12   13

−a ————

————— −s

a ———— ———— s

ΔHOMO < ΔLUMO

−a ————

————— −s

a ————

ΔHOMO = ΔLUMO

14   15

−a ————

————— −s

a ———— ———— s

ΔHOMO = ΔLUMO

−a ————

————— −s

a ———— ———— s

ΔHOMO < ΔLUMO

Figure 8. Expected orbital energy patterns for structures derived from a $C_{20}H_{20}^{2+}$ perimeter.

ΔLUMO were equal to 0.28 and 0.80 eV in 12, 1.07 and 1.08 eV in 13, 0.14 and 0.73 eV in 14, and 0.12 and 1.92 eV in 15. Except for the orbital splitting in 14, this is in perfect qualitative agreement with PMO expectations. PPP calculations for secophyrin 3 gave the a, s, −s, −a ordering and predicted a soft chromophore character for this compound (ΔHOMO = 0.58 eV, ΔLUMO = 0.57 eV).

A numerical computation of the *B* term of the L_1 and L_2 bands of 12–15 at the PPP–CI level produced the signs expected from the relative ΔHOMO and ΔLUMO values.

Conclusion

The MCD spectra of porphyrins 1[8-11] and their isomers, the porphycenes 2,[13] have been investigated previously in great detail and have been found to exhibit the qualitative behavior expected from the simple perimeter model.[2a] This makes it likely that the MCD spectra of other related macrocycles will do so as well, similarly as the numerous other cyclic π-electron systems derived from (4*N* + 2)-electron perimeters that have been examined in the past.[2b] Indeed, in the following paper[16] the MCD spectra of texaphyrins 4 are shown to be readily interpretable in terms of the perimeter model.

Presently, we have emphasized that the striking difference in the MCD spectral behavior of the nearly double-soft porphyrins and the negative-hard porphycenes readily follows from the difference in their topology by inspection and can be understood without any calculation whatever. We have then proceeded to apply the same principles to a series of the so far unknown related macrocycles 3 and 5–15 and used their topology alone to classify them into a group of soft MCD chromophores 3, 5–8, 13, and 14 and negative-hard chromophores 9–12 and 15, with obvious consequences for their MCD signs and response to perturbation by substituents.

A priori prediction is the true test of a theory. It would not be surprising to find that a numerically complex PPP or INDO/S computer calculation correctly predicts the character of a π-electron MCD chromophore, but it will be a remarkable achievement for a simple procedure based on nothing more than an inspection of molecular structure (topology) to predict correctly a property as complicated as magnetic optical activity, even if it is just for a few low-energy transitions. We leave a verification of the predictions as a challenge to those interested in the preparation and utilization of new macrocyclic ligands.

Magnetic Circular Dichroism of Metallotexaphyrins

Jacek Waluk,[1] Gregory Hemmi, Jonathan L. Sessler, and Josef Michl*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-1167

UV–vis absorption and magnetic circular dichroism (MCD) are reported for a series of metal salts of hexaalkyltexaphyrins, recently synthesized novel porphyrinoid structures. The results are interpreted in terms of the standard perimeter model. It is found that texaphyrin is a soft MCD chromophore and that the arrangement of frontier orbitals in metallohexaalkyltexaphyrins is s, a, −s, −a in order of increasing energy.

The derivatives of texaphyrin (1), a recently synthesized[2] "expanded" porphyrin-like system, possess intense near-IR absorption bands and photosensitize the production of singlet oxygen in high yields.[3,4] They are of current interest as possible phototherapeutic agents, and the use of these compounds in magnetic resonance imaging has also been discussed.[5] In addition, texaphyrins are of interest simply as novel ligands, since they are able to support rare coordination geometries such as pentagonal, pentagonal pyramidal, and pentagonal bipyramidal.[6]

Spectral studies of these molecules are in their initial stages. Electronic absorption and fluorescence spectra

(1) Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44, Poland.
(2) Sessler, J. L.; Murai, T.; Lynch, V.; Cyr, M. *J. Am. Chem. Soc.* **1988**, *110*, 5586.
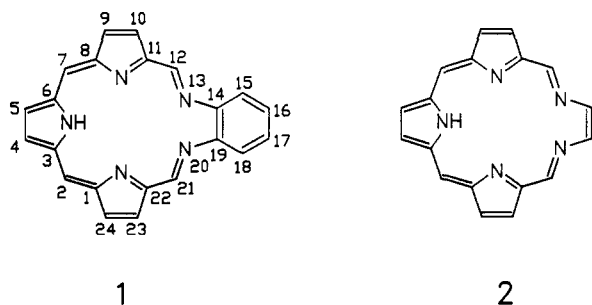(3) Maiya, B. G.; Harriman, T.; Sessler, J. L.; Hemmi, G.; Murai, T.; Mallouk, T. E. *J. Phys. Chem.* **1989**, *93*, 8111.
(4) Harriman, A.; Maiya, B. G.; Murai, T.; Hemmi, G.; Sessler, J. L.; Mallouk, T. E. *J. Chem. Soc., Chem. Commun.* **1989**, 314.

(5) Sessler, J. L.; Murai, T.; Hemmi, G. *Inorg. Chem.* **1989**, *28*, 3390.
(6) Sessler, J. L.; Murai, T.; Lynch, V. *Inorg. Chem.* **1989**, *28*, 1333.

Chart I

1   2

have been published along with triplet lifetime and quantum yield measurements.[3,4] Time-resolved EPR analyses of the triplet states[7,8] have also been performed, and the ^{113}Cd NMR of several derivatives reported.[9] More recently, the effect of substituents upon spectral and redox properties of several cadmium(II) texaphyrins have been investigated.[10]

As is true for the porphyrins, the texaphyrins may be viewed as perturbed derivatives of a $(4N + 2)$ π-electron annulene perimeter, with $N = 4$ (or alternatively, $N = 5$). The perimeter model[11] has proven to be very useful in the interpretation of electronic absorption spectra, and, in particular, of magnetic circular dichroism (MCD). It relates these properties in a simple fashion to orbital splittings and orbital energy ordering. It works well even for many compounds that are only remotely related to a $(4N + 2)$-electron perimeter and has been exceptionally successful for porphyrins[12] and their recently reported isomers, porphycenes.[13]

