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Rotational Isomers and Molecular Structures of (*E*)-Propionaldehyde Oxime as Studied from Electron Diffraction and Microwave Spectroscopic Data

Kinya Iijima,* Mayumi Matsuoka, Takeshi Sakaizumi, and Osamu Ohashi†

Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422

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

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The molecular structures of two rotational isomers (anticlinal and synperiplanar forms) of gaseous (*E*)-propionaldehyde oxime have been determined from electron diffraction and microwave spectroscopic data. The anticlinal form is more stable by 0.15 ±0.10 kcal mol^{-1} than the synperiplanar form. The molecular parameters of the anticlinal form are $r_g(C_1\text{–}C_2) = 1.552(3)$ Å, $r_g(C_2\text{–}C_3) = 1.493(2)$ Å, $r_g(C_3{=}N) = 1.284(2)$ Å, $r_g(N\text{–}O) = 1.429(2)$ Å, $\angle C_1C_2C_3 = 111.5(1)^\circ$, $\angle C_2C_3N = 119.0(3)^\circ$, and $\angle C_3NO = 109.4(2)^\circ$. The $\angle C_2C_3N$, $\angle C_1C_2C_3$, and $r_g(C_3\text{–}N)$ values of the synperiplanar form (122.6(6)°, 112.6(6)°, and 1.291(3) Å, respectively) are not equal to those of the anticlinal form.

Propionaldehyde (propanal) has two rotational isomers in the gas phase. They were determined from the joint analysis of gas electron diffraction data and microwave and infrared spectroscopic data.$^{1)}$ Since propionaldehyde oxime prepared from propionaldehyde and hydroxylamine has two geometrical isomers (*Z*- and *E*-forms),$^{2)}$ several rotational isomers may exist in the gas phase. Separation of the geometrical isomers is essential in order to elucidate the detailed molecular structures of these isomers. The *Z*-form was isolated as a solid from the synthesized mixture by vacuum distillation, and the molecular structure was determined from microwave spectroscopy$^{3)}$ and a joint analysis of gas electron diffraction and microwave spectroscopic data.$^{4)}$ The result was that there exists one rotational isomer with an antiperiplanar form (ap-form) with respect to the C–C bond in the gas phase, though the rotation around the C–C bond is a large amplitude motion.$^{4)}$ The potential barrier height was unusually low ($V_1 = 1.5$ kcal mol^{-1});$^{4)}$ this follows trend similar to those of *Z*-isomers of other oxime compounds.$^{5—7)}$

The *E*-isomer of propionaldehyde oxime could not be isolated from the sample, but microwave spectroscopy confirmed two rotational conformers of the *E*-isomer in the gas phase: anticlinal form (ac-form) and synperiplanar form (sp-form).$^{8,9)}$ This report describes the molecular structures of these two conformers of the *E*-isomer as determined by a joint analysis using electron diffraction data and rotational constants.

Experimental

Propionaldehyde oxime was prepared by reacting propionaldehyde with hydroxylamine hydrochloride according to Dunstan and Dymond's method.$^{10)}$ The *Z*-isomer isolated by vacuum distillation was left for two or three days at room temperature. The interconversion of *Z*-isomer into *E*-isomer took place and the sample became a liquid of the *E*/*Z* mixture.$^{2)}$

Electron diffraction photographs were taken on Kodak electron-image plates using an r^3-sector at the camera distances of 293.81 and 143.88 mm. The sample holder was warmed at about 323 K, and the vapor was introduced to a diffraction chamber through a nozzle warmed at the same temperature as the sample holder. The exposure time was 113 s at the long camera distance and 240 s at the short camera distance with an electron beam current of 1.0 μA. The pressure in the diffraction chamber was 5.3×10^{-4} Pa during the experiment. The wavelength of the electron beam was estimated by measuring the accelerating voltage;$^{4)}$ fluctuation of the voltage was below 0.01% throughout the experiment. Four plates were selected from the long camera-distance photographs and three plates from the short camera-distance photographs. The optical densities of each selected plated were measured by microphotometry.$^{11)}$

