

LCAO MO investigations of lignin model compounds. I. CNDO/2 calculations of intramolecular hydrogen bond O—H...OCH₃ in models of the guaiacol and syringyl type

M. REMKO and J. POLČIN

*Pulp and Paper Research Institute,
890 20 Bratislava*

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The intramolecular hydrogen bond of the O—H...OCH₃ type in 2-methoxyphenol (guaiacol *I*) and its derivatives 2-methoxy-4-methylphenol (*II*), 3-methoxy-4-hydroxybenzyl alcohol (vanillyl alcohol *III*), 3-methoxy-4-hydroxybenzaldehyde (vanillin *IV*), 3-methoxy-4-hydroxyacetophenone (acetoguaiacone *V*), 2,6-dimethoxy-4-methylphenol (*VI*) was studied by means of the semiempirical SCF CNDO/2 method. The compounds investigated form weak intramolecular hydrogen bonds with the energy of 6.3—6.5 kJ mol⁻¹

Был применен метод ППДП/2 для изучения внутримолекулярной водородной связи типа O—H...OCH₃ в 2-метоксифеноле (гваякол *I*) и его производных 2-метокси-4-метилфеноле (*II*), 3-метокси-4-гидроксibenзилалкоголе (ванилиновый спирт *III*), 3-метокси-4-гидроксibenзальдегиде (ванилин *IV*), 3-метокси-4-гидроксиацетофеноне (ацетогваякол *V*) и 2,6-диметокси-4-метилфеноле (*VI*). Изучаемые соединения образуют слабые внутримолекулярные водородные связи, энергия которых приобретает значение 6,3—6,5 кДж моль⁻¹

Intermolecular forces and especially hydrogen bond forces play an important role in the determination of properties of polymers. Well known classical examples are cellulose and polyamides which were intensively studied from this point of view, both experimentally and theoretically. Recently, attention was paid to the investigation of similar problems in lignin in connection with utilization of this natural aromatic material.

Lindberg et al. [1—6] carried out experimental investigations of hydrogen bonds in lignin model compounds and in the macromolecule of lignin. In this work we investigated the intramolecular hydrogen bond of the O—H...OCH₃ type both in guaiacol and syringyl building units (Table 1) using the semiempirical quantum mechanical CNDO/2 method [7—9].

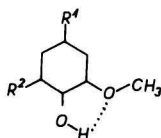
Recently, this method has been used with success for general investigations of the hydrogen bond [10—14] because it provides valuable information on the properties of hydrogen bonded systems. A deeper theoretical study of molecules with intramolecular hydrogen bonds may explain several interesting physical and chemical properties of such molecules.

Method of calculation and geometry

For the calculation of the intramolecular hydrogen bond energy and the electronic structure of the compounds studied the CNDO/2 method with the original parametrization [7—9] has been used. The

Table 1

Energy of the intramolecular hydrogen bond O—H...OCH₃, dipole moments, and bond orders $P_{H...O}$ in the studied lignin model compounds



No.	Compound	R ¹	R ²	E_{HB} kJ mol ⁻¹	$\mu \cdot 10^{29}$ m.A.s.	$P_{\text{H...O}}$
I	2-Methoxyphenol	H	H	6.27	0.96	0.0831
II	2-Methoxy-4-methylphenol	CH ₃	H	6.19	1.00	0.0761
III	3-Methoxy-4-hydroxybenzyl alcohol	CH ₂ OH	H	6.32	1.15	0.0762
IV	3-Methoxy-4-hydroxybenzaldehyde	CHO	H	6.44	0.07	0.0767
V	3-Methoxy-4-hydroxyacetophenone	CO·CH ₃	H	6.53	0.16	0.0967
VI	2,6-Dimethoxy-4-methylphenol*	CH ₃	OCH ₃	9.58	1.52	0.0758

* The energy of the hydrogen bond is defined as $E_{\text{HB}} = E_{\text{total}}^{\Theta=90^\circ} - E_{\text{total}}^{\Theta=0^\circ}$, where Θ is the angle of rotation of the hydroxyl group around the C—O bond.

hydrogen bond energy (E_{HB}) has been defined as a difference between the total energy of a conformer with *trans*-oriented O—H group (E_{trans}) and the total energy of a *cis* conformer (E_{cis}) forming an intramolecular hydrogen bond

$$E_{\text{HB}} = E_{\text{trans}} - E_{\text{cis}}$$

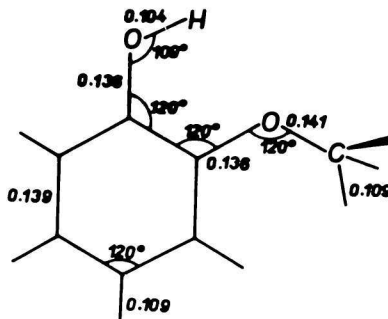
Table 2

CNDO/2 charges in the studied lignin model compounds with an intramolecular hydrogen bond O—H...OCH₃

