



HF–DFT calculations of ^{14}N and ^{35}Cl quadrupole coupling constants on optimized molecular structures of pyridine and the monochloropyridines

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Abstract

^{14}N and ^{35}Cl nuclear quadrupole coupling constants in the monochloropyridines and ^{14}N in pyridine have been determined in the principal axes of both the inertia and coupling constant tensors by HF–DFT calculations of the molecular electric field gradients on B3P86/6-31G(3d,3p) optimized molecular structures.

In the case of 4-chloropyridine, the calculated ^{14}N coupling constants are probably more accurate than the experimental values.

Investigation of the substitution effect shows that the differences in nitrogen nqccs between 2-chloropyridine and pyridine are largely due to the presence of the chlorine substituent (as opposed to distortion of the ring). The small differences found in 3-chloropyridine can be understood as due to near cancellation of effects due to the substituent and ring distortion. In 4-chloropyridine, on the other hand, these effects are additive, accounting for the differences for this molecule. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nuclear quadrupole coupling constants (nqcc) have been measured for both ^{14}N [1,3] and ^{35}Cl [1–9] in the monochloropyridines as a means for study of the substitution effects. However, only the diagonal components in the axes of the inertia tensor could be determined. For chlorine, because the angle between the C–Cl bond and the principal inertia a -axis and that between the C–Cl bond and the principal nqcc z -axis are both expected to be small, the inertia axes (a , b , c) are expected to be near coincidence with the nqcc axes (x , y , z). Thus, reasonably valid comparison may be

made of the nqccs among the different chlorine substitution sites (2, 3, and 4). For nitrogen, however, because of the differing orientation of the pyridine ring with respect to the inertia axes, only the components of the nqcc tensors perpendicular to the planes of the molecules are directly comparable.

To enable comparison of all components, we have undertaken calculation of the complete nqcc tensors for both nitrogen and chlorine in these molecules as well as for nitrogen in pyridine. The molecular structures are optimized, and the different optimization models assessed by calculation of the nqccs. On those structures where good agreement between the calculated and experimental nqccs is found for the diagonal components in the principal axes of the inertia tensor, it is assumed that the calculated off-diagonal

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components are equally accurate. These coupling constants are then transformed to the principal axes of the nqcc tensor.

The effect of chlorine substitution on the differences in nitrogen nqccs between the chloropyridines and pyridine is investigated within the framework of an approximation that separates the effect into two parts, ring distortion and the presence in the molecule of the substituent. Their separate contributions to the nqccs are estimated.

2. Nuclear quadrupole coupling constant

The nqcc is the spectroscopic measurement of the energy of interaction of the electric quadrupole moment of the nucleus of the atom with the gradient of the molecular electric field (efg) at the site of the nucleus. The components of the nqcc tensor χ_{ij} are related to those of the efg tensor q_{ij} by

$$\chi_{ij} = (eQ/h)q_{ij}, \quad (1)$$

where e is the proton electric charge, Q the electric quadrupole moment of the nucleus, and h is Planck's constant; $i, j = a, b, c$ (principle axes of the inertia tensor), or x, y, z (principle axes of the efg tensor).

An 'asymmetry parameter' that measures the degree of deviation from axial or cylindrical symmetry of the nqcc tensor is defined as

$$\eta = |(\chi_{xx} - \chi_{yy})/\chi_{zz}|. \quad (2)$$

With eQ/h taken as a best-fit parameter determined by linear regression analysis of the calculated efgs versus the experimental nqccs, the B3PW91/6-311+G(df,pd) model has been shown to yield accurate nitrogen nqccs for 39 molecules containing 45 nitrogen sites [10]. These calculations were made on the experimental structures. The residual standard deviation (RSD) was found to be 30 kHz (1.3% of the average absolute experimental nqcc), and eQ/h to be 4.5617(43) MHz/a.u. This model is applied here for calculation of the nitrogen nqccs.

For chlorine, the efgs were calculated using the B3LYP, B3P86, and B3PW91 methods with Pople type 6-31G and 6-311G bases, each augmented with different combinations of diffuse and polarization functions. These several models are assessed by linear

regression analyses of the calculated efgs versus the experimental nqccs for the monochloropyridines.

