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# Magnetic Circular Dichroism of Cyclic $\pi$ -Electron Systems. 23.<sup>1</sup> Monocyclic $\pi$ -Excessive Nitrogen Heterocycles. 1,4-Dihydro-1,4-diazocines

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Consequences of the perimeter model for magnetic circular dichroism of heterocycles derived from  $(4N + 2)$ -electron  $[n]$ annulenide anions by replacement of  $\text{CH}^-$  by  $\text{NH}$ , such as pyrrole, 1,2-dihydro-1,2-diazocine, 1,4-dihydro-1,4-diazocine, and azonine, are analyzed. The predicted effects of further introduction of nitrogens of the aza type and of  $+E$  or  $-E$  substituents should depend sensitively on the position of substitution, leading to large predicted differences among tautomers and isomers and suggesting possible analytical applications. The theoretical results are in very good agreement with the few spectra already published and with the newly obtained spectra of 1,4-dihydro-1,4-diazocine and its simple derivatives. The effects of nonplanarity are considered and account for the observed effects of electron-withdrawing substituents on the nitrogens in the eight-membered ring on MCD and absorption spectra. An extension of the results to  $\pi$ -excessive heterocycles with oxygen, sulfur, and similar heteroatoms, such as furan and thiophene, is outlined.

Magnetic circular dichroism (MCD) of cyclic  $\pi$ -electron systems derived from  $(4N + 2)$ -electron  $[n]$ annulene perimeters can be interpreted in terms of the perimeter model without recourse to complicated calculations.<sup>3-5</sup> In the general case  $[N \neq 0, N \neq (n/2) - 1]$ , the model predicts the presence of two low-energy relatively weak transitions in the electronic absorption spectra (Platt's  $L$  bands) and two high-energy strong transitions (Platt's  $B$  bands). We refer to these four transitions as  $L_1$ ,  $L_2$ ,  $B_1$ , and  $B_2$  in the order of increasing energy and to their  $B$  terms in MCD spectra as  $B(L_1)$ ,  $B(L_2)$ ,  $B(B_1)$ , and  $B(B_2)$ , respectively. The magnitude of a  $B$  term of a transition is related to the area under an MCD peak due to the transition:  $B = -33.53^{-1} \int d\epsilon[\theta]_M/\bar{\nu}$ , where  $\bar{\nu}$  is wavenumber and  $[\theta]_M$  is molar ellipticity per unit magnetic field. Since MCD peaks frequently overlap, it is not always easy to determine the magnitude of the  $B$  term, but the observed sign is rarely in doubt. A negative MCD peak corresponds to a positive  $B$  term and a positive MCD peak to a negative  $B$  term.

According to the perimeter model, the  $B$  term for each of the four transitions contains two contributions. One of these is proportional to a small magnetic moment  $\mu^-$  and shows little sensitivity to structure. For most values of  $n$  and  $N$ ,  $\mu^-$  is weakly negative (for a tabulation see ref 3), and the contributions to the four  $B$  terms are as follows:  $B(L_1)$ , small positive or zero;  $B(L_2)$ , small positive or zero if  $L-B$  magnetic mixing dominates and small negative or zero if  $L-L$  magnetic mixing dominates;  $B(B_1)$ , larger positive;  $B(B_2)$ , larger negative. The second contribution is proportional to a large magnetic moment  $\mu^+$  (tabulated in ref 3 as a function of  $n$  and  $N$ ) but appears only if molecular orbital energies are such that  $\Delta\text{HOMO} \neq \Delta\text{LUMO}$ , where  $\Delta\text{HOMO}$  is the energy separation of the two molecular orbitals resulting from the degenerate highest occupied molecular orbital (HOMO) of the parent perimeter upon conversion into the molecule in question, and  $\Delta\text{LUMO}$  is the energy difference of the MOs resulting similarly from the degenerate lowest unoccupied molecular orbital (LUMO) of the parent perimeter. The  $\mu^+$  contribution is very sensitive to molecular structure: if  $\Delta\text{HOMO} - \Delta\text{LUMO} > 0$ , the signs of its contributions to the four  $B$  terms are  $+$ ,  $-$ ,  $+$ , and  $-$ , in the order of increasing

transition energy, and if  $\Delta\text{HOMO} - \Delta\text{LUMO} < 0$ , the signs are  $-$ ,  $+$ ,  $-$ , and  $+$ . The magnitude of the  $\mu^+$  contributions at first increases with increasing  $|\Delta\text{HOMO} - \Delta\text{LUMO}|$ , then reaches a limiting value, and subsequently begins to decrease.

The model is based on a series of simplifying assumptions, whose validity is discussed in some detail in ref 4. In the previous papers of this series it has been tested on various structural types of molecules and found to work very well for the first three of the four transitions and occasionally also for the  $B_2$  transition. One of the assumptions is that the molecule is planar. However, minor deviations from planarity should have almost no effect, and even gross distortions may not make the method inapplicable provided, of course, that cyclic conjugation is at least partly preserved and that the perimeter transitions can still be recognized. A nonmathematical description of the model was given in ref 5-8.

