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Analysis of Permanent Electric Dipole Moments of Aliphatic Amines.

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Abstract

Motivation. The Mulliken permanent electric dipole moments have been calculated for several aliphatic primary amines (ammonia, methylamine, ethylamine and propylamine). These calculated dipole moments were compared to the experimental dipole moments obtained in the gas-phase in order to find a reliable ab initio quantum chemistry model of calculating these quantities.

Method. The Hartree-Fock calculations are carried out for the geometry optimization and calculating the dipole moments. An important number of basis sets incorporating diffuse and polarization functions are used and compared.

Results. 6-31G(3df) and 6-31++G(3df,3pd) were found to be the most reliable ab initio models for the calculation of equilibrium molecular geometries and permanent electric dipole moments of aliphatic primary amines. This method allowed us to obtain calculated dipole moments very concordant with experimental ones for the four molecules studied.

Conclusions. Ab initio quantum chemistry models can be used to predict dipole moments with a good accuracy. The choice of the basis set used for the calculations is of great importance and the best basis set is neither the one including the most complicated polarization functions nor the one including the most important number of diffuse and polarization functions.

Keywords. Aliphatic primary amines; Ab initio quantum chemistry model; Dipole moments.

Abbreviations and notations

HF, Hartree-Fock

SCF, Self Consistent Field

1 INTRODUCTION

The permanent electric molecular dipole moment μ is one of the most frequently studied and applied physical observable, since it provides fundamental information on the structure and polarity of molecules. By definition, the dipole moment vector points from the center of the positive charge distribution to the center of the negative charge distribution. Its scalar value is the norm of the dipole moment vector: $\mu=(\mu_x^2+\mu_y^2+\mu_z^2)^{1/2}$. Consequently, the electric dipole moment is highly dependent on the geometry of the molecule. This dependence is manifested in the intensities of the absorption bands in the infrared spectra.

Either experiments or quantum-chemical calculations allow the determination of these electric molecular dipole moments. Thus we used ab initio quantum-chemical calculations to obtain the components of the electric molecular dipole moment of four different molecules: ammonia, methylamine, ethylamine and propylamine. Then the resulting dipole moments were compared to the experimental values. These calculations were carried out at the Hartree-Fock level of theory and we tested different basis sets in order to find the most reliable method of calculating the dipole moments of these aliphatic primary amines.

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2 MATERIALS AND METHODS

2.1 Chemical Data

The four aliphatic primary amines studied were optimized at the Hartree-Fock HF/6-31G level, before their dipole moments were calculated using Hartree-Fock method combined with different basis sets. Resulting optimized structures are shown Figure 1.

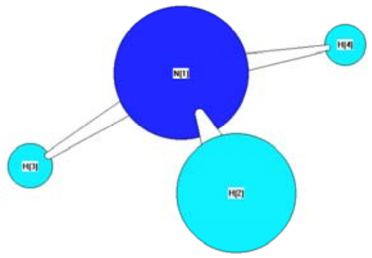
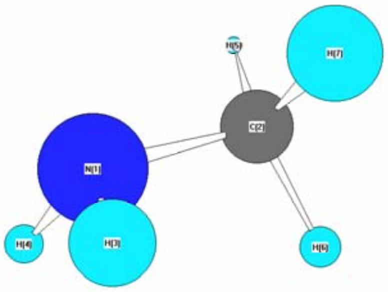
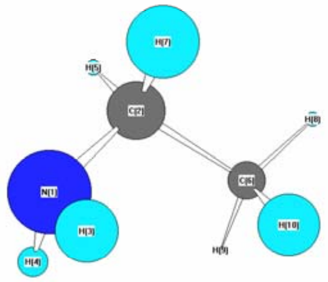
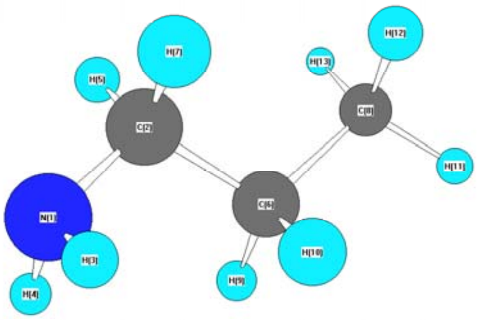
	
Ammonia	Methylamine
	
Ethylamine	Propylamine

Figure 1: Optimized structures of ammonia, methylamine, ethylamine and propylamine.