B3LYP is Becke's [11] hybrid Hartree–Fock theory/density functional theory method (HF–DFT) in conjunction with the correlation functional of Lee et al. [12,13]; B3P86 is Becke's method with the correlation functional of Perdew [14]; and B3PW91 is Becke's method with the correlation functional of Perdew and Wang [15].

All calculations were performed using the GAUSSIAN 94 package of programs [16].

3. Results

The experimental nitrogen and chlorine nqccs for pyridine [17] and the monochloropyridines [1–3] are

Table 1
Calculated and experimental ^{14}N and ^{35}Cl quadrupole coupling constants, χ_{ij} (MHz), in pyridine and the monochloropyridines. Calc. = B3PW91/6-311+G(df,pd) for N, and B3LYP/6-31+G(2df,3p) for Cl

Molecule	χ_{ij}	Calculated	Experimental	References
Pyridine	$\chi_{aa}(\text{N})$	−4.920	−4.908(5)	[17]
	$\chi_{bb}(\text{N})$	1.438	1.434(5)	
	$\chi_{cc}(\text{N})$	3.482	3.474(5)	
2-CP	$\chi_{aa}(\text{N})$	−0.087	−0.09(2)	[2]
	$\chi_{bb}(\text{N})$	−2.924	−2.94(2)	
	$\chi_{cc}(\text{N})$	3.012	3.03(3)	
	$\chi_{ab}(\text{N})$	−2.899		
3-CP	$\chi_{aa}(\text{N})$	+0.010	−0.009(13)	[1]
	$\chi_{bb}(\text{N})$	−3.483	−3.473(10)	
	$\chi_{cc}(\text{N})$	3.474	3.482(16)	
	$\chi_{ab}(\text{N})$	2.676		
4-CP	$\chi_{aa}(\text{N})$	−4.842	−4.81(1)	[3]
	$\chi_{bb}(\text{N})$	1.516	1.64(4)	
	$\chi_{cc}(\text{N})$	3.326	3.17(4)	
2-CP	$\chi_{aa}(\text{Cl})$	−70.385	−70.42(4)	[2]
	$\chi_{bb}(\text{Cl})$	39.714	39.69(2)	
	$\chi_{cc}(\text{Cl})$	30.671	30.73(4)	
	$\chi_{ab}(\text{Cl})$	0.226		
3-CP	$\chi_{aa}(\text{Cl})$	−72.263	−72.255(19)	[1]
	$\chi_{bb}(\text{Cl})$	38.427	38.500(13)	
	$\chi_{cc}(\text{Cl})$	33.836	33.755(23)	
	$\chi_{ab}(\text{Cl})$	−2.156		
4-CP	$\chi_{aa}(\text{Cl})$	−71.676	−71.65(2)	[3]
	$\chi_{bb}(\text{Cl})$	39.271	39.25(11)	
	$\chi_{cc}(\text{Cl})$	32.405	32.40(11)	

shown in Table 1. (The monochloropyridines are hereafter collectively referred to as MCPs, and separately as 2-, 3-, and 4-CP.)

3.1. Nitrogen

The molecular structures of pyridine and the MCPs were optimized using the B3LYP, B3P86, and B3PW91 methods with 6-31G bases augmented with polarization function combinations ranging from d,p to 3d,3p. On these structures, the B3PW91/6-311+G(df,pd) model was applied to calculation of the nitrogen efgs. In Table 2, the RSD and the slope eQ/h of the linear regression line are given as functions of optimization model. These data do not include 4-CP for which the calculated and experimental nqccs are rather different. The smaller RSDs are obtained with the B3P86 method and the smallest, 11.5 kHz (0.45% of the average absolute experimental nqcc), is obtained on the B3P86/6-31G(2d,2p) structures, for which $eQ/h = 4.5670(59)$ MHz/a.u. With the B3P86/6-31G(3d,3p) model, although the RSD is somewhat larger, namely 13.9 kHz (0.55%), eQ/h is 4.5621(71) MHz/a.u., which lies well within the standard error in the calibration value of 4.5617(43) MHz/a.u. This latter is therefore a little more compatible than the former with the experimental structures of the molecules used for calibration of the model. We choose for this reason to go forward with these structures.

