The Electron Spectra of a Blue S-Tetrazine Derived Betaine and its Protonated Forms

A Comparison with the Radical Anion 1,5-Dimethyl-5-oxoverdazyl-3-olate

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Dedicated to Prof. Dr. D. Schulte-Frohlinde on the occasion of his 60th anniversary

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Electronic Spectra, Betaines, Verdazyls

The striking similarities of the hypsochromic shifts of the longest wavelength absorption observed in the series 1—3 and 4—6 are rationalized by means of simple molecular orbital theory.

The betaine 1,4-dimethyl-3,6-dioxo-1,2,4,5-tetrazin-1-ium-5(4H)-id (1) impresses by its deep blue colour which is quite unusual for a simple six-membered ring betaine (in dioxane: \( \lambda_{\text{max}} \) (log \( e \)) = 603 (3.49), 571 (3.50), 227 nm (4.23)) [1]. In acidic solution 1 is protonated; it dissolves in weak acids, e.g. in HCOOH, with red colour (monoprotonated form 2; 524 nm (3.56)) and in 70% perchloric acid with yellow colour (probably diprotonated form 3; 464 nm (3.47), 217 (4.13)) [1]. The longest wavelength absorption of 1—3 is displayed in Fig. 2.

Almost exactly the same colour pattern is observed for the blue-violet verdazyl anion 4 (in 0.01 M NaOH: 575 nm), its red-brown protonated form 5 (in CH₃COOH: 499 nm) and the corresponding yellow cation 6 (in 70% HClO₄: 451 nm) which is formed by disproportionation of 4 in strong acids besides 7 [2].

The similarity of the hypsochromic shifts in the series 1—3 and 4—6 is striking since their structures are quite different, e.g. 4 and 5 constitute free radicals with 11 electrons in the \( \pi \)-system in contrast to 1, 2, 3 and 6 with 10 electrons. The treatment of 1—6 and the study of their electronic spectra with sophisticated semiempirical or \( \text{ab initio} \) approaches is hampered by the necessity of comparing closed and open shell systems. In this communication we will show that the resembling colour pattern of 1—3 and 4—6 can be rationalized within simple molecular orbital theory.

Fig. 1. Survey of studied compounds. For 1—6 the longest wavelength absorptions \( \lambda_{\text{max}} \) (in nm) are given.

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Computational Procedures

For 1—3, 6 and the related compounds s-tetrazine 9 and its dimethoxy derivative 10 we performed calculations using the CNDO/S Hamiltonian [3] utilizing the available experimental [1, 4] and standard bond lengths [5]. The excited singlet states were obtained by configuration interaction between all singly excited configurations which exhibit excitation energies under 10 eV with respect to the Hartree-Fock ground state.

Furthermore 1—6 were studied by means of the ordinary Hückel procedure with Coulomb and resonance integrals $\alpha_\pi = h_\pi \beta$ and $\beta_{\alpha\beta} = k_{\alpha\beta} \beta$ where $\beta$ denotes the negative standard resonance integral. The parameters $h_\pi = 0, 0.42, 1.25, 0.86, 0.91,$ and 1.76 for C, N, N, O, O, and O (the dots represent the electrons contributed to the $\pi$-system) were taken from ref. [6]. In analogy to the $h_\pi$ values for O, O$^-$ and O we obtained $h_{N^-} = 0.47$ from $h_N$ and $h_N$ by interpolation. For the methyl substituents the heteroatom model was applied with $h_{CH_3} = 1.94$ and $k_{N-CH_3} = 0.6$, see ref. [7]. All other resonance integral parameters were chosen as $k_{\alpha\beta} = 1$.

The resonance structures given in Fig. 1 for compounds 1 and 3—6 are not unique since in each case another equivalent resonance structure can be formulated. This does not affect our treatment of 3 due to the fact that both resonance structures differ only in the assignment of double and single bonds in the six-membered ring which are not differentiated in our Hückel procedure. On the contrary the two resonance structures of 1 and 4—6 differ additionally in the assignment of the types of nitrogen and hence of corresponding Coulomb integrals. However, it turned out that the orbital energies depend mainly on the mean of the $h_\pi$ values of the nitrogens in the six-membered ring which does not vary significantly in the series 1—6. Consequently it is a sufficient approximation to assign the Coulomb integrals according to the formulae given in Fig. 1, although the true electronic structures will be between those indicated by the two equivalent resonance structures, cf. the X-ray structure of 1 [1].