Structure Analysis

Scattering intensities in the range $s = 3.125$—17.000 Å^{-1} were obtained at intervals of 0.125 Å^{-1} from the long camera-distance plates and those in the range $s = 8.50$—33.25 Å^{-1} at intervals of 0.25 Å^{-1} from the short camera-distance plates. The intensities were leveled by using theoretical backgrounds. The averaged intensities were reduced to molecular intensities by drawing smooth backgrounds. The elastic and inelastic scattering factors were taken from Refs. 12, 13, 14, and 15. The experimental molecular intensities are shown by dots in Fig. 1. Figure 2 shows the molecular model at the anticlinal position ($\phi = 60^\circ$) and the numbering of the atoms. The rotational angle around the C_2–C_3 bond, ϕ, was taken to be 0° at the antiperiplanar position in the present study.

Figure 3 shows the radial distribution function, where the damping factor was 0.002. The peak of 3.6 Å in the ex-

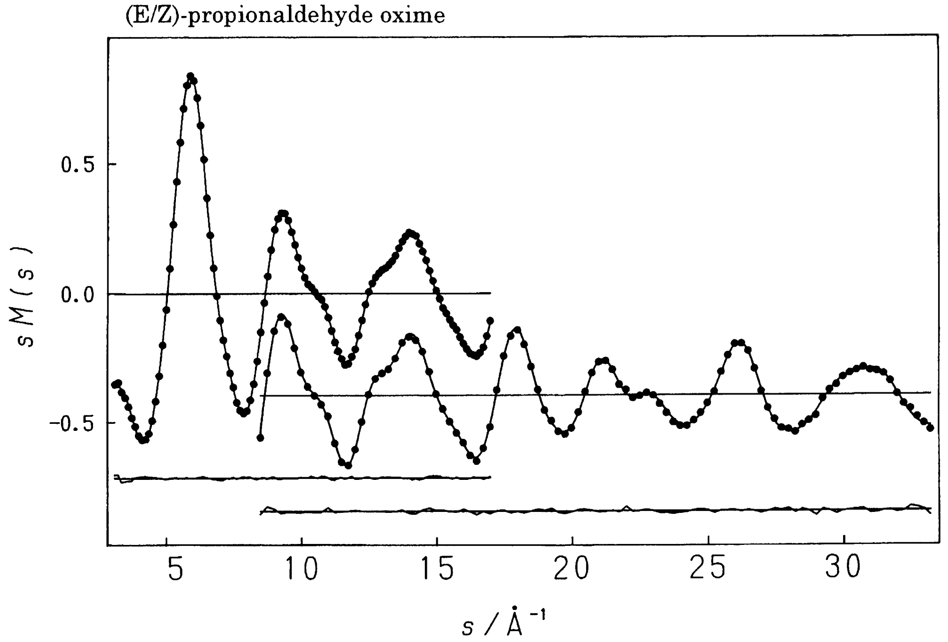

Fig. 1. Molecular intensities for gaseous propionaldehyde oxime. The upper curve corresponds to the long camera-distance data and the lower one to the short camera-distance data. The dots represent observed data, the solid curve the best-fit calculated ones, and the differences between them are given below.

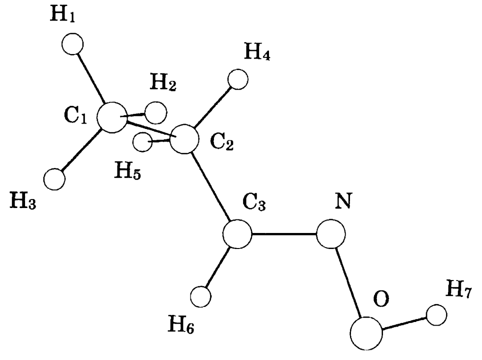

Fig. 2. Molecular model and numbering of the atoms for the ac-form of (*E*)-propionaldehyde oxime.

perimental radial distribution curve indicates that the main species is the *E*-isomer in the gas phase. However, the fact that there are small and broad peaks in the region of 3.9 to 4.7 Å indicates the existence of several rotational conformers with a large amplitude motion. Preliminary analysis showed that there existed the *E*-sp and *Z*-ap forms besides the *E*-ac form. Some trial radial distribution curves are shown in Fig. 3.

