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# $^{14}\text{N}$ nuclear quadrupole coupling and methyl internal rotation in 3-methylpyrrole investigated by microwave spectroscopy

Thuy Nguyen <sup>a</sup>, Wolfgang Stahl <sup>b</sup>, Ha Vinh Lam Nguyen <sup>a,c</sup>, Isabelle Kleiner <sup>a,†</sup>

<sup>a</sup> Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, Institut Pierre Simon Laplace, 61 avenue du Général de Gaulle, 94010 Créteil, France

<sup>b</sup> Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen, Germany

<sup>c</sup> Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris cedex 05, France

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## A B S T R A C T

The molecular structure of 3-methylpyrrole in the gas phase has been determined using a combination of high-resolution spectroscopy and quantum chemical calculations. The rotational spectrum was recorded using a molecular jet Fourier transform microwave spectrometer covering the frequency range from 2.0 to 26.5 GHz. The experimental data were analyzed using the programs XIAM and BELGI-*C<sub>s</sub>-hyperfine*. Because the internal rotor axis accidentally lies along the principal *a*-axis of inertia, the rho axis system and the principal axis system coincide, enabling a direct comparison of the fits. With the program XIAM, the rotational constants  $A = 8631.1629(12)$ ,  $B = 3342.19750(43)$ , and  $C = 2445.73846(42)$  MHz were obtained. Torsional splittings due to internal rotation of the methyl group were observed, leading to the determination of the  $V_3$  potential of  $245.92445(31)$   $\text{cm}^{-1}$ . Hyperfine splittings arising from the nuclear quadrupole coupling of the  $^{14}\text{N}$  nucleus could be resolved, and the quadrupole coupling constants  $\nu_{aa} = 1.4159(49)$  and  $\nu_{bb} - \nu_{cc} = 4.1622(86)$  MHz were found.

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## 1. Introduction

Many studies on monomethyl-substituted five-membered heterocycles have been carried out in the microwave region in great detail, i.e. 2-methylfuran [1], 3-methylthiophene [2], the three isomers of methylthiazole [3–5], the three isomers of methyloxazole [6], 3- and 5-methylisoxazole [7], and the four isomers of methylimidazole [8]. Such molecules exhibit intramolecular dynamics, arising from the internal rotation of the methyl group, being important in physics, chemistry, and biology. Though a number of studies are available, still no effective, phenomenological rule for predicting the torsional barrier of the methyl group could be deduced. In other words, how the steric effects and the electronic environment affect the barrier to internal rotation of the methyl group in five-membered heterocycles is still a puzzling quantitative question, which might be answered by the complementary use of microwave spectroscopy and quantum chemical calculations.

Pyrrole is a nitrogen containing five-membered ring which appears as a structural component of several biologically important compounds, e.g. serotonin (5-hydroxytryptamine), a neuro-

transmitter and vasoconstrictor active in the central nervous system. It is also a subunit of some vitally important compounds called porphyrines, e.g. porphine, and substituted derivatives that form metal complexes like chlorophyll or hemoglobin. The derivatives of pyrrole are studied extensively by pharmacology [9]. Therefore, basic knowledge on the structure and dynamics of pyrrole derivatives underpins investigations and developments in biology.

Recently, the microwave spectrum of a mono-methyl substituted pyrrole derivative, 2-methylpyrrole (2MP), was studied, revealing torsional splittings from the three-fold hindered internal rotation of the methyl group and hyperfine structures from the quadrupole coupling of the  $^{14}\text{N}$  nucleus [10]. The molecular structure as well as the effective  $V_3$  potential and the  $^{14}\text{N}$  nuclear quadrupole coupling constants (NQCCs) were determined with high accuracy. In order to answer how the steric effect and the electronic environment affect the methyl internal rotation, it is plausible to study substitution isomers, i.e. 3-methylpyrrole (3MP), and compare the methyl torsional barrier with that of 2MP. Moreover, the study on the  $^{14}\text{N}$  NQCCs of 2MP states that the effect of methylation on  $\nu_{cc}$  can be almost neglected. The NQCCs of 3MP will provide valuable data to confirm or deny the general validity of this statement.