The nqccs calculated on the B3P86/6-31G(3d,3p) structures are given along with the experimental values in Table 1. In the case of 4-CP, the calculated nqccs are probably more accurate than the experimental values. The experimental nqccs and uncertainties (in the last digit) given in Table 1, namely $-4.81(1)$, $1.64(4)$, and $3.17(4)$ MHz, are taken from the original work [3]. But in a subsequent publication by the same authors [1], the uncertainties appear to have been re-evaluated and are given as (3), (7), and (8), respectively.

Fig. 1 is a plot the calculated efgs versus the experimental nqccs. The open circles are 4-CP; the two points farthest from the line are those with the largest experimental uncertainties. The open squares are pyridine calculated on the experimental r_s structure of Mata et al. [18]. These are included to demonstrate graphically the agreement between the results for the optimized and experimental structures.

Table 2

Linear regression analysis of ^{14}N efgs versus experimental nqccs, RSD (kHz) and slope eQ/h (MHz/a.u.) as functions of optimization model, Method/Basis. Pyridine, 2-, and 3-chloropyridine

Basis	Method	Method		
		B3LYP	B3P86	B3PW91
6-31G(d,p)	RSD	40.0	19.9	23.8
	eQ/h	4.586	4.572	4.579
6-31G(2d,p)	RSD	27.1	11.7	14.8
	eQ/h	4.581	4.567	4.576
6-31G(2d,2p)	RSD		11.5	
	eQ/h		4.567	
6-31G(2d,3p)	RSD		12.1	
	eQ/h		4.568	
6-31G(3d,p)	RSD	27.9	14.4	17.4
	eQ/h	4.575	4.562	4.570
6-31G(3d,2p)	RSD		14.2	
	eQ/h		4.562	
6-31G(3d,3p)	RSD		13.9	
	eQ/h		4.562	

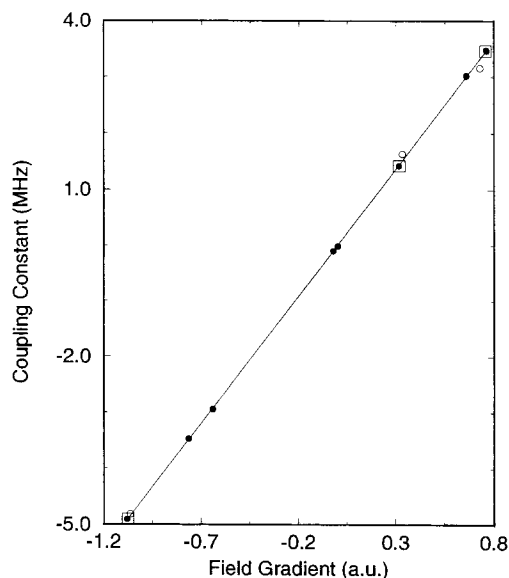


Fig. 1. B3PW91/6-311 + G(df,pd) efgs calculated on B3P86/6-31G(3d,3p) structures versus experimental nqccs. Open circles are 4-chloropyridine. Open squares are pyridine calculated on experimental r_s structure [18]. RSD = 13.9 kHz and eQ/h (slope) = 4.5621(71) MHz/a.u.

Table 3

Molecular structure parameters of pyridine, experimental and B3P86/6-31G(3d,3p) (Å and degrees). Experimental and calculated nqccs (MHz), root mean square (rms) difference

Parameter	r_o^a	r_s^b	r_s^c	B3P86
N(1)C(2)	1.3402	1.3402	1.3376	1.3337
C(2)C(3)	1.3970	1.3945	1.3938	1.3902
C(3)C(4)	1.3936	1.3944	1.3916	1.3885
C(2)H(2)	1.0843	1.0843	1.0865	1.0879
C(3)H(3)	1.0806	1.0805	1.0826	1.0845
C(4)H(4)	1.0811	1.0773	1.0818	1.0851
C(6)N(1)C(2)	117.05	116.83	116.94	117.04
N(1)C(2)C(3)	123.72	123.88	123.80	123.79
C(2)C(3)C(4)	118.49	118.53	118.53	118.44
C(3)C(4)C(5)	118.52	118.33	118.40	118.51
N(1)C(2)H(2)	116.12	115.88	116.01	115.94
C(2)C(3)H(3)	120.00	121.30	120.12	120.24
C(3)C(4)H(4)	120.74	120.83	120.80	120.75
<i>Experimental</i> ^d	<i>Calculated</i>			
χ_{aa} -4.908(3)	-4.915	-4.892	-4.908 ^e	-4.920
χ_{bb} 1.434(3)	1.468	1.452	1.450	1.438
χ_{cc} 3.474(3)	3.446	3.440	3.458	3.482
Rms	0.026	0.024	0.013	0.009

