Magnetic Circular Dichroism of the Long-Wavelength π-π^* Transitions in Nitrogen-Containing Heteroconjugated Aromatic Compounds and in Selected Ruthenium Complexes

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

The long-wavelength magnetic circular dichroism (MCD) spectra of some nitrogen-containing heteroconjugated aromatic compounds have been recorded and interpreted on the basis of quantum-chemical model calculations. In particular, the dependence of the MCD bands on the positions of the N-atoms inside the aromatic rings and on substituents has been investigated.

Some of the compounds considered form Ru^{2+} complexes. The influence of complexation on the long-wavelength π-π^* bands of the ligands has also been recorded and discussed.

1. Introduction. – Magnetic circular dichroism (MCD) is a spectroscopic method that reveals the influence of a magnetic field on the electronic states of molecules. It is the manifestation inside absorption bands of the well-known *Faraday* effect. MCD is, thus, related to *Faraday* rotation in the same way as natural CD is related to natural optical rotation. While natural CD occurs only in chiral media, MCD is induced by a magnetic field in all matter, irrespective of symmetry.

There exists a large amount of literature on the MCD spectra of paramagnetic molecules, and of diamagnetic molecules of high symmetry, where MCD signals are comparatively large and mainly may be classified as (temperature-dependent) C terms and/or bisignate A terms [1].

In diamagnetic molecules without orbital degeneracies, such as those studied here, one detects only the so-called MCD B terms. These spectra are, in general, more complicated and weaker, and their measurement requires relatively high magnetic fields. In special classes of compounds, particularly in molecules containing aromatic rings, the spectra may be interpreted at least semi-quantitatively by quantum-chemical models and methods. The identification of electronic bands in the long-wavelength part of the absorption spectrum is thereby improved.

The systematic study of the MCD spectra of substituted aromatic compounds has been pioneered mainly by *Michl* and co-workers [2]. They developed and successfully applied a Perturbed-Perimeter Model to the interpretation and classification of their experimental data.

We here report the MCD spectra of the near-UV electronic bands of some chosen N-containing heteroconjugated aromatic molecules, in particular also of bipyridine derivatives and of bipyrazine. Some of these compounds act as ligands in tris-Ru^{II} complexes. A comparison of the MCD spectra of the free ligands with those of their complexes shows the influence of complexation on the ligand π-π^* excited states. This investigation [3] is the continuation of similar previous MCD work on quinones and related compounds [4]. The interpretation is based on SCF-MO-single-CI calculations within the semi-empirical PPP approximation.

As is long-since known [5], in many of the molecules considered here, the lowest excited state is not of π-π^* but of n-π^* type. However, in most cases, the contributions of the n-π^* transitions to the MCD is weak, overshadowed by the π-π^* bands, and not distinctly identifiable. Exceptions will be noted and discussed.

2. Methods. – The MCD spectra were recorded in solution with a *Jasco 500C* circular dichrograph modified in such a way that an *Oxford Instruments SM-1* cryomagnet could be fitted into the probe compartment. The measurements were carried out in a magnetic field of *ca.* 5T and at a probe temperature of 10°. Further technical details, in particular concerning the magnetic shielding of the optical and electronic components, are given in [4a] and [6].

The theoretical quantity B was computed for the long-wavelength transitions by the sum-over-states formula indicated in [4a]. Information on the calculation of the excitation energies, the electric and magnetic dipole transition moments, as well as on the state dipole moments are also to be found there.

The relation between the theoretical quantity B and the integrated molar ellipticity per Tesla $[\theta_{\mathrm{M}}]$ of a band is given by the expression:

$$B = -(1/33.53) \int_{band} d\nu([\theta_{\mathrm{M}}]/\nu). \tag{1}$$

Notice the minus sign. The formula is, of course, applicable only where bands arising from different electronic transitions do not overlap too strongly.

3. Results and Discussion. – 3.1. *The Phenylpyridines.* The measured spectra in MeCN, as well as the computed data, are displayed in *Figs. 1–3*.

Calculations were performed for different dihedral angles around the bond connecting the two aromatic rings. The most-consistent results were obtained for 30°. A striking feature of the experimental MCD data with respect to the sign and absolute value of the longest-wavelength band is the difference between the spectra of the 2-phenyl- and 3-phenylpyridines (*o*- and *m*-compounds) on the one hand, and that of the 4-phenyl (*p*) compound on the other. The particular aspect of the spectrum of the 4-Ph compound was already noted in preliminary investigations by *Meier* [6], and a tentative explanation was given there.

We focus our attention on the values of the B terms for the transitions from the respective ground-state G to the singlet excited states $|1\rangle$ and $|3\rangle$, and $B(G \rightarrow 1)$ and $B(G \rightarrow 3)$. The quantity $B(G \rightarrow 2)$ is comparatively much smaller in all three molecules, and does not appear to influence the MCD spectrum appreciably. An analysis of the computations reveals that a sign-determining contribution to the sum-over-states expression for $B(G \rightarrow 1)$ is proportional to:

$$(E_3 - E_1)^{-1} \operatorname{Im} \langle 1 | \boldsymbol{m} | 3 \rangle \cdot \langle G | \boldsymbol{\mu} | 1 \rangle \times \langle 3 | \boldsymbol{\mu} | G \rangle \tag{2}$$

