Microwave Spectrum of Mono-deuterated Acetyl Cyanide CH_2DCOCN and Complete r_s- and r_0-structure of Acetyl Cyanide

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Microwave spectra of symmetric and asymmetric forms of monodeuterated acetyl cyanide CH_2DCOCN have been observed and measured. Significant differences occur between our assignment and those of Krisher and Wilson[1]. We have confirmed all our assignments with the help of microwave — microwave double resonance (MW-MW-DR) experiments. By fitting about twelve low J transition frequencies to a rigid rotator, accurate values for the rotational constants have been obtained. From the analysis of the quadrupole hyperfine splittings of some of the transitions, the nuclear quadrupole coupling constants are also determined.

Using the measured rotational constants for a number of molecular isotopic species of Reference (1), and in addition those measured in this laboratory for the ^{15}N, monodeuterated and normal species (determined with greater accuracy), a complete r_s- and r_0-structure has been calculated. The important conclusions are — i) the methyl group does not possess C_{3v} symmetry and ii) the $C_{carbonyl}$, — $C_{cyanide}$ and C — N bonds are collinear within the accuracy of measurements.

Introduction

Recently, we became interested in the excited torsional and vibrational state spectra of acetyl cyanide, with a purpose of testing the rotation-torsion-vibration interaction model** developed in this laboratory[2,3] to describe the rotational spectra of molecules in the ground and excited torsional and vibrational states simultaneously. The spectrum of the normal species was recently observed and analyzed in terms of RTV model by Scappini et al.[4,5]. In this case it was applied in its simple form where the methyl top is symmetric, the molecule contains a plane of symmetry and the considered vibration lies in the symmetry plane. The model needs in principle, the r_e-structure of the molecule. Previous structure determination by Krisher and Wilson[1] assumed C_{3v} symmetry for the methyl top, although they reported some measured lines for the monodeuterated (both symmetric and asymmetric) and doubly deuterated species of the molecule. Moreover, they did not make isotopic substitution for the nitrogen atom. Our attempt to work out a more detailed structure of the molecule using the rotational constants of the isotopic species measured by Krisher and Wilson[1] (including those for the monodeuterated species determined by fitting low J lines to rigid rotor) and that of normal and ^{15}N isotopic species measured in this laboratory gave unreasonable coordinates for the symmetric and asymmetric hydrogen atoms. We could easily ascribe the reason to wrong assignment and/or measurement of the rotational transitions for the monodeuterated species by Krisher and Wilson[1]. Our conclusion was supported from the following observations too. We obtained the rotational constants for both the symmetric and asymmetric species with the help of three low J transitions (viz. $2_{11} - 3_{12}$, $2_{02} - 3_{13}$, and $3_{13} - 4_{04}$; Table 6 of Reference [1]) and then calculated the entire spectrum with the help of these rotational constants. The difference between these calculated line frequencies to those reported by Krisher and Wilson for $J = 6$ to 10 rotational transitions were too large to be ascribed to the centrifugal distortion effects.

With the basic aim of working out a detailed structure of the molecule, we undertook the study of the monodeuterated species of the molecule. Our interest was related to i) the methyl group: to see how closely it is actually symmetric (a simplifying assumption made in the application of the RTV model) and ii) the CCN group: to see whether the C-C and C-N bonds are actually collinear. It may be mentioned that as the considered excited state vibrations in the observation and subsequent interpretation of the spectra in terms of the RTV model are the methyl torsion and C-C-N in plane bending

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** Henceforth referred to as RTV model.

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vibration, it is the structure of this part of the molecule, which is of particular interest to us.

Experimental

For the sample preparation, monodeuterated acetyl bromide was first prepared by carefully mixing ketene (obtained by pyrolysis of acetone[6]) and deuterium bromide (purchased from the Company MSD Sharp & Dohme GMBH, München) at −78 °C in the absence of air. 8 mMol of monodeuterated acetyl bromide was then added to 9 mMol of dry cuprous cyanide (CuCN) contained in an ice cooled ampul. Sufficient dry cyclohexane was added to wet all the cuprous cyanide and the ampul was sealed off. After standing for three days at room temperature, the contents was distilled and separated by gas — liquid chromatography (2 m PORAPAK Q 80—100 mesh). Yield was 75 to 80 per cent.