In the immediately preceding paper,[14] we have employed the perimeter model to analyze the expectations for the spectral intensities and MCD signs for a series of porphyrinoid macrocycles derived from the $C_{20}H_{20}^{2+}$ perimeter, including secophyrin (2), from which texaphyrin (1) is formally derived by benzoannelation (Chart I). In the present paper, we report the MCD spectra of 10 metallotexaphyrins with different central metal atoms and six alkyl groups on the pyrrole rings as well as different substituents on the macrocyclic skeleton (3–12) and of two more highly benzoannelated analogues, a naphthosecophyrin (13), and a phenanthrosecophyrin (14). Their structures are summarized in Chart II. The observation of different responses of MCD spectra to electron-donating and electron-withdrawing substituents allows us to draw conclusions about the energy pattern of the frontier π-orbitals in metallohexaalkyltexaphyrin. Comparison of absorption and MCD spectra demonstrates the much
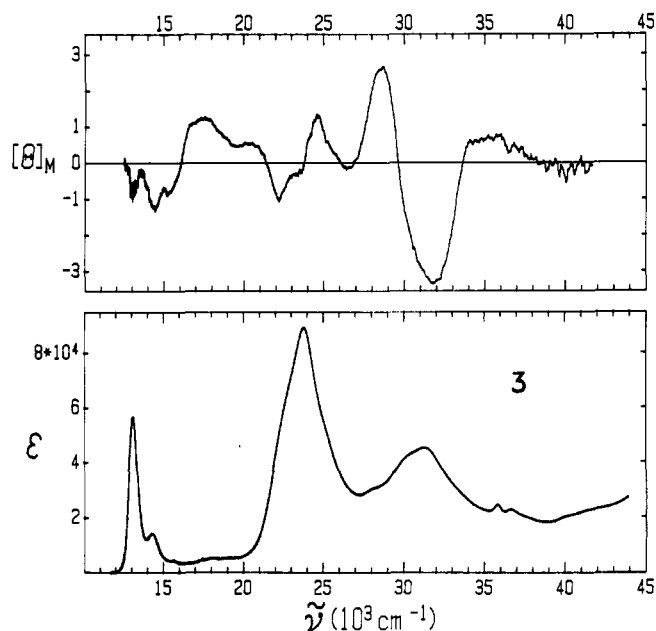

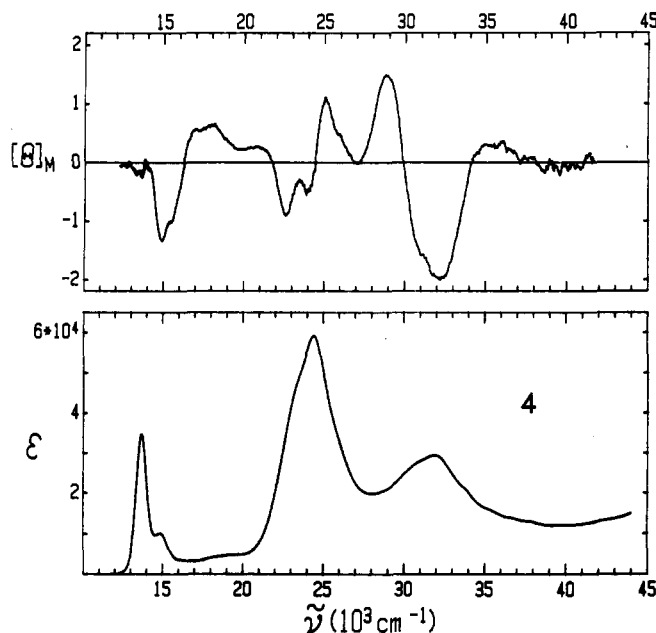Figure 1. Key: top, MCD; bottom, absorption spectra of 3.

Figure 2. Key: top, MCD; bottom, absorption spectra of 4.

greater spectral resolution of the latter, which enabled us to detect nine electronic transitions in the region below 35 000 cm^{-1}. We also compare the experimental data with results of semiempirical calculations and perform a geometry optimization of the parent nonmetallated compound at the QCFF/PI and AM1 levels.

Experimental Part and Computations

The synthesis and purification of the texaphyrins have been described.[2,10] The cadmium compounds (which are cationic complexes) were prepared and measured as the nitrate salts and the zinc, europium, and gadolinium salts as the acetates.

MCD spectra were recorded on a JASCO J-600 spectropolarimeter, equipped with a 15-kG electromagnet. Absorption spectra were run on a Varian 2300 spectrophotometer. Spectral-grade methanol (Malinckrodt) was used as solvent. All spectra were run at room temperature.

For the calculation of electronic transition energies, oscillator strengths, transition moment directions, and MCD B terms, we used the PPP[15] and INDO/S[16] methods. We tried two input
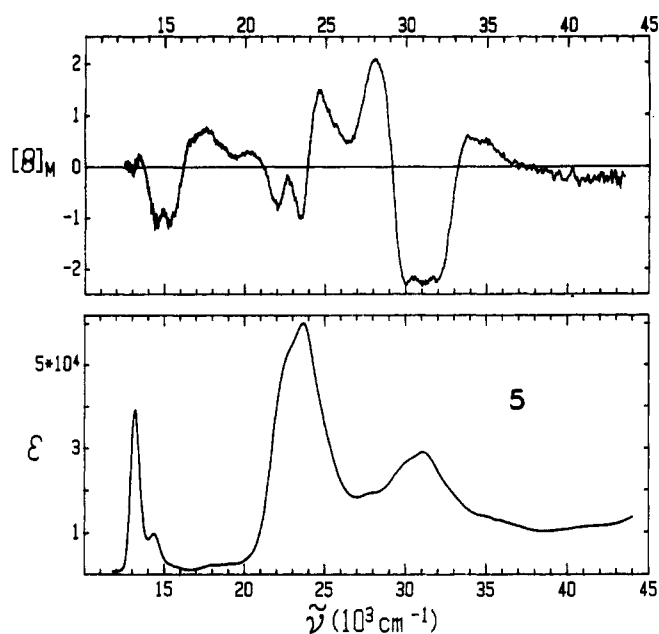
(7) Regev, A.; Berman, A.; Levanon, H.; Murai, T.; Sessler, J. L. *Chem. Phys. Lett.* **1989**, *160*, 401.

(8) Regev, A.; Levanon, H.; Murai, T.; Sessler, J. L. *J. Chem. Phys.* **1990**, *92*, 4718.

(9) Kennedy, M. A.; Sessler, J. L.; Murai, T.; Ellis, P. D. *Inorg. Chem.* **1990**, *29*, 1050.

