On the Odd-Even Effect in the Helix of Non-Sterol Cholesterogens

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A model is proposed to explain the alternation of the screw-sense of the helix with the number of bonds between the chiral centre and the ring system in chiral compounds with nematic-like molecular structure.

Non-sterol cholesterogens can be obtained from a nematogen through the replacement of a hydrogen atom of their alkyl or alkoxy chain by an alkyl group, thus creating a branching point at the chain and consequently a chiral centre at that point. These systems exhibit an odd-even effect, i.e. the handedness of the helix alternates with the number of bonds between the chiral centre and the ring system [1, 2]. The purpose of this note is to explain this effect in terms of a simple model.

In these systems the handedness of the helix appears to depend on the position of the chiral centre at the chain as well as on the absolute configuration of the centre. A convenient definition of the configuration of a chiral centre at the chain is the following. Consider a molecule with a chiral centre having for instance a H-group and a CH_3-group attached to it, see Figure 1a. Next we proceed along the chain towards the ring system with the long axis of the molecule in a horizontal position and the H- and CH_3-groups pointing obliquely upwards. Now the centre is labeled with a R (rectus, righthanded), if the CH_3-group is to the right and with a S (sinister, lefthanded), if the CH_3-group is to the left. This definition is in complete agreement with the convention of Cahn et al. [3]. The centres in Fig. 1a and 1b are therefore R-centres. The sign of the helix in a system of molecules with the chemical structure of Fig. 1a can be reversed by changing the absolute configuration of the chiral centre (R → S) or by shifting the branching point from a carbon atom n, counted from the ring system, to a carbon $n-1$ (Figure 1a and 1b). Note that the latter case can be obtained by means of an inversion operation through the point P located halfway between n and $n-1$ (Figure 1).

In the model we propose the spontaneous twist in these non-sterol systems is due to an orientational interaction between the substitutiongroup (CH_3 in Fig. 1) and the neighbouring molecules. The substitution group tends to align with the neighbouring molecule. This can be simply rephrased by stating that a certain axis of the substitution group, which in general deviates slightly from the symmetry axis of this group, tends to align with the long axes of neighbouring molecules. This additional interaction can be described by a Maier-Saupe model

$$V' = -\sum_i J P_2(\boldsymbol{e}_0 \cdot \boldsymbol{a}_i) \qquad (1)$$

where $\boldsymbol{e}_0$ is a unit vector along the axis of the group, P_2 is the second Legendre polynomial, $P_2(z) = \frac{3}{2} z^2 - \frac{1}{2}$, and J is a coupling constant depending on the distance $r'_{0i} = |\boldsymbol{r}_{0i} - s\,\boldsymbol{d}_0|$ from the substitution group on molecule o to the long axis $\boldsymbol{a}_i$ of molecule i; r_{0i} is the distance between the

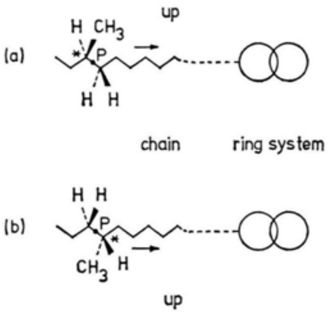

Fig. 1. Chiral molecules consisting of two parts: the ring system (benzene rings or cyclohexane rings and linkage groups) and the chain (alkyl or alkoxy chain). The asymmetric centre is marked with an asterisk. The difference between the number of bonds between the centre and the ring system in (a) and (b) equals one. Both the upperside and direction are indicated in order to facilitate the definition of the absolute configuration.

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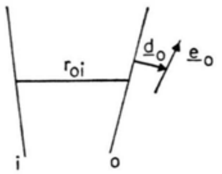

Fig. 2. Schematic representation of two interacting molecules. The substitution group is drawn on only one of the molecules.

centres of mass of the molecules; s denotes the distance between the substitution group and the long axis $\boldsymbol{a}_0$ of molecule o; $\boldsymbol{d}_0$ is a unit vector pointing from the long axis of o towards the group, $\boldsymbol{d}_0\cdot\boldsymbol{a}_0=0$. This situation is schematically represented in Fig. 2 (see also Figure 3). The summation in (1) runs over the nearest neighbours. Whether this interaction is due to steric or to dispersion forces is not relevant for the following argument. Assuming that the distance from the substitution group to the long axis is smaller than the intermolecular distance, we can approximate the interaction (1) by

$$V'=-\sum_i\left(J-s\,\boldsymbol{d}_0\cdot\boldsymbol{u}_{0i}\,\mathrm{d}J/\mathrm{d}r_{0i}\right)P_2(\boldsymbol{e}_0\cdot\boldsymbol{a}_i) \quad (2)$$

where $\boldsymbol{u}_{0i}$ is a unit vector from o towards i. The unit vectors $\boldsymbol{d}_0$ and $\boldsymbol{e}_0$ can be written as

$$\begin{aligned}\boldsymbol{d}_0&=\phantom{e_{0z}\,\boldsymbol{a}_0+{}}d_{0x}\,\boldsymbol{b}_0+d_{0y}\,\boldsymbol{c}_0\,,\\ \boldsymbol{e}_0&=e_{0z}\,\boldsymbol{a}_0+e_{0x}\,\boldsymbol{b}_0+e_{0y}\,\boldsymbol{c}_0\,,\end{aligned} \quad (3)$$

where $\boldsymbol{b}_0$ can $\boldsymbol{c}_0$ denote unit vectors along the short axes of molecule o with $\boldsymbol{b}_0\wedge\boldsymbol{c}_0=\boldsymbol{a}_0$. Next we assume that the molecules rotate more or less uncorrelated. This means that we are allowed to average over all orientations of $\boldsymbol{b}_0$ and $\boldsymbol{c}_0$ such that

$$\boldsymbol{a}_0\cdot\boldsymbol{b}_0=\boldsymbol{b}_0\cdot\boldsymbol{c}_0=\boldsymbol{a}_0\cdot\boldsymbol{c}_0=0\,.$$