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† Corresponding author.

E-mail address: [isabelle.kleiner@lisa.u-pec.fr](mailto:isabelle.kleiner@lisa.u-pec.fr) (I. Kleiner).

The details of the present study will be divided into sections which describe the quantum chemical calculations, the experimental setup, the assignment of the spectra, the fits with molecular parameters deduced from the experimental data, followed by a discussion and our conclusion.

## 2. Quantum chemical calculations

In order to get reasonable starting values for the spectral assignment, the GAMESS [11] program package was used to quantum-chemically optimize the structure of 3MP, to predict the barrier to internal rotation of the methyl group, and to compute the  $^{14}\text{N}$  NQCCs.

### 2.1. Geometry optimizations

To obtain the molecular geometry of 3MP, optimizations were performed using the Kohn-Sham density functional theory [12] employing Becke’s three parameters hybrid exchange functional [13], the Lee-Yang-Parr correlation functional [14] (B3LYP) and the second order Møller-Plesset perturbation method (MP2) [15] in combination with the Dunning basis sets cc-pVDZ and cc-pVTZ [16]. In Table 1, the rotational constants and the angle  $\angle(i,a)$  between the principal  $a$  axis and the internal rotor axis  $i$  are given along with the level of theory at which the calculation was performed.

All calculations yielded only one stable conformer. The geometrical structure of 3MP optimized at the MP2/cc-pVDZ level of theory is illustrated in Fig. 1, showing that the internal rotor axis is almost collinear with the principal inertial  $a$  axis. The Cartesian coordinates are given in Table S1 in the Supporting Information.

### 2.2. Methyl torsional barrier

The height and shape of the torsional potential of the methyl group were retrieved by optimizing the molecular geometry of 3MP in steps of  $10^\circ$  of the dihedral angle  $\alpha = \angle(\text{C}_2\text{C}_3\text{C}_6\text{H}_{12})$  at the MP2/cc-pVDZ level of theory. The

$V_3$  term was determined to be  $189.8\text{ cm}^{-1}$ . The potential curve is illustrated in Figure S2, the fitted Fourier coefficients obtained by fitting the step-wise computed potential function are given in Table S3 in the Supporting Information.

### 2.3. $^{14}\text{N}$ nuclear quadrupole coupling constants

It is known from a number of previous studies that the method introduced by Bailey [17] to compute the  $^{14}\text{N}$  NQCCs is rather reliable [10,18–20]. Therefore, we also apply this method for 3MP. With the molecular geometry optimized at the MP2/cc-pVDZ level of theory, the electric field gradient (EFG) tensor at the site of the  $^{14}\text{N}$  nucleus was calculated at the B3PW91/6-311+G(d,p) level of theory, which is recommended for modeling of conjugated  $\pi$ -electron systems [21]. The quadrupole coupling tensor is directly proportional to the EFG tensor by the calibration factor  $eQ/h = -4.599\text{ MHz/a.u}$  [21]. The NQCCs were found to be  $\nu_{aa} = 1.5054$ ,

Fig. 1. The geometry of 3MP optimized at the MP2/cc-pVDZ level of theory. Atomic numbers and the inertial principal axes are given. The N atom is presented in blue; C atoms are given in grey and H atoms in white. The hydrogen atom  $\text{H}_{13}$  is located behind  $\text{H}_{12}$ . The internal rotor axis is almost collinear with the inertial principal  $a$  axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\nu_{bb} = 1.4234$ ,  $\nu_{cc} = -2.9288$ , and  $\nu_{ab} = 0.1481\text{ MHz}$ . The off-diagonal  $\nu_{ac}$  and  $\nu_{bc}$  are zero due to symmetry.

## 3. Experimental section

### 3.1. Measurements

The sample of 3MP was purchased from TCI Europe, Zwijndrecht, Belgium, with a stated purity of over 99% and used without further purification. A drop of 3MP was put on a pipe cleaner which

is inserted into a stainless-steel tube placed upstream the nozzle.

