# Molecular Structure of Formamide as Studied by Gas Electron Diffraction

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(Received September 10, 1973)

The structure of formamide $HCONH_2$ has been determined by gas electron diffraction. The rotational constants determined in previous microwave studies have also been used for determining the hydrogen parameters. From a joint least-squares analysis of the diffraction intensity and the rotational constants, where the out-of-plane vibrations are treated as finite-amplitude motions in the corrections for vibrational effects, the following $r_g$ bond distances and $r_z$ angles have been derived: C–N = 1.368±0.003 Å, C=O = 1.212±0.003 Å, ∠N–C=O = 125.0±0.4°, N–H(average) = 1.027±0.006 Å, C–H = 1.125±0.012 Å, ∠C–N–H(*cis* to C=O) = 118.7±1.0°, and ∠C–N–H (*trans* to C=O) = 119.7±1.0°, where the uncertainties represent estimated limits of experimental error. The C–N bond is about 0.07 Å longer, whereas the C=O bond is about 0.04 Å shorter, in the free molecule than in the crystal studied by X-ray diffraction. The C–N and C=O bonds are about 0.01 Å or more shorter, and the N–C=O angle is about 3° larger than the corresponding parameters in acetamide and *N*-methylacetamide.

The primary purpose of the present study is to determine the skeletal structure of formamide as accurately as possible, since neither spectroscopic nor diffraction studies have yet afforded a structure accurate enough to enable a critical comparison with analogous amide structures determined in the vapor and crystal phases. Particularly, a comparison of the skeletal structure of formamide with those of acetamide[1] and *N*-methylacetamide[2] determined in our preceding studies is intended in order to appraise the effect of methyl substitutions on simple amide structures. The $r_g$ distances and $r_z$ angles[3,4] should provide more consistent and suitable measures for this comparison than the $r_s$ parameters, since the skeletal $r_s$ parameters in formamide determined by microwave studies[5–7] suffer from appreciable uncertainties in the carbon coordinates, and no $r_s$ structures are yet available for other amides.

On the other hand, the rotational constants of formamide determined by microwave spectroscopy[5–8] for the normal and deuterated species supply valuable information on the positions of the hydrogen atoms, particularly on the planarity of the molecule and the potential function in regard to the $NH_2$ wagging motion,[7] which is hard to determine precisely by the diffraction experiment.[4] Therefore, the diffraction intensity measured in the present study has been merged with the rotational constants in a least-squares analysis. Because of the relatively low frequencies of the out-of-plane vibrations, a finite-amplitude treatment[9] instead of the conventional treatment based on infinitesimal vibrational amplitudes[3] has been made for the vibrational corrections in the comparison of the diffraction and spectroscopic observables.

## Experimental

A commercial guaranteed reagent was heated to about 160 °C by a high-temperature nozzle,[10] and diffraction photographs were taken with 40 kV electrons at camera distances of 112.30 mm (short) and 246.86 mm (long).[11] The scale factors of the diffraction patterns were calibrated to within 0.1% with reference to the $r_a$ (C=O) distance of carbon dioxide (1.1646 Å).[11] The densities of four plates taken at each

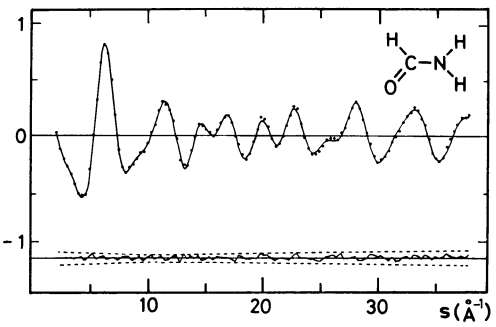


Fig. 1. Experimental and theoretical molecular intensities for formamide. Typical observed $sM(s)$ values are shown in dots, and the best-fit theoretical is shown in the solid curve. The indices of resolution for long and short camera-distances are 0.752 and 0.912, respectively. The lower solid and broken curves represent the residuals and the error limits in the $sM(s)$ to a fractional error of $1\times10^{-3}$ of the original photocurrent,[12] respectively.

