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Theoretical Study of Cyclic Isomers of HNO_x (x=2—6)

Yumin Li and Suehiro Iwata*

Institute for Molecular Science, Myodaiji, Okazaki 444

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A series of cyclic isomers of HNO_x (x=2—6) are examined with ab initio MO methods. All of these cyclic isomers have a ring comprised of one nitrogen atom and two to five oxygen atoms. They are classified under the following three types. Type A: NO_x ring with an *exo* hydrogen bonded to a nitrogen; type B: NO_x ring with an *exo* OH bonded to a nitrogen, and type C: NO_x ring with an *exo* OOH bonded to a nitrogen. The geometry optimizations are carried out at the HF and MP2 levels of approximation with 6-31G** basis set, and the energies are evaluated at the MP4SDTQ approximation. We have failed to locate a five-membered ring HNO_x at the MP2 level. The geometries and vibrational frequencies are discussed by comparing with the data of the related known stable molecules. The conformational preferences among the isomers are interpreted in terms of an intramolecular long-range hydrogen-oxygen interaction.

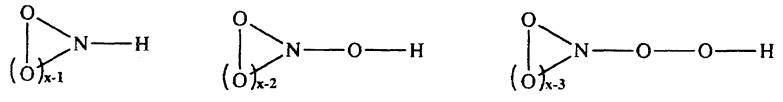
Both NO_x and HNO_x are important molecules in air pollution and atmosphere chemistry. In order to gain a complete understanding of the chemistry that takes place in the earth's atmosphere and on its surface, it is necessary to examine their thermal and photochemical reactions. Due to the conditions in the atmosphere, most notably to the temperature and the concentration of possible reactant molecules, the reactions involving NO_x and HNO_x in both the stratosphere and troposphere are very complicated; in particular, recent human activity has greatly enhanced complicacy, and it is possible to form some isomers that may be short-lived species and remain yet unrevealed. The searching for these isomers, either experimental observation or theoretical prediction, is undoubtedly of necessity and significance, since characterization of any new isomers would lead to further insight into the processes and mechanisms involved in the atmospheric reactions. Recently, we have predicted theoretically, for the first time, a number of unusual cyclic radicals NO_x by ab initio methods.[1] In this paper, we pay our attention to the cyclic isomers of HNO_x species. Although some isomers of HNO_x (x = 1—4) have been investigated both experimentally and theoretically, only in one case has the cyclic isomer of HNO_2 been examined, but the authors did not pay much attention to this isomer because of its relative unstability.[2] Our recent results on the novel radical rings NO_x encourage us to carry out a systematic examination of HNO_x, with x from 2 to 6, which has a similar cyclic geometry to that of NO_x. This paper describes the details of characterization of cyclic HNO_x (x = 2—6) isomers by ab initio molecular orbital methods.

Computational Procedure

We have carried out ab initio SCF MO calculations for a series of cyclic HNO_x species. The equilibrium geometries, which have closed shell singlet structures, are determined by using the GAUSSIAN 92 program.[3] Optimizations are carried out at the HF and MP2 levels with 6-31G** basis set. The harmonic vibrational frequencies are evaluated at the equilibrium geometries determined at each level of approximations. To estimate the energy, the fourth order Møller–Plesset perturbation method (MP4SDTQ) with frozen core approximation is used with the 6-31G** basis functions at the MP2 optimized geometries. For three-membered ring HNO_2 and four-membered ring HNO_3, the equilibrium geometries and corresponding harmonic vibrational frequencies are also evaluated at the MP2 level with large basis set 6-311G(2df,2p).

Results and Discussion

In the light of our works on the cyclic NO_x radicals, [1] here we examine three types of cyclic isomers for $2 \leq x \leq 6$: (Chart 1). In type A, a hydrogen is bonded with the nitrogen, while in the other types B and C, a hydrogen is bonded with the terminal exo oxygen. The geometry optimizations are carried out at the HF/6-31G** and the MP2/6-31G**



A HNO_x B $HONO_{x-1}$ C HO_2NO_{x-2}

Chart 1.

levels, and harmonic frequencies are evaluated to examine whether the optimized geometry is a true local minimum or not. All of the cyclic isomers shown in Fig. 1 are at real local minima at both levels of approximations. Some of cyclic

