Supplementary Information

Single-conformation UV and IR spectroscopy of model G-type lignin dilignols: the β-O-4 and β-β linkages

Jacob C. Dean, Patrick S. Walsh, Bidyut Biswas, P. V. Ramachandran, and Timothy S. Zwier*

Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084 U.S.A.

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1. Low-energy conformers of β-O-4

The two conformers found in the β-O-4 dilignol were assigned as the *syn/anti* pair (about the internal rotation of R1) of the α-C8/γ-C5 linkage family, determined by their characteristic signatures in the OH stretch region of the IR and confirmed by the observed shifts in their UV absorptions. The simulated spectra of these conformers match the pattern of the experimental IR spectra quite well, and a plot comparing the experimental RIDIR spectra with all of the calculated structures within 5 kJ/mol is shown in Figure S1. The first three structures shown below the simulated spectra of the assigned conformers show a band predicted to be red-shifted well below those observed (< 3550 cm^{-1}), and at much larger intensity. This OH stretch is representative of a strong H-bond interaction with the OCH_3 acceptor on R2, which is stronger than the assigned structures due to the out-of-plane OCH_3 orientation positioning the lone pair of the oxygen toward the incoming OH donor. This out-of-plane orientation comes at an energetic cost based on the calculated energies. Also found within these structures are interactions between the α- and γ-OH groups, which themselves display characteristic red-shifts which would be discernible in the experimental spectra.
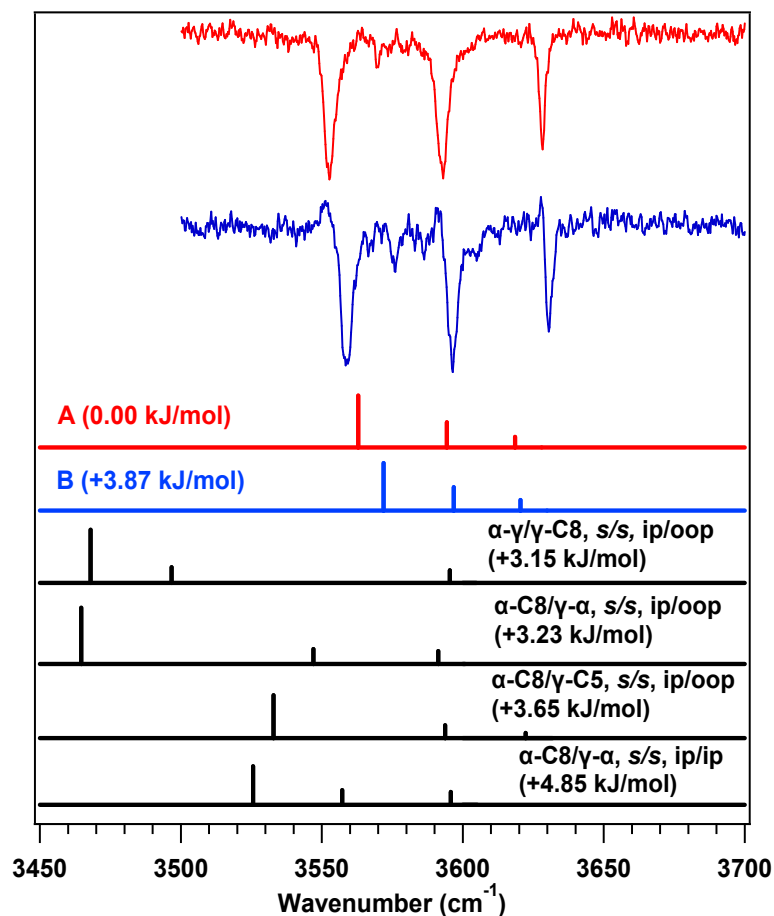
Fig. S1. Experimental RIDIR spectra of conformers A (red) and B (blue), along with the simulated spectra for the assigned structures and remaining structures within 5 kJ/mol of the global minimum.

2. Minor conformers of β-O-4

As discussed in the Results and Analysis section (erythro β-O-4 Spectroscopy), it is expected that one or more minor conformers of the β-O-4 dilignol exists in the supersonic expansion, based on the observation of several small bands in the IRIG spectrum (Figure 4, right) that were not accounted for in RIDIRS. In the calculated structures, the most likely candidate H-bond that would coincide with the small band at 3535 cm^{-1} would be a $\gamma \rightarrow \alpha$ H-bond, reporting a α-C8/γ-α (*s/s*) structure calculated to be 3.23 kJ/mol above the global minimum (slightly lower than conformer B). This structure has a very strong α-C8 H-bond due to an out-

of-plane bend of the R2 methoxy group, orienting its lone pair directly toward the OH hydrogen as shown in **Figure S2** (left). The predicted position of this band is ~3465 cm^{-1} and is represented in its stick spectrum in **Figure S3**. The low energy predicted for this conformation yields it a plausible candidate for one unaccounted conformer that is present in low abundance in the expansion.

