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# CHIRAL INDUCTION BY OPTICALLY ACTIVE AMINOANTHRAQUINONES IN NEMATIC PHASES

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Abstract The helical twisting power of chirally substituted mono- and bis-aminoanthraquinones in ZLI 1695 is only weakly temperature dependent. An exception are the naphthyl substituted compounds where the temperature dependence is correlated with the temperature dependent equilibrium between at least two conformers.
The order of the chiral dopant in the cholesteric phase is described approximately by the order parameters S*, D* and the orientation of the principal axes ($x_i^*$) of the order tensor against the molecular skeleton. Whereas there is no significant dependence of the HTP on S* and D*, the HTP is very sensitive to the orientation of the $x_i^*$ axes. Varying their direction by different types of substitution it can be shown that an approximate additivity rule of the HTP contributions from equal chiral structures holds only if the orientation axis ($x_3^*$) is the same for the molecules compared.

## INTRODUCTION

Chiral compounds solved in a nematic phase induce cholesteric $N^*$ phases. The strength of this chiral induction can be measured by the helical twisting power [1]

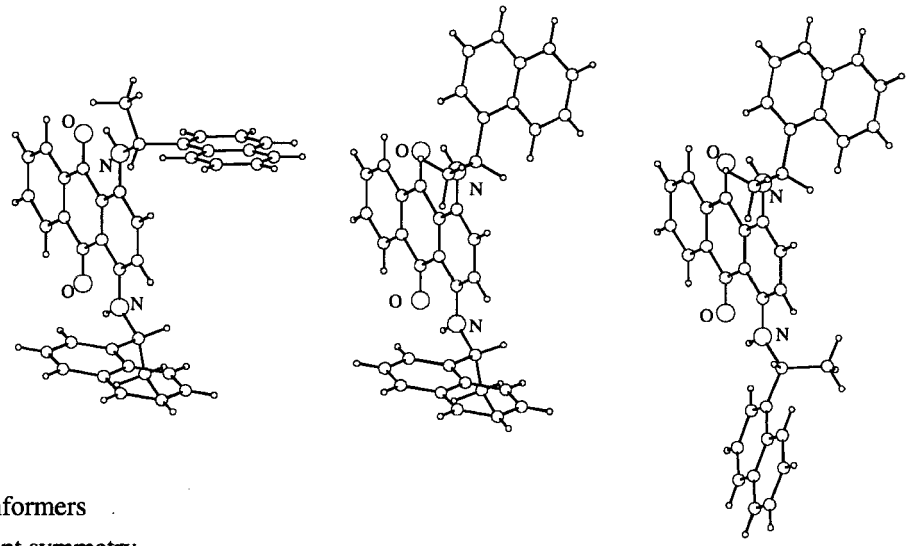
$$HTP = \left( \frac{dP^{-1}}{dx} \right)_{x=0} \tag{1}$$

where P is the pitch of the cholesteric phase in μm and x the mole fraction of the solute (guest).

The HTP depends on the molecular structure of the guest (dopant) and host (nematic phase) molecules. A general and suitable structure/HTP relation is not known

nowadays, and although there exist several kinds of approach, there are obviously no quantitative descriptions of or well-known mechanisms for the HTP. For different molecular structures different effects may be dominant. In the following we discuss an approach to a mechanism of chiral induction [2] by decomposing the effect into an intra- and an intermolecular chirality transfer. Intramolecular transfer means the way in which the chiral molecular structure - i. e. chiral conformers and their chiral electronic distortion - comes into being from "elements of chirality" in the molecule. Elements of chirality are - in accordance with the theory of optical activity - chiral centers, chiral axes and chiral planes [3]. For inherently dissymmetric molecules intramolecular chirality transfer needs, in general, not to be discussed. Intermolecular chirality transfer means the process of induction of the cholesteric phase by the individual species of the chiral guest molecule.

For analyzing the intra- and intermolecular chirality transfer, compounds are chosen which possess a large rigid and achiral skeleton - realized by mono- or bis-aminoanthraquinones - substituted by different chiral groups in different positions. All chiral substituents used in this program are of similar structure and their chirality stems from an asymmetric carbon atom.




