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

I. MOLECULAR FORM

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Quantum-chemical calculations of the electronic structure of molecules of model compounds of lignin in the ground and electronically excited states have been made by the CNDO/S method. The paper gives results on the energies and strengths of the oscillators of the electronic transitions and on the type of excited singlet and triplet states, shows the main configurations of the HOMOs and LUMOs participating in the transitions and their energies and statistical weights, and gives the distribution of charges and their redistribution on the passage of the molecules from the ground into the excited states. Donor-acceptor interactions in the molecules under investigation are discussed on the basis of the results obtained.

Electronically excited states of lignin chromophors arise in the basic technological processes of the production of cellulose [1] and play a decisive role in the light-ageing of lignin-cellulosic materials [2].

The high reactivity of electronically excited states is due not only to the presence of excess energy but also to an electronic structure different from that in the ground state [3]. The change in the electronic structure of the molecules causes a change in bond lengths, polarizabilities, and dipole moments and a rise in both the electron-donating and the elec-

TABLE 1. Geometric Parameters of the Molecules Calculated

Molecules	Numbers of the atoms in the bonds	Bond length, Å	Angles, deg.
I–VII	5—11	1,364	
	11—12	0,950	$C_5O_{11}H_{12}=109,5$
	6—13	1,361	$C_6O_{13}C_{14}=120,0$
	13—14	1,423	
	14—15, 16. 17	1,106	
II	1—19	1,515	
	1—26	1,421	$C_{19}C_{22}H=109,5$
	19—22	1,532	
	26—27	0,950	$C_1C_{19}C_{22}=109,5$
III	1—2	1,475	
	1—18	1,212	$C_2C_1O_{18}=124,0$
	1—19	1,106	
IV	1—18	1,212	
	1—19	1,515	
	19—22	1,532	
V	1—2	1,480	
	1—19	1,345	
	1—18	1,090	
	19—20	1,090	
	19—21	1,510	
VI	19—21	1,484	
	21—22	1,217	$C_{19}C_{21}O_{22}=124,0$
VII	19—21	1,470	$C_{19}C_{21}O_{22}=124,0$
	21—22	1,202	$C_{19}C_{21}O_{23}=113,0$
	21—23	1,343	$C_{21}O_{23}H_{24}=106,0$
	23—24	0,975	

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

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4\ e^-$ (at. units)			
					Ar ring	OH	OCH_3	R
S_1 $\pi\pi^*$	4,501 (4,435)	0,023 (0,031)	64,0 (66.1)	$1 \to 1'$ $(1 \to 1')$	—929 (—965)	423 (427)	507 (434)	— (129)
S_2 $\pi\pi^*$	5,551 (5,471)	0,112 (0,135)	79,3 (81.5)	$1 \to 2'$ $(1 \to 2')$	—1019 (—1120)	451 (454)	567 (467)	— (135)
S_3 $\pi\pi^*$	6,346 (6,337)	1,083 (1,091)	62,2 (63,8)	$2 \to 2'$ $(2 \to 2')$	—600 (—602)	257 (197)	341 (323)	— (87)
T_1 $\pi\pi^*$	2,416 (2.492)	— —	55,4 (60,1)	$1 \to 2'$ $(1 \to 2')$	—1027 (—1053)	388 (375)	640 (482)	— (177)
T_2 $\pi\pi^*$	3,584 (3,513)	— —	82,1 (84,0)	$1 \to 1'$ $(1 \to 1')$	—1157 (—1229)	529 (562)	629 (499)	— (167)
T_3 $\pi\pi^*$	3,710 (3,686)	— —	58,4 (60.1)	$2 \to 1'$ $(2 \to 1')$	—679 (—686)	308 (256)	372 (345)	— (87)

