Estimation of the conformation of 2,2'-dihydroxybenzophenone from electronic absorption spectra and Pariser—Parr—Pople calculations

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Basing on the comparison of the theoretical calculations with the experimental electronic absorption spectra of 2,2'-dihydroxybenzophenone (2,2'-diOHBPh) the conformations of this derivative were estimated. Two interesting results were obtained. Both aromatic rings of 2,2'-diOHBPh in cyclohexane are twisted from the plane defined by the π system of the carbonyl group by equal angle $\Theta_I = -\Theta_{II} = 15-30°$ while in polar solvent (methanol) only one aromatic ring is twisted by angle $60-90°$ and the second ring is coplanar with carbonyl group.

Considerable attention has been devoted to the electronic spectroscopy of the derivatives of 2-OHBPh especially because of photosensitizing properties of some derivatives of BPh [1, 2, 4] as well as their ability to transform the absorbed u.v. energy without radiation [3, 4]. In this respect 2-hydroxybenzophenones are of special interest, since they are widely used as effective stabilizers to protect organic polymers against undesirable effect of u.v. irradiation. Some papers of our laboratory deal with the u.v. spectra of various derivatives of 2-OHBPh from the point of view of their interpretation by the standard PPP method [5—7]. Owing to the steric repulsion between *ortho* hydrogens in aromatic rings (or bulky substituents in *ortho* positions) a twisting of benzene rings out of the plane defined by sp^2-hybridization of carbonyl carbon may be expected in BPh derivatives. There are many experimental studies as well as theoretical calculations by the HMO, EH, and CNDO methods available which are concerned with the conformation of BPh and its derivatives [8—10]. Particular attention has been paid in these papers to the steric effect of *ortho* substituents on the conformation. Moreover, in the case of 2,2'-diOHBPh the angle of twisting of aromatic rings is affected without doubt by other stronger effects, such as formation of intramolecular hydrogen bond, formation of intermolecular hydrogen bond between proton-acceptor solvent and hydroxy group or protonation of carbonyl group and ionization of hydroxyl group.

In the case of 2-OHBPh itself it may be stated on the basis of experimental studies [11—14] and theoretical calculations [6] that the 2-hydroxyphenyl group is coplanar with carbonyl group. Although there are no first-hand data concerning the magnitude of the twisting of unsubstituted ring (in 2-OHBPh) available in literature, it may be assumed that the magnitude of the dihedral angle between two benzene rings (equal to the angle of twisting of unsubstituted ring) must be similar to the dihedral angle in BPh itself [8, 10] (*i.e.* 40—60°).

In our preceding paper [15] the estimation of the conformation in 2-OH-4,6-diCH₃BPh depending on the proton-acceptor properties of solvent, protonization of the carbonyl group and ionization of the 2-hydroxyl group was treated.

This paper extends the application of PPP calculations to 2,2'-diOHBPh in order to establish the conformations in this derivative by comparing experimental absorption spectra and theoretical ones which have been calculated for different twisting angles of 2-hydroxyphenyl rings.

Experimental and calculation

2,2'-diOHBPh was a commercial sample purified by several crystallizations from ethanol. The electronic spectra of this derivative were measured in cyclohexane and methanol.

The measurements were carried out on a SPECORD (Zeiss, Jena) spectrometer.

The experimental oscillator strengths were estimated from absorption curves according to equation [16]

$$f = 4.32 \times 10^{-9} \times \varepsilon_{max} \times \Delta\tilde{v}.\tag{1}$$

ε_{max} and $\Delta\tilde{v}$ being the molar absorption coefficient at the absorption maximum and the half-band width respectively.

