Calculation of Cl and N Nuclear Quadrupole Coupling Constants on Approximate Equilibrium Molecular Structures

IV. F, Cl, C≡N - Ethanes

William C. Bailey

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Contents

Calculations have been made of Cl and N nuclear quadrupole coupling constants on approximate equilibrium molecular structures of the following substituted ethanes:

1. Ethyl Chloride, CH_3-CH_2Cl
2. 1-Chloro-1-Fluoroethane, $CH_3-CHFCl$
3. 1-Chloro-1,2,2,2-Tetrafluoroethane, $CF_3-CHFCl$
4. 1-Chloro-1,1-Difluoroethane, CH_3-CF_2Cl
5. *trans-1-Chloro-1,1,2-Trifluoroethane*, t-CH_2F-CF_2Cl
6. Methyl Chloroform, CH_3-CCl_3
7. 1,1-Dichloroethane, CH_3-$CHCl_2$
8. 1,1-Dichloro-2,2,2-Trifluoroethane, CF_3-$CHCl_2$
9. *gauche-1,2-Dichloroethane*, g-CH_2Cl-CH_2Cl
10. *trans-1-Chloro-2-Cyanoethane*, t-$CH_2Cl-CH_2C\equiv N$
11. 1-Chloro-1-Cyanoethane, $CH_3-CHClC\equiv N$
12. Ethyl Cyanide, $CH_3-CH_2C\equiv N$

[1] Modified July 2016

Introduction

Approximate equilibrium structures of the subjects of this investigation - listed above - were derived by MP2/aug-cc-pVTZ(G03)[2] optimization with empirically corrected bond lengths, as summarized in the following section (see reference [1] for details). NQCC's calculated on these structures, as well as on the optimized structures, are compared with experimental values, where available, in Tables 1 - 12.

Approximate Equilibrium Molecular Structures (~ r_e)

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

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

CCl $\sim r_e$ (Å) = 0.99872 × r_{opt} – 0.00097, RSD = 0.0021 Å,

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

C≡N $\sim r_e$ (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, r_e. CH bond lengths and interatomic angles are those calculated by MP2/aug-cc-pVTZ (G03) optimization, without correction.

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.

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[2] 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.

Calibration 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

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

$$\chi_{ij}(^{37}Cl) = (-15.120 \text{ MHz/a.u.})\, q_{ij}, \quad RSD = 0.44 \text{ MHz},$$

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

where q_{ij} are the calculated efg's. (See reference [1] for details.)

(Note: The G03 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 G03 "standard orientation" to a,b,c and x,y,z principal axes is available in reference [1].)

Results

The results of this investigation - structure parameters and nuclear quadrupole coupling constants - are collected below in Tables 1 - 12.

In Tables 1 - 12; r_{opt}, ~ r_e, and experimental structure parameters, where available, 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 nqccs (percentage of the average magnitude of the experimental nqcc's). φ (degrees) is the angle between its subscriped parameters. $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

Table 1. Ethyl Chloride, CH_3-CH_2Cl. Structure parameters (Å and degrees) and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_m^{ρ} [a]	Expt. [b]
CC	1.5112	1.5096	1.5096(22)	
CCl	1.7916	1.7883	1.7888(18)	
CH	1.0864	1.0864	1.0862(22)	
CH_a	1.0880	1.0880	1.0904(98)	
CH_s	1.0908	1.0908	1.0894(25)	

CCCl	110.78	110.78	111.02(7)	
CCH_a	110.66	110.66	110.53(13)	
H_aCH_a	108.54	108.54	108.26(37)	
CCH_s	109.58	109.58	109.30(105)	
CCH	112.00	112.00	111.81(27)	
HCH	109.13	109.13	108.99(31)	
χ_{aa} (^{35}Cl)	-49.60	-49.47	-49.69	-49.29(9)
χ_{bb}	13.77	13.71	13.89	13.65
χ_{cc}	35.83	35.76	35.80	35.64
$\lvert\chi_{ab}\rvert$	42.77	42.74	42.64	
RMS	0.22 (0.7 %)	0.13 (0.4 %)	0.28 (0.8 %)	
χ_{xx}	35.31	35.26	35.28	
χ_{yy}	35.83	35.76	35.80	
χ_{zz}	-71.14	-71.03	-71.08	
η	0.0072	0.0071	0.0074	
$\varphi_{z,a}$	26.74	26.76	26.64	
$\varphi_{a,CCl}$	25.86	25.88	25.78	
$\varphi_{z,CCl}$	0.88	0.89	0.87	
χ_{aa} (^{37}Cl)	-39.29	-39.19	-39.36	-39.11(8)
χ_{bb}	11.05	11.00	11.14	10.94
χ_{cc}	28.24	28.19	28.22	28.16

