# DFT and HF–DFT calculations of $^{14}$N quadrupole coupling constants in molecules

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## Abstract

The efficacy of several DFT and HF–DFT methods for the calculation of $^{14}$N quadrupole coupling constants in molecules has been investigated. Valence triple-zeta quality Pople and Dunning correlation consistent type bases were used. Assessment of the different methods was made by linear regression analysis of the calculated efg's versus the experimental nqcc's. The HF–DFT methods were found superior to the DFT methods. The least residual standard deviation was obtained with the B3PW91/6-311 + G(df,pd) model. For 39 molecules containing 45 nitrogen sites, the standard deviation is 30 kHz (1.3%). Regarding the Dunning type aug-cc-pVTZ basis, it was found that the addition to nitrogen of core–valence correlation functions significantly improves the results. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* $^{14}$N; efg; nqcc; DFT; HF–DFT

## 1. Introduction

The nuclear quadrupole coupling constant (nqcc) is the spectroscopic measurement of the energy of interaction of the electric quadrupole moment of the nucleus of an atom with the gradient of the molecular electric field (efg) at the site of the nucleus.

Quantum chemistry calculation of the efg permits calculation of the nqcc, the nqcc being proportional to the efg. For accurate calculation of the efg, the need to include electron correlation, along with a fairly large basis, is generally conceded. This requirement places severe restrictions on the size of the molecule that may be investigated. To overcome somewhat these restrictions, Huber et al. have shown that the basis need be of high quality principally on

and in the area of the nucleus of interest, and that smaller bases may be used on atoms further removed. These authors have applied this method with good results at the level of fourth-order Møller–Plesset perturbation theory to calculation of the efg's and nqcc's for $^2$H [1], $^{14}$N [2], $^{17}$O [3], and $^{33}$S [4].

In two recent papers on $^2$H [5] and $^{17}$O [6] we have shown that results competitive with fourth-order Møller–Plesset perturbation theory can be obtained with much less computational cost using Becke's [7] hybrid Hartree–Fock/Density Functional (HF–DFT) method in conjunction with relatively small Pople type bases, thus enabling calculations on still larger molecules.

As a continuation of these studies, we report the results of our investigation of the efficacy of several DFT and hybrid HF–DFT methods in conjunction with augmented valence triple-zeta (VTZ) quality

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Table 1

$^{14}$N quadrupole coupling constants $\chi_{ij}$ (MHz), calculated and experimental. Model I = B3PW91/6-311 + G(df,pd) with $eQ/h = 4.5617$ MHz/a.u. Model II = B3PW91/aug-cc-pC(N)VTZ with $eQ/h = 4.5694$ MHz/a.u. The first reference is for the experimental nqcc, the second for the molecular structure

