



Mobility inhibition of 1-phenylethanol chiral molecules in strong magnetic fields



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ABSTRACT

Experimental evidences are first obtained to demonstrate the effect of external magnetic field on the mobility of 1-phenylethanol molecules characterized by conjugated ring bonds. Enantiomers of these molecules are shown to have different mobilities in chiral polarized mediums composed of these enantiomers taken in various proportions. The difference diminishes when the external magnetic field increases.

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1. Introduction

The influence of magnetic field on transport properties of molecules has been widely discussed [1–7]. The problem becomes especially interesting when considering transport properties of chiral molecules [8–11]. The interpretation of interactions and effects with participation of chiral molecules is still questionable, including the interpretation of the data obtained with nuclear magnetic resonance (NMR) methods. The researches in this area originate from the fact that NMR chemical shifts and spin-spin coupling constants are identical for ‘left’ and ‘right’ molecules but demonstrate a difference in chiral polarized mediums (consisting of two enantiomers in different concentrations) [12–18]. Recently a new approach to detect differences in NMR parameters for enantiomers was proposed. The approach is based on studying the precessions of the nuclear magnetic moment and the induced electric dipole moment in the molecules [19,20]. Interestingly, in the presence of an external magnetic field, a number of molecules with ringed conjugated bonds, e.g. benzene, demonstrate induced electric currents in the ring to create additional induced magnetic field and additional induced magnetic moment. Chiral molecules with such bonds may be of particular interest in NMR studies of chiral effects. For example, magnetic moments induced in molecules by electric currents affect the mobility of chiral molecules by changing their orientation with respect to the external magnetic field [21].

Since diffusion parameters start changing when magnetic fields reach some critical values, studying such thresholds is important for the goals of enantiomer separation in both practical and purely scientific terms.

Here we first present ¹H NMR data to show the effect of external magnetic fields on the mobility of chiral 1-phenylethanol molecules.

2. Experiment and calculations

2.1. Samples

The samples were chosen based on the results of preliminary quantum-chemical calculations of various enantiomers with ringed conjugated bonds. Such molecules are characterized by magnetic fields produced in the centers of the rings by induction currents. The intensity of the induction field can be estimated by calculating magnetic shielding tensors in the centers of the rings [22].

The calculations were performed with ADF 2013 program package [23]. Geometry optimization was carried out within spin-restricted density functional theory using hybrid PBE0 functional [24,25]. Standard all-electron Slater-type-orbital core double zeta, valence triple zeta, doubly polarized basis set (TZ2P) was used for all atoms [26]. Calculated vibrational spectra contained no imaginary frequencies.

Magnetic shielding tensors at nonnuclear points of space were calculated with GIAO method [27,28]. Since the rings in the considered systems are formed by various atoms, a simple choice of geometric centers of the rings is not justified since the nature of interactions between inequivalent atoms at these points is unclear.

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Table 1
Isotropic parts of the magnetic shielding tensor (σ_{iso}) in rcp points for a number of *R*- and *S*-enantiomers.

	σ_{iso} ppm	
	<i>R</i>	<i>S</i>
Carvone	−2.412	−2.412
1,2-Diaminocyclohexane	2.939	2.940
Menthol	3.088	3.088
Phenyl-1-propanol	7.900	7.900
1-Phenylethanol	7.895	7.895
Mandelic acid	7.168	7.168

So the tensors of magnetic shielding were calculated in the positions of QTAIM ring critical points (rcp) [29], i.e. points of space with zero $\nabla\rho$ of electron density and the lowest electron density in the ring plane which makes it possible to minimize the influence of electron density on the magnetic shielding [30].

We calculated the isotropic part (σ_{izo}) of the magnetic shielding tensor for dextrorotatory (*R*) and levorotatory (*S*) chiral molecules such as menthol, 1-phenylethanol, carvone, etc. 1-Phenylethanol molecule, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$, with $\sigma_{\text{izo}} = 7.9$ ppm (for example, benzene molecule $\sigma_{\text{izo}} = 9.7$ ppm [22]) has the minimum number of spectral lines and high value of the isotropic magnetic shielding tensor in the center of the ring and therefore was chosen as the most appropriate for the experiment (Table 1). Therefore, for sample preparation we used *S*(−)-1-phenylethanol and *R*(+)-1-phenylethanol forms of reagent grade quality. The chirally polarized mixture (*RS*) consisted of 80% *R*- and 20% *S*-forms.

2.2. ^1H NMR experiment

The studies were conducted using Bruker Avance NMR 500, 600, and 700 spectrometers in external magnetic fields (H_0) 11.7, 14.1, and 16.4 T, respectively. To determine diffusion coefficients, a pulse method of NMR Diffusion Ordered Spectroscopy (DOSY) was used implying a bipolar longitudinal-eddy-current delay sequence (BPP-LED) [31–33]. BPP-LED method not only effectively reduces the influence of the inhomogeneity of the gradient of external magnetic field, but also significantly diminishes the impact of eddy currents and allows recording high-resolution spectral lines. The parameters of BPP-LED sequence were as follows: 0.0080 s pulse duration; 0.0499 s eddy current decay time, 64 points of the pulsed gradient, and 16 accumulated signals at each point. The Monte Carlo method was used to determine diffusion coefficients and their errors with the confidence level 95%. To determine chemical shifts, an ^1H spectrum of the sample with a capillary with a standard (CDCl_3) was taken before each DOSY measurement. The experiments were performed at 298 K on the sensor of the spectrometer. In all experiments and for all NMR spectrometers the same sample was used in the same standard 5 mm diameter ampoule.

