

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

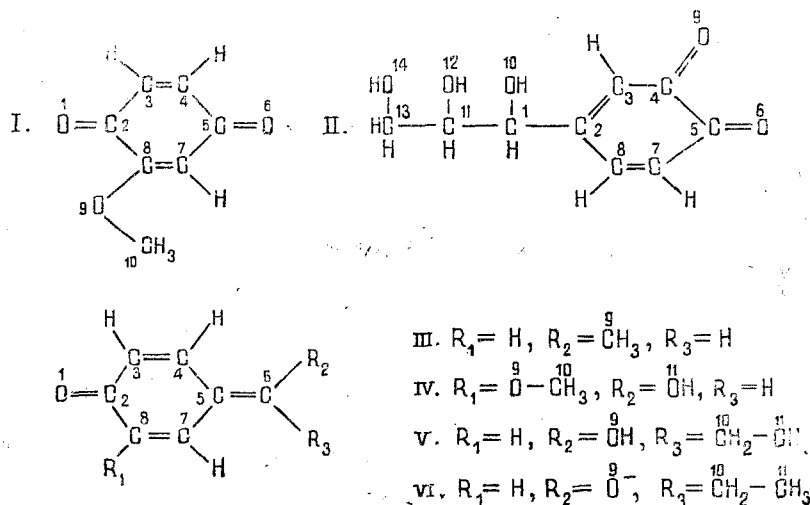
III. QUINONES AND QUINONE METHIDES

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An investigation has been made by the CNDO/S method with allowance for configurational interaction (the lowest six vacant and the highest eight occupied MMOs) of the electronic structure of a number of quinones and quinone methides forming component parts of the structural unit of lignin. The energies of the first singlet-singlet and singlet-triplet transitions and the redistribution of charges on excitation have been obtained, and the dependence of the energy of the transitions on the chromophores present in the molecule has been discussed. The change in the donor-acceptor properties of the fragments in excited states, leading to a change in the pathways in nucleophilic and electrophilic reactions has been shown.

The formation of quinones and quinone methides on the oxidation of lignin is assumed almost unanimously by the majority of research workers. Quinone and quinone methides [1] are highly reactive compounds and, therefore, their steady-state concentrations in solution cannot be in any way appreciable. However, it is just this circumstance that predetermines their fundamental role in reactions leading to an increase in the MM of lignin in autocatalytic processes. Particularly important is the fact that quinones and quinone methides have the longest-wave absorption ($\lambda \sim 420-435$ nm). This determines the flow of the energy of electronic excitation to them (for example, on oxidation), accompanied by the passage of the molecules into the triplet state and by chemiluminescence. The triplet states of quinones and quinone methides are the longest-lived and possess the highest reactivity, which greatly complicates their direct experimental investigation. In view of the diversity of the fragments composing lignin, considerable interest is presented in a determination of the degree to which individual model quinone methides agree or differ in their ground, singlet, and triplet states.



The model compounds calculated by the CNDO/S method.

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TABLE 1. Geometric Parameters Used in the Calculations

| Compound | Numbers of the atoms forming the bonds | Bond length, Å | Angle, deg |
|----------|----------------------------------------|----------------|---------------------------|
| I | 1-2, 5-6 | 1,225 | C7C8O9=126 C8O9C10=124 |
| | 2-3, 4-5, 5-7, 2-8 | 1,481 | |
| | 3-4, 7-8 | 1,344 | |
| | 8-9 | 1,355 | |
| | 9-10 | 1,408 | |
| II | 1-2 | 1,51 | C5O6C9=125 |
| | 3-4 | 1,481 | |
| | 4-5 | 1,50 | |
| | 1-10, 11-12, 13-14 | 1,421 | |
| | 1-11 | 1,52 | |
| III | 11-13 | 1,53 | |
| | 5-6 | 1,354 | |
| IV | 6-9 | 1,510 | |
| | 6-9 | 1,355 | |
| V | 6-10 | 1,515 | |
| VI | 6-9 | 1,28 | |

All the angles not shown in the table are 120°; in the methyl group the CCH angle is 110°; the lengths of C-H bond at sp²-carbon is 1.09 Å and the angle 120°; at sp³-carbon the bond length is 1.06 Å and the angle is 109.6°. The lengths of an O-H bond is 0.945 Å, and the C-OH bond angle is 108°.