| Molecule | ij | Model I | Model II | Expt. | Ref. |
|---|---|---|---|---|---|
| $N_2$ | aa | −5.315 | −5.358 | −5.39(5)[a] | [16],[44] |
| $NO^+$ | aa | −6.782 | −6.800 | −6.76(10) | [17],[44] |
| PN | aa | −5.197 | −5.206 | −5.1718(5) | [18],[18] |
| HCN | aa | −4.693 | −4.705 | −4.70783(6) | [19],[45] |
| FCN | aa | −2.617 | −2.659 | −2.67(5) | [20],[46] |
| ClCN | aa | −3.573 | −3.593 | −3.62277(90) | [21],[47] |
| FCCCN | aa | −4.288 | −4.297 | −4.23913(77) | [22],[48] |
| HCCCN | aa | −4.366 | −4.378 | −4.31924(1) | [23],[49] |
| HCCNC | aa | 0.956 | 0.979 | 0.9454(8) | [24],[50] |
| AlNC | aa | −2.190 | −2.185 | −2.1508(19) | [25],[51] |
| $CH_3CN$ | aa | −4.209 | −4.216 | −4.2292(6) | [26],[52] |
| $CH_3NC$ | aa | 0.534 | 0.543 | 0.4894(4) | [27],[53] |
| $CF_3CN$ | aa | −4.707 | −4.702 | −4.666(4) | [28],[28] |
| $CF_3NC$ | aa | 1.104 | 1.093 | 1.06(3) | [29],[29] |
| $CH_2CHCN$ | aa | −3.792 | −3.800 | −3.78913(40) | [30],[30] |
|  | bb | 1.677 | 1.672 | 1.68607(43) |  |
|  | cc | 2.115 | 2.128 | 2.10306(49) |  |
|  | ab | −1.750 | −1.748 |  |  |
| $CH_3CD_2CN$ | aa | −3.414 | −3.417 | −3.449(16) | [31],[31] |
|  | bb | 1.369 | 1.367 | 1.399(15) |  |
|  | cc | 2.045 | 2.050 | 2.050(17) |  |
|  | ab | 2.066 | 2.064 | −2.01(18) |  |
| C$N$CN | aa | 1.300 | 1.313 | 1.32152(45) | [32],[54] |
| CNC$N$ | aa | −3.830 | −3.853 | −3.78113(32) | [32],[54] |
| $CH_2(CN)(C^{15}N)$ | aa | −2.366 | −2.368 | −2.364(9) | [33],[33] |
|  | bb | 0.340 | 0.336 | 0.313(6) |  |
|  | cc | 2.026 | 2.033 | 2.051(6) |  |
|  | ab | −3.021 | −3.020 |  |  |
| $N$CCNO | aa | −4.332 | −4.339 | −4.21853(53) | [34],[34] |
| NCC$N$O | aa | 0.443 | 0.455 | 0.4416(13) | [34],[34] |
| $N$NO | aa | −0.747 | −0.802 | −0.77376(27) | [35],[55] |
| N$N$O | aa | −0.232 | −0.212 | −0.26758(38) | [35],[55] |
| ONCl | aa | 1.004 | 0.998 | 1.0[b] | [36],[36] |
|  | bb | −4.796 | −4.782 | −4.8[b] |  |
|  | cc | 3.791 | 3.784 | 3.8[b] |  |
|  | ab | 1.926 | 1.947 |  |  |
| DNCO | aa | 2.139 | 2.074 | 2.1237(15) | [37],[56] |
|  | bb | −0.569 | −0.561 | −0.5528[c] |  |
|  | cc | −1.570 | −1.513 | −1.5710[c] |  |
|  | ab | 1.008 | 1.030 |  |  |
| $BH_2NH_2$ | aa | 0.129 | 0.138 | 0.095(9) | [38],[57] |
|  | bb | 2.108 | 2.097 | 2.091(8) |  |
|  | cc | −2.238 | −2.235 | −2.186(8) |  |
| $CH_2NOH$ | aa | 2.932 | 2.877 | 3.0002(32) | [39],[58] |
|  | bb | −4.655 | −4.634 | −4.6900(20) |  |
|  | cc | 1.723 | 1.757 | 1.6898(20) |  |
|  | ab | 3.509 | 3.457 |  |  |
| $CH_2NH$ | aa | −0.919 | −0.932 | −0.9131(16) | [40],[59] |
|  | bb | −2.663 | −2.625 | −2.6688(14) |  |
|  | cc | 3.582 | 3.557 | 3.5819(21) |  |
|  | ab | −2.521 | −2.480 |  |  |

Table 1 (continued)

| Molecule | $ij$ | Model I | Model II | Expt. | Ref. |
|---|---|---|---|---|---|
| $NH_3$ | aa | −4.084 | −4.012 | −4.08965[b] | [41],[60] |
| $NF_3$ | aa | −7.053 | −7.011 | −7.093(8) | [42],[61] |
| $N(CH_3)_3$ | aa | −5.519 | −5.468 | −5.5024(25) | [43],[62] |
| $RSD^d$ | | 0.030 | 0.037 | | |

[a] Solid state value corrected for lattice vibrations.
[b] No uncertainty reported.
[c] Derived from $\chi_{aa}$ and $\chi_{bb} - \chi_{cc} = 1.0182(21)$ MHz.
[d] Residual standard deviation.

6-311G Pople type and cc-pVTZ Dunning type bases for the calculation of $^{14}$N nqcc's in gaseous state molecules.

Our primary goal is to determine and calibrate a model, both reliable and computationally efficient, that may be useful to molecular spectroscopists.

