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Gas-phase molecular structure of nicotinamide studied by electron diffraction combined with MP2 calculations

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Abstract

The molecular structure of nicotinamide has been determined at 467 K by gas electron diffraction combined with MP2/6-31G** calculations. In the analysis of diffraction data, the potential function for torsion of the pyridine ring was assumed to be $V(\phi) = V_1(1 - \cos \phi)/2 + V_2(1 - \cos 2\phi)/2 + V_4(1 - \cos 4\phi)/2$, where ϕ denotes the torsional angle around the C_{ring}–C(=O) bond. The following potential parameters (V/kJ mol^{−1}) and structural parameters of (*E*)-nicotinamide ($r_g/\text{\AA}$ and $\angle_d/^\circ$) have been obtained: $V_1 = 5_{-7}^{+10}$, $V_2 = 11.5$ (assumed), $V_4 = -9(4)$, $\langle r(\text{C}_{\text{ring}} - \text{C}_{\text{ring}}) \rangle = 1.403(4)$, $\langle r(\text{N}_{\text{ring}} - \text{C}_{\text{ring}}) \rangle = 1.328(6)$, $r(\text{C}_{\text{ring}} - \text{C}(=\text{O})) = 1.498(8)$, $r(\text{C}=\text{O}) = 1.216(5)$, $r(\text{O}=\text{C}-\text{N}) = 1.362(12)$, $\angle \text{C}_{\text{ring}}\text{N}_{\text{ring}}\text{C}_{\text{ring}} = 117.5(2)$, $\langle \angle \text{C}_{\text{ring}}\text{C}_{\text{ring}}\text{C}_{\text{ring}} \rangle = 118.0$ (dependent parameter), $\langle \angle \text{N}_{\text{ring}}\text{C}_{\text{ring}}\text{C}_{\text{ring}} \rangle = 124.3$ (dependent parameter), $\angle \text{C}_{\text{ring}}\text{CO} = 121.9(6)$, $\angle \text{C}_{\text{ring}}\text{C}(=\text{O})\text{N} = 115.0$ (dependent parameter), $\angle \text{C}_{\text{cis}}\text{CC}(=\text{O}) = 120.5(17)$, where C_{cis} denotes the ring carbon atom at the *cis* position against the nitrogen atom of the NH₂ group. Parenthesized numbers denote the estimated limits of error and the angle bracket denotes average values. These structural parameters are close to the corresponding parameters of pyridine and acetamide except for $r(\text{N}_{\text{ring}} - \text{C}_{\text{ring}})$ and $\angle \text{C}_{\text{ring}}\text{N}_{\text{ring}}\text{C}_{\text{ring}}$. The N_{ring}–C_{ring} and C=O bonds are shorter than the corresponding parameters in the crystal by 0.01 Å and the (O=C)–N bond is longer than that in the crystal by 0.03 Å. These differences are ascribed to the effect of intermolecular hydrogen bonding on the structure in the crystal.

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Keywords: Nicotinamide; Molecular structure; Gas electron diffraction; Ab initio calculations; Hydrogen bonding

1. Introduction

Nicotinamide is known as a component of the vitamin B complex as well as a component of a coenzyme, nicotinamide adenine dinucleotide (NAD). Therefore, the structure of nicotinamide has been the subject of many experimental studies [1–8]. The crystal structure determined by X-ray and neutron diffraction [1,2] shows that nicotinamide

takes a non-planar (*E*)-form, in which the dihedral angle C2C1C7N9 is 23° [1] (see Fig. 1). In the crystal of NAD [9,10], the conformation of a nicotinamide moiety is similar to that of (*E*)-nicotinamide. On the other hand, Vogelsanger et al. [3] detected the (*E*)- and (*Z*)-conformers of nicotinamide in the gas phase by microwave spectroscopy and showed that the (*E*)-conformer is more stable than the (*Z*)-conformer. In their study, the dihedral angles C2C1C7N9 of the (*E*)- and (*Z*)-conformers were estimated to be 14(2) and 158(2)°, respectively [3].

