

Bond Dissociation Enthalpies of a Pinoresinol Lignin Model Compound

Thomas Elder*

Southern Research Station, United States Forest Service (USFS), United States Department of Agriculture (USDA), Pineville, Louisiana 71360, United States

Supporting Information

ABSTRACT: The pinoresinol unit is one of the principal interunit linkages in lignin. As such, its chemistry and properties are of major importance in understanding the behavior of the polymer. This work examines the homolytic cleavage of the pinoresinol system, representing the initial step in thermal degradation. The bond dissociation enthalpy of this reaction has been evaluated using M06-2X density functional calculations. Products that allow for extensive electron delocalization are energetically favored. Calculations on subsequent reactions reveal a preference of intermediates with two unpaired electrons over a proposed four unpaired electron structure.

INTRODUCTION

Lignin accounts for approximately 25% by weight of terrestrial plants and results from the polymerization of radicals generated by the enzymatic dehydrogenation of the cinnamyl alcohols.¹ Because of the number of resonance forms that the radicals can assume, a variety of interunit linkages occur (Figure 1), such that the polymer is amorphous, without a specific repeat unit. With renewed interest in alternative sources of energy and chemicals from sustainable sources has come a concomitant increase in work on the utilization of lignin in such applications.² Among the processes that have been proposed for the conversion of lignin are the thermal methods, such as pyrolysis and oxidative thermostabilization. The chemical mechanisms associated with the thermal degradation of lignin have been the topic of both experimental and computational studies.

The former includes work on phenethyl phenyl ether and derivatives thereof, representing the ubiquitous β -O-4 linkage.³⁻⁶ From this work, it was proposed that the initial steps in thermal degradation involved homolytic cleavage of carbon-carbon and ether bonds, with subsequent radical-mediated reactions. Methoxylated models have been extensively examined by Kawamoto and Saka and their co-workers, addressing the effect of structure and substitution on primary reaction products,⁷⁻¹¹ secondary reactions,¹²⁻¹⁴ and more recently char formation.¹⁵⁻¹⁸

Computational work on the pyrolysis of lignin models has been dominated in the recent past by the work of Beste and co-workers, with contributions related to reaction selectivity¹⁹⁻²¹ and kinetics.²²⁻²⁵ Bond dissociation enthalpy calculations, as related to thermal degradation mechanisms, have been the subject of comprehensive reports^{26,27} and devoted to more specific models, including β -O-4 linkages,²⁸⁻³¹ a phenyl-coumaran structure,³² and dibenzodioxocin.^{33,34} It is in the spirit of the latter papers that the current work was undertaken. As indicated, there has been considerable computational work reported on reactions of the various open-chain structures of lignin.²⁶⁻³¹ In contrast, there have been relatively few papers

concerned with cyclic lignols.³²⁻³⁴ As such, the objective of this paper is to evaluate the bond dissociation enthalpies of homolytic ring-opening reactions of a pinoresinol model that may occur at elevated temperatures. Specific literature related to the behavior of this structure at elevated temperatures is limited, but a recent paper on the pyrolysis of kraft lignin³⁵ proposed the formation of a quintet (four unpaired electrons) by homolysis of the two α -O linkages, followed by cleavage of the remaining β - β' bond, resulting in two coniferyl alcohol radicals. The only computational work that has been reported for pinoresinol is concerned with its antioxidant activity and, therefore, the cleavage of the phenolic group³⁶ rather than the interunit linkage.

EXPERIMENTAL SECTION

The structures for the reactant and initial products are as shown in Figure 2, along with the labels for the rings in the systems and designations that are consistent with lignin chemistry nomenclature. In accordance with the previous experimental and computational literature,^{2,3,19-34} homolytic cleavage reactions resulting in neutral products are examined. A crystal structure has been reported for the pinoresinol reactant³⁷ and was used as the starting point for the calculations, all of which were performed with Gaussian09, revision C01,³⁸ executing on a SGI Ultraviolet 2000 or Dense Memory Cluster (DMC) administered by the Alabama Supercomputer Authority. The initial calculation was performed using the M06-2X density functional method with the 6-31+G(d) basis set and the ultrafine grid, consisting of 99 radial shells and 590 angular points per shell, with geometry optimization. On the basis of the geometry from this step, a second optimization with a frequency calculation was performed with the M06-2X method, the 6-311++G(d,p) basis set, and the ultrafine grid. Furthermore, to verify the quality of the crystal structure geometry, it was used as the starting point for a 500 step Monte Carlo search, with optimization using the PM3 semi-empirical method, as implemented in Spartan.³⁹ The lowest 10 conformers identified were optimized using M06-2X/6-31+G(d) with the ultrafine grid. The lowest energy

Received: November 23, 2013

Revised: January 22, 2014

Published: January 23, 2014

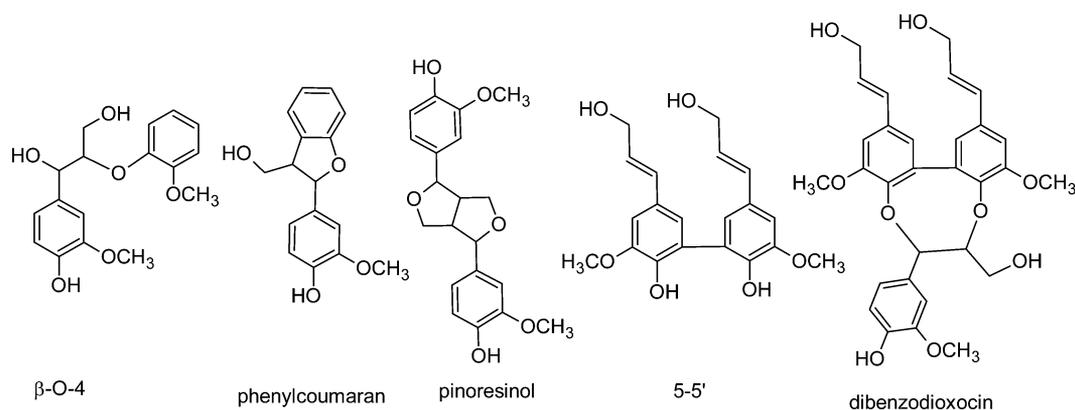


Figure 1. Principal interunit linkages in lignin.