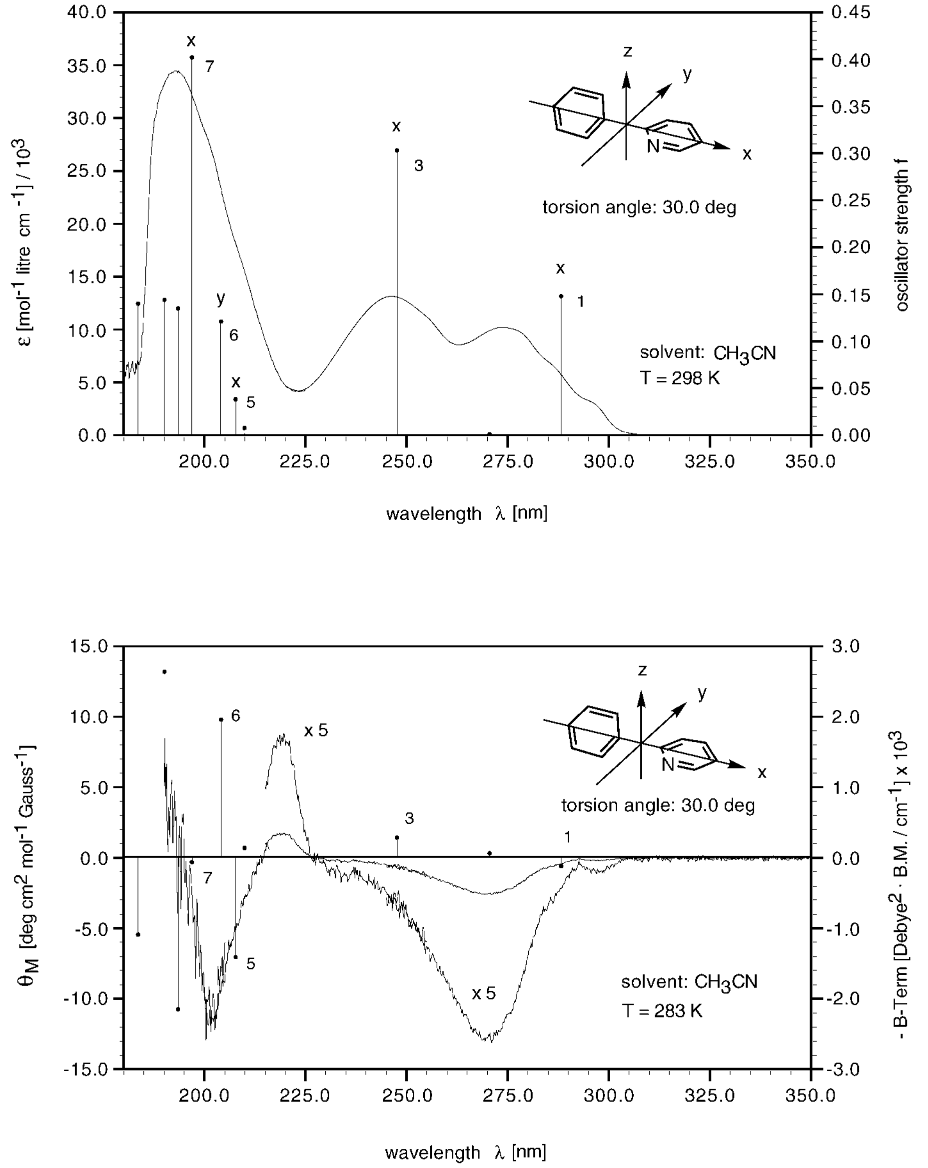


Fig. 1. *2-Phenylpyridine:* upper: *measured and computed absorption spectrum*; lower: *measured* (ellipticity per unit field strength) *and computed* (negative *B* term) *MCD spectrum*

$\boldsymbol{m}$ and $\boldsymbol{\mu}$ being the magnetic and electric dipole operators, respectively. For the term $B(G \rightarrow 3)$, there is a similar contribution, but with $|3\rangle$ and $|1\rangle$ interchanged, which then inverts the sign. In all three compounds, the magnetic dipole transition moment $\langle 1 | \boldsymbol{m} | 3\rangle$ lies in the y,z-plane with a large component in the z-direction (see *Figs.*). The electric dipole transition moment $\langle 3 | \boldsymbol{\mu} | G\rangle$ shows a dominant x-component in the 2-Ph and 3-

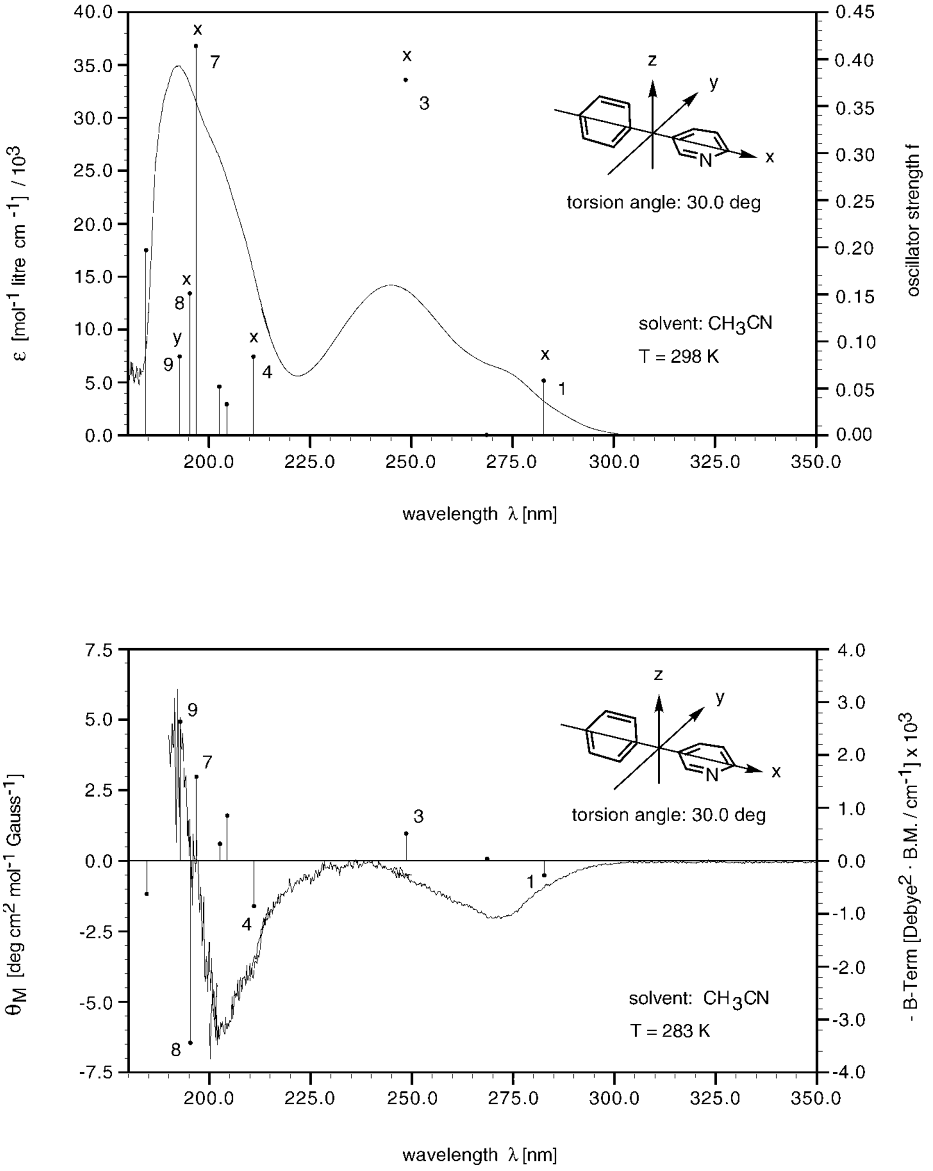


Fig. 2. *3-Phenylpyridine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

Ph compounds, and lies exclusively in the x-direction in the 4-Ph compound (because of exact symmetry C_2). Finally, the transition moment $\langle G \,|\, \boldsymbol{\mu} \,|\, 1 \rangle$ is mainly x-*directed* in the 2-Ph and 3-Ph isomers, but predominantly y-*directed* in 4-Ph isomer, albeit with a smaller absolute value.

