



Rotational spectra and nuclear quadrupole coupling constants of 4- and 2-iodoimidazole

Graham A. Cooper^a, Cara J. Anderson^b, Chris Medcraft^c, Nicholas R. Walker^{b,*}

^a School of Chemistry, Cantock's Close, University of Bristol, Bristol BS8 1TS, United Kingdom

^b Chemistry – School of Natural and Environmental Sciences, Newcastle University, Bedson Building, Newcastle-upon-Tyne NE1 7RU, UK

^c Department of Physics and Astronomy, LaserLab, VU University, de Boelelaan 1081, 1081 HV Amsterdam, the Netherlands

ARTICLE INFO

Article history:

Received 13 August 2018

In revised form 12 September 2018

Accepted 13 September 2018

Available online 15 September 2018

Keywords:

Haloimidazole

Iodoimidazole

Nuclear quadrupole coupling

Hyperfine structure

ABSTRACT

Pure rotational spectra of 4-iodoimidazole and 2-iodoimidazole have been measured and assigned to determine rotational, centrifugal distortion and nuclear quadrupole coupling constants. Samples of each isomer were laser-vaporised from the surface of a solid target rod using the focussed pulse of a Nd:YAG laser prior to cooling via supersonic co-expansion with argon buffer gas. Microwave spectra were recorded by chirped-pulse Fourier transform microwave spectroscopy between 2.0 and 18.5 GHz. Inertial defects of 4-iodoimidazole and 2-iodoimidazole were determined to be 0.0906(1) a.m.u. Å² and 0.0814(2) a.m.u. Å² respectively, consistent with rigid planar geometries for these molecules. The evaluated nuclear quadrupole coupling constants of iodine atoms imply that approximately 1% of an electron is transferred from the iodine lone pair into aromatic π orbitals when iodine is substituted for a hydrogen atom in either the 4- or 2-position. Results are compared with data for other halogenated aromatic molecules and discussed in context of the extent of conjugation across the range.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Recent work by our group [1] explored the nuclear quadrupole coupling constants of 4-bromopyrazole and 4-iodopyrazole and concluded that each of these molecules may form halogen bonds of comparable strength to those formed by CH₃X and CF₃X (where X is Br or I). 4-Halopyrazoles are known to coordinate to a very wide range of protein-binding sites, probably as a result of excellent hydrogen- and halogen-bonding capabilities in solution and in the solid state. These molecules fulfil an important role in facilitating biochemical structure determination by X-ray crystallographic screening. Microwave spectroscopy allows the determination of molecular structure and hyperfine interactions [2,3]. The present work reports the first pure rotational spectra of 4-iodoimidazole and 2-iodoimidazole and has the aim of furthering knowledge of the hyperfine interactions of halogenated hetero-aromatics such that broader trends can be identified.

The imidazole ring is a common motif in biological chemistry, primarily because of its occurrence in the amino acid histidine and its multifunctional derivative, histamine. It has an important role in medicinal chemistry with special prominence in antifungal compounds [4–7]. The microwave spectrum of imidazole has been

studied extensively and the geometry of a hydrogen-bonded dimer of imidazole was recently reported [8–12]. Imidazole-containing compounds including histamine and histidine have also been studied by microwave spectroscopy [13–17]. Each of 4-iodoimidazole and 2-iodoimidazole has been used extensively as a synthetic reagent since their first syntheses in 1928 and 1977 respectively [18–22]. It will be shown that 4-iodoimidazole and 2-iodoimidazole can each be prepared for spectroscopic study by a method that combines laser vaporisation of the solid precursor with cooling by subsequent supersonic co-expansion with argon. The present work and the previous study of 4-halopyrazoles present an opportunity to draw useful comparisons between molecules that are similar in size and composition but different in respect of their detailed structure. Nuclear quadrupole coupling constants will be interpreted to quantify electron transfer from halogen atoms into aromatic systems. Results for 4-iodoimidazole, 2-iodoimidazole and similar molecules will be discussed with reference to standard interpretations of conjugation within aromatic systems.

2. Experimental methods

Prior to each experiment, an iodoimidazole sample was mixed with copper powder (Sigma-Aldrich, <75 μm, 99%) in an equimolar

* Corresponding author.

E-mail address: Nick.walker@ncl.ac.uk (N.R. Walker).

ratio and the resulting mixture compressed into a solid target rod of 5 mm in diameter. Isomerically-pure samples of each of 2-iodoimidazole (Sigma-Aldrich, 97%) and 4-iodoimidazole (Sigma-Aldrich^{CPR}) were purchased such that each could be studied in isolation of the other. Deuteration of 4-iodoimidazole was achieved at the pyrrolic nitrogen by proton exchange with D₂O (Sigma-Aldrich, 99.9 atom%) in the solution phase prior to drying of the solid sample of deuterated 4-iodoimidazole.

Experiments to record spectra were performed using a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer operating between 2.0 and 18.5 GHz which has been described in detail previously [1,23,24]. The rod target (prepared as described above) is continually rotated and translated to expose fresh material prior to each laser pulse. The focussed output of a Nd:YAG laser (wavelength of 532 nm, pulse duration of 10 ns, energy of 16 mJ pulse⁻¹) is used to vaporise material from the surface of the target. Vaporised material is entrained within a flow of argon gas (BOC Pureshield Argon) introduced from a pulsed valve at backing pressure of 7 bar. The gas flow and laser are synchronised at a repetition rate of 2 Hz. Molecules are cooled to a temperature approaching 3 K by supersonic co-expansion with argon prior to recording of their microwave spectra.

