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SIMPLE MO-CALCULATIONS OF THE CHARGE-TRANSFER ABSORPTION IN QUINHYDRONES

H. Vogler, G. Ege* and H. A. Staab
Institut für Organische Chemie der Universität Heidelberg, D-69 Heidelberg, Im Neuenheimer Feld 7, Germany

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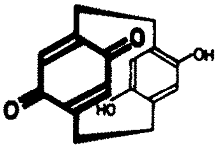
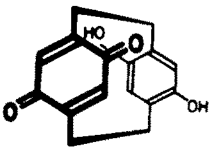
Abstract—HMO-calculations of charge-transfer absorptions are reported for the "pseudoortho" and "pseudogeminal" orientations of 1,4-benzoquinone and hydroquinone. This approach is used to explain the difference in the charge-transfer absorptions which have been observed for the corresponding intramolecular quinhydrones 1 and 2.

Recently the syntheses of several intramolecular charge-transfer (CT) systems of the [2.2]paracyclophane series were reported where donor/acceptor pairs are fixed in different orientations.[1-3] The two diastereomeric intramolecular quinhydrones 1 and 2 are typical examples.



1



2

The "pseudogeminal" compound 1 and the "pseudoortho" compound 2 differ remarkably in their charge-transfer spectra:[2] 1 shows a strong broad CT absorption between 400 and 600 nm with $\lambda_{max} = 500$ nm and $\epsilon \sim 1700$; in 2, however, this absorption is considerably reduced in intensity ($\epsilon \sim 170$) and somewhat shifted to longer wavelength ($\lambda_{max} = 515$ nm). Furthermore the spectrum of 2 shows a shoulder at $\lambda \sim 377$ nm ($\epsilon \sim 730$) whereas 1 has a marked absorption minimum in this wavelength area ($\lambda_{min} = 355$ nm).

We made simple HMO-calculations to explain the difference in the spectra of 1 and 2 which must be due to the different donor/acceptor orientations. We used one-electron theory because we were mainly interested in qualitative conclusions. For this purpose, extended all-valence calculations were not considered advantageous since they do not seem to be able to reproduce the stability of such CT complexes correctly.[4,5]

Theory

P^0 is the bond-order matrix of a donor (D)-acceptor (A) system without any interaction between D and A. The total charge on D is $Q_D^0 = \sum_s^D P_{ss}^0$. The interaction between D and A shall be characterized by the parameter σ. $P = P(\sigma)$ is the bond-order matrix of the D-A system with $\sigma \neq 0$. Analogous to Q_D^0 one gets Q_D. Now it is possible to formulate the following criterion:

$$K_0\colon Q_D^0 > Q_D \wedge Q_A^0 < Q_A.$$

The first order CT-effect CT^1 is defined as follows[6]

$$CT^1\colon \Leftrightarrow K_0 \quad \text{true}$$

CT^1 describes the fact that charge is transferred from D to A in the ground-state. Now consider an excitation from orbital φ_i to φ_k. The bond-order matrix of the excited state is $P^{i\to k}$. The total charge $Q_D^{i\to k}$ on D is calculated analogous to Q_D. The criterion K_1 is defined as follows

$$K_1\colon Q_D - Q_D^{i\to k} > Q_A - Q_A^{i\to k} \wedge Q_D - Q_D^{i\to k} > 0.$$

The sum of Q_D and Q_A resp. $Q_D^{i\to k}$ and $Q_A^{i\to k}$ in our case being constant, criterion K_1 can be simplified to

$$K_1\colon \; Q_D - Q_D^{i\to k} > 0 \wedge Q_A - Q_A^{i\to k} < 0.$$

The sum R of the bond indices[7] between D and A can serve as a measure of binding between D and A:

$$R = \sum_s^D \sum_t^A (P_{st})^2 \text{ resp. } R^{i\to k} = \sum_s^D \sum_t^A (P_{st}^{i\to k})^2.$$

A further criterion K_2 may be obtained:

$$K_2\colon \; R < R^{i\to k}.$$

The second order CT-effect CT^2 is defined as follows[6]

$$CT^2\colon \Leftrightarrow K_1 \quad \text{true} \wedge K_2 \quad \text{true}.$$

Since

$$\varphi_i = \sum_s c_{is}\chi_s$$

with

$$\langle \chi_s | \chi_t \rangle = \delta_{st}$$

K_1 and K_2 can be formulated in terms of the coefficients c_{is}:

$$K_1\colon \sum_s^D (c_{is}^2 - c_{ks}^2) > 0 \wedge \sum_t^A (c_{it}^2 - c_{kt}^2) < 0$$

$$K_2\colon \sum_s^D \sum_t^A (c_{ks}c_{kt} - c_{is}c_{it})(c_{ks}c_{kt} - c_{is}c_{it} + 2 \,.\, P_{st}) > 0.$$

The norm $|\mu_{i\to k}|$ of the transition moments $\mu_{i\to k}$ are simply taken as

$$|\mu_{i\to k}| = (\mu_{i\to k,x}^2 + \mu_{i\to k,y}^2 + \mu_{i\to k,z}^2)^{1/2}$$

with

$$\mu_{i\to k,x} = \sum_s c_{is}c_{ks}X_s$$

(x_s: x-coordinate of atom s) and likewise for y and z.