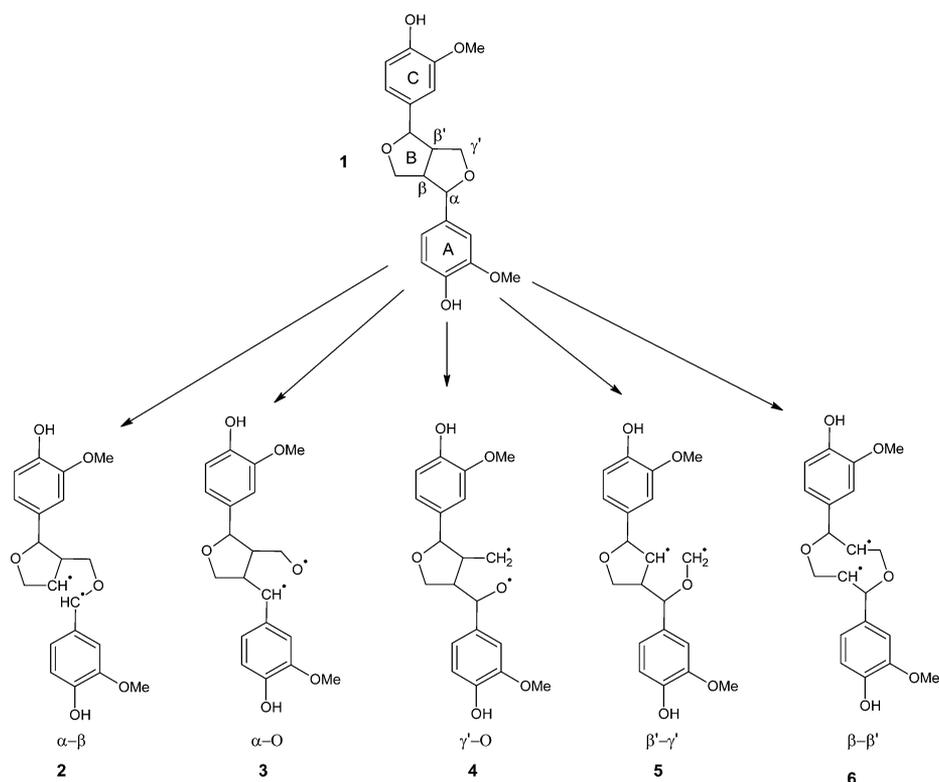


Figure 2. Reactant and products under study in the current work.

conformation was used as the input for an optimization and frequency calculation using M06-2X/6-311++G(d,p) with the ultrafine grid.

The products from the ring-opening reaction were first examined by deleting the appropriate bond and increasing the interatomic distance to 2.5 Å. The structures were optimized as triplets with M06-2X/6-311++G(d) with the ultrafine grid, followed by an optimization and frequency calculation with M06-2X/6-311++G(d,p) and the ultrafine grid. The structures were treated as triplets in accordance with the results from Younker et al.,³² who found small singlet–triplet gaps for a phenylcoumaran model. The initial interatomic distance was set to 2.5 Å to prevent the structure from reverting back to the original geometry.

As was performed for the reactant, a second set of calculations was executed by subjecting the ring-opened products to a Monte Carlo search and the same sequence of density functional calculations previously described. The two sets of calculations can be thought of as representing the structure at various points during the thermal degradation process, with the initial bond rupture corresponding to an early stage, which could, at elevated temperatures, be followed by bond

rotations, as illustrated by the conformational analyses, and identification of alternative geometries.

After complementation of the bond dissociation enthalpy calculations, the geometries of the reactant and all products were evaluated by determining the interatomic distances associated with ring-opening, plane angles formed between the rings within the pinoresinol structure and distances between the centers of the rings. The electronic structure of each reactant was examined by plots of the spin densities and unpaired molecular orbitals, with isovalues of 0.005 and 0.05, respectively.

Furthermore, as was mentioned in the Introduction, Hu and co-workers³⁵ have proposed the degradation mechanism for pinoresinol shown in Figure 3A by invoking an intermediate with four unpaired electrons. While this will account for the observed products, the mechanism shown in Figure 3B could represent an alternative with two unpaired electrons. In addition, the presence of vanillin is reported in the reaction mixture,³⁵ and although this could arise from numerous points in the lignin polymer, it could specifically come from pinoresinol, as shown in mechanisms C and D of Figure 3. The

