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Research Article

CONFORMATIONAL ANALYSIS OF THETHREO AND ERYTHRO DIASTEREOMERIC FORMS OF A GUAIACYL β-O-4 DIMER USING MOLECULAR MECHANICS CALCULATIONS

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ABSTRACT

The dynamical conformational behavior of a guaiacyl β-O-4 lignin model compounds have been investigated by molecular calculation. Stereoisomerism can influence the shape of the lignin molecules. The stereochemistry and conformation of the lignin molecules are of interest in connection with the interpretation of NMR spectra of lignins. It is proposed that both structural differences and conformation are the main reasons for the broadness of the signals in NMR spectra of lignins. Here DFT is validated for preliminary conformational screening of β-O-4 structures. The results is shown that molecular calculation holds great potential for studying lignin and can provide valuable information.

Keywords: DFT, lignin model compounds, lignin conformation, aryl glycerol β-guaiacyl ethers.

INTRODUCTION

A major problem with paper manufactured from potential brightness reversion upon exposure to sunlight[1,2]. The low brightness stability, caused by high concentrations of chromophores, limits its utilization[3]. There is also a general agreement that the initial color reversion processes are associated with photochemical processes. In this regard, a number of researchers have attempted to elucidate the mechanism of photo degradation of wood[4], pulp[5,6] , extracted lignin[7] and lignin model compounds[8-11]. Therefore structure of lignin is of great importance for optimizing the processes and understanding the reactions involved in its removal.

Lignin remains a complex enigma, and structural details of the phenylpropanoid polymers in plants are still emerging. Applications of new and traditional methods continue to reveal a fascinating complexity. The number of monomers or monomer conjugates that undergo radical coupling reactions with typical monolignols to generate complex phenylpropanoid polymers continues to grow. Whether these are true lignins or not continues to be debated. However, components that act as monomers, coupling and cross-coupling with monolignols and oligolignols to become intimately incorporated into the structure are obviously important components of the plants architecture. These components will always analyze as lignin and for some industries such as the pulp and paper industry, will remain the troublesome polymeric phenolic components that must be removed during pulping or bleaching to produce high-end products such as white paper. Structural analysis of normal and perturbed plant systems reveals a lot about the phenylpropanoid component and interacting biochemical pathways, providing a basis for in-depth biochemical studies. Structural elucidation remains a key entry point into understanding these complex plant systems.

Indeed, the β-O-4 linkage represents the predominant interunit linkage in lignin and is an excellent model system for studying major conformational features of the lignin polymer such as H-bonding interactions and flexibility. For this reason, we chose to begin with the study of β-O-4 model compounds[12].

The aryl glycerol β-aryl ether substructures that arise from β-O-4 coupling exist in two diastereomeric forms, referred to as erythro and threo isomers. The isomer ratio has been found to correlate with the syringyl:guaiacyl ratio[13]. The erythro isomer is predominant in hardwood lignins, while softwood lignins contain about equal amounts of the erythro and threo forms.

The appearance of the resulting oligomers shows that stereoisomerism can be expected to influence the shape of the lignin molecules to a great extent. The constructed oligomers provide an idea about the contribution to the complexity of lignins by stereochemistry alone. It is proposed that structural differences, together with confor mational variations, are the main reasons for the broadness of the signals in NMR spectra of lignins.

Lignin consists of various intermolecular linkages between phenyl propane units and contains a number of asymmetric carbons. The structural nature of lignin is thought to be racemic macromolecule, therefore, its side chain parts constructed by asymmetric carbons consist of both enantiomeric forms.

Studies of lignin structure and reactivity have been re-energized by the emergence of modern technologies, new analytical and theoretical methods. Computational studies constitute an alternative approach to study the conformation of this type of structural elements[14,15] .

MATERIALS AND METHODS

All calculations were carried out with the Gaussian program series 2009, as basic program and Gaussian Viewer as graphical medium. As in our previous work, density functional theory (DFT) was employed[11]. DFT calculations were carried out by using the three parameter Becke 3LYP functional. The usual 6-31G* basis set was employed in the DFT calculations. Following the standard nomenclature the latter calculation will be referred to as B3LYP/6-31G*.

Synthesis of erythro form of 1 was reported recently[16]. The threo form of 1 was lately obtained in crystalline form, and its crystal structure was determined[17]. The conformational options of such structural elements had studied based on X-ray crystallography of lignin model compounds[16-19].

