J. Phys. Chem. A **2001,** *105,* 2085−2090

Molecular Structure of 2-Butanimine, an Unstable Imine, as Studied by Gas Electron Diffraction Combined with MP2 and DFT Calculations

Toru Egawa and Shigehiro Konaka*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received: November 14, 2000; In Final Form: January 3, 2001

The molecular structure of 2-butanimine ($C(4)H_3-C(3)H_2-C(2)(-C(5)H_3)=N(1)H$) was determined by means of gas electron diffraction. The sample of 2-butanimine, an unstable imine, was prepared by vacuum gas−solid reaction of *N*,*N*-dichloro-2-butanamine ($(C_2H_5)(CH_3)CH-NCl_2$) and KOH in a glass column. The column temperature and sample pressure were optimized by measuring FTIR spectra of the reaction products in a separate experiment. The results of MP2 and DFT calculations were used as supporting information. The coexistence of the (*E*)-*sp* and (*E*)-*ac* conformers was assumed. The structural parameters (r_g and $\angle_\alpha$) obtained for the (*E*)-*sp* conformer are as follows: $r(C{=}N) = 1.285(3)$ Å; $\langle r(C-C)\rangle = 1.514(2)$ Å; $\langle r(C-H)\rangle = 1.113(3)$ Å; $r(N-H) = 1.046$ Å (dependent); $\angle N{=}C-C(3) = 115.8(5)°$; $\angle N{=}C-C(5) = 125.0(5)°$; $\angle C-C-C(4) = 115.2(12)°$; $\angle C-C(4)-H = 113.5(14)°$; $\angle C{=}N-H = 109.3$ (assumed). Angle brackets denote averaged values, and parenthesized values are the estimated limits of error (3σ) referring to the last significant digit. The dihedral angle, ϕNCCC, of the (*E*)-*ac* conformer was assumed to be 117.6°. The abundance of the (*E*)-*sp* conformer was determined to be 60 ± 10% at room temperature.

Introduction

After a long and successful history of structural determination by gas electron diffraction (GED), its application to unstable species has not yet been a routine project. There have been some (not many) GED studies reported in this field, which are reviewed briefly in ref 1. Recently, we have carried out structural determination by GED of some unstable species having a C=N double bond.[2,3] In these studies, unstable species including imines, *N*-methylmethyleneimine ($CH_2{=}N-CH_3$), and *trans*-*N*-methylethylidenimine ($CH_3-CH{=}N-CH_3$) were formed as products of thermal decomposition or thermal rearrangement of amines heated to about 500 °C. The reaction products were monitored by using a mass spectrometer equipped in the GED apparatus. Although the molecular structures of the unstable species were determined successfully, the limitation of our method became clear at the same time. First, the unstable species formed by a thermal reaction are inevitably exposed to the high temperature environment in the nozzle tip and hence some unexpected byproducts can be formed quite easily. This situation prevents us from using other thermal reactions to form unstable species that have been found by spectroscopic studies. Second, mass spectroscopy is not always a useful technique for the identification of the reaction products, especially when they have some isomers.

Very recently, we have reported the FTIR spectroscopic studies of vacuum gas−solid reaction (VGSR) products of *N*,*N*-dichloroalkylamines with solid KOH in a glass column.[4] This reaction system is similar to the VGSR of *N*-chloroalkylamines with solid base that had been reported by Denis et al.[5−7] to synthesize unstable imines with a C=N bond. In both reaction systems, unstable imines were formed at the column temperature of 100 °C or below. This reaction system of dichloroamine and KOH is more suitable for the GED study than thermal reactions because the former requires much lower temperature and, hence, reduces possible side reactions. However, application of the GED method to this reaction system is not straightforward because the sample pressure applied in ref 4 was only 250−500 mTorr, that is much lower than those adopted in the typical GED experiment. Therefore, it is necessary to confirm if the unstable imines are formed with high purity at the gas-flow condition (pressure and conductivity) suitable for the GED experiment. In addition, the column temperature has to be optimized at that condition. As mentioned in ref 4, it was confirmed that the FTIR spectroscopy combined with the theoretical vibrational spectra of DFT calculation is quite a convenient technique for the identification of unstable reaction products. Therefore, FTIR has been used for that purpose also in this study. Because it is very difficult, if not impossible, to measure the FTIR spectra of the reaction products coming out of the nozzle tip placed in the GED apparatus, we have made a setup for the measurement of FTIR spectra with almost the same gas-flow condition as the GED experiment.

As the first target of this line, 2-butanimine ($(C_2H_5)(CH_3)C{=}NH$) was chosen that was found to be formed by a reaction with *N*,*N*-dichloro-2-butanamine ($(C_2H_5)(CH_3)CH-NCl_2$) and KOH.[4] The results of the theoretical calculations of MP2 and DFT methods are used to assist the GED data analysis.

Experimental Section

Materials. The sample of *N*,*N*-dichloro-2-butanamine was prepared by *N*,*N*-dichorination of *sec*-butylamine (Nacalai Tesque Inc.) by condensing it on an excess amount of *N*-chlorosuccinimide powder.[8] The reaction vessel was kept overnight at room temperature. The progress of the dichlorination was checked by measuring an infrared spectrum.

Infrared Spectra. Prior to the electron diffraction experiment, the condition of the reaction was optimized by monitoring the infrared spectrum of the reaction products by using the setup

---

* Corresponding author. Fax: +81−11−706−4924. E-mail: konaka@sci.hokudai.ac.jp.

