DFT study on structure, electronic properties, and reactivity of *cis*-isomers of $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$

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Abstract. Three *cis*-isomers of $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$, models for the active site of [Fe] hydrogenase, have been examined by computational method at DFT B3LYP/6–311+G(d,p) level. The computed geometric parameters are remarkably close to experimental values. DFT global chemical reactivity descriptors (chemical hardness, total energy, electronic chemical potential, and electrophilicity) are calculated for the isomers and used to predict their relative stability and reactivity. The chemical reactivity indices are found to be related to the bond angle defined by the *cis* carbonyls and the iron center.

Keywords. Chemical hardness; computational chemistry; isomer; hydrogenase model; iron carbonyl; transition metal.

1. Introduction

Organometallic units composing of iron–carbonyl (Fe–CO) tethered to thiolate ligands are present in many biological systems where they are involved in electron transfer and catalytic processes.^{1–8} The active sites of hydrogenase enzymes, responsible for the reversible oxidation of hydrogen, have been structurally characterized and shown to contain Fe–CO thiolate moieties.^{1–7} These active sites are being studied in order to develop efficient synthetic catalysts for the production and/or utilization of hydrogen for fuel cell technology. The structures, (a) and (b), are two descriptions of the active site of the iron–sulfur cluster free hydrogenase ([Fe]-hydrogenase) enzyme (X is unknown). Both structures contain an Fe(II) center bound to two *cis* CO, cysteinyl thiolate (*trans* to CO), and nitrogen of a pyridinol. In the most recent structure, (b), the nitrogen atom is *trans* to a CO.⁸ Studies on [Fe]-hydrogenase suggest that the activation of H₂ is determined by neighbouring base, lewis acidity of Fe(II), and donor strength of the pyridinol.^{8–11}

Structural models for the active site of [Fe]-hydrogenase have been prepared and examined by X-ray crystallography and spectroscopic techniques.^{12–22} One such model, $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$, contains the {Fe(*cis*-CO)} unit and its infra-red spectrum correlates with that of the enzyme.⁸ The crystal structure of *cis*- $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$ **1**, shows pyridine-2-thiolate as an S, N-bidentate ligand with both nitrogen atoms posi-

tioned *trans* to the carbonyls.¹⁶ However, there are two possible *cis* isomers of compound **1** that have not been

identified. One of the isomers, complex **2**, has one nitrogen and one sulfur *trans* to the carbonyls. The other isomer, compound **3**, has both sulfur atoms *trans* to the carbonyls. Isomer **2** is most closely related to the active

site (b), since both have nitrogen and sulfur atoms *trans* to carbonyls. An investigation on the three isomers may

shed light on the structural disposition and electronic properties of the active site of [Fe]-hydrogenase.

In this computational study, an examination of the structural and electronic properties of the three *cis* isomers of $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$ using Density Functional Theory (DFT) is performed. Global chemical reactivity descriptors such as chemical hardness (η), electrophilicity (ω), and electronic chemical potentials (μ) are calculated and used to probe the relative stability and reactivity of compounds **1** to **3**. The apparent preference of the structural arrangement in **1** over those of the other isomers is examined using Parr and Pearson's principle of maximum hardness.

2. Experimental

The computations were performed using Gaussian 09 with WebMO interface.²³ The geometries **1** to **3** were optimized at the DFT B3LYP level of theory with a 6-311+G(d,p) basis set. The structures are minima on potential energy surface with positive harmonic vibrational frequencies. Validation of the computational method was obtained by comparing the results with available experimental values.

3. Results and discussion

3.1 Structural and electronic properties

Optimized geometries of **1** to **3** were obtained using B3LYP level of theory. The structural parameters were

calculated and are presented in table 1. The calculated bond lengths and bond angles of **1** are remarkably close to the experimental values obtained by X-ray crystal diffraction.¹⁶ This result serves as a validation of the computational method. A significant structural difference among the isomers is the bond angle defined by the *cis* carbonyls and the Fe center ($\angle\text{OC-Fe-CO}$). This bond angle is 92.596° for **1**, 94.435° for **2**, and 96.506° for **3**. The OC-Fe-CO bond angle is a measure of electron richness of the Fe center and the extent of backbonding to the CO. Therefore, **1** with the smallest OC-Fe-CO bond angle has the weakest backbonding to CO while **3** with the largest bond angle has the strongest backbonding to CO. The relatively weak backbonding to CO in compound **1** may be due to the π -accepting property of nitrogen atoms of the pyridine-2-thiolate ligands located *trans* to the carbonyls. On the contrary, only one nitrogen is *trans* to CO in **2** and none in **3**. This thermodynamic phenomenon, referred to as *trans* influence, is also related to the hard and soft acids and bases (HSAB) principle. HSAB principle states that, 'hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties'.^{24,25}

