Electronic Properties of Triplet States of Azabenzenes

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The electronic properties of the $\pi\pi^*$ and $n\pi^*$ triplet states of azabenzenes are studied by means of semiempirical calculations of zero-field-splitting parameters.

Key words: triplet states – ZFS parameters – azabenzenes

The lowest excited states of benzene **1** (see Fig. 1) are $\pi\pi^*$ states since they consist of excitations from occupied π orbitals into virtual π^* orbitals. The replacement of CH groups by the isoelectronic nitrogen atoms leads to azines possessing σ orbitals which are localized predominantly at the nitrogen atoms and are thus called n orbitals. Consequently in azines also $n\pi^*$ excited states with transitions from n into π^* orbitals are possible besides the $\pi\pi^*$ ones.

The electronic properties of $\pi\pi^*$ and $n\pi^*$ states differ considerably. For example, the two unpaired electrons in a triplet $\pi\pi^*$ state cannot be at the same atom at a given time if we disregard in-out correlation effects, whereas this is possible in a $n\pi^*$ state. According to Sternlicht [1] this should lead to considerably larger zero-field-splitting (ZFS) parameters D in $n\pi^*$ than in $\pi\pi^*$ triplet states.

In this paper we report on our theoretical study of ZFS parameters D and E of the diazines **2**–**6** and s-tetrazine **7**, which are isoelectronic to benzene **1** (see Figure 1). Low temperature electronic spectra for **2**–**5** revealed [2] that the lowest triplet state of these compounds is an $n\pi^*$ state. However, in case of **2**, **4** and **5** this $n\pi^*$ state is nearly degenerate with the lowest $\pi\pi^*$ triplet. For **7** an $n\pi^*$ lowest triplet state is expected due to the large number of nitrogen atoms.

Computational Procedure

We utilized the semiempirical CNDO/S method [3], which reproduces generally correctly the sequence of higher occupied and lower virtual orbitals [4, 5] and type and energetical spacing of lower singlet and triplet states [4]. The triplet wavefunctions ${}^3\Psi = \Sigma_{(ik)}\, C_{ik}\, \Omega_{ik}$ were obtained by configuration interaction between all singly excxited triplet configurations Ω_{ik} with energies below 10 eV with respect to the ground state and excitations from occupied σ orbitals $\sigma_i = \Sigma_s^\sigma a_{is} \chi_s$ into virtual π orbitals $\pi_k^* = \Sigma_t^\pi b_{kt} \chi_t$. All calculations were carried out using geometries with standard bond lengths [6].

Calculation of ZFS Parameters

All compounds except **6** belong to pointgroups where the magnetic axes [7] $\bar{x}$, $\bar{y}$, $\bar{z}$ agree with the molecular ones shown in Figure 1. In case of **6** the in-plane axes $\bar{x}$, $\bar{y}$ are not fixed by the molecular symmetry. Within coordinate system $\bar{x}$, $\bar{y}$, $\bar{z}$ the ZFS parameters D and E are obtained as expectation

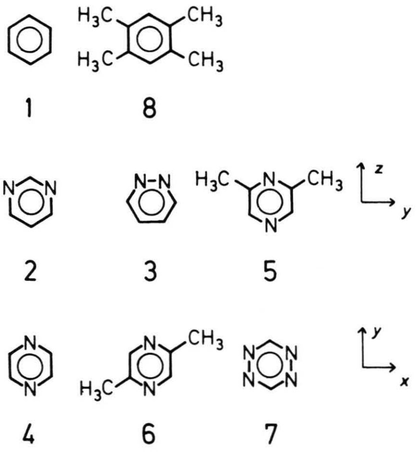

Fig. 1. Compounds under study.

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values of the operator [7] $\hat{D} = c\,(r_{12}^2 - 3\bar{z}_{12}^2)\, r_{12}^{-5}$ and $\hat{E} = c\,(\bar{y}_{12}^2 - \bar{x}_{12}^2)\, r_{12}^{-5}$, where $c = (3/4)\,(g\,\beta)^2$ with the Bohr magneton β and the gyromagnetic ratio g. If one takes into account only spin-spin interaction the ZFS parameters are calculated as [7, 8]

$$\begin{pmatrix} D \\ E \end{pmatrix} = \Sigma_s^\sigma \Sigma_t^\pi f_{st} \begin{pmatrix} D_{st} \\ E_{st} \end{pmatrix}$$

with

$$\begin{aligned} f_{st} = {} & \Sigma_{(ik)} (C_{ik}\, a_{is}\, b_{kt})^2 \\ & + 2\,\Sigma_{(ik)}\, \Sigma_{(jl) > (ik)}\, C_{ik}\, C_{jl}\, a_{is}\, a_{js}\, b_{kt}\, b_{lt} \end{aligned}$$

and the one- and two-centre integrals D_{st} and E_{st}.