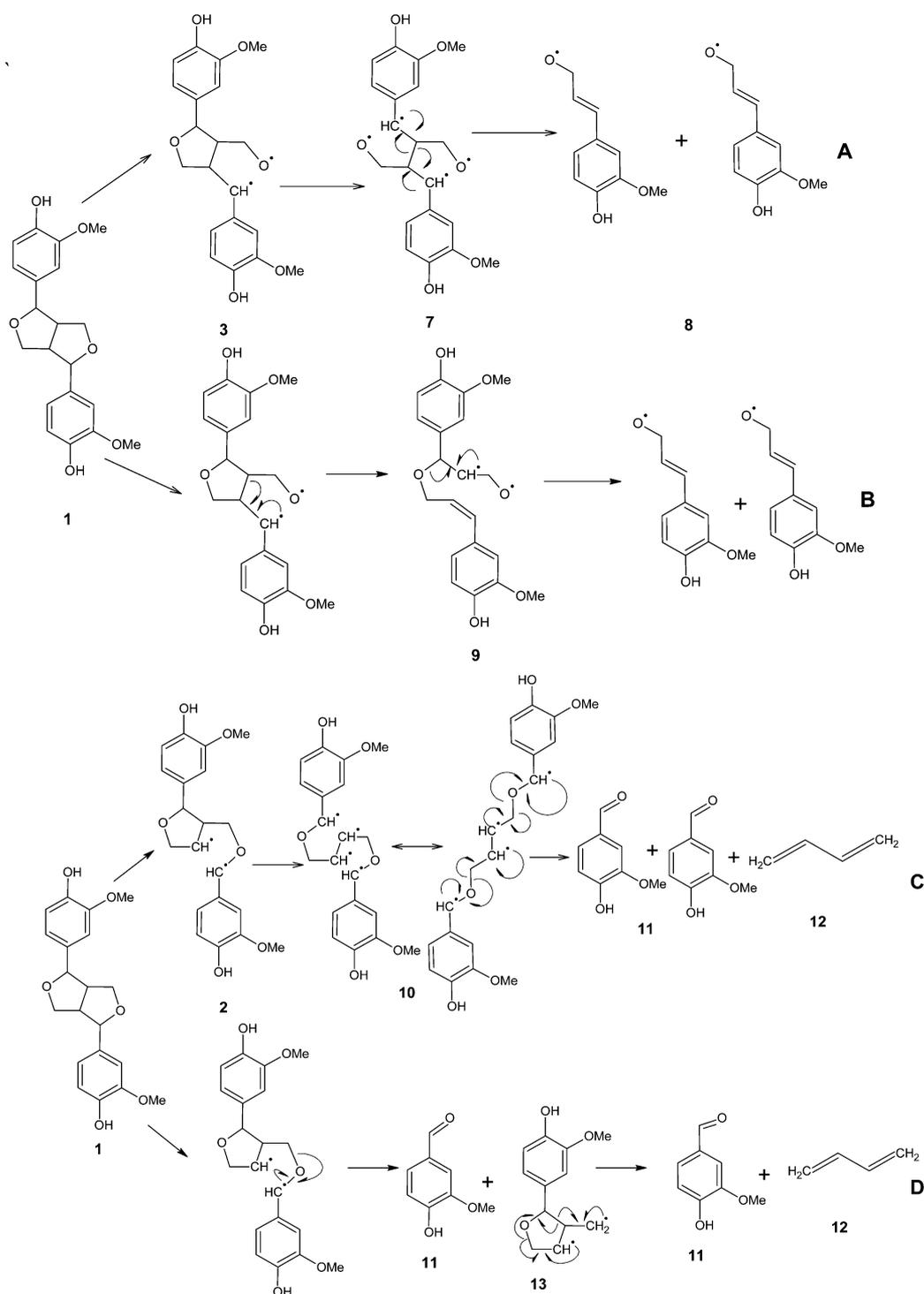


Figure 3. Proposed reaction mechanisms of structures 2 (α - β) and 3 (α -O).

former mechanism, with a four unpaired electron intermediate, would be consistent with Figure 3A, while the latter is an alternative with a triplet intermediate. It is recognized that with four unpaired electrons, quintet, triplet, and singlet configurations may be assumed. A comprehensive examination of this, analogous to the singlet biradical/triplet comparisons reported for phenylcoumaran,³² using multiconfiguration self-consistent field theory would represent a highly involved and computationally intense separate study. As a consequence and for the sake of the current work, a quintet (all spins parallel) was assumed and the reactions were evaluated using the same computational methods as described for the initial products.

RESULTS

The sum of the electronic energy and thermal enthalpy at 298 K for the pinoresinol reactant and each of the products, the bond dissociation enthalpies, calculated as the difference in enthalpy between the reactants, and the final interatomic distances are shown in Table 1. In general, the structures identified by conformational searching are slightly more stable (ranging from 0.03 to 3.25 kcal mol⁻¹), with the exception of compound 6, the β - β' structure. The bond dissociation enthalpies are also very similar for a given product, whether on

Table 1. Enthalpy, Bond Dissociation Enthalpy, and Interatomic Distances for Each of the Ring-Opened Products

product	optimized	conformational search	optimized		conformational search	
	sum of electronic and thermal enthalpies (hartrees)	sum of electronic and thermal enthalpies (hartrees)	bond dissociation enthalpy (kcal mol ⁻¹)	distance (Å)	bond dissociation enthalpy (kcal mol ⁻¹)	distance (Å)
1 (reactant)	-1226.114600	-1226.116232				
2 (α - β)	-1226.007947	-1226.012079	66.93	4.04	65.36	4.51
3 (α -O)	-1226.006385	-1226.007286	67.91	3.01	68.36	4.32
4 (γ' -O)	-1225.989357	-1225.989402	78.95	2.94	79.59	3.26
5 (β' - γ')	-1225.985173	-1225.990357	81.22	4.11	78.99	4.03
6 (β - β')	-1225.985361	-1225.985140	81.10	3.12	82.62	3.18

