Solvent effect investigation on the Conformational behaviors of 1-fluoro-N, N-dimethylmethanamine and analogs containing P, As atoms

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Abstract

NBO analysis, hybrid density functional theory (B3LYP/6-311+G**) based methods were used to study the anomeric effects (*AE*), Stereoelectronic interactions, dipole-dipole interactions on the conformational properties of 1-Fluoro-N, N-dimethylmethanamine (1) and phosphorus (2) and arsenic (3) analogues. Moreover, relationships between stability of the anti-conformations of 1-Fluoro-N, N-dimethylmethanamine (1) and the analogs containing P and As (2, 3) compared to the gauche conformations of these compounds in solvents with different dielectric constants were investigated. Results indicated that the anomeric effect depended on the nature of the substitution present in the compounds and decreased when the dielectric constant of the environment, increased. The anomeric effect was confirmed by electron transfers from donor non-bonding orbitals to antibonding orbitals through using bond-length changes. The structures of compounds (1-3) were then investigated employing the theoretical method. The values of Gibbs free energy (ΔG), the anomeric effect (AE), dipole moment, structural parameters, and electron transfers of the stereoisomers in solvents with different dielectric constants were calculated. Results showed that the anti conformers of compounds (1-3) were more stable than the gauche conformers, and this stability trend was explained by changes in dipole moment and in anomeric effect. Furthermore, the change from the N to the P heteroatom increased the stability of the anti form compared to the gauche form. Moreover, the anti conformers were more stable than the gauche conformers when non-polar solvents were used instead of polar ones, but this trend was completely reversed with the change from the P to the As heteroatom.

Keywords: anomeric effects, NBO, 1-fluoro-N, N-dimethylmethanamine, Stereoelectronic interactions.

Introduction

Computational chemistry, in particular, quantum mechanical calculations, is a new approach to well-known physical and chemical phenomena, which can lead to a better understanding of the world around us. Today, with the advancement of computers, we can study various phenomena in very complex matrices such as biological systems and nanotechnology.

The need for such studies primarily requires a comprehensive understanding of the physical and chemical phenomena, the invention and innovation of modern methods of study and analysis, are documented and purposeful [1].

Many molecules may undergo rotational isomyration around one or more chemical bonds, and this affects the behavior of the spectrum, the orientation of the substrates in active regions, and the synthesis of flexible composites in terms of rotation. Electron delocalization from occupied to nearly unoccupied orbitals has shown to be at least competitive with classical interactions operating in simple systems, such as the ethane molecule [1–4].

Hyperconjugation is also assumed to be an important/major factor controlling the gauche effect in 1,2-disubstituted ethanes,[5–8], though the origin of this effect may also be due to electrostatic interaction [9,10] . One of the most recognized 2 electrons–2 orbitals interaction, which plays an important role in conformational isomerism, is the anomeric effect (formally a negative hyperconjugation), firstly observed in pyranose rings by Edward in 1955 [11]. Antiperiplanar symmetry is required for such interaction and it is well established when oxygen lone pairs are taken into account, but sulfides and sulfoxides also demonstrated significant ability in donating sulphur lone pairs to vicinal C—Cl antibonding orbitals [12]. Other higher-row elements containing lone pair(s) have also shown to be electron donors, and thus the corresponding compounds experience the anomeric effect, though in weaker extent when compared to compounds based on first-row elements [13–18].

In this work, the impacts of the stereoelectronic interactions associated with the *AE*, electrostatic ,steric interactions and solvent effect on the conformational and structural properties of 1-fluoro-N,N-dimethylmethanamine (1) and its phosphorus (2), arsenic (3) analogues were investigated computationally using hybrid-DFT based methods and natural bond orbital (NBO) analysis (see Scheme 1 and Figure 1).