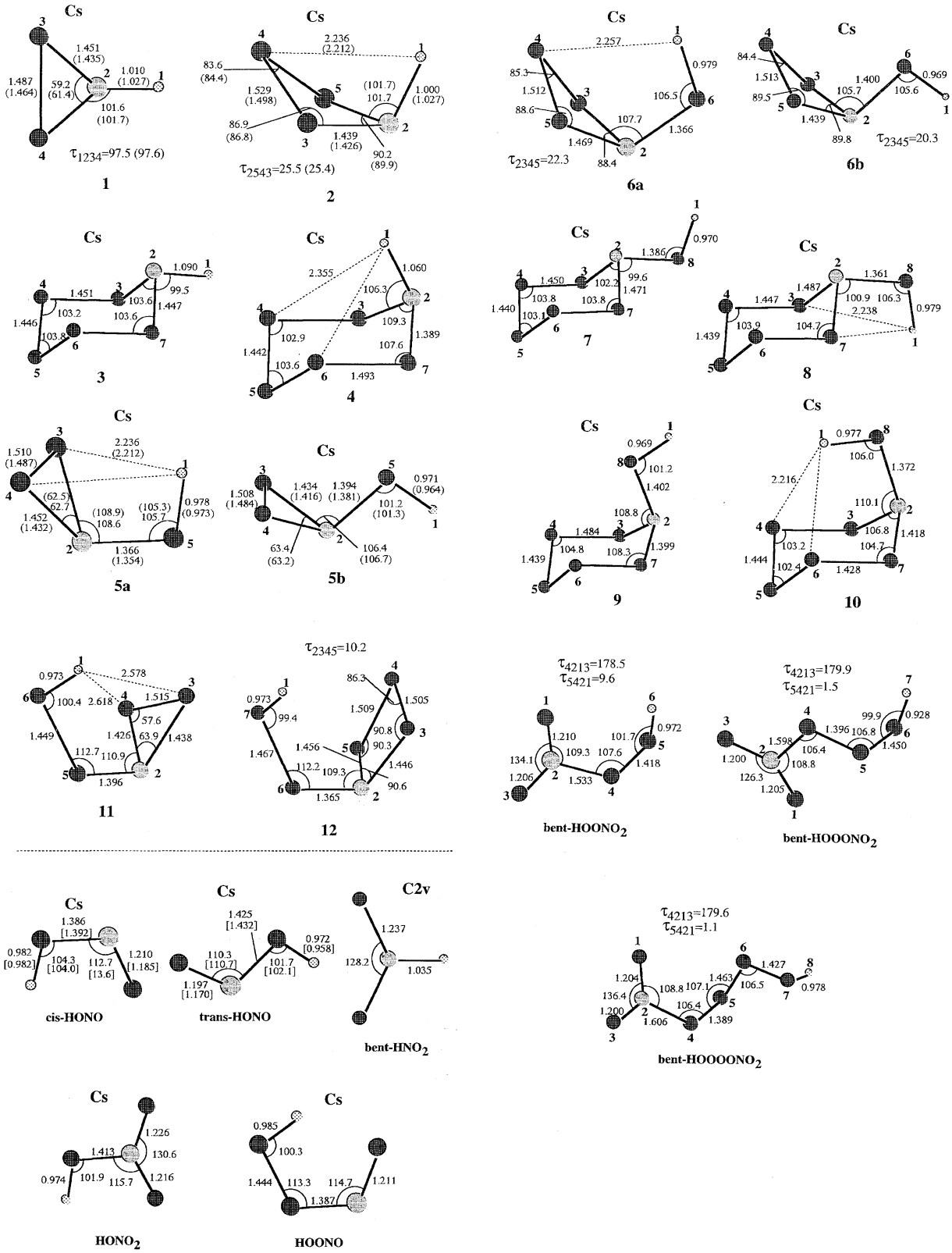


Fig. 1. The optimized geometrical parameters for cyclic and noncyclic HNO_x isomers, bond lengths are in angstrom and angles are in degree. The data in parentheses are obtained at MP2/6-311G(2df,2p), the data in square brackets are experimental results, other data are obtained at MP2/6-31G**.

isomers are local minima at the HF/6-31G** level, but not at the MP2/6-31G** level; they are not shown here. For optimized structures with MP2/6-31G**, the zero point energies and the energies with MP4SDTQ//MP2/6-31G** are listed in Table 1. The scaled harmonic vibrational frequencies and atomic charges are listed in Tables 2 and 3, respectively. For comparison, the energies of noncyclic isomers of HNO_x species are also listed in Table 1.

HNO_2. For most chemists, the chemical form HNO_2 implies nitrous acid HO–N=O, which has cis and trans forms of C_s symmetry. The electron configuration of the ground state is $(1\text{-}8)\sigma^2 1\pi^2 9\sigma^2 2\pi^2 10\sigma^2$, having four electrons in the π orbitals. The acid has been well studied with the ab initio MO calculations.[2,4] In our calculation with MP4SDTQ//MP2/6-31G**, the cis form is slightly more stable by 4.2 kJ mol^{-1} than the trans form. The calculated (experimental) O–N and N=O bond lengths for cis form are 1.386 (1.392) Å and 1.210 (1.185) Å, and those for trans form are 1.425 (1.432) Å and 1.197 (1.170) Å. It is noted that the N–O "single" bond of cis form is substantially shorter than that of trans form. The other planar isomer HNO_2 of C_{2v} symmetry is also known and has been well studied with the ab initio MO calculations;[2,4,5] two oxygens are equivalent, but not bonded to each other. Its electron configuration is given by $(1\text{-}8)\sigma^2 1\pi^2 (9\text{-}10)\sigma^2 2\pi^2$, having also four electrons in the π orbitals. The isomer has the biradical nature, and is less stable by 41.2 kJ mol^{-1} than the most stable cis form with MP4SDTQ//MP2/6-31G** in our calculation. The calculated N–O bond length is 1.237 Å and the angle O–N–O is 128.2 degrees. In this paper, we have studied its cyclic isomer, **1** in Fig. 1, which is the smallest one among all the cyclic isomers in question and has been suggested to be an intermediate involved in the reaction between NH ($^1\Delta$) and O_2 ($^1\Delta_g$).[4] As mentioned above, this cyclic isomer was studied previously with ab initio MO calculations. When they studied the isomers of HNO_2 at HF/4-31G* level, Nakamura et al. calculated this cyclic isomer and found it is less stable than its noncyclic isomer.[2] In this work, we optimize the geometry of the cyclic isomer with 6-31G** basis set at HF and MP2 levels; in both approximations, it is a local minimum. Our HF/6-31G** result is consistent with the result obtained by Nakamura et al with HF/4-31G*.[2] Its electron confiuration is given by $(1\text{-}6)\sigma^2 1\pi^2 (7\text{-}9)\sigma^2 (2\text{-}3)\pi^2$, having six electrons in the π orbitals, where the π orbital is antisymmetric to a plane of NO_2. Thus, though the cyclic isomer **1** has a structure similar to the C_{2v} HNO_2, the main electron configuration of the two isomers are so different from each other, and the barrier height connecting two isomers is expected to be high; the estimation of the height at least requires the well balanced multi-configuration SCF calculation.