TABLE 2. Calculation of the Electronic Spectrum of para-Benzoquinone

| state | Calculation | | | Experiment | |
|----------------|--------------------------|-------|--------------------|--------------------------|------------|
| | ν , cm ⁻¹ | f | type of transition | ν , cm ⁻¹ | ϵ |
| S ₁ | 20500 | 0,000 | n, π^* | 21800 | 20 |
| S ₂ | 21400 | 0,000 | n, π^* | 23090 | 20 |
| S ₃ | 38100 | 0,000 | π, π^* | 36220 | 340 |
| S ₄ | 45100 | 0,833 | π, π^* | 41700 | 20000 |

TABLE 3. Characteristics of the Electronically Excited States of Compound (I)

| Excited states | E , eV | f | I^a , % | $n-h'$ | Changes in the charges on the fragments ($\Sigma \Delta q \cdot 10^4$ at. units) | | | | |
|-----------------------------|----------|-------|-----------|--------|-----------------------------------------------------------------------------------|-----------|-----------|-----------|---------|
| | | | | | $C_1=O_1$ | $C_4=C_3$ | $C_5=O_5$ | $C_7=C_8$ | OCH_3 |
| S ₁ n, π^* | 2,965 | 0,000 | 72,8 | 3-1' | -270 | -390 | 812 | -231 | 79 |
| S ₂ n, π^* | 3,060 | 0,000 | 67,1 | 4-1' | 255 | -780 | 697 | -327 | 152 |
| S ₃ π, π^* | 4,370 | 0,056 | 79,1 | 1-1' | -2161 | -984 | -1316 | 3439 | 1022 |
| T ₁ π, π^* | 2,268 | | 57,2 | 1-1' | -1451 | -1865 | 706 | 2911 | 1110 |
| T ₂ π, π^* | 2,543 | | 59,8 | 2-1' | -1053 | 3183 | 704 | -1555 | 129 |

| serial number of the MO | energy of the MO, eV | type of MO | contributions (%) of the fragments of the MO | | | | |
|-------------------------|----------------------|-------------|----------------------------------------------|-----------|-----------|-----------|---------|
| | | | $C_1=O_1$ | $C_4=C_3$ | $C_5=O_5$ | $C_7=C_8$ | OCH_3 |
| 1' | -2,66 | π^* | 27,99 | 25,90 | 23,46 | 21,02 | 1,62 |
| 1 | -10,55 | π | 4,44 | 1,89 | 9,56 | 69,47 | 14,64 |
| 2 | -11,15 | π | 11,49 | 75,17 | 12,02 | 0,34 | 0,10 |
| 3 | -11,36 | n, σ | 25,63 | 20,76 | 35,33 | 16,92 | 1,36 |
| 4 | -11,79 | n, σ | 37,20 | 11,25 | 34,62 | 13,97 | 2,95 |

In [2, 3], the results of an investigation of the electronic structures of molecular and phenolate-anionic forms in the ground and lowest singlet and triplet states were given. By the same methods (CNDO/S and MNDO) we have performed quantum-chemical calculations of

TABLE 4. Characteristics of the Electronically Excited States of Compound (II)

| Excited states | E, eV | f | I ² , % | n-k' | Changes in the charges on the fragments ($\Sigma\Delta q \cdot 10^4$ at. units) | | | | |
|----------------------|-------|-------|--------------------|------|----------------------------------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------------------------|
| | | | | | C ₂ =C ₃ | C ₄ =O ₆ | C ₅ =O ₈ | C ₇ =C ₈ | C ₉ O ₂ H ₇ |
| S ₁ n, π* | 2,389 | 0,000 | 76,7 | 2-1' | -1207 | 1638 | 689 | -1760 | 638 |
| S ₂ n, π* | 3,938 | 0,001 | 25,5 | 2-2' | -1237 | 92 | -267 | -1378 | 2791 |
| S ₃ π, π* | 4,146 | 0,153 | 97,2 | 1-1' | 2909 | -1301 | -2027 | -13 | 431 |
| T ₁ π, π* | 1,969 | | 79,0 | 1-1' | 2462 | -1352 | -1833 | 19 | 764 |
| T ₂ n, π* | 2,389 | | 76,7 | 2-1' | -1207 | 1638 | 689 | -1760 | 638 |

