

Calculation of ^{14}N and ^{35}Cl quadrupole coupling constants on optimized molecular structures of pyrimidine, 2-X- and 5-X-pyrimidine, with X = F, Cl, Br, and CN

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Abstract

$^{14}\text{N}(1,3)$ quadrupole coupling constants (nqcc's) were calculated on B3P86/6-31G(3d,3p) optimized molecular structures of pyrimidine (PRM), 2-X-PRM, and 5-X-PRM, with X = F, Cl, Br, and CN.

For PRM, the root mean square difference between calculated and experimental nqcc's is 6 kHz (0.3%).

For 2-F-PRM, the calculated value of -5.254 MHz for $(\chi_{bb} - \chi_{cc})$ lies within the rather large uncertainty ($\approx 1\%$) in the experimental value. Hyperfine structure due to χ_{aa} was unresolved – its calculated value is -0.062 MHz.

In the remaining molecules, for which no experimental data are available, nitrogen nqcc's are predicted. In the Cl-PRMs, ^{35}Cl nqcc's are predicted.

In the halogen substituted PRMs, differences in nqcc's correlate with differences in carbon–halogen bond lengths. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pyrimidine; ^{14}N ; ^{35}Cl ; Nuclear quadrupole coupling constant; NQCC

1. Introduction

The results of a comprehensive investigation of the rotational spectrum of pyrimidine (PRM) over a broad range of frequencies have recently been reported by Kisiel et al. [1]. Complete heavy atom r_s and r_o molecular structures were determined, as well as the complete ^{14}N quadrupole coupling constant (nqcc) tensor. The diagonal nqcc's χ_{aa} , χ_{bb} , and χ_{cc} represent an improvement in accuracy over previously reported values [2], while the off-

diagonal component χ_{ab} was determined for the first time.

Microwave spectra of 2-fluoropyrimidine (2-F-PRM) and 2-bromopyrimidine (2-Br-PRM) were investigated by Chen et al. [3,4]. These are shown to be planar molecules with C_{2v} symmetry. In 2-F-PRM [3], the asymmetry in the nitrogen nqcc tensor $(\chi_{bb} - \chi_{cc})$ was measured, but hyperfine splitting due to χ_{aa} was unresolved. In 2-Br-PRM [4], nitrogen nqcc's were not determined.

In this work, assuming planarity with C_{2v} symmetry, B3P86/6-31G(3d,3p) optimized molecular structures were determined of PRM, and 2-X-pyrimidine (2-X-PRM) and 5-X-pyrimidine (5-X-PRM), with X = F, Cl, Br, and CN. ^{14}N nqcc's

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were calculated on these structures, as well as on the r_s and r_o structures of PRM. ^{35}Cl nqcc's were calculated in the Cl-PRMs.

Reliable calculation of the nqcc's, when compared with accurate experimental nqcc's, provides for assessment of different structure types of a given molecule – in this case, PRM.

2. Method

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 is 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 in Eq. (1) determined by least-squares linear regression analysis of the calculated efg's versus the experimental nqcc's, the B3PW91/6-311+G(df,pd) model for calculation of the efg's has been shown to yield accurate nqcc's on the experimental structures of 39 molecules containing 45 inequivalent nitrogen sites. With $eQ/h = @4.5617(43)$ MHz/a.u., the root mean square (rms) difference between the calculated and experimental nqcc's was found to be 30 kHz (1.3% of the average absolute experimental nqcc) [5].

Accurate nitrogen nqcc's were recently calculated using this model on B3P86/6-31G(3d,3p) optimized molecular structures of pyridine and the monochloropyridines (MCP). In addition, accurate results were obtained for chlorine in the MCPs using the B3LYP/6-31+G(2df,3p) model for calculation of the efg's, and $eQ/h = -18.9642(64)$

MHz/a.u. for conversion of the efg's to nqcc's [6]. The current investigation follows along these lines.

B3LYP is Becke's [7] hybrid Hartree–Fock theory/density functional theory method (HF-DFT) in conjunction with the correlation functional of Lee et al. [8,9]; B3P86 is Becke's method with the correlation functional of Perdew [10]; and B3PW91 is Becke's method with the correlation functional of Perdew and Wang [11].

All calculations were performed using the GAUSSIAN 94 package of programs [12].

3. Results

3.1. Pyrimidine

The PRM molecule is shown in Fig. 1. The nitrogen atoms are numbered 1 and 3, the carbon atoms are numbered accordingly.