The Stark modulation spectrograph and the MW-MW-DR spectrographs are the same as used in previous studies and have been described elsewhere [7].

Ground State Spectra

The ground state spectra were readily assigned with the help of MW-MW-DR experiments. For setting the approximate pump frequency and the appropriate region where the signal should be searched, use was made of the r_0-structure of the molecule, which was calculated with the help of the rotational constants of the previously studied isotopic species of the molecule. It had been the general experience, that for predicting the spectrum of a new isotopic species of a molecule, r_0-structure is the better choice. Table 1 gives the details of the MW-MW-DR experiments performed. The hyperfine structure of the lines was resolved, wherever it was conveniently possible. Table 2 and 3 list the measured ground state rotational transitions for the symmetric and asymmetric species respectively. From the hyperfine structure, the nuclear quadrupole coupling constants were determined. The rotational constants were determined by a least square rigid rotor fit to the extrapolated unsplit frequencies of the rotational transitions. The results are mentioned in Table 4 for both the species.

Table 1. Microwave — microwave double resonance (MW-MW-DR) experiments performed in the present studies.

Pump	Signal
$4_{13}-3_{22}$	$4_{23}-3_{22}$
$4_{13}-4_{04}$	$5_{15}-4_{04}$
	$5_{05}-4_{04}$
	$4_{13}-3_{12}$
	$4_{04}-3_{03}$
	$4_{04}-3_{13}$
$2_{12}-1_{11}$	$2_{20}-1_{11}$
$2_{11}-1_{10}$	$3_{12}-2_{11}$
$2_{02}-1_{01}$	$3_{13}-2_{02}$
$4_{13}-3_{22}$	$3_{22}-2_{11}$ *

* Performed only for the asymmetric species.

For the asymmetric species, some of the transitions were also found to be split into doublets due to the tunneling of the deuterium atom between two equivalent out of plane positions. Table 5 gives the observed splittings. In this publication, we do not make an attempt to analyse this splitting with a possible determination of barrier to internal rotation. This could, however, be done in terms of the theory developed by Quade and Lin[8].

Structure

i) *r_s-structure*

For the determination of structure, the substitution method proposed by Kraitchman[9] and Costain[10] was employed with CH_3COCN as the parent molecule and the assumption of C_s configuration symmetry. Table 6 summarizes the moments of inertia of all the measured isotopic species of acetyl cyanide along with the quantity $I_a + I_b - I_c$, which should change only slightly with the substitution of an atom in the symmetry plane. A maximum change of 0.043 amu Å^2 can, however, be noticed in the case of CH_2DCOCN (sym).

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 at a time and eliminating the third by the equation $\Delta I_a + \Delta I_b - \Delta I_c = 0$. In Table 7, in plane bond distances and bond angles are given with respect to the sets of ΔI's used. The spread of the data in Table 7 reflects the methodical error of the substitution method. These errors dominate over those derived by the error propagation from the uncertainties in the measured rotational constants.

Table 2. Measured rotational transitions for monodeuterated acetyl cyanide (symmetric species), all frequencies are in MHz.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	$F - F'$	ν_{ob}	$\nu_{unsplit}$ [a]	ν_{cal} [b]	Deviation
$2_{20} - 1_{11}$	$3 - 2$ $1 - 0$	34079.11 [c]	34079.35	34079.22	0.13
	$2 - 1$	34080.05 [c]			
$2_{02} - 1_{01}$	$3 - 2$ $2 - 1$	13620.94	13620.88	13620.08	0.80
$3_{12} - 2_{11}$	$4 - 3$ $2 - 1$	22174.30 [c]	22174.17	22174.15	0.02
	$3 - 2$	22173.88 [c]			
$3_{13} - 2_{02}$	$4 - 3$ $3 - 2$	23972.42 [c]	23972.35	23972.28	0.07
$4_{13} - 4_{04}$	$5 - 5$ $3 - 3$	13495.56	13495.67	13495.52	0.15
	$4 - 4$	13495.87			
$4_{23} - 3_{22}$	$5 - 4$ $3 - 2$	27404.53 [c]	27404.33	27404.59	0.26
	$4 - 3$	27403.89 [c]			
$4_{13} - 3_{12}$	$5 - 4$ $3 - 2$ $4 - 3$	29382.23 [c]	29382.24	29382.20	0.04
$4_{04} - 3_{03}$	$5 - 4$ $3 - 2$ $4 - 3$	26270.06 [c]	26270.07	26269.93	0.14
$4_{04} - 3_{13}$	$5 - 4$ $3 - 2$	22404.07 [c]	22403.98	22403.81	0.17
	$4 - 3$	22403.77 [c]			
$5_{23} - 5_{14}$	$6 - 6$ $4 - 4$	16311.21 [c]	16311.36	16311.48	0.12
$5_{15} - 4_{04}$	$6 - 5$ $4 - 3$ $5 - 4$	33866.00 [c]	33866.01	33866.07	0.06
$5_{05} - 4_{04}$	$6 - 5$ $4 - 3$ $5 - 4$	32151.12 [c]	32151.12	32150.98	0.14
				RMS Deviation	0.26

