Rotational Spectra and Nuclear Quadrupole Coupling Constants of 4- and 2-Iodoimidazole

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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.

1. Introduction

Recent work by our group¹ 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 CH_3X and CF_3X (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 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 μ s) 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 μ s. The cycle of microwave pulse followed by FID detection is repeated eight times following each gas valve pulse with FIDs 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 to 8.0 GHz or the 7.0 to 18.5 GHz frequency ranges were 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 potential³⁴ obtained from the EMSL Basis Set Exchange.^{35, 36} Figure 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 480k and 420k FIDs respectively. For the purposes of illustration, Figure 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 Figure 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 Figure 2. Each panel displays transitions that share the same $J' \rightarrow J''$ assignment but which are distinct in respect of changes in either or both of K_{-1} or K_{+1} . Significant hyperfine splittings were observed and result from nuclear quadrupole coupling interactions of the iodine and nitrogen nuclei.

Proton transfer is known to occur between pyrrolic and pyridinic nitrogen atoms of imidazole in the solid state.^{55, 56} If the equivalent proton transfer were occurring within 4-iodoimidazole, whether in the solid phase or subsequent to vaporisation of the sample, a fraction of the sample would be expected to convert to 5-iodoimidazole and could be distinguished in the spectra if present in sufficiently high abundance. Transitions of 5-iodoimidazole were not observed for either 4-iodoimidazole or its deuterated isotopologue (where the deuterium is attached to the pyrrolic nitrogen) confirming that the described proton transfer is inefficient under the experimental conditions employed herein. The spectrum of the *N*-deuterated isotopologue (respectively recorded as the average of 630k FIDs between 2.0 and 8.0 GHz; and the average of 480k FIDs between 7.0 and 18.5 GHz) also revealed transitions of many deuterated fragmentation products including CH₂DCN,^{57, 58} CHD₂CN,^{58, 59} CD₃CN,³⁹ DC₃N,⁶⁰ DC₅N,⁴⁵ DC₇N,⁶¹ and both *cis*- and *trans*-CHD=CHCN.⁶² The observed isotopic shifts and hyperfine splittings confirm the assignment of transitions of both the *N*-deuterated and parent isotopologues (see Section 4.2).

Spectra of 2-iodoimidazole were recorded in the 2.0–8.0 and 7.0–18.5 GHz frequency ranges with each spectrum being an average of 480k FIDs. These data were combined to generate the spectrum displayed in Figure 3. The range of species generated by fragmentation of the 2-iodoimidazole sample was similar to that resulting from fragmentation of 4-iodoimidazole, but further included HC₉N⁶¹ and trace amounts of cyanoallene.^{63, 64} Some transitions assigned to fragmentation products and impurities have been subtracted from the data displayed in Figure 3. The most intense features are *b*-type transitions confirming the different relative orientations of the dipole moment and inertial axes in 4-iodoimidazole and 2-iodoimidazole. An intense Q-branch is apparent between 8 and 11 GHz with R-branch lines found throughout the frequency range surveyed. Examples of Q- and R-branch series are shown in the inset of Figure 3 and illustrate the

effects of hyperfine interactions. Each $J'_{K'-1, K'+1} \rightarrow J''_{K''-1, K''+1}$ transition is further split by the effects of nuclear quadrupole coupling of (iodine and nitrogen) nuclei having $I \geq 1$.

4.2 Determination of spectroscopic parameters

Preliminary assignments and fits of transitions were performed using Western's PGOPHER software package⁶⁵⁻⁶⁷ with final fits performed using SPFIT.⁶⁸ The Hamiltonian used was:

$$H = H_R - \frac{1}{6}\mathbf{Q}(\text{I}):\nabla\mathbf{E}(\text{I}) - \frac{1}{6}\mathbf{Q}(\text{N1}):\nabla\mathbf{E}(\text{N1}) - \frac{1}{6}\mathbf{Q}(\text{N3}):\nabla\mathbf{E}(\text{N3}), \quad (1)$$

where H_R is the energy operator (Watson's A -reduction) for a semi-rigid asymmetric rotor. The remaining terms represent nuclear quadrupole coupling interactions for nuclei having $I \geq 1$ where $\mathbf{Q}$ is the nuclear electric quadrupole moment dyadic and $\nabla\mathbf{E}$ is the dyadic of the electric field gradient at the nucleus under consideration. The iodine atom is represented by I, and the pyrrolic and pyridinic nitrogen atoms are represented by N1 and N3 respectively. This numbering (omitting "N2") is chosen to correspond with the standard numbering convention used when labelling atoms within a heteroaromatic ring. The resolution of the experiment was insufficient to record hyperfine effects introduced by hydrogen or deuterium nuclei.