Figure 1: The anti conformations of X: and gauche forms N (1), P (2), As (3)
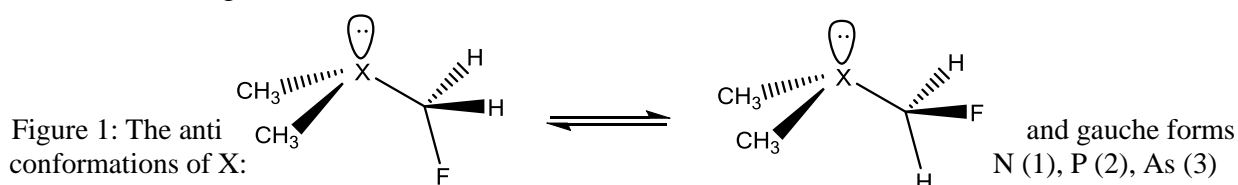
Theoretical calculations

The structures of the molecules were first drawn using the Chem3D and ChemDraw programs and then, using the Gaussian 09 program and considering the polar solvent H_2O and the non-polar solvent n-Hexane, the Z-matrix of the anti and gauche conformations of compounds (1-3) was studied [20].

The thermodynamic parameters and their relative values in these solvents of different polarities were also calculated. Natural bond orbital (NBO) analyses were used to calculate stability energies resulting from effective electron transfer, non-diametric elements, and structural parameters of the mentioned analogs [19].

Correlations between the corrected relative energy of the electrons, the Gibbs free energy, the enthalpy of the mentioned conformations, the anomeric effect of electron transfers, and the

structural parameters resulting from molecular orbitals were studied. Moreover, the stabilities of the stereoisomers of compounds (1-3) and their anomeric effect and dipole moments in the two solvents (H_2O and n-Hexane) were also investigated.

Discussion and results

The thermodynamic for the most stable anti and gauche conformations of compounds 1-3 are calculated at the B3LYP/6-311+G** levels of theory (Table 1). The results gave the Gibbs free energy difference between the anti and gauche conformations of compounds (1-3) in the solvents (H_2O and n-Hexane) were calculated at the B3LyP//6-311+G** level of theory.

$$\Delta G = \Sigma \, (GE_{gauche}) - \Sigma \, (GE_{anti}) \qquad (Eq. \ 1)$$

The results of methods used showed that the differences between the Gibbs free energy difference $(\Delta G_{gauche\text{-}anti})$ values between the anti and gauche conformations (anti preferences) increase from compound 1 to compound 2 and decreases from compound 2 to compound 3 in the polar solvent compared to the non-polar solvent . (Table 1)

Table 1. B3lyp/6-311+G**calculated thermodynamic functions [enthalpies, Gibbs free energies (in hartree) and entropies (in cal mol^{-1}K^{-1})], for the energy-minimum and energy-maximum geometries of compounds 1-3.

Solvent	Geometries	H	S	G	ΔH^a	ΔS^a	ΔG^a
Water ε=78.3553	N-Gauche	-273.692134	77.158	-273.728795	0.000	0.017	0.000002(0.001)^b
	N-Anti	-273.692128	77.175	-273.728797	6×10^{-6}	0.000	0.000
	P-Gauche	-560.315033	83.958	-560.354924	-0.002	0.000	0.001283(0.805)^b
	P- Anti	-560.316852	82.829	-560.356207	0.000	-1.129	0.000
	As-Gauche	-454.813768	89.034	-454.856071	-0.001	0.000	0.00029(0.182)^b
	As- Anti	-454.814738	87.601	-454.856361	0.000	-0.433	0.000
n-Hexan ε=1.8819	N-Gauche	-273.688179	76.880	-273.724707	-2×10^{-6}	0.004	0.000005(0.003)^b
	N-Anti	-273.688181	76.884	-273.724712	0.000	0.000	0.000
	P-Gauche	-560.310899	84.026	-560.350822	-0.003	0.000	0.002052(1.288)^b
	P-Anti	-560.313552	82.759	-560.352874	0.000	-1.267	0.000
	As-Gauche	-454.810230	88.818	-454.852431	-0.002	0.000	0.000961(0.603)^b
	As-Anti	-454.811784	87.572	-454.853392	0.000	-1.246	0.000

^{a}Relative to the ground state.

^{b}Numbers in parentheses are the corresponding thermodynamic function values in kcal mol^{-1}.

