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Skeleton Deformations and Electronic Structure of *p*-Quinonemethide

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The electronic structure of the lignin subunit *p*-quinonemethide (4-alkylidene-2,5-cyclohexadiene-1-one) was calculated by the CNDO/S3 method. The results indicate a quinoid structure for the ground state, the transformation into diradical being possible only by photoexcitation. There is no reason to ascribe zwitterionic structure to any *p*-quinonemethides. Chemical reactivity of *p*-quinonemethides and the effect of skeleton deformations on reactivity are analyzed in detail.

INTRODUCTION

The electronic structure of *p*-quinonemethides (4-alkylidene-2,5-cyclohexadiene-1-ones) is of interest because of their place in the chemistry of lignin[1,2] and sterically hindered phenols.[3] In spite of theoretical[4,5] and experimental[6] arguments in favour of the »classic« quinoid structure of these compounds in the ground state many assumptions may be found in literature that some thermal reactions proceed through *p*-quinonemethide intermediates in their diradical or zwitterionic forms, these assumptions being based on obsolete and probably erroneous data.[3] Therefore, we have examined theoretically in detail the electronic structure of *p*-quinonemethides and its dependence on molecular geometry. It should also be mentioned that the high chemical reactivity of the simplest compounds belonging to this series imposes limitations on experimental approaches.

RESULTS

CNDO/S3 calculations[7] have been performed for *p*-benzoquinone (*1*, test compound) and the simplest *p*-quinonemethide using geometry parameters corresponding to quinoid (*2*), planar zwitterionic (*3*), and zwitterionic with perpendicular orientation of benzenoid and methylene fragment (*4*) forms.

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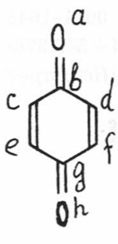
In addition, calculations have been performed for a more complicated compound resembling *p*-quinonemethide subunits of the lignin macromolecule more closely, in its quinoid (*5*) and planar zwitterionic (*6*) forms.



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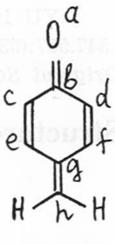

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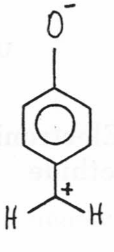

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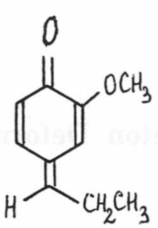

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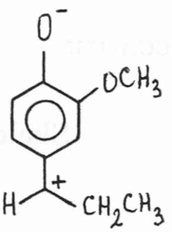

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The geometry parameters were chosen on the basis of experimental data for *p*-quinodimethane,[8] *p*-benzoquinone and related compounds.[9] The accepted bond lengths are listed in Table I, the C—H length being 110 pm. Valence angles of the quinonemethide framework in the zwitterionic forms were made equal to 120°, in the quinoid forms (*cbd*) to 118°, and (*egf*) to 122°. For details of the geometry accepted for *5* and *6* see ref.[5] Wave functions and excited states energies were calculated taking into account 80 single excited configurations, corresponding to singlet-singlet electron excitations from one of ten highest occupied levels to one of eight lowest unoccupied levels.

TABLE I

Bond Lengths Accepted for the Systems 1—6, *pm*

Bond	*1*	*2, 5*	*3, 4, 6*
ab	123	123	140
bc	148	148	140
ce	136	136	140
eg	148	146	140
gh	123	138	151

The results are presented in Tables II—VI*. The calculated (Table II) and experimental electron absorption spectra of *1* are in good agreement, corroborating the adequacy of parametrization used.[10] The CNDO/S3 method being parametrized for electron level calculations may give unsatisfactory results for other molecular properties. So, in order to check the reliability of qualitative conclusions, CNDO/2 calculations of bond indices, atomic charges, valence indices, and relative energies of different forms were performed, as well. It is to be mentioned that the CNDO/2 method was parametrized to reproduce the *ab initio* density matrix.

Bond indices (I_{AB} and I_{AB}', Table III) were calculated according to formulae:[11–13]

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* Bond indices I_{AB} and atomic charges q_A of *5* and *6* are listed in paper[5].