2.2 Computer Software

Ab initio calculations were performed at the Hartree-Fock [1] level of theory with Gaussian 98W [2] using the split valence, incorporating polarization and diffuse functions [3]. For the calculations, the standard 6-31G, 6-31+G, 6-31++G, 6-31G(d), 6-31G(2d), 6-31G(3d), 6-31G(df), 6-31G(2df), 6-31G(3df), 6-31G(d,p), 6-31G(d,2p), 6-31G(d,3p), 6-31G(d,pd), 6-31G(d,2pd), 6-31G(d,3pd), 6-31++G(3df,3pd) and 6-311++G(3df,3pd) basis sets were used. The geometry optimization calculations were obtained with a Self-Consistent Field (SCF) optimization. Thus these quantum-chemical calculations allowed us to access the dipole moments of each molecule by solving the Self-Consistent Field equations for 298.15 K at 1 atm. in the gas-phase.

3 RESULTS AND DISCUSSION

The experimentally determined gas-phase dipole moments referring to the ground vibrational state of the ground electronic state of molecules were taken from a reference book [4]. The first line in Table 1 gives these experimental values μ_{exp}. Data compiled in Table 1 reveals that the scalar magnitudes of the experimental dipole moments of aliphatic primary amines are usually small since they are inferior to 1.5D. One can also observe that their dipole moment is smaller when the chain of the aliphatic primary amine is longer.

The ground electronic state equilibrium geometries were determined with full geometry optimization at the Hartree-Fock level. The permanent electric dipole moments were calculated by using the SCF wavefunctions. Indeed, since the electric dipole moment is a one-electron property, it can be expected that for neutral closed shell molecules, in their ground electronic state, the quality of the HF SCF wavefunction will be adequate for the provision of good calculated values. Table 1 gives the calculated scalar magnitudes of the permanent electric dipole moments for different basis sets using both polarization and diffuse functions.

Table 1 reveals that experimental and calculated dipole moments of the molecules studied are concordant when 6-31G, 6-31G(3df), 6-31G(d,3p) or 6-31G(d,3pd) basis sets are used. Indeed, for these latter basis sets, the average difference between experimental and calculated values are inferior to 5%. On the contrary, when 6-31G(d), 6-31G(df), 6-31G(d,p) or 6-31G(d,pd) basis sets are used, the average difference is superior to 10%. Consequently, these basis sets are not efficient for providing accurate dipole moments of aliphatic primary amines. However, such a difference is not very surprising since previous studies showed that the difference between experimental and calculated dipole moments of aliphatic hydrocarbon molecules may reach 20% when calculations are made at the Hartree-Fock level of theory with 6-31G(d) basis set [5]. From these results, we can consider that the accuracy of the calculated dipole moments is strongly dependent on the basis set used for these calculations.

If we are looking closely to the results compiled in Table 1, we can also observe that the addition of diffuse functions does not provide more accurate calculated dipole moments. Indeed the average difference between experimental and calculated values is more important for 6-31+G and 6-31++G than for 6-31G basis set.

The consequences of the addition of polarization functions is much more complicated. For example, the results obtained with the 6-31G(d,p) basis set, which consists in the addition of p functions on hydrogen atoms and d functions on heavy atoms, does not give a calculated dipole moment concordant with the experimental one (average difference of 16.8%). However, the resulting dipole moment is more concordant when using 6-31G(d,2p) basis set (12.0%), and far more concordant when using 6-31G(d,3p) basis set (3.9%). Such a result can be observed when adding different types of functions on hydrogen and heavy atoms (see Table 1).

