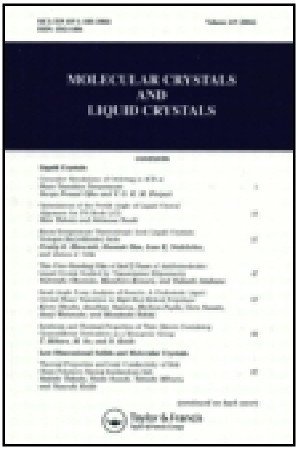

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Chain Ordering In The Smectic C, Smectic A and Nematic Phases Of Terephtal-bis-butyl-aniline (TBBA) and its Temperature Dependence: A Study in Terms of Intermolecular Potentials and Changes in the Molecular Free Volume

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ERRATUM

Chain Ordering In The Smectic C, Smectic A and Nematic Phases Of Terephtal-bis-butyl-aniline (TBBA) and its Temperature Dependence: A Study in Terms of Intermolecular Potentials and Changes in the Molecular Free Volume

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This paper contains a serious mathematical error which affects most results of the analysis. This error is associated with the values of Euler angles of the rotations which bring the frame $C_i x_i^0 y_i^0 z_i^0$ on to the frame $C_{i-1} x_{i-1}^0 y_{i-1}^0 z_{i-1}^0$ ($i = 2,3,4$): there is no alternation in the sign of the second Euler angle u_c and the third angle is 0 instead of π. The resulting correct expressions for the four splittings are (Eqs. 16 to 19).

$$\Delta\nu_1 = \frac{3}{2} c_1 S \sum_{m_1} d^2_{m_1 0}(\epsilon) d^2_{m_1 0}(u_D) \cos m_1\phi \cos m_1 \varphi_D \langle \cos m_1 \varphi_1 \rangle \quad (16)$$

$$\Delta\nu_2 = \frac{3}{2} c_2 S \sum_{m_1,m_2} d^2_{m_1 0}(\epsilon) d^2_{m_1 m_2}(u_c)\, d^2_{m_2 0}(u_D)$$

$$\times \cos m_1\phi \;\; \cos m_2\varphi_D \; \langle \cos m_1\varphi_1 \; \cos m_2\varphi_2 \rangle \qquad (17)$$

$$\Delta\nu_3 = \frac{3}{2} c_3 S \sum_{m_1,m_2,m_3} d^2_{m_1 0}(\epsilon) d^2_{m_1 m_2}(u_c) d^2_{m_2 m_3}(u_c) d^2_{m_3 0}(u_D)$$

$$\times \cos m_1\phi \; \cos m_3\varphi_D \; \langle \cos m_1\varphi_1 \; \cos m_2\varphi_2 \; \cos m_3\varphi_3 \rangle \qquad (18)$$

$$\Delta\nu_4 = \frac{3}{2} c_4 S \sum_{m_1,m_2,m_3} d^2_{m_1 0}(\epsilon)\, d^2_{m_1 m_2}(u_c) d^2_{m_2 m_3}(u_c)\, d^2_{m_3 0}(u_c)\, d^2_{00}(\mu_{DM})$$

$$\times \cos m_1\phi \; \langle \cos m_1\varphi_1 \; \cos m_2\varphi_2 \; \cos m_3\varphi_3 \rangle \qquad (19)$$

It turns out that, although these expressions are different from those of the original paper, due to the properties of the d^2_{mn}, only the expression of $\Delta\nu_2$, Eq. (17) of the original paper, was wrong.

The main consequences are the following:

(i) the values of the ratios R_{i1} for the isolated molecule are different (section 4). The correct values calculated with $u_c = 67.5°$, $u_D = 68.8°$, $u_{DM} = 70.6°$, $\epsilon = 8°$, $\phi = \pi$ (instead of 68, 69.8, 70.6, 7.9, 100° respectively) are

$R_{21} = -0.1267 \quad R_{31} = 0.1925 \quad R_{41} = -0.0303$ with Table 1.

