Molecular Structure, Quadrupole Coupling Tensor and Dipole Moment of Ethyl Cyanide

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The microwave spectra of CD_3CH_2CN, $^{13}CH_3CH_2CN$, $CH_3{}^{13}CH_2CN$ and $CH_3CH_2C^{15}N$ have been measured. In addition the spectrum of $CH_3CH_2{}^{13}CN$ has been remeasured with greater accuracy. From these spectra and those previously reported – CH_3CH_2CN, CH_3CD_2CN, CH_2DCH_2CN (sym) and CH_2DCH_2CN (asym) – a complete r_S-structure has been calculated by the equations of Kraitchman and Chutjian. r_0-structure calculations were performed with different assumptions due to the symmetry of the molecule. A comparison between r_0- and r_S-structure was made and showed good agreement especially for the atoms of the frame.

The quadrupole coupling constants of the above mentioned isotopes of ethyl cyanide were obtained from the hyperfine structure of the spectra with the exception of $CH_3CH_2C^{15}N$, which has no nucleus with quadrupole moment. The quadrupole coupling tensor in its principal axis system was determined from the constants of CD_3CH_2CN and CH_3CD_2CN using the angle ε between their principal axes of inertia in the a-b-plane.

From Stark effect measurements the dipole moment of CH_3CH_2CN was reevaluated. To determine the direction of the dipole moment Stark effect measurements for CD_3CH_2CN and CH_3CD_2CN were carried out.

Ethyl cyanide has been the subject of several investigations in microwave spectroscopy. With the aid of further experimental information it is now possible to determine the r_s-structure of this molecule. Until now only r_0-structures were proposed by Lerner and Dailey [1] and more recently by Mäder et al. [2]. Further emphasis in microwave studies was on the determination of the ^{14}N-quadrupole coupling, dipole moment and internal rotation by Laurie [3]. Extended studies were made by Li and Harmony [4] for ^{14}N-quadrupole coupling, likewise by Mäder et al. who also examined the rotation-torsion-vibration-interaction in ethyl cyanide.

The microwave spectra of $^{13}CH_3CH_2CN$, $CH_3{}^{13}CH_2CN$, $CH_3CH_2C^{15}N$, CD_3CH_2CN were measured in the region of 8 – 41 GHz and assigned. The spectrum of $CH_3CH_2{}^{13}CN$ was reinvestigated with greater accuracy. From the moments of inertia of these isotopic molecules and those previously reported [2] – CH_3CH_2CN, CH_3CD_2CN, CH_2DCH_2CN (sym) and CH_2DCH_2CN (asym) – a complete r_s-structure could be determined. For comparison a r_0-structure was calculated. In terms of the r_s-structure more reliable calculations of the ^{14}N-quadrupole coupling tensor and dipole moment were possible.

* This work is a part of the thesis of H. M. Heise and that of H. Lutz.

Experimental

The spectra were recorded with a conventional microwave spectrometer [5, 6] using 100 kHz Stark modulation and employing phase stabilized BWO's as microwave sources. The measurements were carried out with absorption cells cooled to temperatures of approximately -70 °C and sample pressures of several microns.

The samples of the isotopic ethyl cyanides $^{13}CH_3CH_2CN$, $CH_3{}^{13}CH_2CN$, CD_3CH_2CN were prepared from the corresponding ^{13}C-substituted ethyl iodides, $^{13}CH_3CH_2J$ and $CH_3{}^{13}CH_2J$ (both 90% C-13, Sharp & Dohme, München), respectively, and from the deuterated species, CD_3CH_2J (99% D, Roth, Karlsruhe), by a modified Kolbe-reaction [2]. For the species $CH_3CH_2{}^{13}CN$ and $CH_3CH_2C^{15}N$ normal ethyl iodide from Merck (Darmstadt) and $Na^{13}CN$ (90% C-13, Sharp & Dohme), in the other case $KC^{15}N$ (51% N-15, Isocommerz) were used. For Stark effect measurements a digital voltmeter Dymec 2401 B was used to determine the Stark field while recording the lines. The cell was calibrated using the transition $J = 1 \rightarrow 2$ of OCS with $\mu_{OCS} = 0.71521$ D [7].

Description of the Spectra

The isotopes of ethyl cyanide are nearly symmetric tops ($\varkappa = -0.94$ to $\varkappa = -0.96$). Due to the

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Table 1. Rotational transitions (MHz) of CD_3CH_2CN.

Transition $J_{K_-K_+} - J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl} - \nu_{calc}$
$0_{00} - 1_{01}$	1 — 2	8 005.11	8 005.00	8 005.04	0.11	0.16	— 0.04
	1 — 1	8 004.28			— 0.72	— 0.80	
	1 — 0	8 006.66			1.66	1.60	
$1_{01} - 1_{10}$	2 — 2	19 064.51	19 064.76	19 064.86	— 0.25	— 0.26	— 0.10
	1 — 1	19 066.07			1.31	1.32	
	2 — 1	19 065.10			0.34	0.35	
	1 — 2	19 065.46			0.70	0.70	
	0 — 1	19 063.69			— 1.07	— 1.09	
	1 — 0	19 064.51			— 0.25	— 0.23	
$0_{00} - 1_{11}$	1 — 2	26 665.23	26 665.29	26 665.35	— 0.06	— 0.06	— 0.06
	1 — 1	26 665.57			0.29	0.29	
	1 — 0	26 664.73			— 0.56	— 0.57	
$1_{01} - 2_{02}$	2 — 3	16 003.50	16 003.45	16 003.56	0.05	0.07	— 0.11
	1 — 2	16 003.50			0.05	0.00	
	0 — 1	16 002.58			— 0.87	— 0.80	
	2 — 2	16 002.58			— 0.87	— 0.96	
	1 — 1	16 005.10			1.65	1.61	
$1_{10} - 2_{11}$	2 — 3	16 414.80	16 414.62	16 414.61	0.18	0.18	0.01
	1 — 2	16 413.82			— 0.80	— 0.80	
	0 — 1	16 415.93			1.31	1.32	
	2 — 2	16 414.43			— 0.19	— 0.19	
	1 — 1	16 414.43			— 0.19	— 0.23	
$1_{11} - 2_{12}$	2 — 3	15 605.85	15 605.64	15 605.53	0.21	0.20	0.11
	1 — 2	15 604.85			— 0.79	— 0.80	
	0 — 1	15 606.73			1.09	1.09	
	2 — 2	15 605.18			— 0.46	— 0.46	
	1 — 1	15 605.85			0.21	0.23	
$2_{02} - 2_{11}$	3 — 3	19 475.90	19 476.03	19 475.91	— 0.13	— 0.15	0.12
	2 — 2	19 476.55			0.52	0.52	
	1 — 1	19 475.48			— 0.55	— 0.52	
	3 — 2	19 475.48			— 0.55	— 0.52	
	2 — 1	19 477.04			1.01	1.09	
	2 — 3	19 477.04			1.01	0.89	
	1 — 2	19 474.87			— 1.16	— 1.09	

μ_a-component of the dipole moment in comparison to μ_b the μ_a-lines are about eight times more intense than μ_b-lines of equivalent line strength. Both spectra – a- and b-type – were measured. The rotational transitions were identified either by their Stark pattern or by their nuclear quadrupole hyperfine structure or both.

