Magnetic Circular Dichroism (MCD) of Four-membered Rings with four π-Electrons

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On the basis of the perimeter model for 4*N*-electron [*n*]annulenes, algebraic expressions for the B values of perturbed four-membered rings ($n = 4$) with four π electrons ($N = 1$) have been derived. The results are used to interpret the MCD spectrum of 1,3-di-*tert*-butyl-2,4-diethyl-1,3,2,4-diazadiboretidine.

Key words: 4*N*-electron [*n*]annulenes; Perimeter Model; Magnetic Circular Dichroism.

1. Introduction

Michl extended the perimeter model of cyclic π-electron systems, which was originally developed by Platt [1] and Moffit [2], to the interpretation of absolute signs in magnetic circular dichroism (MCD) [3–5]. A set of rules was derived by him that accounted for a large number of MCD signs in the spectra of all kinds of aromatic π systems, i.e. those derived from a $(4N+2)$-electron perimeter.

More recently the model was also applied to 4*N*-electron perimeters [6–9]. In the first paper of this series, perfect biradicals at their most symmetrical D_{nh} geometries were treated. Especially interesting for the present work are the results for the 4-electron [4]annulene with D_{4h} symmetry.

In the following papers Michl and coworkers treated perturbed 4*N*-electron [*n*]annulenes with $N \geq 2$ and $n \geq 7$ [7–9]. Tractable analytical expressions for the B values of these molecules could be obtained if at least a symmetry plane perpendicular to the molecular plane was present and when the number of configurations which were used to study the parent perimeter was reduced.

To interpret the MCD-spectrum of a diazadiboretidine derivative, which was recently measured by us, we derived formulas for the B values of perturbed four-membered rings. The results are rather different from those for $N \geq 2$ and $n \geq 7$ because the number of parameters is smaller. In contrast to Michl et al. we therefore needed not to reduce the number of basis functions to get tractable expressions. As is the case for the investigated molecule we assume one symmetry plane perpendicular to the molecular plane and passing through diagonally opposite atoms.

2. Theory

In the perimeter model the four atoms of the 4-electron [4]annulene are located on a circle (Figure 1).

The complex molecular orbitals of the four-membered ring are

$$\psi_k = \frac{1}{2} \sum_{\mu=0}^{3} e^{\frac{\pi i k \mu}{2}} \chi_\mu, (k = 0, \pm 1, 2). \tag{1}$$

The χ_μ are orbitals which have been constructed from nonorthogonal atomic orbitals $2p_{z\mu}$ by an explicit Löwdin orthogonalization [3]. In contrast to the general case, the HOMO (ψ_0) and the LUMO ($\psi_{\pm 2}$) are not degenerate. The one electron energies are $E(\mathrm{HO})$ for the HOMO, $E(\mathrm{LO})$ for the LUMO and $E(\mathrm{SO})$ for the SOMO. A perturbation is described in this model by five parameters h_D, l_D, s_D, Δs and the phase angle σ:

$$h_D = \langle \psi_0 | \hat{a} | \psi_0 \rangle, \tag{2}$$

$$l_D = \langle \psi_{+2} | \hat{a} | \psi_{+2} \rangle, \tag{3}$$

$$s_D = \langle \psi_{+1} | \hat{a} | \psi_{+1} \rangle = \langle \psi_{-1} | \hat{a} | \psi_{-1} \rangle, \tag{4}$$

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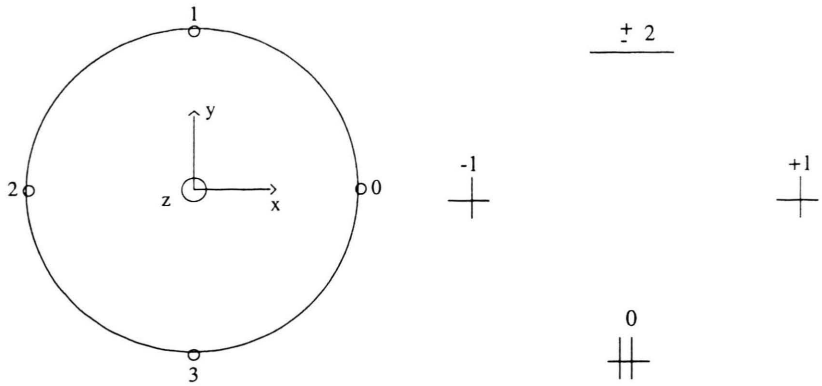

Fig. 1. Left, the coordinate system and the assumed geometry of a regular [4]annulene perimeter. Right, the electron occupancy of the unperturbed ground state. The complex orbitals are labeled by the subscript k of the irreducible representation ε_k in the C_4 symmetry group.

$$\frac{\Delta s}{2} e^{i\sigma} = \langle \psi_1 | \hat{a} | \psi_{-1} \rangle, (\Delta s \geq 0, 0 \leq \sigma \leq 2\pi). \tag{5}$$

$\hat{a}$ is a one electron operator. Its matrix elements in the chosen basis are

$$a_{ij} = \langle \chi_i | \hat{a} | \chi_j \rangle. \tag{6}$$

The symmetry plane Σ, which shall be present and which is perpendicular to the molecular plane, shall pass through the atoms 0 and 2 (Figure 1). As is shown in [8] and [9], the phase angle σ can then only have the value 0 or π (if Σ passes through bonds, σ can only be $\pm\frac{\pi}{2}$, as is easily seen by looking at the integral $\langle \psi_{+1} | \hat{a}\hat{\Sigma} | \psi_{+1} \rangle$ and recognizing that $\hat{a}$ and $\hat{\Sigma}$ commute).