^a Ref. [2].^b Ref. [19].^c Ref. [18].^d Ref. [17].^e Ref. [10].

The B3P86/6-31G(3d,3p) structure parameters for pyridine are given in Table 3 along with the experimental parameters of Meyer et al. [2], Bak et al. [19], and Mata et al. With these several structures are given the nqccs calculated on each, and for each the root mean square (rms) difference between the calculated and experimental nqccs. The smaller rms differences are found for the Mata et al. and B3P86 structures; namely 13 and 9 kHz, respectively.

The B3P86/6-31G(3d,3p) structure parameters for 2-, 3-, and 4-CP are given in Table 4. Atomic numbering is described in Fig. 2.

3.2. Chlorine

On the B3P86/6-31G(3d,3p) structures, the efgs were calculated at the sites of the chlorine nuclei in the MCPs. The results of linear regression analyses of the several models are presented in Table 5, where the RSD is given as a function of model. To put these

Table 4

B3P86/6-31G(3d,3p) structure parameters of the monochloropyridines (Å and degrees); X = H or Cl

Parameter	2-CP	3-CP	4-CP
C(6)N(1)	1.3359	1.3332	1.3328
N(1)C(2)	1.3169	1.3298	1.3328
C(2)C(3)	1.3929	1.3921	1.3899
C(3)C(4)	1.3856	1.3873	1.3875
C(4)C(5)	1.3908	1.3878	1.3875
C(5)C(6)	1.3870	1.3896	1.3899
C(2)X(2)	1.7394	1.0866	1.0875
C(3)X(3)	1.0825	1.7301	1.0829
C(4)X(4)	1.0848	1.0836	1.7286
C(5)H(5)	1.0836	1.0842	1.0829
C(6)H(6)	1.0869	1.0870	1.0875
C(6)N(1)C(2)	117.00	117.83	116.85
N(1)C(2)C(3)	124.91	122.61	124.22
C(2)C(3)C(4)	117.21	119.58	117.54
C(3)C(4)C(5)	119.16	117.72	119.65
C(4)C(5)C(6)	118.17	118.80	117.54
C(5)C(6)N(1)	123.54	123.45	124.22
N(1)C(2)X(2)	116.61	117.33	116.18
C(2)C(3)X(3)	120.56	119.81	121.29
C(3)C(4)X(4)	120.05	120.48	120.18
C(4)C(5)H(5)	121.42	120.70	121.17
C(5)C(6)H(6)	120.82	120.50	119.60

RSDs in perspective, 100 kHz corresponds to about 0.2% of the average absolute experimental nqcc. For the 6-31G models, with few exceptions, the RSDs are less than 1%, whereas for the 6-311G models, the RSDs are all greater than 2%.

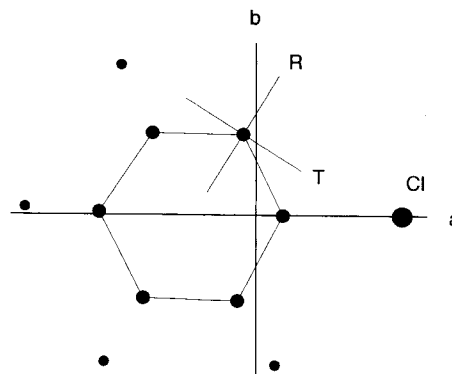


Fig. 2. 2-Chloropyridine. *R* and *T*, centered on N(1), are the in-plane principal axes of the nqcc tensor. Carbon atoms are numbered clockwise C(2), C(3), etc.