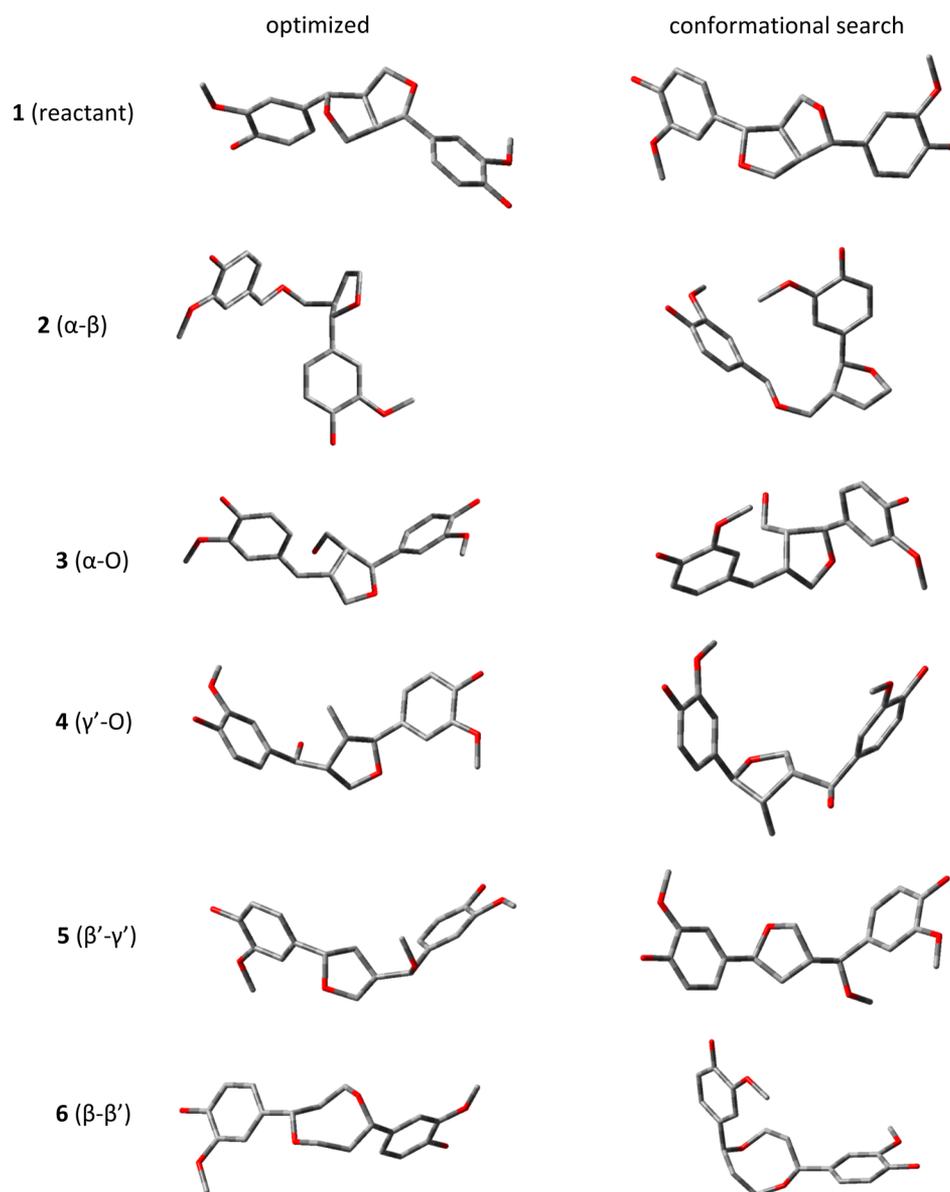


Figure 4. Geometries of reactants and products.

the basis of the ring-opened optimized structures or the geometries identified through conformational searching, with the largest differences being associated with the α - β and β - β' ring openings, at 1.57 and 1.52 kcal mol⁻¹, respectively. Among the products, the 2 (α - β) and 3 (α -O) structures exhibit the lowest bond dissociation enthalpies of about 65–68 kcal mol⁻¹, which are somewhat higher than the related bond cleavages in phenylcoumaran,³² with structures 4 (γ' -O), 5 (β' - γ'), and 6

(β - β') in the range of \sim 79–82 kcal mol⁻¹. On the basis of these values and the assumption that bond dissociation enthalpy is proportional to activation energy, structures 2 (α - β) and 3 (α -O) would be the dominant products of the reaction. This assumption is based on reports from work on other lignin model compounds, in which transition states were not identified on the potential energy surface and, as such, the bond dissociation enthalpies are used to approximate activation

