Calculation of N and Cl Nuclear Quadrupole Coupling Constants

on Approximate Equilibrium Molecular Structures

II. F, Cl - Acetonitriles

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Abstract

Calculations were made of N and Cl nuclear quadrupole coupling constants on molecular structures of F, Cl substituted acetonitriles derived by MP2 optimization, with empirically corrected bond lengths. The molecules are

Acetonitrile, CH_3CN Fluoroacetonitrile, CH_2FCN

Difluoroacetonitrile, CHF_2CN Trifluoroacetonitrile, CF_3CN

Chloroacetonitrile, CH_2ClCN Chlorofluoroacetonitrile, $CHFClCN$

MP2 optimizations were made in conjunction with Method (1) Dunning aug-cc-pVTZ and Method (2) Pople-type triple-zeta bases. Methods (1) and (2) give similar results for CH_3CN, CH_2FCN, CHF_2CN, and CF_3CN; but quite different results for CH_2ClCN and $CHFClCN$. In the case of CH_2ClCN, agreement between calculated and experimental nuclear quadrupole coupling constants is good for calculation on structure (1), poor for calculation on structure (2). The difference lies in optimization of the interatomic angles. In this regard, Method (1) is more reliable than Method (2).

Introduction

In Part I of this series, approximate equilibrium molecular structures of CH_3Cl, CH_2FCl, CHF_2Cl, CF_3Cl, CH_2Cl_2, $CHFCl_2$, CF_2Cl_2, $CHCl_3$, and $CFCl_3$ were derived by MP2/aug-cc-pVTZ(G03)[1] optimization with empirically corrected bond lengths. Assessment of these structures was made by comparison of calculated and experimental Cl nuclear quadrupole coupling constants (nqcc's). Because of the sensitivity of calculated nqcc's

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[1] All calculations were made on a Mac G5 from Apple Inc. using the G03M quantum chemistry package of Gaussian Inc. This package contains Dunning bases that have been modified somewhat for computational efficiency. That these bases are not the originals is denoted here by the appendage G03.

to molecular structure, the good agreement that was found is taken as validation of the structures.

Approximate equilibrium structures of the subjects of this investigation - CH_3CN, CH_2FCN, CHF_2CN, CF_3CN, CH_2ClCN, and $CHFClCN$ - were derived as in Part I and, for comparison, by the methods of Demaison et al. [1 - 8]; that is, MP2 in conjunction with Pople bases. Assessment of these structures is made by calculation of the nqcc's.

Molecular Structures

Methods 1 and 2 for derivation of approximate equilibrium structures are described in detail in Ref. [9], and summarized below:

Method 1. The structures were optimized at the MP2/aug-cc-pVTZ(G03) level of theory, the CF, CCl, C-C, and CN optimized bond lengths then corrected via the following equations:

CF $\qquad \sim r_e$ (1) (Å) = 0.97993 × r_{opt} + 0.02084, RSD = 0.0014 Å,

CCl $\qquad \sim r_e$ (1) (Å) = 0.99872 × r_{opt} − 0.00097, RSD = 0.0022 Å,

C-C $\qquad \sim r_e$ (1) (Å) = 0.95547 × r_{opt} + 0.06567, RSD = 0.0012 Å,

C≡N $\qquad \sim r_e$ (1) (Å) = 0.69449 × r_{opt} + 0.34294, RSD = 0.0006 Å,

where r_{opt} is the optimized bond length. RSD is the standard deviation of the residuals which may be taken as an estimate of the uncertainty in the corrected bond length, $\sim r_e$. CH bond lengths and interatomic angles are those calculated by MP2/aug-cc-pVTZ optimization, without correction.

Method 2. The structures were optimized at the MP2/6-311+G(2d,p), MP2/6-311+G (d,p), and MP2/6-31G(d,p) levels of theory. Then, the MP2/6-311+G(2d,p) optimized CCl bond length; and MP2/6-311+G(d,p) optimized CF, C-C, and CN bond lengths were corrected as follows:

CF $\qquad \sim r_e$ (2) (Å) = 0.96166 × r_{opt} + 0.04418, RSD = 0.0019 Å,

CCl $\qquad \sim r_e$ (2) (Å) = 0.99534 × r_{opt} − 0.00877, RSD = 0.0029 Å,

C-C $\qquad \sim r_e$ (2) (Å) = 0.94032 × r_{opt} + 0.08339, RSD = 0.0016 Å,

C≡N $\qquad \sim r_e$ (2) (Å) = 0.59767 × r_{opt} + 0.45394, RSD = 0.0009 Å.