(10) Maiya, B. G.; Mallouk, T. E.; Hemmi, G.; Sessler, J. L. *Inorg. Chem.* **1990**, *29*, 3738.

(11) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801, 6812, 6819. *Tetrahedron* **1984**, *40*, 3845.

(12) Keegan, J. D.; Stolzenberg, A. M.; Lu, Y.-C.; Linder, R. E.; Barth, G.; Moscowitz, A.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1982**, *104*, 4305, 4317. Goldbeck, R. A. *Acc. Chem. Res.* **1988**, *21*, 95. Djerassi, C.; Lu, Y.; Waleh, A.; Shu, A. Y. L.; Goldbeck, R. A.; Kehres, L. A.; Crandell, C. W.; Wee, A. G. H.; Knierzinger, A.; Gaete-Holmes, R.; Loew, G. H.; Clezy, P. S.; Bunnenberg, E. *J. Am. Chem. Soc.* **1984**, *106*, 4241. Goldbeck, R. A.; Tolf, B.-R.; Wee, A. G. H.; Shu, A. Y. L.; Records, R.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1986**, *108*, 6449.

(13) Waluk, J.; Mueller, M.; Boersch-Pulm, B.; Koecher, M.; Vogel, E.; Hohlneicher, G.; Michl, J. *J. Am. Chem. Soc.*, in press.

(14) Waluk, J.; Michl, J. Immediately preceding paper in this issue.

Figure 3. Key: top, MCD; bottom, absorption spectra of **5**.
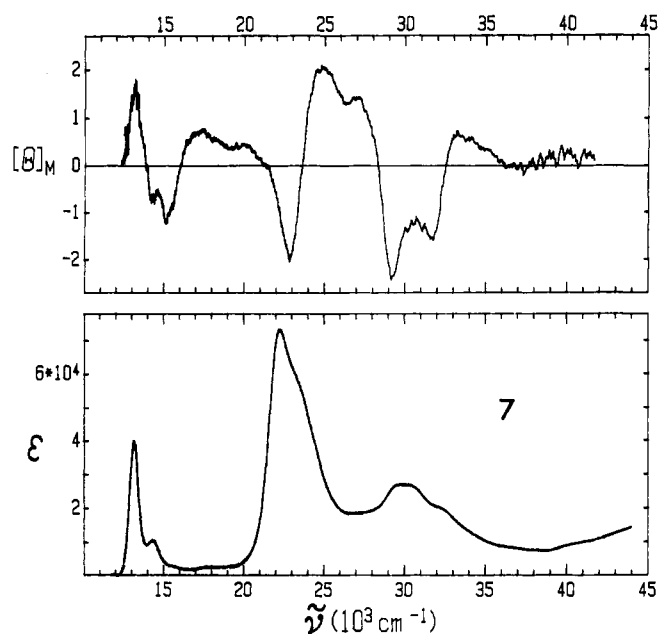

Figure 5. Key: top, MCD; bottom, absorption spectra of **7**.
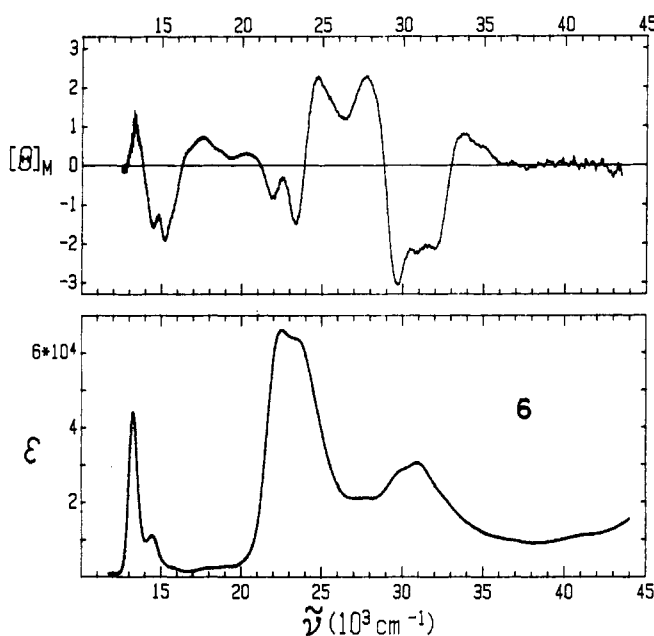

Figure 4. Key: top, MCD; bottom, absorption spectra of **6**.
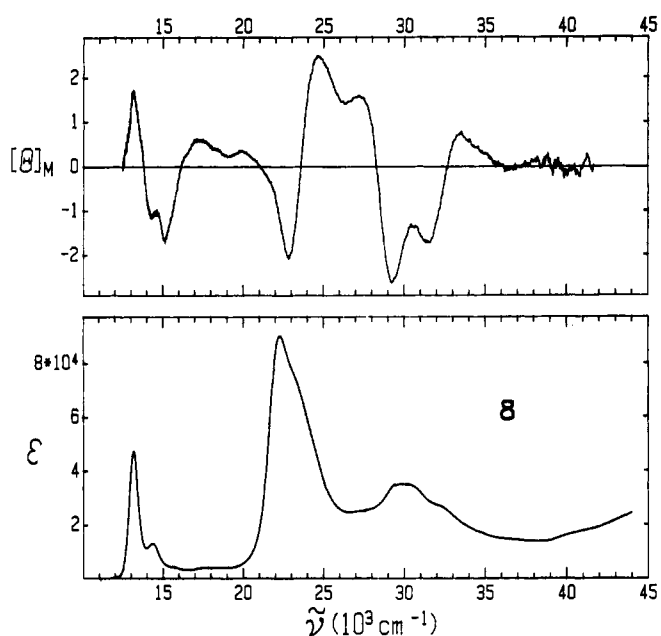

Figure 6. Key: top, MCD; bottom, absorption spectra of **8**.

geometries: (i) the X-ray structure that was determined[2] for the bis(pyridine) complex of **3** and (ii) the geometry of parent texaphyrin (**1**) optimized by the QCFF/PI[17] and AM1[18] methods. While the dependence of the calculated spectral properties on the input geometry was not severe, the QCFF/PI and AM1 methods each gave a completely different picture of the ground-state geometry of the parent, nonmetallated texaphyrin. By use of the former method, strong alternation of bond lengths was obtained, whereas the latter procedure predicted all C–C and C–N bonds to be equal at 1.40 ± 0.01 Å. Comparison with the X-ray data for the bis(pyridine)cadmium(II) complex shows that the QCFF/PI method works much better in predicting the ground-state structure, although even here, the agreement with experiment is far from perfect.