Helium, used as carrier gas, flowed over the substance at a backing pressure of 200–250 kPa. The spectra of 3MP were recorded using a molecular jet Fourier-transform microwave spectrometer covering the frequency region from 2.0 to 26.5 GHz [22].

Guided by the theoretical spectrum using the rotational constants predicted at the MP2/cc-pVDZ level of theory, a broadband scan from 10 to 12 GHz in steps of 0.25 MHz was recorded for the spectral assignment. Subsequently, all lines were remeasured at higher resolution. The line widths are approximately 15–30 kHz for isolated lines, the measurement accuracy is about 2.5 kHz.

### 3.2. Spectral assignment

In the first approach, the effects arising from the nuclear quadrupole coupling were neglected and 3MP was treated as a one-top molecule. The values of the rotational constants, the barrier to internal rotation of the methyl group, and the angle  $\angle(i,a)$  calculated at the MP2/cc-pVDZ level of theory were used as initial values in the program XIAM [23] to predict the spectrum of 3MP. The dipole moment components of 3MP were predicted to be  $|\mathbf{I}_a| = 1.49$ ,  $|\mathbf{I}_b| = 1.17$ , and  $|\mathbf{I}_c| = 0.00\text{ D}$ . Therefore, the spectrum should contain only  $a$ - and  $b$ -type transitions. By comparing the theoretical spectrum and the broadband frequency scan, we were able to identify the A and E torsional components of the  $1_{11} \rightarrow 0_{00}$ ,  $2_{12} \rightarrow 1_{11}$ , and  $4_{13} \rightarrow 4_{04}$  transitions. Fitting the frequencies of those transitions by adjusting the three linear combinations of the rotational constants  $B_K = A - 0.5(B + C)$ ,  $B_j = 0.5(B + C)$ ,

Table 1  
The rotational constants (in MHz) and the angle  $\angle(i,a)$  (in degrees) of 3MP obtained at various levels of theory.

	A	B	C	$\angle(i,a)$
MP2/cc-pVDZ	8553.8	3305.9	2420.8	0.25
MP2/cc-pVTZ	8470.2	3445.8	2486.9	0.01
B3LYP/cc-pVDZ	8602.5	3321.6	2432.9	0.42
B3LYP/cc-pVTZ	8697.2	3352.1	2456.2	0.44
Experimental	8631.2	3342.2	2445.7	0.00

$B_- = 0.5(B-C)$ , and the  $V_3$  potential minimized the root-mean-square (rms) deviation to about 0.5 MHz. This fit allowed us to record further lines at high resolution with sufficient accuracy. The quadrupole hyperfine structures due to the  $^{14}\text{N}$  nucleus are well-resolved for all lines. The assignment of the hyperfine components was straightforward because the observed frequencies agreed fairly well with the predictions based on the calculated NQCC values. Finally, 89 rotational transitions including 36 A species and 53 E species lines with a total of 264 hyperfine components were measured and fitted with the program *XIAM*. The frequencies are given in Table S4 of the [Supporting Information](#).

Since the final rms deviation of 12.1 kHz obtained with *XIAM* is much higher than the measurement accuracy, the program *BELGI-C<sub>s</sub>-hyperfine* [24] was applied on the same data set, aiming to reduce the rms deviation to measurement accuracy. The *BELGI-C<sub>s</sub>-hyperfine* code is an extension of the *BELGI-C<sub>s</sub>* code. While *BELGI-C<sub>s</sub>* is suitable to treat the microwave spectra of molecules with one methyl internal rotation and  $C_s$  frame symmetry, the *BELGI-C<sub>s</sub>-hyperfine* code takes into account in addition one weak nuclear quadrupole interaction, i.e.  $^{14}\text{N}$ , using a perturbation approach to calculate the hyperfine splittings. The rotation-torsion eigenvalues and eigenvectors are first obtained from the usual two-step diagonalization of the rotation-torsion Hamiltonian in the rho axis system. Subsequently, the numerical values of the quadratic angular momentum components  $hP_a^2\mathbf{i}$ ,  $hP_b^2\mathbf{i}$ ,  $hP_c^2\mathbf{i}$ , and  $hP_aP_b\mathbf{i}$ ,  $hP_bP_c\mathbf{i}$ ,  $hP_cP_a\mathbf{i}$  are quantified, and then put into the standard hyperfine energy expression as given in Eq. (1) of Ref. [24].