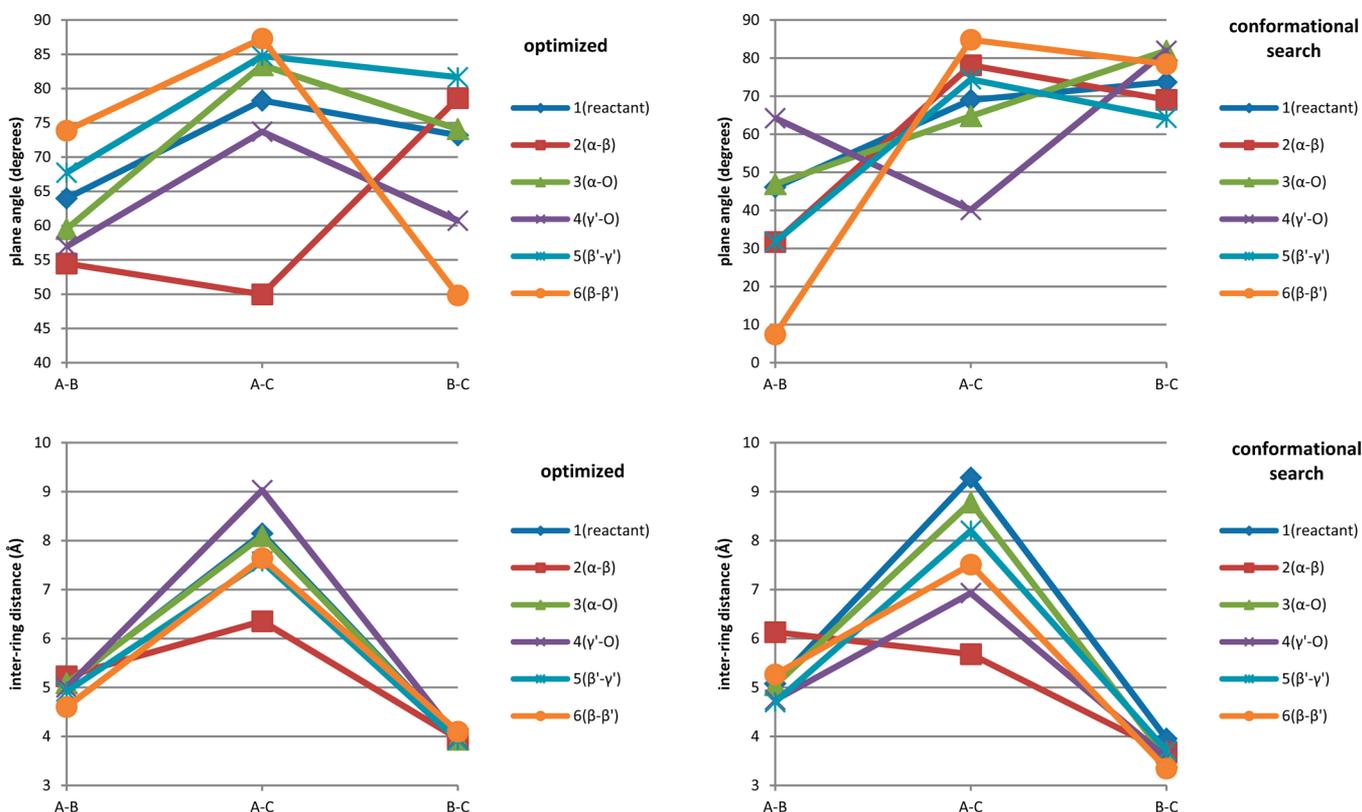


Figure 5. Results from measurements of ring plane angles and inter-ring distances for optimized and conformational search geometries.

energies.^{6,32,34} It should also be noted that, on the basis of a test set of 177 main group compounds, the mean unsigned accuracy of M06-2X thermochemical calculations⁴⁰ was $1.3 \text{ kcal mol}^{-1}$. Given this accuracy, structures differing by less than this value cannot be energetically differentiated. In addition, while the interatomic distances because of the ring openings are, as might be expected, generally greater after conformational searching, they do not differ markedly between two sets of structures. Figure 4 shows the final geometry for the reactant and each product.

It should be noted that the current results are based on the harmonic oscillator rather than the hindered rotor approximation. While the latter method could be invoked to address low-frequency vibrations, a comparison of enthalpies and free energies of structures 1–6 indicates a very high correlation ($R^2 = 0.9995$). On the basis of this result, while the entropy term would affect the absolute values for the cleavage reaction, the relative values would be consistent.

Figure 5 shows the inter-ring plane angles and distances for both the ring-opened optimized structures and the low-energy conformers from the conformational search. Among the optimized structures, the plane angles exhibit similar trends, not differing markedly from the reactant, with the exception of structure 2 ($\alpha-\beta$), in which the aromatic rings (A–C) are more aligned. The results from the conformational search procedure generally show less variability between the aromatic rings, which are oriented more perpendicular to each other, the exception to which is the 4 ($\gamma'-\text{O}$) product. Similarly, after conformational searching, the B–C plane angles for all products are quite tightly clustered in the range of about $65\text{--}80^\circ$. The inter-ring distances are very similar for the A–B and B–C separations, with values of ~ 5 and 4 \AA , respectively, for both the optimized and conformational search results. There is,

not unsurprisingly, more variability for the A–C inter-ring distance ranging from just below 6 to over 9 \AA . In all cases, this distance has decreased with the ring-opening reaction, with structure 2 ($\alpha-\beta$) exhibiting the smallest separation.

Figures 6 and 7 show the plots of spin density and the two singly occupied molecular orbitals for the optimized products and the low-energy structures identified by conformational searching, respectively. It can be seen from the spin density plots that structures 2 ($\alpha-\beta$) and 3 ($\alpha-\text{O}$) exhibit extensive delocalization of the unpaired electrons, which is in accordance with the bond dissociation enthalpy calculations, showing that these products are the most stable. Conversely, structures 4 ($\gamma'-\text{O}$), 5 ($\beta'-\gamma'$), and 6 ($\beta-\beta'$) with higher bond dissociation enthalpies show highly localized spin density. While the concentration of spin density at the salient positions is qualitatively similar among these products, with conformational searching, structure 6 ($\beta-\beta'$) is found to have a somewhat higher bond dissociation enthalpy. Although the eight-membered ring is probably quite flexible, the ring-opening reactions associated with products 2 ($\alpha-\beta$), 3 ($\alpha-\text{O}$), 4 ($\gamma'-\text{O}$), and 5 ($\beta'-\gamma'$) may have rotational degrees of freedom that would not be accessible to structure 6 ($\beta-\beta'$) and may account for the slightly higher bond dissociation enthalpy upon conformational searching. With respect to the orbital plots, there are individual products, such as the optimized structures 2 ($\alpha-\beta$), 6 ($\beta-\beta'$), and 5 ($\beta'-\gamma'$) from conformational searching, in which there is close correspondence with the spin densities, while in general, the orbitals display typical aromatic character.