Serial No. of the MO		Energy of the MO, eV	Type of MO	ΣC^2, %			
				Ar ring	OH	OCH_3	R
HOMO	2′	—0,435 (—0,369)	π^*	96,9 (96,3)	1,6 (1,7)	1,5 (1,3)	— (0,62)
	1′	—0.543 (—0,489)	π^*	98,7 (98 4)	0,5 (0,4)	0,8 (1,0)	— (0,20)
LUMO	1	—9,189 (—9,001)	π	85,0 (84,3)	6,8 (7,0)	8,2 (6,5)	— (2,15)
	2	—9,776 (—9,697)	π	95,7 (94,8)	2,0 (1,2)	2,3 (3,5)	— (0,62)

tron-accepting properties. Changes in the redox and acid-base properties and bond energies on the excitation of the molecules are extremely large, thanks to which the reactivity increases and it proves possible to perform reactions during the lifetime of the excited molecules. In view of this, the study of the electronic structure and nature of the excited states of model compounds is of considerable interest for understanding the mechanism of the transformations of lignin in processes accompanying the appearance and reactivation of excited states of its chromophores.

The considerable overlapping of the absorption and luminescence bands of the chromophores of lignin complicates the interpretation of the experimental spectra [4], while information on the electronic structure and charge distribution on the atoms can be obtained only by the use of quantum-chemical methods of calculation.

The calculation of the electronic structures of a number of lignin-modeling compounds by the PPP method in the π-electronic approximation [5] describes the nπ*-excited states insufficiently fully, while calculations by the CNDO/S method were made without taking into account the triplet states [6] that are the most reactive in chemical and photochemical processes. Furthermore, the differing geometric parameters used in the calculation do not permit a strict comparison within the framework of a single method of the change in the electronic structure of the lignin chromophors on the passage into excited states.

We have performed calculations of the electronic structure of the ground and lowest excited states of lignin-modeling compounds in molecular, ionic, and quinoid forms within the framework of a single method and a single system of parameters selected from literature information [7].

The present communication gives the results of quantum-chemical calculations of the characteristics of electronic transitions from the ground (S_0) to the lowest excited singlet (S_1, S_2, and S_3) and triplet (T_1, T_2, T_3) states of the molecules of model compounds of the structural unit of lignin: guaiacol (I), α-guaiacylpropanol (II), vanillin (III), α-guaiacylpropanone (IV), isoeugenol (V), coniferyl aldehyde (VI), and ferulic acid (VII).

For calculation we used the CNDO/S method included in the Viking group of quantum-chemical programs [8]. The geometric parameters of the molecules of the model compounds of lignin

TABLE 3. Characteristics of Electronically Excited States of the Vanillin and α-Guaiacylpropanone Molecules

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4 e^-$ (at. units)			
					Ar ring	OH	OCH_3	C=O
S_1 $n\pi^*$	3,435 (3,492)	0,000 (0,000)	50,5 (51,4)	$3 \to 1'$ $(3 \to 1')$	−3199 (−3672)	−74 (−93)	204 (114)	2240 (2363)
S_2 $\pi\pi^*$	4,402 (4,409)	0,039 (0,036)	33,0 (33,1)	$1 \to 1'$ $(1 \to 1')$	316 (197)	365 (365)	525 (518)	−1207) (−1046
S_3 $\pi\pi^*$	5,169 (5,205)	0,296 (0,281)	57,0 (55,0)	$1 \to 1'$ $(1 \to 1')$	434 (253)	404 (496)	665 (641)	−1504 (−1265)
T_1 $\pi\pi^*$	2,514 (2,535)	— —	37,4 (36,5)	$1 \to 1'$ $(1 \to 1')$	305 (164)	381 (370)	567 (541)	−1291 (−1098)
T_2 $n\pi^*$ (T_2 $\pi\pi^*$)	3,435 (3,491)	— —	50,5 (53,3)	$3 \to 1'$ $(1 \to 1')$	−3199 (−3672)	−74 (−93)	204 (114)	3069 (4)—27)
T_3 $\pi\pi^*$	3,462 (3,485)	— —	52,6 (51,4)	$1 \to 1'$ $(1 \to 1')$	110 (43)	397 (394)	515 (547)	−1087 (−967)

