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Induction of chirality in donor–acceptor spiro compounds

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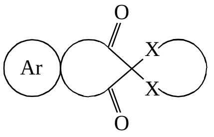
HOMO–LUMO transitions observed in chiral donor–acceptor spiro compounds 1 and 2 are of the n–π^* type, based on the high dissymmetry factor $\Delta\varepsilon/\varepsilon \cong 10^{-2}$ determined from their CD and absorption spectra.

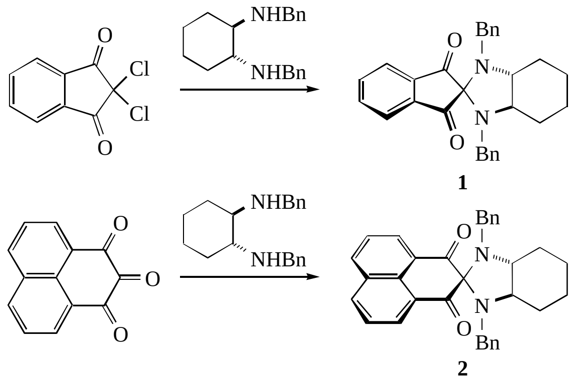
Spiro compounds **A** are known to display long-wavelength transitions in the visible region of the absorption spectrum, making these compounds coloured. Neither the conjugated aromatic (acceptor) part nor the heterocyclic (donor) part are capable to absorb in the visible region; however, when combined they form a donor–acceptor system, whose long-wavelength electronic absorption band due to the HOMO–LUMO transition usually lies in the visible region of the electronic absorption spectrum.



X = N, O, S

A

A comparison between the photoelectron spectra of spiro compounds **A** and their fragments indicated only a very weak interaction.[1] Nevertheless, this interaction is responsible for the red shift of the first absorption band in **A**. In order to clarify the nature of the long-wavelength transition, we have synthesised two spiro compounds **1** and **2**, in which the heterocyclic part derived from *N,N*′-dibenzyl-(*R,R*)-*trans*-1,2-diaminocyclohexane is chiral (Scheme 1).[†] In such derivatives, the absorption bands can be active in the circular dichroism (CD) spectra.



Scheme 1

The long-wavelength (250–520 nm) part of the CD spectra of **1** and **2**, corresponding to the weak absorption in the UV-VIS spectrum, is shown in Figure 1.

The long-wavelength transition of **1**, which is responsible for its red colour, is clearly seen in the isotropic (ε 270 at 420 nm in acetonitrile) and CD spectrum ($\Delta\varepsilon$ +4 at 420 nm in acetonitrile). This transition is followed by another Cotton effect ($\Delta\varepsilon$ –12 nm at 295 nm in acetonitrile) for which the UV band is situated on the slope of the strong π–π^* absorption band in the short-wavelength spectral region. The UV band is red shifted in a less polar benzene solution, ε 285 at 428 nm, a value very close to that reported for a similar achiral spiro compound.[2,3] In a more polar methanol solution, a small blue shift is observed, ε 280 at 417 nm. Both the solvent effect and the value of $\Delta\varepsilon/\varepsilon = 1.5\times10^{-2}$ for the long-wavelength band of **1** are typical characteristics of the n–π^* transition in ketones.

The spectral behaviour of **2** is similar to that of **1**: the Cotton effects are more red-shifted but are of the same sign, $\Delta\varepsilon$ +4 at 433 nm and $\Delta\varepsilon$ –9 at 346 nm. This is despite different molecular symmetry of **1** and **2**. In **1**, the acceptor ring is planar and the molecule has C_2 symmetry (the donor molecule retains a chair conformation with equatorial C–N bonds). In **2**, the six-membered ring containing the spiro substituent cannot be planar, and it forms a C2-sofa structure. The overall symmetry of **2** is C_1. This is readily seen in the ^{1}H NMR spectra, where the corresponding signals displayed by **1** are doubled in the case of **2**. For example, the two ring CHN protons in **1** give one resonance signal at 3.0 ppm, while there are two signals at 2.95 and 3.35 ppm in the case of **2**; the benzylic CH_2 protons of **1** give two doublets at 3.50 and 3.95 ppm, whereas those of **2** appear as four doublets at 3.30, 3.40, 3.70 and 3.82 ppm.