In the present paper, we summarize the predictions of the model for selected representatives of an important class of simple heterocyclic analogues of  $(4N + 2)$ -electron  $[n]$ annulenide anions:  $\pi$ -excessive nitrogen heterocycles. These are derived by replacement of one or more  $\text{CH}^-$  groups in the parent anionic perimeter by the isoelectronic but more strongly electronegative  $\text{NH}$  group, producing an electroneutral heterocycle (Chart I). The predictions are compared with the newly measured MCD spectra of the 10- $\pi$ -electron aromatic system of 1,4-dihydro-1,4-diazocine<sup>9</sup> and also with literature data for several heterocycles of the pyrrole<sup>10</sup> and imidazole<sup>11</sup> series.

## Results and Discussion

**Parent Anions 1-3.** The parent  $(4N + 2)$ -electron  $[n]$ annulenide anions selected for consideration are the [5]annulenide anion (1), the [8]annulenide dianion (2), and the [9]annulenide anion (3). Extension of the arguments to other ring sizes is straightforward. In the parent perimeters, symmetry demands  $\Delta\text{HOMO} = \Delta\text{LUMO} = 0$  and

(1) Part 22: J. Waluk and J. Michl, submitted for publication.

(2) (a) University of Utah. (b) University of Cologne.

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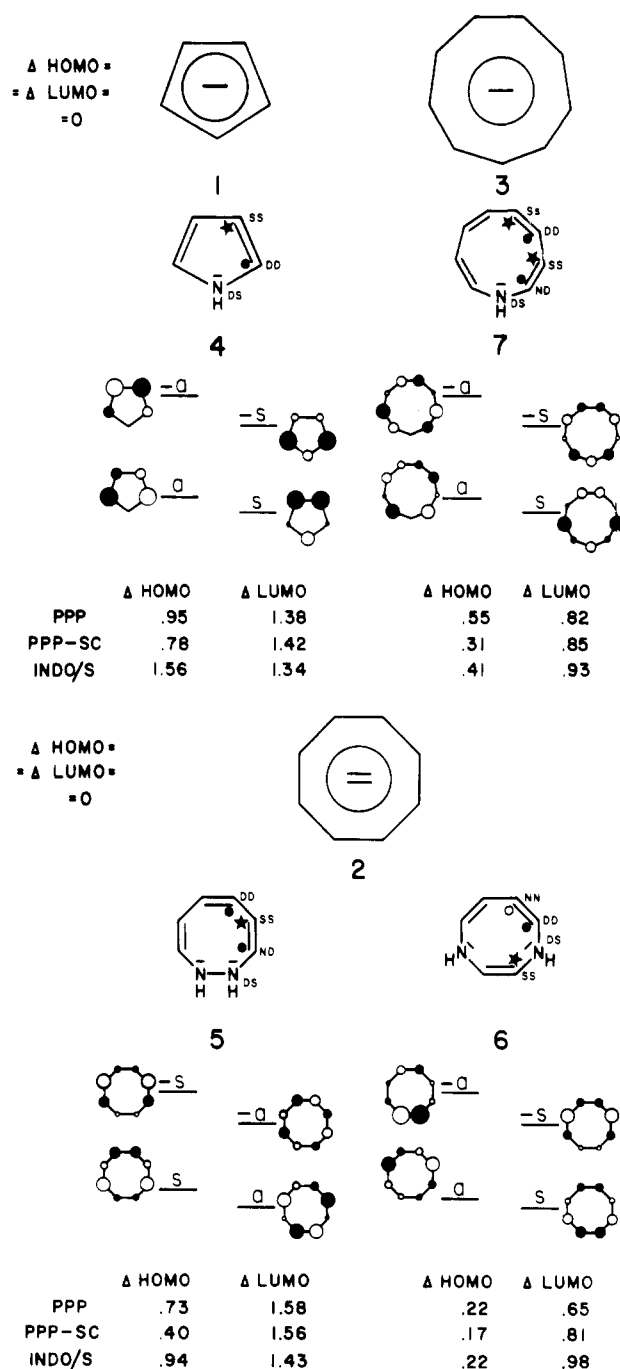
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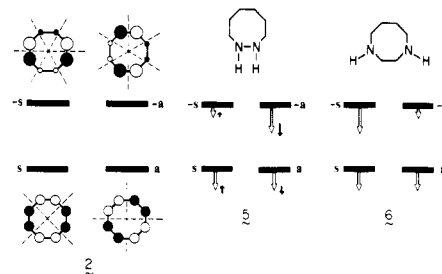
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Chart I



vanishing intensity for both L transitions, which are degenerate and appear in the absorption spectra only weakly as a result of vibronic interactions ( $\sim 45\,000\text{ cm}^{-1}$  in 1,<sup>12</sup>  $\sim 26\,000\text{ cm}^{-1}$  in 2,<sup>13</sup> and  $\sim 31\,000\text{ cm}^{-1}$  in 3<sup>14</sup>). The two higher energy B transitions are also degenerate and are allowed in absorption (above  $50\,000\text{ cm}^{-1}$  and unobserved in 1,  $35\,000\text{ cm}^{-1}$  in 2,<sup>13</sup> and  $\sim 40\,000\text{ cm}^{-1}$  in 3<sup>14</sup>). The MCD spectra of the parent annulenes tend to be dominated by vibronic interactions.