Serial No. of the MO		Energy of the MO, eV	Type of MO	ΣC^2, %			
	3′	0,609 (0,720)	π^*	43,0 (42,1)	0,9 (0,9)	0,5 (0,5)	55,6 (55,1)
HOMO	2′	−0,740 (−0,682)	π^*	97,6 (97,5)	0,0 (0,0)	2,0 (2,0)	0,4 (0,5)
	1′	−1,318 (−1,211)	π^*	73,3 (75,8)	1,8 (1,7)	0,1 (0,1)	24,8 (21,8)
	1	−9,442 (−9,385)	π	81,1 (81,4)	6,2 (6,2)	8,4 (8,2)	4,3 (4,1)
LUMO	2	−10,039 (−9,976)	π	93,7 (94,0)	2,2 (2,1)	2,1 (2,2)	2,0 (1,6)
	3	−11,280 (−10,798)	n	26,2 (23,9)	0,3 (0,2)	1,5 (0,9)	72,0 (60,8)

TABLE 4. Characteristics of Electronically Excited States of the Isoeugenol Molecule (V)

Excited states	E, eV	f	l^2, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4 e^-$ (at. units)				
					Ar ring	OH	OCH_3	HC==CH	CH_3
S_1 $\pi\pi^*$	4,229	0,043	59,6	$1 \to 2'$	−1400	288	284	698	129
S_2 $\pi\pi^*$	4,717	0,563	90,2	$1 \to 1'$	−233	351	226	−186	123
S_3 $\pi\pi^*$	5,862	0,737	64,1	$2 \to 1'$	487	74	356	−1244	28
T_1 $\pi\pi^*$	2,065	—	69,3	$1 \to 1'$	−217	336	326	−591	146
T_2 $\pi\pi^*$	2,849	—	37,7	$1 \to 3'$	−323	291	427	−559	159
T_3 $\pi\pi^*$	3,400	—	72,8	$1 \to 2'$	−2507	409	180	1727	190

Serial No. of the MO		Energy of the MO, eV	Type of MO	ΣC^2, %				
	3′	0,632	π^*	43,6	0,9	0,5	54,2	0,8
HOMO	2′	−0,463	π^*	97,9	0,0	1,8	0,3	0,0
	1′	−0,909	π^*	62,2	1,4	0,1	35,3	1,0
	1	−12,286	π	62,2	4,9	2,4	28,3	2,2
LUMO	2	−13,591	π	88,3	0,0	7,3	4,0	0,4
	3	−13,606	π	39,2	6,5	3,0	46,9	4,4

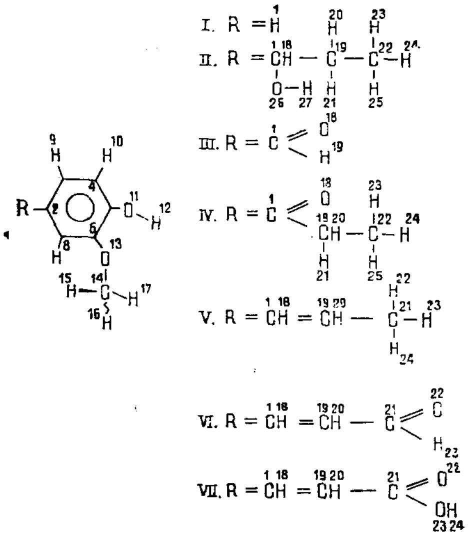
TABLE 5. Characteristics of Electronically Excited States of the Molecules of Coniferyl Aldehyde and of Ferulic Acid (VI (VII))

Excited states	E, eV	f	P, %	$n \to k'$	$\Sigma\Delta q \cdot 10^4\ e^-$ (at units)					
					Ar ring	OH_{phe}	OCH_3	HC=CH	C=O	OH_{carbox}
$S_1\ n\pi^*$	3,475	0,000	43,3	$4 \to 1'$	—3064	—61	63	—1421	4484	—
($S_1\ \pi\pi^*$)	(4,264)	(0,001)	(44,4)	($1 \to 2'$)	(—1877)	(—23)	(218)	(—1059)	(2535)	(205)
$S_2\ \pi\pi^*$	4,237	0,147	39,3	$1 \to 2'$	658	303	389	—629	—712	—
($S_2\ n\pi^*$)	(4,255)	(0,126)	(40,8)	($4 \to 1'$)	(536)	(301)	(370)	(—632)	(—541)	(—33)
$S_3\ \pi\pi^*$	4,510	0,631	72,4	$1 \to 1'$	1723	402	361	—1465	—1021	—
	(4,542)	(0,617)	(74,5)	($1 \to 1'$)	(1617)	(405)	(354)	(—1526)	(—802)	(—48)
$T_1\ \pi\pi^*$	2,166	—	66,9	$1 \to 1'$	1501	381	408	—1149	—1141	—
	(2,232)	—	(69,2)	($1 \to 1'$)	(1459)	(382)	(366)	—1239	(—916)	(—46)
$T_2\ \pi\pi^*$	2,996	—	33,0	$2 \to 2'$	—189	295	435	336	—876	—
	(3,089)	—	(36,1)	($2 \to 2'$)	(—308)	(286)	(370)	(362)	(—680)	(—30)
$T_3\ n\pi^*$	3,475	—	43,3	$4 \to 1'$	—3064	—61	63	—1421	4484	—
($T_3\ \pi\pi^*$)	(3,546)	—	(62,4)	($1 \to 2'$)	(—1092)	(367)	(307)	(682)	(—246)	(—19)

