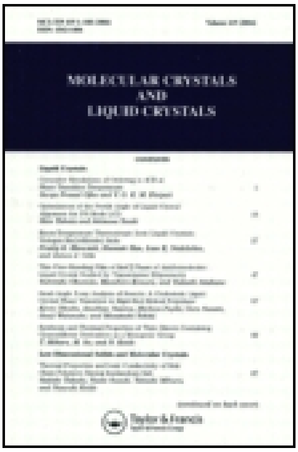

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Induced Cholesteric Phases of Chiral Aminoanthraquinones

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INDUCED CHOLESTERIC PHASES OF CHIRAL AMINOANTHRAQUINONES

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Abstract The temperature dependence of the HTP of 1,4–bis–(S–1–(1-naphthyl)ethylamino)–9,10–anthraquinone [S–5] or [R–5] and of 1,8–bis–(S–1–(1–naphthyl)ethylamino)–9,10–anthraquinone [S–6] in ZLI 1695 (Merck) is expounded to be a consequence of a shift of an equilibrium between at least two conformers $A \rightleftarrows B$ with an equilibrium constant $K < 1$, derived from the temperature dependence of a CD couplet. Conditional on this equilibrium, the HTP(T) is a linear function of the amplitude of the couplet. The sign of the CD of the isotropic solution is determined by the conformer A whereas the sign of the HTP is given by B. The helix inversion for [S–5] in ZLI 1132 (Merck) appears to be a result of a slightly increasing concentration of the conformer B.

Keywords: induced cholesteric, circular dichroism, chiral conformers

INTRODUCTION

Chiral molecules solved in a nematic phase induce cholesteric phases. The strength of the induction is given by the helical twisting power (HTP) of the guest molecule which is strongly dependent on the molecular structure. There are many models describing the HTP/structure relation in literature which work in a qualitative sense but a quantitative description by such models is not possible at the moment. A comprehensive review is given by Solladié et al. [1].

We have started an analysis of the HTP for molecules built up by a planar – and thus achiral – group which is substituted by one or two equal chiral substituents in different positions of the planar skeleton [2]. From these results the genesis of the

$$\mathrm{HTP} = \left(\frac{dp^{-1}}{dx}\right)_{x=o} = a \qquad (1)$$

(p^{-1} is the inverse pitch in μm^{-1} and x the mole fraction) of mono– and diamino–anthraquinones has been separated in the following way:

1. Order and Porter Effect

Here, the dependence of the HTP on the order of the guest and the host (order effect) should be discussed. Furthermore, groups substituted in different positions of the achiral skeleton possess a distinct orientational order in the liquid crystal phase which, however, depends on the order of the skeleton. Therefore, the task of the skeleton to carry chiral substituents in different ways into the phase (porter effect) – depending on the position of substitution – should be discussed, also.

2. Chirality transfer

Here, the intramolecular transfer of "chirality" from the substituent to the achiral and planar skeleton should be discussed. This view of the problems resembles the discussion of sector rules in the CD spectroscopy where the molecules are divided into an achiral and a chiral part or two achiral parts in a special orientation with respect to each other.

3. Chirality transmission

Here, the intermolecular transfer of chirality, i.e. the transmission of chirality from the guest molecule to the liquid crystal host sytem should be discussed. The notion "chirality transmission" used here is meant in a more general sense than by Gottarelli et.al. [3], who have introduced it to describe a shift of an equilibrium of chiral conformers which is often called Pfeiffer effect.

For the mono– and diamino–substituted anthraquinones analyzed earlier [2], the effect of the chirality transfer can be shown directly and there are some hints for a chirality transmission depending on the molecular structure. For an order and porter effect there is no evidence in experiments given there. For these compounds no contribution can be seen. In this paper an example will be given where a conformational change contributes to the HTP.

RESULTS AND DISCUSSION

The amino– and diamino–anthraquinone skeleton is the essential part for the order of the guest which will be modified by the substituents. The HTP of these compounds is only weakly temperature dependent in the temperature region measured except for 1,4–bis–(S–1–(1–naphthyl)ethylamino)-9,10–anthraquinone [S–5] and to some extent for 1,8–bis–(S–1–(1–naphthyl)-ethylamino)–9,10–anthraquinone [S–6].

