MICROWAVE SPECTRUM OF 1,1'-DIMETHYL-2,2'-DICYANOETHYLENE

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ABSTRACT

The microwave spectra of 1,1'dimethyl-2,2'dicyanoethylene and 1,1'dimethyl-2,2'dicyanoethylene-d₆ have been recorded in the frequency region 18–40 GHz. The measured ground state lines have been fitted to a semi-rigid rotor model. From the resulting six moments of inertia some structural information has been obtained.

INTRODUCTION

The vibrational analysis of 1,1'dimethyl-2,2'dicyanoethylene, $(CH_3)_2C=C-(CN)_2$, which is under way [1], has stimulated the present MW investigation. The structural information obtainable from the MW results will be of importance in the force field calculation.

Some similar molecules have been studied by MW spectroscopy, particularly 1,1'-dicyanoethene [2-4] and isobutene [5-7]. Structural parameters and, in the latter case, the internal rotation barrier were determined. An increase of V_3 with a decrease of the H₃C-C-CH₃ angle was observed in the series: dimethylketene [8], dimethylallene [9], and isobutene [5, 7]. This same angle is expected not to vary much in 1,1'-dimethyl-2,2'-dicyanoethylene with respect to isobutene, as the repulsive interactions between the atoms at C_1 and C_2 , see Fig. 1, appear, at first sight, of the same order in both cases.

The heavy atoms configuration of $(CH_3)_2C=C(CN)_2$ will be of use also in the vibrational study of the more complex molecule 1,2-carbodicyanocyclobuten-3,4-dione [1].

EXPERIMENTAL

The sample of $(CH_3)_2C=C(CN)_2$ was obtained as follows. Redistilled malonodinitrile (10 g) and acetone (50 ml, distilled from a solution of KMnO₄) were introduced into a 200 ml flask provided with reflux condenser and poly-



Fig. 1. Molecular structure of $(CH_3)_2C=C(CN)_2$ referred to the principal axes of inertia.

tetrafluoroethylene-covered magnetic stirring bar. When the solid was dissolved, a solution of β -alanine (0.100 g) in water (2.00 ml) was added rapidly with strong agitation. Within 5 min the mixture became hot and refluxing was started. After 30 min the solution was washed several times with water in a separatory funnel, discarding the lower layer. The crude product was dried with CaCl₂, and distilled twice at 7–8 mm Hg in a mist-removing apparatus [10]. The product consisted of 15 g (nearly quantitative yield) of water-clear liquid, boiling at 84°C and lacking in gas-chromatographically (Apiezon column) detectable impurities. The NMR shift in CCl₄ solution at 37°C was 2.38 ppm; the IR spectrum was the same as that of a five-times distilled sample prepared after the method of ref. 11 which, however, gives a much lower yield because the crude product contains large quantities of other compounds.

The hexadeuterated species, $(CD_3)_2C=C(CN)_2$, was obtained as follows. Redistilled malonodinitrile (3.5 g) was dissolved in D₂O (12 ml) contained into a bulb connected by means of a side arm and a polytetrafluoroethylene pipe to a tank of UPP nitrogen. While a slow nitrogen stream flowed out, acetone-d₆ was added (6.0 ml, 99.8% D, Stohler Isotope Chemicals) and then a solution of β -alanine (30 mg) in D₂O (1 ml, 99.8% D, Fluka) by means of two syringes and hypodermic needles. The system was agitated for 10 min and allowed to stand in a water bath at 45°C for a further 30 min. Then the nitrogen stream was started again, the lower layer discarded, and the remaining product washed twice with 2 ml portions of D₂O. The liquid was then dried with fused CaCl₂ and distilled as the hydrogen compound. The product consisted of 5 g of water-clear liquid, b.p. 52°C at about 1 mm Hg, with no gas-chromatography detectable impurities. No NMR signal and negligible IR absorptions were found in the positions characteristic of the hydrogenated species.

The spectra were recorded with a HP 8400 C Stark modulated spectrometer. For the assignment of a number of transitions of $(CH_3)_2C=C(CN)_2$ use was made of the microwave—microwave double resonance (MWMWDR) technique in the arrangement described elsewhere [12].