Table 5

Linear regression analysis of ^{35}Cl efgs versus experimental nqccs. RSD (kHz) as function of model, method/basis, for calculation of efgs on the B3P86/6-31G(3d,3p) optimized structures of the monochloropyridines

Basis	Method		
	B3LYP	B3P86	B3PW91
6-31+G(d,p)	82	131	121
(2d,p)	58	107	88
(3d,p)	704	837	829
(df,p)	134	110	122
(2df,p)	90	70	76
(3df,p)	592	719	714
6-31+G (2d)	84	85	85
6-31G (2d,p)	202	266	255
6-31++G(2d,p)	76	158	134
6-31+G (2d,2p)	70	147	119
(2d,3p)	84	175	147
6-31G (2df,p)	178	217	216
6-31+G (2df)	126	83	104
(2df,2p)	56	93	76
(2df,3p)	51	122	100
(2df,pd)	105	122	123
6-311G	1188	1126	1185
6-311G (d,p)	1360	1328	1393
6-311+G(2d,p)	1307	1275	1354
(2df,p)	1306	1269	1348

The least RSD, namely 51.1 kHz (0.11%), is obtained with the B3LYP/6-31+G(2df,3p) model, for which $eQ/h = -18.9642(64)$ MHz/a.u., and the correlation coefficient is 0.9999996. Q_{eff} , defined as $(eQ/h)/234.9649$, is $-80.71(3)$ mb, which differs from the most recent high-level calculation [20] of $Q(^{35}\text{Cl})$ of $-81.65(80)$ mb by 1.2%. The calculated nqccs are given in Table 1, along with the experimental values.

With the more efficient B3LYP/6-31+G(2d,p) model, the RSD is 58.5 kHz (0.12%), the correlation coefficient is 0.9999995, and eQ/h is $-19.3281(75)$ MHz/a.u. Q_{eff} for this model is $-82.26(3)$ mb, which differs from $Q(^{35}\text{Cl})$ by 0.8%, and lies within the given uncertainty.

4. Principal values and principal axes of the nqcc tensor

In Table 6, the B3LYP/6-31+G(2df,3p) chlorine

Table 6

Calculated ^{35}Cl quadrupole coupling constants (MHz), on B3P86/6-31G(3d,3p) structures, in the principal axes of the nqcc tensor. The y -axis is perpendicular to the plane of the molecule. Angles in degrees

Parameter	2-CP	3-CP	4-CP
χ_{xx}	39.714	38.469	39.271
χ_{yy}	30.671	33.836	32.405
χ_{zz}	-70.385	-72.305	-71.676
η	0.128	0.064	0.096
$\angle z, \text{CCl}$	0.16	0.19	0 ^a
$\angle a, \text{CCl}$	0.28	1.30	0 ^a
$\angle z, a$	0.12	1.12	0 ^a

^a Symmetry.

nqccs and asymmetry parameters are given in the principal x -, y -, and z -axes of the nqcc tensor. The y -axis is chosen perpendicular to the plane of the molecule, and the z -axis 'coincident' with the C–Cl bond direction, where $\angle z, \text{CCl}$ is the angle of deviation from coincidence. In 2-CP, $\chi_{zz} = -70.385$ MHz, $\eta = 0.128$, and $\angle z, \text{CCl} = 0.16^\circ$; in 3-CP, $\chi_{zz} = -72.305$ MHz, $\eta = 0.064$, and $\angle z, \text{CCl} = 0.19^\circ$; and in 4-CP, $\chi_{zz} = -71.676$ MHz, $\eta = 0.096$, and $\angle z, \text{CCl} = 0^\circ$ (by symmetry). The assumption of near coincidence of the principal axes of the inertia and nqcc tensors is seen to be reasonable; in 2-CP, $\angle z, a = 0.12^\circ$, and in 3-CP, it is 1.12° .

In Table 7, the nitrogen nqccs are given in the principal axes of the nqcc tensor. The axes, in this case, are described according to a scheme introduced by Palmer [21]. They are labeled R , T , and II . The R -axis is 'radial' and deviates from the external bisector of $\angle \text{CNC}$ by an angle α , T is 'tangent to the arc' formed by the CNC atoms, and II (equivalent to the

Table 7

Calculated ^{14}N quadrupole coupling constants (MHz), on B3P86/6-31G(3d,3p) structures, in the principal axes of the nqcc tensor. α (degrees) is the angle between the R -axis and the external bisector of $\angle \text{CNC}$

Parameter	2-CP	3-CP	4-CP	Pyridine
χ_R	-4.733	-4.932	-4.842	-4.920
χ_T	1.722	1.459	1.516	1.438
χ_{II}	3.012	3.474	3.326	3.482
α	0.20	1.15	0 ^a	0 ^a

^a Symmetry.