$\lvert\chi_{ab}\rvert$	33.56	33.53	33.45	
RMS	0.13 (0.5 %)	0.06 (0.2 %)	0.18 (0.7 %)	

[a] Ref. [2]. [b] Ref. [3]. BACK TO TOP

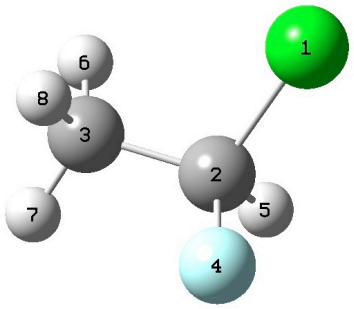


Table 2. 1-Chloro-1-Fluoroethane, CH_3−CHFCl. Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e		Expt. [a]
CC	1.5018	1.5006		
CCl	1.7810	1.7778		
CF	1.3734	1.3666		
CH	1.0867	1.0867		
CCCl	110.97	110.97		
CCF	109.78	109.78		
CCH	113.66	113.66		
ClCF	108.28	108.28		
ClCH	106.24	106.24		
HCF	107.70	107.70		
CH(6)	1.0872	1.0872		
CH(7)	1.0889	1.0889		

CH(8)	1.0875	1.0875		
CCH(6)	109.92	109.92		
CCH(7)	109.04	109.04		
CCH(8)	109.63	109.63		
H(6)CH(7)	109.42	109.42		
H(6)CH(8)	109.31	109.31		
H(7)CH(8)	109.50	109.50		
χ_{aa} (^{35}Cl)	-62.89	-62.62		-62.4014(109)
χ_{bb}	34.41	34.30		34.2641(138)
χ_{cc}	28.48	28.32		28.1373(138)
$\lvert\chi_{ab}\rvert$ [b]	0.48	0.66		
$\lvert\chi_{ac}\rvert$	26.68	26.63		25.5(64)
$\lvert\chi_{bc}\rvert$	2.04	1.97		
RMS	0.36 (0.9 %)	0.17 (0.4 %)		
χ_{xx}	32.86	32.76		
χ_{yy}	37.26	37.09		
χ_{zz}	-70.11	-69.85		
η	0.0628	0.0619		
$\varphi_{z,CCl}$	0.60	0.66		
χ_{aa} (^{37}Cl)	-49.62	-49.40		-49.210(60)
χ_{bb}	27.12	27.03		26.982(60)

χ_{cc}	22.50	22.37		22.227(60)
$\lvert\chi_{ab}\rvert$ [b]	0.29	0.42		
$\lvert\chi_{ac}\rvert$	20.94	20.90		
$\lvert\chi_{bc}\rvert$	1.64	1.58		
RMS	0.29 (0.9 %)	0.14 (0.4 %)		

[a] Ref. [4]. [b] The algebraic sign of the product $\chi_{ab}\,\chi_{ac}\,\chi_{bc}$ is positive. BACK TO TOP

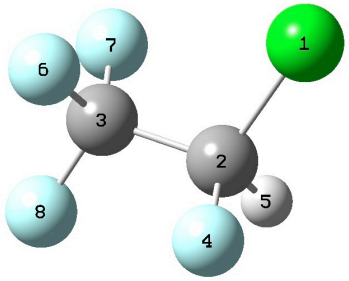


Table 3. 1-Chloro-1,2,2,2-Tetrafluoroethane, CF_3−CHFCl. Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e		Expt. [a]
CC	1.5299	1.5274		
CCl	1.7544	1.7512		
CF	1.3582	1.3518		
CH	1.0872	1.0872		
CCCl	110.49	110.49		
CCF	108.10	108.10		
CCH	109.39	109.39		
ClCF	110.34	110.34		
ClCH	108.88	108.88		