The root-mean-square amplitudes, l, and the shrinkage corrections, $r_a - r_\alpha^{\circ}$[16] for the *E*-isomer were calculated from the same force field as that used in the analysis of (*Z*)-propionaldehyde oxime.[4] The torsional motion around the C_2–C_3 bond was excluded because the system was treated as a large amplitude motion, which will be described later. The results are listed in Table 1; these were used in the subsequent analysis. The asymmetry parameters[16] were ignored. The geometrical parameters of the *Z*-isomer were also taken from Ref. 4 and were fixed in the present analysis, but the concentration of the *Z*-isomer in the sample gas was refined in the least-squares calculations.

The potential function around the C_2–C_3 bond of the *E*-isomer was assumed as follows:

$$V(\phi) = (1/2)V_1(1-\cos\phi) + (1/2)V_3(1+\cos 3\phi),$$

where ϕ is the rotational angle around the C_2–C_3 bond. The molecular intensities were calculated at 20° intervals of the rotational angle around the C_2–C_3 bond and were summed with the weighting of the Boltzmann distribution. The V_1 and V_3 values were varied alternatively until self-consistent values were obtained in the least-squares analysis. The root-mean-square amplitudes of the atomic pairs of $C_1 \cdots N$ and $C_1 \cdots O$ were strongly dependent on the rotational angle around the C_2–C_3 bond. The relation between the amplitudes and the rotational angle is shown in Fig. 4; this was used in the calculations of molecular intensities.

The refined molecular parameters are $r(C_1–C_2)$, $r(C_2–C_3)$, $r(C_3=N)$, $r(N–O)$, $r(O–H)$, average $r(C–H)$, difference between $r(C_3–H_6)$ and $r(C_1–H_1)$, $\angle C_1C_2C_3$, $\angle C_2C_3N$, $\angle C_3NO$, $\angle HCH$, and $\angle NOH$. Since the positions of hydrogen atoms could not be accurately determined due to the small scattering powers, the following assumptions were made: (1) The methyl group has C_{3v} symmetry, (2) the C–H bond distance in the $–CH_2–$ group are equal to the C–H bond distance in the methyl group, (3) the H_4 and H_5 atoms are symmetrically place on the plane bisecting the angle $C_1C_2C_3$, and (4) the H_6 atom is on the line bisecting the angle C_2C_3N.

The analysis with the assumption that the angle C_2C_3N was independent of the rotational angle could not yield a good agreement between the experimental and calculated molecular intensities. When the angle C_2C_3N was taken to be