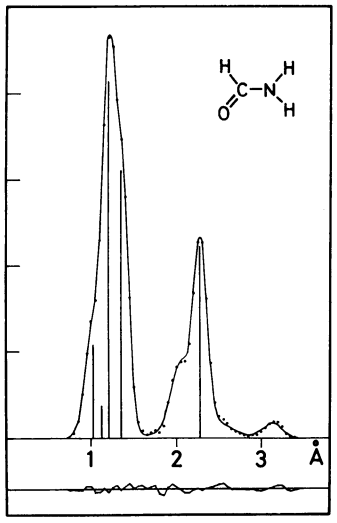


Fig. 2. Experimental (dots) and theoretical radial distribution curves for formamide. The lower curve represents residuals. Vertical bars correspond to principal internuclear distances. A damping factor, $\exp(-0.0016\ s^2)$, is used.

camera distance were measured by a digital microphotometer.[12] Other experimental procedures have been described elsewhere.[11,13]

Molecular intensities were obtained in the ranges of $s=$ 2.2—15.7 Å$^{-1}$ and 9.4—37.7 Å$^{-1}$ from the long and short camera-distance data, respectively.[14] They agreed with each other in the overlapping region within experimental error of about 0.03 in the absolute $sM(s)$ scale, and hence were joined at $s=12.7$ Å$^{-1}$ (Fig. 1). A hand-drawn background was adjusted to get the radial distribution curve shown in Fig. 2. Most calculations were carried out on a HITAC 5020E and 8700/8800 in the Computer Center of the University of Tokyo.

## Analysis of Electron Diffraction Data

The skeletal parameters, $r_g$(C–N), $r_g$(C=O), and $\phi_\alpha$(N–C=O), and the average $r_g$(N–H) distance were determined by a least-squares analysis of the molecular intensity with a uniform empirical weight function.[15] The molecule was assumed to be planar in equilibrium,[7] and the $r_\alpha$(C–H) distance and all the $\phi_\alpha$ angles involving the hydrogen atoms were fixed to the corresponding $r_s$-values.[7] The mean amplitudes and the vibrational corrections $(r_a-r_\alpha)$[3,16] were calculated by the use of an approximate set of the modified Urey-Bradley force constants for the in-plane vibrations shown in Table 1; they were taken from those reported by Suzuki[17]

TABLE 1. APPROXIMATE IN-PLANE FORCE CONSTANTS FOR FORMAMIDE[a] (in md/Å)

| | I | II | | I | II |
|---|---|---|---|---|---|
| $K$(N–H) | 6.58 | 5.80 | $H$(H–C=O) | 0.20 | 0.20 |
| $K$(C–H) | 3.50 | 3.74 | $H$(N–C=O) | 0.14 | 0.34 |
| $K$(C=O) | 9.00 | 8.80 | $F$(H···H) | 0 | 0 |
| $K$(C–N) | 6.15 | 6.15 | $F$(H···C) | 0.41 | 0.46 |
| $H$(H–N–H) | 0.45 | 0.40 | $F$(H···N) | 0.70 | 0.70 |
| $H$(H–N–C) | 0.18 | 0.32 | $F$(H···O) | 0.92 | 0.92 |
| $H$(H–C–N) | 0.24 | 0.18 | $F$(O···N) | 1.50 | 1.50 |

a) See Ref. 17 for definitions of the modified Urey-Bradley force constants, $K$, $H$, and $F$.
I: Present estimates, II: Estimated by Suzuki, Ref. 17.

and adjusted slightly to reproduce the vibrational frequencies observed recently by King[18] in the gas phase. For the $NH_2$ rocking frequency, however, that assigned tentatively by King (602 cm$^{-1}$) seems to be unlikely, since the calculated value (about 958 cm$^{-1}$) deviated significantly from it and it was impossible to reporduce the former value by a reasonable adjustment of the force constants. A further spectroscopic work, particularly on the deuteride vapors, is necessary to make a decisive assignment.

