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Commentationes

Theoretical Investigation of the Carbon Nitrogen Double Bond

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Ab initio Gaussian type calculations are reported for the ground and excited states of the hypothetical molecule formaldimine (H_2CNH). The C=N group is compared with the C=O group.

Die Ergebnisse einer *ab initio* Rechnung mit Gauß-Orbitalen für das hypothetische Formaldimin-Molekül (H_2CNH) werden mitgeteilt. Es werden sowohl Grundzustand als auch einige angeregte Zustände untersucht und die beiden Gruppen C=O und N=O verglichen.

On présente les résultats de calculs *ab initio* utilisant une base Gaussienne pour la molécule hypothétique de formaldimine (H_2CNH). L'étude porte sur l'état fondamental et quelques états excités. Une comparaison est faite entre le groupement C=N et le groupement C=O.

Introduction

The carbonyl (C=O) function has been the object of extensive studies for many decades. Much less is known about the azomethine (C=N) group, however, and we therefore felt that a theoretical investigation of this functional group was in order. It was decided to study the simplest system with a C=N function, namely the hypothetical molecule of formaldimine (H_2CNH).

Calculations

The *ab initio* calculations were done using a 4-31G Gaussian basis set [1]. The computer programs were modified versions of the Polyatom system [2, 3]. The $n - n^*$ singlet state was done using Huz, a program we built which is based on Huzinaga's first scheme [4]. This program will be submitted to the Quantum Chemistry Program Exchange very shortly.

Ground State

Complete optimization of the ground state geometry (Fig. 1) of formaldimine gives a planar structure having a total energy of -93.8824 a.u. (Table 1).

Experimentally, the C=N bond length is of the order of 1.29 – 1.30 Å for non conjugated imines (see Ref. [5]), i.e. imines containing alkyl substituents only. The value we obtain for H_2CNH is 1.257 Å.

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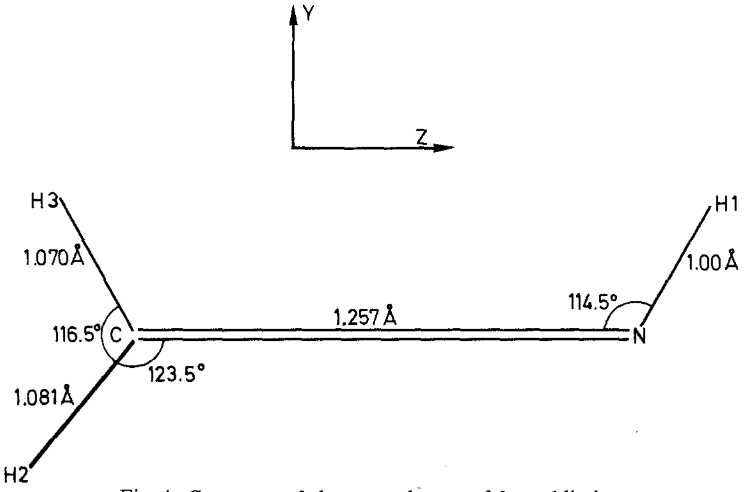

Fig. 1. Geometry of the ground state of formaldimine

Table 1. Results of SCF calculation on the ground state of formaldimine

	Energy breakdown (a.u.)		Orbital eigenvalues (a.u.)
Kinetic	93.9724	$1a'$	−15.5395
One-el. pot.	−286.2296	$2a'$	−11.2622
One-el. energy	−192.2573	$3a'$	− 1.2292
Two-el. pot.	65.0770	$4a'$	− 0.8521
Total el. pot.	−221.1525	$5a'$	− 0.6925
Nuclear pot.	33.2978	$6a'$	− 0.6142
Total pot.	−187.8547	$1a''(\pi)$	− 0.4499
Total electron	−127.1802	$7a'(n)$	− 0.4119
		$2a''(\pi^*)$	0.1646
Total energy	− 93.8824	$8a'$	0.2414
		$9a'$	0.2806
Virial	− 1.9990	$10a'$	0.3411

The following ground state electronic configuration of formaldimine results from the calculations (under C_s symmetry):

$$^1A' : (1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')^2 (1a'')^2 (7a')^2 .$$

The first two molecular orbitals are the Nitrogen and Carbon inner-shell orbitals respectively. The $3a'$ orbital is strongly C=N bonding, with most of the charge centered on the Nitrogen. An individual breakdown of the charges in terms of the basis functions (atomic orbitals) shows that 90% of the charge on Nitrogen and 80% of the charge on Carbon are due to the respective $2s$ basis functions. This MO is therefore mainly a $2s-2s$ bonding orbital, with slight contributions from the p_y and p_z orbitals.