Results and Discussion

Numerical results

As long as we can exclude first order configuration interaction [8], it is assumed within Hückel theory that the longest wavelength $\pi\pi^*$ absorption in the electron spectrum results from that one-electron transition $\phi_i \rightarrow \phi_k$ from occupied orbital $\phi_i$ with energy $\varepsilon_i$ to virtual orbital $\phi_k$ with energy $\varepsilon_k$ which exhibits the smallest excitation energy $E_{ik} = \varepsilon_k - \varepsilon_i$. In case of the closed shell systems 1—3 and 6 the minimum $E_{ik}$ is associated with the excitation from the highest occupied orbital $\phi_h$ to the lowest virtual orbital $\phi_l$ (type A, cf. Fig. 3). On the contrary either excitation $\phi_h \rightarrow \phi_i$ (type B) or $\phi_{h-1} \rightarrow \phi_h$ (type C) can lead to the smallest $E_{ik}$ with the radicals 4 and 5.

<table>
<thead>
<tr>
<th>$\phi_h$</th>
<th>$\phi_i$</th>
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<td>$\phi$</td>
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Fig. 3. Excitation types.

Obviously Hückel theory can be used in order to rationalize the colour pattern of series 1—3 and 4—6 only if the longest wavelength absorption gains its intensity mainly from a $\pi\pi^*$ type transition which is dominated by a single orbital excitation. Our CNDO/S results (see Table I) for 9 (which is related to the
six-ring moiety in 1–6), 10, 1–3 and 6 demonstrate that the lowest excited singlet \( \pi\pi^* \) state of these compounds consists predominantly of a transition from the highest occupied to the lowest virtual \( \pi \)-orbital corresponding to the \( \phi_{h-1} \rightarrow \phi_I \) excitation. Only for 9 it is the \( \phi_{h-1} \rightarrow \phi_I \) excitation since here CNDO/S correctly yields a \( \sigma \)-orbital \( \phi_s \) [9]. In case of 9 four \( \sigma\pi^* \) excited singlet states are lower in energy than the \( \pi\pi^* \) singlet state. The difference between first \( \sigma\pi^* \) and \( \pi\pi^* \) state amounts to nearly 3 eV in good agreement with experiment [10]. Only three \( \sigma\pi^* \) singlet states are more stable than the lowest singlet \( \pi\pi^* \) state if dimethoxy substituents are introduced into 9. The \( \sigma\pi^* \) transitions lead to the two longest wavelength absorption bands in the experimental UV-VIS spectrum of 10 [11] whereas according to our CNDO/S results the third band should derive from the \( \pi\pi^* \) excitation. In agreement with experiment [10, 11] the long wavelength \( \sigma\pi^* \) excitations of 9 are characterized by much smaller oscillator strengths than the \( \pi\pi^* \) excitation whereas the opposite applies to its dimethoxy derivative 10.

According to our CNDO/S calculations one \( \sigma\pi^* \) excitation occurs at longer wavelength than the first \( \pi\pi^* \) transition in 1–3 and 6 but the energy separation is reduced to about 0.3 eV. As in case of 9 the oscillator strength of the \( \pi\pi^* \) excitation is considerably larger than that of the \( \sigma\pi^* \) transition. The first absorption band in the UV-VIS spectrum of 1 exhibits two maxima. A band analysis assuming Gaussian line shapes yields two transitions (see Fig. 2) at 620 nm (log \( \varepsilon = 3.2 \), halfwidth 19 nm) and 571 nm (log \( \varepsilon = 3.5 \), halfwidth 59 nm). This is in good agreement with our CNDO/S results if we assign these two transitions to the \( \sigma\pi^* \) and \( \pi\pi^* \) excitations. The CNDO/S calculations reproduce the observed hypsochromic shift in the series 1–3 of the longest wavelength absorption which is obviously mainly due to the \( \pi\pi^* \) and to a minor degree to the \( \sigma\pi^* \) excitation. Although we correctly calculate larger \( \sigma\pi^* \) and \( \pi\pi^* \) excitation energies for 6 with respect to 2 it is obvious from Table I that these are too large for 3 but too small for 6. This is most likely due to inadequacies in the chosen geometries for these compounds.