For our purpose it seemed sufficient to use simplified geometries, e.g. the 1,4-benzoquinone (A) and hydroquinone (D) rings parallel to each other, bond length all 1·397 Å and bond angles 120°. The distance between D and A was fixed at 2·95 Å (cf. mean value in [2.2]benzoquinophane[8]). The following HMO-parameter values have been adopted[9] (all values in units of the resonance integral):

$$\alpha_C = 0, \quad \alpha_O = 1, \quad \alpha_{O^-} = 2{\cdot}5 \quad \text{(simulating the OH-group)}$$

$$\beta_{CC} = 1, \quad \beta_{CO} = 1, \quad \beta_{CO^-} = 0{\cdot}8.$$

For 1 and 2 the influence of the $-CH_2-CH_2-$ bridges is simulated by $\alpha_{C-CH_2} = -0{\cdot}2$. I and II correspond to 1 and 2, resp. the $-CH_2-CH_2-$ bridges, however, are not taken into account. The resonance integrals σ of the p_σ-p_σ-type overlap between D and A were chosen between $\sigma = 0$ and $\sigma = 0{\cdot}25$. The last value might be in the right order of magnitude for an interplanar spacing of about 3 Å (*cf* ref.[10]). Only overlap between opposite C atoms was taken into account. The sign of σ is dependent on the orientation of the p_z-orbitals in D and A against each other; it can be chosen arbitrarily, since HMO-theory with only one p_z-atomic orbital per atom is invariant against rotations of 180°.[11]

Orbital energies ϵ, electronic transition energies $\Delta\epsilon_{i\rightarrow k}$ and transition moments $\mu_{i\rightarrow k}$ were calculated for the 1,4-benzoquinone/hydroquinone pair in the pseudogeminal and pseudoortho orientation (I and II, resp.) and the corresponding [2.2]paracyclophane quinhydrones 1 and 2.

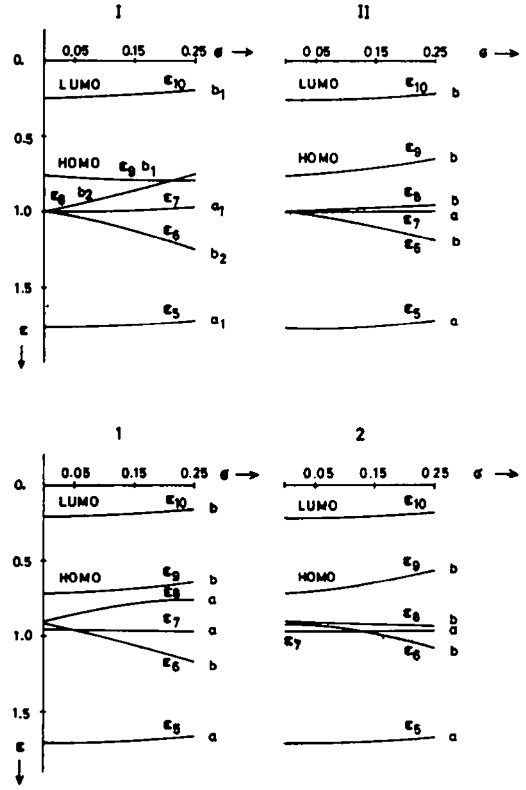


Fig. 1. Orbital energies ϵ_5 to ϵ_{10} in units of the (negative) resonance integral for the quinhydrone geometries I and II and for the compounds 1 and 2 as a function of σ.

Results

Both compounds 1 and 2 (resp. I and II) show a CT[1]-effect for $\sigma \neq 0$. Compound 1 (resp. I) is more stabilized than 2 (resp. II) when σ increases from $\sigma = 0$ to $\sigma = 0{\cdot}25$. The four lowest transitions of 1 and 2 are excitations from the four highest occupied orbitals φ_6 to φ_9 to the lowest unoccupied orbital φ_{10} (LUMO). The excitation to the next higher unoccupied orbital φ_{11} requires much higher transition energies (>1·4). Figure 1 shows for the 1,4-benzoquinone/hydroquinone orientations I and II and for the corresponding intramolecular quinhydrones 1 and 2 the orbital energies ϵ for the four highest occupied (φ_6 to φ_9) and the lowest unoccupied (LUMO, φ_{10}) orbitals as a function of σ. The resulting four lowest electronic transition energies $\Delta\epsilon_{i\rightarrow k}$ together with the transition moments $\mu_{i\rightarrow k}$ are shown in Fig. 2. Three of these excitations ($\varphi_9 \rightarrow \varphi_{10}$, $\varphi_8 \rightarrow \varphi_{10}$, $\varphi_6 \rightarrow \varphi_{10}$) are

