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Conformational preferences for *N*,*N*-dimethyl-2-haloacetamides (halo = F, Cl, Br and I) through theoretical and experimental studies: An unexpected orbital interaction

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Abstract

Conformational preferences and orbital interactions of *N*,*N*-dimethyl-2-fluoroacetamide (**1**), *N*,*N*-dimethyl-2-chloroacetamide (**2**), *N*,*N*-dimethyl-2-bromoacetamide (**3**) and *N*,*N*-dimethyl-2-iodoacetamide (**4**) were analyzed using experimental infra-red data, theoretical calculations and NBO analysis. The conformational equilibria of compounds **1**–**4** can be represented by their *cis* and *gauche* rotamers. The *gauche* form of **1** is stable in the vapor phase and in a non-polar solvent, but the *cis* is predominant in a polar solvent. For **2**–**4** the *gauche* form is more stable than the *cis*, in both the vapor and liquid phases. These conformational preferences were attributed to the orbital interaction between two antibonding orbitals, $\pi^*_{C=O} \rightarrow \sigma^*_{C-X}$. This unexpected interaction was possibly due to the high (0.3) electron density on $\pi^*_{C=O}$, which results from the interaction between one nitrogen lone pair and $\pi^*_{C=O}$.

Keywords: Conformational analysis; Haloacetamides; Theoretical calculations; Infra-red spectroscopy

1. Introduction

Simple amides have been widely used as model compounds for experimental and theoretical studies [1]. Much of this attention stems from the importance of amide functional groups in biologically important systems as the building blocks of proteins and enzymes [2].

The amide bond and its importance in structural organic chemistry have been recently reviewed [3]. The conjugation of the nitrogen lone-pair is usually described in terms of resonance between two Lewis structures **I** and **II** (Scheme 1). However, this model has been challenged by Wiberg et al. [4] on the basis of comparisons of the calculated C, N, O electron densities of planar and twisted amides. Significantly, while distortion of the amide linkage introduces large variations in the CO–N bond length, the corresponding carbonyl bond length is hardly changed. In an attempt to rationalize these results, a third resonance structure (**III**) was introduced, so the dominant structures representing the amide bond become **II** and **III**. This implies that the carbonyl group of amides is best written as $C^+–O^-$.

There is a great deal of interest in the amides as complexing agents for selective extraction of actinides and lanthanides. In designing these host molecules, the knowledge of their stable conformations and of the rotational barriers is of the most importance, and have been extensively studied by theoretical methods, together with gas phase electron diffraction data and crystal structure data [5,6].

As a consequence, most of the recent studies on amides are related to the substituent effects on the rotational barrier of C–N bond [1,7–16]. It is generally accepted that the rotational barriers in amides are governed by steric and electronic effects [1,10–16] and these interactions (steric and electronic) are due to a direct or remote (through an aromatic ring) substituent interaction with the carbonyl group, which affects the C–N rotational barrier [3–12].

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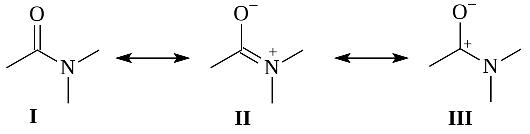
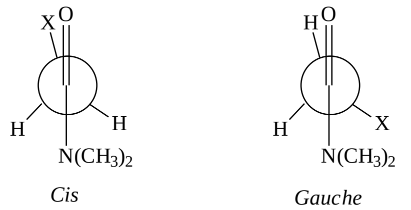


Scheme 1.



Scheme 2. The most stable rotamers *cis* and *gauche*, for *N*,*N*-dimethyl-2-haloacetamides (halo = F, Cl, Br and I).

In the special case of α-fluoro- and β′-fluoro-substituted amides, it was showed the relevant effect of the fluorine atom in determining the most stable conformer in aliphatic amides [17]. Despite most of the recent papers include theoretical calculations to describe the geometries and energies for the stable conformers, the energies due to the substituent interaction and the relevant orbitals involved in these interactions have remained virtually unexplored.