In the following CI calculation, two-electron repulsion integrals

$$\int\int \psi_r^*(1)\, \psi_s(1) \left(\frac{e^2}{r_{12}}\right) \psi_t^*(2)\, \psi_u(2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \tag{7}$$

have to be evaluated. For symmetry reasons they are nonzero only if $s - r = t - u \bmod 4$. They are denoted by $[l]$, where $l = \min(|s-r|, 4-|s-r|)$ [6]. For the four-membered ring the only nonvanishing integrals are the coulombic repulsion integral [0] and the two exchange integrals [1] and [2] (for details see [6]). Following Michl and coworkers [7–9] we will use for the perturbed systems real molecular orbitals:

$$s_+ = \frac{1}{\sqrt{2}} \left\{ e^{\frac{i\sigma}{2}} \psi_{+1} + e^{\frac{-i\sigma}{2}} \psi_{-1} \right\} \tag{8}$$

and

$$s_- = \frac{1}{i\sqrt{2}} \left\{ e^{\frac{i\sigma}{2}} \psi_{+1} - e^{\frac{-i\sigma}{2}} \psi_{-1} \right\}. \tag{9}$$

The HOMO $h \equiv \psi_0$ and the LUMO $l \equiv \psi_2$ are already real. The one-electron energies of these orbitals are

$$\varepsilon(l) = E(\mathrm{LO}) + l_\mathrm{D}, \tag{10}$$

$$\varepsilon(s_+) = E(\mathrm{SO}) + s_\mathrm{D} + \frac{\Delta s}{2}, \tag{11}$$

$$\varepsilon(s_-) = E(\mathrm{SO}) + s_\mathrm{D} - \frac{\Delta s}{2}, \tag{12}$$

$$\varepsilon(h) = E(\mathrm{HO}) + h_\mathrm{D}. \tag{13}$$

With these real orbitals we form seven CI basis functions [7–9]:

$$\psi_\mathrm{R} = |h\bar{h}s_-\bar{s}_-|, \tag{14}$$

$$\psi_{s_-}^{s_+} = \left(\frac{1}{\sqrt{2}}\right)\left\{|h\bar{h}s_-\bar{s}_+| + |h\bar{h}s_+\bar{s}_-|\right\}, \tag{15}$$

$$\psi_{s_-s_-}^{s_+s_+} = |h\bar{h}s_+\bar{s}_+|, \tag{16}$$

$$\psi_h^{s_+} = \left(\frac{1}{\sqrt{2}}\right)\left\{|s_-\bar{s}_-h\bar{s}_+| + |s_-\bar{s}_-s_+\bar{h}|\right\}, \tag{17}$$

$$\psi_{s_-}^{l} = \left(\frac{1}{\sqrt{2}}\right)\left\{|h\bar{h}s_-\bar{l}| + |h\bar{h}l\bar{s}_-|\right\}, \tag{18}$$

$$\psi_{s_-h}^{s_+s_+} = \left(\frac{1}{\sqrt{2}}\right)\left\{|s_+\bar{s}_+h\bar{s}_-| + |s_+\bar{s}_+s_-\bar{h}|\right\}, \tag{19}$$

$$\psi_{s_-s_-}^{s_+l} = \left(\frac{1}{\sqrt{2}}\right)\left\{|h\bar{h}s_+\bar{l}| + |h\bar{h}l\bar{s}_+|\right\} \tag{20}$$

and obtain the following CI matrix:

$$
\begin{array}{cccccccc}
 & \psi_{\mathrm{R}} & \psi_{s_-}^{s_+} & \psi_{s_-s_-}^{s_+s_+} & \psi_h^{s_+} & \psi_{s_-}^{l} & \psi_{s_-h}^{s_+s_+} & \psi_{s_-s_-}^{s_+l} \\
\psi_{\mathrm{R}} & E(\psi_{\mathrm{R}}) & \frac{-[2]}{\sqrt{2}}\sin 2\sigma & \frac{[2]}{2}(1-\cos 2\sigma) & 0 & 0 & 0 & 0 \\
\psi_{s_-}^{s_+} & \frac{-[2]}{\sqrt{2}}\sin 2\sigma & E(\psi_{s_-}^{s_+}) & \frac{[2]}{\sqrt{2}}\sin 2\sigma & 0 & 0 & 0 & 0 \\
\psi_{s_-s_-}^{s_+s_+} & \frac{[2]}{2}(1-\cos 2\sigma) & \frac{[2]}{\sqrt{2}}\sin 2\sigma & E(\psi_{s_-s_-}^{s_+s_+}) & 0 & 0 & 0 & 0 \\
\psi_h^{s_+} & 0 & 0 & 0 & E(\psi_h^{s_+}) & [1]\sin\sigma & 0 & [1]\cos\sigma \\
\psi_{s_-}^{l} & 0 & 0 & 0 & [1]\sin\sigma & E(\psi_{s_-}^{l}) & -[1]\cos\sigma & 0 \\
\psi_{s_-h}^{s_+s_+} & 0 & 0 & 0 & 0 & -[1]\cos\sigma & E(\psi_{s_-h}^{s_+s_+}) & [1]\sin\sigma \\
\psi_{s_-s_-}^{s_+l} & 0 & 0 & 0 & [1]\cos\sigma & 0 & [1]\sin\sigma & E(\psi_{s_-s_-}^{s_+l})
\end{array} \tag{21}
$$

with

$$E(\psi_{\mathrm{R}}) = -\Delta s + \frac{[2]}{2}(1+\cos 2\sigma), \tag{22}$$

$$E(\psi_{s_-}^{s_+}) = -[2]\cos 2\sigma, \tag{23}$$

$$E(\psi_{s_-s_-}^{s_+s_+}) = \Delta s + \frac{[2]}{2}(1+\cos 2\sigma), \tag{24}$$

$$E(\psi_h^{s_+}) = c + \frac{\Delta HSL}{4} - \frac{\Delta s}{2} + \frac{l_{\mathrm{D}} - h_{\mathrm{D}}}{2} + [1], \tag{25}$$

$$E(\psi_{s_-}^{l}) = c - \frac{\Delta HSL}{4} - \frac{\Delta s}{2} + \frac{l_{\mathrm{D}} - h_{\mathrm{D}}}{2} + [1], \tag{26}$$

$$E(\psi_{s_-h}^{s_+s_+}) = c + \frac{\Delta HSL}{4} + \frac{\Delta s}{2} + \frac{l_{\mathrm{D}} - h_{\mathrm{D}}}{2} + [1], \tag{27}$$

$$E(\psi_{s_-s_-}^{s_+l}) = c - \frac{\Delta HSL}{4} + \frac{\Delta s}{2} + \frac{l_{\mathrm{D}} - h_{\mathrm{D}}}{2} + [1]. \tag{28}$$