The excitation energies and oscillator strengths were calculated by the SCF method with LCI in π approximation. The approximations put forward by *Pople* [17] and *Pariser* and *Parr* [18] were applied in the method used. Semiempirical parameters used are listed in Table 1. For details of calculations see paper [15]. In all transitions the validity of the Franck—Condon principle was considered.
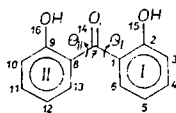
Table 1

Values of the semiempirical parameters for the PPP LCI calculation

Bond	Atom	I_μ [eV]	$\gamma_{\mu\mu}$ [eV]	$\beta_{C\mu}$ [eV]	$r_{C\mu}$ [A]	Z
C—C	C	11.22	10.98	−2.39	1.39	1
C=O	O	17.30	14.00	−2.30	1.23	1
C—OH	O	33.00	23.00	−2.10	1.40	2

Results and discussion

In comparison with BPh the conformation of 2,2'-diOHBPh* (structure *I*) is affected by the formation of intramolecular hydrogen bond of both hydroxyl groups with carbonyl oxygen. In proton-acceptor solvents the formation of intermolecular hydrogen bond between 2-OH groups and solvent may occur which effects the change in the conformation of molecule (by twisting aromatic rings) and in the electronic spectrum as well.

* The second OH group is substituted in position 9 (structure *I*) according to our designation.

The experimental spectrum of 2,2'-diOHBPh measured in cyclohexane and methanol is presented in Table 2 and Figs. 1a and 1b. A considerable shift of the band positions as well as the change in intensities indicate rather great changes in conformation owing to the change of solvent.

Table 2

Experimental values of excitation energies and oscillator strengths for 2,2'-diOHBPh in cyclohexane and methanol

Solvent	E_1 [eV]	f_1	E_2 [eV]	f_2	E_3 [eV]	f_3	E_4 [eV]	f_4
Cyclohexane	3.48	0.195	4.56	0.237	5.16	0.15	5.73	0.412
Methanol	3.69	0.1345	4.76	0.26	—	—	5.82	0.50

The calculated excitation energies and oscillator strengths for different twisting of aromatic rings are given in Table 3. A comparison of the experimental values of the spectrum of 2,2'-diOHBPh in cyclohexane with the theoretical ones shows that the first absorption band is due to the two transitions, i.e. $\varphi_9 \to \varphi_{10}$ and $\varphi_8 \to \varphi_{10}$. If one of the benzene rings is twisted, the $\varphi_9 \to \varphi_{10}$ transition shifts hypsochromically and its oscillator strength decreases (to zero at 90°). The energy of the $\varphi_8 \to \varphi_{10}$ transition does not change essentially while the oscillator strength increases. If we

Table 3

Excitation energies and oscillator strengths calculated for 2,2'-diOHBPh

Θ_I [°]	Θ_{II} [°]	ψ_{9-10}	ψ_{8-10}	ψ_{6-10}	ψ_{7-10}	ψ_{9-11}	ψ_{8-11}	ψ_{9-12}	ψ_{8-12}
0	0	3.5034	3.7381	4.6275	4.7062	5.2199	5.2365	5.6762	5.7993
15	0	3.5082	3.7420	4.6267	4.7142	5.1989	5.2513	5.6719	5.8063
45	0	3.5511	3.7667	4.7609	4.6044	5.0483	5.3878	5.6527	5.8239
60	0	3.5827	3.7637	4.7787	4.5882	4.9482	5.4727	5.6431	5.8429
ΔE 75	0	3.6167	3.7422	4.7909	4.5583	4.8609	5.5657	5.6231	5.8724
90	0	3.6450	3.7255	4.8272	4.5442	4.7905	5.5821	5,6209	5.8814
15	−15	3.5204	3.7494	4.6392	4.7169	5.1633	5.1816	5.6802	5.7902
30	−30	3.5567	3.7623	4.6591	4.7225	5.1592	5.1573	5.6863	5.7827
45	−45	3.6191	3.7835	4.6779	4.7233	5.1419	5.1030	5.6872	5.7467
0	0	0.4189	0.0060	0.1447	0.0744	0.0635	0.0361	0.0762	0.8521
15	0	0.4085	0.0081	0.1348	0.0797	0.0556	0.0490	0.0923	0.8437
45	0	0.3267	0.0252	0.1531	0.0465	0.0636	0.0792	0.1628	0.7964
60	0	0.2394	0.0508	0.1893	0.0086	0.0512	0.1187	0.2736	0.7531
f 75	0	0.1115	0.1173	0.2093	0.0023	0.0509	0.1790	0.2841	0.7338
90	0	0.0000	0.2092	0.2252	0.0000	0.0426	0.2308	0.2716	0.7318
15	−15	0.4021	0.0021	0.1390	0.0720	0.0660	0.0512	0.1263	0.8224
30	−30	0.3651	0.0005	0.1210	0.0681	0.0691	0.0717	0.2284	0.7792
45	−45	0.2896	0.0022	0.0508	0.0685	0.0712	0.1066	0.3654	0.6328