TABLE II

*Calculated Electron Transitions**

Compound or form	Excited state	Excitation energy, eV	Wave length, nm	Oscillator strength	Dominating electron transition
1	S_1	3.03	409	0	$\sigma_- \to \pi^*$
	S_2	3.67	338	0	$\sigma_- \to \pi^*$
	S_3	4.05	306	0	$\pi_- \to \pi_+^*$
	S_4	5.05	245	0.654	$\pi_+ \to \pi_+^*$
	S_5	5.77	215	0	$\sigma_- \to \pi_-^*$
2	T_1	1.46	850	0	$\pi_+ \to \pi_+^*$
	T_2	2.77	448	0	$\pi_- \to \pi_+^*$
	T_3	3.55	350	0	$\pi_- \to \pi_-^*$
	T_4	3.66	339	0	$\sigma_- \to \pi_+^*$
	S_1	3.66	339	0	$\sigma_- \to \pi_+^*$
	S_2	4.27	290	0.837	$\pi_+ \to \pi_+^*$
	S_3	4.48	277	0.007	$\pi_- \to \pi_+^*$
3	T_1	0.71	1750	0	$\pi_+ \to \pi_+^*$
	T_2	2.22	558	0	$\pi_- \to \pi_+^*$
	T_3	3.16	392	0	$\pi_- \to \pi_-^*$
	S_1	3.26	380	0.009	$\pi_- \to \pi_+^*$
	S_2	3.34	372	0.767	$\pi_+ \to {}_+\pi^*$
	S_3	3.53	352	0	$n_- \to \pi_+^*$
	T_4	3.53	352	0	$n_- \to \pi_+^*$
4	T_1	1.11	1118	0	$\pi_+ \to \surd\,^*$
	S_1	1.11	1118	0	$\pi_+ \to \surd\,^*$
	T_2	2.55	487	0	$\pi_- \to \surd\,^*$
	S_2	2.55	487	0	$\pi_- \to \surd\,^*$
5	T_1	1.42	871	0	$\pi \to \pi^*$
	T_2	2.77	447	0	$\pi \to \pi^*$
	T_3	3.59	446	0	$\pi \to \pi^*$
	S_1	3.82	325	0.677	$\pi \to \pi^*$
	S_2	3.84	323	0	$n \to \pi^*$
	T_4	3.84	323	0	$n \to \pi^*$
	S_3	4.31	288	0.177	$\pi \to \pi^*$
6	T_1	0.87	1426	0	$\pi \to \pi^*$
	T_2	2.30	538	0	$\pi \to \pi^*$
	S_1	2.94	422	0.405	$\pi \to \pi^*$
	T_3	3.28	379	0	$\pi \to \pi^*$
	S_2	3.28	378	0.386	$\pi \to \pi^*$
	S_3	3.68	337	0	$n \to \pi^*$
	T_4	3.68	337	0	$n \to \pi^*$

* MO classification for *1* corresponds to the symmetry point group of *p*-quinonemethide (C_{2v}). Oscillator strengths were calculated according to formula $f_{0n} = 2/3\, E_n\, \mu_{0n}^2$ (E_n-energy, and μ_{0n}-dipole moment of electron transition).

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} \left| (S^{1/2} P S^{1/2})_{ab} \right|^2;$$

$$I'_{AB} = \sum_{a \in A} \sum_{b \in B} (PS)_{ab}\, (PS)_{ba},$$

TABLE III

Bond Indices

Bond	I_{AB} (CNDO/2)				I_{AB}				I'_{AB}			
	1	*2*	*3*	*4*	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
ab	1.81	1.79	1.54	1.28	1.73	1.68	1.29	1.18	1.71	1.65	1.27	1.17
bc	1.06	1.06	1.18	1.26	0.96	0.99	1.16	1.25	0.92	0.95	1.12	1.21
ce	1.86	1.84	1.70	1.54	1.84	1.80	1.61	1.46	1.80	1.75	1.56	1.42
eg	1.06	1.07	1.16	1.24	0.96	1.03	1.15	1.28	0.92	0.99	1.11	1.24
gh	—	1.80	1.62	1.18	—	1.76	1.47	0.91	—	1.72	1.43	0.85

TABLE IV

Atomic Charges, a. u.