Fitted values of rotational (A_0, B_0, C_0), centrifugal distortion ($\Delta_J, \Delta_{JK}, \Delta_K$ and δ_J) and nuclear quadrupole coupling constants ($\chi_{aa}(\text{I})$, $[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})]$, $|\chi_{ab}|(\text{I})$) for 4-iodoimidazole and 2-iodoimidazole are compared with those calculated using DFT in Tables 1 and 2 respectively. The high precision of the determined parameters reflect that many transitions were measured, of both a - and b -type; and that iodoimidazole is sufficiently heavy that many $J' \rightarrow J''$ transitions are

accessible within the spectrometer bandwidth. The agreement between the measured parameters and those calculated *ab initio* is good confirming high accuracy of the calculated geometry. It should be noted that the experimentally-determined rotational constants reflect the molecular structure in the $v=0$ vibrational state while the *ab initio* calculations yield an equilibrium geometry. There is good agreement between the experimental and *ab initio* calculated nuclear quadrupole coupling constants of the nitrogen atoms for both 4-iodoimidazole and 2-iodoimidazole. In the case of the former, this is an important verification that the observed spectrum should indeed be assigned to 4-iodoimidazole rather than 5-iodoimidazole. These two isomers would otherwise be very similar with respect to their rotational constants and parameters that describe nuclear quadrupole coupling of the iodine atom. Fortunately, the differing orientations with respect to the inertial axes of the various nitrogen atoms in these two isomers lead to values of $\chi_{aa}(N)$, $[\chi_{bb}(N)-\chi_{cc}(N)]$ and $|\chi_{ab}|(N)$ that are highly distinctive of the molecular carrier. Values of $\chi_{aa}(N1)$, $[\chi_{bb}(N1)-\chi_{cc}(N1)]$, $\chi_{aa}(N3)$ and $[\chi_{bb}(N3)-\chi_{cc}(N3)]$ calculated *ab initio* for 5-iodoimidazole are 1.224 MHz, 4.323 MHz, -2.181 MHz and -2.654 MHz respectively. These are a significantly worse fit to the experimental data than the equivalent results appropriate to 4-iodoimidazole presented in Table 1. The molecular carrier of the spectrum assigned herein as 4-iodoimidazole is therefore unambiguous.

4.3 Molecular geometries of 4- and 2-iodoimidazole

The primary aim of the present study was to determine the nuclear quadrupole coupling constants of the nitrogen and iodine atoms within isomers of iodoimidazole and compare these with others in halogenated, heteroaromatic molecules. However, the molecular geometries are

worthy of brief examination. Inertial defects calculated from the experimental data for 4-iodoimidazole and 2-iodoimidazole are 0.0906(1) a.m.u. Å² and 0.0814(2) a.m.u. Å² while both isomers are also confirmed to be near-prolate asymmetric tops ($\kappa = -0.978$ and -0.976 respectively). Small, positive inertial defects are consistent with values expected for rigid, planar molecules and similar to the results for pyrrole (C₄H₅N) and imidazole (C₃H₄N₂) of 0.01621(3) a.m.u. Å² and 0.0287(3) a.m.u. Å² respectively.^{10, 69}

The experimental data allow the accurate determination of a single structural parameter for 4-iodoimidazole which provides further confirmation that the spectrum of 4-iodoimidazole has been assigned to the correct molecular carrier. Kraitchman's equations⁷⁰ allow the coordinates of an atom to be determined provided that an isotopic substitution is available at that atom. The coordinates of the hydrogen atom attached to the pyrrolic nitrogen in 4-iodoimidazole were thus determined as (−3.8739(4), 1.156(1), 0) Å with uncertainties calculated to include Costain errors of $\delta a = 0.0015/|a|$ with the out-of-plane coordinate fixed at zero.^{2, 71} These results are consistent with coordinates of (−3.8952, 1.157, 0) Å calculated *ab initio*. Substitution coordinates of hydrogen atoms are generally not determined with very high accuracy using Kraitchman's equations due to assumptions within the model employed and a relatively large change in zero-point vibrational energy on deuteration.

