A CNDO/S3′ study of lignin model quinone methides and related cations

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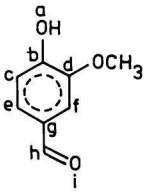
The electronic structure and chemical reactivity of some typical lignin model *p*-hydroxybenzaldehydes and *p*-quinone methides as well as products of their protonization have been studied by means of the semiempirical CNDO/S3′ method (corrected parameters were implemented). The results indicate a benzyl cation structure of protonated *p*-hydroxybenzaldehydes and *p*-quinone methides. Protonization drastically changes electron affinity and electronegativity of quinone methides, but not their hardness which is much lower than the hardness of related aldehydes. The calculations explain a pronounced regioselectivity of FMO-controlled reactions of quinone methides and corresponding cations.

The electronic structure of *p*-quinone methides is a subject of a paramount interest because of their role as important intermediates in lignification and delignification processes [1—3]. Theoretical research has led to definite conclusions concerning physicochemical properties and chemical reactivity of these compounds [4—11]. The properties of quinone methides as electrophiles are well known, and reactions of nucleophilic addition to these substrates as well as electrochemical reduction of quinone methides were analyzed more than once [8, 10, 12]. In wood chemistry, processes such as these take place mostly in alkaline or neutral media. In acidic media, quinone methides exist in their protonated forms as corresponding cations, the structure of the latter being not quite clear till now. It is evident that proton adds to the oxygen atom of a quinone methide, but widely used statements that a result of this process is a formation of the oxonium ion [2, 3, 13] seem to be doubtful. With the aim to determine the electronic structure of protonated quinone methides and to estimate the effect of transition from quinone methides or *p*-hydroxybenzaldehydes to related (and similar in both cases) cations we have implemented some semiempirical quantum-chemical calculations on the systems *I*—*VIII*.

Besides the cations *III* and *IV*, we have calculated two aldehydes *I* and *II* as well as a set of *p*-quinone methides *V*—*VIII* to obtain more opportunities for

I



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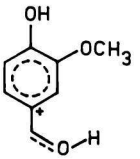

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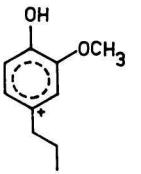

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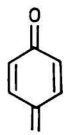

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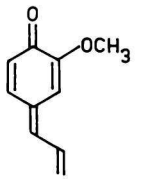
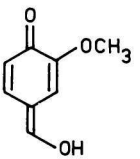
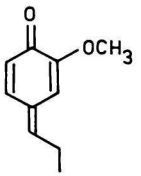


VI



VII



VIII

direct comparisons (in our previous calculations we used a bit different parametrization). The compound *VII* is the quinonoid isomer of the phenolic aldehyde *II*; a comparison between these two forms has been made earlier [7]. The cations *III* and *IV* should be regarded as protonated forms of neutral molecules *II* (or *VII*) and *VIII*, correspondingly.

Calculation method

For the calculations of the electronic structure and electron absorption spectra of the compounds investigated, the CNDO/S3′ method was applied. It differs from the standard CNDO/S3 method [14] only in a minor correction of some parameters (Table 1, see the discussion [10]). Wave functions and excited

Table 1

The CNDO/S3′ parameters (eV) [10, 13]

Atom	U_s	U_p	γ	β_s°	β_p°	ξ/a.u.
H	13.60	—	12.85	10	—	1.233
C	53.23	43.43	10.63	20	17	2, 1.625*
O	98.68	81.66	13.10	31	26	2.286

* Exponential parameters of 3- and 4-coordinated atoms, correspondingly.

state energies were calculated taking into account 80 single excited configurations, corresponding to singlet—singlet electron excitations from one of the ten highest occupied levels to one of the eight lowest unoccupied levels. The geometry parameters are listed in Table 2. The choice of geometry was discussed elsewhere [6—9]; for the cations, the standard parameters were chosen, the C-h—O-i bond length being an average between C=O and C—O bond lengths.