Study of changes in the anomeric effect (AE) based on using the B3LyP//6-311+G** method for optimizing the base state and for performing the NBO analysis on the interaction between the donor-acceptor orbitals revealed that the values for the anomeric effect of the compounds (1-2) increased in H_2O and n-Hexane, respectively, but those for the compounds (2-3) decreased (Table 2).

$$AE = \Sigma \, (GAE_{gauche}) - \Sigma \, (GAE_{anti}) \qquad (Eq. \ 2)$$

Table 2. Calculated stabilization (resonance) energies associated with donor–acceptor interactions (E_2, in kcal mol−1), anomeric effect (AE, in kcal mol−1) and off-diagonal elements (Fij, in a.u.), for the equatorial and axial

conformations of compounds 1–3, using NBO analysis based on the optimized structures at the B3LYP/6–311+G∗∗ level of theory

E_2(kcalmol^{-1})	Water ε=78.3553		Water ε=78.3553		Water ε=78.3553	
	N-Gauche	N-Anti	P-Gauche	P- Anti	As-Gauche	As- Anti
($\sigma_{C2-H6} \to \sigma^*_{X-C5}$)	5.22	-	0.82	-	0.65	-
($\sigma_{X-C4} \to \sigma^*_{C2-H7}$)	1.30	-	-	-	-	-
($\sigma_{X-C4} \to \sigma^*_{C2-H6}$)	-	1.30	-	1.21	-	0.98
($\sigma_{X-C4} \to \sigma^*_{C5-H11}$)	-	1.01	-	-	-	-
($\sigma_{X-C2} \to \sigma^*_{C4-H8}$)	7.12	2.84	1.54	1.40	1.29	1.20
($\sigma_{X-C2} \to \sigma^*_{C5-H11}$)	7.13	2.84	1.46	1.40	1.25	1.20
($\sigma_{X-C5} \to \sigma^*_{C4-H9}$)	1.02	1.01	1.46	1.39	1.29	1.22
($\sigma_{X-C5} \to \sigma^*_{C2-H6}$)	1.30	-	1.08	-	0.89	-
(LPX$\to \sigma^*_{C4-H10}$)	-	-	3.08	2.94	1.80	1.72
(LPX $\to \sigma^*_{C2-H7}$)	-	-	-	-	1.25	-
(LPX $\to \sigma^*_{C2-F}$)	-	-	-	6.03	-	3.34
∑	23.09	9	9.44	14.37	8.42	9.66
AE(kcalmol^{-1})	-14.09		4.93		1.24	
Fij(a.u.)						
(LPX $\to \sigma^*_{C2-F}$)	-	-	-	0.053	-	0.042

E_2(kcalmol^{-1})	n-Hexan ε=1.8819		n-Hexan ε=1.8819		n-Hexan ε=1.8819	
	N-Gauche	N-Anti	P-Gauche	P- Anti	As-Gauche	As- Anti
($\sigma_{C2-H6} \to \sigma^*_{X-C5}$)	5.24	-	0.82	-	0.65	-
($\sigma_{X-C4} \to \sigma^*_{C2-H7}$)	1.31	-	-	-	-	-
($\sigma_{X-C4} \to \sigma^*_{C2-H6}$)	-	1.31	-	1.22	-	0.98
($\sigma_{X-C2} \to \sigma^*_{C4-H8}$)	-	0.75	1.56	1.44	1.31	1.22
($\sigma_{X-C2} \to \sigma^*_{C5-H11}$)	-	0.75	1.51	1.44	1.30	1.22
($\sigma_{X-C5} \to \sigma^*_{C4-H9}$)	1.11	1.11	1.49	1.41	1.30	1.24
($\sigma_{X-C5} \to \sigma^*_{C2-H6}$)	1.31	-	1.11	-	0.93	-
(LPX$\to \sigma^*_{C4-H10}$)	2.28	7.48	3.06	2.89	1.80	1.69
(LPX $\to \sigma^*_{C2-H6}$)	1.69	1.70	-	-	-	-
(LPX $\to \sigma^*_{C2-H7}$)	1.70	1.70	2.25	-	1.22	-
(LPX $\to \sigma^*_{C2-F}$)	25.78	25.81	0.71	5.81	-	3.22
∑	40.42	40.61	12.51	14.21	8.51	9.57
AE(kcalmol^{-1})	0.19		1.7		1.06	
Fij(a.u.)						
(LPX $\to \sigma^*_{C2-F}$)	0.096	0.096	0.019	0.052	-	0.042