The other bands to the blue centered at 3648 cm^{-1} are likely due to free α-OH stretch fundamentals as this is just red of those observed for HMPPT. The lowest energy structure incorporating this is a α-free/γ-C8 (-/*a*) conformer at 5.74 kJ/mol above the global minimum. This structure is labeled as "-" in its relative ring orientation because R2 is nominally perpendicular to R1, perhaps signifying that an α-OH H-bond locks the structure down to a more linear, unfolded structure (as in conformers A and B). This structure is also likely giving rise to the shoulder to the red of the central G band, with the γ-C8 being predicted there. Additional structures with a free α-OH display a larger degree of folding with some structures having a stacked ring configuration.
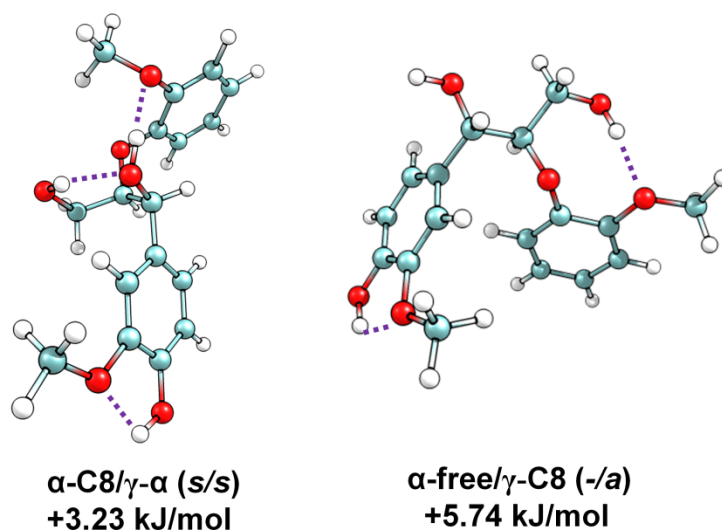

α-C8/γ-α (*s/s*)
+3.23 kJ/mol

α-free/γ-C8 (-/*a*)
+5.74 kJ/mol

Fig. S2 Tentative structural assignments for possible minor conformers of the β-O-4 dilignol.
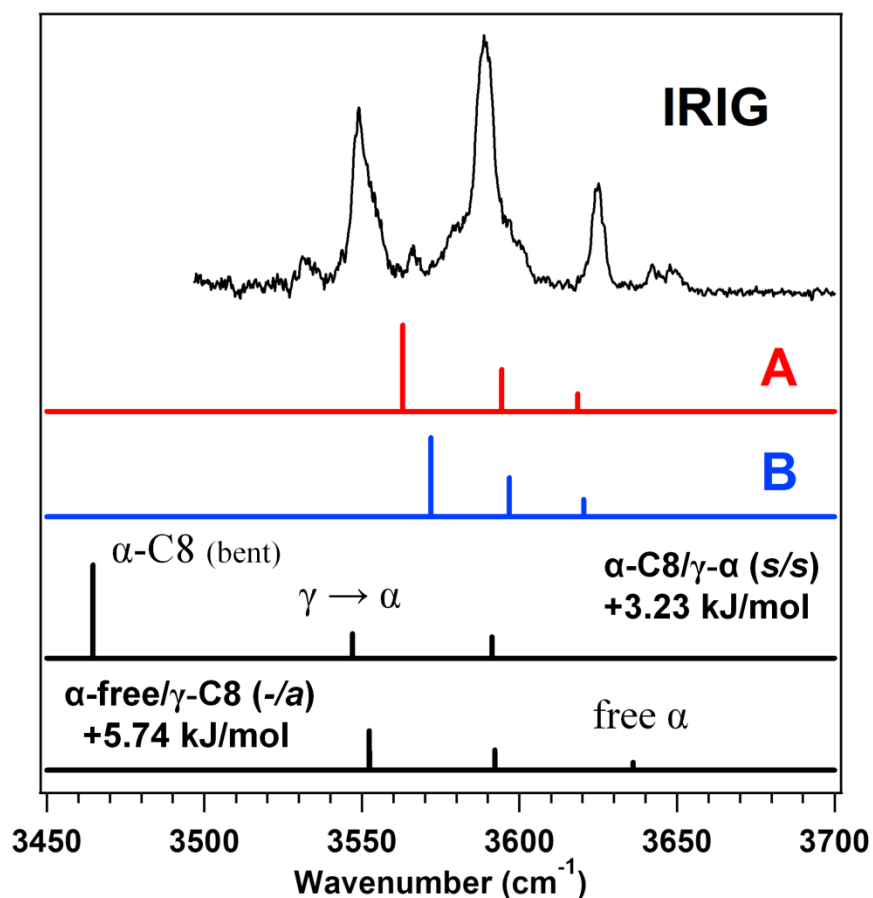
Fig. S3 IRIG spectrum of the β-O-4 dilignol along with the simulated spectra for the major conformers A and B (red and blue), and tentative minor conformers (black).