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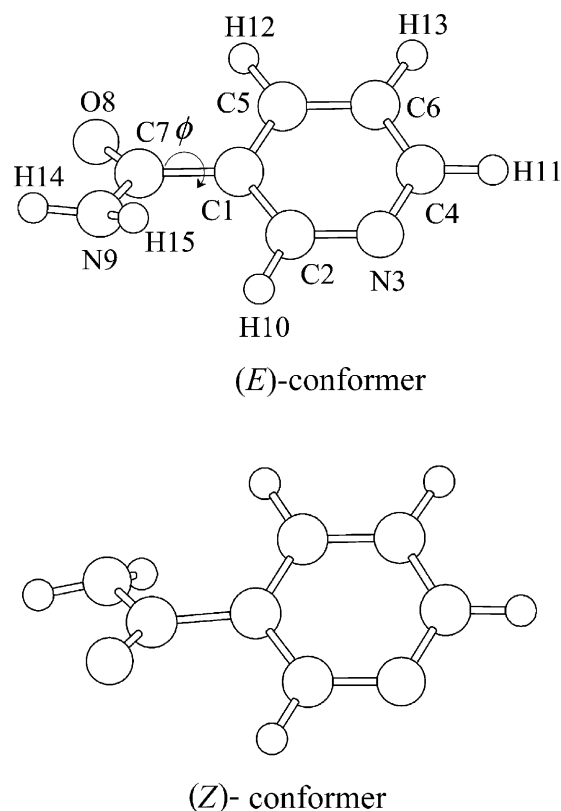


Fig. 1. Structural model of nicotinamide with atom numbering.

Recently, the molecular structure of benzamide [11], a related compound of nicotinamide, has been determined in our laboratory by gas electron diffraction (GED). The results obtained for benzamide show that the C–N bond length in the crystal is considerably shorter than that in the gas phase and the C=O bond length in the crystal is considerably longer than that in the gas phase. This has been ascribed to intermolecular hydrogen bonding. As shown in Fig. 2, the network of hydrogen bonds in the crystal of nicotinamide is different from that of benzamide. However, the bond lengths and angles of nicotinamide are not available in the gas phase and thus the effect of hydrogen bonding on the structure of nicotinamide is not elucidated. In the present study, the molecular structure of nicotinamide is determined by GED augmented by *ab initio* calculations and the result is used to discuss the effect of the hydrogen bonding on the structure of nicotinamide.

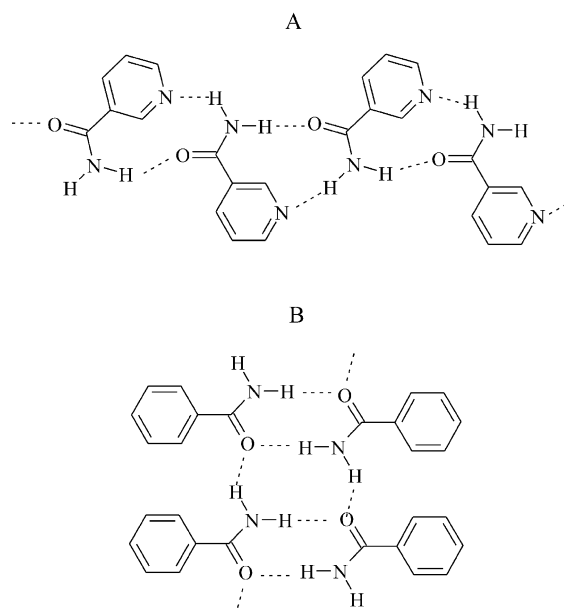


Fig. 2. Schematic drawing of hydrogen bonds in the crystal: (A) nicotinamide; (B) benzamide.

2. Experimental

A commercial sample of nicotinamide (Tokyo Chemical Co., Ltd) with a purity of 99% was used. An apparatus [12] equipped with an r^3 -sector was used to record the diffraction patterns on 8×8 in. Kodak projector slide plates. A high-temperature nozzle [13] was used to vaporize the sample and the temperature of the nozzle tip was kept at 467 K. Photographic plates were developed in Kodak Dektol developer diluted 1:1 for 4.5 min. The camera distance was 244.4 mm, the energy of incident electrons was about 37 keV and the scale factor was determined from the diffraction patterns of carbon disulfide ($r_a(\text{C}-\text{S}) = 1.5570 \text{ \AA}$) [14]. Other experimental conditions are as follows: beam current, 1.5 μA ; exposure time, 75 s; background pressure, 3×10^{-6} Torr; uncertainty in the scale factor (3σ), 0.04%.

