LCAO MO investigations on lignin model compounds. IV.* CNDO/CI calculations of electronic spectra of oxybenzaldehyde type models

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CNDO method in Del Bene and Jaffé modification was used for investigation of the electronic spectra of benzaldehyde, 2-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, and 4-hydroxybenzaldehyde.

Метод МО ЛКАО ССП в приближении ППДП по Дел Бенэ и Джаффе был использован для изучения электронных спектров бензальдегида, 2-гидроксибензальдегида, 3-гидроксибензальдегида и 4-гидроксибензальдегида.

Within the systematic research of chromophore systems of lignified materials this series of papers is devoted to the study of the spectral properties of basic structures from which building units of lignin macromolecule are derived. Carbonyl conjugated with the benzene ring is one of very important parent chromophores in lignin [1—3].

The present paper is dealing with the theoretical calculation of electronic spectra of benzaldehyde, the simplest representative of such carbonyl, with a particular attention to the auxochromic influence of an OH substitution of the benzene ring.

The electronic spectra of benzaldehyde and its hydroxy-substituted derivatives were studied experimentally by many authors [4—7]. In theoretical interpretations of these spectra mostly PPP method [8] was used. However, application of this method is limited to the study of π electrons only. On the other hand, σ electrons play also an important role in electronic spectroscopy and therefore they cannot be ignored.

We applied the semiempirical CNDO/2 method in *Del Bene* and *Jaffé* modification [9] to the present theoretical study of electronic spectra of compounds of the

* For Part III see Ref. [27].

given type. This method proved to be most suitable for the study of transition energies and is now extensively used in investigations of electronic spectra [10—18].

Method of calculation and geometry

The original CNDO method in *Del Bene* and *Jaffé* modification with the original parametrization [9] has been used for calculations of the electronic structure and electronic spectra of the molecules under study. The computer programme from QCPE was applied on a Siemens 4004/150 computer in the Computer Centre of the Komenský University, Bratislava. In calculations of two-centre repulsion integrals we used *Pariser—Paar* (P—P) approximation [19] and *Mataga—Nishimoto* (M—N) [20] approximation. It was found that these approximations give substantially different results. In the configuration interaction we took into account in all cases 20 lowest monoexcited configurations.

The following experimental data for geometry were used: $(C—C)_{arom} = 0.139$ nm, C—C = = 0.141 nm, C=O = 0.121 nm, C—H = 0.109 nm, C—O = 0.136 nm, O—H = 0.104 nm, with valence angles set equal to 120°. All molecules were considered to be planar with C_s group of symmetry.

Results and discussion

Energies of lower excited singlet states calculated according to *Pariser—Paar* (P—P) [19] and *Mataga—Nishimoto* (M—N) [20] approximations as well as oscillator strengths (f) are summarized in Table 1 together with experimental data. The shown $\pi \rightarrow \pi^*$ transitions have all the A' symmetry; the transitions of $n \rightarrow \pi^*$ type with the A'' symmetry are symmetry forbidden. It can be seen that the P—P approximation gives somewhat better results for the $n \rightarrow \pi^*$ transition in benzaldehyde. Because the $\pi \rightarrow \pi^*$ transitions calculated by the M—N approximation are in a better agreement with the experimental spectra, results obtained by this approximation have been used in the further discussion.

Benzaldehyde

The first band in the experimental spectrum is of the $n \rightarrow \pi^*$ type and in a non-polar solvent (hexane) shows a vibrational structure. This band is accompanied by other two intense bands corresponding to the $\pi \rightarrow \pi^*$ transitions, which are in the near u.v. region followed by another intense $\pi \rightarrow \pi^*$ band.

By both approximations calculated energy (Table 1) of the first $n \rightarrow \pi^*$ transition is lower than the experimental value. This band is accompanied mainly by the following monoexcited configurations

Table 1

CNDO/CI calculated according to P—P and M—N approximation and observed spectral data of the studied compounds