[a] Hyperfine center frequency calculated with the constants of Table 4.
[b] Calculated with the help of the rotational constants of Table 4.
[c] Confirmed by MW-MW-DR experiments.

The coordinates of the methyl carbon, oxygen, nitrogen, symmetric and asymmetric hydrogen and the 'a' coordinate of the cyanide carbon atom were determined from the observed changes in the moments of inertia between the normal and $^{13}CH_3COCN$, $CH_3C^{18}OCN$, $CH_3COC^{15}N$ [10], CH_2DCOCN (sym), CH_2DCOCN (asym) and $CH_3CO^{13}CN$ isotopic species respectively. The coordinates of the carbonyl carbon were determined in the principle axes system of CD_3COCN from the observed changes in the moments of inertia between CD_3COCN and $CD_3{}^{13}COCN$. The appropriate translation and rotation of the axes were then made to obtain its coordinates in the principle axes system of the parent CH_3COCN molecule. This translation and rotation of the axes was readily calculated from the determinied coordinates of the symmetric and asymmetric hydrogen atoms. * The *b* coordinate of

* The CH_3COCN and CD_3COCN principal axes systems are related by the coordinates of the substituted hydrogen atoms only.

Table 3. Measured rotational transitions[c] for monodeuterated acetyl cyanide (asymmetric species), all frequencies are in MHz.

Transition $J_{K-K+} - J'_{K-'K+'}$,	$F - F'$	ν_{ob}	$\nu_{unsplit}$[a]	ν_{cal}[b]	Deviation
$3_{22} - 2_{11}$	4 — 3	37140.60	37140.68	37140.68	0.00
	2 — 1	37140.01			
	3 — 2	37141.19			
$3_{12} - 2_{11}$	4 — 3, 2 — 1	22747.89	22747.80	22747.43	0.37
	3 — 2	22747.57			
$3_{13} - 2_{02}$	4 — 3	23592.61	23592.67	23592.54	0.13
	2 — 1	23592.14			
	3 — 2	23592.95			
$4_{22} - 3_{21}$	5 — 4, 3 — 2	29544.47	29544.26	29544.12	0.14
	4 — 3	29543.83			
$4_{23} - 3_{22}$	5 — 4, 3 — 2	28007.04	28006.90	28006.87	0.03
	4 — 3	28006.64			
$4_{13} - 3_{12}$	5 — 4, 3 — 2, 4 — 3	30088.76	30088.77	30088.87	0.10
$4_{04} - 3_{03}$	5 — 4, 3 — 2, 4 — 3	26603.44	26603.45	26603.24	0.21
$4_{04} - 3_{13}$	5 — 4, 3 — 2, 4 — 3	23451.02	23450.91	23450.54	0.37
$5_{14} - 4_{13}$	6 — 5, 4 — 3, 5 — 4	37178.01	37178.01	37178.26	0.25
$5_{15} - 4_{04}$	6 — 5, 4 — 3, 5 — 4	33685.12	33685.12	33685.35	0.23
$5_{05} - 4_{04}$	6 — 5, 4 — 3, 5 — 4	32480.44	32480.44	32480.43	0.01
				RMS Deviation	0.21

[a] Hyperfine center frequency calculated with the constants of Table 4.
[b] Calculated with the help of the rotational constants of Table 4.
[c] All measured transitions confirmed by MW-MW-DR experiments.