Table 2

The bond lengths (*l*/pm) accepted for the molecules of compounds *I—VIII*

Bond*	*I—IV*	*V—VIII*
a—b	136	123
b—c, b—d	140	148
c—e, d—f	140	136
e—g, f—g	140	146
g—h	151	138
h—i	123 (*I*, *II*), 129 (*III*), 151 (*IV*)	146 (*VI*), 136 (*VII*), 151 (*VIII*)
i—j	153 (*IV*)	136 (*VI*), 153 (*VIII*)

* C—H 110, O—H 95, O—Me 136.

Oscillator strengths f_{0n} were calculated according to the formula $f_{0n} = \frac{2}{3} E_n \mu_{0n}^2$ (E_n is the energy and μ_{0n} the dipole moment of the electron transition). The application of reactivity indices $F_A = |C_{\pi A,\mathrm{LUMO}}|^4$ has been discussed earlier [10]. Bond indices W_{AB} and atomic valencies V_A were calculated according to publications [15—18]. The ionization potential I and electron affinity A were determined according to the empirical formulae $I = -e - 0.80$ eV and $A = -e^* - 1.00$ eV (e, e^* are the HOMO and LUMO energies, correspondingly). These formulae enable to reproduce experimental values of I for benzene [14] and of A for 1,4-benzoquinone. The formulae for electronegativity χ and hardness η are: $\chi = 1/2(I + A)$ [19], $\eta = 1/2(I - A)$ [20] (the softness $s = 1/\eta$).

Results and discussion

The calculated electron absorption spectra are presented in Table 3; in some cases comparisons with experimental data can be made. Ionization potentials for the molecules of *I* and *II* (Table 4) demonstrate coincidence between the experimental and theoretical data. Regarding the spectral data as a test of calculations, we may conclude that the method applied should give reliable predictions of electronic structure of the molecules under consideration.

Table 3

The calculated wavelengths (λ/nm) and oscillator strengths f of the π-electron transitions $S_0 \rightarrow S_n$

Compound	λ_{calc}	λ_{exp}	f	λ_{calc}	λ_{exp}	f	λ_{calc}	λ_{exp}	f
I	279	285[a]	0.006	248	222[a]	0.410	215		0.274
II	292	312[b]	0.039	255	280[b]	0.283	222	231[b]	0.543
III	371		0.192	319		0.230	256		0.113
IV	394		0.148	334		0.320	255		0.083
V	289	281[c]	0.875	270		0.004	242		0.001
VI	352	336[d]	1.108	293		0.234	257		0.085
VII	332		0.704	280		0.127	259		0.141
VIII	325	321[e]	0.668	283	290	0.186	255		0.083

a) Ref. [21], *b*) [7], *c*) [22], *d*) [9], *e*) [10].

Table 4

The calculated first ionization potential (I/eV), electron affinity (A/eV), electronegativity (χ/eV), and hardness (η/eV)

Parameter	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
I	8.94[a]	8.54[b]	11.98	11.80	8.63	7.90	7.93	7.99
A	0.55	0.55	5.48	5.52	1.63	1.77	1.38	1.39
χ	4.75	4.55	8.73	8.66	5.14	4.84	4.66	4.69
η	4.20	4.00	3.25	3.14	3.51	3.07	3.28	3.30

a) The experimental value 8.92, *b*) 8.51 [23].

