SHORT REPORTS

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THEORETICAL STUDY OF THE N_2H_2 MOLECULE.

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Abstract

Theoretical investigation of the diimide molecule using the semi-empirical technique MNDO, predicts that the trans-*diimide (3) is more stable than the* cis-*diimide (5) by 1.8 kcal mole^{-1} and* cis-*diimide (5) is 27.61 kcal mole^{-1} below the aminonitrene (1).*

To our knowledge, there is a lot of information in the literature about the diimide molecule[1-5]. There were a few semi-empirical calculations[6-8]. The author wishes to report the theoretical investigation of diimide molecule using the MNDO method[8].

Structures

Three equilibrium and two transition state structures of the N_2H_2 system are shown in Fig. 1. The aminonitrene (1) geometries are given in Table 1. The previous calculations are shown in the Table 1. There was a fairly wide variation in the predicted structure of aminonitrene (1), with difference in θ_{NNH} angle values being as large as 3°. These differences are partly due to the choice of the basis set, and the inclusion or neglect of polarization and electron correlation effects. The MNDO method predicts the structure in reasonable agreement with the DZ + P/SCEP values.

The transition state (2) and transition state (4) structures are given in the Table 1. The MNDO method predicts rather unsatisfactory N-N bond distances for both transition states.

The geometry of *trans*-diimide (3) whose structure has been determined experimentally[9], are given in Table 1. The MNDO method predicts reasonable bond length for *trans*-diimide (3), but too large θ_{NNH} angle.

There is no experimental results of *cis*-diimide (5). The MNDO method predicts θ_{NNH} too large by 1-2° compared to other basis set and the N-N bond length turns out considerally too small.

Energies and Heat of Formation

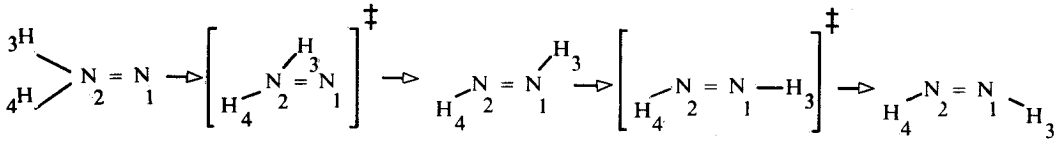
In 1976 R.A. Back *et al.*[10] investigated the experimental heat of formation of *trans*-diimide (3) via mass spectroscopic method. The MNDO calculated heat of formation for *trans*-diimide (3) differs from the experimental value by 4.1 kcal mole^{-1}.

The relative energies are given in Table 2. The MNDO method predicts that the *trans*-diimide (3) is more stable than *cis*-diimide (5) by 1.8 kcal mole^{-1} and that the *cis*-isomer (5) is 27.61 kcal mole^{-1} below the aminonitrene (1). This is in qualitative agreement, but the quantitative data are rather far away from the best values.

The MNDO calculated HOMO energies in eV for the N_2H_2 system are 9.2503, 9.1838, 10.8025, 8.9918 and 11.2540 compared with Parson and Dykstra values[12] 9.7963, 9.2521, 10.8848, 9.2521 and 10.8848.

The MNDO calculated dipole moments of the N_2H_2 system are 3.29, 2.13, 0.0, 1.84 and 2.44 D.

Fig. 1. Three equilibrium and two transition state structures of N_2H_2 system.



Aminonitrene (1) Transition state (2) Transdiimide (3) Transition state (4) Cis-diimide (5)

TABLE 1. COMPARISON OF CALCULATED STRUCTURES OF THE N_2H_2 SYSTEM

Aminonitrene (1)

Calculations	R_{NN} (A)	R_{NH} (A)	θ_{NNH}	Reference
MNDO	1.201	1.026	125.1	
TZ + P	1.215	1.011	122.6	(5)
DZ + P/SCEP	1.233	1.028	123.2	(5)

Transition state (2)

Calculations	R_{NN} (A)	$R_{N_2H_3}$ (A)	$R_{N_2H_4}$ (A)	$\theta_{N_1N_2H_4}$	$\theta_{N_1N_2H_3}$	Reference
MNDO	1.226	1.030	1.191	123.8	70.8	
DZ	1.294	1.011	1.165	121.7	62.9	(5)
DZ + P	1.259	1.020	1.112	120.5	65.6	(5)
DZ+P/SCEP	1.286	1.032	1.040	121.5	77.5	(5)

Trans-diimide (3)

Calculations	R_{NN} (A)	R_{NH} (A)	θ_{NNH}	Reference
MNDO	1.230	1.025	11.3	
Experiment	1.252 ± 0.002	1.028 ± 0.005	106.85 ± 0.047	(10)

Transition state (4)

Calculations	R_{NN} (A)	$R_{N_1H_3}$ (A)	$R_{N_2H_4}$ (A)	$\theta_{N_2N_1H_3}$	$\theta_{N_1N_2H_4}$	Reference
MNDO	1.187	0.979	1.054	180.0	112.6	
NZ + P	1.213	0.983	1.030	178.6	110.0	(5)
DZ + P/SCEP	1.237	0.993	1.048	177.8	109.0	(5)

Cis-diimide (5)

Calculations	R_{NN} (A)	R_{NH} (A)	θ_{NNH}	Reference
MNDO	1.208	1.029	118.7	
4-31G	1.230	1.020	116.0	(5)
TZ + P	1.215	1.017	113.0	(5)

TABLE 2. COMPARISON OF BARRIER ENERGIES (kcal $mole^{-1}$) TO OTHER CALCULATIONS.

Calculations	E_{31}	E_{35}	E_{32}	E_{34}	E_{12}	E_{45}	Ref.
MNDO	29.4	1.8	98.9	41.3	69.4	39.4	
DZ	7.1	8.3	89.9	46.9	82.8	38.6	(5)
DZ + P	18.7	6.3	87.9	55.7	69.2	49.4	(5)
TZ + 2P	18.1	5.8	86.7	55.5	68.6	49.7	(5)
DZ + P/SCEP	25.5	5.7	82.8	55.9	57.3	50.2	(5)
TZ + 2P/SCEP	24.5	7.2	82.6	55.1	58.1	47.9	(5)

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บทคัดย่อ

การศึกษาทางด้านทฤษฎีของ N_2H_2 โมเลกุลโดยใช้ semiempirical technique MNDO พบว่า trans-diimide (3) stable กว่า cis-diimide (5) โดย 1.8 kcal $mole^{-1}$ และ cis-diimide (5) มีค่า energy ต่ำกว่า aminonitrene (1) โดย 27.61 kcal $mole^{-1}$