In this report, DFT is validated for preliminary conformational screening of guaiacyl β-O-4 structures.

RESULTS AND DISCUSSION

Aryl glycerol-β-guaiacyl ether is one of the most important phenolic compound for studying the chemistry and biochemistry of lignin. This compound contains two asymmetric carbons at the alpha and beta positions of its side chain, therefore theoretically it can exist as four different stereoisomers contain R-R, R-S, S-R and S-S (Fig.1). As in our previous work[11] the optimized geometry and structural parameters of all stereoisomer's of compound 1 calculated by DFT/B3LYP levels with the 6-31G* basis set.

The conformation of compounds of the aryl glycerol β-guaiacyl ether type is largely determined by two torsion angles: Caryl-Cα-Cβ-O and Caryl-O-Cβ-Cα (Fig. 2).

The molecular dipole moment is perhaps the simplest experimental measure of charge density in a molecule. Theoretically computed total energies, Dipole moment, HOMO and LUMO energies, ionization potential and electron affinity for all stereo isomers are shown in below (table 1).

Torsion angles of all stereo isomers are shown in Table 2.

As is observed a good agreement between calculated and experimental torsion angles is observed in the stereoisomers with R-configuration at Cα[19].

In the following discussion we have considered the isomers with R-configuration at Cα. Therefore total configuration in erythro and threo form of compound 1 is R,S and R,R respectively.

In the erythro form of dimeric lignin model 1 the Caryl-Cα-Cβ-O angle is about 61° and the Caryl-O-Cβ-Cα angle is about -156°. In contrast, the Caryl-Cα-Cβ-O angle is about -173° in the threo forms, while the Caryl-O-Cβ-Cα angle is about 121°. The aromatic rings are planar and well separated. The distance for C_3-C_{21} is 4.73 Å in threo and 4.02 Å in erythro isomer.

As is shown in Fig 1, in erythro isomer an intramolecular hydrogen bonding exists between the hydroxyl oxygen atom γ- position and hydroxyl hydrogen atom α- position. The calculated Dipole moment in this isomer is 4.8793 that is bigger than 2.4124 in threo isomer.

Molecular orbital and their properties like energy are very useful to the physicists and chemists and their frontier electron density used for predicting the most reactive position in π-electron system and also explained several types of reaction in conjugated systems[20]. Moreover, the eigen values of highest occupied molecular orbitals HOMOs (π donor) and lowest unoccupied molecular orbitals LUMOs (π acceptor) and their energy gap reflect the chemical activity. Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intra-molecular charge transfer (ICT)[21].

The frontier orbitals (HOMO, LUMO) of all stereoisomer's of compound 1, are shown in Fig.

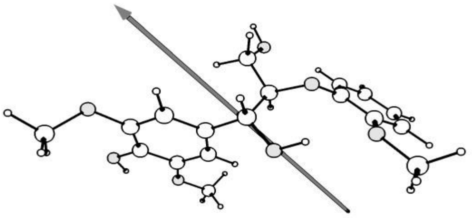
3. The HOMO–LUMO energy gap of all stereoisomers are reported in Table 1. The HOMO is located over the phenolic ring . By contrast, the LUMO is located over the phenoxy ring. The HOMO→LUMO transition implies an electron density transfer to phenoxyring from the phenolic ring.

The frontier molecular orbitals are mainly composed of p atomic orbital, so, electronic transitions from the HOMO to the LUMO are mainly derived from the electronic transitions of π–π*.

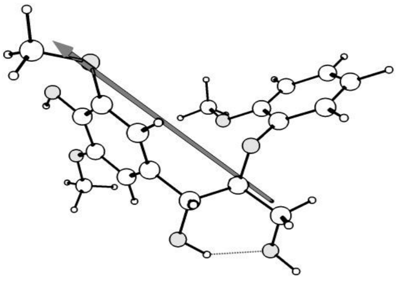
CONCLUSION

Stereochemistry and conformation have a decisive influence on the shape of the lignin molecules. The sequences of aryl glycerol β-guaiacyl ethers studied exist in a very large number of stereo isomeric forms. This provides an idea about the considerable contribution of stereo isomerism alone to the complexity of the lignin structure. Lignin stereochemistry is of importance in connection with analytical lignin work.

Computational studies constitute an usefull approach to study the conformation of this type of structural elements. A good agreement between calculated and experimental torsion angles is observed in the stereoisomers with R-configuration at Cα. Evidently the examined lignin models adopt similar conformations regardless of structural variation. Therefore we think that the conformational results obtained in model compound studies are applicable to lignin too.



