December, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 3647—3648 (1985)* 3647

The Microwave Spectrum of (*Z*)-(Acrylaldehyde Oxime)

Mariko Terashima and Osamu Ohashi*

Department of Chemistry, Faculty of Science and Technology, Sophia University, Chiyoda-ku, Tokyo 102

(Received August 8, 1985)

Synopsis. The microwave spectrum of (*Z*)-(acrylaldehyde oxime) was observed in the frequency region from 10 to 40 GHz.

Several a-type R-branch transitions in the ground vibrational state were identified and the rotational constants in MHz were determined to be A=17430.7(35), B=3022.514(15), and C=2576.504(16). The conformation of (*Z*)-(acrylaldehyde oxime) has been plausibly deduced to be the s-trans Z-form from the rotational constants experimentally determined. The angle of C–C=N is discussed.

The gas chromatogram and proton magnetic resonance spectrum of acrylaldehyde oxime have suggested that this molecule has two geometrical isomers.[1] One of them is an E-form of which the microwave spectroscopic study has been reported.[2] The other one is a Z-form which has not been determined to be whether the s-trans Z-form or s-cis Z-form, or both (See Fig. 1). It is interesting to determine the molecular conformation of (*Z*)-(acrylaldehyde oxime) in gas phase. We have observed the microwave spectrum of (*Z*)-(acrylaldehyde oxime) and discussed its conformation and the angle of C–C=N.

Experimental

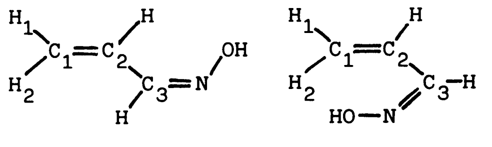
Acrylaldehyde oxime was prepared and purified by the method described elsewhere.[2] No attempt was made to separate the E- and Z-species; all measurements were made with the equilibrium mixture of the isomers at room temperature, using a flowing system in which the sample was put into a sample cell at the one end and pumped out from the other end during the measurement of the spectrum.

The spectrometer used has been described elsewhere.[2]

Results and Discussion

The first survey of the rotational spectrum was made in the frequency region of 26.5 to 40 GHz at the Stark field of 100 V/cm.

Bunches of relatively weak absorption lines that might be ascribed to the Z conformer were found with the frequency interval of about 5600 MHz, while groups of strong lines which had been assigned to the E-conformer were observed with the frequency interval of about 4600 MHz.



s-trans Z-form s-cis Z-form

Fig. 1. Two possible geometrical isomers and the numbering of carbon and hydrogen atoms of (*Z*)-(acrylaldehyde oxime).

In the first place, four transitions of J=5←4 and J=6←5 with K_{-1}=1 and six lines of J=5←4, 6←5, and 7←6 with K_{-1}=2 in the frequency region of 26.5 to 40 GHz were tentatively assigned and they led to the prelimenary rotational constants which were employed to predict the other transition lines. Then, forty a-type R-branch transition lines in the ground vibrational state were assigned in the frequency region of 10 to 40 GHz as listed in Table 1. The rotational and centrifugal distortion constants finally determined are shown in Table 2, together with the rotational

Table 1. Observed transition frequencies (MHz) of (*Z*)-(acrylaldehyde oxime)

Transition	Obsd	$\Delta\nu$[a]	Transition	Obsd	$\Delta\nu$[a]
$2_{12}-1_{11}$	10752.05	0.02	$5_{14}-4_{13}$	29063.63	0.02
$2_{02}-1_{01}$	11187.84	0.02	$6_{16}-5_{15}$	32177.93	−0.04
$2_{11}-1_{10}$	11644.15	0.12	$6_{06}-5_{05}$	33242.38	0.01
$3_{13}-2_{12}$	16121.73	0.02	$6_{25}-5_{24}$	33547.80	−0.06
$3_{03}-2_{02}$	16756.12	−0.11	$6_{52}-5_{51}$	33620.67	0.15
$3_{22}-2_{21}$	16797.18	0.08	$6_{51}-5_{50}$		0.15
$3_{21}-2_{20}$	16837.65	−0.20	$6_{43}-5_{42}$	33629.17	0.06
$3_{12}-2_{11}$	17459.57	0.01	$6_{42}-5_{41}$		0.00
$4_{14}-3_{13}$	21483.88	−0.09	$6_{34}-5_{33}$	33646.25	0.15
$4_{04}-3_{03}$	22294.24	−0.00	$6_{33}-5_{32}$	33654.08	−0.17
$4_{23}-3_{22}$	22388.23	0.11	$6_{24}-5_{23}$	33898.89	−0.01
$4_{32}-3_{31}$	22416.76	0.54	$6_{15}-5_{14}$	34845.88	0.06
$4_{31}-3_{30}$		−0.33	$7_{17}-6_{16}$	37506.39	0.07
$4_{22}-3_{21}$	22489.78	0.02	$7_{07}-6_{06}$	38637.93	0.07
$4_{13}-3_{12}$	23267.13	0.04	$7_{26}-6_{25}$	39113.17	−0.01
$5_{15}-4_{14}$	26836.62	−0.06	$7_{62}-6_{61}$	39223.26	−0.01
$5_{05}-4_{04}$	27792.39	−0.01	$7_{61}-6_{60}$		−0.01
$5_{24}-4_{23}$	27972.25	−0.02	$7_{53}-6_{52}$	39230.07	−0.05
$5_{42}-4_{41}$	28018.55	0.34	$7_{52}-6_{51}$		−0.05
$5_{41}-4_{40}$		0.33	$7_{44}-6_{43}$	39243.94	−0.01
$5_{33}-4_{32}$	28029.10	0.27	$7_{43}-6_{42}$		−0.22
$5_{32}-4_{31}$	28031.38	−0.41	$7_{35}-6_{34}$	39268.54	−0.02
$5_{23}-4_{22}$	28174.57	−0.02	$7_{34}-6_{33}$	39286.78	−0.06
			$7_{25}-6_{24}$	39667.21	−0.02

a) $\Delta\nu=\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$.