**$\pi$ -Excessive Heterocycles 4-7.** Simple heterocycles which can be derived from these parent perimeters are pyrrole (4), 1,2-dihydro-1,2-diazocine (5), 1,4-dihydro-1,4-diazocine (6), and azonine (7) (Chart I). We shall concentrate on their L transitions in the following, since they



**Figure 1.** Symmetry MO's of 2 and a qualitative consideration of first-order effects on their energies due to perturbations by heteroatom electronegativity (double arrows) and reduced heteroatom-heteroatom resonance integral (dark arrows).

appear in a spectral region which is more easily accessible and in which interference from other types of transitions such as Rydberg transitions is less likely. Actually, in 4, whose L transitions are at  $45\,000\text{--}50\,000\text{ cm}^{-1}$ , the presence of a Rydberg transition in the same region<sup>15</sup> may well cause complications. At first, we shall assume that 4-7 are all planar. Eventually, we shall recognize that this need not be so for 5-7, depending on further substitution, and shall consider the changes nonplanarity will cause in our conclusions.

In the case of 4 and 7, molecular symmetry dictates that one of the HOMOs derived from the parent perimeter (a) as well as one of the LUMOs (-a) have a node going through the position of the heteroatom. The other two orbitals (s and -s) have an antinode in this position. Perturbation theory<sup>16</sup> then suggests that the orbital ordering will be s, a, -s, and -a in the order of increasing energy, since the  $\pi$  orbital of NH lies at lower energy than that of  $\text{CH}^-$ . To the first order in perturbation energy,  $\Delta \text{HOMO} = |\epsilon(a) - \epsilon(s)|$  will be equal to  $\Delta \text{LUMO} = |\epsilon(-a) - \epsilon(-s)|$ . Since the perturbation is quite strong, the first-order approximation may be inadequate, and  $\Delta \text{HOMO}$  and  $\Delta \text{LUMO}$  may differ. Numerical estimates were obtained in the  $\pi$ -electron PPP approximation and in the all-valence electron INDO/S approximation, as described in more detail below. They confirm the expected orbital ordering and suggest that the difference  $\Delta \text{HOMO} - \Delta \text{LUMO}$  is fairly close to zero in the case of 4 (the three methods of calculation disagree in this case) and somewhat negative in the case of 7 (Chart I).

In the case of 5 and 6, the symmetry is such that one of the HOMOs derived from the parent perimeter (a) and one of the LUMOs (-a) are antisymmetric with respect to the mirror plane which images one nitrogen into the other, while the other HOMO (s) and LUMO (-s) are symmetric with respect to this symmetry operation. In order to use perturbation theory arguments for prediction of the energy ordering of the four orbitals, the explicit form of the MOs of the parent perimeter 2 is needed. This is dictated by symmetry and is shown in Figure 1. A consideration of the increased electronegativity of nitrogen relative to carbon and of the somewhat smaller absolute value of the resonance integral  $\beta_{\text{N-N}}$  relative to  $\beta_{\text{C-C}}$  readily produces the conclusion that the energy ordering will be a, s, -a, and -s in 5 and a and s (approximately degenerate) followed by -s and then -a for 6 and suggests that  $\Delta \text{HOMO} < \Delta \text{LUMO}$  both in 5 and in 6 (Figure 1). Numerical estimates confirm these expectations. The calculated energies of the a and s orbitals of 6 are equal within 0.2 eV, the

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(16) For fundamentals of perturbation MO theory, see, for instance, M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, 1975.

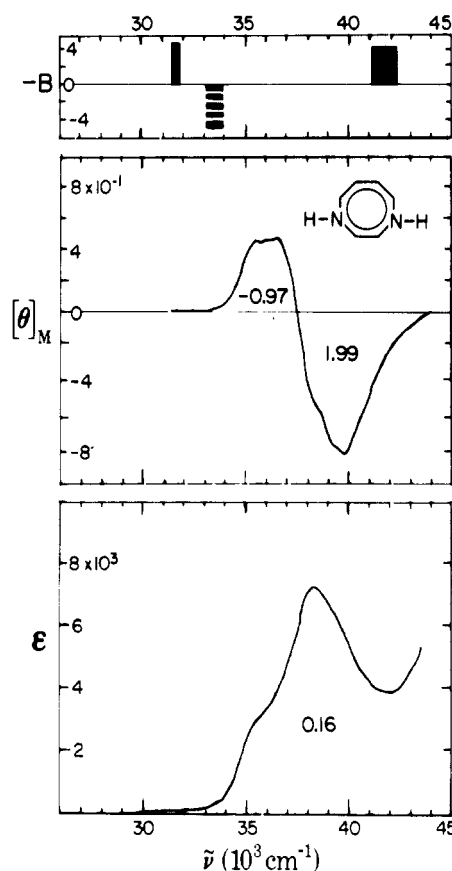
ordering of the others is as expected, and  $\Delta\text{HOMO} - \Delta\text{LUMO}$  is negative both in 5 and in 6 (Chart I).

In summary, the  $\pi$ -excessive nitrogen heterocycles are expected to present borderline cases between single-soft MCD chromophores<sup>4</sup> ( $\Delta\text{HOMO} = \Delta\text{LUMO}$ ) and negative-hard MCD chromophores<sup>4</sup> ( $\Delta\text{HOMO} < \Delta\text{LUMO}$ ), with 4 most nearly single-soft, 6 and 7 more distinctly single-soft, and 5 most clearly negative-hard. The  $\mu^+$  contributions to the  $B$  terms of the  $L$  transitions in their MCD spectra should be nearly zero for 4 and negative and positive for  $B(L_1)$  and  $B(L_2)$ , respectively, in 5-7.