The rotational line frequencies of CD_3CH_2CN, $^{13}CH_3CH_2CN$, $CH_3{}^{13}CH_2CN$, $CH_3CH_2{}^{13}CN$ and $CH_3CH_2C^{15}N$ are listed in Tables 1 – 5. They were measured up to the rotational quantum number $J = 3$. In the spectrum of $CH_3CH_2{}^{13}CN$ the transitions $J = 2 \rightarrow 3$ were reexamined and their hyperfine structure was resolved. Note that the same set of transitions was measured in each case. The same set of rotational transitions up to the quantum number $J = 2$ was fitted by a program using the asymmetric rigid rotor model. Thus the distortion effects are negligible and the rotational constants are comparable. The rotational constants of the isotopes together with those determined in Ref. [2] are given in Table 6.

All spectra except that of $CH_3CH_2C^{15}N$, which has no nucleus with a quadrupole moment, showed resolvable hyperfine structure due to the interaction of the ^{14}N-quadrupole moment with the overall rotation. From the hyperfine structure of the lowest transitions up to $J = 2$ the quadrupole coupling constants $\chi_+ = -\chi_{aa}$ and $\chi_- = \chi_{bb} - \chi_{cc}$ * of the corresponding isotopes were determined by a least squares analysis.

For the determination of the dipole moments of CH_3CH_2CN, CD_3CH_2CN and CH_3CD_2CN Stark satellites of the transitions $1_{01} - 2_{02}$, $2_{11} - 3_{12}$ and $2_{02} - 3_{03}$ were used.

* χ_{aa}, χ_{bb} and χ_{cc} are the diagonal elements of the quadrupole coupling tensor with respect to the principal axes of inertia.

Table 1 continued

Transition $J_{K_-K_+} - J'_{K'_-K'_+}$	$F - F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl} - \nu_{calc}$
$1_{01} - 2_{12}$	2 — 3	34 265.88	34 265.89	34 265.84	— 0.01	— 0.01	0.05
	1 — 2	34 266.17			0.28	0.28	
	0 — 1	34 264.80			— 1.09	— 1.09	
	2 — 2	34 265.20			— 0.69	— 0.68	
	1 — 1	34 267.20			1.31	1.31	
$2_{20} - 3_{21}$	3 — 4	24 041.74	24 041.50	24 041.12	0.24	0.23	0.38
	2 — 3	24 040.70			— 0.80	— 0.80	
	1 — 2	24 042.29			0.79	0.80	
	3 — 3	24 041.74			0.24	0.24	
	2 — 2	24 040.70			— 0.80	— 0.81	
$2_{02} - 3_{03}$	3 — 4	23 988.86	23 988.87	23 989.09	— 0.01	0.04	— 0.22
	2 — 3	23 988.86			— 0.01	— 0.00	
	1 — 2	23 988.86			— 0.01	— 0.16	
	3 — 3	23 987.81			— 1.06	— 1.04	
	2 — 2	23 990.30			1.43	1.45	
$2_{11} - 3_{12}$	3 — 4	24 617.74	24 617.65	24 617.82	0.09	0.08	— 0.17
	2 — 3	24 617.45			— 0.20	— 0.20	
	1 — 2	24 617.74			0.09	0.10	
	3 — 3	24 617.09			— 0.56	— 0.57	
	2 — 2	24 618.32			0.67	0.67	
$2_{12} - 3_{13}$	3 — 4	23 404.40	23 404.31	23 404.26	0.09	0.09	0.05
	2 — 3	23 404.09			— 0.22	— 0.20	
	1 — 2	23 404.40			0.09	0.06	
	3 — 3	23 403.44			— 0.87	— 0.86	
	2 — 2	23 405.39			1.08	1.09	
$2_{21} - 3_{22}$	3 — 4	24 015.90	24 015.68	24 015.11	0.22	0.23	0.57
	2 — 3	24 014.90			— 0.78	— 0.80	
	1 — 2	24 016.46			0.78	0.80	
	3 — 3	24 015.90			0.22	0.23	
	2 — 2	24 014.90			— 0.78	— 0.80	
$3_{03} - 3_{12}$	4 — 4	20 104.54	20 104.69	20 104.63	— 0.15	— 0.11	0.06
	3 — 3	20 104.99			0.30	0.32	
	2 — 2	20 104.54			— 0.15	— 0.25	

[a] Intensity weighted average value.
[b] Calculated with the rotational constants of Table 6.
[c] Hyperfine component shifts $\Delta\nu$ HFS $= \nu_{observed} - \nu_{unsplit}$.
[d] Calculated with the quadrupole coupling constants of Table 7.

Quadrupole Coupling Constants

The hyperfine structure due to ^{14}N-quadrupole coupling to overall rotation could be resolved for all low J-lines of the appropriate isotopic molecules. The hyperfine structure was analysed with first order perturbation theory [see, for example, Eq. (9.75), Reference [8]].

The diagonal elements χ_{gg} of the quadrupole coupling tensor, determined from lines up to $J = 2$ are listed in Table 7. Since the molecule has C_s-symmetry the only non-zero off-diagonal tensor element is χ_{ab}. The quadrupole coupling tensor is assumed to be invariant with isotopic substitution. By rotating the principal inertial axis system with isotopic substitution and combining the diagonal elements χ_{gg} of two molecules, the off-diagonal element χ_{ab} may be calculated. We used the two isotopic molecules CD_3CH_2CN and CH_3CD_2CN. In this case the angle of rotation ε between the principal axis systems is the largest of all pairs of measured isotopes. The angle of rotation ε and its error are found to be $3.21 \pm 0.20°$. These were determined from the r_s-structure and its uncertainties. However no account was taken for the error in the determination of the principal axes of the two isotopic molecules assumed to have the same r_s-structure. An r_s-structure does not necessarily give zero inertial products. The details of the further calculation are given elsewhere [9]. The results are shown in Table 7.