D (and analogously E) can be partitioned into a one-centre term D_1 and a two-centre term D_2:

$$\begin{aligned} D &= D_1 + D_2\,, \\ D_1 &= \Sigma_{\mathrm{A}}\, \Sigma_s^{\sigma,\mathrm{A}}\, \Sigma_t^{\pi,\mathrm{A}} f_{st}\, D_{st}^{\mathrm{AA}}\,, \\ D_2 &= \Sigma_{\mathrm{A}}\, \Sigma_s^{\sigma,\mathrm{A}}\, \Sigma_{\mathrm{B} \neq \mathrm{A}}\, \Sigma_t^{\pi,\mathrm{B}} f_{st}\, D_{st}^{\mathrm{AB}}\,, \end{aligned}$$

where Σ_{A} denotes a sum over all atoms (except hydrogen atoms whose contribution to the ZFS parameters is negligible).

The integrals D_{st} (analogous formulae are valid for E_{st}) are defined as [7, 8]

$$\begin{aligned} D_{st} &= \langle \chi_s(1)\, \chi_t(2) - \chi_t(1)\, \chi_s(2)\, |\, \hat{D}\, |\, \chi_s(1)\, \chi_t(2) \rangle \\ &:= \{\chi_s \chi_t\}_D\,. \end{aligned}$$

The one-centre integrals with respect to orbitals at atom A with Slater exponent ζ_{A} are given as [9]

$$\begin{aligned} \{2\mathrm{s}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{A})\}_D &= -\,7\,\zeta_{\mathrm{A}}^3/240\,, \\ \{2p_{\bar{x}}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{A})\}_{D,E} &= \{2p_{\bar{y}}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_{\mathrm{D}} \\ &= -\,\{2p_{\bar{y}}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_E \\ &= -\,7\,\zeta_{\mathrm{A}}^3/480\,. \end{aligned}$$

By utilizing the half-electron charge model [8–10] we derived the following formulae for the two-centre integrals with respect to σ orbitals at atom A and the π orbitals at atom B:

$$\begin{aligned} \{2s(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_D &= c\,(R_{\mathrm{AB}}^2 - 2\,d_{\mathrm{B}}'^2)\,(R_{\mathrm{AB}}^2 + d_{\mathrm{B}}'^2)^{-5/2}\,, \\ \{2s(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_E &= -\,c\,R_{\mathrm{AB}}^2\,(R_{\mathrm{AB}}^2 + d_{\mathrm{B}}'^2)^{-5/2} \cos 2\,\gamma_{\mathrm{AB}}\,, \\ \{2p_{\bar{x}}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_{D,E} &= \cos^2\gamma_{\mathrm{AB}}\, I_{D,E}^1 + \sin^2\gamma_{\mathrm{AB}}\, I_{D,E}^2\,, \\ \{2p_{\bar{y}}(\mathrm{A})\, 2p_{\bar{z}}(\mathrm{B})\}_{D,E} &= \sin^2\gamma_{\mathrm{AB}}\, I_{D,E}^1 + \cos^2\gamma_{\mathrm{AB}}\, I_{D,E}^2\,, \end{aligned}$$

$$\begin{aligned} I_D^1 = {} & (c/2)\,[((R_{\mathrm{AB}} + d_{\mathrm{A}})^2 - 2\,d_{\mathrm{B}}^2)\,((R_{\mathrm{AB}} + d_{\mathrm{A}})^2 + d_{\mathrm{B}}^2)^{-5/2} \\ & + ((R_{\mathrm{AB}} - d_{\mathrm{A}})^2 - 2\,d_{\mathrm{B}}^2)\,((R_{\mathrm{AB}} - d_{\mathrm{A}})^2 + d_{\mathrm{B}}^2)^{-5/2}]\,, \end{aligned}$$

$$I_D^2 = c\,(R_{\mathrm{AB}}^2 + d_{\mathrm{A}}^2 - 2\,d_{\mathrm{B}}^2)\,(R_{\mathrm{AB}}^2 + d_{\mathrm{A}}^2 + d_{\mathrm{B}}^2)^{-5/2}\,,$$

$$\begin{aligned} I_E^1 = {} & -\,(c/2)\,[(R_{\mathrm{AB}} + d_{\mathrm{A}})^2\,((R_{\mathrm{AB}} + d_{\mathrm{A}})^2 + d_{\mathrm{B}}^2)^{-5/2} \\ & + (R_{\mathrm{AB}} - d_{\mathrm{A}})^2\,((R_{\mathrm{AB}} - d_{\mathrm{A}})^2 \\ & + d_{\mathrm{B}}^2)^{-5/2}] \cos 2\,\gamma_{\mathrm{AB}}\,, \end{aligned}$$

