*Journal of Molecular Structure (Theochem)*, 236 (1991) 97–111
Elsevier Science Publishers B.V., Amsterdam



# Conformers of *cis*-*N*-methylacetamide. Ab initio study of geometries and vibrational spectra

Noemi G. Mirkin and Samuel Krimm

*Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, MI 48109 (USA)*

(Received 25 January 1991)

**Abstract**

Energies and geometries have been obtained, at the Hartree-Fock 4-31G* level, for the four stable conformers of *cis*-*N*-methylacetamide that result from conformational isomerism of the $CH_3$ groups. Ab initio force fields were obtained for these four structures, the scale factors being transferred from the experimentally refined ones for the trans molecule with the minimum change required to give agreement with the available data on the cis molecule. The latter required a change only in the scale factor for the CN stretch, and resulted in good agreement between observed and calculated bands. Comparisons of properties are made between the four cis conformers and between the lowest energy conformers of *trans*- and *cis*-*N*-methylacetamide.

## INTRODUCTION

In a recent paper [1], we calculated the ab initio geometries, energies and force fields of the four stable conformers of *trans*-*N*-methylacetamide (*t*-NMA) that result from conformational isomerism of the $CH_3$ groups. The force constants were scaled to reproduce the experimental matrix-isolated frequencies [2–4], taking into account the fact that, because of the very small predicted energy differences, the conformers could be expected to co-exist in the matrix. The observed bands could be interpreted in terms of predicted modes that differed detectably in frequency between the four conformers. Since the fully relaxed geometries also resulted in planar peptide groups, the satisfactory vibrational assignments to the four conformers indicated that it is not necessary to invoke the existence of a non-planar peptide group [3] in order to account for the unexpected additional bands in the spectra.

Comparison of room-temperature-nozzle and high-temperature-nozzle matrix isolation spectra of NMA [4] suggested the presence of *cis*-NMA (*c*-NMA) in the latter case, a conclusion supported by normal mode calculations [4]. The latter, however, were based on a force field and internal geometry transferred from *t*-NMA, assumptions that may not be warranted. Further interest

in *c*-NMA results from the proposal [5], recently confirmed [6], that *c*-NMA is formed in aqueous solutions by photoisomerization of *t*-NMA in the presence of high energy laser pulses.

We have, therefore, thought it worthwhile to perform an ab initio study of the geometries, energies and force fields of conformers of *c*-NMA. This paper reports the results for the isolated molecule, which already show [7] that its vibrational dynamics cannot be obtained by simply transferring the geometry and force field from *t*-NMA. A subsequent paper [8] discusses the normal modes of a hydrogen-bonded NMA molecule, modeled by NMA to which are bonded two $H_2O$ molecules, one at the C=O group and the other at the NH group. Not surprisingly [7], its normal modes differ significantly from those of the isolated molecule.

TABLE 1

Relative ab initio energies (in kcal $mol^{-1}$) of equilibrium conformers of *cis*-*N*-methylacetamide

| Conformer | 3-21G | 4-31G | 4-31G* | 6-31G | 6-31G* |
|---|---|---|---|---|---|
| **I** | 0 | 0 | 0 | 0 | 0 |
| **II** | 0.79 | 0.67 | 0.53 | 0.66 | 0.54 |
| **III** | 1.58 | 1.07 | 0.91 | 0.98 | 0.86 |
| **IV** | 2.96 | 2.37 | 2.09 | 2.28 | 2.05 |

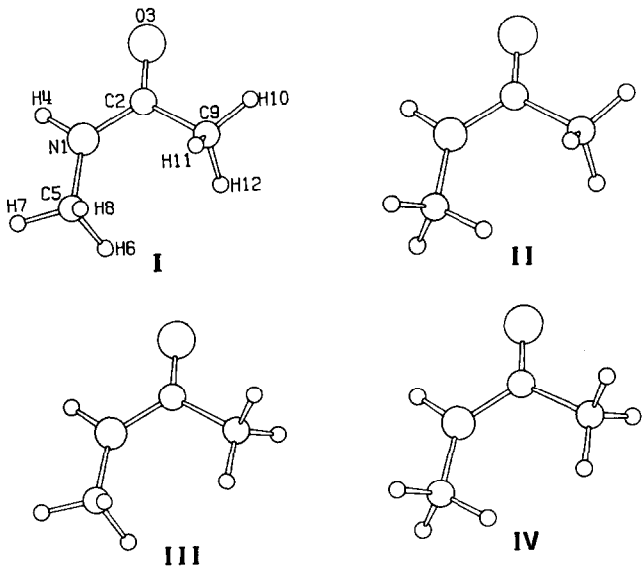


Fig. 1. Equilibrium conformers of *cis*-*N*-methylacetamide.

ENERGIES AND GEOMETRIES

As with *t*-NMA [1], we determined the equilibrium geometry of each conformer from a minimization of the total energy using the gradient method and with simultaneous relaxation of all geometric parameters and no initial assumption of planar symmetry. Calculations were carried out at the Hartree–Fock level with 3-21G, 4-31G, 4-31G*, 6-31G and 6-31G* basis sets, using GAUSSIAN 86.