$R_{21} = -0.1263 \quad R_{31} = 0.1741 \quad R_{41} = -0.0413$ with Table 2.

Note that these values are practically independent of ϕ.

The conclusions concerning the validity of the uncoupled model to describe the differences in ordering between the isolated chains and the chains in the liquid crystalline medium are not changed.

(ii) the results concerning the actual behaviour of the chains in the liquid crystalline phases are affected:

a) the assumption that the first methylene group flips around C_BC_1 is certainly not valid. On the contrary, the corresponding rotation (angle φ_1) appears to be highly hindered and the long molecular axis Oz_0 lies in the plane of the all-trans chain, implying $\phi = \pi$. In all calculations, we have assumed a small, temperature independent, librational motion around $\varphi_1 = \pi$, characterized by $\langle\cos\varphi_1\rangle = -0.98$, $\langle\cos 2\varphi_1\rangle = 0.92$ (mean amplitude fluctuation of ~10°).

b) the only reasonable combination of signs for the R_{i1} is now $[+,+,-]$ instead of $[-,+,-]$. However, the assignment of splittings in the nematic phase is the same: $|\Delta\nu_3| < |\Delta\nu_2|$

c) as a consequence, Figure 7 of the original paper is wrong. The correct one will not be reproduced here since equivalent information is contained in section 6.

(iii) The analysis in terms of intermolecular potentials (section 6), using the same Eqs. (26) and (27) yields significantly different results. They are summarized in the new figures 9, 10 and 11:

a) comparison between Figure 10a and 11a shows that the potential hindering the rotation around C_1C_2 (φ_2 rotation) is dominated by the external contribution. Complete rotation as well as jumps to gauche positions are not possible. However, libration around $\varphi_2 = \pi$ (the trans position) is easier than in the isolated molecule since the intermolecular potential tends to reduce the barrier height between trans and gauche positions. The total

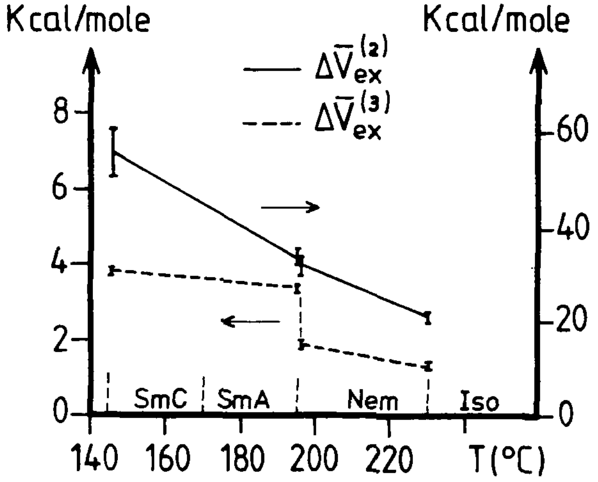

FIGURE 9 Temperature variation of the full heights $\Delta\overline{V}_{ex}^{(2)}$ and $\Delta\overline{V}_{ex}^{(3)}$ of the mean intermolecular potentials $\overline{V}_{ex}(\varphi_2)$ and $\overline{V}_{ex}(\varphi_3)$.

