

NOTE

Semi-empirical Calculations for the Electronic Structure of Schiff Base

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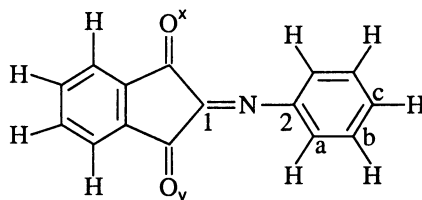
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Ninhydrin is a triketo compound which is stable in hydrated form and is used in the detection and estimation of amino acids. It reacts with amino acids producing purple coloured Schiff base. Experimental data are available for this compound, so it prompted us to study the electronic structure of the reaction with substituted amines, by using quantum mechanical calculations. The theoretical study reveals that the *para* position of amines makes ninhydrin a high-potential ligand, when they react with each other.

Ninhydrin, a triketo compound, is used in the detection and estimation of amino acids. The product formed is a purple-coloured Schiff base. Nenberg¹ studied extensively the reaction of ninhydrin with various amines. These bases may be having good biological activities, being an important reagent in biomolecular reactions².

Recently, Mallikarjuna *et al.*³ were prompted to synthesise few complexes of Sn(IV) with ninhydrin-amine (Schiff base) because of its considerable physiological and biological importance. These workers extensively synthesised and characterised the tin-complexes by doing various substitutions, *viz.*, in Cl, Br, OCH₃, CH₃ phenyl ring of Schiff base. In the present work, we have attempted to study the substitutions at various positions in the phenyl ring, through quantum-mechanical calculations⁴.



The molecular geometry of the ligand is optimised by using Parametric Method Third (PM3) for different substituted Schiff bases.

For any ligand, to be used for stable complex formation, it is of utmost importance to look for the bonding site, with which the metal ion will react. In this regard, the net atomic charges become the vital parameters to assign the attacking site and stability of the complex.

The net atomic changes at two carbonyl oxygen, carbon and nitrogen are given in Table-1. It can be that for all time, the high value of net atomic changes of C-position in the phenyl ring for various substitutions (see figure) make one of the carbonyl oxygens (x) to be more active for complex formation in comparison to the other carbonyl oxygen (y), which has the tentative value 0.26 electrons. It is observed experimentally also³ that the bond due to one of the (C=O) shows considerable low frequency shift and is located in the region 1720–1610 cm⁻¹ in the complexes. This shift to the lower frequency is suggestive of coordination of (C=O) to the Sn(IV) *via* oxygen.

TABLE 1
NET CHANGES ON CARBONYL OXYGEN AND CARBON,
NITROGEN ATOMS OF SUBSTITUTED NINHYDRIN

System		>C=O	>C=O	C(1)	N(1)
CH ₃	a	-0.272	-0.260	-0.2276	-0.1255
	b	-0.300	-0.263	-0.2446	-0.1140
	c	-0.300	-0.265	-0.2475	-0.1167
Cl	a	-0.272	-0.255	-0.2164	-0.1220
	b	-0.296	-0.262	-0.2359	-0.1085
	c	-0.300	-0.262	-0.2399	-0.1106
Br	a	-0.266	-0.259	-0.2124	-0.1153
	b	-0.295	-0.261	-0.2354	-0.1079
	c	-0.299	-0.261	-0.2358	-0.1069
CH ₃ O	a	-0.278	-0.260	-0.2219	-0.1390
	b	-0.292	-0.263	-0.2373	-0.1083
	c	-0.305	-0.266	-0.2575	-0.1260

In addition, the atomic charges on carbon and nitrogen in various substituted Schiff bases remain in the range of 0.22 ± 0.01 and 0.11 ± 0.01 respectively, showing that the (C=N) of the ligand does not take part in the coordination. Hence, the substitution at the *para* position in the phenyl ring makes the ligand more reactive for complex formation with other metal ions also.

Furthermore, the CH₃, Cl, Br substituted ligands are found to be endothermic whereas methoxy-ligand is exothermic (Table 2). The heat of formation values are also confirming the *para* position substitution to be making more active ligands (Schiff base). The rest of the parameters like dipole moment,, hardness and electronegativity are for academic interest.

Conclusion

The quantum mechanical calculations can be successfully used to predict the stability of the complex and making the more active ligands., used for biological interests.

TABLE 2
CALCULATED HEAT OF FORMATION (kcal), DIPOLE MOMENTS
(DEBYE), HARDNESS (ev) AND ELECTRONEGATIVITY (χ)
OF SUBSTITUTED NINHYDRIN

System		ΔH	μ	η	χ
CH ₃	a	5.56	2.76	4.05	5.11
	b	4.97	2.48	4.13	5.36
	c	4.70	2.13	4.09	5.31
Cl	a	8.24	3.06	4.03	5.15
	b	8.00	1.93	4.04	5.34
	c	7.68	2.68	4.00	5.38
Br	a	24.8	2.48	4.16	5.25
	b	22.4	1.93	4.18	5.57
	c	22.3	2.95	4.14	5.55
CH ₃ O	a	-22.8	3.22	3.99	4.98
	b	-17.5	1.97	4.00	5.23
	c	-26.5	3.20	3.96	5.16

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REFERENCES

1. C. Nenberg, *Z. Biochem*, **56**, 495 (1914).
2. A. Aniello, G. Onofrio, M. Pischetola and L. Strazzulto, *Anal. Biochem.*, **144**, 610 (1985).
3. N.N. Mallikarjuna, S.D. Angadi and V.H. Kulkarni, *Asian J. Chem.*, **12**, 902 (2000).
4. J.J.P. Stewart, Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado, USA (1989)..

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