Moreover, while the rotational barrier of C–N bond in amides was widely explored, the same attention was not dedicated to the C–C(O) bond, which was the subject of a few studies from this laboratory (POCL) involving fluoroamides [18–20] and *N*,*N*-diethyl-α-haloacetamides [21,22] (Scheme 2).

In the present paper, a theoretical approach was applied to describe which orbital interactions are involved in the conformers stability and the corresponding energies for these interactions. The theoretical data were supported by IR spectral data in solvents of varying polarity. To this end, the halogenated derivatives amides (Scheme 2) were chosen to perform these studies.

2. Experimental

N,*N*-dimethylfluoroacetamide (**1**), *N*,*N*-dimethylchloroacetamide (**2**), *N*,*N*-dimethylbromoacetamide (**3**) and *N*,*N*-dimethyliodoacetamide (**4**) were prepared by literature procedures [10,18].

The carbonyl stretching bands in the fundamental (1850–1600 cm^{-1}) were obtained from the infrared spectra, recorded in a Bomem FT–IR MB-100 spectrometer, using 0.02 M solutions for compounds **1–3** in CCl_4, **4** in CH_2Cl_2 (non-polar solvents) and **1–4** in CH_3CN (polar solvent), using a 0.5 mm sodium chloride matched cell. All spectra were obtained with 64 scans and a resolution of 1 cm^{-1} and the deconvolution was performed through the GRAMS/32 curve fitting program which utilizes Gaussian and Lorentzian functions.

2.1. Computational details

All structures for the studied amides were fully optimized (Table 1) at the B3LYP/aug-cc-pVTZ levels using the Gaussian 98 program [23]. The aug-cc-pVTZ basis set was chosen for the correct description of fluorine, chlorine and bromine atoms. This basis set includes additional diffuse functions (prefix aug-), which were used to take into account the relatively diffuse nature of the lone

Table 1
Calculated parameters for *N*,*N*-dimethyl-2-haloacetamides (halo = F, Cl, Br and I) at the B3LYP/aug-cc-pVTZ level

Parameter	F		Cl		Br		I	
	Cis	*Gauche*	*Cis*	*Gauche*	*Cis*	*Gauche*	*Cis*	*Gauche*
$r(C{=}O)$[a]	1.214	1.223	1.214	1.220	1.214	1.221	1.216	1.221
$r(C–X)$	1.372	1.397	1.778	1.806	1.944	1.976	2.142	2.174
$r(C–N)$	1.366	1.358	1.364	1.361	1.365	1.362	1.365	1.364
$R(C–C)$	1.532	1.529	1.533	1.527	1.530	1.522	1.528	1.518
$\angle(C–C{=}O)$[b]	121	117	123	118	123	118	123	118
$\angle(C–C–X)$	110	113	112	112	112	112	113	112
$\angle(C–C–N)$	114	119	114	118	114	118	121	118
$\angle(O{=}C–N)$	124	123	122	123	123	122	122	123
$\theta(X–C–C–O)$	0.0	135	0.0	109	0.0	105	0.0	99
$E_{\text{rel.}}$[c]	2.2	0.0	3.2	0.0	3.7	0.0	3.7	0.0
$\mu(D)$	5.53	3.17	5.46	3.72	5.38	3.77	5.11	3.80
$\nu_{C{=}O}(\text{cm}^{-1})$[d]	1697	1661	1686	1661	1682	1658	1673	1655
$\nu_{C{=}O}(\text{cm}^{-1})$[e]	1691	1662	1688	1667		1664	1671	1647

[a] Angstrom.
[b] Degree.
[c] kcal mol^{-1}
[d] Corrected values obtained by multiplying the calculated frequencies by 0.967 (the correction factor).
[e] Experimental frequencies.