HCF	109.64	109.64		
CF(6)	1.3289	1.3231		
CF(7)	1.3349	1.3290		
CF(8)	1.3374	1.3314		
CCF(6)	112.01	112.01		
CCF(7)	110.09	110.09		
CCF(8)	109.00	109.00		
F(6)CF(7)	108.95	108.95		
F(6)CF(8)	108.47	108.47		
F(7)CF(8)	108.23	108.23		
χ_{aa} (^{35}Cl)	-34.54	-34.37		-34.247(44)
χ_{bb}	4.30	4.35		4.487(47)
χ_{cc}	30.24	30.02		29.760(44)
$\lvert\chi_{ab}\rvert$ [b]	47.72	47.46		
$\lvert\chi_{ac}\rvert$	27.60	27.49		
$\lvert\chi_{bc}\rvert$	16.51	16.46		
RMS	0.34 (1.5 %)	0.19 (0.8 %)		
χ_{xx}	35.76	35.61		
χ_{yy}	40.56	40.32		
χ_{zz}	-76.32	-75.93		
η	0.0628	0.0619		
$\varphi_{z,CCl}$	1.17	1.21		

χ_{aa} (^{37}Cl)	-28.25	-28.12		-26.95(51)
χ_{bb}	4.41	4.44		4.53(27)
χ_{cc}	23.84	23.67		22.42(49)
$\lvert\chi_{ab}\rvert$ [b]	37.18	36.97		
$\lvert\chi_{ac}\rvert$	21.91	21.83		
$\lvert\chi_{bc}\rvert$	12.70	12.66		
RMS	1.11 (6.2 %)	0.99 (5.5 %)		

[a] Ref. [5]. [b] The algebraic sign of the product $\chi_{ab}\chi_{ac}\chi_{bc}$ is negative. BACK TO TOP

Table 4. 1-Chloro-1,1-Difluoroethane, $CH_3{-}CF_2Cl$. Structure parameters (Å and degrees) and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		Expt. [a]
CC	1.4994	1.4984		
CCl	1.7763	1.7730		
CF	1.3505	1.3442		
CH_a	1.0857	1.0857		
CH_s	1.0879	1.0879		
CCCl	112.13	112.13		
CCH_a	109.37	109.37		
H_aCH_a	109.84	109.84		
CCH_s	108.17	108.17		

CCF	110.91	110.91		
FCF	106.71	106.71		
χ_{aa} (^{35}Cl)	-72.64	-72.22		-72.0861(57)
χ_{bb}	36.97	36.74		36.719(13)
χ_{cc}	35.66	35.48		35.368(13)
$\lvert\chi_{ab}\rvert$	0.56	0.50		
RMS	0.39 (0.8 %)	0.10 (0.2 %)		
χ_{xx}	36.98	36.74		
χ_{yy}	35.66	35.48		
χ_{zz}	-72.64	-72.22		
η	-0.018	-0.017		
$\varphi_{z,a}$	0.30	0.26		
$\varphi_{a,CCl}$	0.07	0.05		
$\varphi_{z,CCl}$	0.22	0.31		
χ_{aa} (^{37}Cl)	-57.25	-56.92		-56.8162(73)
χ_{bb}	29.14	28.95		28.911(19)
χ_{cc}	28.11	27.96		27.905(19)
$\lvert\chi_{ab}\rvert$	0.60	0.56		
RMS	0.30 (0.8 %)	0.07 (0.2 %)		

[a] Ref. [6]. BACK TO TOP

Table 5. *trans*-1-Chloro-1,1,2-Trifluoroethane, t-CH_2F-CF_2Cl. Structure parameters (Å and degrees) and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		Expt. [a]
C(1)C(2)	1.5144	1.5126		
C(1)Cl	1.7699	1.7666		
C(1)F	1.3422	1.3360		
C(2)C(1)Cl	108.78	108.78		
C(2)C(1)F	111.08	111.08		
FC(1)F	107.47	107.47		
C(2)F	1.3756	1.3688		
C(2)H	1.0877	1.0877		
C(1)C(2)F	109.00	109.00		
C(1)C(2)H	108.92	108.92		
HC(2)H	109.49	109.49		
χ_{aa} (^{35}Cl)	-58.19	-57.84		-57.958(10)
χ_{bb}	21.15	21.02		21.231(11)
χ_{cc}	37.04	36.82		36.727(11)
$\lvert\chi_{ab}\rvert$	36.79	36.54		
RMS	0.23 (0.6 %)	0.15 (0.4 %)		
χ_{xx}	35.59	35.35		

χ_{yy}	37.04	36.82		
χ_{zz}	-72.62	-72.17		
η	0.020	0.020		
$\varphi_{z,a}$	21.42	21.41		
$\varphi_{a,CCl}$	22.03	22.08		
$\varphi_{z,CCl}$	0.61	0.67		
χ_{aa} (^{37}Cl)	-46.46	-46.19		-46.268(11)
χ_{bb}	17.28	17.17		17.319(13)
χ_{cc}	29.19	29.02		28.949(13)
$\lvert\chi_{ab}\rvert$	28.33	28.14		
RMS	0.18 (0.58 %)	0.11 (0.34 %)		

[a] Ref. [7]. BACK TO TOP

Table 6(a). 1,1,1-Trichloroethane (Methyl Chloroform), $CH_3C^{35}Cl_3$. Structure parameters (Å and degrees) and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column. χ_{uu} is the component of the nqcc tensor along the threefold axis, χ_{vv} and χ_{ww} are the components along the v- and w- axes for the Cl atom in the uv-plane.