Turning to the mechanisms proposed in Figure 3, the results from the calculations are shown in Table 2. It can be seen that, as expected, the quintets are on the order of $40\text{--}60 \text{ kcal mol}^{-1}$ less stable than the triplets. Although all of the reactions are

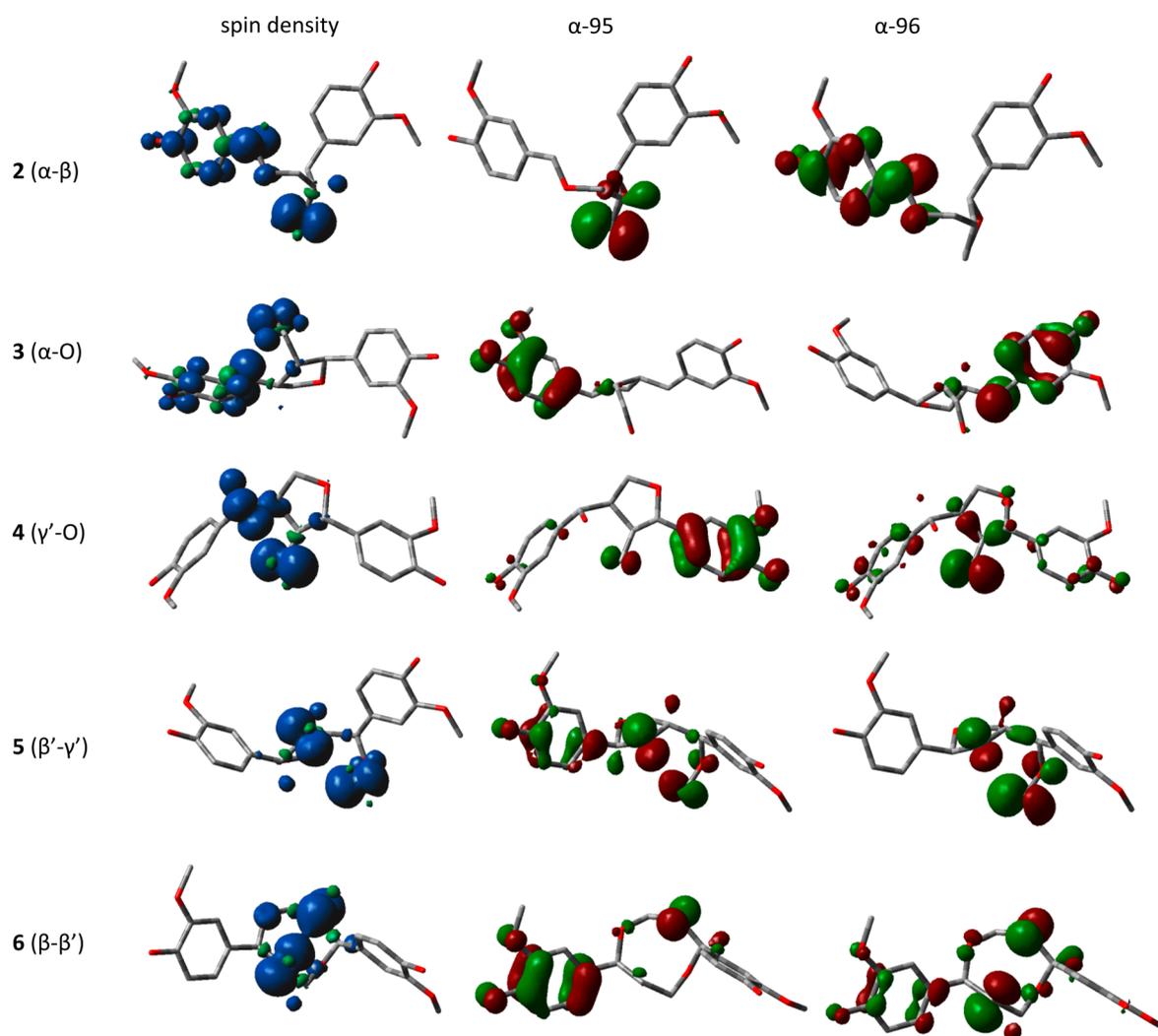


Figure 6. Spin density and orbital plots for optimized structures.

endothermic, those that proceed through the quintets (mechanisms A and C of Figure 3) have enthalpies of reaction in the range of ca. 68–77 kcal mol⁻¹, while those associated with the triplets range from ca. 16 to 26 kcal mol⁻¹, with the reaction responsible for vanillin formation (Figure 3D) representing the lower range of the latter. Parenthetically, as an alternative to the assumed quintet state, preliminary calculations were subsequently performed on structures 7 and 10 with the singlet configuration, in which the electrons have opposite spins, resulting in markedly lower enthalpy values. While beyond the scope of the current paper, these results indicate that a more detailed examination of the electronic nature of these structures is warranted.

The model compound addressed in this work and those from the literature are consistent with known interunit linkages of lignin. Although such studies are necessitated by the complex and indefinite structure of lignin, the limitations should also be kept in mind. Among these is the conformational flexibility of smaller models that may differ from the native polymer, thus impacting electron delocalization and, therefore, energetics and chemistry. A study on the main lignin linkages using layered calculations would be an interesting problem.