Coherent polarisation of the molecular ensemble is induced by a microwave pulse (of duration of 1 μs) that sweeps from low to high frequency. After each polarising pulse, the free induction decay (FID) of the coherent molecular polarisation is recorded over a period of 20 μs. The cycle of microwave pulse followed by FID detection is repeated eight times following each gas valve pulse. FIDs are digitised and recorded by a 100 GS/s oscilloscope, then co-added in the time domain prior to Fourier transformation using a high resolution window function to obtain peaks with estimated full-widths at half-maximum of ca. 100 kHz and estimated precision of peak frequency of ca. 10 kHz. Either the 2.0–8.0 GHz or the 7.0–18.5 GHz frequency range was probed during any single experiment. Some figures included herein were prepared by combining the data recorded across each of the above frequency ranges.

3. Computational methods

Density functional theory (DFT) was used to perform geometry optimisation calculations using the Gaussian09 software package

[25]. The B3LYP functional was used [26–29], in conjunction with the aug-cc-pVTZ basis set for all atoms except iodine [30–33], where the aug-cc-pVTZ-PP basis set was used with an electron core potential [34] obtained from the EMSL Basis Set Exchange [35,36]. Fig. 1 shows the results of these calculations including the magnitudes and orientations of the dipole moments of each isomer. In the case of 2-iodoimidazole, the highest projection of the dipole moment onto an inertial axis is onto the *b*-axis (3.30 D) such that *b*-type transitions were the most intense in the spectrum observed of this isomer. On the other hand, the dipole moment of 4-iodoimidazole is closer to being aligned with the *a*-axis (3.78 D), consistent with intense *a*-type transitions being observed for this molecule.

4. Results

4.1. Detection and assignment of microwave spectra

Spectra of 4-iodoimidazole were recorded in the 2.0–8.0 GHz and 7.0–18.5 GHz ranges, where data were averaged for 480 k and 420 k FIDs respectively. For the purposes of illustration, Fig. 2 displays the results of experiments performed across each of the above frequency ranges on the same plot. The presence of transitions assigned to (HCN)₂ [37,38], CH₃CN [39], CH₃CCCN [40,41], HC₃N [42–44], HC₅N [45], HC₇N [46], ICN [47], ICCCN [48], CH₂(CN)₂ [49,50], and vinyl cyanide (CH₂=CHCN) [51,52] confirms that some 4-iodoimidazole molecules disintegrate into smaller units following vaporisation from the surface of the rod target. Some features [53,54] were assigned to transitions of (H₂O)₂ and CH₃OH which result from trace impurities. Transitions of the species listed above did not impede assignment of the spectrum of 4-iodoimidazole and have been removed from Fig. 2. Over one thousand transitions of 4-iodoimidazole were distinguished from those of fragmentation products or impurities and unambiguously assigned. For the reasons discussed in Section 3, the spectrum of 4-iodoimidazole is dominated by strong *a*-type transitions with *b*-type transitions being observed with lower intensity within the spectrum. Two series of *a*-type, R-branch transitions are shown in detail in the inset of Fig. 2. Each panel displays transitions that share the same *J'* → *J''* assignment but which are distinct in respect of changes in either or both of *K*₋₁ or *K*₊₁.

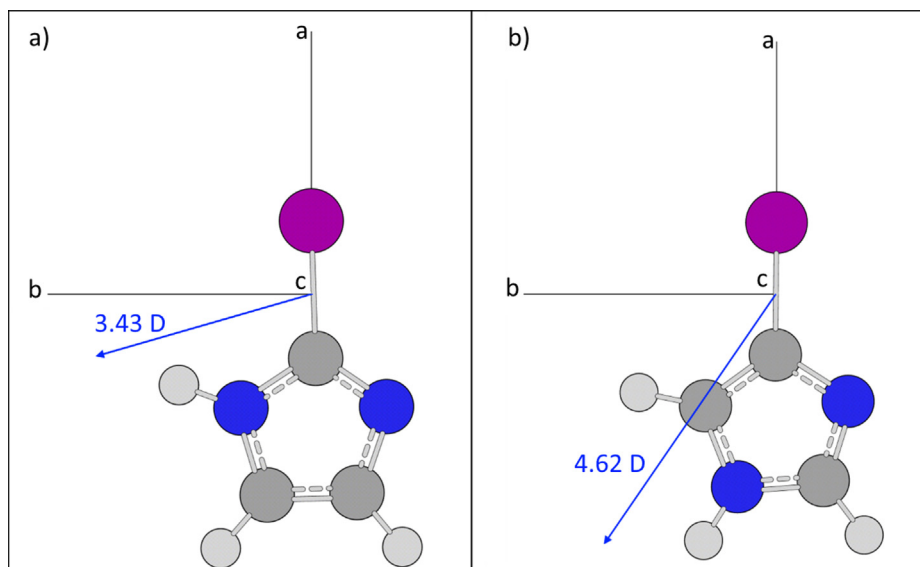


Fig. 1. Molecular geometries of (a) 2-iodoimidazole and (b) 4-iodoimidazole calculated using the B3LYP/aug-cc-pVTZ (aug-cc-pVTZ-PP with ECP for iodine) method with calculations performed in Gaussian 09. Inertial axes are indicated for each molecule with the *c*-axis oriented out of the page. Blue arrows indicate the orientation and relative magnitude of the dipole moment for each species.

Download English Version:

<https://daneshyari.com/en/article/11011469>

Download Persian Version:

<https://daneshyari.com/article/11011469>

[Daneshyari.com](https://daneshyari.com)