Parameter	r_{opt}	$\sim r_e$	r_o [a]	Expt. [b]
CC	1.5101	1.5085	1.541	
CCl	1.7776	1.7744	1.7712	
CH	1.0878	1.0878	1.090	

CCCl	110.03	110.03 [c]	109.55	
ClCCl	108.91	108.91		
CCH	109.04	109.04	108.90	
HCH	109.90	109.90		
χ_{uu} (^{35}Cl)	27.44	27.36	28.06	26.8907(9)
χ_{vv}	-66.33	-66.18	-66.87	-65.5378(12)
χ_{ww}	38.89	38.82	38.81	38.6472(12)
$\lvert\chi_{uv}\rvert$	36.26	36.22	35.29	36.510(23)
RMS	0.57 (1.3 %)	0.47 (1.1 %)	1.03 (2.3 %)	
χ_{xx}	39.83	39.74	39.74	39.571(14)
χ_{yy}	38.89	38.82	38.81	38.6472(12)
χ_{zz}	-78.72	-78.56	-78.55	-78.218(14)
η	-0.0120	-0.0118	-0.0119	-0.0118(2)
$\varphi_{z,u}$	71.14	71.12	71.68	70.846(9)
$\varphi_{u,CCl}$	69.97	69.97	70.45	
$\varphi_{z,CCl}$	1.17	1.15	1.24	

[a] Ref. [8]. [b] Ref. [9]. [c] Calculation on the ~ r_e structure but with CCCl = 110.20° gives χ_{uu} = 26.98, χ_{vv} = -65.83, and χ_{ww} = 38.84 MHz, for which RMS = 0.21 MHz (0.48 %). See CH_3CCl_3.

Table 6(b). 1,1,1-Trichloroethane (Methyl Chloroform), $CH_3C^{37}Cl^{35}Cl_2$. ^{35}Cl and ^{37}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column. Structure parameters are given in Table 6(a).

Parameter	r_{opt}	$\sim r_e$	r_o [a]	Expt. [b]
χ_{aa} (^{35}Cl)	12.99	12.98		13.0190(13)
χ_{bb}	-40.02	-39.93		-39.4898(13)
χ_{cc}	27.03	26.95		26.4708(6)
$\lvert\chi_{ac}\rvert$ [c]	18.29	18.27		18.294(59)
$\lvert\chi_{ab}\rvert$	45.20	45.11		44.7363(42)
$\lvert\chi_{bc}\rvert$	31.92	31.88		32.128(29)
RMS	0.45 (1.7 %)	0.38 (1.4 %)		
χ_{aa} (^{37}Cl)	-52.91	-52.79	-53.33	-52.3028(16)
χ_{bb}	30.65	30.59	30.59	30.4585(16)
χ_{cc}	22.26	22.20	22.74	21.8443(11)
$\lvert\chi_{ac}\rvert$	27.74	27.70	26.95	28.032(76)
RMS	0.44 (1.3 %)	0.36 (1.0 %)	0.79 (2.3 %)	

[a] Ref. [8]. [b] Ref. [9]. [c] The algebraic sign of the product $\chi_{ac}\chi_{ab}\chi_{bc}$ is negative.
BACK TO TOP

Table 7. 1,1-Dichloroethane, CH_3-$CH^{35}Cl_2$ (C_s). Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_s [a]	Expt. [b]
CC	1.5073	1.5058	1.517(3)	
CCl	1.7799	1.7766	1.775(1)	
CCCl	110.51	110.51	110.78(16)	
ClCCl	110.11	110.11	110.45(12)	
CH	1.0846	1.0846	1.085	
CH_s	1.0877	1.0877	1.100(5)	
CH_a	1.0887	1.0887	1.098(27)	
CCH_s	109.85	109.85	109.16(38)	
CCH_a	109.47	109.47	109.0(29)	
H_aCH_a	109.53	109.53	110.78	
χ_{aa} (^{35}Cl)	-39.73	-39.62	-40.01	-39.0405(22)
χ_{bb}	11.08	11.06	11.25	10.6742(30)
χ_{cc}	28.65	28.56	28.76	28.3663(30)
χ_{ab} [c]	±44.30	±44.22	±44.42	±44.22(36)
χ_{ac}	±25.24	±25.22	±25.32	±24.08(74)
χ_{bc}	-16.14	-16.13	-16.04	-16.27(29)
RMS	0.49 (1.9 %)	0.42 (1.6 %)	0.69 (2.6 %)	
χ_{xx}	35.75	35.70	35.96	34.79(93)