For the CH bond, $\sim r_e$ (2) (Å) = 1.001 × r_{opt}, where r_{opt} = MP2/6-31G(d,p) optimization. Interatomic angles used here are those given by MP2/6-311+G(d,p) optimization.

Nuclear Quadrupole Coupling Constant

The components of the nqcc tensor χ are related to those of the electric field gradient (efg) tensor q by

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

where e is the fundamental electric charge, Q is the electric quadrupole moment of the nucleus, and h is Planck's constant. Subscripts ij refer to coordinate axes. Experimental nqcc's are measured in the principal axes system of the molecular inertia tensor. These axes are associated with the rotational constants A, B, and C; and are labeled a, b, and c. Principal axes of the nqcc tensor are labeled x, y, and z.

Calibration [9] of the B1LYP/TZV(3df,2p) model for calculation of the ^{35}Cl nqcc's, and the B3PW91/6-311+G(df,pd) model for calculation of the ^{14}N nqcc's yields

$$\chi_{ij}\,(^{35}\text{Cl}) = (\text{-19.185 MHz/a.u.})\, q_{ij}, \ \ \text{RSD} = 0.49 \text{ MHz},$$

$$\chi_{ij}\,(^{14}\text{N}) = (\text{4.5586 MHz/a.u.})\, q_{ij}, \ \ \text{RSD} = 0.030 \text{ MHz},$$

where q_{ij} are the calculated efg's.

(Note: The G03M code calculates the efg tensor in a coordinate system other than the inertia system. A fortran program used here for transformation of the efg tensor from G03M axes to a,b,c and x,y,z principal axes is available in Ref. [9].)

Results

The results of this investigation - structure parameters and nuclear quadrupole coupling constants - are collected below in Tables 1 - 6; and displayed in Fig. 1, which is a plot of calculated versus experimental diagonal inertia axes ^{14}N nqcc's.

In Tables 1 - 6; ~ r_e (1), ~ r_e (2), and experimental structure parameters are compared. Coupling constants calculated on each structure are compared with experimental nqcc's. RMS is the root mean square difference between calculated and experimental diagonal nqcc's (percent of average experimental nqcc). $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ and φ (degrees) is the angle between its subscripted parameters.

Table 1. Acetonitrile, CH_3CN. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)	r_e [a]	expt. nqcc [b]
CH	1.0884	1.0873	1.087(3)	
C-C	1.4588	1.4578	1.457(2)	
C≡N	1.1555	1.1553	1.156(2)	
HCC	109.89	109.93	110.1(3)	
χ_{zz} (^{14}N)	-4.212	-4.214	-4.208	-4.22473(8)

[a] Ref. [8]. [b] Ref. [10]. [Back to Top](#)

Table 2. Fluoroacetonitrile, CH_2FCN. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)		expt. nqcc [a]
CH	1.0909	1.0883		
C-C	1.4660	1.4662		
C≡N	1.1555	1.1552		
CF	1.3727	1.3732		
CCH	109.60	109.66		
FCC	110.07	110.05		
CCN	178.84	178.90		
HCH	109.99	109.86		

χ_{aa} (^{14}N)	-3.712	-3.712		-3.7039(26)
χ_{bb}	1.945	1.943		1.8918(26)
χ_{cc}	1.766	1.769		1.8122(37)
$|\chi_{ab}|$	2.233	2.238		2.119
RMS	0.041 (1.6 %)	0.039 (1.6 %)		
χ_{xx}	2.720	2.721		2.604
χ_{yy}	1.766	1.769		1.812
χ_{zz}	-4.487	-4.490		-4.416
η	-0.212	-0.212		
$\varphi_{z,a}$	19.14	19.18		
$\varphi_{a,CN}$	18.96	19.02		
$\varphi_{z,CN}$	0.18	0.16		

[a] Ref. [11]. Back to Top

Table 3. Difluoroacetonitrile, CHF_2CN. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)		expt. nqcc [a]
CH	1.0896	1.0882		
C-C	1.4736	1.4762		
C≡N	1.1557	1.1554		