| serial number of MO | energy of the MO, eV | type of MO | contributions (%) of the fragments to the MO | | | | |
|---------------------|----------------------|------------|----------------------------------------------|-------|-------|-------|------|
| 2' | -0,40 | π* | 38,75 | 14,39 | 10,27 | 35,81 | 0,75 |
| 1' | -2,54 | π* | 23,64 | 21,56 | 24,93 | 29,34 | 0,50 |
| 1 | -10,03 | π | 53,60 | 7,96 | 4,04 | 29,42 | 4,96 |
| 2 | -10,78 | n, σ | 11,63 | 40,87 | 33,94 | 9,89 | 3,53 |

TABLE 5. Characteristics of the Electronically Excited States of Compound (III)

| serial number of MO | E, eV | f | I ² , % | n-k' | Changes in the charges on the fragments ($\Sigma\Delta q \cdot 10^4$ at. units) | | | | |
|----------------------|-------|-------|--------------------|------|----------------------------------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------|-----------------|
| | | | | | C ₂ =O ₁ | C ₃ =C ₄ | C ₅ =C ₆ | C ₇ =C ₈ | CH ₃ |
| S ₁ n, π* | 3,073 | 0,000 | 67,2 | 3-1' | 3552 | 25 | -3649 | 133 | -62 |
| S ₂ π, π* | 4,470 | 1,102 | 93,8 | 1-1' | -627 | -194 | 493 | 151 | 177 |
| S ₃ π, π* | 4,975 | 0,023 | 97,9 | 2-1' | -2061 | 3122 | -3794 | 2869 | -137 |
| T ₁ π, π* | 1,563 | | 86,5 | 1-1' | -612 | -149 | 395 | 173 | 192 |
| T ₂ π, π* | 2,781 | | 51,4 | 2-1' | -797 | 651 | -448 | 527 | 66 |

| serial number of the MO | energy of the MO, eV | type of MO | contributions (%) of the fragments to the MO | | | | |
|-------------------------|----------------------|------------|----------------------------------------------|-------|-------|-------|------|
| 1' | -2,12 | π* | 21,00 | 19,91 | 38,97 | 18,68 | 1,42 |
| 1 | -9,09 | π | 14,59 | 17,47 | 44,45 | 20,17 | 3,32 |
| 2 | -10,65 | π | 0,01 | 51,89 | 0,02 | 48,03 | 0,03 |
| 3 | -10,73 | n, σ | 62,59 | 17,94 | 1,65 | 17,66 | 0,17 |

TABLE 6. Characteristics of the Electronically Excited States of Compound (IV)

| Excited states | E, eV | f | I ² , % | n-k' | Changes in the charges on the fragments ($\Sigma\Delta q \cdot 10^4$ at. units) | | | | | |
|--------------------|-------|-------|--------------------|------|----------------------------------------------------------------------------------|-----------------------------------|----------------------------------|------|----------------------------------|------------------|
| | | | | | C ₂ =O ₁ | HC ₃ =C ₄ H | C ₅ =C ₆ H | OH | C ₇ =C ₈ H | OCH ₃ |
| S ₁ nπ* | 3,141 | 0,000 | 65,6 | 3-1' | 3631 | -143 | -3593 | -198 | 124 | 179 |
| S ₂ ππ* | 4,273 | 0,908 | 90,1 | 1-1' | -940 | -670 | 19 | 236 | 829 | 456 |
| S ₃ ππ* | 4,892 | 0,155 | 92,9 | 2-1' | -1886 | 2937 | -3327 | -213 | 1809 | 681 |
| T ₁ ππ* | 1,516 | | 84,8 | 1-1' | -869 | -647 | 111 | 266 | 682 | 457 |
| T ₂ ππ* | 2,607 | | 47,1 | 2-1' | -762 | 298 | -186 | 124 | -31 | 557 |