It was possible to determine the principal axis elements χ_{zz}, χ_{xx} and χ_{yy} of the coupling tensor. The z-axis of the coupling tensor defines with the a-inertial axis an angle α_Q. This angle agrees within the error limits with α_s, the angle between the C — N-bond and the a-inertial axis. The agreement would be better if $\sphericalangle$CCN were assumed to be 180°.

Table 2. Rotational transitions (MHz) of $^{13}CH_3CH_2CN$.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl}-\nu_{calc}$
$0_{00}-1_{01}$	1 — 2	8 731.99	8 731.84	8 731.82	0.15	0.16	0.02
	1 — 1	8 731.04			— 0.80	— 0.82	
	1 — 0	8 733.49			1.65	1.65	
$1_{01}-1_{10}$	2 — 2	23 208.19	23 208.44	23 208.49	— 0.25	— 0.27	— 0.05
	1 — 1	23 209.77			1.33	1.33	
	2 — 1	23 208.79			0.35	0.35	
	1 — 0	23 208.19			— 0.25	— 0.20	
	1 — 2	23 209.16			0.72	0.72	
	0 — 1	23 207.30			— 1.14	— 1.13	
$0_{00}-1_{11}$	1 — 2	31 475.89	31 475.95	31 476.03	— 0.06	— 0.06	— 0.08
	1 — 2	31 476.26			0.31	0.31	
	1 — 0	31 475.34			— 0.61	— 0.62	
$1_{01}-2_{02}$	2 — 3	17 456.53	17 456.47	17 456.61	0.06	0.07	— 0.14
	1 — 2	17 456.53			0.06	— 0.00	
	0 — 1	17 455.56			— 0.91	— 0.82	
	2 — 2	17 455.56			— 0.91	— 0.99	
	1 — 1	17 458.14			1.67	1.65	
$1_{10}-2_{11}$	2 — 3	17 928.15	17 927.96	17 927.94	0.19	0.19	0.02
	1 — 2	17 927.14			— 0.82	— 0.82	
	0 — 1	17 929.28			1.32	1.33	
	2 — 2	17 927.76			— 0.20	— 0.21	
	1 — 1	17 927.76			— 0.20	— 0.20	
$1_{11}-2_{12}$	2 — 3	16 999.67	16.999.46	16 999.36	0.21	0.21	0.10
	1 — 2	16 998.64			— 0.82	— 0.82	
	0 — 1	17 000.61			1.15	1.13	
	2 — 2	16 999.02			— 0.44	— 0.45	
	1 — 1	16 999.67			0.21	0.20	
$2_{02}-2_{11}$	3 — 3	23 679.76	23 679.91	23 679.82	— 0.15	— 0.15	0.09
	2 — 2	23 680.43			0.52	0.51	
	1 — 1	23 679.78			— 0.53	— 0.51	
	3 — 2	23 679.38			— 0.53	— 0.55	
	2 — 1	23 681.04			1.13	1.13	
	2 — 3	23 680.85			0.94	0.91	
	1 — 2	23 678.76			— 1.15	— 1.13	
$1_{01}-2_{12}$	2 — 3	39 743.58	39 743.60	39 743.56	— 0.02	— 0.02	0.04
	1 — 2	39 743.92			0.32	0.31	

Table 3. Rotational transitions (MHz) of $CH_3{}^{13}CH_2CN$.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl}-\nu_{calc}$
$0_{00}-1_{01}$	1 — 2	8 905.24	8 905.06	8 905.03	0.18	0.17	0.03
	1 — 1	8 904.22			— 0.84	— 0.83	
	1 — 0	8 906.68			1.62	1.67	
$1_{01}-1_{10}$	2 — 2	22 838.05	22 838.31	22 838.43	— 0.26	— 0.27	— 0.12
	1 — 1	22 839.66			1.35	1.34	
	2 — 1	22 838.65			0.34	0.34	
	1 — 2	22 839.05			0.74	0.73	
	0 — 1	22 837.15			— 1.16	— 1.16	
	1 — 0	22 838.05			— 0.26	— 0.18	
$0_{00}-1_{11}$	1 — 2	31 252.45	31 252.51	31 252.57	— 0.06	— 0.07	— 0.06
	1 — 1	31 252.82			0.31	0.33	
	1 — 0	31 251.86			— 0.65	— 0.66	
$1_{01}-2_{02}$	2 — 3	17 802.04	17 801.97	17 802.06	0.07	0.07	— 0.09
	1 — 2	17 802.04			0.07	0.00	
	0 — 1	17 801.00			— 0.97	— 0.83	
	2 — 2	17 801.00			— 0.97	— 1.00	
	1 — 1	17 803.68			1.71	1.67	
$1_{10}-2_{11}$	2 — 3	18 301.19	18 300.99	18 300.95	0.20	0.20	0.04
	1 — 2	18 300.15			— 0.84	— 0.83	
	0 — 1	18 302.35			1.36	1.34	
	2 — 2	18 300.79			— 0.20	— 0.23	
	1 — 1	18 300.79			— 0.20	— 0.18	
$1_{11}-2_{12}$	2 — 3	17 319.32	17 319.11	17 319.17	0.21	0.21	— 0.06
	1 — 2	17 318.27			— 0.84	— 0.83	
	0 — 1	17 320.29			1.18	1.16	
	2 — 2	17 318.67			— 0.44	— .044	
	1 — 1	17 319.32			0.21	0.18	