Conformers (Point symmetry group): α ($C_2$) β ($C_1$) γ($C_2$)

FIGURE 1 Conformers of 1,4-bis-(R-1-(1-naphthyl)ethylamino)-9,10-anthraquinone (R-**5**) derived from molecular modelling (CHARMM); energy ratio: $E_\alpha:E_\beta:E_\gamma = 1:1.023:1.032$.

By this chiral center, three chiral conformers are produced in the case of the bis-naphthyl compounds by way of intramolecular chirality transfer as can be derived by molecular modelling [4] and partially proven from the temperature dependence of the circular dichroism spectra in the spectral region of the couplet at about $40 \cdot 10^3\,cm^{-1}$ [4,5]. Comparing the temperature dependence of the HTP and that of the CD of the couplet it can be concluded that one of the conformers (fig. 1: $\gamma(C_2)$) is responsible for the HTP and another one (fig. 1: $\alpha(C_2)$) $1\alpha$) for the CD [5].

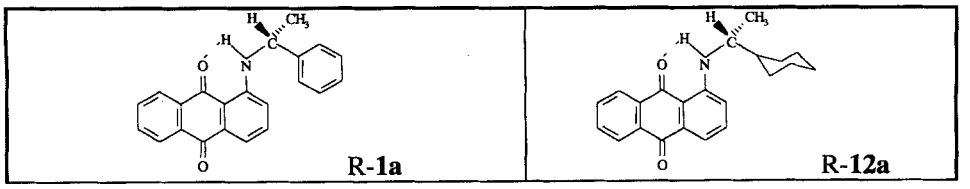
It is frequently stated that the HTP is not very sensitive to the local order of the phase as described by the order parameters S* and D* because in

$$P^{-1} = \frac{\lambda}{k_{22}}, \tag{2}$$

where $\lambda$ is an interaction parameter and $k_{22}$ the elastic twist constant, both quantities depend on the order in the same way [6]. This is confirmed also for the compounds analyzed here (fig. 2) where only a small temperature dependence has been found. But it will be shown in this paper that in spite of this fact the direction of the orientation axis ($x_3^*$, [7]) with respect to the molecular skeleton is very important for the strength of the chiral induction. If this direction is changed by achiral ligands in parts of the molecule far away from the chiral substituents, a significant variation of the HTP is to be expected.

## EXPERIMENTAL

The HTP has been measured by the Cano method [8] with an automatic apparatus [9]. The compounds (fig. 2) have been synthesized and purified by chromatographic methods [10]. The liquid crystal phase ZLI 1695 (Merck, Darmstadt) is a mixture of four 4-n-alkyl-4'-cyanobicyclohexanes with a clearing point at about 72,5°C.