The  $\mu^-$  contributions are expected to be particularly small for the  $(4N + 2)$ -electron  $[n]$ annulenide anions 1-3 and their derivatives. As discussed in more detail in ref 3,  $\mu^-$  is negative for most combinations of  $n$  and  $N$  but tends to more positive values as more electrons are added to the perimeter. It is always positive if only one unoccupied perimeter MO is left, as would happen, say, in  $\text{C}_4\text{H}_4^{2-}$  and as has been verified experimentally on inorganic heterocycles.<sup>17</sup> It so happens that 1-3 are very near the border line where  $\mu^-$  is expected to change sign, and its value probably is very close to zero. The  $\mu^+$  contributions should therefore be particularly dominant in systems derived from these parent anions, such as 4-7.

Pyrrole absorption begins in the region above  $45\,000\text{ cm}^{-1}$  where the degenerate  $L$  transition of 1 is located. Some or all of this absorption may be due to Rydberg rather than perimeter transitions,<sup>15</sup> although the former are usually suppressed in solution spectra. Moreover, this is a difficult region for MCD measurement. The published spectrum<sup>10</sup> is indistinct and noisy, permitting no useful conclusions. Its weakness is certainly compatible with the notion that 4 is a nearly exactly soft chromophore, so that  $\mu^+$  does not contribute and that  $\mu^-$  for a  $6\pi$ -electron five-membered ring is very small.

A more definitive test of the theoretical concepts should be possible with 1,4-dihydro-1,4-diazocine (6). The very weak degenerate  $L$  transition of 2 begins at  $26\,000\text{ cm}^{-1}$ , in a much more readily investigated spectral region. The absorption spectrum of 6 (Figure 2) starts with a broad intense band in the region  $35\,000$ – $42\,000\text{ cm}^{-1}$ , with some indications of composite structure. This is followed by more intense absorption above  $44\,000\text{ cm}^{-1}$ . The MCD spectrum displays clearly the composite nature of the first absorption band. The shoulder near  $35\,000$  is positive in MCD, and the peak near  $38\,000$  is negative. This is exactly as expected for the  $L_1$  and  $L_2$  transitions of a negative-hard MCD chromophore, and we propose this assignment of the observed spectra [ $B(L_1) < 0$ ,  $B(L_2) > 0$ ]. The near degeneracy of the two transitions is in keeping with the expected near degeneracy of the two MOs originating in the degenerate HOMO of 2, i.e., with the very small predicted value of  $\Delta\text{HOMO}$ . The numerical calculations suggest that the antisymmetric orbital  $a$  is about  $0.2\text{ eV}$  ( $1600\text{ cm}^{-1}$ ) above  $s$  in energy. Since the symmetrical orbital  $-s$  is certainly well below  $-a$ , the singly excited configurations  $a \rightarrow -s$  and  $s \rightarrow -s$  can be expected to predominate in the  $L_1$  and  $L_2$  excited states, respectively, with  $s \rightarrow -a$  providing a minor contribution to the former and  $a \rightarrow -a$  to the latter. Numerical calculations indeed produce this result, with  $L_1$  about  $2000\text{ cm}^{-1}$  below  $L_2$  (the experimental separation is about  $3000\text{ cm}^{-1}$ ). It should be noted that the ordering of the two states cannot be determined from the MCD spectrum of 6 but could be determined from a measurement of linear polarization. The  $a \rightarrow -s$  transition will be polarized along the line connecting the two nitrogen



**Figure 2.** 1,4-Dihydro-1,4-diazocine: bottom, absorption (oscillator strength given); center, MCD ( $B$  terms in units of  $10^{-3} \beta_e D^2/\text{cm}^{-1}$ ); top, PPP calculation. A full bar indicates vertical polarization and a broken bar horizontal polarization with respect to the formula shown. The thickness of the bar indicates intensity: thin line,  $f \leq 0.05$ ; medium line,  $0.05 < f < 0.5$ ; thick line,  $f \geq 0.5$ .

atoms and the  $s \rightarrow -s$  transition along a line perpendicular to the above. Unfortunately, problems with limited solubility prevented us from determining the polarization directions both in stretched polyethylene and in nematic liquid crystals. While the knowledge of the ordering of the  $a$  and  $s$  orbitals is immaterial for the MCD spectrum of 6 itself, which depends only on the absolute value of their energy difference,  $\Delta\text{HOMO}$ , it is important for the prediction of the effect of weakly perturbing substituents on the magnitude of  $\Delta\text{HOMO}$  and thus on the MCD spectrum and is discussed in more detail below.