Compound	P—P			M—N			Experiment[a]	
	Sym.	$\nu \cdot 10^{-3}$ cm^{-1}	f	Sym.	$\nu \cdot 10^{-3}$ cm^{-1}	f	$\nu \cdot 10^{-3}$ cm^{-1}	f
Benzaldehyde	A''	25.4	0.0	A''	23.7	0.0	26.9	5×10^{-4}
	A'	37.6	0.004	A'	37.2	0.003	35.4	0.026
	A'	40.8	0.027	A'	44.7	0.171	42.8	0.29
	A''	50.5	0.0	A''	47.6	0.0	—	—
	A'	52.7	0.505	A''	49.4	0.0	—	—
	A''	53.1	0.0	A'	52.1	0.351	51.2	0.45
3-Hydroxy-benzaldehyde	A''	25.4	0.0	A''	23.6	0.0	—	—
	A'	35.5	0.024	A'	35.0	0.023	32.2	0.05
	A'	39.2	0.021	A'	43.4	0.085	40.7	0.17
	A''	50.1	0.0	A''	47.2	0.0	—	—
	A'	50.6	0.563	A'	48.4	0.52	45.0	—
	A'	53.1	0.445	A''	50.0	0.0	—	—
2-Hydroxy-benzaldehyde (*cis*)	A''	25.8	0.0	A''	22.6	0.0	—	—
	A'	34.3	0.06	A'	33.8	0.055	30.6	0.08
	A'	38.9	0.002	A'	42.19	0.037	39.7	0.23
	A''	47.7	0.0	A''	43.8	0.0	—	—
	A''	49.6	0.0	A''	44.6	0.0	—	—
	A'	49.9	0.201	A'	48.6	0.398	46.4	—
2-Hydroxy-benzaldehyde (*trans*)	A''	25.8	0.0	A''	23.6	0.0	—	—
	A'	35.4	0.041	A'	34.8	0.034		
	A'	39.0	0.005	A'	42.5	0.055		
	A''	48.5	0.0	A''	45.4	0.0		
	A''	50.5	0.0	A''	46.7	0.0		
	A'	51.2	0.316	A'	49.7	0.635		
4-Hydroxy-benzaldehyde	A''	25.8	0.0	A''	23.5	0.0	—	—
	A'	36.3	0.007	A'	35.8	0.003	35.7	weak
	A'	38.8	0.079	A'	41.3	0.251	38.5	0.26
	A''	51.7	0.0	A''	48.2	0.0	—	—
	A'	51.8	0.398	A''	48.6	0.0	—	—
	A''	52.4	0.0	A'	50.4	0.365	46.0	—

a) Ref. [8].

$$^1A''\ (23.7\times10^3\ \mathrm{cm}^{-1});\ 55\%\ [18\rightarrow21],\ 36\%\ [18\rightarrow23]$$

The orbital 18 of the n type is localized mainly on C=O group (70%). The π^*

orbitals 21 and 23 are delocalized on the whole molecule (23 and 53% on C=O, respectively). As it follows from the atomic population analysis (Table 2), this transition is accompanied by the internal charge transfer from carbonyl oxygen to the aromatic ring. The following two $\pi \rightarrow \pi^*$ type transitions arise mainly from these monoexcited configurations

$$^1A'\ (37.2 \times 10^3\ \mathrm{cm}^{-1});\ 53\%\ [19 \rightarrow 21],\ 40\%\ [20 \rightarrow 22]$$

$$^1A'\ (44.7 \times 10^3\ \mathrm{cm}^{-1});\ 86\%\ [20 \rightarrow 21],\ 10\%\ [19 \rightarrow 22]$$

The π orbitals 19 and 20 are mostly delocalized on the whole ring, the orbital 22 is a ring localized π^* orbital (25% on each C (4, 5, 7, 8)). While the first $\pi \rightarrow \pi^*$ transition is accompanied by a change of the electron density on all atoms, the configuration 20, 21 with a charge transfer from the benzene ring to the carbonyl group (Table 2) is dominant in the second $\pi \rightarrow \pi^*$ transition. Besides the two $\sigma \rightarrow \pi^*$ transitions ($47.6 \times 10^3\ \mathrm{cm}^{-1}$ and $49.4 \times 10^3\ \mathrm{cm}^{-1}$) which were not observed in experimental spectrum, the third calculated short-wave $\pi \rightarrow \pi^*$ transition with the energy $52.1 \times 10^3\ \mathrm{cm}^{-1}$ consists mainly of 19, 21, further 20, 22 and 19, 22 monoexcited configurations and is accompanied by a significant charge transfer from the C=O group to the benzene ring (Table 2).