No.		Charges			
		O	—	H	O
I	<i>cis</i>	-0.2365		+0.1386	-0.2169
	<i>trans</i>	-0.2298		+0.1297	-0.2086
II	<i>cis</i>	-0.2371		+0.1369	-0.2169
	<i>trans</i>	-0.2303		+0.1287	-0.2086
III	<i>cis</i>	-0.2369		+0.1379	-0.2169
	<i>trans</i>	-0.2298		+0.1284	-0.2085
IV	<i>cis</i>	-0.2339		+0.1433	-0.2159
	<i>trans</i>	-0.2268		+0.1338	-0.2074
V	<i>cis</i>	-0.2344		+0.1430	-0.2164
	<i>trans</i>	-0.2269		+0.1331	-0.2079

The calculations were carried out on a Siemens 4004/150 computer at the Computer Centre of the Komenský University, Bratislava using the QCPE 141 standard programme.

For the theoretical calculations the experimental geometry (shown in Scheme 1 for guaiacol) was used.



Scheme 1

Results and discussion

Table 1 shows the energy of intramolecular hydrogen bonds $\text{O}-\text{H}\dots\text{OCH}_3$, calculated by the CNDO/2 method, dipole moments and the $P_{\text{H}\dots\text{O}}$ bond orders of the compounds investigated.

In all compounds studied formation of weak intramolecular hydrogen bonds with a low $P_{\text{H}\dots\text{O}}$ value has been found indicating their low stability.

Generally, the energy of the $\text{O}-\text{H}\dots\text{OCH}_3$ intramolecular hydrogen bond is increasing with increasing electron-donor ability of a substituent in *para* position to the phenolic hydroxyl group. By methylating one of the $\text{O}-\text{H}$ groups in 1,2-benzenediol the hydrogen bond energy of the corresponding 2-methoxyphenol increased by 0.4 kJ mol^{-1} in comparison with the value calculated for 1,2-benzenediol [15].

The formation of five-membered rings with hydrogen bonds in the compounds investigated is less favourable mainly because of the stereochemical hindrance (distance $\text{O}\dots\text{H} \cong 0.21 \text{ nm}$). Besides, the hydrogen of the $\text{O}-\text{H}$ group is not directed precisely to one of the free-electron pairs of the methoxyl group.

Fig. 1 shows the dependence of the total energy of 2-methoxy-4-methylphenol on the rotation of the phenolic hydroxyl group around the $\text{C}-\text{O}$ bond.

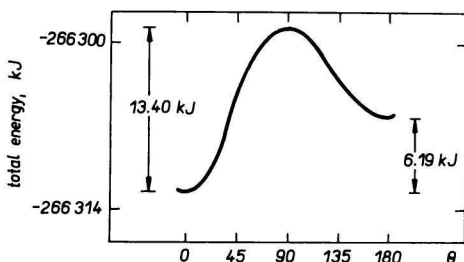
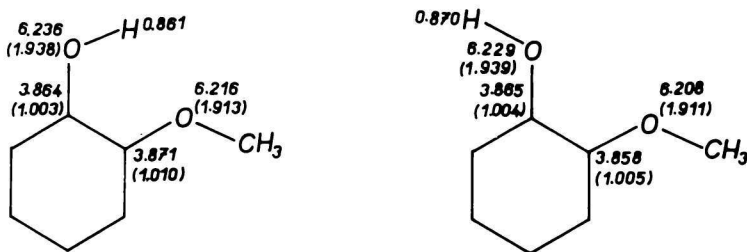


Fig. 1. Variation of the energy in the 2-methoxy-4-methylphenol as a function of the angle of rotation θ of the phenolic hydroxyl group.

The most stable is the conformer with an intramolecular hydrogen bond ($\theta = 0^\circ$). The height of the rotation barrier calculated as an energy difference of the two configurations $\theta = 0^\circ$ and $\theta = 90^\circ$ has been found equal to 13.4 kJ.

The study of the electron distribution in the 2-methoxyphenol *cis* and *trans* isomers has shown (Scheme 2) that the formation of the hydrogen bond causes a change in the σ -electron density in both oxygen atoms without any significant change in the π -electron density. The oxygen atom of the methoxyl group generally acts as a weak π acceptor and a good σ acceptor, whereas the phenolic hydroxyl oxygen atom acts as a weak π donor and a good σ acceptor. The electron density on the neighbouring carbon atoms remains practically unchanged. The hydrogen bond causes weakening of the electron density in the hydrogen atom.



Scheme 2

In Table 2 the total charges of atoms forming a hydrogen bond directly are given. According to listed values, the formation of a hydrogen bond causes an increase of the electron density on both oxygens with a simultaneous increase of the positive charge on hydrogen bonded by the H bond. A substitution in the *para* position to the phenolic hydroxyl changes primarily the electron density on oxygen of the phenolic hydroxyl group, while the electron density on oxygen of the methoxyl group remains practically constant.

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