In 1–3 and 6 \( \phi_h, \phi_I \) and \( \phi_{h-1} \) are \( \pi \)-orbitals which should match with \( \phi_{h-1}, \phi_h \) and \( \phi_I \) of 4 and 5 due to the additional electron in the latter molecules. Consequently we can assume that in 4 and 5 \( \phi_h \rightarrow \phi_I \) (type B) and \( \phi_{h-1} \rightarrow \phi_I \) (type C) will be \( \pi\pi^* \) excitations which should be lower in energy than \( \sigma\pi^* \) transitions. By considering the orbital symmetries in the carboconjugated system 8 we can conclude that the excitations B and C do not significantly interact with each other in the related systems 4 and 5.

The CNDO/S calculations and above considerations suggest that a Hückel approach should account for the characteristic colour pattern in the series 1–3 and 4–6. This is indeed corroborated by Fig. 4 where the calculated wavelengths \( \lambda \) of the electron transi-

<table>
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<th>Compound</th>
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<th>Experimental values</th>
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* This work and refs. [1, 2].
tions with the lowest energy $E_{\text{ik}}$ are compared with observed $\lambda_{\text{max}}$ values. The wavelengths were calculated by the formula $\lambda/nm = 1239/(a \cdot E_{\text{ik}}/\beta + b)$ from transition energies $E_{\text{ik}}$. The constants $a = 1.70$, $b = 1.08$ \((1-3)\) and $a = 4.00$, $b = -0.80$ \((4-6)\) in the denominator were determined by linear regression analysis of experimental vs. calculated transition energies. A single regression line for 1-6 does not lead to different conclusions. Based on our Hückel results the longest wavelength absorption of 4 should be due to a type C excitation and probably a type B excitation in case of 5. The hypsochromic shift in the series 1-3 derives from the increasing stabilization of $\phi_h$ whereas in the series 4-6 it is due to two effects, i.e. the stabilization of $\phi_{h-1}$ in 5 and 6 with respect to 4 and the different number of electrons in 4 or 5 and 6.

![Fig. 4. Energies of Hückel orbitals $\phi_{h-1}$, $\phi_h$, and $\phi_l$ for 1-6 and experimental (calculated) wavelengths $\lambda$ (in nm).](image)

**Rationalization of results**

The Hückel orbitals of 1-6 are similar to those of the topologically related hydrocarbon 8 and exhibit the same nodal properties, see Fig. 5. Therefore it is possible to explain the orbital energy changes $\Delta\epsilon_i$ caused by the structural changes in the series 1-3 and 4-6 within first order perturbation theory. We can write $\Delta\epsilon_i = \sum c_i^0 \delta\alpha_i$ where $\delta\alpha_i$ denotes the change of Coulomb integrals $\alpha_i$ and $c_i$ is the coefficient of orbital $\phi_i$ at atom s. Except for 2 and 6 or 4 and 5 all compounds differ in the type of at least one nitrogen. Nevertheless the orbital changes $\Delta\epsilon_i$ caused by the replacement of carbons by nitrogens are approximately the same for all compounds 1-6 since due to the symmetry of 8 only the mean value of all nitrogen $\delta\alpha_i$ values is important which turns out to be nearly constant. Thus 1-6 will exhibit significantly different $\Delta\epsilon_i$ values for orbitals $\phi_i$ only if the associated orbitals of 8 are characterized by numerically large coefficients at the exocyclic atoms and the electronegativity of at least one oxygen atom is altered.

The frontier orbitals $\phi_h$ and $\phi_l$ of 1-3 and 6 are derived from $\phi_5$ and $\phi_6$ of 8 whereas $\phi_{h-1}$, $\phi_h$ (singly occupied) and $\phi_l$ of 4 and 5 are associated with $\phi_5$, $\phi_6$, and $\phi_l$ of 8. Numerically large orbital coefficients at the exocyclic atoms of 8 are found in $\phi_5$ but not in $\phi_h$ or $\phi_l$ (cf. Fig. 5). Consequently only those frontier orbitals of 1-6 which correspond to $\phi_5$ of 8 will experience important $\Delta\epsilon_i$ shifts if an oxygen substituent is altered. In the series 1-3 the substituents $=\text{O}$ are successively replaced by the more electronegative $-\text{OH}$ (negative $\delta\alpha$). Thus $\phi_h$ is stabilized whereas $\phi_l$ remains unchanged leading to the observed hypsochromic shift in this series. The substituent $-\text{O}^-$ of 4 is superseded by the more electronegative $-\text{OH}$ in 5. On the other hand 5 and 6 do not differ in their oxygen substitution pattern. Due to the nodal properties of $\phi_5 - \phi_7$ of 8 $\phi_{h-1}$ is stabilized from 4 to 5.