3. Comparison of β-O-4 and pinoresinol alkyl CH stretch spectra

The alkyl CH stretch spectra of the β-O-4 dilignol and pinoresinol were each found to display a set of bands associated with OCH_3 modes, along with various linkage CH fundamentals. **Figure S4** shows the alkyl CH stretch RIDIR spectra of conformer A of β-O-4 and pinoresinol for comparison, along with the stick spectra of their assigned structures. Perhaps the most immediate similarity between the experimental spectra are the OCH_3 bands representative of the guaiacyl rings of both molecules (red sticks in stick spectrum). This shows that these bands are relatively linkage independent, and similar patterns of those bands suspected

to be members of either the symmetric or antisymmetric CH_2 stretch modes can be matched between these molecules since the linkage CH fundamentals are distinct. This provides further insight into Fermi resonance couplings involving the OCH_3 modes, particularly the symmetric stretch which represents the most apparent discrepancy between experiment and harmonic frequency calculations.
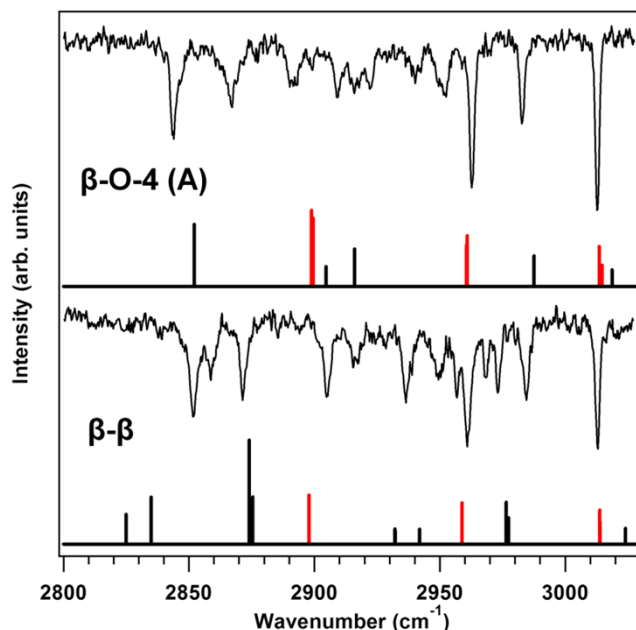

Fig. S4 RIDIR spectra and simulated IR spectra of conformational assignment (sticks) for β-O-4 conformer A (top) and pinoresinol/β-β (bottom).

4. Comparison of RIDIR spectra between three low-energy conformers of pinoresinol

The conformational landscape of pinoresinol is largely limited to torsional minima about the guaiacyl ring internal rotation, with minima in characteristic *syn/anti* orientations (see Figure 11). In principle then, the reporting IR probes on the guaiacyl rings (OH, OCH_3) can act as reporters on the individual ring orientations. **Figure S5** shows the experimental RIDIR spectra with simulated spectra of the three low-energy structures differing only in their ring configurations. Slight differences in the OH stretch frequencies are predicted for rings oriented