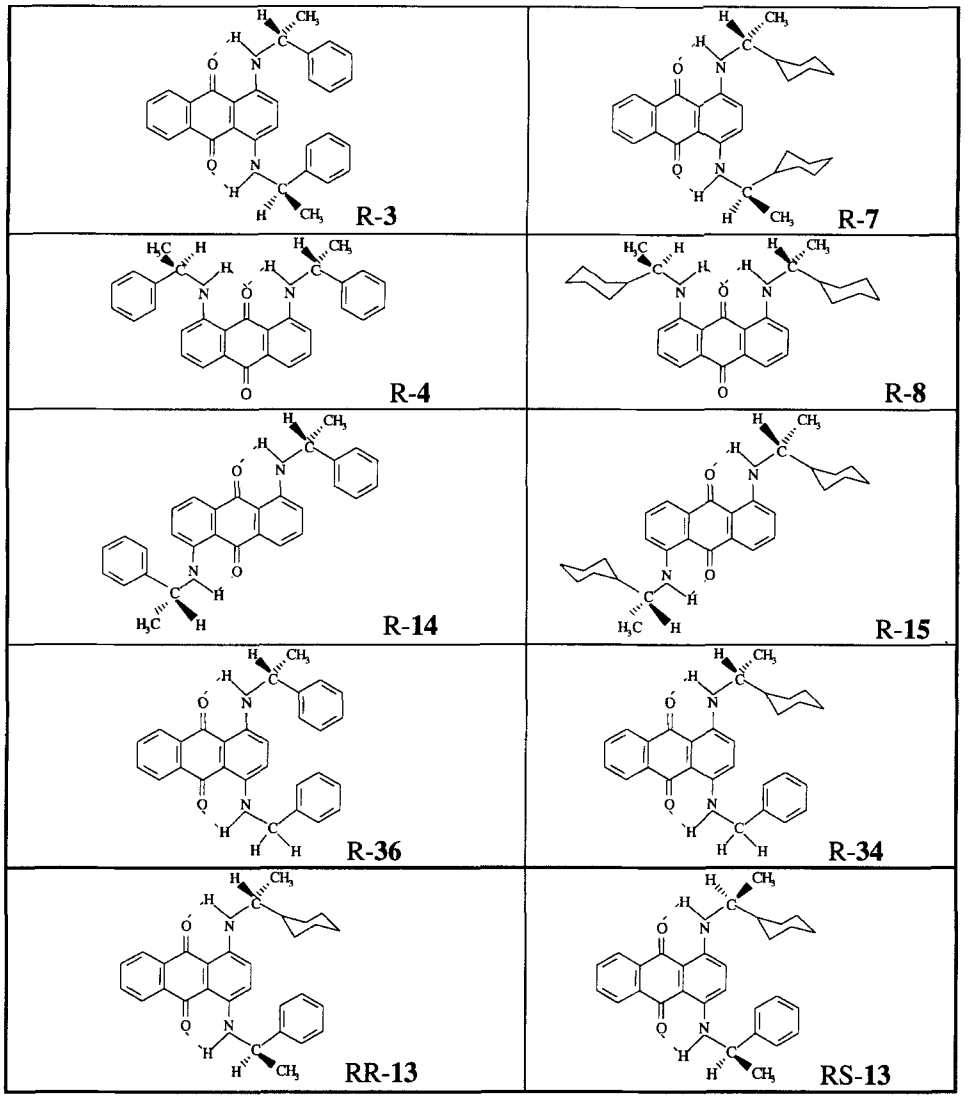



FIGURE 2 1-(R-1-phenylethylamino)-9,10-anthraquinone (R-**1a**); 1-(R-1-cyclohexylethylamino)-9,10-anthraquinone (R-**12a**); 1,4-bis-(R-1-phenylethylamino)-9,10-anthraquinone (R-**3**); 1,4-bis-(R-1-cyclohexylethylamino)-9,10-anthraquinone (R-**7**); 1,8-bis-(R-1-phenylethylamino)-9,10-anthraquinone (R-**4**); 1,8-bis-(R-1-cyclohexylethylamino)-9,10-anthraquinone (R-**8**); 1,5-bis-(R-1-phenylethylamino)-9,10-anthraquinone (R-**14**); 1,5-bis-(R-1-cyclohexylethylamino)-9,10-anthraquinone (R-**15**); 1-(R-1-phenylethylamino)-4-phenylmethylamino-9,10-anthraquinone (R-

**36**); 1-(R-1-cyclohexylethylamino)-4-phenylmethylamino-9,10-anthraquinone (R-**34**); 1-(R-1-cyclohexylethylamino)-4-(R-1-phenylethylamino)-9,10-anthraquinone (RR-**13**); 1-(S-1-cyclohexylethylamino)-4-(R-1-phenylethylamino)-9,10-anthraquinone (RS-**13**).

## RESULTS AND DISCUSSION

For the aminoanthraquinones S-**5**, S-**6**, S-**11a**, and S-**16** (fig. 3) the HTP (in ZLI 1695 (Merck, Darmstadt)) as well as the CD (in n-heptane) have been measured as a function of temperature.