The relative energies of the four conformers with these basis sets are given in Table 1, and the structures are shown in Fig. 1. The order of stability, dis-

TABLE 2

Optimized 4-31G* geometric parameters of conformers of *cis-N*-methylacetamide

| Parameter[a] | Conformer | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| CC | 1.512 | 1.514 | 1.514 | 1.514 |
| CO | 1.198 | 1.198 | 1.199 | 1.200 |
| CN | 1.355 | 1.355 | 1.353 | 1.354 |
| NH | 0.995 | 0.996 | 0.995 | 0.997 |
| NC | 1.443 | 1.441 | 1.443 | 1.442 |
| (N)CH[b] | 1.080 | 1.078 | 1.081 | 1.077 |
| (N)CH[c] | 1.084 | 1.084 | 1.084 | 1.084 |
| (C)CH[b] | 1.079 | 1.079 | 1.080 | 1.078 |
| (C)CH[c] | 1.084 | 1.084 | 1.083 | 1.082 |
| CCN | 116.5 | 117.7 | 118.3 | 120.2 |
| OCN | 121.4 | 120.9 | 121.2 | 120.4 |
| CNH | 113.9 | 113.0 | 113.3 | 111.8 |
| CNC | 127.5 | 129.5 | 128.6 | 131.6 |
| NCH[b] | 108.2 | 110.6 | 107.9 | 111.1 |
| NCH[c] | 112.2 | 111.0 | 112.2 | 110.8 |
| CCH[b] | 108.2 | 107.7 | 114.9 | 116.0 |
| CCH[c] | 111.1 | 111.3 | 108.0 | 107.6 |
| OCNH | 0 | 0 | 0 | 0 |
| OCNC | 180.0 | 180.0 | 180.0 | 180.0 |
| CCNH | 180.0 | 180.0 | 180.0 | 180.0 |
| CNCH[b] | 180.0 | 0 | 180.0 | 0 |
| CNCH[c] | −61.2 | −119.7 | −61.4 | −119.9 |
| CNCH[c] | 61.2 | 119.7 | 61.4 | 119.9 |
| NCCH[b] | 180.0 | 180.0 | 0 | 0 |
| NCCH[c] | −60.0 | −60.3 | −122.1 | −122.3 |
| NCCH[c] | 60.0 | 60.3 | 122.1 | 122.3 |

[a]Bond lengths in Å, bond angles in degrees.
[b]In-plane H atoms.
[c]Out-of-plane H atoms.

tinct from the case of *t*-NMA [1], is the same for all basis sets; however, the energy differences between conformers are much larger than for *t*-NMA, where the maximum differences were 0.1–0.2 kcal $mol^{-1}$ for the 4-31G(G*) and 6-31G(G*) basis sets. As in the case of *t*-NMA [1], 4-31G* frequencies were found to be about the same as 6-31G* frequencies, and we therefore report here the 4-31G* geometries (Table 2) and force fields. It is interesting to note that the lowest energy cis conformer has the same local $CH_3$ group conformations as does the comparable trans conformer. The energy difference between these structures is 2.45 kcal $mol^{-1}$, consistent with that found in other ab initio studies [9,10] and with that obtained from temperature-dependent matrix-isolation studies (about 2.3 kcal $mol^{-1}$) [4].

## FORCE CONSTANTS AND VIBRATIONAL FREQUENCIES

Force constants were calculated for the optimized 4-31G* geometries of each of the four conformers by analytically computing the second derivatives of the energy at the Hartree–Fock level. These force constants in cartesian coordinates were then transformed into force constants in internal coordinates. The internal coordinates for *c*-NMA are given in Table 3, and in Table 4 we give the local symmetry coordinates (for conformer **I**) used in the normal mode calculations. The equilibrium structure has a plane of symmetry, and the 30 normal modes of vibration are divided into 19 in-plane (A′) and 11 out-of-plane (A″) modes.

TABLE 3

International coordinates of *cis-N*-methylacetamide[a]

| | |
|---|---|
| $R_1 = \Delta r(C_2\text{-}N_1)$ | $R_{18} = \Delta\theta(C_2\text{-}C_9\text{-}H_{10})$ |
| $R_2 = \Delta r(C_2\text{-}O_3)$ | $R_{19} = \Delta\theta(C_2\text{-}C_9\text{-}H_{11})$ |
| $R_3 = \Delta r(C_2\text{-}C_9)$ | $R_{20} = \Delta\theta(C_2\text{-}C_9\text{-}H_{12})$ |
| $R_4 = \Delta r(N_1\text{-}C_5)$ | $R_{21} = \Delta\theta(H_{10}\text{-}C_9\text{-}H_{11})$ |
| $R_5 = \Delta r(N_1\text{-}H_4)$ | $R_{22} = \Delta\theta(H_{10}\text{-}C_9\text{-}H_{12})$ |
| $R_6 = \Delta r(C_9\text{-}H_{10})$ | $R_{23} = \Delta\theta(H_{11}\text{-}C_9\text{-}H_{12})$ |
| $R_7 = \Delta r(C_9\text{-}H_{11})$ | $R_{24} = \Delta\theta(N_1\text{-}C_5\text{-}H_6)$ |
| $R_8 = \Delta r(C_9\text{-}H_{12})$ | $R_{25} = \Delta\theta(N_1\text{-}C_5\text{-}H_7)$ |
| $R_9 = \Delta r(C_5\text{-}H_6)$ | $R_{26} = \Delta\theta(N_1\text{-}C_5\text{-}H_8)$ |
| $R_{10} = \Delta r(C_5\text{-}H_7)$ | $R_{27} = \Delta\theta(H_6\text{-}C_5\text{-}H_7)$ |
| $R_{11} = \Delta r(C_5\text{-}H_8)$ | $R_{28} = \Delta\theta(H_6\text{-}C_5\text{-}H_8)$ |
| $R_{12} = \Delta\theta(C_9\text{-}C_2\text{-}O_3)$ | $R_{29} = \Delta\theta(H_7\text{-}C_5\text{-}H_8)$ |
| $R_{13} = \Delta\theta(C_9\text{-}C_2\text{-}N_1)$ | $R_{30} = \Delta\omega(C_2O_3)$ |
| $R_{14} = \Delta\theta(O_3\text{-}C_2\text{-}N_1)$ | $R_{31} = \Delta\omega(N_1H_4)$ |
| $R_{15} = \Delta\theta(C_2\text{-}N_1\text{-}C_5)$ | $R_{32} = \Delta\tau(C_2N_1)$ |
| $R_{16} = \Delta\theta(C_2\text{-}N_1\text{-}H_4)$ | $R_{33} = \Delta\tau(C_9C_2)$ |
| $R_{17} = \Delta\theta(C_5\text{-}N_1\text{-}H_4)$ | $R_{34} = \Delta\tau(N_1C_5)$ |