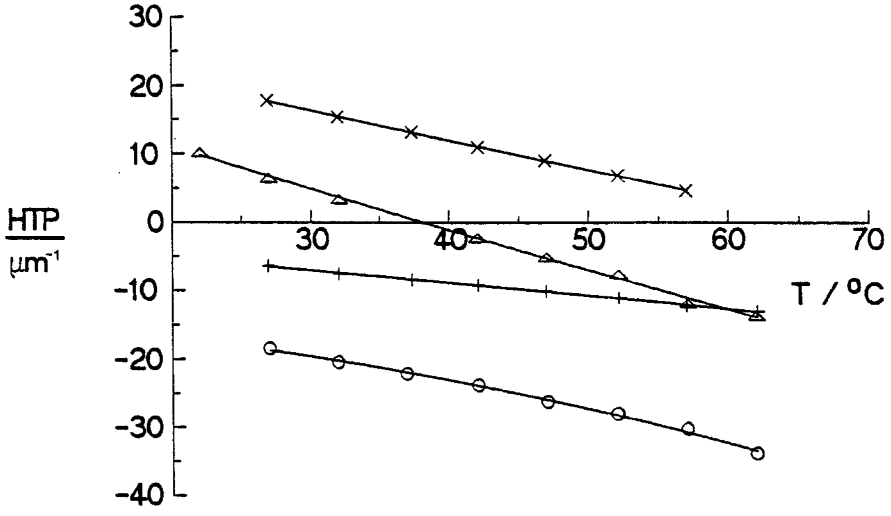

FIGURE 1 HTP as a function of temperature for S–5 and S–6, resp. in ZLI 1695 (o, +, resp.; Merck: mixture of four 4–n–alkyl–4'-cyanobicyclohexanes) and in ZLI 1132 (▵, x, resp.; Merck: mixture of three 4–cyano–1 [4–n–alkylcyclohexyl]–benzenes and 4–[4–n–alkyl-cyclohexyl]-4'–cyano–biphenyl).

The HTP as a function of the reduced temperature is linear for all compounds analyzed here with a high coefficient of correlation. The temperature dependence of S–5 and S–6 in ZLI 1695 in comparison to that in ZLI 1132 is

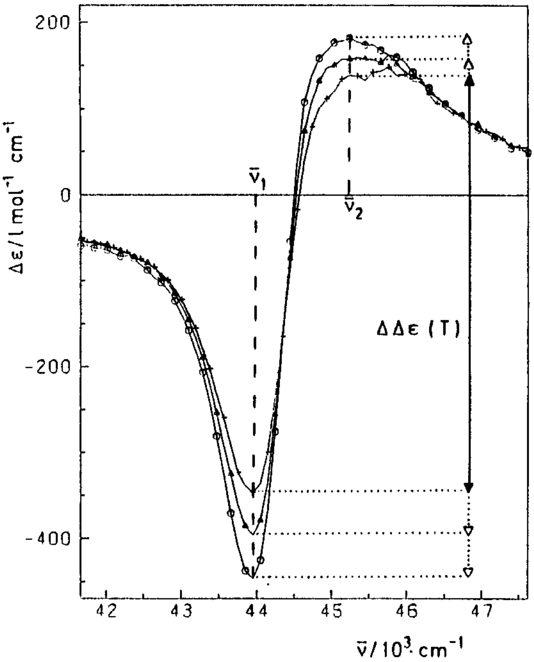

FIGURE 2 CD spectra ($\Delta\epsilon$) of R–5 in n–heptane for T = 20 °C (O), 50 °C (Δ), and 80 °C (+). Amplitude $\Delta\Delta\epsilon(T) = \Delta\epsilon(\bar{\nu}_1, T) - \Delta\epsilon(\bar{\nu}_2, T)$; $\bar{\nu}_1 < \bar{\nu}_2$).

shown in fig. 1. Fig. 2 represents a part of the CD spectrum of R–5 in which the couplet is shown for three temperatures. S–6 shows a similar but smaller temperature dependence. Following Moscowitz [4] this temperature dependence can be interpreted by an equilibrium between conformers. Assuming two conformers with suitable CD the rotational strength of the positive and negative band of the couplet or, in some approximation, the amplitude of the couplet $\Delta\Delta\epsilon$ is given then by

$$\Delta\Delta\epsilon(T) = \Delta\Delta\epsilon_B + (\Delta\Delta\epsilon_A - \Delta\Delta\epsilon_B)\frac{1}{1+\exp\{-\frac{\Delta G_0}{RT}\}} \quad . \qquad (2)$$

If there are equilibria between more than two conformers of the molecule, the structure of eq. (2) is preserved. Only the $\Delta\Delta\epsilon$'s have to be multiplied by factors which take into account the different equilibria. ΔG_0 then describes a mean value.