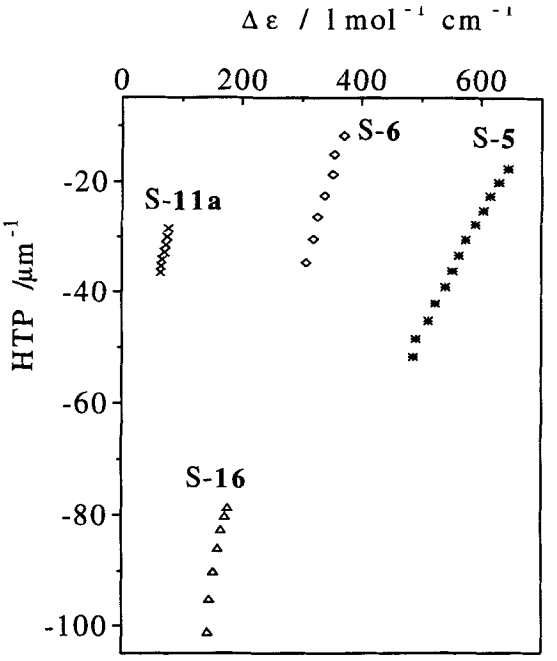



FIGURE 3 HTP(T) as a function of the amplitude of the couplet for 1,4-bis-(S-1-(1-naphthyl)ethylamino)-9,10-anthraquinone (*; S-**5**), and of $\Delta\varepsilon(\bar{\nu},T)$, $\bar{\nu}$ = $44.4\cdot10^3\,cm^{-1}$, $44.3\cdot10^3\,cm^{-1}$ and $44.6\cdot10^3\,cm^{-1}$ for 1,8-bis-(S-1-(1-naphthyl)ethylamino)-9,10- anthraquinone (✧; S-**6**), 1-(S-1-(1-naphthyl)ethylamino)-9,10- anthraquinone (×; S-**11a**), 1,5-bis-(S-1-(1-naphthyl)ethylamino)-9,10-anthraquinone (Δ; S-**16**).

As shown earlier for S-5 [5], the relation between the HTP and the CD of the couplet $\Delta\varepsilon(\bar{\nu}_{max})$ is approximately a linear function (fig. 3) from which follows that the conformers of different energy determine the temperature dependence of the HTP in the same way as that of the CD. One may conclude here directly that each conformer contributes to the HTP in a different manner. Furthermore, the HTP of the aminoanthraquinones given in fig. 2 has been measured as a function of temperature (fig. 4).

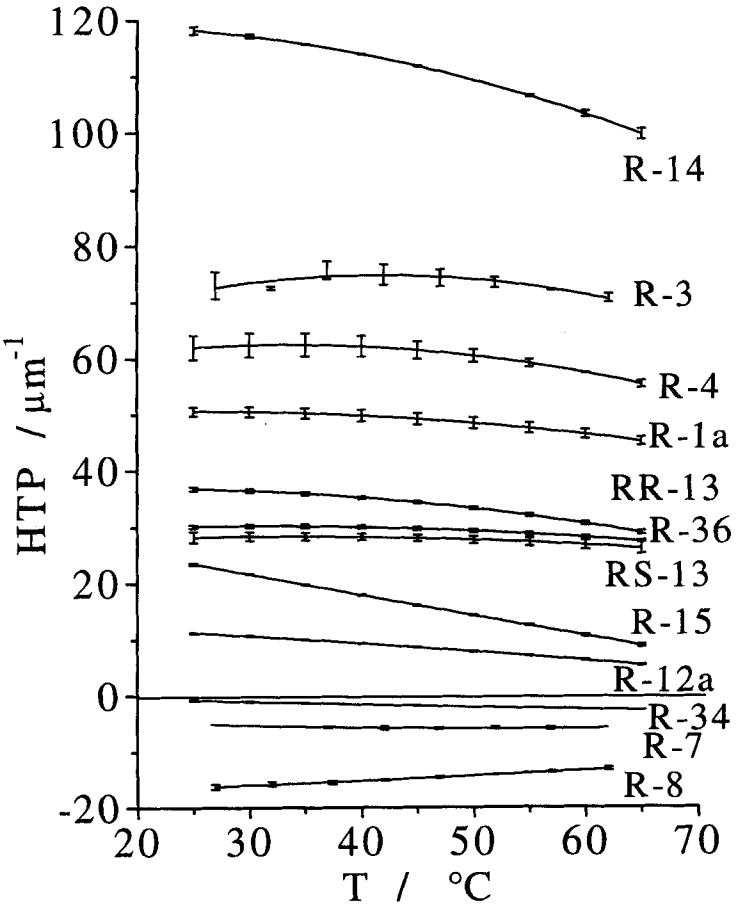



FIGURE 4 HTP as a function of temperature in ZLI 1695.