Serial No. of the MO		Energy of the MO, eV	Type of MO	$\Sigma\ C^2$, %					
		—0,784	π^*	97,9	0,0	1,8	0,2	0,1	—
HOMO	2′	(—0,746)		(97,9)	(0,0)	(1,8)	(0,2)	(0,1)	(0,0)
	1′	—1,730	π	41,0	1,0	0,1	41,9	16,2	—
		(—1,653)		(43,2)	(1,6)	(0,1)	(42,1)	(12,8)	(0,7)
	1	—9,055	π^*	65,9	5,4	3,6	21,5	3,7	—
		(—9,026)		67,0	(5,5)	(3,6)	(21,4)	(3,1)	(0,2)
LUMO	2	—9,946	π	88,8	0,1	6,4	4,0	0,7	—
		(—9,909)		(88,9)	(0,1)	(6,4)	(4,1)	(0,6)	(0,0)
	4	—11,345	n	6,2	0,1	0,5	17,3	75,7	
		—11,593)		(16,3)	(0,3)	(1,7)	(22,3)	(55,8)	(3,5)

(Table 1) were selected by extrapolating standard distances and angles between the structural groups of molecules close in composition [9]. The bond lengths and angles in the benzene ring were fixed: C$\overset{\cdot\cdot\cdot}{-}$C (1.398 Å), C–H (1.1 Å); all angles 120°C. For the guaiacol molecule, using the MNDO method [10] a simultaneous optimization was carried out for the bond lengths $O{-}C_{Phe}$, O–H, and $O{-}C_{methoxy}$ and of the angles CCO, COH, and COC, and these optimized values of the parameters of this fragment were used in the subsequent calculations.

The numbering of the atoms used in Tables 1 and 6 was based on the guaiacyl fragment, which is present in all the molecules investigated.



The characteristics of the electronic structures of the excited states were calculated by the method of configurational interactions, with consideration of 49 singly excited configurations corresponding to electronic transitions from the seven highest occupied molecular orbitals (HOMOs) to the seven lowest unoccupied orbitals (LUMOs). Tables 2-5 show the values of the energies and serial numbers of the HOMOs (n) and LUMOs (k'), the statistical weights of the configurations (1^2, %) making the main contributions to the structure of the wave function of the corresponding excited state, the total contributions of the atomic orbitals (AOs) and of individual fragments of the molecules (ΣC^2, %) to the MOs, the orbital type ($\pi\pi^*$ or $n\pi^*$) of the excited states, and the energies (E, eV) and strengths of the oscillators of the electronic transitions (f).

We have considered the spectral-luminescent properties of compounds (I-VII) and possible directions of the transfer of excitation energy between these chromophores of lignin in [11], and therefore in this paper we shall limit ourselves to a consideration of the results of a calculation of the electron-donor and electron-acceptor properties, the distributions of the charges on the atoms, and the types and degree of participation of the determining configurations in the formation of the excited states.

For more convenient consideration of the results, in Tables 2-5 the total change in charges (with allowance for the charges on the hydrogen atom in the individual fragments of the molecules ($\Sigma\Delta q\cdot 10^4$) are given. A minus sign in these Tables means a rise in the negative charge to the given value, and its absence, correspondingly, a decrease on transition into the excited S_i and T_i states. Table 6 gives the values of the charges ($q\cdot 10^4$) on the carbon and oxygen atoms in the S_0, S_1, and T_1 states.

