Tetrahedron Letters,Vol.24,No.21,pp 2159-2162,1983
Printed in Great Britain

0040-4039/83/212159-04$03.00/0

THEORETICAL STUDY OF THE LOWER SINGLET EXCITATIONS OF [2.2]PARACYCLOPHANE QUINHYDRONES

Helmut Vogler

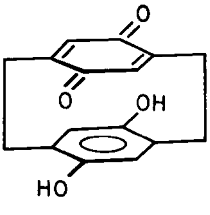
Max-Planck-Institut für Medizinische Forschung

Abteilung Organische Chemie

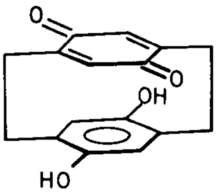
Jahnstr. 29, D-6900 Heidelberg, West-Germany

The lower excited singlet states of the diastereomeric [2.2]paracyclophane quinhydrones 1 and 2 are studied by means of semiempirical π-theory.

The diastereomeric [2.2]paracyclophane quinhydrones 1 and 2 differ by the mutual orientation of the hydroquinone (H) and p-benzoquinone (Q) moiety. Correspondingly differences can be seen in the experimental uv-vis spectra[1] of the pseudogeminal 1 and the pseudo-*ortho* 2 (cf. Fig. 1): (i) The extinction of the longest wavelength absorption band is considerably smaller and slightly red-shifted for 2. (ii) At λ=377 nm 2 exhibits a shoulder which becomes even a band maximum in the case of the analogous [3.3]paracyclophane[2] whereas minimum absorption is found for 1 in this region. (iii) At $\lambda \cong 250$ nm 1 shows two well separated absorption bands whereas only one band is found for 2. (iv) In contrast to the afore-mentioned differences between the orientational isomers both compounds are characterized due to a strong absorption band at $\lambda \cong 317$ nm.



1



2

A first theoretical interpretation of the longest wavelength part of the uv-vis spectra of 1 and 2 was given within simple Hückel theory[3]. However, such an approach without explicit consideration of electron interaction cannot be used for studying the shorter wavelength absorptions. Therefore we report in this communication on our π-SCF calculations with subsequent configuration interaction[4)] of the lower excited singlet states of 1 and 2. The inductive effect of the methylene groups, the through-bond interaction via the bridges and the deformations of the conjugated subsystems are neglected since they seem not to affect crucially the energies and characters of the lower excited states of quinhydrones. Furthermore n→π* transitions are not treated here since they do not contribute significantly to the shape of the absorption spectra due to their low intensities.