Table 1. Energies $E_{MP4SDTQ}$ and E_{ZP} (in Hartrees) and Relative Energies ΔE (in kJ mol^{-1}) for the Cyclic and Noncyclic HNO_x Isomers at the Optimized Structures with MP2/6-31G**

Molecule[a]	No.	$E_{MP4SDTQ}$	E_{ZP}	ΔE
HNO_2	**1**	−205.07655	0.02000	347.0
bent-HNO_2 (C_{2v})		−205.19554	0.02250	41.2
trans-HONO (C_s)		−205.20730	0.02019	4.2
cis-HONO (C_s)		−205.20911	0.02040	0
HNO_3	**2**	−280.01682	0.02425	498.2
$HONO_2$	**5b**	−280.09043	0.02312	302.0
$HONO_2$	**5a**	−280.09452	0.02340	291.9
HOONO		−280.16453	0.02362	108.7
bent-$HONO_2$		−280.20916	0.02685	0
$HONO_3$	**6b**	−355.02702	0.02704	348.8
$HONO_3$	**6a**	−355.03012	0.02719	341.1
HO_2NO_2	**11**	−355.04414	0.02628	301.9
bent-$HOONO_2$		−355.16211	0.02927	0
HNO_5	**3**	−429.97785	0.03154	384.0
HO_2NO_3	**12**	−429.98219	0.03002	368.6
HNO_5	**4**	−429.99169	0.03142	347.3
bent-$HOOONO_2$		−430.12469	0.03213	0
$HONO_5$	**7**	−504.98164	0.03443	271.7
$HONO_5$	**8**	−504.98342	0.03442	267.0
$HONO_5$	**9**	−504.98778	0.03399	254.4
$HONO_5$	**10**	−504.99074	0.03421	247.2
bent-$HOOOONO_2$		−505.08588	0.03518	0

a) Molecule No. is given in Fig. 1.

The electron correlation with the MP2 level lengthens the N–O and O–O bonds and shortens slightly the N–H bond length. The isomer has a nonplanar structure with C_s symmetry, and the N–O and O–O bonds are nearly normal single bonds, since all three π orbitals are doubly occupied and therefore they do not contribute to the bonding. Furthermore, we also optimize this isomer with MP2/6-311G-(2df,2p), which are given in parentheses in Fig. 1. The geometric parameters are very similar to those of MP2/6-31G**. The harmonic vibrational frequency calculation with MP2/6-311G (2df,2p) also shows that it is at a local minimum. In our calculations, the cyclic HNO_2 is less stable by 347.0 kJ mol^{-1} than the cis form of HO–N=O with MP4SDTQ//MP2/6-31G**.

HNO_3. So far two isomers have been reported for HNO_3; one is well-known and commonly called nitric acid, $HONO_2$, which is the lowest energy form for HNO_3; its electron configuration of the ground state is $(1\text{-}9)\sigma^2 1\pi^2 (10\text{-}11)\sigma^2 2\pi^2 (12\text{-}13)\sigma^2 3\pi^2$. The other isomer is peroxonitrous acid, HOONO, whose electron configuration of the ground state is also $(1\text{-}9)\sigma^2 1\pi^2 (10\text{-}11)\sigma^2 2\pi^2 (12\text{-}13)\sigma^2 3\pi^2$. The latter lies roughly 146.3 kJ mol^{-1} higher than nitric acid in energy, via correlated calculations of moderate accuracy.[6] The relative energies and vibrational frequencies of some conformers of peroxonitrous acid have recently been calculated,[7] which indicated the lowest energy conformer of peroxonitrous acid is planer with an intramolecular hydrogen bond. Experimentally, HOONO has also been detected in argon matrices as a recombination product of the photolysis of nitric acid,[8,9] and also it is believed to have been observed in solution.[10] The theoretical studies of nitric acid and peroxonitrous acid have also attracted much attention in recent years, because

Table 2. The Scaled Harmonic Vibrational Frequencies[a] (cm^{-1}) and IR Intensities (km $mole^{-1}$) for the Cyclic HNO_x Isomers at MP2/6-31G** Level

1	Symmetry	a′	a″	a′ [b]	a″	a′	a′ [c]			
	Scled freq.	748	761	1035	1140	1344	3177			
	Unscaled freq.	801	814	1107	1219	1437	3398			
	IR intensity	0.3	2.9	0.5	39.3	34.8	2.6			
bent-HNO_2	Symmetry	a_1	b_1	a_1	b_2	b_2	a_1			
(C_{2v})	Scaled freq.	717	968	1275	1435	1538	3114			
	Unscaled freq.	767	1035	1364	1535	1842	3334			
	IR intensity	26.9	32.3	31.6	15.9	84.8	4.5			
trans-HONO	Symmetry	a″	a′	a′	a′	a′	a′			
	Scaled freq.	561	588	808	1216	1549	3562			
(C_s)	Unscaled freq.	600	629	864	1301	1657	3810			
	IR intensity	114.1	100.9	184.8	191.6	67.4	73.7			
	Exp freq. [e]	583	625	815	1298	1684	3558			
cis-HONO	Symmetry	a′	a″	a′	a′	a′	a′			
	Scaled freq.	611	695	885	1259	1513	3408			
(C_s)	Unscaled freq.	654	743	947	1346	1618	3645			
	IR intensity	13.5	116.7	326.4	4.6	117.4	27.6			
	Exp freq. [f]	610	637	850	1265	1633	3412			
2	Symmetry	a′	a′	a″	a′	a″	a′ [b]	a′	a″	a′ [c]
	Scaled freq.	394	605	636	776	814	890	1287	1344	3164
	IR intensity	6.3	1.1	1.4	9.2	6.1	3.6	40.1	13.7	4.2
3	Symmetry	a″	a′	a″	a″	a′	a′ [b]	a′	a″	a″
	Scaled freq.	354	360	464	490	509	554	671	711	743
	IR intensity	2.2	13.7	0.3	2.7	0.9	6.0	4.9	14.4	26.0
	Symmetry	a′	a′	a′	a′	a″	a′ [c]			
	Scaled freq.	751	780	850	1142	1327	3235			
	IR intensity	1.7	0.9	3.9	69.8	14.1	16.2			
4	Symmetry	a″	a′	a″	a″	a′	a′ [b]	a′	a″	a′
	Scaled freq.	322	368	401	495	503	532	640	652	719
	IR intensity	5.3	4.5	2.3	1.4	12.9	6.7	1.5	0.9	53.6
	Symmetry	a″	a′	a″	a′	a″	a′ [c]			
	Scaled freq.	779	835	840	1183	1398	3231			
	IR intensity	4.5	8.9	11.8	57.4	5.3	6.8			
5a	Symmetry	a″	a″	a′	a″	a′	a′	a′ [b]	a′	a′ [d]
	Scaled freq.	371	528	532	698	700	954	968	1349	3461
	IR intensity	67.3	66.2	23.1	20.6	5.4	191.1	33.2	46.1	39.7
5b	Symmetry	a″	a″	a′	a″	a′	a′	a′ [b]	a′	a′ [d]
	Scaled freq.	197	485	533	705	750	910	999	1329	3582
	IR intensity	89.9	20.7	1.4	25.4	27.0	142.7	53.3	65.1	91.3
HOONO	Symmetry	a″	a′	a″	a′	a′	a′	a′	a′	a′
	Scaled freq.	268	378	475	709	777	907	1365	1478	3337
	IR intensity	91.7	7.3	27.6	171.8	41.6	15.5	88.3	132.6	30.7
bent-$HONO_2$	Symmetry	a″	a′	a′	a″	a′	a′	a′	a′	a′
	Scaled freq.	464	541	617	706	850	1264	1271	1777	3532
	IR intensity	136.7	11.3	3.8	9.4	191.2	190.7	132.8	192.2	86.3
	Exp freq. [g]	456	579	647	762	879	1324	1330	1708	3550