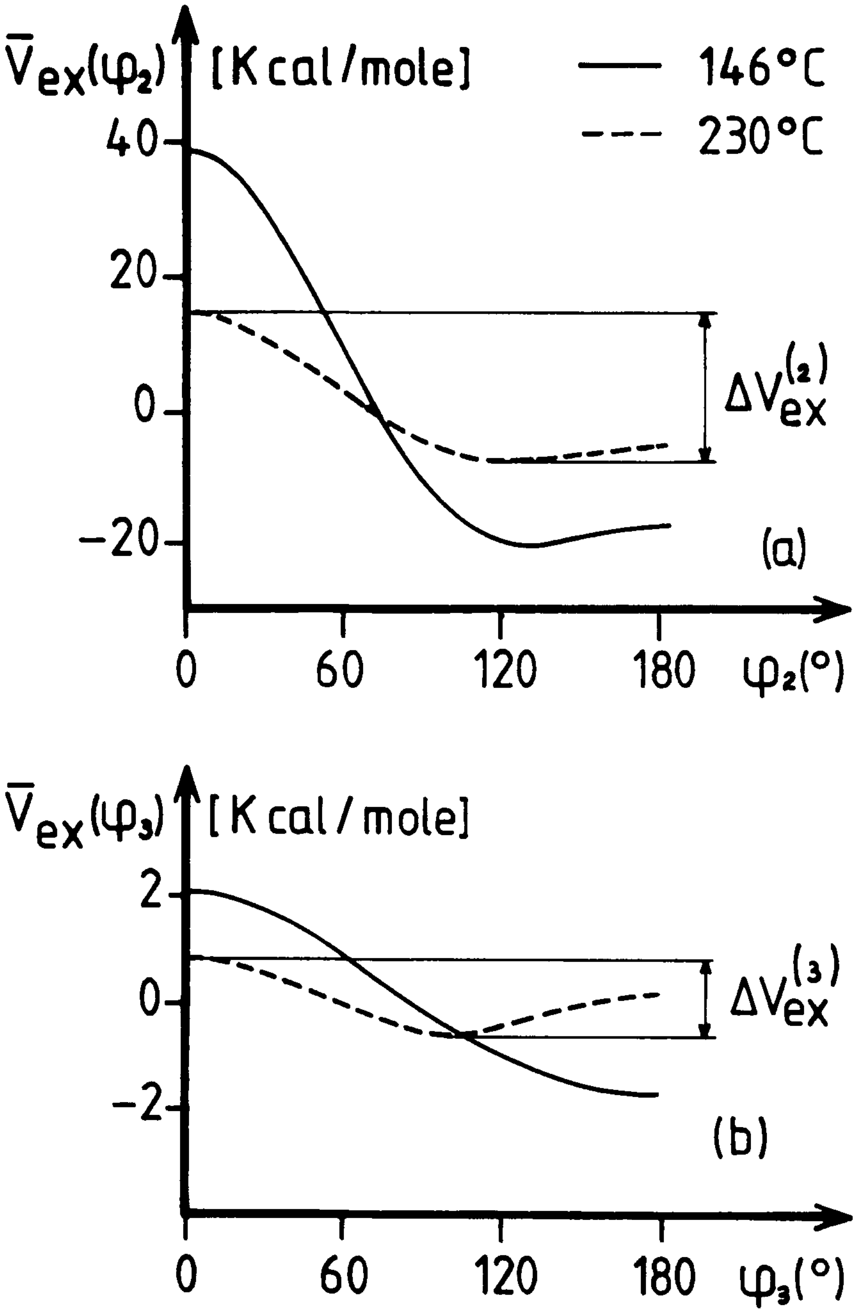

FIGURE 10 Shape of the mean intermolecular potentials for the two extreme temperatures 146 and 230°C (a) $\bar{V}_{ex}(\varphi_2)$; (b) $\bar{V}_{ex}(\varphi_3)$.

