Table 1. A comparison between the values of the barriers, obtained by different methods, has shown that if the rotation occurs about the O(5)—O(4) bond, the allowance for d-functions on the N and O atoms (on going from the 6-31G to the 6-31G* basis set) results in different values of these barriers. On going from the UHF/6-31G to the UHF/6-31G* approximation, the value of the first barrier ($Q = 0°$) remains unchanged, whereas the value of the second barrier ($Q = 180°$) increases by 3 kJ mol^{-1}. Taking into account the correlation energy (going from the UHF/6-31G* to MP2/6-31G* and MP4/6-31G* approximations) has no appreciable effect on the height of the barriers to the internal rotation about the O(5)—O(4) bond. In the case of the most precise of the approximations used, MP4/6-31G*, the barriers are equal to 8.6 and 14.7 kJ mol^{-1}. The *cis*-conformer evidently has a lower barrier owing to the formation of a hydrogen bond, as the H—O(2) distance does not exceed 1.948 Å.



For comparison, the length of the intermolecular hydrogen H...O bond in various hydroperoxides[12—14] is ~1.8 Å, while the length of the intramolecular hydrogen bond in peroxyacetic acid[15] is 1.82 Å. The main factor determining the height of the barriers to the rotation about the O(5)—O(4) bond might be the mutual repulsion of the electrons of the nonbonding p-orbitals of the O atoms in the peroxide bond. Electrostatic repulsion of similarly charged and attraction of oppositely charged atoms make a considerable contribution to the values of the barriers to internal rotation. The effective charges calculated according to the Mulliken scheme change a little as the *Q* angle changes from 0 to 360°. The values of the effective charges of the atoms of PNA in the ground state are: H, 0.489; O(5), −0.368; O(4), −0.368; N, +0.923; O(3), −0.424; and O(2), −0.396. For comparison, in the HOOH molecule, in which the values of the barriers are mostly determined by mutual repulsion of the p-orbitals of the O atoms and that of positively charged H atoms, the value of the barrier is 30.9 kJ mol^{-1} according to the quantum-chemical calculation in the framework of the GVB+1+2QC method[7] and 29 kJ mol^{-1} according to the experimental data[13,16] at $Q = 0°$. The calculated and experimentally determined values of the barrier are 4.4 and 4.6 kJ mol^{-1}, respectively, at $Q = 180°$. Considering that our calculation and the calculations in Ref. 4 were performed using different approximations, it is only possible to compare the ratio of the heights of the barriers for each of two molecules. If the heights of the barriers in *cis*- and *trans*-positions of the H and N atoms in $HOONO_2$ differ from each other approximately by a factor of 1.7, the barriers for the *cis*- and *trans*-positions of the H atoms in HOOH molecule differ by a factor of ~6.5—7. Thus, the substitution of an electroneutral nitro group for the H atom in the HOOH molecule results in the energetic convergence of the *cis*- and *trans*-positions of the terminal atoms on going from hydrogen peroxide to PNA.

As can be seen from Table 2, the heights of the barriers to rotation about the N—O(4) bond (in contrast to the barriers to the rotation about the O(5)—O(4) bond) are approximately equal to each other in each of the approximations used,* but their values are considerably larger than those of the barriers to rotation about the O(5)—O(4) bond. The barriers to rotation about the N—O(4) bond are 19.2 kJ mol^{-1} in the UHF/6-31G approximation; they increase to 30.8 kJ mol^{-1} on going to the UHF/6-31G* approximation. In this case, as also for the rotation about the O(5)—O(4) bond, the allowance for the correlation energy is less significant than the expansion of the basis set by using polarization d-functions, and results in an increase in both barriers to 36.1 kJ mol^{-1} and 33.5 kJ mol^{-1} in the MP2/6-31G* and MP4/6-31G* approximations, respectively. Hence, the structure of the O(4)—NO(2)O(3) fragment is more rigid as compared with that of the HO(5)—O(4)N fragment. This is also confirmed by large changes in geometric parameters in the case of "forced" rotation about the N—O(4) bond. The greater rigidity is due to a fairly strong interaction between the electrons of the O(2),

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*It follows from the equivalency of the O(2) and O(3) atoms in the case of such rotation.

O(3) and O(4) atoms. Such an assumption is favored by the fact that the O(4)NO(3)O(2) nitro group remains nearly planar as the angles Q and τ change along both potential curves. No hydrogen bonds between the H atoms and O(2) (or O(3)) atom are formed in the case of the rotation about the N—O(4) bond, since in this case the internuclear H—O(2) (or H—O(3)) distances vary in the range from ~2.6 to 3.3 Å (R(O(2)—H) ≈ 2.6 Å at τ = 157.4° while R(O(3)—H) ≈ 3.3 Å at τ = 334.8°).

Thus, the mutual repulsion of the nonbonding p-orbitals of the O atoms is assumed to make the major contribution to the height of the barriers to conformational rotation in the case of rotation about the O(5)—O(4) bond. In the case of the rotation about the N—O(4) bond, the main contribution comes from the interaction between the π- and p-orbitals in the nearly planar nitro group O(4)NO(3)O(2) and the violation of their coplanarity caused by rotation.

Ab initio calculations of various conformers of the molecule of peroxynitrous acid HOONO were performed;[17] in accordance with our notations of the atoms in PNA its formula can be written as HO(5)O(4)NO(3). In contrast to peroxynitric acid, only one NO fragment in this molecule can be conjugated with the N—O(4) bond. Only a semiquantitative comparison of the results obtained for peroxynitrous acid[17] with the results of our calculations for PNA can be made, since other approximations were used both to optimize the geometry of the conformers (MP2/6-31G(d)) and to make an estimate of the heights of the barriers (MP2/6-311+G(3df,2p)) in the first case.[17] The *cis-cis*-configuration*, in which all atoms form a half-ring with an intramolecular hydrogen H...O(3) bond, corresponds to the ground state of the molecule of peroxynitrous acid. The *cis-trans*-conformer has the highest energy with regard to the *cis-cis*-conformer if mutual *cis*-position of the terminal O(5) and O(3) atoms persists. The energy of the *cis-trans*-conformer is 10.5 kJ mol^{-1} higher than those of two other calculated conformers.[17] Therefore, the barrier to rotation about the O(5)—O(4) bond in peroxynitrous acid can be assumed to be about 10.5 kJ mol^{-1}, which is fairly close to the barriers to rotation about the O(5)—O(4) bond we calculated for PNA (8.6 and 14.7 kJ mol^{-1}). However, if all atoms of peroxynitrous acid in its ground state lie in the same plane, the planes of the HO(5)O(4) and O(5)O(4)N atomic groups in the ground state of PNA are mutually perpendicular.

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*In the description of the conformation the first notation corresponds to the mutual position of the terminal O atoms, and the second to the mutual position of the N and H atoms in the molecule of peroxynitric acid.

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