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Circular dichroism spectra of planar chiral 2-substituted ferrocenecarboxaldehydes and 2-ferrocenyl-1,1-dicyanoethylenes

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Abstract—Circular dichroism spectra of a series of planar chiral 2-substituted ferrocene carboxaldehydes and 2-ferrocenyl-1,1-dicyanoethylenes are reported. They show Cotton effects associated with intramolecular charge transfer transitions and are related to the absolute configuration of these compounds.

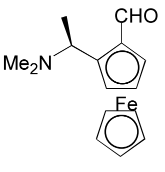
1. Introduction

Planar chiral ferrocenyl 'push–pull' compounds, Fc-π bridge-acceptor group, have attracted considerable attention as nonlinear optical materials exhibiting large second harmonic generation efficiencies in the solid state.[1] Their electronic absorption spectra were thoroughly studied and two intense bands observed in the visible region assigned to metal-to-ligand charge transfer (MLCT) and intraligand charge transfer (ILCT) transitions.[2] We became interested in whether these transitions in a homochiral environment would lead to Cotton effects (CE's) in circular dichroism (CD) spectra of ferrocenyl 'push–pull' derivatives. CE's associated with MLCT transitions constitute a valuable tool in assignment of stereochemistry of coordination compounds,[3] but we are not aware of the studies of such effects in chiral ferrocenyl 'push–pull' compounds.

Herein CD spectra of a series of planar chiral 2-substituted ferrocenecarboxaldehydes **1**–**4** ('push-pull' systems with a rather weak acceptor group, formyl) and 2-ferrocenyl-1,1-dicyanoethylenes **5**–**8**, in which the 'push-pull' character is more pronounced are reported.

2. Results and discussion

The electronic absorption spectra of compounds **1**–**8**[4] are presented in Figures 1 and 2 and the data are collected in Table 1. Similar to ferrocene, compounds **1**–**8** display, in the region 300–600 nm, two distinct absorption bands. For ferrocene these bands are situated at 325 nm and 442 (ε<100)[5], and are usually attributed to the Lapporte-forbidden d–d ligand field transitions. In the case of compounds **1**–**4** these bands are shifted bathochromically and are much more intense (hyperchromic effect), both facts being explicable assuming the admixture of the metal-to-ligand charge transfer transitions, leading



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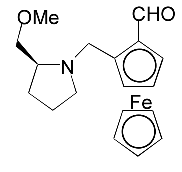

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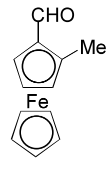

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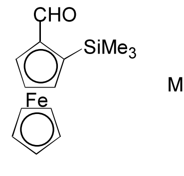

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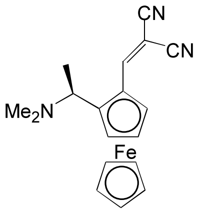

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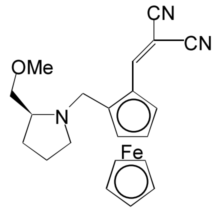

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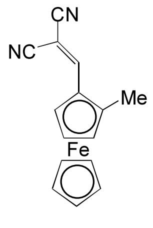

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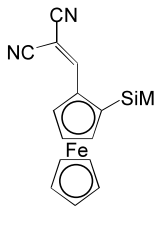

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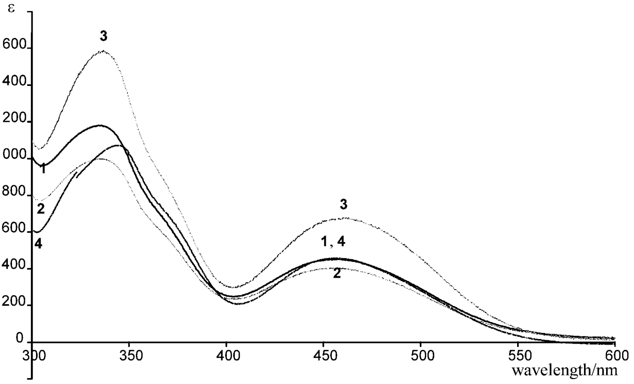


Figure 1. Electronic absorption spectra of compounds **1**–**4**.

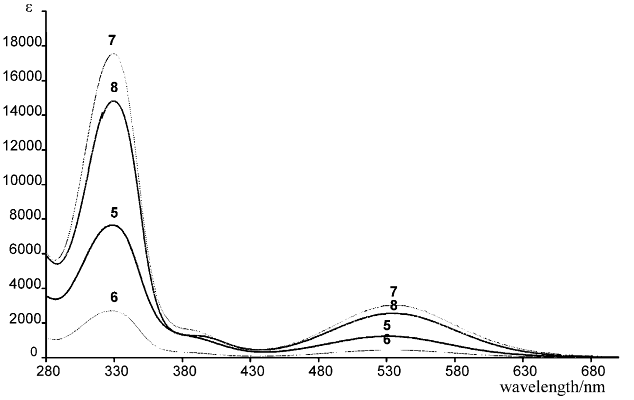
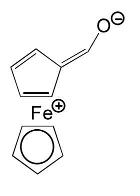
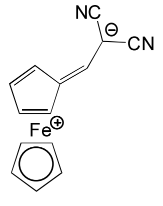


Figure 2. Electronic absorption spectra of compounds **5**–**8**.

to a charge-separated excited state represented by the structure **A**.[6] In the case of **5**–**8** the charge-separated structure **B** is even more stable bringing about additional bathochromic and hyperchromic effects. In fact, for these compounds we can assume that bands observed in the visible region correspond to almost pure MLCT transitions.