$$\begin{aligned} I_E^2 = {} & c\,[(d_{\mathrm{A}}^2 - R_{\mathrm{AB}}^2) \cos 2\,\gamma_{\mathrm{AB}} \\ & + 4\,d_{\mathrm{A}}\, R_{\mathrm{AB}} \sin \gamma_{\mathrm{AB}} \cos 2\,\gamma_{\mathrm{AB}}]\,(R_{\mathrm{AB}}^2 + d_{\mathrm{A}}^2 + d_{\mathrm{B}}^2)^{-5/2} \end{aligned}$$

$$\sin \gamma_{\mathrm{AB}} = (\bar{y}_{\mathrm{B}} - \bar{y}_{\mathrm{A}})/R_{\mathrm{AB}}\,, \quad \cos \gamma_{\mathrm{AB}} = (\bar{x}_{\mathrm{B}} - \bar{x}_{\mathrm{A}})/R_{\mathrm{AB}}\,.$$

R_{AB} is the distance between atoms A and B. For $R_{\mathrm{AB}} \rightarrow 0$ the two-centre integrals become identical with the corresponding one-centre integrals. Thus the parameters d and d' are given by the equations $d_{\mathrm{A}} = [960/7.32^{1/2}]^{1/3}/\zeta_{\mathrm{A}}$ and $d'_{\mathrm{A}} = [480/7]^{1/3}/\zeta_{\mathrm{A}}$. Using the Slater exponents $\zeta = 1.59, 1.91, 2.23$ for C, N, O we obtain $d/\text{Å} = 0.76, 0.64, 0.55$, and $d'/\text{Å} = 1.36, 1.13, 0.97$.

Results and Discussion

The calculated and experimental ZFS parameters for **1–4**, **6** and **7** are collected in Table 1. For $n\pi^*$ states the magnetic and molecular axes can be attached to each other in three different ways, leading to different sets of D and E values. These are given by

$$D = (D^\circ \pm 3\,E^\circ)/2 \quad \text{and} \quad E = \pm\,(D^\circ \mp 3\,E^\circ)/2\,,$$

where D° corresponds to a $\bar{z}$ = out-of-plane molecular axis. A unique D, E pair is selected by the condition [7] $|D| > 3\,|E|$.

The calculated D value for s-tetrazine **7** is 12% larger than the experimental one. Considerably larger errors of about 40% occur for the $n\pi^*$ states of **2** and **4**. Here the $n\pi^*$ state is nearly degenerate with the lowest $\pi\pi^*$ triplet [2] whereas in **7** the first two triplet states are separated by more than 1 eV [11]. Therefore we can assume that in **2** and **4** spin-orbit coupling, which was not taken into account in our calculation of ZFS parameters, leads to a reduction of D similar as in case of some enones and benzaldehyde derivatives [12]. Also the vibronic coupling between both states [2] could influence the magnitude of the ZFS parameters of the lowest

Table 1. Calculated and experimental ZFS parameters D and E, and one- and two-centre terms D_1 and D_2 (all values in cm^{-1}), and magnetic out-of-plane axis $\bar{z}$ (see Fig. 1) for **1–4**, **6** and **7**.

Compound	Calculated values						Experimental values		
	State	$\lvert D\rvert$	$\lvert E\rvert$	$\bar{z}$	D_1	D_2	$\lvert D\rvert$	$\lvert E\rvert$	Ref.
1	$\pi\pi^*$	0.159 [a]	0 [a]				0.158	0.006	[18]
2	$n\pi^*$	0.260	0.074	x	−0.245	− 0.015	0.173	0.015	[19]
	$n\pi^*$	(0.241	0.093	z	0.275	0.035) [b]			
3	$n\pi^*$	0.496	0.064	y	0.503	− 0.006			
4	$n\pi^*$	0.467	0.040	y	0.481	− 0.014	0.331	0.007	[19]
6	$n\pi^*$	0.437	0.040 [c]	y	0.459	− 0.022	0.177	0.057	[20]
	$\pi\pi^*$	0.150−0.194 [d]		z					
7	$n\pi^*$	0.461	0.049	y	0.480	− 0.019	0.410	0.021	[11, 20]

[a] Taken from [15]. – [b] Different attachment between $(\bar{x}, \bar{y}, \bar{z})$ and (x, y, z) with $|D| < 3|E|$. – [c] Assuming the same in-plane magnetic axes as for **4**. – [d] Value for **4** taken from [16, 17].

triplet. For **3** the second triplet state with $\pi\pi^*$ nature is much higher in energy than the $n\pi^*$ one. Hence we expect that our calculated D will be only slightly larger than the experimental one which is not yet known to the best of our knowledge.