![Fig. 5. Schematic representation of Hückel $\pi$-orbitals $\phi_{h-1}$, $\phi_h$, and $\phi_l$ of 1 and 4 and associated orbitals $\phi_5$, $\phi_6$, and $\phi_7$ of 8. Corresponding orbitals of 2, 3, 5 and 6 do not differ considerably from those given here.](image)
whereas $\phi_h$ and $\phi_l$ are not significantly shifted in energy. Consequently the hypochromic shift in the series 4–6 has to be attributed to the stabilization of $\phi_{h-1}$ (4→5) and to the decrease in the number of electrons (5→6) both leading to a change in the type of excitation (C→B→A).

Compounds 2 and 6 possess the same types of nitrogen and oxygen atoms. According to first order perturbation theory both should exhibit the same longest wavelength absorption. But we observe $\lambda_{\text{max}}$ (2) > $\lambda_{\text{max}}$ (6) which is correctly reproduced by our numerical calculations and is obviously due to higher order effects. This can be rationalized by applying the interlacing rule [12] since 2 and 6 are topologically related molecules with non-isomorphic partial structures. Also for 1, 3, 4 and 5 isomers can be formulated which are likewise topologically related as 2 and 6. However, either they are not known hitherto (isomers of 1 and 3) or can be traced only by means of ESR (isomers of 4 and 5).

How can we explain the deep blue colour of 1? Our CNDO/S calculations revealed that although part of the blue colour can be attributed to a $\sigma\pi^*$ transition most of the intensity is due to a $\pi\pi^*$ excitation. The orbital energy difference between $\phi_3$ and $\phi_6$ of 8 which correspond to $\phi_h$ and $\phi_l$ of 1 is $E_h = -0.689 \beta$. By using first order perturbation theory it is straightforward to show (cf. Fig. 5) that both orbitals are almost equally stabilized by the introduction of the heteroatoms so that $E_{hl} = -0.638 \beta$ for 1 is only slightly smaller than $E_{56}$ of 8. On the other hand $E_{hl}$ of 10 is considerably enlarged with respect to $E_{56}$ of 8 since here the heteroatoms lower $\phi_l$ in energy more than $\phi_h$. This explains the much higher $\pi\pi^*$ excitation energy of 10 with respect to 1–3 and 6, cf. Table I. The $E_{56}$ value of 8 is bracketed by the $E_{hl}$ values of anthracene ($E_{hl} = -0.828 \beta$) and naphthacene ($E_{hl} = -0.590 \beta$). Consequently 1 should not absorb over 450 nm if we disregard the $\pi\pi^*$ transition and apply the regression line [13] between Hückel $E_{hl}$ values and experimental excitation energies for the $1L_\alpha$ (p) band with dominant $\phi_h \rightarrow \phi_l$ transition of polyacenes. However, by taking electron interaction explicitly into account the energy of an excitation being dominated by the $\phi_h \rightarrow \phi_l$ transition is given as $S_{hl} = E_{hl} - (J_{hl} - 2K_{hl})$ where $J_{hl}$ and $K_{hl}$ denote the Coulomb and exchange integral of orbitals $\phi_h/\phi_l$. Generally $J_{hl}$ decreases with increasing extension of the $\pi$-system similar to $E_{hl}$. The same applies to $K_{hl}$ which depends on the overlap density $\phi_h/\phi_l$ and hence $K_{hl}$ are large since $\phi_h$ and $\phi_l$ differ only in the sign of the orbital coefficients due to the pairing theorem [14]. On the contrary $\phi_3$ and $\phi_6$ of 8 exhibit no pairing properties, cf. Fig. 5. Consequently $\phi_h/\phi_l$ and hence $K_{hl}$ of 1 are small. Thus $S_{hl}$ of 1 is considerably smaller than that of polyacenes. This is explicitly taken into account in our regression lines for 1–6. Obviously two features are responsible for the deep blue colour of 1: the absence of at least an approximate pairing relationship between $\phi_h$ and $\phi_l$ in 1 which is also responsible for the blue colour of azulene [15], and the occurrence of heteroatoms in such a manner that the small $E_{56}$ value of 8 is retained in $E_{hl}$ of 1 in contrast to 10.

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