The discussion starts from the fact that the circular dichroism is an anisotropic property. The measurable quantity for oriented molecules $\Delta\varepsilon^A$ (ACD; [11, 12]) is a chirality observation. For an observation with an ensemble of molecules completely

oriented along an axis (orientation axis ($x_3^*$)) and distributed uniformly about this axis there results

$$\Delta\varepsilon^A = \Delta\varepsilon_{33}^* \tag{3}$$

for the ACD. If by any method the direction of the orientation axis can be changed, $\Delta\varepsilon_{33}$ varies as a function of this direction. Fig. 5 shows the calculated variation of $\Delta\varepsilon^A$ with the angle $\beta$ (fig. 5). We see that $\Delta\varepsilon^A$ may even change its sign.

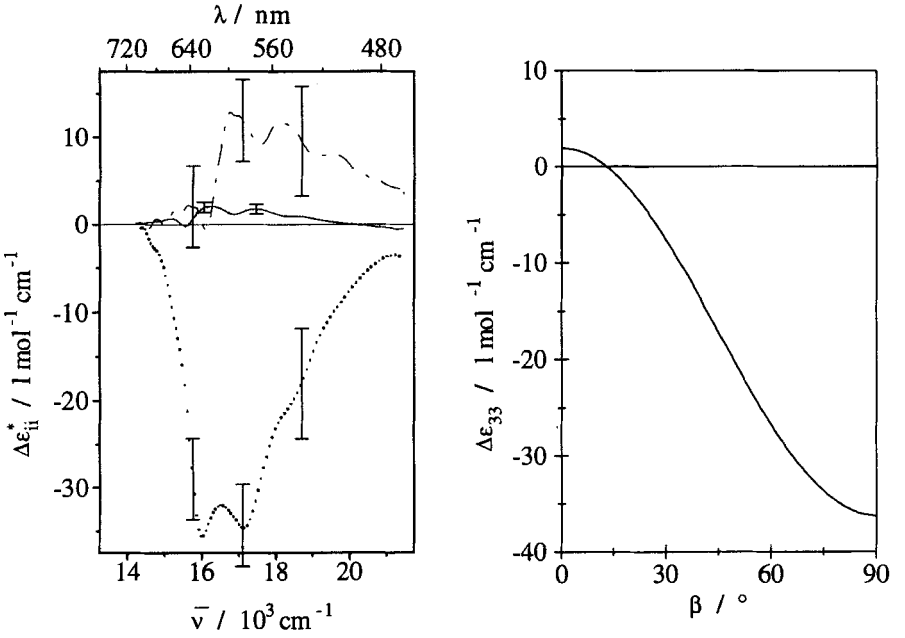
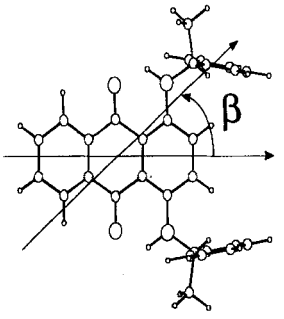



FIGURE 5 Left: The coordinates $\Delta\varepsilon_{ii}(\bar{\nu})$ of the circular dichroism tensor for R-**3** (in ZLI 1695);
Right: The calculated circular dichroism corresponding to a measurement at $\bar{\nu} = 16 \cdot 10^3\,\mathrm{cm}^{-1}$ along different directions relative to the molecule. The orientation axis is assumed to be parallel to this direction for each $\beta$.



Transferring these findings to the effect of chiral induction we may expect that the intermolecular chirality transfer and hence the HTP value will possibly depend strongly on the direction of the orientation axis ($x_3^*$) or, in the case of biaxiality, of all three principal axes ($x_i^*$) of the order tensor relative to the molecular skeleton. The oriented chiral molecule imprints its chirality onto the phase in different ways so that different HTP values should result.



