5. Yu. R. Dzelme, Ya. Ya. Slezhis, Ya. A. Gravitis, Yu. K. Yakobson, and P. P. Érin'sh, Cell Chem. Technol., No. 13, 175 (1979).
6. M. Remko and J. Polcin, Z. Naturforsch., No. 33a, 59 (1978).
7. G. Kuennlenz and H. Jaffe, J. Chem. Phys., 58, No. 6, 2238 (1973).
8. G. A. Shchembelov, Yu. A. Ustynyuk, and V. M. Mamaev, Quantum-Chemical Methods of Calculating Molecules [in Russian], Moscow (1980), p. 256.
9. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, Determination of the Electronic Structures of Free Molecules [in Russian], Leningrad (1978), p. 224.
10. M. J. S. Dewar, J. Am. Chem. Soc., 99, No. 15, 4899 (1977).
11. V. M. Burlakov, É. I. Chupka, D. D. Chuvashev, and G. V. Ratovskii, Cell. Chem. Technol., No. 6, 651 (1986).
12. É. S. Stern and C. J. Timmons, Gillem and Stern's introduction to Electronic Absorption Spectra in Organic Chemistry, 3rd edn., Arnold (London (1970) [Russian translation, Moscow (1974), p. 295].
13. K. Kimura and S. Nagakura, Mol. Phys., 9, No. 2, 117 (1965).
14. D. A. Warwick and C. H. J. Wells, Spectrochim., Acta, 24A, 589 (1968).
15. T. Takemura and H. Baba, Bull. Chem. Soc. Jpn., 42, No. 10, 2756 (1969).
16. C. Steelink, Tetrahedron Lett., 57, 5041 (1969).
17. M. G. Kuz'min, Physical Chemistry, Modern Problems [in Russian], Moscow (1985), p. 264.

INTRAMOLECULAR INTERACTIONS AND NATURE OF THE LOWEST ELECTRONICALLY EXCITED STATES IN COMPOUNDS MODELING THE STRUCTURAL UNIT OF LIGNIN.

II. PHENOLATE ANIONS

V. M. Burlakov, É. I. Chupka,
D. D. Chuvashev, G. V. Ratovskii,
and L. B. Maksimova

UDC 547.992.3

Quantum-chemical calculations of the electronic structures of the phenolate ions of compounds modeling lignin in the ground and electronically excited states have been made by the CNDO/S method. The intramolecular electron donor-acceptor interactions in the phenolate anion on excitation and the nature of the lowest electronically excited states are discussed on the basis of the results obtained.

Under the conditions of alkaline methods of delignifying wood, structural fragments of the lignin macromolecule are present in the form of phenolate anions. The reactivities of the ionized fragments of lignin undergo substantial changes in comparison with their molecular forms [1]. Even greater changes in reactivity may be expected on the passage of the ionized lignin macromolecule into electronically excited states. The chemiluminescence accompanying the oxidation of lignin in an alkaline medium in the caustic soda and sulfate methods of delignification and in the bleaching of cellulose by hydrogen peroxide, sodium hypochlorite, and chlorine dioxide [2] indicate the occurrence of these processes via exothermic elementary stages with the appearance in the system of electronically excited states of the lignin chromophores. An experimental proof of the participation of excited lignin chromophores in redox reactions on its alkaline treatment is the change in the intensity of chemiluminescence with time as a function of parameters determining the rate of the reaction such as the initial concentration of lignin, the amount of oxidant, the pH of the medium, and the temperature.

We have previously [3] pointed out the necessity for studying the electronic structures and properties of electronically excited states of the chromophores of lignin for a deeper understanding of the mechanism of its transformations both in photochemical processes and in the processes taking place on the delignification of wood.

Siberian Scientific-Research Institute of Pulp and Board, Bratsk. A. A. Zhdanov Irkutsk State University. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 275-282, March-April, 1988. Original article submitted April 9, 1987; revision submitted June 30, 1987.