syn versus *anti* as shown in Figure S5a). Using the scale factor determined previously, the global minimum *syn/syn* structure is an exact fit, albeit the frequencies between calculated structures vary at most only 5 cm^{-1}. In the alkyl CH stretch region (Figure S5b), the asymmetric *syn/anti* structure displays a splitting in its OCH$_3$ symmetric and antisymmetric CH$_2$ fundamentals as one would expect. Given the congestion and Fermi resonance coupling in this region of the RIDIR spectrum however, this is more difficult to exploit in assigning the conformation of pinoresinol.
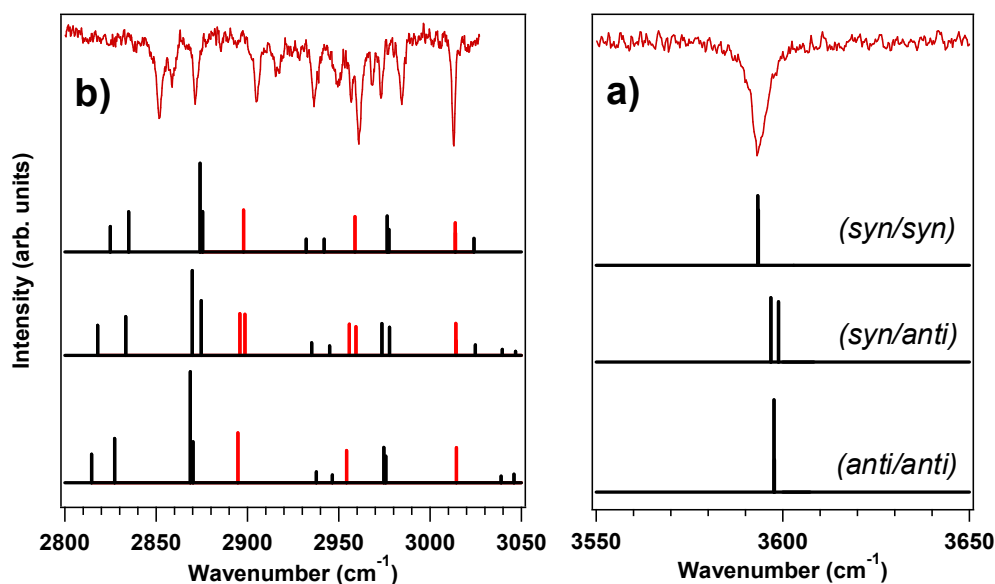

Fig. S5 Comparison of the RIDIR spectra of pinoresinol with the simulated IR spectra of the three low-energy conformers in the (a) OH stretch and (b) alkyl CH stretch regions.

5. Further discussion of vibrational quenching of the excitonic splitting

The interpretation of the overestimation of excitonic splittings comes in the breakdown of the Born-Oppenheimer approximation, i.e. vibronic coupling, when exciting to the excited electronic surfaces. In the excitation, the pure electronic coupling element is quenched at every spectroscopically-allowed vibronic band by its Franck-Condon factor, which by definition is less than one: $V_{AB}^{vibron} = V_{AB}^{el} * |\langle X_{v'} | X_0 \rangle|^2$. In short, the pure Born-Oppenheimer based excitonic

splitting is spread out between every Franck-Condon active vibration, breaking it into individual "vibronic" fragments (See figure 3 in reference 1).[1,2] This effect has been modeled by taking the two localized diabatic potentials of the monomer excited states, each displaced along a particular vibrational coordinate, and forming a pair of adiabatic surfaces for S_1 and S_2.[1] The adiabatic potential for S_1 forms a double-minimum potential with minima displaced from the ground state minimum an amount representative of the change in geometry. The Born-Oppenheimer splitting is treated as the difference in energy between the two surfaces vertically from the ground state equilibrium position. The vibrationally-quenched splitting however, is the nonadiabatic tunneling splitting in the lower adiabatic potential.[1] This vibrationally *quenched* dipole-dipole picture has reproduced experimental splittings quite accurately.[2,3]

In the case of pinoresinol with its identical UV chromophores, the excitonic coupling is small, and we have surmised based on calculation that the Franck-Condon quenched excitonic splitting is no more than a few wavenumbers. In this weak coupling limit, the excited state surfaces produce an adiabatic lower surface that is a double-well in which electronic excitation is localized on one (|A*B>) or the other (|AB*>) ring, with an S_1/S_2 splitting that is best thought of as a tunneling splitting on this lower adiabatic surface, where both nuclear motion and electronic excitation must be transferred from one ring to the other during the tunneling process. In the absence of high resolution UV spectroscopy or dispersed fluorescence, we have been unable to firmly identify the magnitude of the splitting, which is inversely proportional to the timescale for electronic energy transfer between the two rings.

References

1.   S. Kopec, P. Ottiger, S. Leutwyler and H. Koppel, *J. Chem. Phys.*, 2012, **137**, 184312.

2.   P. Ottiger, S. Leutwyler and H. Koppel, *J. Chem. Phys.*, 2012, **136**, 174308.
3.   E. G. Buchanan, P. S. Walsh, D. F. Plusquellic and T. S. Zwier, *J. Chem. Phys.*, 2013, **138**, 204313.