Let us consider the results presented in Tables 2-6.

In guaiacol and α-guaiacylpropanol, the lowest – S_1, S_2, and S_3, and T_1, T_2, and T_3 – states belong to the $\pi\pi^*$ type. For the MOs describing these states it is characteristic that the vacant π^* orbitals are localized in the benzene ring and the occupied orbitals involve mainly the benzene ring and to a small degree the hydroxy and methoxy groups (Table 2). All the transitions are therefore accompanied by a partial transfer of the negative charge to the benzene ring (~0.06-0.12e^-). The oscillator strength of the $S_0 \rightarrow S_1$ transition, which is forbidden in benzene, increases under the influence of the substituting groups (OH and OCH_3) but remains small. The probability and energy of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions rise substantially, which is in harmony with result for phenol and anisole [12].

TABLE 6. Charge on the Atoms ($q \cdot 10^4$) in the Ground and Lowest Excited Singlet and Triplet States on the Molecules of (I-VII) ($S_0/S_1/T_1$)

Atoms	Compounds modeling the structural units of lignin						
	I	II	III	IV	V	VI	VII
2	−388 −257 709	109 394 −371	−70 −78 333	−101 −173 220	61 482 −220	−27 −643 951	−30 571 458
3	−364 −274 −669	−435 −351 −647	−12 −244 −171	−40 −239 −209	−484 −958 −179	−304 −701 −70	−308 −431 −71
4	−343 −1153 −280	−321 −1304 −321	−377 −894 −366	−380 −1027 −858	−343 −1256 −342	−333 −623 −165	−337 −636 −152
5	1243 1555 999	1161 1711 969	1452 −466 1573	1423 −532 1514	1174 1816 1107	1348 90 1790	1340 1864 1753
6	1198 1394 942	1190 1176 905	1152 930 1522	1140 852 1459	1204 597 1442	1208 949 1774	1206 1278 1814
7	−456 −1305 −420	−634 −1514 −530	−318 −677 −758	−374 −1096 −797	−553 −1021 −965	−421 −758 −859	−415 −650 −896
11	−2914 −2492 −2526	−2930 −2503 −2556	−2862 −2941 −2481	−2870 −2965 −2500	−2926 −2638 −2591	−2881 −2944 −2501	−2884 −2583 −2500
13	−2645 −2168 −2116	−2645 −2235 −2206	−2653 −2490 −2110	−2655 −2066 −2154	−2644 −2379 −2359	−2641 −2594 −2276	−2643 −2293 −2302
14	466 471 424	468 471 481	472 500 491	472 491 480	465 469 478	471 482 484	472 475 477
>C=O							
C	—	—	2470 1391 1471	2762 1930 1869	—	2428 1897 1594	—
O	—	—	−4101 −782 −4393	−4369 −1174 −4573	—	−4124 112 −4431	
1	—	—	—	—	−622 −299 −638	118 −1175 −1072	191 −687 −1046
19					−309 66 −884	−533 −832 −491	−526 −280 −528
26	—	−3252 −3225 −3217	—	—	—	—	—
21	—	—	—	—	—	—	3986 3568 3272
22	—	—	—	—	—	—	−4499 −4622 −4701
23	—	—	—	—	—	—	−2709 −2742 −2755

The energies of the first and second complex transitions in phenol and guaiacol calculated by the PPP method in [5] proved to be close, with $f_1 > f_2$, which contradicts our results and those obtained by Japanese workers [13]. The contribution of the AOs of the propanol fragment to the MOs participating in the transitions under discussion does not exceed 2%, and therefore the characteristics of the electronic structures of the molecules of (I) and (II) are analogous.

The facts given in Table 3 show that vanillin and α-guaiacylpropanone have very close characteristics of their electronically excited states.