The method of analysis and some computational details are discussed in Section 2. In Section 3, the results of calibration of the several models are presented. In Section 4, the calculated nqcc's are transformed to the principal axis system of the nqcc (efg) tensor. Section 5 summarizes this study.

## 2. Method

The components of the nqcc tensor $\chi_{ij}$ are related to those of the efg tensor $q_{ij}$ by

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

where $e$ is the proton electric charge, $h$ is Planck's constant, $Q$ is the electric quadrupole moment of the nucleus, and $i,j = a,b,c$ (the principle axes of the inertia tensor) or $x,y,z$ (the principal axes of the nqcc tensor). An asymmetry parameter that measures the degree of deviation from axial or cylindrical symmetry of the nqcc (efg) tensor is defined as

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

Following the procedure previously employed [5,6,8], the coefficient $eQ/h$ in Eq. (1) is determined from least-squares, linear regression analysis of the calculated efg's versus the experimental nqcc's. Although not independent, all three diagonal components of the calculated efg tensor are plotted against the corresponding components of the nqcc tensor.

This assures, because the tensors are traceless, that the least-squares line pass through the origin. In this way, the model is calibrated for a given set of molecules by the best-fit value of $eQ/h$, which may then be used for calculation and prediction of nqcc's in other molecules. Equivalently, a model-dependent effective value of the nuclear quadrupole moment $Q_{eff}$ may be calculated, where $Q_{eff}$ (barns) is given by $eQ/h$(MHz/a.u.)/234.9649.

All calculations were performed using the GAUSSIAN 94 [9] package. Numerical integrations were performed over a grid consisting of 75 radial shells with 302 angular points per shell, which is pruned to about 7500 integration points per atom. This is the default in the GAUSSIAN 94 package. This same grid, which 'unpruned' consists of 22 650 integration points per atom, was used for a set of calculations with the B3PW91/6-311 + G(3df,3pd) model. No significant differences in either $eQ/h$ or the residual standard deviation were observed between this larger calculation and one using the default grid. Furthermore, convergence criteria tighter than the default do not significantly alter the results. Thus, the results reported in this work are those obtained with the default settings.

## 3. Calibration

The DFT methods investigated are Becke's [10] exchange functional in combination with the correlation functionals of Lee et al. (LYP) [11,12], Perdew (P86) [13], Perdew and Wang (PW91) [14], and Vosko et al. (VWN5) [15]. These methods are designated BLYP, BP86, BPW91, and BVWN5, respec-

tively. The HF–DFT methods are Becke's [7] three parameter method in combination with each of the above cited LYP, P86, and PW91 correlation functionals, designated B3LYP, B3P86, and B3PW91, respectively.

The molecules chosen for initial calibration, along with the experimental nqcc's [16–43], are listed in Table 1. These 28 molecules provide 31 inequivalent nitrogen sites and represent a variety of sp, $sp^2$, and $sp^3$ bond hybridizations. The efg's were calculated on the experimental structures [18,28–31,33,34, 36,44–62].

For evaluation of the several methods, each was calibrated using the 6-311 + + G(3df,3pd) and aug-cc-pVTZ bases. Calibration was also made of the Hartree–Fock (HF) method, which is included for comparison. The results are given in Table 2. The accuracy of a particular model is judged by the value of the residual standard deviation (RSD). The value of $eQ/h$ is included as an indication of the relative magnitudes of the calculated efg's. HF calculations with these fairly large bases, although efficient, are completely unreliable. The RSD's are respectively 347 and 364 kHz for the 6-311 + + G(3df,3pd) and aug-cc-pVTZ bases. These RSD's are 15–16% of the average absolute experimental nqcc. Better results are obtained with the DFT methods where the RSD ranges from about 100 to 120 kHz. The most accurate models, however, as the table clearly shows, are the hybrid HF–DFT methods in conjunction with the 6-311 + + G(3df,3pd) basis. For these, the RSD ranges from 33 to 45 kHz. The most accurate is the

Table 2
Calibration of the HF, DFT, and HF-DFT methods using 6-311 + + G(3df,3pd) and aug-cc-pVTZ bases. RSD (residual standard deviation) is in kHz, $eQ/h$ (slope) is in MHz/a.u.