Table 4. Derived molecular parameters.

Parameter		CH_2DCOCN (sym)	CH_2DCOCN (asym)
A	(MHz)	9987.22 ± 0.08	9948.54 ± 0.08
B	(MHz)	3982.71 ± 0.03	4103.74 ± 0.03
C	(MHz)	2894.76 ± 0.02	2931.69 ± 0.02
χ_{aa}	(MHz)	− 4.72 ± 0.07	− 3.88 ± 0.09
χ_{bb}	(MHz)	1.93 ± 0.29	2.38 ± 0.31
χ_{cc}	(MHz)	2.79 ± 0.29	1.50 ± 0.31

Table 5. Observed tunneling splitting of some of the rotational transitions for the asymmetric species of CH_2DCOCN.

Transition	Splitting (MHz)
$4_{22} - 3_{21}$	0.66
$4_{23} - 3_{22}$	0.48
$4_{13} - 3_{12}$	0.58
$5_{14} - 4_{13}$	0.74

Table 6. The rotational constants and moments of inertia of the different isotopic species of acetyl cyanide used for the structure determination.

	A (MHz)	B (MHz)	C (MHz)	I_a (amu Å^2)	I_b (amu Å^2)	I_c (amu Å^2)	$I_a + I_b - I_c$ (amu Å^2)
CH_3COCN *	10185.22	4157.36	3002.79	49.63378[a]	121.5990	168.3538	2.87906
$CH_3CO^{13}CN$ †	10184.58	4125.37	2986.21	49.63690	122.5420	169.2885	2.89038
$^{13}CH_3COCN$ †	9906.07	4105.57	2951.68	51.03245	123.1330	171.2689	2.89650
$CH_3C^{18}OCN$ †	9657.42	4085.73	2918.86	52.34638	123.73088	173.1947	2.88259
CD_3COCN †	8728.40	3875.60	2772.32	57.91795	130.4394	182.3494	6.00791
$CD_3{}^{13}COCN$ †	8722.81	3870.29	2769.23	57.95506	130.6184	182.5529	6.02052
$CH_3COC^{15}N$ ††	10183.66	4011.07	2925.28	49.64139	126.0339	172.8145	2.86079
CH_2DCOCN (sym)**	9987.22	3982.71	2894.76	50.61781	126.9314	174.6364	2.91282
CH_2DCOCN (asym)**	9448.54	4103.74	2931.69	53.50363	123.1878	172.4368	4.25464

* Reference (3); ** present work; † Reference (1); †† Reference (11); [a] Conversion factor $5.05531 \cdot 10^5$ MHz · amu Å^2; mass scale ^{16}O.

Table 7. Variation of the in plane r_s-strucutral parameters with the choice of ΔI's (Distances in Å, angles in degrees).

Parameter	$\Delta I_a, \Delta I_b, \Delta I_c$	$\Delta I_a, \Delta I_b$	$\Delta I_a, \Delta I_c$	$\Delta I_b, \Delta I_c$
$C\text{-}H_{sym}$	1.083	1.082	1.083	1.084
$C_{methyl}\text{-}C_{carb}$	1.471	1.487	1.494	1.453
$C_{carb}\text{-}O$	1.248	1.225	1.232	1.259
$C_{carb}\text{-}C_{cyan}$	1.458	1.483	1.448	1.469
$C_{cyan}\text{-}N$	1.159	1.151	1.164	1.170
$\sphericalangle$ $C_{carb}\text{-}C_{meth}\text{-}H_{sym}$	111.12	110.53	111.06	111.28
$\sphericalangle$ $C_{cyan}\text{-}C_{carb}\text{-}C_{meth}$	119.58	116.39	116.77	122.29
$\sphericalangle$ $C_{cyan}\text{-}C_{carb}\text{-}O$	116.58	118.55	119.60	113.84

Table 8. The r_s coordinates of acetyl cyanide in the principle axes system of CH_3COCN using all the changes in moments of inertia.