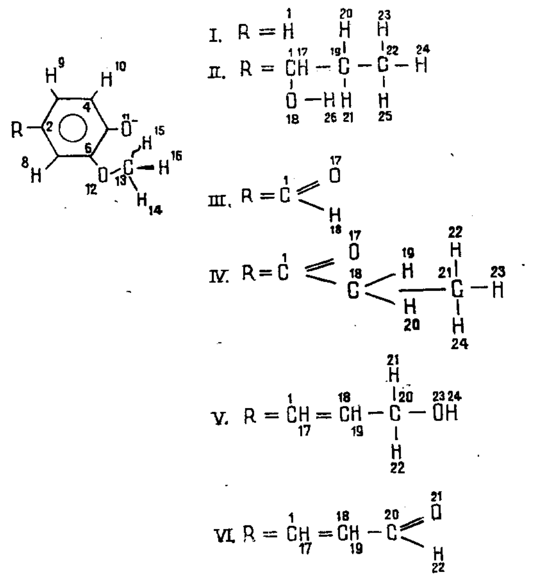
0009-3130/88/2402-0235$12.50

TABLE 1. Geometric Parameters of the Phenolate Anions Calculated

Compound	Numbers of the atoms forming the bonds	Bond length, Å	Angles, degrees
I	5—11	1,30	$C_4C_5O_{11}$=118.2
	6—12	1.38	$C_5C_6O_{12}$=127.7
	12—13	1,40	$C_6O_{12}C_{13}$=126,4
II—IV, VI	Geometries of the corresponding constituents similar to those in [4]		
V	18—20	1,515	$C_1C_{18}C_{20}$=122

In a preceding communication [4] we considered the characteristics of the ground and lowest electronically excited states of the molecules of compounds modeling lignin that had been obtained with the aid of quantum-chemical calculations. In the present paper we give the results of quantum-chemical calculations by the CNDO/S method of the electronic structures of the phenolate anions of compounds modeling lignin.

The method of calculation and the system of parameters taken were similar to those in [4]. Since the conformation with the minimum total energy for phenolate anions and molecular forms of compounds may differ, simultaneous optimization was carried out for the bonds and the valence and dihedral angles by the MNDO method.[5] on the basis of the phenolate anion of guaiacol. The optimum conformation found and the optimized values of the geometric parameters were used in the subsequent calculations. In the benzene ring the C$\overset{...}{—}$C bond was fixed at 1.398 Å, the C—H bond at 1.1 Å, and all the angles at 120°. The geometry of the other phenolate anions was obtained either by construction using the values of the bond lengths and angles in individual fragments from the literature [6] or by optimization by means of the MNDO method. The numbering of the atoms use in Table 1 was based on the guaiacyl fragment, which is present in all the phenolate anions investigated — those of guaiacol (I), α-guaiacylpropanol (II), vanillin (III), α-guaiacylpropanone (IV), coniferyl alcohol (V), and coniferyl aldehyde (VI):



Tables 2-6 contain the same characteristics of the electronically excited states of the phenolate anions as the corresponding Tables 2-6 in [4] for the molecular forms of the comounds.

In the present communication we consider the results of quantum-chemical calculations for the distribution of charges on the atoms of the phenolate anions (I-VI) the redistribution of electron density on their passage into electronically excited states, and the types and contributions of the determining contributions forming the excited states.

TABLE 2. Characteristics of Electronically Excited States of the Phenolate Ions of Guaiacol and of α-Guaiacylpropanol (I (II))

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4$ e^- (at. units)			
					Ar. ring	O^-	OCH_3	R
S_1 $\pi\pi^*$	3,757 (3,752)	0,154 (0,163)	92,2 (92,6)	1 → 1′ (1 → 1′)	—3014 (—2960)	2724 (2598)	289 (278)	— (84)
S_2 $n\pi^*$	3,957 (3,953)	0,000 (0,000)	67,6 (67,3)	2 → 2′ (2 → 2′)	—6558 (—6366)	6197 (6215)	359 (337)	— (−186)
S_3 $\pi\pi^*$	4,722 (4,682)	0.363 (0,377)	92,0 (92,0)	1 → 2′ (1 → 2′)	—2398 (—2335)	1990 (1904)	408 (400)	— (30)
T_1 $\pi\pi^*$	2,328 (2,272)	—	95,2 (95,8)	1 → 1′ (1 → 1′)	—3083 (—3095)	2806 (2743)	277 (260)	— (93)
T_2 $\pi\pi^*$	2,542 (2,458)	—	79,0 (81,4)	1 → 2′ (1 → 2′)	—2363 (—2338)	1926 (1885)	437 (410)	(42)
T_3 $\pi\pi^*$	3,196 (3,183)	— —	76,7 (78,2)	3 → 1′ (3 → 1′)	—1092 (—1030)	547 (502)	545 (534)	— (—5)

