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

III. XC≡CY; X, Y = H, F, Cl, C≡N, CH_3, CF_3

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Abstract

Calculations have been made of Cl and N nuclear quadrupole coupling constants on approximate equilibrium molecular structures of the following substituted acetylenes derived by MP2/aug-cc-pVTZ(G03) optimization, with empirically corrected bond lengths.

1. Chloroacetylene, HC≡CCl
2. Chlorofluoroacetylene, FC≡CCl
3. Chloromethylacetylene, CH_3C≡CCl
4. Chlorocyanoacetylene, ClC≡CC≡N
5. Cyanoacetylene, HC≡CC≡N
6. Cyanofluoroacetylene, FC≡CC≡N
7. Cyanomethylacetylene, CH_3C≡CC≡N
8. Cyanotrifluoromethylacetylene, CF_3C≡CC≡N
9. Dichloroacetylene, ClC≡CCl
10. Dicyanoacetylene, N≡CC≡CC≡N

For chloroacetylene and cyanoacetylene, as well as accetylene and fluoroacetylene, derived molecular structures are in good agreement with experimental equilibrium structures. For all the above, where accurate experimental coupling constants are known, good agreement is obtained with the calculated values.

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[1] Modified January 2008.

Introduction

Approximate equilibrium structures of the subjects of this investigation - HC≡CCl, FC≡CCl, $CH_3C{\equiv}CCl$, ClC≡CCl, ClC≡CC≡N, HC≡CC≡N, FC≡CC≡N, $CH_3C{\equiv}CC{\equiv}N$, $CF_3C{\equiv}CC{\equiv}N$, and C≡NC≡CC≡N - have been derived by MP2/aug-cc-pVTZ(G03)[2] optimization, with bond length corrections as discussed in the following section. ^{35}Cl, ^{37}Cl, and ^{14}N nuclear quadrupole coupling constants (nqcc) calculated on these structures are shown below in Tables 1 - 8, and compare favorably with experimental values, where available.

The purpose of this work is to calculate molecular structures on which accurate nqcc's may be calculated.

Molecular Structures

The 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 [1]:

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 = 0.0022 Å,

C≡C $\sim r_e$ (Å) = 0.79708 × r_{opt} + 0.23575, RSD = 0.0005 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, $\sim r_e$. CH bond lengths 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

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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.

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

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. For the molecules of this work, $\chi_{zz} = \chi_{aa}$. and $\chi_{xx} = \chi_{yy} = -\frac{1}{2}\chi_{zz}$.

Calibration [1] 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 [1]

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

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

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

where q_{ij} (a.u.) are the calculated efg's.

Results

The results of this investigation - structure parameters and nuclear quadrupole coupling constants - are collected below in Tables 1 - 8.

In Tables 1 - 8; r_{opt}, ~ r_e, and experimental structure parameters are compared. Coupling constants calculated on each structure are compared with experimental nqcc's.

Table 1. Chloroacetylene, HCCCl. Structure parameters (Å and degrees) and 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_e [a]	expt. χ_{zz} [b]
HC	1.0606	1.0606	1.0605	
C≡C	1.2136	1.2031	1.2030	
CCl	1.6386	1.6353	1.6353	

χ_{zz} (^{35}Cl)	-80.02	-79.62	-79.60	-79.7358(19)
χ_{zz} (^{37}Cl)	-63.06	-62.75	-62.73	-62.8451(27)

[a] Ref. [2]. [b] Ref. [3].

Table 2. Chlorofluoroacetylene, FCCCl. Structure parameters (Å and degrees) and 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_o [a]	expt. χ_{zz} [a]
FC	1.2824	1.2775	1.278	
C≡C	1.2044	1.1958	[1.200]	
CCl	1.6423	1.6392	1.636	
χ_{zz} (^{35}Cl)	-83.60	-83.14	-82.82	-83.0(1)
χ_{zz} (^{37}Cl)	-65.89	-65.52	-65.27	-65.6(1)

[a] Ref. [4]. Value in brackets is assumed.

Table 3. Chloromethylacetylene, $CH_3C{\equiv}CCl$. Structure parameters (Å and degrees) and 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}	$\sim r_e$		
ClC	1.6424	1.6394		
C≡C	1.2154	1.2045		
C-C	1.4574	1.4582		
CH	1.0890	1.0890		
CCH	110.66	110.66		
χ_{zz} (^{35}Cl)	-80.05	-79.66		
χ_{zz} (^{37}Cl)	-63.09	-62.78		

Table 4. Chlorocyanoacetylene, ClC≡C-C≡N. Structure parameters (Å and degrees) and nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	$\sim r_e$	r_s [a]	expt. χ_{zz} [a]
ClC	1.6260	1.6229	1.6245	
C≡C	1.2204	1.2085	1.2090	
C-C	1.3669	1.3717	1.3690	
C≡N	1.1785	1.1614	1.1602	
χ_{zz} (^{35}Cl)	-79.90	-79.52	-79.72	-75(4)

χ_{zz} (^{37}Cl)	-62.97	-62.68	-62.83	-62(3)
χ_{zz} (^{14}N)	-4.092	-4.279	-4.295	---

[a] Ref. [5].