Investigation of the dipole moment ($\Delta\mu$) based on B3LyP//6-311+G** calculations showed that the difference in dipole moment between the anti and gauche forms increased from compound

(1) to compound (2), from the H2O solvent to the n-Hexane solvent, and from compound 2 to compound 3, respectively (Table 3).

Table 3. Calculated orbital occupancies(e),orbital energies [in atomic unit, (a.u.)], dipole moments (μ, in Debye) for the Gauche and Anti conformations of compounds 1–3, using NBO analysis based on the optimized structures at the B3LYP/6–311+G∗∗ level of theory

	Water ε=78.3553		Water ε=78.3553		Water ε=78.3553	
	N-Gauche	N-Anti	P-Gauche	P- Anti	As-Gauche	As- Anti
Orbital energy differences						
$\Delta(E\,\sigma^*_{\text{C4-H10}}\text{- LPX})$	0.38880	0.38397	0.78319	0.78999	0.88338	0.89043
$\Delta(E\,\sigma^*_{\text{C2-H6}}\text{– LPX})$	0.39424	0.39425	0.7629	0.75346	0.85987	0.85069
$\Delta(E\,\sigma^*_{\text{C2-H7}}\text{- LPX})$	0.39439	0.39411	0.76056	0.75355	0.85935	0.85069
$\Delta(E\,\sigma^*_{\text{C2-F}}\text{– LPX})$	0.48375	0.48402	0.58805	0.57064	0.68151	0.66904
Orbital occupancies						
LPX	-	-	1.94923	1.93182	1.97248	1.96106
$\sigma^*_{\text{C4-H10}}$	0.01079	0.02181	0.01553	0.01354	0.01042	0.00939
$\sigma^*_{\text{C2-H6}}$	0.02219	0.02226	0.01967	0.01932	0.01901	0.01872
$\sigma^*_{\text{C2-H7}}$	0.02223	0.02226	0.02770	0.01932	0.02353	0.01872
$\sigma^*_{\text{C2-F}}$	0.08828	0.08797	0.02376	0.04554	0.02058	0.03296
Dipole moments						
μ (Debye)	2.8205	2.8086	3.8030	0.9099	3.4731	1.0995
$\Delta(\mu_{\text{anti}}\text{-}\mu_{\text{gauche}})$	-0.0119		-2.8931		-2.3736	

	n-Hexan ε=1.8819		n-Hexan ε=1.8819		n-Hexan ε=1.8819	
	N- Gauche	N-Anti	P- Gauche	P- Anti	As- Gauche	As- Anti
Orbital energy differences						
$\Delta(E\,\sigma^*_{\text{C4-H10}}\text{- LPX})$	0.65221	0.65216	0.78714	0.79418	0.88663	0.89365
$\Delta(E\,\sigma^*_{\text{C2-H6}}\text{– LPX})$	0.64165	0.64159	0.7658	0.7559	0.86185	0.85222
$\Delta(E\,\sigma^*_{\text{C2-H7}}\text{- LPX})$	0.64164	0.64159	0.76256	0.7559	0.86056	0.85222
$\Delta(E\,\sigma^*_{\text{C2-F}}\text{– LPX})$	0.43069	0.43036	0.60124	0.58123	0.69358	0.67877
Orbital occupancies						
LPX	1.80126	1.80112	1.95099	1.93446	1.97346	1.96259
$\sigma^*_{\text{C4-H10}}$	0.01064	0.02233	0.01556	0.01343	0.01048	0.00937
$\sigma^*_{\text{C2-H6}}$	0.02403	0.02402	0.02042	0.01986	0.01969	0.01924
$\sigma^*_{\text{C2-H7}}$	0.02404	0.02402	0.02847	0.01986	0.02429	0.01924
$\sigma^*_{\text{C2-F}}$	0.11809	0.11825	0.02224	0.04339	0.01939	0.03148
Dipole moments						
μ (Debye)	2.2111	2.2153	3.0952	0.7963	2.8187	0.9292
$\Delta(\mu_{\text{anti}}\text{-}\mu_{\text{gauche}})$	0.0042		- 2.2989		-1.8895	