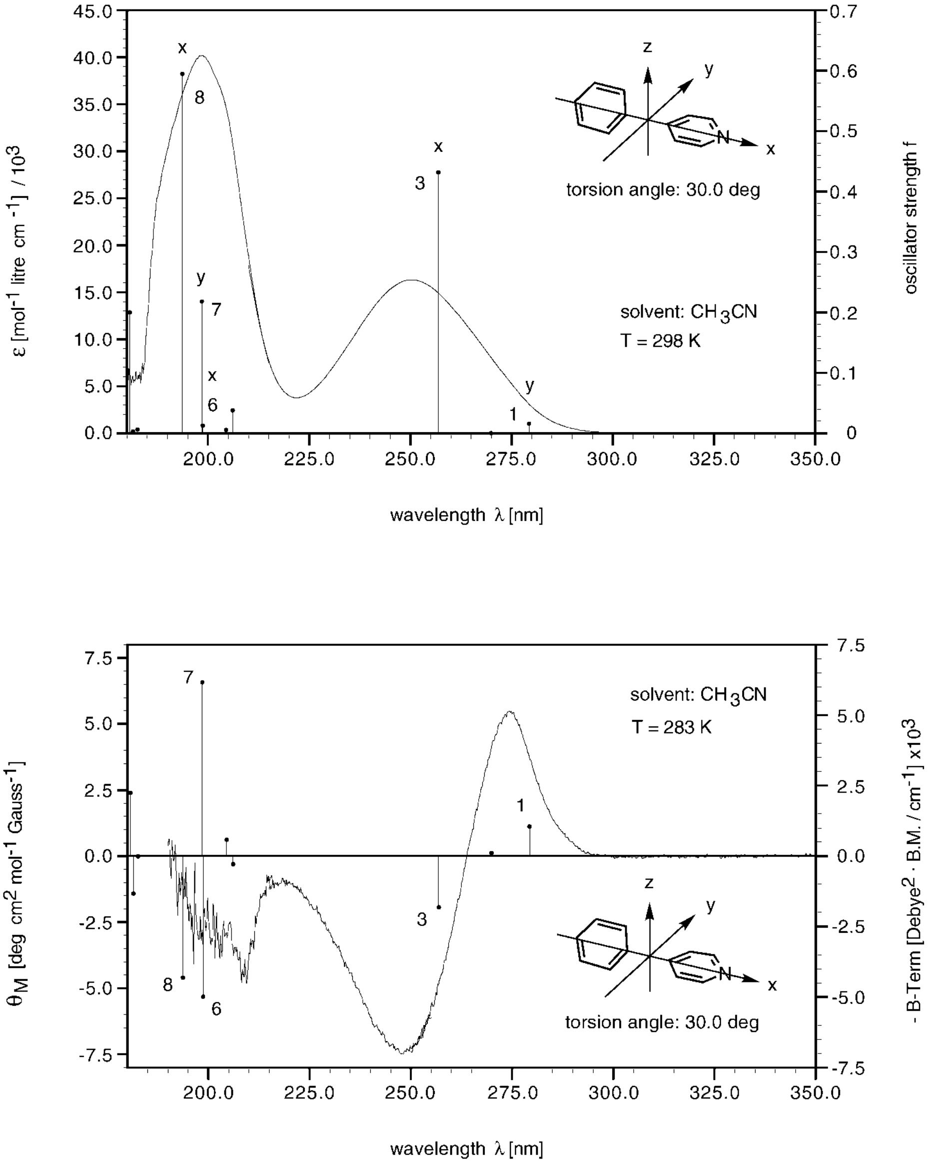


Fig. 3. *4-Phenylpyridine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

Looking at the measured MCD spectra, we notice that the longest-wavelength band (*1*) is negative in 2-Ph and 3-Ph compounds, in qualitative agreement with the computed positive value for $B(G \rightarrow 1)$. The predicted positive band (*3*) is not directly identifiable in the spectrum. It may possibly be overshadowed by the shorter-wavelength negative band *5* in 2-Ph compound, and by the negative band *4* in 3-Ph compound. In the 4-Ph isomer, the longest-wavelength transition *1*, though weak and hardly visible in the absorption spectrum, is predicted to be predominantly y-*polarized* and leads, in conjunction with the x-*polarized* transition *3*, to a strong and characteristic bisignate, positive-negative, pseudo-A term [4] in the MCD spectrum, in qualitative agreement with the calculation.

The question then remains, why, in the 2-Ph and 3-Ph isomers, is the longest-wavelength transition predominantly x-*polarized*, while, in the 4-Ph isomer, it is mainly y-*polarized* albeit weak. From the calculations, we notice that the first excited singlet state $|1\rangle$ in the 2-Ph and 3-Ph compounds contains, to a large extent, the HOMO-LUMO excitation $6 \rightarrow 7^*$, with CI coefficients of 0.78 for 2-Ph and 0.64 for 3-Ph compound. In 4-Ph compound, on the other hand, the MOs *6* and *7**, which are of symmetry a under C_2 (*Fig. 4*), both show a significant N AO coefficient. Due to the electronegativity of N, expressed in its high valence-state ionization potential, MOs *6* and *7** are lowered with respect to MO *5*, which is of symmetry b. The y,z-*polarized* excitation $5 \rightarrow 7^*$ becomes lowest in energy, and the singlet state $|1\rangle$ turns out to be of symmetry B under C_2, and not of symmetry A, as one would expect from the two other isomers.

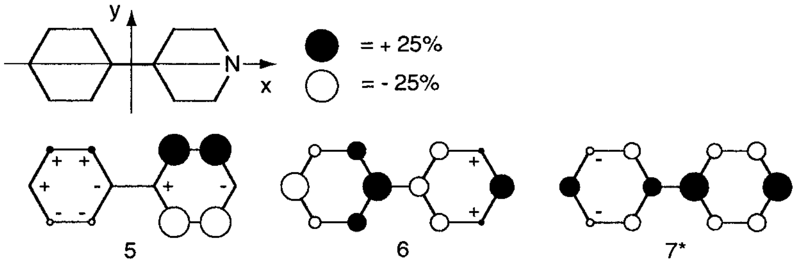
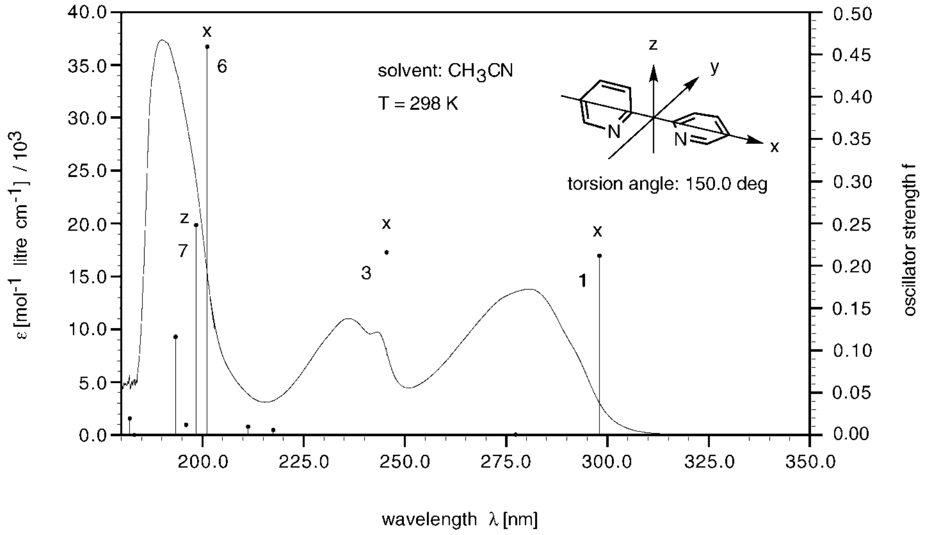


Fig. 4. *4-Phenylpyridine: relative magnitude and sign of the AO coefficients of the two highest occupied* (*5* and *6*) *and the lowest unoccupied* (*7**) *MOs*

3.2. *The Bipyridines.* The measured spectra of the compounds 2,2′-, 3,3′-, and 4,4′-bipyridine, as well as the computed data, are displayed in *Figs. 5–7.* The dihedral angles between the aromatic rings adopted in the calculations were those for which agreement with the spectroscopic data was best.