Optical densities were measured with a microphotometer of a double-beam autobalanced type. The average densities obtained at intervals of 0.5 mm along the diameter of the halo were converted to total intensities [15], which were then divided by theoretical backgrounds to obtain leveled total

Table 1

Molecular structures, energies and relative abundances of the (*E*)- and (*Z*)-nicotinamide obtained by RHF/6-31G** and MP2/6-31G** calculations

Conformer	RHF/6-31G**		MP2/6-31G**	
	(<i>E</i>)	(<i>Z</i>)	(<i>E</i>)	(<i>Z</i>)
<i>Bond lengths</i>				
C1–C2	1.388	1.391	1.399	1.400
C2–N3	1.320	1.318	1.344	1.342
N3–C4	1.320	1.322	1.344	1.346
C4–C6	1.386	1.384	1.397	1.395
C5–C6	1.379	1.382	1.390	1.393
C1–C5	1.389	1.387	1.397	1.397
C1–C7	1.498	1.497	1.498	1.497
C7–O8	1.200	1.198	1.230	1.230
C7–N9	1.358	1.362	1.372	1.375
C2–H10	1.076	1.074	1.085	1.083
C4–H11	1.077	1.077	1.084	1.084
C5–H12	1.074	1.075	1.082	1.083
C6–H13	1.074	1.074	1.082	1.082
N9–H14	0.995	0.995	1.008	1.008
N9–H15	0.992	0.992	1.005	1.006
<i>Bond angles</i>				
C1C2N3	123.7	123.6	123.7	123.7
C2N3C4	117.8	117.9	116.9	116.9
N3C4C6	123.6	123.6	123.7	123.7
C4C6C5	118.2	118.2	118.8	118.8
C1C5C6	118.9	118.9	118.4	118.3
C2C1C5	117.8	117.8	118.5	118.5
C2C1C7	123.8	118.2	123.1	118.2
C5C1C7	118.4	124.0	118.4	123.3
C1C7O8	121.2	121.6	121.8	122.2
C1C7N9	116.8	116.4	115.3	115.0
O8C7N9	122.0	122.0	122.8	122.8
C1C2H10	120.8	119.2	120.6	119.3
H10C2N3	115.5	117.2	115.7	117.0
N3C4H11	116.1	116.2	115.8	115.9
H11C4C6	120.3	120.2	120.5	120.5
C4C6H13	120.4	120.5	120.1	120.2
H13C6C5	121.4	121.3	121.1	121.0
C6C5H12	121.9	120.1	122.3	120.9
H12C5C1	119.2	121.0	119.2	120.7
C7N9H14	115.6	115.1	115.4	114.9
C7N9H15	121.0	120.3	119.7	119.1
H14N9H15	117.1	116.6	117.0	116.5
<i>Dihedral angles</i>				
C2C1C7O8	–159.6	21.6	–152.8	28.4
C2C1C7N9	19.7	–159.4	25.7	–153.2
C5C1C7O8	18.7	–157.0	25.1	–150.0
C5C1C7N9	–162.0	22.0	–156.4	28.4
C1C7N9H14	173.7	173.0	172.4	171.5
C1C7N9H15	22.4	25.3	24.2	26.4
O8C7N9H14	–7.0	–8.0	–9.1	–10.1

(continued on next page)

Table 1 (continued)

Conformer	RHF/6-31G**		MP2/6-31G**	
	(E)	(Z)	(E)	(Z)
O8C7N9H15	−158.3	−155.7	−157.3	−155.2
<i>Total and relative energies</i>				
E^a	−414.49650	−414.49521	−415.77904	−415.77788
ΔE^b	0.0	3.37	0.0	3.06
<i>Relative abundances</i>				
x	0.70	0.30	0.69	0.31

Bond lengths in angstroms and angles in degrees.

^a In E_h (hartree).

^b In kJ mol^{-1} .

intensities. The leveled total intensities averaged for three plates were used for data analysis. Elastic scattering factors were calculated as described in Ref. [16] and inelastic scattering factors were taken from Ref. [17].