CONCLUSION

The work reported in this paper is concerned with the calculation of homolytic bond dissociation enthalpies for a pinoresinol lignin model compound, by the application of the density functional theory. The reactions under consideration are consistent with those proposed for the initial steps in the thermal degradation of lignin, which represents an integral part of the biorefinery concept for the conversion of biomass to chemicals and fuels. The model compound examined extends previous work on both acyclic and cyclic dilignols from this and other laboratories. The current results show that, while the linkage may be broken at several points during the initial steps of thermal degradation, marked energetic differences exist. The cleavage of the α -O and α - β bonds exhibits considerably lower bond dissociation enthalpies, which are consistent with the extensive delocalization of the unpaired electrons, as observed in spin density plots. Furthermore, the bond dissociation enthalpies of the α -O and α - β bonds are in the lower range of such values for acyclic dilignols.²⁷ Interestingly, the α -O results are higher than those reported for ether linkages in phenylcoumaran³² and dibenzodioxocin.³⁴ The bond dissociation enthalpy of the α - β bond is higher than that reported for phenylcoumaran³² and lower than that in dibenzodioxocin.³⁴ In subsequent reactions of these initial

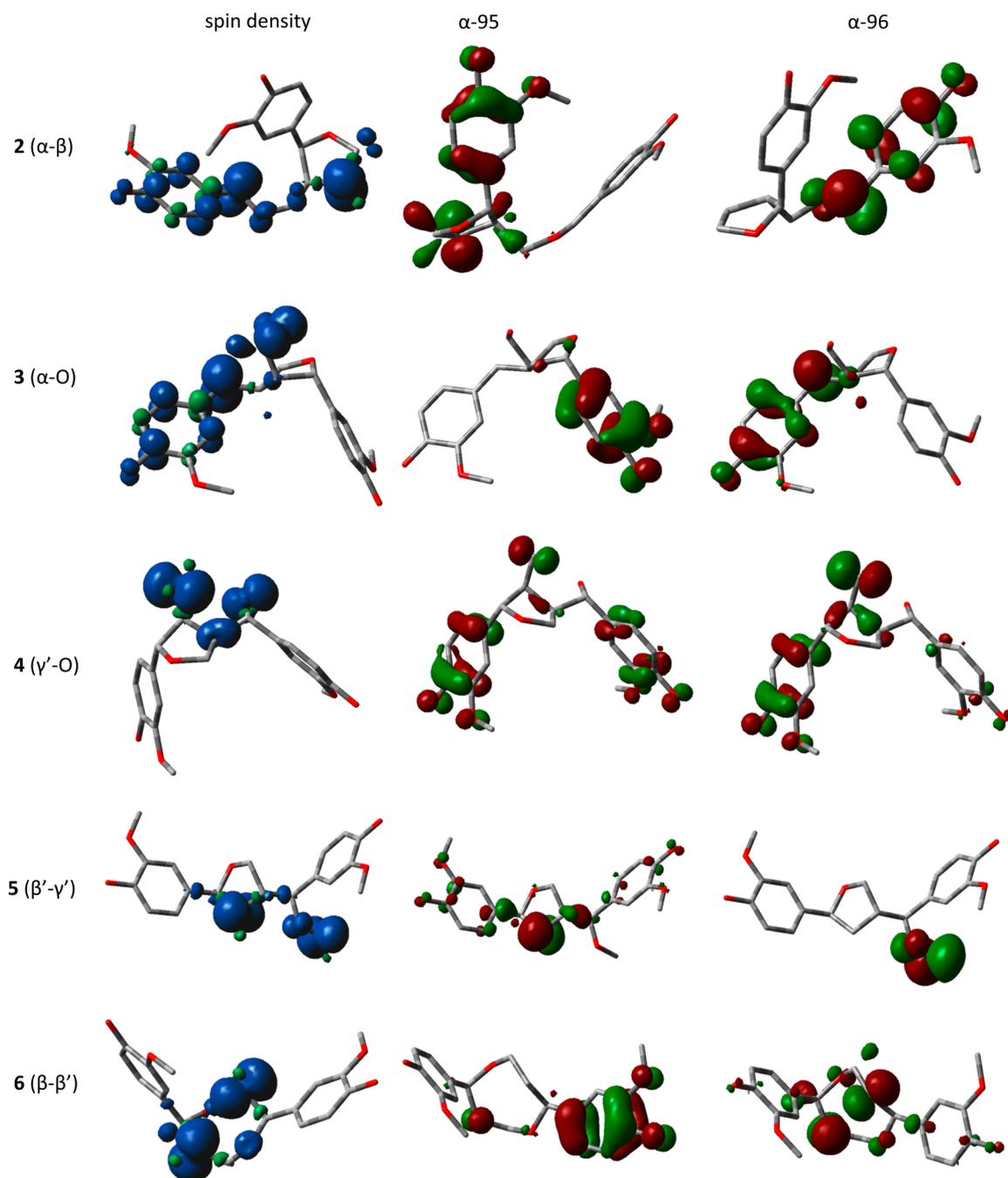


Figure 7. Spin density and orbital plots for optimized structures of low-energy conformers.

Table 2. Enthalpy and Enthalpy of Reaction for Mechanisms Proposed in Figure 3

product	optimized	conformational search	optimized	conformational search
	sum of electronic and thermal enthalpies (hartrees)	sum of electronic and thermal enthalpies (hartrees)	enthalpy of reaction (kcal mol ⁻¹)	enthalpy of reaction (kcal mol ⁻¹)
2 (α - β)	-1226.007947	-1226.012079		
10 (quintet product)	-1225.896644	-1225.889514	69.84	76.91
11 + 13 (triplet product)	-1225.981075	-1225.982391	15.88	18.63
3 (α -O)	-1226.006385	-1226.007286		
7 (quintet product)	-1225.897242	-1225.899666	68.49	67.53
9 (triplet product)	-1225.965415	-1225.969552	25.71	23.68

products, a structure with four unpaired electrons was proposed in the previous literature.³⁵ Calculations were performed on this mechanism and an alternative invoking an intermediate

with two unpaired electrons. The latter was found to be much more energetically favorable and, as such, may represent a more feasible route to the experimentally observed products.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: telder@fs.fed.us.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The author is indebted to Raymond C. Fort, Jr. and Ariana Beste for their comments and suggestions and Dr. David C. Young for his support in the performance of this work.

