



Quantum mechanical calculations of dipole moment of diverse imines

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In this study, the dipole moment of imine derivatives is discussed in detail. Both the aldimines and ketimines are considered for this investigation. The influence of the substituted group at nitrogen and carbon position on the polarity is also investigated. Quantum mechanical AM1 method is chosen to calculate dipole moment of these molecules. Best of our knowledge, this is the first study on the dipole moment of imine derivatives. This theoretical analysis may help to realize the reactivity of the imines in diverse chemical reactions.

Keywords: Dipole moment, aldimines, ketimines.

Introduction

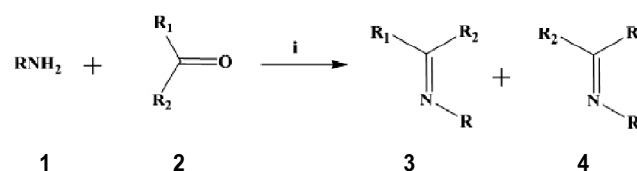
Imines have a carbon-nitrogen double bond and these are also called Schiff bases¹⁻⁴. The carbon atom has two additional single bonds. Aldimines and ketimines can be obtained from aldehydes and ketones by their reaction with a primary amine. These imine derivatives are useful starting materials for the synthesis of several heterocyclic compounds⁵⁻⁸.

Over the past decade, our group has widely studied the imine-based synthesis of β -lactams⁹. We also have carried out the synthesis of several other medicinally important compounds and the computational studies¹⁰. In this study, we present quantum mechanical dipole moment calculations of imine derivatives. Both the aldimines and ketamines derivatives are considered for this investigation. According to our knowledge, this is the first study on the dipole moment calculation of imine derivatives. The dipole moment data has shown a consistent trend in all of these imines regardless of the substituted groups at the nitrogen and carbon position.

Materials and methods

We have considered two different classes of Schiff bases, aldimines and ketimines for dipole moment calculation. The synthesis of aldimines and ketimines is shown in Scheme 1.

A reaction of a primary amine **1** with a carbonyl compound **2** in toluene under reflux produces an imine or a mixture of two imines **3** and **4** in almost quantitative yields. In general, aromatic compounds are used for this study.



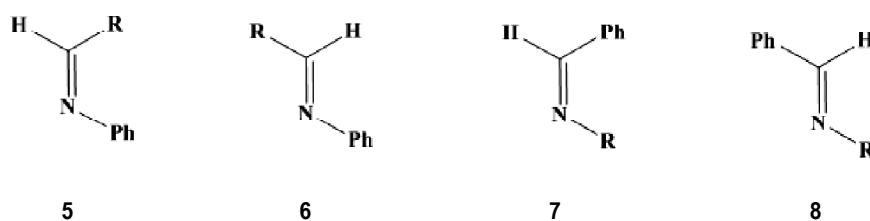
Aldimine: R = Aromatic rings; R₁ = H; R₂ = Aromatic rings

Ketimines: R = Aromatic rings; R₁ = CH₃; R₂ = Aromatic rings

Scheme 1. Synthesis of aldimines and ketimines. (i: solvent, heat).

Aldimine:

In this study we are considered the aldimine derivatives, in which carbon atom is attached to both an aryl group and a hydrogen atom and the substituent on the nitrogen atom is an aryl group. Both the *Z*-aldimines and *E*-aldimines are evaluated. The chemical structures of all these derivatives are shown in Scheme 2. Fourteen derivatives of aldimines are considered in this study by changing the groups at nitrogen and carbon position. The aryl groups substituted at the nitrogen and carbon positions have phenyl, anthracene, phenanthrene and chrysene ring systems.



5a, 6a: R = Phenyl; 5b, 6b, 7b, 8b: R = Anthracene; 5c, 6c, 7c, 8c: R = Phenanthrene; 5d, 6d, 7d, 8d: R = Chrysene.

Scheme 2. Chemical structures of the aldimines.

Ketimines:

Secondary ketimine derivatives studied in this work are shown in Scheme 3. Carbon atom is attached to both an aryl group and a methyl group and nitrogen atom is attached to an aryl group. Both the *Z*-ketimines and *E*-ketimines are analyzed as well. The substituted aryl groups at the nitrogen and carbon positions were phenyl, anthracene, phenanthrene and chrysene.

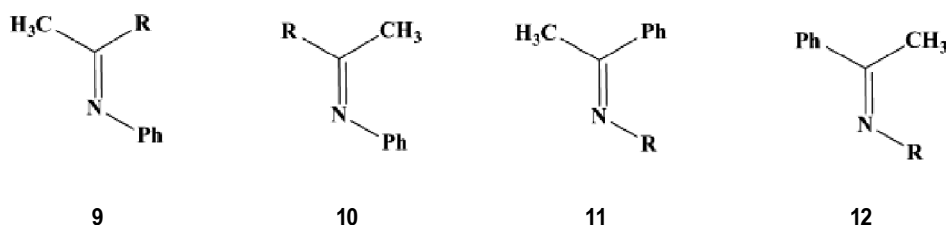
All the dipole moment calculations for imine derivatives were performed using the SPARTAN 18 software package. All the measurements are taken with equilibrium geometry at ground state, using semi-empirical quantum chemistry

method, Austin Model 1 (AM1) method, the method is based on the Neglect of Differential Diatomic Overlap (NDDO) integral approximation. All the imine structures were drawn in 2D and then converted into their 3D forms using the same software followed by their energy minimization procedure.

