Induction of Preferred Conformation in Achiral Solutes Dissolved in Chiral Liquid Crystals

M. M. Labes* and Wen Shang

Department of Chemistry, Temple University
Philadelphia, Pennsylvania 19122

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In this work it is demonstrated that achiral solutes which normally show degeneracy of their enantiomeric twist states can behave as if they have a unique twist sense in a chiral liquid crystal environment. In the most dramatic example, the addition of ~0.2 mol % of 4,4‴-bis[(2-butyloctyl)oxy]-*p*-quaterphenyl (QP) to a cholesteric solvent causes a 22% reduction of the pitch, an effect much larger than that of a typical chiral solute.

It is well-known that chiral solutes added to nematic liquid crystals induce cholesteric phases[1-5] and that each member of an enantiomeric pair will produce opposite handedness of these phases.[6-8] In the limit of low concentrations, the pitch p of the cholesteric helix is inversely proportional to the concentration C of chiral solute ($p^{-1} = \beta C$).[9,10] The proportionality constant β is referred to as the "helical twisting power" (HTP) of the solute, and a number of studies have attempted to correlate β with size and shape related parameters.[11-14]

Here the question is raised whether there can be perturbation of conformational equilibria of enantiomeric twisted molecules in the presence of a chiral solvent. Further, if the solvent phase itself consists of molecules such as biphenyls or terphenyls, can the conformational equilibrium be perturbed by the presence of a chiral dopant? It occurred to us that a direct assessment of the induction of chirality in such molecules can come from a measurement of their effective HTP in a cholesteric phase.

Aromatic rings in an oligophenyl can be viewed as normally showing either an M or P twist sense. A preferred conformation can be locked into the structure in, for example, optically active bridged biaryl compounds. Solladie and Gotarelli studied the HTPs of such optically active biaryls in nematic liquid crystals and demonstrated that the chiral conformation leads to a cholesteric phase of the same helicity.[12-14] They proposed that chirality transfer from a chiral solute to a nematic phase proceeded through conformational interactions. What is explored in this work is the possibility that a *non optically active* oligophenyl will adopt a preferred twist conformation in a choleseric medium. Strong evidence is presented that this is indeed the case.

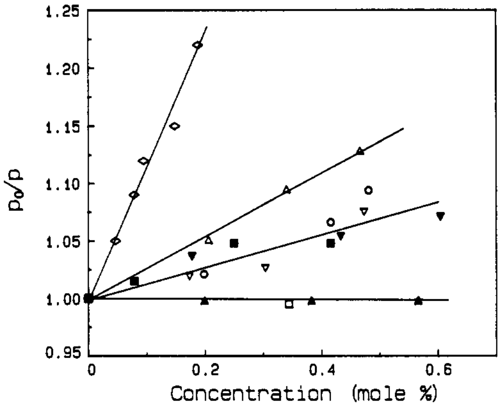

Figure 1. Relationship between p_0/p (initial pitch/final pitch) and concentration (mol %) for a group of achiral solutes and a reference chiral solute in the cholesteric solvent 0.4 wt % CP in MBBA at 20 °C. Proceeding from top to bottom: line 1, QP (◇); line 2, C15 (△); line 3, M27 (▽), T15 (■), TP (▼), S1114 (○); line 4, BC (□), S1185 (▲).

The cholesteric solvent employed consisted of *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) doped with 0.4 wt% of cholesteryl propionate (CP). This solvent was chosen because it can be easily aligned between glass slides by coating them with octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride (Petrarch). The pitch of this cholesteric solvent at 20 °C is ~110 μm. One achieves the so-called "fingerprint texture" of cholesterics in this manner in which the helix axis is parallel to the glass walls, and the molecular optical axis is precessing with a helical periodicity. When viewed between crossed polars on a polarizing microscope, one observes a series of black and light regions as the molecular axis proceeds from registry alternatively perpendicular or parallel to the observation direction.[15] A large number of fingerprint sizes are averaged to obtain the pitch (two fingerprints = 360° rotation of the optic axis). Measurements were made at 20 °C on samples 12 μm thick.

The achiral solutes employed were QP, *p*-terphenyl (TP), 4-*n*-pentyl-4″-cyano-*p*-terphenyl (T15), 4-(*n*-nonyloxy)-4′-cyanobiphenyl (M27), 4-cyano-1-(*trans*-4-*n*-pentylcyclohexyl)benzene (S1114), bicyclohexyl (BC), and 4-*n*-pentyl-4′-cyanobicyclohexyl (S1185). For comparison purposes, the chiral solute 4-[[(*S*)-(−)-2-methylbutyl]oxy]-4′-cyanobiphenyl (C15) was also studied. All materials were obtained from E. Merck, Aldrich Chemical, or Eastman Kodak.

Figure 1 is a plot of p_0/p, where p_0 is the initial pitch of CP in MBBA and p is the measured pitch when solute is added. The most profound shortening of the pitch was observed for QP, which has an apparent HTP greater than that of the optically active solute C15! Terphenyls, biphenyls, and phenylcyclohexanes produced small decreases in pitch and have HTPs of the same order of magnitude. Both BC and S1185 do not perturb the pitch significantly. Since all work was performed in the limit of very low concentration, these pitch fluctuations cannot be expected to be caused by any other factor than a preferred conformational effect. The order parameters of all these solutes are expected to be quite different, but at these concentrations it is unreasonable to assume that the order parameter of MBBA fluctuates strongly. Changes in p due to suppressions of the phase-transition temperature are also known to be very small when one is far from the phase transition, as is the case at 20 °C in MBBA.