CF	1.3461	1.3455		
CCF	109.45	109.42		
HCC	111.55	111.56		
CCN	177.60	177.71		
FCF	108.55	108.45		
χ_{aa} (^{14}N)	-4.428	-4.426		-4.3899(33)
χ_{bb}	2.436	2.435		2.4017(39)
χ_{cc}	1.992	1.991		1.9883(39)
$|\chi_{ac}|$	1.240	1.247		
RMS	0.030 (1.0 %)	0.028 (1.0 %)		
χ_{xx}	2.223	2.225		
χ_{yy}	2.436	2.435		
χ_{zz}	-4.659	-4.660		
η	0.046	0.045		
$\varphi_{z,a}$	10.56	10.62		
$\varphi_{a,CN}$	9.84	9.93		
$\varphi_{z,CN}$	0.72	0.68		

[a] Ref. [12]. Back to Top

Table 4. Trifluoroacetonitrile, CF_3CN. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)	r_z [a]	expt. nqcc [a]
CF	1.3266	1.3251	1.328	
C-C	1.4748	1.4792	1.492	
C≡N	1.1555	1.1552	1.154	
FCF	108.62	108.64	109.2	
χ_{zz} (^{14}N)	-4.719	-4.716	-4.704	-4.666(4)

[a] Ref. [13]. Back to Top

Table 5(a). Chloroacetonitrile, $CH_2{}^{35}ClCN$. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)	partial r_o [a]	expt. nqcc [b]
CCl	1.7747	1.7771	1.767	
CH	1.0881	1.0863	[1.070]	
H····H	1.7808	1.7758	1.728	
C-C	1.4570	1.4563	1.472	
C≡N	1.1559	1.1558	[1.158]	
CCCl	111.49	110.93	111.4	
CCH	109.37	110.12	[109.5]	
C-C≡N	178.52	179.00	[180]	

χ_{aa} (^{14}N)	-2.792	-2.743	-2.743	-2.721(22)
χ_{bb}	0.868	0.800	0.818	0.760(15)
χ_{cc}	1.924	1.943	1.925	1.961(37)
$|\chi_{ab}|$	2.867	2.897	2.868	
RMS	0.078 (4.3 %)	0.028 (1.6 %)	0.041 (2.3 %)	
χ_{xx}	2.439	2.424		
χ_{yy}	1.924	1.943		
χ_{zz}	-4.363	-4.367		
η	-0.118	-0.110		
$\varphi_{z,a}$	28.72	29.28		
$\varphi_{a,CN}$	28.65	29.29		
$\varphi_{z,CN}$	0.07	0.01		

[a] Ref. [14]. Values in square brackets are assumed. [b] Ref. [15].

Table 5(b). Chloroacetonitrile, $CH_2{}^{35}ClCN$. Structure parameters (Å and degrees) and ^{35}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)	partial r_o [a]	expt. nqcc [b]
CCl	1.7747	1.7771	1.767	
CH	1.0881	1.0863	[1.070]	
H$\cdots$H	1.7808	1.7758	1.728	

C-C	1.4570	1.4563	1.472	
C≡N	1.1559	1.1558	[1.158]	
CCCl	111.49	110.93	111.4	
CCH	109.37	110.12	[109.5]	
C-C≡N	178.52	179.00	[180]	
χ_{aa} (^{35}Cl)	-36.11	-35.25	-34.70	-34.873(20)
χ_{bb}	-5.20	-6.04	-6.34	-6.145(15)
χ_{cc}	41.32	41.29	41.33	41.018(35)
$|\chi_{ab}|$	58.81	58.95	59.04	
RMS	0.92 (3.3 %)	0.27 (1.0 %)	0.35 (1.3 %)	
χ_{xx}	40.15	40.09		
χ_{yy}	41.32	41.29		
χ_{zz}	-81.47	-81.38		
η	0.014	0.015		
$\varphi_{z,a}$	37.64	38.04		
$\varphi_{a,CCl}$	38.38	38.79		
$\varphi_{z,CCl}$	0.74	0.75		