The $S_0 \rightarrow S_1$ transition belongs to the nπ* type, has a zero oscillator strength, and, in the main, is determined by a configuration which corresponds to excitation from HOMO 3 covering mainly the unshared electron pair (UEP) of the oxygen of the carbonyl group and the aromatic ring to LUMO 1', having the main contributions of the AOs of the same fragments. On the realization of the transition, there is a considerable transfer of charge (0.32-0.37 e^-) to the benzene ring from the carbonyl group (~0.22-0.24 e^-). The $S_0 \rightarrow S_2$ transition belongs to the ππ* type and has a low probability. It takes place in the benzene ring with the participation of the other fragment of the molecules and is accompanied by a partial transfer of negative charge to the carbonyl group (~0.10-0.12 e^-). The $S_0 \rightarrow S_3$ transition possesses a considerably higher probability and is characterized by analogous configurations and by the participation of the AOs of the same fragments of the molecules as in the $S_0 \rightarrow S_2$ transition that is accompanied by somewhat greater transfer of charge (~0.13-0.15 e^-) to the carbonyl group. The $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_3$ transitions are close to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions in the nature, magnitude, and direction of the transfer of electron density. It is desirable to mention that the results of calculations on the nature of the S_1 and T_1 states of the (III) and (IV) molecules agree with conclusions based on experimental investigations of the UV absorption and luminescence spectra of related compounds [14, 15]. The $S_0 \rightarrow T_1$ transition in the molecule of (III) belongs to the nπ* type and is analogous in its characteristics to the $S_0 \rightarrow S_1$ transition.

In isoeugenol, all the transitions shown in Table 4 belong to the ππ* type.

The $S_0 \rightarrow S_1$ electronic transition is described by a configuration corresponding to excitation from HOMO 1, covering the benzene ring and the vinyl group to the vacant MO 2', delocalized over the π-system of the aromatic ring. The transition is accompanied by the passage of electron density (~0.14 e^-) to the benzene ring, but its oscillator strength is inconsiderable. The transition $S_0 \rightarrow S_1$ with a high probability is due to the excitation of an electron from HOMO 1 to LUMO 1', which are very close with respect to the total contributions of the AOs of the fragments. On excitation there is a small redistribution of electron density in the benzene ring and the vinyl fragment. The $S_0 \rightarrow S_3$ transition, having a high oscillator strength, takes place predominantly in the benzene ring and is accompanied by charge transfer (~0.12 e^-) to the vinyl group. The $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions are close to the $S_0 \rightarrow S_2$ transition with respect to the magnitude and direction of the transfer of charges, and the $S_0 \rightarrow T_3$ transition is similar to the $S_0 \rightarrow S_1$ transition.

The first singlet-singlet transition in coniferyl aldehyde is of the nπ* type and is described by a basic configuration corresponding to excitation from HOMO 4, including the UEP of the oxygen of the carbonyl group, the vinyl group, and the aromatic nucleus to the vacant π*-orbital 1' covering the same fragments of molecule (VI) (Table 5).

The $S_0 \rightarrow S_1$ transition is accompanied by a considerable transfer of electron density from the carbonyl group to the benzene ring (~0.31 e^-) and, in smaller degree, to the vinyl group (~0.14 e^-). In ferulic acid, this transition is of the ππ* type and is due to the excitation of an electron from occupied MO 1, localized mainly in the benzene ring and in the vinyl group, to vacant MO 2', concentrated almost completely in the benzene ring. The direction of the transfer of negative charges in excitation remains the same as in compound (VI) but their magnitude changes considerably. In the second singlet-singlet transition, $S_0 \rightarrow S_2$, the types and numbers of the MOs participating in the transition change to the opposite, respectively, for compounds (VI) and (VII). However, in comparison with the $S_0 \rightarrow S_1$ transition in this case charge transfer takes place from the guaiacyl fragment in the direction to the vinyl-carbonyl grouping. For compounds (VI) and (VII) the $S_0 \rightarrow S_3$ transitions have practically identical characteristics: close energies and oscillator strengths and types and numbers of the MOs participating in the transitions, values of the change in the charges on the fragments, and the direction of transfer. As in the $S_0 \rightarrow S_2$ transition, charge transfer takes place from the guaiacyl fragment to the vinyl and carbonyl groups. Thanks to p,π conjugation in the carbonyl group, charge transfer to the carbonyl in ferulic acid is smaller than in coniferyl aldehyde. In its characteristics, the $S_0 \rightarrow T_1$ ππ* transition is similar to the $S_0 \rightarrow S_3$ transition. For (VI) and (VII), the $S_0 \rightarrow T_2$ transition has the same ππ* nature, takes place mainly in the benzene ring, and is accompanied by a small transfer of negative charge to the ring and the carbonyl group from the other fragments. For compound (VI) the $S_0 \rightarrow T_3$ transition is completely identical in its characteristics with the $S_0 \rightarrow S_1$ transition, while for compound (VI) it differs mainly by the magnitude of the change in charge on the benzene ring and the opposite direction of transfer in the vinyl-carbonyl grouping.