More, 6-31G(3df) was found to be the most reliable ab initio model for the calculation of permanent electric dipole moments of aliphatic primary amines since the average difference between calculated and experimental dipole moment is equal to 2.1%.

Despite the fact that HF/6-31++G(3df,3pd) and HF/6-311++G(3df,3pd) levels of theory are supposed to be the most accurate HF methods used in this work, they do not provide more accurate dipole moments than some other cheaper computation methods. In particular they are less accurate than HF/6-31G(3df) method which is a less complicated and cheaper method.

	ammonia	methylamine	Ethylamine	propylamine	Average difference between experimental and calculated values
Experimental value μ_{exp} in the gas-phase	1.47	1.31	1.22	1.17	
6-31G	1.3708 (6.7%)	1.2549 (4.2%)	1.2165 (0.3%)	1.1609 (0.8%)	3.0%
6-31+G	1.1961 (18.6%)	1.2104 (7.6%)	1.1872 (2.7%)	1.1172 (4.5%)	8.3%
6-31++G	1.2301 (16.3%)	1.2266 (6.4%)	1.1960 (2.0%)	1.1249 (3.9%)	7.1%
6-31G(d)	1.9196 (30.6%)	1.5321 (17.0%)	1.4593 (19.6%)	1.4007 (19.7.%)	21.7%
6-31G(2d)	1.6821 (14.4%)	1.3817 (5.5%)	1.3240 (8.5%)	1.2663 (8.2%)	9.2%
6-31G(3d)	1.5912 (8.2%)	1.3319 (1.7%)	1.2770 (4.7%)	1.2258 (4.8%)	4.8%
6-31G(df)	1.8126 (23.3%)	1.4590 (11.4%)	1.3914 (14.0%)	1.3355 (14.1%)	15.7%
6-31G(2df)	1.6277 (10.7%)	1.3369 (2.1%)	1.2824 (5.1%)	1.2247 (4.7%)	5.6%
6-31G(3df)	1.5381 (4.6%)	1.2836 (2.0%)	1.2327 (1.0%)	1.1811 (0.9%)	2.1%
6-31G(d,p)	1.8384 (25.1%)	1.4717 (12.3%)	1.4008 (14.8%)	1.3462 (15.1%)	16.8%
6-31G(d,2p)	1.7550 (19.4%)	1.4121 (7.8%)	1.3454 (10.3%)	1.2929 (10.5%)	12.0%
6-31G(d,3p)	1.5990 (8.8%)	1.3059 (0.3%)	1.2609 (3.4%)	1.2081 (3.3%)	3.9%
6-31G(d,pd)	1.8124 (23.3%)	1.4555 (11.1%)	1.3857 (13.6%)	1.3318 (13.8%)	15.5%

6-31G(d,2pd)	1.7236 (17.3%)	1.3921 (6.3%)	1.3246 (8.6%)	1.2738 (8.9%)	10.2%
6-31G(d,3pd)	1.5832 (7.7%)	1.2900 (1.5%)	1.2460 (2.1%)	1.1945 (2.1%)	3.4%
6-31++G(3df,3pd),	1.5655 (6.5%)	1.3546 (3.4%)	1.3186 (8.1%)	1.2537 (7.2%)	6.3%
6-311++G(3df,3pd)	1.5620 (6.3%)	1.3473 (2.8%)	1.3064 (7.1%)	1.2442 (6.3%)	5.6%

Table 1: Experimental and calculated dipole moments (in D) of aliphatic primary amines.

Linear regression analysis according to the expression $\mu_{experimental} = \beta\ \mu_{calculated}$ was performed for the data given in Table 1. The resulting regression coefficients β and the linear correlation coefficients ρ are compiled in Table 2.