Type of MO		Energy of the MO, eV	Type of MO	ΣC^2, %			
LUMO	3′	6,150 (6,081)	π^*	91,80 (89,01)	7,55 (7,55)	0,61 (0,60)	— (2,80)
	2′	4,002 (3,886)	π^*	91,77 (91,25)	8,22 (8,02)	0,01 (0,01)	— (0,70)
	1′	3,360 (3,288)	π^*	98,47 (98,37)	0,04 (0,04)	1,47 (1,50)	— (0,07)
HOMO	1	—3,893 (—3,885)	π	66,58 (66,43)	29,30 (28,55)	4,10 (3,94)	— (1,06)
	2	—5,632 (—5,672)	n	26,05 (26,11)	70,38 (70,24)	3,57 (3,54)	— (0,09)
	3	—5,829 (—5,898)	π	92,37 (92,22)	0,77 (0,75)	6,89 (6,85)	— (0,16)

Let us consider the results presented in Tables 2-6. In the phenolate anions of guaiacol and of α-guaiacylpropanol (Table 2), the $S_0 \to S_1$ and $S_0 \to T_1$ electronic transitions belong to the ππ* type and correspond to excitation from HOMO 1 to the lowest vacant MO 1'; the HOMO comprises the benzene ring, the ionized oxygen (11) and, to a slight degree, the methoxy group. The LUMO is localized almost completely in the benzene ring, and therefore the transitions are accompanied by a considerable transfer of charge (~0.30 e⁻) to the benzene ring. The oscillator strength of the $S_0 \to S_1$ transition is substantially higher than for the corresponding transitions in the molecular forms of the compounds. On the ionization of the oxygen of the phenolic hydroxyl, there is a change in the type of the second singlet transition $S_0 \to S_2$, which in the phenolate ions (I) and (II) has a nπ* nature and takes place from HOMO 2, comprising the unshared electron pair (UEP) of oxygen 11 to the vacant π*-orbital 2', concentrated mainly in the benzene ring. The oscillator strength of this transition is equal to zero, but on its realization a considerable transfer of charge (~0.65 e⁻) to the benzene ring is predicted. The $S_0 \to S_3$ transition is a ππ* transition from HOMO 1 to π*-orbital 2', localized in the benzene ring. The transition has a high probability and is accompanied by the transfer of charge (~0.24 e⁻) to the benzene ring. With respect to the contribution of the determining configurations, to type, and to donor-acceptor interaction, the $S_0 \to T_2$ transition is analogous to it. The $S_0 \to T_3$ transition is practically localized in the benzene ring. In comparison with (I), in the phenolate anion of (II) the AOs of the alkyl substituent participates only very slightly both in the occupied and in the unoccupied MOs, and therefore it has practically no influence on the change in the donor-acceptor properties of compound (II).

The first singlet transitions $S_0 \to S_1$ and $S_0 \to S_2$ in the phenolate anions of vanillin and α-guaiacylpropanone are of the nπ* type and have zero oscillator strength (Table 3). For (III), MO 2, covering the UEPs of oxygen 11 and, partially, the benzene ring, and the vacant 1' MO, concentrated in the benzene ring and on the carbonyl group participate, in the $S_0 \to S_1$ transition. The transition is accompanied by a considerable transfer of charge (~0.60 e⁻)

TABLE 3. Characteristics of the Electronically Excited States of the Phenolate Anions of Vanillin and of α-Guaiacylpropanone [III, (IV)]