Table 2. (Continued)

6a	Symmetry	a′	a″	a′	a″	a′	a″			
	Scaled freq.	214	392	542	560	568	693			
	IR intensity	2.9	38.9	12.5	77.0	43.7	38.0			
	Symmetry	a′ [b]	a′	a″	a′	a′	a′ [d]			
	Scaled freq.	793	821	821	945	1360	3452			
	IR intensity	14.7	10.7	11.2	178.8	55.3	33.0			
6b	Symmetry	a′	a″	a″	a′	a′	a″			
	Scaled freq.	207	230	487	542	521	698			
	IR intensity	0.7	100.1	10.3	3.0	38.9	17.7			
	Symmetry	a′ [b]	a′	a″	a′	a′	a′ [d]			
	Scaled freq.	817	825	855	898	1326	3591			
	IR intensity	90.8	61.5	14.7	48.1	63.6	95.4			
7	Symmetry	a′	a″	a″	a″	a′	a″	a′	a″	a′ [b]
	Scaled freq.	206	274	329	358	465	469	484	515	556
	IR intensity	2.9	71.5	10.0	4.2	1.9	23.3	4.3	0.4	0.3
	Symmetry	a′	a″	a′	a′	a″	a′	a′	a′	a′ [d]
	Scaled freq.	675	721	729	765	817	855	1011	1320	3579
	IR intensity	29.6	14.1	5.6	40.3	35.9	14.7	64.5	70.2	127.6
8	Symmetry	a′	a″	a″	a″	a′	a′	a″	a″	a′ [b]
	Scaled freq.	198	307	338	421	462	482	508	513	543
	IR intensity	5.2	10.0	25.1	40.4	0.3	1.4	69.2	0.4	6.4
	Symmetry	a′	a″	a′	a′	a″	a′	a′	a′	a′ [d]
	Scaled freq.	667	713	724	753	814	857	1019	1366	3437
	IR intensity	37.3	13.8	7.5	3.1	34.9	6.4	122.0	70.2	39.5
9	Symmetry	a″	a′	a″	a″	a′	a″	a′ [b]	a″	a′
	Scaled freq.	165	209	264	401	414	480	525	563	595
	IR intensity	91.2	3.6	11.1	13.3	1.5	0.0	0.7	2.2	0.3
	Symmetry	a′	a″	a′	a′	a″	a′	a′	a′	a′ [d]
	Scaled freq.	634	685	721	798	803	828	957	1317	3589
	IR intensity	4.1	0.3	7.8	0.5	29.0	90.2	50.8	61.8	106.9
10	Symmetry	a′	a″	a″	a″	a′	a″	a′ [b]	a′	a″
	Scaled freq.	226	272	337	410	387	482	524	572	576
	IR intensity	2.1	7.0	34.2	41.6	3.4	11.1	0.4	9.6	25.7
	Symmetry	a′	a″	a′	a″	a′	a′	a′	a′	a′ [d]
	Scaled freq.	603	684	702	774	791	848	983	1375	3467
	IR intensity	5.4	0.8	4.3	35.2	1.4	13.8	123.3	68.0	34.7
11	Scaled freq.	192	247	315	463	630	703			
	IR intensity	55.8	66.9	6.1	3.6	8.9	16.6			
	Scaled freq.	728	777	848	1028[b]	1314	3451[d]			
	IR intensity	88.5	10.1	6.9	30.6	66.8	34.1			
12	Scaled freq.	175	197	252	290	463	598	636	737	763
	IR intensity	1.5	4.5	89.9	28.6	7.2	3.3	77.2	8.3	19.9
	Scaled freq.	776	810[b]	880	914	1290	3539[d]			
	IR intensity	29.2	3.0	12.1	44.7	63.8	38.9			

a) The scale factor, 0.935, is determined by fitting the experimental vibrational frequencies of trans- and cis-nitrous acids. b) Cyclic breath vibration. c) *exo* N–H stretching vibration. d) *exo* O–H stretching vibration. e) Ref. 17. f) Ref. 18. g) Ref. 19.