The quantitiy c is related to the one-electron energy difference of the HO and LO levels and is defined by

$$c = \frac{E(\mathrm{LO}) - E(\mathrm{HO})}{2} + [1] - [2]. \tag{29}$$

As will be seen later, the sign of the quantity

$$\begin{aligned}\Delta HSL &= 2(2E(\mathrm{SO}) + 2s_{\mathrm{D}} - E(\mathrm{HO}) \\ &\quad - h_{\mathrm{D}} - E(\mathrm{LO}) - l_{\mathrm{D}}) \\ &= 4s_{\mathrm{D}} - 2h_{\mathrm{D}} - 2l_{\mathrm{D}}\end{aligned} \tag{30}$$

is decisive in predicting the signs of the B values. From all the diagonal elements, $E = 2h_{\mathrm{D}} + 2s_{\mathrm{D}} + 2E(\mathrm{HO}) + 2E(\mathrm{SO}) + 6[0] - 2[1]$ has been substracted.

The CI matrix is blocked into a 3×3 and a 4×4 matrix. The 3×3 block is diagonal for $\sigma = 0$ or π. The solution of the 4×4 block is also easily done because for $\sigma = 0$ or π it decomposes into two 2×2 matrices.

Whether ψ_{R} or ψ_{-s}^{+s} is the ground state ψ_{G} will depend on whether $\Delta s > 2[2]$ ($\psi_{\mathrm{G}} = \psi_{\mathrm{R}}$) or $\Delta s < 2[2]$ ($\psi_{\mathrm{G}} = \psi_{s_-}^{s+}$). For the parent molecule [6], $\psi_{s_-}^{s+}$ is the ground state. For the perturbed systems we will look here at both cases. Table 1 gives the energies and wave functions for the 3×3 block of the CI matrix. Table 2 shows these properties for the four higher excited states for $\sigma = 0$ and $\sigma = \pi$.

If the ground state is not degenerate and if one ignores vibrational fine structure, the dipole strength ($D_{\mathrm{G}\to\mathrm{F}}$) and the B value ($B_{\mathrm{G}\to\mathrm{F}}$) of a transition from the ground state

Table 1. Energies and wave functions of the 3×3 matrix for $\sigma = 0$ and π.

Energy[a]	Wave function
$-[2]$	$\psi_{s_-}^{s+}$
$-\Delta s + [2]$	ψ_{R}
$\Delta s + [2]$	$\psi_{s_-s_-}^{s+s+}$

[a] The order of the two lowest energies depend on whether $\Delta s >$ or $< 2[2]$.

Table 2. Energies and wave functions of the 4×4 matrix for $\sigma = 0$ and π.

Energy[a]	Wave function[b]	
	$\sigma = 0$	$\sigma = \pi$
$A + \sqrt{[1]^2 + (\Delta s/2 + \Delta HSL/4)^2}$	$\psi_4 = \sin\beta\psi^{s_+s_+}_{s\_h} - \cos\beta\psi^{l}_{s_-}$	$\psi_3 = \cos\beta\psi^{s_+s_+}_{s\_h} + \sin\beta\psi^{l}_{s_-}$
$A + \sqrt{[1]^2 + (\Delta s/2 - \Delta HSL/4)^2}$	$\psi_1 = \cos\alpha\psi^{s_+}_{h} + \sin\alpha\psi^{s_+l}_{s\_s_-}$	$\psi_2 = \sin\alpha\psi^{s_+}_{h} - \cos\alpha\psi^{s_+l}_{s\_s_-}$
$A - \sqrt{[1]^2 + (\Delta s/2 - \Delta HSL/4)^2}$	$\psi_2 = \sin\alpha\psi^{s_+}_{h} - \cos\alpha\psi^{s_+l}_{s\_s_-}$	$\psi_1 = \cos\alpha\psi^{s_+}_{h} + \sin\alpha\psi^{s_+l}_{s\_s_-}$
$A - \sqrt{[1]^2 + (\Delta s/2 + \Delta HSL/4)^2}$	$\psi_3 = \cos\beta\psi^{s_+s_+}_{s\_h} + \sin\beta\psi^{l}_{s_-}$	$\psi_4 = \sin\beta\psi^{s_+s_+}_{s\_h} - \cos\beta\psi^{l}_{s_-}$

[a] $A = c + [1] + (l_D - h_D)/2$

[b] $\alpha = (1/2)\tan^{-1}\{-[1]B/(\Delta s/2 - \Delta HSL/4)\}$; $\beta = (1/2)\tan^{-1}\{-[1]B/(\Delta s/2 + \Delta HSL/4)\}$; $B = \delta_{0\sigma} - \delta_{\pi\sigma}$; $\delta_{\omega,\sigma}$ equals 1 if $\sigma = \omega$, and 0 otherwise.