The sample cells were operated at room temperature, with a sample pressure of about 50 μ Hg. The accuracy of the frequency measurements is estimated to be ±200 kHz, due to line broadening.

MICROWAVE SPECTRUM

The spectra of $(CH_3)_2C=C(CN)_2$ and $(CD_3)_2C=C(CN_2)$ appeared rather dense with weak lines due to many low-lying vibrational states [1].

The molecule is an oblate asymmetric rotor with μ_a transitions. Since it is rather heavy, a number of families of Q-branch transitions fall into the frequency region studied. The unresolved effects of nuclear quadrupole coupling of the nitrogen and of the two methyl tops internal rotation produce a broadening of the lines of the order of 1 MHz. The vibrational satellites, which in many cases overlap the ground state lines, contribute to the linewidth. Both Q- and R-branch transitions were taken into consideration in the process of assigning the spectra, but, since the Q-branch transitions pile up into bands, only the R-branch transitions were eventually retained. The measured frequencies are given in Table 1 and the fitted rotational parameters in Table 2. All the measured lines were easily Stark modulated. Typical Stark fields of the order of 500—1000 V cm⁻¹ were usually required for proper modulation. In the MWMWDR experiments, Q-branch transitions were pumped while observing R-branch transitions. The lines assigned by this technique are indicated in Table 1.

STRUCTURE CONSIDERATIONS

From the six effective moments of inertia, determined by assuming a semi-rigid rotor model, some structural parameters can be determined.

In order to minimize the zero point vibrational effects, differences of the moments of inertia for the normal and deuterated species are used [13].

From the relationship

$$\Delta_c = \Delta I_c^0 - \Delta I_a^0 - \Delta I_b^0 = -2\Delta P_c \tag{1}$$

in the present case, $-2\Delta P_c$ is characteristic of a molecule possessing a plane of symmetry with two pairs of hydrogens being out-of-plane atoms, as shown in Table 3. In this hypothesis it is

$$\Delta P_{\rm e} = 2(m_{\rm D} - m_{\rm H})r_{\rm s}^2 \tag{2}$$

where r_s is the distance between the out-of-plane H atoms in the two methyl

TABLE 1

Transition	$(CH_3)_2C=C(CN)_2$		(CD ₃) ₂ C=C(CN) ₂	
	Obs.	Diff. ^a	Obs.	Diff.ª
634-533	18724.2	0.2		
624 - 523	18724.2	0.2		
744-643	23 106.1	0.1		
734-633	23106.1	-0.1		
726-625	18781.5	0.0		
716-615	18781.5	0.0		
853-752			27157.0	0_0
854-753	27488.4	0.2		
8 4 4-7 4 3	27488.4	-0.1		
845 - 744	25 325.8	0.1		
835-734	25 325.8	0.1		
836-735	23 163.5	0.1		
826-725	23 163.5	0.1		
827-726	21 001.3	0.1	19078.2	0.1
817-716	21 001.3	0.1	19078.2	0.1
8 1 8-7 1 7	18838.9	-0.1		
808-707	18 838.9	-0.1		
955-854	29707.9	0.1		
945-844	29 707.9	0.1		
946-845	27 545.4	0.0		
936835	27 545.4	0.0		
937—836	25 383.1	0.0		
927-826	25 383.1	0.0		
928-827	23221.0	0.1		
918-817	23 221.0	0.1		
91 9— 818	21 058.8	0.0	19175.0	0.0
909808	21058.8	0.0	19175.0	0.0
1056-955	31 927.3 ^b	0.1	28 910.9	0.1
1046-945	31927.3 ^b	-0.1	28 910.9	0.3
10 4 7-9 4 6	$29.765.2^{b}$	0.1		
1037-936	29765.2^{b}	0.1		
1038-937	27 602.8	0.0		
10 2 8-9 2 7	27 602.8	0.0		
10 2 9-9 2 8	25 440.6	0.0	23 1 25.2	0.1
1019-918	25 440.6	0.0	23 125.3	0.1
10 1 10-9 1 9	23 278.3	-0.1		
10 0 10-9 0 9	23 278.3	-0.1		
1175-1074	38472.2	0.0		
1165-1064	38 472.2 ^b	0.0		
11 5 6-10 6 5	36 309.4 [°]	0.0		
11561055	36 309.4 ^b	0.0		
1157-1056	$34146.9^{ m b}$	0.0		
11 4 7-10 4 6	34146.9^{b}	0.0		
11 4 8-10 4 7	31 984.9	0.2		
11 3 8-10 3 7	31984.9	0.2		
11 3 9-10 3 8	29 822.6	0.1		