In Table 1 the experimental heavy atom r_s and r_o structure parameters are compared with the B3P86/6-31G(3d,3p) optimized parameters. The B3P86/6-31G(3d,3p) structure is hereafter referred

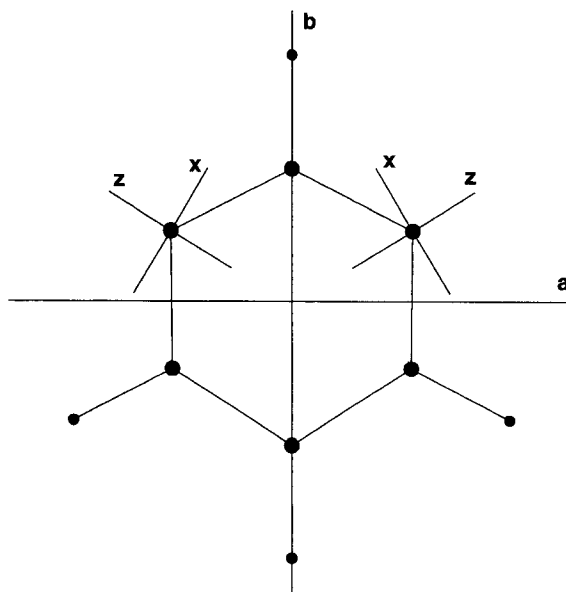


Fig. 1. PRM – x and z , centered on N(1,3) are the in-plane principal axes of the nqcc tensor. Carbon and hydrogen atoms are numbered accordingly.

Table 1
PRM – experimental (r_s and r_o) and B3P86/6-31G(3d,3p) (r_{opt}) structure parameters (Å and degrees)^a

Parameter	r_s [Å]	r_o [Å]	r_{opt}
C(2)N(3)	1.337(2)	1.338(4)	1.3320
N(3)C(4)	1.332(3)	1.339(5)	1.3330
C(4)C(5)	1.393(3)	1.393(4)	1.3877
C(2)H(2)			1.0876
C(4)H(4)			1.0879
C(5)H(5)			1.0835
N(1)C(2)N(3)	127.2(3)	127.4(4)	127.39
C(2)N(3)C(4)	115.8(3)	115.7(4)	115.69
N(3)C(4)C(5)	122.4(3)	122.3(4)	122.40
C(4)C(5)C(6)	116.4(2)	116.3(3)	116.44
C(5)C(4)H(4)			121.18
Experimental [1]	Calculated	Calculated	Calculated
$\chi_{aa} = -3.1004(7)$	-3.073	-3.139	-3.106
$\chi_{bb} = -0.2554(7)$	-0.286	-0.148	-0.258
$\chi_{cc} = 3.3558(7)$	3.360	3.288	3.364
$\chi_{ab} = \pm 2.76(7)$	± 2.740	± 2.703	± 2.716
rms ^b	0.024	0.077	0.006

^a Experimental and B3PW91/6-311+G(df,pd) calculated ¹⁴N quadrupole coupling constants (MHz). For calculation of the coupling constants on the experimental structures, the CH bond lengths and CCH angle were set to the r_{opt} values.

^b Root mean square difference between calculated and experimental diagonal coupling constants.

to as r_{opt} . The experimental nitrogen nqcc's are given along with those calculated on each of the three structures and, for each, the rms difference between the calculated and experimental diagonal nqcc's.

For calculations on the experimental structures, the CH bond lengths and CCH angle were set to the r_{opt} values. Linear regression analysis of the calculated efg's versus the experimental nqcc's was made with PRM added to the molecules of Ref. [5]. With the r_s structure, the overall rms difference between calculated and experimental nqcc's is 30 kHz, and eQ/h is 4.5620(42) MHz/a.u. This result is the same as that obtained without PRM – the slight difference in eQ/h is not significant. For PRM, the rms difference is 24 kHz, which is agreeable with the overall rms difference. With the r_o structure, on the other hand, analyzed as above, the PRM rms difference is 77 kHz. Comparison of the r_s and r_o structure parameters shows that the only substantial difference between the two is the

N(3)C(4) bond lengths, which differ by 0.007 Å. The nqcc calculations argue for the shorter r_s value.