Table 2 continued

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl}-\nu_{calc}$
	0 — 1	39 742.46			— 1.14	— 1.13	
	2 — 2	39 742.92			— 0.68	— 0.68	
	1 — 1	39 744.96			1.36	1.33	
$2_{20}-3_{21}$	3 — 4	26 224.56	26 224.32	26 223.61	0.24	0.23	0.71
	2 — 3	26 223.49			— 0.83	— 0.82	
	1 — 2	26 225.14			0.82	0.82	
	3 — 3	26 224.56			0.24	0.24	
	2 — 2	26 223.49			— 0.83	— 0.83	
$2_{02}-3_{03}$	3 — 4	26 166.99	26 167.01	26 167.34	— 0.02	0.04	— 0.33
	2 — 3	26 166.99			— 0.02	0.00	
	1 — 2	26 166.99			— 0.02	— 0.16	
	3 — 3	26 165.91			— 1.10	— 1.06	
	2 — 2	26 168.46			1.45	1.49	
$2_{11}-3_{12}$	3 — 4	26 887.29	26 887.21	26 887.48	0.08	0.08	— 0.27
	2 — 3	26 887.03			— 0.18	— 0.21	
	1 — 2	26 887.29			0.08	0.10	
	3 — 3	26 886.53			— 0.68	— 0.61	
	2 — 2	26 887.82			0.61	0.72	
$2_{12}-3_{13}$	3 — 4	25 494.84	25 494.85	25 494.67	— 0.01	0.09	0.18
	2 — 3	25 494.84			— 0.01	— 0.21	
	1 — 2	25 494.84			— 0.01	0.06	
	3 — 3	25 494.00			— 0.85	— 0.86	
	2 — 2	25 495.95			1.10	1.09	
$2_{21}-3_{22}$	3 — 4	26 196.55	26 196.32	26 195.47	0.23	0.24	0.85
	2 — 3	26 195.51			— 0.81	— 0.82	
	1 — 2	26 197.13			0.81	0.82	
	3 — 3	26 196.55			0.23	0.24	
	2 — 2	26 195.51			— 0.81	— 0.82	
$3_{03}-3_{12}$	4 — 4	24 400.19	24 400.34	24 399.96	— 0.15	— 0.10	0.38
	3 — 3	24 400.67			0.33	0.31	
	2 — 2	24 400.19			— 0.15	— 0.25	
	4 — 3	24 399.40			— 0.94	— 0.79	
	3 — 2	24 401.46			1.12	1.24	
	3 — 4	24 401.28			0.94	1.00	
	2 — 3	24 399.09			— 1.25	— 1.18	

Footnotes see Table 1.

Table 3 continued

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl}-\nu_{calc}$
$2_{02}-2_{11}$	3 — 3	23 337.25	23 337.38	23 337.32	— 0.13	— 0.15	0.06
	2 — 2	23 337.86			0.49	0.51	
	1 — 1	23 336.86			— 0.52	— 0.51	
	3 — 2	23 336.86			— 0.52	— 0.57	
	2 — 1	23 338.51			1.13	1.16	
	2 — 3	23 338.33			0.95	0.93	
$1_{01}-2_{12}$	2 — 3	39 666.81	39 666.83	39 666.71	— 0.02	— 0.02	0.12
	1 — 2	39 667.14			0.31	0.33	
	0 — 1	39 665.66			— 1.17	— 1.16	
	2 — 2	39 666.14			— 0.69	— 0.67	
	1 — 1	39 668.19			1.36	1.34	
$2_{03}-3_{03}$	3 — 4	26 682.92	26 682.93	26 683.10	— 0.01	0.04	— 0.17
	2 — 3	26 682.92			— 0.01	0.00	
	1 — 2	26 682.92			— 0.01	— 0.17	
	3 — 3	26 681.81			— 1.12	— 1.08	
	2 — 2	26 684.42			1.49	1.51	
$2_{12}-3_{13}$	3 — 4	25 974.11	25 974.05	25 973.79	0.06	0.09	0.26
	2 — 3	25 973.84			— 0.20	— 0.21	
	1 — 2	25 974.11			0.06	0.07	
	2 — 2	25 975.14			1.09	1.08	
$3_{03}-3_{12}$	4 — 4	24 100.45	24 100.60	24 100.59	— 0.15	— 0.10	0.01
	3 — 3	24 100.90			0.30	0.30	
	2 — 2	24 100.45			— 0.15	— 0.24	
	4 — 3	24 099.77			— 0.83	— 0.82	
	3 — 2	24 101.72			1.12	1.27	
	3 — 4	24 101.72			1.12	1.02	
	2 — 3	24 099.40			— 1.20	— 1.21	

Footnotes see Table 1.