In calculations of the vibrational corrections, the contributions from the out-of-plane vibrations were excluded, since their amplitudes cannot be treated as infinitesimal[9] (see next section). All but the skeletal mean amplitudes were fixed to the calculated values listed in Table 2. The asymmetry parameters $\kappa$ for the bonded C–H and N–H distances were assumed to be $1.8\times10^{-5}$ Å$^3$, and the rest of the $\kappa$ parameters were ignored.[19]

The structural parameters and the mean amplitudes

TABLE 2. MEAN AMPLITUDES AND VIBRATIONAL CORRECTIONS FOR FORMAMIDE[a] (in $10^{-4}$ Å)

| | $l$ | $r_a-r_\alpha$ | | $l$ | $r_a-r_\alpha$ |
|---|---|---|---|---|---|
| C=O | 394 | 4 | N···$H_a$ | 981 | −11 |
| C–N | 427 | 2 | O···$H_a$ | 923 | 9 |
| C–$H_a$ | 800 | 1 | O···$H_c$ | 1402 | 40 |
| N–H | 715 | 30 | O···$H_t$ | 923 | 83 |
| N···O | 563 | −17 | $H_a$···$H_c$ | 1196 | 55 |
| C···$H_c$ | 1001 | −18 | $H_a$···$H_t$ | 1634 | 64 |
| C···$H_t$ | 982 | −21 | $H_c$···$H_t$ | 1151 | 20 |

a) Calculated at 160 °C. The aldehyde hydrogen atom is denoted as $H_a$. The amide hydrogen atoms which are *trans* and *cis* to the C=O bond are denoted as $H_t$ and $H_c$, respectively.

TABLE 3. STRUCTURAL PARAMETERS FOR FORMAMIDE[a]

| | ED[b] | | ED+MW[c] | | MW[d] |
|---|---|---|---|---|---|
| | $r_g$ | $r_\alpha$ | $r_g$ | $r_z$ | $r_s$ |
| C=O | 1.211(4) | 1.209 | 1.212(3) | 1.210 | 1.219(12) |
| C–N | 1.367(4) | 1.365 | 1.368(3) | $1.366_5$ | 1.352(12) |
| N–$H_{av}$ | 1.021(9) | 1.013 | 1.027(6) | $1.018_5$ | 1.002( 3) |
| C–$H_a$ | 1.12 fix | 1.115 | 1.125(12) | 1.119 | 1.098(10) |
| ∠N–C=O | | 124.9(5) | | 125.0( 4) | 124.7( 3) |
| ∠C–N–$H_c$ | | 118.5 fix | | 118.7(10) | 118.5( 5) |
| ∠C–N–$H_t$ | | 120.0 fix | | 119.7(10) | 120.0( 5) |
| ∠$H_a$–C–N | | 112.7 fix | | 112.7 fix | 112.7(20) |
| $l$(C=O)[e] | 0.043(3) | | 0.043(3) | | |
| $l$(C–N) | 0.050(4) | | 0.050(4) | | |
| $k_l$[f] | 0.75 (2) | | 0.75 (2) | | |
| $k_s$ | 0.91 (5) | | 0.91 (5) | | |

a) Distances in Å and angles in degrees. The numbers in parentheses represent uncertainties attached to the last significant figures. For definitions of $r_g$, $r_\alpha$, $r_z$, and $r_s$, see Ref. 3.
b) Structures based on the analysis of electron-diffraction intensity with estimated limits of error.
c) Structures based on the analysis of electron-diffraction intensity and rotational constants, with estimated limits of error. The $r_z$ structure derived in this procedure is sometimes denoted as $r_{av}$.[22]
d) The $r_s$ structure determined by Hirota *et al.* by microwave spectroscopy. Ref. 7.
e) Mean amplitudes with estimated limits of error.
f) Indices of resolution for diffraction intensities taken with the long (l) and short (s) camera-distances.

derived from the least-squares analysis are listed in Table 3. The quoted limits of error were estimated as 2.5 times the random errors plus systematic errors.[20,21]

## Joint Analysis of Diffraction Intensity and Rotational Constants

A further analysis was made by the use of the observed rotational constants for the normal and four deuterated species for the ground vibrational state[6] for testing the accuracy of the diffraction parameters and for refinement of the hydrogen parameters.[22] The analysis was

based on the rotational constants $A_z$, $B_z$, and $C_z$ (hereafter represented, as a set, by $B_z$) corresponding to a hypothetical set of the planar nuclear positions averaged over the in-plane vibrations.