For the r_{opt} structure, the calculated efg's in PRM are combined with those for the r_{opt} structures of pyridine, 2-MCP, and 3-MCP [6]. Fig. 2 is a plot of the efg's versus the experimental nqcc's for these four molecules. The residual standard deviation (RSD) is 12 kHz (0.5%) (rms = 11 kHz), and eQ/h is 4.5594(56) MHz/a.u. This value of eQ/h is essentially the same as the above, and shows that these r_{opt} structures are agreeable with the experimental structures. For PRM, the rms difference between the calculated and experimental nqcc's is 6 kHz (0.3%).

Comparison of the r_s and r_{opt} structure parameters suggests that the r_s values of the C(2)N(3) and C(4)C(5) bond lengths are too long each by perhaps as much as 0.005 Å.

Principal values of the calculated nqcc tensor are compared with the experimental results in Table 2. Orientation and labeling of the principal axes are shown in Fig. 1. In Table 2, $\theta_{str,a}$ is the

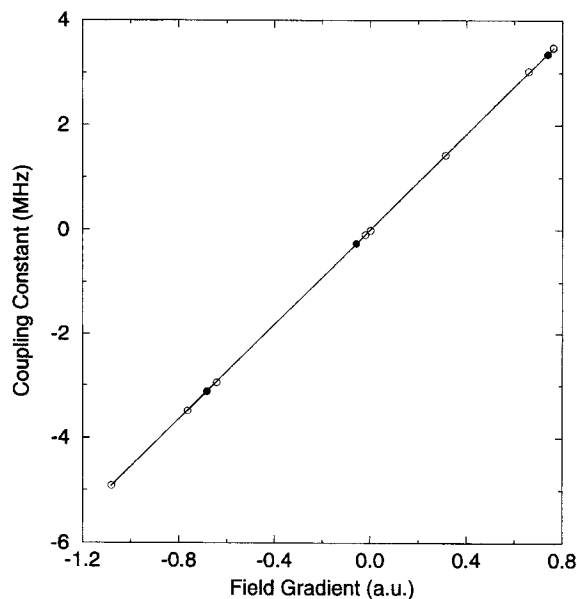


Fig. 2. B3PW91/6-311+G(df,pd) efg's calculated on B3P86/6-31G(3d,3p) (r_{opt}) molecular structures versus experimental nqcc's. Open circles are pyridine, 2-chloropyridine, and 3-chloropyridine [6]. Solid circles are PRM. RSD = 12.2 kHz. eQ/h (slope) = 4.5594(56) MHz/a.u.

Table 2

PRM – calculated and experimental ^{14}N nuclear quadrupole coupling constants (MHz) in the principal axes of the coupling constant tensor^a

	Calculated	Experimental [1]
χ_{zz}	–4.749	–4.78(6)
χ_{xx}	1.385	1.43(6)
$\chi_{yy} = \chi_{cc}$	3.364	3.3558(7)
θ_{za}	31.2	31.4(3)
$\theta_{str,a}$	31.5 ^b	31.5(2) ^c

^a Calculated = B3PW91/6-311+G(df,pd) with $eQ/h = 4.5594$ (56) MHz/a.u. θ_{za} (deg) is angle between z -axis of coupling constant tensor and the a -axis of the inertia tensor. $\theta_{str,a}$ (deg) is the angle between the $\angle\text{NCN}$ bisector and the a -axis.

^b B3P86/6-31G(3d,3p) structure, r_{opt} .

^c r_s structure.

angle between the $\angle\text{NCN}$ bisector and the a -axis. It is 31.5° for both r_{opt} and r_s structures. θ_{za} is the angle between the z -principal axis of the nqcc tensor and the a -axis. It is 31.2° for the calculated nqcc's, and 31.4° for the experimental nqcc's. Deviation of the z -axis from the bisector is, therefore, 0.3° for the calculated nqcc's on the r_{opt} structure, and $0.1(3)^\circ$ for the experimental nqcc's on the r_s structure.

The principal values of the nitrogen nqcc tensor may be compared with the experimental results for pyridine [13]: χ_{zz} is -4.749 MHz in PRM compared with $-4.908(3)$ MHz in pyridine, χ_{xx} is 1.385 MHz compared with $1.434(3)$ MHz, and χ_{yy} is 3.364 MHz compared with $3.474(3)$ MHz. It is seen that the nqcc's in PRM are uniformly about 3.3% smaller in magnitude than the corresponding coupling constants in pyridine.

3.2. Substituted pyrimidines

The r_{opt} structure parameters are given for 2-X-PRM in Table 3, and for 5-X-PRM in Table 4.

