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Experimental and theoretical determination of the stable conformation of α,α,2,6-tetrachlorotoluene

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Abstract

The stable conformation of α,α,2,6-tetrachlorotoluene molecule is determined at low temperature by analysis of the proton spectra with natural abundance satellites C-13, and also of ^{1}H and ^{13}C spectra, both in isotropic as well as in oriented solvents. The analysis of the ^{1}H and ^{13}C NMR data, including 2D correlation spectroscopy by the combination of homo- and hetero-nuclear experiments COSY, HMQC and HMBC in isotropic solvent is established. The experimental data are further supported by theoretical quantum chemistry calculations. The correct assignment of chemical shift of carbon atoms was revisited with the help of 2D spectra. We conclude that the hydrogen atom of the methylene dichloride functional group lies in the plane of the benzene ring.

Keywords: NMR; α,α,2,6-Tetrachlorotoluene; Liquid crystals

1. Introduction

Nuclear Magnetic Resonance spectroscopy of molecules aligned in liquid crystal provides information on molecular structure and on order parameters [1–7]. The partial alignment of the molecules in the anisotropic phase of the liquid crystals gives rise to residual intramolecular dipolar couplings that are dependent of the internuclear distances and therefore yields information on the geometry of molecules. The spectra of these aligned molecules become rapidly complex with the increasing number of interacting spins and with the decreasing symmetry of the molecules. The analysis of the experimental data issued from the liquid crystal NMR spectra can be complicated by the molecular motion and by the electronic structure contributions to the signal. The direct use of the spectral parameters with an approximate theory [8,9] without paying attention to these contributions gives a rough estimate of the molecular shape. For example, harmonic vibrations [10] increase by several percents the contribution of the observed anisotropic couplings, $D_{ij\mathrm{exp}}$, used to determine the molecular average (r_α) or equilibrium (r_e) geometry. The difference between these two internally consistent geometries is due to the anharmonicity of the molecular vibration [11], which affects the former and makes it temperature dependent.

The main aim of the present paper is the experimental determination of the structure of α,α,2,6-tetrachlorotoluene molecule by using the liquid crystal NMR method to show whether the C–H bond of the methylene dichloride functional group and those of the aromatic part, shown in Fig. 1, are coplanar or not in the lowest-energy conformation at low temperature. The present experimental studies are performed simultaneously with theoretical calculations, which have become reliable recently with the improvement in computational resources, to complete the geometrical characterization.

2. Experiment

The α,α,2,6-tetrachlorotoluene is obtained from Fluka, and the liquid crystal solvent is purchased from Merck (Dramstadt). 1D NMR experiments were performed on a Bruker high resolution spectrometer equipped with a 5 mm diameter $^{1}H/^{13}C$ dual probe and operating at frequencies of 300.130 MHz for proton and 75.470 MHz for carbon-13. The 2D NMR experiments in isotropic solvent were performed on a high-resolution Bruker DRX 400 spectrometer equipped with

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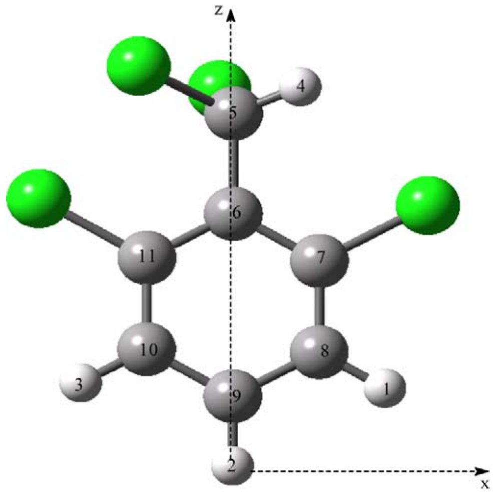

Fig. 1. Numbering of the nuclei and labeling system for the α,α,2,6-tetrachlorotoluene molecule.

a standard variable-temperature unit (BVT3000) by using a broadband inverse probe and a Z-gradient unit. The temperature was kept constant at 268 K. The indirect coupling constants between protons and protons–carbon-13 were measured. A 50% by weight solution in hexadeuterioacetone added with CS_2 was placed in 5 mm sample tube, sealed and degassed under vacuum. Before the NMR spectra were measured, the sample was kept for about 1 h in the magnetic field in order to achieve a good thermal equilibration. Four hundred scans were accumulated into 16 K data points.