Table 4. Rotational transitions (MHz) of $CH_3CH_2{}^{13}CN$.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	observed frequencies	unsplit frequencies[a]	calculated frequencies[b]	$\Delta\nu$ HFS observed[c]	$\Delta\nu$ HFS calculated[d]	$\nu_{unspl}-\nu_{calc}$
$0_{00}-1_{01}$	1 — 2	8 904.86	8 904.70	8 904.71	0.16	0.17	0.01
	1 — 1	8 903.87			— 0.83	— 0.84	
	1 — 0	8 906.38			1.68	1.67	
$1_{01}-1_{10}$	2 — 2	23 419.92	23 420.16	23 420.25	— 0.24	— 0.27	— 0.09
	1 — 1	23 421.50			1.34	1.35	
	2 — 1	23 420.50			0.34	0.35	
	1 — 0	23 419.92			— 0.24	— 0.19	
	1 — 2	23 420.89			0.73	0.73	
	0 — 1	23 419.02			— 1.14	— 1.16	
$0_{00}-1_{11}$	1 — 2	31 849.69	31 849.76	31 849.84	— 0.07	— 0.06	— 0.08
	1 — 1	31 850.08			0.32	0.32	
	1 — 0	31 849.13			— 0.63	— 0.65	
$1_{01}-2_{02}$	2 — 3	17 802.04	17 801.99	17 802.12	0.05	0.07	— 0.13
	1 — 2	17 802.04			0.05	0.00	
	0 — 1	17 801.06			— 0.93	— 0.84	
	2 — 2	17 801.06			— 0.93	— 1.01	
	1 — 1	17 803.67			1.68	1.68	
$1_{10}-2_{11}$	2 — 3	18 284.74	18 284.55	18 284.54	0.19	0.19	0.01
	1 — 2	18 283.71			— 0.84	— 0.84	
	0 — 1	18 285.89			1.34	1.35	
	2 — 2	18 284.35			— 0.20	— 0.22	
	1 — 1	18 284.35			— 0.20	— 0.19	
$1_{11}-2_{12}$	2 — 3	17 334.64	17 334.43	17 334.31	0.21	0.21	0.12
	1 — 2	17 333.59			— 0.84	— 0.84	
	0 — 1	17 335.58			1.15	1.16	
	2 — 2	17 333.97			— 0.46	— 0.45	
	1 — 1	17 334.64			0.21	0.19	
$2_{02}-2_{11}$	3 — 3	23 902.65	23 902.79	23 902.67	— 0.14	— 0.15	0.12
	2 — 2	23 903.31			0.52	0.51	
	1 — 1	23 902.27			— 0.52	— 0.51	
	3 — 2	23 902.27			— 0.52	— 0.56	
	2 — 1	23 903.88			1.09	1.16	
	2 — 3	23 903.70			0.91	0.93	
	1 — 2	23 901.59			— 1.20	— 1.16	
$1_{01}-2_{12}$	2 — 3	40 279.47	40 279.49	40 279.44	— 0.02	— 0.02	0.05
	1 — 2	40 279.81			0.32	0.32	
	0 — 1	40 278.34			— 1.15	— 1.16	
	2 — 2	40 278.82			— 0.67	— 0.68	
	1 — 1	40 280.84			1.35	1.35	
$2_{20}-3_{21}{}^{L}$	3 — 4	26 744.26	26 744.01	26 743.33	0.25	0.24	0.68
	2 — 3	26 743.18			— 0.83	— 0.83	
	1 — 2	26 744.80			0.79	0.84	
	3 — 3	26 744.26			0.25	0.24	
	2 — 2	26 743.18			— 0.83	— 0.84	
$2_{02}-3_{03}{}^{L}$	3 — 4	26 684.58	26 684.58	26 684.94	0.00	0.04	— 0.36
	2 — 3	26 684.58			0.00	0.00	
	1 — 2	26 684.58			0.00	0.16	
	3 — 3	26 683.51			— 1.07	— 1.08	
	2 — 2	26 686.07			1.49	1.51	
$2_{12}-3_{13}{}^{L}$	3 — 4	25 997.13	25 997.07	25 996.93	0.06	0.09	0.11
	2 — 3	25 996.90			— 0.17	— 0.21	
	1 — 2	25 997.13			0.06	0.07	
	3 — 3	25 996.21			— 0.86	— 0.87	
	2 — 2	25 998.16			1.09	1.09	
$2_{21}-3_{22}{}^{L}$	3 — 4	26 715.22	26 714.95	26 714.13	0.27	0.24	0.82
	2 — 3	26 714.17			— 0.78	— 0.84	
	1 — 2	26 715.77			0.82	0.84	
	3 — 3	26 715.22			0.27	0.24	
	2 — 2	26 714.17			— 0.78	— 0.84	
$3_{03}-3_{12}$	4 — 4	24 639.99	24 640.14	24 639.94	— 0.15	— 0.10	0.20
	3 — 3	24 640.44			0.30	0.31	
	2 — 2	24 639.99			— 0.15	— 0.25	
	4 — 3	24 639.34			— 0.80	— 0.81	
	3 — 2	24 641.20			1.06	1.27	
	3 — 4	24 641.20			1.06	1.02	
	2 — 3	24 638.95			— 1.19	— 1.21	

[L] Transitions measured by Lerner and Dailey [1], remeasured with greater accuracy other footnotes see Table 1.

Table 5. Rotational transitions (MHz) of $CH_3CH_2C^{15}N$.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	observed frequencies	calculated[a] frequencies	$\nu_{obs}-\nu_{calc}$
$0_{00}-1_{01}$	8694.31	8694.29	0.02
$1_{01}-1_{10}$	23422.15	23422.08	0.07
$0_{00}-1_{11}$	31660.92	31661.02	−0.10
$1_{01}-2_{02}$	17381.76	17381.88	−0.12
$1_{10}-2_{11}$	17843.97	17843.94	0.03
$1_{11}-2_{12}$	16933.36	16933.23	0.13
$2_{02}-2_{11}$	23884.16	23884.14	0.02
$1_{01}-2_{12}$	39899.96	39899.96	0.00
$2_{20}-3_{21}$	26110.30	26109.69	0.61
$2_{02}-3_{03}$	26055.77	26056.07	−0.30
$2_{11}-3_{12}$	26761.44	26761.69	−0.25
$2_{12}-3_{13}$	25395.73	25395.69	0.04
$2_{21}-3_{22}$	26083.70	26082.88	0.82
$3_{03}-3_{12}$	24589.95	24589.76	0.19

[a] Calculated with the rotational constants from Table 6.

The field gradient asymmetry η points out a cylindrical symmetry. These results agree with those of Li and Harmony[4], who analysed the hyperfine structure of normal ethyl cyanide, although they assumed implicitely that the C – N-bond is collinear with the z-principal axis of the quadrupole coupling tensor.

Structure

For the determination of the structure the substitution method proposed by Kraitchman[10] [formula (23)] and Costain[11] was employed using CH_3CH_2CN as parent molecule and the assumption of C_s-symmetry.

The determination of the H (methylene) position was based on Chutjian's[12] method using the rotational constants of CH_3CH_2CN and CH_3CD_2CN. The b-coordinate of H (methyl – in plane) was calculated by the center of mass condition.

In Table 8 the moments of inertia of all measured isotopic molecules of ethyl cyanide are listed, as well as the quantity $I_c - I_a - I_b$, which should change only slightly with a substitution of an atom in the a-b-plane. However a remarkable change can be noticed in the case of CH_2DCH_2CN (sym), which may be explained by a change in the ground vibrational state of the deuterium relative to the hydrogen atom.

For the coordinates of the atoms in the a-b-plane different values could be calculated either by making use of the complete set of the three ΔI's or by taking two ΔI's, having eliminated one by the equation

Table 6. Rotational constants (MHz) for all investigated isotopic species of ethyl cyanide.