The relationship between OC-Fe-CO bond angles and backbonding to CO for the isomers discussed above is consistent with their calculated infra-red CO stretching frequencies. Computed IR spectra of **1**, **2**, and **3** show two $\nu_{(\text{CO})}$ frequencies typical of *cis*-CO arrangement. The $\nu_{(\text{CO})}$ values of the isomers (table 1) shift to lower wavenumbers as the OC-Fe-CO bond angle or backbonding to CO increases. The IR CO frequencies for isomer **1** are shifted to higher values by $\sim 7\text{ cm}^{-1}$ from those of compound **2** and $\sim 14\text{ cm}^{-1}$ from values of isomer **3**.

Table 1. Calculated bond lengths ($\text{\AA}$), bond angles ($^\circ$), and IR data (cm^{-1}) for isomers **1** to **3**.

	1 ^a	1 ^b	2 ^b	3 ^b
Fe-S	2.325 ^c	2.380	2.376, (2.419-CO) ^d	2.412
Fe-N	1.995 ^c	2.021	1.997, (2.011-CO) ^d	1.992
Fe-C	1.764 ^c	1.811	1.815, (1.805-N) ^d	1.808
S-Fe-S	163.061	161.843	98.104	92.954
N-Fe-N	87.302	87.422	94.939	159.64
S-Fe-N	71.142	70.362	70.205 ^a	70.144
OC-Fe-CO	91.64	92.596	94.435	96.506
$\nu_{(\text{CO})}$	2047, 2000 ^e	2128, 2092 ^f	2123, 2085 ^f	2116, 2078 ^f

^aExperimental values from reference 16; ^bDFT computed values; ^caverage values; ^dbonds *trans* to the indicated atoms or ligands; ^erecorded in hexanes. ^fThe computed frequencies are not scaled

Table 2. Global chemical reactivity indices for isomers **1** to **3**.

	1	2	3
E (Hartree)	−2782.506	−2782.499	−2782.497
HOMO (eV)	−5.88	−5.77	−5.69
LUMO (eV)	−1.77	−1.70	−1.68
μ (eV)	−3.83	−3.74	−3.70
η (eV)	2.06	2.04	2.01
ω (eV)	3.56	3.43	3.41

3.2 Chemical reactivity

Investigations into the mechanism of hydrogen cleavage by [Fe]-hydrogenase suggest involvement of the Fe center, a neighbouring base, and electron donating/withdrawing properties of the ligands.^{9–12} With the aid of models, the reactivity of the active site of [Fe]-hydrogenase can be elucidated by computation using global chemical reactivity indices. The chemical reactivity descriptors calculated using DFT are; total energy (E), chemical hardness (η), electronic chemical potential (μ), and electrophilicity (ω).

Chemical hardness is associated with the stability and reactivity of a chemical system. In a molecule, it measures the resistance to change in the electron distribution or charge transfer. On the basis of frontier molecular orbitals, chemical hardness corresponds to the gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). Chemical hardness is approximated using equation 1.

$$\eta = (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) / 2, \quad (1)$$

where $\varepsilon_{\text{LUMO}}$ and $\varepsilon_{\text{HOMO}}$ are the LUMO and HOMO energies.

The larger the HOMO–LUMO energy gap, the harder and more stable/less reactive the molecule.^{24–31} Table 2 (row 5) contains the computed chemical hardness values for compounds **1** to **3**. The results indicate that isomer **1** is harder and less reactive than **2** which is harder and less reactive than **3**.

Electronic chemical potential is defined as the negative of electronegativity of a molecule³⁰ and determined using equation 2.

$$\mu = (\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}) / 2. \quad (2)$$

Physically, μ describes the escaping tendency of electrons from an equilibrium system.²⁴ The values of μ for isomers **1** to **3** are presented in table 2 (row 4). The trend in electronic chemical potential for the isomers is **3** > **2** > **1**. The greater the electronic chemical potential, the less stable or more reactive is the isomer. Therefore, **3** is the most reactive and **1** is the least reactive of the isomers.