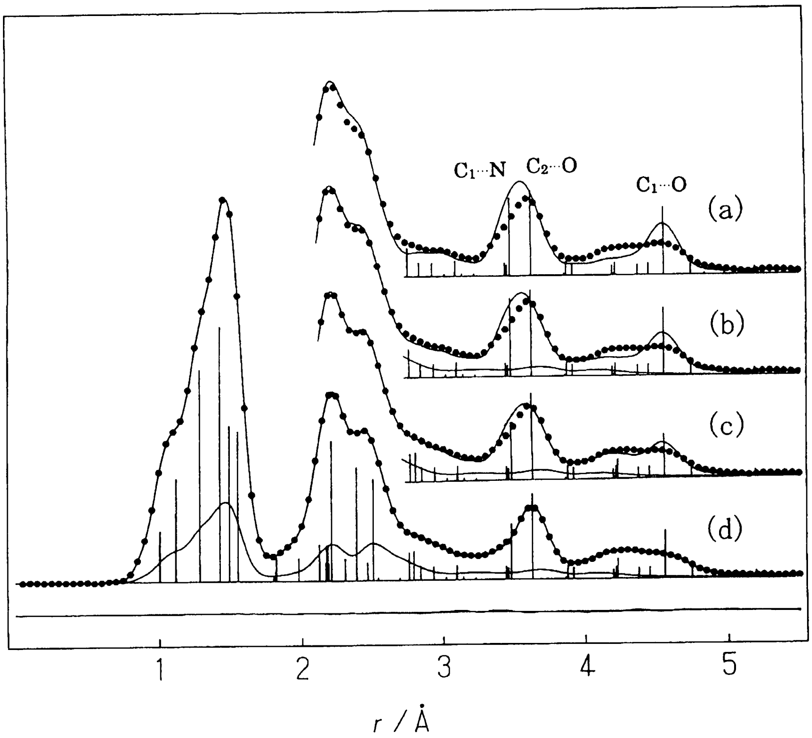

Fig. 3. Radial distribution curves for gaseous propionaldehyde oxime. The dots represent the experimental data and the solid curves the theoretical ones. The theoretical curves correspond to the models of (a) ac-form of *E*-isomer (*R*-factor = 0.16, see text), (b) ac-form of *E*-isomer plus *Z*-isomer (*R*-factor = 0.11), (c) ac- and sp-forms of *E*-isomer plus *Z*-isomer (*R*-factor = 0.075), and (d) *E*-isomer with large amplitude motion plus *Z*-isomer (*R*-factor=0.023). The contribution from the *Z*-isomer is shown as the solid curve at the under part of each theoretical one. The vertical bars represent bond distances and the scattering powers at the *E*-ac and *E*-sp positions.

Table 1. Calculated Root-Mean-Square Amplitudes and Shrinkage Corrections for (*E*)-Propionaldehyde Oxime ($\times 10^4$ Å)

	l	$r_a - r_\alpha^\circ$		l	$r_a - r_\alpha^\circ$
C_3–N	391	6	O–H_7	807	212
$C_3 \cdots O$	636	−6	$O \cdots C_2$	686	−9
$C_3 \cdots H_7$	1010	54	$O \cdots H_4$	1213	−6
C_3–C_2	508	11	$O \cdots C_1$	636	−6
$C_3 \cdots H_4$	1065	26	$O \cdots H_1$	1131	16
$C_3 \cdots C_1$	775	−15	$O \cdots H_2$	2149	−67
$C_3 \cdots H_1$	1057	40	$O \cdots H_6$	1425	−7
$C_3 \cdots H_2$	1724	−37	C_2–H_4	789	94
C_3–H_6	778	149	C_2–C_1	508	11
N–O	483	1	$C_2 \cdots H_1$	1057	70
$N \cdots H_7$	1050	88	$C_2 \cdots H_6$	1001	57
$N \cdots C_2$	655	−8	$H_4 \cdots H_5$	1310	74
$N \cdots H_4$	1230	7	$H_4 \cdots C_1$	1069	10
$N \cdots C_1$	695	−10	C_1–H_1	796	174
$N \cdots H_1$	1229	18	$C_1 \cdots H_6$	1057	40
$N \cdots H_2$	1717	−30	$H_1 \cdots H_2$	1281	218
$N \cdots H_6$	937	50			

Numbering is shown in Fig. 2. Atomic pairs with small scattering power are omitted. The values are calculated at the *E*-ac position, but the $l(C_1 \cdots N)$ and $l(C_1 \cdots O)$ were treated as variables depending on the rotation around the C_2–C_3 bond in the analysis (see Fig. 4).

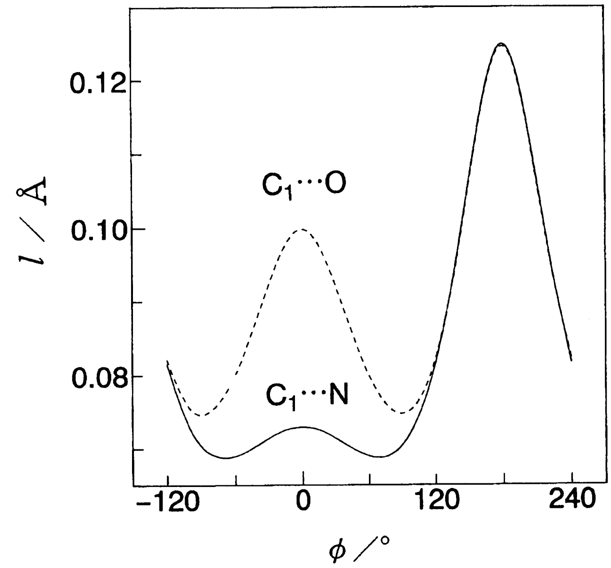

Fig. 4. Correlation curves of root-mean-square amplitudes of the atomic pair $C_1 \cdots O$ and $C_1 \cdots N$ versus rotational angle around the C_2–C_3 bond.