[a] Ref. [14]. Values in square brackets are assumed. [b] Ref. [15]. Back to Top

Table 6(a). Chlorofluoroacetonitrile, $CHF^{35}ClCN$. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)		
CH	1.0884	1.0867		
CF	1.3576	1.3558		
CCl	1.7592	1.7630		
C-C	1.4643	1.4652		
C≡N	1.1562	1.1561		
ClCH	108.15	107.69		
ClCF	110.00	109.86		
ClCC	110.46	109.78		
C-C≡N	177.79	178.57		
χ_{aa} (^{14}N)	-3.062	-3.011		
χ_{bb}	1.147	1.094		
χ_{cc}	1.915	1.917		
$|\chi_{ab}|$ [a]	2.526	2.548		
$|\chi_{ac}|$	1.161	1.181		
$|\chi_{bc}|$	0.770	0.803		
χ_{xx}	2.060	2.056		
χ_{yy}	2.480	2.484		
χ_{zz}	-4.540	-4.540		
η	0.092	0.094		

$\varphi_{z,CN}$	0.50	0.31

[a] The product $\chi_{ab} \chi_{ac} \chi_{bc}$ is negative.

Table 6(b). Chlorofluoroacetonitrile, $CHF^{35}ClCN$. Structure parameters (Å and degrees) and ^{35}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	~ r_e (2)	~ r_e (1)		
CH	1.0884	1.0867		
CF	1.3576	1.3558		
CCl	1.7592	1.7630		
C-C	1.4643	1.4652		
C≡N	1.1562	1.1561		
ClCH	108.15	107.69		
ClCF	110.00	109.86		
ClCC	110.46	109.78		
C-C≡N	177.79	178.57		
χ_{aa} (^{35}Cl)	-31.41	-29.80		
χ_{bb}	0.86	-0.55		
χ_{cc}	30.55	30.35		
$|\chi_{ab}|$ [b]	50.48	50.88		
$|\chi_{ac}|$	27.87	27.77		
$|\chi_{bc}|$	16.58	17.09		

χ_{xx}	35.78	35.79		
χ_{yy}	42.11	42.07		
χ_{zz}	-77.88	-77.86		
η	0.081	0.081		
$\varphi_{z,CCl}$	1.43	1.42		

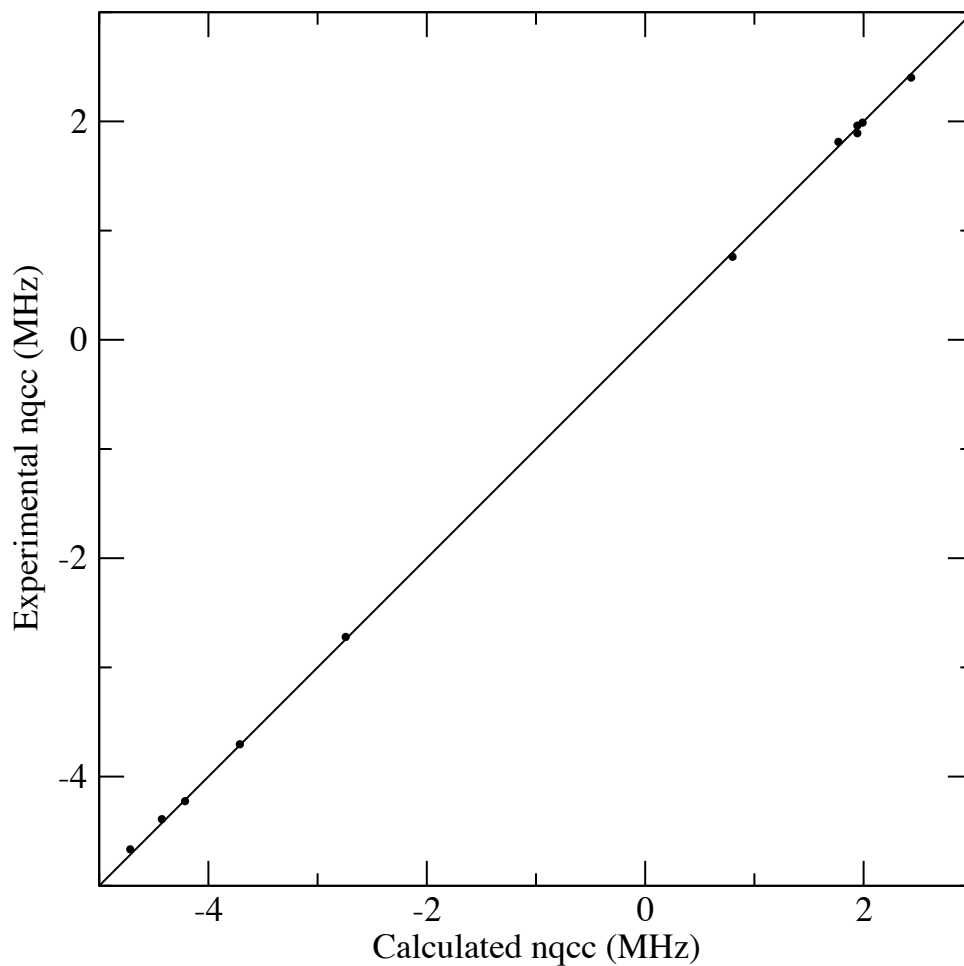[a] The product $\chi_{ab}\,\chi_{ac}\,\chi_{bc}$ is negative. [Back to Top](#)