of its atmospheric significance, photochemical importance and structural interests. In our knowledge the present work is the first examination of cyclic isomers containing three- and four-membered ring. We have successfully obtained one four-membered ring isomer **2** in Fig. 1 and two three-membered ring isomers **5a** and **5b** in Fig. 1. Isomer **2** has been confirmed with all harmonic frequencies, being real at HF/6-31G**, MP2/6-31G**, and MP2/6-311G(2df,2p) levels, and its all bonds are nearly single bonds; the cyclic O–O bonds are somewhat longer than a normal O–O single bond (1.529 Å vs. 1.475 Å of the normal O–O single bond length in HOOH[11]) at MP2/6-31G** level. It is also noted in isomer **2** that the distance between hydrogen and the oxygen numbered 4 is 2.298 Å with HF/6-31G**, 2.236 Å

Table 3. The Mulliken Charges for the Cyclic and Noncyclic HNO_x Isomers at the Optimized Structures with MP2/6-31G** Approximation

Molecule[a)]	No.	1(H)	2(N)	3(O)	4(O)	5(O)	6(O)	7(O)	8(O)
HNO_2	**1**	0.341	0.063	−0.202	−0.202				
bent-HNO_2 (C_{2v})		0.351	0.482	−0.417	−0.417				
trans-HO(3)NO (C_s)		0.370	0.384	−0.483	−0.271				
cis-HO(3)NO (C_s)		0.364	0.446	−0.469	−0.340				
HNO_3	**2**	0.338	0.101	−0.188	−0.064	−0.188			
$HO(3)NO_2$		0.398	0.868	−0.429	−0.446	−0.390			
HO(3)O(4)NO		0.411	0.491	−0.315	−0.221	−0.367			
HNO_5	**3**	0.347	0.082	−0.196	−0.014	−0.009	−0.014	−0.196	
HNO_5	**4**	0.337	0.108	−0.165	−0.058	0.002	−0.058	−0.165	
$HONO_2$	**5a**	0.383	0.440	−0.199	−0.199	−0.426			
$HONO_2$	**5b**	0.384	0.369	−0.165	−0.165	−0.423			
$HONO_3$	**6a**	0.387	0.417	−0.158	−0.073	−0.158	−0.415		
$HONO_3$	**6b**	0.385	0.368	−0.153	−0.024	−0.153	−0.420		
$HONO_5$	**7**	0.395	0.370	−0.146	−0.024	−0.001	−0.024	−0.146	−0.422
$HONO_5$	**8**	0.385	0.443	−0.185	−0.010	−0.005	−0.010	−0.185	−0.423
$HONO_5$	**9**	0.392	0.366	−0.145	−0.021	−0.004	−0.021	−0.145	−0.421
$HONO_5$	**10**	0.395	0.409	−0.129	−0.068	0.014	−0.068	−0.129	−0.424
HO_2NO_2	**11**	0.393	0.466	−0.150	−0.209	−0.210	−0.289		
HO_2NO_3	**12**	0.393	0.471	−0.156	−0.009	−0.205	−0.191	−0.304	

a) Molecular No. is given in Fig. 1.

with MP2/6-31G**, and 2.212 Å with MP2/6-311G (2df,2p), respectively, which indicates a weak intramolecular interaction between oxygen and hydrogen atoms. The interaction is electrostatic between the positively charged hydrogen atom and the negatively charged oxygen atom, and might be called an intramolecular hydrogen bond. The other two three-membered isomers **5a** and **5b** have also been predicted with all harmonic frequencies being real at all three approximation levels. Both of them have C_s symmetry and all their bonds are nearly single bonds with exceptions of a little longer cyclic O–O bond and a slightly shorter *exo* N–O bond. Interestingly, the *exo* N–O bond is substantially shorter than the cyclic N–O bonds and is almost the same as that of cis form HO–N=O. In isomer **5a**, the distance between hydrogen and two of cyclic oxygens is 2.230 Å with HF/6-31G**, 2.236 Å with MP2/6-31G**, and 2.212 Å with MP2/6-311G (2df,2p), which indicates an intramolecular bifurcated hydrogen–oxygen interaction. This type of interaction is not noted in isomer **5b**, which may be the reason that isomer **5a** is more stable than **5b** by 10.1 kJ mol^{-1} with MP4SDTQ//MP2/6-31G** and its O–H stretching vibrational frequency is smaller than that of **5b** by 128 cm^{-1} with MP2/6-31G** (see Table 2). From Table 1, it can be seen that isomer **2** is less stable by 206.3 kJ mol^{-1} than isomer **5a**, by 389.5 kJ mol^{-1} than the most stable conformer among several HOONO (peroxonitrous acid) isomers and by 498.2 kJ mol^{-1} than bent-HNO_3 (nitric acid).

HNO_4. For HNO_4, the only known isomer either experimentally or theoretically is peroxonitric acid HO_2NO_2. Although this molecule was identified in the gas phase by Niki et al. in 1977,[12] it was 1985 when Saxon and Liu reported the first theoretical study of the ground state geometry and excited state of HO_2NO_2.[13] In this work, we have examined its isomers with three types of rings; the first one is a five-membered NO_4 ring with an additional *exo* N–H moiety, the second one is a four-membered NO_3 ring with an *exo* N–O–H moiety, and the third one is a three-membered NO_2 ring with an *exo* N–O–O–H moiety. Both full-optimization and optimization under the C_s constraint for the isomer containing a five-membered NO_4 ring at the HF/6-31G** level gives the expected structure and all the harmonic vibrational frequencies are real, but at the MP2/6-31G** level the reoptimization results in the decomposition of the isomer to O_2+HNO_2. On the other hand, for the other two types of isomers, at both ab initio levels, they are confirmed to be at true local minima. Two isomers containing a four-membered NO_3 ring **6a** and **6b** in Fig. 1 are found. Both of them have C_s symmetry. As in the other isomers containing a three- or four-membered ring discussed before, all bonds are nearly single bonds, though the cyclic O–O bond is a little longer than the normal O–O single bond. In addition, the *exo* N–O bond is shorter than the cyclic N–O bonds, and the *exo* N–O bond of cis form **6a** is shorter than that of trans form **6b**. The tendencies in N–O bonds are similar to those found in isomers **5a** and **5b**. It is also noted that the intramolecular interaction between hydrogen and cyclic oxygen numbered 4 exists in isomer **6a**, but not in **6b**. The distance between hydrogen and the cyclic oxygen numbered 4 in isomer **6a** is 2.257 Å with MP2/6-31G**. The intramolecular hydrogen bond in isomer **6a** also may be the reason that isomer **6a** is more stable than **6b** by 7.7 kJ mol^{-1} with MP4SDTQ//MP2/6-31G** and its O–H stretching vibrational frequency is smaller than that of **6b** by 149 cm^{-1} with MP2/6-31G**. Isomer **11** has a three-membered NO_2 ring with *exo* N–O–O–H moiety. This isomer has no symmetry plane and all bonds are nearly single bonds except for a little longer cyclic O–O bond and slightly shorter *exo* N–O bond. From Table 1, it can be seen that isomer **11** is more stable than **6a** by 39.2 kJ mol^{-1} and is less