Table 2. Results of Mulliken population analysis on formaldimine

MO	Gross populations					Overlap populations			
	H_2	H_3	C	N	H_1	N–H_1	N–C	CH_2	CH_3
$1a'$	0.0000	0.0000	0.0047	1.9942	0.0010	0.0018	0.0075	0.0000	0.0000
$2a'$	0.0017	0.0014	1.9956	0.0016	0.0000	0.0000	0.0027	0.0027	0.0025
$3a'$	0.0141	0.0122	0.5329	1.3613	0.0795	0.1069	0.5183	0.0134	0.0126
$4a'$	0.2580	0.1740	0.8886	0.4870	0.2024	0.2630	−0.1952	0.2905	0.2182
$5a'$	0.0026	0.4033	0.7845	0.5877	0.2219	0.1399	0.2470	0.0031	0.3516
$6a'$	0.4259	0.0504	0.8585	0.5634	0.1017	0.1332	0.0809	0.3903	0.0504
$1a''$	0.0000	0.0000	0.8829	1.1171	0.0000	0.0000	0.4867	0.0000	0.0000
$7a'$	0.1276	0.2098	0.1297	1.4395	0.0934	0.0086	−0.1350	0.0689	0.1360
Total a'	0.8197	0.8512	5.1955	6.4347	0.6999	0.6534	0.5261	0.7689	0.7750
Total a''	0.0000	0.0000	0.8829	1.1171	0.0000	0.0000	0.4867	0.0000	0.0000
Total	0.8197	0.8512	6.0774	7.5518	0.6999	0.6534	1.0127	0.7689	0.7750

In MO's $4a'$, $5a'$, and $6a'$ most of the charge is on C and N. The $4a'$ MO is slightly antibonding in CN, and $6a'$ is practically non bonding in CN. Orbital $7a'$, which is associated with the free pair orbital has most of the charge localized on the Nitrogen. This orbital is slightly antibonding in CN, and only slightly bonding in $C-H_3$; there is of course a slight delocalization over the entire molecule.

The $1a''$ MO is the MO which is formed from the $2p_x$ orbitals of Nitrogen and Carbon. The orbital is strongly bonding, and, as expected, is polarized towards the Nitrogen atom.

Taking the sum of populations over all occupied MO's, we see that the Hydrogens bonded to the Carbon lose about 0.16 electrons each while the one bonded to the Nitrogen loses 0.30.

The Carbon atom transfers $0.12\,\pi$ electrons to the Nitrogen while gaining $0.19\,\sigma$ electrons. The Nitrogen atom gains $0.43\,\sigma$ electrons.

Formaldimine is isoelectronic with formaldehyde and we can expect similarities between these molecules. From a qualitative point of view, both molecules are predicted to be planar with formaldimine having a bent $C{=}N-H_1$ part (symmetry group C_s). In both molecules, the ordering of the highest two occupied orbitals, and lowest virtual orbital is predicted to be π, n, π^* [6, 7].

Our calculation and that of Winter, Dunning and Letcher on formaldehyde [8] bear these predictions out. Table 3 contains the orbital eigenvalues, gross atomic and overlap populations of formaldehyde taken from Ref. [8].