4.4 Interpretation and analyses of nuclear quadrupole coupling interactions

In order to compare the nuclear quadrupole coupling constants determined for 2- and 4-iodoimidazole with those of similar molecules, it is first necessary to establish a common frame of reference. For each molecule, the quantities determined experimentally are the projections of

the nuclear quadrupole coupling tensor onto the a , b and c inertial axes. The inertial axes are differently oriented (with respect to the orientation of the imidazole ring) within the various molecules featured in Table 3. When comparing quantities across the range, it is convenient to analyse the components of the coupling tensor along the principal nuclear axes which are defined for each nucleus by the electron distribution in its vicinity. These components are comparable for atoms in similar environments in analogous molecules (e.g. the pyrrolic nitrogen in various imidazole derivatives), giving information about changes to the electron distribution between the molecules. The experimental data allow the nuclear quadrupole coupling tensors to be diagonalized and thence transformed from the inertial axis (a , b , c) framework onto a principal nuclear axis (x , y , z) framework using the QDIAG program available from the PROSPE database.⁷²

Each of 4- and 2-iodoimidazole is planar requiring that the out-of-plane c -axis is parallel to one of the principal nuclear axes. The a - and b -axes are rotated through an angle of $\phi(X)$, where X is the nucleus on which the axes are centred. The labelling system used for the nitrogen atoms was chosen to be consistent with that used by Christen *et al.* in their study of imidazole.¹⁰ For the pyrrolic nitrogen atom (N1), the z -axis is out of the molecular plane, and ϕ is the angle between the a - and x -axes for 2-iodoimidazole, and between the a - and y -axes for 4-iodoimidazole. For the pyridinic nitrogen (N3), the y -axis is perpendicular to the plane of the molecule, and ϕ is the angle between the a - and x -axes in both cases. The z -axis for the iodine atom points along the direction of the C-I bond, with the y -axis out of the plane of the molecule and the x -axis parallel to the ring. In order to determine the angle ϕ , the absolute value of χ_{ab} must be determined; in most cases, this was successfully fitted from the spectrum. However, with respect to the pyrrolic nitrogen of 4-iodoimidazole, this constant could not be resolved due to its small magnitude and the *ab initio*

value was used instead. Illustrations to graphically represent the axis transformations are provided as Supplementary Data.

5. Discussion

Nuclear quadrupole coupling tensors for the isomers of iodoimidazole studied herein are compared with results for a range of other species in Table 3. It is interesting to analyse the evaluated nuclear quadrupole coupling constants to determine the extent of electron transfer into aromatic π orbitals which can be evaluated using the parameter δ (also called the Goldstein parameter) which is calculated from nuclear quadrupole coupling constants of the halogen atom as follows;

$$\delta = \frac{2}{3} \frac{\chi_{xx} - \chi_{yy}}{eQq_{n10}},$$

where eQq_{n10} is the contribution of a single p -electron to nuclear quadrupole coupling, and is equal to +2292.712(20) MHz for iodine.^{2, 73, 74} In reasonable approximation, the value of δ quantifies the difference in electron density between the p_x and p_y orbitals. The electron lone pair in the p_y orbital on the iodine atom of either 2- or 4-iodoimidazole is able to donate electron density into aromatic π orbitals of the imidazole sub-unit. Given that the p_x orbital is unable to overlap with the orbitals in the ring and is therefore nominally occupied by two electrons, δ is assumed equal to the deficit in electron density in the p_y orbital relative to occupation by a full lone pair. This can be understood as the double bond character in the C–I bond, or, equivalently, the electron density donated into aromatic π orbitals by the iodine atom, expressed as percentage of an electron. Tables 4 and 5

compare the values of δ found for brominated and iodinated compounds containing six-membered aromatic rings for which microwave spectral data are available. The broad trend can be explained with reference to the varying degrees of conjugation in these molecules.