10.1021/jp004184f CCC: $20.00

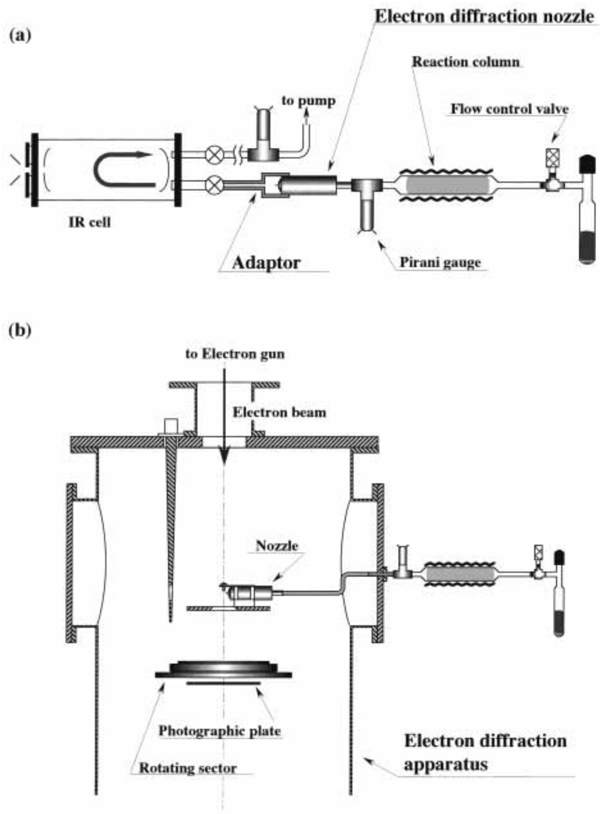


Figure 1. Experimental setup (a) the setup for the measurement of FTIR spectra of 2-butanimine and (b) the setup for the GED experiment of 2-butanimie.

shown in Figure 1a. This setup is basically the same as described previously.[4] The only difference is that the electron diffraction nozzle was inserted between the column and the infrared cell in order to reproduce the same gas-flow condition as that of electron diffraction experiment. The size of the nozzle tip used was 0.55 mm in inner diameter and 6 mm in length. The vapor of *N*,*N*-dichloro-2-butanamine was passed through a Pyrex-glass column (20 mm (i.d.) × 200 mm) containing KOH powder. The pushing pressure was monitored by a pirani gauge attached to the end of the column and was controlled by using a needle valve placed between the sample holder of the dichloroamine and the column. Prior to the experiment, the column was evacuated for hours while heated to 90 °C in order to remove the adsorbed water from the KOH surface. FTIR spectra were measured by using a BOMEM DA3.16 spectrometer with a spectral range of 450−4000 cm^{-1} and a resolution of 0.5 cm^{-1}. A long path cell with a 10 m path length and with KBr windows was used. The cell was continuously evacuated by a vacuum pump.

Figure 2 shows the results of the optimization. Trace (a) is the spectrum of the parent molecule, *N*,*N*-dichloro-2-butanamine. At the column temperature of 80 °C (trace (b)), some vibrational bands of 2-butanimine[4] appeared; however, the vibrational band at about 700 cm^{-1} indicates that the parent molecule still remains in this condition. On the other hand, the parent molecule disappears completely when the column temperature was set at 90 °C (trace (c)). The sample pressure measured between the column and the nozzle for this trace was 3 Torr. When the column temperature was raised to 100 °C, some vibrational bands of the unidentified byproducts appeared, indicating that the column temperature was too high (trace (d)). As a result, it was concluded that the combination of the column temperature of 90 °C and the sample pressure of 3 Torr was the best for this reaction system.

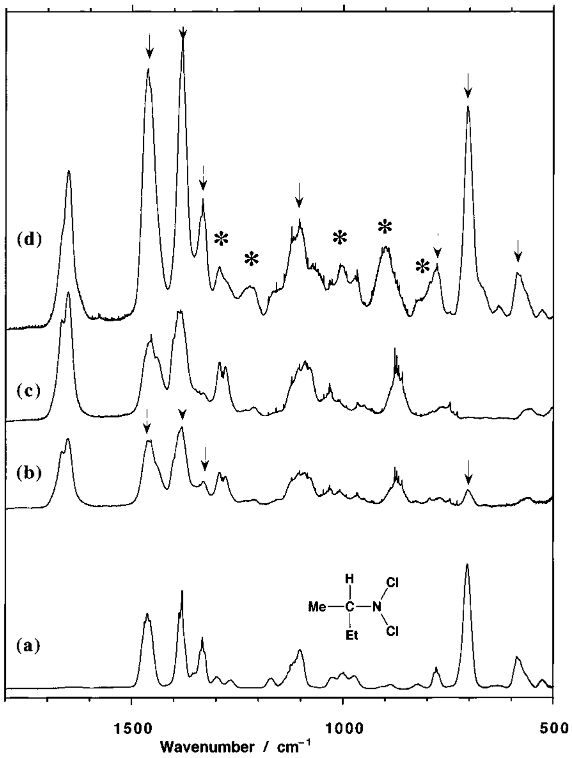


Figure 2. Infrared spectra of the reaction product of *N*,*N*-dichloro-2-butanamine and KOH: (a) *N*,*N*-dichloro-2-butanamine; (b) reaction product at the column temperature of 80 °C; (c) reaction product at the column temperature of 90 °C; (d) reaction product at the column temperature of 100 °C. The sample pressure was about 3 Torr. The arrows indicate the parent molecule and the asterisks indicate the byproducts.