ΔE in eV; ψ_{i-j} stands for an excited state where the configuration ψ_{i-j} predominates.

consider the first band to be a superposition of these two transitions then this band is shifted from 3.5 to 3.72 eV, *i.e.* by 0.22 eV and the oscillator strength decreases to 50% of its value at 0° owing to the twisting $\Theta_I = 90°$ and $\Theta_{II} = 0°$. The second possibility of the change in geometry is simultaneous twisting of both aromatic rings by equal angle in the opposite direction. In the change of geometry from $\Theta_I = \Theta_{II} = 0°$ to $\Theta_I = -\Theta_{II} = 45°$ the first absorption band is characterized merely by the $\varphi_9 \rightarrow \varphi_{10}$ transition and the $\varphi_8 \rightarrow \varphi_{10}$ transition is practically forbidden for such conformations. Then the energetic shift of the first band from 3.5 eV ($\Theta_I = \Theta_{II} = 0°$) to 3.619 eV ($\Theta_I = -\Theta_{II} = 45°$) appears and the theoretical oscillator strength of the first band decreases from 0.418 to 0.289, *i.e.* to 70%. Let us assume that the aromatic rings of 2,2'-diOHBPh in cyclohexane are twisted by equal angle and in methanol only one ring is twisted whereas the second one is coplanar with
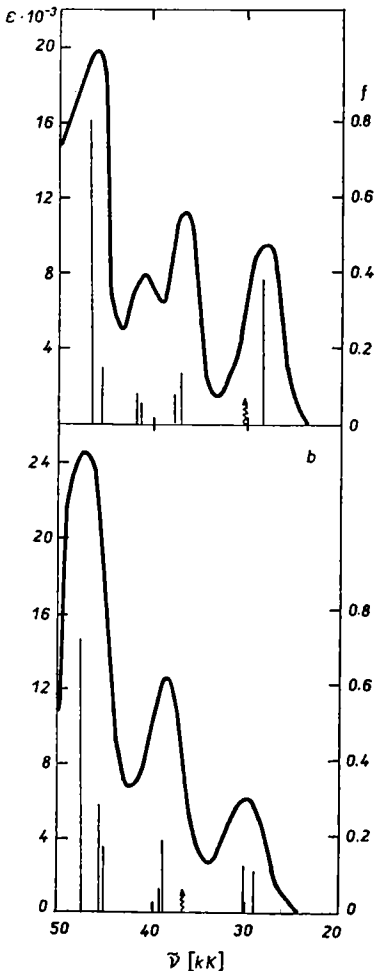

Fig. 1.

a) Experimental absorption curve of 2,2'-diOHBPh in cyclohexane and the LCI SCF excitation energies and oscillator strengths calculated for $\Theta_I = -\Theta_{II} = 20°$.

b) Experimental absorption curve of 2,2'-diOHBPh in methanol and the LCI SCF excitation energies and oscillator strengths calculated for $\Theta_I = 75°$, $\Theta_{II} = 0°$.

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C=O group. The comparison of the experimental values of the first band as well as of its changes accompanying the change of solvent with the theoretical values then indicates that the twisting of the aromatic rings of 2,2′-diOHBPh in cyclohexane is in the range from 0 to 30° while it is near to the conformation $\Theta_{II} \simeq 0°$, $\Theta_I = 60—90°$ in methanol.