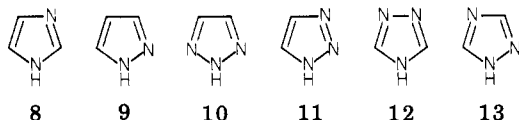
**Aza Derivatives of the  $\pi$ -Excessive Heterocycles 4-7.** Replacement of a  $\text{CH=}$  moiety by the  $\text{N=}$  moiety represents a simple example of further purely inductive perturbation. Numerous heterocycles of this type derived from 4 are known and have considerable importance (pyrazole, imidazole, etc.). Knowledge of the form of the four frontier orbitals of 4-7 permits an application of first-order perturbation theory<sup>16</sup> to predict the effect of electron-withdrawing inductive perturbation on the magnitude of the  $\Delta\text{HOMO}-\Delta\text{LUMO}$  difference and thus on the signs of  $B(L_1)$  and  $B(L_2)$  in the MCD spectra. Here, we recognize that the aza replacement is a weaker perturbation than the initial replacement of  $\text{CH}^-$  by  $\text{NH}$  which produced the heterocycles 4-7.

In the first approximation, the shift in the energy of an orbital upon aza replacement is proportional to the square of its expansion coefficient in the position of replacement. The effects on  $\Delta\text{HOMO}-\Delta\text{LUMO}$  predicted by using this simple tool are shown in Chart I. Those positions in which aza replacement should make  $\Delta\text{HOMO}-\Delta\text{LUMO}$  more positive ("I subdominant") are labeled with a star, those

(17) J. W. Waluk and J. Michl, *Inorg. Chem.*, in press.

in which such replacement should make  $\Delta\text{HOMO}$ – $\Delta\text{LUMO}$  more negative ("I dominant") are labeled with a dot, and those in which such replacement should have little effect on  $\Delta\text{HOMO}$ – $\Delta\text{LUMO}$  ("I neutral") are labeled with a circle. The results obtained from the three methods of calculation (PPP, PPP-SC, INDO/S) were qualitatively similar. Since the MCD spectra are expected to be dominated by  $\mu^+$  contributions alone, a knowledge of the effect of aza replacement permits an immediate conclusion concerning its effect on the  $B$  terms of the  $L$  transitions. Thus, aza replacement in a starred position should make a positive contribution to  $B(L_1)$  and a negative one to  $B(L_2)$ , the opposite should be true in a dotted position, and little effect should be observed at a circled position.

The predictions are particularly straightforward for aza analogues of **4** which has almost vanishing  $B$  terms to start with. Unfortunately, their  $L$  transitions occur in a difficult spectral region. The signs of  $B$  terms anticipated for imidazole (**8**) are  $B(L_1) > 0$  and  $B(L_2) < 0$ , and those antic-



ipated for pyrazole (**9**) are just the opposite,  $B(L_1) < 0$  and  $B(L_2) > 0$ . The MCD spectra of imidazole and a series of simple derivatives (alkyl, halogen) have been measured recently<sup>11</sup> and indeed show this expected sign pattern.

Possible exploitation of this behavior in investigations of tautomerism and isomerism can be envisaged. For instance, the 2-H tautomer of *vic*-triazole (**10**) should show a strong +,– MCD sign sequence in the order of increasing energy [ $B(L_1) < 0$ ,  $B(L_2) > 0$ ], since the action of both of its aza nitrogens is additive, while the 1-H tautomer (**11**) should have very weak MCD peaks similar to those of pyrrole itself, since its two aza nitrogens counteract each other. Similarly, the 4-H tautomer of 1,3,4-triazole (**12**) can be expected to exhibit a strong –,+ peak sequence in its MCD spectrum [ $B(L_1) > 0$ ,  $B(L_2) < 0$ ], while the MCD spectrum of the 1-H tautomer (**13**) should be very weak. Analogous differences can be expected for N-methylated isomers, etc.

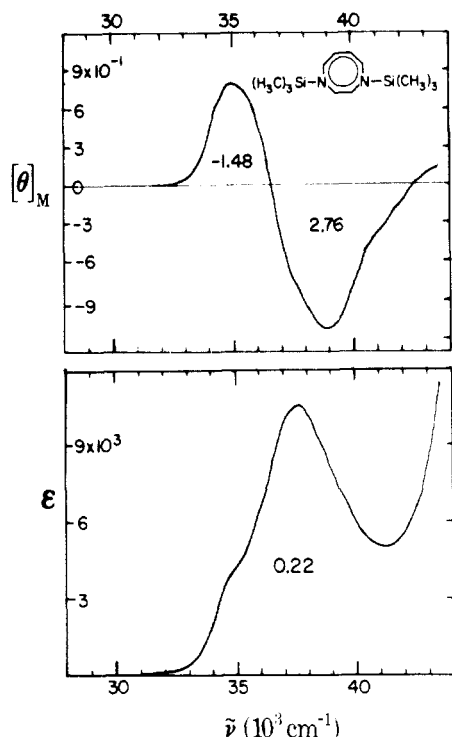
**$\pi$  Effect of Substituents on MCD of the  $\pi$ -Excessive Heterocycles 4–7.** A substituent which possesses either vacant or occupied orbitals of  $\pi$  symmetry has the potential of acting as a  $\pi$  acceptor (+E) or  $\pi$  donor (–E), respectively. Many substituents possess orbitals of both kinds, and one or the other characteristic dominates their behavior, depending on the substrate to which they are attached (vinyl is a  $\pi$  acceptor on  $\text{C}_5\text{H}_5^-$  but a  $\pi$  donor on  $\text{C}_7\text{H}_7^+$ ). When the effect of a conjugative substituent is described in the simplest MO terms, it is found that a +E substituent affects primarily the  $\Delta\text{LUMO}$  and a –E substituent affects primarily the  $\Delta\text{HOMO}$ .<sup>5</sup> The direction of the effect is predicted readily if the ordering of the orbitals and the LCAO expansion coefficients are known.