Gas Electron Diffraction. An electron diffraction experiment was carried out by using the setup shown in Figure 1b. The reaction system and the nozzle tip are the same as those used in the measurement of the infrared spectrum. The column temperature was kept at 90 °C during the experiment.

Electron diffraction patterns of 2-butanimine were recorded on 8 × 8 in. Kodak projector slide plates with an apparatus equipped with an r^3-sector[9] at the nozzle temperature of 294 K (21 °C). Because the sample pressure had to be kept below 3 Torr to prevent the parent molecule from surviving, an exposure time of 153−180 s was necessary with the beam current of 1.55 μA, which is longer than our usual condition. The accelerating voltage was about 37 kV. The diffraction patterns of CS_2 were recorded in the same sequence of exposures as 2-butanimine. The photographic plates were developed for 4.5 min in Dektol developer diluted 1:1. The photometry process was described in details elsewhere.[10] The experimental intensities and backgrounds are available as Supporting Information (Table S1). The electron wavelength was calibrated to the r_a (C═S) distance of CS_2 (1.5570 Å).[11] Other experimental conditions are as follows: camera distance, 244.2 mm; electron wavelength, 0.06329 Å; uncertainty of the scale factor, 0.03%; background pressure during exposure, 4×10^{-6} Torr; number of plates used, 4; range of s values, 4.5−33.8 $\mathrm{Å}^{-1}$. This s range is, in our experience, considered to be sufficient for the molecules of this size.

Elastic atomic scattering factors were calculated as described in ref 12, and inelastic scattering factors were taken from ref 13. The experimental molecular scattering intensities are shown

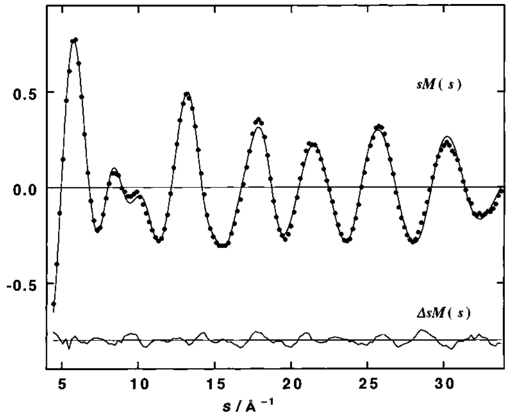
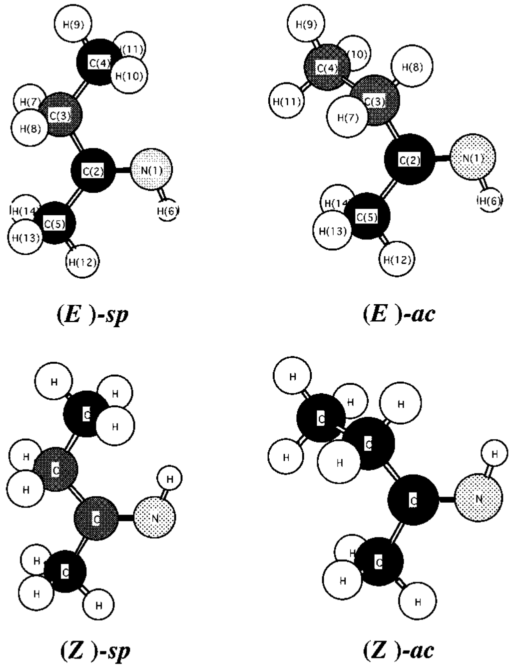


Figure 3. Experimental (dots) and theoretical (solid curves) molecular scattering intensities of 2-butanimine; $\Delta sM(s) = sM(s)^{obs} - sM(s)^{calc}$. The theoretical curves were calculated from the best-fit parameters.



(*E*)-*sp* (*E*)-*ac*

(*Z*)-*sp* (*Z*)-*ac*

Figure 4. Molecular models and atom numbering for the four conformers of 2-butanimine.

in Figure 3 along with the calculated intensities in the final data analysis. A diagonal weight matrix was used in the analysis.[14] Two Gaussian functions have been used to express the weight function.

Ab Initio and DFT Calculations. 2-Butanimine is expected to have four stable forms, (*E*)-*sp*, (*E*)-*ac*, (*Z*)-*sp*, (*Z*)-*ac* (see Figure 4), where (*E*) and (*Z*) designate the configuration of the N−H bond (trans and cis to the ethyl group, respectively) and *sp* and *ac* designate the conformation of the ethyl group. Structure optimizations of all of these forms were carried out with the program Gaussian 94.[15] The level of theory applied is MP2 (frozen core)[16] with the 6-31G** basis set. The obtained structural parameters and conformational energies are listed in Table 1. These results predict that the (*E*)-*sp* form is the most stable. The $N_1{=}C_2{-}C_3$ angles of the (*E*) conformers are about 7° smaller than the $N_1{=}C_2{-}C_5$ angles of these conformers. On the other hand, this relationship is reversed for the (*Z*) conformers. This feature is ascribed to the steric repulsion between the H_6 atom and methylene or methyl hydrogens.