The $B_z$ constants were estimated in the following steps of eliminating the effect of in-plane and out-of-plane vibrations.

From the spectroscopic side, the $B_z$ constants were obtained from the corresponding $B_0$ constants by making the following corrections:[23]

$$B_z = B_0 + \Delta B_{\text{electronic}} + \Delta B_{\text{centrifugal}} + \Delta B_{\text{Coriolis}} + \sum_s \Delta B_s + \sum_t \Delta B_t \quad (1)$$

where the electronic corrections were estimated by Oka's formulation[24] from the molecular $g$-values observed by Flygare and Benson,[25] and the centrifugal corrections[24] were ignored. The Coriolis corrections and the vibrational corrections for the in-plane modes were calculated in a conventional way by the use of the force constants given in Table 1 as[3,23]

$$\Delta B_{\text{Coriolis}} = -4B_e^2 \sum_s \omega_s \sum_{s'} (\zeta_{ss'}^{(\alpha)})^2/(\omega_s^2 - \omega_{s'}^2) \quad (2)$$

and

$$\Delta B_s = -(B_e^2/\omega_s)[3A_{ss}^{(\alpha\alpha)} - 4\sum_{s'}(\zeta_{ss'}^{(\alpha)})^2] \quad (3)$$

where Nielsen's notations[26] are followed. Individual in-plane and out-of-plane modes are represented by $s$ and $t$, respectively, and $s'$ includes all $s$ and $t$. The vibrational corrections for the out-of-plane motions were approximated on the assumption that the $NH_2$ wagging, torsion and C–H out-of-plane bending motions were independent of one another,

$$\sum_t \Delta B_t \cong \Delta B_{\text{wag}} + \Delta B_{\text{torsion}} + \Delta B_{\text{bend}} \quad (4)$$

The correction for the wagging motion followed the calculation by Hirota *et al.*,[7]

$$\Delta B_{\text{wag}} = -B_1\langle\tau^2\rangle_0 - B_2\langle\tau^4\rangle_0 \quad (5)$$

where the coefficients $B_1$, $B_2$ and the average values of the $NH_2$ wagging displacement $\tau$ for the ground state are given in their paper. The corrections for the torsion and the C–H bending motion were estimated in a similar way. A two-fold harmonic potential for the torsion with $V_2$=20 kcal/mol[27] and the C–H bending frequency[18] of 1050 $cm^{-1}$ were assumed, and only quadratic averages of the displacements were taken into account. The correction terms are listed in Table 4. The inertia defects calculated from the present $B_z$ do not vanish exactly, as mentioned by Hirota *et al.*,[7] but they fall within the limits of uncertainty in the correction terms estimated above ($-0.04\pm0.10$ amu. $Å^2$ for all the isotopic species).

From the diffraction side, the $r_g$ parameters were related to the $r_a$ parameters by making conventional shrinkage corrections[3] for the in-plane contributions, and for the nonbonded distances which vary with the out-of-plane vibrations, classical averages over the motions based on a rigid frame, analogous to Karle's shrinkage correction for internal rotation,[28] were made[9] by the use of the mean displacements used in the spectroscopic corrections. Then the $r_a$ parameters were assumed to be equal to the corresponding $r_z$ parameters, since the frequencies of the in-plane vibrations are so high that thermal effects are unimportant.[3,29]

Table 4. Corrections for rotational constants,[a] $B_z-B_0$ (in $10^{-5}$ $cm^{-1}$)

