Microwave spectrum, structure, tautomeric, and conformational composition of 4-vinylimidazole

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(Received 30 April 2012; accepted 19 July 2012; published online 8 August 2012)

The microwave spectra of the two conformers each, of the 1H and 3H tautomers of 4-vinylimidazole, have been measured in the 48–72 GHz spectral region. The 4-vinylimidazole was generated in situ by the facile decarboxylation of urocanic acid at its vaporization temperature of 220 °C. The recognition of this reaction casts doubt on the reliability of a previous published spectroscopic study apparently mistakenly thought to be of uncontaminated vaporized urocanic acid, a natural product of great interest in skin cancer etiology. Quantum chemical theoretical predictions of the structures of each of ten possible conformers/tautomers of urocanic acid and four of 4-vinylimidazole were performed at the ab initio MP2/cc-pVTZ level, with vibrational predictions at the B3LYP/cc-pVTZ and M062X/cc-pVTZ levels. The predicted values of rotational constants for all the urocanic acid species were found to be quite inconsistent with those of the four observed spectra. For the 4-vinylimidazole isomers, the calculated relative energies suggested that all four species would have substantial equilibrium mole fractions at 220 °C. The isomers were identified by matching the observed and calculated rotational constants. The resulting assignment was found to be consistent with the predicted and observed 14N nuclear quadrupole hyperfine multiplet patterns for a suitable rotational transition, and with the observed versus empirically calculated inertial defects. With one exception, the predicted structures were found to be planar. Resembling the case of 1-vinylimidazole, where one conformer is nonplanar, one isomer of 4-vinylimidazole was found to be quasiplanar. This seems to belong to a class of spontaneous symmetry-breaking observed in the molecular structure of some otherwise planar vinyl aromatic compounds. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4742061]

I. INTRODUCTION

Despite the importance of the imidazole heterocycle moiety in numerous key compounds in biology, including an essential amino acid, histidine, 2-amino-3-(1H-imidazol-4-yl)propanoic acid, and the ubiquitous multifunctional agent histamine, 2-(1H-imidazol-4-yl)ethanamine, there have been only a few experimental structural studies of isolated molecules of imidazole and its derivatives. Gas phase microwave spectroscopy has been reported for unsubstituted imidazole1 and the substituted variants histamine2 and 1-vinylimidazole.3 In general, imidazole compounds occurring in biology follow histidine in having ring substituents at the 4-position carbon.

Typical of such compounds is trans-urocanic acid, (E)-3-(1H-imidazol-4-yl)prop-2-enoic acid, which has attracted much interest because of its potential role as an epidermal chromophore in skin-cancer photochemistry.4 In this context, a gas-phase electronic spectroscopy and photoisomerization study of trans-urocanic acid in a supersonic jet was reported.5 Subsequently, we attempted to conduct a structural investigation of urocanic acid under analogous physical conditions in our Stark-modulated free-jet microwave absorption spectrometer. As described in this report, the microwave spectrum detected could not be reconciled with that of urocanic acid (1), but consisted exclusively of four different tautomeric and conformational isomers of its break-down product, 4-vinylimidazole (2). In retrospect, we should have anticipated this result since the thermolysis of urocanic acid (Figure 1) in vacuo at ca. 220 °C has been, for many decades, a popular route for the synthesis of this much-utilized polymer chemistry formulant.6,7 In hindsight, it seems highly likely that the compound actually studied in the purported electronic spectroscopy study of urocanic acid vapor in a supersonic jet6 was actually that of 4-vinylimidazole. This observation in no way casts doubt on the abundant literature dealing with spectroscopic studies of urocanic acid in the condensed phase at lower temperatures.4,8

The compound 4-vinylimidazole has received considerable attention as a component of proton-conducting copolymers9 in applications such as polymer membrane fuel cells.10 Polymers containing 4-vinylimidazole also have been found to exhibit catalytic activity, functioning as potential coenzyme mimics.11

In our own study, the attempted vapor-phase microwave spectroscopic structural study of (1) has led fortuitously to a similar study of the comparably important compound (2).