Results and discussion

The calculated ground-state dipole moment (μ) value in Debye (D) for imine derivatives, is shown in Table 1.

Dipole moment values of aldimines and corresponding ketimines are very close to each other. It appears steric crowding of the methyl group and the hydrogen atom is similar in



9a, 10a: R = Phenyl; 9b, 10b, 11b, 12b: R = Anthracene; 9c, 10c, 11c, 12c: R = Phenanthrene; 9d, 10d, 11d, 12d: R = Chrysene.

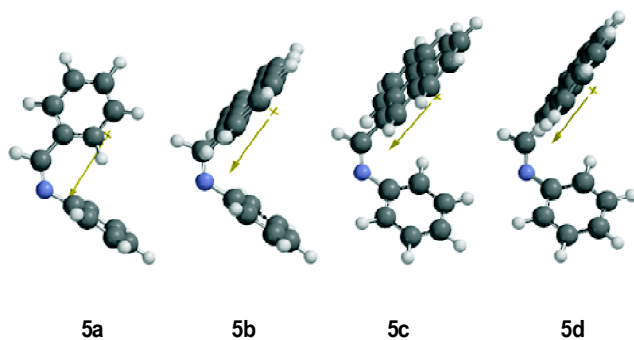
Scheme 3. Chemical structures of the ketimines.

Table 1. Calculated dipole moment values of aldimines and ketimines. Values are in Debye (D)

Aldimines				Ketimines			
Z-Aldimine		E-Aldimine		Z-Ketimine		E-Ketimine	
Compounds	Dipole moment (D)	Compounds	Dipole moment (D)	Compounds	Dipole moment (D)	Compounds	Dipole moment (D)
5a	2.33	6a	1.7	9a	2.06	10a	1.91
5b	2.19	6b	1.52	9b	2.15	10b	2.10
7b	2.44	8b	1.89	11b	2.38	12b	2.08
5c	2.18	6c	1.39	9c	2.16	10c	1.85
7c	2.28	8c	1.43	11c	2.09	12c	1.9
5d	2.2	6d	1.33	9d	2.15	10d	1.83
7d	2.33	8d	1.45	11d	2.15	12d	1.81

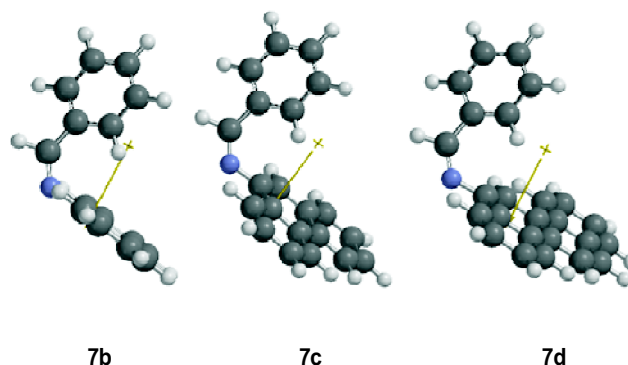
open chain imines. Methyl group does not have electronegative atom or atoms with lone pair of electrons, although it has a weak electron donating power. The calculated dipole moment values of all aldimines and ketimines remain very similar. Compounds **7b**, **8b**, **10b** and **11b** showed higher dipole moment, which has an anthracene group as the substituted groups at either carbon atom or nitrogen atom. In both aldimines and ketimines, *Z*-imines showed higher dipole moment than corresponding *E*-imines. The higher number of aromatic rings in *Z*-imine and *E*-imine increases the dipole moment. For instance, the difference in dipole moment in compound **5b** and **6b** is 0.67D and the difference in dipole moment in compound **5d** and **6d** is 0.87D.

The energy minimized structure of the derivatives of *Z*-aldimine **5** is shown in Scheme 4. The arrow representing the direction of dipole. It is observed that all the four compounds, **5a-5d**, the resultant dipole vector pointing towards nitrogen atom. In these compounds, lone pair effect of nitrogen predominates over the electron withdrawing effects of aromatic group at carbon. This is particularly valid because the aromatic groups are not directly connected to nitrogen in these systems.



Scheme 4. The energy minimized structure of the derivatives of *Z*-aldimine **5**.

The energy minimized structure of the derivatives *Z*-aldimine **7** is shown in Scheme 5. It is observed that all the compounds, **7b-7d**, the resultant dipole vector pointing towards aromatic ring. In these compounds, aromatic rings are directly connected to nitrogen. It appears electron withdrawing effect of the aromatic groups predominates than the lone pair effect of nitrogen.



Scheme 5. The energy minimized structure of the derivatives of *Z*-aldimine **7**.

Conclusions

In this study twenty-eight imine derivatives are analyzed with semi-empirical quantum mechanical dipole moment calculations. Both aldimines and ketimines are considered for this study. Dipole moment is observed to be high for *Z*-imines regardless of the group present in the nitrogen and carbon position. The dipole moment values of all aldimines and ketimines remain very similar. On the basis of these dipole moment studies, the reactivity of these imines can be differentiated and therefore, different products can be obtained. This study is significant and novel, since dipole moment values have played an important role in determining the biological activity of many medicinally important compounds. But, this type of study has not been investigated with imines that have a wide range of applications. These results may open a way to design and synthesize more active imine-based compounds for chemical manipulations.

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Supporting materials

All the supporting materials will be available on request.

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