Global electrophilicity index (ω), introduced by Parr, is calculated using the electronic chemical potential and chemical hardness as shown in equation 3.

$$\omega = \mu^2 / 2\eta. \quad (3)$$

Electrophilicity index measures the propensity or capacity of a species to accept electrons.^{31,32} It is a measure of the stabilization in energy after a system accepts additional amount of electronic charge from the environment.^{33,34} The electrophilicity values (table 2, row 6) for the isomers are 3.56 eV for **1**, 3.43 eV for **2** and 3.41 eV for **3**. Among the isomers, **3** is

Figure 1. Frontier molecular orbitals of isomers **1** to **3**.

the strongest nucleophile while **1** is the strongest electrophile. Experimentally, **1** has been shown to react with the nucleophile, $[\text{SC}_5\text{H}_4\text{N}]^-$, to form $[\text{Fe}(\text{SC}_5\text{H}_4\text{N})_3]^-$ at 60°C .¹⁶ The electrophilicity values are observed to follow the hardness trend in violation of the minimum electrophilicity principle (MEP: for equilibrium geometries, ‘more stable isomers correspond to lesser electrophilicity values’).^{34–36} This apparent violation may be attributed to the improper behaviour of the chemical potential.

The HOMO and LUMO orbital energies are related to gas phase ionization energies (I) and electron affinities (A) of the isomers according to the Koopmans’ theorem through equations 4 and 5.^{30,32}

$$A = -\varepsilon_{\text{LUMO}}. \quad (4)$$

$$I = -\varepsilon_{\text{HOMO}}. \quad (5)$$

Diagrams and energies of the HOMO and LUMO of compounds **1**, **2**, and **3** are displayed in figure 1 and table 2 (rows 2 and 3) respectively. Except for the HOMO of **3**, all the frontier orbitals contain some contribution from the Fe center. This suggests that the metal center may be involved in the reactivity of the isomers as observed for the active site of [Fe] hydrogenase.^{8–11}

Plots of the chemical reactivity indices (μ , η , ω) against the geometric parameter, ($\angle \text{OC-Fe-CO}$), are presented in figure 2. The plots show that chemical hardness and electrophilicity index decrease with increase in $\angle \text{OC-Fe-CO}$. On the other hand, electronic chemical potential increases with increase in $\angle \text{OC-Fe-CO}$. Hence the OC–Fe–CO bond angle of similar models for the active site of [Fe] hydrogenase may be used to predict their relative chemical reactivity.

As mentioned earlier, though compound **1** has been synthesized, isolated and structurally characterized, the isomers **2** and **3** have not been identified. The structural arrangement of **1** seems to be thermodynamically preferred over the structural dispositions of **2** and **3**. This geometric preference can be explained by the Principle of Maximum Hardness (PMH). PMH states ‘there seems to be a rule of nature that molecules arrange themselves to be as hard as possible’.^{26,31,37–40} The geometric arrangement of **1** provides for maximum hardness and hence **1** is the thermodynamically stable *cis* isomer. The computed energies, (E , table 2, row 1) at the DFT B3LYP/6–311+G(d,p) level confirms that **1** is more stable than the isomers **2** and **3**. The energy difference between isomers **1** and **2** is 4.4 kcal/mol. Isomer **1** is more stable than isomer **3** by 5.6 kcal/mol.

Figure 2. Plot of chemical reactivity indices against the OC–Fe–CO bond angles of isomers **1**, **2** and **3**.

4. Conclusions

A comparative DFT B3LYP/6–311+G(d,p) study on *cis* isomers of $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$ has been accomplished. B3LYP calculated reactivity descriptors: E , μ , η , ω , consistently predict **1** to be the most stable *cis* isomer of $[(\text{NC}_5\text{H}_4\text{-S})_2\text{Fe}(\text{CO})_2]$. A relationship between the geometric parameter, $\angle \text{OC-Fe-CO}$, and the chemical reactivity descriptors is observed. This study shows that compared to **1** and **3**, isomer **2** with similar coordination chemistry to the active site of [Fe] hydrogenase has moderate stability, a useful property for catalytic systems. Therefore, isomer **2** provides a useful example for the design of models for the active site of [Fe] hydrogenase.

