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Research Note

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Research Note

On the Helical Twisting Power of α-Phenethylamine in Nematic Liquid Crystals†

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It is the purpose of this Note to point out that the extraordinarily high helical twisting power reported for (+) and (−) forms of α-phenethylamine (PEA) dissolved in Schiff base-type nematic liquid crystals[1,2] is solely due to amine exchange reactions.

It is well known that chiral solutes, in general, induce cholesteric behavior in nematic liquid crystals,[3–5] and that if one substitutes a chiral center into a nematogen, a "chiral nematic" liquid crystal results with optical properties identical to conventional cholesteric liquid crystals.[6] Small optically active solute molecules produce minor perturbations of a nematic array, and the helical twisting power (defined as the reciprocal helix pitch extrapolated to 100% solute concentration[3]) is smaller than that of a typical cholesteric or chiral nematic molecule. The only exception is PEA[1,2] for which the helical twisting power has been reported to be higher than that of cholesteryl chloride.

PEA reacts rapidly at room temperature with N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline or its *p*-ethoxy-analog (EBBA).[7] The expected reaction product of EBBA and PEA was readily prepared by refluxing *p*-ethoxybenzaldehyde and (−) PEA in ethanol (Structure I below, EBPEA; infrared and nmr spectra consistent with structure). As can be seen from Figure 1, the high helical twisting power of PEA can easily be explained by amine exchange according to the reaction:

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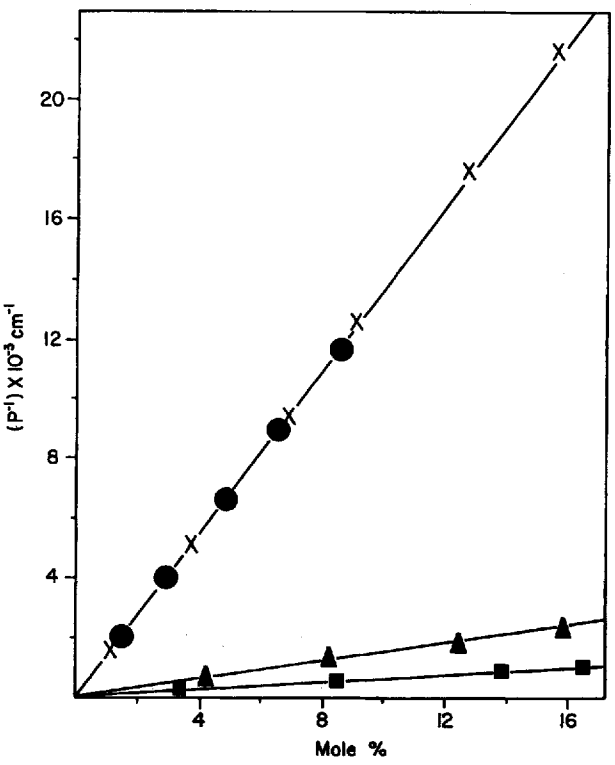
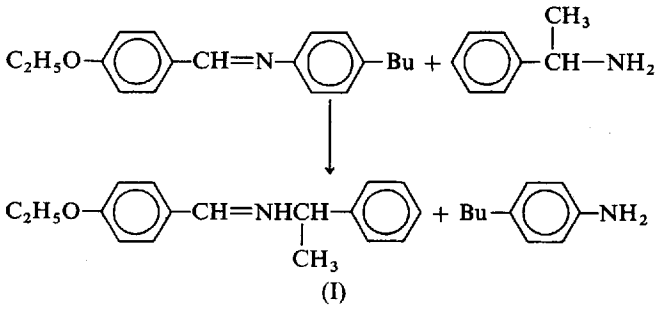


FIGURE 1 Reciprocal pitch vs mole % of solutes. PEA in Nematic Phase V (■); PEA in EBBA (●); EBPEA in EBBA (×); and α-phenethyl-alcohol in EBBA (▲). Nematic Phase V is a eutectic mixture of *p*-methoxyazoxybenzenes which are *p'* substituted with ethyl and *n*-butyl groups; it is commercially available from E. Merck.



(I)

PEA in other nematic solvents that undergo no reaction has a normal helical twisting power and the structurally related α-phenethylalcohol has a comparable twisting power in EBBA, as can be seen in Figure 1.

NMR spectra of EBBA, EBPEA and a 1:1 mixture of PEA and EBBA were taken and the equilibrium constant for the amine exchange reaction, calculated from the ratio of aldehydic proton peaks in the mixture, is about 5.5 at room temperature. EBPEA is *not* a nematic liquid crystal (m.p. 33.6°) but its similarity in shape to nematogenic Schiff bases undoubtedly leads to substantial cooperativity in its interaction with them and the concomitant high helical twisting power.

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