a good agreement was attained,

$$\angle C_2C_3N = c_1 + c_2(1 - \cos \phi)/2,$$

where ϕ is a rotational angle around the C_2–C_3 bond and c_1 and c_2 are variables in the least-squares calculations. The

Table 2. Results of Least-Squares Analysis for (*E*)-Propionaldehyde Oxime[a)]

	$r_\alpha^\circ(1)$[b)]	ε[c)]	$r_\alpha^\circ(2)$[d)]	ε[c)]
$r(C_1–C_2)$/Å	1.547	0.003	1.550	0.003
$r(C_2–C_3)$/Å	1.492	0.002	1.490	0.002
$a_1(C_3{=}N)$/Å [e)]	1.282	0.002	1.280	0.002
$a_2(C_3{=}N)$/Å [e)]	0.0	fixed	0.010	0.004
$r(N–O)$/Å	1.425	0.002	1.428	0.002
$<r(C–H)>$/Å [f)]	1.086	0.005	1.085	0.005
$\Delta r(C–H)$Å [g)]	−0.098	0.038	−0.113	0.030
$r(O–H)$/Å	0.991	0.027	0.986	0.023
$b_1(C_1C_2C_3)$/° [h)]	112.0	0.3	111.2	0.3
$b_2(C_1C_2C_3)$/° [h)]	0.0	fixed	1.4	0.9
$c_1(C_2C_3N)$/° [i)]	116.9	0.6	117.8	0.5
$c_2(C_2C_3N)$/° [i)]	7.4	1.2	4.8	1.0
$\angle C_3NO$/°	109.7	0.2	109.4	0.2
$\angle HCH$/°	108.4	1.2	108.9	0.2
$\angle NOH$/°	95.6	3.0	95.7	2.0
k[j)]	0.21	0.02	0.21	0.02

a) The potential values of V_1 and V_3 for the rotation around the $C_2–C_3$ bond were assumed to the best ones of 0.2 and 1.0 kcal mol^{-1}, respectively (see text). b) Result from the analysis of electron diffraction data. c) Limits of error. d) Results from the joint analysis of electron diffraction data and rotational constants. e) $r(C{=}N)=a_1+a_2(1-\cos\phi)/2$. f) Mean value of C–H bonds. g) $r(C_3–H_6)-r(C_1–H_1)$. h) $\angle C_1C_2C_3=b_1+b_2(1+\cos 2\phi)/2$. i) $\angle C_2C_3N=c_1+c_2(1-\cos\phi)/2$. j) Concentration of the *Z*-form in the sample gas. The ϕ in e), h), and i) means the rotational angle around the $C_2–C_3$ bond, which is 0° at the antiperiplanar position.

calculated rotational constants for the ac- and sp-forms of the *E*-isomer obtained in this analysis are listed in Table 3 as $B_{\alpha\mathrm{calcd}}^\circ(1)$. The agreement between the experimental and the calculated rotational constants were not very good, though qualitative agreement was achieved. This result shows that the molecular parameters of the ac- and sp-forms are different with each other, as are the rotational angle around the $C_2–C_3$ bond and the C_2C_3N angle, and these differences could not be elucidated from electron diffraction data alone. Thus the joint analysis using electron diffraction data and rotational constants were carried out.

Table 3. Observed and Calculated Rotational Constants for (*E*)-Propionaldehyde Oxime (in MHz)

	B_{obsd}[a)]	B_{corr}[b)]	B_z[c)]	$B_{\alpha\mathrm{calcd}}^\circ(1)$[d)]	$B_{\alpha\mathrm{calcd}}^\circ(2)$[e)]	w[f)]
ac-form						
A	19400(400)	−73	19327	19472(88)	19332(40)	1×10^2
B	2278.16(3)	−1.3	2276.9	2269(6)	2277(1)	1×10^5
C	2204.09(3)	−1.1	2203.0	2199(6)	2203(1)	1×10^5
sp-form						
A	14996(8)	−76	14920	15117(92)	14923(14)	1×10^3
B	2706.74(3)	−4.0	2702.7	2687(12)	2704(1)	5×10^4
C	2360.24(4)	−0.7	2359.5	2350(8)	2359(1)	2×10^5

Estimated error are in parentheses. a) Observed rotational constants.[8,9)] b) Vibrational corrections.[16)] c) Rotational constants corrected for the vibrational effects. d) Rotational constants calculated from the results obtained in the analysis of the electron diffraction data. e) Rotational constants calculated in the joint analysis. f) Weights of the rotational constants used in the least-squares calculation of the joint analysis.