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\ \Delta q \cdot 10^4\ e^-$ (at. units)			
					Ar ring	O⁻	OCH_3	C=O
$S_1\ n\pi^*$	3,774 (3,768)	0,000 (0,000)	56,8 (54,7)	$2 \to 1'$ $(2 \to 1')$	—3804 (—2958)	6205 (5507)	408 (335)	—2808 (—2938)
$S_2\ n\pi^*$	3,850 (3,666)	0,000 (0,000)	50,0 (46,4)	$4 \to 1'$ $(4 \to 1')$	—2185 (—2135)	—276 (497)	86 (126)	2374 (568)
$S_3\ \pi\pi^*$	3,930 (3,949)	0,129 (0,175)	91,0 (77,0)	$1 \to 2'$ $(1 \to 2')$	—2845 (—2144)	2528 (2426)	327 (341)	—8 (—604)
$T_1\ \pi\pi^*$	2,493 (2,586)	— —	91,3 (60,8)	$1 \to 2'$ $(1 \to 2')$	—3054 (—1582)	2570 (2360)	323 (365)	160 (—1121)
$T_2\ \pi\pi^*$	2,553 (2,405)	— —	81,2 (59,0)	$1 \to 1'$ $(1 \to 1')$	100 (—8)	2152 (2252)	449 (403)	—2701 (—2590)
$T_3\ \pi\pi^*$	3,116 (3,115)	— —	79,8 (77,5)	$3 \to 2'$ $(3 \to 2')$	—754 (—841)	423 (516)	597 (557)	—267 (—232)

Serial number of the MO		Energy of the MO, ev	Type of MO	$\Sigma\ C^2$, %			
LUMO	2′	3,100 (3,063)	π^*	97,70 (97,17)	0,27 (0,06)	1,47 (1,40)	0,55 (1,33)
	1′	3,045 (2,683)	π^*	64,86 (49,92)	6,56 (5,63)	0,01 (0,11)	28,57 (43,24)
HOMO	1	—4,310 (—4,384)	π	63,94 (63,28)	28,14 (27 65)	4,41 (4,29)	3,51 (4,57)
	2	—6,064 (—6,151)	n	26,27 (27,03)	69,27 (68,58)	3,91 (4,30)	0,02 (0,21)
	3	—6,130 (—6,194)	π	91,94 (92,11)	0,78 (0,94)	7,08 (6,81)	0,19 (0,07)
	4	—7,348 (—7,513)	n	28,39 (27,30)	0,52 (1,36)	0,68 (0,70)	70,37 (57,70)

TABLE 4. Characteristics of the Electronically Excited States of the Phenolate Ion of Coniferyl Alcohol (V)

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4\ e^-$ (at. units)			
					Ar ring	O⁻	OCH_3	HC=CH
$S_1\ \pi\pi^*$	3,694	0,622	93,3	$1 \to 1'$	2616	2120	338	—5037
$S_2\ \pi\pi^*$	3,756	0,190	88,2	$1 \to 2'$	—2949	2266	244	384
$S_3\ n\pi^*$	3,784	0,000	42,9	$2 \to 1'$	—2945	6428	352	—3776
$T_1\ \pi\pi^*$	1,899	—	72,0	$1 \to 1'$	1849	1878	298	—4104
$T_2\ \pi\pi^*$	2,341	—	93,0	$1 \to 2'$	—3587	2353	212	949
$T_3\ \pi\pi^*$	2,839	—	56,1	$1 \to 3'$	—754	1539	329	—1272

Serial number of the MO		Energy of the MO, eV	Type of O	ΣC_2, %			
LUMO	3′	4,292	π^*	65,09	5,92	0,05	28,58
	2′	3,152	π^*	98,43	0,03	1,52	0,02
	1′	2,518	π^*	30,52	3,67	0,02	64,61
HOMO	1	—3,967	π^*	60,33	25,10	3,44	10,42
	2	—5,922	n	26,55	69,45	3,69	0,08

from the ionized oxygen to the benzene ring and to the carbonyl group. In (IV) this transition takes place from MO 4, covering mainly the carbonyl groups and the benzene ring to LUMO 1' and is accompanied by a partial transfer of charge (~0.55 e^-) from the UEP of the ionized oxygen. In the $S_0 \rightarrow S_2$ transition the configurations of the participating MOs change correspondingly for (III) and (IV). A similar situation exists with the $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions. The $S_0 \rightarrow T_1$ transition in (III) is determined by the particiation of HOMO 1, localized in the

TABLE 5. Characteristics of the Electronically Excited States of the Phenolate Ion of Coniferyl Aldehyde (VI)

