The Application of Computational Chemistry to Lignin

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Abstract

Computational chemical methods have become an important technique in the examination of the structure and reactivity of lignin. The calculations can be based either on classical or quantum mechanics, with concomitant differences in computational intensity and size restrictions. The current paper will concentrate on results developed from the latter type of calculations for lignin model compounds. These methods can provide information on molecular geometry, thermodynamic properties, kinetics and electronic structure. Using density functional theory, the energies associated with bond dissociation and radical oxidation have been determined for β-O-4 dimers and trimers, pinoresinols, dibenzodioxocins, catechol-alcohol based dimers, spirodienones, and combinations with tricin, catechins and epicatechins. Ongoing work is concerned with homo-coupled ferulates and cross-coupled lignin-ferulates. Exhaustive examinations of stereochemistry reveals the existence of thermodynamic differences with configuration.

Keywords: lignin; density functional theory; bond dissociation energy.

Introduction

The application of quantum mechanically based electronic structure calculations on lignin dates back to 1966 and the work of Lindberg and co-workers [1-3]. In the intervening years there have been massive improvements in computer hardware and software, rendering even relatively large lignin models accessible to highly accurate, computationally intense methods. Results from such calculations include energetically optimized geometries, thermodynamic properties, spectroscopic information (IR, UV, NMR), and electronic structure (dipole moments, atomic charge, orbital densities, spin densities). These data can be used to determine relative reactivities, conformer distributions and rates of reaction [4].

Experimental

The work discussed has been done using the M06-2X density functional method [5] as implemented in Gaussian [6] using the resources of the Alabama Supercomputer Authority, the Pittsburgh Supercomputer System and the Texas Advanced Computing Center.

Results and Discussion

Lignins based on the catechol alcohols, caffeyl and 5-hydroxyconiferyl alcohol (Figure 1) have been the topic of recent experimental scrutiny due to the homogeneous nature of the former and the formation of benzodioxane rings connecting subsequent lignin units [7,8]. Lignins based on these units were examined computationally [9,10] and it was found that the initial dehydrogenation of 5-hydroxyconiferyl alcohol was ~3 kcal mol^{-1} less exothermic than coniferyl alcohol, while the coupling to form the quinone methide was ~10 kcal mol^{-1} more exothermic, indicating that the reactions involving 5-hydroxyconiferyl alcohol would be thermodynamically favored.
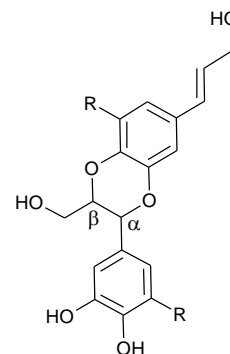