Transition frequencies (MHz) in the ground state of (CH₃)₂C=C(CN)₂ and (CD₃)₂C=C(CN)₂

Transition	$(CH_3)_2C=C(CN)_2$		$(CD_3)_2C=C(CN)_2$	
	Obs.	Diff. ^a	Obs.	Diff.ª
11 2 9-10 2 8	29 822.6	0.1		
11 2 10-10 2 9	27 660.5	0.1	25 148.6	0.0
11 1 10—10 1 9	27660.5	0,1	25148.6	0.0
11 1 11-10 1 10	25 498.2	0.0		
11 0 11—10 0 10	25498.2	0.0		
1266—1165			36 827.9	0.0
1267—1166	38 528.7	-0.2	34 886.1	0.0
1257-1156	38 528.7	-0.2	34886.1	-0.1
1258-1157	36 366.6	0.0	32954.5	-0.1
1248-1147	36 366.6	0.0	32954.5	-0.1
1249-1148	34 204.4	0.1		
1239-1138	34 204 4	0.1		
12 3 10-11 3 9	320424	0.2		
12210-1129	320424	0.2		
12211-11210	29 879 9	-0.1	27 1 7 9 1	0.0
12111-11110	298799	-01	27 179 1	0.0
12112-11111	277178	0.0	21 1/2,1	0,0
12012-11011	27 717 8	0.0		
1359-1258	38 586 4	0.0	34 977 3	0.0
1349-1248	38 586 4	0.2	34 977 3	0.0
13410-1249	36423.9	-0.2	33 049 2	-0.0
13 3 10-12 3 9	36423.0	-0.2	330492	-0.2
13311-19310	34 961 7	01	33043.4	0.2
13 2 11 12 2 10	34 961 7	01		
13 2 11 12 2 10	22000 7	-0.1		
13 1 19-19 1 11	32033.1	0.0		
13 1 13-19 1 19	29 937 A	-0.1	97 968 9	0.2
13 0 13-12 0 12	20 007.4	01	27 268 9	0.2
14 5 10-13 5 9	23 301.4	0,1	37 000 3	0.2
14410-1349			27000.3	0.0
14410 1040	386434	-0.3	25 072 0	0.0
14 + 11 + 10 + 10 14 + 11 - 12 + 10	28 642 4	-0.3	35072.5	0.1
14 3 12 13 3 10	36 481 9	0.3	221458	0.1
14012 10011 14019 - 19011	36481.2	-0.3	33145.0	0.0
1421213211	24 210 1	-0.3	33 145.0	0.0
14210 10212	24 210 1	-0.2		
14 1 13 - 13 1 12	291579	0.2		
14 0 14 19 0 19	29157.2	0.0		
14014 - 13013	32 LJ1.2	0.0	95 100 4	0.1
	30701.0	0.1	35169.4	0.1
	38701.0	-0.1	35169.4	0.1
	30 338.9 20 528 0	-0.1	33242.8	0.2
	30 338,9	-0.1	33 242.8	0.2
	34376.8	0.0		
15 0 15-14 0 14	34 376.8	U.U		. .
16 3 14-15 3 13			37192.8	0.1
16 2 14-15 2 13			37 192.8	0.1
16 2 15-15 2 14	38758.7	0.1		
16 1 1515 1 14	38758.7	0.1		

TABLE 1 (continued)