(15) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

(16) Zerner, M. Z. *Theor. Chim. Acta* **1973**, *32*, 111.

(17) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *97*, 5613. Lifson, S.; Warshel, A. *J. Chem. Phys.* **1968**, *49*, 5116.

(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Steward, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Results

Figures 1–12 present the absorption and MCD spectra of the metallotexaphyrins. The shape of the absorption curves remains very similar for all compounds except **14**. Different central metal atoms have some effect on the shape of MCD curves in the region 20 000–28 000 cm⁻¹ (cf. Figures 4–6). The most characteristic feature of the MCD spectra is the substituent effect on the lowest energy band, which can be either positive or negative, depending on the substituents in positions 16 or 17 (see Chart I for position numbering). A similar situation, i.e., substituent-dependent MCD sign, most probably occurs also for at least one transition in the spectral region 20 000–26 000 cm⁻¹ (cf., for instance, Figures 6 and 10). However, this region is very difficult to interpret, since at least three partially overlapping electronic transitions contribute to the total MCD intensity.

Comparison of absorption and MCD spectra demonstrates the advantages of the latter in locating and sepa-
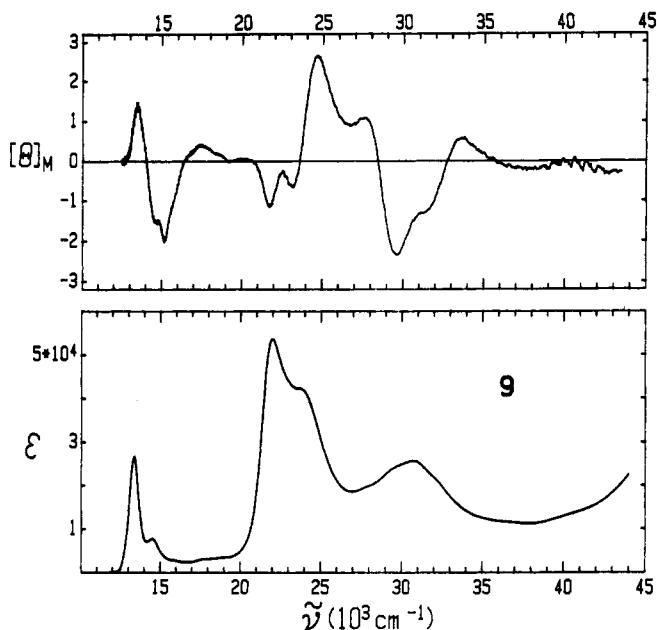
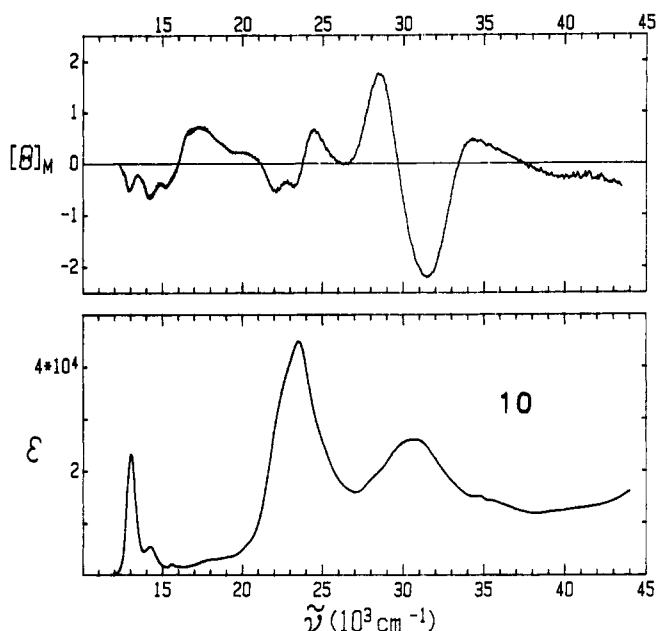**Figure 7.** Key: top, MCD; bottom, absorption spectra of 9.

Figure 9. Key: top, MCD; bottom, absorption spectra of 11.

Figure 8. Key: top, MCD; bottom, absorption spectra of 10.
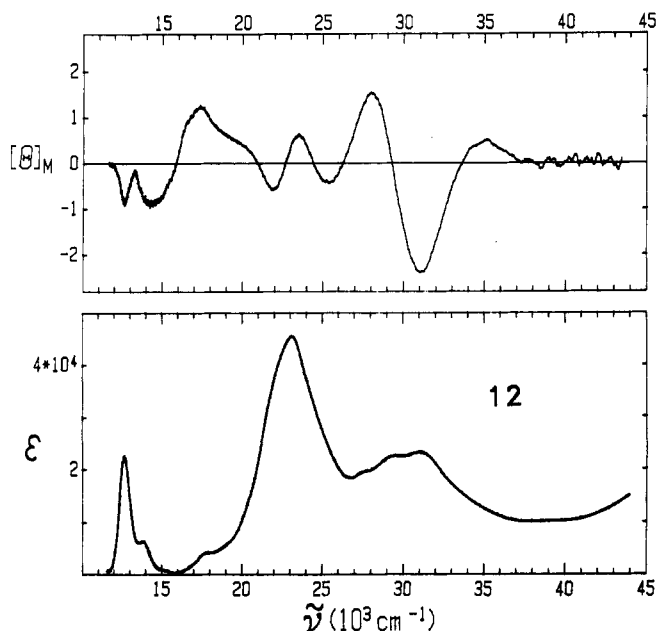
Figure 10. Key: top, MCD; bottom, absorption spectra of 12.

rating electronic transitions. At least nine excited states were identified in the region below 35000 cm^{-1}, more than twice the number that could be deduced on the basis of absorption spectra alone. This was possible since (i) both positive and negative MCD signs are present, (ii) different relative intensities appear in absorption and in MCD for different transitions (e.g., the band near 17000 cm^{-1} is very weak in absorption but has considerable intensity in MCD), and (iii) the spectra respond differently to different substituents or central metal atoms.