	Linear regression $\mu_{experimental} = \beta\ \mu_{calculated}$
6-31G	$\beta = 0.670$, $\rho = 0.99313$
6-31G(d)	$\beta = 1.731$, $\rho = 0.97461$
6-31G(2d)	$\beta = 1.376$, $\rho = 0.97898$
6-31G(3d)	$\beta = 1.210$, $\rho = 0.98171$
6-31G(df)	$\beta = 1.590$, $\rho = 0.97576$
6-31G(2df)	$\beta = 1.331$, $\rho = 0.97892$
6-31G(3df)	$\beta = 1.179$, $\rho = 0.98076$
6-31G(d,p)	$\beta = 1.644$, $\rho = 0.97511$
6-31G(d,2p)	$\beta = 1.542$, $\rho = 0.97570$
6-31G(d,3p)	$\beta = 1.292$, $\rho = 0.97265$
6-31G(d,pd)	$\beta = 1.605$, $\rho = 0.97562$
6-31G(d,2pd)	$\beta = 1.502$, $\rho = 0.97689$
6-31G(d,3pd)	$\beta = 1.285$, $\rho = 0.97167$
6-31+G	$\beta = 0.203$, $\rho = 0.64435$
6-31++G	$\beta = 0.294$, $\rho = 0.79313$
6-31++G(3df,3pd),	$\beta = 1.006$, $\rho = 0.98291$
6-311++G(3df,3pd)	$\beta = 1.031$, $\rho = 0.98444$

Table 2: Linear regressions $\mu_{experimental} = \beta\ \mu_{calculated}$ of aliphatic primary amines.

From these results, we have the confirmation that the addition of diffuse functions does not give good calculated dipole moments since the fitting is not good: neither β nor ρ are close to 1. Consequently, 6-31+G and 6-31++G are really unefficient to provide good dipole moment values.

The consequences of the addition of polarization functions on the regression and linear regression coefficients is similar to the effects of the addition of these latter functions on the average difference between experimental and calculated values given in Table 1. For example, the calculations computed with the 6-31G(d,p) basis set were: $\beta = 1.644$ and $\rho = 0.97511$. So, it can be seen that the fitting is not very good. But, when the calculations were computed with the 6-31G(d,2p) basis set the coefficients were: $\beta = 1.542$ and $\rho = 0.97511$ and with 6-31G(d,3p) basis set they were: $\beta = 1.292$ and $\rho = 0.97265$, the fitting is getting better and better. We can also observe that the best fittings have been obtained when the calculations were made at the HF/6-31++G(3df,3pd) and HF/6-311++G(3df,3pd) levels of theory. Consequently, since the regression coefficient and linear regression coefficient are close to one, it is possible to predict accurately the dipole moments of an important number of aliphatic primary amines after the linear regression have been made for few amines.

4 CONCLUSIONS

In this study, we have calculated, using Hartree-Fock calculations combiend with different basis sets, the permanent electric dipole moments of ammonia, methylamine, ethylamine and propylamine. The calculated dipole moments of these primary amines have been compared to their experimental values in the gas-phase. It appeared that 6-31G(3df) and 6-31++G(3df,3pd) basis sets were the most reliable ab initio models for the calculation of permanent electric dipole moments of aliphatic primary amines. Indeed, these basis sets allowed us to obtain calculated dipole moments very concordant with experimental ones for the four molecules studied. Consequently, ab initio quantum chemistry models can be used to predict dipole moments with a good accuracy even if the choice of the basis set was of great importance since the best basis set was neither the one including the most complicated polarization functions nor the one including the most important number of diffuse and polarization functions.

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Biographies

Boris Lakard is teaching physics at the Pharmacology Department of the University of Bourgogne. After obtaining a Ph.D. degree in physical chemistry and quantum chemistry from the University of Franche-Comté. His research includes the determination of polymerization mechanisms as well as the determination of chemical properties of compounds including amino groups using ab initio calculations through the use of Hartree-Fock and DFT methods.