Transition	$(CH_3)_2C=C(CN)_2$		$(CD_3)_2C=C(CN)_2$	
	Obs.	Diff. ^a	Obs.	Diff.ª
16 1 16-15 1 15	36 596.5	0.1	33 339.6	-0.0
16 0 16-15 0 15	36 596.5	0.1	33 339.6	-0.0
17 2 16-16 2 15			37 289.8	0.2
17 1 16-16 1 15			37 289.8	0.2
17 1 17-16 1 16	38 816.2	0.3	35 362.9	-0.2
17017-16016	38 816.2	0.3	35 362.9	-0.2
18 1 18-17 1 17			37 386.6	-0.0
18 0 18-17 0 17			37 386 6	0.0
19 1 19-18 1 18			39 409 9	-01
19 0 19-18 0 18			39 409.9	-0.1

TABLE 1 (continued)

^aDifferences (MHz) between observed and calculated frequencies. ^bFrequencies checked by MWMWDR.

tops; see Fig. 1 (the methyl top conformations are assumed as in isobutene [5, 6]).

The next relationship to be used is

$$\Delta P_b = \frac{1}{2} \left(\Delta I_a^0 + \Delta I_c^0 - \Delta I_b^0 \right) \tag{3}$$

which yields the H₃C--C--CH₃ angle (α) by assuming the C--C distance between the methyl and ethylenic carbon atoms, H₃C--C equal to 1.507 Å, C--H (out-of-plane H) = 1.095 Å, C--H (in-plane H) = 1.072 Å, \angle HCC (inplane H) = 112.9°, and \angle HCC (out-of-plane H) = 110.7° [6].

Finally, using the planar moments of inertia P_a , together with the above assumptions and results, and taking C=C = 1.341 Å, C—CN = 1.438 Å, and C=N = 1.160 Å the NC—C—CN angle (β) can be obtained.

TABLE 2

Molecular constants for the ground state of (CH₃)₂C=C(CN)₂^a and (CD₃)₂C=C(CN)₂^b

	(CH ₃) ₂ C=C(CN) ₂	$(CD_3)_2C=C(CN)_2$	
-4 (MHz)	2199.677 (5) ^c	2025.116 (6)	
B (MHz)	2182.323 (3)	1927.392 (4)	
C (MHz)	1109.9 (4)	1011.76 (2)	
`	0.9681	0.8071	
^d (MHz) ^d	(0.552 ± 0.057) × 10 ⁻⁴	(0.106 ± 0.053) × 10 [→]	
P _u (uA ²) ^e	228.59 (9)	256.078 (4)	
$P_{b}^{-}(uA^{2})^{\circ}$	226.76 (9)	243.425 (4)	
$P_{c}(\mathbf{u} \mathbf{A}^{2})^{e}$	2.99 (9)	6.131 (4)	

^aCalculated by least squares fit of 92 frequencies, standard deviation $\sigma = 0.129$ MHz. ^bBy least squares fit of 46 frequencies, $\sigma = 0.118$ MHz. ^cParenthesized values are the standard deviation on the last figure. ^d Watson's centrifugal distortion constant [16]. ^eP are the planar moments of inertia.

TABLE 3

	Δ _c	Reference	
(CH,),CC(CN),	-5.984	This work	
$(CD_1), CC(CN),$	-12.262	This work	
(CH,),CCO	-6.0405	8	
¹³ CH,CCO	-6.0327	8	
(CD,),CCO	-12.3388	8	
(CH,),CCH,	-6.1444	5	
¹ ³ CH,CH,CCH,	-6.1411	6	
CH, CHCHCN (cis)	-2.8875	17	
CH ₃ CHCHCN (trans)	-3.0693	18	

Inertial quantity $\Delta_c = I_c^s - I_a^s - F_b^s$, in units of uA^{2a}, for a number of molecules possessing a plane of symmetry with pairs of hydrogens being the only out-of-plane atoms

^aThe moments of inertia are calculated using the conversion factor 505379.1 uA² MHz.

The assumed and calculated structural parameters are presented in Table 4. The rotational constants for $(CH_3)_2C=C(CN)_2$ and $(CD_3)_2C=C(CN)_2$ are reproduced with a maximum deviation of 2.5 MHz.

