Calculation of the ^{14}N nuclear quadrupole coupling constant tensor in ethyl cyanide was made on the ab initio (ai) r_e, semi-experimental (se) r_e, r_o, $r_m^{(1)}$, $r_m^{(2)}$, and r_s-fit molecular structures of Demaison et al. [1]. These are compared with the experimental coupling constants [2 - 4] in Tables 1 - 7.

Electric field gradients calculated at the B3PW91/6-311+G(df,pd) (tight convergence option and default integration grid) level of theory are converted to nuclear quadrupole coupling constants by multiplication by 4.5586(40) MHz/a.u. Details of calibration of this model are given here. A fortran program for transformation of the coupling constant tensor from "standard coordinates" of Gaussian Inc. to inertia a,b,c axes is available here.

For calibration of the model, the standard deviation of residuals (RSD) is 0.030 MHz. Thus, calculations for which the root mean square difference (rms) between calculated and experimental coupling constants is less than this is considered to lie within the computational uncertainty. This is the case for most results shown below.

Table 1. CH_3CH_2CN. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental coupling constants. ϕ (degrees) is the angle between its subscripted parameters.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [2]
X_{aa}	-3.357	-3.381	-3.331	-3.339	-3.336	-3.308	-3.309(33)
X_{bb}	1.291	1.301	1.279	1.289	1.287	1.276	1.265(13)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.044(20)
$\|X_{ab}\|$	2.171	2.188	2.169	2.162	2.171	2.151	
rms	0.034	0.051	0.016	0.022	0.020	0.010	

X_{xx}	2.148	2.080	2.139	2.142	2.147	2.127	
X_{yy}	2.065	2.164	2.052	2.050	2.049	2.032	
X_{zz}	-4.213	-4.244	-4.191	-4.192	-4.196	-4.159	
η	-0.0196	-0.0197	-0.0209	-0.0218	-0.0232	-0.0230	
$\phi_{a,z}$	21.52	21.53	21.63	21.53	21.60	21.59	
$\phi_{a,CN}$	21.79	21.80	21.89	21.82	21.86	22.11	
$\phi_{z,CN}$	0.26	0.27	0.26	0.29	0.26	0.52	

Table 2. CH_3CD_2CN. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental diagonal coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [3]
X_{aa}	-3.447	-3.472	-3.422	-3.429	-3.428	-3.398	-3.449(16)
X_{bb}	1.382	1.392	1.370	1.379	1.378	1.366	1.399(15)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.050(17)
$\|X_{ab}\|$	2.069	2.084	2.068	2.061	2.069	2.051	2.01(18)
rms	0.013	0.022	0.023	0.016	0.017	0.037	

Table 3. CD_3CH_2CN. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental diagonal coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [3]
X_{aa}	-3.203	-3.226	-3.177	-3.188	-3.182	-3.157	-3.209(17)
X_{bb}	1.138	1.145	1.125	1.137	1.133	1.125	1.150(16)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.059(18)
$\|X_{ab}\|$	2.324	2.343	2.322	2.313	2.324	2.301	2.27(12)
rms	0.009	0.016	0.024	0.015	0.019	0.037	

Table 4. $^{13}CH_3CH_2CN$. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [3]
X_{aa}	-3.319	-3.344	-3.294	-3.302	-3.299	-3.271	-3.290(11)
X_{bb}	1.254	1.263	1.241	1.252	1.250	1.239	1.242(10)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.048(12)
$\lvert X_{ab}\rvert$	2.210	2.227	2.208	2.201	2.210	2.190	
rms	0.021	0.038	0.003	0.009	0.007	0.014	

Table 5. $CH_3{}^{13}CH_2CN$. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [3]
X_{aa}	-3.376	-3.401	-3.350	-3.358	-3.356	-3.327	-3.377(21)
X_{bb}	1.311	1.320	1.298	1.308	1.306	1.296	1.334(17)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.043(19)
$\vert X_{ab}\vert$	2.150	2.166	2.148	2.141	2.150	2.130	
rms	0.018	0.027	0.026	0.019	0.020	0.037	

Table 6. $CH_3CH_2{}^{13}CN$. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [3]
X_{aa}	-3.352	-3.376	-3.326	-3.334	-3.331	-3.303	-3.349(11)
X_{bb}	1.286	1.296	1.274	1.284	1.282	1.271	1.297(10)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.052(12)
$\|X_{ab}\|$	2.176	2.194	2.174	2.167	2.176	2.156	
rms	0.010	0.023	0.019	0.012	0.013	0.032	

Table 7. CD_3CD_2CN. ^{14}N nuclear quadrupole coupling constants (MHz). Calculation was made on the structures given in the first row. Experimental coupling constants are given in the last column. rms (MHz) is the root mean square difference between calculated and experimental coupling constants.

	ai r_e	se r_e	r_o	$r_m^{(1)}$	$r_m^{(2)}$	r_s-fit	expt [4]
X_{aa}	-3.278	-3.301	-3.253	-3.262	-3.258	-3.231	-3.213(20)
X_{bb}	1.213	1.221	1.200	1.212	1.208	1.200	1.168(20)
X_{cc}	2.065	2.080	2.052	2.050	2.049	2.032	2.045(20)
$\lvert X_{ab} \rvert$	2.252	2.270	2.250	2.241	2.252	2.230	
rms	0.047	0.061	0.030	0.038	0.035	0.022	

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