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An *ab initio* SCF-LCAO-MO Study of the Nitrogen Inversion Barriers in Methylenimine, Diimide and Carbodiimide*

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The calculated values of the barriers to nitrogen inversion in methylenimine, diimide and carbodiimide are found to be respectively: 27.9, 50.1, and 8.4 kcal/mole.

Inversion barriers of pyramidal nitrogen have been computed for ethylenimine [1, 2] and for oxaziridine [2] in addition to the numerous calculations performed on ammonia [1, 3 and references therein].

Continuing our theoretical studies [1] of nitrogen inversion within the *ab-initio* SCF-LCAO-MO framework, we have investigated three compounds containing planar, "sp^2", nitrogen sites: methylenimine, I, diimide, II, and carbodiimide, III. Although semi-empirical computations on diimide [4, 5, 6] and on carbodiimide [6] have been published, no *ab initio* SCF calculations of the nitrogen inversion barriers in compounds I, II, and III have yet been reported[1]. The present calculations are of the SCF-LCAO-MO type using gaussian functions ($9s$ and $5p$ for N and C, $4s$ for H) as basis set[2].

Methylenimine, I

Bond lengths and bond angles for the ground state I have been taken from the microwave study of $H_2C{=}N{-}CH_3$ [8] using $N{-}H = 1.0$ Å. Optimization of the C=N–H angle gave a value of 67°. The shape of the nitrogen inversion curve has been calculated. The energy of the "linear" transition state I(l) is 27.9 kcal/mole above the ground state I and the energy of the singlet state of the twisted, "perpendicular", form I(*perp*) 57.5 kcal/mole above I (see table).

This means that the thermal isomerization of imines $R_1R_2C{=}NR_3$ will probably occur by nitrogen inversion [through form I(l)] and not by rotation around the C=N bond [through form I(*perp*)].

No experimental data on the isomerization of methylenimine are available. However related imines (where $R_3{=}CH_3$; R_1 and R_2 = alkyl or aryl) show thermal

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* Theoretical Conformational Analysis. Part II. (Part I see Ref. [1]).

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[1] Reference 7 in [5] cites two non-empirical calculations on diimide as private communications by L. C. Allen and by L. J. Schaad. An SCF study of the electronic states of the azoalkanes (including diimide) has been reported [7].

[2] IBMOL program; for the exponents of the GTF and coefficients for construction of the "contracted" basis functions see [1].

isomerization barriers higher than 23 kcal/mole (of the order of 25–27 kcal/mole) [9, 10, 11 and references therein][3].

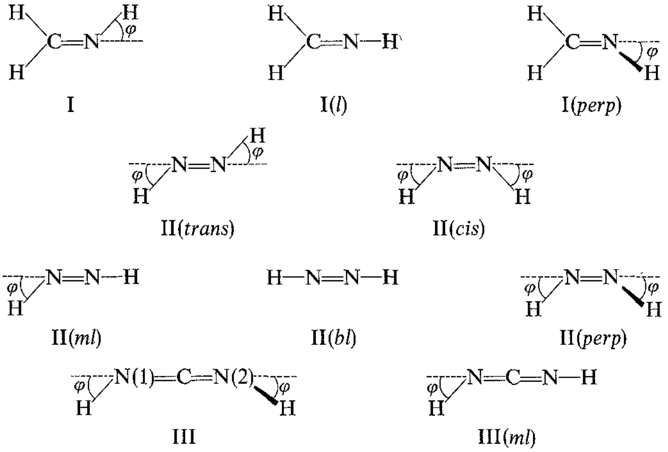
Diimide, II

Bond lengths for diimide have been taken from Ref. [13]. The N=N–H angles have been optimized. The results are given in the table. It is seen that the optimum N=N–H angles may be appreciably different in the various forms. We find that *trans*-diimide is *more stable* than the *cis* form by 10.5 kcal/mole. This is in sharp contrast with the results of the semi-empirical calculations which yield a lower energy for the *cis* form (4–8 kcal/mole; [5, 6]) but seems in agreement with other SCF calculations[4]. Thermal interconversion of *trans* and *cis* diimide should occur by inversion at one nitrogen through the "monolinear" form II(*ml*) (activation energy of 50 kcal/mole) and not by rotation around the N=N bond through the "perpendicular" form II(*perp*) (activation energy of 84 kcal/mole).