The calculated ZFS parameters E are generally less accurate than the D values. Nevertheless we see in Table 1 that the errors in $|E|$ for **2** and **4** are more than twice than those for **7**. This again is in agreement with our conclusion that spin-orbit or vibronic coupling is important in case of **2** and **4**.

The lowest triplet for **5** is an $n\pi^*$ state [2]. Further methyl substitution stabilizes the lowest $\pi\pi^*$ triplet, and so in **8** the lowest triplet has $\pi\pi^*$ nature [2]. The comparison between the experimental D value for **6** and those calculated for the $n\pi^*$ and $\pi\pi^*$ states reveals that the lowest triplet of **6** should be a $\pi\pi^*$ state. This is in agreement with our CNDO/S calculations, which show that 2,5-methyl substitution as in **6** lowers the $\pi\pi^*$ state more than the 2,6-methyl substitution as in **5**, although CNDO/S underestimates the effect of a methyl group [13]. Thus pyrazine **4** represents an interesting system where either an $n\pi^*$ or a $\pi\pi^*$ lowest triplet state can be realized by different methyl substitution, leading to largely differing ZFS parameters.

The magnetic $\bar{z}$ axis is in-plane with all compounds except **2** where, however, another attachment of the magnetic and molecular axes also leads to an in-plane $\bar{z}$ axis. Since both attachments do not differ significantly in their D and E values, it is impossible to decide upon the magnetic axes in **2** due to the inaccuracy of the calculated E values. An in-plane $\bar{z}$ axis was also evidenced for the $n\pi^*$ triplet of thiouracil [14].

The one-centre terms D_1 are numerically much larger than the two-centre terms D_2 in case of all $n\pi^*$ states. Furthermore D_1 and D_2 exhibit opposite sign if $\bar{z}$ is in-plane, and so D_2 reduces $|D|$. The $n\pi^*$ triplet state of **2**, **4** and **7** is dominated by an excitation $\sigma_{\mathrm{h}} \rightarrow \pi_{\mathrm{l}}^*$ from the highest occupied n orbital σ_{h} to the lowest virtual orbital π_{l}^*. Neglecting the other small terms in the wave function, D_1 is given by the formula

$$D_1 = \Sigma_{\mathrm{A}} \Sigma_s^{\sigma,\mathrm{A}} \Sigma_t^{\pi,\mathrm{A}} a_{\mathrm{h}s}^2 b_{\mathrm{l}t}^2 D_{st}^{\mathrm{AA}} .$$

Thus we obtain significant contributions to D_1 only if σ_{h} and π_{l}^* exhibit large values for $a_{\mathrm{h}s}^2$ and $b_{\mathrm{l}t}^2$ at

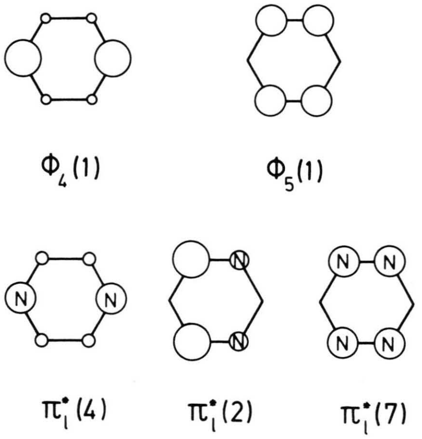

Fig. 2. Schematical representation of squared coefficients $b_{\mathrm{l}t}^2$ of lowest virtual π orbitals Φ_4 and Φ_5 of **1** and π_{l}^* of **2**, **4** and **7**.

the same atoms. Since σ_h is mainly localized at the nitrogen atoms, a numerically large D_1 requires numerically large coefficients of π_1^* also at the nitrogen atoms. In the studied compounds π_1^* is related to the degenerated orbitals Φ_4 and Φ_5 of benzene **1**, see Figure 2. Due to their nodal properties and the nitrogen pattern in **2**, **4** and **7**, π_1^* of **4** is derived from Φ_4 (**1**) whereas π_1^* of **2** and **7** is related to Φ_5 (**1**). Therefore π_1^* of all these compounds exhibits the largest coefficients b_{1t}^2 just at the nitrogen atoms causing the numerically large D_1 and hence D values. The differences in the b_{1t}^2 values also rationalize the larger D values of **4** and **7** with respect to **2**. Much smaller D values would have been obtained if π_1^* of **4** would be related to Φ_5 (**1**) and π_1^* of **2** and **7** to Φ_4 (**1**). However, the corresponding $n\pi^*$ states are much higher in energy.

A more detailed study of the triplet state and ZFS parameters of s-tetrazine **7** and some derivatives will be published elsewhere [11].

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