ψ_G to a final state ψ_F can be calculated, from the expressions [10]

$$D_{G\to F} = \left|\left\langle G\middle|\hat{M}\middle|F\right\rangle\right|^2 \tag{31}$$

and

$$B_{G\to F} = \sum_{I\neq F} B^F_{I,F} + \sum_{I\neq G} B^F_{I,G}, \tag{32}$$

where

$$B^F_{I,F} = \mathrm{Im}\langle F|\hat{\mathcal{M}}|I\rangle\cdot\left\langle G\middle|\hat{M}\middle|F\right\rangle \times\left\langle I\middle|\hat{M}\middle|G\right\rangle/(E_I - E_F) \tag{33}$$

and

$$B^F_{I,G} = \mathrm{Im}\langle I|\hat{\mathcal{M}}|G\rangle\cdot\left\langle G\middle|\hat{M}\middle|F\right\rangle \times\left\langle F\middle|\hat{M}\middle|I\right\rangle/(E_I - E_G). \tag{34}$$

In these expressions, Im stands for "imaginary part of". The summation runs over all electronic states besides F resp. G. E_K is the energy of the K-th electronic state. $\hat{M} = \Sigma_i \hat{m}_i$ is the total electric dipole moment operator and $\hat{\mathcal{M}} = \Sigma_i \hat{\mu}_i$ is the total magnetic dipole moment operator, where the summation is over the four π-electrons.

The only nonvanishing matrix elements of the electric $\hat{m}$ and magnetic $\hat{\mu}$ one-electron dipole moment operators in the complex MO basis are [3]

$$\left\langle\psi_k\middle|\hat{m}\middle|\psi_{k\pm1}\right\rangle = m(n,|2k\pm1|)(\boldsymbol{x}\pm i\boldsymbol{y})/\sqrt{2} \tag{35}$$

and

$$\left\langle\psi_k\middle|\hat{\mu}\middle|\psi_k\right\rangle = \mu(n,k)\,\boldsymbol{z}. \tag{36}$$

Analytical expressions for the negative quantities $m(n, |2k\pm1|)$ and $\mu(n,k)$ are given in [3]. For the nonvanishing matrix elements of $\hat{M}$ and $\hat{\mathcal{M}}$ between the CI basis functions one then gets

$$\left\langle\psi_R\middle|\hat{M}\middle|\psi^l_{s_-}\right\rangle = \sqrt{2}\,m(4,3)\left(\boldsymbol{x}\sin\frac{\sigma}{2} - \boldsymbol{y}\cos\frac{\sigma}{2}\right), \tag{37}$$

$$\left\langle\psi_R\middle|\hat{M}\middle|\psi^{s_+}_{h}\right\rangle = \sqrt{2}\,m(4,1)\left(\boldsymbol{x}\cos\frac{\sigma}{2} - \boldsymbol{y}\sin\frac{\sigma}{2}\right), \tag{38}$$

$$\left\langle\psi^{s_+s_+}_{s\_s_-}\middle|\hat{M}\middle|\psi^{s_+s_+}_{s\_h}\right\rangle = \sqrt{2}\,m(4,1)\left(\boldsymbol{x}\sin\frac{\sigma}{2} + \boldsymbol{y}\cos\frac{\sigma}{2}\right) \tag{39}$$

$$\left\langle\psi^{s_+s_+}_{s\_s_-}\middle|\hat{M}\middle|\psi^{s_+l}_{s\_s_-}\right\rangle = \sqrt{2}\,m(4,3)\left(\boldsymbol{x}\cos\frac{\sigma}{2} + \boldsymbol{y}\sin\frac{\sigma}{2}\right) \tag{40}$$

$$\left\langle\psi^{s_+}_{s_-}\middle|\hat{M}\middle|\psi^{l}_{s_-}\right\rangle = m(4,3)\left(\boldsymbol{x}\cos\frac{\sigma}{2} + \boldsymbol{y}\sin\frac{\sigma}{2}\right) \tag{41}$$

$$\left\langle\psi^{s_+}_{s_-}\middle|\hat{M}\middle|\psi^{s_+}_{h}\right\rangle = -\,m(4,1)\left(\boldsymbol{x}\sin\frac{\sigma}{2} + \boldsymbol{y}\cos\frac{\sigma}{2}\right) \tag{42}$$

$$\left\langle\psi^{s_+}_{s_-}\middle|\hat{M}\middle|\psi^{s_+s_+}_{s\_h}\right\rangle = -\,m(4,1)\left(\boldsymbol{x}\cos\frac{\sigma}{2} - \boldsymbol{y}\sin\frac{\sigma}{2}\right) \tag{43}$$

$$\left\langle\psi^{s_+}_{s_-}\middle|\hat{M}\middle|\psi^{s_+l}_{s\_s_-}\right\rangle = m(4,3)\left(\boldsymbol{x}\sin\frac{\sigma}{2} - \boldsymbol{y}\cos\frac{\sigma}{2}\right), \tag{44}$$

Table 3. Dipole strengths D and B terms for transitions from the ground state $\psi_G = \psi_{s_-}^{s+}$ $(\Delta s < 2[2])$