The facts given in Table 6 show that a distribution of the charges on the atoms of the (I-VII) molecules in the electronically excited states are different from those in the ground states. The redistribution of electron density when the molecules pass into the excited S_i and T_i states is determined by intramolecular interactions which are due to the donor-acceptor properties of the groupings present in the molecules [3].

A considerable redistribution of electron density on excitation takes place on the carbon atoms of the benzene ring. In the S_1 state for all the molecules investigated the negative charge increases greatly on atoms 4 and 7 and their nucleophilic properties are thereby increased. The charges on carbon atoms 5 and 6, which are electrophilic sites in the ground state of the molecules, change differently for molecules of different types when they pass into excited states. For the (I) and (II) molecules in the S_1 state the positive charges on them rise, while in the T_1 state they fall. For the (III), (IV) and (VI) molecules, conversely, in the S_1 state the positive charge decreases and in the triplet state it increases. The negative charge on atom 3 for the (III)-(VII) molecules is the greatest in the S_1 state, and for the (I) and (II) molecules in the T_1 state. The sign and magnitude of the charge on carbon atom 2 of the benzene ring varies for different molecules and is probably determined by the donor-acceptor properties of the substituent R. The negative charges on the oxygen atoms of the phenolic hydroxy group (11) and of the methoxy group (13) for compounds (I-VII) amount to a considerable magnitude (~0.21-0.29 e^-) both in the ground and in the excited states. Large negative charges are concentrated on oxygen (26) of the α-hydroxy group of compound (II) and the oxygen (23) of the hydroxyl of the carboxy group of compound (VII), which scarcely change when the molecules pass into excited states.

The highest negative charges in the ground state (~0.41-0.44 e^-) are possessed by the oxygen atoms of the carbonyl groups of compounds (III), (IV), (VI), and (VII). The size of the negative charges on them rises still further when the molecules pass into the excited T_1 states, with a consequent increase in their nucleophilic properties which is also probably connected with the high reactivity of the carbonyl compounds in excited triplet states. Conversely, the carbon atoms attached to the oxygens of the carbonyl groups experience a deficiency of electron density and are electrophilic centers of these molecules. In the vinyl groups of compounds (V)-(VII), the carbon atoms in the ground state do not bear large charges, but on passing into the S_1 and T_1 states the negative charge on atom 1 of compounds (VI) and (VII) rises sharply.

Thus, the redistribution of electron density on the passage of molecules of compounds modeling the structural unit into excited singlet and triplet states is due to intramolecular interactions of electron-donating and electron-accepting substituents with the aromatic ring that are determined by the contributions of the AOs and MOs participating in the transition. In the lignin macromolecule, which has conjugated structural elements with electron-donating and electron-accepting substituents in the phenylpropane units, a considerable transfer of electron density through the conjugated system from the donors to the acceptors may be expected with the formation of intramolecular-transfer states and, in polar media, even of radical ions, a confirmation of which is the identification of semiquinoid radicals [16] in alkaline solutions of lignin.

SUMMARY

The characteristics of the electron systems of compounds modeling the structural unit of lignin obtained by the CNDO/S method and the intramolecular donor-acceptor interactions described on their basis agree well with general ideas of the redistribution of electron density in aromatic molecules on excitation [3, 17].

The results presented in this paper show that in the electronically excited states molecules of compounds modeling the structural unit of lignin not only possess an excess of energy but also have a distribution of the charges on the atoms different from that in the ground state and, consequently, also different reactivities of their functional groups.

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

II. PHENOLATE ANIONS

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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.

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