[a]For atom numbering see Fig. 1.

TABLE 4

Symmetry coordinates of *cis*-*N*-methylacetamide[a]

| Symmetry coordinate | Description[b] |
|---|---|
| A′ Modes | |
| $S_1 = R_1$ | CN s |
| $S_2 = R_2$ | CO s |
| $S_3 = R_3$ | CC s |
| $S_4 = R_4$ | NC s |
| $S_5 = R_5$ | NH s |
| $S_6 = R_6 + R_7 + R_8$ | $CCH_3$ ss |
| $S_7 = 2R_6 - R_7 - R_8$ | $CCH_3$ as |
| $S_8 = R_9 + R_{10} + R_{11}$ | $NCH_3$ ss |
| $S_9 = 2R_{10} - R_9 - R_{11}$ | $NCH_3$ as |
| $S_{10} = 2R_{13} - R_{12} - R_{14}$ | CCN d |
| $S_{11} = R_{12} - R_{14}$ | CO ib |
| $S_{12} = R_{12} + R_{13} + R_{14}$ | Red 1 |
| $S_{13} = 2R_{15} - R_{16} - R_{17}$ | CNC d |
| $S_{14} = R_{16} - R_{17}$ | NH ib |
| $S_{15} = R_{15} + R_{16} + R_{17}$ | Red 2 |
| $S_{16} = R_{21} + R_{22} + R_{23} - R_{18} - R_{19} - R_{20}$ | $CCH_3$ sb |
| $S_{17} = 2R_{18} - R_{19} - R_{20}$ | $CCH_3$ r |
| $S_{18} = 2R_{23} - R_{22} - R_{21}$ | $CCH_3$ ab |
| $S_{19} = R_{18} + R_{19} + R_{20} + R_{21} + R_{22} + R_{23}$ | Red 3 |
| $S_{20} = R_{27} + R_{28} + R_{29} - R_{24} - R_{25} - R_{26}$ | $NCH_3$ sb |
| $S_{21} = 2R_{25} - R_{24} - R_{26}$ | $NCH_3$ r |
| $S_{22} = 2R_{28} - R_{27} - R_{29}$ | $NCH_3$ ab |
| $S_{23} = R_{24} + R_{25} + R_{26} + R_{27} + R_{28} + R_{29}$ | Red 4 |
| A″ Modes | |
| $S_{24} = R_7 - R_8$ | $CCH_3$ as |
| $S_{25} = R_9 - R_{11}$ | $NCH_3$ as |
| $S_{26} = R_{19} - R_{20}$ | $CCH_3$ r |
| $S_{27} = R_{22} - R_{21}$ | $CCH_3$ ab |
| $S_{28} = R_{24} - R_{26}$ | $NCH_3$ r |
| $S_{29} = R_{27} - R_{29}$ | $NCH_3$ ab |
| $S_{30} = R_{30}$ | CO ob |
| $S_{31} = R_{31}$ | NH ob |
| $S_{32} = R_{32}$ | CN t |
| $S_{33} = R_{33}$ | CC t |
| $S_{34} = R_{34}$ | NC t |

[a]Coordinates given for conformer I. Normalization constants are not shown.

[b]s = stretch, ss = symmetric stretch, as = antisymmetric stretch, sb = symmetric bend, ab = antisymmetric bend, ib = in-plane bend, ob = out-of-plane bend, d = deformation, r = rock, t = torsion, Red = redundancy.