The observed rotational constants for the ac- and sp-forms of the *E*-isomer[8,9)] were corrected for the vibrational effects[16)] by the force field, as listed in Table 3. The relative weightings of the rotational constants to the electron diffraction data were adjusted so as to fit the calculated rotational constants with the observed ones within the estimated errors. Since the experimental errors for the rotational constants *A*'s of the ac- and sp-forms were large,[8,9)] the relative weights of them were reduced in the least-squares calculations. The final weights were listed in Table 3.

An analysis removing the assumptions about the hydrogen positions did not improve the agreement. The best agreement was obtained when the $r(C{=}N)$ and $\angle C_1C_2C_3$ values were varied as a function of the rotational angle as follows:

$$r(C{=}N)=a_1+a_2(1-\cos\phi)/2$$
$$\angle C_1C_2C_3=b_1+b_2(1+\cos 2\phi)/2,$$

and when a_1, a_2, b_1, and b_2 were refined in the least-squares calculations. An analysis assuming the function for $\angle C_1C_2C_3$ as b_1+b_2 $(1-\cos\phi)/2$ increased the *R*-factor by 10%.

The computations were performed on an AV3100 and a HP9000/720RX in the Information Processing Center of Shizuoka University.

Results and Discussion

The best-fit molecular intensities are shown in Fig. 1 as the solid curve. The final parameters obtained from least-squares calculations are listed in Table 2, and the calculated rotational constants in the joint analysis are listed in Table 3 as $B_{\alpha\mathrm{calcd}}^\circ(2)$. The limits of error of the molecular parameters were estimated from the systematic errors and the random errors in the least-squares calculation.[4)]

The concentration of the *Z*-isomer in the sample gas (21±2%) was small under the present experimental condition, though the concentration is about fifty in the liquid phase.[2)] This shows the small vapor pressure of the *Z*-form.

The relations between the *R*-factor $([\Sigma w(sM_{\mathrm{obsd}}-sM_{\mathrm{calcd}})^2/\Sigma w(sM_{\mathrm{obsd}})^2]^{1/2})$ and the coefficients of the potential function (V_1 and V_3) are shown in Fig. 5. The best V_1 and V_3 values were 0.2±0.1 and 1.0±0.2 kcal mol^{-1}, respectively, where the limits of error were estimated by Hamilton's method.[17)] The potential function around the $C_2–C_3$ bond is drawn in Fig. 6. The ac-form is more stable by 0.15 kcal mol^{-1} than the sp-form. The potential barrier height separating the ac- and sp-forms is 1.1 kcal mol^{-1}, and the one separating the two ac-forms is 0.95 kcal mol^{-1}. Taking into account the statistical weights, the ratios of *E*-ac, *E*-sp, and *Z*-ap forms were determined to be 0.56, 0.23, and 0.21, respectively, in the vapor at 323 K. Thus the main conformer in the gas phase is the ac-form of (*E*)-propionaldehyde oxime.

Since there were several species in the sample gas, the

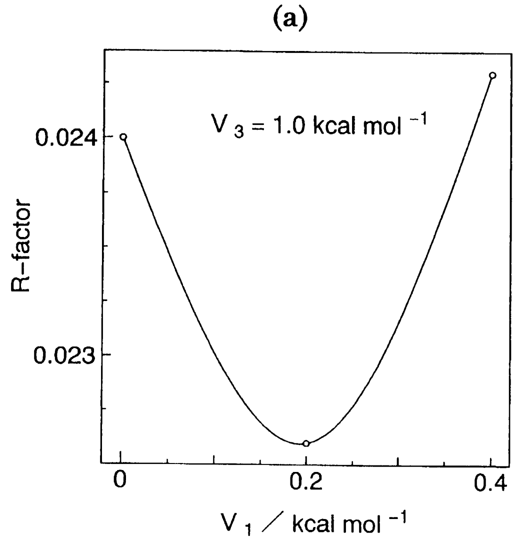

Fig. 5. Correlation curves of R-factor versus (a) V_1 and (b) V_3 values of the potential function (see text).