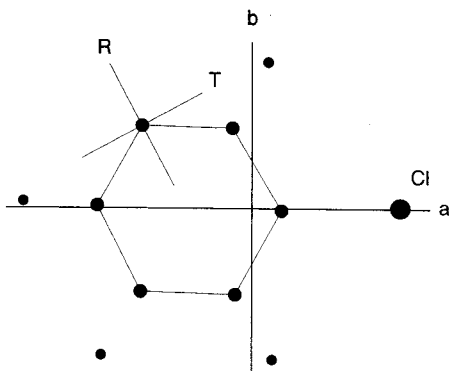


Fig. 3. 3-Chloropyridine. *R* and *T*, centered on N(1), are the in-plane principal axes of the nqcc tensor. Carbon atoms are numbered clockwise C(2), C(3), etc.

c-axis) is perpendicular to the plane of the molecule. The nqccs in 2-CP differ most from those in pyridine. In 3-CP, Heineking and Dreizler [1] note that χ_{cc} (χ_{II}) is equal (within the error limits) to the value found in pyridine and that there is, therefore, no detectable effect due to chlorine substitution. As shown in Table 7, the nqccs are all three about equal to those in pyridine, the largest difference being 0.021 MHz (1.5%) for χ_T .

The B3P86/6-31G(3d,3p) structures of 2- and 3-CP are shown in Figs. 2 and 3, respectively. *R* and *T*, centered on the nitrogen atom, are the in-plane principal axes of the nqcc tensor. In 2-CP, $\alpha = 0.20^\circ$ away from the chlorine atom; in 3-CP, $\alpha = 1.15^\circ$ toward the chlorine atom.

5. Discussion

5.1. Pyridine ring distortion

The nature and degree of distortion of the pyridine ring can be seen in the data given in Table 8. In this table are given the differences between the regular pyridine ring bond lengths and angles (Table 3, B3P86) and the corresponding bond lengths and angles for the MCPs (Table 4). The former is subtracted from the latter. Thus, compared with pyridine, a positive (negative) difference corresponds to a longer (shorter) bond length or larger (smaller) angle.

In 2-CP, the bond lengths are seen to be alternately

Table 8

Differences in ring bond lengths and angles between the monochloropyridines and pyridine. Compared with pyridine, + (–) is a longer (shorter) bond length or larger (smaller) angle. B3P86/6-31G(3d,3p) structures (Å and degrees)

Parameter	2-CP	3-CP	4-CP
C(6)N(1)	+0.0022	–0.0005	–0.0009
N(1)C(2)	–0.0168	–0.0039	–0.0009
C(2)C(3)	+0.0027	+0.0019	–0.0003
C(3)C(4)	–0.0029	–0.0012	–0.0010
C(4)C(5)	+0.0023	–0.0007	–0.0010
C(5)C(6)	–0.0032	–0.0006	–0.0003
C(6)N(1)C(2)	–0.04	+0.79	–0.19
N(1)C(2)C(3)	+1.12	–1.18	+0.43
C(2)C(3)C(4)	–1.23	+1.14	–0.90
C(3)C(4)C(5)	+0.65	–0.79	+1.14
C(4)C(5)C(6)	–0.27	+0.36	–0.90
C(5)C(6)N(1)	–0.25	–0.34	+0.43

longer and shorter than in pyridine, whereas in 3- and 4-CP, with one exception the bond lengths are all shorter. The differences are greatest in 2-CP, least in 4-CP. The perimeter of the ring compared with pyridine, is -0.0157 \AA for 2-CP, -0.0050 \AA for 3-CP, and -0.0044 \AA for 4-CP. In each case the ring is contracted, and is contracted most in 2-CP. In both 2- and 3-CP, the largest single difference is the N(1)C(2) bond length, -0.0168 and -0.0039 \AA , respectively. In 3-CP, the distortion is somewhat one-sided, with larger differences for N(1)C(2), C(2)C(3), and C(3)C(4) than for C(4)C(5), C(5)C(6), and C(6)N(1). The larger distortion is on the side of the substituent.