On the parent annulene,  $\Delta\text{HOMO} = \Delta\text{LUMO} = 0$ , a  $\pi$ -acceptor (+E) substituent will induce  $\Delta\text{HOMO} < \Delta\text{LUMO}$ , and thus  $B(L_1) < 0$  and  $B(L_2) > 0$ . A  $\pi$ -donor (–E) substituent will induce  $\Delta\text{HOMO} > \Delta\text{LUMO}$ , and thus  $B(L_1) > 0$  and  $B(L_2) < 0$ . The same will be true in more complex derivatives as long as a  $\pi$  substituent represents the strongest perturbation of the parent perimeter among all those present. In this sense, these sign orders represent the "natural" sign sequences for a +E and –E substituent, respectively. Physically, they are related to the fact that an acceptor substituent hinders the circulation along the perimeter in a magnetic field for an excited electron in the

LUMO by attempting to extract it out on itself but does not hinder that of the "hole" which it left behind in the HOMO, while a donor substituent hinders the circulation of the "hole" by pulling it out on itself and not that of the electron. The opposite charges of the circulating electron and the "hole" lead to opposite signs of magnetic moments and opposite MCD signs.

On an already perturbed annulene such as 4–7, the situation is more complicated.<sup>5</sup> In certain positions of substitution, referred to as "dominant" (D), the substituent acts in its natural mode; i.e., a +E acceptor increases  $\Delta\text{LUMO}$ , and a –E donor increases  $\Delta\text{HOMO}$ . This happens when the substituent acceptor orbital interacts more strongly with the LUMO of the substrate than with its second LUMO or if the substituent donor orbital interacts more strongly with the HOMO than with the second HOMO. In other positions of substitution, referred to as "subdominant" (S), the effect of a weak substituent is the opposite of the natural one: a +E acceptor decreases  $\Delta\text{LUMO}$ , and a –E donor decreases  $\Delta\text{HOMO}$ . This occurs when the substituent orbital interacts more strongly with the second LUMO or second HOMO than with the LUMO or HOMO, respectively. As the substituent effect is allowed to become stronger, however, its action will interchange the order of the orbitals (of the second LUMO and the LUMO in the case of a +E substituent and of the second HOMO and the HOMO in the case of –E substituent), and, as already noted, a very strong substituent will dominate the MCD signs as if no other perturbations were present. Other things being equal, the strength of the substituent needed for the reversal of its effect in an S position will depend on the initial value of  $\Delta\text{LUMO}$  in the case of an acceptor and of  $\Delta\text{HOMO}$  in the case of a donor. For instance, if  $\Delta\text{HOMO}$  is very small, as happens in **6**, only the weakest donors will induce a decrease in  $\Delta\text{HOMO}$ , and all others will interchange the orbitals and induce an increase in  $\Delta\text{HOMO}$ . It is with this proviso that we list the positions in 4–7 as S or D in Chart I. The first label refers to the expected effect of a +E acceptor and the second to the expected effect of a –E donor. Positions in which the effects should be weak are labeled N for neutral. The predictions were made by accepting the perimeter orbital ordering deduced above and inspecting the LCAO coefficients of the four orbitals, assuming for simplicity that the magnitude of the interaction between the perimeter orbital and the substituent orbital is proportional to the square of the MO coefficient at the position of attachment. This approximation becomes progressively poorer as the substituent increases in strength, but as explained above, for very strong substituents all positions act as if they were of type D anyway.

Comparison with experiment is possible in the cases of **4** and **6**. The interpretation of the MCD spectra of methylpyrroles is not very clear-cut since more than two peaks appear in some of them in what is presumed to be the region of  $L$  transitions.<sup>10</sup> This might be due to vibronic effects, since the spectra are quite weak, or to the presence of an additional transition, either of Rydberg nature or analogous to the "doubly excited" state presumably present in butadiene. *N*-Methyl substitution produces the +,– sign sequence as expected for –E substitution in a DS position. These MCD peaks are reduced in the presence of an additional methyl in position 2 as expected since the latter is of type DD. Addition of a third methyl in position 5 continues this trend as it should, but complications with a third peak appear. Similarly, 2,5-dimethyl substitution on pyrrole produces the –,+ sign sequence expected for a DD position, but once again, a third peak is present. The

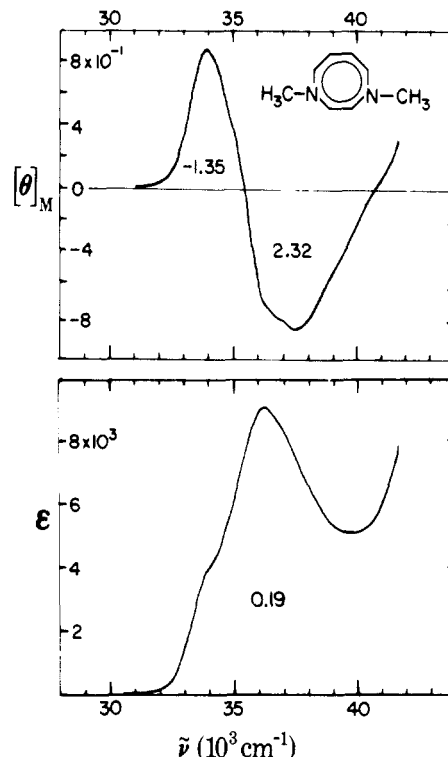


**Figure 3.** *N,N'*-Bis(trimethylsilyl)-1,4-dihydro-1,4-diazocine: bottom, absorption (oscillator strength given); top, MCD (*B* terms in units of  $10^{-3} \beta_e D^2 / \text{cm}^{-1}$ ).