Except for the relative stabilities of II(*trans*) and of II(*cis*), the present results for II(*ml*), II(*bl*) and II(*perp*) are similar to the values obtained from semi-empirical INDO calculations [6], but are very different from the much lower energies obtained from EHT calculations [5]. No experimental measurements of the relative energies of the various forms of II are available, but the existence of *cis* and *trans* diimide has been established spectroscopically [15].

Carbodiimide, III

Bond lengths of 1.25 Å and 1.0 Å have been used for the C=N [16] and N–H bonds respectively. The C=N–H angle has been optimized in the ground state III.



[For I(*perp*), II(*perp*), and IIIa dihedral angle of 90° has been used.]

Fig. 1. Structures calculated for Methylenimine I, Diimide II and Carbodiimide III

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[3] When heteroatoms are present on C or on N new effects are introduced which have to be taken into consideration. For instance when $R_3 = \mathrm{Cl}$ or $\mathrm{OCH_3}$ the nitrogen inversion barriers are expected to be much higher than for $R_3 = \mathrm{H}$ or $\mathrm{CH_3}$ [9] as has also been shown for other N-halogeno compounds [12].

[4] See footnote 1 on precedent page. This point will be discussed later with respect to the chemical reactivity of the "diimide" species. See for instance [14].

Also in this case the transition state for nitrogen inversion is the "monolinear" form I(*ml*). The barrier to inversion is calculated to be of 8.4 kcal/mole. This value is comparable to the result of INDO calculations on the same compound (8.0 kcal/mole barrier; [6]). No experimental data on compound III are available[5].

Nitrogen Inversion Barriers and Population Analysis

It has been pointed out previously [1] that nitrogen inversion is accompanied by a $2s \rightarrow 2p$ electronic population transfer at the inverting nitrogen atom. In the present cases a decrease of ca. 0.3 and 0.1 electron is observed respectively for the nitrogen $2s$ and hydrogen (on the inverting nitrogen) $1s$ populations. Simultaneously the population of the nitrogen $2p$ orbital lying in the direction of the "lone pair" increases by 0.45, 0.47, and 0.18 electron for I → I(*l*), II → II(*ml*), and III → III(*ml*) respectively. It is seen that a high inversion barrier corresponds to a large population transfer.

Furthermore, the population of the nitrogen $2p$ orbital belonging to the N(1) = C π bond [and therefore lying in the same plane as the lone-pair of N(2)] on the non-inverting nitrogen N(1), increases by 0.13 electron as N(2) inverts from III to III(*ml*). This change corresponds to an electron transfer in the sense of a conjugation of the lone-pair on N(2) with N(1) = C double bond. Such a "conjugation" may explain the low inversion barrier calculated for III as compared to I.

Calculations of the barrier to rotation about the C=N bonds in III are under way. A detailed analysis of the electronic structure of the present compounds and a discussion of their properties will be given in the final account of this work.

Table. *Computed angles and energies for compounds* I–III

Structure	Angle φ optimized	Total energy a.u.	Energy barriers kcal/mole
I	67°	−93.947306	
I(*l*)	0°	−93.929830	I(*l*)-I = 27.9
I(*perp*)	67° [a]	−93.882763	I(*perp*)-I = 57.5
II(*trans*)	70°	−109.924240	
II(*cis*)	63°	−109.907558	II(*cis*)-II(*trans*) = 10.5
II(*ml*)	68°	−109.844374	II(*ml*)-II(*trans*) = 50.1
II(*bl*)	0°	−109.737979	II(*bl*)-II(*trans*) = 116.9
II(*perp*)	56° [a]	−109.790334	II(*perp*)-II(*trans*) = 84.1
III	60°	−147.794927	
III(*ml*)	60° [a]	−147.781594	III(*ml*)-III = 8.4

[a] Angle not optimized for this structure.

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[5] N.M.R. studies show that the nitrogen inversion barrier in substituted carbodiimides is lower than 10 kcal/mole: Lehn, J. M., and J. Wagner, unpublished results.

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