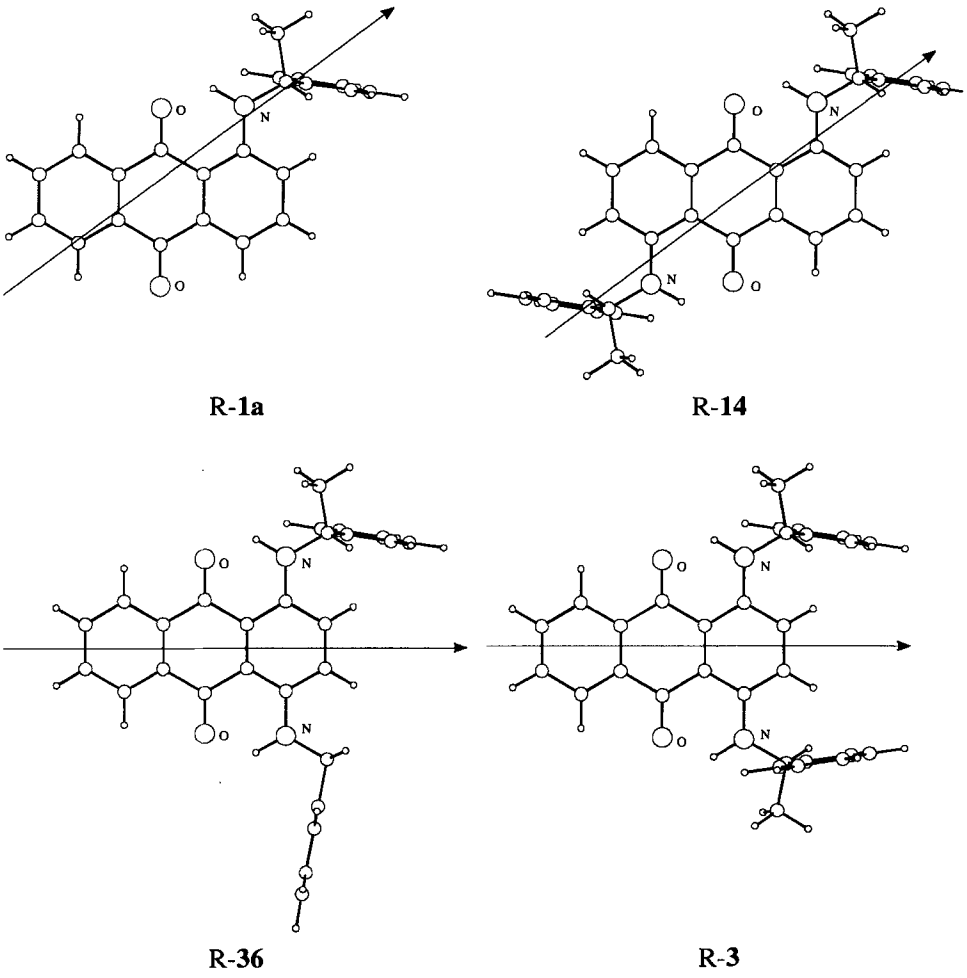



FIGURE 6 Estimated orientation axis for the conformers of lowest energy of the phenyl-substituted aminoanthraquinones.

In order to demonstrate the dependence on the direction of the orientation axis experimentally, the compounds of fig. 2 have been analyzed where the chirality can be led back to one or to two identical asymmetric carbon atoms. The intramolecular chirality transfer produces a chiral environment of the asymmetric carbon atom in form of a specific orientation of the substituent with respect to the rigid aminoanthraquinone skeleton (figs. 1 and 6). Molecular modelling for the compounds with two chiral centers yields that the structure of each pair, substituent - anthraquinone skeleton, is independent of the structure of the other one, i.e., in the disubstituted compounds each substituent acts independently of the other one. Except for the naphthyl substituted compounds the temperature dependence of the HTP (fig. 4) is small as generally found for such types of compounds but the variation of the substituents leads to a variation of the HTP of two orders of magnitude.