Both the PPP and INDO/S methods predict over 10 electronic transitions below 35000 cm^{-1} in the parent nonmetallated texaphyrin (Figure 13). A large number of overlapping bands was calculated above 23000 cm^{-1}. However, only two states are computed to lie below 20000 cm^{-1}. These should, therefore, be fairly well separated from the other transitions. These states correspond quite well to excitations from the HOMO into the LUMO orbitals and may thus be described in terms of the perimeter model as L$_1$ and L$_2$ or in terms of the usual porphyrin nomen-
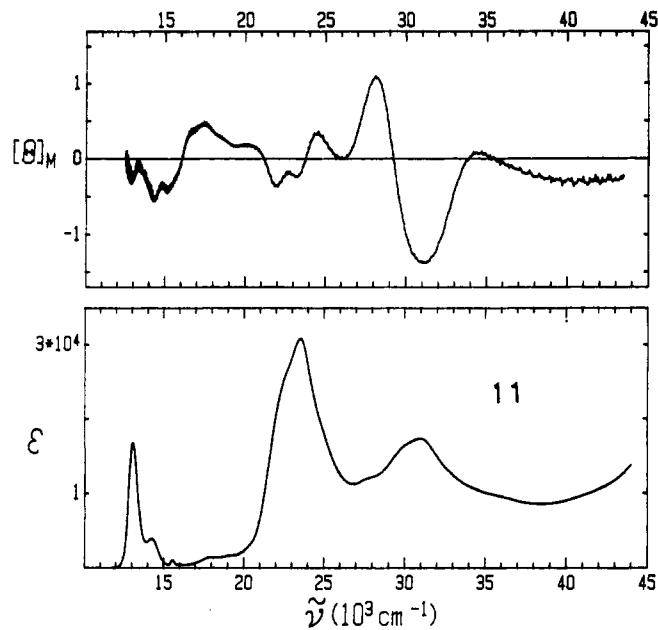
clature as Q$_x$ and Q$_y$. Another pair of transitions corresponding to electronic jumps between the frontier orbitals is calculated to lie ~10000 cm^{-1} higher in energy. These may be labeled B$_1$ and B$_2$ and treated as analogues of the Soret bands of porphyrins. The calculated intensity ratios between the pairs of B and L transitions (or, between Soret and Q bands, using "porphyrin" terminology) is ~10 for the PPP and 6 for the INDO/S method. The latter agrees quite well with experiment, if we assume that most of the absorption intensity in the region 20000–25000 cm^{-1} is provided by the Soret bands.

Discussion

The principles of interpretation of the MCD spectra of cyclic π-electron systems derived from a (4N + 2) π-electron perimeter have been summarized in the immediately preceding paper.[14] The four low-energy electronic excitations resulting from the simple perimeter model are L$_1$, L$_2$, B$_1$, and B$_2$, in order of increasing energy. Their MCD intensities contain two contributions of different origin.
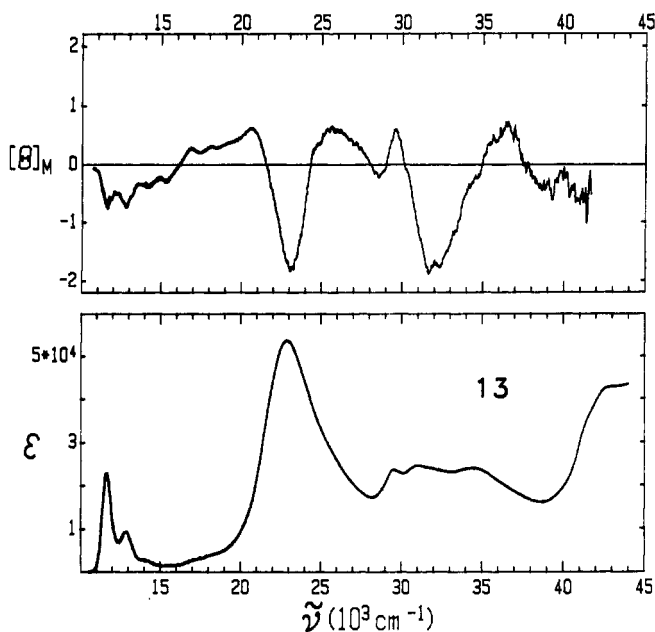
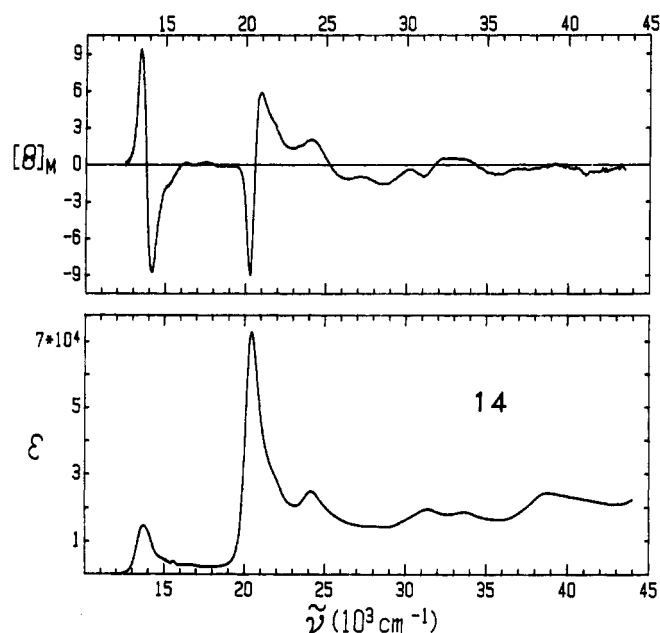**Figure 11.** Key: top, MCD; bottom, absorption spectra of **13**.

Figure 12. Key: top, MCD; bottom, absorption spectra of **14**.

The first are the μ^- contributions, always present, with signs independent of molecular structure. The second are the μ^+ contributions, arising when the energy splitting between the HOMO pair (ΔHOMO) is not equal to the splitting between the LUMO orbitals (ΔLUMO). For the L_1 and L_2 transitions, the latter are much larger than the former and their signs are sensitive to molecular structure. If ΔHOMO > ΔLUMO, their signs lead to a +, −, +, − sequence of the MCD B terms for L_1, L_2, B_1, and B_2 transitions, respectively. If ΔHOMO < ΔLUMO, a −, +, −, + sequence is expected. If ΔHOMO = ΔLUMO, even a small perturbation may change the sign pattern, depending on whether ΔHOMO or ΔLUMO becomes larger ("soft MCD chromophores").[11] On the contrary, for structures with ΔHOMO ≠ ΔLUMO, the signs of B terms are difficult to change by small perturbations ("hard chromophores").[11] Note that the sign of a B term is defined as opposite to the sign of an observed MCD peak.