Therefore, the changes in the anomeric effect and dipole moment well explained the changes in Gibbs free energy (ΔG) and increases in the anti conformer compared to the gauche conformer (Table 2). NBO results showed that the population of nonbonding orbitals (LP) of compounds (1-3) in the anti and gauche conformers in both solvents increased but the population of

antibonding orbitals (σ^*_{C2-F}) decreased (Table 3). The population of the non-bonding orbitals (LP$_X$) and the population of the antibonding orbitals (σ^*_{C2-F}) of the anti and gauche conformations can be explained by studying the changes in the anomeric effect of compounds (1-3). Therefore, the donor-receiver interaction is an effective factor in the bonding, non-bonding, and antibonding populations of the various conformations of these compounds.
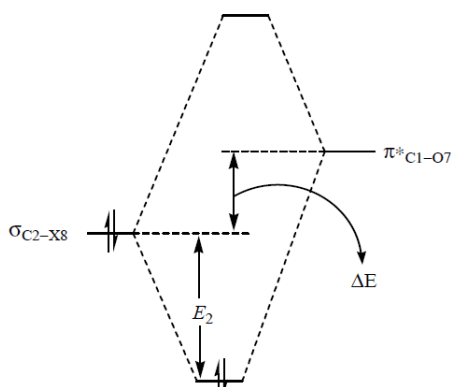
Based on NBO results, the energy difference (ΔE) between the donor orbitals (anti E$_{LPX}$) and the acceptor orbitals (Eσ^*_{C2-F}) of compounds (1-3) increased with heteroatom change from N to P and to AS in both solvents, respectively (Table 3). Therefore, differences in energy (ΔE) cannot well explain the changes in resonance energy (E_2).

However, based on NBO results, values for the non-diametric elements (F_{ij}) related to lack of electron establishment LP x → σ^*_{C2-F} in compounds (1-3) in H$_2$O increased and then decreased, respectively, and there was a parallel change in the values for the resonance energy (E_2)LP x → σ^*_{C2-F}. In the n-Hexane solvent, the values for the LP x → σ^*_{C2-F} transfer decreased in compounds (1-3) and, in parallel with it, the values for the E$_2$ energy changed.

$$\text{(Eq. 3)} \qquad E_2 = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i}$$

Where qi is the ith donor orbital occupancy, $\varepsilon_i, \varepsilon_j$ are off-diagonal elements (orbital energies) and $F(i,j)$ off-diagonal elements, respectively associated with the NBO Fock matrix (Figure 2). There is a direct relationship between F(i,j) off-diagonal elements and orbital overlap (S). In the NBO method, the donor-acceptor electron interactions can be studied separately because this method allows separation of the energy contribution due to donor-acceptor electron interactions from those caused by steric and electrostatic interactions, therefore the NBO approach permits consideration of charge delocalization [21-26].

Figure 2: Schematic representation of the correlation between the second order perturbation energies (i.e. stabilization energies E$_2$) and the energy gaps between donor and acceptor orbitals in the axial conformations of compounds 1-3.

Therefore, we can say that changes in non-diametric elements (F_{ij}) can well explain changes in resonance energy E$_2$ (Table 2). The structural parameters introduced for the anti and gauche forms of compounds (1-3) were calculated at the B3LyP//6-311+G** level of theory. Study of the structures of these compounds suggests that lack of the electron establishment LP N is observed in n-Hexane but not in water because the N atom is covered by the water solvent whereas lack of establishment of LP$_P$ and LP$_{As}$ electrons is observed in both solvents. This shows that P and As are not covered by the solvent because of their larger compared to N (Table 4).