3. Ab initio calculation

Calculations were carried out with the GAUSSIAN 94 program [18]. Geometry was optimized for the (E)- and (Z)-conformers at RHF/6-31G** and MP2/6-31G** levels of theory. Table 1 lists resultant

structural parameters. Moreover, MP2 calculations were performed to estimate the potential function for torsion of the pyridine ring. In the calculations, the values of $\phi(\text{C2C1C7N9})$ were fixed at an interval of 15° whereas all the other structural parameters were varied. The result is shown in Fig. 3. According to the MP2 calculations, the energy of the (Z)-form is larger than that of the (E)-form by 3.06 kJ mol^{-1} .

Cartesian force constants derived from MP2/6-31G** calculations were converted to the force constants in local symmetry coordinates and modified by using scale factors [19]. Scale factors were adjusted so that calculated vibrational wavenumbers might reproduce the wavenumbers observed in the gas phase [7] and liquid phase [8] as shown in Section 6.

4. Structural analysis

In the data analysis, the following assumptions were made: (1) the pyridine ring is planar, (2) the skeleton of the amide group is planar, (3) differences, $r(\text{C2-N3}) - r(\text{N3-C4})$, $r(\text{C1-C5}) - r(\text{C1-C2})$, $r(\text{C4-C6}) - r(\text{C1-C2})$, $r(\text{C5-C6}) - r(\text{C1-C2})$, $\angle \text{C1C2N3} - \angle \text{C2N3C4}$, $\angle \text{C6C4N3} - \angle \text{C2N3C4}$ and $\angle \text{C1C7O8} - \angle \text{C1C7N9}$, are equal to the corresponding differences given by the MP2/6-31G** calculations, (4) the N–H bond lengths are equal to the observed value of acetamide, 1.022 \AA (r_g) [20], (5) the C–H bond lengths of the pyridine ring are the same, (6) in the pyridine ring, the C–H bonds bisect the XCC bond angles ($X = \text{N, C}$) and (7) the CNH

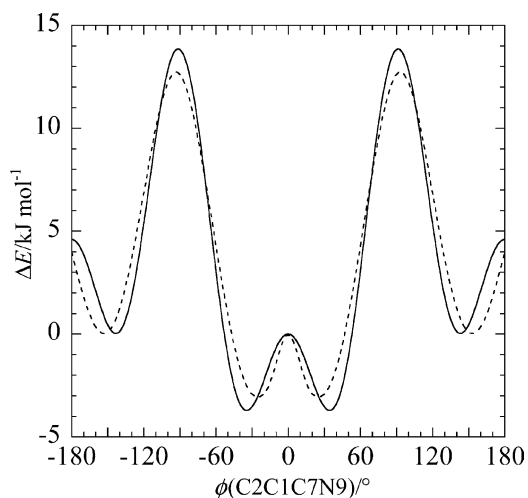


Fig. 3. Experimental potential function of nicotinamide (solid curve) and theoretical one given by MP2/6-31G** calculations (dashed curve).

Table 2
Mean amplitudes l and interatomic distances r_a of nicotinamide (\AA)