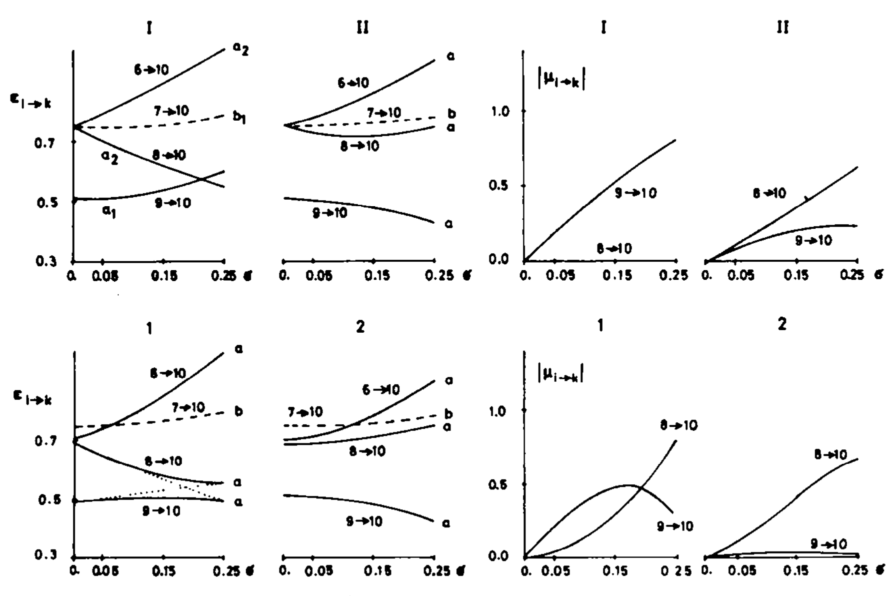


Fig. 2. Transition energies $\Delta\epsilon_{i\rightarrow k}$ and the norm $|\mu_{i\rightarrow k}|$ of the transition moments $\mu_{i\rightarrow k}$ for the lowest CT-transitions of I, II and 1, 2 as a function of σ (—— no CT-transition).

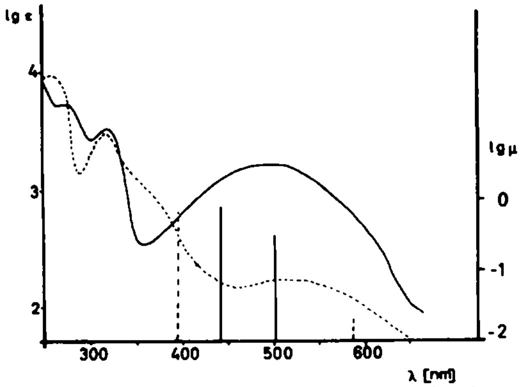


Fig. 3. Experimental electronic spectra vs calculated reciprocal transition energies (λ [nm] = $195 + 149/\Delta\epsilon_{l\to k}$) and transition moments for $\sigma = 0{\cdot}25$ of **1** (——) and **2** (----).

z-polarized CT^2-transitions for $\sigma \neq 0$ (in I, however, $\mu_{8\to10} = \mu_{6\to10} = 0$ for symmetry reasons). The transition ($\varphi_7 \to \varphi_{10}$) is polarized parallel to the ring planes and is no CT^2-transition.

As can be seen from Fig. 1 the orbital energies of **1** and **2** (as those of I and II, resp.) differ mainly in the behaviour of the highest occupied orbital φ_9, HOMO) and of the one below (φ_8): in **1** (and I) both get about the same energy when approaching $\sigma = 0{\cdot}25$ whereas in **2** (and II) φ_8 remains almost unaffected by changes of σ. Therefore, for **1** (and I) two CT-transitions of nearly the same energy are derived for the absorptions at longest wavelength (Fig. 2). In contrast, the two corresponding CT-transitions of **2** (and II) have different energies, the first being shifted to longer, the second to shorter wavelength as compared to **1** (or I, resp.). The first CT-transition $\varphi_9 \to \varphi_{10}$ shows a high transition moment only in **1** whereas the second CT-excitation $\varphi_8 \to \varphi_{10}$ shows a high transition moment for both **1** and **2**.

Our HMO calculations agree well with the experimental data assuming

(i) the broad CT-band of **1** to be composed of two electronic transitions with nearly the same energy,

(ii) the low intensity of the first CT-band in **2** being the result of the low transition moment of the first symmetry allowed CT-transition, and

(iii) the strong second CT-transition of **2** being responsible for the shoulder at $\lambda = 377$ nm.

This is demonstrated in Fig. 3 where a direct comparison is made between the experimental spectra (from ref.2) and the calculated transition energies and transition moments.

Note added in proof. PPP-calculations[5] with inclusion of configuration interaction lead to similar qualitative results as compared to HMO-calculations.

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