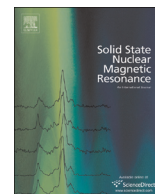




Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

Carbon-13 chemical-shift tensors in indigo: A two-dimensional NMR-ROCSA and DFT Study

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ARTICLE INFO

Article history:

Received 4 June 2015

Received in revised form

25 August 2015

Accepted 27 August 2015

Keywords:

¹³C NMR

Recoupling of chemical-shift anisotropy

Density-functional theory

Indigo

Indole

Purine

Hypoxanthine

Adenosine

Natural product

ABSTRACT

The principal components of the ¹³C NMR chemical-shift tensors for the eight unique carbon sites of crystalline indigo have been measured using the ROCSA pulse sequence. The chemical shifts have been assigned unambiguously to their respective nuclear sites through comparison of the experimental data to the results of density-functional calculations employing a refined X-ray diffraction structure. These measurements expand the database of measured aromatic ¹³C chemical-shift tensors to the indole ring. Magnetic shielding calculations for hypoxanthine and adenosine are also reported. Comparisons of calculations that include the effect of the crystalline lattice with calculations that model indigo as an isolated molecule give an estimate of the intermolecular contribution to the magnetic shielding.

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1. Introduction

Indigo, 2,2'-bis(2,3-dihydro-3-oxoindolylidene), is a blue dye with technological, industrial, cultural, and biological significance [1]. The molecular structure and atom-labeling scheme of indigo are given in Fig. 1. Traditionally, indigo has been obtained as a tryptophan-derived natural product extracted from tropical plants. The synthesis of indigo has been important in the history of industrial chemistry through processes such as those developed by Baeyer [2–4], including the Baeyer–Drewson reaction [5], and later synthetic routes appropriate to large-scale production by Heumann [6] and by Pfeleger [7]. Other than its use as a textile dye, indigo and its derivatives have been used as components of organic semiconductors [8–10].

Nuclear magnetic resonance (NMR) spectroscopy has been used in combination with computational chemistry to study the interaction between indigo molecules and porous clays [11–16]. Complexation of indigo derivatives with model fibers has been the subject of investigation by NMR spectroscopy [17,18]. Chemical analyses of cultural heritage objects with NMR spectroscopy have

detected indigo [18,19]. NMR has been used to study the biodegradation of indigo dye and its derivatives [20,21], as well as the biosynthesis of indigo and indigo precursors in plants [22] and bacteria [23].

The ubiquity of indigo makes it an excellent model for the study of indole rings, which are found in such places as the amino acid tryptophan and its derivatives. To our knowledge, ¹³C chemical-shift tensors have not been reported for carbons in indole rings in any material containing such rings. Careful measurements of the ¹³C chemical-shift parameters of crystalline indigo are important in understanding the crystalline structure, the molecular structure, and the electronic state of the solid. An analysis of structural effects on the ¹³C NMR parameters, particularly the chemical shifts, of indigo may be of significance in the interpretation of NMR data on indole-containing materials like tryptophan.

The link between chemical shifts and crystal structure is established through quantum-chemical calculations such as those based on density-functional theory (DFT). In this work, experimental ¹³C chemical-shift tensors for all sites in indigo are assigned to their respective lattice sites by comparison to computed values based on a refined X-ray diffraction structure. We also perform calculations on the purine derivative hypoxanthine, and the purine nucleoside adenosine, both of which are

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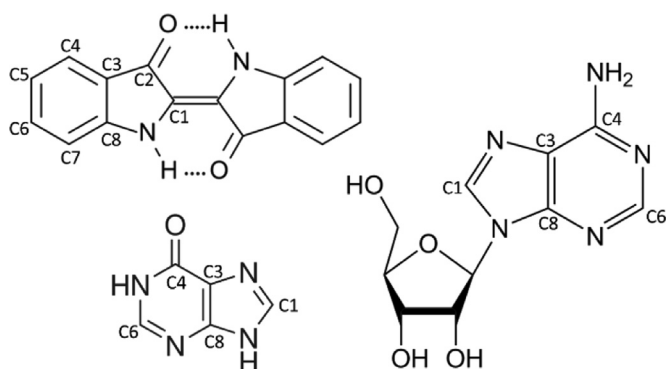


Fig. 1. Structures of indigo (upper left), hypoxanthine (lower left), and adenosine (right). The labeling schemes for the aromatic carbons sites are shown.

structurally similar to indigo (Fig. 1).