Table 5. Cyanoacetylene, HC≡C-C≡N. Structure parameters (Å and degrees) and 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_e [a]	expt. χ_{zz} [b]
HC	1.0631	1.0631	1.0624	
C≡C	1.2174	1.2061	1.2058	
C-C	1.3722	1.3768	1.3764	
C≡N	1.1771	1.1604	1.1605	
χ_{zz} (^{14}N)	-4.186	-4.364	-4.364	-4.31924(1)

[a] Ref. [6]. [b] Ref. [7].

Table 6. Cyanofluoroacetylene, FC≡C-C≡N. Structure parameters (Å and degrees) and 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_o [a]	expt. χ_{zz}
FC	1.2698	1.2652	1.2702	

C≡C	1.2102	1.2003	1.2011	
C-C	1.3705	1.3751	1.3688	
C≡N	1.1768	1.1602	1.1597	
χ_{zz} (^{14}N)	-4.092	-4.271	-4.285	-4.23913(77) [b]
				-4.2513(47) [c]

[a] Ref. [8]. [b] Ref. [9]. [c] Ref. [10].

Table 7. Cyanomethylacetylene, $CH_3C{\equiv}CC{\equiv}N$. Structure parameters (Å and degrees) and 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_o [a]	expt. χ_{zz} [a]
C≡N	1.1780	1.1611		
N≡C-C	1.3697	1.3744		
C≡C	1.2204	1.2086		
C-CH_3	1.4530	1.4540		
CH	1.0889	1.0889		
CCH	110.36	110.36		
χ_{zz} (^{14}N)	-4.028	-4.214	-4.257	-4.0(2)

[a] Ref. [11].

Table 8. Cyanotrifluoromethylacetylene, $CF_3C{\equiv}CC{\equiv}N$. Structure parameters (Å and degrees) and 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. χ_{zz} [a]
C≡N	1.1775	1.1607		
N≡C-C	1.3707	1.3754		
C≡C	1.2178	1.2064		
C-CF_3	1.4662	1.4666		
CF	1.3361	1.3302		
CCF	110.81	110.81		
χ_{zz} (^{14}N)	-4.335	-4.509		-4.40(4)

[a] Ref. [12].

Summary

The results given above in Tables 1 - 8 are summarized below in Tables 9 and 10, which include $\sim r_e$ and χ_{zz} calculated for ClC≡CCl and N≡CC≡CC≡N.

Table 9. XC≡CCl; X = H, F, CH_3, C≡N. Approximate equilibrium structure parameter, $\sim r_e$ (Å), and calculated ^{35}Cl nuclear quadrupole coupling constants (MHz).

	X-C	C≡C	C-Cl	χ_{zz}
HC≡CCl	1.0606	1.2031	1.6353	-79.62
FC≡CCl	1.2775	1.1958	1.6392	-83.14

$CH_3C{\equiv}CCl$	1.4582	1.2045	1.6394	-79.66
$N{\equiv}CC{\equiv}CCl$	1.3717	1.2085	1.6229	-79.52
$ClC{\equiv}CCl$	1.6347	1.2037	1.6347	-80.81

Table 10. $XC{\equiv}CC{\equiv}N$; X = H, F, CH_3, CF_3, Cl, $C{\equiv}N$. Approximate equilibrium structure parameters, $\sim r_e$ (Å), and calculated ^{14}N nuclear quadrupole coupling constants (MHz).

	X-C	C≡C	C-C	C≡N	χ_{zz}
$HC{\equiv}CC{\equiv}N$	1.0631	1.2061	1.3768	1.1604	-4.364
$FC{\equiv}CC{\equiv}N$	1.2652	1.2003	1.3751	1.1602	-4.271
$CH_3C{\equiv}CC{\equiv}N$	1.4540	1.2086	1.3744	1.1611	-4.214
$CF_3C{\equiv}CC{\equiv}N$	1.4666	1.2064	1.3754	1.1607	-4.509
$ClC{\equiv}CC{\equiv}N$	1.6229	1.2085	1.3717	1.1614	-4.279
$N{\equiv}CC{\equiv}CC{\equiv}N$	1.3709	1.2122	1.3709	1.1620	-4.535

Discussion

Comparison of $\sim r_e$ structures with experimental r_e structures of chloroacetylene and cyanoacetylene are made in Tables 1 and 5. For $HC{\equiv}CH$, $\sim r_e$ and r_e [13] (in parentheses) are C≡C = 1.2018 Å (1.2024 Å) and CH = 1.0616 Å (1.0625 Å); and for $HC{\equiv}CF$ [14], HC = 1.0592 Å (1.0591 Å), C≡C = 1.1965 Å (1.1961 Å), and CF = 1.2755 Å (1.2765 Å). Agreement between $\sim r_e$ and r_e for these four molecules - and presumably for the others as well - is good, the largest difference being 0.0010 Å for CF in $HC{\equiv}CF$.

^{35}Cl and ^{37}Cl nqcc's calculated on the $\sim r_e$ structures of $HC{\equiv}CCl$ and $FC{\equiv}CCl$ compare favorably with the experimental nqcc's, the differences being all less than 0.2 %. For $ClC{\equiv}CC{\equiv}N$, the differences are comparable to the large uncertainties in the experimental values.

^{14}N nqcc's calculated on the ~ r_e structures of HC≡CC≡N, FC≡CC≡N, and CF_3C≡CC≡N differ from the experimental nqcc's by 1.0, 0.75, and 2.5 % respectively; in CH_3C≡CC≡N, the difference is comparable to the large uncertainty in the experimental value.

References

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