Microwave Spectrum of Malononitrile, $CH_2(CN)_2$. I. The Molecular Structure in the Ground Vibrational State

By Eizi HIROTA and Yonezo MORINO

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The vibration-rotation interaction in polyatomic molecules has been studied extensively by Nielsen and others[1]. The interaction manifests itself in several ways in the observed spectra; for example, the rotational constant differs slightly in each vibrational state and the centrifugal force results in the elongation of molecules. An interesting feature of the interaction is given by the Coriolis force which can be observed most clearly in the degenerate vibrational states. Microwave investigation has been made on the Coriolis interaction in linear and symmetric top molecules, in the name of *l*-type doubling[2]. However, it may be pointed out that, if the two vibrational states are nearly or accidentally degenerate, the Coriolis interaction is expected to become large. Malononitrile has been studied for this purpose, since the Coriolis interactions are expected between four low-lying C–C≡N bending modes[3].

The Raman effect of malononitrile was observed by Kohlrausch and Ypsilanti[4] and the infrared absorption spectrum was measured by Halverson and Francel[5]. The latter authors assigned the spectra and carried out the normal coordinate analysis. However, no data have yet been reported on the structure of the molecule. The present paper will give the molecular structure in the ground vibrational state. The vibration-rotation interaction will be treated in the near future.

Experimental

The apparatus used was a conventional Stark modulation spectrograph, a 100 kc. sine wave being used for simplicity[6]. In addition to the normal molecule, three kinds of molecules isotopically substituted, $CHD(CN)_2$, $CD_2(CN)_2$, and $CH_2CNC^{15}N$, were synthesized to observe their rotational spectra. The hydrogen atoms of malononitrile exchange readily with the hydrogen of water; thus, the deuterated molecules were obtained by mixing the normal malononitrile with heavy water, made slightly alkaline by adding a small quantity of anhydrous sodium carbonate. The ^{15}N substituted molecules were obtained as follows. Ammonium sulfate containing 23.5% ^{15}N was mixed with barium hydroxide and heated. The ammonia thus evolved was led into cold water. The reaction of aqueous ammonia with ethylcyanoacetate gave cyanoacetic amide, which was dehydrated by phosphorous oxychloride to $CH_2CNC^{15}N$[7].

Rotational Spectra and Rotational Constants

The malononitrile molecule has a two-fold symmetry axis and the moment of inertia about this axis is of an intermediate magnitude. Thus, the selection rule allows only the *b*-type rotational transitions. The *a*-axis lies on a plane made by the two cyano groups and the central carbon atom. The *c*-type transitions are allowed for $CHD(CN)_2$ and the *a*-type transitions for $CH_2CNC^{15}N$, but neither of them was observed. Microwave absorption was observed only at room temperature since the vapor pressure is low. Owing to the large dipole moment (~3.6 D), the small rotational constants, and the presence of many vibrational states of low energies, the molecule was found to have many rotational lines: at least, one absorption line was observed in every 10 Mc./sec. Hence, the assignment seemed at first to be difficult. Fortunately, a *Q*-branch series $J_{0,J} \rightarrow J_{1\,J-1}$ was found to be assigned most easily*: the Stark effects are large and the intensities, in particular of high *J* members, are very strong. It was possible to resolve three or four Stark components of $J=5$, 6 and

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[1] H. H. Nielsen, *Revs. Modern Phys.*, **23**, 90 (1951).

[2] See, for example, R. G. Shulman and C. H. Townes, *Phys. Rev.*, **77**, 421 (1950).

[3] E. B. Wilson, Jr., *J. Chem. Phys.*, **4**, 313 (1936).

[4] K. W. F. Kohlrausch and Gr. P. Ypsilanti, *Z. physik. Chem.*, **B29**, 274 (1935).

[5] F. Halverson and R. J. Francel, *J. Chem. Phys.*, **17**, 694 (1949).

[6] E. Hirota, T. Oka and Y. Morino, ibid., **29**, 444 (1958); This Bulletin, to be published.

[7] H. Gilman, "Organic Syntheses", Vol. 1, John Wiley & Sons, Inc., New York (1948), p. 179; A. H. Blatt, ibid., Vol. 2 (1948), p. 379; A. R. Surrey, ibid., Vol. 25 (1945), p. 63.

* It can be easily shown by use of the rotational constants that the $J_{0J} \rightarrow J_{1,J-1}$ transitions are the single series of the *Q*-branch of this molecule in the region accessible by the present technique, 7000 to 30000 Mc./sec.

TABLE I. OBSERVED AND CALCULATED FREQUENCIES (Mc./sec.)