Wave function	$D^{a, b}$	$B^{a, b}$
$\psi_{s_-}^{s+}$	–	–
ψ_R	0	0
$\psi_{s_-s_-}^{s+s+}$	0	0
ψ_1	$m^2(\cos\alpha \pm \sin\alpha)^2$	$2\mu m^2(\cos\alpha \pm \sin\alpha)\left(\frac{\cos\alpha}{-\Delta s + 2[2]} \mp \frac{\sin\alpha}{\Delta s + 2[2]}\right)$ $+\mu\cos(\alpha-\beta)\, m^2(\cos\alpha \pm \sin\alpha)(\cos\beta \mp \sin\beta)/(E_3 - E_1)$ $\mp\mu\sin(\alpha-\beta)\, m^2(\pm\cos\alpha + \sin\alpha)(\pm\cos\beta + \sin\beta)/(E_4 - E_1)$
ψ_2	$m^2(\cos\alpha \mp \sin\alpha)^2$	$2\mu m^2(\sin\alpha \mp \cos\alpha)\left(\frac{\sin\alpha}{-\Delta s + 2[2]} \pm \frac{\cos\alpha}{\Delta s + 2[2]}\right)$ $+\mu\sin(\alpha-\beta)\, m^2(\sin\alpha \mp \cos\alpha)(\sin\beta \mp \cos\beta)/(E_3 - E_2)$ $+\mu\cos(\alpha-\beta)\, m^2(\sin\alpha \mp \cos\alpha)(\sin\beta \pm \cos\beta)/(E_4 - E_2)$
ψ_3	$m^2(\cos\beta \mp \sin\beta)^2$	$2\mu m^2(\cos\beta \mp \sin\beta)\left(\frac{\pm\sin\beta}{-\Delta s + 2[2]} + \frac{\cos\beta}{\Delta s + 2[2]}\right)$ $-\mu\cos(\alpha-\beta)\, m^2(\cos\alpha \pm \sin\alpha)(\cos\beta \mp \sin\beta)/(E_3 - E_1)$ $-\mu\sin(\alpha-\beta)\, m^2(\sin\alpha \mp \cos\alpha)(\sin\beta \mp \cos\beta)/(E_3 - E_2)$
ψ_4	$m^2(\cos\beta \pm \sin\beta)^2$	$2\mu m^2(\pm\cos\beta + \sin\beta)\left(\frac{\mp\cos\beta}{-\Delta s + 2[2]} + \frac{\sin\beta}{\Delta s + 2[2]}\right)$ $\pm\mu\sin(\alpha-\beta)\, m^2(\pm\cos\alpha + \sin\alpha)(\pm\cos\beta + \sin\beta)/(E_4 - E_1)$ $-\mu\cos(\alpha-\beta)\, m^2(\sin\alpha \mp \cos\alpha)(\sin\beta \pm \cos\beta)/(E_4 - E_2)$

[a] $m \equiv m(4, 1) = m(4, 3)$; $\mu \equiv \mu(4, 1)$; [b] The upper signs are for $\sigma = 0$ and the lower signs for $\sigma = \pi$.

and

$$\langle \psi_R | \hat{\mathcal{M}} | \psi_{s_-}^{s_+} \rangle = \langle \psi_{s_-}^{s_+} | \hat{\mathcal{M}} | \psi_{s_-s_-}^{s_+s_+} \rangle iz\sqrt{2}\,\mu(4,1), \quad (45)$$

$$\langle \psi_{s_-}^{l} | \hat{\mathcal{M}} | \psi_{s_-s_-}^{s_+l} \rangle = \langle \psi_{s_-h}^{s_+s_+} | \hat{\mathcal{M}} | \psi_{h}^{s_+} \rangle = iz\,\mu(4,1). \quad (46)$$

With these transition moment integrals and the wave functions in Table 1 and 2 one can now easily evaluate the dipole strengths and B values for the different transitions from the ground state. In Table 3 these properties are given for $\psi_G = \psi_{s_-}^{s+}$ and in Table 4 for $\psi_G = \psi_R$. The mixing angles α and β are

$$\alpha = \frac{1}{2}\tan^{-1}\left\{\frac{-[1]B}{\Delta s/2 - \Delta HSL/4}\right\} \quad (47)$$

and

$$\beta = \frac{1}{2}\tan^{-1}\left\{\frac{-[1]B}{\Delta s/2 + \Delta HSL/4}\right\} \quad (48)$$

Table 4. Dipole strengths D and B terms for transitions from the ground state $\psi_G = \psi_R$ $(\Delta s > 2[2])$.

Wave function	D^{a}	$B^{a, b}$
ψ_R	–	–
$\psi_{s_-}^{s+}$	0	0
$\psi_{s_-s_-}^{s+s+}$	0	0
ψ_1	$2m^2\cos^2\alpha$	$2\mu m^2\cos\alpha(\cos\alpha \pm \sin\alpha)/(\Delta s - 2[2])$ $\pm\mu m^2\cos(\alpha-\beta)\cdot 2\cos\alpha\sin\beta/(E_3 - E_1)$ $\pm\mu m^2\sin(\alpha-\beta)\cdot 2\cos\alpha\cos\beta/(E_4 - E_1)$
ψ_2	$2m^2\sin^2\alpha$	$2\mu m^2\sin\alpha(\sin\alpha \mp \cos\alpha)/(\Delta s - 2[2])$ $\pm\mu m^2\sin(\alpha-\beta)\, 2\sin\alpha\sin\beta/(E_3 - E_2)$ $\mp\mu m^2\cos(\alpha-\beta)\, 2\sin\alpha\cos\beta/(E_4 - E_2)$
ψ_3	$2m^2\sin^2\beta$	$2\mu m^2\sin\beta(\pm\cos\beta - \sin\beta)/(\Delta s - 2[2])$ $\mp\mu m^2\sin(\alpha-\beta)\cdot 2\sin\alpha\sin\beta/(E_3 - E_2)$ $\mp\mu m^2\cos(\alpha-\beta)\cdot 2\cos\alpha\sin\beta/(E_3 - E_1)$
ψ_4	$2m^2\cos^2\beta$	$2\mu m^2\cos\beta(\mp\sin\beta - \cos\beta)/(\Delta s - 2[2])$ $\mp\mu m^2\sin(\alpha-\beta)\cdot 2\cos\alpha\cos\beta/(E_4 - E_1)$ $\pm\mu m^2\cos(\alpha-\beta)\cdot 2\sin\alpha\cos\beta/(E_4 - E_2)$

[a] $m \equiv m(4, 1) = m(4, 3)$; $\mu \equiv \mu(4, 1)$; [b] The upper signs are for $\sigma = 0$ and the lower signs for $\sigma = \pi$.