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II. EXPERIMENT

A. Microwave spectroscopy

trans-Urocanic acid was purchased from Aldrich and used without further purification. The mm-wave region (48–72 GHz) spectrum was recorded with a Stark-modulated free-jet spectrometer developed from that employed in the spectroscopy of histamine\(^2\) which has been described previously.\(^1\) In the currently-used enhanced instrument developed during the mid-1990s, the klystron sources were replaced with dual-ganged, computer-driven solid state YIG-FET sweep oscillators to provide automated frequency tuning ability and to improve sensitivity by the use of heterodyne detection. Sensitivity was further enhanced by replacing the original horn-lens transmission microwave optics with a computer-tuned confocal-mirror resonant cavity used in a reflex mode, having a coupling iris to a waveguide feed in the center of one of the cavity mirrors. Parallel-plate electrodes, on either side of the cavity-mode beam waist, separated by ca. 3.5 cm provided a 33 kHz Stark modulation field, transverse to the molecular beam. In an adjacent heated chamber, the solid or molten sample (trans-urocanic acid) was heated to 220 °C, selected to provide a sample vapor pressure of ca. 1 Torr, in a stream of argon at a pressure of ~30 kPa. The sample vapor, entrained in hot argon, was introduced into the spectrometer via a 350 μm diameter pinhole nozzle heated to 230 °C. The resulting jet-cooled molecular beam was directed across the microwave cavity beam waist, between the parallel-plate Stark electrodes. The spectrometer was continuously evacuated by a He closed-cycle refrigerator cryopump, achieving under normal jet-flow conditions (ca. 5 mmol min\(^{-1}\) Ar), a background pressure of ca. 10\(^{-3}\) Torr. The rotational temperature in the expanded beam was ca. 10 K. Electric fields of up to 1700 V cm\(^{-1}\) were used to provide an adequate degree of Stark modulation. A search spectrum was first recorded over a wide frequency range (48–72 GHz) using a strip chart. All observed lines subsequently were recorded individually by digitally averaging repetitive narrow-band scans. Line profiles were fitted with a Lorentzian line shape function giving typical full width half height for transitions of 200–300 kHz, leading to experimental line center-frequency uncertainties of 20–60 kHz.

B. Quantum chemistry calculations

The assignment of the observed rotational transitions was assisted by pattern comparison with theoretical microwave spectra computed using predicted molecular structures and electric dipole moments from quantum chemical geometry optimizations.

The rotational constants, dipole moments, harmonic vibrational frequencies, and quartic centrifugal distortion constants of all candidate molecules were predicted from computed geometry optimizations using GAUSSIAN 09,\(^1\)\(^3\) first at the B3LYP/cc-pVTZ level. Subsequently, more reliable values of the geometric parameters, rotational constants, and dipole moments were predicted from optimizations at the more expensive MP2/cc-pVTZ level. Planarity was not assumed. All energetically plausible conformers were considered in these geometry optimizations.

Structure optimizations were completed at the MP2/cc-pVTZ level for cis-(3H)-urocanic acid, cis-(1H)-urocanic acid, four rotamers each of trans-(1H)-urocanic acid, and trans-(3H)-Urocanic acid, respectively. Subsequently, following observations discussed below, similar structure optimizations were completed for two rotamers each of 4-vinyl-(1H)-imidazole and 4-vinyl-(3H)-imidazole, respectively. In each case harmonic vibrational frequency and centrifugal distortion constant predictions were made at the less expensive B3LYP/cc-pVTZ level. Detailed results from representative chemical computations are provided in the supplementary material.\(^1\)\(^4\)

C. Rotational spectroscopy calculations

Spectral predictions from theoretical rotation constants and best-fit rotational and centrifugal distortion constants from experimental line frequency, measurements were made using unpublished software developed by the Monash microwave spectroscopy group, as was the calculation of best-fit spectroscopic constants from observed spectra.