Calculated N(1,3) nqcc's in both the principal inertial axes and principal quadrupolar axes are given in Table 5. In the substituted PRMs, the inertial a - and b -axes are interchanged with respect to PRM (Fig. 1). Therefore, to provide direct comparison with PRM, $\theta_{str,b}$ in Table 5 is the angle between the $\angle\text{NCN}$ bisector and the b -axis, and θ_{zb} is the angle between the z - and b -axes.

Table 3

2-X-PRM, where X = F, Cl, Br, and CN. B3P86/6-31G(3d,3p) structure parameters (Å and degrees)^a

Parameter	2-F-PRM	2-Cl-PRM	2-Br-PRM	2-CN-PRM
C(2)N(3)	1.3178	1.3240	1.3226	1.3332
N(3)C(4)	1.3338	1.3332	1.3334	1.3310
C(4)C(5)	1.3876	1.3874	1.3868	1.3885
C(2)X(2)	1.3234	1.7305	1.8779	1.4457
C(4)H(4)	1.0871	1.0872	1.0870	1.0871
C(5)H(5)	1.0823	1.0826	1.0827	1.0830
N(1)C(2)N(3)	129.64	128.43	128.32	127.90
C(2)N(3)C(4)	114.58	115.17	115.28	115.36
N(3)C(4)C(5)	122.46	122.51	122.47	122.36
C(4)C(5)C(6)	116.28	116.20	116.18	116.65
C(5)C(4)H(4)	121.48	121.52	121.47	121.41

^a For 2-CN-PRM, X = C (cyano) where CN = 1.1556 Å.

Table 4

5-X-PRM, where X = F, Cl, Br, and CN. B3P86/6-31G(3d,3p) structure parameters (Å and degrees)^a

Parameter	5-F-PRM	5-Cl-PRM	5-Br-PRM	5-CN-PRM
C(2)N(3)	1.3319	1.3317	1.3310	1.3328
N(3)C(4)	1.3308	1.3302	1.3294	1.3268
C(4)C(5)	1.3843	1.3891	1.3886	1.3979
C(2)H(2)	1.0862	1.0868	1.0859	1.0869
C(4)H(4)	1.0871	1.0867	1.0866	1.0869
C(5)X(5)	1.3351	1.7235	1.8691	1.4238
N(1)C(2)N(3)	127.12	127.09	126.91	127.20
C(2)N(3)C(4)	116.38	116.30	116.31	116.19
N(3)C(4)C(5)	120.68	121.33	121.64	121.93
C(4)C(5)C(6)	118.76	117.66	117.20	116.55
C(5)C(4)H(4)	120.87	120.96	120.84	120.62

^a For 5-CN-PRM, X = C (cyano) where CN = 1.1578 Å.

Chen et al. report for 2-F-PRM a small (unresolved) value of χ_{aa} , and $(\chi_{bb} - \chi_{cc}) = (-)5.206(57)$ MHz (the negative sign is here inserted, its absence in Ref. [3] appears to be an error in the text). The calculated values are $\chi_{aa} = -0.062$ MHz, and $(\chi_{bb} - \chi_{cc}) = -5.254$ MHz. This latter lies within the rather large uncertainty in the experimental value.

Calculated cyano nitrogen nqcc's are given in Table 6 along with, for comparison, the experimental values for benzonitrile [14]. In 5-CN-PRM, the nqcc's are similar to those in benzonitrile,

Table 5

$^{14}\text{N}(1,3)$ quadrupole coupling constants (MHz) in the substituted PRMs. θ_{zb} (deg) is angle between z -axis of coupling constant tensor and the b -axis of the inertia tensor^a

	2-F-PRM ^b	2-Cl-PRM	2-Br-PRM	2-CN-PRM
χ_{aa}	−0.062	−0.084	−0.053	−0.366
χ_{bb}	−2.596	−2.824	−2.909	−2.966
χ_{cc}	2.658	2.908	2.962	3.332
χ_{ab}	±2.804	±2.885	±2.878	±2.893
χ_{zz}	−4.406	−4.648	−4.693	−4.837
χ_{xx}	1.748	1.740	1.731	1.506
$\chi_{yy} = \chi_{cc}$	2.658	2.908	2.962	3.332
θ_{zb}	32.8	32.3	31.8	32.9
$\theta_{\text{str},b}$	32.1	31.8	31.8	31.6
	5-F-PRM	5-Cl-PRM	5-Br-PRM	5-CN-PRM
χ_{aa}	−0.112	−0.138	−0.123	−0.242
χ_{bb}	−3.263	−3.212	−3.217	−3.144
χ_{cc}	3.375	3.351	3.340	3.386
χ_{ab}	±2.732	±2.691	±2.671	±2.731
χ_{zz}	−4.841	−4.775	−4.757	−4.785
χ_{xx}	1.466	1.424	1.416	1.399
$\chi_{yy} = \chi_{cc}$	3.375	3.351	3.340	3.386
θ_{zb}	30.0	30.1	30.0	31.0
$\theta_{\text{str},b}$	31.8	31.7	31.6	31.7

^a $\theta_{\text{str},b}$ (deg) is the angle between the $\angle\text{NCN}$ bisector and the b -axis.