A comparison of the calculated α and β angles in $(CH_3)_2C=C(CN)_2$ with respect to the corresponding ones in isobutene, shows that the differences are of the order of the uncertainties estimated taking into account the effects of vibrations.

Since a dipole moment determination was impossible, due to spectral difficulties, a calculated value, $\mu_{calc} = 4.8$ D, was obtained using the plausible structure of Table 5 and bond moments from ref. 14.

TABLE 4

		Assumed from reference
C—H (out-of-plane H)	1.095	6
C—H (in-plane H)	1.072	6
H,C-C	1.507	6
∠HCC (out-of-plane H)	110.7	6
∠HCC (in-plane H)	112.9	6
α	117.6	
C=C	1.341	4
C-CN	1.438	4
C≡N	1.160	4
β	115.1	
r _s (HH)	1.766 (26) ^a	

Proposed structural parameters for $(CH_3)_2C=C(CN)_2$; bond lengths are in A and bond angles in degrees

^aValue of the standard deviation on the two last figures.

DISCUSSION

The consideration of the inertial quantity Δ_c in $(CH_3)_2C=C(CN)_2$ and $(CD_3)_2C=C(CN)_2$ leads to the conclusion that the heavy atom skeleton is planar.

The molecule features many low energy vibrational states, as indicated by the intensity of the numerous vibrational satellites accompanying the groundstate lines. The corresponding vibrations are associated with the torsional motions of the two methyl tops and the bending motions of the terminal groups [1].

As already discussed, several concurrent effects broaden the lines and prevent further resolution. Consequently there is no experimental indication of the height of the methyl tops internal rotation barrier. However, test calculations with a tentative barrier of $V_3 = 2100$ cal mol⁻¹, upon consideration of related molecules [5-9], using the structural parameters of Table 4 and Woods' program [15], show splittings which are well below the FWHM of the measured lines. An evaluation of the barrier height should come, hopefully, from the frequencies of the torsional bands in the FIR, whose measurements are presently in progress [1].

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REFERENCES

- 1 B. Lunelli, to be published.
- 2 B. T. Tan, J. Demaison and H. D. Rudolph, J. Mol. Spectrosc., 71 (1978) 471.
- 3 B. T. Tan, J. Demaison and H. D. Rudolph, J. Mol. Spectrosc., 76 (1979) 104.
- 4 H. Rück, private communication, 1983.
- 5 V. W. Laurie, J. Chem. Phys., 34 (1961) 1516.
- 6 L. H. Scharpen and V. W. Laurie, J. Chem. Phys., 39 (1963) 1732.
- 7 J. Demaison and H. D. Rudolph, J. Mol. Spectrosc., 24 (1975) 325.
- S K. P. R. Nair, H. D. Rudolph and H. Dreizler, J. Mol. Spectrosc., 48 (1973) 571.
- 9 J. Demaison and H. D. Rudolph, J. Mol. Spectrosc., 40 (1971) 445.
- 10 B. Lunelli, Rev. Sci. Instrum., 51 (1980) 832.
- 11 D. M. W. Anderson, F. Bell and J. L. Duncan, J. Chem. Soc., (1961) 4705.
- 12 F. Scappini, P. G. Favero and R. Cervellati, Chem. Phys. Lett., 33 (1975) 499.
- 13 W. Gordy and R. L. Cook, Microwave Molecular Spectra, Cap. XIII, Interscience, New York, 1970.
- 14 V. I. Minkin, O. A. Ossipov and Yu A. Zhdanov, Dipole Moments in Organic Chemistry, Plenum Press, New York, 1970.
- 15 R. C. Woods, J. Mol. Spectrosc., 22 (1967) 49.
- 16 J. K. Watson, J. Chem. Phys., 46 (1967) 1935.
- 17 R. A. Beaudet, J. Chem. Phys., 38 (1963) 2548.
- 18 M. Suzuki and K. Kozima, J. Mol. Spectrosc., 33 (1970) 407.