3-Hydroxybenzaldehyde

The experimental spectrum of 3-hydroxybenzaldehyde measured in cyclohexane shows three well resolved bands corresponding to the three lowest $\pi \rightarrow \pi^*$ transitions. These bands show a bathochromic shift caused by the introduced auxochromic substituent — hydroxyl group. Therefore the long-wave $n \rightarrow \pi^*$ transition, generally weak, is not resolved. The calculated transition with the energy $23.6 \times 10^3\ \mathrm{cm}^{-1}$ is accompanied by a charge transfer from the carbonyl group to the benzene ring with the dominant configurations 21, 24 and 21, 26. The following two calculated $\pi \rightarrow \pi^*$ type transitions consist mostly of these monoexcited configurations

$$^1A'\ (35.0 \times 10^3\ \mathrm{cm}^{-1});\quad 56\%\ [23 \rightarrow 24],\ 21\%\ [22 \rightarrow 25]$$

$$^1A'\ (43.4 \times 10^3\ \mathrm{cm}^{-1});\quad 46\%\ [22 \rightarrow 24],\ 31\%\ [23 \rightarrow 25]$$

In the ground state occupied π orbitals 22 and 23 are mostly localized on the benzene ring. The delocalized π^* orbital 24 contains an important contribution of AO's from the carbonyl group, while the π^* orbital 25 is ring localized with 25% on each C (4, 5, 7, 8). The atomic population analysis (Table 3) has shown that the first $\pi \rightarrow \pi^*$ transition is accompanied by a charge transfer from the substituents to the benzene ring, while the second $\pi \rightarrow \pi^*$ transition is, on the contrary, accompanied by a charge transfer from the region of the benzene ring to the C=O group.

Table 2

Calculated charge densities and dipole moments for the ground state and some lower excited singlet states of benzaldehyde

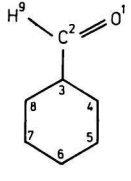
State	$\nu \cdot 10^{-3}$ cm^{-1}	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	H(9)	$\mu \cdot 10^{29}$ C.m.
A'	0	−0.320	0.203	0.008	0.015	−0.020	0.006	−0.022	0.0	0.032	1.12
A''	23.7	0.111	0.110	−0.026	−0.035	−0.071	−0.203	−0.061	−0.051	0.112	1.96
A'	37.2	−0.219	0.141	−0.070	0.0	0.080	−0.145	0.030	0.025	0.058	0.74
A'	44.7	−0.325	0.100	0.096	0.015	−0.024	0.029	0.049	−0.073	0.033	1.51
A'	52.1	0.326	0.258	0.018	−0.205	−0.160	−0.132	−0.194	−0.189	0.034	3.74

Table 3

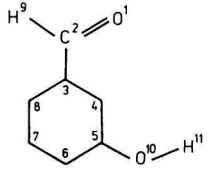
Calculated charge densities and dipole moments for the ground state and some lower excited singlet states of 3-hydroxybenzaldehyde

State	$\nu \cdot 10^{-3}$ cm^{-1}	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	H(9)	O(10)	H(11)	$\mu \cdot 10^{29}$ C.m.
A'	0	−0.316	0.203	0.005	−0.002	0.103	−0.004	−0.024	−0.013	0.034	−0.202	0.146	0.64
A''	23.6	−0.004	0.199	−0.035	−0.113	0.068	−0.093	−0.125	−0.054	0.088	−0.160	0.148	1.75
A'	35.0	−0.300	0.052	−0.052	−0.006	0.174	−0.055	−0.065	0.078	0.051	−0.093	0.146	0.92
A'	43.4	−0.356	0.096	0.002	0.119	0.080	−0.032	0.142	−0.099	0.034	−0.203	0.146	1.17
A'	48.4	0.124	−0.120	0.032	−0.011	0.031	−0.236	−0.132	0.062	0.131	−0.151	0.148	2.00

Formula referring to *Table 2*



Formula referring to *Table 3*



The third $\pi \rightarrow \pi^*$ transition in the experimental spectrum with the energy $45.0 \times \times 10^3$ cm^{-1} corresponds to a theoretically calculated transition with the energy 48.4×10^3 cm^{-1}. This transition with the dominant configurations 22, 24 and 23, 25 is accompanied by a significant charge transfer from carbonyl oxygen to the region of the benzene ring.

