Polymer Bulletin 28, 81–85 (1992)

Polymer Bulletin

An interpretation of NMR data of 4-ethoxy-4′-cyanobiphenyl in the nematic state – internal rotation around the O-CH$_2$ bond

Noritaka Kimura and Akihiro Abe*

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

Summary

Conformation of the ethoxy tail flanking the cyanobiphenyl core has been studied in the liquid-crystalline state. The compound exhibits a monotropic nematic phase at 91.9 °C. The ^{2}H NMR analysis indicates that the fraction of the trans conformer around the O-CH$_2$ bond amounts to 0.79 at the temperature slightly below the isotropic-to-nematic transition point. The result was found to be consistent with those reported for some related compounds by Celebre et al.

Introduction

Liquid-crystalline compounds often contain flexible tails or spacers jointed through oxygen to aromatic mesogenic cores. In our previous studies (1), we have examined conformation of main-chain type dimer and polymer liquid crystals carrying spacers such as -O(CH$_2$)$_n$O-. As may be easily shown by an inspection of a proper model, the conformational characteristics of the O-CH$_2$ (spacer) bond is quite important. The ^{2}H NMR analyses of the aforementioned liquid crystals lead to a conclusion that the conformation of the bond should be nearly entirely in trans. Molecular mechanics calculations for small molecules suggest that the bond favors trans, but the gauche form may be permitted as well in the free state (2).

Celebre et al. (3) have studied conformation of molecules such as X-ϕ-OCH$_2$CH$_3$ (with X=H, F, Cl) dissolved in a nematic solvent. The observed dipolar and quadrupolar NMR data are analyzed according to the Emsley-Luckhurst-Stockley (ELS) theory. In this study, the profiles of the rotational potential about the C^{ph}O-CC bond were adjusted so as to reproduce experimental observations. The energy difference ΔE (gauche - trans) was thus estimated to be of the order of 1.4 to 1.7 kcal mol^{-1}.

In contrast, Galland and Volino (4) have shown that the NMR data of Celebre et al. (3) can be equally well interpreted in terms of a model in which the molecule is assumed to exist essentially in one conformation. These authors concluded that the conformation in a liquid-crystalline state is similar to those existing in the solid phase at lower temperatures. The conformation

---

*To whom offprint requests should be sent thus derived requires some fairly large displacement of the rotational minima around the O-C and C-C bonds. The biaxiality of the molecule is also substantially large in the liquid-crystalline phase.

In this work, we have attempted to investigate the conformational characteristics inherent to the O-CH_2 bond involved in 4-ethoxy-4′-cyanobiphenyl (2OCB) in the liquid-crystalline state. The molecule has approximately C_{2v} symmetry around the C^{ph}-O bond. The rotational minima about this bond are assumed to occur at 0 and π, thus the O-CH_2 bond of the the alkoxy tail being coplanar with the phenyl plane. The trans (t) and gauche forms ($g^{\pm}$) defined around the C^{ph}O-CC bond are the only distinguishable conformers of the molecule.

Experimental Results

The Compound exhibits a monotropic nematic state at 91.9 °C on cooling from the isotropic melt. Deuterated samples such as $NC\phi\phi OCD_2CD_3$ (2OCB-d_7) were prepared starting from 4-hydroxy-4′-cyanobiphenyl deuterated at the ortho position (5). ^2H NMR spectra were recorded on JEOL GSX-270 spectrometer operating at 41.3 MHz deuterium resonance frequency. The measurements were also carried out under the proton-decoupled condition. The quadrupolar and dipolar splittings observed in the nematic state at the temperature $T = T_{NI} - 1.8$ K are as follows: $\Delta\nu_1 = 33.62$, $\Delta\nu_2 = 20.27$, $\Delta\nu_3 = 8.40$, and $D_{HD} = 0.494$, all units being kHz. The innermost doublet ($\Delta\nu_3$) which exhibits dipolar splittings (D_{HD}) originates from the aromatic C-D bond at the ortho position. The splittings $\Delta\nu_1$ and $\Delta\nu_2$ are due to the α-CD_2 and the terminal CD_3 group, respectively.

The order parameters of the mesogenic core axis can be estimated from the observed values of D_{HD} and $\Delta\nu_3$ according to the conventional procedure (6). From the experimental data given above, we obtained $S^R_{ZZ} = 0.409$ and $S^R_{XX}-S^R_{YY} = 0.027$. The contribution from the biaxiality term may be negligible as a first approximation.