The analysis of further bands confirms these assumptions. The second absorption band $E = 4,56$ eV (in cyclohexane) shifts in polar solvent (methanol) hypsochromically to 4.76 eV and the experimental oscillator strength from 0.237 to 0.26. In the corresponding part of the theoretical spectrum there are two transitions. Provided Θ_I and Θ_{II} are close to zero the energies of the $\varphi_6 \to \varphi_{10}$ and $\varphi_7 \to \varphi_{10}$ transitions are very near (4.6275 and 4.7062 eV resp.) and are assigned only to the second band. By twisting one aromatic ring from 0 to 90° (the second remains in the plane with carbonyl group) the $\varphi_6 \to \varphi_{10}$ transition is shifted hypsochromically by 0.2 eV (the oscillator strength changes from 0.1447 to 0.2252). The $\varphi_7 \to \varphi_{10}$ transition shifts bathochromically by 0.15 eV but its oscillator strength decreases owing to twisting with respect to the f_{6-10} so that the $\varphi_6 \to \varphi_{10}$ transition predominates in this region. The simultaneous twisting of both rings by equal angle results only in a small energetic shift of the mentioned transitions. Moreover, the sum of oscillator strengths of both transitions decreases. By comparing the experimental values with the theoretical ones we come to the same conclusion as in the case of the first band referring to the effect of methanol on the twisting of rings I and II.

The existence of the third absorption band ($E = 5.16$ eV and $f = 0.15$) in the spectrum in nonpolar solvent seems to be the most important evidence for the conformation $\Theta_I = -\Theta_{II} = 0—30°$ in cyclohexane and the conformation $\Theta_I = 60—90°$, $\Theta_{II} = 0°$ in methanol, while no distinct band appears in this region in methanol (see Figs. 1a and 1b). Two transitions, i.e. $\varphi_9 \to \varphi_{11}$ and $\varphi_8 \to \varphi_{11}$ which are energetically very near for conformation $\Theta_I = \Theta_{II} = 0°$ (5.2199 eV, $f = 0.0744$ and 5.2365 eV, $f = 0.0635$, respectively) correspond to the third band in the spectrum. By twisting only one ring from 0 to 90° $\varphi_9 \to \varphi_{11}$ transition shifts bathochromically by as much as 0.43 eV and, vice versa, the $\varphi_8 \to \varphi_{11}$ transition is shifted hypsochromically by 0.35 eV so that no transition occurs in the region of spectrum from 4.95—5.5 eV for the conformations close to $\Theta_I = 60—90°$, $\Theta_{II} = 0°$ Since the energy of both transitions changes just very little in simultaneous twisting of both rings by equal angle and, moreover, their oscillator strength increases, the spectrum of 2,2′-diOHBPh in methanol ought to show a band in this region (even more intensive than in cyclohexane) if both the rings were equally twisted (from 0 to 45°). The analysis of the fourth absorption band could lead to similar conclusions. Figs. 1a and 1b show the theoretical spectrum at $\Theta_I = -\Theta_{II} = 20°$ and $\Theta_I = 75°$, $\Theta_{II} = 0°$, respectively.

A qualitative and simple interpretation of the first absorption band of 2,2′-diOHBPh with respect to the first band of 2-OHBPh may be done by using a simple reasoning based on perturbation theory.

If φ_8 is the highest occupied MO in 2-OHBPh and φ_8' is the highest occupied MO in the reflected image of 2-OHBPh (mirror plane is perpendicular to the π system and goes through C=O bond), then the two highest occupied MO, i.e. ψ_8 and ψ_9 in 2,2′-diOHBPh may be produced by their combination, i.e.

$$\psi_8 = \frac{1}{\sqrt{2}} (\varphi_8 + \varphi_8'), \tag{2}$$

$$\psi_9 = \frac{1}{\sqrt{2}} (\varphi_8 - \varphi_8'). \tag{3}$$

Owing to the perturbation, the magnitude of which depends on the conjugation between both 2-hydroxyphenyl groups, the originally degenerated φ_8 and φ_8' levels split while the orbital with bonding combination corresponds to lower energy. The transition moment of the first $\varphi_8 \rightarrow \varphi_9$ transition in 2-OHBPh is almost perpendicular to C=O bond [6] and thus it holds approximately

$$\langle \varphi_8 | \vec{r} | \varphi_9 \rangle \doteq - \langle \varphi_8' | \vec{r} | \varphi_9 \rangle. \tag{4}$$

Assuming that the lowest antibonding orbitals in 2-OHBPh (φ_9) and in 2,2'-diOHBPh (ψ_{10}) are approximately equal (with respect to the localization on a carbonyl group) it holds

$$\langle \varphi_8 | \vec{r} | \varphi_9 \rangle \doteq \langle \varphi_8 | \vec{r} | \psi_{10} \rangle. \tag{5}$$