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4$ e^-(at. units)				
					Ar ring	O$^-$	OCH$_3$	HC= =CH	C=O
S_1 $\pi\pi^*$	3,257	0,856	94,5	$1 \to 1'$	3756	2153	370	−3700	−2580
S_2 $n\pi^*$	3,614	0,000	40,7	$2 \to 1'$	−1372	6316	379	−2775	−2549
S_3 $n\pi^*$	3,750	0,000	45,5	$5 \to 1'$	−112	132	188	−1605	1397
T_1 $\pi\pi^*$	1,967	—	77,7	$1 \to 1'$	3234	2087	358	−2992	−2685
T_2 $\pi\pi^*$	2,438	—	87,4	$1 \to 2'$	−3272	2200	265	736	70
T_3 $\pi\pi^*$	3,051	—	37,2	$3 \to 2'$	93	1182	483	−429	−1330

Serial number of the MO		Energy of the MO, eV	Type of MO	ΣC^2, %				
LUMO	3′	3,356	π^*	42,80	4,13	0,00	6,92	46,13
	2′	2,825	π^*	98,39	0,03	1,53	0,03	0,00
	1′	1,597	π^*	19,89	3,05	0,05	48,53	28,24
HOMO	1	−4,421	π	59,42	24,97	3,77	9,57	2,26
	2	−6,372	n	27,22	68,60	3,98	0,17	0,07
	3	−6,420	π	91,14	0,42	7,51	0,78	0,15
	5	−8,499	n	21,66	1,85	1,39	20,27	54,82

TABLE 6. Charges on the Atoms ($q \cdot 10^4$ e^-) in the Ground and Lowest Excited Singlet and Triplet States of the Phenolate Anions (I-VI) (S_0, S_1, T_1)

Atoms	Compounds modeling the structural unit of lignin		
	I	II	III
2	−1484, 413, 677	−972, 958, 1239	−1063, −2288, 949
3	−487, −2464, −2524	−493, −2386, −2458	−336, −1821, −1967
4	−1277, −1854, −2001	−1240, −1875, 56	−1248, −1025, −1838
5	1985, 2232, 2304	1973, 2231, 2317	2108, 1178, 2254
6	348, −17, −121	351, −65, −184	409, 667, 0
7	−506, −2728, −2840	−610, −2813, −2952	−230, −1075, −2811
11	−6724, −4000, −3918	−6718, −4120, −3975	−6528, −323, −3958
12	−2876, −2608, −2621	−2876, −2620, −2638	−2854, −2626, −2559
13	453, 459, 460	455, 462, 462	461, 545, 470
>C = O			
C	—	—	2393, 573, 2332
O	—	—	−4096, −5101, −3875
18	—	−3280, −3255, −3253	—

	IV	V	VI
2	−1058, −1094, 487	−905, 850, 237	−942, 1114, 814
3	−114, −550, −1471	−430, −1286, −1023	−292, −885, −845
4	−1227, −995, 370	−1176, 106, 8	−1120, 193, 131
5	2132, 1084, 1595	2035, 1817, 1631	2138, 2051, 1939
6	407, 480, 1554	440, 2066, 1765	501, 2213, 2100
7	−404, −1556, −2067	−502, −1474, −1305	−409, −1052, 1029
11	−6483, −5986, −4231	−6598, −4478, −4720	−6420, −4267, −4333
12	−2871, −2792, −2502	−2859, −2542, −2589	−2848, −2505, −2520
13	460, 492, 471	457, 463, 467	461, 469, 470
>C = O			
C	2562, 996, 642	—	2232, 601, 448
O	−4878, −2744, −5548	—	−4603, −5551, −5504
1	—	−366, −3234, −2748	275, −3132, −2619
18	—	−1083, 3250, −2804	−1296, −1587, −1394
23	—	−3267, −3265, −3253	—

benzene ring and partially on the ionized oxygen, and of LUMO 2', which covers the benzene ring almost completely, and in (IV) by that of HOMO 1 and LUMO 1', while in the $S_0 \to T_2$ transition the numbers of the participating orbitals change correspondingly. In the first triplet transition there is a transfer of charge predominantly to the benzene ring, while in the second it is to the carbonyl group. The $S_0 \to S_3$ transition has a $\pi\pi^*$ nature and in the phenolate anions of both (III) and (IV) it takes place between one and the same MOs: occupied 1 and unoccupied 2'. It is accompanied by partial charge transfer (~0.21-0.28 e^-) to the benzene ring. The $S_0 \rightarrow T_3$ transition has a ππ* nature and is practically completely localized in the benzene ring and is therefore accompanied by only slight donor-acceptor interactions.