The bromine or iodine atom of C_6H_5X , where X is Br or I, is able to donate ca. 2.5% or 1.9% respectively of an electron into the benzene ring;^{75,76} similar values are found for *para*-halotoluene.⁷⁷ These values are somewhat lower than those for vinyl halides where simple conjugation between a bromine or iodine atom and a C=C double bond results in δ values of 3.6(2)% and 2.91(4)% respectively.⁷⁸ The implication is that donation of the lone pair by the halogen atom actively disrupts the aromaticity and hence the stability of a benzene ring, disfavouring the conjugation. While examining conjugation in different halogenated aromatic molecules, it is useful to model the conjugated structure as the sum of a series of resonance canonicals which contribute to the overall resonance. Effects on the stability of a canonical will change its contribution to the overall sum. The value of δ can be thought of as the sum of the contributions to the overall resonance of canonicals in which the halogen lone pair is delocalised around the ring. A similar model has previously been used in the analysis of nuclear quadrupolar coupling constants of other halogenated heteroatomic rings.^{79,80,81,82} It has previously been noted that in heteroaromatic rings, δ can be increased when resonance canonicals exist in which the negative charge from the halogen lone pair can be located on an electronegative atom, such as in 2- and 4-halopyridine and 2-bromopyrimidine, but that when this is not possible, such as in 3-halopyridine, the value of δ is similar to that of halobenzene.

It has previously been observed that thiophenes and furans are poorer acceptors of electron density from halogen atoms⁸³ and have lower values of δ than six-membered rings of similar composition. The values of δ are compared for a range of compounds containing five-membered

rings in Table 5. It is apparent that these molecules are generally less stabilised by donation of a halogen lone pair than each of the six-membered rings featured in Table 4. A negative value is calculated for 4-iodopyrazole confirming that assumptions in the model employed cause δ to be calculated less accurately than implied by the uncertainties given in parentheses (which are calculated from standard deviations in the experimentally-determined parameters). The resonance canonicals for 2- and 4-iodoimidazole are shown in Figure 4. For the resonance forms in which the halogen lone pair is donated into the ring, the heteroatom lone pair is restricted in its ability to delocalise effectively around the ring. There are few canonicals where both the halogen and heteroatom lone pairs are delocalised. There is one such canonical form (Figure 4a) for 2-substituted rings but the implication of adjacent negative charges is that this form will not contribute significantly to the overall resonance; figure 4b shows that there are two canonical structures that allow delocalisation of the heteroatom lone pair in 4-iodoimidazole but only one of these will contribute significantly given the presence of adjacent negative charges in the other. This suggests a large disruption of aromaticity, disfavouring the conjugation.

The degree of conjugation in the iodoimidazole isomers featured herein is slightly higher than that in other five-membered, iodinated rings studied previously (Table 5). The additional heteroatom in iodoimidazoles, when compared with iodothiophenes, allows that canonicals of the former can be drawn with electron density delocalised onto an electronegative heteroatom. The result is that δ for each iodoimidazole isomer is higher than for 2- or 3- iodothiophene. This effect is analogous to that which leads 2- and 4-halopyridines to have higher values of δ than does halobenzene. The pyridinic nitrogen is located adjacent to a pyrrolic nitrogen in 4-halopyrazole¹ such that any resonance canonical that locates the negative charge on the nitrogen atom carries

charges on adjacent atoms which are unfavourable to the overall stability. 4-Halopyrazoles are consequently associated with very low degrees of conjugation.

Components of the nuclear quadrupole coupling tensors determined for the nitrogen atoms can also be rationalised with a conceptual model that uses resonance canonicals. There are high uncertainties in the determined values of $\chi_{xx}(\text{N1})$, $\chi_{yy}(\text{N1})$, $\chi_{xx}(\text{N3})$ and $\chi_{zz}(\text{N3})$ so it is not meaningful to compare these quantities with parameters determined for other molecules. However, the out-of-plane components of the nuclear quadrupole coupling tensors (χ_{zz} for the pyrrolic nitrogen atom (N1) and χ_{yy} for the pyridinic nitrogen atom (N3)) retain a high degree of precision. The value of $\chi_{yy}(\text{N3})$ is lower in each of the iodoimidazoles studied here than in unhalogenated imidazole. The extended Townes-Dailey method described by Novick confirms that a p -orbital of nitrogen makes the largest contribution to $\chi_{yy}(\text{N3})$ with further contributions from σ -orbitals.³ The magnitude of this effect is equivalent to a change of roughly 2% of an electron in the occupation of the aromatic π -orbitals relative to the sp^2 σ -orbitals.