There are characteristic general differences between the lignin model electrophiles investigated (Table 4). At first we may note that substituent effects on the electronic structure (ring methoxy group, α-ethyl, α-ethenyl, and α-hydroxy groups) seem to be logical and are in concordance with our conclusions made previously [7—10], so there is no reason to reproduce here all explanations. It is interesting that there are no serious differences between the influence of α-ethyl and α-hydroxy group. As to the neutral lignin, the calculations demonstrate that usually quinone methide subunits have lower ionization potentials and hardness and higher electron affinity than α-carbonyl subunits. *p*-Quinone methides are very soft electrophiles. Consequently, these compounds are inclined to reactions with soft nucleophiles, the regioselectivity of these reactions being governed by AO contributions to LUMO. The cations have much higher ionization potential, electron affinity and electronegativity than the parent quinone methides and aldehydes (compare *II*, *VII* and *III*; *VIII* and *IV*). On the other hand, cations are soft electrophiles such as parent quinone methides. Reactivity indices F_A characterize relative rate of a nucleophilic attack on different atoms of an electrophile. These indices are applicable to soft-soft interactions only. The calculations demonstrate that it is possible for a nucleophile to attack different positions of an aldehyde molecule (in the case of the compounds *I* and *II* nonzero F_A values are for the atoms: C-b 0.05 for *I* and 0.04 for *II*, C-h 0.04, C-g 0.03, C-e, C-f, O-i 0.01—0.02). Regioselectivity of a nucleophilic addition to quinone methides should be more pronounced: F_A values for the C-h atom are 0.10 (*V*, *VII*), 0.09 (*VIII*), and 0.06 (*VI*), but only C-e (*VII*, *VIII*) and C-j (*VI*) have F_A values of 0.02, for another atoms $F_A = 0.01$. A difference in chemical reactivity of different atoms becomes much more pronounced in the case of the cations (F_A value of C-h atom is 0.33 for *III* and 0.39 for *IV*): it is quite clear that the only path for a nucleophilic reaction is an addition to the C-h atom.

The exocyclic C-h atom also may be regarded as a centre of a positive charge of the cations. The data (Table 5) demonstrate that C-h atom of *p*-quinone

Table 5

Atomic charges (q_A/e) and populations of the $2p\pi$ orbitals (p)

Denotation of the atom	*I*		*II*		*III*		*IV*		*V*		*VI*		*VII*		*VIII*	
	q_A	p	q_A	p	q_A	p	q_A	p	q_A	p	q_A	p	q_A	p	q_A	p
a	−0.25	1.92	−0.25	1.93	−0.21	1.90	−0.21	1.90	−0.32	1.39	−0.31	1.38	−0.32	1.39	−0.31	1.38
b	+0.09	0.91	+0.08	0.97	+0.15	0.86	+0.15	0.84	+0.19	0.72	+0.21	0.73	+0.21	0.73	+0.21	0.73
c	−0.09	1.08	−0.08	1.06	−0.06	1.06	−0.07	1.07	−0.09	1.03	−0.09	1.06	−0.10	1.07	−0.10	1.07
d	−0.10	1.09	+0.05	1.02	+0.08	1.01	+0.07	1.02	−0.09	1.03	+0.07	0.95	+0.06	0.98	+0.07	0.96
e	−0.05	0.95	−0.07	0.99	−0.01	0.91	−0.01	0.89	−0.05	0.95	−0.04	0.93	−0.04	0.93	−0.04	0.92
f	−0.03	0.93	−0.07	1.00	−0.05	0.99	−0.05	0.97	−0.05	0.95	−0.11	1.09	−0.10	1.08	−0.12	1.09
g	−0.07	1.07	−0.06	1.05	−0.07	1.17	−0.07	1.14	−0.04	1.00	−0.04	1.00	−0.06	1.09	−0.06	1.04
h	+0.16	0.70	+0.16	0.70	+0.27	0.46	+0.17	0.34	−0.09	0.94	−0.06	0.96	+0.05	0.92	−0.05	0.92
i	−0.31	1.35	−0.31	1.35	−0.11	1.74	+0.01	1.01	—	—	−0.08	1.00	−0.24	1.91	−0.01	1.00
j	—	—	—	—	+0.24	—	−0.08	1.02	—	—	−0.12	0.99	+0.21	—	−0.09	1.00

methides (*V*, *VI*, *VIII*) bears a small negative charge being not an appropriate site for an attack by a charged particle in the case of charge-controlled reactions. Protonization leads to a decrease of a negative charge on the O-a atom and at the same time to the rise of a positive charge on the C-h atom. Charge distribution in that case resembles the distribution in aldehydes. Also there is a close similarity between protonated *p*-hydroxybenzaldehydes and *p*-quinone methides in their atomic charges. The centres of a positive charge are depicted on the formulae of cations *III* and *IV* according to the data of the calculations.