A



B

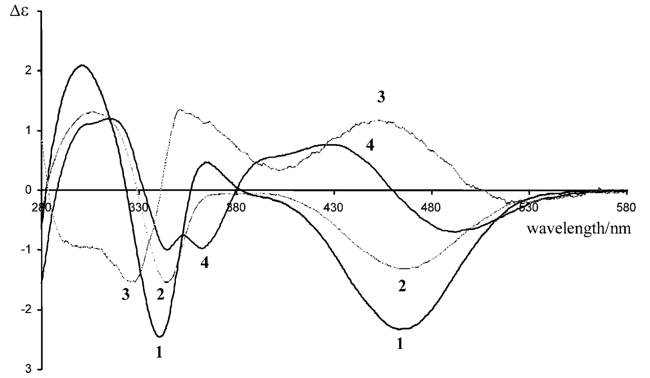


Figure 3. CD spectra of compounds **1**–**4**.

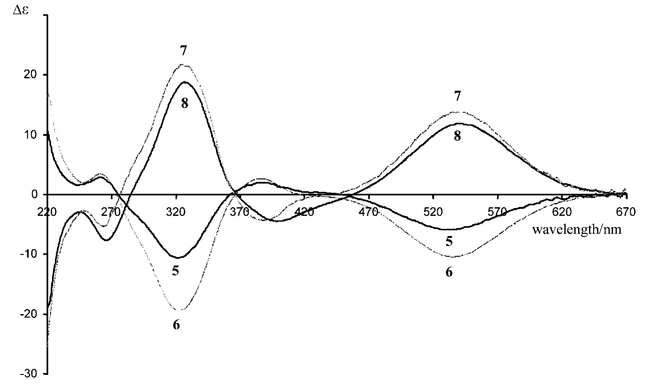


Figure 4. CD spectra of compounds **5**–**8**.

The CD spectra of compounds **1**–**4** are shown in Figure 3 and those of **5**–**8** in Figure 4 and the data are gathered in Table 2.

Figure 3 reveals that multiple CE's are present in the CD spectra of aldehydes **1**–**4**. However, there is no simple correlation between signs of the CE's and the stereochemistry of the aldehyde (e.g. compare spectra of **3** and **4**). This situation changes dramatically in the case of compounds **5**–**8**. The CE's are observed at higher wavelengths and are significantly stronger. Note the roughly enantiomeric relationship between spectra of **5**–**6** and those of **7**–**8**, presumably reflecting pseudo-enantiomeric relationship between these molecules (they would be enantiomers if the substituent in the 2 position was the same).

Table 1. Electronic absorption data for compounds **1**–**8**

Compound	Solvent	λ_{max} (ε_{max})[a]	Compound	Solvent	λ_{max} (ε_{max})[a]
1	MeCN	334 (1200) 458 (450)	**5**	CH_2Cl_2	329 (7650) 530 (1240)
2	MeCN	334 (1000) 454 (390)	**6**	CH_2Cl_2	329 (13490) 534 (2200)
3	MeCN	337 (1590) 460 (670)	**7**	CH_2Cl_2	329 (13200) 534 (2140)
4	MeCN	344 (1080) 458 (461)	**8**	CH_2Cl_2	330 (14800) 537 (2570)

[a] λ_{max} in nm; ε_{max} in M^{-1} cm^{-1}.

Table 2. CD data for compounds **1**–**8**

Compound	Solvent	λ_{max} (nm)	$\Delta\varepsilon$
1	Acetonitrile	301	2.09
		340	−2.45
		364	0.46
		464	−2.32
2	Acetonitrile	268	−2.11
		306	1.31
		344	−1.54
		464	−1.31
3	Acetonitrile	325	−1.52
		352	1.36
		425	1.16
		529	−0.19
4	Acetonitrile	315	1.20
		362	−0.97
		427	0.77
		492	−0.70
5	CH_2Cl_2	252	2.90
		322	−10.62
		390	1.97
		531	−5.90
6	CH_2Cl_2	260	3.43
		322	−19.50
		388	2.58
		535	−10.48
7	CH_2Cl_2	264	−2.66
		325	10.85
		387	−2.18
		534	6.88
8	CH_2Cl_2	266	−7.68
		326	18.74
		398	−4.49
		540	11.86

In conclusion, we have demonstrated that MLCT electronic transitions in ferrocenyl 'push–pull' molecules are 'cottonogenic' i.e. give rise to CE's in CD spectra. For weakly polarized systems such as ferrocenecarboxaldehydes the CE's are weak and hardly correlated with the absolute configuration of the metallocene. On the other hand in stronger 'push-pull' systems such as **5**–**8** the CE's are stronger and seem to be directly correlated with the stereochemistry of metallocene. Of course, more examples are needed to find out if our model is general and such research is currently underway in our laboratory.

It is also noteworthy that 2-ferrocenyl-1,1-dicyanoethylenes can be readily prepared from ferrocenecarboxaldehydes via Knoevenagel condensation with malononitrile. Such a transformation and measurement of the CD spectrum of the 2-ferrocenyl-1,1-dicyanoethylenes may constitute a way for determination of the absolute configuration of the aldehyde.

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4. Compounds **1**, **3**, **4** were obtained according to the literature methods (Lu, X.; Chen, G. *Tetrahedron* **1998**, *54*, 12539. Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan H. B. *J. Org. Chem.* **1997**, *62*, 6733.) Compound **2** was prepared by lithiation of (*S*)-(2-methoxymethylpyrrolydin-1-yl)ferrocene (Ganter, C.; Wagner, T. *Chem. Ber.* **1995**, *128*, 1157) followed by quenching with DMF. Complexes **5**–**8** were obtained by reaction of **1**–**4** with malononitrile. Details of syntheses and characterisation of new compounds will be published elsewhere.
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