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The combined use of deuterium NMR and computer simulations for conformational investigation of flexible molecules in nematic solutions

Giorgio Celebre*, Giuseppina De Luca, Gloria Mazzone

Dipartimento di Chimica, Università della Calabria—v. P. Bucci, 87036 Rende (CS), Italy

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Abstract

In this paper, we suggest a new methodological approach to get in a very simple way a crude (but meaningful) conformational analysis of flexible molecules in fluid condensed phases (a very interesting matter where inter- and intra-molecular interactions are deeply involved). The test case we have chosen is the never-studied-before temperature dependence of inter-ring angle of biphenyl in a nematic solution. Undemanding ^{2}H NMR experiments were carried out on perdeuterated biphenyl dissolved in the mesophase at different temperatures, to obtain deuterium quadrupolar splittings. Since the experimental data alone are not sufficient to allow the determination of the inter-ring angle for each temperature, they were supplemented with simulated orientational information: this 'hybrid' set of data was enough to obtain the searched conformational distribution versus *T*. The results, showing a very slight tendency of the inter-ring angle to increase with the temperature, lend themselves to immediate interesting speculations and encourages the accomplishment of more sophisticated and expensive experiments to investigate more in detail the phenomenology. In our opinion the suggested methodology, appealing for its easiness, could be useful, for example, for coarse grained conformational investigations of large flexible systems (as, e.g. biomolecules) in liquid media.

Keywords: Liquid crystal NMR; Computer simulations; Biphenyl structure in liquid phase

1. Introduction

Biphenyl is a challenging molecule because it represents one of the few examples in which the molecular structure, characterized by its inter-ring angle φ (see Fig. 1), changes dramatically depending on the material's phase; the twist angle of biphenyl can then be exploited as a kind of 'probe' of molecular interactions.

In the gas phase, the province of intra-molecular forces, the twist angle is regulated by the optimization between the mutual repulsion of the rings (minimum at $\varphi=90°$, maximum at $\varphi=0°$) and the loss in conjugation energy stabilization of π systems (minimum at $\varphi=0°$, maximum at $\varphi=90°$): as a matter of fact, electron diffraction gives the two rings twisted of about 45° [1] (the same value has been also obtained by sophisticated theoretical calculations [2]). On the contrary in the solid, mainly ruled by inter-molecular forces, the rings are coplanar or just slightly twisted (X-ray studies indicate a planar structure above 40 K [3,4] and a twist of approximately 10° at lower temperatures [5,6]; ^{13}C NMR techniques gave an angle of 15–12° [7,8]). Between the solid and the gas there is the liquid phase, where a delicate, temperature-dependent equilibrium between inter- and intra-molecular forces is established. The study of this equilibrium via the observation of φ can be useful to investigate the nature of molecular interactions, in particular when the analysis is carried out by changing the temperature. Unfortunately, the twist angle of biphenyl in liquid phase is elusive: the φ angle is believed to be in the range 30–40° [8–12], but also lower values (about 20°) are reported [13]. A powerful, well established, high quality technique to study the conformational distribution of solutes in fluid condensed phases is the proton NMR of small molecules dissolved in liquid crystal solvents [14] (shortly, ^{1}H-LXNMR). Three ^{1}H-LXNMR studies of biphenyl in different nematic phases exist [15–17], one of these [16] carried out in the same nematic solvent of the present work (the so-called 'magic' mixture; vide infra). In those papers, the authors found a φ angle in the range 34–37°; anyway, due to the complexity of the method, the experiments [15,16] were carried out only at

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* Corresponding author. Tel.: +39 984493321; fax: +39 984493301.
E-mail address: giorgio.celebre@unical.it (G. Celebre).

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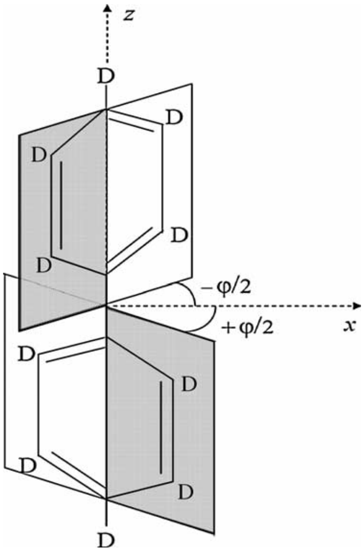

Fig. 1. Structure of perdeuterated biphenyl.

room temperature. Here, we suggest a simple but effective method to tackle the problem of crudely determining the T dependence of inter-ring angle of biphenyl in liquid phase at temperatures around the room temperature. In this approach, ^{2}H NMR experiments were carried out on perdeuterated biphenyl dissolved in a nematic phase at temperatures ranging from ~17 to 33 °C to obtain deuteron quadrupolar splittings. Since the experimental data alone are not sufficient to allow the determination of the inter-ring angle for each value of temperature, they were supplemented by Monte Carlo simulated orientational information: this 'hybrid' set of data was enough to obtain the searched conformational distribution versus T.