| serial number of the MO | energy of the MO, eV | type of MO | contributions (%) of the fragments to the MO | | | | | |
|-------------------------|----------------------|------------|----------------------------------------------|-------|-------|------|-------|------|
| 1' | -2,01 | π* | 20,80 | 20,34 | 37,48 | 2,69 | 17,67 | 1,04 |
| 1 | -8,86 | π | 11,50 | 12,02 | 39,59 | 5,33 | 26,22 | 5,34 |
| 2 | -10,36 | π | 1,25 | 52,24 | 1,77 | 0,21 | 36,69 | 7,85 |
| 3 | -10,73 | n | 62,92 | 16,52 | 1,21 | 0,01 | 17,03 | 2,26 |

quinones and quinone methides forming component parts of the structural unit of lignin. The methods of assigning geometry were similar to those in [2, 3]. The bond lengths and angles used are given in Table 1. For a check, the electronic spectrum of para-benzoquinone was calculated (Table 2).

The first two singlet-singlet transitions take place from the σ-orbitals, which cover the unshared electron pairs (UEPs) of the oxygen atoms, to the vacant π*-orbitals. Their

TABLE 7. Characteristics of the Electronically Excited States of Compound (V)

| Excited states | E, eV | f | I ² , % | n → k' | Changes in the charges on the fragments (ΣΔq · 10 ⁴ at. units) | | | | | |
|-------------------------|----------------------|------------|----------------------------------------------|--------|---------------------------------------------------------------------------|-----------------------------------|--------------------------------|-----------------------------------|------|-------------------------------|
| | | | | | C ₆ =O ₁ | HC ₃ =C ₄ H | C ₅ =C ₆ | HC ₇ =C ₈ H | OH | C ₂ H ₅ |
| S ₁ nπ* | 3,117 | 0,007 | 60,4 | 2-1' | 3747 | 4 | -3644 | 113 | -198 | -27 |
| S ₂ ππ* | 4,330 | 1,093 | 95,0 | 1-1' | -395 | -270 | 108 | 292 | 160 | 97 |
| S ₃ ππ* | 5,148 | 0,057 | 48,4 | 3-1' | -159 | -158 | 141 | 33 | 91 | 51 |
| T ₁ ππ* | 1,705 | | 87,2 | 1-1' | -382 | -214 | 28 | 289 | 160 | 121 |
| T ₂ ππ* | 2,841 | | 43,5 | 3-1' | -480 | 140 | -75 | 264 | 81 | 68 |
| serial number of the MO | energy of the MO, eV | type of MO | contributions (%) of the fragments to the MO | | | | | | | |
| 1' | -1,90 | π* | 18,04 | 20,08 | 40,49 | 17,10 | 2,98 | 1,31 | | |
| 1 | -8,86 | π | 14,03 | 17,09 | 41,80 | 20,06 | 4,60 | 2,42 | | |
| 2 | -10,55 | n | 64,17 | 17,01 | 1,43 | 17,08 | 0,06 | 0,21 | | |
| 3 | -10,59 | π | 0,00 | 51,00 | 0,05 | 48,87 | 0,03 | 0,03 | | |

TABLE 8. Characteristics of the Electronically Excited States of Compound (VI)