■ DEDICATION

This paper is dedicated to the memory of Dr. Wayne K. Murphey.

■ REFERENCES

- (1) Boerjan, W.; Ralph, J.; Boucher, M. *Annu. Rev. Plant Biol.* **2003**, *54*, 519–546.
- (2) Bozell, J. J.; Holladay, J. E.; Johnson, D.; White, J. F. *Top Value Added Candidates from Biomass, Vol. II: Results of Screening for Potential Candidates from Biorefinery Lignin*; Pacific Northwest National Laboratory (PNNL): Richland, WA, 2007.
- (3) Britt, P.; Buchanan, A., III; Cooney, M.; Martineau, D. *J. Org. Chem.* **2000**, *65*, 1376–1389.
- (4) Britt, P.; Kidder, M.; Buchanan, A., III *Energy Fuels* **2007**, *21*, 3102–3108.
- (5) Klein, M.; Virk, P. *Ind. Eng. Chem.* **1983**, *22*, 35–45.
- (6) Jarvis, M.; Daily, J.; Castensen, H.-H.; Dean, A.; Sharma, S.; Dayton, D.; Robichaud, D.; Nimlos, M. *J. Phys. Chem. A* **2011**, *115*, 428–438.
- (7) Kawamoto, H.; Horigoshi, S.; Saka, S. *J. Wood Sci.* **2007**, *53*, 168–174.
- (8) Kawamoto, H.; Saka, S. *J. Wood Chem. Technol.* **2007**, *27*, 113–120.
- (9) Kawamoto, H.; Horigoshi, S.; Saka, S. *J. Wood Sci.* **2007**, *53*, 268–271.
- (10) Kawamoto, H.; Ryoritani, R.; Saka, S. *J. Anal. Appl. Pyrolysis* **2008**, *81*, 88–94.
- (11) Kawamoto, H.; Nakamura, T.; Saka, S. *Holzforschung* **2008**, *62*, 50–56.
- (12) Nakamura, T.; Kawamoto, H.; Saka, S. *J. Wood Chem. Technol.* **2007**, *27*, 121–133.
- (13) Hosoya, T.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2008**, *83*, 71–77.
- (14) Hosoya, T.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2008**, *83*, 78–87.
- (15) Hosoya, T.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2009**, *84*, 79–83.
- (16) Asmadi, M.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 77–87.
- (17) Asmadi, M.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 88–98.
- (18) Asmadi, M.; Kawamoto, H.; Saka, S. *Holzforschung* **2012**, *86*, 323–330.
- (19) Beste, A.; Buchanan, A., III; Britt, P.; Hathorn, B.; Harrison, R. *J. Phys. Chem. A* **2007**, *111*, 12118–12126.
- (20) Beste, A.; Buchanan, A., III; Harrison, R. *J. Phys. Chem. A* **2008**, *112*, 4982–4988.
- (21) Beste, A.; Buchanan, A., III *J. Phys. Chem. A* **2008**, *117*, 3235–3242.
- (22) Beste, A.; Buchanan, A., III *Energy Fuels* **2010**, *24*, 2857–2867.
- (23) Beste, A.; Buchanan, A., III *J. Org. Chem.* **2011**, *76*, 2195–2203.
- (24) Beste, A.; Buchanan, A., III *Chem. Phys. Lett.* **2012**, *545*, 19–24.
- (25) Beste, A.; Buchanan, A., III *J. Phys. Chem. A* **2012**, *116*, 12242–12248.
- (26) Kim, S.; Chmely, S.; Nimlos, M.; Bomble, Y.; Foust, T.; Paton, R.; Beckham, G. *J. Chem. Phys. Lett.* **2011**, *2*, 2846–2852.
- (27) Parthasarathi, R.; Romero, R.; Redondo, A.; Gnankaran, S. *J. Chem. Phys. Lett.* **2011**, *2*, 2660–2666.
- (28) Beste, A.; Buchanan, A. J., III *Org. Chem.* **2009**, *74*, 2837–2841.
- (29) Wang, H.; Zhao, Y.; Wang, C.; Fu, Y.; Guo, Q. *Acta Chim. Sin.* **2009**, *9*, 893–900.
- (30) Elder, T. *Holzforschung* **2010**, *84*, 435–440.
- (31) Younker, J.; Beste, A.; Buchanan, A., III *ChemPhysChem* **2011**, *12*, 3556–3565.
- (32) Younker, J.; Beste, A.; Buchanan, A., III *Chem. Phys. Lett.* **2012**, *545*, 100–106.
- (33) Gardrat, C.; Ruggerio, R.; Rayez, M.-T.; Rayez, J.-C.; Castellan, A. *Wood Sci. Technol.* **2013**, *47*, 27–41.
- (34) Elder, T. *Energy Fuels* **2013**, *27*, 4785–4790.
- (35) Hu, J.; Shen, D.; Xiao, R.; Wu, S.; Zhang, H. *Energy Fuels* **2013**, *27*, 285–293.
- (36) Nenadis, N.; Wang, L.-F.; Tsimidou, M.; Zhang, H.-Y. *J. Agric. Food Chem.* **2005**, *53*, 295–299.
- (37) Lundquist, K.; Stomberg, R. *Holzforschung* **1988**, *42*, 375–384.
- (38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*; Gaussian, Inc.: Wallingford, CT, 2010.
- (39) Wavefunction, Inc. *Spartan'04*; Wavefunction, Inc.: Irvine, CA, 2004.
- (40) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.