Atom pair	(E)-form ($\phi = 30^\circ$)				(Z)-form ($\phi = 150^\circ$)			
	r_a	l^{calc}	l^{obs}	Group ^a	r_a	l^{calc}	l^{obs}	Group ^a
N9–H15	1.018	0.072	0.065(5)	1	1.018	0.072	0.065(5)	1
N9–H14	1.018	0.072	0.065	1	1.018	0.072	0.065	1
C6–H13	1.093	0.077	0.070	1	1.093	0.077	0.070	1
C5–H12	1.093	0.077	0.070	1	1.093	0.077	0.070	1
C4–H11	1.093	0.077	0.070	1	1.093	0.077	0.070	1
C2–H10	1.093	0.077	0.070	1	1.093	0.076	0.070	1
C7–O8	1.216	0.039	0.032	1	1.215	0.039	0.032	1
N3–C4	1.327	0.045	0.038	1	1.329	0.045	0.039	1
C2–N3	1.327	0.046	0.039	1	1.325	0.045	0.039	1
C7–N9	1.361	0.048	0.041	1	1.364	0.048	0.042	1
C5–C6	1.396	0.046	0.040	1	1.399	0.046	0.040	1
C1–C5	1.402	0.046	0.039	1	1.403	0.046	0.039	1
C4–C6	1.403	0.046	0.040	1	1.401	0.046	0.040	1
C1–C2	1.405	0.047	0.041	1	1.406	0.047	0.041	1
C1–C7	1.497	0.053	0.046	1	1.496	0.052	0.046	1
C2...C4	2.267	0.056	0.061(3)	2	2.268	0.056	0.061(3)	2
O8...N9	2.261	0.059	0.064	2	2.263	0.059	0.064	2
C1...O8	2.373	0.064	0.070	2	2.374	0.064	0.070	2
C4...C5	2.389	0.056	0.062	2	2.390	0.056	0.062	2
C2...C5	2.390	0.057	0.062	2	2.391	0.057	0.062	2
C1...C6	2.413	0.058	0.063	2	2.415	0.058	0.063	2
C1...N9	2.411	0.067	0.073	2	2.409	0.067	0.073	2
N3...C6	2.408	0.056	0.061	2	2.407	0.056	0.061	2
C1...N3	2.412	0.056	0.062	2	2.411	0.056	0.062	2
C5...C7	2.536	0.073	0.078	2	2.590	0.073	0.079	2
C2...C7	2.515	0.074	0.080	2	2.454	0.075	0.080	2
C2...C6	2.723	0.062	0.070(8)	3	2.723	0.062	0.070	3
C1...C4	2.729	0.062	0.070	3	2.729	0.062	0.070	3
N3...C5	2.789	0.066	0.074	3	2.789	0.067	0.074	3
C2...N9	2.850	0.112	0.120	3	3.603	0.077	0.077 ^b	
C5...O8	2.943	0.111	0.118	3	3.629	0.074	0.074 ^b	
C2...O8	3.573	0.076	0.076 ^b		2.820	0.118	0.126	3
C5...N9	3.657	0.079	0.079 ^b		2.972	0.114	0.122	3
N3...C7	3.753	0.072	0.072 ^b		3.706	0.073	0.073 ^b	
C6...C7	3.797	0.072	0.072 ^b		3.831	0.072	0.072 ^b	
N3...N9	4.147	0.119	0.119 ^b		4.752	0.085	0.085 ^b	
C4...C7	4.214	0.072	0.072 ^b		4.205	0.072	0.072 ^b	
C6...O8	4.304	0.115	0.115 ^b		4.750	0.082	0.082 ^b	
N3...O8	4.728	0.083	0.083 ^b		4.121	0.123	0.123 ^b	
C6...N9	4.773	0.086	0.086 ^b		4.330	0.119	0.119 ^b	
C4...N9	4.905	0.105	0.105 ^b		5.011	0.105	0.105 ^b	
C4...O8	4.987	0.101	0.101 ^b		4.882	0.105	0.105 ^b	

The mean amplitudes for O...H, N...H, C...H and H...H atom pairs are not listed although they were included in the data analysis. The numbers in parentheses are the estimated limits of error (3σ).

^a The groups are divided at $r_a = 1.65$, 2.65 , and 3.15 \AA . The mean amplitudes with the same number were refined as one group.

^b Fixed value.

Table 3

Structural and potential parameters of nicotinamide (r_g, \angle_α)

Parameter	(E)-form ($\phi = 30^\circ$)	(Z)-form ($\phi = 150^\circ$)	Parameter	(E)-form ($\phi = 30^\circ$)	(Z)-form ($\phi = 150^\circ$)
C2–N3	1.328(6) ^a	1.326	C4–N3	1.328 ^a	1.330
C1–C2	1.406(4) ^b	1.407	C1–C5	1.404 ^b	1.404
C4–C6	1.404 ^b	1.402	C5–C6	1.397 ^b	1.400
C1–C7	1.498(8)	1.497	C=O	1.216(5)	1.216
C7–C9	1.362(12)	1.366	$\langle C-H \rangle$	1.097(12)	1.097
$\langle N-H \rangle$	1.022 ^c	1.022			
C2N3C4	117.5(2) ^d	117.5	C1C2N3	124.3 ^d	124.3
C6C4N3	124.3 ^d	124.3	C1C5C6	119.5 ^e	119.4
C2C1C5	117.0 ^e	117.1	C4C6C5	117.4 ^e	117.4
C1C7O8	121.9(6)	122.1	C1C7N9	115.0 ^f	114.8
N9C7O8	123.1 ^e	123.1	C2C1C7	120.5(17)	115.9
N3C2H10	117.9 ^e	117.8	N3C4H11	117.9 ^e	117.9
C1C5H12	120.3 ^e	120.3	C4C6H13	121.3 ^e	121.3
ϕ^g	34(6) ^h	143(6) ^h			
V_1	5 ⁺¹⁰ ₋₇				
V_2	11.5 ^c				
V_4	–9(4)				
R^i	0.045				

Bond lengths in angstroms, angles in degrees and potential coefficients in kJ mol^{-1} . The numbers in parentheses are the estimated limits of error. The index of resolution is 0.96(2).