III. RESULTS

A. Measurement and assignment of observed microwave absorption transitions

From broad chart-scans and subsequent narrow digitally averaged scans, ca. 140 microwave absorption lines were measured in the 48–72 GHz region. All but ca. 15 of the measured lines was found to fit to one of four distinct rotational spectra, indicating that the vaporized trans-urocanic acid was producing a mixture of four molecular species, designated w, x, y, and z, in the Ar-entrained free-jet molecular beam. The measured lines in each spectrum consisted of a mix of \(\mu_w\)-type and \(\mu_y\)-type transitions of generally comparable observed intensities. Detailed results including measured microwave absorption frequencies and the four rotational spectrum fits are provided in the supplementary material.\(^1\)\(^4\)

The predicted structures of the four 4-vinylimidazole isomers, designated I, II, III, and IV, are shown in Figure 2 and their predicted rotational constants are listed in Table II. The calculated principal axis electric dipole moment components and equilibrium mole fractions at the vaporization temperature of 225 °C are shown in Table III.
IV. DISCUSSION

A. Elimination of urocanic acid as the carrier of the observed spectrum

The sets of fitted rotational constants $A$, $B$, and $C$, for observed spectra designated $w$, $x$, $y$, and $z$, shown in Table I, had similar values of ca. 8.1, 2.0, and 1.6 GHz, respectively, for each species. This was close to the values predicted for the isomers of 4-vinylimidazole but quite dissimilar to any of the ten energetically plausible cis- or trans-urocanic acid species considered, all of which had $A$, $B$, and $C$ values in the region of 4–5, 0.6–0.8, and 0.5–0.7 GHz, respectively. Following this observation, urocanic acid was eliminated from consideration as a candidate carrier of the observed spectra. We have not eliminated the possibility that the ca. 15 unidentified lines detected belong to the spectrum of urocanic acid.

TABLE I. Rotational constants $A$, $B$, and $C$, calculated from fits to the observed spectra $w$, $x$, $y$, and $z$. Standard deviations in units of the last quoted digit are shown in parenthesis.

<table>
<thead>
<tr>
<th>Sp.</th>
<th>$N^b$</th>
<th>$A$ (MHz)</th>
<th>$B$ (MHz)</th>
<th>$C$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w$</td>
<td>63</td>
<td>8024.468(4)</td>
<td>2059.551(1)</td>
<td>1639.578(1)</td>
</tr>
<tr>
<td>$x$</td>
<td>22</td>
<td>8030.152(3)</td>
<td>2019.481(2)</td>
<td>1615.959(2)</td>
</tr>
<tr>
<td>$y$</td>
<td>45</td>
<td>8123.955(3)</td>
<td>2032.040(1)</td>
<td>1626.435(2)</td>
</tr>
<tr>
<td>$z$</td>
<td>25</td>
<td>8095.394(4)</td>
<td>2001.101(1)</td>
<td>1607.398(1)</td>
</tr>
</tbody>
</table>

$^a$Arbitrary identification label of observed spectrum.

$^b$Number of measured line frequencies used in fit.

Theoretical prediction of the spectrum of the anticipated predominant isomer indicates that the strongest lines would be expected to be ca. one tenth of the intensity of those of 4-vinylimidazole, as are most of the unidentified lines. All the detectable transitions in our frequency range would lack resolvable hyperfine splitting, consistent with the shape of the unidentified line profiles. However, we have not been able to fit the unidentified lines to an asymmetric rotor spectrum, consistent or not with urocanic acid.

B. Assignment of the observed spectra to isomers of 4-vinylimidazole

The observation in each spectrum of both $\mu_a$-type and $\mu_b$-type transitions is consistent with the dipole moment predictions shown in Table III. Owing to the erratic frequency dependence of sensitivity in our cavity spectrometer, the relative intensities of observed transitions are not as useful an assignment diagnostic as they are in other classes of microwave spectroscopy. Because of the similarity in the values of the sets of rotational constants, and bearing in mind the anticipated range of systematic errors when making a direct comparison between $ab$ initio and experimental rotational constants, the definite assignment of each of the carriers of $w$, $x$, $y$, and $z$ to isomers I, II, III, and IV is quite challenging. The initially hypothesized assignment was based on a comparison of the differences between the MP2 $R_e$ equilibrium geometry values and spectral fit values of all three constants $A$, $B$, and $C$ for each possible association of particular MP2 and fit species. Figure 3 shows the results of this procedure. To better compare like with like, MP2 estimates of the vibrational ground state rotational constants were calculated using vibration-rotation $\alpha$ values from anharmonic frequency calculations at the B3LYP/cc-pVTZ level. Considering each of the constants $A$, $B$, and $C$, the most consistent match between

TABLE II. Predicted rotational constants $A$, $B$, $C$, calculated from $ab$ initio geometry optimizations, at MP2/cc-pVTZ level, of the of 4-vinylimidazole isomers I, II, III, and IV.