Table 2. Observed and calculated rotational constants of (*Z*)-(acrylaldehyde oxime)

	Obsd	Calcd[a]	
		s-trans	*s-cis*
A/MHz	17430.7(35)	16309	9111
B/MHz	3022.514(15)	3232.61	6040.54
C/MHz	2576.504(16)	2697.87	3632.41
Δ_J/kHz	0.74(13)		
Δ_{JK}/kHz	−5.21(35)		
κ	−0.939948	−0.92143	−0.12099
ΔI[b]/amu · Å^2	−0.0493788		

Numbers in parentheses represent 2.5 times the standard deviation. a) Calculated from the molecular parameters in Table 3. b) $\Delta I=I_c-I_a-I_b$.

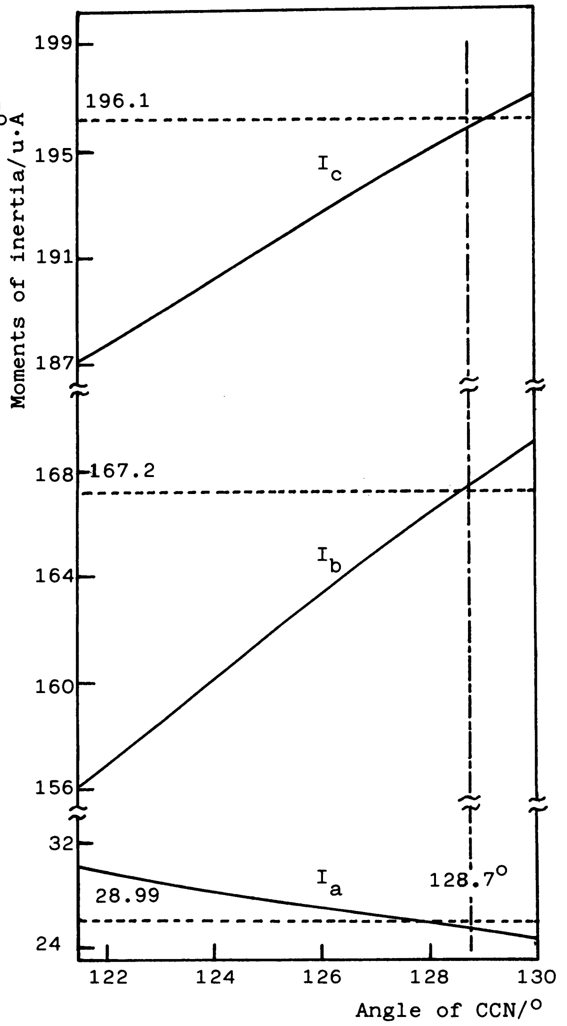


Fig. 2. The dependence of the moments of inertia, I_a, I_b, and I_c, on the angle of CCN. The solid lines indicate the calculated moments of inertia and the dotted lines show the observed ones.

constants calculated from the molecular models (See Fig. 1 and Table 3).

From the comparison of the experimental and calculated rotational constants shown in Table 2, it is conclued that the s-trans Z conformer is attributed to the spectrum analyzed in this work.

TABLE 3. STRUCTURAL PARAMETERS ASSUMED FOR (*Z*)-(ACRYLALDEHYDE OXIME)

Bond length	l/Å	Bond angle	θ/°
C=C	1.345$^{a)}$	H_1-C=C	121.45$^{a)}$
C=C	1.470$^{a)}$	H_2-C=C	119.97$^{a)}$
C_1-H	1.086$^{a)}$	C_1=C_2-H	122.83$^{a)}$
C_2-H	1.084$^{a)}$	C=C-C	119.83$^{a)}$
C=N	1.276$^{b)}$	C-C=N	121.77$^{b)}$
N-O	1.408$^{b)}$	H-C=N	115.55$^{b)}$
O-H	0.956$^{b)}$	C=N-O	110.20$^{b)}$
C_3-H	1.086$^{b)}$	N-O-H	102.68$^{b)}$

The numbering of carbon and hydrogen atoms is given in Fig. 1. a) Ref. 3, Cherniak and Costain, *J. Chem. Phys.*, **45**, 104 (1966). b) Ref. 4, Levine, *J. Chem. Phys.*, **38**, 2326 (1963).

No spectrum of any other conformer has been detected. This suggests that the population or dipole moment, or both of the other conformer is too small to be detected.

Figure 2 shows how the moments of inertia, I_a, I_b, and I_c, depend on the angle of C-C=N keeping the other structural parameters constant. According to Fig. 2, the angle of C-C=N may be plausibly determined to be 128.7°. This unexpectedly large angle is thought to be due to the steric effect between the vinyl and hydroxyl groups. However, the moments of inertia, I_a, I_b, and I_c, may largely depend on the other structural parameters, particularly the bond length of C_2-C_3 and C=N, and the angle of C=C-C and C=N-O.

The more data than we have now are needed in order to come to the final conclusion about this angle.

References

1) S. Masuda, H. Kihara, and T. Ota, *Nippon Kagaku Kaishi*, **1974**, 608.

2) M. Niwase, K. Kubota, K. Yoshida, T. Sakaizumi, M. Onda, O. Ohashi, and I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **57**, 2408 (1984).

3) E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966).

4) I. N. Levine, *J. Chem. Phys.*, **38**, 2326 (1963).