Transition	$CH_2(CN)_2$		$CH_2CNC^{15}N$		$CHD(CN)_2$		$CD_2(CN)_2$		$CH_2CN^{13}CN$
	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
$1_{01} \to 1_{10}$	18265.36	18265.36	18088.67	18088.66	15916.73	15916.82	14077.66	14077.62	
$2_{02} \to 2_{11}$	18595.54	18595.46	18405.56	18405.88	16268.84	16268.81	14444.84	14444.81	
$3_{03} \to 3_{12}$	19098.79	19098.82	18889.37	18889.37	16807.95	16807.47	15008.56	15008.67	
$4_{04} \to 4_{13}$	19785.23	19785.23	19548.66	19548.23	17545.41	17545.45	15784.72	15784.65	
$5_{05} \to 5_{14}$	20667.93	20667.53	20394.99	20394.50	18498.82	18499.29	16791.92	16792.84	
$6_{06} \to 6_{15}$	21761.79	21761.37	21443.07	21442.81	19688.76	19688.98	18055.72	18057.16	
$7_{07} \to 7_{16}$	23084.25	23084.74	22709.58	22710.03	21135.78	21137.12	19601.55	19604.16	
$8_{08} \to 8_{17}$	24656.01	24657.52	24213.27	24214.85	22864.92	22867.70	21456.12	21461.10	
$9_{09} \to 9_{18}$	26497.38	26500.21	25973.43	25976.61	24899.76	24904.63	23645.34	23653.46	26367.03
$10_{0,10} \to 10_{19}$	28626.87	28632.98	28008.57	28014.56	27261.51	27269.52	26189.70	26202.06	28456.41
$0_{00} \to 1_{11}$	23498.82	23498.91	23189.52	23189.62	21086.78	21086.64	19191.00	19191.03	
$1_{01} \to 2_{12}$	28732.50	28732.46	28290.63	28290.58	26256.39	26256.46	24304.47	24304.45	
$5_{15} \to 6_{06}$	17414.02	17419.57							
$6_{16} \to 7_{07}$	23738.22	23746.58							
$5_{14} \to 4_{23}$	24093.24	24096.38							
$6_{15} \to 5_{24}$	17595.24	17586.45							

TABLE II. ROTATIONAL CONSTANTS AND PRINCIPAL MOMENTS OF INERTIA[a)]

	$CH_2(CN)_2$	$CH_2CNC^{15}N$	$CD_2(CN)_2$	$CHD(CN)_2$
A	20882.137	20639.146	16634.324	18501.730
B	2942.477	2863.585	2916.905	2931.189
C	2616.774	2550.477	2556.710	2584.910
b	-8.9961×10^{-3}	-8.7304×10^{-3}	-1.29590×10^{-2}	-1.09974×10^{-2}
I_a	24.208777	24.493794	30.390835	27.323445
I_b	171.8046	176.5378	173.3108	172.4662
I_c	193.1886	198.2104	197.7272	195.5701

$CH_2CN^{13}CN$

$A-(B+C)/2=18120.8\pm5.$ Mc./sec.

$(B-C)/2=160.3\pm4.$ Mc./sec.

a) Rotational constants are given in Mc./sec. and principal moments of inertia in amu Å^2. Conversion factor 505531 Mc. amu Å^2 is used.

7 lines and thus to check the J numbers of these lines by the technique of Golden and Wilson[8)]. Six low J transitions of P- and R-branches were also observed for $CH_2(CN)_2$, and two R-branch transitions for isotopically substituted molecules. The Q-branch members, $9_{09}\to9_{18}$ and $10_{0,10}\to10_{19}$ of the $CH_2CN^{13}CN$ molecule in natural abundance were measured and assigned. The measured frequencies are listed in Table I.

The rotational constants given in Table II were determined by four Q-branch ($J=1$ to 4) and two R-branch ($0_{00}\to1_{11}$ and $1_{01}\to2_{12}$) transitions, the centrifugal distortion being neglected. $A-(B+C)/2$ and $(B-C)/2$ were obtained for $CH_2CN^{13}CN$. The results are also given in Table II. The frequencies calculated by using the constants obtained above are compared with the observed frequencies in Table I.

Structure Analysis

The structure of malononitrile is specified by five parameters: the C—H, the C—C, and the C≡N bond length, and the HCH and the CCC bond angle. If the linearity of the C—C≡N group is abandoned, an additional parameter, ∠CCN, is necessary.