| | | $\Delta B_1$ | $\Delta B_2$ | $\Delta B_3$ | $\Delta B_4$ | $\Delta B_5$ | $\Delta B_6$ |
|---|---|---|---|---|---|---|---|
| $HCONH_2$ | $A$ | −38 | 2549 | 994 | −1099 | −170 | 199 |
| | $B$ | −1 | 81 | 41 | 122 | −15 | −9 |
| | $C$ | 0 | 47 | −29 | 137 | 15 | 10 |
| $DCONH_2$ | $A$ | −28 | 1542 | 606 | −627 | −95 | 131 |
| | $B$ | −1 | 86 | 43 | 122 | −17 | −8 |
| | $C$ | 0 | 47 | −32 | 126 | 14 | 8 |
| *c*-HCONHD[b] | $A$ | −32 | 1981 | 659 | −699 | −33 | 157 |
| | $B$ | 1 | 83 | 43 | 150 | −20 | −9 |
| | $C$ | 0 | 46 | −30 | 164 | 10 | 9 |
| *t*-HCONHD[c] | $A$ | −37 | 2763 | 834 | −1797 | −295 | 182 |
| | $B$ | 1 | 78 | 31 | 148 | −8 | −7 |
| | $C$ | 0 | 44 | −29 | 156 | 15 | 8 |
| $HCOND_2$ | $A$ | −31 | 2110 | 548 | −1103 | −144 | 143 |
| | $B$ | 1 | 79 | 33 | 164 | −14 | −8 |
| | $C$ | 0 | 43 | −30 | 172 | 13 | 8 |

a) $\Delta B_1$: electronic, $\Delta B_2$: Coriolis, Eq. (2), $\Delta B_3$: in-plane vibrational, Eq. (3), $\Delta B_4$: $NH_2$ wagging, Eq. (5), $\Delta B_5$: torsion, $\Delta B_6$: C–H out-of-plane bending. See text.
b) The deuterium atom is *cis* to the C=O bond.
c) The deuterium atom is *trans* to the C=O bond.

The relative statistical weights assigned to the rotational constants were such that their standard errors were approximately equal to their estimated uncertainties.[20] They were taken by a trial and error procedure as $1\times10^2$, $2\times10^5$, and $1\times10^6$ for $A_z$, $B_z$, and $C_z$, respectively, for all the isotopic species, whereas a unit weight was assigned to each molecular intensity of electron diffraction from $s$=6.3 to 26.7 $Å^{-1}$ taken at unit $q$ ($10\ s/\pi$) intervals.

All the independent structural parameters were varied except that the $r_z$(N–H) distances were set equal to each other and that the $\phi_z$(H–C–N) angle was fixed to 112.7°, the $r_s$ angle reported by Hirota *et al.*[7] As for the mean amplitudes, all but the bonded C–N and C=O amplitudes were fixed to the calculated values given in Table 2. The isotopic differences for the $r_z$(N–H)$-r_z$(N–D) and $r_z$(C–H)$-r_z$(C–D) distances were initially estimated by use of an approximate formula,[22,29]

$$r_z(\text{H}) - r_z(\text{D}) \cong \frac{3}{2}a_3[\langle\Delta z^2\rangle_0(\text{H}) - \langle\Delta z^2\rangle_0(\text{D})] - [\langle\Delta x^2\rangle_0(\text{H}) - \langle\Delta x^2\rangle_0(\text{D})]/2r_z \quad (6)$$

where the anharmonicity parameters $a_3$ for N–H and C–H were assumed to be[30] 2.19 $Å^{-1}$ and 1.98 $Å^{-1}$, respectively, and the in-plane relative displacements of the nuclei parallel and perpendicular to the equilibrium bond axes, $\Delta z$ and $\Delta x$, respectively, were taken into account. In line with the finite-amplitude treatment mentioned above, contributions from the out-of-plane displacements, $\Delta y$, were not included in the calculation. The isotopic differences were estimated to be $0.003_2$ and $0.002_0$ Å, respectively, for N–H and C–H. (A conventional treatment including the out-of-plane contributions resulted in $-0.004_8$ and $0.000_6$ Å, respec-

TABLE 5. ROTATIONAL CONSTANTS FOR FORMAMIDE (in $cm^{-1}$)