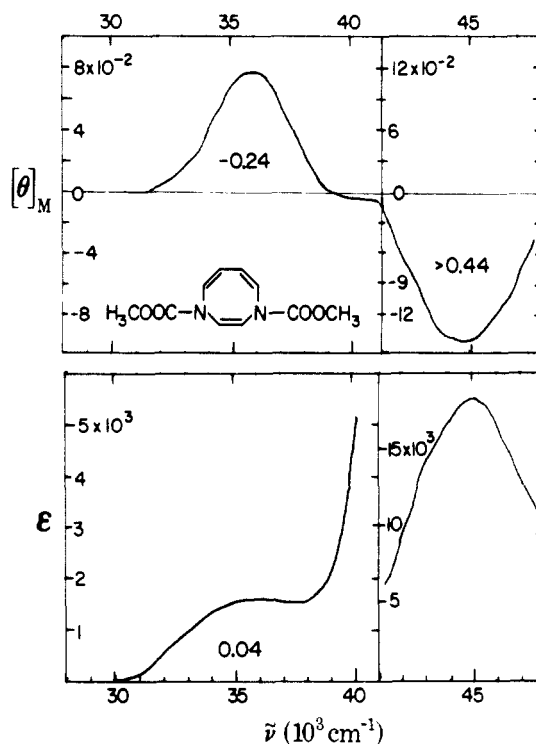
MCD spectrum of 2,4-dimethylpyrrole is almost the same as that of the 2,5-dimethyl isomer. This is not unreasonable on considering that the effect of a  $-E$  substituent in the dominant position 2 (= position 5) should be much stronger than in the subdominant position 3 (= position 4) (the differences of squares of MO coefficients are  $\sim 0.4$  in the former and  $\sim 0.2$  in the latter). It would be interesting to perform MCD measurements on more strongly perturbed pyrroles in which the effects would be stronger and the transitions shifted to lower energies where they can be more easily measured. Such measurements have been performed on a series of substituted imidazoles, and very good agreement with expectations based on the simple theory was found.<sup>11</sup>

Predictions for the presently investigated 1,4-dihydro-1,4-diazocines (**6**) are interesting in that for very weak substituents the response should be clearly different in the three possible positions of substitution on carbon, but as  $\Delta\text{HOMO}$  is very small, the direction of response to stronger donors should be the same in all three. Experimental information is presently available only for substitution on nitrogen. This is a position of type DS, and we expect a  $+E$  acceptor to make  $\Delta\text{HOMO} - \Delta\text{LUMO}$  even more negative than it already is in the parent **6** and a weak  $-E$  donor to act the same way, while a strong  $-E$  donor should have the opposite effect. Figure 3 shows that the introduction of two weak  $+E$  substituents,  $\text{SiMe}_3$ , on the nitrogens indeed enhances the *B* terms already present in **6** (Figure 2). Figure 4 shows that the weak  $-E$  substituent, methyl, acts similarly. This result is in perfect agreement with expectations and supports our previous assignment of the ordering of the occupied orbitals in **6**, a above *s* (methyl substitution should have the opposite effect if the order were the opposite).

**Effects of Nonplanarity.** Figure 5 shows the effects of double carbomethoxy substitution. The strong  $+E$  effect of these substituents should make the  $\Delta\text{HOMO} - \Delta\text{LUMO}$  difference even more negative by stabilizing  $-s$ . However, this substitution apparently disturbs the aromatic stabilization of **6** to such a degree that it no longer can overcome bond angle distortions required by planarity, and NMR evidence suggests that this compound, similarly as the dimethanesulfonate derivative, is nonplanar and olefinic.<sup>9</sup> This difference is also reflected strikingly in the absorption and MCD spectra.



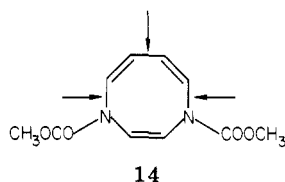
**Figure 4.** *N,N'*-Dimethyl-1,4-dihydro-1,4-diazocine. See caption to Figure 3.