	a	b	c
C_{methyl}	-1.230 ± 0.004	1.196 ± 0.001	0.0 *
H_{sym}	-2.2991 ± 0.0002	1.0213 ± 0.0002	0.0 *
H_{asym}	-0.9293 ± 0.0005	1.7878 ± 0.0003	$\pm (0.8663 \pm 0.0006)$
$C_{carbonyl}$	-0.483 ± 0.012	-0.076 ± 0.002	0.0 *
O	-1.026 ± 0.002	-1.196 ± 0.001	0.0 *
$C_{cyanyde}$	0.974 ± 0.005	-0.054 ± 0.012	0.0 *
N	2.126 ± 0.002	0.122 ± 0.007	0.0 *

* Assumed by symmetry.

Table 9. Derived structural parameters[a].

	α	β	γ
$C\text{-}H_{sym}$	1.102 ± 0.017	1.102 ± 0.013	1.083 ± 0.004
$C\text{-}H_{asym}$	1.067 ± 0.002	1.067 ± 0.003	1.091 ± 0.002
$C_{methyl}\text{-}C_{carb}$	1.488 ± 0.034	1.488 ± 0.022	1.476 ± 0.014
$C_{carb}\text{-}O$	1.219 ± 0.027	1.218 ± 0.024	1.245 ± 0.006
$C_{carb}\text{-}C_{cyanide}$	1.489 ± 0.053	1.489 ± 0.049	1.457 ± 0.016
$C_{cyanide}\text{-}N$	1.149 ± 0.014	1.149 ± 0.013	1.166 ± 0.017
$\sphericalangle$ $H_{sym}\text{-}C_{methyl}\text{-}H_{asym}$	109.5 ± 1.5	109.5 ± 1.4	111.1 ± 2.1
$\sphericalangle$ $H_{asym}\text{-}C_{methyl}\text{-}H_{asym}$	104.6 ± 1.5	104.6 ± 1.3	105.1 ± 1.6
$\sphericalangle$ $C_{cyan}\text{-}C_{carb}\text{-}C_{methyl}$	114.3 ± 1.9	114.2 ± 1.5	119.6 ± 1.8
$\sphericalangle$ $C_{methyl}\text{-}C_{carb}\text{-}O$	125.4 ± 4.9	125.3 ± 3.7	123.7 ± 1.7
$\sphericalangle$ $C_{carb}\text{-}C_{cyan}\text{-}N$	179.8 ± 2.4	180.0[b]	176.2 ± 4.3
Sum of weighted squared defects[c]	1.2×10^{-8}	1.2×10^{-8}	

[a] Bond lengths in Å, bond angles in degrees. [b] Assumed. [c] in GHz^2.

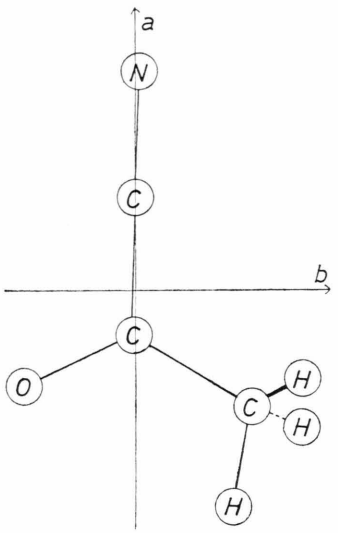

Fig. 1. The structure of Acetyl Cyanide, showing the location of atoms in the principal axis system of the parent molecule CH_3COCN.

the cyanide carbon is very small and the r_s method becomes impractical here. This coordinate is, therefore, obtained from the center of mass condition. The coordinates of the atoms in the principle axes system of the parent molecule is given in Table 8, along with the propagated uncertainties due to the error in the measured rotational constants. The derived molecular structure is given in column 3 of Table 9 and shown in Figure 1.

ii) *r_0-structure*

Inspite of the fact that many isotopic species of acetyl cyanide were previously studied, its r_0-structure was not reported in the literature. In the present work, we utilize all the available experimental data of Ref. [1] as well as those measured in this laboratory (Ref. [4, 11] and the present work). The structure fitting calculations are based on a least square procedure, in which the error equations are weighted with the relative uncertainties of the rotational constants *.