TABLE 5

Scale factors for *cis*-*N*-methylacetamide

| Internal coordinate | Scale factor |
|---|---|
| CN stretch | 0.840 |
| CO stretch | 0.717 |
| CC stretch and NC stretch | 0.859 |
| NH stretch | 0.808 |
| CH stretch | 0.826 |
| Non-hydrogen in-plane deformations | 0.998 |
| CNH bend | 0.763 |
| NCH bend and CCH bend | 0.782 |
| HCH bend | 0.778 |
| Out-of-plane bend and torsion | 0.880 |

The number of observed bands specifically assignable to *c*-NMA from the temperature-dependent matrix-isolation studies [4] is relatively small, and it was therefore not feasible to depend on a totally independent refinement of scale factors, as we did for *t*-NMA [1]. Conversely, it is reasonable to expect that the scale factors for *t*-NMA should be a good first approximation to those for *c*-NMA, and to proceed at this stage by making the minimal changes consistent with obtaining agreement with observation. In the spirit of this approach, we have found (see discussion below) that satisfactory agreement is obtained by changing only one scale factor, that for the CN stretch s being changed from 0.74 to 0.84. The resulting scale factors, used for all conformers of *c*-NMA, are given in Table 5, and the scaled force constants are given in Table 6 (diagonal) and Table 7 (off-diagonal $\geq 0.03$).

In calculating the normal mode frequencies, we found that one of the lowest frequencies, a methyl torsion, was negative. As in the case of *t*-NMA, where we encountered two negative torsions, we believe that this is a result of the large and in some cases negative off-diagonal force constants involving CC torsion t and NC t. Since these diagonal force constants are positive and very small (e.g. 0.04 and 0.02, respectively, for conformer **I**), we believe, as before [1], that this part of the potential surface is probably not well described at this basis set level, and we have again [1] chosen to exclude these two coordinates from the calculation (equivalent to assuming free rotation of the $CH_3$ groups). This approximation has no effect on the A′ frequencies and eigenvectors nor on the higher frequency A″ modes, but it will influence the lower frequency A″ modes (those below about 600 $cm^{-1}$), and therefore quantitative aspects of these must be accepted with care at present. In Table 8 we present the calculated frequencies of the four conformers and the eigenvectors for conformer **I**, and compare these with the observed bands for *c*-NMA [4].

TABLE 6

Scaled diagonal force constants of *cis*-*N*-methylacetamide

| Force constant[a] | Value[b] | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| A′ Modes | | | | |
| CN s | 6.652 | 6.669 | 6.710 | 6.735 |
| CO s | 10.965 | 10.927 | 10.888 | 10.819 |
| CC s | 4.252 | 4.254 | 4.257 | 4.248 |
| NC s | 5.424 | 5.384 | 5.400 | 5.367 |
| NH s | 6.679 | 6.618 | 6.663 | 6.591 |
| $CCH_3$ ss | 4.959 | 4.964 | 4.992 | 5.012 |
| $CCH_3$ as | 4.920 | 4.920 | 4.903 | 4.936 |
| $NCH_3$ ss | 4.939 | 4.964 | 4.940 | 4.982 |
| $NCH_3$ as | 4.832 | 4.902 | 4.834 | 4.936 |
| CCN d | 1.378 | 1.477 | 1.459 | 1.622 |
| CO ib | 1.464 | 1.438 | 1.391 | 1.436 |
| CNC d | 0.905 | 0.993 | 0.927 | 1.100 |
| NH ib | 0.490 | 0.493 | 0.499 | 0.503 |
| $CCH_3$ sb | 0.528 | 0.530 | 0.537 | 0.537 |
| $CCH_3$ r | 0.609 | 0.619 | 0.605 | 0.603 |
| $CCH_3$ ab | 0.520 | 0.524 | 0.514 | 0.516 |
| $NCH_3$ sb | 0.601 | 0.600 | 0.602 | 0.599 |
| $NCH_3$ r | 0.776 | 0.764 | 0.782 | 0.759 |
| $NCH_3$ ab | 0.560 | 0.563 | 0.566 | 0.563 |
| A″ Modes | | | | |
| $CCH_3$ as | 4.766 | 4.778 | 4.844 | 4.848 |
| $NCH_3$ as | 4.709 | 4.693 | 4.715 | 4.697 |
| $CCH_3$ r | 0.529 | 0.529 | 0.571 | 0.581 |
| $CCH_3$ ab | 0.519 | 0.525 | 0.520 | 0.517 |
| $NCH_3$ r | 0.766 | 0.776 | 0.765 | 0.780 |
| $NCH_3$ ab | 0.540 | 0.542 | 0.543 | 0.538 |
| CO ob | 0.843 | 0.819 | 0.829 | 0.833 |
| NH ob | 0.061 | 0.070 | 0.061 | 0.082 |
| CN t | 0.272 | 0.285 | 0.285 | 0.218 |
| CC t | 0.044 | 0.072 | 0.015 | 0.027 |
| NC t | 0.023 | 0.001 | 0.046 | 0.013 |

[a]s = stretch, ss = symmetric stretch, as = antisymmetric stretch, sb = symmetric bend, ab = antisymmetric bend, ib = in-plane bend, ob = out-of-plane bend, d = deformation, r = rock, t = torsion.

[b]mdyn $Å^{-1}$ for stretch and stretch, stretch constants; mdyn for stretch, bend constants; mdyn Å for all others.