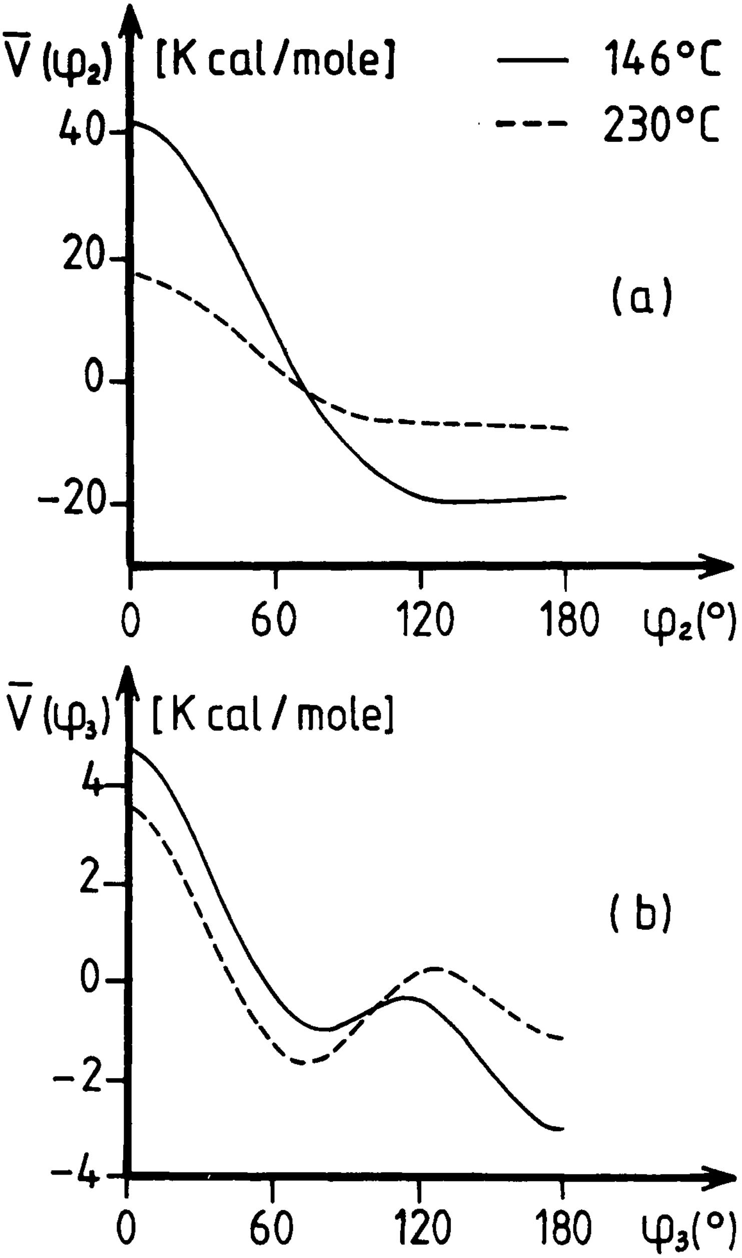

FIGURE 11 Shape of the mean total potentials for the two extreme temperatures 146 and 230°C (a) $\bar{V}(\varphi_2) = \bar{V}_{in}(\varphi_2) + \bar{V}_{ex}(\varphi_2)$; (b) $\bar{V}(\varphi_3) = \bar{V}_{in}(\varphi_3) + \bar{V}_{ex}(\varphi_3)$

height $\Delta \overline{V}_{ex}^{(2)}$ decreases smoothly with increasing temperature with no discontinuity at the various transitions (Figure 9).

b) comparison between Figure 10b, 11b and 9 shows that the situation is completely different for rotation around C_2C_3(φ_3 rotation). First, the intermolecular potential is comparable or smaller than the intramolecular one. Second, the situations in the smectic and nematic phases are different. In the Sm C and Sm A phases, the external potential tends to favor the trans position by slightly increasing the energy difference between the trans and gauche states, compared to the isolated chain. The total height $\Delta \overline{V}_{ex}^{(3)}$ slightly decreases with increasing temperature. At the Sm A – Nematic transition, this height decreases drastically (cf. Figure 9) and simultaneously the minimum shifts from 180 to ~100°. The intermolecular potential now favors thet gauche states and the energy of the gauche positions becomes slightly lower than that of the trans position (Figure 11b). Thus, transition to the nematic phase is characterized by a qualitative change of the intermolecular potential resulting in a large increase of rotational disorder around C_2C_3 bond.

c) these two points, together with the fact that in all phases, rotation of the first methylene group around C_BC_1 is strongly hindered and rotation of the methyl groups around their three-fold C_3C_4 axis is rather free, represent the main results concerning chain ordering in the Sm C and Sm A and nematic phases of TBBA, as predicted by the model used. These results replace those given in the original paper.