Constructing simple resonance canonicals, electron density transferred from the iodine atom can delocalise onto the pyridinic nitrogen atom by a direct mechanism in 2-iodoimidazole; or by an indirect mechanism, by increasing the contribution of canonicals such as the third in Figure 4b which feature delocalisation of the pyrrolic nitrogen lone pair onto the pyridinic nitrogen atom, in 4-iodoimidazole. The values of $\chi_{yy}(\text{N3})$, which are lower for each of 2-iodoimidazole and 4-iodoimidazole than for $\chi_{yy}(\text{N3})$ of imidazole, are therefore explained by an increase in π -electron density at the pyridinic nitrogen atom on the attachment of iodine to imidazole. Examining the evaluated components of the nuclear quadrupole coupling tensor at the pyrrolic nitrogen atom of each molecule, it is apparent that $\chi_{zz}(\text{N1})$ of 2-iodoimidazole is more negative than the same parameter of either 4-iodoimidazole or imidazole. Consistent with this observation, resonance

canonicals can be constructed for each of 4-iodoimidazole and imidazole in which the pyrrolic nitrogen lone pair is favourably delocalised onto the pyridinic nitrogen atom. However, for canonicals which feature the iodine lone pair delocalised into the ring, which contribute to about 1% of the overall resonance (as shown above), there are no stable structures wherein the pyrrolic nitrogen lone pair is delocalised around the ring, as shown in Figure 4a. This suggests that the increase in π -electron density shown by $\chi_{zz}(\text{N1})$ is due to the lone pair becoming increasingly localised on the nitrogen atom.

While comparing imidazole with each of 2-iodoimidazole and 4-iodoimidazole, it should finally be noted that replacing a hydrogen atom with a more electronegative iodine atom will anyway tend to reduce $\chi_{yy}(\text{N3})$ and $\chi_{zz}(\text{N1})$ through withdrawal of electrons from σ -bonds within the ring. This effect will be more significant in 2-iodoimidazole than in 4-iodoimidazole given that the iodine atom is positioned closer to the pyrrolic and pyridinic nitrogen atoms in the former. Observed changes in π -electron density on the nitrogen atoms are thus broadly consistent with expectations derived from the standard model of resonance in aromatic systems. The attachment of iodine to imidazole (whether in the 2- or 4- position) is associated with a greater increase in conjugation than that seen following the attachment of bromine or iodine to pyrazole.

6. Conclusions

The pure rotational spectra of two isomers of iodoimidazole have been recorded for the first time. Rotational, centrifugal distortion and nuclear quadrupole coupling constants have been determined. The evaluated nuclear quadrupole coupling constants are consistent with $\delta(\text{C-I})$ of 1% where $\delta(\text{C-I})$ approximates the electron density donated into aromatic π orbitals by the iodine

atom, expressed as percentage of an electron. The density of electron transfer from the halogen atom into the ring is thus slightly greater than observed during spectroscopic studies of other 5-membered heteroaromatics but is significantly less than typically seen in 6-membered heteroaromatics.

Acknowledgements

The authors thank the European Research Council for postdoctoral fellowships awarded to G.A.C. and C.M. and for project funding (Grant No. CPFTMW-307000). We are grateful to Dr. Alistair Henderson of NewChem Technologies for preparation of the deuterated samples.

Appendix A. Supplementary Material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at <http://xxxxxxxxxxxxxxxxxxxxxx>. The supplementary data includes the atom coordinates and molecular geometries calculated ab initio; illustrations to represent the axis transformations described in Section 4.

Figure 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.

Figure 2. Microwave spectrum of 4-iodoimidazole recorded in the 2.0 – 18.5 GHz region. The experimental data are displayed as positive-going peaks with simulations generated from the experimentally-determined parameters displayed as negative-going peaks. Two features from the main R-branch are shown in detail. Peaks labelled with asterisks assign to $J' \rightarrow J''$ transitions of 4-iodoimidazole other than that indicated by the label.

Figure 3. Microwave spectrum of 2-iodoimidazole recorded in the 2.0 – 18.5 GHz region. The experimental data are displayed as positive-going peaks with simulations generated from the experimentally-determined parameters displayed as negative-going peaks. One feature from each of the main Q- and R-branches is shown in detail. Peaks labelled with asterisks assign to $J' \rightarrow J''$ transitions of 2-iodoimidazole other than that indicated by the label.

Figure 4. Resonance structures for the delocalisation of iodine lone pair electrons in a) 2-iodoimidazole and b) 4-iodoimidazole.

Table 1. Ground-state spectroscopic constants of 4-iodoimidazole and its N-deuterated isotopologue determined experimentally and computationally.

