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Structural parameters, charge distribution and vibrational frequency analysis using theoretical SCF methods

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ABSTRACT

A Schiff base namely 3-{4-[4-(Benzylideneamino)benzenesulfonyl]-phenyl}-2-phenylquinazolin-4(3H)-one has been considered here. Theoretical characterization was done by Gaussian-03. The AM1 route has been used. The various parameters such as bond length, bond angle, atomic charge distribution and vibrational frequency analysis have been discussed. The theoretically observed IR values are found to be in accordance with the experimentally obtained values.

Introduction

Quinazolinones and their derivatives constitute an important class of heterocyclic compounds. Many of them show insecticidal, analgesic, antifungal, antibacterial, anticancer, anti-inflammatory activities. Quinazolinone nucleus is found in many bioactive natural products. Because of these reasons much attention is being paid for the synthesis of quinazolinone derivatives. A Schiff base namely 3-{4-[4-(Benzylideneamino) benzenesulfonyl]-phenyl}-2-phenylquinazolin-4(3H)-one was synthesized in the lab by R.Thilagavathy et. al., ealier[1]. Here the molecule is taken up for ab-initio study. Gaussian package[2] was used to characterize the molecule.

Computational Details

The Calculations of the structural parameters and atomic charges have been performed AM1 method using the Gaussian-03 program . The molecule was completely optimized and the optimized parameters were used for determining the theoretical vibrational frequencies. A scaling factor of 0.9352 were applied to the theoretically obtained values and were compared with the experimental values. The characteristic regions have been identified using these calculations.

Results and Discussion

When an atom in a molecule is substituted with another atom, the geometries of the interatomic bonds undergo changes. The structural parameters obtained using the AM1 route was compared to the un-optimized values. In the given system(Figure 1) it is observed that C_4-C_5 bond length where the fusion of rings occur elongates by 0.08Å to 1.4176 Å. Distinct elongation is of 0.15observed in C_8-C_{35} where it elongates to 1.4915 Å. This C-C bond connects two rings and it is obvious that the rings are pushed apart. All the C-C bonds attached to Nitrogen atoms exhibit a comparatively overestimated value to 1.416 Å as compared to other endocyclic C-C bonds which also get over estimated, but to values between 1.38 to 1.40 Å. C_{28}-C_{29} being a bond attached to N atom also elongates but by a high degree of 0.13 Å to 1.4683 Å. It has to be observed that C_{28} is an unsaturated carbon atom and is not a member of the aromatic ring. C_5-C_{10} is also considerably overestimated to 1.48 Å and this perhaps may be attributed to the fact that C_{10} is attached to unsaturated Oxygen atom while also being connected to the Nitrogen atom.

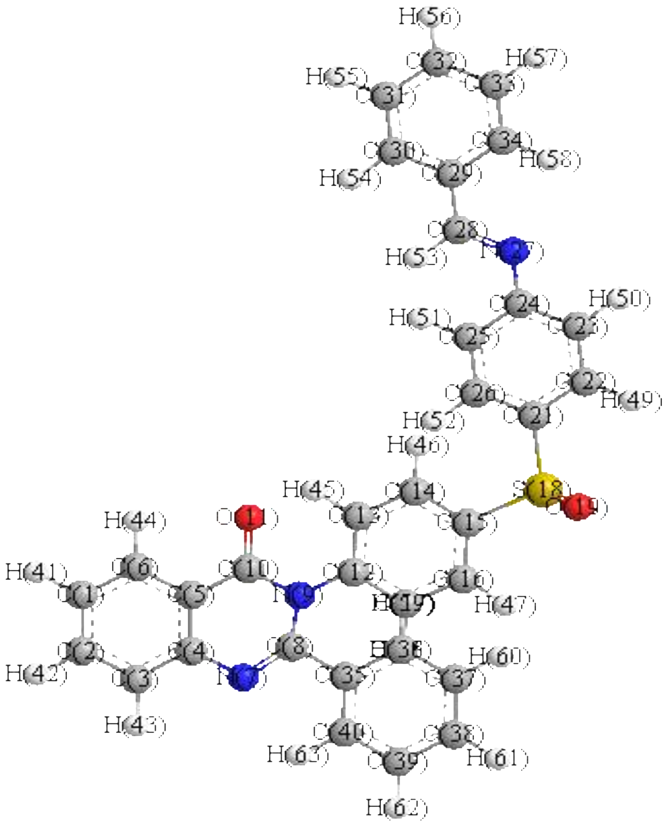

Figure 1

While discussing the C-N bonds almost all C-N bonds lengthen by 0.15 Å to 1.42 Å. C_4-N_7 elongates by just 0.13 Å. C_4 is a member of the fused C-C bond. C_8-N_9 elongates by around

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0.17 Ǻ. The overestimation is considerably lesser in the unsaturated C-N bonds. N_7=C_8 and N_{27}=C_{28} elongate by just around 0.03 Ǻ. All the endocyclic C-N bonds elongate indicating a strong likeliness for hydrogen bonding as indicated by Halina Szatilowiz where she suggests such a result when N atom is an inherent part of the aromatic ring like the Pyridine[3]. These C-N bonds are highly overestimated compared to those proposed by J.Peszke et al[4].Only the bond N_{27}=C_{28} is underestimated to 1.2564 as expected.