In our opinion, the interest of the suggested approach goes beyond the specific conformational problem outlined above. From a methodological point of view, this work shows that it is possible to complete not exhaustive sets of experimental data (coming from simple, undemanding experiments) with reliable 'virtual' data from computer simulations; this, in order to obtain self-consistent sets of 'hybrid' data, useful to get significant (even though only coarse grained) conformational information about very complex systems (e.g. biomolecules in a liquid medium). The results obtained by this method could be also considered as a useful preliminary step (a kind of 'low cost' test) to decide if it is worth to proceed with more sophisticated, demanding and expensive experiments.

2. Experimental

A 10 wt% solution was prepared by dissolving perdeuterated biphenyl (from Aldrich) in the 'magic' 55 wt% ZLI1132+EBBA nematic mixture, where orienting effects at room temperature (and in the vicinity of room temperature) are claimed to be due essentially to short-range 'size-and-shape' mechanisms [18]. In Fig. 2, the structures of ZLI1132 (from Merck) and EBBA (synthesized following standard procedures [19]) are shown.

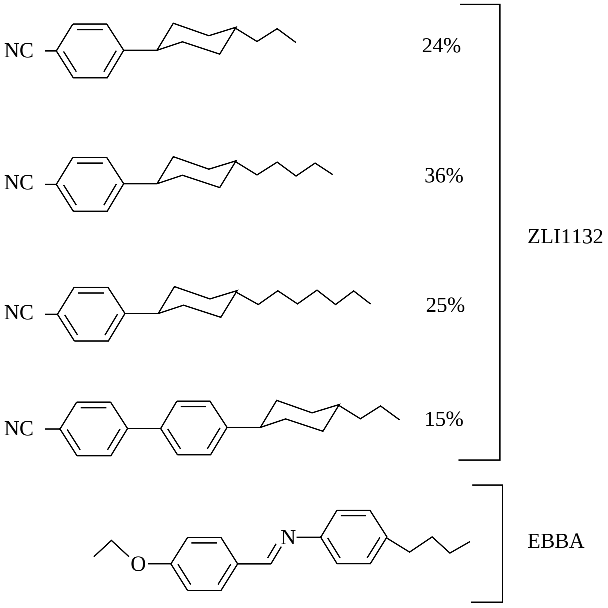

Fig. 2. Structure of solvent molecules.

Deuterium NMR spectra were recorded every ~2.5 °C from 16.7 to 33.2 °C on a Bruker AVANCE 500 (11.7 T) to obtain the experimental *ortho–meta* $(\Delta\nu_{o,m}^{\mathrm{exp}})$ and *para* $(\Delta\nu_{p}^{\mathrm{exp}})$ deuteron quadrupolar splittings (Figs. 3 and 4).

3. Theory

In a uniaxial liquid-crystalline environment (typically, a nematic mesophase) where the director aligns along the external applied magnetic field, the above mentioned experimental quadrupolar splitting of the ith deuterium is given by [20]

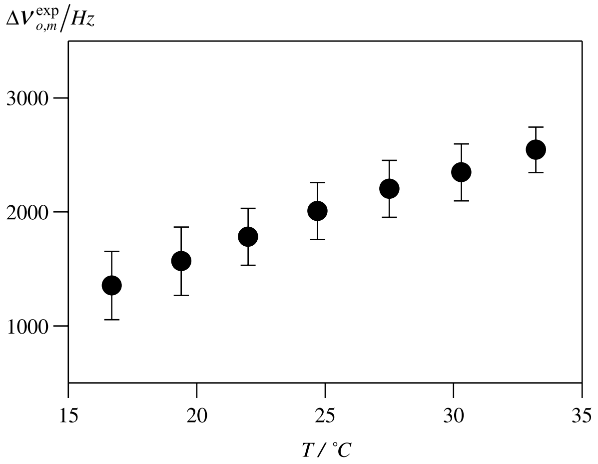

Fig. 3. Experimental quadrupolar splitting of *ortho–meta* deuterons as a function of T.