χ_{yy}	38.36	38.28	38.40	38.41(57)
χ_{zz}	-74.11	-73.98	-74.36	-73.19(71)
η	0.035	0.035	0.033	0.049(21)
$\varphi_{z,CCl}$	1.09	1.08	1.11	

[a] Ref. [10]. [b] Ref. [11]. [c] The algebraic sign of the product $\chi_{ab}\chi_{ac}\chi_{bc}$ is negative.
BACK TO TOP

Table 8(a). 1,1-Dichloro-2,2,2-Trifluoroethane, CF_3-$CH^{35}Cl_2$ (C_s). Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		Expt. [a]
CC	1.5296	1.5272		
CCl	1.7601	1.7568		
CCCl	109.85	109.85		
ClCCl	111.93	111.93		
CH	1.0856	1.0856		
CF_s	1.3297	1.3238		
CF_a	1.3369	1.3309		
CCF_s	112.33	112.33		
CCF_a	109.76	109.76		
F_aCF_a	107.81	107.81		
χ_{aa} (^{35}Cl)	12.29	12.29		12.385(35)
χ_{bb}	-42.72	-42.56		-42.284(31)

χ_{cc}	30.43	30.27		29.899 [b]
χ_{ab} [c]	±46.80	±46.62		
χ_{ac}	-17.36	-17.31		
χ_{bc}	±29.66	±29.62		
RMS	0.40 (1.4 %)	0.27 (0.97 %)		
χ_{xx}	39.02	38.91		
χ_{yy}	41.15	41.00		
χ_{zz}	-80.17	-79.91		
η	0.027	0.026		
$\varphi_{z,CCl}$	0.53	0.51		

[a] Ref. [12]. [b] Derived here from zero trace condition. [c] The algebraic sign of the product $\chi_{ab}\chi_{ac}\chi_{bc}$ is negative.

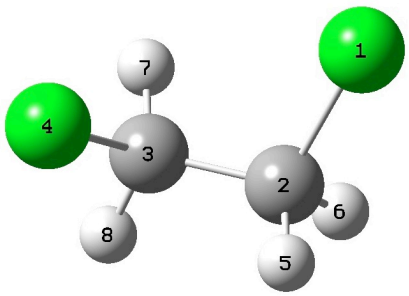
Table 8(b). 1,1-Dichloro-2,2,2-Trifluoroethane, CF_3-$CH^{35}Cl^{37}Cl$ ("C_s"). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column. Structure parameters are given in Table 7(a).

	r_{opt}	~ r_e		Expt. [a]
χ_{aa} (^{35}Cl)	18.05	18.02		17.639(51)
χ_{bb}	-48.47	-48.29		-47.670(67)
χ_{cc}	30.42	30.27		30.031 [b]
$\lvert\chi_{ab}\rvert$ [c]	42.89	42.74		
$\lvert\chi_{ac}\rvert$	15.42	15.39		

$\lvert\chi_{bc}\rvert$	30.72	30.68		
RMS	0.58 (1.8 %)	0.44 (1.4 %)		
χ_{aa} (^{37}Cl)	4.78	4.81		4.701(54)
χ_{bb}	-28.77	-28.68		-28.331(83)
χ_{cc}	23.99	23.87		23.630 [b]
$\lvert\chi_{ab}\rvert$ [c]	39.36	39.21		
$\lvert\chi_{ac}\rvert$	15.14	15.10		
$\lvert\chi_{bc}\rvert$	22.44	22.41		
RMS	0.33 (1.8 %)	0.25 (1.3 %)		

[a] Ref. [12]. [b] Derived here from zero trace condition. [c] The algebraic sign of the product $\chi_{ab}\,\chi_{ac}\,\chi_{bc}$ is negative. BACK TO TOP

Table 9. *gauche* 1,2-Dichloroethane (C_2 symmetry), g-CH_2Cl-CH_2Cl. Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.