<table>
<thead>
<tr>
<th>Species</th>
<th>$A$ (MHz)</th>
<th>$B$ (MHz)</th>
<th>$C$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8074.7</td>
<td>2067.5</td>
<td>1646.1</td>
</tr>
<tr>
<td>II</td>
<td>8178.9</td>
<td>2035.5</td>
<td>1629.9</td>
</tr>
<tr>
<td>III</td>
<td>8056.4</td>
<td>2029.2</td>
<td>1620.9</td>
</tr>
<tr>
<td>IV</td>
<td>8115.8</td>
<td>2008.7</td>
<td>1612.0</td>
</tr>
</tbody>
</table>

TABLE III. Principal axis electric dipole moment components and mole fractions calculated from $ab$ initio geometry optimizations, at MP2/cc-pVTZ level, of the of 4-vinylimidazole isomers I, II, III, and IV.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\mu_a$</th>
<th>$\mu_b$</th>
<th>$\mu_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3.30</td>
<td>2.18</td>
<td>0.43</td>
</tr>
<tr>
<td>II</td>
<td>2.46</td>
<td>2.26</td>
<td>0.33</td>
</tr>
<tr>
<td>III</td>
<td>2.18</td>
<td>3.19</td>
<td>0.15</td>
</tr>
<tr>
<td>IV</td>
<td>1.49</td>
<td>3.31</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$^a$In debye. For each species the value of $\mu_c$ was 0.0 D.

$^b$Equilibrium mole fraction at 225 $^\circ$C, from MP2/cc-pVTZ internal energy including B3LYP/cc-pVTZ zero-point vibrational energy correction.
theory and experiment is found with the assignments ($w \leftrightarrow I$), ($x \leftrightarrow III$), ($y \leftrightarrow II$), ($z \leftrightarrow IV$).

C. $^{14}N$ nuclear quadrupole coupling hyperfine patterns

As in the case of histamine where 20 possible isomers were considered,\textsuperscript{2} comparison of predicted and observed $^{14}N$ nuclear quadrupole coupling hyperfine multiplet patterns can be used to test the reliability of isomer assignments. Such a test is illustrated in Figure 4 which shows the observed and calculated hyperfine multiplets for the rotational transition $^{13}_2,^{12}_1,^{11}_1$ of the four isomers of 4-vinylimidazole. For each isomer, the match between the theoretical and experimental multiplet pattern is satisfactory. Also, except between the pairs ($w \leftrightarrow I$) and ($z \leftrightarrow IV$), the patterns are clearly distinctly different in shape, independently confirming the assignments ($x \equiv III$) and ($y \equiv II$) as unique. In the lower right of Figure 4, the comparison between the observed and calculated transitions is confused by the right-hand component in the observed profile for $z$ being merged with the single-component $^{13}_3,^{11}_1$ transition of $z$.

D. Consideration of inertial defect values

For a rigid planar molecule, a quantity that can be calculated from the rotational constants, the inertial defect $\Delta_0$, will be zero. For real molecules with a planar equilibrium structure, but having zero-point vibrational motion (“v = 0”), the calculation of the inertial defect $\Delta_0$ from A, B, and C yields a value other than zero, but generally much smaller in magnitude than the always negative $\Delta_0$ for a real molecule with a
TABLE IV. Inertial defect values $\Delta_0$ from the observed spectra $w, x, y,$ and $z$ compared with empirically calculated values for the corresponding assigned species. Standard deviations in units of the last quoted digit are shown in parentheses.

<table>
<thead>
<tr>
<th>Sp. $^a$</th>
<th>$\Delta_0^{b}$ from spectrum fit$^c$</th>
<th>Assigned species $^d$</th>
<th>$\Delta_0^{b}$ Calc.$^e$</th>
<th>(o-c)$^f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w$</td>
<td>$-0.1257(2)$</td>
<td>I</td>
<td>$-0.14$</td>
<td>$-13$</td>
</tr>
<tr>
<td>$x$</td>
<td>$-0.4446(2)$</td>
<td>III</td>
<td>$-0.34$</td>
<td>$24$</td>
</tr>
<tr>
<td>$y$</td>
<td>$-0.1858(1)$</td>
<td>II</td>
<td>$-0.19$</td>
<td>$0$</td>
</tr>
<tr>
<td>$z$</td>
<td>$-0.5702(2)$</td>
<td>IV</td>
<td>$-0.42$</td>
<td>$27$</td>
</tr>
</tbody>
</table>

$^a$Arbitrary identification label of observed spectrum.

