Ab Initio Calculation of the Molecular Structure and Electronic Properties of Carbodi-imide, HN=C=NH

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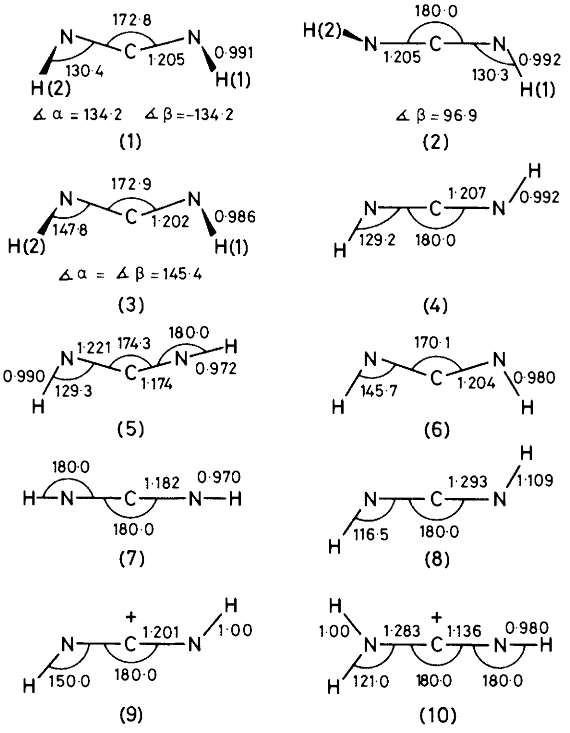
Results of *ab initio* SCF calculations on carbodi-imide (HN=C=NH) are reported. The geometry is optimized by the analytical-gradient method using the split-valence 4-31G basis set. The most stable geometry exhibits the non-linear $-N=C=N-$ frame with an $\widehat{NCN}$ angle of 172.8°. The calculated rotational and inversion barriers of the N–H group are shown to be very low and are almost the same (3.84 and 3.54 kcal mol^{-1} for rotation and inversion, respectively), confirming the configurational instability of this species. Some molecular properties have been calculated by the 6-31G** basis set.

Carbodi-imides, R–N=C=N–R, play important roles as condensing agents in the preparation of nucleotides and peptides in organic and biological chemistry. Recent advances in carbodi-imide chemistry have been reviewed by Williams and Ibrahim[1] and Mikolajczyk and Kielbasinsky.[2] The simplest member of the carbodi-imide family is HN=C=NH, for which the i.r. spectrum of the argon matrix-isolated species is available.[3] The existence of the transient HN=C=NH species as a tautomeric form of cyanamide at high temperatures, $NH_2CN \rightleftharpoons HNCNH$, has been positively identified.

There are some semi-empirical MO studies available for substituted carbodi-imides.[4,5] For HN=C=NH itself, there are also some *ab initio* SCF studies on the structure, inversion barrier, and one-electron properties.[6–9] One of these *ab initio* studies was by Moffat[8] who carried out a geometry optimization assuming a linear $-N=C=N-$ structure, while other studies assumed all geometrical parameters. The $-N=C=N-$ structure, however, was found to be non-linear in a recent *X*-ray crystallographic study, with the $\widehat{NCN}$ bond angle varying from 166 to 170° for several aliphatic and aromatic substituted carbodi-imides.[10]

The internal rotation and inversion of the N–H group are important with respect to the problem of the configurational instability of carbodi-imide. A previous *ab initio* study[6] employed an unrelaxed (non-optimized) geometry and obtained 8.4 kcal mol^{-1} for the inversion barrier. The INDO study with geometry optimization exhibited 7.8 kcal mol^{-1} for the internal rotation of the N–H group.[4] It would seem, therefore, interesting to obtain a completely optimized geometry for HN=C=NH in various conformations in order to determine relative energies and barriers to internal rotation and inversion from an *ab initio* SCF study.

In this work, we have considered seven possible conformers of HN=C=NH and calculated rotational and inversion barriers by completely optimizing all geometrical parameters by a gradient method. Furthermore, the triplet state, the cation, and the protonated species have been considered. A set of harmonic-force constants and some one-electron properties have also been calculated for the most stable conformer.