In the phenolate anion of coniferyl alcohol, the $S_0 \rightarrow S_1$ transition belongs to the ππ* type and has a high probability (Table 4). For it, as for the ππ* transition $S_0 \rightarrow T_1$ the main configuration is one corresponding to excitation from HOMO 1, which covers the benzene ring, oxygen 11, and the vinyl group, to LUMO 1', concentrated mainly on the vinyl group and the benzene ring. The S_1 and T_1 excited states are characterized by a considerable transfer of negative charge (~0.41-0.50 e^-) to the vinyl group. The first $S_0 \rightarrow S_2$ transition, similar in energy, has a lower probability. With respect to the nature and contributions of the determining configurations, and also to donor-acceptor interactions, it is similar to the $S_0 \rightarrow T_2$ transition. They take place from HOMO 1 to unoccupied MO 2', which is localized almost completely in the benzene ring. The transitions are accompanied by the transfer of charge (~0.29 and 0.36 e^-) to the benzene ring. The $S_0 \rightarrow S_3$ transition belongs to the nπ* type and is effected from the occupied MO 2, covering the ionized oxygen 11 and the benzene ring, to the unoccupied MO 1'. The probability of this transition is close to zero, but on its realization the transfer of a considerable charge (~0.64 e^-) from the oxygen of the phenolic hydroxyl to the benzene ring and the vinyl group is expected. The $S_0 \rightarrow T_3$ transition is not accompanied by a large charge transfer, but is close in its nature to the $S_0 \rightarrow T_1$ transition.

In the phenolate ion of coniferyl aldehyde (VI), the lowest, $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$, transitions belong to the ππ* type and are due to the participation of identical basic configurations (Table 5). They take place from HOMO 1, covering the benzene ring, the oxygen ion, and the vinyl fragment, to LUMO 1', delocalized over the benzene ring and the vinyl-carbonyl substituent. The transitions are accompanied by partial charge transfer from the benzene ring (~0.38 and 0.32 e^-) and from the ionized oxygen (~0.21 e^-) to the vinyl and carbonyl groups. The two S_2 and S_3 states, close in energy, belong to the nπ* type. In the first, the UEP of oxygen has the decisive contribution, and in the second it is the unshared electron pair of the oxygen of the carbonyl group, and therefore the transfer of charges in these states has different magnitudes and directions. For the $S_0 \rightarrow S_2$ transition the transfer is to the benzene ring (~0.14 e^-), the vinyl group (~0.28 e^-), and the carbonyl group (~0.26 e^-), while for the $S_0 \rightarrow S_3$ transition it is from the carbonyl to the vinyl group. The $S_0 \rightarrow T_2$ and $S_0 \rightarrow T_3$ triplet transitions belong to the ππ* type. The first of them takes place from HOMO 1 to the unoccupied MO 2' which is 98% localized in the benzene ring, and therefore charge transfer (~0.32 e^-) takes place to the benzene ring. The $S_0 \rightarrow T_3$ transition is concentrated in the benzene ring, and therefore it is accompanied by only a slight redistribution of the charges on the other fragments.