For convenience a Cartesian coordinate system is fixed in the molecule; its origin coincides with the center of gravity and the x-axis is taken along to the c-axis, the y-axis to the a-axis, and the z-axis to the b-axis, respectively (see Fig. 1). For isotopically substituted molecules the origin is shifted to the new center of gravity,

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8) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

TABLE III. THE x-, y- AND z-MOMENTS (amu Å^2)

	$CH_2(CN)_2$	$CH_2CNC^{15}N$	$CD_2(CN)_2$	$CHD(CN)_2$
$\sum m_i x_i^2$	1.4124	1.4106	2.9872	2.1805
$\sum m_i y_i^2$	170.3922	175.1228	170.3236	170.3564
$\sum m_i z_i^2$	22.7964	23.0876	27.4036	25.1430

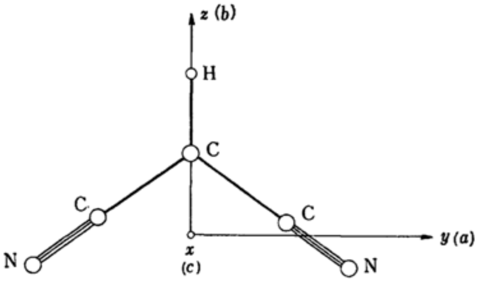

Fig. 1. Schematic diagram of malononitrile molecule.

but the x-, y-, and z-axes are kept parallel to those in the original molecule. For $CD_2(CN)_2$ the (x, y, z) system evidently coincides with the principal axes of moment of inertia, but for $CHD(CN)_2$ and $CH_2CNC^{15}N$ a slight rotation of axes is necessary, in transforming from the (a, b, c) system to the (x, y, z) system. Thus, in evaluating $\sum m_i x_i^2$, $\sum m_i y_i^2$, and $\sum m_i z_i^2$ (which are called the x-moment, the y-moment, and the z-moment, respectively) from I_a, I_b and I_c for the latter two molecules, some minor corrections are necessary and they are easily calculated by assuming a structure close to the real one. The x-, y- and z-moments thus obtained are listed in Table III.

a) x-Coordinates. — The x-moment is a function only of the x-coordinate of the hydrogen atom, x_H: that is,

$$\sum m_i x_i^2 = 2m x_H^2 \tag{1}$$

where $2m = 2m_H$ for $CH_2(CN)_2$ and $CH_2CN \cdot C^{15}N$, $2m = [(3m_C + 2m_N)(m_D + m_H) + 4m_D m_H] / (3m_C + 2m_N + m_D + m_H)$ for $CHD(CN)_2$, and $2m = 2m_D$ for $CD_2(CN)_2$. The value of x_H, given in Table IV, increases with the mass of hydrogen, just as in the case of methylene chloride. Laurie[9] has explained this effect by the inertia defect, in analogy with planar molecules. By taking into consideration the inertia defect Δ, Eq. 1 is modified as follows:

$$\sum m_i x_i^2 + (1/2)\Delta = 2m x_H^2 \tag{1'}$$

where a single value of the inertia defect Δ is assumed for all molecules, since the inertia defect is considered to originate from the in-plane vibrations of low frequencies. In fact, four observed x-moments can be reproduced by Eq. 1′, if two parameters, x_H and Δ, are assumed to be 0.8847 Å and 0.3379 amu Å^2, respectively. The calculated x-moments are compared with those observed in Table V. The inertia defect Δ of 0.3379 amu Å^2 is large compared with that of methylene chloride 0.167 amu Å^2, or of other molecules[9]. It is consistent with the fact that there are more normal modes of low frequencies in malononitrile.

TABLE IV. VALUES OF x_H DETERMINED WITHOUT THE INERTIA DEFECT CORRECTION (Å)

Molecule	x_H
$CH_2(CN)_2$	0.8370
$CH_2CNC^{15}N$	0.8364
$CHD(CN)_2$	0.8514
$CD_2(CN)_2$	0.8610

TABLE V. OBSERVED AND CALCULATED x-MOMENTS (amu Å^2)

Molecule	$\sum m_i x_i^2$	
	obsd.	calcd.[a]
$CH_2(CN)_2$	1.4124	1.4091
$CH_2CNC^{15}N$	1.4106	1.4091
$CHD(CN)_2$	2.1805	2.1851
$CD_2(CN)_2$	2.9872	2.9848

[a] $x_H = 0.8847$ Å and $\Delta = 0.3379$ amu A^2 are assumed.