TABLE 7

Scaled off-diagonal force constants ($\geq 0.03$) of *cis*-*N*-methylacetamide

| Force constant[a] | Value[b] | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| A′ Modes | | | | |
| 1-2 | 1.294 | 1.318 | 1.311 | 1.346 |
| 1-3 | 0.336 | 0.332 | 0.305 | 0.310 |
| 1-4 | 0.165 | 0.168 | 0.169 | 0.180 |
| 1-5 | 0.080 | 0.073 | 0.079 | 0.077 |
| 1-7 | 0.003 | −0.005 | −0.021 | −0.041 |
| 1-8 | −0.067 | −0.090 | −0.066 | −0.104 |
| 1-9 | 0.028 | −0.049 | 0.030 | −0.069 |
| 1-10 | 0.241 | 0.277 | 0.258 | 0.332 |
| 1-11 | −0.437 | −0.448 | −0.434 | −0.467 |
| 1-13 | 0.214 | 0.253 | 0.239 | 0.313 |
| 1-14 | 0.115 | 0.120 | 0.118 | 0.127 |
| 1-16 | −0.053 | −0.052 | −0.058 | −0.070 |
| 1-17 | −0.016 | −0.018 | 0.048 | 0.074 |
| 1-18 | 0.024 | 0.030 | −0.008 | −0.009 |
| 1-20 | 0.028 | 0.022 | 0.029 | 0.014 |
| 1-21 | 0.038 | 0.065 | 0.031 | 0.083 |
| 2-3 | 0.498 | 0.504 | 0.531 | 0.534 |
| 2-4 | −0.012 | −0.019 | −0.031 | −0.021 |
| 2-6 | 0.030 | 0.027 | 0.026 | 0.025 |
| 2-8 | 0.033 | 0.034 | 0.035 | 0.035 |
| 2-10 | −0.480 | −0.486 | −0.465 | −0.484 |
| 2-11 | −0.135 | −0.094 | −0.106 | −0.110 |
| 2-13 | 0.035 | 0.051 | 0.046 | 0.049 |
| 2-16 | −0.046 | −0.048 | −0.046 | −0.047 |
| 2-17 | −0.061 | −0.055 | 0.070 | 0.074 |
| 2-20 | −0.039 | −0.037 | −0.036 | −0.038 |
| 2-21 | 0.010 | −0.042 | 0.006 | −0.042 |
| 3-4 | 0.001 | 0.030 | 0.023 | 0.049 |
| 3-6 | 0.046 | 0.050 | 0.035 | 0.025 |
| 3-7 | −0.034 | −0.033 | −0.034 | −0.044 |
| 3-10 | 0.177 | 0.206 | 0.238 | 0.231 |
| 3-11 | 0.294 | 0.301 | 0.282 | 0.302 |
| 3-13 | 0.014 | 0.056 | 0.075 | 0.123 |
| 3-16 | −0.221 | −0.225 | −0.239 | −0.240 |
| 3-17 | 0.065 | 0.065 | 0.016 | 0.005 |
| 3-21 | −0.003 | 0.021 | −0.012 | 0.036 |
| 4-8 | 0.263 | 0.245 | 0.251 | 0.235 |
| 4-9 | −0.097 | −0.120 | −0.099 | −0.127 |
| 4-10 | 0.019 | 0.057 | 0.015 | 0.098 |
| 4-13 | 0.139 | 0.177 | 0.092 | 0.178 |
| 4-14 | −0.172 | −0.149 | −0.176 | −0.155 |
| 4-17 | −0.025 | −0.036 | 0.023 | 0.051 |
| 4-20 | −0.469 | −0.459 | −0.467 | −0.460 |

TABLE 7 (continued)

| Force constant[a] | Value[b] | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| 4-21 | −0.041 | −0.052 | −0.035 | −0.056 |
| 5-10 | 0.095 | 0.064 | 0.066 | 0.067 |
| 5-11 | 0.061 | 0.058 | 0.056 | 0.063 |
| 5-13 | −0.061 | −0.089 | −0.077 | −0.089 |
| 5-14 | 0.016 | 0.052 | 0.068 | 0.054 |
| 6-7 | 0.092 | 0.091 | 0.040 | 0.063 |
| 6-10 | −0.057 | −0.013 | −0.043 | −0.074 |
| 6-13 | −0.049 | −0.025 | −0.057 | −0.085 |
| 6-16 | 0.094 | 0.088 | 0.101 | 0.109 |
| 6-17 | 0.042 | −0.003 | −0.025 | −0.038 |
| 7-9 | 0.007 | −0.013 | −0.015 | 0.043 |
| 7-10 | 0.085 | 0.102 | −0.178 | −0.222 |
| 7-11 | −0.079 | −0.081 | 0.073 | 0.076 |
| 7-13 | 0.006 | 0.012 | −0.076 | −0.115 |
| 7-16 | −0.026 | −0.003 | 0.021 | 0.031 |
| 7-17 | 0.106 | 0.090 | 0.057 | 0.037 |
| 7-18 | −0.098 | −0.106 | −0.115 | −0.117 |
| 8-9 | 0.065 | 0.116 | 0.061 | 0.137 |
| 8-10 | −0.014 | −0.075 | −0.029 | −0.102 |
| 8-11 | −0.027 | −0.026 | −0.029 | −0.027 |
| 8-13 | 0.024 | −0.065 | −0.007 | −0.089 |
| 8-20 | 0.106 | 0.115 | 0.110 | 0.120 |
| 9-10 | 0.027 | −0.098 | 0.022 | −0.135 |
| 9-13 | 0.069 | −0.144 | 0.052 | −0.179 |
| 9-21 | 0.055 | 0.045 | 0.071 | 0.031 |
| 9-22 | −0.140 | −0.135 | −0.134 | −0.136 |
| 10-11 | 0.141 | 0.129 | 0.152 | 0.159 |
| 10-13 | 0.131 | 0.236 | 0.198 | 0.404 |
| 10-14 | 0.093 | 0.092 | 0.094 | 0.092 |
| 10-16 | −0.037 | −0.040 | −0.071 | −0.090 |
| 10-17 | 0.106 | 0.094 | −0.045 | −0.003 |
| 10-18 | 0.053 | 0.063 | −0.026 | −0.026 |
| 10-20 | −0.001 | −0.017 | 0.002 | −0.036 |
| 10-21 | −0.035 | 0.093 | −0.044 | 0.127 |
| 11-13 | −0.092 | −0.099 | −0.097 | −0.090 |
| 11-14 | 0.056 | 0.055 | 0.057 | 0.055 |
| 11-16 | −0.032 | −0.032 | −0.024 | −0.025 |
| 11-17 | −0.094 | −0.091 | 0.119 | 0.118 |
| 13-16 | −0.011 | −0.014 | −0.029 | −0.053 |
| 13-17 | −0.062 | −0.068 | 0.091 | 0.139 |
| 13-18 | 0.022 | 0.035 | −0.005 | −0.004 |
| 13-20 | −0.032 | −0.053 | −0.024 | −0.065 |
| 13-21 | 0.051 | −0.015 | 0.042 | 0.009 |
| 13-22 | 0.023 | −0.015 | 0.036 | −0.016 |
| 14-21 | 0.034 | −0.060 | 0.033 | −0.060 |
| 17-21 | 0.007 | −0.016 | −0.010 | 0.036 |
| 21-22 | −0.048 | −0.037 | −0.055 | −0.036 |