Differences in interatomic angles at the sites of the substitution are essentially the same for each; that is, $+1.12^\circ$, $+1.14^\circ$, and $+1.14^\circ$ for 2-, 3- and 4-CP, respectively. The adjacent interatomic angles, on either side of the substitution site, are smaller (negative). Thus, the rings are somewhat flattened (pushed-in) at these sites.

5.2. Quadrupole coupling

The principal values of the nitrogen nqccs in the MCPs differ most from those in pyridine in the case of 2-CP. This is a consequence, one would assume, of the degree of distortion of the pyridine ring, particularly with regard to the nitrogen–carbon bond lengths, and

of the proximity to the nitrogen atom of the chlorine substituent.

The differences in nqccs between 2-CP and pyridine are $(\Delta\chi_R, \Delta\chi_T, \Delta\chi_{II}) = (0.187, 0.284, -0.470 \text{ MHz})$. An estimate of the contribution of the distortion of the ring to these differences was made by calculation of the nqccs on a 2-CP structure consisting of a regular pyridine ring (Table 3, B3P86) with Cl(2) substituted for H(2) using the C(2)Cl(2) and N(1)C(2)Cl(2) parameters for 2-CP (Table 4). The result is $\chi_R = -4.766$, $\chi_T = 1.760$, and $\chi_{II} = 3.006 \text{ MHz}$. The differences between these nqccs and those calculated on the ring distorted structure of 2-CP (Table 4) are $(0.033, -0.038, -0.006 \text{ MHz})$, which cannot at all account for the differences between 2-CP and pyridine. The larger remaining part, therefore, is presumably due to the presence in the molecule of the chlorine substituent. This part is $(0.154, 0.322, -0.464 \text{ MHz})$.

In the case of 3-CP, the differences are $(-0.012, 0.021, 0.008 \text{ MHz})$. On a 3-CP structure with a regular pyridine ring the nqccs are $\chi_R = -4.838$, $\chi_T = 1.426$, and $\chi_{II} = 3.411 \text{ MHz}$. Thus, the differences in nqccs calculated with and without distortion are $(-0.094, 0.033, 0.063 \text{ MHz})$, which more than account for the small differences between 3-CP and pyridine. Thus, the chlorine contribution must be similar in magnitude but opposite in algebraic sign, namely $(0.084, -0.012, -0.055 \text{ MHz})$.

In 4-CP compared with pyridine, the differences in nqccs are $(0.078, 0.078, -0.156 \text{ MHz})$. On a structure with a regular pyridine ring, the nqccs are $\chi_R = -4.887$, $\chi_T = 1.508$, and $\chi_{II} = 3.379 \text{ MHz}$. The ring distortion contribution is therefore estimated to be $(0.045, 0.008, -0.053 \text{ MHz})$; and the chlorine contribution, accounting for the remaining part of the difference, is $(0.033, 0.070, -0.103 \text{ MHz})$. In this case the separate contributions are seen to be additive.

6. Summary

Excellent agreement between the calculated and experimental nqccs for both ^{14}N and ^{35}Cl in pyridine and the MCPs is obtained on molecular structures optimized with the B3P86/6-31G(3d,3p) model. For calculation of the nqccs for nitrogen, the B3PW91/6-311+G(df,pd) model was employed, and for chlorine, the B3LYP/6-31+G(2df,3p) model.

In the case of 4-CP, the calculated nitrogen nqccs are probably more accurate than the experimental values.

Complete nitrogen and chlorine nqcc tensors are given in the principal axes of both the inertia and nqcc tensors.

As for substitution effects, the differences between the nqccs for 2-CP and pyridine are estimated to be largely due to the chlorine substituent, with surprisingly little contribution from distortion of the ring.

The near equivalence of the nqccs for 3-CP and pyridine can be understood as due to near cancellation of the effects of the chlorine substituent and ring distortion.

In 4-CP, on the other hand, these effects are additive, accounting for the differences for this molecule.

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