In analogy with the phenylpyridines, we notice also here a striking difference between the MCD spectra of the 2,2′- and 3,3′-bipyridines on one hand, and that of the 4,4′-bipyridine on the other. The origin of this difference is basically the same as in the phenylpyridines.

In 2,2′- and 3,3′-bipyridine the long-wavelength absorption and MCD spectrum are dominated by the transitions $G \rightarrow 1$ and $G \rightarrow 3$, which are both x-*polarized*, *i.e.*, of symmetry B under C_2. A dominant contribution to $B(G \rightarrow 1)$ is, as previously seen, the term given by *Expression 2*. An important influence in $B(G \rightarrow 3)$ is represented by the corresponding term with states $|1\rangle$ and $|3\rangle$ interchanged. We notice that the agreement of the computed MCD spectra with experiment is, in general, better than for the phenylpyridines. The influence of the term $B(G \rightarrow 3)$ is experimentally clearly detectable. This may be due to the higher molecular symmetry making selection rules clear-cut.



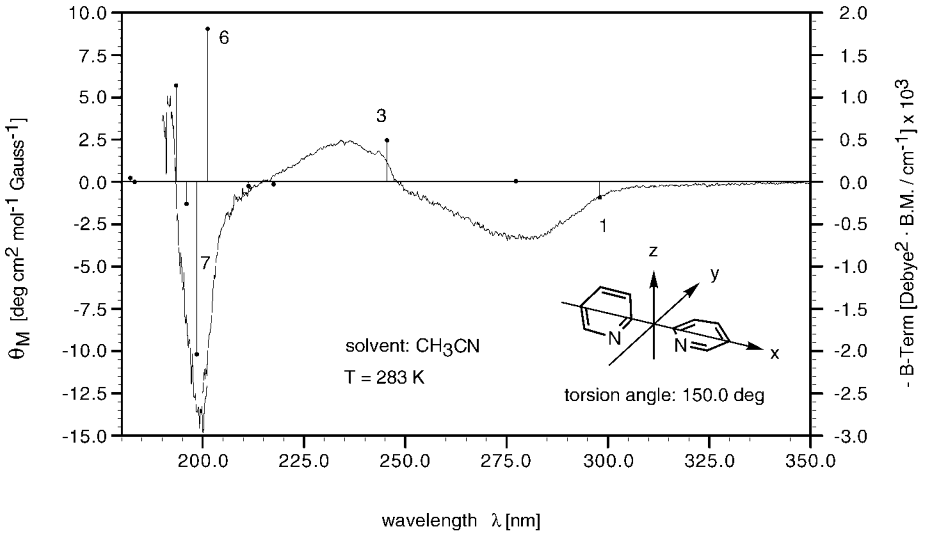


Fig. 5. *2,2′-Bipyridine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

In 4,4′-bipyridine, the transition $G \rightarrow 1$ is predicted to be *z-polarized*, *i.e.*, of symmetry B_1 under D_2, in contrast to the situation in 2,2′- and 3,3′-bipyridines. Indeed, we find the magnetic transition moment $\langle 1 | \boldsymbol{m} | 3 \rangle$ to be *y*-directed, and the electric transition moments $\langle G | \boldsymbol{\mu} | 1 \rangle$ and $\langle 3 | \boldsymbol{\mu} | G \rangle$ to lie along $(-z)$ and $(+x)$, respectively. Furthermore, the transition $G \rightarrow 2$, predicted to be of symmetry B_2 and *y-polarized*, is

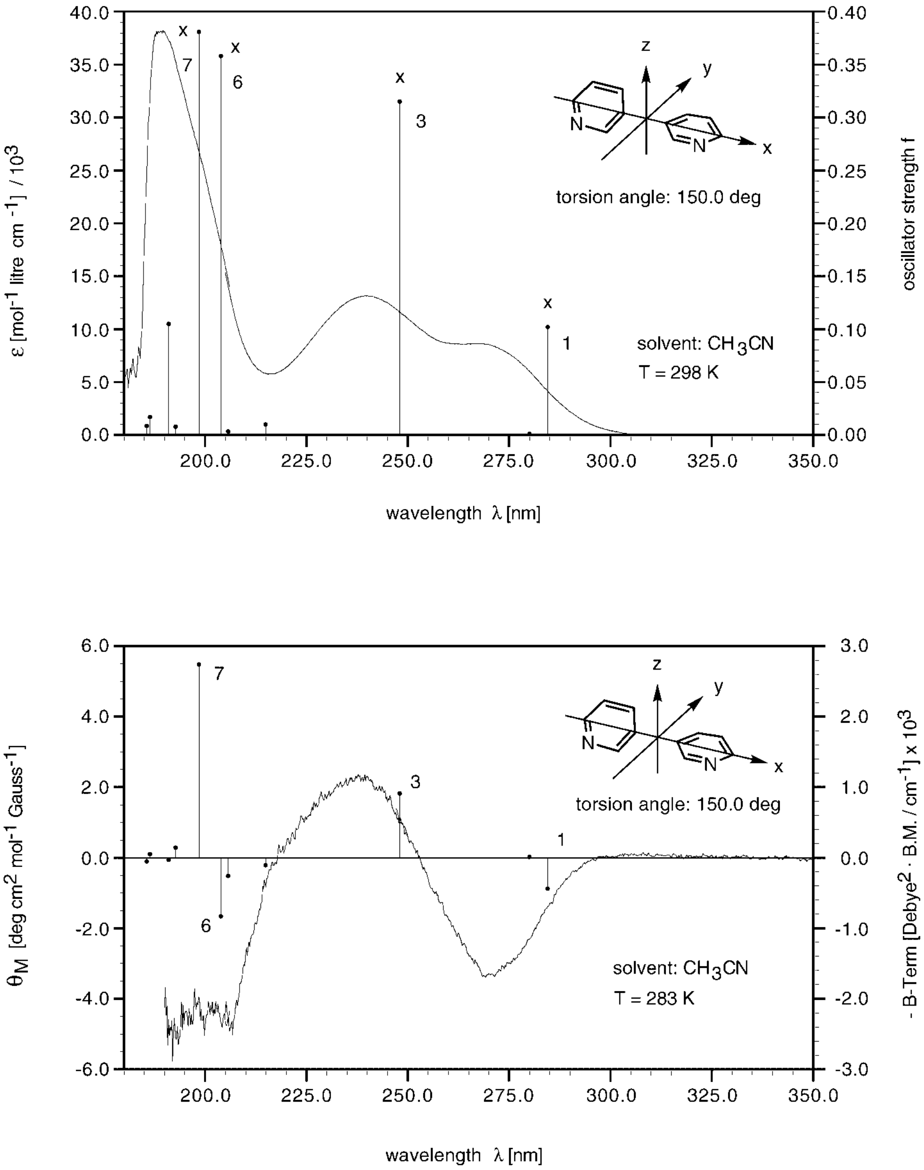


Fig. 6. *3,3'-Bipyridine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

almost degenerate with $G \rightarrow 1$ and influences strongly the MCD spectrum. An important contribution to $B(G \rightarrow 2)$ is:

$$(E_3 - E_2)^{-1} \operatorname{Im} \langle 2 | \boldsymbol{m} | 3 \rangle \cdot \langle G | \boldsymbol{\mu} | 2 \rangle \times \langle 3 | \boldsymbol{\mu} | G \rangle \tag{3}$$

