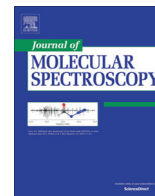




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A study of the conformational isomerism of 1-iodobutane by high resolution rotational spectroscopy

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ABSTRACT

The first microwave study of 1-iodobutane, performed by Steinmetz et al. in 1977, led to the determination of the $B + C$ parameter for the anti-anti- and gauche-anti-conformers. Nearly 40 years later, this reinvestigation of 1-iodobutane, by high-resolution microwave spectroscopy, led to the determination of rotational constants, centrifugal distortion constants, nuclear quadrupole coupling constants (NQCCs), and nuclear-spin rotation constants belonging to both of the two previously mentioned conformers, in addition to the gauche-gauche-conformer, which was observed in this frequency regime for the first time. Comparisons between the three conformers of 1-iodobutane and other iodo- and bromoalkanes are made, specifically through an analysis of the nuclear quadrupole coupling constants belonging to the iodine and bromine atoms in the respective chemical environments.

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1. Introduction

It has been commonly accepted that the electric field gradient of a nucleus remains unchanged in most simple molecules even as they take on different conformations or as they form van der Waals complexes. A field gradient caused by a charge is proportional to $1/r^3$, where r is the distance from the charge to the nucleus. It is presented by Townes and Dailey [1] and outlined in Gordy and Cook [2], how the field gradient found at a nucleus can be assumed to have been produced by the bonds made by that atom. This analysis was originally for bonding p orbitals, but was later extended to include hybrid orbital contributions by Novick in 2011 [3]. This unchanging nature of a field gradient was recently used to correctly determine the structure of HOD-N₂O [4].

The assumption that the field gradient will remain unchanged upon the formation of a complex, conformational change, or isotopic substitution has, of course, exceptions. Choosing N₂O and the complexes it forms as an example [5–16], it was shown repeatedly that there are subtle changes in the electronic environment of near atoms as complexes are formed. For HCCH \cdots N₂O [5,7], as

studied by Leung and coworkers, it was shown that in forming the complex there is a significant change in the electric field gradient of the central nitrogen, while the field gradient at terminal nitrogen remained unchanged. Through molecular multipole analysis, the authors showed that this change is caused by redistribution of electrons about the central nitrogen.

To observe changes in electronic structure from perturbations smaller in magnitude than those observed upon forming a van der Waals complex, such as conformational changes, a more sensitive nucleus is required to act as a probe for this change. Iodine, with its large nuclear electric quadrupole moment, $-69.6(12) fm^2$ [17] for ¹²⁷I, compared to the ¹⁴N value of $2.001(10) fm^2$ [18], makes the observed nuclear quadrupole coupling constants significantly more sensitive to small changes in electron distribution near the iodine nucleus. For example, in a recent study of iodobenzene and the Ne-iodobenzene complex [19], there is a <0.3% change in the iodine NQCC upon forming the complex with neon. We have recently reported a small, but significant, change in electronic structure from carbon-13 isotopic substitution in 2-iodobutane [20].

Continuing a series of studies on the subtle changes in electric structure determined by changes in nuclear quadrupole coupling constants, we report here on the conformational effects on a terminal iodine group in a hydrocarbon chain.

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2. Experimental

The high-resolution rotational spectrum of 1-iodobutane was measured from 7 to 13 GHz with a chirped-pulse Fourier transform microwave (FTMW) spectrometer. Detailed specifications of this spectrometer, which is based on the design of Pate and coworkers [21], have been presented previously [22]. In short, a chosen microwave center frequency, ν , and a 6 μ s linear frequency sweep are mixed from DC to 1 GHz. The resulting radiation, $\nu \pm 1$ GHz, is broadcast directly into a vacuum chamber through a microwave horn antenna. This transmitted radiation then induces a polarization in the coincident molecular beam. A second microwave horn antenna collects the free induction decay (FID) after a 1 μ s delay. With the aid of a Tektronix TDS6124C Digital Oscilloscope, the FID is fast Fourier transformed and directly digitized. A total of 800,000 points, over a time of 20 μ s, are collected from the FID. On average, the molecular rotational transitions have a line width of 80 kHz with an uncertainty of |8| kHz in the center frequency.

The sample was acquired from Sigma-Aldrich® ($\geq 99\%$ C₄H₉I). Further purification was not necessary. The sample (bp 130–131 °C) was contained in a glass U-form tube at room temperature and one atmosphere of dry argon (99.999%, Airgas®) was bubbled directly through the liquid. The final mixture of carrier gas and sample was pulsed through a solenoid valve into the chamber, held at an ambient pressure of 10^{-6} Torr, allowing the molecules to undergo supersonic expansion, where the molecules become rotationally cold (1–2 K).