Rotational Isomeric State Analysis

In a previous treatment of 4-n-alkyl-4′-cyanobiphenyls (nCB) (7), we have developed a model based on the assumption that [1] the molecular axis (Z) lies in the direction parallel to the line connecting both terminals of the molecule, and [2] the molecules are approximately axially symmetric around the Z-axis, and thus the orientation of these anisotropic molecules can be described by a single order parameter S_{ZZ}, the biaxiality of the system $S_{XX} - S_{YY}$ being ignored for simplicity. In this scheme, the quadrupolar splitting $\Delta\nu_i$ of the i-th C-D bond may be expressed as

$$\Delta\nu_i = (3/2)(e^2qQ/h)S_{ZZ}(<3\cos^2\theta_i> - 1)/2 \qquad (i = 1,\ 2) \qquad (1)$$

where e^2qQ/h (= 174 kHz) is the quadrupolar coupling constant, and the bracket indicates a conformational average. Comparison of the calculated and observed results may be facilitated by taking a ratio such as

$$\Delta\nu_2/\Delta\nu_1 = (<3\cos^2\theta_2> - 1)/(<3\cos^2\theta_1> - 1) \qquad (2)$$

The order parameter S_{ZZ} may be approximately related to S_{ZZ}^{R} of the mesogenic core by

$$S_{ZZ}^{R} = S_{ZZ}(<3\cos^2\psi> - 1)/2 \qquad (3)$$

where ψ denotes the inclination angle of the para-axis of the cyanobiphenyl group with respect to the molecular axis. Structural parameters required were mostly taken from literatures. The cyanobiphenyl group is treated as a simple straight rod: the length spanning the rigid core, $N{\equiv}C\text{-}\phi\text{-}\phi$, is taken to be 7.66 Å. The bond angles adopted for the ethoxy tail are as follows: ∠COC = 120°, ∠OCC = 110°, and ∠DCD=107.9°. For the terminal C-C bond, a threefold symmetric rotational potential was assumed. It has been suggested that the direction of the C^{ph}-O bond may be slightly disoriented from the exact para axis of the phenyl core: the distortion angle δ ranges from 0 to 4° in literatures (8).

The relative stability of the trans and gauche states about the C^{ph}O-CC bond can be easily deduced by simulation according to the expression given in eq. 2. Use of eq. 1 then leads to an estimate of S_{ZZ}. Since angles ψ are unambiguously defined for individual conformers in the framework of the assumed model, the value S_{ZZ}^{R} can be calculated from eq. 3. The fraction of the trans conformer f_t (= 1-f_g) and the order parameter S_{ZZ}^{R} thus derived vary quite sensitively with the structural parameters chosen in the simulation. Shown in Figure 1 are the dependence of (a) S_{ZZ}^{R} and (b) f_t on δ estimated by simulation for the observed quadrupolar splitting data. The broken curves indicate the results obtained by using ∠OCC = 112°. As may be easily demonstrated by an inspection of a molecular model, the effect arising from bond angle δ and ∠OCC are somewhat compensative: adoption of a larger bond angle (∠OCC = 112°) shifts the S_{ZZ}^{R} and f_t vs. δ curves to the right by about 1°. The horizontal thin line represents the value of S_{ZZ}^{R} (= 0.409) observed in the nematic phase. The value of δ (= 1.3°) thus derived falls within the range (0 to 4°) reported in literatures. The corresponding value of f_t was calculated to be 0.79 (cf. Figure 1b).