B3LYP/6-31G** DFT calculations[17,18] had also been carried out to obtain the vibrational frequencies and force constants of

TABLE 1: Geometrical Parameters and Relative Energies for the Possible Four Conformers of 2-Butanimine Obtained from the MP2(frozen core)/6-31G ab Initio Calculations**

parameters[a]	(*E*)-*sp*	(*E*)-*ac*	(*Z*)-*sp*	(*Z*)-*ac*
bond lengths (in Å)				
$N_1{=}C_2$	1.2856	1.2869	1.2856	1.2870
$N_1{-}H_6$	1.0234	1.0242	1.0227	1.0242
$C_2{-}C_3$	1.5094	1.5074	1.5159	1.5124
$C_2{-}C_5$	1.5093	1.5096	1.5046	1.5050
$C_3{-}C_4$	1.5205	1.5298	1.5214	1.5301
$C_3{-}H_7$	1.0948	1.0939	1.0940	1.0938
$C_3{-}H_8$	1.0948	1.0889	1.0940	1.0922
$C_4{-}H_9$	1.0894	1.0889	1.0884	1.0889
$C_4{-}H_{10}$	1.0872	1.0896	1.0896	1.0895
$C_4{-}H_{11}$	1.0872	1.0892	1.0896	1.0884
$C_5{-}H_{12}$	1.0892	1.0889	1.0861	1.0862
$C_5{-}H_{13}$	1.0906	1.0906	1.0911	1.0910
$C_5{-}H_{14}$	1.0906	1.0904	1.0911	1.0903
bond angles (in degree)				
$C_2{=}N_1{-}H_6$	109.3198	109.3324	109.8943	109.1279
$N_1{=}C_2{-}C_3$	118.9577	117.8935	126.4783	125.1823
$N_1{=}C_2{-}C_5$	125.5079	125.3235	118.1067	117.9678
$C_3{-}C_2{-}C_5$	115.5345	116.7767	115.4150	116.8495
$C_2{-}C_3{-}C_4$	114.3792	112.9665	115.4198	113.0989
$C_2{-}C_3{-}H_7$	107.9295	108.9486	107.7298	108.6495
$C_2{-}C_3{-}H_8$	107.9295	107.2440	107.7298	108.8296
$C_2{-}C_5{-}H_{12}$	111.2971	111.0249	109.6724	109.2995
$C_2{-}C_5{-}H_{13}$	110.3908	110.6356	110.5538	110.7637
$C_2{-}C_5{-}H_{14}$	110.3908	110.6611	110.5538	110.9007
$C_4{-}C_3{-}H_7$	110.4779	109.3614	110.0445	109.2540
$C_4{-}C_3{-}H_8$	110.4779	110.3520	110.0445	109.8009
$C_3{-}C_4{-}H_9$	110.3963	110.5295	110.4818	110.5701
$C_3{-}C_4{-}H_{10}$	110.6590	110.4736	111.2199	110.6428
$C_3{-}C_4{-}H_{11}$	110.6590	111.7753	111.2199	111.4277
$H_7{-}C_3{-}H_8$	105.1969	107.8194	105.3617	107.0209
$H_9{-}C_4{-}H_{10}$	108.8434	108.0261	107.7631	108.1158
$H_9{-}C_4{-}H_{11}$	108.8434	107.6711	107.7631	107.8022
$H_{10}{-}C_4{-}H_{11}$	107.3582	108.2334	108.2517	108.1597
$H_{12}{-}C_5{-}H_{13}$	108.7028	108.7857	109.4185	109.6272
$H_{12}{-}C_5{-}H_{14}$	108.7028	108.3356	109.4185	108.8594
$H_{13}{-}C_5{-}H_{14}$	107.2435	107.2834	107.1803	107.3487
dihedral angles (in degree)				
$H_6{-}N_1{=}C_2{-}C_3$	180.0000	−179.7767	0.0000	−0.0614
$H_6{-}N_1{=}C_2{-}C_5$	0.0000	−0.7272	180.0000	179.6872
$N_1{=}C_2{-}C_3{-}C_4$	0.0000	117.6120	0.0000	119.4511
$N_1{=}C_2{-}C_3{-}H_7$	123.3897	−120.6394	123.3917	−119.0615
$N_1{=}C_2{-}C_3{-}H_8$	−123.3897	−4.1940	−123.3917	−2.8619
$N_1{=}C_2{-}C_5{-}H_{12}$	0.0000	10.2130	0.0000	7.8722
$N_1{=}C_2{-}C_5{-}H_{13}$	120.8020	131.1033	120.7389	128.7621
$N_1{=}C_2{-}C_5{-}H_{14}$	−120.8020	−110.1266	−120.7389	−112.1505
$C_5{-}C_2{-}C_3{-}C_4$	180.0000	−61.5193	180.0000	−60.3000
$C_5{-}C_2{-}C_3{-}H_7$	−56.6103	60.2293	−56.6083	61.1874
$C_5{-}C_2{-}C_3{-}H_8$	56.6103	176.6747	56.6083	177.3870
$C_3{-}C_2{-}C_5{-}H_{12}$	180.0000	−170.7280	180.0000	−172.3581
$C_3{-}C_2{-}C_5{-}H_{13}$	−59.1980	−49.8377	−59.2611	−51.4682
$C_3{-}C_2{-}C_5{-}H_{14}$	59.1980	68.9324	59.2611	67.6192
$C_2{-}C_3{-}C_4{-}H_9$	180.0000	−175.9470	180.0000	−176.2826
$C_2{-}C_3{-}C_4{-}H_{10}$	−59.4384	−56.4402	−60.3707	−56.5285
$C_2{-}C_3{-}C_4{-}H_{11}$	59.4384	64.1433	60.3707	63.8445
$H_7{-}C_3{-}C_4{-}H_9$	57.9931	62.5372	57.8383	62.5712
$H_7{-}C_3{-}C_4{-}H_{10}$	178.5547	−177.9560	177.4677	−177.6748
$H_7{-}C_3{-}C_4{-}H_{11}$	−62.5685	−57.3725	−61.7910	−57.3018
$H_8{-}C_3{-}C_4{-}H_9$	−57.9931	−55.9074	−57.8383	−54.5136
$H_8{-}C_3{-}C_4{-}H_{10}$	62.5685	63.5995	61.7910	65.2405
$H_8{-}C_3{-}C_4{-}H_{11}$	−178.5547	−175.8170	−177.4677	−174.3866
ΔE/kcal mol^{-1} [b]	0.0	0.944	0.251	0.965
ΔG (at 294 K)/ kcal mol^{-1} [c]	0.0	1.003	0.606	1.086
abundance (at 294 K)/% [d]	49.4	17.7	17.5	15.4
B3LYP/6-31G** calculations				
ΔE/kcal mol^{-1} [e]	0.0	1.038	0.088	1.045
ΔG (at 294 K)/ kcal mol^{-1} [c]	0.0	0.979	0.406	1.026
abundance (at 294 K)/% [d]	45.0	16.9	22.5	15.6