^a C–N3 bond lengths were refined in a group.

^b C–C bond lengths in the pyridine ring were refined in a group.

^c Assumed.

^d CCN3 and C2N3C4 bond angles were refined in a group.

^e Dependent value.

^f C1C7O8 and C1C7N9 bond angles were refined in a group.

^g ϕ denotes dihedral angle C2C1C7N9.

^h Obtained from the potential parameters, V_1 , V_2 and V_4 .

ⁱ $R = \{ \sum_i W_i (sM(s)_i^{\text{obs}} - sM(s)_i^{\text{calc}})^2 / \sum_i W_i (sM(s)_i^{\text{obs}})^2 \}^{1/2}$, where W_i is a diagonal element of the weight matrix.

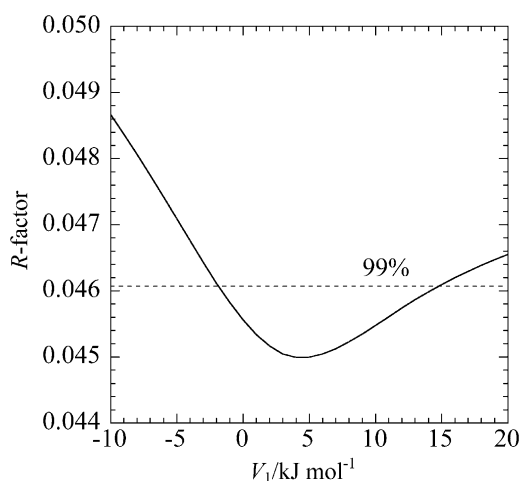


Fig. 4. Plot of the R -factor against V_1 . See Table 3 for the definition of R -factor. The dashed line shows the 99% confidence level.

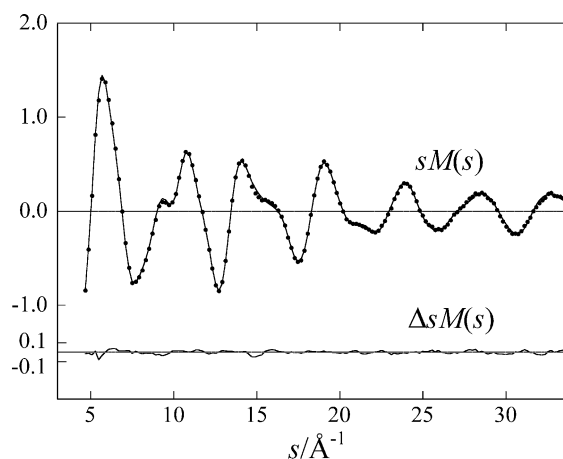


Fig. 5. Experimental (●) and theoretical (—) molecular scattering intensities of nicotinamide: $\Delta sM(s) = sM(s)^{\text{obs}} - sM(s)^{\text{calc}}$.

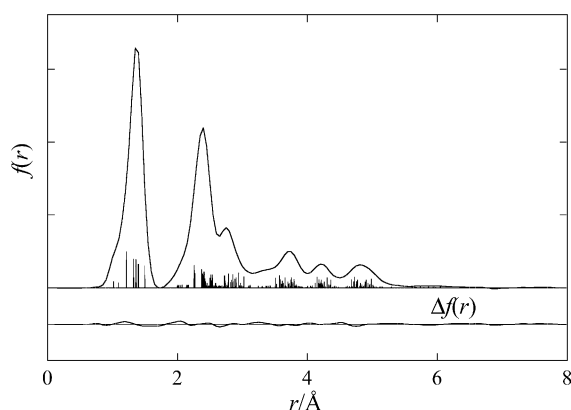


Fig. 6. Experimental radial distribution curve of nicotinamide: $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. An artificial damping function, $\exp(-0.002s^2)$, is used. Relatively important atom pairs are indicated by vertical bars.

bond angles and CCNH dihedral angles are equal to the MP2/6-31G** values. The assumptions of (4)–(7) are due to the difficulty in determining the positions of hydrogen atoms by GED.