Figure 1. Calculated versus experimental ^{14}N diagonal inertia axes nqcc's. Calculated nqcc's are those calculated on $\sim r_e$ (1) structures. Solid line is calculated = experimental.

Discussion

Comparison of the $\sim r_e$ structures with the experimental r_e structure of acetonitrile is made in Table 1. Agreement among these three structures is good, and the calculated χ_{zz} are essentially the same.

An *ab initio* "best estimate" r_e structure of acetonitrile was recently derived by Puzzarini and Cazzoli [16] at the CCSD(T) level of theory in conjunction with a basis set of sextuple-zeta quality and with core-correlation corrections. This structure is CN = 1.1553 Å, C-C = 1.4590 Å, CH = 1.0865 Å, and CCH = 109.84°, with which our r_c structures are in good agreement. On this structure, we calculate χ_{zz} = -4.209 MHz. Puzzarini and Cazzoli, at the CCSD(T)/cc-pwCVQZ level of theory with all-electron correlation, calculate -4.22 MHz. The experimental value is -4.22473(8) MHz.

For fluoro-, difluoro-, and trifluoro- acetonitrile, molecular structures $\sim r_e$ (1) and $\sim r_e$ (2) are not much different. The largest bond length differences are Δ(C-C) = 0.0044 Å in CF_3CN, Δ(CH) = 0.0026 Å in CH_2FCN, and Δ(C-C) = 0.0026 Å in CHF_2CN; all other bond lengths differ only in the 4th decimal place. The largest interatomic angle differences are Δ(HCH) = 0.13° in CH2FCN and Δ(CCN) = 0.11° in CHF_2CN. There is, therefore, little difference between calculated nqcc's. The less computationally demanding r_c (2) works as well as the more demanding r_c (1).

However - and this is the main conclusion to be drawn from this investigation - there are significant differences between $\sim r_e$ (1) and $\sim r_e$ (2) for CH_2ClCN and CHFClCN.

Consider ^{35}Cl in CH_2ClCN. For calculation of the nqcc's on the $\sim r_e$ (1) structure, the RMS difference between calculated and experimental nqcc's is 0.27 MHz compared with 0.92 MHz for calculation of the $\sim r_e$ (2) structure. Note in particular the difference between the two structures in the angle between CCl and the a-axis: namely, 0.41° (and between CN and the a-axis: 0.64°). The difference in CCl bond length is 0.0024 Å. That the largest part of the difference in RMS differences are due to interatomic angles, rather than bond lengths, is manifest by calculation of the nqcc's on structures consisting of the $\sim r_e$ (2) bond lenghts and interatomic angles given by MP2/6-311+G (d,p) (Table 6), MP2/6-311++G(3df,3pd), and MP2/aug-cc-pVTZ (Table 6) optimizations. On these structures respectively, the RMS difference between calculated and experimental nqcc's decreases from 0.92 to 0.64 to 0.19 MHz (and for ^{14}N, from 0.078 to 0.050 to 0.029 MHz).

As a final observation, we note the $\sim r_e$ (1) structural changes with increasing fluorine substitution - namely, a pronounced shortening of CF, accompanied by a less pronounced lengthening of C-C; while CN is essentially unchanged. Going from CH_2FCN to CHF_2CN to CF_3CN, CF decreases from 1.3732 to 1.3461 to 1.3266 Å. In CF_4, which completes this sequence, $\sim r_e$ (1) is 1.3154 Å. Going from CH_3CN to CH_2FCN to CHF_2CN to CF_3CN, C-C increases from 1.4578 to 1.4662 to 1.4762 to 1.4792 Å. Meanwhile, CN holds at 1.1553(1) Å.

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