Parameter	r_{opt}	~ r_e	r_s [a]	Expt. [b]
CC	1.5079	1.5065	1.491(3)	
CCl	1.7808	1.7775	1.787(4)	
CCCl	111.69	111.69	112.1(3)	

ClCCCl	67.69	67.69	68.1(7)	
CH(5,7)	1.0864	1.0864	1.108(6)	
CH(6,8)	1.0883	1.0883	1.098(4)	
CCH(5,7)	111.15	111.15	107.5(8)	
CCH(6,8)	109.58	109.58	111.3(4)	
ClCH(5,7)	107.45	107.45	105.7(4)	
ClCH(6,8)	107.05	107.05	109.6(8)	
χ_{aa} (^{35}Cl)	-0.52	-0.51	-0.76	-1.1523(14)
χ_{bb}	-28.19	-28.13	-28.80	-27.5129(14)
χ_{cc}	28.71	28.64	29.56	28.6651(14)
$\lvert\chi_{ab}\rvert$ [c]	50.04	49.93	50.48	49.89(4)
$\lvert\chi_{ac}\rvert$	16.43	16.41	16.02	16.51(6)
$\lvert\chi_{bc}\rvert$	22.98	22.96	22.39	22.70(9)
RMS	0.53 (2.8 %)	0.51 (2.7 %)	0.93 (4.9 %)	
χ_{xx}	36.03	35.96	36.37	
χ_{yy}	38.00	37.93	38.08	
χ_{zz}	-74.03	-73.89	-75.45	
η	0.026	0.027	0.023	
$\varphi_{z,CCl}$	0.64	0.65	0.48	

[a] Ref. [10]. [b] Ref. [17]. [c] The algebraic sign of the product $\chi_{ab}\chi_{ac}\chi_{bc}$ is negative.
BACK TO TOP

Table 10(a). *trans* 1-Chloro-2-Cyanoethane (3-Chloropropionitrile), t-CH_2Cl-$CH_2C{\equiv}N$. Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		Expt. [a]
C_1C_2	1.5235	1.5214		
C_1Cl	1.7801	1.7768		
C_1H	1.0861	1.0861		
C_2C	1.4602	1.4608		
$C{\equiv}N$	1.1708	1.1560		
C_2H	1.0895	1.0895		
C_2C_1Cl	109.51	109.51		
C_2C_1H	111.22	111.22		
HC_1H	109.51	109.51		
C_1C_2C	110.10	110.10		
$C_2C{\equiv}N$	178.24	178.24		
C_1C_2H	110.02	110.02		
HC_2H	107.92	107.92		
χ_{aa} (^{35}Cl)	-61.21	-61.01		-58.8(9)
χ_{bb}	23.62	23.51		
χ_{cc}	37.59	37.50		
$\lvert\chi_{ab}\rvert$	35.03	35.05		
χ_{xx}	36.21	36.15		

χ_{yy}	37.59	37.50		
χ_{zz}	-73.80	-73.66		
η	0.0186	0.0183		
$\varphi_{z,a}$	19.78	19.84		
$\varphi_{a,CCl}$	19.20	19.24		
$\varphi_{z,CCl}$	0.57	0.60		
χ_{aa} (^{37}Cl)	-48.26	-48.10		-47.6(9)
χ_{bb}	18.63	18.54		
χ_{cc}	29.62	29.55		
$\lvert\chi_{ab}\rvert$	27.59	27.61		

[a] Ref. [13].

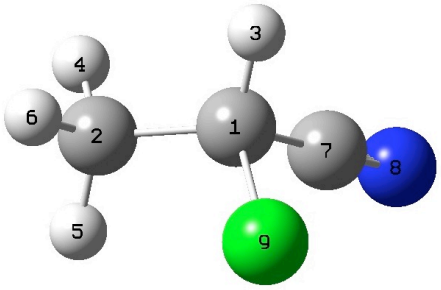
Table 10(b). *trans* 1-Chloro-2-Cyanoethane (3-Chloropropionitrile), t-CH_2Cl-$CH_2C{\equiv}N$. Structure parameters (Å and degrees) and ^{14}N quadrupole coupling constants (MHz) in ^{35}Cl species. Coupling constants in a given column were calculated on the molecular structure given in the heading of that column. Structure parameters are given in Table 9(a).