[a] See Figure 4 for the atom numberings. [b] Absolute value of the energy is −211.905498 E_h for the (*E*)-*sp* conformer. [c] Estimated from the energy difference, ΔE, theoretical vibrational wavenumbers, and theoretical rotational constants. [d] Estimated from the theoretical ΔG values. [e] Absolute values of the energy is −212.603139 E_h for the (*E*)-*sp* conformer.

TABLE 2: Observed and Calculated Vibrational Wavenumbers (in cm^{-1}) and Assignment of 2-Butanimine

mode[a]	obsd.[b]	intensity [c]	calc. [d]	assignments
ν_1	3263	w	3248.4	N−H stretch
ν_2	2971	vs	2967.8	CH$_3$ anti−symmetric stretch
ν_3			2965.7	CH$_3$ anti−symmetric stretch
ν_4	2894	s	2899.9	CH$_3$ symmetric stretch
ν_5			2879.5	CH$_3$ symmetric stretch
ν_6	2747	vw	2857.4	CH$_2$ symmetric stretch
ν_7	1652	vs	1696.5	C═N stretch
ν_8			1498.3	CH$_3$ anti−symmetric deform
ν_9	1455	s	1481.2	CH$_3$ anti−symmetric deform
ν_{10}			1462.6	CH$_2$ scissors
ν_{11}			1412.5	CH$_3$ symmetric deform
ν_{12}	1385	vs	1408.4	CH$_3$ symmetric deform
ν_{13}			1393.4	CH$_3$ symmetric deform
ν_{14}	1286	m	1309.6	CH$_2$ wag + CNH bend
ν_{15}			1100.2	CH$_3$ rock
ν_{16}	1091	m	1089.4	C−C stretch + CH$_3$ rock + CNH bend
ν_{17}	1008	vw	994.5	C−C stretch + CH$_3$ rock
ν_{18}	967	w	945.0	CH$_3$ rock + C−C stretch
ν_{19}			770.4	C−C stretch
ν_{20}	557	w	558.0	skeletal rock
ν_{21}			405.8	C−C−C bend
ν_{22}			260.9	C−C−C bend
ν_{23}	2981	vs	2979.6	CH$_3$ anti−symmetric stretch
ν_{24}	2938	vs	2936.0	CH$_3$ anti−symmetric stretch
ν_{25}			2880.4	CH$_2$ anti−symmetric stretch
ν_{26}			1488.9	CH$_3$ anti−symmetric deform
ν_{27}			1474.1	CH$_3$ anti−symmetric deform
ν_{28}			1282.3	CH$_2$ twist
ν_{29}			1120.5	CH$_3$ rock + CH2 rock
ν_{30}	1032	m	1054.4	CH$_3$ rock + C═N torsion
ν_{31}	878	s	873.8	C═N torsion
ν_{32}	746	w	744.9	CH$_2$ rock
ν_{33}			460.2	C═N out of plane bend
ν_{34}			217.8	C−C torsion
ν_{35}			139.3	C−C torsion
ν_{36}			61.7	C−C torsion

[a] Vibrational modes were numbered assuming C_s point group, where ν_1 to ν_{22} belong to the A' species and ν_{23} to ν_{36} to the A'' species. [b] Reference 4. [c] Abbreviations used: s; strong, m; medium, w; weak, v; very. [d] Calculated from the scaled force constants.

these four forms as reported in ref 4. These calculations also predicted that the (*E*)-*sp* form is the most stable. Only the energy differences and the predicted abundances for the conformers are given in Table 1 for the B3LYP calculations.