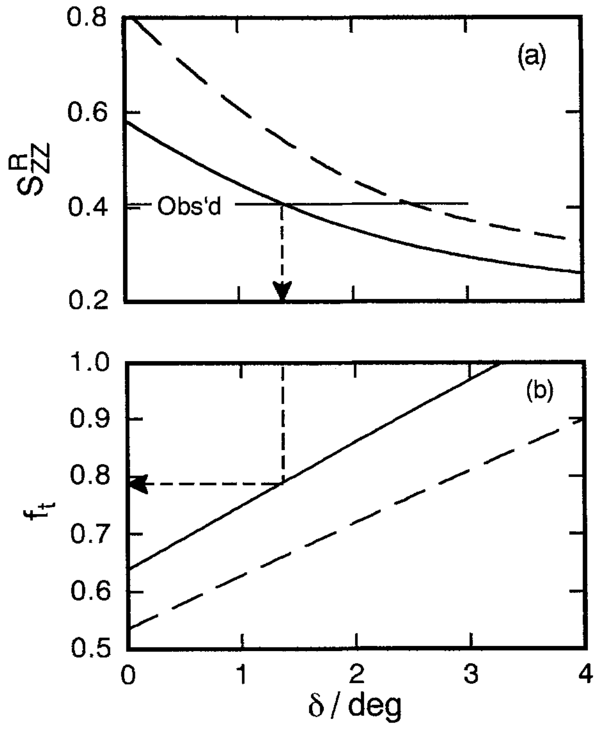

Figure 1. Variation of (a) S^{R}_{ZZ} and (b) f_t with disorientation angle δ. The curves shown are those calculated by adopting ∠OCC = 110° (solid) and 112° (broken), the other geometrical parameters being kept invariant. The horizontal (thin) line designates the observed value of S^{R}_{ZZ}. An appropriate value of δ and the corresponding fraction f_t may be estimated from the figure as indicated by the dotted lines.

Discussion

As given in eq. 3, the ratio $\Delta\nu_2/\Delta\nu_1$ is free from the external order parameter, and varies only sensitively with the conformation of the ethoxy tail. In the work cited in the introduction, Celebre et al. (3) have measured the deuterium quadrupolar splittings for 4-ethoxybenzene and 4-chloroethoxybenzene: the ratios are calculated to be 1.786 and 1.665, respectively. The corresponding ratio of 2OCB is in the same range: 1.659. These results immediately suggest that the conformational characteristics of the tail are similar, although the axial ratios of the mesogenic core are quite different. The conformational energies given by Celebre et al. (3) correspond to the fraction f_t = 0.75 to 0.81 in terms of the Boltzmann distribution. As stated above, our estimate is $f_t = 0.79$ in agreement with Celebre et al.'s results. It should be emphasized however that our method allows us to elucidate conformations without resort to any thermodynamic theories.

We believe that the bond rotation should be permitted in the liquid-crystalline state as long as the coresponding molecular configurations are compatible with the uniaxial order set by the environment. The single conformation model proposed by Galland et al. (4) is unrealistic from the thermodynamic point of view. More detailed studies including the conformational analysis in the isotropic solution are in progress and will be reported elsewhere.

Acknowledgment

This work was supported by Grants-in-Aid for Scientific Reserch from the Ministry of Education, Science and Culture. (03453108)

References

1. A. Abe, H. Furuya, *Polym. Bull.* **19**, 403 (1988); H. Furuya, A. Abe, *Polym. Bull.* **20**, 467 (1988); A. Abe, H. Furuya, *Macromolecules* **22**, 2982 (1989).
2. A. Abe, N. Kimura, unpublished results.
3. G. Celebre, M. Longeri, J. W. Emsley, *Liq. Cryst.* **6**, 689 (1989); J. W. Emsley, N. J. Heaton, M. K. Kimmings, M. Longeri, *Mol. Phys.* **61**, 433 (1987); G. Celebre, M. Longeri, J. W. Emsley, *J. Chem. Soc., Faraday Trans. 2* **84**, 1041 (1988).
4. D. Galland, F. Volino, *J. Phys. (Orsay, Fr.) II* 209 (1991).
5. J. W. Emsley, G. R. Luckhurst, G. N. Shilstone, *Mol. Phys.* **53**, 1023 (1984).
6. "*Nuclear Megnetic Resonance of Liquid Crystals*", edited by J. W. Emsley, Vol D. Reidel Publishing Co., Dordrecht 1985.
7. A. Abe, H. Furuya, *Mol. Cryst. Liq. Cryst.* **159**, 99 (1988).
8. H. M. Seip, R. Seip, *Acta Chem. Scand.* **27**, 4024 (1973); G. M. Anderson III, P. A. Kollman, L. N. Domelsmith, K. N. Houk, *J. Am. Chem. Soc.* **101**, 2344 (1979); D. Catalano, G. Celebre, M. Longeri, C. A. Veracini, *Gazzetta Chim. Italica* **115**, 233 (1985).

Accepted December 27, 1991 Sae