The use of the perimeter model for MCD interpretations is justified if the energies of the excited states under
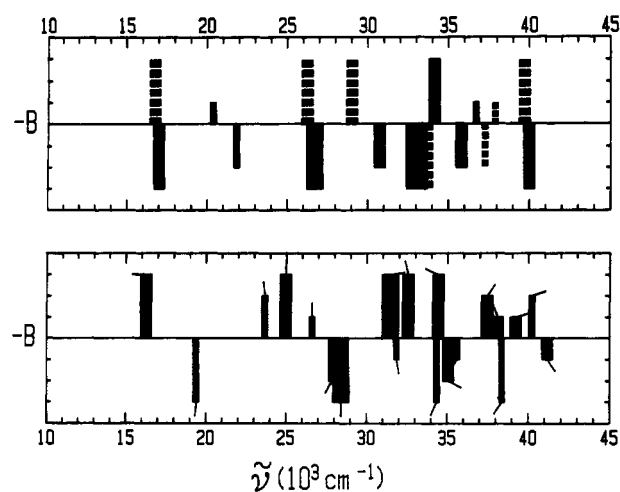
Figure 13. Results of calculations for unsubstituted non-metallated texaphyrin. Top: PPP method ("ideal" geometry), solid and broken bars denote horizontal and vertical polarization, respectively, in the formula (Chart I). Bottom: INDO/S results (X-ray geometry[2]), polarization of transitions shown with respect to the formula. Three different widths of the bars correspond to f < 0.1, 0.1 < f < 0.5, and f > 0.5; three heights indicate B < 1, 1 < B < 5, and B > 5, respectively. B terms in units of $10^{-3}\beta_e D^2/cm^{-1}$.

consideration lie reasonably far below the energies of higher energy states. If this is not the case, magnetic mixing with other states may become dominant and simple rules for the B terms no longer hold. In texaphyrins, it seems that the model may be applied to the lowest two excited states only, since the higher energy region contains many closely spaced electronic transitions. Our calculations confirm that wavefunctions of the first two excited singlet states indeed correspond to those expected from the simple model (the dominant configurations are HOMO → LUMO and second HOMO → LUMO).

In the preceding paper,[14] we outlined the first-order expectations for the frontier orbital energy ordering in texaphyrin (1) and its precursor, secophyrin (2). While the prediction of an a, s, −s, −a sequence seemed quite secure for secophyrin (2), it was not clear what should be the ordering of the top two highest occupied MO's in texaphyrin (1). This was caused by the fact that the a orbital of secophyrin (2) should be destabilized as a result of interaction with the HOMO orbital of cis-butadiene when going to the benzo analogue, texaphyrin (1). If this interaction is strong enough, the initial, a, s ordering in secophyrin (2) may be reversed in texaphyrin (1). The LUMO ordering may be safely assumed to be −s, −a in both cases, since it is the −s orbital of secophyrin (2) that becomes stabilized after the interaction with the LUMO orbital of cis-butadiene.

For the unsubstituted parent texaphyrin, our INDO/S calculations predict the s, a, −s, −a sequence of frontier orbitals, while the PPP results give an a, s, −s, −a order, with the HOMO orbitals nearly degenerate (ΔHOMO = 0.14 eV). The order of the two HOMO's clearly is difficult to predict from calculations. As we shall see in the following text, it can be established unequivocally for the known metallohexaalkyltexaphyrins from the effect of substitution on the observed MCD spectra, as demonstrated previously in the case of 1,6-methano[10]-annulene.[19] Since this is such a close call, it is possible that the order is different in the parent texaphyrin and

(19) Klingensmith, K. A.; Püttmann, W.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3375.
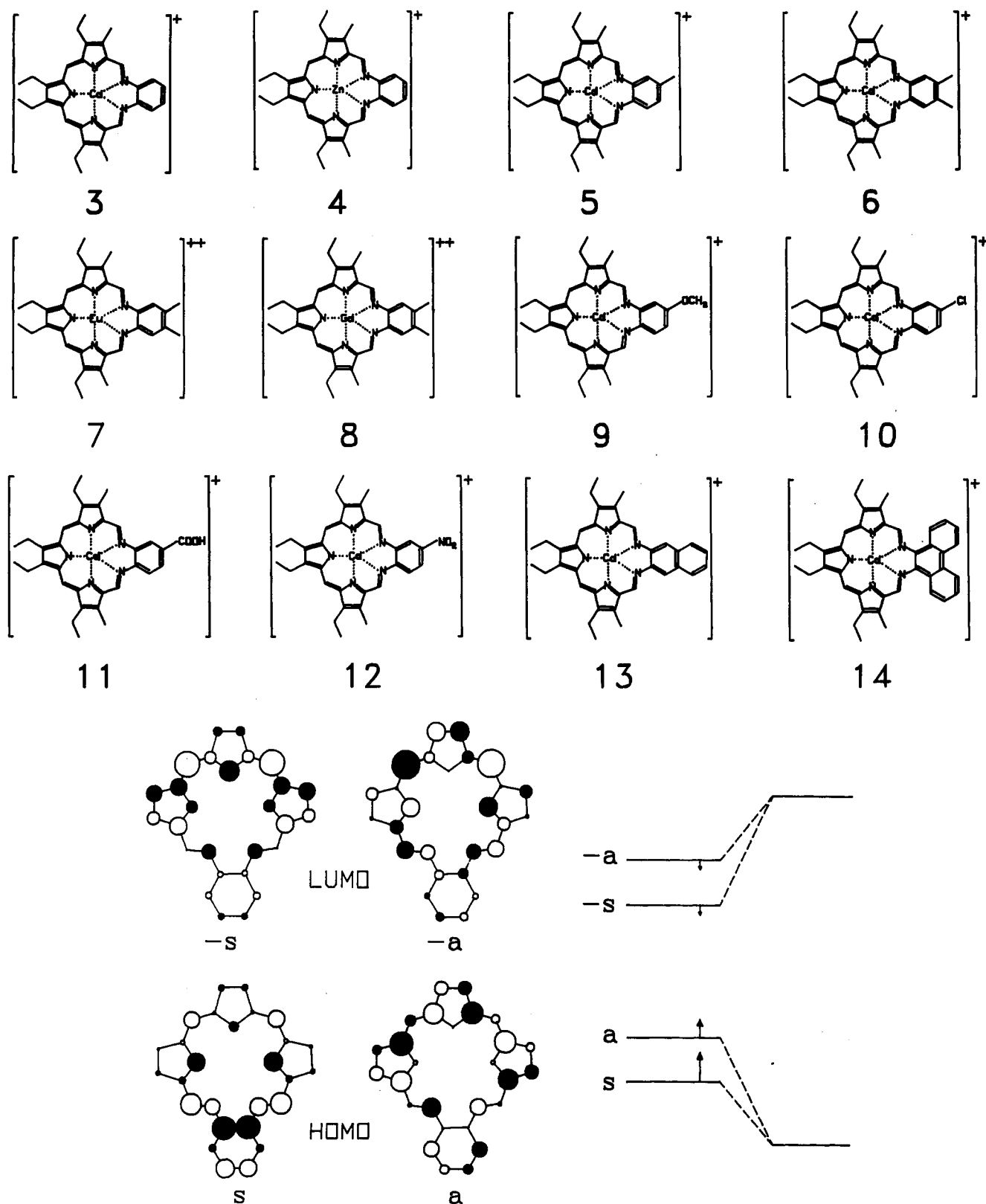
Chart II