Comparing Table 3 with Table 1 and Table 2, we find that the two molecules are not only qualitatively similar, but, except for the sixth molecular orbital, the eigenvalues, gross and overlap populations on Carbon, Nitrogen and Oxygen are quantitatively quite close for each occupied MO. The functional group bonds C=N and C=O have similar overlap populations for corresponding molecular orbitals, and the gross populations on Carbon and Nitrogen in formaldimine correspond very well to the Carbon and Oxygen populations in formaldehyde. The σ, π, and total charge on Carbon is less in formaldehyde

Table 3. Orbital eigenvalues and population analysis of formaldehyde (Results taken from Ref. [8])

MO	ε_i (a.u.)	Gross populations		Overlap populations
		C	O	C–O
$1a_1$	−20.6072	0.0015	1.9985	0.0029
$2a_1$	−11.3576	1.9993	−0.0002	−0.0004
$3a_1$	− 1.4304	0.4042	1.5817	0.4552
$4a_1$	− 0.8609	1.0835	0.3809	−0.1190
$1b_2$	− 0.6893	0.9485	0.6046	0.2609
$5a_1$	− 0.6318	0.4478	1.3731	0.1126
$1b_1(\pi)$	− 0.5238	0.7715	1.2285	0.4270
$2b_2(n)$	− 0.4269	0.1142	1.2528	−0.1169
$2b_1(\pi^*)$	0.1465	—	—	—
σ Sub total		5.0291	7.1914	0.5952
π Sub total		0.7715	1.2285	0.4270
Total		5.8006	8.4199	1.0222

Table 4. Inversion barriers for formaldimine

Configuration	Total energy	Barrier (kcal/mole)	Ref. [9]
Ground state	−93.8824 a.u.		
Rotated transition state	−93.7947 a.u.	55.1	57.5
Planar transition state	−93.8404 a.u.	26.3	27.9

than in formaldimine because of the greater electronegativity of Oxygen relative to Nitrogen. These results exemplify the close relationship these molecules have from a bonding point of view.

Experimental evidence supports a planar inversion mechanism for isomerization of imines [11, 20]. Our results predict that the isomerization process in formaldimine would occur through planar inversion rather than rotation about the molecular axis. From Table 4, we see that our results are quite similar to those of Lehn and Munsch [9], although they used a much better basis than ours. Our calculated value of 26.3 kcal/mole is in good agreement with experimental values for alkyl substituted imines which range from 25 to 27 kcal/mole [10–12].

We obtain a dipole moment of 2.44 D for formaldimine which is quite close to the value obtained for formaldehyde (2.59 D) [8]. The experimental value for formaldehyde's dipole moment is 2.34 D [13].

The positive ion of formaldimine was calculated using the Polyatom open shell SCF program based on Roothaan's [14] one-determinant formalism. We obtain an energy of −93.5499 a.u. This gives us a vertical ionization potential of 0.3325 a.u., which is of course inferior to the Koopmans' theorem value of 0.4119 a.u. since the latter does not take into account the rearrangement of the molecular orbitals in the ion.

Table 5. Transition energies (vertical) for formaldimine

State	CI	SCF
$(n \to \pi^*)^3$	4.68 eV	3.49 eV
$(n \to \pi^*)^1$	5.84 eV	4.21 eV
$(\pi \to \pi^*)^3$	4.57 eV	4.05 eV
$(\pi \to \pi^*)^1$	10.33 eV	—
$(n \to \sigma^*)^3$	9.59 eV	—

Excited States

The $n \to \pi^*$ transition energy should be about the same for most alkyl substituted imines, since the transition goes from a non bonding orbital largely localized on the Nitrogen, to a π^* orbital which is still largely localized on the C=N group. The transition energies for various excited states of formaldimine are given in Table 5. The energies were calculated by two different methods: singly excited configuration interaction using the ground state molecular orbitals, and the open-shell SCF procedure applied to the excited state wavefunctions. Because of the limited size of our basis set, CI did not lower the transition energies very much. The calculations were done with the ground state geometry, and therefore correspond to the vertical transitions.

Experimentally, the far ultra-violet spectrum of alkyl substituted imines [5] consists of broad bands and this feature makes the interpretation difficult. The fact that all types of transitions are permitted does not simplify matters either. There is a strong and diffuse band centered around 1700 Å (7.3 eV), with a molecular extinction coefficient of nearly 8000. This transition occurs at too low a frequency to be caused by the alkyl groups, and the molecular extinction coefficient would seem to indicate that in all likelihood, this is the first $(\pi \to \pi^*)^1$ transition. The asymmetrical shape of the band, which extends to 2000 Å indicates a composite character, probably due to a $(n \to \sigma^*)^1$ or $(n \to 3s)^1$ Rydberg transition. The $(n \to \pi^*)^1$ transition is usually located between 5.0 and 5.4 eV in this type of molecule [15, 16].