| | | $HCONH_2$ | $DCONH_2$ | *c*-HCONHD[a] | *t*-HCONHD[b] | $HCOND_2$ |
|---|---|---|---|---|---|---|
| $A_0$ | (obs)[c] | 2.425548 | 1.832881 | 2.046279 | 2.374296 | 1.991907 |
| $A_z$ | (est)[d] | 2.40119 | 1.81761 | 2.02594 | 2.35779 | 1.97668 |
| $A_z$ | (cal)[e] | 2.420(15) | 1.827(13) | 2.037(13) | 2.365(16) | 1.978(14) |
| $B_0$ | (obs) | 0.379387 | 0.379365 | 0.367250 | 0.349352 | 0.340021 |
| $B_z$ | (est) | 0.37720 | 0.37712 | 0.36479 | 0.34695 | 0.33749 |
| $B_z$ | (cal) | 0.3771(4) | 0.3771(4) | 0.3647(6) | 0.3472(6) | 0.3377(5) |
| $C_0$ | (obs) | 0.328018 | 0.314207 | 0.311352 | 0.304626 | 0.290545 |
| $C_z$ | (est) | 0.32623 | 0.31257 | 0.30936 | 0.30269 | 0.28848 |
| $C_z$ | (cal) | 0.3623(2) | 0.3126(3) | 0.3093(3) | 0.3028(3) | 0.2885(3) |

a) The deuterium atom is *cis* to the C=O bond.
b) The deuterium atom is *trans* to the C=O bond.
c) Rotational constants observed by Costain and Dowling by microwave spectroscopy. Ref. 6.
d) Rotational constants estimated from $A_0$ (obs), *etc.*, by the corrections listed in Table 4.
e) Rotational constants calculated by the most probable set of $r_z$ parameters given in Table 3 with 2.5 times the estimated standard errors enclosed in parentheses.

TABLE 6. ERROR MATRIX FOR FORMAMIDE[a]

| | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $X_5$ | $X_6$ | $X_7$ | $l_1$ | $l_2$ | $k_1$ | $k_s$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_1$ | 7 | 4 | 6 | 14 | −10 | −8 | −4 | −3 | −5 | 5 | 8 |
| $X_2$ | | 10 | −10 | −15 | −14 | −8 | 9 | 6 | 5 | 19 | 25 |
| $X_3$ | | | 31 | −26 | 10 | −29 | −31 | −10 | −8 | −31 | 13 |
| $X_4$ | | | | 58 | 27 | −32 | 21 | 6 | 7 | −28 | −49 |
| $X_5$ | | | | | 27 | −25 | −34 | −6 | 3 | −24 | −27 |
| $X_6$ | | | | | | 108 | −68 | −6 | 5 | 35 | −37 |
| $X_7$ | | | | | | | 127 | 6 | 4 | 17 | −39 |
| $l_1$ | | | | | | | | 11 | 9 | 16 | 43 |
| $l_2$ | | | | | | | | | 12 | 14 | 36 |
| $k_1$ | | | | | | | | | | 93 | 60 |
| $k_s$ | | | | | | | | | | | 236 |

a) The error matrix refers to the analysis ED+MW listed in Table 3. $X_1$ through $X_7$ represent $r$(C=O), $r$(C–N), $r$(N–$H_{av}$), $r$(C–$H_a$), ∠N–C=O, ∠C–N–$H_c$, and ∠C–N–$H_t$, respectively; $l_1$=$l$(C=O), $l_2$=$l$(C–N); $k_1$ and $k_s$ are indices of resolution for the long and short camera-distance data, respectively. Units ($\times 10^{-4}$) for the distances are Å, those for the angles are rad, and those for the indices are dimensionless.

tively.) When the differences were varied to minimize the residuals of the rotational constants, the optimum values were found to be 0.002±0.002 Å and 0.003±0.003 Å, respectively. The rest of the isotopic differences were ignored.

The results of the joint analysis are listed in Table 3. The skeletal structure is essentially the same as that determined in the analysis of the diffraction intensity alone. All the rotational constants calculated from the most probable parameters are consistent with those estimated from the observed $B_0$ constants, as shown in Table 5. The molecular intensity and the radial distribution curves calculated by the use of the most probable parameters are compared in Figs. 1 and 2, respectively, with the observed curves. The error matrix is given in Table 6.

## Discussion

In comparison with the $r_s$-structure determined by microwave spectroscopy,[5-7] listed in Table 2, the $r_g$(C–N) and $r_g$(C=O) distances appear to be about 0.01 Å longer and shorter, respectively, although uncertainties of more than 0.01 Å in the microwave $r_s$-structure rule out a more definitive discussion. The difference of about 0.02 Å between the $r_g$ and $r_s$ distances involving hydrogen atoms (N–H and C–H) is a reasonable order of magnitude.[4] On the other hand, the $\phi_z$(N–C=O) angle is essentially equal to the corresponding angle in the $r_s$ structure.