Substitution of (3) into (2) and next making use of the following two relations valid for all vectors $\boldsymbol{n}$ and $\boldsymbol{m}$, which are not affected by the rotation of molecule o (e.g. $\boldsymbol{a}_i$ and $\boldsymbol{u}_{0i}$) [4]:

$$\text{(1)}\quad \overline{(\boldsymbol{b}_0\cdot\boldsymbol{n})(\boldsymbol{b}_0\cdot\boldsymbol{m})}^{av}=\overline{(\boldsymbol{c}_0\cdot\boldsymbol{n})(\boldsymbol{c}_0\cdot\boldsymbol{m})}^{av}=\tfrac{1}{2}(\boldsymbol{n}\cdot\boldsymbol{m})-\tfrac{1}{2}(\boldsymbol{n}\cdot\boldsymbol{a}_0)(\boldsymbol{m}\cdot\boldsymbol{a}_0), \quad (4\text{a})$$

$$\text{(2)}\quad \overline{(\boldsymbol{b}_0\cdot\boldsymbol{n})(\boldsymbol{c}_0\cdot\boldsymbol{m})}^{av}=\tfrac{1}{2}\,\boldsymbol{n}\wedge\boldsymbol{m}\cdot\boldsymbol{a}_0\,, \quad (4\text{b})$$

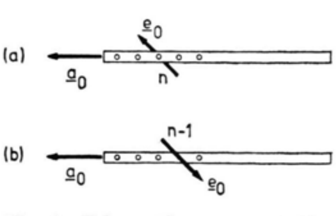

Fig. 3. Schematic representation of a molecule with a chiral centre at n (a) and at $n-1$ (b).

where the average has been taken over $\boldsymbol{b}_0$ and $\boldsymbol{c}_0$, yields the following twist-producing interaction:

$$\tfrac{3}{2}\sum_i s\,\mathrm{d}J/\mathrm{d}r_{0i}\left[(\boldsymbol{a}_0\cdot\boldsymbol{e}_0)(\boldsymbol{a}_0\wedge\boldsymbol{e}_0\cdot\boldsymbol{d}_0)\right]\cdot\left[(\boldsymbol{a}_0\cdot\boldsymbol{a}_i)(\boldsymbol{a}_0\wedge\boldsymbol{a}_i\cdot\boldsymbol{u}_{0i})\right], \quad (5)$$

where we used the relation

$$e_{0x}\,d_{0y}-e_{0y}\,d_{0x}=\boldsymbol{e}_0\wedge\boldsymbol{d}_0\cdot\boldsymbol{a}_0=\boldsymbol{a}_0\wedge\boldsymbol{e}_0\cdot\boldsymbol{d}_0\,. \quad (6)$$

According to the continuum theory [5] the helical wavenumber $q=2\pi/\text{pitch}$ is given by

$$q=k_2/k_{22}\,, \quad (7)$$

where k_{22} is the elastic constant for twist and k_2 is the elastic constant for spontaneous twist; k_{22} is always positive, whereas k_2 can be positive or negative; $q>0$ $(k_2>0)$ corresponds with a righthanded and $q<0$ $(k_2<0)$ corresponds with a lefthanded helix. As follows from the molecular theory of the cholesteric phase [4, 6], the interaction (5) determines k_2 and therefore the sign of the helix. The following proportionality relation holds

$$q\sim(\boldsymbol{a}_0\cdot\boldsymbol{e}_0)(\boldsymbol{a}_0\wedge\boldsymbol{e}_0\cdot\boldsymbol{d}_0)\,. \quad (8)$$

The odd-even effect in the twisting power becomes obvious immediately. As explained above, a shift of the branching point from a carbon atom n to a neighbouring atom $n-1$ (Fig. 1a and 1b), while keeping the same absolute configuration of the chiral centre, is equivalent to an interchange of the groups attached to carbon atom n and $n-1$ by means of an inversion through the point P located halfway between n and $n-1$. Under this inversion operation the vectors $\boldsymbol{e}_0$ and $\boldsymbol{d}_0$ transform according to

$$\boldsymbol{d}_0\to-\boldsymbol{d}_0\,,\quad \boldsymbol{e}_0\to-\boldsymbol{e}_0\,. \quad (9)$$

Then we see from (8) that the helix changes sign. Consequently we describe the odd-even effect. The transformation (9) is illustrated in Figure 3a and b). This figure may also be helpful to visualize the odd-even effect. The orientational perturbation of the substitution group with axis $\boldsymbol{e}_0$ is the strongest on the side where the group sticks out from the axis. In Fig. 3a, therefore, the group induces a righthanded helix, whereas it gives rise to a lefthanded helix in the situation of Figure 3b.

If the number of bonds between the chiral centre and the ring system increases, the factor

$$(\boldsymbol{a}_0\cdot\boldsymbol{e}_0)(\boldsymbol{a}_0\wedge\boldsymbol{e}_0\cdot\boldsymbol{d}_0)$$

will decrease on the average due to an increase of the flexibility of that part of the alkyl chain. As a consequence the pitch will become larger with an increasing number of bonds between the branching point and the ring system. This is observed experimentally [2].

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