Optimized geometry (4-31G basis set) for carbodi-imide (1)—(7), the triplet state (8), the cation (9), and the protonated species (10). Distances in Å and angles in degrees; $\measuredangle\alpha = H_1NCN$, $\measuredangle\beta = H_2NCN$

Calculation

Ab initio SCF calculations of structures and properties of HN=C=NH have been carried out employing the split-valence 4-31G and 6-31G** basis sets.[11] The molecular geometry was optimized by the force-gradient method, with analytical gradient[12] as implemented in the MONSTERGAUSS program.[13] The force constants were obtained from the VAo5AD sum of square optimization technique[14] and the triplet state and cation have been calculated by the spin-unrestricted Hartree–Fock method.

Results and Discussion

The optimized geometries of seven conformations of carbodi-imide (1)—(7), the triplet state (8), the cation (9), and the protonated species (10) are shown in the Figure. The calculated SCF energies and relative energies with respect to the most stable conformer are summarized in Table 1. The 6-31G** basis set calculation employed the optimized geometry with the 4-31G basis set. The most stable conformer turned out to have the non-linear $-N=C=N-$ frame with an $\widehat{NCN}$ angle of

Table 1. Calculated total and relative energies of HN=C=NH

Molecule	E_T(4-31G)/ a.u. [a]	E_T(6-31G**)/ a.u.	ΔE(4-31G)/ kcal mol^{-1}	ΔE(6-31G**)/ kcal mol^{-1}
(1)	−147.661 58	−147.900 16	0.0	0.0
(2)	−147.660 37	−147.898 69	0.76	0.92
(3)	−147.654 30	−147.883 97	4.57	10.16
(4)	−147.655 45	−147.888 06	3.84	7.59
(5)	−147.655 93	−147.887 35	3.54	8.03
(6)	−147.654 96	−147.885 63	4.15	9.11
(7)	−147.651 13	−147.875 01	6.55	15.78
(8)	−147.540 61	−147.772 09	75.88	80.34
(9)	−147.354 29	−147.580 43	192.77	200.57
(10)	−148.014 81	−148.240 72	−221.59	−213.64

[a] A.u. = atomic units.

Table 2. Moments of inertia and rotational constants of HN=C=NH

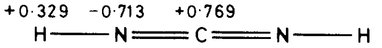
	Molecule	
Parameter	(1)	(2)
I_a [a]	0.9599	1.0329
I_b	48.3273	48.2763
I_c	48.3703	48.3458
A [b]	526 483.26	489 248.39
B	10 457.36	10 468.39
C	10 448.06	10 453.36

[a] A.m.u. Å^2 units. [b] MHz units.

172.8°. The energy difference between this and the linear −N=C=N− frame is calculated as 0.76 (4-31G) or 0.92 (6-31G**) kcal mol^{-1}. The calculated rotational barrier of 3.84 (4-31G) or 7.59 (6-31G**) kcal mol^{-1} turned out to be almost the same as the inversion barrier of 3.54 (4-31G) or 8.03 (6-31G**) kcal mol^{-1} in both basis sets. The completely linear structure H−N=C=N−H has been calculated to lie only 6.55 (4-31G) or 15.78 (6-31G**) kcal mol^{-1} above the most stable conformer and this evidence shows that the molecule as such is structurally very flexible. A previous INDO study [4] predicted 8.1 kcal mol^{-1} for the rotational barrier and 7.8 kcal mol^{-1} for the inversion barrier of the N−H group and the completely linear structure was calculated to be 16.8 kcal mol^{-1} above the most stable one. An experimental value of 6.7 kcal mol^{-1} has been reported from a recent n.m.r. study on the barrier of *cis–trans* racemization of carbodi-imide.[15]

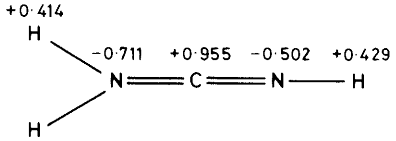
The calculated barriers of carbodi-imide may be contrasted to those of ketenimine, CH_2=C=NH. A recent *ab initio* study [16] predicted that the inversion barrier of the N−H group in ketenimine, 9.22 (4-31G) or 13.85 (6-31G**) kcal mol^{-1}, is much smaller than the rotational barrier of 26.72 (4-31G) or 25.12 (6-31G**) kcal mol^{-1}, and thus inversion is more likely in this species confirming the assignment of the configurational instability of CH_2=C=NH to nitrogen inversion. For HN=C=NH, the configurational instability is not only due to the nitrogen inversion but also to the N−H rotation, since the calculated barriers for both motions are shown to be almost the same and both are low.