The C-S bonds exhibit underestimated values.and shoten by around 0.1 Ǻ to nearly 1.68 Ǻ .Similarly both the S-O bonds shorten to 1.40 Ǻ by 0.04 Ǻ The C-S bond length is underestimated to those suggested by Bradley.T.Lougrey et al at around 1.78 Ǻ [5]. S-O bondlengths present negligible change. The S-O bond length is marginally underestimated compared to the S-O bond length suggested by Bradley.T.Lougrey et. al., in their work on the structure on 4-(Benzylideneamino)benzene sulfonamide.[6] .C-O bond elongates by 0.004 Ǻ . The bond angles also reflect the fact that the ring structure is disturbed.

Atomic Charges

Partial charges on atoms in a molecule arise from differences in electron affinity. Charge is transferred from one atom to the next through the covalent bond joining them. Groups of tightly bonded atoms are often electrically neutral with the partial charge on one atom balanced by the negative partial charge on the other atom.

All the carbon atoms attached to the Nitrogen atoms gain a positive charge and the magnitude of charge gained is more in case of C_8 which is attached to Nitrogen atoms and C_{10} which is attached to a Nitrogen and an Oxygen atom. Nitrogen atoms gain a negative charge and the negative charge gained by N_{27} is the least presumably because it is not a member of the ring. Again this significant change in the charge of N_9 which is a part of the aromatic ring was predicted by Halina Szatilowiz[7] which she predicts is because of H-boding. The Oxygen atom also gains a mentionable negative charge by withdrawing electrons from C_{10} as stated by M. Levitt *et al*[8] in their paper on "Aromatic rings act as hydrogen bond acceptors", where they state that carbon atoms are negatively charged when bonded to hydrogen atoms and positively charged when bonded to oxygen or nitrogen atoms. Almost all other Carbon atoms gain a negative charge. This negative charge is more for the carbon atoms attached to a sulphur atom and sulphur gains very positive charge which is roughly a sum of the electrons donated to the attached carbon atom and the two oxygen atoms attached to it. The magnitude of charge on the thiocarbonyl atom is smaller than the carbonyl atom [9]. The charge variations in the Hydrogen atoms are negligible.

Vibrational Frequency Analysis

The IR spectra (KBr pellets) was recorded Shimadzu FT-IR model 8010 spectrometer. Theoretical values for IR spectral assignments were obtained using the route AM1. The theoretical and the experimental values are listed in Table 1.

C-S stretching assignments are found in the region 780-510cm^{-1} in aromatic sulphides[10,11] and the value 553 and 572 in experimental and theoretical values are assigned to this.

S=O vibrational assignments are found only for the asymmetric regions and are comparable.

C-H bending assignments are found to be very closely assigned in both the experimental and theoretical methods at around 720 cm^{-1}.

The presence of a benzene ring in the compound throws up several bands for C-C stretching. C-C stretching vibrations(theoretical values in brackets) at 1470(1430) and 1500(1443) and 1593(1563) are comparable to those assigned by Mohan et al [12] .

The region above 3100 can be either assigned to O-H or N-H stretching. In secondary amines the bands due to N-H vibrations are generally strong and those due to O-H are weak.

Conclusion

An attempt has been made to predict the structural parameters and the atomic charge distribution using the Hartree-Method. Theoretical Vibrational frequencies were also predicted using the AM1 method and were found to be comparable with those obtained by experimental methods. Any deviations may be ascribed to the fact that he calculations are done on a single molecule in gas state where as the experimental values are recorded in the presence of intermolecular reactions.

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Table 1 -Significant Assignments

Experimental	Theoretical	Assignments
553	572	C-S stretch
606.67	608	-SO (Scissoring)
726	716	C-H Bend
1283	1320	C-N vibrations
1470	1430	C-C stretch
1500	1544	C-C stretch
1593.31	1563	C-C stretch
1764	1806	N-C=O(quinazoline)
3379	2991	C-N vibrations