Assuming that the acetyl cyanide has a C_s configuration symmetry and that deuterium substitution does not change bond distances and bond angles, the number of independent structural parameters reduces to 12. An attempt to fit all these parameters to 27 rotational constants yielded an r_0-structure mentioned in column 1 of Table 9. This analysis gives a deviation of about 12′ from 180° for $\sphericalangle$ CCN, with this angle sufficiently uncorrelated to the C_{meth}-$C_{cyanide}$ and C-N bond lengths. As this is well within the error limits propagated from the uncertainties in the measured rotational constants, the next fit was tried with only 11 structural parameters as adjustable ($\sphericalangle$ CCN = 180° fixed). The results are given in column 2 of Table 9. As can be seen, the RMS deviation for the fitted rotational constants remained the same, but the standard deviation for the fitted rotational parameters improved. This could be taken as a positive evidence in favour of $\sphericalangle$ CCN being equal to 180°. The two r_0 structures (columns 1 and 2 of Table 9), however, agree within error limits.

* Computer program VT 12, written by V. Typke, Ulm.

Discussion

A comparison of the determined r_s- and r_0-structure (columns β and γ of Table 9) shows some remarkable differences worthy of discussion. These are $\sphericalangle$ C_{methyl}-$C_{carbonyl}$-$C_{cyanide}$ and ii) C-H_{sym} and C-H_{asym} bond lengths. As has been mentioned earlier also, the b coordinate of $C_{cyanide}$ was too small to be determined from the changes in the observed moments of inertia. This was therefore determined from the center of mass condition and was found to be -0.054 Å. The r_0 structure calculation showed this to be $+0.005$ Å. Moreover, the r_s-structure calculates a deviation of about (3.8 $\pm$4.3)° from 180° for $\sphericalangle$ CCN, whereas in the r_0 calculation (column β of Table 9) this was fixed at 180°. The mentioned uncertainty of 1.8° for $\sphericalangle$ C-C-C in the r_s structure has been derived from the projected error in the determined coordinates. For the b coordinate of the $C_{cyanide}$ atom the uncertainty was calculated from the total uncertainty in the quantity $\sum_i m_i b_i$. However, for almost all determined r_s structures, the center of mass condition is not exactly reproduced. The extent of deviation depends upon zero point vibrational effects. An example is served from the quantity $\sum m_i a_i$ (Table 8) for the determined structure, which is 0.307 amu Å^2, rather than zero. In determining the coordinate of an atom by the center of mass condition, these zero point vibrational effects further worsen the accuracy of the results to an extent which cannot be readily estimated. We believe that the somewhat large difference (beyond the error limits) in $\sphericalangle$ CCC as determined by the two methods

is a result of the breakdown of the r_s-method for the b coordinate determination of $C_{cyanide}$ atom and its subsequent determination from the center of mass condition.

The second point concerns the C-H bond lengths in the methyl group. The r_0-structure calculation shows that $C\text{-}H_{asym} < C\text{-}H_{sym}$, whereas the r_s-structure calculates $C\text{-}H_{asym} > C\text{-}H_{sym}$. This reversal of the trend in the two structures is peculier and needs discussion. There is a difference of 0.026 Å (much beyond the standard error) in the determined C-H bond lengths in the two structures. To be sure, use was also made of a computer program DRSSTR.F4 * for the r_s-structure calculation. This calculation gave structural parameters which agree to those mentioned in column γ of Table 9 within error limits. A closer examination of the input data revealed the following facts. The quantity $I_a + I_b - I_c$ for the normal species, which should be equal to I_α § (for a molecule with C_s configuration symmetry in which the out of plane atoms are the two asymmetric hydrogen atoms only) is substantially lower from its value in similar molecules. (Observed value 2.871 amu Å^2, typical value 3.14 amu Å^2.) The reason for such a remarkably low value of $I_a + I_b - I_c$ could be the following.