Threo(R,R)



Erythro (R,S)

Fig. 1: The structure and dipole direction of compound I

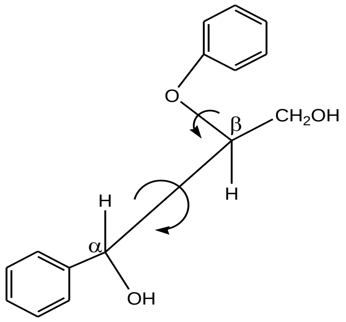


Fig. 2: Important torsion angles for the conformation of aryl glycerol β-aryl ethers: Caryl-Cα-Cβ-O and Caryl-O-Cβ-Cα.

Table 1: Theoretically computed total energies, Dipole moment, HOMO and LUMO energies, ionization potential and electron affinity for all stereo isomers

Compound	Threo		Erythro	
parameter	S,S	R,R	S,R	R,S
Total energy(a.u)	-1225.73	-1225.74	-1225.73	-1225.73
Dipole moment	3.9368	2.4124	2.8288	4.8793
HOMO Energy	-0.21274	-0.21788	-0.21353	-0.20609
LUMO Energy	-0.00831	-0.02941	-0.01316	-0.04765
H-L gap	0.20443	0.18847	0.20037	0.15844
ionization potential(IP)	0.21274	0.21788	0.21353	0.20609
electron affinity(EA)	0.00831	0.02941	0.01316	0.04765

Table 2: Torsional angles (◦)

stereoisomer	Threo			Erythro	
torsion angles	S,S	R,R	Exp	S,R	R,S
C_3-C_9-C_{10}-C_{34}	-175.18	66.59	61.2	76.06	178.68
C_3-C_9-C_{10}-O_{23}	63.97	-173.56	-179.2	-162.64	61.80
C_{24}-O_{23}-C_{10}-C_9	-160.65	121.58	126.3	111.56	-156.99
O_{44}- C_9-C_{10}-C_{34}	59.42	-172.52	-177.8	-52.49	-59.67
O_{37}-C_{34}-C_{10}-C_9	67.58	-169.83	-159.9	-162.91	68.47
O_{44}- C_9-C_{10}-O_{23}	-61.41	-52.68	-58.3	68.79	-176.55

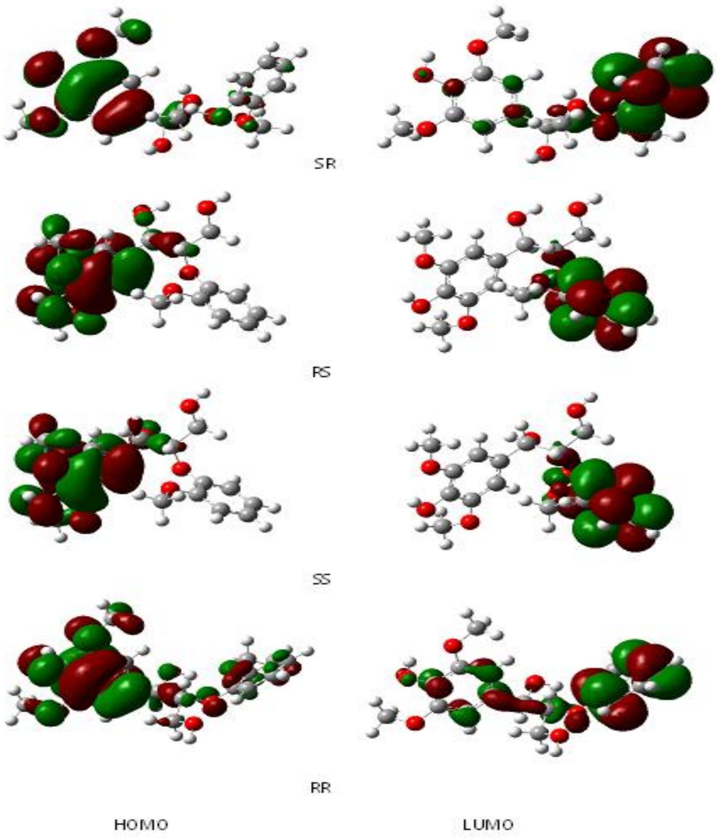


Fig. 3: Plots of the frontier orbitals of compound 1 by B3LYP/6-31+G(d,p)

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