From results of the approximation shown in fig. 3 for S–5 $\Delta G_0 = 6{,}6 \pm 1$ kJ mol^{-1} and from an analogous curve follows for S–6 $\Delta G_0 = 11{,}8 \pm 1$ kJ mol^{-1}.

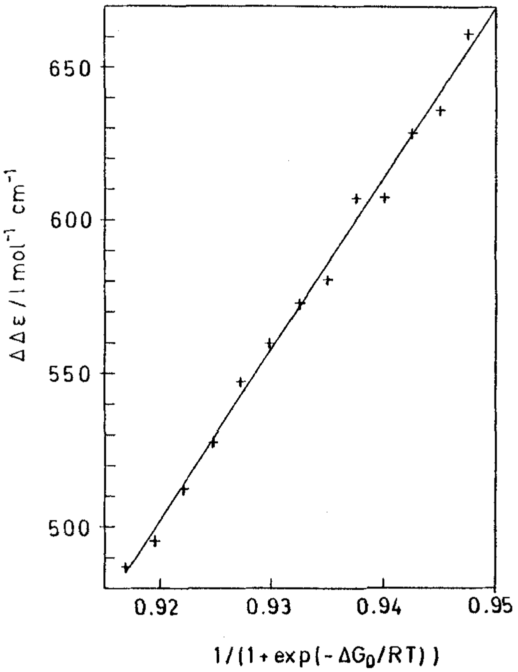

FIGURE 3 $\Delta\Delta\epsilon(T)$ as a function of $1/(1 + \exp\{-\Delta G_0/RT\})$ for S–5 in n–heptane.

In the temperature interval between 20 °C and 80 °C in n–heptane a variation of concentration of the conformer B about 6 to 10 % for S–5 and 1 to 2 % for S–6 appears.

Assuming the additivity of the helical twisting power, as Heppke et al.

[5] have shown to be acceptable,

$$p^{-1}x = \sum_i a_i x_i \qquad (3)$$

a calculation of ΔG_0 according to eq. (2) can be done. Because of the small temperature dependence the non linear fitting of these curves is not reliable. But combining eq. (2) and the analogous equation basing on eq. (3) the HTP can be given as a linear function

$$\mathrm{HTP(T)} = -\frac{(a_A - a_B)\ \Delta\Delta\epsilon_B}{\Delta\Delta\epsilon_A - \Delta\Delta\epsilon_B} + a_B + \frac{a_A - a_B}{\Delta\Delta\epsilon_A - \Delta\Delta\epsilon_B}\,\Delta\Delta\epsilon(\mathrm{T}). \qquad (4)$$

This is experimentally shown in fig. 4a,b for S–5 and S–6.

The linear relation between the HTP(T) and the CD amplitude $\Delta\Delta\epsilon$(T) is – corresponding to eq. (4) – fulfilled (fig. 4a,b). For this the existence of two conformers A and B is necessary.

For the discussion of these curves it should kept in mind that the temperature independence of the constants for the HTP, a_A and a_B, and the circular dichroism, $\Delta\epsilon_A$ and $\Delta\epsilon_B$, is the presupposition for eq. (4). Furthermore, the temperature dependence of the HTP is measured in ZLI 1695 and $\Delta\epsilon$ in n–heptane as a solvent because there is no adequate temperature region to measure $\Delta\epsilon$ in ZLI 1695 (Merck) in order to get the equilibrium constant and thus ΔG_0. A comparison of $\Delta\Delta\epsilon(T = 80\ ^0C)$ of S–5 in n–heptane and in ZLI 1695 shows a decrease of 10 %. Furthermore, it should be mentioned, that it is of no influence on the calculated equilibrium constant whether the CD band structure is a couplet of an exciton coupling or only an overlapping of a CD band of two independent transitions with different signs.