| Theory | 6-311 + + G(3df,3pd) | | aug-cc-pVTZ | |
|---|---|---|---|---|
| | RSD | $eQ/h$ | RSD | $eQ/h$ |
| HF | 347 | 3.849 | 364 | 3.863 |
| BLYP | 103 | 4.652 | 115 | 4.643 |
| BP86 | 108 | 4.768 | 111 | 4.753 |
| BPW91 | 119 | 4.773 | 104 | 4.763 |
| VWN5 | 114 | 4.622 | 96 | 4.619 |
| B3LYP | 45 | 4.449 | 94 | 4.443 |
| B3P86 | 34 | 4.532 | 75 | 4.525 |
| B3PW91 | 33 | 4.546 | 64 | 4.539 |

Table 3
Calibration of the B3PW91/6-311G model augmented with different combinations of diffuse and polarization functions. RSD (residual standard deviation) is in kHz, $eQ/h$ (slope) is in MHz/a.u.

| Basis | RSD | $eQ/h$ |
|---|---|---|
| 6-311 + + G(3df,3pd) | 33 | 4.546 |
| + + G(2df,3pd) | 69 | 4.492 |
| + + G(df,3pd) | 31 | 4.562 |
| + + G(3d,3pd) | 64 | 4.581 |
| + + G(2d,3pd) | 52 | 4.542 |
| + + G(d,3pd) | 126 | 4.632 |
| 6-311G(3df,3pd) | 49 | 4.492 |
| 6-311 + G(3df,3pd) | 33 | 4.546 |
| + G(3df,2pd) | 34 | 4.548 |
| + G(3df,pd) | 33 | 4.545 |
| + G(3df,3p) | 34 | 4.548 |
| + G(3df,2p) | 33 | 4.547 |
| + G(3df,p) | 33 | 4.546 |
| 6-311 + G(df,3pd) | 31 | 4.562 |
| + G(df,2pd) | 31 | 4.562 |
| + G(df,pd) | $29_9$ | 4.558 |
| + G(df,3p) | 32 | 4.563 |
| + G(df,2p) | 32 | 4.562 |
| + G(df,p) | $30_4$ | 4.559 |

B3PW91 method (33 kHz), which is only slightly more accurate than the B3P86 method (34 kHz).

In Table 3, the results are given of linear regression analysis of the B3PW91 method using the 6-311G basis augmented with various combinations of diffuse and polarization functions. Accurate results are obtained with 6-311 + G(3df) and 6-311 + G(df) bases on the heavy atoms, the latter (RSD = 30–32 kHz) slightly better than the former (RSD = 33–34 kHz). The least RSD is found for the B3PW91/6-311 + G(df,pd) model, namely 29.9 kHz (1.3%). The correlation coefficient is 0.99994, and $eQ/h$ is 4.5580(52) MHz/a.u. Very similar statistics are obtained for the 6-311 + G(df,p) model. In this case,

Table 4
Calibration of the B3PW91 method in conjunction with cc-pVTZ Dunning type bases. RSD (residual standard deviation) is in kHz, $eQ/h$ (slope) is in MHz/a.u.

| Nitrogen | Other atoms | RSD | $eQ/h$ |
|---|---|---|---|
| aug-cc-pVTZ | aug-cc-pVTZ | 64 | 4.539 |
| aug-cc-pCVTZ | aug-cc-pVTZ | 37 | 4.569 |
| cc-pCVTZ | cc-pVTZ | 50 | 4.516 |

Table 5

$^{14}N$ quadrupole coupling constants $\chi_{ij}$ (MHz), calculated and experimental. Calc. = B3PW91/6-311 + G(df,pd) with $eQ/h = 4.5617$ MHz/a.u. The first reference is for the experimental nqcc, the second for the molecular structure.