2.1. Quantum chemical calculations

Using a 321G* basis set at the APFD level of theory, a coordinate scan of the C–C–C and C–C–I dihedral angles was performed, in order to identify the most probable ground state molecular geometries. Three of the lowest energy structures from the scan were optimized at the MP2 level of theory. A 6311G* basis set was imported from the EMSL Basis Set Library [23,24] specifically chosen to handle the iodine atom, while a 6311G++(2d,2p) basis set was used for the remaining carbon and hydrogen atoms. All calculations were performed with the GAUSSIAN09 Revision D suite [25]. Results from the *ab initio* optimizations are presented in Table 1. Illustrations of the corresponding structures can be found in Fig. 1. More on predicting the NQCCs will be discussed in the subsequent sections.

2.2. Spectral assignments

All three of the lowest energy conformers obtained from the *ab initio* investigation were successfully assigned from the rotational spectrum collected in the frequency range of 7–13 GHz. A 70 MHz portion of this spectrum is shown in Fig. 2. The three broadband assignments were accomplished with the help of both the AABS package [26] and Pickett's programs, SPFIT/SPCAT [27,28]. The final rotational constants, centrifugal distortion constants, NQCCs, and nuclear spin-rotation constants for each conformer can be found in Table 2. Although there is a large discrepancy between the *ab initio* and experimental NQC tensors belonging to the iodine atom in each of the three species, there is at most only a 7% difference between the rotational constants obtained from the *ab initio* study and those determined experimentally. This seems to suggest that the actual geometries of the three conformers present in the molecular beam are quite similar to those that were calculated, whereas the only agreement in the NQCCs was in the trend of their respective magnitudes.

The poor *ab initio* NQCC values made the first assignment, of the ga-conformer, quite challenging. In order to make the assignment

Table 1

Rotational constants and NQCCs for three conformers of 1-iodobutane as determined from *ab initio* optimization at the MP2 level of theory.

Parameters	gg	ga	aa
A (MHz)	6033	7388	15,123
B (MHz)	1077	937	706
C (MHz)	1013	867	686
$^{127}\chi_{aa}$ (MHz)	−397	−274	−682
$^{127}\chi_{bb}$ (MHz)	74	−167	223
$^{127}\chi_{cc}$ (MHz)	322	441	459
$^{127}\chi_{ab}$ (MHz)	−570	−670	−511
$^{127}\chi_{ac}$ (MHz)	−330	−109	0 ^b
$^{127}\chi_{bc}$ (MHz)	−226	−104	0
ΔE^a (cm ^{−1})	385	160	0

^a Relative energies from MP2 optimizations.

^b χ_{ac} and χ_{bc} are zero by symmetry.

process more efficient and less tedious, alternate methods of prediction were employed. Taking advantage of the fact that changes in the geometry of the butane chain have a very small effect on the electric field gradient at the iodine nucleus (more on this to come later), the experimental NQC tensor of iodine in the ga-conformer was used to make predictions of the NQC tensors of iodine in both of the two remaining unassigned conformers. This predictive process was simply an exercise in tensor rotation. Using QDIAG [29], the *ab initio* tensors of the two unassigned conformers were diagonalized. In doing this, the rotation matrices, specific to the *ab initio* geometries of these species, were obtained. Then, these respective rotation matrices were used to transform the experimental NQC tensor of the ga-conformer into the inertial axes systems of the gg- and aa-conformers. The resulting hybrid tensors were based on *ab initio* geometries, specific to the unassigned conformers, and experimental NQCCs, belonging to the already assigned ga-conformer. To best illustrate the power of this method, the NQC tensor predictions of the aa-conformer will be used as an example. Eq. (1) contains the *ab initio* tensor belonging to the aa-conformer, Eq. (2) contains the hybrid tensor, and Eq. (3) contains the experimental tensor based only on rotational transitions belonging to the aa-conformer. It is perhaps immediately obvious that the hybrid tensor, again based on the *ab initio* geometry of the aa-conformer and the rotated experimental NQC tensor of the ga-conformer, offers a much better prediction than the purely *ab initio* tensor. To further highlight this point, Fig. 3 presents small portions of the rotational spectra corresponding to these respective tensors. It is worth noting here that the similarities between the NQC tensors of iodine in various iodoalkanes, such as iodoethane, t-1-iodopropane, and aa-1-iodobutane, which will be discussed later, suggest that this method can be applied to quite a large range of problems. This method, based on straightforward linear algebra, can lead to very accurate predictions without the need for expensive computations.

It should be noted there are other methods used to make accurate predictions of NQCCs, especially for species with large quadrupoles, as shown by Professor W. C. Bailey [30]. Post-analysis, we received calculations from Professor Bailey, which can be found in Table 3 alongside the predictions from our hybrid approach [31,32]. These calculations involve the calibration of a specific combination of level of theory and basis set, by linear regression, of the calculated electric field gradients versus the experimental NQCCs of a selected group of molecules. Once calibrated, the specific combination of level of theory and basis set can be applied to other systems. Upon comparison of Tables 2 and 3, it can be seen that this method yields excellent results. The differences between the hybrid method explained previously and these calculations are small. Although it is clear that these calculations are quite accurate,

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