HTPs can be calculated from the slope of the curves in Figure 1; the following values, which are consistent with general values of HTP in the literature,[12-15] are obtained (p in μm, C in mole fraction): C15, 0.31; QP, 1.14; the average value for the achiral biphenyls and terphenyls is 0.17.

The results not only furnish a rather clear case of induced conformational preference but also indicate that appropriate selection of achiral additives may be used to assist in the creation of highly chiral liquid crystals. An important role of conformational preference in the properties of cholesteric phases from biphenyl, terphenyl, and phenylcyclohexane type liquid crystals is clearly implied by these results. Conformational state selection should also be possible in polymer liquid crystals.[16]

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There are also implications in this work for the possibilities of asymmetric induction in cholesteric media. Eskanazi et al.[17] critically reexamined such studies up to 1979 and concluded that such induction can generally be expected to result in only low optical yields *except* for cases where strong solute–solvent interactions exist. Several additional studies since 1979 have claimed small enantiomeric excesses for reactions in cholesteric media;[18-20] one claim of a rather large (16%) excess has been made for some hydrogenation reactions.[21] The very large values of HTP for QP implies that this may be a case of a very strong solute–solvent interaction, and an attempt to capture these twist states in appropriate chemical reactions is therefore an intriguing possibility.

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Triplet States of Fullerenes C_{60} and C_{70}: Electron Paramagnetic Resonance Spectra, Photophysics, and Electronic Structures

Michael R. Wasielewski,*,† Michael P. O'Neil,†
Keith R. Lykke,†,‡ Michael J. Pellin,†,‡ and
Dieter M. Gruen†,‡

Chemistry and Materials Science Divisions
Argonne National Laboratory, Argonne, Illinois 60439

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The recent macroscopic preparation of C_{60} and C_{70} (buckminsterfullerenes) has resulted in renewed interest in these materials from both theoretical and practical standpoints.[1-4] As yet, no detailed X-ray structures exist for these molecules. Estimates of the sizes and symmetries of these molecules from theoretical work[5-13] combined with recent scanning tunneling microscopy[14,15] and ^{13}C NMR[16,17] observations. While the photophysics of these molecules have been studied in the gas phase,[18] only one report has appeared recently that presents data on the photophysics of C_{60} in condensed media.[19] We now report optical and magnetic resonance measurements on the lowest excited triplet states of C_{60} and C_{70} that yield structural information.

C_{60} and C_{70} solutions in degassed toluene[20] (5×10^{-4} M) at 295 K were excited directly within their low-lying, weak optical transitions with 4-ps laser flashes at 515 and 450 nm, respectively.[21]

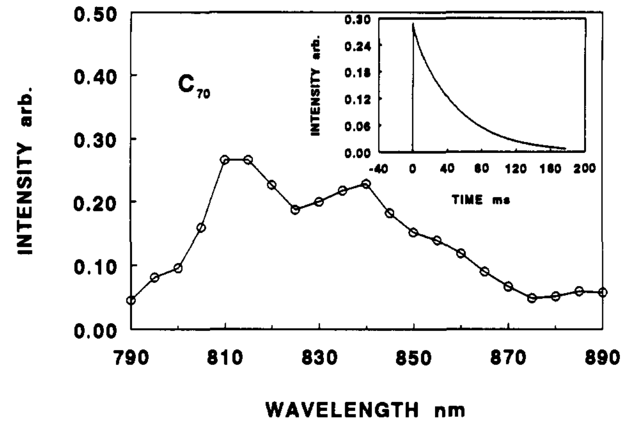

Figure 1. Phosphorescence spectrum of C_{70} in toluene/10% poly(α-methylstyrene) at 77 K obtained 10 ms after a 5-ns, 532-nm laser flash. A Burle (RCA) 8852 photomultiplier tube and a Jarrell-Ash 0.25-m monochromator were used for detection. Inset: phosphorescence decay at 810 nm.

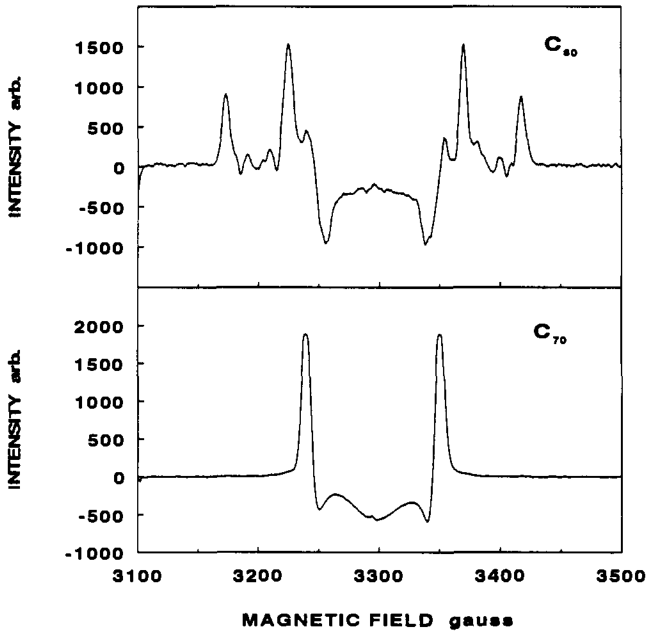

Figure 2. EPR spectra of $^3C_{60}$ and $^3C_{70}$ at 5 K, $\nu = 9.248$ GHz, microwave power = 1 mW, $\lambda > 400$ nm, 1-kHz light modulation, phase-sensitive detection, four field scans averaged, Varian E-9 spectrometer.

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† Chemistry Division.

‡ Materials Science Division.

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