| Excited states | E, eV | f | I ² , % | n → k' | Changes in the charges on the fragments (ΣΔq · 10 ⁴ at. units) | | | | | |
|-------------------------|----------------------|------------|----------------------------------------------|--------|---------------------------------------------------------------------------|-----------------------------------|--------------------------------|-----------------------------------|----------------|-------------------------------|
| | | | | | C ₂ =O ₁ | HC ₃ =C ₄ H | C ₅ =C ₆ | HC ₇ =C ₈ H | O ⁻ | C ₂ H ₅ |
| S ₁ nπ* | 3,575 | 0,000 | 35,1 | 4-1' | -237 | -1159 | -1943 | -318 | 2808 | 849 |
| S ₂ nπ* | 3,668 | 0,000 | 35,3 | 2-1' | 1638 | -836 | -2223 | -79 | 1060 | 442 |
| S ₃ ππ* | 4,144 | 0,902 | 97,7 | 1-1' | -870 | -891 | 1416 | 237 | 159 | -51 |
| T ₁ ππ* | 2,512 | | 91,3 | 1-1' | -858 | -801 | 1305 | 239 | 139 | -26 |
| T ₂ ππ* | 2,889 | | 82,2 | 1-2' | 903 | -2035 | 2824 | -2621 | 900 | 29 |
| serial number of the MO | energy of the MO, eV | type of MO | contributions (%) of the fragments to the MO | | | | | | | |
| 2' | 3,28 | π* | 0,38 | 45,04 | 0,21 | 54,25 | 0,08 | 0,03 | | |
| 1' | 2,60 | π* | 24,50 | 26,36 | 23,02 | 15,28 | 10,11 | 0,73 | | |
| 1 | -4,62 | π | 15,45 | 17,13 | 37,75 | 17,76 | 11,44 | 0,46 | | |
| 2 | -6,78 | n | 57,28 | 14,20 | 3,47 | 15,57 | 7,18 | 2,30 | | |
| 4 | -7,05 | n | 9,95 | 3,09 | 17,57 | 5,01 | 51,94 | 12,45 | | |

probability is therefore very low. The corresponding UV-absorption bands [4] have frequencies close to those calculated and are characterized by a very low intensity. The difference between the first two transitions is also well reproduced (0.146 eV being the experimental value and 0.114 eV the calculated value). The S₀ → T₁ transition is analogous to the S₀ → S₄ transition with respect to the determining configurations and the magnitude of the charge transfer.

Compound (I) has characteristics close to those of para-benzoquinone. The S₀ → S₁ and S₀ → S₂ transitions, also of the n, π* type, are made from MOs 3 and 4, comprising mainly the UEPs of the oxygen atoms in the carbonyl groups, to the π* orbital 1', and their energy has somewhat increased (Table 3).

The probability of the S₀ → S₃ transition corresponding to excitation from the highest occupied MO 1, comprising the C=C-O-Me fragment, to the lowest vacant MO, 1', has increased in comparison with para-benzoquinone and gives rise to a UV absorption band (ν = 29,200 cm⁻¹, ε = 1100) of low intensity [4]. On excitation, a transfer of electron density (~0.44 e⁻) from the vinyloxy group is predicted. The lowest singlet-triplet transition is close, with respect to the determining configurations and the magnitude and direction of charge transfer, to the S₀ → S₃ transition. The S₀ → T₂ transition, which is due to configurations with the participation of the MOs 1, 2, 1', and 2', also belongs to the π, π* type. The energy of the S₁ state has risen and that of the T₁ state has fallen in comparison with para-benzoquinone.

In compound (II), the S₀-S₁ and S₀-S₂ transitions belong to the n, π* type with a large participation of the UEPs of the oxygens of the carbonyl groups and of the C-O, C-C σ-bonds. Both are calculated with a close-to-zero oscillator strength and are accompanied by a partial transfer of electron density to vinyl groups (Table 4). The S₀-S₃ and S₀-T₁ transitions, of the π, π* type, are determined completely by excitation from the highest occupied MO, localized in the π-system of the vinyl groups, to the lowest vacant MO, which covers the car-

TABLE 9. Changes on the Atoms ($\Delta g \cdot 10^4 e^-$) in the Ground and Lowest Electronically Excited Singlet and Triplet (S_0, S_1, T_1) States of the Molecules (I-VI)