To determine absolute values of diffusion coefficient, precision calibration of NMR spectrometers is required [34]. In our Letter, we study how diffusion coefficients depend on the external magnetic field. We believe that this effect can be detected only by comparing the mobility of chiral molecules in a chirally pure medium with the mobility of the same molecules in a chiral polarized medium in the same external conditions. In this case, it is only meaningful to consider the ratios D_{RS}/D_R rather than absolute values of diffusion coefficients, because this allows avoiding the impact of various external factors:

$$D_R = kD_R^0 \text{ and } D_{RS} = kD_{RS}^0$$

where D_R and D_{RS} are measured diffusion coefficients in pure and chiral polarized mediums, respectively; D_R^0 and D_{RS}^0 are the true

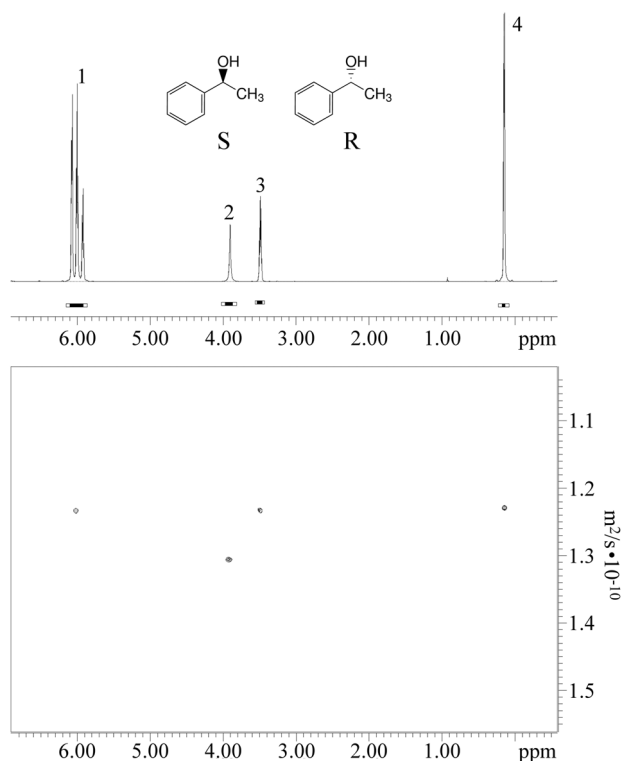


Figure 1. Top: ^1H NMR spectrum for *RS* mixture: the lines correspond to hydrogen atoms in C_6H_5 ring (1) —OH groups (2) —CH group (3) and — CH_3 group (4). Bottom: diffusion coefficients obtained for the corresponding lines. The scale of chemical shifts is imagined relative to TMS.

values of diffusion coefficients in pure and chiral polarized mediums, respectively; k is a parameter determined by the design of the spectrometer. As is seen, the ratios D_R/D_{RS} and D_R^0/D_{RS}^0 have the same values. We, therefore, studied ratios D_{RS}/D_R rather than absolute values of diffusion coefficients. The uncertainty of identifying D_{RS}/D_R ratios is determined by the sum of uncertainties of identifying D_{RS} and D_R coefficients with the Monte-Carlo method and did not exceed ± 0.004 . Note also that the uncertainty of studying the effect of induction fields on the diffusion coefficients due to different densities of studied mediums is in this case avoided because both pure and racemic forms have the close values of their densities (1.013 g/mL for the racemate and 1.010 g/mL for pure forms) [35].

3. Results and discussion

Figure 1 shows a typical ^1H NMR spectrum for *RS* mixture at $H_0 = 14.1$ T (other H_0 values demonstrate the same pattern of spectral lines). ^1H NMR spectra of pure *R*-, *S*-forms are similar to those of *RS* mixture and differ only in the values of chemical shifts. The distribution and the values of diffusion coefficients for each spectral line are shown in Figure 1 and Table 2.

Table 2

Diffusion coefficients ($10^{-10} \text{ m}^2/\text{c}$) for spectral components of ^1H NMR spectrum for pure *R*-form and *RS* mixture of 1-phenylethanol in various magnetic fields. N is the number of the spectral line (Figure 1).

N	11.7 T		14.1 T		16.4 T	
	<i>R</i>	<i>RS</i>	<i>R</i>	<i>RS</i>	<i>R</i>	<i>RS</i>
1	1.47	1.37	1.31	1.23	2.07	2.04
2	1.77	1.45	1.49	1.30	2.12	2.12
3	1.47	1.38	1.31	1.23	2.08	2.04
4	1.47	1.37	1.31	1.23	2.08	2.03

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