| Molecule | | $ij$ | Calc. | Expt. | Ref. |
|---|---|---|---|---|---|
| BrCN | | aa | −3.796 | −3.78(2) | [64],[75] |
| GeH$_3$CN | | aa | −4.974 | −5.0(1) | [65],[65] |
| Benzonitrile | | aa | −4.226 | −4.244(4) | [66],[76] |
| | | bb | 2.284 | 2.290(5) | |
| | | cc | 1.942 | 1.954(5) | |
| Pyridine | | aa | −4.908 | −4.908(3) | [67],[77] |
| | | bb | 1.450 | 1.434(3) | |
| | | cc | 3.458 | 3.474(3) | |
| Pyridine–N–O | | aa | 0.824 | 0.838(3) | [68],[78] |
| | | bb | −0.831 | −0.858(2) | |
| | | cc | 0.007 | 0.020(2) | |
| Pyrrole | | aa | 1.415 | 1.412(3) | [69],[79] |
| | | bb | 1.215 | 1.292(4) | |
| | | cc | −2.630 | −2.704(2) | |
| Pyrazole | N(1) | aa | 1.434 | 1.391(6) | [70],[80] |
| | | bb | 1.643 | 1.662(6) | |
| | | cc | −3.078 | −3.053(12) | |
| | | ab | 0.735 | −0.730(21) | |
| | N(2) | aa | −3.909 | −3.960(5) | |
| | | bb | 3.081 | 3.140(5) | |
| | | cc | 0.828 | 0.820(10) | |
| | | ab | 2.042 | −1.943(6) | |
| Imidazole | N(1) | aa | 1.295 | 1.281(7) | [71],[81] |
| | | bb | 1.256 | 1.278(7) | |
| | | cc | −2.550 | −2.559[a] | |
| | | ab | 0.143 | | |
| | N(3) | aa | −3.948 | −3.981(5) | |
| | | bb | 1.733 | 1.753(8) | |
| | | cc | 2.214 | 2.228[a] | |
| | | ab | 0.793 | | |
| d$_1$-Furazan | N(2) | aa | 3.538 | 3.546(10) | [72],[82] |
| | | bb | −4.688 | −4.690(10) | |
| | | cc | 1.150 | 1.144(10) | |
| | | ab | −2.792 | 2.764[b] | |
| | N(5) | aa | −5.073 | −5.044(10) | |
| | | bb | 3.923 | 3.900(10) | |
| | | cc | 1.150 | 1.144(10) | |
| | | ab | 2.118 | −2.144[b] | |
| Thiazole | | aa | −2.708 | −2.7481(15) | [73],[83] |
| | | bb | 0.059 | 0.08505[c] | |
| | | cc | 2.649 | 2.6630[c] | |
| | | ab | 2.583 | | |

Table 5 (continued)

| Molecule | $ij$ | Calc. | Expt. | Ref. |
|----------|------|-------|-------|------|
| Oxazole  | aa   | −3.991 | −3.92(2) | [74],[84] |
|          | bb   | 1.578  | 1.54(2)  |          |
|          | cc   | 2.412  | 2.38[a]  |          |
|          | ab   | −0.921 | 0.81[b]  |          |

[a] Derived from zero trace.

[b] No experimental uncertainty reported.

[c] Derived from $\chi_{aa}$ and $\chi_{bb} - \chi_{cc} = -2.5780(32)$ MHz.

the RSD is 30.4 kHz, the correlation coefficient is 0.99994, and $eQ/h$ is 4.5586(52) MHz/a.u. Considering only the hydrogen containing compounds in Table 1, the root mean square (rms) differences between the calculated and experimental nqcc's are respectively 23.7 and 25.1 kHz for the 6-311 + G(df,pd) and 6-311 + G(df,p) bases.

In Table 4, the results are given of linear regression analysis of the B3PW91 method with the cc-pVTZ type bases. The most notable result here is that the addition of core–valence correlation functions 'C' [63] to the nitrogen aug-cc-pVTZ basis reduces the RSD by nearly half, that is, from 64 kHz to 37 kHz. 'C' adds two sets each of s and p functions and one set of d functions to the core of the nitrogen basis. The statistics for the B3PW91/ aug-cc-pC(N)VTZ model (C(N) means that C-functions are on N only, for all other atoms the basis is aug-cc-pVTZ.) are as follows: The RSD is 37 kHZ (1.6%), the correlation coefficient is 0.99991, and $eQ/h$ is 4.5694(64) MHz/a.u. The calculated nqcc's are given in Table 1.