In the anisotropic medium, the sample was prepared using 5% by weight of the α,α,2,6-tetrachlorotoluene molecule dissolved in the Merck ZLI 2081 nematic liquid crystal which possess an anisotropy of diamagnetic susceptibility greater than zero; placed in 5 mm double wall tube using hexadeuterioacetone in the inter-wall space as a lock substance. The sample is degassed and sealed under vacuum thereafter. One half hour was allowed to achieve temperature equilibration before spectra were accumulated. About 10,000 and 41,000 scans are accumulated into 32 K data points, respectively, for the ^{1}H and the ^{13}C nuclei. The ^{1}H spectrum required about 4 h of accumulation (pulse duration, 4 μs; number of points in the FID signal, 8 K). The temperature was kept constant at 268 K during the accumulations. Fig. 2 gives the ^{1}H NMR spectrum with ^{13}C satellites of α,α,2,6-tetrachlorotoluene molecule oriented by phase ZLI 2081 (268 K, 5 mol%).

3. Computational details

All calculations have been performed with the Gaussian suite of programs [12]. Among all the available methods we chose one issued from Density Functional Theory (DFT) since it produces accurate results—the electronic correlation is taken into account—with affordable computational cost. The B3 [13] hybrid exchange functional in conjunction with the LYP [14] electronic correlation functional were selected with the triple-ζ polarized basis set 6-311G**. This level of theory is known to give reliable geometric and energetic parameters. The geometry has been fully optimized with the 'tight' convergence criteria, with 'ultrafine' integration grid, and requiring the convergence criteria of the self-consistent field (SCF) equation to reach 10^{-12} atomic units. The nature of the critical point found was further analyzed by means of force constants calculation—all eigenvalues of the hessian matrix were positive. Furthermore, the energetic profile of the rotation around the single C_5–C_6 bond (see Fig. 1 for atom numbering) is obtained by constrained geometry optimization varying the H_4–C_5–C_6–C_7 dihedral angle by steps of 10° from 0 to 90°.

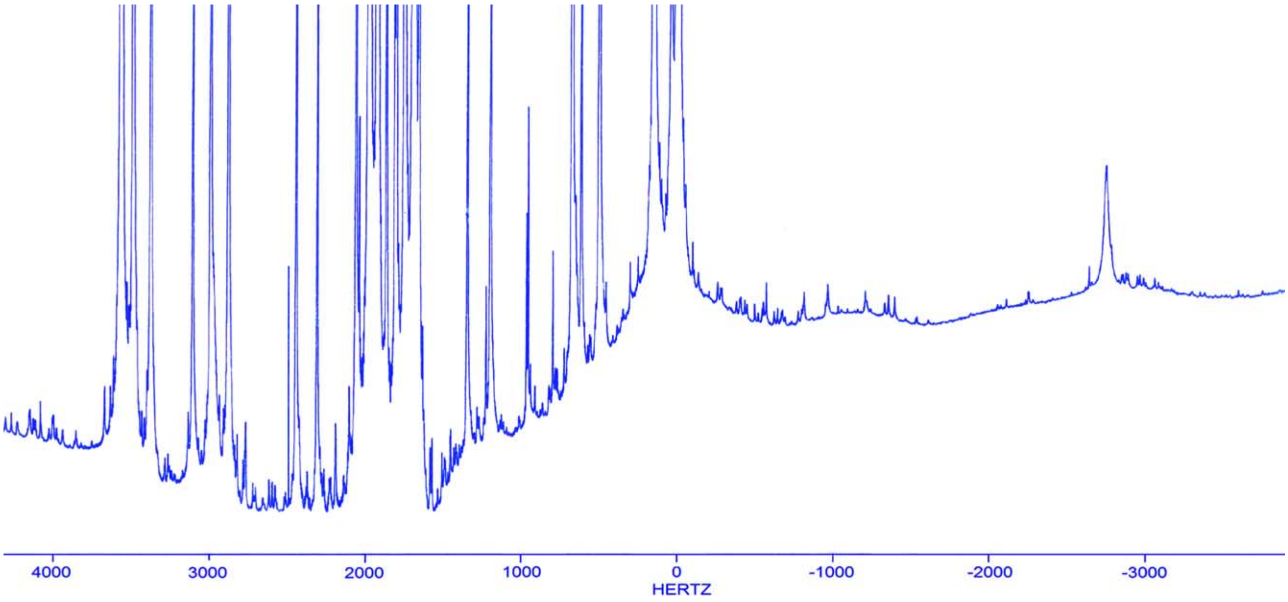

Fig. 2. ^{1}H NMR spectrum with C-13 satellites of α,α,2,6-tetrachlorotoluene molecule oriented by phase ZLI 2081 (268 K, 5 mol%).