From this model it follows that the transition moments for the first two transitions in 2,2'-diOHBPh ($\psi_8 \rightarrow \psi_{10}$) and ($\psi_9 \rightarrow \psi_{10}$) may be expressed as follows

$$\vec{Q}_{8-10} = \langle \psi_8 | \vec{r} | \psi_{10} \rangle = \frac{1}{\sqrt{2}} [\langle \varphi_8 | \vec{r} | \psi_{10} \rangle + \langle \varphi_8' | \vec{r} | \psi_{10} \rangle] = 0, \tag{6}$$

$$\vec{Q}_{9-10} = \langle \psi_9 | \vec{r} | \psi_{10} \rangle = \frac{1}{\sqrt{2}} [\langle \varphi_8 | \vec{r} | \psi_{10} \rangle - \langle \varphi_8' | \vec{r} | \psi_{10} \rangle] = \sqrt{2} \langle \varphi_8 | \vec{r} | \varphi_9 \rangle. \tag{7}$$

It follows from this simple model that the first absorption band of 2,2'-diOHBPh ought to be shifted bathochromically with respect to the first band of 2-OHBPh and its oscillator strength should be twofold (assuming the planarity of both molecules).

A detailed calculation confirms, in principle, the rightness of this assumption. The theoretical value of f_{9-10} (2,2'-diOHBPh, $\Theta_{\mathrm{I}} = \Theta_{\mathrm{II}} = 0°$) is equal to $1.87 \times \times f_{8-9}$ (2-OHBPh, $\Theta_{\mathrm{I}} = 0°$, $\Theta_{\mathrm{II}} = -45°$). If we change in this proportion the experimental value of f_1 (2-OHBPh), we obtain the hypothetical value of the experimental value of oscillator strength f_1^{hyp} (2,2'-diOHBPh) $= 0.222$ (*i.e.* $\Theta_{\mathrm{I}} = \Theta_{\mathrm{II}} = 0°$). Now if we compare the real experimental value $f_1 = 0.195$ (for 2,2'-diOHBPh in cyclohexane) with the hypothetical value (and in conformity with preceding considerations we suppose a simultaneous twisting of both aromatic rings) we obtain the following theoretical oscillator strength

$$f_\Theta^{\mathrm{theor}} = \frac{f_1^{\mathrm{exp}}}{f_1^{\mathrm{hyp}}} f_{\Theta=0°}^{\mathrm{theor}} = 0.368. \tag{8}$$

This value corresponds to $\Theta_{\mathrm{I}} = -\Theta_{\mathrm{II}} = 27°$. In the same manner, for 2,2'-diOHBPh in methanol it holds $f_\Theta^{\mathrm{theor}} = 0.257$. In this case the value of $f_\Theta^{\mathrm{theor}}$ corresponds to $\Theta_{\mathrm{I}} = 67°$, $\Theta_{\mathrm{II}} = 0°$.

It follows from the above results involving twisting angles that both hydroxyl groups form in nonpolar solvent an intramolecular hydrogen bond with carbonyl oxygen but owing to the mutual repulsion of *ortho* hydrogens both the rings are twisted by 15—30° from the π plane of carbonyl group. In a polar proton-acceptor solvent one intramolecular hydrogen bond disappears owing to the formation of an

intermolecular hydrogen bond with solvent (the twisting angle of the aromatic ring bearing this hydroxy group increases) while the second hydrogen bond is strengthened so that the second aromatic ring becomes more coplanar with C=O group. Besides the mentioned repulsive conjugation and hydrogen bond energies also the solvation energy influences the value of total energy. From the calculated values of π components of the dipole moment it may be concluded that the conformation $\Theta_I \simeq 0°$, $\Theta_{II} = 60—90°$ (D.M. $\cong$ 2.9 Debye) will have preference over the conformations $\Theta_I = \Theta_{II} = 0°$ (D.M. = 0.47 Debye) and $\Theta_I = -\Theta_{II} = 45°$ (D.M. = = 0.88 Debye) in polar solvents.

We are aware of possible inaccuracy in the estimation of twisting angles because of approximations used. However, we believe that the estimated conformations of 2,2'-diOHBPh are realistic and a similar approach may be used for determining the conformations of other molecules where excitation energy and oscillator strength are strongly dependent on the conformation.

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