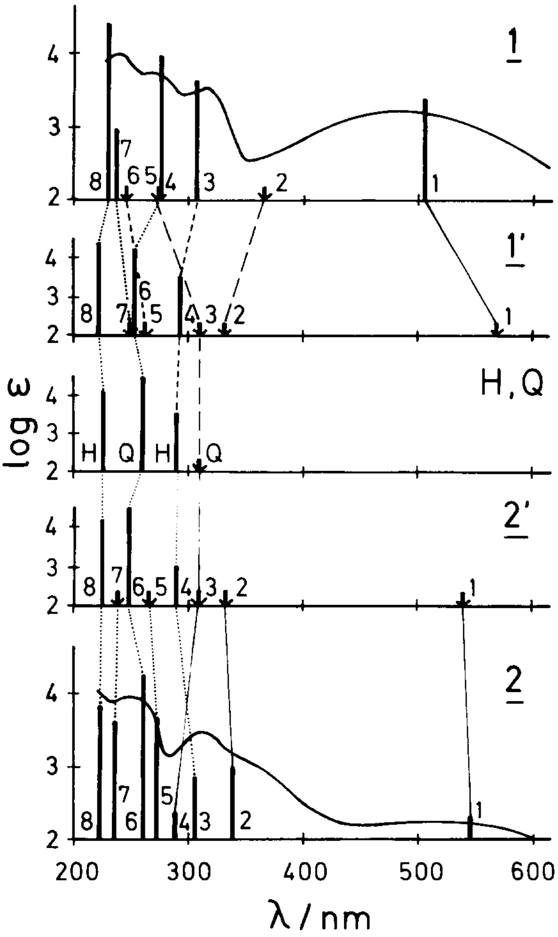


Fig. 1. Experimental uv-vis spectra of 1 and 2 and calculated transitions of H, Q, 1', 1, 2' and 2. Weak (log ε≦2) or forbidden transitions are indicated by arrows. The excitations are correlated according to their symmetries.

The two lowest calculated π→π* excitations of H and Q are in good agreement with experiment[5)]. 1' and 2' correspond to 1 and 2, but transanular one-electron interaction between H and Q via the transanular resonance integrals is not taken into account. The orbitals ϕ_i of 1' and 2' are either localized in H or Q and can be mapped uniquely with the orbitals ϕ_i^H of H or ϕ_j^Q of Q, although they need not to be identical. Besides the local excitations (LE's) either in H or Q the charge-transfer excitations (CE's) can be discriminated. For the lower excited states only the following CE's with an electron transfer q=1 are of interest: $\phi_h^H \to \phi_l^Q$, $\phi_{h-1}^H \to \phi_l^Q$, $\phi_h^H \to \phi_{l+1}^Q$ and $\phi_{h-2}^H \to \phi_l^Q$, which are arranged due to increasing energy. $\phi_{h(l)}$ indicates the highest occupied (lowest virtual) orbital. In 1' and 2' CE's or LE's can couple one another but CE's and LE's cannot. The four CE's given above form predominantly the transitions 1, 2, 5 and 7 of 1' and 2'. The transitions 1 and 2 consist just of the first two CE's whereas the other ones are coupled with energetically higher CE's.

The transitions 3 and 4 correspond to the first LE in Q and H. They are not coupled despite of their similar energies[5)] since they belong to different irreducible representations. This does not apply to the second LE of Q and H. Both are coupled but nevertheless transition 6 is predominantly the second LE of Q whereas transition 8 that of H since the latter is higher in energy by about 0.7 eV.

The transanular resonance integrals cause a covalent mixing of the orbitals of H and Q and the coupling of CE's with LE's becomes possible. Generally the resultant orbitals ϕ_i remain localized mainly in either H or Q, e.g., ϕ_h and ϕ_l are localized by more than 96 % in H or Q and we have $\phi_h \cong \phi_h^H$, $\phi_l \cong \phi_l^Q$. However, (near) degenerate orbitals of H and Q belonging to the same irreducible representation can lead to orbitals ϕ_i which are fully delocalized over H and Q, e.g., ϕ_{l+1} is localized by 40 % in H and results mainly from the covalent mixing of the near-degenerate orbitals ϕ_l^H and ϕ_{l+1}^Q. But even the small covalent admixtures of orbitals from the other conjugated subsystem as in the case of ϕ_h or ϕ_l is important since it may lead to allowed transitions being predominantly CE's which would be forbidden otherwise (see the CE's of 1' and 2'). An example is provided by the first transition of 1 and 2 with an almost complete electron transfer. Also the second transition is mainly a CE with a slightly smaller $q=0.79$ (1) or 0.87 (2) due to the weak coupling with the first LE in Q. The third transition is dominated by the excitation $\phi_h \rightarrow \phi_{l+1}$ which is no longer tantamount to the first LE in H (dominated by the $\phi_h^H \rightarrow \phi_l^H$ excitation) as in 1' or 2'. Due to the afore-mentioned nature of the orbitals ϕ_h and ϕ_{l+1} it is rather a combination of that LE and the third CE of 1' or 2' (transition 5) leading to the large $q \cong 0.5$ value. The corresponding higher energy combination forms transition 6 (1) or 5 (2) with a $q \cong 0.4$. The first and second LE in Q are the major components of the transitions 4 and 5 (1) or 6 (2), respectively. Both are nearly degenerate in the case of 1. The transition 7 corresponds to the same type of CE as with 1' and 2' now with $q \cong 0.8$ and gains its intensity from the small covalent mixing of orbitals of H with those of Q and v.v. The second LE in H is the leading part of transition 8 with a $q \cong 0.3$ which derives from the significant coupling with CE's.