Table 4. B3lyp/6-31G* calculated structural parameters for the axial and equatorial conformations of compounds 1-3.Compound

	Water ε=78.3553		Water ε=78.3553		Water ε=78.3553	
Bond lengths (Å)	**N- Gauche**	**N-Anti**	**P- Gauche**	**P- Anti**	**As- Gauche**	**As- Anti**
r_{C2-X}	1.385	1.386	1.870	1.858	1.998	1.992
r_{C2-F}	1.489	1.488	1.418	1.423	1.417	1.417
r_{C2-H6}	1.088	1.088	1.092	1.092	1.091	1.091
Bond angles (°)						
$\theta_{C4-X-C5}$	114.253	114.255	100.801	101.101	98.107	98.466
$\theta_{C2-X-C5}$	116.999	116.994	99.936	100.366	97.468	97.602
$\theta_{C2-X-C4}$	117.041	116.994	97.224	100.366	95.068	97.602
θ_{X-C2-F}	113.484	113.502	109.612	114.060	109.627	113.373
Torsion angels (°)						
$\phi_{F-C2-X-C4}$	70.620	-70.488	176.412	-51.720	177.466	-49.826
$\phi_{H7-C2-X-C4}$	-172.996	45.940	-64.498	68.177	-63.575	69.892
$\phi_{H6-C2-X-C4}$	-45.773	173.084	58.660	-171.617	59.540	-169.543

Compound	**n-Hexan ε=1.8819**		**n-Hexan ε=1.8819**		**n-Hexan ε=1.8819**	
Bond lengths (Å)	**N-Gauche**	**N-Anti**	**P-Gauche**	**P- Anti**	**As-Gauche**	**As- Anti**
r_{C2-X}	1.395	1.395	1.873	1.861	2.000	1.995
r_{C2-F}	1.460	1.460	1.408	1.415	1.407	1.409
r_{C2-H6}	1.090	1.090	1.093	1.093	1.092	1.092
Bond angles (°)						
$\theta_{C4-X-C5}$	113.877	113.893	100.269	100.686	97.758	98.149
$\theta_{C2-X-C5}$	116.277	116.283	99.231	99.815	96.725	97.117
$\theta_{C2-X-C4}$	116.269	116.283	96.768	99.815	94.676	97.117
θ_{X-C2-F}	113.624	113.620	109.800	114.115	109.705	113.329
Torsion angels (°)						
$\phi_{F-C2-X-C4}$	69.194	-69.196	-179.998	-51.381	-178.359	-49.590
$\phi_{H7-C2-X-C4}$	-173.467	48.129	-60.667	68.783	-59.244	70.361
$\phi_{H6-C2-X-C4}$	-48.140	173.479	61.865	-171.545	63.300	-169.541

Conclusions and recommendations

-By examining the values of ΔG in each solvent, by changing the heteroatom from N to P and AS, anti conformer is more stable than gauche conformer.

- By changing the heteroatom, the stability of anti increases from N to P and decreases from P to AS. In H$_2$O solvent, if the heteroatom is N, due to its solvent encapsulation, the anti form would be more stable than gauche form; however in non-polar solvent of n-hexane, for all of the mentioned heteroatoms, anti form is more stable than gauche form.

In both solvents, the changes in Gibbs free energy ΔG and changes in the anomeric effect AE are in alignment with each other and the stability of conformations (1-3) is justified by the variations of the anomeric effect (AE) and dipole moments($\Delta\mu$).

-Investigating the electron density of orbitals indicated that there is no population for LPN in H$_2$O solvent because N is covered by this polar solvent; however, in n-hexane non-polar solvent, this phenomenon is not observed and LP$_N$ has a population.

-The r_{c2-X} bond length increases by increasing the atomic radii of the heteroatoms in conformations (1-3), and the r_{c2-X} bond length decreases at the same time.

-The investigations revealed that the variations in the resonance energy (E_2) and the non-diagonal elements (F_{ij}) are in alignment with each other and are justified; however, the changes in energy ΔE do not play a decisive role in determining the value of resonance energy (E_2).

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