TABLE 7 (continued)

| Force constant[a] | Value[b] | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| A″ Modes | | | | |
| 24-26 | 0.092 | 0.113 | 0.113 | 0.112 |
| 24-27 | −0.138 | −0.129 | 0.123 | 0.124 |
| 24-30 | −0.071 | −0.046 | −0.046 | −0.048 |
| 25-28 | 0.072 | −0.057 | 0.051 | 0.056 |
| 25-29 | 0.133 | −0.137 | 0.141 | 0.137 |
| 25-31 | −0.034 | 0.023 | −0.022 | 0.021 |
| 26-30 | −0.122 | −0.127 | −0.120 | −0.118 |
| 26-32 | −0.022 | −0.037 | −0.034 | −0.047 |
| 28-29 | 0.029 | 0.040 | 0.026 | 0.040 |
| 28-30 | 0.009 | 0.031 | 0.017 | −0.032 |
| 28-31 | −0.046 | −0.035 | −0.046 | 0.034 |
| 28-32 | −0.031 | −0.035 | −0.031 | 0.045 |
| 30-31 | 0.056 | 0.051 | 0.042 | 0.048 |
| 30-32 | −0.083 | −0.092 | −0.064 | −0.104 |
| 31-32 | 0.051 | 0.048 | 0.078 | 0.091 |

[a]Numbers designate symmetry coordinates of Table 4.
[b]mdyn $Å^{-1}$ for stretch and stretch, stretch constants; mdyn for stretch, bend constants; mdyn Å for all others.

## DISCUSSION

The energy differences between conformers of *c*-NMA (Table 1) are significantly larger than those between conformers of *t*-NMA [1]. In the latter case, the maximum difference was about 0.2 kcal $mol^{-1}$, which led to our presumption, fulfilled by the analysis, that all conformers could be present in a matrix-isolated sample. For *c*-NMA, with a nozzle temperature of 770 K [4], conformers **I** and **II** will predominate in the matrix (about 68% if the gas-phase proportion is maintained in the 20 K matrix) over conformers **III** and **IV**.

As for the geometries, the variations in bond lengths and angles between conformers are comparable to what we found for *t*-NMA [1]. In comparing the two isomers, cis and trans, the bond lengths are generally similar, except for the CN bond, which, for the lowest energy conformers, is 0.004 Å longer in *c*-NMA, and the NH bond, which is 0.003 Å longer in *c*-NMA. The CCN and OCN bond angles are within about 1° of each other, but the CNH angle is 5.6° smaller and the CNC angle is 6.1° larger in *c*-NMA. The isomer differences for these bond length and angle parameters follow similar results for formamide and *N*-methylformamide [11]. Such differences would clearly not warrant assuming the same geometric parameters for the two isomers [4].