The small difference (0.25%) between the above value of $eQ/h$ and that for the B3PW91/6-311 + G(df,pd) model, together with similarly small rms deviations, implies little difference on average in the calculated values of the efg's.

We choose for the remainder of this paper the B3PW91/6-311 + G(df,pd) model. For final calibration of this model, the molecules and experimental nqcc's [64–74] listed in Table 5 are added to those in Table 1. The total number of molecules is now 39, and the number of nitrogen sites is 45. Calculations of the efg's were made on the experimental structures [75–84].
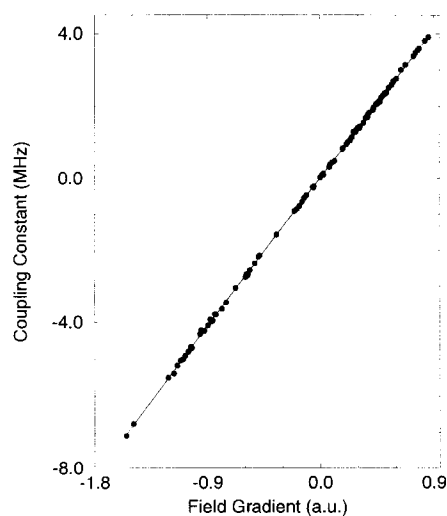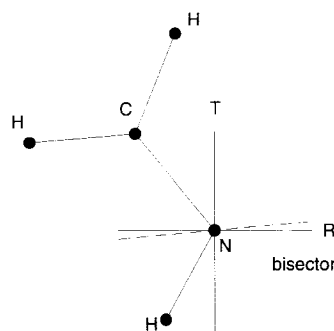


Fig. 1. B3PW91/6-311 + G(df,pd) calibration curve. Calculated efg's (a.u.) vs. experimental nqcc's (MHz). The residual standard deviation is 30 kHz, the correlation coefficient is 0.99994, and the slope ($eQ/H$) is 4.5617 MHz/a.u.



Fig. 2. Methanimine, $CH_2NH$. Principal axes R and T of the nqcc tensor. The molecule is planar and the $\pi$-axis is perpendicular to the molecular plane. The R-axis is tilted 5.2° ($\alpha$) toward H from the external bisector (dashed line) of $\angle HNC$.

Table 6

sp$^2$ compounds. Quadrupole coupling in the principal axes of the nqcc tensor, calculated and experimental. $\chi$ is in MHz. Angles $\angle$XNY are from the experimental structures referenced in Table 1Table 5.

| Molecule | | $\chi$ | Calc. | Expt. | Orientation |
|---|---|---|---|---|---|
| CH$_2$NH[a] | | R | −4.459 | | $\alpha = 5.2°$ |
| | | T | 0.877 | | toward H |
| | | $\pi$ | 3.582 | | $\angle$HNC $= 110.4°$ |
| CH$_2$NOH | | R | −6.029 | | $\alpha = 23.5°$ |
| | | T | 4.306 | | toward OH |
| | | $\pi$ | 1.723 | | $\angle$CNO $= 110.2°$ |
| ONCl | | R | −5.377 | | $\alpha = 32.7°$ |
| | | T | 1.586 | | toward Cl[b] |
| | | $\pi$ | 3.791 | | $\angle$ONCl $= 113.4°$ |
| DNCO | | R | −0.903 | | $\alpha = 2.8°$ |
| | | T | 2.473 | | toward CO |
| | | $\pi$ | −1.570 | | $\angle$DNC $= 123.9°$ |
| Thiazole | | R | −4.254 | | $\alpha = 2.0°$ |
| | | T | 1.605 | | toward C(4)[c] |
| | | $\pi$ | 2.649 | | $\angle$CNC $= 115.81°$ |
| Oxazole | | R | −4.139 | −4.04[d] | $\alpha = 5.0°$ and |
| | | T | 1.727 | 1.66 | $\alpha_{\text{expt}} = 5.7$[od] |
| | | $\pi$ | 2.412 | 2.38 | toward C(4)[e] $\angle$CNC $= 103.9°$ |
| Furazan | N(2,5) | R | −5.546 | −5.53(4)[f] | $\alpha = 24.4°$ and |
| | | T | 4.396 | 4.39(4) | $\alpha_{\text{expt}} = 24.60°$[f] |
| | | $\pi$ | 1.150 | 1.14(4) | toward O $\angle$CNO $= 105.53°$ |
| Imidazole | N(1)[g] | R | 1.419 | | $\alpha = 13.2°$ |
| | | T | 1.131 | | toward C(2) |
| | | $\pi$ | −2.550 | | $\angle$CNC $= 106.90°$ |
| | N(3)[h] | R | −4.057 | | $\alpha = 2.2°$ |
| | | T | 1.842 | | toward C(4) |
| | | $\pi$ | 2.214 | | $\angle$CNC $= 104.93°$ |
| Pyrazole | N(1)[g] | R | 0.796 | 0.791(36)[i] | $\alpha = 27.9°$ and |
| | | T | 2.281 | 2.277(29) | $\alpha_{\text{expt}} = 29.1°$[i,j] |
| | | $\pi$ | −3.078 | −3.068(9) | toward N(2) $\angle$CNN $= 113.0°$ |
| | N(2)[h] | R | −4.462 | −4.473(10)[i] | $\alpha = 17.7°$ and |
| | | T | 3.633 | 3.621(4) | $\alpha_{\text{expt}} = 17.0°$[i,j] |
| | | $\pi$ | 0.828 | 0.853(10) | toward N(1) $\angle$NNC $= 104.1°$ |