Atom	q_A (CNDO/2)				q_A				q'_A			
	1	*2*	*3*	*4*	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
a	—0.22	—0.26	—0.33	—0.52	—0.42	—0.46	—0.60	—0.66	—0.45	—0.49	—0.60	—0.66
b	+0.23	+0.24	+0.20	+0.19	+0.28	+0.27	+0.21	+0.16	+0.29	+0.28	+0.20	+0.16
c	—0.02	—0.06	—0.04	—0.08	—0.04	—0.08	—0.07	—0.09	—0.07	—0.10	—0.10	—0.11
e	—0.02	+0.03	+0.03	+0.07	—0.04	—0.04	—0.03	—0.06	—0.07	—0.08	—0.07	—0.09
g	+0.22	+0.03	+0.03	—0.10	+0.28	—0.04	—0.05	—0.13	+0.29	—0.04	—0.05	—0.11
h	—	—0.02	+0.01	+0.33	—	—0.08	+0.04	+0.26	—	—0.15	—0.06	+0.12
H^c	+0.02	+0.01	+0.02	+0.01	+0.11	+0.10	+0.10	+0.10	+0.15	+0.13	+0.14	+0.14
H^e	+0.02	+0.01	—0.00	—0.02	+0.11	+0.09	+0.08	+0.07	+0.15	+0.13	+0.12	+0.10
H^h	—	+0.02	+0.03	+0.07	—	+0.09	+0.12	+0.16	—	+0.12	+0.16	+0.21

TABLE V

Atomic Valence Indices

Atom	V_A (CNDO/2)				V_A				V'_A			
	1	*2*	*3*	*4*	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
a	2.04	2.03	1.91	1.51	1.93	1.88	1.51	1.37	1.91	1.87	1.50	1.37
b	3.97	3.97	3.97	3.92	3.77	3.78	3.78	3.84	3.71	3.72	3.73	3.78
c	3.99	3.99	3.99	3.98	3.91	3.91	3.91	3.90	3.82	3.82	3.83	3.8
e	3.99	3.99	3.99	3.98	3.91	3.92	3.92	3.91	3.82	3.84	3.84	3.83
g	3.97	4.00	4.00	3.86	3.77	3.90	3.88	3.71	3.71	3.84	3.81	3.6
h	—	3.99	3.97	3.35	—	3.93	3.74	2.94	—	3.84	3.65	2.83

where P is the density matrix, and S is the overlap matrix of all the atomic orbitals.

Atomic charges (q_A and q_A', Table IV) were calculated according to formulae:

$$q_A = Z_A - \sum_{a \in A} n_a, \quad n_a = (S^{1/2} P S^{1/2})_{aa};$$

$$q'_A = Z_A - \sum_{a \in A} n_a', \quad n_a' = (PS)_{aa},$$

where n_a and n_a' are the Löwdin and Mulliken a-th orbital electron populations of atom A, respectively; Z_A — core charge of the latter.[14,15]

TABLE VI

*HOMO and LUMO Energies, eV**

Energy level	*1*	*2*	*3*	*4*	*5*	*6*
2	—1.23 (π_-^*)	—0.77 (π_-^*)	—1.07 (π_-^*)	—1.41 (σ^*)	—0.56 (π^*)	—0.79 (π^*)
1	—3.57 (π_+^*)	—2.85 (π_+^*, 33% $2p_zC^h$)	—3.85 (π_+^*, 57% $2p_zC^h$)	—4.20 (v*, 94% $2p_yC^h$)	—2.65 (π^*, 32% $2p_zC^h$)	—3.52 (π^*, 56% $2p_zC^h$)
—1	—11.44 (π_-)	—9.71 (π_+)	—9.47 (π_+)	—8.21 (π_+, 34% $2p_zO$)	—9.09 (π)	—8.86 (π)
—2	—11.57 (π_+)	—10.93 (π_-)	—10.53 (π_-)	—10.21 (π_-)	—10.43 (π)	—10.02 (π)
—3	—11.57 (σ_-, 16% $2p_yO \times 2$)	—11.18 (σ_-, 38% $2p_yO$)	—11.12 (n_-, 72% $2p_yO$)	—10.21 (n_-, 78% $2p_yO$)	—11.16 (n)	—10.85 (n)

* MO classification for *1* corresponds to the C_{2v} symmetry group.
AO contributions (%) correspond to the Löwdin population analysis.

Atomic valence indices (V_A and V_A', Table V) were calculated according to formulae:[14,16]

$$V_A = \sum_{a \in A} (2\,n_a - n_a^2) - \sum_{a \neq a' \in A} \left| (S^{1/2} P S^{1/2})_{aa'} \right|^2;$$

$$V_A' = \sum_{a \in A} (2\,n_a' - n_a'^2) - \sum_{a \neq a' \in A} (PS)_{aa'} (PS)_{a'a}.$$

All the data obtained using different approaches are in good agreement, leading to the same general conclusions. It is essential to note the similarity of properties of the simplest *p*-quinonemethide and the substituted one, resembling the lignin subunits more closely. Therefore, we think that the conclusions based on the investigation of simple molecules are transferable to the natural polymer.