**Figure 5.** *N,N'*-Bis(carbomethoxy)-1,4-dihydro-1,4-diazocine. See caption to Figure 3.

A distortion from planarity will reduce overlaps between some adjacent  $2p_z$  orbitals on the ring atoms and can be modeled by a reduction of the resonance integrals for those bonds along which twisting occurs. X-ray structure

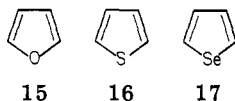
analysis of the dimethanesulfonate shows that these are the bonds 1-8, 4-5, and 6-7, and it is reasonable to expect that the same type of distortion occurs in the bis(carbomethoxy) derivative 14. The bonds along which twisting



is assumed are indicated by arrows in formula 14. Inspection of the nodal properties of the four frontier orbitals shown in Figure 1 shows that the twisting will remove the near degeneracy of the *a* and *s* orbitals by stabilizing *a* and destabilizing *s*. Development of double bond character will shorten three of the bonds and increase the magnitudes of the corresponding resonance integrals. This will further stabilize *a*, destabilize *s* and  $-a$ , and have little effect on  $-s$ . An immediate consequence of the loss of the near degeneracy of *a* and *s* should be a loss of the near degeneracy of the  $L_1$  and  $L_2$  transitions in the absorption and MCD spectra. This result follows from qualitative reasoning and is reinforced by numerical calculations. The observed spectra indeed show a much increased splitting between the  $L_1$  transition at  $35\,000\text{ cm}^{-1}$  and the  $L_2$  transition near  $45\,000\text{ cm}^{-1}$ . The observed MCD signs suggest, however, that  $\Delta\text{HOMO}$  remains smaller than  $\Delta\text{LUMO}$  in spite of the considerable increase in the former upon going to 14.

Similar considerations concerning the effects of nonplanarity on the absorption and MCD spectra will be necessary for other olefinic derivatives of 6-7.

**Other  $\pi$ -Excessive Heterocycles.** Replacement of a  $\text{CH}$  group by moieties other than  $\text{NH}$  is possible, and  $\pi$ -excessive heterocycles containing O, S, Se, and other isoelectronic moieties are common. The MCD spectra of these heterocycles and their derivatives can be predicted qualitatively by the methods employed in the present study. Thus, for instance, furan (15) is qualitatively similar



to pyrrole in its orbital energy ordering (*s*, *a*,  $-s$ ,  $-a$ ), in its LCAO coefficients, and in the approximate equality of  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  which makes it a soft MCD chromophore. Methyl ( $-E$ ) substitution in positions 2 and 5 has indeed been found to make its  $B(L_1)$  more positive and  $B(L_2)$  more negative, while bromo ( $-E$ ) substitution in position 3 had the opposite effect, as would be expected from the MO coefficients of 4 itself (Chart I).<sup>10</sup>

On the other hand, thiophene (16) and selenophene (17) are distinctly negative-hard MCD chromophores, with  $\Delta\text{HOMO} < \Delta\text{LUMO}$ .<sup>10</sup> This difference is probably not primarily due to the lower electronegativity of these heteroatoms, which raises the energy of orbital *s* so that it is essentially degenerate with *a* but raises also the energy of  $-s$ , so that the net effect on  $\Delta\text{HOMO} - \Delta\text{LUMO}$  is small. Rather, it appears to be caused by the much smaller value of the C-heteroatom resonance integral, which should cause a preferential stabilization of orbital  $-s$  (Chart I) and thus favor  $\Delta\text{LUMO}$  over  $\Delta\text{HOMO}$ . In a negative-hard MCD chromophore with an approximately degenerate HOMO pair (*a*, *s*),  $\pi$ -electron-donating ( $-E$ ) substitution in any position should make  $\Delta\text{HOMO} - \Delta\text{LUMO}$  less negative. The observed effect of methyl and bromo substitution in both positions 2 and 3 indeed is to reduce the negative value of  $B(L_1)$ .<sup>10</sup>  $\pi$ -Electron-withdrawing ( $+E$ ) substitution in position 2 ( $\text{COOH}$ ,  $\text{CHO}$ ) should stabilize  $-s$ , making  $\Delta\text{LUMO}$  even larger and  $\Delta\text{HOMO} - \Delta\text{LUMO}$  even more negative. Little effect on  $B(L_1)$  is observed,<sup>10</sup> as is reasonable if  $\Delta\text{HOMO} - \Delta\text{LUMO}$  is already quite large. One can expect similar  $+E$  substitution in position 3 to stabilize *a*, reducing  $\Delta\text{LUMO}$ , making  $\Delta\text{HOMO} - \Delta\text{LUMO}$  less negative, and thus leading to a less negative  $B(L_1)$ , but no experimental data are available.

### Experimental Section

**Materials.** The samples of the 1,4-dihydro-1,4-diazocine were those of ref 9. The solvent was spectral grade purity acetonitrile.

**Measurements.** Absorption and linear dichroism were measured on a Cary 17 spectrophotometer. MCD was measured on a JASCO 500C spectropolarimeter equipped with a 15-kG electromagnet. The measurement on 6 was repeated twice, once with vacuum line techniques to remove oxygen and the second time with a freshly degassed solvent but otherwise ordinary conditions, with the same result.

**Calculations.** Three types of semiempirical calculations were performed. First, simple PPP calculations of the type described in ref 18, second, PPP calculations modified by iterating to self-consistency the relation between bond orders and bond lengths as in ref 19 (PPP-SC), and finally, INDO/S calculations with the procedure described in ref 20.

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**Registry No.** 6, 56039-49-7; *N,N'*-bis(trimethylsilyl)-1,4-dihydro-1,4-diazocine, 72160-98-6; *N,N'*-dimethyl-1,4-dihydro-1,4-diazocine, 72160-99-7; *N,N'*-bis(carbomethoxy)-1,4-dihydro-1,4-diazocine, 58672-89-2.

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