Not surprisingly, force constants vary between conformers (see Table 6). The variation in most cases is within a few percent, as in the case of *t*-NMA

TABLE 8

Observed and calculated frequencies (in $cm^{-1}$) of conformers cis-N-methylacetamide

| Observed[a] | Calculated | | | | PED[b] |
|---|---|---|---|---|---|
| | I | II | III | IV | |
| A′ Modes | | | | | |
| 3458 | 3471 | 3454 | 3467 | 3446 | NH s(100) |
| (3008) | 3031 | 3032 | 3019 | 3051 | $CCH_3$ as(93) |
| (2973) | 3001 | 3027 | 3000 | 3021 | $NCH_3$ as(93) |
| (2958) | 2923 | 2924 | 2939 | 2943 | $CCH_3$ ss(86) |
| (2915) | 2914 | 2915 | 2915 | 2917 | $NCH_3$ ss(86) |
| (1707) | 1717 | 1712 | 1709 | 1701 | CO s(78) CCN d(12) |
| 1485 | 1481 | 1502 | 1485 | 1510 | $NCH_3$ ab(54) CN s(16) $NCH_3$ r(14) |
| 1454 | 1465 | 1464 | 1474 | 1462 | $NCH_3$ sb(41) $NCH_3$ ab(25) CN s(17) |
| 1432 | 1438 | 1447 | 1441 | 1447 | NH ib(34) $NCH_3$ sb(27) NC s(16) $NCH_3$ ab(14) |
| (1419) | 1424 | 1424 | 1429 | 1443 | $CCH_3$ ab(77) $NCH_3$ sb(18) |
| 1387 | 1392 | 1392 | 1383 | 1383 | $CCH_3$ sb(44) NH ib(21) $NCH_3$ sb(13) |
| 1325 | 1331 | 1335 | 1343 | 1345 | $CCH_3$ sb(51) CN s(17) NH ib(12) CO ib(12) |
| | 1204 | 1180 | 1206 | 1180 | NC s(40) $NCH_3$ r(30) |
| 1075 | 1083 | 1086 | 1079 | 1080 | $NCH_3$ r(31) NC s(21) $CCH_3$ r(15) NH ib(12) |
| (980) | 983 | 976 | 997 | 991 | $CCH_3$ r(52) $NCH_3$ r(16) |
| | 798 | 791 | 787 | 776 | CC s(52) CN s(20) NC s(10) |
| 607 | 596 | 596 | 598 | 597 | CO ib(28) NC s(17) CCN d(12) CC s(10) |
| 510 | 523 | 523 | 514 | 509 | CCN d(43) CO ib(41) CNC d(26) $CCH_3$ r(23) |
| (279) | 294 | 320 | 309 | 352 | CNC d(53) CCN d(33) |
| A″ Modes | | | | | |
| | 2973 | 2976 | 2996 | 2997 | $CCH_3$ as(95) |
| | 2959 | 2955 | 2963 | 2956 | $NCH_3$ as(95) |
| 1454 | 1453 | 1454 | 1454 | 1448 | $NCH_3$ ab(73) $CCH_3$ ab(21) |
| 1432 | 1437 | 1439 | 1434 | 1433 | $CCH_3$ ab(72) $NCH_3$ ab(22) |
| | 1114 | 1115 | 1113 | 1116 | $NCH_3$ r(92) |
| (1037) | 1047 | 1048 | 1052 | 1053 | $CCH_3$ r(60) CO ob(23) |
| (619) | 634 | 640 | 660 | 672 | CO ob(58) $CCH_3$ r(26) CN t(12) NH ob(11) |
| 510 | 516 | 508 | 534 | 513 | CN t(36) CO ob(26) NH ob(17) $CCH_3$ r(13) |
| | 112 | 133 | 97 | 82 | NH ob(116) CN t(85) CO ob(16) |

[a]From ref. 4. Frequencies without ( ): bands that clearly develop in the high-temperature-nozzle matrix-isolated spectra. Frequencies with ( ): bands present in room-temperature-nozzle matrix-isolation spectra (see text).

[b]Potential energy distribution (contributing $\geq 10$) for conformer I.

[1], but some force constants vary by much more (about 10–25%) and the variation is generally larger for conformers of *c*-NMA than for *t*-NMA. A comparison of diagonal force constants of *c*-NMA and *t*-NMA (Table 9) shows some modest (1–4%) and some large (10–30%) differences, the latter in CN s, CCN d (deformation), NH ob (out-of-plane bend), and CN t force con-

TABLE 9

Scaled diagonal force constants of lowest energy conformers of *trans*-*N*-methylacetamide and *cis*-*N*-methylacetamide

| Force constant[a] | Isomer[b] | |
|---|---|---|
| | *t*-II | *c*-I |
| A′ Modes | | |
| CN s | 5.966 | 6.652 |
| CO s | 10.984 | 10.965 |
| CC s | 4.279 | 4.252 |
| NC s | 5.388 | 5.424 |
| NH s | 6.775 | 6.679 |
| $CCH_3$ ss | 4.948 | 4.959 |
| $CCH_3$ as | 4.908 | 4.920 |
| $NCH_3$ ss | 4.979 | 4.939 |
| $NCH_3$ as | 4.847 | 4.832 |
| CCN d | 1.246 | 1.378 |
| CO ib | 1.412 | 1.464 |
| CNC d | 0.846 | 0.905 |
| NH ib | 0.501 | 0.490 |
| $CCH_3$ sb | 0.530 | 0.528 |
| $CCH_3$ r | 0.600 | 0.609 |
| $CCH_3$ ab | 0.521 | 0.520 |
| $NCH_3$ sb | 0.606 | 0.601 |
| $NCH_3$ r | 0.761 | 0.776 |
| $NCH_3$ ab | 0.543 | 0.560 |
| A″ Modes | | |
| $CCH_3$ as | 4.755 | 4.766 |
| $NCH_3$ as | 4.798 | 4.709 |
| $CCH_3$ r | 0.543 | 0.529 |
| $CCH_3$ ab | 0.520 | 0.519 |
| $NCH_3$ r | 0.770 | 0.766 |
| $NCH_3$ ab | 0.531 | 0.540 |
| CO ob | 0.810 | 0.843 |
| NH ob | 0.043 | 0.061 |
| CN t | 0.312 | 0.272 |
| CC t | 0.007 | 0.044 |
| NC t | 0.013 | 0.023 |

[a]s = stretch, ss = symmetric stretch, as = antisymmetric stretch, sb = symmetric bend, ab = antisymmetric bend, ib = in-plane bend, ob = out-of-plane bend, d = deformation, r = rock, t = torsion.

