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Theoretical Study of the Barriers to Internal Rotation in Nitrous Acid

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Nitrous acid, HONO, has been studied for three geometries by the *ab initio* LCAO SCF MO method with a basis of accurate gaussian atomic orbitals. The *trans* geometry is correctly predicted to be most stable, lying about 2 kcal/mole lower than the *cis* form, and 9 kcal/mole lower than the *90°* form (experimental estimates being 0.4 and 11.6 kcal/mole, respectively). Population analysis, dipole moment components, and properties related to nuclear-nuclear and nuclear-electron potentials all show a partial breaking of the hydroxyl oxygen-nitrogen bond at *90°* compared to *cis* and *trans*, as well as the effects of electronic rearrangement for nuclear screening in the high nuclear repulsion *cis* form. The *cis* to *90°* barrier is dominated by the attractive components of the total energy, while the *trans* to *90°* one is dominated by repulsive components, in agreement with our analysis and an earlier prediction by Allen.

In the manner of our previous paper on formic acid [1], we report here a study of the relative energies and geometries of the 24-electron system nitrous acid (HONO) by the *ab initio* LCAO SCF MO method. Nitrous acid is interesting both for its similarities to, and differences from, the isoelectronic formic acid. Both molecules have double bond character hindering internal rotation of the OH group. In formic acid both planar geometries having good opportunity for this double-bonding have unfavorable nuclear-nuclear repulsion, and the equilibrium geometry is, in fact, the high-nuclear repulsion form with H *cis* to the carbonyl O, this being a compromise between higher nuclear repulsion and the apparent greater ability of the carbonyl O to accumulate electronic charge for screening of the nuclear repulsion [1]. But in nitrous acid the planar form with H *trans* to the nitrosyl O does not have a hydrogen eclipsed against a hydrogen as in formic acid, and this lowest nuclear repulsion conformer is also the lowest total energy one, though by only about 0.4 ± 1 kcal/mole according to experimental estimates [2]. The energy of the *90°* form of nitrous acid with the "broken" partial double bond is deduced from spectral data [2] to be 11.6 kcal/mole higher than that of the trans form. As with formic acid, we hope our theoretical study will describe these relative energies, and also give some insight into the "barrier mechanism" *via* analysis of the electronic structure as a function of geometry.

Table 1. *Summary of calculated energy quantities for nitrous acid*[a]

	cis	*90°*	*trans*
E_t	−204.4140	−204.4029	−204.4173
V_{nn}	68.0207	67.7381	67.5540
V_{ne}	−618.4503	−618.0910	−617.7162
V_{ee}	141.9325	141.8314	141.7025
T	204.0832	204.1186	204.0424
$-V/2T$	1.000810	1.000696	1.000919

[a] E_t = total energy; V_{nn} = nuclear repulsion energy; V_{ne} = electron-nuclear attraction; V_{ee} = electron-electron repulsion; T = electronic kinetic energy; V = total potential energy = $V_{nn} + V_{ne} + V_{ee}$. All in atomic units: 1 a.u. = 627.5 kcal/mole.

Table 2. *Mulliken gross atomic and overlap populations calculated for nitrous acid*

	cis	*90°*	*trans*
Gross atomic			
H	0.585	0.580	0.574
O_A	8.414	8.433	8.433
N	6.785	6.812	6.811
O_B	8.216	8.174	8.182
Overlap			
H–O_A	0.595	0.593	0.600
O_A–N	0.348	0.299	0.326
N–O_B	0.652	0.652	0.670
H–N	−0.069	−0.054	−0.065
H–O_B	−0.001	0.000	0.004
O_A–O_B	−0.131	−0.123	−0.121

We use geometrical parameters from experimental studies [2]: $R(\text{O–H}) = 0.96$ Å, $R(\text{O–N}) = 1.46$ Å, $R(\text{N=O}) = 1.20$ Å, $\sphericalangle\text{HON} = 104°$, and $\sphericalangle(\text{ONO}) = 118°$. The molecule is aligned with hydroxyl O at the origin, N along the $+Z$ axis, nitrosyl O in the $+X$ direction in the XZ plane; H is rotated about the Z axis for this fixed framework. We denote the hydroxyl O as O_A, the nitrosyl O as O_B. Basis functions for the LCAO expansions are the "double-zeta" quality gaussian atomic SCF orbitals previously discussed [1], with the scale factor of the 5-term gaussian H 1*s* orbital set at $\sqrt{2}$.