Myers and Gwinn[10] have analyzed their data on methylene chloride by plotting x_H against $1/2m$. The meaning of this procedure is evident from Eq. 1′; if $\Delta \ll \sum m_i x_i^2$ is assumed, x_H is given by $(\sum m_i x_i^2/2m)^{1/2} \cdot (1 + \Delta/4\sum m_i x_i^2) = x_H^0 + (\Delta/4x_H^0)(1/2m)$, where $x_H^0 = (\sum m_i x_i^2/2m)^{1/2}$ means the value of x_H, when Δ is ignored. Thus, the x_H obtained here corresponds to x_H^0 in the limit of $1/2m \rightarrow 0$.

b) y-Coordinates. — If the effect of zero-point vibration is negligible, the same y-moment should be obtained for three molecules; $CH_2(CN)_2$, $CHD(CN)_2$ and $CD_2(CN)_2$, since the y-moment is a function depending only upon the coordinates of the cyano groups. The observed y-moments,

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[9] V. W. Laurie, ibid., **28**, 704 (1958).

[10] R. J. Myers and W. D. Gwinn, ibid., **20**, 1420 (1952).

170.3922, 170.3564 and 170.3236 amu Å^2, show a small discrepancy, presumably due to zero-point vibration, but the effect is not so large as in the x-moment.

By combining the y-moment for $CH_2CN\cdot C^{15}N$, $(\sum m_i y_i^2)_{15}$, with that of $CH_2(CN)_2$, $(\sum m_i y_i^2)_{14}$, the y-coordinate of nitrogen, y_N, in the normal molecule is obtained as follows:

$$y_N^2 = [(M+\varDelta m_N)/M\varDelta m_N] \times [(\sum m_i y_i^2)_{15} - (\sum m_i y_i^2)_{14}] \qquad (2)$$

where M is the total mass of $CH_2(CN)_2$, and $\varDelta m_N$ is the mass difference of ^{15}N and ^{14}N. Then y_N is found to be 2.1943 Å.

In order to determine the y-coordinate of the carbon atom in a cyano group, y_C, it is desirable to substitute the carbon atom with its isotope, ^{13}C[11]. As mentioned earlier, two Q-branch transitions have been observed for $CH_2CN^{13}CN$ molecule, but the rotational constants could not be determined accurately enough for the structure analysis. Hence y_C is evaluated through the y-moment combined with the value of y_N obtained above. Three values of the y-moments for $CH_2(CN)_2$, $CHD(CN)_2$, and $CD_2(CN)_2$ give accordingly three y_C's: 1.2161, 1.2155 and 1.2149 Å, respectively. As the difference between them is not large, the average of the three values is used for y_C: that is, 1.2155 Å.

c) z-Coordinates. — The z-moments of $CH_2(CN)_2$, $(\sum m_i z_i^2)_2$, and of $CHD(CN)_2$, $(\sum m_i z_i^2)_3$, give the z-coordinate of hydrogen in the normal molecule, z_H, by the relation similar to Eq. 2:

$$z_H^2 = [(M+\varDelta m_H)/M\varDelta m_H] \times [(\sum m_i z_i^2)_3 - (\sum m_i z_i^2)_2] \qquad (3)$$

where $\varDelta m_H$ is the mass difference of D and H. If the z-moment of $CD_2(CN)_2$, $(\sum m_i z_i^2)_4$, is used in place of $(\sum m_i z_i^2)_3$, the equation

$$z_H^2 = [(M+2\varDelta m_H)/2M\varDelta m_H] \times [(\sum m_i z_i^2)_4 - (\sum m_i z_i^2)_2] \qquad (4)$$

must be applied. Eq. 3 gives z_H of 1.5384 Å, whereas Eq. 4 gives 1.5357 Å. The average value, 1.5371 Å, is used in the following analysis of the structure.

A similar procedure is used to determine the z-coordinate of the nitrogen atom, z_N. The relevant equation is

$$z_N^2 = [(M+\varDelta m_N)/M\varDelta m_N] \times [(\sum m_i z_i^2)_{15} - (\sum m_i z_i^2)_{14}] \qquad (5)$$

where $(\sum m_i z_i^2)_{14}$ means $(\sum m_i z_i^2)_2$ in Eqs. 3 and 4. It may be noted that, since the effect of zero-point vibration entering in $\sum m_i x_i^2$ is probably similar for the two molecules $CH_2(CN)_2$ and $CH_2CNC^{15}N$, I_{yy} is used in place of $(\sum m_i z_i^2)$. In doing so, the accuracy attained becomes considerably better, for the value of I_{yy} is determined by the rotational constant A, whereas $\sum m_i z_i^2$ is evaluated by three rotational constants, A, B and C. Under this assumption z_N is found to be -0.5427_3 Å.