Table 5. Energies and wave functions of the 3×3 matrix for $\sigma = \pm\frac{\pi}{2}$.

Energy	Wave function[a]
$-\sqrt{[2]^2 + (\Delta s)^2}$	$\psi_G = \sin\omega\psi_R - \cos\omega\psi^{s_+s_+}_{s_-s_-}$
$[2]$	$\psi_S = \psi^{s_+}_{s_-}$
$+\sqrt{[2]^2 + (\Delta s)^2}$	$\psi_D = \cos\omega\psi_R + \sin\omega\psi^{s_+s_+}_{s_-s_-}$

[a] The mixing angle ω is $\frac{1}{2}\tan^{-1}(-[2]/\Delta s)$.

where $B \equiv \delta_{0\sigma} - \delta_{\pi\sigma}$. $\delta_{\omega,\sigma}$ equals 1 if $\sigma = \omega$, and 0 otherwise.

For completeness we give in Tables 5, 6, and 7 also the results for the case $\sigma = \pm\frac{\pi}{2}$, in which the perpendicular symmetry plane passes through bonds.

3. Results

For both cases ($\psi_G = \psi_R$ and $\psi_G = \psi^{s_+}_{s_-}$) the dipole strengths and therefore also the B values of transitions

Table 6. Energies and wave functions of the 4×4 matrix for $\sigma = \pm\frac{\pi}{2}$.

Energy[a]	Wave function[b] $\sigma = \frac{\pi}{2}$	Wave function[b] $\sigma = -\frac{\pi}{2}$
$A + \frac{\Delta s}{2} + \sqrt{[1]^2 + (\Delta HSL/4)^2}$	$\psi_4 = \cos\alpha\psi^{s_+s_+}_{s_-h} + \sin\alpha\psi^{s_+l}_{s_-s_-}$	$\psi_3 = \sin\alpha\psi^{s_+s_+}_{s_-h} - \cos\alpha\psi^{s_+l}_{s_-s_-}$
$A + \frac{\Delta s}{2} - \sqrt{[1]^2 + (\Delta HSL/4)^2}$	$\psi_3 = \sin\alpha\psi^{s_+s_+}_{s_-h} - \cos\alpha\psi^{s_+l}_{s_-s_-}$	$\psi_4 = \cos\alpha\psi^{s_+s_+}_{s_-h} + \sin\alpha\psi^{s_+l}_{s_-s_-}$
$A - \frac{\Delta s}{2} + \sqrt{[1]^2 + (\Delta HSL/4)^2}$	$\psi_2 = \cos\alpha\psi^{s_+}_{h} + \sin\alpha\psi^{l}_{s_-}$	$\psi_1 = \sin\alpha\psi^{s_+}_{h} - \cos\alpha\psi^{l}_{s_-}$
$A - \frac{\Delta s}{2} - \sqrt{[1]^2 + (\Delta HSL/4)^2}$	$\psi_1 = \sin\alpha\psi^{s_+}_{h} - \cos\alpha\psi^{l}_{s_-}$	$\psi_2 = \cos\alpha\psi^{s_+}_{h} + \sin\alpha\psi^{l}_{s_-}$

[a] $A = c + [1] + (l_D - h_D)/2$;
[b] $\alpha = (1/2)\tan^{-1}\{4B[1]/\Delta HSL\}$; $B = \delta_{\sigma,\frac{\pi}{2}} - \delta_{\sigma,\frac{-\pi}{2}}$; $\delta_{\sigma,\omega}$ equals 1 if $\sigma = \omega$, and 0 otherwise.

Table 7. Dipole strengths D and B terms for transitions from the ground state ψ_G, $\left(\sigma = \pm\frac{\pi}{2}\right)$.

Wave function	D[a, b]	B[a, b]
ψ_G	–	–
ψ_S	0	0
ψ_D	0	0
ψ_1	$2\sin^2\omega m^2(1 \mp \sin 2\alpha)$	$-2\mu m^2\sin\omega(\sin\omega + \cos\omega)\cos 2\alpha/(E_S - E_G)$ $-2\mu m^2\sin\omega\cos\omega\cos 2\alpha(1 \mp \sin 2\alpha)/(E_3 - E_1)$ $\mp 2\mu m^2\sin\omega\cos\omega\sin 2\alpha/(E_4 - E_1)$
ψ_2	$2\sin^2\omega m^2(1 \pm \sin 2\alpha)$	$2\mu m^2\sin\omega(\sin\omega + \cos\omega)\cos 2\alpha/(E_S - E_G)$ $\mp 2\mu m^2\sin\omega\cos\omega\sin 2\alpha/(E_3 - E_2)$ $+2\mu m^2\sin\omega\cos\omega\cos 2\alpha(1 \pm \sin 2\alpha)/(E_4 - E_2)$
ψ_3	$2\cos^2\omega m^2(1 \mp \sin 2\alpha)$	$-2\mu m^2\cos\omega(\sin\omega + \cos\omega)\cos 2\alpha/(E_S - E_G)$ $+2\mu m^2\sin\omega\cos\omega\cos 2\alpha(1 \mp \sin 2\alpha)/(E_3 - E_1)$ $\pm 2\mu m^2\sin\omega\cos\omega\sin 2\alpha/(E_3 - E_2)$
ψ_4	$2\cos^2\omega m^2(1 \pm \sin 2\alpha)$	$2\mu m^2\cos\omega(\sin\omega + \cos\omega)\cos 2\alpha/(E_S - E_G)$ $\pm 2\mu m^2\sin\omega\cos\omega\sin 2\alpha/(E_4 - E_1)$ $-2\mu m^2\sin\omega\cos\omega\cos 2\alpha(1 \pm \sin 2\alpha)/(E_4 - E_2)$

[a] $m \equiv m(4,1) = m(4,3)$; $\mu \equiv \mu(4,1)$; [b] The upper signs are for $\sigma = \frac{\pi}{2}$ and the lower signs for $\sigma = \frac{-\pi}{2}$.