DISCUSSION

The data presented here enable us to analyze the problem of electronic structure of *p*-quinonemethides in different terms. Let us consider the possibility for *p*-quinonemethide to exist in zwitterionic form. The calculated electron transitions of quinoid and zwitterionic forms are quite different (Table II), being in agreement with experiment[6,17,18] only in the case of quinoid structures (*2*, *5*). Moreover, CNDO/2 calculation has predicted a considerable increase of energy as a result of the conversion of *2* to *3*. However, such energy estimations cannot help to decide whether the high energy form corresponds to a minimum on the potential energy surface. The data presented in Table III indicate that this is not the case. In fact, bond indices of form *3* calculated under the assumption of its benzenoid structure (*i. e.* equal bond lengths in the ring) alternate appreciably. Consequently, in-plane geometry deformation of *2*, making it more similar to the hypothetic zwitterion *3*, is not accompanied by the expected change in electronic structure. It is characteristic that atomic charges (Table IV) are also insensitive to this deformation, so formula *3* in principle does not reflect even the structure of related vibrational exicited states.

The analysis of atomic valence indices (Table V), being now a popular method to differentiate between »normal« molecules, diradicals and zwitterions,[19,20] leads us to the same conclusion. All the atoms of *2* have »normal« indices, undoubtedly indicating the quinoid structure; a transformation into *3* brings about only an insignicifant change in the valence index of atom O^a.

Thus, it may be supposed that no in-plane skeleton vibration of *p*-quinonemethides changes their »classic« quinoid structure. In spite of this, the twisting of the methylene »tail«, just as expected, results in a significant change of electronic structure. The calculation of the saddle point of twist transition *4* has predicted a decrease of ring bonds alternation (Table III), considerable polarization (Table IV), and obvious deviation of valence indices of the atoms O^a and C^h (Table V) from »normal« values (»subvalent«[20] atoms).

Consequently, *p*-quinonemethide has zwitterionic structure only near the saddle point of the twist transition. However, it is well known that torsion barriers are extremely high in the alkene series. The CNDO/2 calculation has resulted in 2.8 eV energy difference between *3* and *4*; experimental estimation of the alkene torsional barrier is about 2.5 eV.[21] In general, the electronic structure of such a reactive intermediate as *p*-quinonemethide is of interest primarily with respect to its reactivity. It is evident that the structure *4* corresponds to the high energy saddle point on the potential energy surface, and must not be considered as an intermediate (the latter corresponding to local minimum). This opinion is supported by high stereoselectivity of the reactions of nucleophilic addition to substituted *p*-quinonemethides,[22] the srereoselectivity being improbable if the reaction proceeds through a twisted form like *4*.

Consequently, there is no reason to connect the chemical reactivity of *p*-quinonemethides and the possibility of their existance in zwitterionic form. However, it must be pointed out that thermal excitation of in-plane and twist vibrations must raise their reactivity as substrates in nucleophilic addition reactions. The data listed in Table VI in all the cases show a significant energy difference between the LUMO π_+^* and other MO levels, and consequently high probability of *p*-quinonemethides reacting with mild nucleophiles to be orbitally controlled. In this case the reaction rate increases with decreasing LUMO energy. LUMO energy decreases during the transition of quinoid structure *2* to structures *3* and *4*. The regioselectivity of orbitally controlled reactions is determined by AO contributions in the frontier MO. Even in the classic quinoid structure *2* a contribution of AO (C^h) prevails, being the reason for the well known high regioselectivity of *p*-quinonemethide reactions.[23] It is of interest that skeleton deformations accompanied by increased reactivity (transformation of *2* into *3* or *4*) also result in a more pronounced LUMO localization on atom C^h, and consequently in higher regioselectivity, which is in contradiction with the widespread view on the »activity — selectivity« relationship. This feature is helpful in explaining the high regioselectivity of the reactions of nucleophilic addition to *p*-quinonemethides at elevated temperatures. A comparison of data obtained for simple *p*-quinonemethide and its derivative resembling typical lignin subunits more closely demonstrates no qualitative differences.