| Compound | State | Serial number of the atom | | | | | | | | | | | | | |
|----------|-------|---------------------------|------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|-----|-------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| I | S_0 | -3857 | 2912 | -66 | 58 | 2761 | -4113 | -539 | 1888 | -2372 | 500 | - | - | - | - |
| | S_1 | -3262 | 2047 | -492 | -344 | 2221 | -2761 | -552 | 1440 | -2362 | 543 | - | - | - | - |
| | T_1 | -4382 | 1986 | -932 | -941 | 1993 | -4051 | 1934 | 2356 | -1401 | 535 | - | - | - | - |
| II | S_0 | 1129 | 515 | -477 | 2853 | 2922 | -3650 | -228 | -130 | -3771 | -3127 | 1220 | -3174 | 782 | 3211 |
| | S_1 | 1379 | -458 | -870 | 3069 | 2893 | -2931 | -993 | -1358 | -2303 | -3036 | 1292 | -3108 | 825 | -3180 |
| | T_1 | 1311 | 871 | 1628 | 1899 | 1820 | -4441 | 344 | -689 | -4129 | -3025 | 1445 | -3094 | 880 | -3196 |
| III | S_0 | -4522 | 2760 | -214 | -228 | -48 | 121 | -191 | -265 | -539 | - | - | - | - | - |
| | S_1 | -837 | 2617 | 171 | -996 | -979 | -2612 | -909 | 1861 | -512 | - | - | - | - | - |
| | T_1 | -4174 | 1799 | 342 | -933 | 973 | -515 | -821 | 538 | -433 | - | - | - | - | - |
| IV | S_0 | -4286 | 2806 | -489 | 50 | -212 | 1235 | -531 | 1449 | -2470 | 483 | - | - | - | - |
| | S_1 | -527 | 2678 | -133 | -823 | -1235 | -1349 | -1043 | 1879 | -2365 | 556 | - | - | - | - |
| | T_1 | -4219 | 1870 | -208 | -878 | 662 | 472 | -435 | 20.6 | -2049 | 497 | - | - | - | - |
| V | S_0 | -4503 | 2699 | -449 | -99 | -508 | 1861 | 18 | -530 | -2791 | -224 | - | - | - | - |
| | S_1 | -571 | 2514 | -83 | -845 | -1451 | -840 | -701 | -78 | -2491 | -189 | - | - | - | - |
| | T_1 | -4074 | 1888 | 115 | -877 | 944 | 435 | -676 | 383 | -2630 | -150 | - | - | - | - |
| VI | S_0 | -5419 | 2381 | -1268 | -109 | -1581 | 2465 | 99 | -1313 | -5637 | -306 | - | - | - | - |
| | S_1 | -4376 | 1100 | -1275 | -1410 | -1841 | 782 | -581 | -1083 | -2.29 | 513 | - | - | - | - |
| | T_1 | -5015 | 1119 | -71 | -2106 | 1392 | 797 | -1218 | 243 | -6458 | -288 | - | - | - | - |

bonyl and vinyl groups equally. Here, there is a transfer of electron density ($\sim 0.33 e^-$) to the carbonyl groups. The S_0 - T_2 transition is identical to the S_0 - S_1 transition. The S_1 and S_2 states in compounds (I) are formed by transitions from almost degenerate n levels (MOs 3 and 4) to one and the same vacant orbital. In compound (II), the UEPs of the carbonyl oxygens interact not only through the system of σ -bonds but also through space. This leads to a greater splitting of the n levels. The S_0 - S_1 and S_0 - S_2 transitions are therefore described basically by transitions from one and the same occupied MO to the MOs 1' and 2', differing considerably in energy, respectively. The difference in the energies of all the S_1 and S_2 states in compound (II) therefore increase considerably.

In compound (III), the S_0 - S_1 transition belongs to the n, π^* type, and its probability is close to zero. It is determined mainly by a configuration corresponding to excitation from MO 3, which covers the UEPs of the oxygen of the carbonyl group, to the lowest vacant MO, which covers all the fragments of the molecule fairly equally (Table 5). Here there is a considerable transfer of electron density ($\sim 0.36 e^-$) to the vinyl group, more remote from the carbonyl group. The $S_0 \rightarrow S_2$ transition, of the π, π^* type, which is due almost completely to excitation from the highest occupied to the lowest vacant MO possesses the highest oscillator strength. The two orbitals have close percentage contributions of the fragments, and, therefore, the transfer of charge is insignificant. The $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions have practically the same nature. The replacement of one carbonyl group by a vinyl group has led not only to a change in the nature of the highest occupied MO but also to a substantial (~ 1.0 eV) change in its energy. By comparison with compound (II), therefore, the energy of the first singlet-triplet transition has decreased considerably.