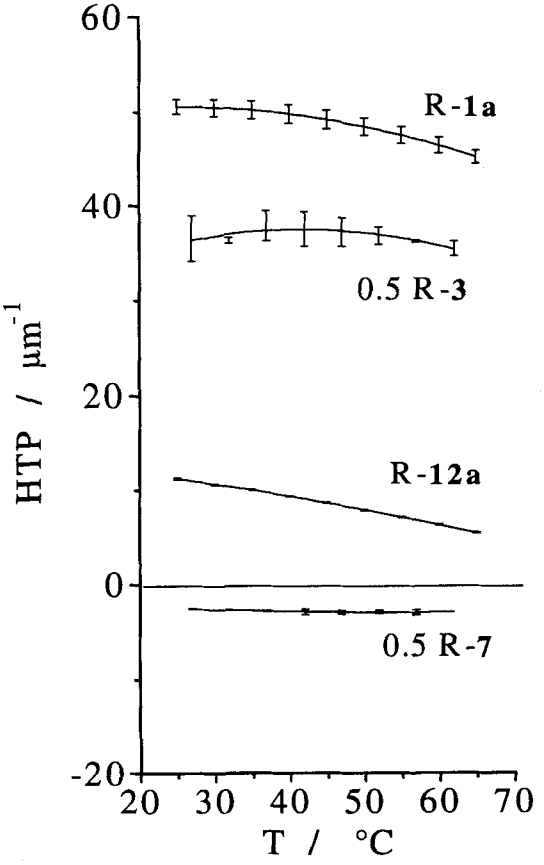



FIGURE 7 Comparison of the HTP values of R-**1a**, R-**12a**, R-**3**, and R-**7** in ZLI 1695