The torsion of the pyridine ring was treated as a large amplitude motion. The $\phi(\text{C2C1C7N9})$ values of pseudo conformers were taken at an interval of 15° . The differences between structural parameters of pseudo-conformers were fixed at the corresponding MP2 values. The potential function was assumed to be

$$V(\phi) = \frac{V_1}{2}(1 - \cos \phi) + \frac{V_2}{2}(1 - \cos 2\phi) + \frac{V_4}{2}(1 - \cos 4\phi).$$

The relative abundance of each pseudo conformer was calculated according to a Boltzmann distribution. In the analysis, the V_2 value could not be determined probably because, unlike V_1 and V_4 , V_2 represents the barrier height of the internal rotation and has no direct

Table 4
Molecular structures of (*E*)-nicotinamide, benzamide, pyridine and acetamide

Parameter	<i>(E)</i> -nicotinamide		Benzamide		Pyridine, ^a gas, r_g , \angle_α	Acetamide, ^b gas, r_g , \angle_α
	Gas, ^c r_g , \angle_α	Crystal, ^d r_α	Gas, ^c r_g , \angle_α	Crystal, ^f r_α		
$\langle \text{C}-\text{N} \rangle_{\text{ring}}$	1.328(6)	1.340(2)			1.344(1)	
C1–C7	1.498(8)	1.492(3)	1.511(5)	1.498(3)		
$\langle \text{C}-\text{C} \rangle_{\text{ring}}$	1.403(4)	1.385(2)	1.401(2)	1.397(1)	1.399 ^g	
C=O	1.216(5)	1.230(3)	1.225(3)	1.245(3)		1.220(3)
C–N _{amide}	1.362(12)	1.337(3)	1.380(11)	1.340(3)		1.380(4)
C2N3C4	117.5(2)	118.0(3)			116.1(1)	
C6C4N3	124.3 ^g	123.1(3)			124.6 ^g	
C1C2N3	124.3 ^g	123.1(2)			124.6 ^g	
C1C5C6	119.5 ^g	119.5(3)			119.1 ^g	
C2C1C5	117.0 ^g	118.0(3)			117.8 ^g	
C4C6C5	117.4 ^g	118.3(3)			117.8 ^g	
C1C7O8	121.9(6)	119.7(3)	121.2(17)	120.3(3)		123.0 ^g
C1C7N9	115.0 ^g	117.8(2)	117.8(16)	117.3(3)		115.1(16)
N9C7O8	123.1 ^g	122.5(3)	121.0 ^g	122.3(3)		122.0(6)
C2C1C7	120.5(25)	124.1(2)	121.8(17)	122.1(3)		
ϕ	34(6) ^h	23.0(3)	19(5)	25.3(3)		

Bond lengths in angstroms and angles in degrees. The numbers in parentheses are 3σ .

^a Ref. [24]. The uncertainties are quoted from Ref. [25].

^b Ref. [20].

^c The present work.

^d Result obtained by neutron diffraction at 295 K [1].

^e Ref. [11].

^f Result obtained by neutron diffraction at 15 K [26].

^g Dependent value.

^h Obtained from the potential parameters, V_1 , V_2 and V_4 .

relationship with the molecular structure or conformational composition. Therefore, it was fixed at the value of 11.5 kJ mol^{-1} obtained from the MP2 calculations. In the final analysis, adjustable structural and potential parameters were selected to be: $\langle r(\text{N}_{\text{ring}}-\text{C}_{\text{ring}}) \rangle$, $\langle r(\text{C}_{\text{ring}}-\text{C}_{\text{ring}}) \rangle$, $r(\text{C}=\text{O})$, $r(\text{C}-\text{C}(=\text{O}))$, $r(\text{C}-\text{N})$, $\langle r(\text{C}-\text{H}) \rangle$, $\angle \text{C}_{\text{ring}}\text{N}_{\text{ring}}\text{C}_{\text{ring}}$, $\angle \text{C2C1C7}$, $\angle \text{CCO}$, V_1 and V_4 , where angle brackets denote average values.