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References

- Peters J W, Lanzilotta W N B, Lemon J and Seefeldt, L C 1998 *Science* **282** 1853
- Nicolet Y, Piras C, Legrand P, Hatchikian C E and Fontecilla-Camps J C 1999 *Structure* **13** 7
- Zirngibl C, Hedderich R and Thauer R K 1990 *FEBS Lett.* **112** 261
- Shima S, Pilak O, Vogt S, Schick M, Stagni M S, Meyer-Klaucke W, Warkentin E, Thauer R and Ermler K U 2008 *Science* **321** 572
- Volbeda A, Charon M H, Piras C, Hatchikian E C, Frey M and Fontecillacamps J C 1995 *Nature (London)* **580** 373
- Garcin E, Vernede X, Hatchikian E C, Volbeda A, Frey M and Fontecilla-Camps J C 1999 *Structure* **7** 557
- Volbeda A, Garcin E, Piras C, deLacey A L, Fernandez V M, Hatchikian E C, Frey M and FontecillaCamps J C 1996 *J. Am. Chem. Soc.* **118** 12989
- Tard C and Pickett C J 2009 *Chem. Rev.* **109** 2245
- Yang X and Hall M B 2008 *J. Am. Chem. Soc.* **130** 14036
- Yang X and Hall M B 2009 *J. Am. Chem. Soc.* **131** 10901
- Hiramoto T, Warkentin E, Moll J, Priv-Doz U E and Shima S 2009 *Chem. Asian J.* **48** 6457
- Wang X F, Li Z M, Zeng X R, Luo Q Y, Evans D J, Pickett C J and Liu X M 2008 *Chem. Commun.* (30) 3555
- Sadique A R, Brennessel W W and Holland P L 2008 *Inorg. Chem.* **47** 784
- Guo Y S, Wang H X, Xiao Y M, Vogt S, Thauer R K, Shima S, Volkens P I, Rauchfuss T B, Pelmentschikov V, Case D A, Alp E E, Sturhahn W, Yoda Y and Cramer S P 2008 *Inorg. Chem.* **47** 3969
- Takacs J, Soos E, Nagy-Magos Z, Marko L, Gervasio G and Hoffmann T 1989 *Inorg. Chim. Acta* **39** 166
- Liaw W F, Chen C H, Lee G H and Peng S M 1998 *Organometallics* **17** 2370
- Mauro A E, Casagrande O L, Nogueira V M, Santos R H A, Gambardella M T P, Lechat J R and Filho M F J 1993 *Polyhedron* **12** 29
- Li B, Liu T, Popescu C V, Bilko A and Darensbourg M Y 2009 *Inorg. Chem.* **48** 11283
- Chen D, Scopelliti R and Hu X 2010 *J. Am. Chem. Soc.* **132** 928
- Obrist B V, Chen D F, Ahrens A, Schunemann V, Scopelliti R and Hu X L 2009 *Inorg. Chem.* **48** 3514
- Liu T, Li B, Popescu C V, Bilko A, Pérez L M, Hall M B and Darensbourg M Y 2010 *Chem. Eur. J.* **16** 3083
- Royer A M, Rauchfuss T B and Gray D L 2009 *Organometallics* **28** 3618
- Frisch M J *et al.* 2009 Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT
- Chattaraj P K and Maiti B 2003 *J. Am. Chem. Soc.* **125** 2705
- Pearson R G 1973 *Hard and soft acids and bases*, Stroudsburg, PA: Dowden, Hutchinson & Ross
- Pearson R G 1993 *Acc. Chem. Res.* **26** 250.
- Pearson R G 1997 *Chemical hardness: Application from molecules to solid*, Weinheim: Wiley-VCH
- Sen K D and Mingos D M P 1993 *Chemical hardness: Structure and bonding*, Berlin: Springer
- Parr R G and Yang W 1989 *Density functional theory of atoms and molecules*, Oxford: Oxford University Press
- Parr P G and Pearson R G 1983 *J. Am. Chem. Soc.* **105** 7512
- Vektariene A, Vektaris G and Svoboda J 2009 *ARKIVOC* **7** 311
- Parr R G, Szentpaly L and Liu S 1999 *J. Am. Chem. Soc.* **121** 1922
- Koopmans T 1933 *Physica* **1** 104
- Liu S 2005 *J. Chem. Sci.* **117** 477
- Parthasarathi R, Elango M, Subramanian V and Chattaraj P K 2005 *Theor. Chem. Acc.* **113** 257
- Chattaraj P K, Sarkar U and Roy D R 2006 *Chem. Rev.* **106** 2065
- Pearson R G 1987 *J. Chem. Ed.* **64** 561
- Parr R G and Chattaraj P K 1991 *J. Am. Chem. Soc.* **113** 1854
- Pearson R G 1985 *J. Am. Chem. Soc.* **107** 6801
- Parr R G and Pearson R G 1983 *J. Am. Chem. Soc.* **105** 7512