Figure 14. Key: left, frontier π-orbitals obtained by PPP method; right, their interaction with electron-donating and electron-accepting substituents.

in the hexaalkylated metallo derivatives.

The two compounds unsubstituted in positions 16 and 17, 3 and 4, reveal the same weakly positive sign of MCD B terms for the lowest two electronic transitions. Such a sequence is characteristic of soft chromophores and suggests the equality ΔHOMO = ΔLUMO, since in the case

of vanishing μ^+ contributions the MCD intensity is determined by the μ^- contributions and these have the same weakly positive signs for the L_1 and L_2 transitions. The conclusion that ΔHOMO and ΔLUMO are approximately equal but both quite different from zero in both the parent texaphyrin and its hexaalkylmetallo derivatives is quite
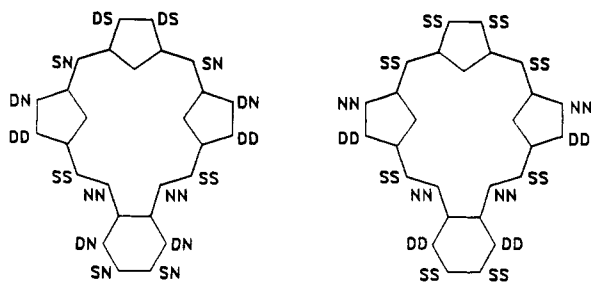
Figure 15. Texaphyrin: predicted responses to mesomeric (left) and inductive (right) substitutions; first letter, the position type with respect to a −E (−I) effect; second letter, the position type with respect to a +E (+I) effect. See text for details.

firm regardless of the order of the orbitals s and a and is nicely compatible with the much stronger absorption intensity of the L_1 transition compared with L_2, as expected from the perimeter model in this instance.[11]

We can now proceed to analyze the effect of substitution in positions 16 and 17 upon the MCD spectra, assuming at first the s, a, −s, −a orbital energy ordering. Electron-donating substituents will affect primarily the energies of the HOMO orbitals and electron-withdrawing ones those of the LUMO orbitals, as dictated by the energy differences between the interacting orbitals. To first order in perturbation theory, the net effect of the interaction will depend on the square of the LCAO coefficients of the frontier orbitals at the position of substitution. For the HOMO orbitals, both PPP and INDO/S methods predict that these coefficients are larger for the s orbital (Figure 14). Hence, the interaction of the HOMO orbitals with the donor orbitals of electron-donating substituents should raise the energy of the s orbital more than that of the a orbital and lead to ΔHOMO < ΔLUMO, inducing a −, + sequence of B terms for the L transitions. Exactly this behavior is observed for all compounds with electron-donating substituents in positions 16 or 17 that we have studied (Figures 3–8), except the chlorine derivative 10. In the latter, chlorine is a weak π-electron donor, but it

also has an opposite inductive effect. One may thus expect that the two effects will cancel, at least partly, and the orbital splitting will not change much with respect to the unsubstituted derivative. This is indeed observed (cf. Figures 1 and 8).

If one now assumes the opposite orbital energy ordering, a below s, the electron-donating substituents still increase the energy of the s orbital, but now this increases ΔHOMO relative to ΔLUMO, inducing a +, − sequence of B terms. This is opposite to what is observed, and we conclude that in the metallohexaalkyltexaphyrin chromophore, s lies below a.

For the −s and −a orbitals, calculations predict very similar values of the LCAO coefficients in positions 16 and 17 (Figure 14). Thus, both orbitals should interact with orbitals of electron-withdrawing substituents to a more or less similar degree and no change in the LUMO splitting is to be expected. Thus, a +, + pattern of the B terms, observed for the unsubstituted compounds, should be preserved. Indeed, this is what we observe (Figures 9 and 10).

Similar arguments may now be applied for predicting the spectral response to E and I substitution at any position in texaphyrin (1). Figure 15 shows the position types obtained on the basis of PPP calculations and the just verified assumption of s, a, −s, −a orbital ordering. The electron-donating substituents, which cause ΔHOMO < ΔLUMO when put in positions 16 and 17, should cause the opposite effect in positions 15 and 18 (ΔHOMO > ΔLUMO, a +, − sequence of B terms for the L transitions). Electron-withdrawing substituents are not expected to change the MCD pattern in any of these positions. They should induce ΔHOMO < ΔLUMO only when applied in positions 10 and 23.