The triplet state that lies 75.88 (4-31G) or 80.34 (6-31G**) kcal mol^{-1} above the most stable conformer has the linear −N=C=N− frame. Also, the cationic and protonated species have the linear −N=C=N−frame, as shown in Figure 1. The proton affinity of carbodi-imide was calculated as 221.59 (4.31G) or 213.64 (6-31G**) kcal mol^{-1}, which is found to be similar to the 232.5, 230.0, and 194.0 kcal mol^{-1} of CH_2=C=NH, CH_2=C=CH_2, and CH_2=C=O, respectively.[17] The moments of inertia and rotational constants of NH=C=NH for the most stable conformer and the linear −N=C=N− frame conformer are compared in Table 2.



$$\overset{+0.329}{H}-\overset{-0.713}{N}=\overset{+0.769}{C}=N-H$$

(I)



(II)

The quadratic force constants of carbodi-imide at the predicted equilibrium geometry (1) are summarized in Table 3. The N=C=N bending force constant of 0.787 mdyn Å rad^{-2} is shown to be relatively small reflecting the structural flexibility of this species with respect to this motion.

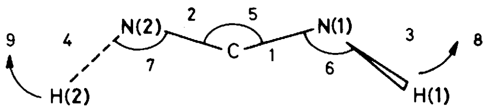
The photoelectron spectra of dialkylcarbodi-imides have been studied by Kroner *et al.*[18] and by Schouten and Oskam.[19] Dimethylcarbodi-imide, CH_3−N=C=N−CH_3, showed bands at 9.5, 11.55, and 12.26 eV. The first maximum consists of two ionizations that were assigned to represent two orbitals on the NCN part with both π- and *n*-character. The orbital ordering obtained both from the 4-31G and 6-31G** basis-set calculations supports this assignment, in that the two highest lying MOs correspond to the *n*- and π-orbitals of the NCN part, which are almost degenerate with MO energy of 10.25 eV. Another degenerate set of *n*- and π-orbitals is also present at the next higher lying band system.

The first ionization potential obtained from the SCF energy difference between the neutral and the cationic species, which was calculated by the spin-unrestricted Hartree-Fock SCF method, amounts to 8.35 eV (4-31G) and 8.70 eV (6-31G**).

The net charge distribution obtained from the 6-31G** basis set calculation for the equilibrium geometry is as in (I), and the overlap population of the N=C double bond amounts to 1.252 e. The net charge distribution for the protonated species from the 6-31G** basis set is given in (II), and the overlap population of the N=C double bond amounts to 0.814 e. In the presence of catalytic agents, such as metal ions, carbodi-imides react exothermally with alcohols and diols.[2] It was assumed that protonation or complex formation on the N atom increase the electrophilicity of the central carbodi-imide C atom considerably. Comparing the calculated net charges between the neutral and protonated species, it is evident that the central C atom becomes much more positive owing to the protonation, and thus the electrophilic nature becomes enhanced.

Table 3. Calculated 4-31G harmonic force constants (uncorrected) for carbodi-imide (1), mdyn Å^{-1} or mdyn Å rad^{-2}. The definition of the internal co-ordinates is given below [a]

1	2	3	4	5	6	7	8	9
15.056	1.446	−0.145	−0.110	0.104	0.501	−0.087	0.000	0.013
	15.056	−0.110	−0.145	0.103	−0.087	0.501	0.013	0.000
		7.891	0.000	0.011	0.185	0.013	0.001	0.003
			7.891	0.011	0.013	0.185	0.003	0.001
				0.787	0.000	0.000	0.000	0.000
					0.804	0.000	0.000	0.000
						0.804	0.000	0.000
							0.302	0.000
								0.302



[a] Co-ordinates 8 and 9 are out-of-plane bends.

Table 4. Molecular properties of carbodi-imide, H−N=C=N−H calculated by the 6-31G** basis set

Parameter	Molecule	
	(1)	(2)
Dipole moment [a]		
|μ|	2.165	2.044
Magnetic shielding [b]		
xx(C)	−5.3397	−5.3426
yy(C)	−5.3429	−5.3439
zz(C)	−3.9243	−3.9189
xx(N)	−6.4665	−6.3960
yy(N)	−6.4600	−6.5267
zz(N)	−5.4103	−5.4134
xx(H)	−0.4893	−0.0848
yy(H)	−0.4650	−0.8661
zz(H)	−0.0371	−0.0387
Potential [c]		
$1/r$ (C)	−14.6069	−14.6055
$1/r$ (N)	−18.3367	−18.3360
$1/r$ (H)	−0.9914	−0.9897
Quadrupole moment [d]		
Q_{xx}	−4.513	−4.781
Q_{yy}	−1.335	−0.876
Q_{zz}	5.848	5.657
Electric field gradient [e]		
q_{xx}(N)	0.112	0.082
q_{yy}(N)	0.471	0.518
q_{zz}(N)	−0.583	−0.600
η [f]	0.618	0.728

[a] Debye units. [b] Atomic units. [c] Atomic units. [d] Atomic units. [e] Atomic units. [f] Asymmetry parameter.