#### 4. Fit results

The experimental data were analyzed using two programs, *XIAM* [23] and *BELGI-C<sub>s</sub>-hyperfine* [24]. The *XIAM* code uses a combined axis method where the internal rotation Hamiltonian of each single top is set up in the rho axis system and then transformed into the principal axis system, while in *BELGI-C<sub>s</sub>-hyperfine* the Hamiltonian is written exclusively in the rho axis system. Therefore, molecular parameters obtained from *XIAM* and *BELGI-C<sub>s</sub>-hyperfine* refer to different axis systems. For a comparison, parameters obtained from *BELGI-C<sub>s</sub>-hyperfine* have to be transformed into the principal axis system, which is often not possible for all resultant parameters. In all previous investigations where the two approaches have been compared, this procedure could only be applied for the rotational constants [25,26] and the NQCCs [24]. Details of the conversions are given in Refs. [27,28].

Though *ab initio* calculations suggested that the angle  $\angle(i,a)$  between the  $a$  principal axis and the internal rotor axis is approximately zero (see Table 1), we still tried to float this angle in the *XIAM* fit. However, it turned out to be badly determined and was highly correlated with the  $V_3$  parameter with a correlation coefficient of 0.998. Therefore, we finally fixed the value of  $\angle(i,a)$  at zero. In the *BELGI* code, the angle  $\angle(i,a)$  is not available as a fit parameter, but another parameter called  $D_{ab}$  multiplying the  $P_aP_b + P_bP_a$  off-diagonal Hamiltonian term.  $D_{ab}$  is related to the angle between the rho axis system and the principal axis system. A detailed explanation can be found in Ref. [29]. Similar to the situation observed during the fitting with the program *XIAM*, attempts to float  $D_{ab}$  led to divergence. We then fixed  $D_{ab}$  at various values varying in the range from  $1 \cdot 10^{-5} \text{ cm}^{-1}$  (about 0.3 MHz) to  $5 \cdot 10^{-3} \text{ cm}^{-1}$  (about 150 MHz). In Fig. 2, the rms deviation of the fits is plotted as a function of the fixed value of  $D_{ab}$ . The bottom of the curve is extremely flat until  $D_{ab}$  reaches the value of about  $0.002 \text{ cm}^{-1}$  where the rms deviation started to increase. Therefore, we decided to fix  $D_{ab}$  at zero. This means that in the case of 3MP, the principal axis system and the rho axis system coincide within the measure-

Fig. 2. Root-mean-square deviation of the *BELGI* fit as a function of  $D_{ab}$ .

ment accuracy and the results of the *XIAM* and *BELGI-C<sub>s</sub>-hyperfine* fits are directly comparable for all resultant parameters.

In the *XIAM* fit, the main geometrical parameters (three rotational constants), the internal rotation parameters (barrier to inter-

nal rotation and the rotation distortion operators in the principal axis system  $D_{pi2j}$ ,  $D_{pi2k}$ , and  $D_{pi2l}$ ), the NQCCs ( $v_{aa}$  and  $v_{bb}$   $v_{cc}$ ) together with four centrifugal distortion constants using Watson's A reduction ( $D_j$ ,  $D_{JK}$ ,  $d_j$ ,  $d_K$ ) were fitted and determined with high accuracy. The rms deviation is 12.1 kHz which is approximately 5 times the estimated measurement accuracy.

The *BELGI-C<sub>s</sub>-hyperfine* code succeeded to reproduce the experimental data of *N-tert-butylacetamide* [24], 3-nitrotoluene [30], and recently 2MP [10] with a satisfactory rms deviation. For 3MP, with 14 floated parameters (and fixing the two parameters  $F$  and  $D_{ab}$ ), the rms deviation of 2.9 kHz obtained with *BELGI-C<sub>s</sub>-hyperfine* is almost the measurement accuracy. The molecular parameters of 3MP obtained from the two fits and the results from *ab initio* calculations at the MP2/cc-pVDZ level of theory are presented in Table 2.