stable than peroxonitric acid by 301.9 kJ mol^{-1}.

HNO_5 and HNO_6. To the best of our knowledge, no reports have addressed these species HNO_x with $x \geq 5$ even by theoretical predictions. In this paper, cyclic HNO_x with $x \geq 5$ have been predicted. For HNO_5, three types of isomers containing a NO_x ring have been studied. For isomers containing a six-membered NO_5 ring, we have examined its boat and chair conformers. As expected, the vibrational analysis for a boat conformer gives one imaginary frequency at both HF/6-31G** and MP2/6-31G** levels. For its chair conformer, on the other hand, two conformers, equatorial isomer **3** and axial isomer **4**, are found; both have a symmetry plane. Both conformers are verified to be at real local minima by vibrational analyses at both levels. Both isomer **3** and **4** have normal N–O, O–O, and N–H single bonds. Again, we have failed to locate the five-membered isomer for HNO_5 though the corresponding isomer of NO_5 was established as a true local minimum previously.[1] As in the search for a five-membered HNO_4, the HF/6-31G** full optimization for the isomer reaches the expected ring geometry and all the calculated harmonic vibrational frequencies are real, but the MP2/6-31G** full optimization results in the decomposition of the isomer into O_2+$HONO_2$. For isomers containing NO_3 four-membered ring, the full optimization gives isomer **12** in Fig. 1 without any symmetry at both levels of approximation, and the characteristics of bond lengths are similar to those for smaller x. As in the other isomers containing a three- or four-membered ring, at MP2/6-31G** level, the cyclic O–O bonds are also a little longer than the normal O–O single bond. We have also succeeded in obtaining an isomer containing NO_2 three-membered ring with *exo* –O–O–O–H moiety, but we will not discuss it in detail, because we mainly discuss three types of ring isomers as mentioned above. In addition, we have also obtained one of its chain isomers for HNO_5. As given in Table 1, the chain isomer, bent-$HOOONO_2$, is the most stable, and is more stable than isomer **4** by 347.3 kJ mol^{-1}, than isomer **12** by 368.6 kJ mol^{-1} and than isomer **3** by 384.0 kJ mol^{-1}.

For isomers **3** and **4**, their relative stability is interesting. It is well-known that for monosubstituted cyclohexane, the equatorial conformer is generally more stable than the axial conformer. But in our case, the equatorial isomer **3** is less stable than the axial isomer **4** by 36.7 kJ mol^{-1} with MP4SDTQ//MP2/6-31G**. It is not a surprise if we compare the axial/equatorial preference of **3** and **4** with that of the piperidine (C_5H_5NH), which has a similar skeleton with the six-membered ring of HNO_5. There are controversial reports on the axial/equatorial preference of piperidine, and there are also several explanations for different results.[14] One of these explanations in support of preference for the NH-axial conformation is that the axial proton on nitrogen has attractive interactions with the β-axial protons and the β-carbons;[15] this is deduced from theoretical considerations. But in our case of isomers **3** and **4**, no axial proton is present at β-position. The most possible explanation for the preference of axial isomer **4** over equatorial isomer **3** is intramolecular bifurcated interaction between the proton and two β-oxygens; the calculated distance between H and β-O in isomer **4** is 2.336 Å with HF/6-31G** and 2.355 Å with MP2/6-31G**.

In the case of HNO_6, although there are many possible cyclic isomers of five-, four-, three-membered rings, we examine only isomers containing seven- and six-membered rings. In our calculations, we have failed in determining a seven-membered ring isomer at the MP2 level. For the six-membered ring isomers, we examine only the most stable chair conformers, and there are four possible conformers : **7**, **8**, **9**, and **10** in Fig. 1. For convenience, we refer to the different isomers by the orientation both of the *exo* N–O bond (axial or equatorial) and of the O–H bond (cis or trans with respect to the cyclic N–O bond), and thus we have equatorial-trans (isomer **7**), equatorial-cis (isomer **8**), axial-trans (isomer **9**), and axial-cis (isomer **10**) conformers, which are all at true local minima with both HF/6-31G** and MP2/6-31G** levels. In all cases, the optimized geometries have C_s symmetry and all the bonds for each conformer are nearly single bonds. The *exo* N–O bond is shorter than the cyclic N–O bonds except for isomer **9**, in which the *exo* N–O bond is slightly longer than the cyclic N–O bonds at MP2/6-31G**. In addition, we have also obtained one of its chain isomers for HNO_6. As shown in Table 1, the chain isomer, bent-$HOOOONO_2$, is the most stable isomer of HNO_6.