Calculated molecular properties of HN=C=NH with the 6-31G** basis set for the equilibrium geometry (1) and the linear −N=C=N− frame geometry (2) are summarized in Table 4. They include the dipole moment, magnetic shielding and potentials at nuclei, quadrupole moment, and the electric-field gradient at nitrogen. The calculated dipole moment at equilibrium geometry amounts to 2.165 Debye, which is smaller in magnitude compared with a previous *ab initio* value of 2.591 Debye.[8] It should be mentioned that the geometrical parameters were not optimized in this previous study. The diamagnetic-shielding values for H in the equilibrium geometry and in the linear −N=C=N− frame geometry are shown to be considerably different to each other, while potentials at nuclei are shown to be almost the same in both conformations. Of interest is the electric-field gradient, since it is a sensitive measure of the electronic-charge distribution in the immediate neighbourhood of the quadrupole nuclei, such as the nitrogen. The calculated quadrupole coupling constant (eQq) employing the quadrupole moment of nitrogen, $Q(^{14}N) = 1.56 \times 10^{-26}$ cm^2,[20] amounts to 2.20 MHz with an asymmetry parameter (η) of 0.618 for ^{14}N in the equilibrium geometry. The calculated eQq value is similar to the value of a previous *ab initio* SCF study by Kochanski *et al.*[7] of 2.55 MHz, but it is much smaller than the value 4.34 MHz of Hart.[8] Unfortunately there are, as yet, no experimental molecular properties reported for carbodi-imide itself to be compared with the calculated data reported here.

In conclusion, it should be stressed that the carbodi-imide-species, NH=C=NH, which is only about 18 kcal mol^{-1} less stable than cyanamide, NH_2CN,[9] owes its configurational stability to the lower lying rotational and inversion barriers of the N−H group and to its very flexible −N=C=N− group, as shown in the present study.

References

1 A. Williams and I. T. Ibrahim, *Chem. Rev.*, 1981, **81**, 589.
2 M. Mikolajczyk and P. Kielbasinsky, *Tetrahedron*, 1981, **37**, 233.
3 S. T. King and J. H. Strope, *J. Chem. Phys.*, 1971, **54**, 1289.
4 M. S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 2471.
5 D. R. Williams and R. Damrauer, *Theor. Chim. Acta*, 1971, **23**, 195.
6 J. M. Lehn and B. Munsch, *Theor. Chim. Acta*, 1968, **12**, 91.
7 E. Kochanski, J. M. Lehn, and B. Levy, *Theor. Chim. Acta*, 1971, **22**, 111.
8 B. T. Hart, *Aust. J. Chem.*, 1973, **26**, 463, 477.
9 J. B. Moffat, *J. Mol. Struct.*, 1973, **52**, 275.
10 H. Irgartigen and H. U. Jeager, *Acta Crystallogr.*, 1978, **B34**, 3262.
11 R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
12 H. B. Schlegel, Ph.D. Thesis, Queen's University, Canada, 1975.

13 M. R. Peterson and R. A. Poirier, Department of Chemistry, University of Toronto, Canada.
14 M. J. D. Powell, AERE subroutine library, Harwell, U.K.
15 I. Yavari and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 4689.
16 J. Kaneti and M.-T. Nguyen, *J. Mol. Struct.*, THEOCHEM. 1982, **87**, 205.
17 T.-K. Ha and M.-T. Nguyen, *J. Mol. Struct.*, THEOCHEM, 1982, **87**, 355.
18 J. Kroner, W. Strack, F. Holsboer, and W. Kosbahn, *Z. Naturforsch., Teil B*, 1973, **28**, 188.
19 S. Schouten and A. Oskam, *Inorg. Chim. Acta*, 1977, **22**, 149.
20 C. T. O'Konski and T.-K. Ha, *J. Chem. Phys.*, 1968, **49**, 5354.

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