2-Hydroxybenzaldehyde

The experimental spectrum of 2-hydroxybenzaldehyde consists of three intense bands bathochromically shifted in comparison with the same bands of benzaldehyde. They belong to the $\pi \rightarrow \pi^*$ transitions.

The calculated forbidden $n \rightarrow \pi^*$ transition with the energy 22.6×10^3 cm^{-1} is in the experimental spectrum overlapped by the first $\pi \rightarrow \pi^*$ transition. It consists predominantly of the monoexcited configurations 22, 24 and 22, 26. The $n \rightarrow \pi^*$ transition is followed by two intense $\pi \rightarrow \pi^*$ transitions. The calculated energies of these transitions are somewhat higher than those found experimentally and consist mostly of the following monoexcited configurations

$$^1A'\ (33.8 \times 10^3\ \text{cm}^{-1});\quad 79\%\ [23 \rightarrow 24],\ 16\%\ [21 \rightarrow 25]$$

$$^1A'\ (42.2 \times 10^3\ \text{cm}^{-1});\quad 46\%\ [23 \rightarrow 25],\ 38\%\ [21 \rightarrow 24]$$

The occupied π orbitals 21 and 23 are ring localized; the orbital 23 contains also a non-negligible contribution of AO of hydroxyl oxygen. The π^* orbital 24 contains an important contribution of AO on the carbonyl group. The π^* orbital 25 is ring localized (25% on each C (4, 5, 7, 8)). The first $\pi \rightarrow \pi^*$ transition is accompanied by a charge transfer from the OH group to the region of the benzene ring (Table 4). The second $\pi \rightarrow \pi^*$ transition is accompanied mostly by a charge transfer from carbonyl and hydroxyl oxygen to the region of the benzene ring. The third short-wave experimental $\pi \rightarrow \pi^*$ transition with the energy 46.4×10^3 cm^{-1} is preceded in the theoretical spectrum by two forbidden $\sigma \rightarrow \pi^*$ transitions (43.8×10^3 cm^{-1} and 44.6×10^3 cm^{-1}) unobserved in the experimental spectrum. The calculated value 48.6×10^3 cm^{-1} is in a good agreement with the experiment. This transition consists of several monoexcited $\pi \rightarrow \pi^*$ configurations, with the highest statistical weights belonging to the configurations 23, 25 (31%), 21, 25 (29%), and 23, 26 (25%). The transition is accompanied by a charge transfer from the substituents to the region of the benzene ring.

The physicochemical properties of 2-hydroxybenzaldehyde in the ground state are significantly influenced by the formation of an intramolecular hydrogen bond, which is, as shown by experimental [21—23] and theoretical studies [24], very stable. In the u.v. spectrum the presence of the hydrogen bond is caused by a hypsochromic $n \rightarrow \pi^*$ and bathochromic $\pi \rightarrow \pi^*$ shift [25]. Therefore, we

calculated spectra of both isomers of 2-hydroxybenzaldehyde: *cis* with the intramolecular hydrogen bond, and *trans* without the intramolecular hydrogen bond. As it follows from Table 1 this simple model, however, does not describe well hypso- $n \rightarrow \pi^*$ shift (M—N calculation predicts, on the contrary, batho- $n \rightarrow \pi^*$ shift). On the other hand, bathochromic shift of the first $\pi \rightarrow \pi^*$ transition (1000 cm^{-1}) is qualitatively correctly described by this method. It is necessary to add that after the recent CNDO/CI calculations of *Simonetta et al.* [26] the alone effect of a hydrogen bond cannot explain the observed trends in u.v. spectra caused by interaction with a solvent.

4-Hydroxybenzaldehyde

In the experimental spectrum of 4-hydroxybenzaldehyde measured in a non-polar solvent (hexane) a new long-wave $\pi \rightarrow \pi^*$ transition appears, not present in the spectra of 2- and 3-hydroxybenzaldehydes, with both low energy (35.7×10^3 cm^{-1}) and intensity. The energy of this band is close to that of another intense $\pi \rightarrow \pi^*$ transition (38.5×10^3 cm^{-1}) so that the resulting long-wave band consists of two partially overlapped bands, the separation of which is difficult because of their different intensities. This band is followed in the short-wave region by another intense band corresponding to the $\pi \rightarrow \pi^*$ transition.