#### 5. Discussion

##### 5.1. Geometry parameters

The rotational constants obtained with the *XIAM* and *BELGI-C<sub>s</sub>-hyperfine* codes agree fairly well. The small differences in the two approaches probably arise from altered constraints that come with the different sets of parameters used in the two fits. When comparing the values obtained from the *XIAM* fit with those from quantum chemical calculations at the MP2/cc-pVDZ level of theory, we found deviations of  $-0.90\%$  for A,  $-1.09\%$  for B, and  $-1.02\%$  for C (with respect to the *XIAM* values). Such deviations are frequently observed while comparing the experimental rotational constants, which refer to the vibrational ground state, with equilibrium constants calculated at the MP2/cc-pVDZ level.

Using the same data set, the *BELGI-C<sub>s</sub>-hyperfine* code enables us to retrieve all five quartic centrifugal distortion constants  $D_j$ ,  $D_{JK}$ ,  $D_K$ ,  $d_j$ ,  $d_K$  whereas  $D_K$  cannot be determined with *XIAM*. Generally, a direct comparison between the centrifugal distortion constants obtained with *BELGI-C<sub>s</sub>-hyperfine* and *XIAM*, except for  $D_j$ , is not possible. However, in the case of 3MP where the rho axis and the principal axis systems accidentally coincide, the parameters can be directly compared. While the values of  $D_j$ ,  $D_{JK}$ , and  $d_j$  from the *XIAM* fit, the *BELGI-C<sub>s</sub>-hyperfine* fit, and *ab initio* calculations at

Table 2  
Molecular parameters of 3MP in the principal axis system obtained from fits with the *XIAM* and the *BELGI-C<sub>s</sub>-hyperfine* programs.

Operator	Par. <sup>a</sup>	Unit	Fit <i>XIAM</i>	Fit <i>BELGI</i>	<i>ab initio</i> <sup>b</sup>
$P_a^2$	$A$	MHz	8631.1629(12)	8631.0585(40)	8553.8
$P_b^2$	$B$	MHz	3342.19750(43)	3341.8407(43)	3305.9
$P_c^2$	$C$	MHz	2445.73846(42)	2445.5916(45)	2420.8
$\{P_a, P_b\}$	$D_{ab}$	—	—	0 <sup>c</sup>	—
$-\mathbf{P}^4$	$D_J$	kHz	0.2460(89)	0.2191(27)	0.2142
$-\mathbf{P}^4$	$D_{JK}$	kHz	1.487(42)	1.586(10)	1.4488
$-\mathbf{P}_{a_2}^4$	$D_K$	kHz	—	0.525(14)	0.6462
$-2P_a^2(P_b - P_c)^2$	$d_j$	kHz	0.0645(32)	0.0608(78)	0.0582
$-(P_a, P_a - P_c)$	$d_K$	kHz	0.445(70)	1.129(17)	0.3413
$(P_a - qP_a)^2$	$F_0$	GHz	158 <sup>d</sup>	—	158
$(1/2)(1 - \cos 3a)$	$F$	GHz	167.130 <sup>e</sup>	167.130 <sup>f</sup>	—
$P_a P_a$	$V_3$	cm <sup>-1</sup>	245.92445(31)	245.14101(89)	189.8
$2(P_a - qP_a)^2 P^2$	$q$	—	0.0546 <sup>g</sup>	0.05400716(72)	—
$\{(P_a - qP_a)^2, P^2\}$	$D_{pi2j}$	kHz	21.9(19)	—	—
$\{(P_a - qP_a)^2, P^2\}$	$D_{pi2K}$	MHz	1.3505(60)	—	—
$\{(P_a - qP_a)^2, (P_b^2 - P_c^2)\}$	$D_{pi2-}$	kHz	13.20(89)	—	—
$2(P_a^2 - P_b^2)$	$C$	MHz	—	0.05832(93)	—
$2(P_a^2 - P_b^2)$	$c_a^v$	MHz	—	0.01200(22)	—
$v_{aa}$	$v_{aa}$	MHz	1.4159(49)	1.41345(12)	1.5054
$v_{bb}$	$v_{bb}$	MHz	1.3732(68)	1.37535(12)	1.4234
$v_{cc}$	$v_{cc}$	MHz	-2.7890(19)	-2.78880(24)	-2.9288
$\backslash(i, a)$	$\backslash(i, a)$	°	—	—	0.25
$\backslash(i, c)$	$\backslash(i, c)$	°	90 <sup>g</sup>	90 <sup>g</sup>	90
$rms^h$	$rms^h$	kHz	12.1	2.9	—
$N_A/N_E/N_q^i$	$N_A/N_E/N_q^i$	—	36/53/264	36/53/264	—