Analyses

Normal Vibration Analysis. According to the results of the structure optimization, it was assumed that the most abundant conformer is the (*E*)-*sp*. The Cartesian force constants of this conformer obtained from the B3LYP/6-31G** calculation[4] were transformed by using the formula given in ref 19 into the symmetrized internal force constants, F_{ij}, which were then modified by the scaling method so as to reproduce the vibrational wavenumbers that have been reported in our previous work.[4] The linear scaling formula[20] F_{ij} (scaled) = $(c_i\ c_j)^{1/2}$ F_{ij} (unscaled) was adopted where c_i is the scale factor. It was chosen to be 0.90 for NH, CH$_2$ and CH$_3$ stretching modes, 0.95 for skeletal stretching modes, and 0.98 for other vibrational modes after some trials of normal coordinate calculations. Resultant vibrational wavenumbers are listed in Table 2. For most of the vibrational modes, the agreement between the observed and calculated wavenumbers is better than 2% as shown in the Table. The definitions of symmetry coordinates and the corresponding scaled force constants are listed in Tables S2 and S3 of Supporting Information, respectively.

TABLE 3: Mean Amplitudes, l, r_a Distances, Shrinkage Corrections, $r_\alpha - r_a$, and Anharmonicity Parameters, κ, for the (*E*)-*sp* Conformer of 2-Butanimine (in Å)

atom pair [a]	l_{calc} [b]	l_{obs} [c]	r_a	group	$r_\alpha - r_a$	κ[d]
$N_1{=}C_2$	0.040	0.044(2)	1.284	2	−0.0036	8
$N_1\cdots C_3$	0.060	0.053(10)	2.363	3	−0.0021	0
$N_1\cdots C_4$	0.113	0.106	2.749	3	−0.0476	386
$N_1\cdots C_5$	0.060	0.053	2.476	3	−0.0100	0
N_1-H_6	0.074	0.067(3)	1.041	1	−0.0152	102
C_2-C_3	0.051	0.056	1.508	2	−0.0054	23
$C_2\cdots C_4$	0.069	0.061	2.533	3	−0.0074	0
C_2-C_5	0.051	0.056	1.508	2	−0.0111	23
C_3-C_4	0.051	0.056	1.520	2	−0.0305	23
$C_3\cdots C_5$	0.070	0.062	2.603	3	−0.0158	0
C_3-H_7	0.080	0.072	1.112	1	−0.0520	133
$C_4\cdots C_5$	0.083	0.083 (fix)	3.872		0.0348	−237
C_4-H_9	0.079	0.071	1.105	1	−0.0402	128
C_4-H_{10}	0.078	0.071	1.105	1	−0.0764	125
C_5-H_{12}	0.079	0.071	1.107	1	−0.0673	127
C_5-H_{13}	0.079	0.072	1.107	1	−0.0928	129

[a] See Figure 4 for the atom numberings. Nonbonded atom pairs containing H atoms are not listed for the simplicity although they are included in the analysis. [b] Calculated at 294.3 K. [c] Numbers in parentheses are estimated error limits (3σ) referring to the last significant digit. [d] In 10^{-7} Å^3.

TABLE 4: Molecular Structures of the (*E*)-*sp* Conformer of 2-Butanimine Determined by Gas Electron Diffraction (in Å and Degree)

parameters[a]	ED (r_g and $\angle_\alpha$)[b]		MP2/6-31G** (r_e)	B3LYP/6-31G** (r_e)
bond lengths (in Å)				
$N_1{=}C_2$	1.285	(3)	1.286	1.277
C_2-C_3	1.510	(2)	1.509	1.517
C_3-C_4	1.521		1.521	1.527
C_2-C_5	1.510		1.509	1.516
N_1-H_6	1.046	(3)	1.023	1.026
⟨C−H⟩	1.113		1.090	1.096
bond angles (in degree)				
$N_1{=}C_2-C_3$	115.8	(5)	119.0	119.3
$N_1{=}C_2-C_5$	125.0	(5)	125.5	125.3
$C_2-C_3-C_4$	115.2	(12)	114.4	115.0
C_3-C_4-H	113.5	(14)	110.6	110.8
$C_2{=}N_1-H$	109.3	(assumed)	109.3	110.3
dihedral angle (in degree)				
$N_1{=}C_2-C_3-C_4$[c]	117.6	(assumed)	117.6	111.7
abundance (in %)				
C (*E-sp*)	60	(10)	66.9[d]	67.5[d]

[a] See Figure 4 for the atom numberings. Angle brackets denote averaged values. [b] Numbers in parentheses are estimated error limits (3σ) referring to the last significant digit. [c] (*E*)-*ac* conformer. [d] Sum of the abundances of the (*E*)-*sp* and (*Z*)-*sp* conformers.

Analysis of Electron Diffraction Data. As mentioned in the previous section, the (*E*) and (*Z*) conformers differ not only in the direction of the N−H bond but also in the N═C−C angles. However, our trial analysis of the GED data to distinguish the (*E*) and (*Z*) conformers failed, even when this conformational difference in the N═C−C angles was included into the structural constraints. It is because the scattering power of the H atom is small. Therefore, only the (*E*)-*sp* and (*E*)-*ac* conformers were assumed to coexist in the analysis, and the abundance of the former was varied as an independent parameter. This assumption is equivalent to combining the (*E*)-*sp* and (*Z*)-*sp* conformers and combining the (*E*)-*ac* and (*Z*)-*ac* conformers. Similar geometrical parameters were bound together and were refined as groups in order to reduce the correlation among the adjustable parameters. The differences among the bound parameters were fixed at the MP2/6-31G** values. The methyl groups were assumed to have C_{3v} symmetry with the same C−C−H angles, and the bond angles for the C$_3$ methylene group were fixed at