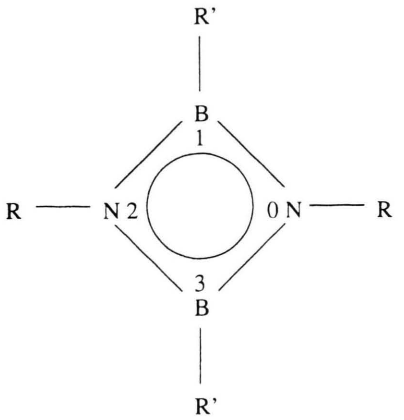

Fig. 2. 1,3-di-*tert*-butyl-2,4-diethyl-1,3,2,4-diazadiboretidine ($R' = Et$, $R = tBu$) [11].

from the ground state into one of the other two states resulting from the 3×3 block should be zero and can possibly get some intensity if vibronic coupling is taken into account. This result is in accordance with what Michl and coworkers discussed already in the general case ($N \geq 2$ and $n \geq 7$) for ($\psi_G = \psi_R$ [7–9].

Let us first look at the unperturbed parent four-membered ring with $\Delta s = l_D = h_D = s_D = 0$ ([6], Table 4). Because $\Delta s = 0$, the results have to be independent of the value of the phase angle σ. Let us take $\sigma = 0$. The mixing angles α and β are then both $\frac{\pi}{4}$ because $\Delta s = \Delta HSL = 0$ (see (47) and (48)). The lower one, to which the wave functions ψ_2 and ψ_3 belong, has the energy c and the higher one, with the functions ψ_1 and ψ_4, the energy $c + 2[1]$. These are the energies of the $E_{1u}^{-}(c)$ and of the E_{1u}^{+} states ($c + 2[1]$) of the parent ring [6].

From Table 3 one recognizes that the dipole strength for the transition into the (ψ_1, ψ_4) state is $4\,m^2$, whereas the dipole strength to the lower (ψ_2, ψ_3) state is 0. The B values for both states are 0.

These findings are identical with those of Michl et al. for the parent ring [6]. We will now try to interpret the MCD spectrum of 1,3-di-*tert*-butyl-2,4-diethyl-1,3,2,4-diazadiboretidine ([11], Fig. 2) which was recently measured by us (Figure 3). The MCD spectrum was taken on a JASCO J41 spectropolarimeter equipped with an electromagnet JASCO MCD-1B (1.5 T); solvent: isooctane; $c = 4.14\ 10^{-3}$ mol/l, $d = 0.1$ cm.

From an MCD spectrum the B value of a transition $G \rightarrow F$ can be obtained from the magnetically induced molar ellipticity $[\Theta]_m$ per unit magnetic field in deg L m^{-1} mol^{-1} G^{-1} by

$$B = -33{,}53^{-1} \int \frac{d\tilde{\nu}\,[\Theta]_m}{\tilde{\nu}}, \qquad (49)$$

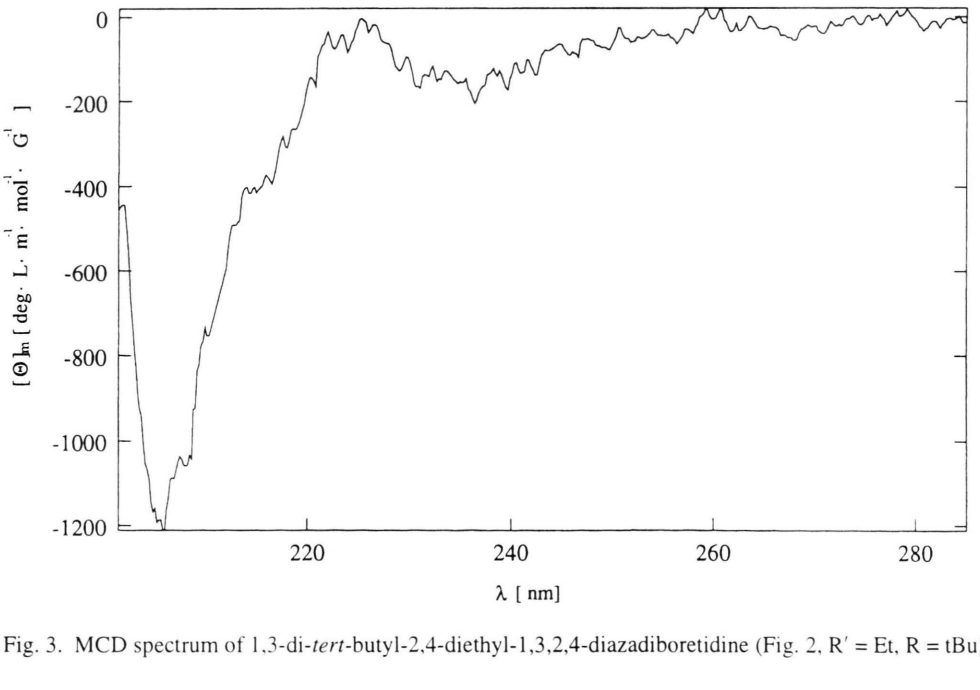

Fig. 3. MCD spectrum of 1,3-di-*tert*-butyl-2,4-diethyl-1,3,2,4-diazadiboretidine (Fig. 2, $R' = Et$, $R = tBu$).