The figures given in Table 6 show that the maximum positive charge in the phenolate anions (I-VI) is concentrated on the ionized oxygen atom, and in passing to the excited S_1 and T_1 states the magnitude of the charge decreases. In the substituents of the benzene ring, all the oxygen atoms bear negative charges of different magnitudes both in the ground and in the excited states. According to the literature [7], because of a delocalization of electron density the negative charges in phenolate ions may be concentrated not only on the oxygen atoms but also in the ortho- or para- positions of the aromatic ring. The possibility of such a concentration of charge leads to the appearance of an ambident anion in which there are two nucleophilic reaction centers – the atom of ionized oxygen and the aromatic nucleus. Such a dual reactivity of phenolate anions is a common property of compounds with conjugated bonds [8 (sic)]. However, it must be mentioned that this property is characteristic for the ground thermodynamic state of phenolate anions and while on the whole, it is retained when they pass into excited states, the distribution of negative charges in the aromatic nucleus then changes substantially. Thus, while in the ground state the greatest electron density is concentrated on carbon atoms 2 and 4, present, respectively, in the para- and ortho- positions with respect to the ionized oxygen, on passing to excited states of the phenolate anions (I-VI) a migration of the nucleophilic centers into the benzene ring is observed. In compounds (I) and (II) the greatest negative charges are acquired by carbon atoms 3 and 7, in ions (IV) and (V) by carbon atom 7, and in (VI) the greatest negative charges in the singlet excited state are possessed by carbon atoms 2 and 7 and in the T_1 state by carbon atoms 7 and 3, respectively. It is difficult to detect a definite relationship between the particular excited state that a phenolate anion is present in and the direction of the redistribution of the nucloephilic centers in the benzene ring. However, it must be observed that the changes in the charges on the atoms of the aromatic nucleus are fairly considerable and involve a migration of reaction centers. Consequently, on passing to excited S_1 and T_1 states the reaction properties of the phenolate anion will be different from those in the ground state — the positions of the nucleophilic centers in the benzene change, which leads to a change of the direction of attack of electrophilic reagents.

SUMMARY

The passage of ionized lignin chromophores (phenolate anions) into electronically excited state is accompanied by the transfer of negative charge between the individual functional groups and by a redistribution of the electron density in the aromatic ring, which leads to a change in the donor-acceptor properties of the excited phenolate anions of compounds modeling the structural unit of lignin and, consequently, to a change on their reactivity in electrophilic and nucleophilic reactions as compared with their ground thermodynamic state.

LITERATURE CITED

1. N. N. Shorygina, V. M. Reznikov, and V. V. Elkin, The Reactivity of Lignin [in Russian], Moscow (1976), p. 368.
2. V. M. Burlakov, D. D. Chuvashev, and G. V. Ratovskii, Theoretical Problems of New Methods of Delignifying Wood [in Russian], Bratsk, 1985, p. 23.
3. V. M. Burlakov, É. I. Chupka, D. D. Chuvashev, and G. V. Ratovskii, Cellulose Chem. Technol., No. 6, 651 (1986).
4. V. M. Burlakov, É. I. Chupka, D. D. Chuvashev, G. V. Ratovskii, and L. B. Maksimova, Khim. Prir. Soedin., 265 (1988) [in this issue].
5. M. J. S. Dewar, J. Am. Chem. Soc., 99, No. 15, 4899 (1977).
6. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, Determination of the Electronic Structures of Free Molecules [in Russian], Leningrad (1978), p. 224.
7. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically Hindered Phenols [in Russian], Moscow (1972), p. 352.

---

^{1}H and ^{13}C NMR SPECTRA OF BIOLOGICALLY ACTIVE COMPOUNDS.

III. DIASTEREOMERS OF (±)-7-THIA- AND 13-THIA-16-ARYLOXY ANALOGS OF 11-DEOXYPROSTAGLANDINS OF THE E_1 SERIES

L. M. Khalluov, A. A. Panasenko
E. V. Vasil'eva, N. A. Danilova,
Ya. L. Vel'der, and G. A. Tolstikov

UDC 543.422.25+547.915

The structure has been established and stereochemical assignments have been made of two complete sets of diastereomers of the 7-thia and 13-thia analogs of 11-deoxyprostaglandins of the E_1 series by the ^{13}C NMR method. It is proposed to determine the diastereomeric effects of the ^{13}C NMR chemical shifts, which are differential parameters bearing information on the stereochemistry of the molecules. Diagnostic diastereomeric effects have been found for assigning stereoisomers with respect to the C-15-hydroxy group and also with respect to the C-8 and C-12 chiral centers of the cyclopentane ring.

The introduction of a sulfur atom into the α- or ω-chain of a prostaglandin molecule may lead to considerable changes in its biological activity [2]. It is also known that the properties of prostaglandins depend substantially on the mutual configurations of the chiral centers [3].

Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 282-287, March-April, 1988. Original article submitted June 3, 1987; revision submitted September 29, 1987.