Table 6

Bond indices (W_{AB})

Bond	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
a—b	1.04	1.04	1.08	1.08	1.77	1.79	1.78	1.78
b—c	1.34	1.36	1.33	1.32	0.98	0.98	0.98	0.98
b—d	1.34	1.30	1.25	1.24	0.98	0.94	0.95	0.94
c—e	1.42	1.41	1.44	1.45	1.81	1.79	1.78	1.79
d—f	1.42	1.37	1.42	1.43	1.81	1.70	1.71	1.71
e—g	1.35	1.36	1.29	1.27	1.03	1.04	1.04	1.04
f—g	1.35	1.35	1.27	1.25	1.03	1.04	1.04	1.03
g—h	0.95	0.95	1.07	1.16	1.76	1.65	1.65	1.70
h—i	1.88	1.88	1.39	1.02	—	1.06	1.07	1.01
i—j	—	—	0.95	1.05	—	1.86	0.95	1.05

It should be concluded that the electronic structure of the cations related to *p*-hydroxybenzaldehydes and *p*-quinone methides corresponds to benzylic carbocations, but not oxonium ions with bond alteration in the ring (*cf.* [2, 3, 13]). Besides the data on atomic charges, the data on populations of $2p\pi$ orbitals (Table 5) lead to the same conclusion. It is obvious that a protonization is followed by a transformation of corresponding C=O double bond into an ordinary bond. The comparison of populations for the C-h atoms of the cations *III* and *IV* enables us to make also a conclusion about the delocalization of a lone pair of the atom O-i of the compound *III*. Bond indices (Table 6) of the cations demonstrate an alteration of bonds in the ring that is much less pronounced than in quinone methides and similar to this characteristic of aromatic aldehydes. The C-h—O-i bond index of the cation *III* also corresponds to a partial delocalization of a lone pair of the O-i atom, the bond C-h—O-i being not a real double bond yet. There are some very characteristic changes in the valencies of the atoms during protonization (Table 7): the C-h atoms become hypovalent (and O-i atom becomes hypervalent in the case of the transformation *II* → *III*).

Table 7

Valencies of the atoms (V_A)

Denotation of the atom	*I, II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
a	2.10	2.14	2.15	2.00	2.01	2.00	2.00
b	3.90	3.89	3.88	3.83	3.84	3.84	3.83
c	3.92	3.91	3.90	3.91	3.88	3.90	3.90
d	3.91	3.90	3.90	3.91	3.88	3.88	3.88
e	3.92	3.91	3.91	3.92	3.92	3.92	3.92
f	3.92	3.92	3.92	3.92	3.91	3.91	3.90
g	3.89	3.83	3.86	3.90	3.90	3.89	3.90
h	3.82	3.55	3.44	3.93	3.92	3.90	3.93
	2.01	2.39	3.95	—	3.93	2.14	3.98
j	—	0.94	3.98	—	3.94	0.96	3.99

The data presented enable us to conclude that the electronic structure of protonated *p*-hydroxybenzaldehydes and *p*-quinone methides should be represented by the formulae of corresponding benzyl (but not oxonium!) cations. These cations are extremely soft electrophiles inclined to highly regioselective reactions with soft nucleophiles with a preferred attack on the exocyclic C-h atom. In this aspect, chemical reactivity of these *p*-hydroxybenzyl cations is similar to chemical reactivity of the related quinone methides, the affinity to a nucleophile being higher and regioselectivity being more pronounced. The α-OH group has only a minor effect on the electronic structure features governing a chemical reactivity, therefore a reactivity of protonated *p*-hydroxybenzaldehydes and *p*-quinone methides is very similar.

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