Theoret. Chim. Acta (Berl.) 64, 313–316 (1984)

THEORETICA CHIMICA ACTA

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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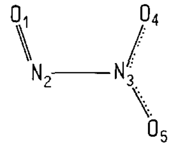
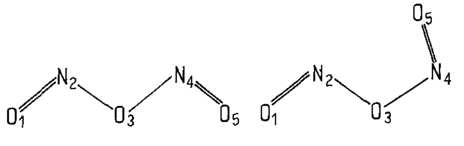


asymmetric

Ia



cis-symmetric trans-symmetric

Ib

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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Received August 9, 1983