$^b$I in $\text{Å}^2$.

$^c$ $\Delta_0 = I_{xx} - I_{yy} - I_{zz}$.

$^d$ $\Delta_0 = -33.715/\nu_{\text{op}} + 0.00803\sqrt{T}$, $\nu_{\text{op}}$ is the wavenumber value of the out-of-plane vinyl torsional mode from B3LYP/cc-pVTZ level calculation.

$^e$(o-c) = ($\Delta_{\text{fit}} - \Delta_{\text{calc.}}$)/$\Delta_{\text{fit}}$.

nonplanar equilibrium structure. The source of this small non-zero value is from rotation-vibration interaction and is well understood, although challenging to predict theoretically. For molecules with a planar equilibrium structure, in-plane vibrations contribute positive contributions to $\Delta_0$ and low-frequency out-of-plane vibrations, negative contributions. For vinylimidazoles, an out-of-plane torsional vibration involving the vinyl group is expected to have a low frequency and so $\Delta_0$ is anticipated to be negative. Values in the range 0.1 to 0.8 $\text{Å}^2$ have been found for a wide variety of monosubstituted aromatics (but not including any imidazole derivatives).

In a definitive treatment of the topic of inertial defects in molecules with planar equilibrium structures, Oka shows that, where a single low-frequency out-of-plane vibration is present, a simple formula involving the reciprocal of that frequency successfully predicts the approximate value of the inertial defect in the ground vibrational state $\Delta_0$. For a set of about 15 substituted benzenes (thought to have planar equilibrium structures) reported by Oka, the errors in the predicted values of $\Delta_0$ show a standard deviation of ca. 20%. Table IV compares the value of $\Delta_0$ found for each of the four spectra analyzed with empirically predicted values of $\Delta_0$ for the isomers that have been assigned to the observed spectra from the evidence already discussed. The mismatch between the spectral fit and empirically calculated values of $\Delta_0$ for each assignment is <30%, a result not significantly inconsistent with a planar equilibrium structure for each species.

The optimized structure from a high-level $ab\text{ initio}$ calculation purported to approach the true equilibrium structure. This is consistent with the $ab\text{ initio}$ MP2/cc-pVTZ structure optimizations for I, II, and III which result in values of $|\Delta_{\text{el}}|$ of $<10^{-4}$ $\text{Å}^2$. For 4-vinylimidazoles I, II, and III the converged structures have no dihedral angles deviating from 0° or 180° by more than 0.01°. In contrast, for IV, the dihedral angle CCCC involving the vinyl group and the two adjacent ring C atoms is almost 8°. This results in a value for $\Delta_e$ of ca. 0.35 $\text{Å}^2$ for this isomer. The actual value of $\Delta_0$ for $z$ (assigned to IV) is ca. 0.6 $\text{Å}^2$. Isomer IV appears to have an equilibrium structure that is best described as quasiplanar. The out-of-plane vibration involving torsion of the vinyl group would have a low-barrier double-minimum potential function. The empirical formula of Oka would not be expected to be all reliable for such an anharmonic vibration, so any similarity between the values of $\Delta_0$ for $z$ and the empirical value for IV (which is based on harmonic vibrations) is probably fortuitous. It should be noted that the vibrational frequencies employed in the empirical predictions of $\Delta_0$ were calculated at the more approximate B3LYP/cc-pVTZ level. At this level, the optimized structure for isomer IV was found to be planar.

E. Nonplanarity: Comparison with 1-vinylimidazole

It is interesting to compare the case of the 4-vinylimidazole isomers with that of 1-vinylimidazole. As mentioned previously, a thorough microwave spectroscopic structural investigation of 1-vinylimidazole and associated quantum chemical calculations has been published recently. Two conformers, here designated (i) and (ii), are possible. As illustrated in Figure 5, the shapes and atom dispositions are reminiscent of those of isomers IV and II of 4-vinylimidazole, respectively, differing only in the interchange of C with N between the ring vinyl junction and an adjacent ring atom.