Mean amplitudes and shrinkage corrections, $r_\alpha - r_a$ [21], were calculated from the quadratic force constants obtained in Section 3. Asymmetry parameters, k , were estimated by the conventional method [22]. Most of mean amplitudes were refined in groups as shown in Table 2. The differences between the mean amplitudes in each group were fixed at the calculated values.

The rotational constants of nicotinamide had been determined by microwave spectroscopy [3]. However, no joint analysis of GED data and rotational constants was carried out. This is because it is difficult to calculate vibrational corrections for rotational constants $B_0 - B_e$ and shrinkage corrections $r_\alpha^0 - r_a$ with reliable precision for molecules undergoing a large-amplitude vibration.

Adjustable structural parameters, V_4 , mean amplitudes and the index of resolution were determined by least-squares calculations on molecular scattering intensities. In the calculations, the V_1 value was fixed at various values. Resulting R -factors (see the footnote *i* of Table 3 for the definition) are shown in Fig. 4. Molecular scattering intensities and radial distribution curves are shown in Figs. 5 and 6, respectively.

5. Results and discussion

Fig. 4 shows that the V_1 value is $5_{-7}^{+10} \text{ kJ mol}^{-1}$ in the 99% confidence interval [23]. Determined structural and potential parameters of nicotinamide are listed in Table 3. The limits of error were estimated from three times standard deviations in the least-squares calculations and the systematic errors due to the uncertainties in the scale factor and V_1 .

The determined V_1 and V_4 values are consistent with the values obtained from the MP2/6-31G** calculations, 3.4 and -7.2 kJ mol^{-1} . From

the potential coefficients, V_1 , V_2 and V_4 , the population and the dihedral angle C2C1C7N9 of the (*E*)-conformer are calculated to be $73_{-41}^{+27}\%$ and $34(6)^\circ$, respectively. The corresponding values of the (*Z*)-conformer are $27_{-27}^{+41}\%$ and $143(6)^\circ$, respectively. The ratio of the relative abundances of (*E*)- and (*Z*)-conformers is consistent with the corresponding one of about 150:8 determined by microwave spectroscopy [3]. Table 3 shows that the differences in the bond lengths and angles except the C2C1C7 bond angle between (*E*)- and (*Z*)-forms are smaller than 0.003 \AA and 0.3° , respectively.

As shown in Table 4, most of the structural parameters of (*E*)-nicotinamide in the gas phase are in fair agreement with the corresponding parameters of pyridine [24,25] and acetamide [20]. However, the $\langle r(\text{N}-\text{C}_{\text{ring}}) \rangle$ and $\angle \text{CNC}_{\text{ring}}$ of nicotinamide are different from the corresponding parameters of pyridine.

The skeletal structures of nicotinamide and benzamide are non-planar (see Table 4). This can be ascribed to the effect of steric repulsion between the H10 and H15 atoms [11]. The dihedral angle C2C1C7N9 of nicotinamide, $34(6)^\circ$, is larger than the corresponding value of benzamide, $19(5)^\circ$ [11]. This is consistent with the experimental result that the C1–C7 bond length of nicotinamide is shorter than that of benzamide and hence the stronger repulsion is expected for nicotinamide.

The gas-phase geometry of nicotinamide is compared with the molecular geometry in the crystal determined by neutron diffraction [1] in Table 4. The dihedral angle C2C1C7N9 in the gas phase, $34(6)^\circ$, is larger than that in the crystal by 11° . The bond angles of nicotinamide determined by GED are close to those in the crystal.

The C=O bond length of nicotinamide in the gas phase is shorter than that in the crystal by 0.01 \AA , while the C–N bond length in the gas phase is longer than that in the solid phase by 0.03 \AA . These changes are close to those found for benzamide [11,26] and thus they are ascribed to the effect of hydrogen bonding on the structure in the crystal [11].

As shown in Fig. 2, the nitrogen atom in the pyridine ring acts as a proton acceptor. The N–C_{ring} bond length of nicotinamide in the gas phase, $1.328(6) \text{ \AA}$, is shorter than that in the crystal, $1.340(2) \text{ \AA}$. This shortening is also attributed to the effect of hydrogen bonding.

6. Supplementary material

Tables of the leveled total intensities and background, correlation matrix, structural parameters of pseudo-conformers, local symmetry coordinates, scale factors, scaled force constants, and observed and calculated wavenumbers with potential energy distribution are deposited with B.L.L.D. as publication No. SUP 26692 (14 pages).

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