The lowest singlet-triplet and singlet-singlet transitions in compounds (IV) and (V) differ little from one another and are close to the corresponding transitions in compound (III) with respect to energy, nature, and electron-density transfer. The lowest singlet-singlet transition is due to excitation from the MO describing the UEP of the oxygen in the carbonyl group to vacant π^* orbitals. The calculated oscillator strength is close to zero, and the transfer of electron density from the carbonyl group is ($\sim 0.37 e^-$) (Tables 6 and 7). The S_0 - S_2 transition is determined almost completely by excitation from the highest occupied MO, covering the π system of conjugated double bonds, to the lowest vacant π^* orbital, which is close with respect to the contribution of the fragments. Consequently, charge transfer of excitation is insignificant. This transition possesses a high oscillator strength and determines the UV absorption of compounds (IV) and (V). The lowest singlet-triplet transition is similar to $S_0 \rightarrow S_2$ in nature and in participating configurations. The substituents at the conjugated double bonds (OCH₃, OH, Alk) participate little in the transitions under consideration and change only slightly the redistribution of electron density on excitation. Their influence is detected in some change in the energies of the transitions and their probabilities.

Table 8 gives information on an anion - compound (VI). The two close-lying $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions with zero probability are due to excitation from the occupied σ -orbitals 2 and 4, which correspond to the UEPs of the carbonyl oxygen atom and the isolated (9) oxygen atom, to the vacant π^* orbital 1' and 2'. Both transitions are accompanied by a transfer of electron density to the vinyl groups. The $S_0 \rightarrow S_3$ and $S_0 \rightarrow T_1$ transitions of the π, π^* type are described by practically a single configuration. This configuration corresponds to a transition from MO 1 to MO 1', which are close in percentage contributions of the AOs of the fragments and, therefore, the transfer of electron density is low.

On excitation of the compounds considered, both a considerable change in the magnitude of the charge on the atom or group as a whole and a change in the sign of the charge are observed, which may lead to the conversion of an electrophilic center into a nucleophilic center, and conversely. This appears particularly clearly for the carbon of the carbonyl group and in the vinyl groups. The polarity of the double bonds also changes considerably in magnitude and even in direction. Substituents at the conjugated double bonds (OH, OCH₃, Alk) change the charge distribution only slightly and practically retain their properties on passage to the lowest electronically excited states. Thus, the main changes in reactivity are due to the carbon atoms of the carbonyl and vinyl groups. Features of the change in donor-acceptor properties in the transition from the S_0 to the S_1 and T_1 states are given in Table 9.

CONCLUSIONS

The redistribution of electron density and also the change in the energies of the lowest singlet and triplet excited states in quinone and quinone methides depends to a considerable degree on the chromophores present in them. The substantial differences in these properties permit the assumption of dissimilar participations of the chromophores under consideration in the transformation processes of lignin. A change in the donor-acceptor properties of the fragments in excited states leads to a change in the pathways of electrophilic and nucleophilic reactions as compared with the ground state.

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COMPETITIVE BINDINGS OF HISTONES WITH DNA IN FORMATION OF PLANT NUCLEOHISTONES

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The nature of the relative affinity of histones for DNA has been studied with the aid of the electrophoretic analysis of the DNP complexes obtained by the addition of the total histone to a nuclear histone with a DNA:histone ratio of 1:1. It has been established that, on the addition of histone, complexes are formed the composition of which changes according to the degree of competition of the histone fractions. Some differences have been detected in the nature of the formation of nuclear histones of plant and animal origin due to features of the primary structure of the histones. The results obtained confirm a hypothesis put forward previously about the different strengths of the bonds of histones with DNA and the role of dissociation in the functioning of the genetic apparatus of the cells of higher organisms.

Advances of recent years in the study of the structural-functional state of chromatin have considerably promoted our understanding of the mechanisms of the functioning of the genetic apparatus of eukaryotes. General features of the nucleosomal organization of the chromosomal fibrils have become known [1, 2]. Information has been obtained on the nature of the packing of the nucleosomes into structures of higher order [3-5]. However, so far the role of certain histones and nonhistone proteins in the packing of DNA has been unclear. There is little information on the structural organization of the chromatin of higher plants [6].

The study of the main components of chromatin and the elucidation of the nature and specificity of their interaction form one of the key points in the solution to these questions.

In connection with a comparative study of the histones of the calf thymus and the cotton plant - objects remote from one another in the evolutionary series - and in order to deter-

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