In the published study of 1-vinylimidazole, it was found at the MP2/cc-pVTZ level that isomer (i) was significantly nonplanar, with the vinyl group tilted ca. 17° to the plane of the imidazole ring. Conformer (ii) was found to be essentially planar at the same level. This result qualitatively mimics the planarity status of the similarly disposed isomers IV and II of 4-vinylimidazole.

For both compounds it is not easy to arrive at a distinct underlying cause of the deviation from planarity found in isomers (i) and IV, but not in any of the other isomers. Indicative trends arising from systematically differing

FIG. 5. Comparison of the MP2/cc-pVTZ structures of the two possible isomers (i) and (ii) of 1-vinylimidazole with isomers (IV) and (II) of 4-vinylimidazole.
hydrogen-hydrogen non-bonded distances or varying double bond character in the bond between the junction ring atom and the vinyl group seem not to apply. With the calculations using the elaborate cc-pVTZ atomic orbital basis functions, optimized structures that are nonplanar at the MP2 level become planar at the simpler RHF and B3LYP levels, which are more neglectful of the effects of electron correlation. However, for (i) and IV, DFT methods more elaborate than B3LYP, such as M062X/cc-pVTZ also results in nonplanar structures.

The methods MP2 and CCSD that include some of the electron correlation consequences of configuration interaction at different levels of approximation, were applied with a range of less elaborate basis functions. Both methods predicted planar structures with the minimal STO-3G basis set but nonplanar with 3-21G, 4-31G, and 6-31G.

The structural deviations from planarity discussed here are a manifestation of spontaneous symmetry-breaking. In this case the molecular point group moves from $C_{1}$ to $C_{2}$ contrary to the expectation of the generally accepted rules for the structure of organic molecules, where conjugated double bonds are usually coplanar about the intervening single bond. This effect is analogous to the case of propadiene, where the cumulated double bonds are found to be non-collinear. This case aroused interest particularly among quantum chemists since it was apparently the first example in which the inclusion of electron correlation terms in the Hamiltonian was vital to the satisfactory prediction of the observed symmetry point group.

An analogous case of quasiplanarity has also been encountered in quantum chemical calculations for the simplest vinyl-substituted benzene–styrene. In the latter study, a structurally related compound $p$-hydroxystyrene was also found to be quasiplanar.

V. CONCLUSIONS

The microwave spectra of the four isomers of 4-vinylimidazole produced from the vaporization at ca. 220 °C of trans-urocanic acid have been measured. While not being able to unequivocally eliminate urocanic acid as a significant component of the resultant vapor, it was concluded that the vapor contained a substantial mole fraction of 4-vinylimidazole, consequently casting doubt on the reliability of previously reported vapor phase electronic spectroscopy of trans-urocanic acid. Comparisons between observed and quantum chemically predicted rotational constants, and between observed and predicted $^{14}$N nuclear quadrupole coupling patterns led to consistent identification of each of the observed spectra with one of the four possible isomers of 4-vinylimidazole. These structural assignments were supported by comparison between observed and calculated estimates of the inertial defect $\Delta_{0}$ for each isomer. As with one of the isomers of 1-vinylimidazole, the isomer IV of 4-vinylimidazole, with a similar skeletal shape, also showed a small deviation from planarity. A similar quasiplanarity has been detected in styrene, indicating a class of spontaneous symmetry-breaking in the molecular structure of some otherwise planar vinyl aromatic compounds. The effect requires the explicit inclusion of electron correlation in order to show itself in quantum chemical predictions.

ACKNOWLEDGMENTS

Financial support was from the Australian Research Council and from Monash University. Quantum chemistry calculations were carried out using the Australian Partnership for Advanced Computing (APAC) National Facility and the computational resources of the NCI Australia National Facility through the National Computational Merit Allocation Scheme.

13M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 09, Revision B.01, Gaussian Inc., Wallingford, CT, 2010.
14See supplementary material at http://dx.doi.org/10.1063/1.4742061 for detailed results from representative chemical computations and for measured microwave absorption frequencies and the four rotational spectrum fits.