The first calculated transition in the theoretical spectrum is of the $n \rightarrow \pi^*$ type and was not experimentally found in a non-polar solvent. This band is accompanied predominantly by the monoexcited configurations 21, 24 (53%) and 21, 26 (36%). As it follows from the atomic population analysis (Table 5) this transition is accompanied by a significant charge transfer from carbonyl to the hydroxyl group. The following two $\pi \rightarrow \pi^*$ transitions consist mostly of these monoexcited configurations

$$^1A'\ (35.8 \times 10^3\ cm^{-1});\quad 59\%\ [23 \rightarrow 25],\ 37\%\ [22 \rightarrow 24]$$

$$^1A'\ (41.4 \times 10^3\ cm^{-1});\quad 92\%\ [23 \rightarrow 24],\ 6\%\ [22 \rightarrow 25]$$

In the ground state occupied π orbital 22 is ring localized (25% on each C (4, 5, 7, 8)); the π orbital 23 contains also a non-negligible AO contribution of both oxygens. The delocalized π^* orbital 24 contains a significant contribution of AO from the carbonyl group. The π^* orbital 25 is ring localized (25% on each C (4, 5, 7, 8)). The first $\pi \rightarrow \pi^*$ transition is accompanied by a significant charge transfer from the both substituents to the region of the benzene ring (Table 5). The second absorption band with a dominant weight of the monoexcited configuration 23, 24 is accompanied by a charge transfer from hydroxyl to the carbonyl group. The third short-wave $\pi \rightarrow \pi^*$ transition accompanied by a charge transfer (Table 5) from the

Table 4

Calculated charge densities and dipole moments for the ground state and some lower excited singlet states of 2-hydroxybenzaldehyde (*cis* isomer)

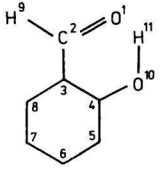
State	$\nu \cdot 10^{-3}$ cm^{-1}	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	H(9)	O(10)	H(11)	$\mu \cdot 10^{29}$ C.m.
A′	0	−0.309	0.216	−0.012	0.151	−0.025	−0.003	−0.025	−0.012	0.039	−0.272	0.188	1.27
A″	22.6	−0.008	0.179	−0.012	0.069	−0.071	−0.146	−0.036	−0.180	0.088	−0.150	0.192	1.87
A′	33.8	−0.297	0.046	0.019	0.169	0.071	−0.216	0.183	−0.172	0.054	−0.114	0.189	0.69
A′	42.2	0.046	−0.083	−0.003	0.183	−0.097	−0.174	−0.107	−0.005	0.108	−0.136	0.193	1.65
A′	48.6	−0.264	0.042	0.031	0.121	0.097	−0.155	0.072	−0.087	0.057	−0.196	0.190	0.90

Table 5

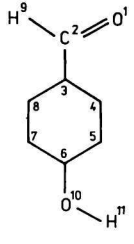
Calculated charge densities and dipole moments for the ground state and some lower excited singlet states of 4-hydroxybenzaldehyde

State	$\nu \cdot 10^{-3}$ cm^{-1}	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	H(9)	O(10)	H(11)	$\mu \cdot 10^{29}$ C.m.
A′	0	−0.326	0.194	0.014	−0.002	−0.026	0.120	−0.018	−0.019	0.031	−0.196	0.147	0.79
A″	23.5	−0.005	0.142	−0.100	−0.006	0.055	0.122	0.066	−0.041	0.080	−0.214	0.148	0.70
A′	35.8	0.328	0.185	0.597	−0.562	−0.402	0.415	−0.379	−0.535	0.105	0.015	0.147	2.59
A′	41.4	−0.388	−0.041	0.199	−0.123	0.119	0.009	0.201	−0.225	0.031	−0.011	0.147	3.09
A′	50.4	0.457	0.287	0.211	−0.372	−0.298	0.127	−0.297	−0.361	0.139	−0.150	0.148	4.65

Formula referring to *Table 4*



Formula referring to *Table 5*



carbonyl group to the region of the benzene ring consists mostly of the monoexcited configurations 22, 24 (59%) and 23, 25 (36%). This band is preceded by two forbidden $\sigma \rightarrow \pi^*$ transitions with the calculated values 48.2×10^3 cm^{-1} and 48.6×10^3 cm^{-1} both unobserved in the experimental spectrum.

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