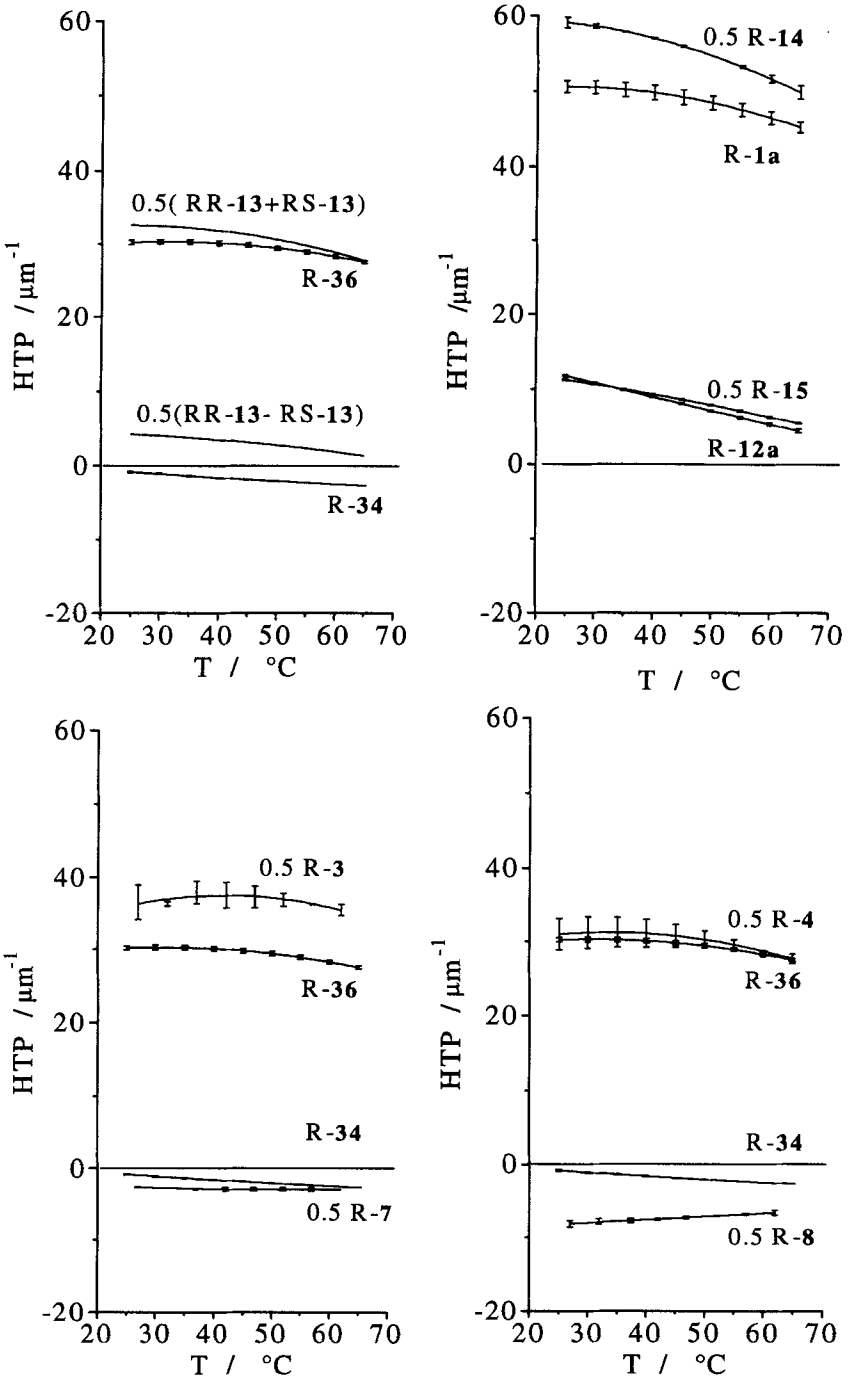



FIGURE 8 Comparison of the HTP values of R-3, R-4, R-7, R-8, R-34, and R-36 in ZLI 1695

The HTP values of R-**3** and R-**14** are different by a factor of about 1.6 (fig. 4) in spite of the fact that they are built up from the same groups and differ only in the positions of substitution. The analogue holds for R-**7** and R-**15** where the HTP values even are of different sign. Furthermore, HTP(R-**1a**) ≠ 1/2 HTP(R-**3**) and HTP(R-**12a**) ≠ 1/2 HTP(R-**7**) (fig. 7). On the other hand the following relations hold: HTP(R-**1a**) ≈ 1/2 HTP(R-**14**); HTP(R-**12a**) ≈ 1/2 HTP(R-**15**) (figs. 4, 8). It is conspicuous that in these cases R-**1a** and R-**14**, R-**12a**, and R-**15** the molecules possess approximately the same orientation axis; with the 1- and 1,5-substituted molecules this axis should be found in the direction from the 1- to the 5-position of the anthraquinone skeleton as shown in fig. 6. This means that the effects of the -NH-$CHCH_3$-$C_6H_5$ resp. -NH-$CHCH_3$-$C_6H_{11}$- groups are additive if both groups interact with the phase in the same orientation.

Transferring this idea, if one wants to compare R-**3** and R-**7** with molecules possessing only one chiral substituent like R-**1a** and R-**12a**, one has to take care that the orientation axis of the latter is parallel to that of R-**3** and R-**7**. In the symmetrically substituted molecules the orientation axis is approximately parallel to the long axis of the anthraquinone skeleton as has been found from polarized UV spectroscopy [7, 11]. The rotation of the orientation axis of R-**1a** and R-**12a** into this position can be achieved by a substitution in the 4-position. In order to have no additional chiral center this must be done by a substituent without an asymmetric carbon atom as in the case of R-**36** and R-**34**. Comparing R-**1a** with R-**36** and R-**12a** with R-**34**, one finds a drastic variation of the HTP values (fig. 4). As the chiral center is the same in each pair of molecules, this effect should be due to the alteration of the orientation axes. From fig. 8 it can be seen that the additivity rule HTP(R-**36**) ≈ 1/2 HTP(R-**3**) and HTP(R-**34**) ≈ 1/2 HTP(R-**7**) is approximately fulfilled. If the additivity holds, the following relations should also be true: HTP(R-**36**) ≈ 1/2 [HTP(RR-**13**) + HTP(RS-**13**)] and HTP(R-**34**) ≈ 1/2 [HTP(RR-**13**) - HTP(RS-**13**)]. For R-**36** this is indeed the case whereas for R-**34** a small positive value is calculated and a small negative value has been found. This error may come from the fact that here a small difference of two numbers is formed. Furthermore, HTP(R-**36**) ≈ 1/2 HTP(R-**4**) and HTP(R-**34**) ≈ 1/2 HTP(R-**8**) should hold (fig. 8). Whereas the first equation is fulfilled adequately, in the second case a large deviation is found.

From this discussion we conclude that the chiral induction depends on the direction of the orientation axis resp. of the entire $x_i^*$ (i=1,2,3) system. An increment system with additivity of the effects of different and non-interacting chiral centers in a molecule seems to make sense when the orientation axis is the same in the compounds compared. For two reasons this conclusion is not hampered by the fact that there exist different conformers for all our compounds. At first for all conformers of one compound

the orientation axis is approximately the same - this means that each conformer has to be discussed separately. Secondly there are some arguments that in each case only one conformer plays the important role in determining the HTP.

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