From the results given in fig. 4a,b the amplitudes of the couplet $\Delta\Delta\epsilon_A$ and $\Delta\Delta\epsilon_B$ and a_A and a_B of the conformers (tabl. 1) can be determined by eq. (2) and eq. (4). To estimate the errors due to the assumptions discussed above is difficult. For S–5, R–5 the situation is better than for S–6 because of the large temperature dependence.

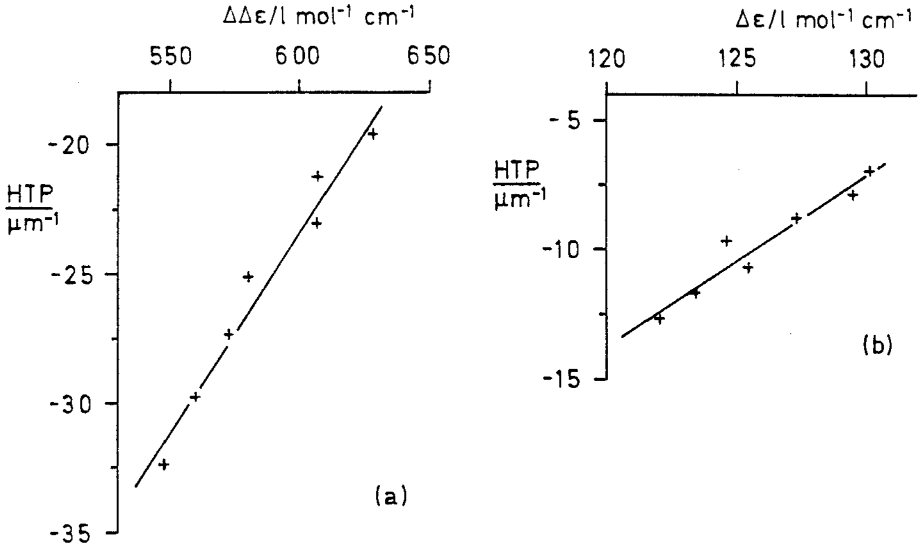

FIGURE 4 HTP(T) in ZLI 1695 (Merck) as a function of $\Delta\Delta\epsilon(T)$ or $\Delta\epsilon(T)$ in n–heptane according eq. (4) for S–5 (a) and S–6 (b), resp..

TABLE 1 Amplitude ($\Delta\Delta\epsilon_i$) or $\Delta\epsilon_i(\bar{\nu} = 44\,400\ \mathrm{cm}^{-1})$ and HTP (a_i) of the conformers A and B of S–5 and S–6

	$\Delta\Delta\epsilon_A$	$\Delta\Delta\epsilon_B$	a_A	a_B
S–5	950	– 4630	31	– 830
	$\Delta\epsilon_A$	$\Delta\epsilon_B$		
S–6	150	– 1680	4	– 1200

If there are more than two conformers which take part in the equilibrium of 5 and 6, the values given in tab. 1 are no longer pure spectroscopic constants. In general, they are then spectroscopic values multiplied by a function which is determined by the equilibrium constants between the distinct conformers. The molecular structures of the conformers contributing to the CD or HTP are not known. This is not essential for the experimental proof that conformers contribute to the HTP with different amounts. In a short hand notation one may say: the more stable conformer A of S–5 and S–6 determines the sign of $\Delta\Delta\epsilon$, whereas the sign of the HTP is given by B.

The amplitude of the couplet of S–5 depends on the solvent: $\Delta\Delta\epsilon$ (n–heptane) > $\Delta\Delta\epsilon$ (ZLI 1695) > $\Delta\Delta\epsilon$ (CH_3CN) (for 80 ^{0}C + 487, + 448, + 350 (extrapolated)). With increasing polarity the amplitude $\Delta\Delta\epsilon$ decreases which can be interpreted as the consequence of an increasing amount of the conformer B. An increase of the concentration of A and thus a decrease of B would shift the HTP of S–5 towards zero or a sign inversion of the induced helix. Only a small increase of the concentration of the conformer B is necessary for a sign inversion as found for S–5 in ZLI 1132 (fig. 1).

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