The electronic transitions of **1** have been computed by the DFT mpw1pw91/cc-pvdz method, for the structure optimised at the b3lyp/6-31(d) level of theory.[7] Whereas we did not obtain the lowest lying transitions of correct energy, the signs of rotational strength were correctly computed, positive for the lowest energy band (computed at 494 nm) and negative for the second band (computed at 306 nm).[‡] According to the computation, for the lowest-energy transition the HOMOs involved are the pyramidalised nitrogen atom non-bonded orbitals, whereas the LUMO orbitals are the conjugated carbonyl π^* orbitals.

In summary, we have demonstrated that the lowest-lying transition in spiro compounds **1** and **2** is of an intramolecular n–π^* character (between the nitrogen donor and a carbonyl group acceptor). The sign of the Cotton effect associated with this transition can be correlated with the helical path between the HOMO–LUMO orbitals involved (positive for the *R,R* con-

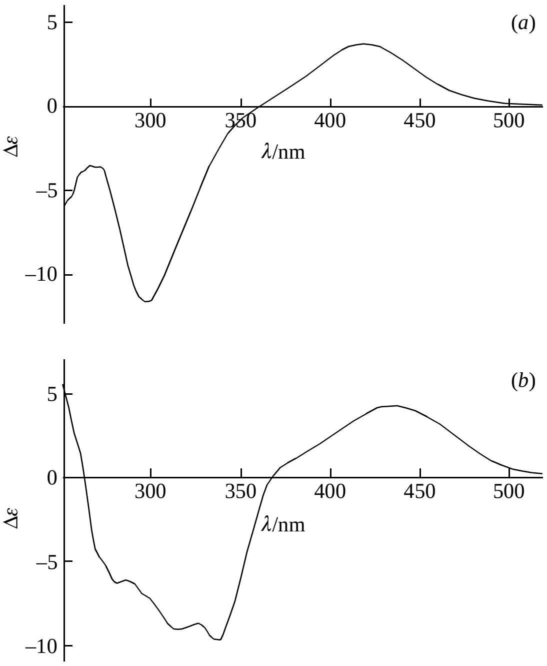


Figure 1 The CD spectra of (*a*) **1** and (*b*) **2** measured in acetonitrile solutions.

[†] Compounds **1** and **2** were prepared by the condensation of enantiomerically pure *N,N*′-dibenzyl-(*R,R*)-*trans*-1,2-diaminocyclohexane with either 2,2-dichloro-1,3-indandione[4] or 1,2,3-trioxo-2,3-dihydrophenalene[5,6] according to published procedures.[1,2]

figuration of the donor diamine). The splitting of the *n*–π* transition leads to a second higher energy band with a negative Cotton effect in the CD spectrum.

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‡ Replacing the cc-pvdz basis set with the larger 6-31++g(d,p) basis set did not improve the DFT calculations. The lowest lying transitions were computed at 514 nm (positive rotational strength) and 314 nm (negative rotational strength). All calculations were performed for 20 excited states.

1: mp 164–167 °C (ethyl acetate–hexane); $[\alpha]_D$ –60.7 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.2–1.4 (m, 4H), 1.8 (m, 2H), 1.9 (m, 2H), 3.0 (m, 2H), 3.50 (d, 2H, *J* 13.7 Hz), 3.94 (d, 2H, *J* 13.7 Hz), 6.8–7.0 (m, 10H), 7.3–7.5 (m, 4H). IR (KBr, ν/cm^{-1}): 2932, 1736, 1707, 1594, 1495, 1453, 1353, 1333, 1243, 1209, 1185, 1150, 913, 742, 696. EIMS, *m*/*z*: 436.5 (M^+).

2: solidified oil. ^{1}H NMR ($CDCl_3$) δ: 1.0–2.0 (m, 8H), 2.95 (m, 1H), 3.31 (d, 1H, *J* 13.6 Hz), 3.32 (m, 1H), 3.40 (d, 1H, *J* 14.3 Hz), 3.70 (d, 1H, *J* 14.3 Hz), 3.80 (d, 1H, *J* 13.7 Hz), 6.56 (m, 2H), 6.72 (m, 3H), 6.95 (m, 3H), 7.03 (m, 2H), 7.4–7.5 (m, 2H), 7.7–7.85 (m, 4H). IR (KBr, ν/cm^{-1}): 2930, 2858, 1723, 1603, 1493, 1453, 1193, 783, 743, 697. EIMS, *m*/*z*: 458 (M^+ – CO), 430 (M^+ – 2CO).