Parameter	r_{opt}	$\sim r_e$		Expt.
χ_{aa} (^{14}N)	-3.412	-3.536		
χ_{bb}	1.465	1.506		
χ_{cc}	1.948	2.030		
$\lvert\chi_{ab}\rvert$	2.035	2.113		
χ_{xx}	2.202	2.275		

χ_{yy}	1.948	2.030		
χ_{zz}	-4.150	-4.304		
η	-0.0614	-0.0569		
$\varphi_{z,a}$	19.92	19.99		
$\varphi_{a,CN}$	20.37	20.40		
$\varphi_{z,CN}$	0.45	0.42		

BACK TO TOP

Table 11(a). 1-Chloro-1-Cyanoethane (2-Chloropropionitrile), $CH_3-CHClC{\equiv}N$. Structure parameters (Å and degrees) and chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.



Parameter	r_{opt}	$\sim r_e$		Expt. [a]
C(1)C(2)	1.5192	1.5172		
CCl	1.7922	1.7890		
C(1)C(7)	1.4596	1.4603		
C≡N	1.1717	1.1567		
C(1)H	1.0882	1.0882		
C(2)C(1)Cl	110.39	110.39		
CCC	111.64	111.64		
CC≡N	177.99	177.99		
C(2)C(1)H	111.18	111.18		

ClC(1)C(7)	108.83	108.83		
ClCH	105.92	105.92		
HC(1)C(7)	108.68	108.68		
CH(4)	1.0895	1.0895		
CH(5)	1.0876	1.0876		
CH(6)	1.0874	1.0874		
CCH(4)	109.48	109.48		
CCH(5)	110.07	110.07		
CCH(6)	109.45	109.45		
H(4)CH(5)	109.12	109.12		
H(4)CH(6)	109.45	109.45		
H(5)CH(6)	109.25	109.25		
χ_{aa} (^{35}Cl)	-30.73	-30.87		-28.24(51)
χ_{bb} - χ_{cc}	-27.56	-27.24		-26.30(63)
χ_{bb}	1.58	1.81		0.97 [b]
χ_{cc}	29.14	29.05		27.27 [b]
$\lvert\chi_{ab}\rvert$ [c]	50.86	50.68		
$\lvert\chi_{ac}\rvert$	26.37	26.37		
$\lvert\chi_{bc}\rvert$	19.64	19.54		
RMS	1.83 (9.7 %)	1.90 (10 %)		
χ_{xx}	38.66	38.60		
χ_{yy}	39.36	39.25		

χ_{zz}	-78.02	-77.85		
η	0.0089	0.0084		
$\varphi_{z,CCl}$	1.54	1.53		
χ_{aa} (^{37}Cl)	-25.77	-25.88		-23.41(93)
χ_{bb} - χ_{cc}	-20.33	-20.09		-22.20(86)
χ_{bb}	2.72	2.89		0.60 [b]
χ_{cc}	23.06	22.98		22.80 [b]
$\lvert\chi_{ab}\rvert$ [c]	39.62	39.47		
$\lvert\chi_{ac}\rvert$	20.97	20.96		
$\lvert\chi_{bc}\rvert$	15.01	14.93		
RMS	1.84 (12 %)	1.65 (10 %)		

[a] Ref. [14]. [b] Derived here from the experimental χ_{aa} and χ_{bb} - χ_{cc} [c] The algebraic sign of the product $\chi_{ab}\,\chi_{ac}\,\chi_{bc}$ is negative.

Table 11(b). 1-Chloro-1-Cyanoethane (2-Chloropropionitrile), $CH_3-CHClC{\equiv}N$. Structure parameters (Å and degrees) and ^{14}N nuclear quadrupole coupling constants (MHz) in ^{35}Cl species.. Coupling constants in a given column were calculated on the molecular structure given in the heading of that column. Structure parameters are given in Table 8 (a).

Parameter	r_{opt}	$\sim r_e$		Expt.
χ_{aa} (^{14}N)	-2.694	-2.787		
χ_{bb}	1.021	1.046		
χ_{cc}	1.673	1.741		

$\lvert\chi_{ab}\rvert$	2.354	2.445		
$\lvert\chi_{ac}\rvert$	1.322	1.373		
$\lvert\chi_{bc}\rvert$	0.463	0.499		
χ_{xx}	1.909	1.997		
χ_{yy}	2.258	2.328		
χ_{zz}	-4.167	-4.325		
η	0.0838	0.0766		
$\varphi_{z,CN}$	0.21	0.20		

BACK TO TOP

Table 12. Ethyl Cyanide, $CH_3{-}CH_2C{\equiv}N$. 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 that same column.