Among four chair conformers, as shown in Table 1, isomer **10** (axial-cis) is actually the most stable conformer, and the order of stability for these conformers is isomer **7** < isomer **8** < isomer **9** < isomer **10**. The relative stabilities of isomers **7** and **8**, and of isomers **9** and **10** can be easily explained by an intramolecular bifurcated hydrogen bond. In isomer **8**, the distance between the proton and the α-oxygens is 2.260 Å at HF/6-31G** level and 2.238 Å at MP2/6-31G** level, indicating the intramolecular bifurcated hydrogen bonds. The calculated harmonic vibrational frequencies are also in support of the hydrogen bond, which will be discussed in next section. For isomer **10**, the distance between the proton and the β-oxygen is 2.278 Å at the HF/6-31G** level and 2.216 Å at the MP2/6-31G** level, which is evidence for an intramolecular hydrogen bond, and the calculated harmonic vibrational frequencies are also indicative of the hydrogen-oxygen interaction.

Vibrational Frequencies (Infrared Spectra)

The MP2/6-31G** harmonic vibrational frequencies have been calculated at the optimized geometries for cyclic HNO_x and their noncyclic isomers. Calculated harmonic frequencies which have been scaled by a scale factor of 0.935 are shown in Table 2, together with known related experimental frequencies. The scale factor, 0.935, is determined by fitting the experimental vibrational frequencies of *trans*- and *cis*-nitrous acids. Experimental frequencies are available for the *trans*- and *cis*-nitrous acids and for nitric acid. Our frequencies scaled with a single scale factor are in reasonable agreement with them. We will not discuss in detail the infrared spectra because no experimental data for these cyclic isomers are available, but two remarkable vibrational frequencies are worth mentioning here for future use of the

identification.

N–H and O–H Stretching Frequencies. As shown in Table 2, after scaling, the calculated OH stretching frequencies for the known three molecules, *trans*- and *cis*-HONO and bent-$HONO_2$, are in very good agreement with the experimental band positions. Although we cannot claim this much accuracy for the OH and NH stretching frequencies in the unstable ring isomers, the calculated shifts of the frequencies in these molecules provide us information for future identification of them.

The NH stretching frequencies are 3180 cm^{-1} for **1**, 3160 cm^{-1} for **2**, 3240 cm^{-1} for **3**, and 3230 cm^{-1} for **4**. These are substantially shifted to lower frequencies from the symmetric NH of ammonia (3337 cm^{-1}). The harmonic frequency is not correlated with the N–H distance (1.01 Å for **1**, 1.00 for **2**, 1.09 for **3** and 1.06 for **4**), which might be attributed to the coupling of the NH mode with the ring modes.

The calculated OH frequencies of the *exo* NOH and NOOH are grouped to two frequency regions : around 3460 cm^{-1} and around 3590 cm^{-1}. The isomers **5a** (3460 cm^{-1}), **6a** (3450 cm^{-1}), **8** (3440 cm^{-1}) and **10** (3470 cm^{-1}) belong to the former group. There is a common feature in the geometric structures of these molecules; as indicated in Fig. 1, the hydrogen atom is interacting with one or two oxygen atoms in the ring. It is also noted that the lower frequency of the OH mode is found in the cis form of HONO (3410 cm^{-1} in the calculation and 3412 cm^{-1} in the experimental data), in which the long range intramolecular O–H interaction also exists. In spite of the similarity, a systematic high frequency shift in the exo OH is noticed.

On the other hand, the isomers **5b** (3580 cm^{-1}), **6b** (3590 cm^{-1}), **7** (3580 cm^{-1}), **9** (3590 cm^{-1}), and **12** (3540 cm^{-1}) have no such intramolecular interaction. The calculated frequencies are close to but slightly higher than the trans form of HONO (3560 cm^{-1} in the calculation and 3558 cm^{-1} in the experimental data). These similarities and slight high frequency shifts could be a clue to identify the ring isomers.

Ring Breath Modes. In Fig. 2 the frequencies and vectors of the symmetric breath mode in the three-, four-, and six-membered rings are summarized. Roughly speaking, the frequencies of these modes are nearly equal to each other for those of the same ring size; 1100 to 1040 cm^{-1} for three-membered ring, 950 to 850 cm^{-1} for four-membered ring and 590 to 560 cm^{-1} for six-membered ring. In the six-