^b $\chi_{bb} - \chi_{cc} = -5.254$ MHz compared with experimental value of $-5.206(57)$ MHz [3].

Table 6

Cyano ^{14}N quadrupole coupling constants (MHz) in 2- and 5-cyanopyrimidine (2-CN-PRM and 5-CN-PRM)^a

	2-CN-PRM	5-CN-PRM	$\text{C}_6\text{H}_5\text{CN}$ [14]
$\chi_{zz} = \chi_{aa}$	−4.481	−4.369	−4.244(4)
$\chi_{xx} = \chi_{bb}$	2.009	2.362	2.290(5)
$\chi_{yy} = \chi_{cc}$	2.472	2.006	1.954(5)
η	+0.103	−0.082	−0.079

^a Experimental coupling constants in benzonitrile, $\text{C}_6\text{H}_5\text{CN}$. $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

Table 7

^{35}Cl quadrupole coupling constants (MHz) in 2- and 5-chloropyrimidine (2-Cl-PRM and 5-Cl-PRM)^a

	2-Cl-PRM	5-Cl-PRM	4-MCP [16]	$\text{C}_6\text{H}_5\text{Cl}$ [17]
$\chi_{zz} = \chi_{aa}$	−71.66	−73.56	−71.65(2)	−71.241(7)
$\chi_{xx} = \chi_{bb}$	42.83	39.07	39.25(11)	38.237(10)
$\chi_{yy} = \chi_{cc}$	28.83	34.50	32.40(11)	33.005(10)
η	−0.195	−0.062	−0.096	−0.073

^a Experimental coupling constants in 4-monochloropyridine (4-MCP) and chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$); $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

reflecting similar atomic environments. Furthermore, the CN bond lengths compare favorably. Bak et al. [15] determined an r_s structure of benzonitrile in which the CN bond length is 1.159(2) Å. In the r_{opt} structure of 5-CN-PRM, it is 1.1578 Å. In 2-CN-PRM, on the other hand, the nqcc's – particularly χ_{xx} and χ_{yy} , and therefore the asymmetry parameter η – are quite different from 5-CN-PRM (and benzonitrile). The r_{opt} value of the CN bond length is notably shorter than in 5-CN-PRM, namely 1.1556 Å; and C(2)C(CN) is appreciable longer than C(5)C(CN), that is 1.4457 Å compared with 1.4238 Å.

In Table 7, calculated chlorine nqcc's are given along with the experimental values for 4-MCP [16] and chlorobenzene [17]. As above, the nqcc's in 5-Cl-PRM, 4-MCP, and chlorobenzene are similar, and differ from those in 2-Cl-PRM, particularly with regard to η . In chlorobenzene, Michel et al. [18] report an r_s structure in which CCl is 1.7248(1) Å. In 5-Cl-PRM, the r_{opt} value of CCl is similar, namely 1.7235 Å. In 2-Cl-PRM, it is somewhat longer, namely, 1.7305 Å.

4. Discussion

The effects of substitution on the N(1,3) nqcc's are shown in Table 8, wherein the nqcc's in PRM are subtracted from the corresponding nqcc's in the

Table 8
Effects of substitution on the N(1,3) quadrupole coupling constants, χ^a

	2-F-PRM	2-Cl-PRM	2-Br-PRM	2-CN-PRM
$\Delta\chi_{zz}$	0.343	0.101	0.056	-0.088
$\Delta\chi_{xx}$	0.363	0.355	0.346	0.121
$\Delta\chi_{yy}$	-0.706	-0.456	-0.402	-0.032
	5-F-PRM	5-Cl-PRM	5-Br-PRM	5-CN-PRM
$\Delta\chi_{zz}$	-0.092	-0.026	-0.008	-0.036
$\Delta\chi_{xx}$	0.081	0.039	0.031	0.014
$\Delta\chi_{yy}$	0.011	-0.013	-0.024	0.022

^a $\Delta\chi(\text{MHz}) = \chi$ in the substituted PRMs minus χ in PRM.

substituted PRMs. The data in Table 9 are the differences in r_{opt} ring structure parameters, where the structure parameters for PRM are subtracted from the corresponding parameters for the substituted PRMs. Thus, positive (negative) corresponds to a longer (shorter) bond length and a larger (smaller) interatomic angle compared with PRM.