Parameter	r_{opt}	$\sim r_e$	r_s [a]	Expt. [b]
CC	1.5297	1.5272	1.537(1)	
CC≡N	1.4605	1.4611	1.459(1)	
C≡N	1.1707	1.1560	1.159(1)	
CH	1.0899	1.0899	1.094(1)	
CCC	111.64	111.64	111.98(10)	
CC≡N	178.68	178.68	178.73(22)	
CCH	110.73	110.73	110.62(3)	
HCH	107.23	107.23		
CH_a	1.0878	1.0878	1.091(1)	

CH_s	1.0881	1.0881	1.079(18)	
CCH_a	110.67	110.67	110.47(2)	
H_aCH_a	108.28	108.28		
CCH_s	109.88	109.88	111.08(237)	
H_sCH_a	108.64	108.64		
χ_{aa} (^{14}N)	-3.234	-3.349	-3.322	-3.309(33)
χ_{bb}	1.242	1.278	1.278	1.265(13)
χ_{cc}	1.992	2.070	2.044	2.044(20)
$\lvert\chi_{ab}\rvert$	2.093	2.180	2.165	
RMS	0.054 (2.5 %)	0.028 (1.3 %)	0.011 (0.5 %)	
χ_{xx}	2.068	2.144	2.136	
χ_{yy}	1.992	2.070	2.044	
χ_{zz}	-4.060	-4.214	-4.181	
η	-0.019	-0.017	-0.022	
$\varphi_{z,a}$	21.54	21.65	21.63	
$\varphi_{a,CN}$	21.84	21.92	21.99	
$\varphi_{z,CN}$	0.30	0.27	0.36	

[a] Ref. [15]. [b] Ref. [16]. BACK TO TOP

Summary

The results given above in Tables 1 - 11 for ^{35}Cl and ^{37}Cl nqcc's calculated on the ~ r_e structures are summarized below in Table 13.

Table 13. ^{35}Cl and ^{37}Cl: Root mean square (RMS) difference between calculated and experimental diagonal inertial nqcc's for calculation on ~ r_e structures. (Percentage of the average of the magnitudes of the experimental nqcc's.)

Molecule	RMS (MHz) / ^{35}Cl	RMS (MHz) / ^{37}Cl
CH_3-CH_2Cl	0.13 (0.4 %)	0.06 (0.2 %)
$CH_3-CHFCl$	0.17 (0.4 %)	0.14 (0.4 %)
$CF_3-CHFCl$	0.19 (0.8 %)	0.99 (5.5 %)
CH_3-CF_2Cl	0.10 (0.2 %)	0.07 (0.2 %)
t-CH_2F-CF_2Cl	0.15 (0.4 %)	0.11 (0.3 %)
$CH_3-C^{35}Cl_3$	0.47 (1.1 %)	- - -
$CH_3-C^{37}Cl^{35}Cl_2$	0.38 (1.4 %)	0.36 (1.0 %)
CH_3-$CH^{35}Cl_2$	0.42 (1.6 %)	- - -
CF_3-$CH^{35}Cl_2$	0.27 (1.0 %)	- - -
CF_3-$CH^{35}Cl^{37}Cl$	0.44 (1.4 %)	0.25 (1.3 %)
g-$CH_2{}^{35}Cl-CH_2{}^{35}Cl$	0.88 (4.6 %)	- - -
t-$CH_2Cl-CH_2C\equiv N$		
$CH_3-CHClC\equiv N$	1.90 (10 %)	1.65 (10 %)

As can be seen in Table 13, good agreement (RMS < RSD), with few outliers, is obtained between calculated and experimental ^{35}Cl and ^{37}Cl nuclear quadrupole coupling constants.

Outliers are $CF_3-CHF^{37}Cl$, g-$CH_2{}^{35}Cl-CH_2{}^{35}Cl$, and $CH_3-CH^{35,37}ClC{\equiv}N$.

In t-CH_2Cl-$CH_2C{\equiv}N$, only χ_{aa} has been experimentally determined. Calculated and experimental values are, for ^{35}Cl, -61.01 and -58.8(9) MHz, respectively; and for ^{37}Cl, -48.10 and -47.6(9) MHz. For ^{35}Cl, the difference is 2.2 MHz (3.8 %); for ^{37}Cl, 0.5 MHz, which lies within the uncertainty in the experimental χ_{aa}.

For ^{14}N in ethyl cyanide, the RMS difference between calculated (on $\sim r_e$ structure) and experimental nqccs is 0.028 MHz. In $CH_3-CHClC{\equiv}N$ and t-CH_2Cl-$CH_2C{\equiv}N$, ^{14}N nqccs were not determined, and are here predicted.

In conclusion, the good agreement seen here between calculated and experimental nqcc's validates the $\sim r_e$ structures on which the calculations were made.

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