<sup>a</sup> All parameters refer to the inertial principal axis system.  $P_a, P_b, P_c$  are the components of the overall rotation angular momentum,  $P_a$  is the angular momentum conjugate to the internal rotation angle  $a$  and  $P_r$  is the angular momentum vector along the rho axis. For 3MP, the rho axis is collinear to the principal  $a$  axis, meaning that  $P_r$  lies in the same direction as  $P_a$ . Statistical uncertainties are given as one standard uncertainty in the last digit. Watson's A reduction and I<sup>r</sup> representation were used.  $\{u, v\}$  is the anti-commutator  $uv + vu$ . The product of the parameter and operator from a given row yields the term actually used in the vibration-rotation-torsion Hamiltonian, except for  $F, q$ , and  $A$ , which occur in the Hamiltonian in the form  $F(P_a - qP_a)^2 - AP_a^2$ .

<sup>b</sup> Calculated at the MP2/cc-pVDZ level.

<sup>c</sup> Fixed to zero (see text).

<sup>d</sup> Fixed to the calculated value.

<sup>e</sup> Derived parameter.

<sup>f</sup> Fixed to the value of *XIAM*.

<sup>g</sup> Fixed due to symmetry.

<sup>h</sup> Root-mean-square deviation of the fit.

<sup>i</sup> Number of A and E species rotational transitions as well as number of the hyperfine components.

the MP2/cc-pVDZ level of theory match fairly well, the  $d_K$  value obtained with *BELGI-C<sub>s</sub>-hyperfine* is significantly higher. To test the effects of centrifugal distortion in *BELGI*, we switched to Watson's S reduction, since some studies in the literature, e.g. 1,1-difluoroacetone [31] and aziridine [32], have indicated fitting problems arising from the dependence of  $d_K$  on the ratio  $(2A - B - C)/(B - C)$  [33], from which  $D_J, D_{JK}, D_K, d_j$  and all of five quartic centrifugal distortion terms in the S reduction are free of. A comparison of the quartic centrifugal distortion constants obtained from *BELGI* and *XIAM* is given in Table 3.

Since  $D_K$  (or  $D_K$ ) is not well-determined with *XIAM*, we performed several tests where  $D_K$  (or  $D_K$ ) is fixed to zero, fitted, and fixed to the values obtained from *BELGI-C<sub>s</sub>-hyperfine*. The results from all these tests show that values of all other four quartic centrifugal distortion parameters as well as the rms deviation do not change much upon variations in the value of  $D_K$  (or  $D_K$ ), and the

value of  $d_K$  or  $d_2$  deduced from *XIAM* always differs significantly to that from *BELGI*. This indicates that the reduction is not responsible for the different values of  $d_K$  or  $d_2$ , but the contamination of this parameter by the internal rotation effects reflected in different sets of internal rotation parameters used in *BELGI-C<sub>s</sub>-hyperfine* and *XIAM*.