[a] See Fig. 2.
[b] The T-axis deviates from the NCl bond by 0.55°.
[c] With S = S(1).
[d] Ref. [74].
[e] With O = O(1).
[f] Ref. [72].
[g] Pyrrolic.
[h] Pyridinic.
[i] Ref. [70].
[j] Calculated here from data given in Ref. [70].

Table 7
Cyano compounds. Quadrupole coupling in the principal axes of the nqcc tensor. $\chi$ is in MHz. The $y$-principal axis is perpendicular to the plane of mirror symmetry of the molecule. $\eta$ is the asymmetry parameter, Eq. (2). $\theta_{z,CN}$ (°) is the angular deviation of the $z$-principal axis from the CN bond direction

| Molecule | $\chi_{zz}$ | $\chi_{xx}$ | $\chi_{yy}$ | $\eta$ | $\theta_{z,CN}$ |
|---|---|---|---|---|---|
| $CH_2CHCN$ | −4.304 | 2.189 | 2.115 | 0.017 | 0.21 |
| expt.[a] | −4.18(5) | 2.07(5) | 2.1031(5) | 0.008 | 1.7 |
| $CH_3CH_2CN$ | −4.183 | 2.138 | 2.045 | 0.022 | 0.36 |
| expt.[b] | −4.17(16) | 2.12(16) | 2.05(18) | 0.02(4) | 1.0(17) |
| $CH_2(CN)_2$ | −4.406 | 2.328 | 2.079 | 0.056 | 0.61 |
| expt.[c] | −4.157(17) | 2.092(17) | 2.050 | 0.010 | 0.44 |

[a] Ref. [30], $\theta_{z,CN}$ calculated here from the following reported data: $\angle CN,a = 16.1(9)°$ and $\angle z,a = 14.4(9)°$.
[b] Ref. [31], $\theta_{z,CN}$ calculated here from the following reported data: $\angle CN,a = 20.77(14)°$ and $\angle z,a = 19.8(17)°$.
[c] Ref. [33], calculated results, see the ref. for assumptions and details.

The final statistics (which are not very different from those of the initial calibration) are as follows: The RSD is 30 kHz (1.3%), the correlation coefficient is 0.99994, and $eQ/h$ is 4.5617(42) MHz/a.u. Fig. 1 shows the calculated efg's plotted against the experimental nqcc's (calibration curve). The calculated nqcc's are given in Tables 1 and 5. For all three diagonal components for all molecules given in Tables 1 and 5, the average absolute difference between the calculated and the experimental nqcc's is 23 kHz (1.0%) and the rms difference is 30 kHz (1.3%).

$Q_{eff}$, the model-dependent value of the nuclear electric quadrupole moment, is 19.41(2) mb, which is 3.4% less than the recommended value of 20.1(2) mb [85]. This suggests that the magnitudes of the calculated efg's, without correction for zero point vibration, are roughly this percentage too high.