The effect on the nqcc's is most pronounced in the case of 2-F-PRM, which is due both to the proximity of the substituent to the nitrogens and

to the large degree of distortion of the PRM ring. An appreciable shortening of the C(2)N(3) bond length is accompanied by a large increase in the N(1)C(2)N(3) interatomic angle.

In 2-Cl-PRM and 2-Br-PRM, the effects on both the nqcc's and the ring structures are like those in 2-F-PRM, but smaller in magnitude. The effect on the nqcc's in 2-Cl-PRM is somewhat larger than in 2-Br-PRM, which correlates with the shorter C(2)Cl bond length compared with C(2)Br (Table 3). Distortions of the 2-Cl- and 2-Br-PRM rings are about the same.

In the halogen substituted 5-X-PRMs compared with PRM, differences in the nqcc's are small, as one would expect, due to the remoteness of the substituents and the smaller degree of ring distortions. These differences correlate, as above, with differences in the C(5)X bond lengths.

The halogen substituted PRMs show trends with regard to the nqcc's into which the cyano substituted PRMs clearly do not fit. That the nature of the interaction of the cyano substituent with the PRM ring differs from the halogens is reflected in differences in the ring nitrogen nqcc's.

Table 9
Effects of substitution on the r_{opt} ring structure parameters^a

Δ Parameter	2-F-PRM	2-Cl-PRM	2-Br-PRM	2-CN-PRM
$\Delta\text{C}(2)\text{N}(3)$	-0.014	-0.008	-0.009	0.001
$\Delta\text{N}(3)\text{C}(4)$	0.001	0.000	0.000	-0.002
$\Delta\text{C}(4)\text{C}(5)$	-0.000	-0.000	-0.001	0.001
$\Delta\text{N}(1)\text{C}(2)\text{N}(3)$	2.2	1.0	0.9	0.5
$\Delta\text{C}(2)\text{N}(3)\text{C}(4)$	-1.1	-0.5	-0.4	-0.3
$\Delta\text{N}(3)\text{C}(4)\text{C}(5)$	0.1	0.1	0.1	-0.0
$\Delta\text{C}(4)\text{C}(5)\text{C}(6)$	-0.2	-0.2	-0.3	0.2
	5-F-PRM	5-Cl-PRM	5-Br-PRM	5-CN-PRM
$\Delta\text{C}(2)\text{N}(3)$	-0.000	-0.000	-0.001	0.001
$\Delta\text{N}(3)\text{C}(4)$	-0.002	-0.003	-0.004	-0.006
$\Delta\text{C}(4)\text{C}(5)$	-0.003	0.001	0.001	0.010
$\Delta\text{N}(1)\text{C}(2)\text{N}(3)$	-0.3	-0.3	-0.5	-0.2
$\Delta\text{C}(2)\text{N}(3)\text{C}(4)$	0.7	0.6	0.6	0.5
$\Delta\text{N}(3)\text{C}(4)\text{C}(5)$	-1.7	-1.1	-0.8	-0.5
$\Delta\text{C}(4)\text{C}(5)\text{C}(6)$	2.3	1.2	0.8	0.1

^a Δ Parameter = parameter in the substituted pyrimidines minus parameter in pyrimidine (Å and degrees). Positive (negative) corresponds to a longer (shorter) bond length and a larger (smaller) interatomic angle.

5. Summary

Reliable calculation of nqcc's, when compared with experimental nqcc's, provides a means for assessment of different structure types of a given molecule. Good agreement between calculated and experimental nqcc's in PRM is obtained on the r_s structure (rms = 24 kHz); poor agreement on the r_o structure (rms = 77 kHz); and excellent agreement on the r_{opt} structure (rms = 6 kHz).

The nqcc's in PRM are uniformly smaller in magnitude than the corresponding nqcc's in pyridine by about 3.3%.

In the halogen substituted PRMs, the N(1,3) nqcc's correlate with the carbon-substituent bond length.

There are clear differences in the N(1,3) nqcc's between the halogen and cyano substituents.

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