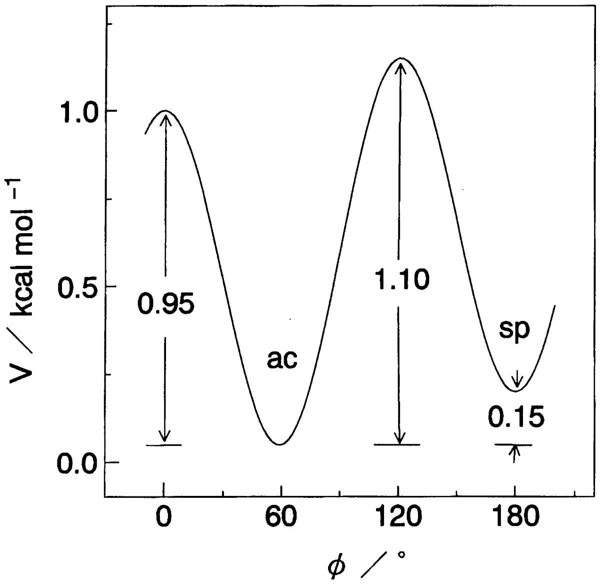

Fig. 6. Potential curve around the C_2–C_3 bond. The position of ϕ=60° represents the ac-form of (E)-propionaldehyde oxime and ϕ=180° the sp-form.

detailed molecular parameters of each species could not be elucidated from gas-phase electron diffraction data alone. It was very helpful to use the rotational constants obtained from the microwave spectroscopic studies for the molecular structure determination. The main molecular parameters of the rotational conformers of the E-isomer deduced in the present joint analysis are compared with those of the Z-isomer[4)] in Table 4. The C_1–C_2, C_2–C_3, N–O distances and the C_3NO angle are almost the same in the E-ac, E-sp, and Z-ap conformers.

However, there are significant differences with respect to the r(C=N), $\angle C_1C_2C_3$, and $\angle C_2C_3N$ values of the E-ac, E-sp, and Z-ap conformers. The differences in the C_2C_3N angles could be explained by the repulsion between the NOH and CH_3CH_2 groups. Since the distance between both groups is the shortest in the Z-ap form and the second shortest in the E-sp form, the C_2C_3N angle is the largest in the Z-ap form and the second largest in the E-sp form. The same interpretation could be applied to the difference in the C=N bond distances.

Table 4. Main Molecular Parameters of Propionaldehyde Oxime

	E-isomer		Z-isomer
	ac-form	sp-form	ap-form
$r_g(C_1$–$C_2)$/Å	1.552(3)		1.549(3)
$r_g(C_2$–$C_3)$/Å	1.493(2)		1.497(2)
$r_g(C_3$=N)/Å	1.284(2)	1.291(3)	1.295(1)
r_g(N–O)/Å	1.429(2)		1.430(2)
$\angle C_1C_2C_3$/°	111.5(1)	112.6(6)	109.4(4)
$\angle C_2C_3N$/°	119.0(3)	122.6(6)	127.5(3)
$\angle C_3NO$/°	109.4(2)		109.3(3)
Ref.	Present study		4

The distance parameter r_g is calculated by the relation of $r_g=r_a+(l^2/r_a)$, where $r_a=r_\alpha{}^\circ+\Delta r$ and Δr is the shrinkage correction listed in Table 1. The angle parameter represents $r_\alpha{}^\circ$ parameter.

On the contrary, the $C_1C_2C_3$ angle is the largest in the E-sp form and the smallest in the Z-ap form. This could be attributed to the repulsion between the NOH and CH_3 groups, because the distance between the NOH and CH_3 groups is the shortest in the E-sp form and the longest in the Z-ap form. It will be interesting to do ab-intio calculation for explaining the energetic and geometrical characteristics of this compound.

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