Calculations on several small molecules made by Cummins et al. [86] employing extensive Gaussian basis sets at the coupled pair functional [87] level of theory yield for $^{14}N$ an uncorrected $Q$ (that is, $Q_{eff}$) of 19.6 mb, and after correction for zero point vibration and basis set truncation, a value for $Q$ of 20.5(2) mb. It is noteworthy that the relatively simple B3PW91/6-311 + G(df,pd) calculations yield very nearly the same $Q_{eff}$ as the more extensive ab initio calculations, the difference between the two being about 1%.

Concerning the calculated nqcc's given in Tables 1 and 5, Gaussian 94 often calculates a different algebraic sign for the off-diagonal $\chi_{ab}$ than is given experimentally. This is the result of a molecular orientation with respect to $a$, $b$ coordinates that may differ from the experimental one by an inversion of one coordinate or the other, that is, $a \rightarrow -a$ or $b \rightarrow -b$. It is the magnitude of the calculated value that should be compared with the magnitude of the experimental value.

## 4. The NQCC tensor

Fig. 2 is a sketch of $CH_2NH$ intended to help define the descriptions of the orientation of the principal axes of the nqcc tensors given in Table 6. The scheme, introduced by Palmer et al. ([88], and references therein), is particularly useful for $sp^2$ hybridized bonding. The principal axes are labeled T, R, and $\pi$. The T-axis is 'tangent to the arc' formed by HNC, the R-axis is 'radial' and deviates from the external bisector of the $\angle HNC$ by an angle $\alpha$, and the $\pi$-axis is perpendicular to the plane of the molecule. Given $\alpha$ and $\angle HNC$, the orientation of the axes is specified. For $CH_2NH$, $\angle HNC$ is 110.4° [59] and the R-axis is tilted 5.2° (that is, $\alpha$) toward H. The principal values of the nqcc tensor, denoted $\chi_R$, $\chi_T$, and $\chi_\pi$, are −4.459, 0.877, and 3.582 MHz, respectively. The results for the $sp^2$ hybrids from Tables 1 and 5 are given in Table 6.

In Table 7, the nqcc tensors are given for the cyanogen compounds $CH_2CHCN$, $CH_3CH_2CN$, and $CH_2(CN)_2$. It is useful here to describe the orientation of the principal axes in the following manner: The $y$-axis is perpendicular to the plane of mirror symmetry, while the $x$- and $z$-axes lie in the plane. The latter is 'coincident' with the CN bond axis. $\theta_{z,CN}$ is the angle by which the z axis deviates from the CN axis, and $\eta$ is the asymmetry parameter (Eq. (2)). These parameters, given in Table 7, show the similarity of the nitrogen coupling in these molecules: $\chi_{zz} = -4.3$, −4.2, and −4.4 MHz; $\eta = 0.02$, 0.02, and 0.06; and $\theta_{z,CN} = 0.2$, 0.4, and 0.6° respectively for $CH_2CHCN$, $CH_3CH_2CN$, and $CH_2(CN)_2$. Thus, the magnitudes of the quadrupole coupling are simi-

lar and, in each case, the deviation from cylindrical symmetry along the CN bond axis is small.

## 5. Summary

For the calculation of ^{14}N nqcc's, the efficacy of HF theory, several DFT methods involving Becke's exchange functional with different correlation functionals, and Becke's HF–DFT method in conjunction with different correlation functionals was investigated. Pople and Dunning correlation consistent type VTZ bases were used.

From among these, the least RSD was obtained with the B3PW91/6-311 + G(df,pd) model. For 39 molecules containing 45 nitrogen sites, which represent a variety of sp, $sp^2$, and $sp^3$ bond hybridizations, the RSD is 30 kHz (1.3%) and $eQ/h$ is 4.5617(43) MHz/a.u. $Q_{eff}$, derived from the latter, is 19.41(2) mb.

Regarding the Dunning type bases, with the B3PW91 method, it was found that the addition of core–valence correlation functions to the aug-cc-pVTZ basis for nitrogen reduces the RSD by nearly half.

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