The naphtho- (13) and phenanthro- (14) annelated secophyrins require a separate treatment. Their MCD spectra are totally different (Figures 11 and 12). The spectrum of the former resembles closely that of the hexaalkylated parent metallotexaphyrins, 3 and 4, while the spectrum of the latter is completely different and much
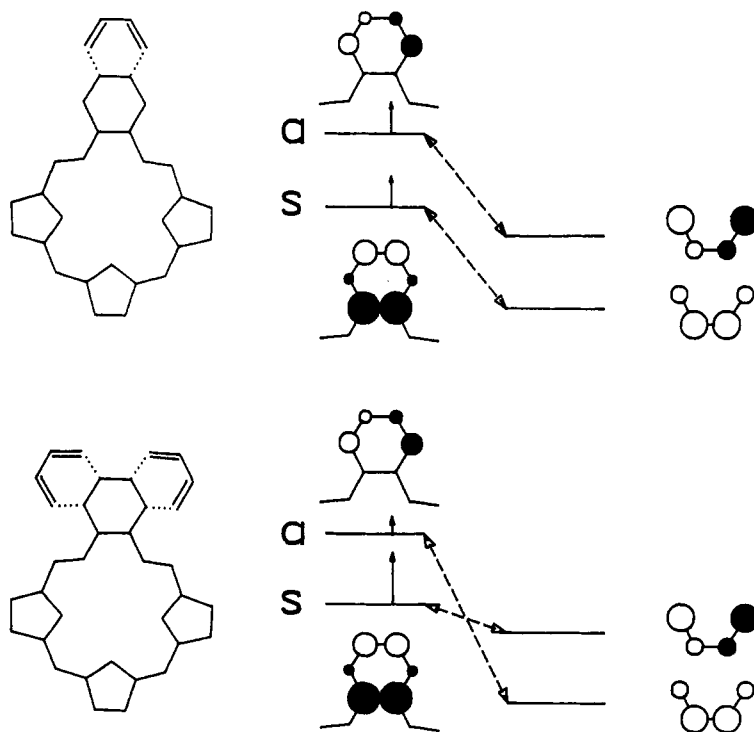

Figure 16. Interaction of orbitals of texaphyrin with orbitals of s-cis-butadiene upon formation of 13 (top) and 14 (bottom).

more intense. This behavior may readily be understood if one formally derives these compounds from **3** by adding one (**13**) or two (**14**) s-cis-1,3-butadiene bridges (Figure 16). For each of these two molecules, different orbitals of texaphyrin and butadiene will interact for symmetry reasons. In the case of **13**, the second HOMO (s) will interact with the lowest π-orbital of butadiene and the HOMO orbital (a) with the second lowest orbital of butadiene. Considering the energy differences and the values of LCAO coefficients (Figure 14), we may expect a similar shift of both HOMO orbitals toward higher energy. Thus, the value of ΔHOMO should remain approximately unchanged. ΔLUMO is not expected to change, either, since the interaction of the LUMO orbitals with the orbitals of butadiene may be neglected due to small values of LCAO coefficients in both LUMO orbitals. Thus, the similarity of the MCD spectra of **3** and **13** is not surprising. One should, however, expect the two lowest excited states of the latter compound to lie at lower energies than the corresponding transitions of the former, since both HOMO orbitals now lie at higher energies. This is indeed observed (cf. Figures 1 and 11).

In compound **14**, the orbital interaction picture is different. Now, the HOMO orbital (s) interacts with the second occupied orbital of butadiene, while the a orbital interacts with the first one. Since the energy difference between the interacting pair of orbitals is much smaller in the former case, one should expect that the s orbital

should be destabilized to a much higher degree than the a orbital. One now predicts ΔHOMO < ΔLUMO, and henceforth a −, + sequence of μ⁺ contributions to the B terms. Additional amplification of this effect with respect to **13** stems from the fact that the shifts now result from the interaction with two butadiene units.

The prediction of a −, + sequence of relatively large B terms for **14** is in perfect agreement with experiment and provides yet another argument for the s, a, −s, −a orbital ordering. The a, s, −s, −a sequence leads to a prediction of benzannelation effects that cannot be reconciled with the observed spectra.

In summary, our results show that the perimeter model accounts in a simple way for the signs of the MCD B terms of the low-lying electronic transitions of metallotexaphyrins. They demonstrate the s, a, −s, −a orbital energy pattern for the hexaalkylated parent metallotexaphyrins, **3** and **4**, and show that in these, the values of ΔHOMO and ΔLUMO are nearly the same, so that they are soft MCD chromophores. This equality may easily be destroyed by substitution in positions 16 or 17 by electron-donating substituents, but not by electron-withdrawing ones.

Heats of Reaction of Resonance-Stabilized Carbenium Ions with Nitrogen Bases

Edward M. Arnett* and Sampath Venimadhavan

Department of Chemistry, Duke University, Durham, North Carolina 27706
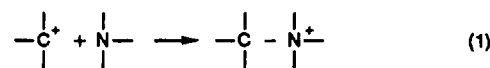
Heats of reaction (ΔH_{rxn}) are reported for five resonance-stabilized carbenium ions with ten aliphatic amines and seven pyridines in sulfolane at 25 °C to produce substituted ammonium ions. Heats of reaction (ΔH_{rxn}) for these neutral bases fall in the same range as the corresponding heats of reaction of the carbenium ions with a variety of resonance-stabilized anions (carbanions, and oxyanions) whose pK_as are comparable to those of the amines and pyridines. Although the ΔH_{rxn}s do not correlate with the aqueous pK_{BH^+}s of the amines, good correlations are obtained using the pK_{R^+}s of the carbenium ions and with the gas-phase heats of reaction of the amines with trimethylboron. Also, the ΔH_{rxn}s of pyridines with the carbenium ions correlate fairly well with the pK_{R^+}s of the carbenium ions and are surprisingly insensitive to steric hindrance.

Introduction

In 1933, Hughes, Ingold, and Patel published their comparison of the attack of hydroxide ion on trimethyl-n-decylammonium and trimethylbenzhydrylammonium ions.[1] The dramatic difference in kinetic order established a duality for displacement reactions which is now familiar to every student of introductory organic chemistry. However, with the exception of Ritchie's equilibrium studies[2] and the recent flash photolysis work of McClel-

land[3] there are no published accounts of the thermodynamics of reaction between amines and carbenium ions in solution (eq 1). In addition, Katritzky's group has studied

$$-\overset{|}{\underset{|}{C}}{}^+ \; + \; \overset{|}{\underset{|}{N}}{-} \; \longrightarrow \; -\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{N}}{\overset{+}{-}} \tag{1}$$

displacements on a wide range of ammonium ions[4] and have also examined the gas-phase fragmentation of a series of alkylpyridinium ions to form carbenium ions and a pyridine molecule.[5]

(1) Hughes, E. D.; Ingold, C. K.; Patel, C. S. *J. Chem. Soc.* **1933**, 526.
(2) (a) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239–50 and references therein. (b) Ritchie, C. D.; Van Verth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491. (c) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1973**, *95*, 1882. (d) Ritchie, C. D.; Minasz, R. J.; Kamego, A. A.; Sawada, M. *J. Am. Chem. Soc.* **1977**, *99*, 3747 and references therein. (e) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.

(3) (a) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918 and references therein. (b) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.
(4) Katritzky, A. R.; Brycki, B. E. *Chem. Soc. Rev.* **1990**, *19*, 83–105 and references therein.