2. Experimental methods

Measurements of the ^{13}C chemical-shift tensors in indigo employed the recoupling-of-chemical-shift-anisotropy (ROCSA) sequence, a two-dimensional magic-angle-spinning (MAS) technique in which rotor-synchronized pulse sequences are used to obtain the recoupled powder patterns [26]. The ROCSA sequence is amenable to high-frequency MAS because the recoupling field is required to be only about four times the MAS frequency. The technique was originally developed for the study of isotopically labeled proteins; however, ROCSA and related sequences have been applied in the analysis of organic systems other than peptides [27–30]. High-power decoupling of ^1H spins used a ^1H 90° pulse of $2.97\ \mu\text{s}$ (SPINAL-64 at 100 kHz). The ROCSA sequence was rotor-synchronized with a MAS frequency of 10.0 kHz. 32 t_1 points, with 544 scans each, were collected with a 6.0 s recycle delay. The isotropic chemical shifts were externally referenced to tetramethylsilane (TMS) using the amide carbon in α -glycine (176.5 ppm) as a secondary reference [31].

Principal components were extracted from the recoupled chemical-shift powder patterns using a numerical simulation with wsolids [32], which identified the principal components of the chemical-shift tensors by searching for singularities in the derivative spectra. The numerical simulations introduced an expansion factor of 0.272, as suggested by Chan and Tycko [26]. The fitted three principal components of the chemical-shift tensor are also reported using Mason's convention [33], the average of the principal components δ_{ave} , the span Ω , and the skew κ , through the following relations:

$$\delta_{ave} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33}), \quad (1)$$

$$\Omega = \delta_{11} - \delta_{33}, \quad (2)$$

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega} \quad (3)$$

The isotropic chemical shift, δ_{iso} , was determined in a separate 1D CP/MAS experiment. Within experimental uncertainty, δ_{iso} and δ_{ave} are the same.

3. Computational methods

Predicted chemical-shift tensors were derived from DFT calculations on molecular clusters representing structures of the

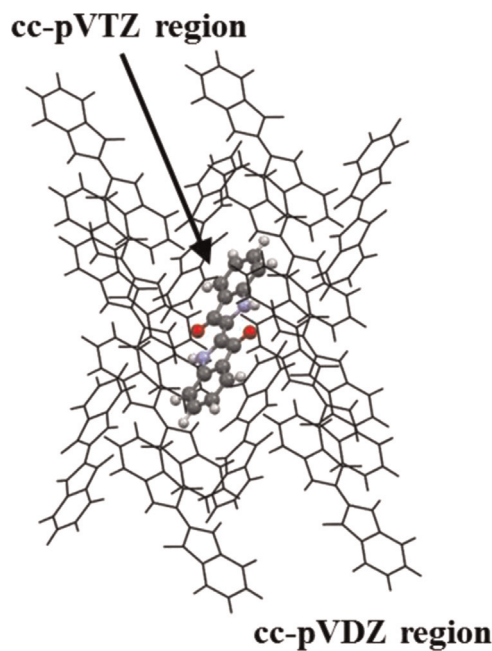


Fig. 2. Crystal packing diagram of indigo (polymorph A, $P2_1/c$ space group) showing the partition into two layers. The central molecule (cc-pVTZ basis set) is shown in ball-and-stick representation and the peripheral molecules (cc-pVDZ basis set) are shown in a wireframe representation. The peripheral molecules present in the model clusters were chosen according to the symmetry-adapted cluster method.

three solids [34,35]. The models of indigo, hypoxanthine, and adenosine were built from thirteen, eleven, and fifteen molecules, respectively (Fig. 2), to represent the local lattice structure around a single molecule, in accordance with the symmetry-adapted-cluster (SAC) model [34]. The cluster models were based on single-crystal diffraction parameters [36–38]. Before first-principles NMR parameters were calculated, the atomic coordinates were optimized, because diffraction-based structures generally give unrealistic hydrogen-atom positions [24,25,34]. Optimization was performed using the cluster model with the PBE functional [39] and the cc-pVDZ basis set [40]. For adenosine, the positions of only the hydrogen atoms were refined, as the structure was obtained from neutron diffraction. For indigo and hypoxanthine, the optimizations were performed in two steps where the first optimization allowed only the positions of hydrogen atoms to relax and the second optimization allowed the entire molecule to relax. The optimization procedure did not alter the structure of the molecule significantly, with changes in bond lengths limited to ranges found in previous studies [41]. Nonetheless, such small refinements to the structure are known to improve the quality of magnetic-shielding calculations in many cases [24,25,34,41,42].

Magnetic shielding was calculated with the gauge-including-atomic-orbital (GIAO) method [43–45] using the τ -dependent hybrid exchange-correlation (XC) functional TPSSh [46]. This model chemistry was selected to provide a rigorous description of electron correlation in the heteroatomic ring. The cluster was partitioned into two layers where the central molecule was given a locally-dense basis set (cc-pVTZ) and the peripheral molecules were given a less-dense basis set (cc-pVDZ). Previous work on organic systems has shown that treating the central molecule of a cluster with a triple- ζ basis set with additional polarization functions and the outlying molecules with a smaller double- ζ basis set yields reliable results [34]. Calculations were also performed on single refined molecules taken in isolation, as a means to examine intermolecular effects on the magnetic shielding.

Calculated magnetic-shielding values were converted to

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