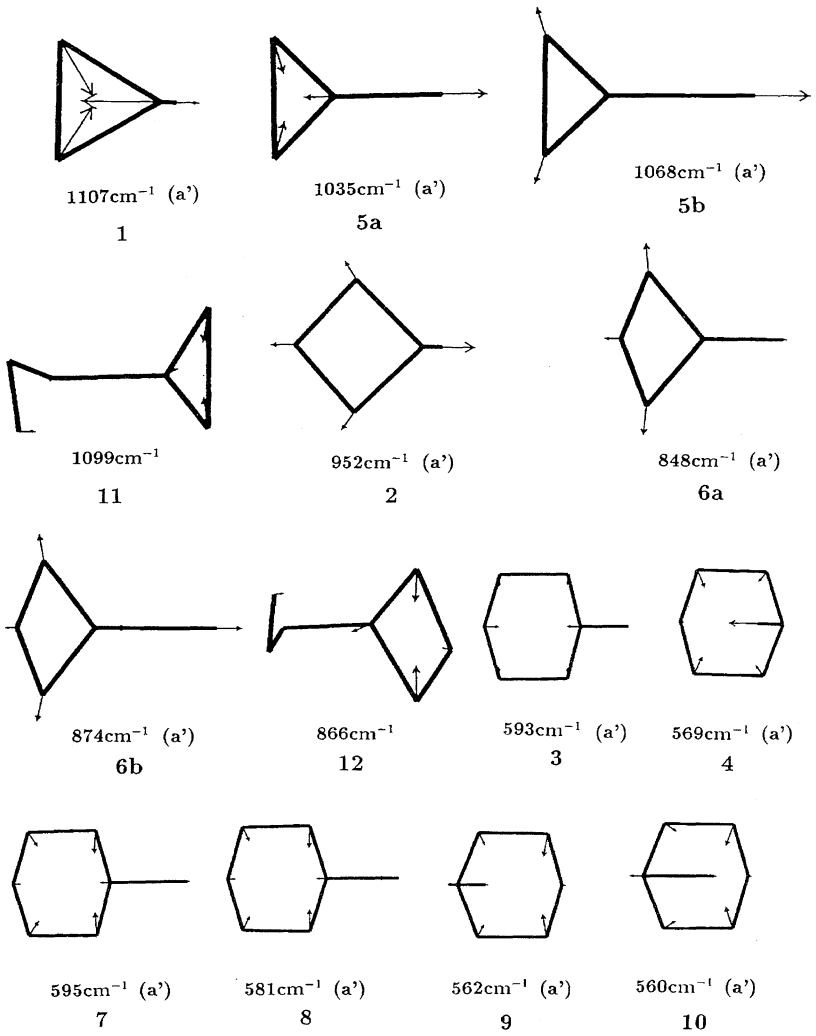


Fig. 2. The calculated harmonic frequencies of ring breath modes for cyclic HNO_x isomers at MP2/6-31G**.

membered ring, the frequencies are almost independent of the *exo* part.

Among the three- and four-membered ring isomers, the isomers (**1** and **2**) without an exo OH have the distinctively highest frequency among the corresponding isomers, which suggests a slightly more rigid ring without an exo OH than those with it. The intramolecular long range O–H interaction reduces also the frequency of the ring breath mode, as is seen in **5a** (1040 cm^{-1}) and **5b** (1070 cm^{-1}), and in **6a** (850 cm^{-1}) and **6b** (870 cm^{-1}).

Some Characteristics of Cyclic Isomers

Some of the geometric parameters determined with the MP2/6-31G** level of approximation are summarized as follows. The N–H and O–H bond lengths of the cyclic isomers are 1.00—1.09 Å and 0.97—0.98 Å, respectively; they are within normal N–H and O–H bond lengths. The bond lengths of the *exo* N–O are 1.36—1.40 Å, which are slightly shorter than the normal single bond. There are some systematic changes in the *exo* N–O bond lengths for pairs of (**5a**, **5b**), (**6a**, **6b**), (**8**, **7**), and (**10**, **9**); in each pair the *exo* N–O bond length of the first one is substantially shorter (1.36 Å) than that of the second (1.39—1.40 Å). The cis and trans conformers of nitrous acid (HONO) are a similar pair; the bond length of the single bond N–O of *cis* is 1.39 Å, while that of *trans* is 1.43 Å. The common feature of *cis*-nitrous acid and the first isomer of each pair is the *cis* form of O–N–O–H. Some kind of electronic factor might be operative, which is clearly seen in the Mulliken charges on the nitrogen atoms shown in Table 3; the nitrogen atoms with a shorter bond length are more positive than that with a longer bond.

The N–O lengths in the rings are ranged from 1.39 to 1.49 Å, mostly 1.44—1.46 Å. In some of the six-membered rings, the exceptionally short N–O bonds are found (for instance, in isomer **4**). The O–O lengths in the three- and four-membered rings are in the range of 1.49—1.53 Å; some of them are substantially longer than the normal single bond. The other O–O lengths (1.44—1.49 Å), in the six-membered ring and the *exo* part, are in the range of the typical O–O single bond.

The Mulliken charges also show some clear trends. The absolute values of all of the atoms of the ring isomers are smaller than those of the corresponding non-cyclic isomers; in other words, the cyclic isomers are less polar molecules. In particular, the N atom with the N–H bond is almost neutral. As is expected, the positive charge on the hydrogen of NH is less than that of OH; they are not much dependent on the size of the ring. The hydrogen of OH with a larger ring and of OOH is more positive (0.39) than that of the others. The bond O–H is as polarized as or more than that of the nitrous acids.

The nitrous acid is one of the most strong acids. One of the measures of the acidity in the ab initio calculations is the heterolytic bond dissociation energy, or deprotonation energy, of AH evaluated for the reaction[16)]

$$HNO_x \rightarrow NO_x^- + H^+. \quad (1)$$

For simplicity the total energy difference ΔE_{depro} of the reaction for some of the molecules are evaluated with the MP2/6-31G** approximation to examine the relative strength of acidity of the ring isomers. Among HNO_2, the order of ΔE_{depro} is *cis*-HONO (359 kJ mol^{-1})>*trans*-HONO (358)> bent-HNO_2 (349)> cyclic-HNO_2 (**1**) (276); distinctively the cyclic isomer's is the smallest. On the other hand, for HNO_3, the order of ΔE_{depro} is cyclic-HNO_3 (**2**) (381 kJ mol^{-1})> HOONO (366)> bent-$HONO_2$ (340)> cyclic-$HONO_2$ (**5a**) (329)> cyclic-$HONO_2$ (**5b**) (327).

Thus, if ever the four-membered ring isomer HNO_3 is synthesized, it is expected that it is a strong acid, stronger than nitrous acid.

Concluding Remarks

Ab initio molecular orbital calculations were carried out to locate and characterize the cyclic HNO_x (x=2—6) local minima. The relationship between the relative stability and the molecular conformation for the isomers containing the same size NO_x ring has been explained in terms of intramolecular interaction of positively charged hydrogen and negatively charged oxygen, which is further indicated in the shift of stretching vibrational frequencies.

Like NO_x radical rings, cyclic isomers of HNO_x are also energy-rich molecules. Therefore, both the theoretical and experimental studies on their syntheses, reactivity and decomposition will have important significance, though it is expected to be difficult; this could be a new target for theoretical and experimental scientists.

This work, along with the work on NO_x radical rings, has introduced the concept of a ringed system, which is very common in both organic and inorganic compounds, into the chemistry of nitrogen oxides.

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