i) Mäder[12] points out that for the case of molecules with a C_s symmetry and possessing a methyl group with relatively low barrier to internal rotation, there happens to be a barrier dependent contribution to the quantity $I_a + I_b - I_c$, which effectively lowers its value. It was also possible for him to determine a reliable barrier value for 2 methyl pyridine[12] from the lowering of this quantity. For acetyl cyanide, we determined this lowering from the known value of the barrier parameter[4, 11]. This was obtained to be only 0.03 amu Å^2, a value much less to account for it in the present case.

ii) For a molecule of this kind one has

$$(I_a + I_b - I_c)_{\text{normal species}} = 4\, m_H\, r_H^2 \ldots \quad (1)$$

where m_H is the mass of the hydrogen atom and r_H is the out of plane distance (c coordinate) of the asymmetric hydrogen atoms.

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§ I_α stands for the moment of inertia of the methyl top about its symmetry axis.

Similarly, for the trideuterated species one has

$$(I_a + I_b - I_c)_{\text{tri deu. species}} = 4\, m_D\, r_H^2 . \quad (2)$$

The value of r_H comes out to be 0.844 and 0.864 Å, when determined from Eq. (1) and (2) respectively. r_H can also be determined from the relation

$$r_H = \frac{(I_a + I_b - I_c)_{\text{tri deu. species}}}{4(m_D - m_H) - (I_a + I_b - I_c)_{\text{normal species}}} . \quad (3)$$

This comes out to be 0.883 Å. The r_0 procedure fits the structural parameters to the observed moments of inertia and is thus expected to yield a value of r_H somewhere between 0.844 and 0.864 Å. The r_s procedure, on the other hand fits the structural parameters to the differences in the observed moments of inertia and should thus yield a value near 0.883 Å. It should be emphasized that the magnitude and sign of this difference in the value of r_H tends to explain successfully the difference between the calculated $C\text{-}H_{asym}$ bond distance in the two structure determinations.

iii) Laurie[13] has pointed out that a negative contribution to $I_a + I_b - I_c$ also comes from an effect similar to 'quantum defect' observed in completely planar molecules and arises mainly from the low frequency motion of the heavy in plane atoms. Thus, it has been proposed that Eqs. (1) and (2) should be modified to

$$(I_a + I_b - I_c)_{\text{normal species}} + \Delta' = 4\, m_H\, r_H^2 , \quad (4)$$

$$(I_a + I_b - I_c)_{\text{tri deu. species}} + \Delta' = 4\, m_D\, r_H^2 \quad (5)$$

where Δ' is the contribution of the quantum defect as mentioned above, and has been shown to be independent of this isotopic substitution. This kind of analysis yields a value of r_H, which is essentially the same as determined from the r_s procedure and $\Delta' = 0.2714$ amu Å^2. The Δ' is similar in magnitude and sign to the values observed for completely planar molecules, which have an intramolecular vibrational mode with a frequency comparable to those in the present molecule[14] (CH_3 torsion 131.5 cm^{-1}, CCN in plane bending 176 cm^{-1}); for example 0.252 amu Å^2 for $COCl_2$ (Cl-C-Cl in plane bending vibration at 191 cm^{-1})[15].

iv) We do not feel that the inherent assumption of the invariance of bond length with deuterium

substitution should be thought of as a possible reason for the present molecule. When considered, it[15] usually gives a change of only 0.003—0.005 Å for the X-H and X-D bond lengths, a value just of the order of the standard error in the determination of the C-H bond length in the present molecule.

Conclusions

The present structure determination indicates that the methyl group does not have C_{3v} symmetry. This can be stated with some confidence, because both the bond lengths and bond angles differ beyond the range of uncertainty for the symmetric and asymmetric hydrogen positions.

The axis through the center of mass of the three methyl hydrogens and the carbon atom is tilted by about 2° towards the C=O bond. This is in agreement to the conclusion reached from the analysis of the ground state internal rotation splitting of the transitions in the normal and ^{15}N isotopic species of the molecule.

So far as the CCN group is concerned, the present structural investigations suggest it to be collinear within the uncertainty of measurements.

From the above discussions we conclude that the r_s-structure (column γ of Table 9) is perhaps the better choice for use in the analysis of the rotational spectrum of the molecule in the ground and the excited torsional and vibrational states simultaneously in terms of the RTV model.

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