The calculated positions and relative intensities of the lower excitations of 1 and 2 are in good agreement with the experimental band maxima (cf. Fig. 1). Our interpretation of the longest wavelength absorption band and the shoulder at $\lambda \cong 377$ nm of 2 agrees with that given earlier[3)]. According to our calculations the absorption at $\lambda \cong 317$ nm corresponds to an excitation which consists of the strongly coupled first LE in H and CE's. Furthermore our results demonstrate that the two bands around 250 nm in the uv-spectrum of 1 arise mainly from the transitions 4 and 8 being predominantly the second LE's of Q and H. Contrary to 1 all transitions 5-8 constitute the single short wavelength band of 2. Consequently this band consists of different types of excitations, viz. the combination of the first LE in H with CE's, the second LE's in Q and H, and linear combinations of CE's.

The good agreement between calculated and experimental uv-vis spectra of 1 and 2 as well as their similarity with those of the corresponding [3.3]paracyclophanes gives evidence of the insignificance of through-bond interaction via the methylene bridges for the lower excited states of quinhydrones. This derives from the fact that a transition can manifest any significant through-bond interaction only if it is dominated by excitations from occupied orbitals being fully delocalized over H and Q. However, there are no such dominant excitations with all transitions studied here. The transitions 3 and 6 (1) or 3, 5 and 8 (2) are dominated by excitations $\phi_i \rightarrow \phi_k$ where the virtual orbital ϕ_k is delocalized over H and Q. But this is ineffective with respect to through-bond interaction due to the large energy differences between the virtual and bridge orbitals6).

Acknowledgements. The author is deeply indebted to Professor H. A. Staab for his continuous interest in this work and for providing the uv-vis spectra of 1 and 2. Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemie is gratefully acknowledged.

REFERENCES AND NOTES

1) H. A. Staab and W. Rebafka, Chem. Ber. 110, 3333 (1977).

2) H. A. Staab and C. P. Herz, Angew. Chem. 89, 839 (1977).

3) H. Vogler, G. Ege and H. A. Staab, Tetrahedron 31, 2441 (1975).

4) The parameters are taken from J. M. Younkin, L. J. Smith and R. N. Compton, Theoret. Chim. Acta 41, 157 (1976), however, the one-centre electron repulsion integral for the quinone oxygen was increased by 2 eV in order to obtain better transition energies for Q. The geometries are chosen as in Ref.3) and the transanular resonance integrals are calculated as described in H. Vogler, Theoret. Chim. Acta 60, 65 (1981) with C=1. The configuration interaction utilized 20 singly excited configurations. The extinctions are calculated according to J. Pancíř, I. Matoušek and R. Zahradník, Collect. Czech. Chem. Commun. 38, 3039 (1973).

5) Calculated (observed) values (in units of eV): 4.0 (4.0-4.4), 4.8 (4.8-5.1) for Q, 4.3 (4.3), 5.5 (5.5) for H. Observed values are taken from: H. P. Trommsdorff, J. Chem. Phys. 56, 5358 (1972); Á. I. Kiss and J. Szöke, Chem. Phys. Lett. 18, 195 (1973); R. W. Bigelow, J. Chem. Phys. 68, 5086 (1978).

6) B. Kovač, M. Mohraz, E. Heilbronner, V. Boekelheide and H. Hopf, J. Am. Chem. Soc. 102, 2314 (1980); B. Kovač, M. Allan and E. Heilbronner, Helv. Chim. Acta 64, 430 (1981).

(Received in Germany 25 February 1983)