Our CI calculation gives a value of 10.33 eV for the $(\pi \to \pi^*)^1$ transition, which is about 30% higher than the experimental value. Del Bene, Ditchfield, and Pople's study of excited states (using the same basis as ours) by configuration interaction [20] shows that for $(\pi \to \pi^*)^1$ transitions, the calculated value is usually between 20% and 30% higher than the experimental values.

Similarly, $(n \to \pi^*)^1$ transitions are between 5% and 15% higher than the experimental values. If we reduce our calculated value by 10%, we obtain 5.2 eV, which is in good agreement with the experimental data for this type of transition.

The open-shell SCF results for the vertical transitions are lower than the CI results and the experimental values. This is presumably because the correlation energy is smaller in the excited states than in the ground state. Buenker and Peyerimhoff [17] obtained similar results for formaldehyde, their CI calculations being quite close to the experimental value while the SCF value was much lower.

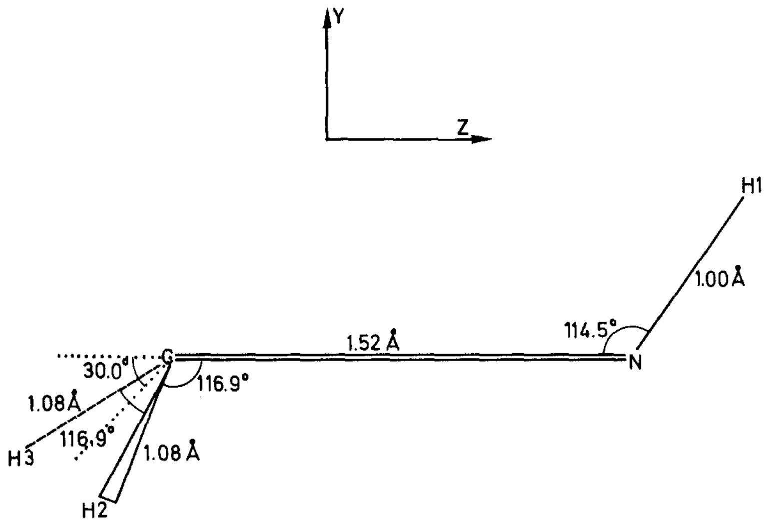

Fig. 2. Geometry of the excited triplet state of formaldimine

Symmetry considerations [6, 7, 18] predict that excitation of a non bonding electron to an anti-bonding orbital ($n \rightarrow \pi^*$) should result in bending the CH_2 group out of the molecular plane and a rotation of the N–H bond about the same plane (Fig. 2).

We have partially optimized the $(n \rightarrow \pi^*)^3$ state geometry, using the open-shell SCF method. The Hydrogen bond lengths were kept constant (1.08 Å for CH, and 1.00 Å for NH), the CNH angle was not varied, and the HCH angle was kept equal to the HCN angle. The minimum energy configuration (Fig. 2) gives an energy of -93.8108 a.u. We note that the CH_2 group is bent out of plane by 30°, the CN bond length is lengthened to 1.52 Å, and the NH bond is rotated 90° out of plane to give a trans conformation. This structure no longer represents the $(n \rightarrow \pi^*)^3$ state however since the geometry variations have destroyed the original symmetry plane. The resulting state is a mixture of the original ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) triplet states. Buenker and Peyerimhoff [18] obtained an out-of-plane bending angle of 32° for the formaldehyde $(n \rightarrow \pi^*)^3$ state: this is quite close to the value we obtain for formaldimine. The experimental out-of-plane bending angle is approximately 35° for formaldehyde (see Ref. [17]).

Conclusion

This paper has attempted to elucidate the structural characteristics of the imine functional group. We have drawn attention to similarities between the imine group and the carbonyl group throughout the article. The results are quite satisfying in that the two groups are very similar in the ground state, and the low-lying electronic states also seem to have a great deal in common.

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