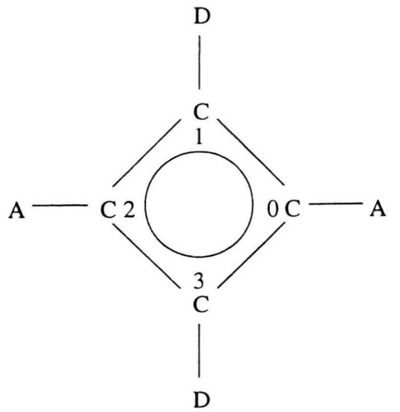

Fig. 4. Molecular formula of a cyclobutadiene, symmetrically substituted by an acceptor group (A) and a donor group (D).

where $\tilde{\nu}$ is the wavenumber and the integration is over the MCD band. From (49) it follows that a negative $[\Theta]$ curve means a positive B value and vice versa. For our example (D_{2h} symmetry) we have two perpendicular symmetry planes. This means that for the matrix elements of the perturbation operator $\hat{a}$ the following relationships should be valid: $a_{00} = a_{22}$, $a_{11} = a_{33}$ and $a_{01} = a_{12} = a_{23} = a_{30}$. With (2)–(5) and (30) one then gets

$$\Delta HSL = -4\,(a_{02} + a_{13}), \tag{50}$$

$$\frac{\Delta s}{2}\, e^{i\sigma} = \frac{1}{2}\,(a_{00} - a_{11} - a_{02} + a_{13})\,. \tag{51}$$

a_{00} and a_{11} should be proportional to the electronegativity difference between nitrogen and carbon, and boron and carbon, respectively, and therefore $a_{00} \approx -a_{11}$ should be a large negative quantity (Figure 2).

According to Linderberg [12] the resonance integrals $a_{02} = \beta^{\mathrm{L}}_{02}$ and $a_{13} = \beta^{\mathrm{L}}_{13}$ between next nearest neighbors are proportional to $\left\langle \chi_0 \middle| \frac{\partial}{\partial x} \middle| \chi_2 \right\rangle$ and $\left\langle \chi_1 \middle| \frac{\partial}{\partial x} \middle| \chi_3 \right\rangle$. In atomic units the resonance integral β^{L}_{ij} between Löwdin orbitals χ_i and χ_j is

$$\beta^{\mathrm{L}}_{ij} = (x_i - x_j)^{-1} \left\langle \chi_i \middle| \frac{\partial}{\partial x} \middle| \chi_j \right\rangle. \tag{52}$$

x_i and x_j are the x-coordinates of atoms i and j. In contrast to benzene, for which the resonance integral between next nearest neighbors is positive [13], we found for cyclobutadiene a negative resonance integral between 0 and 2 and 1 and 3. Using Slaterorbitals ($\xi = 1.625$) for carbon and a bond distance of 1.4 Å we obtained – 0.09 eV for cyclobutadiene, whereas for benzene we found a value of 0.05 eV. The main reason for this is that the distance between atoms 0 and 2 in cyclobutadiene is much smaller than the corresponding value in benzene. It follows that ΔHSL should be positive and small, whereas the positive Δs will be rather large. Therefore the ground state ψ_{G} for our molecule will be ψ_{R}. The phase angle σ should be π because $\frac{\Delta s}{2}\, e^{i\sigma} < 0$. It would be interesting to study also the MCD spectra of four-membered rings of the kind shown in Figure 4.

Here the electronegativity difference between two neighboring carbons can be much smaller, so that perhaps the ground state ψ_{G} will be ψ^{s+}_{s-}. The dipole strength and B values for the low lying transitions of these rings can be evaluated with the expressions given in Table 3.

Because for our molecule $\Delta HSL > 0$ and $\sigma = \pi$, the lowest excited state of the 4×4 block will be described by the wave function ψ_4, and the next higher one by ψ_1 (Table 2). The other two states will be very much higher in energy because Δs is large.

The mixing angles α (47) and β (48) will be small and are nearly equal ($\alpha \approx \beta \approx 0$). ψ_4 is therefore nearly identical (see Table 2) with the configuration ψ^{l}_{s-}, and ψ^{s+s+}_{s-h} contributes nearly nothing. The same is the case for the next higher wave function ψ_1. ψ_1 is nearly identical with ψ^{s+}_{h}, and the contribution of ψ^{s+l}_{s-s-} is negligible. This is in accordance with the fact that Michl and coworkers [7–9] neglected in the general case, where one has two LUMOs (l_- and l_+) and two HOMOs (h_- and h_+), the configurations ψ^{s+l-}_{s-s-}, ψ^{s+l+}_{s-s-}, ψ^{s+s+}_{s-h-}, and ψ^{s+s+}_{s-h+}.

From this it follows (Table 4) that the dipole strength of the lower ψ_4 state should be rather large ($\approx 2\ \mathrm{m}^2$) with a large positive B value. The dipole strength of the ψ_1 state is also large ($\approx 2\ \mathrm{m}^2$), but the B value should be negative.

For both transitions ($\psi_{\mathrm{R}} \rightarrow \psi_4$, $\psi_{\mathrm{R}} \rightarrow \psi_1$) the magnetic mixing of the ground state ψ_{R} with the intermediate state ψ^{s+}_{s-}, which is proportional to $(\Delta s - 2[2])^{-1}$, is decisive, whereas the magnetic mixing of the ψ_4 state with ψ_2 and ψ_1 and of the ψ_1 state with ψ_3 and ψ_4 is negligible (Table 4). These theoretical findings are in accordance with the observed spectrum of the diazadiboretidine derivative (Figure 3). The first small positive B value (at $\lambda \approx 235$ nm) should belong to the first forbidden transition $\psi_{\mathrm{R}} \rightarrow \psi^{s+}_{s-}$.

The large positive B value at about 205 nm is in agreement with the predicted large positive B value of the transition $\psi_R \rightarrow \psi_4$.

The predicted negative B value for the $\psi_R \rightarrow \psi_1$ transition occurs apparently at a too small wavelength and could not be observed by us.

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