The probability for *p*-quinonemethides to exist in diradical form may be estimated by analysis of the data presented in Table II. According to Salem and Rowland[24], diradicals are characterized by singlet-triplet degeneracy. In principle, experiments (ESR, electron absorption spectra), as well as calculations, leave no doubt that in the ground state *p*-quinonemethides are closed-shell compounds. The calculated energies of singlet-triplet excitation in any case are too high to consider the corresponding structure as a diradical. Only some excited states may have diradical nature. Minimum energies of such states, characterized by singlet-triplet degeneracy in cases of *2*, *3*, *5*, and *6*, are unattainable by thermal excitation (Table II). The energy of such a state is low only in the case of *4* (1.11 eV) however, this structure corresponds to the high energy saddle point on the potential energy surface of *p*-quinonemethide. So, diradical forms of *p*-quinonemethides may be created only by photoexcitation, and may play an important role only in photochemical reaction mechanisms. The absence of diradical participation in thermal reactions of *p*-quinonemethides is also supported by the high stereoselectivity of such reactions.[19,23]

REFERENCES

1. J. Gierer, *Holzforschung,* **36** (1982) 43.
2. S. M. Shevchenko and I. P. Deineko, *Khimiya Drevesiny,* N 6 (1983) 3.
3. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, *Sterically Hindered Phenols* (in Russ.), Khimiya, Moscow 1972.
4. S. G. Semenov and S. M. Shevchenko, *Zhurn. Strukt. Khim.* **24** (N 5, 1983) 25.
5. S. G. Semenov and S. M. Shevchenko, *Khimya Drevesiny,* N 3 (1986) 61.
6. S. M. Shevchenko, S. G. Semenov, E. I. Evstigneev, V. A. Gindin, and A. V. Pranovich, *Zhurn. Org. Khim.* **23** (1987) 1891.
7. C. B. Duke, *Intern, J. Quantum Chem. Sympos.* N 13 (1979) 267.
8. P. G. Mahaffy, J. D. Wieser, and L. K. Montgomery, *J. Amer. Chem. Soc.* **99** (1977) 4514.
9. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, *Determination of the Geometrical Structure of Free Molecules,* Mir, Moscow 1983.
10. P. Jacques, J. Faure, O. Chalvet, and H. H. Jaffe, *J. Phys. Chem.* **85** (1981) 473.
11. K. B. Wiberg, *Tetrahedron,* **24** (1968) 1083.
12. S. G. Semenov, in:*Theory of Valence in Progress,* ed. V. I. Kuznetsov, Mir, Moscow 1980, p. 150.
13. M. Giambiagi, M. de Giambiagi, D. R. Grempel, C. D. Heymann, *J. Chim. Phys.* **72** (1975) 15.
14. I. S. Dmitriev and S. G. Semenov, *Quantum Chemistry — Past and Present* (in Russ.), Atomizdat, Moscow 1980.
15. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1833.
16. N. P. Borisova and S. G. Semenov, *Vestn. Leningrad. Univ. N* **16** (1973) 119.
17. L. Musil, M. Pisova, J. Pospišek, and M. Souček, *Coll. Czechosl. Chem. Commun.* **41** (1976) 2238.
18. F. Nakatsubo, *Wood Research,* N 68 (1981) 58.
19. K. Jug, *Tetrahedron Lett.* **26** (1985) 1437.
20. K. Jug, in: *Mathematics and Computational Concepts in Chemistry,* ed. N. Trinajstić, Wiley, New York e.a., 1986, p. 124.
21. V. G. Dashevsky, *Conformational Analysis of Organic Molecules* (in Russ.), Khimiya, Moscow 1982.
22. S. M. Shevchenko and M. A. Kuznetsov, *Zhurn. Org. Khim.* **22** (1986) 688.
23. S. M. Shevchenko, S. G. Semenov, and I. P. Deineko, *Khimiya Drevesiny,* N 6 (1984) 63.
24. L. Salem, C. Rowland, *Angew. Chem., Int. Ed. Engl.* **11** (1972) 92.

SAŽETAK

Deformacija skeleta i elektronska struktura *p*-kinonmetida

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Elektronska struktura podjedinice lignina, *p*-kinonmetida (4-alkiliden-2,5-ciklo-heksadien-1-on), izračunana je s pomoću CNDO/S3 metode. Rezultati upućuju na kinoidnu strukturu temeljnog stanja, pa je transformacija u diradikal moguća jedino fotoekscitacijom. Pokazuje se da ne postoji razlog za pripisivanje zwitterionske strukture bilo kojem *p*-kinonmetidu. U radu se potanko analizira kemijska reaktivnost *p*-kinonmetida kao i utjecaj deformacija skeleta.