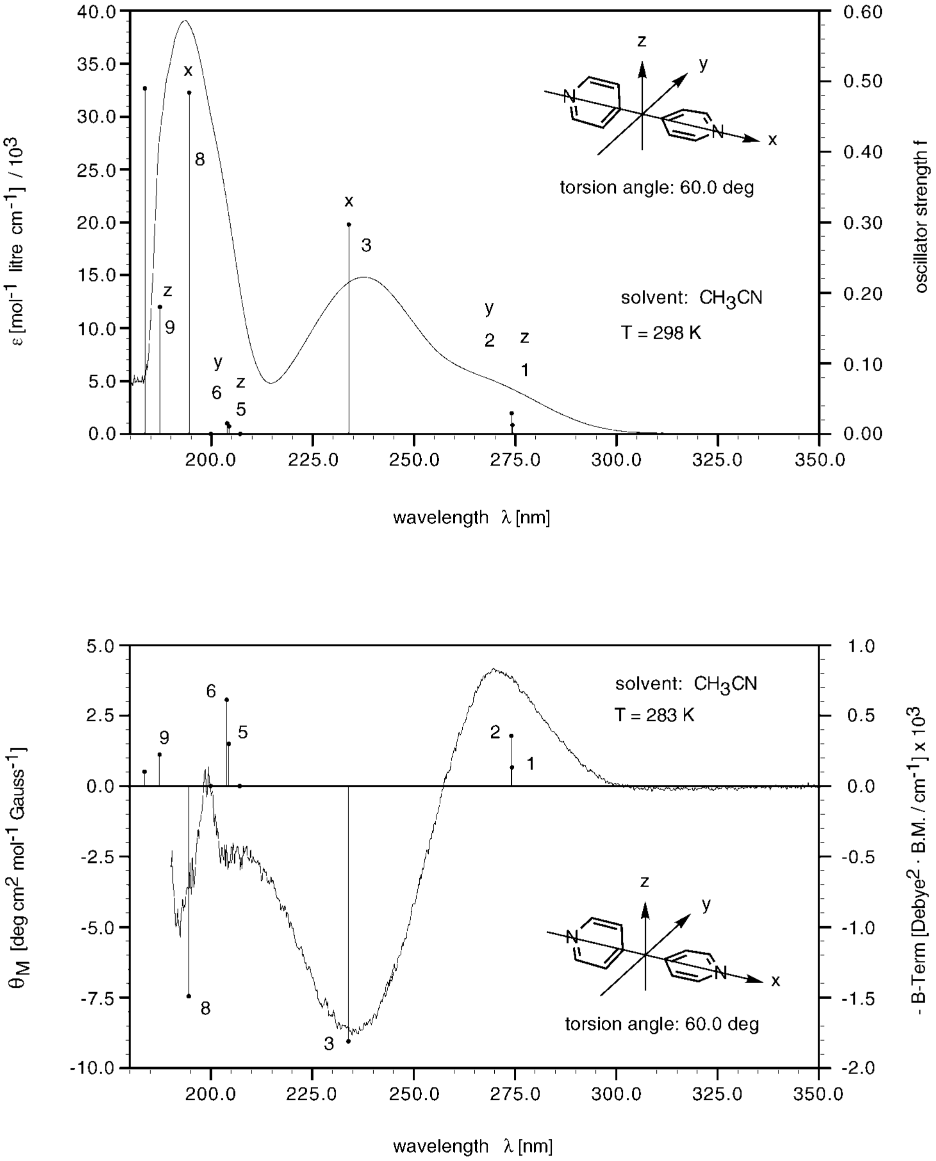


Fig. 7. *4,4′-Bipyridine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

The magnetic transition moment $\langle 2|\boldsymbol{m}|3\rangle$ is $(-z)$-directed, the electric transition moment $\langle G|\boldsymbol{\mu}|2\rangle$ lies along $(-y)$. Both $B(G \rightarrow 1)$ and $B(G \rightarrow 2)$ have the same sign, leading, in conjunction with $B(G \rightarrow 3)$, to a distinct positive-negative pseudo-A term signal (*Fig. 7*). We consequently find also here a satisfactory semiquantitative agreement between theory and experiment.