TABLE 5: C=N Distances 2-Butanimine and Related Molecules (r_g in Å)

species	formulas	r_g(C=N)	stability	refs
N-methylmethyleneimine	$CH_2{=}N{-}CH_3$	1.281(6)	unstable	2
trans-*N*-methylethylideneimine	$CH_3{-}CH{=}N{-}CH_3$	1.278(4)	unstable	3
(*E*)-*sp*−2-butanimine	$C_2H_5{-}C({-}CH_3){=}NH$	1.285(3)	unstable	this work
MBBA	$CH_3{-}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_4H_9$	1.290(12)	stable	10
(*E*)-*sp*-propionaldehyde oxime	$C_2H_5{-}CH{=}N{-}OH$	1.291(3)	stable	27

the MP2/6-31G** values. The planarity around C_2 atom was assumed for the (*E*)-*ac* conformer. In addition, the dihedral angle, ϕNCCC of the (*E*)-*ac* conformer was fixed at the MP2/6-31G** value (117.6 °) because this parameter could not be determined with a good precision. The independent parameters and the constraints are summarized in Table S4 of Supporting Information.

Mean amplitudes, *l*, and shrinkage corrections,[21] $r_a - r_\alpha$, were calculated from the above-mentioned scaled force constants. Those of the (*E*)-*ac* conformer were obtained from the results of the B3LYP/6-31G** calculation and were scaled with the same scale factor c_i as that of the (*E*)-*sp* conformer. The small-amplitude vibration model was adopted with the exception of the $N_1{\cdots}C_4$ and $C_4{\cdots}C_5$ nonbonded pairs of the (*E*)-*sp* conformer for which the $r_a - r_\alpha$ corrections and the mean amplitudes were estimated by using the method described in refs 22 and 23. The mean amplitudes were adjusted in groups. The groups were separated according to the distances of the atomic pairs at $r_a =$ 1.2, 1.65, 3.0 Å. The differences among mean amplitudes in each group were fixed at the calculated values. The first group (r_a = 0.0−1.2 Å) corresponds to the C−H and N−H bonds, the second group (r_a = 1.2−1.65 Å) to the C−C and C=N bonds, and the third group (r_a = 1.65−3.0 Å) to the nonbonded C⋯C, C⋯N, and C⋯H, etc. The mean amplitudes of nonbonded pairs with longer r_a distances were fixed at their calculated values. The mean amplitudes with the corresponding r_a distances and the grouping are listed in Table 3. The anharmonicity parameters,[24] κ, for bonded atom pairs were estimated in a diatomic approximation,[25] $\kappa = (a/6)l$,[4] where the Morse parameter, *a*, was assumed to be 2.0 Å^{-1}. Those for nonbonded atom pairs were assumed to be zero with the exception of the $N_1{\cdots}C_4$ and $C_4{\cdots}C_5$ nonbonded pairs of the (*E*)-*sp* conformer, for which the κ parameters were estimated according to the method described in ref 23. They are also listed in Table 3.

Results and Discussion

Table 4 lists the obtained structural parameters for the (*E*)-*sp* conformer. A radial distribution curve is shown in Figure 5. The possibility of the survival of the parent molecule, *N*,*N*-dichloro-2-butanamine, can be ruled out because there seems to be no significant residual at about 1.76 Å of the radial distribution curve corresponding to the N−Cl bonds.[8] If the methyl or ethyl group as well as the H atom migrate from the α-carbon of the parent molecule to the N atom, *N*-propylidene-methanamine ($(C_2H_5)CH{=}NCH_3$) or *N*-ethylidene-ethanamine ($(CH_3)CH{=}NC_2H_5$) would be formed as a side product of VGSR. The former two species have nonbonded C⋯C pairs that have longer distances than the $C_4{\cdots}C_5$ pair of 2-butanimine. Therefore, if either of these species exists in the products, there will be residual at the region longer than 4 Å of the radial distribution curve. Figure 5 shows that such a possibility is negligible, and this result is consistent with the FTIR investigation. The correlation matrix in the least-squares fitting is given in Table S5 of the Supporting Information. None of the off-diagonal elements exceeded ±0.70. The *R*-factor[26] of the analysis was 0.090, which is not so good as our usual value for the stable molecules (typically 0.05 or better). This is presumably because of the very small amount of unidentified byproducts, the existence of which is inevitable in the GED study of unstable species. The index of resolution, *k*, of the molecular scattering intensities was determined to be 0.93 ± 0.03.

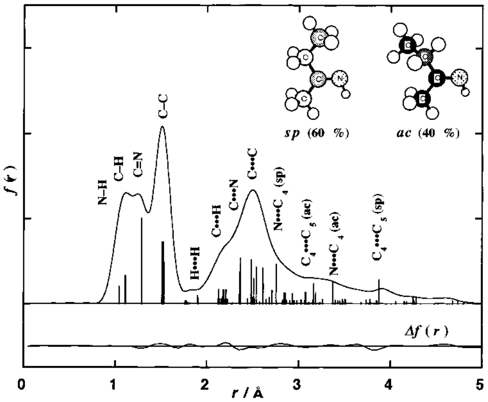


Figure 5. Experimental radial distribution curves of (*E*)-*sp* (60%) and (*E*)-*ac* (40%) mixture of 2-butanimine; $\Delta f(r) = f(r)^{obs} - f(r)^{calc}$. Distance distributions are shown by vertical bars.