The skeletal bond distances in simple amide vapors are compared in Table 7 with those observed in molecular crystals.[31-33] As pointed out for acetamide[1] and *N*-methylacetamide,[2] the C–N and C=O bonds in the gas phase are about 0.07 Å longer and about 0.04 Å shorter, respectively, than those in the crystal phase. Since similar differences have been observed in the corresponding comparisons of the C=O and C–O bond distances in the gas-phase monomers and solids of formic acid[34,35] and acetic acid,[36,37] as shown in Table 7, the trends observed in the amides can be ascribed to the influence of the strong intermolecular hydrogen bonds existing in the amide crystals, which tends to increase and decrease, respectively, the double-bond characters of the C–N and C=O bonds.

A replacement of the hydrogen atom attached to the carbon atom in an N–C=O system by a methyl group has a significant influence on the structure as evidenced

Table 7. Comparison of skeletal bond distances in the gas and crystal phases (in Å)

| | C=O | | C–N | | Ref. | |
|---|---|---|---|---|---|---|
| | gas ($r_g$) | cryst.[a] | gas ($r_g$) | cryst. | gas | cryst. |
| $HCONH_2$ | 1.212(3) | 1.255(13) | 1.368(3) | 1.300(13) | b | 31 |
| $CH_3CONH_2$ | 1.220(3) | 1.260(11) | 1.380(4) | 1.334(17) | 1 | 32 |
| $CH_3CONHCH_3$ | 1.225(3) | 1.236(12) | 1.386(4) | 1.290(13) | 2 | 33 |
| | C=O | | C–O | | Ref. | |
| | gas($r_a$) | cryst. | gas($r_a$) | cryst. | gas | cryst. |
| HCOOH | 1.217(3) | 1.23 ( 3) | 1.361(3) | 1.26 ( 3) | 34 | 35 |
| $CH_3COOH$ | 1.214(3) | 1.220( 6) | 1.364(3) | 1.318( 7) | 36 | 37 |

a) Bond lengths in molecules in the crystal phase studied by X-ray diffraction.
b) Present study.

Table 8. Comparison of carbon valence angles[a]

| | ∠N–C=O | Ref. | | ∠C–C=O | Ref. | | ∠C–C=C | Ref. |
|---|---|---|---|---|---|---|---|---|
| $HCONH_2$ | 125.0(4) | b | $HCOCH_3$ | 124.2(5) | 38, 39 | $CH_3CH=CH_2$ | 124.3(4) | 9 |
| $CH_3CONH_2$ | 122.0(5) | 1 | $CH_3COCH_3$ | 122.0(2) | 40 | $(CH_3)_2C=CH_2$ | 122.2(2) | 42 |
| $CH_3CONHCH_3$ | 121.8(4) | 2 | $CH_3COCH_2CH_3$ | 121.3(7) | 41 | | | |

a) The $r_z$ structures. Numbers in parentheses represent estimated limits of experimental error in 0.1 degrees.
b) Present study.

in Table 7 and also in Table 8, where observed carbon valence angles formed by a single bond and a double bond are listed. The methyl substitutions in formamide forming acetamide and *N*-methylacetamide increase the C–N and C=O bond lengths simultaneously by about 0.01 Å or more and decrease the N–C=O angle by about 3°. Analogous trends are observed in the acetaldehyde[38,39]–acetone[40]–methyl ethyl ketone[41] system and in the propene[9]–isobutene[42] system. These systematic trends conform to those observed in many more methyl-substituted compounds collected by Jacob *et al.*,[43] who accounted for the trends consistently in terms of the influence of interactions among nonbonded atoms.

The $r_g(N–H_{av})$ and $r_g(C–H_a)$ distances listed in Table 3 (ED+MW) are essentially equal to, respectively, the $r_g$(N–H) distance in $NH_3$ ($1.030\pm0.002$ Å)[44] and the $r_g$(C–H) distances in a number of aldehydes (1.13 Å).[4]

The authors are indebted to Professor Eizi Hirota of Kyushu University for his supply of numerical data prior to publication and for his helpful discussions.

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