# A theoretical study of the relative stability of the isomeric forms of $N_2O_3$

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The electronic structure, geometrical parameters and relative stability of the isomeric forms of $N_2O_3$ are analysed by means of *ab initio* calculations. Total energies of the different isomers are given. The energy difference between the most stable conformers of the symmetric $N_2O_3$ is 4.31 Kcal mol$^{-1}$ as provided by 6-31G basis set. The height of the rotational barrier determined by the *ab initio* technique is 7.12 kcal mol$^{-1}$.

**Key words:** $N_2O_3$ isomeric forms—*Ab initio* calculations.

The existence of two isomeric forms of $N_2O_3$ has been reported: one is stable in gaseous phase, the $ONNO_2$ (asymmetric $N_2O_3$) (Fig. 1$_a$) and another one obtained in matrix isolation at low temperature [1, 2] and apparently in solution [3], $ONONO$ (symmetric-$N_2O_3$) (Fig. 1$_b$). the former show an extremely large N–N bond distance, as it was experimentally proved [4].

There have been several attempts to explain the geometry and electronic structure of asymmetric $N_2O_3$ [5, 6, 7] but no attention has been paid to the symmetric $N_2O_3$. The main purpose of this note is to analyse the electronic structure and geometrical parameters for this species and its rotational conformers.

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asymmetric

$I_a$

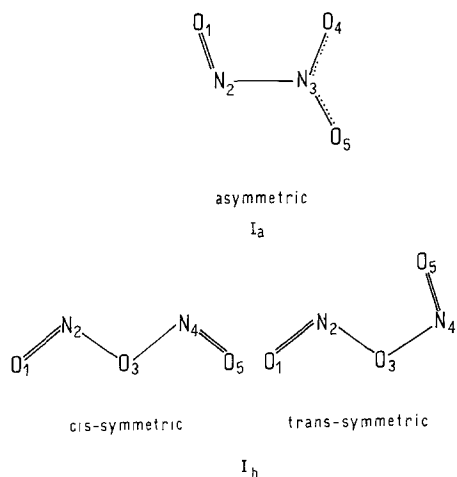cis-symmetric          trans-symmetric

$I_b$

**Fig. 1 a, b**

We have performed *ab initio* calculations with different basis sets using the Gaussian 70 package. The basis sets were those of Pople et al. [8]: STO-3G, 4-31G and 6-31G. Geometry optimization was carried out using the gradient method [9]. The starting geometries were taken from experimental data or the asymmetric $N_2O_3$ [3], while for the symmetric $N_2O_3$ the data were correlated from the one of the HONO [10], since no experimental data are available for this compound.

The optimized bond angles and bond lengths obtained for asymmetric as well as for the cis and trans rotational conformers of symmetric $N_2O_3$ (Fig. 1) are displayed in Table 1.

We also tested the most common semiempirical techniques (CNDO/2 [11], MINDO/3 [12], MNDO [13], PCILO [14] and CNDO/S-CI [15]). All of them

**Table 1.** Optimized bond angles and bond lengths for asymmetric $N_2O_3$, cis- and trans-symmetric $N_2O_3$ obtained by the Gaussian 70 *ab initio* technique

|  | Asymmetric | |  | *cis*-symmetric *trans*-symmetric | |
| --- | --- | --- | --- | --- | --- |
|  | STO-3G | Experimental |  | 6-31G | 6-31G |
| $O_1N_2$ | 1.206 | 1.206 | $O_1N_2$ | 1.221 | 1.221 |
| $N_2N_3$ | 1.779 | 1.864 | $N_2O_3$ | 1.436 | 1.436 |
| $N_3O_4$ | 1.260 | 1.202 | $O_3N_4$ | 1.436 | 1.446 |
| $N_3O_5$ | 1.271 | 1.217 | $N_4O_5$ | 1.221 | 1.217 |
| $O_1N_2N_3$ | 103.08 | 105.10 | $O_1N_2O_3$ | 107.33 | 107.73 |
| $O_4N_3N_2$ | 113.00 | 112.70 | $N_2O_3N_4$ | 104.75 | 111.65 |
| $O_5N_3N_2$ | 120.34 | 117.50 | $O_3N_4O_5$ | 107.33 | 107.73 |
| $O_1N_2N_3O_4$ | 0 | 0 | $O_1N_2O_3N_4$ | 180.00 | 180.00 |
| $O_1N_2N_3O_5$ | 180.00 | 180.00 | $N_2O_3N_4O_5$ | 180.00 | 0 |

**Table 2.** Total energy for the $N_2O_3$ conformers

| Method | | Asymmetric | *cis*-symmetric | *trans*-symmetric |
|---|---|---|---|---|
| GAUSSIAN 70 | STO-3G | −328.791893 | −328.858190 | −328.850770 |
| basis set | 4-31G | | −332.178537 | −332.171609 |
| [au] | 6-31G | | −332.518969 | −332.512102 |
| MNDO [eV] | | −1375.73006 | −1377.18881 | −1376.86351 |

failed to reproduce the experimental N–N bond distance for the asymmetric $N_2O_3$, except for the PCILO technique which describes it better than the STO-3G basis set. Several problems arose when a larger basis set was tried for this species, making extremely difficult the handling of this molecule. This may be attributed to the fact that there is a triplet state near in energy to the ground state [6] which makes it necessary the use of post Hartree–Fock methods.

For the symmetrical $N_2O_3$ the semiempirical technique yielded a geometry that can not be considered as reliable, since as we go from the cis to trans conformers the ONO angle does not show any change, as it should be expected due to the repulsion between $N_2$ and $O_5$ atoms lone pairs and as it is shown by *ab initio* technique.

The total energies for the different isomers are given in Table 2. The energy difference between the conformers of the symmetric-$N_2O_3$ is 4.31 Kcal mol$^{-1}$, as provided by the *ab initio* method (6-31G basis set), whereas from the MNDO method it is 7.5 Kcal mol$^{-1}$. The height of the rotational barrier provided by the *ab initio* technique is 7.12 Kcal mol$^{-1}$ (6-31G basis set).

We also studied the orbital symmetry of the frontier orbitals and their associated eigenvalues in order to correlate the results obtained from different methods for the symmetric $N_2O_3$. It was found that they may be correlated without any order inversion of their eigenvalues. It could also be observed that the HOMO of the cis compound is more stabilized that in the trans one, which may be attributed to the lower lone pair-lone pair repulsion present in the former.

It was experimentally demonstrated [2] as well as estimated [1] by means of heats atomization that the symmetric $N_2O_3$ is the most stable conformer, as it is also found at the Hartree–Fock level of calculations. In spite of the fact that the symmetric $N_2O_3$ is more stable than the asymmetric $N_2O_3$ the latter is found as the unique species in the gas phase. This fact is not contradictory because the asymmetric $N_2O_3$ is kinetically favored since the reaction between the quasi-radicals NO and $NO_2$ has zero or nearly zero activation energy, while the symmetric $N_2O_3$ is thermodinamically favored.

According to the results, we concluded that cis and trans symmetric $N_2O_3$ rotational conformers must be considered as existing in equilibrium. Consequently, they both should be taken into account whenever any spectroscopic study at low temperature is performed when $N_2O_3$ is present.

The next step in the theoretical study of the relative stability of the isomeric forms of $N_2O_3$ is to perform CI calculations in order to study the interconversion process between asymmetric and symmetric conformers.

At present, we are working on this line and further results will be presented elsewhere in a forthcoming paper.

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