Spectroscopic Constant	C ₃ N ₂ H ₃ I		C ₃ N ₂ H ₂ DI	
	Expt. ^a	Comp. ^b	Expt.	Comp.
A_0 / MHz	9431.8375(10)	9534.0170	9209.3525(15)	9306.2964
B_0 / MHz	988.45251(12)	975.73482	960.15903(16)	947.86153
C_0 / MHz	894.54595(11)	885.14673	869.38089(13)	860.24425
Δ_J / kHz	0.03849(74)	0.03590	0.02772(75)	0.03324
Δ_{JK} / kHz	0.5881(97)	0.5600	0.5298(73)	0.5176
Δ_K / kHz	[2.87]c	2.87	4.16(48)	2.80
δ_J / Hz	3.71(15)	3.53	2.59(29)	3.25
δ_K / kHz	[0.39]c	0.39	[0.36]c	0.36
χ_{aa} (I) / MHz	−1980.759(10)	—	−1980.917(13)	—
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})]$ / MHz	37.339(14)	—	37.662(17)	—
$ \chi_{ab} $ (I) / MHz	37.79(14)	—	9.17(54)	—
χ_{aa} (N1) / MHz	1.371(13)	1.409	1.378(17)	1.410
$[\chi_{bb}(\text{N1})-\chi_{cc}(\text{N1})]$ / MHz	3.674(11)	3.705	3.698(13)	3.704
$ \chi_{ab} $ (N1) / MHz	[−0.060]c	−0.060	[−0.057]c	−0.057
χ_{aa} (N3) / MHz	1.159(13)	1.201	1.109(17)	1.159
$[\chi_{bb}(\text{N3})-\chi_{cc}(\text{N3})]$ / MHz	−5.169(11)	−5.745	−5.110(13)	−5.703
$ \chi_{ab} $ (N3) / MHz	1.71(37)	2.22	2.31(92)	2.27
N^d	1092	—	912	—
$\sigma_{r.m.s.}^e$ / kHz	16.7	—	17.0	—

^a. Numbers in brackets are one standard deviation in units of the last significant figure.

^b. Calculated using Gaussian 09 using B3LYP functional and aug-cc-pVTZ basis set (aug-cc-pVTZ-PP with ECP for iodine)

^c Fixed at *ab initio* value

^d. Number of transitions included in the fit.

^e. Root mean square deviation of the fit.

Table 2. Ground-state spectroscopic constants of 2-iodoimidazole determined experimentally and computationally (numbers in brackets indicate standard deviations in units of last digit).

Spectroscopic Constant	Expt. ^a	Comp. ^b
A_0 / MHz	9357.00567(56)	9460.47633
B_0 / MHz	1017.73058(21)	1003.75611
C_0 / MHz	917.75860(22)	907.47327
Δ_J / kHz	0.03655(77)	0.03841
Δ_{JK} / kHz	0.560(11)	0.576
Δ_K / kHz	2.43(10)	2.56
δ_J / Hz	3.664(68)	3.905
δ_K / kHz	0.223(92)	0.409
χ_{aa} (I) / MHz	-2026.5535(80)	—
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})]$ / MHz	4.3916(84)	—
$ \chi_{ab} $ (I) / MHz	93.55(15)	—
χ_{aa} (N1) / MHz	1.3270(73)	1.3839
$[\chi_{bb}(\text{N1})-\chi_{cc}(\text{N1})]$ / MHz	4.1848(60)	4.3573
$ \chi_{ab} $ (N1) / MHz	0.39(26)	0.13
χ_{aa} (N3) / MHz	1.5506(73)	1.6344
$[\chi_{bb}(\text{N3})-\chi_{cc}(\text{N3})]$ / MHz	-5.5700(60)	-6.1574
$ \chi_{ab} $ (N3) / MHz	1.89(24)	1.69
N^c	1219	—
$\sigma_{r.m.s.}$ / kHz ^d	14.1	—

^a. Numbers in brackets are one standard deviation in units of the last significant figure.

^b. Calculated using Gaussian 09 using B3LYP functional and aug-cc-pVTZ basis set (aug-cc-pVTZ-PP with ECP for iodine).

^c. Number of transitions included in the fit.

^d. Root mean square deviation of the fit.

Table 3. Nuclear quadrupole coupling constants of iodoimidazole isomers in the principal quadrupole axis system with angle of rotation from inertial axes (numbers in brackets indicate standard deviations in units of last digit).