Figure 1. Benzodioxane connection

In other work on these lignins [10], 24-mers were constructed from the lowest-energy conformations of caffeoyl alcohol resulting from the dimer optimizations (Figure 2). The exact internal coordinates defining the inter-caffeoyl-alcohol linkages were replicated between each caffeoyl unit, such that the 24-mer repeat preserved this optimized configuration. Distinct differences in polymer curvature and length were found between the stereoisomer-pure polymers. The extent of helical-type twists of the polymer varied, with the (R,R) isomer yielding the greatest number of full rotations along the 24-mer chain. Most notably, the more compact inter-monolignol configuration of the (S,S) isomer yielded a substantially compressed 24-mer polymer length of 98 Å, opposed to the other configurations each around 142 Å, as measured from the terminal phenyl O4 and vinyl alcohol oxygen). This effect is further observed in the comparison of each strand's diameter, as measured by calculating the minimum radius of a cylinder to enclose the strand, where the central axis is defined by the line connecting the midpoints of the α and β carbons on one terminus, and the O4 and O5 of the opposite terminus. This metric determines the diameter of the (S,S) stereoisomer coil to nearly double that of the other isomers at 19.3Å.
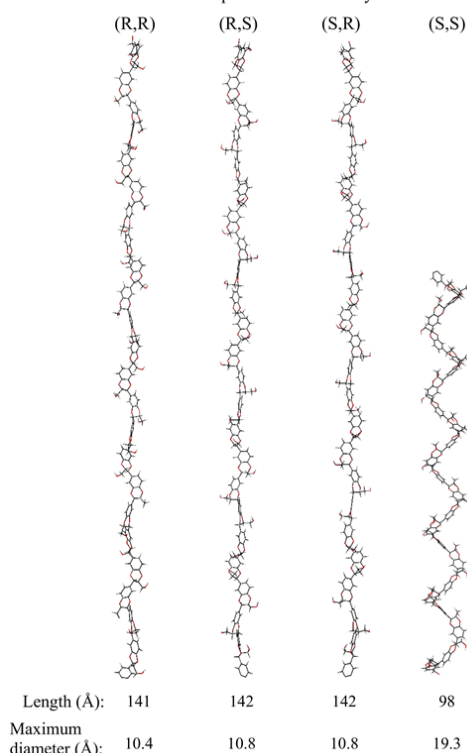
Subsequent calculations have been completed on the relatively recently discovered spirodienone structure [11,12] in lignin (Figure 3). With 5 chiral carbons, this structure is stereochemically complex, but analytically two stereoisomers have been reported, but without assignment of configuration. An exhaustive examination of the possible stereoisomers was undertaken to determine if thermodynamic differences exist that could help identify the experimentally observed stereoisomers. Results from density functional theory calculations (Figure 4) reveal the presence of clusters of stereoisomers with varying stability that may be of use in narrowing the list of possible structures. The RRSRS stereoisomer has been defined as distinct from the others. The
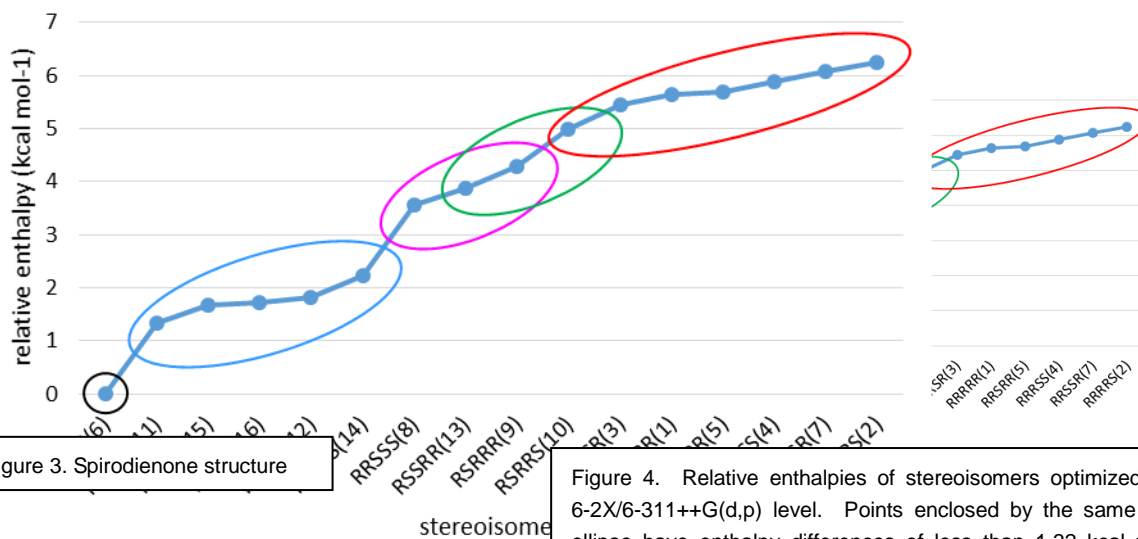
Benzodioxane-coupled caffeoyl 24-mers models of pure stereochemistry:

	(R,R)	(R,S)	(S,R)	(S,S)
Length (Å):	141	142	142	98
Maximum diameter (Å):	10.4	10.8	10.8	19.3

Figure 2. 24-mers of caffeoyl alcohol

Figure 3. Spirodienone structure

Figure 4. Relative enthalpies of stereoisomers optimized at M0 6-2X/6-311++G(d,p) level. Points enclosed by the same color ellipse have enthalpy differences of less than 1.32 kcal mol⁻¹.

Lastly, based on reports of coupling of the flavone tricin to lignols (Figure 5) [13] the bond dissociation enthalpies associated with the reaction shown in Figure 5 have been determined with density functional calculations. The lignols examined were based on p-coumaryl, caffeyl. 5-hydoxyconfieryl, coniferyl and sinapyl alcohols and ethyl ferulate, with stereochemistry taken into account. The various cinnamyl alcohols exhibit fairly similar BDE values, on the order of about 65-70 kcal mol⁻¹ while the ethyl ferulate couple is markedly lower at 55-60 kcal mol⁻¹.
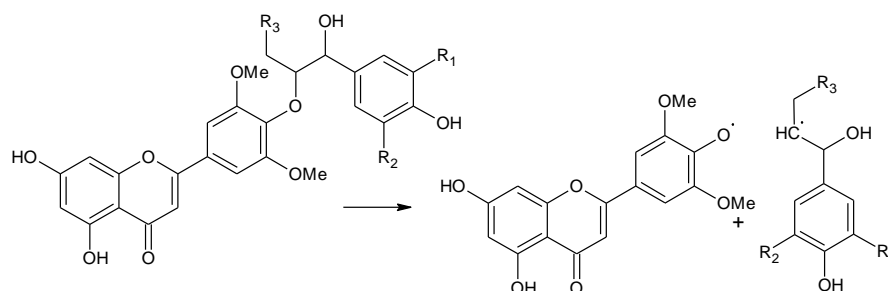
Figure 5. Tricin monolignol couple

Conclusions

It can be seen from these reports that electronic structure calculations can provide useful information on the structure and reactivity of lignin models. These results give insights into reaction mechanisms and rates that can be of use in the development of chemical processes for the production of value-added products.

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