In Table 4, structural parameters obtained from the MP2/6-31G** and B3LYP/6-31G** calculations are also listed for the comparison with the observation. As for the bond angles, these two sets of calculated parameters essentially agree with each other, and they are also in moderate agreement with the observed values. On the other hand, there are significant differences between the bond distances of these calculations, and apparently the set of MP2/6-31G** values shows better agreement with the observation. Therefore, it can be said that the MP2 method is superior to the B3LYP method in the reproduction of the geometrical structure in the present case.

The abundance of the (*E*)-*sp* conformer was determined to be 60 ± 10% at room temperature. As mentioned in the Analysis section, this value corresponds to the sum of (*E*)-*sp* and (*Z*)-*sp* conformers against the (*E*)-*ac* plus (*Z*)-*ac*. According to the energy difference and the entropy difference among the conformers obtained from the theoretical calculations, the relative abundance of (*E*)-*sp* + (*Z*)-*sp* conformers was estimated and listed in Table 4. The agreements of both the MP2 and B3LYP calculations with the experimental values are satisfactory.

In Table 5, the C=N double bond distance is compared with those of some related molecules (stable[10,27] and unstable[2,3]). According to the previous studies, r_g(C=N) of unstable species is about 1.28 Å, that is about 0.01 Å shorter than that of stable species as shown in this table. However, the present result, r_g(C=N) = 1.285 Å, falls into the middle of those of stable and unstable species. So, no clear-cut statement about the relationship between the stability and C=N distance of molecules with C=N double bond can be made without further investigation of other unstable species.

Acknowledgment. We thank the Computing Center of the Institute for Molecular Science, Okazaki National Research

Institutes, for the use of the NEC SX-4 computer and the Library program GAUSSIAN 94. Numerical computations were performed using the HITACHI MP5800/160 at the Hokkaido University Computing Center.

Supporting Information Available: Tables of the leveled total intensities and the backgrounds, definitions of the symmetry coordinates, the scaled harmonic force constants, structural constraints and the correlation matrices. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tremmel, J.; Hargittai, I. *Stereochemical Applications of Gas-phase Electron Diffraction, Part A*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Chapter 6.

(2) Fujiwara, H.; Egawa, T.; Konaka, S. *J. Mol. Struct.* **1995**, *344*, 217.

(3) Fujiwara, H.; Egawa, T.; Konaka, S. *J. Am. Chem. Soc.* **1997**, *119*, 1346.

(4) Egawa, T.; Ito, M.; Konaka, S. *J. Mol. Struct.* **2001**, *56*, 337.

(5) Braillon, B.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Nouv. J. Chim.* **1982**, *6*, 121.

(6) Guillemin, J. C.; Denis, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 690.

(7) Guillemin, J. C.; Denis, J. M. *Tetrahedron* **1988**, *44*, 4431.

(8) Egawa, T.; Ohtsubo, M.; Nakagawa, H.; Kuze, N.; Fujiwara, H.; Konaka, S. *J. Phys. Chem. A* **2000**, *104*, 1311.

(9) Konaka, S.; Kimura, M. In *13th Austin Symposium on Gas Phase Molecular Structure, 12−14 March*; The University of Texas, Austin, TX, 1990; S21.

(10) Kuze, N.; Fujiwara, H.; Takeuchi, H.; Egawa, T.; Konaka, S.; Fogarasi, G. *J. Phys. Chem. A* **1999**, *103*, 3054.

(11) Tsuboyama, A.; Murayama, A.; Konaka, S.; Kimura, M. *J. Mol. Struct.* **1984**, *118*, 351.

(12) Kimura, M.; Konaka, S.; Ogasawara, M. *J. Chem. Phys.* **1967**, *46*, 2599.

(13) Tavard, C.; Nicolas, D.; Rouault, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1967**, *64*, 540.

(14) Konaka, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1693.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; J. P. Stewart; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94; Revision E.2 ed.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(16) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(19) Williams, I. H. *J. Mol. Struct. (THEOCHEM)* **1983**, *94*, 275.

(20) Boggs, J. E. *Stereochemical Applications of Gas-phase Electron Diffraction, Part B*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Chapter 10.

(21) Kuchitsu, K.; Cyvin, S. J. *Molecular Structures and Vibrations*; Cyvin, S. J., Ed.; Elsevier: Amsterdam, 1972; Chapter 12.

(22) Egawa, T.; Maekawa, S.; Fujiwara, H.; Takeuchi, H.; Konaka, S. *J. Mol. Struct.* **1995**, *352/353*, 193.

(23) Egawa, T.; Fukuyama, T.; Yamamoto, S.; Takabayashi, F.; Kambara, H.; Ueda, T.; Kuchitsu, K. *J. Chem. Phys.* **1987**, *86*, 6018.

(24) Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 505.

(25) Kuchitsu, K.; Bartell, L. S. *J. Chem. Phys.* **1961**, *35*, 1945.

(26) R-factor is defined as $R = \{\Sigma_i W_i(\Delta sM(s)_i)^2/\Sigma_i W_i(sM(s)_i^{\mathrm{obs}})^2\}^{1/2}$, where $\Delta sM(s)_i = \Delta sM(s)_i^{\mathrm{obs}} - \Delta sM(s)_i^{\mathrm{calc}}$ and W_i is a diagonal element of the weight matrix.

(27) Iijima, K.; Matsuoka, M.; Sakaizumi, T.; Ohashi, O. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2481.