		observed[a]	calculated[b]	observed-calculated
CH_3CH_2CN[c]	A	27 663.288 (± 0.054)	27 665.020	−1.732
	B	4 714.199 (± 0.029)	4 712.748	1.451
	C	4 235.083 (± 0.021)	4 236.449	−1.366
CH_3CD_2CN[c]	A	21 942.980 (± 0.027)	21 942.985	−0.005
	B	4 600.231 (± 0.015)	4 602.060	−1.829
	C	4 087.830 (± 0.014)	4 085.232	2.598
CH_2DCH_2CN[c] (sym.)	A	27 650.897 (± 0.049)	27 650.992	−0.095
	B	4 425.142 (± 0.027)	4 423.908	1.234
	C	4 000.821 (± 0.019)	4 001.294	−0.473
CH_2DCH_2CN[c] (asym.)	A	25 022.652 (± 0.041)	25 020.702	1.950
	B	4 583.476 (± 0.022)	4 581.048	2.428
	C	4 110.264 (± 0.016)	4 112.796	−2.532
$^{13}CH_3CH_2CN$	A	27 342.259 (± 0.050)	27 341.553	0.706
	B	4 598.057 (± 0.027)	4 596.033	2.024
	C	4 133.767 (± 0.020)	4 134.574	−0.807
$CH_3{}^{13}CH_2CN$	A	27 045.499 (± 0.051)	27 045.540	−0.041
	B	4 697.959 (± 0.028)	4 696.297	1.662
	C	4 207.070 (± 0.020)	4 208.436	−1.366
$CH_3CH_2{}^{13}CN$	A	27 635.046 (± 0.057)	27 636.483	−1.437
	B	4 689.914 (± 0.031)	4 688.519	1.395
	C	4 214.797 (± 0.023)	4 216.196	−1.399
$CH_3CH_2C^{15}N$	A	27 541.550 (± 0.049)	27 540.502	1.048
	B	4 574.825 (± 0.027)	4 573.162	1.663
	C	4 119.468 (± 0.019)	4 120.537	−1.069
CD_3CH_2CN	A	22 865.104 (± 0.053)	22 867.418	−2.314
	B	4 204.788 (± 0.029)	4 201.864	2.924
	C	3 800.247 (± 0.021)	3 803.003	−2.756

[a] Obtained from a rigid rotor fit with the same set of rotational lines up to $J=2$ (Tables 1–5); the uncertainties are standard errors.
[b] Calculated from r_0-structure in Table 11.
[c] From Reference [2].

Table 7. Quadrupole Coupling Constants (MHz).

	CH_3CD_2CN [a]	CD_3CH_2CN	$^{13}CH_3CH_2CN$	$CH_3{}^{13}CH_2CN$	$CH_3CH_2{}^{13}CN$
χ_{aa} [b]	-3.449 ± 0.016	-3.209 ± 0.017	-3.290 ± 0.011	-3.377 ± 0.021	-3.349 ± 0.011
χ_{bb} [b]	1.399 ± 0.015	1.150 ± 0.016	1.242 ± 0.010	1.334 ± 0.017	1.297 ± 0.010
χ_{cc} [b]	2.050 ± 0.017	2.059 ± 0.018	2.048 ± 0.012	2.043 ± 0.019	2.052 ± 0.012
χ_{ab}	-2.01 ± 0.18	-2.27 ± 0.12			
χ_{zz}		$-4.17_3 \pm 0.16$			
χ_{xx}		$2.11_9 \pm 0.16$			
χ_{yy}		$2.05_5 \pm 0.018$			
η [c]		0.02 ± 0.04			
ε		$3.21^\circ \pm 0.20^\circ$			
α_Q	$19.8^\circ \pm 1.7^\circ$				
α_s [d]	$20.77^\circ \pm 0.14^\circ$				

[a] See Reference [2].
[b] Obtained from least squares analysis including all precisely measured hyperfine components from Tables 1–4 up to $J=2$.
[c] $\eta = (\chi_{yy} - \chi_{xx})/\chi_{zz}$.
[d] Obtained from r_s-structure of Table 10.

Table 8. Principal Moments of Inertia [a] (amu Å^2).

Species	I_a	I_b	I_c	$I_c - I_a - I_b$ [c]
CH_3CH_2CN [b]	18.268 83	107.202 94	119.330 84	− 6.140 93
$^{13}CH_3CH_2CN$	18.483 33	109.910 77	122.255 56	− 6.138 54
$CH_3{}^{13}CH_2CN$	18.686 14	107.573 52	120.125 41	− 6.134 25
$CH_3CH_2{}^{13}CN$	18.287 50	107.758 05	119.905 18	− 6.140 37
$CH_3CH_2C^{15}N$	18.349 58	110.468.93	122.679 92	− 6.138 59
CH_2DCH_2CN (sym) [b]	18.277 02	114.205 60	126.318 07	− 6.164 55
CH_2DCH_2CN (asym) [b]	20.196 74	110.260 42	122.954 63	− 7.502 53
CH_3CD_2CN [b]	23.031 32	109.858 83	123.629 40	− 9.260 75
CD_3CH_2CN	22.102 50	120.190 60	132.985 04	− 9.308 06

[a] Conversion factor 505.376 GHz amu Å^2 (Ref. [8], p. 651).
[b] From Reference [2].
[c] Experimental uncertainty is about 0.0010.

Table 9. Variation of r_s-parameters with the choice of ΔI's (distances in Å, angles in degrees).

Parameter	$\Delta I_a, \Delta I_b, \Delta I_c$	$\Delta I_a, \Delta I_b$	$\Delta I_a, \Delta I_c$	$\Delta I_b, \Delta I_c$
r_{C-C}	1.537	1.535	1.532	1.541
r_{C-CN}	1.459	1.456	1.462	1.457
r_{C-N}	1.159	1.158	1.158	1.160
r_{C-H}	1.079	1.075	1.070	1.082
methyl, H in plane				
$\sphericalangle$ CCC	111.98	112.17	112.12	111.85
$\sphericalangle$ CCN	178.73	178.85	178.77	178.68
$\sphericalangle$ HCC	111.08	112.20	111.97	110.93
methyl, H in plane				
$\sum m_i a_i$	0.065	0.094	0.037	0.095
$\sum m_i b_i$	0.000 [a]	0.015	0.015	0.000 [a]
$\sum m_i a_i b_i$	0.029	0.145	0.104	0.174

[a] The b-coordinate of the in-plane H of the methyl group was calculated from the equation $\sum m_i b_i = 0$.

$\Delta I_c - \Delta I_a - \Delta I_b = 0$. In Table 9 bond distances and angles are given with respect to the sets of ΔI's used. The spread of the data in Table 9 reflects the methodical errors of the substitution method. These errors dominate those derived by error propagation from the uncertainties of the rotational constants.

These structure calculations indicate that the methyl group does not have C_{3v}-symmetry. This can be stated although the error of the b-coordinate of H in plane is large as a result of its determination by the center of mass condition.

The axis through the center of mass of the three methyl hydrogens and the C-atom is tilted by an angle of 1.32° towards the CN-group with respect to the C–C-bond. It is noteworthy that the angle $\sphericalangle$CCN is smaller than 180°, bent towards the methyl group even considering the large uncertainty of the b-coordinate of the C-atom. Both fea-

Table 10. Cartesian coordinates (Å) of ethyl cyanide calculated using all ΔI's.