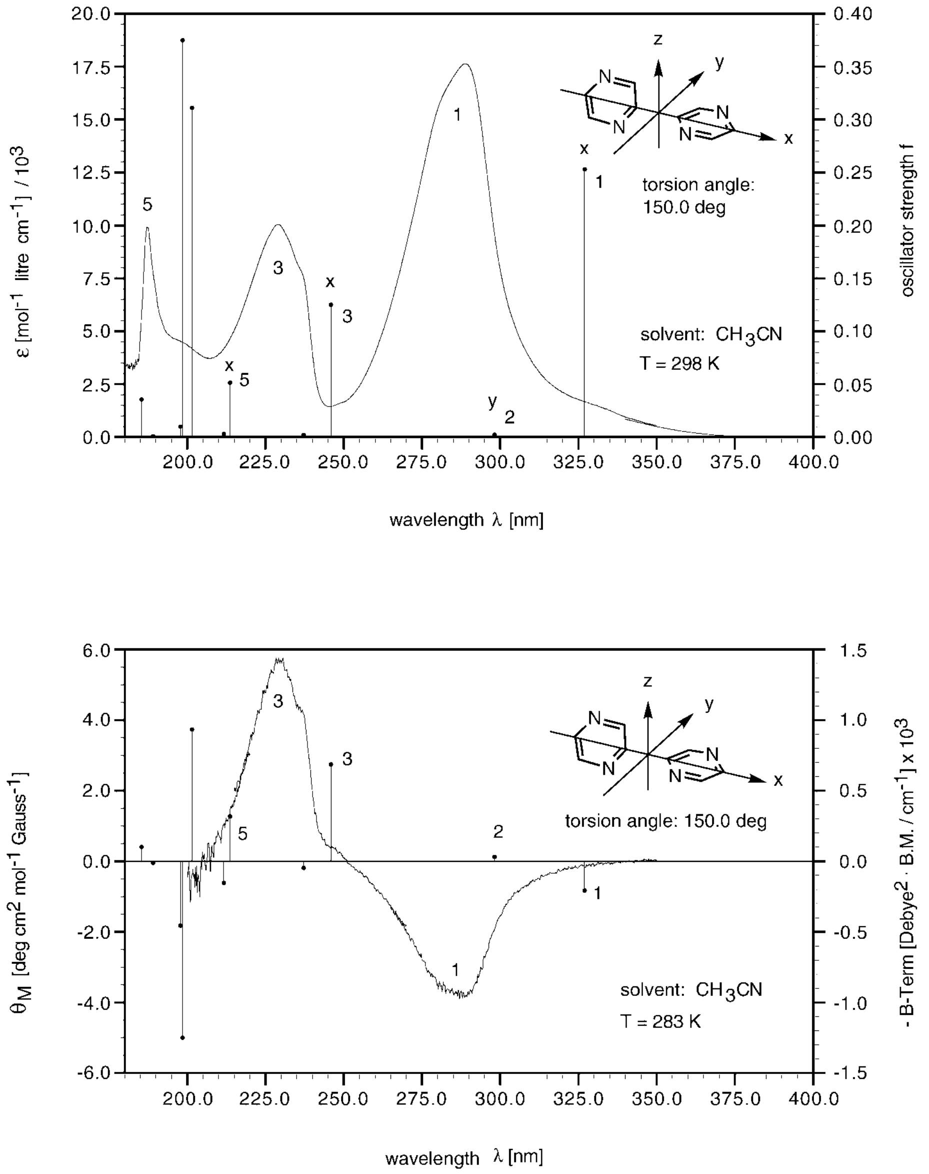


Fig. 8. *2,2′-Bipyrazine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

3.3. *2,2′-Bipyrazine.* The measured spectra of 2,2′-bipyrazine, as well as the corresponding computed data, are displayed in *Fig. 8.*

The long-wavelength absorption spectrum is dominated by the very strong x-polarized 280-nm band (*1*). This band is predicted by the calculation to occur only at 327 nm, but the high oscillator strength and the negative sign of the MCD signal are in qualitative agreement with experiment. It is also instructive to compare the absorption and MCD spectra of 2,2′-bipyrazine with those of 2,2′- and 3,3′-bipyridine (*Figs. 5* and *6*). We notice that, in all three compounds, the signs of the long-wavelength MCD signals coincide.

Until now, we have ignored the longest-wavelength n-π^* states. In the pyridine derivatives, it may safely be assumed that, in both the absorption and MCD spectra, the n-π^* transitions are overshadowed by the π-π^* bands. When there is more than one N-atom inside an aromatic ring, such as in pyrimidine or pyrazine, the longest-wavelength n-π^* bands become red-shifted [5]. It is, however, difficult to unambiguously discern any n-π^* contributions to the spectra of 2,2′-bipyrazine here displayed.

3.4. *Dipyrido[3,2-*c*:2′,8′-*e*]pyridazine.* The recorded spectra of dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, together with the computed data, are shown in *Fig. 9*.

Both in the absorption and the MCD spectrum, we notice the occurrence of a broad but weak ($\varepsilon_{\max} \approx 200$) long-wavelength band centered at *ca.* 415–420 nm, which we tentatively assign to the n-π^* transition originating from the highest nonbonding orbital of the $-$N=N$-$ moiety. This band is absent in the spectra (here not displayed; *cf. Experimental*) of the closely related molecule 1,10-phenanthroline, where $-$N=N$-$ is replaced by $-$C=C$-$.

In the calculated MCD spectrum, the signs of the relatively weak π-π^* transitions $G \rightarrow 1$, $G \rightarrow 2$, $G \rightarrow 3$ agree with experiment, but those for the transitions $G \rightarrow 4$ and $G \rightarrow 5$ should be inverted. We again compare with the molecule 1,10-phenanthroline, where, in this respect, there is better agreement. For this, we consider the main sum-over-states contributions to the B terms, $B(G \rightarrow 4)$ and $B(G \rightarrow 5)$, and we notice the relative importance of:

$$(E_5 - E_4)^{-1}\ \mathrm{Im}\ \langle 4|\boldsymbol{m}|5\rangle \cdot \langle G|\boldsymbol{\mu}|4\rangle \times \langle 5|\boldsymbol{\mu}|G\rangle \tag{4}$$

The $(-z)$-directed magnetic transition moment $\langle 4|\boldsymbol{m}|5\rangle$ and the $(-y)$-directed electric transition moment $\langle 4|\boldsymbol{\mu}|4\rangle$ have equal signs both in dipyrido[3,2-*c*:2′,3′-*e*]pyridazine and in 1,10-phenanthroline, but the $(+x)$-directed electric transition moment $\langle 5|\boldsymbol{\mu}|G\rangle$ in dipyrido[3,2-*c*:2′,3′-*e*]pyridazine has negative sign in 1,10-phenanthroline. Upon analyzing the wavefunctions, one notices that, in the state $|4\rangle$ in 1,10-phenanthroline, the SCF MO excitation *6* $\rightarrow$ *8** plays a dominant role, in the state $|5\rangle$ the excitation *6* $\rightarrow$ *9**. In dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, rather, the excitations *7* $\rightarrow$ *8** and *7* $\rightarrow$ *9** are important. In 1,10-phenanthroline, the highest filled MOs *6* and *7* have the symmetries a_2 and b_1 under C_{2v}, in dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, we find the inverted sequence. This, then, is another instance where sign changes in the computed MCD signals may be traced back to differences in the energetic sequence of SCF MOs.

3.5. *1,10-Phenanthroline-5,6-dione.* The measured and computed spectra of 1,10-phenanthroline-5,6-dione are displayed in *Fig. 10*. The overall accord between the computed and measured MCD signals appears to be better than for dipyrido[3,2-*c*:2′,3′-*e*]pyridazine. In analogy to dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, we notice the pronounced pseudo-A-term character of the y- and x-polarized transitions $G \rightarrow 4$ and $G \rightarrow 5$. There also seems to be qualitative agreement between the calculated and measured weaker long-wavelength bands arising from the transitions $G \rightarrow 1, 2, 3$.