## 5.2. <sup>14</sup>N nuclear quadrupole coupling constants

The NQCCs obtained from the two fits are in very good agreement. The values of  $v_{aa}, v_{bb}$ , and  $v_{cc}$  predicted at the B3PW91/6-311+G(d,p)/MP2/cc-pVDZ level deviate by 6.32%, 3.65%, and 5.01%, respectively, compared to those deduced by the *XIAM* fit. The  $v_{cc}$  value found for 3MP is -2.7890(19) MHz, which is smaller than that found for 2MP (-2.846(36) MHz) and even closer to that of pyrrole (-2.66(2) MHz) [34]. This observation confirmed the negligible methylation effect on  $v_{cc}$  perpendicular to the aromatic rings plane of the methyl derivatives of pyrrole. As  $v_{ab}$  is associated with the expectation value of  $\{P_a, P_b\}$ , it can vanish if the coupling tensor aligns with the inertial principal  $a$ - or  $b$ -axis. This is only approximately true here. However, since the off-diagonal elements only contribute to the second order, an experimental value of  $v_{ab}$  could not be determined for 3MP.

## 5.3. Barrier to methyl internal rotation

The  $V_3$  potential values obtained with the *XIAM* and *BELGI-C<sub>s</sub>-hyperfine* codes give satisfactory agreement. The value obtained

Table 3  
Comparison of quartic centrifugal distortion constants (in kHz) using Watson's S reduction in I<sup>r</sup> representation obtained from fits with the *XIAM* and the *BELGI-C<sub>s</sub>-hyperfine* programs as well as calculations at the MP2/cc-pVDZ level.

Par.	Fit <i>XIAM</i>	Fit <i>BELGI</i>	<i>ab initio</i>
$D_J$	0.2387(90)	0.1777(33)	0.2010
$D_{JK}$	1.592(35)	1.990(11)	1.5284
$D_K$	—	0.292(17)	0.5798
$d_1$	-0.0644(32)	-0.05888(95)	-0.0582
$d_2$	-0.0088(14)	-0.02429(42)	-0.0066

Fig. 3. The barrier to methyl internal rotation  $V_3$ , and the NQCC  $v_{cc}$  of 3MP in comparison with mono-methylated pyrroles, thiazoles, imidazoles, and oxazoles. (1) *N*-methylpyrrole [28], (2) 2-methylpyrrole [10], (3) 3-methylpyrrole (this work), (4) 2-methylthiazole [3], (5) 4-methylthiazole [4], (6) 5-methylthiazole [5], (7) *N*-methylimidazole [8], (8) 2-methylimidazole [8], (9) 4-methylimidazole [8], (10) 5-methylimidazole [8], (11) 2-methyloxazole [6], (12) 4-methyloxazole [6], (13) 5-methyloxazole [6].

from *BELGI* differs only by  $-0.32\%$  from the *XIAM* value. The  $V_3$  value predicted at the MP2/cc-pVTZ level of theory is  $-22.8\%$  lower than the experimental value. At the same level, the difference of  $8.8\%$  observed for 2MP is much smaller [10]. Obviously, even within the same class of molecules, in this case methyl-substituted pyrroles, a level of theory which gives calculated results close to the experimental values for one isomer may not give such a satisfactory agreement for another isomer. It is hard to predict which level of theory is required for trustable value of  $V_3$ , thereby highlighting the need of microwave studies as a reliable source to quantify the large amplitude motion(s) in a molecule.

#### 5.4. Comparison of nitrogen containing mono-methylated aromatic five-membered rings

A comparison between the results obtained for mono-methylated pyrroles, thiazoles, imidazoles, and oxazoles is given in Fig. 3 with focus on the title molecule 3MP.

The planar moment of  $1.5639 \text{ u}\text{\AA}^2$  of 3MP (3) is very close to that of *N*-methylpyrrole (1) ( $1.652 \text{ u}\text{\AA}^2$ ) [35] and 2MP (2) ( $1.6115 \text{ u}\text{\AA}^2$ ) [10], confirming that there are two out-of-plane hydrogen atoms. Regarding the methyl torsion, the  $V_3$  potential value changes significantly if the ring atom or the substitution at the

heteroatom is varied. For mono-methylated thiazoles, imidazoles, and oxazoles, the lowest  $V_3$  value is always found in the 2-isomer while the highest barriers correspond to the 5-isomer. The crucial role of the frame symmetry is also proven by the intermediate barrier of  $123\text{ cm}^{-1}$  observed for 2-methylimidazole (8) [8]. If the hydrogen atom would no longer attach to the N(1) atom in (8), the local frame symmetry of the  $\text{CH}_3$  group would be  $C_{2v}$ , resulting in a leading  $V_6$  potential term. The deviation caused by the small hydrogen atom attached to the nitrogen atom N(1) breaks the  $C_{2v}$  symmetry of the frame as well as the equal electron distribution, and leads to a significant change of the barrier height.