Coupling Tensor Component	2-Iodoimidazole	4-Iodoimidazole	Imidazole ^a
χ_{zz} (I) / MHz	−2029.413(12)	−1981.236(11)	—
χ_{yy} (I) / MHz	996.0809(58)	971.7099(88)	—
χ_{xx} (I) / MHz	1033.333(11)	1009.5263(95)	—
ϕ (I) ^b / °	−1.7512(28)	0.7240(27)	—
χ_{zz} (N1) / MHz	−2.7561(47)	−2.5223(86)	−2.524(12)
χ_{yy} (N1) / MHz	1.77(26)	1.386(23)	1.633(58)
χ_{xx} (N1) / MHz	0.98(26)	1.136(21)	0.890(52)
ϕ (N1) ^b / °	41.3(25)	−14.4(81) ^c	−43.7
χ_{zz} (N3) / MHz	−4.18(14)	−3.76(23)	−4.113(34)
χ_{yy} (N3) / MHz	2.0097(47)	2.0051(86)	2.278(24)
χ_{xx} (N3) / MHz	2.17(14)	1.75(23)	1.835(23)
ϕ (N3) ^b / °	−18.2(17)	19.2(30)	−9.4

^a Results from Christen *et al.*¹⁰

^b Signs of ϕ (I), ϕ (N1) and ϕ (N3) are not available from the experimental results but were deduced by comparison with the molecular geometries calculated *ab initio*. A positive sign of ϕ indicates anticlockwise rotation of the inertial axes into the principal nuclear axes when the molecule is drawn such that the numbering of atoms proceeds anticlockwise. See Supplementary Figures 2-4 for illustrations.

^c Determined from χ_{ab} value calculated *ab initio*.

Table 4. Values of $\delta(\text{C-X})$ calculated from ^{79}Br and ^{127}I nuclear quadrupole coupling constants (numbers in brackets indicate standard deviations in units of last digit) for compounds containing six-membered aromatic rings. The structures of the 2-substituted isomers of halopyridine are shown.

Structure	Molecule	$\delta(\text{C-Br})$	$\delta(\text{C-I})$
<i>p</i> -Halotoluene ^b	2.279(2)%	1.6976(7)%
Halobenzene ^c	2.51297(4)%	1.9073(2)%
2-Halopyridine ^d	4.8(1)%	4.4(1)%
	3-Halopyridine ^e	2.2(2)%	1.7142(1)%
	4-Halopyridine ^d	3.8(2)%	2.3(2)%
2-Halopyrimidine ^f	8.2(6)%	—

^a The structures illustrated for halopyridine and halopyrimidine are those of the 2-substituted isomers.

^b Shubert *et al.*⁷⁷

^c Dorosh *et al.* (Br)⁷⁵ and Neill *et al.* (I)⁷⁶

^d Caminati & Forti^{79, 80}

^e Doraiswamy & Sharma (Br)⁸¹ and Gaster *et al.* (I)⁸⁴

^f Chen *et al.*⁸²

Table 5. Values of $\delta(\text{C-X})$ calculated from ^{79}Br and ^{127}I nuclear quadrupole coupling constants (numbers in brackets indicate standard deviations in units of last digit) for compounds containing five-membered aromatic rings.

Structure	Molecule	$\delta(\text{C-Br})$	$\delta(\text{C-I})$
2-Halothiophene ^b	0.4(2)%	0.35(7)%
	3-Halothiophene ^c	1.536(6)%	0.06(8)%
2-Halofuran ^d	1.2%	-
	3-Halofuran ^d	0.7%	-
4-Halopyrazole ^e	0.179(3)%	-0.3764(2)% ^f
2-Haloimidazole ^g	—	1.0832(2)%
4-Haloimidazole ^g	—	1.0996(3)%

^a. The structures illustrated for halothiophene and halofuran are those of the 2-substituted isomers

^b Mjöberg *et al.* (Br)^{85, 86} and Niide *et al.* (I)⁸⁷

^c Hübner *et al.* (Br)⁸³ and Niide *et al.* (I)⁸⁸

^d Hübner *et al.* and references therein⁸³

^e. Cooper *et al.*¹

^f. The negative sign of this parameter results from limitations of the model employed. Uncertainties that connect with model assumptions are evidently greater than implied by the standard deviation of the experimental data (used to calculate the figure given in brackets).

^g. This work.

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