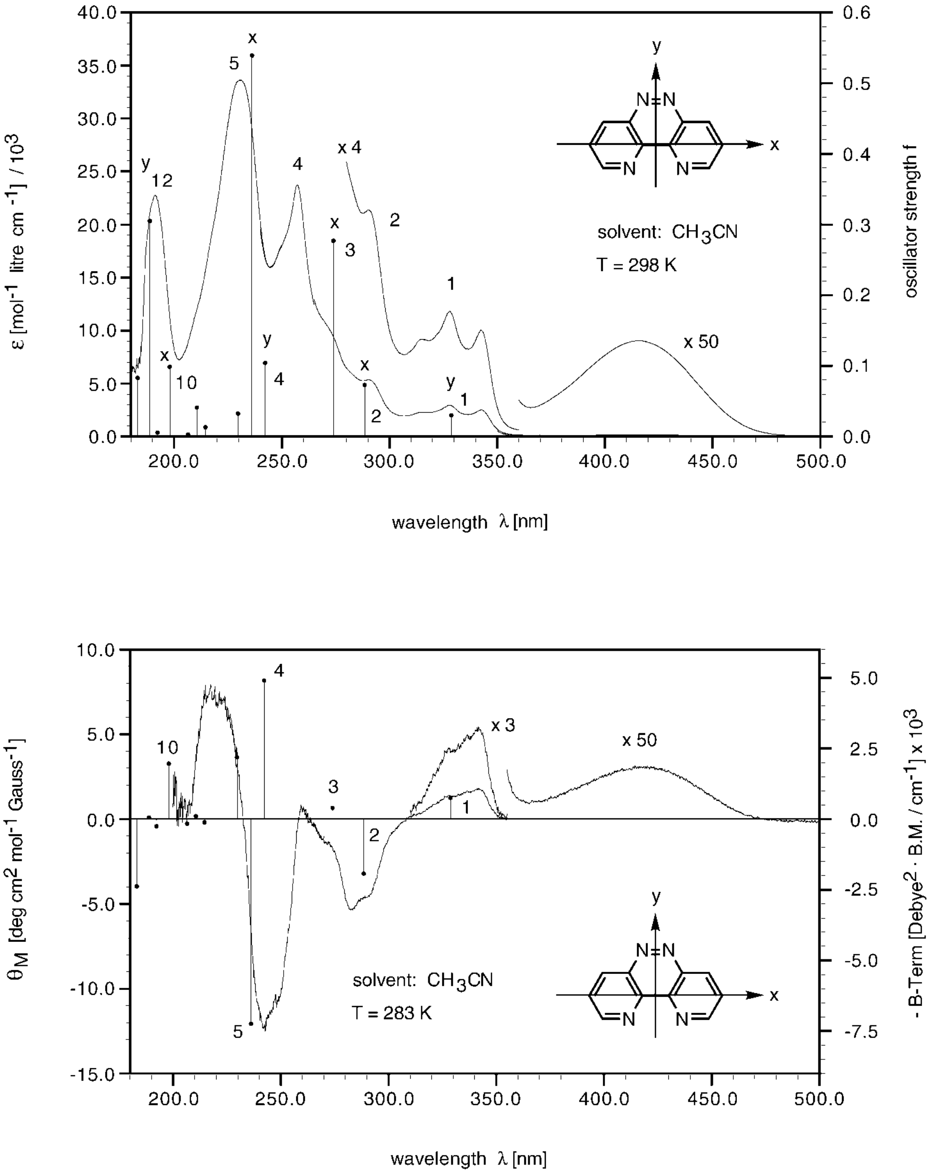


Fig. 9. *Dipyrido[3,2-*c*:2′,3′-*e*]pyridazine:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum*

A particular aspect of the absorption spectrum is the weak tail, extending from *ca.* 430 to beyond 520 nm. It must be ascribed to the n-π^* transitions of the dione moiety. Indeed, in the MO calculations one notices that the LUMO *9** is strongly located on the two C=O groups. At maximum MCD detection sensitivity, we are able to further extend the observation of these signals, and to measure between 525 and 590 nm the

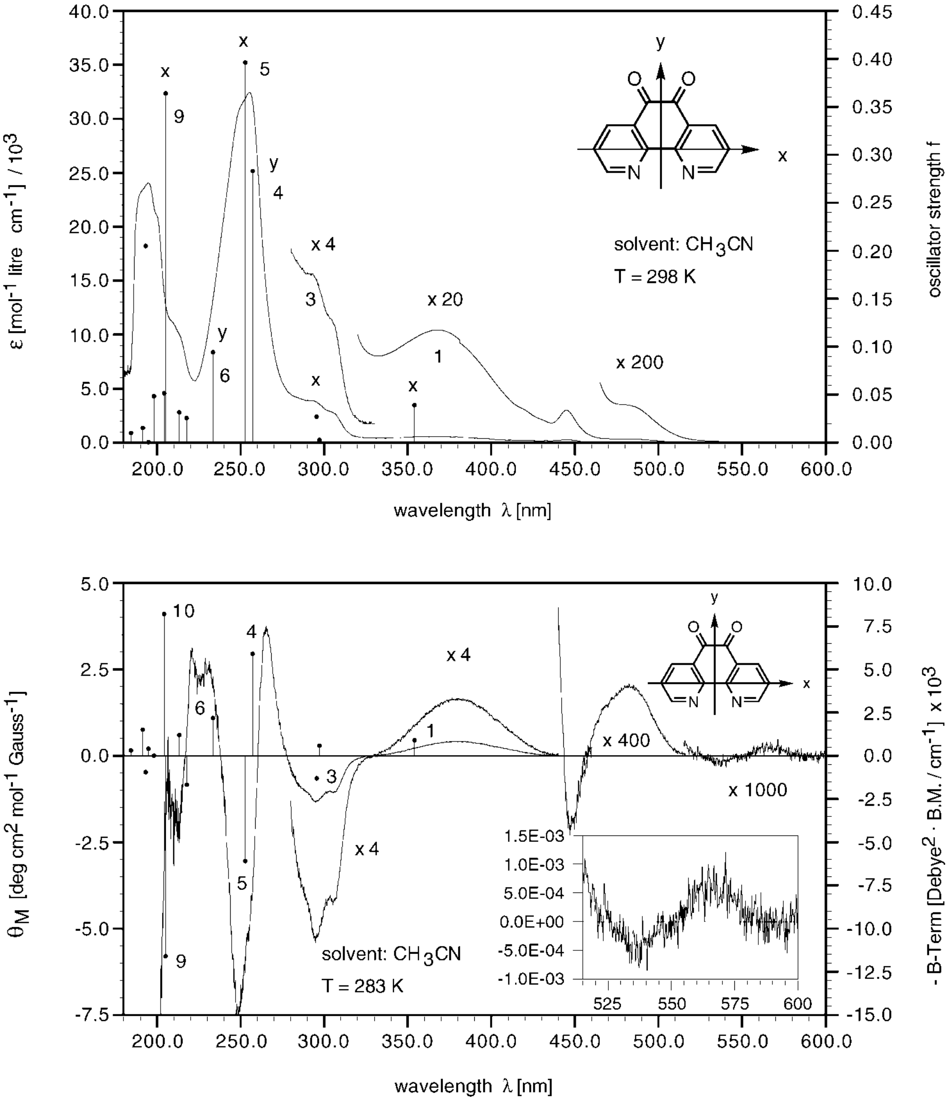


Fig. 10. *1,10-Phenanthroline-5,6-dione:* upper: *measured and computed absorption spectrum*; lower: *measured and computed MCD spectrum.* Notice the weak *A* term in the 550-nm region.

very weak *A* term of the electronically forbidden singlet-triplet $G \rightarrow {}^3(\text{n-}\pi^*)$ transition. This kind of signal was already previously recorded in phenanthrene-9,10-dione and in other diones [4].