Total energies and their components for *cis*, *90°*, and *trans* forms are summarized in Table 1. The *trans* conformer is correctly predicted to be more stable than the *cis*, by 0.0033 a.u. = 2.06 kcal/mole, and more stable than the *90°* form by 0.0144 a.u. = 9.04 kcal/mole. Thus the experimental results are fairly accurately represented.

To analyze the problem in more detail, we have computed the Mulliken gross atomic populations and overlap populations as summarized in Table 2. As in formic acid [1], there are marked shifts in atomic populations for the conformational change *90°* to *cis*. O_B gains about 0.042 e^- at the expense of losses of 0.019 for O_A and 0.027 for N, reflecting the "screening" of O_B which is eclipsed by H.

Table 3. *Summary of calculated potential Φ_n and $\langle 1/r \rangle_n$ at the nuclei in nitrous acid*[a]

	cis	*90°*	*trans*
Φ_n			
H	-0.8722	-0.8717	-0.8779
O_A	-22.260	-22.287	-22.279
N	-17.998	-18.015	-18.010
O_B	-22.183	-22.166	-22.178
$\langle 1/r \rangle_n$			
H	9.0733	8.7902	8.6122
O_A	27.202	27.229	27.220
N	24.699	24.716	24.711
O_B	27.357	27.306	27.294

[a] In atomic units.

This charge shift is no doubt assisted by increased bonding between the O_A–N pair (the partial double bond), as the O_A–N overlap in *cis* is rather larger (by 0.042) than in *90°*. The *trans* conformer also has greater O_A–N bonding than *90*, according to the overlap populations. Note that O_A–N overlap is largest for the *cis* geometry.

Further analysis can be obtained [1] from average dipole moment components, potentials at the nuclei (Φ_n), and the average value of the inverse of the electronic distances from the nuclei ($\langle 1/r \rangle_n$). Since the nuclear contribution to the Z component of the dipole moment does not change with rotation, changes in this component with rotation must be due to electronic rearrangement in the O_A–N direction. As in formic acid [1], we find for planar geometries a large displacement of electrons toward the O_B end of the molecule: 0.066 a.u. more for the *cis* than the *trans* geometry, which is in turn 0.016 more than the *90°* form.

Table 3 presents the calculated Φ_n and $\langle 1/r \rangle_n$. Since rotation of H about the O_A–N line does not change the nuclear potential at O_A and N, the decreased potential (or increased $\langle 1/r \rangle_n$) at these two atoms at *90°* compared to *cis* and *trans* would again reflect less O_A–N bonding.

The larger magnitudes at *cis* compared to *trans* of the O_B population, O_A–N overlap, electronic displacement along O_A–N, and increased potentials at O_A and N, all suggest slightly more O_A–N bonding and charge transfer in the *cis* geometry than *trans*. Again, as in formic acid, this indicates a shift of electrons to "screen" the H–O_B nuclear repulsion which is strongest at *cis*. But the overall effect here is not quite enough to make this *cis* geometry lower in energy than the *trans*, where nuclear repulsion is least.

Finally we examine the barriers in terms of Allen's partitioning [3] of the total energy into attractive and repulsive components. The energy components of Table 1 show that the *cis* to *90°* barrier is dominated by an increase in the attractive (negative) energy larger than the decrease in the repulsive (positive) component. Conversely, the *trans* to *90°* barrier is dominated by a repulsive increase. These are in agreement with Allen's predictions [3], as well as our own previous analysis here. Scaling to satisfy the virial theorem produces the same results.

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References

1. Schwartz, M. E., Hayes, E. F., Rothenberg, S.: J. chem. Physics **52**, 2011 (1970).
2. McGraw, G. E., Bernitt, D. L., Hisatsune, I. C.: J. chem. Physics **45**, 1392 (1966).
3. Allen, L. C.: Chem. Physics Letters **2**, 597 (1968).
4. Rothenberg, S., Kollmann, P., Schwartz, M. E., Hayes, E. F., Allen, L. C.: Int. J. of quant. Chem. S **3**, 715 (1970).

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