[a] The given uncertainties of the coordinates are standard errors derived from the errors of the rotational constants.
[b] Calculated from Chutjian's equations [12] with the rotational constants of CH_3CH_2CN and CH_3CD_2CN.
[c] Calculated from the equation $\Sigma m_i b_i = 0$.

	a	b	c
C (methyl)	-1.6561 ± 2[a]	-0.4750 ± 7	0.0
C (methylene)	-0.6146 ± 5	0.6548 ± 5	0.0
C (cyanide)	0.7507 ± 4	0.1391 ± 26	0.0
N	1.8257 ± 2	-0.2945 ± 11	0.0
H (methylene)[b]	-0.7377 ± 2	1.2922 ± 1	0.8804 ± 1
H (methylene)[b]	-0.7377 ± 2	1.2922 ± 1	-0.8804 ± 1
H (methyl)	-2.6596 ± 1	-0.0778 ± 481[c]	0.0
H (methyl)	-1.5347 ± 2	-1.1059 ± 3	0.8818 ± 3
H (methyl)	-1.5347 ± 2	-1.1059 ± 3	-0.8818 ± 3

Table 11. Structural parameters of ethyl cyanide (distances in Å, angles in degree).

	r_s	r_0[a]	r^*
r_{C-C}	1.537 ± 0.001	1.538 ± 0.012	1.537[b]
r_{C-CN}	1.459 ± 0.001	1.459 ± 0.043	1.455 ± 0.005
r_{C-N}	1.159 ± 0.001	1.162 ± 0.042	1.165 ± 0.005
r_{C-H} (methylene)	1.094 ± 0.001	1.085 ± 0.004	1.094 ± 0.002
r_{C-H} (methyl, H in plane)	1.079 ± 0.018	1.069 ± 0.013	1.082 ± 0.002
r_{C-H} (methyl, H out of plane)	1.091 ± 0.001	1.099 ± 0.003	1.091 ± 0.003
$\sphericalangle$ CCN	178.73 ± 0.22	178.67 ± 1.47	178.16 ± 0.94
$\sphericalangle$ CCC	111.98 ± 0.10	112.15 ± 0.29	112.15 ± 0.35
$\sphericalangle$ CCH (methylene)	110.62 ± 0.03	111.44 ± 1.26	110.68 ± 0.14
$\sphericalangle$ HC(CN)	108.13 ± 0.06	108.90	108.00
$\sphericalangle$ HCH (methylene)	107.19 ± 0.04	103.60	107.15
$\sphericalangle$ HCH (methyl, both H out of plane)	107.85 ± 0.06	110.27	107.96
$\sphericalangle$ HCH (H in plane, H out of plane)	108.44 ± 1.24	107.77	108.64
$\sphericalangle$ HCC (methyl, H out of plane)	110.47 ± 0.02	109.37 ± 0.86	110.43 ± 0.14
$\sphericalangle$ HCC (methyl, H in plane)	111.08 ± 2.37	112.26 ± 0.58	110.66 ± 0.15
$\sphericalangle$ HC—CH (dihedral angle)	59.31	57.60 ± 1.23	59.32 ± 0.17

[a] Compare Table 13, column 1.
[b] This parameter was not fitted.

Table 12 a. r_s-Structures of molecules of the type CH_3CH_2X (distances in Å, angles in degrees).

$X =$	CH_3[15]	CN	F[16]	Cl[17]	Br[18]
r_{C-C}	1.526 ± 0.002	1.537 ± 0.001	1.505 ± 0.004	1.520 ± 0.003	1.518 ± 0.004
$\sphericalangle$ CCX	112.4 ± 0.2	111.98 ± 0.10	109.7 ± 0.3	111.03 ± 0.13	111.03 ± 0.25
Methylene:					
r_{C-H}	1.096 ± 0.002	1.094 ± 0.001	1.095 ± 0.002	1.089 ± 0.010	1.087 ± 0.010
$\sphericalangle$ HCH	106.1 ± 0.2	107.19 ± 0.04	108.8 ± 0.2	109.20 ± 0.50	109.90 ± 0.50
$\sphericalangle$ CCH	109.55	110.62 ± 0.03	112.9 ± 0.5	111.60 ± 0.50	112.40 ± 0.50
$\sphericalangle$ HCX	109.55	108.13 ± 0.06	106.1 ± 0.5	106.58	105.40 ± 0.50
Methyl:					
r_{C-H}	1.091 ± 0.01	1.091 ± 0.001	1.091 ± 0.002	1.091 ± 0.01	1.093 ± 0.01
$\sphericalangle$ HCH	107.7 ± 1.0	107.85 ± 0.06	108.9 ± 0.2	108.50 ± 0.50	108.87 ± 0.50

Table 12 b. Bond distances of Nitriles [Å].

	CH_3CN[11]	CH_3CH_2CN	$(CH_3)_3CCN$[14]
r_{C-N}	1.157 ± 0.001	1.159 ± 0.001	1.159 ± 0.001
r_{C-CN}	1.458 ± 0.001	1.459 ± 0.001	1.495 ± 0.015

tures are reproduced by the r_0-structure given below.

In comparison with propane and the ethyl halides ethyl cyanide may be placed between propane and ethyl fluoride as given in Table 12 a. Furthermore a good agreement with the structure of other nitriles is observed (see Table 12 b). The r_0-structure calculations were made by a least squares analysis including all rotational constants weighted by

Table 13. Various r_0-structure calculations with the following assumptions: α C_s-symmetry of the molecule; β C_{3v}-symmetry of the methyl-group; γ $\sphericalangle$CCN=180°; δ tilt angle of C_{3v}-symmetric methyl group allowed.