Since adequate substitutions are not yet available, a procedure similar to that used for the determination of z_H and z_N can not be applied to the z-coordinates of carbon atoms. Moreover, whatever substitution is possible, the z-coordinate of the carbon atom of the cyano group is close to zero, and the procedure becomes less powerful. Hence the first moment equation and the relation giving the z-moment of $CH_2(CN)_2$ are used to evaluate the z-coordinates of the apex carbon atom, z_0, and of the carbon atom in the cyano group, z_C[11]. They are 0.8994 and 0.0545 Å, respectively.

TABLE VI. COORDINATES OF ATOMS IN $CH_2(CN)_2$ AND MOLECULAR STRUCTURE

Atom	x_i	y_i	z_i
H	±0.8847 Å	0 Å	+1.5371 Å
C (apex)	0	0	+0.8994
C (cyano)	0	±1.2155	+0.0545
N	0	±2.1943	-0.5427_3

C—C	$1.480_3 \pm 0.0056$ Å	∠CCC	110°24′±24′
C≡N	$1.146_6 \pm 0.0064$ Å	∠HCH	108°26′±26′
C—H	$1.090_6 \pm 0.0034$ Å	∠CCN	180°−(3°24′±26′) (outside)

All the coodinates necessary for the structure determination are thus obtained and listed in Table VI. The bond length of C—H is found to be 1.091 Å, that of C—C 1.480 Å, and that of C≡N 1.147 Å. The bond angle of CCC, 110°24′, is about 1° wider than the tetrahedral angle, whereas that of HCH, 108°26′, is smaller than the tetrahedral angle by the same order of magnitude. Myers and Gwinn[10] reported the C—H bond length and the HCH bond angle in methylene chloride to be 1.082 Å and 112°58′, respectively, whereas Lide, Jr.[12], obtained 1.092 Å and 111°52′, for the corresponding quantities in methylene fluoride. The C—H bond length of malononitrile, 1.091 Å, is closer to that of methylene fluoride, rather than to that of methylene chloride, but the

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11) C. C. Costain, ibid., **29**, 864 (1958).

12) D. R. Lide, Jr., *J. Am. Chem. Soc.*, **74**, 3548 (1952).

HCH bond angle 108°26′ is definitely smaller than those of methylene halides. It is noteworthy that the linearity of C—C≡N groups does not hold, the cyano groups being bent outside by about 3.5°. Though zero-point vibration may modify considerably the equilibrium configuration, it seems reasonable to assume an electrostatic repulsion between two electronegative groups such as cyano radicals. Somewhat longer C—C, somewhat shorter C≡N bond length, and the bent C—C≡N indicate that the electron configuration in the cyano groups might be more or less different from that in acetonitrile. In fact, Casabella and Bray[13] found, in the solid state, a quadrupole coupling constant and an asymmetry parameter, definitely larger than those of acetonitrile and of ethyl cyanide.

Dipole Moment

The dipole moment of $CH_2(CN)_2$ was obtained from the Stark effects of the six transitions: four Q-branch lines of $J=1$ to 4 and two R-branch transitions, $0_{00} \rightarrow 1_{11}$ and $1_{01} \rightarrow 2_{12}$. The field strength was calibrated by the $J=1 \rightarrow 2$ transition of OCS, the dipole moment of OCS being assumed to be 0.7124 D[14]. The values of the dipole moment obtained from the six transitions agree well with each other (Table VII). The average of them is 3.735 D, which is compared with 3.6 D obtained by the dielectric constant measurement in benzene solutions[15].

TABLE VII. DIPOLE MOMENT (DEBYE)

Transition	μ
$1_{01} \rightarrow 1_{10}$	3.724
$2_{02} \rightarrow 2_{11}$	3.735
$3_{03} \rightarrow 3_{12}$	3.759
$4_{04} \rightarrow 4_{13}$	3.750
$0_{00} \rightarrow 1_{11}$	3.704
$1_{01} \rightarrow 2_{12}$	3.736
average	3.735 ± 0.017

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

Added in Proof:

October, 1959 Dr. P. W. Moore of Purdue University called the authors' attention to the paper by N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **80**, 3483 (1958). They measured the microwave spectrum of normal species $CH_2(CN)_2$ of malononitrile and obtained rotational constants in close agreement with the authors'. Recently Dr. Muller wrote us that their measurement had been extended to include the rotational spectrum of deuterium substituted species $CD_2(CN)_2$, and the rotational constants obtained were also in agreement with the authors'.

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[13] P. A. Casabella and P. J. Bray, *J. Chem. Phys.*, **29**, 1105 (1958).

[14] S. A. Marshall and I. Weber, *Phys. Rev.*, **105**, 1502 (1957).

[15] P. Trunel, *Ann. chim.*, **12**, 93 (1939).