Finally, the methyl torsional barrier of  $252\text{ cm}^{-1}$  found for 2-methyloxazole (11) is higher than that of 2-methylimidazole (8).

The trend that the barrier to internal rotation increases from methylthiazoles [3–5] over methylimidazoles [8] to methyloxazoles [6] is generally observed not only for the 2-, but also for the 4- and 5-isomers. Obviously, the electronic distribution of a nitrogen atom is closer to that of a sulfur atom than that of a NH group, and the deviation to that of an oxygen atom is even greater. For the 2-isomers, 2MP (2) can also be considered in the comparison, which possesses the highest barrier [10], indicating the largest difference in the electronic distributions between a nitrogen atom and a carbon atom. In conclusion, the barrier to internal rotation of a methyl group strongly depends on the presence of heteroatoms in the ring, since electronic effects are easily propagated in aromatic ring systems through the  $p$  electron conjugation. In this sense, the barrier of a methyl group can be considered as a direct measure for the electronic distribution within the attached ring. However, such interpretations are only intuitive and require proofs from more measurement data as well as theoretical calculations.

Due to the planar structure of all molecules shown in Fig. 3, the principal  $c$ -axis of inertia is collinear with one principal axis of the nitrogen coupling tensor, therefore enabling a direct comparison of the values of  $v_{cc}$  among these molecules. The values of  $v_{cc}$  can be classified into two groups, one with positive values, and the other with negative values. They reflect different bond situations of the nitrogen nucleus. If the nitrogen atom is bonded to a methyl group as in *N*-methylpyrrole (1) or a hydrogen atom as in 2MP (2), 3MP (3), and the case of N(1) in methylimidazoles (7–10), it donates two electrons to create the aromatic system, and  $v_{cc}$  is negative. In methylthiazoles (4–6) and methyloxazoles (11–13),  $v_{cc}$  has a positive value, as the nitrogen atom provides only one electron to the ring systems. Detailed interpretations concerning the field gradient at the site of the nitrogen atom are explained in Ref. [10].

## 6. Conclusion

The rotational spectra of 3MP were recorded using a molecular jet Fourier transform microwave spectrometer. Fine splittings arising from the internal rotation of the methyl group and hyperfine splittings from the  $^{14}\text{N}$  quadrupole coupling were observed and analyzed using the programs *XIAM* and *BELGI-C<sub>s</sub>-hyperfine*. While the program *XIAM* experienced some difficulties in reproducing the data set within the measurement accuracy, the *BELGI-C<sub>s</sub>-hyperfine* yielded satisfactory results. Highly accurate molecular parameters were obtained. Because the internal rotor axis accidentally coincides with the principal  $a$ -axis of inertia, a direct comparison of the *XIAM* and *BELGI-C<sub>s</sub>-hyperfine* parameters is possible. Comparison on the barrier height and the  $v_{cc}$  quadrupole coupling constant among a selection of nitrogen-containing aromatic five-membered rings has given insights into the dependence of these two parameters not only on the methyl position but also on the specific hetero-atom in the planar rings.

## CRedit authorship contribution statement

Thuy Nguyen: Conceptualization, Investigation, Writing - original draft, Visualization. Wolfgang Stahl: Conceptualization, Validation, Writing - review & editing, Supervision, Resources. Ha Vinh Lam Nguyen: Conceptualization, Formal analysis, Visualization, Validation, Writing - review & editing, Resources. Isabelle Kleiner: Software, Formal analysis, Validation, Writing - review & editing, Supervision, Resources.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jms.2020.111351>.

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