	1	2[a]	3	4	5	r_s
Assumption to the moleculare structure	α	$\alpha+\beta+\gamma$	$\alpha+\beta$	$\alpha+\gamma$	$\alpha+\beta+\delta$	α
No. of varied independent parameters	13	9	10	12	11	
Sum of squared defects (kHz)	77	120	110	92	121	
r_{C-C}	1.538 ± 0.012 (0.006)[b]	1.529 ± 0.005	1.509 ± 0.009	1.547 ± 0.006	1.535 ± 0.013 (0.006)[b]	1.537 ± 0.001
r_{C-CN}	1.459 ± 0.043 (0.006)[b]	1.425 ± 0.009	1.534 ± 0.043	1.421 ± 0.006	1.463 ± 0.049 (0.007)[b]	1.459 ± 0.001
r_{C-N}	1.162 ± 0.042 (0.007)[b]	1.215 ± 0.009	1.100 ± 0.046	1.200 ± 0.007	1.160 ± 0.049 (0.008)[b]	1.159 ± 0.001
Θ[c]	1.7	(0.0)	(0.0)	2.1	2.24 ± 0.7	1.32

[a] The same assumption as used by Mäder et al. [2].
[b] These standard errors are obtained by a second fit with 12 or 10 parameters, respectively, and a fixed $\sphericalangle$CCN angle derived in the first fit.
[c] Tilt angle (definition see text).

their standard errors as listed in Table 6. Mäder et al. [2] derived nine structural parameters using 21 rotational constants and assuming that the molecule has C_s-symmetry, the methyl group C_{3v}-symmetry and that the angle $\sphericalangle$CCN equals 180°. We tried several extended r_0-structure calculations for comparison with the r_s-structure and for studying the influence of the above assumptions. The different calculations are described in Table 13.

The first was made using the same assumption as in the r_s-structure calculation. A good agreement in the bond distances and angles of the frame atoms and the asymmetry of the methyl group may be seen.

Further r_0-structure calculations (see Table 13, column 2 – 5) with additional assumptions reducing the number of adjustable parameters resulted in a

Table 14. Stark-effect measurements (field strength in volts/cm, frequencies in MHz).

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$		M	E [V/cm]	$\Delta\nu_{Mobs}$ [a]	$\Delta\nu_{Mcalc}$	$\Delta\nu_{Mobs}-\Delta\nu_{Mcalc}$
CH_3CH_2CN	$2_{02}-3_{03}$	1	855.86	6.70	6.54	0.16
		2	972.80	25.46	25.84	− 0.38
	$2_{11}-3_{12}$	1	430.08	− 11.37	− 11.42	0.05
		2	236.03	− 13.40	− 13.24	− 0.16
		2	323.99	− 24.81	− 24.64	− 0.17
CD_3CH_2CN	$1_{01}-2_{02}$	0	421.24	− 14.65	− 14.57	− 0.08
		1	421.24	9.01	9.37	− 0.36
		1	642.76	21.65	21.71	− 0.06
	$2_{02}-3_{03}$	1	923.89	12.55	12.54	0.01
		2	734.19	16.16	16.43	− 0.27
	$2_{11}-3_{12}$	1	500.96	− 17.94	− 18.11	0.17
		2	261.56	− 19.25	− 19.02	− 0.23
		2	323.41	− 28.96	− 28.74	− 0.22
CH_3CD_2CN	$1_{01}-2_{02}$	0	201.35	19.14	19.00	0.14
		0	154.35	13.87	13.65	0.22
		1	421.46	18.16	18.46	− 0.30
	$2_{02}-3_{03}$	0	207.20	− 22.77	− 22.88	0.11
	$2_{11}-3_{12}$	1	498.15	− 14.67	− 14.83	0.16
		2	261.33	− 15.77	− 15.63	− 0.14
		2	326.10	− 24.21	− 24.13	− 0.08

[a] $\Delta\nu_{Mobs.} = \nu_{Mobs.} - \nu_{obs.}$ The ν_{obs}-values without Stark field are found in Table 1 and Tables 1 and 3 of Reference [2].

Table 15. Dipolmoments (Debye).

Isotopic species	μ_a	μ_b	$\lvert\mu\rvert$	α_D [b]	α_s [c]
CD_3CH_2CN	3.84 ± 0.01	1.37 ± 0.01	4.07 ± 0.02	19.6 ± 0.2	23.98
CH_3CH_2CN [a]	3.85 ± 0.02	1.23 ± 0.02	4.05 ± 0.03	17.7 ± 0.2	21.97
CH_3CD_2CN	3.92 ± 0.02	1.19 ± 0.01	4.10 ± 0.03	16.9 ± 0.2	20.77

[a] The dipole moment of CH_3CH_2CN and its components given previously by Laurie [14] are: $\mu_a = 3.78 \pm 0.04$, $\mu_b = 1.38 \pm 0.04$ and $|\mu| = 4.02 \pm 0.04$.
[b] Angle between μ and a-axis.
[c] Angle between CN-bond and a-axis.

worse fit and/or a large discrepancy of the structural parameters of the frame atoms relative to r_s-values.

In calculation 5 the tilt angle definition equals implicitely that mentioned above in the r_s-structure discussion using C_{3v}-symmetry of the methyl group. Finally the last column of Table 11 shows the results calculated by a program developed by Nösberger [13]. With this program it is possible to fit internal structural parameters directly to differences of moments of inertia. The experimental information was equivalent to that used for the r_s-structure given in column 1.

Dipole Moment

The frequencies of the Stark satellites of the transitions $1_{01} - 2_{02}$, $2_{11} - 3_{12}$ and $2_{02} - 3_{03}$ of the three isotopic species CD_3CH_2CN, CH_3CH_2CN and CH_3CD_2CN and the applied field strengths are listed in Table 14. The calculations were carried out by a least squares fit of the observed Stark shifts ($\Delta\nu_{obs}$) and those obtained by a diagonalisation of a finite submatrix of the energy matrix.

Because the Stark effect only allows the magnitude of the dipole moment to be determined, two directions are possible as shown in Figure 1. A decision may be made by comparing the dipole moment components of the isotopic species. If the dipole moment

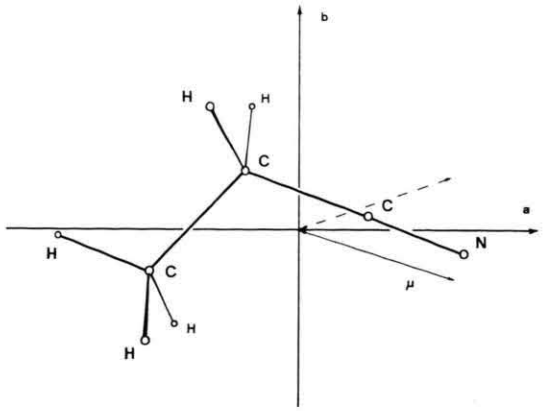

Fig. 1. Ethyl cyanide with possible directions of the dipole moment.

is along the solid arrow, the μ_b component of CH_3CD_2CN should be smaller than that of CD_3CH_2CN, as the angle between C – N-bond and a-inertiae-axis is larger for CD_3CH_2CN.

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