3.6. *The Ruthenium(II) Complexes.* In *Figs. 11* and *12*, we display the MCD spectra of the Ru^{2+} complexes of tris[2,2′-bipyridine] and of tris[dipyrido[3,2-*c*:2′,3′-*e*]pyridazine]. In these spectra, we focus our attention on the wavelength range between 200 and 350 nm, originating in the π-π^* transitions of the ligands. Our aim is a qualitative

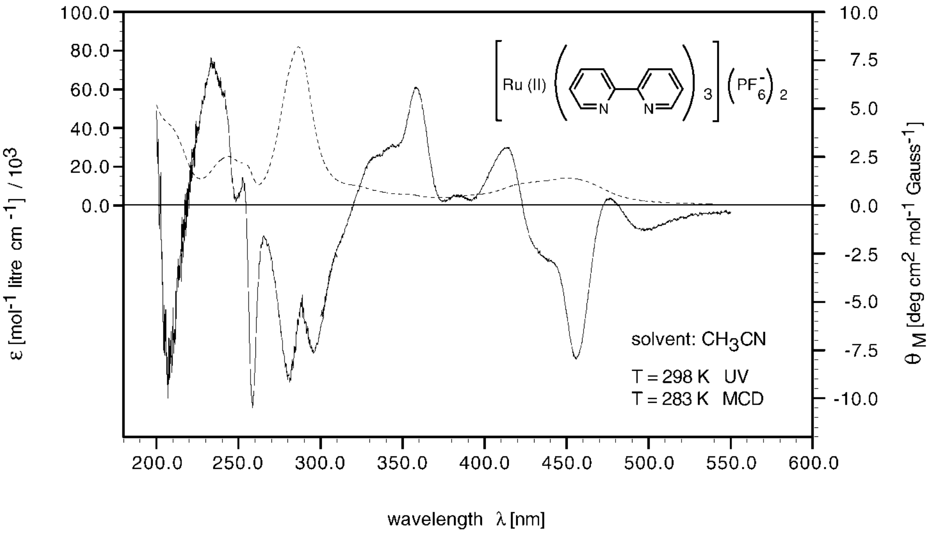


Fig. 11. *Ru^{II} Complex of tris[2,2′-bipyridine]:* dashed line: *absorption spectrum*. Compare with *Fig. 5*. Notice the enhanced band at 280–290 nm. Full line: *MCD spectrum*. The signals beyond 330 nm must have charge-transfer character.

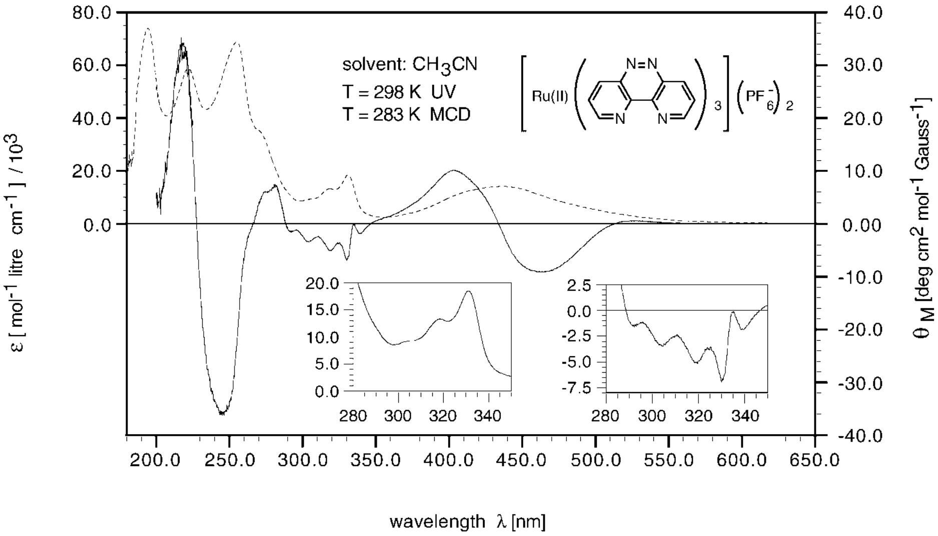


Fig. 12. *Ru^{II} Complex of tris[dipyrido[3,2-*c:*2′,3′-*e*]pyridazine]:* dashed line: *absorption spectrum*; full line: *MCD spectrum*. Compare with *Fig. 9*.

comparison with the spectra of the free ligands. The longer-wavelength parts of the MCD spectra of the complexes, arising from the metal–ligand charge-transfer transitions, are not discussed here in any detail. The MCD spectra of the tris(2,2′-bipyridine)ruthenium(2+) system in the range between 330 and 650 nm has been investigated by other authors [7].

The tris-complexes here considered all have the point-group symmetry D_3. Consequently, the electric (and magnetic) dipole-allowed transitions may be classified as either A_2 or E. The E states being twofold degenerate, one would expect them to give rise to bisignate MCD A terms. As may easily be shown, such A terms can be strong only when there is considerable wave-function overlap between the ligands. This is not the case here, however. It seems reasonable to assume that the interaction between the ligands is predominantly electrostatic, corresponding to the 'coupled oscillator' model [8]. There should consequently be an exciton-type splitting of the monomer transitions in the complex and a concomitant shift and modification of the B terms in the MCD spectrum. This is, qualitatively speaking, what one observes.

Within the frame of the coupled-oscillator model, one notices that only monomer transitions polarized perpendicularly to the local C_2 symmetry axis of the individual ligands contribute to the B terms of the tris-complex. The spectra of the complexes should, therefore, predominantly derive from the x-polarized transitions in the local molecular coordinate system (see also *Figs. 5* and *9*, and the computed monomer spectra).

4. Conclusions. – We have measured the MCD spectra of a series of N-containing heteroconjugated aromatic molecules. It is shown that the spectra may, in general, be interpreted and discussed on the basis of SCF-single-CI calculations within the carefully parametrized semi-empirical PPP model. This is in accord with the results of previous similar investigations on quinoid compounds of aromatic structure [4].

The main conclusions of the present investigation are the following:

– In the phenylpyridines and the bipyridines, there is a marked difference between the MCD spectra of the molecules in which the ring N-atoms are in *p*-position with respect to the bond connecting the two aromatic rings, and of the molecules where the N-atoms are in *o*- or *m*-position. These differences may be clearly interpreted on the basis of the symmetry of the calculated electronic structure.

– In the other compounds, there is, in general, also semiquantitative agreement (with respect to signs) between the measured long-wavelength MCD spectra and the calculations.

– In the molecule 1,10-phenanthroline-5,6-dione, we detect between 525 and 590 nm the electronically forbidden, therefore very weak, A term of the singlet – triplet n-π^* absorption. This agrees with our observations on other, similar, quinoid aromatic compounds [4].

– The MCD spectra of the Ru^{II} complexes are qualitatively compared in the 200 – 350 nm range with those of the free ligands. There is no doubt that the complex bands in this spectral region derive from the π-π^* transitions in the individual ligands, which, in the D_3-symmetric complex, couple mainly electrostatically.

5. Experimental. – The phenylpyridines, as well as 2,2′-bipyridine and 4,4′-bipyridine were of commercial origin and were further purified by recrystallization and sublimation. The compound 3,3′-bipyridine was synthesized by one of the authors (*P. K.*) from 3-bromopyridine [9], purified by distillation, and analyzed by elemental analysis and IR and NMR spectroscopy.

The compounds 2,2′-bipyrazine, 2,2′-bipyrimidine, dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, 1,10-phenanthroline, and 1,10-phenanthroline-5,6-dione were synthesized by one of the authors (*P. B.*). Concerning these syntheses and the preparation of the Ru^{II} complexes, see [10] and refs. cit. therein.

Besides the data reported in this paper, we have also measured the MCD spectra of 2,2′-bipyrimidine and of 1,10-phenanthroline, as well as those of the Ru^{II} complexes of 2,2′-bipyrazine, 2,2′-bipyrimidine, and 1,10-phenanthroline. These spectra are here not displayed for reasons of limited space, but may be obtained from the authors upon request.

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