[b]mdyn $Å^{-1}$ for stretch and stretch, stretch constants; mdyn for stretch, bend constants; mdyn Å for all others.

stants, again emphasizing the inadequacy of assuming transferability of force field [4]. A comparison of off-diagonal force constants shows two features. First, *c*-NMA has many more force constants $\geq 0.03$ than *t*-NMA, 105 vs. 82. Second, many equivalent force constants are different; in sign with comparable magnitudes (probably due to the topological inversion), in sign with different magnitudes, and of different magnitudes but the same sign (probably due to changes in electronic structure between the isomers). Perhaps most surprising is that the CN s force constant is higher in *c*-NMA than in *t*-NMA although the bond in the former is longer than that in the latter, a counter-intuitive situation particularly in view of the fact that the CN t force constants are in a proper order (at least at this basis set level). Of course, this results from using a scale factor of 0.84 for CN s in *c*-NMA instead of the value of 0.74 refined for *t*-NMA [1], and we turn now to the reasoning that justifies this change at present.

As discussed above, in the absence of extensive experimental data on *c*-NMA and believing that the scale factors refined for *t*-NMA should be essentially applicable to *c*-NMA, we have endeavored at this stage to make minimal changes in transferring scale factors. If we make no change (i.e. keep the scale factor for CN s at 0.74), all the modes of conformer **I** remain essentially the same as those given in Table 8 except four: 1476 $NCH_3$ ab(81) $NCH_3$ r(13), 1452 $NCH_3$ sb(67) $CCH_3$ ab(10), 1428 NH ib(49) CN s(16) NC s(14) $NCH_3$ ab(11), and 1317 $CCH_3$ sb(39) CN s(24) CO ib(17) (ab = antisymmetric bend, r = rock, sb = symmetric bend, ib = in-plane bend). The frequency agreement with observed cis bands is probably acceptable (see Table 8), but the resulting absence of a significant contribution from CN s above about 1430 $cm^{-1}$ is troubling. This is particularly true in view of the fact that recent studies of aqueous NMA [5,6] clearly show that a band at 1496 $cm^{-1}$ is primarily CN s, while a calculation with a scale factor of 0.74 in this case [8] results in a mode (at 1480 $cm^{-1}$) with minimal CN s and a significant NH ib component, which the 1496 $cm^{-1}$ band is known not to posses [5,6]. However, if the CN s scale factor is increased to 0.84, this mode is predicted at 1499 $cm^{-1}$ and has CN s as its major component with minimal NH ib [7,8]. We have, therefore, proposed a scale factor of 0.84 for CN s in the isolated molecule, pending further studies on isotopic derivatives to verify this assignment.

With this set of scale factors (Table 5), the agreement between calculated and presently observed frequencies of *c*-NMA is quite good (Table 8). It is worth noting that, while comparable frequency agreement was achieved for some bands in an earlier normal mode calculation [4] (though the overall agreement was poorer), the eigenvectors were quite different, for example: 1487 NH ib(46) $NCH_3$ r(16) CN s(16) and 1441 $CCH_3$ ab(97). This is undoubtedly due to the different geometries and force fields used in the calculations, and reveals the sensitivities of the normal modes to the fine details of these properties of the molecule.

Further evidence of this is seen in comparing the modes of *c*-NMA with those of *t*-NMA [1]. While previous normal mode studies of the cis peptide group in *c*-NMA [4,12] as well as in diketopiperazine [13] have pointed up the significant differences in the amide modes as compared to the trans peptide group, the earlier complete NMA calculation [4] indicated that $CH_3$ modes (ab, sb, r) are essentially unaffected. Our results do not support this conclusion. For example, in *t*-NMA we find the following modes [1] (for conformer **II**): 1469 $NCH_3$ ab(82), 1428 $CCH_3$ ab(56) $NCH_3$ sb(41), 1422 $NCH_3$ sb(54) $CCH_3$ ab(35), and 1375 $CCH_3$ sb(87) CC s(11). Comparison with similar bands in *c*-NMA (Table 8) shows that the modes are significantly different in character. (A similar result was found for *N*-methylformamide [11].) Since the local geometry differences do not seem large enough to account for such changes, we assume that this result derives mainly from differences in the force fields, probably primarily from the previously noted changes in interaction constants (the effect is not likely to be due to changes in kinetic coupling, since it did not show up when the force fields were the same [4]). Larger disparities in frequencies (60–80 $cm^{-1}$) are seen in modes that seem to be superficially similar in character. These results may indicate that the completeness of an ab initio force field is essential to a total understanding of the vibrational spectrum of a molecule.

## CONCLUSIONS

Ab initio calculations of energies, geometries, and force fields of the four conformers of *c*-NMA show that: (1) energy differences, while larger than those for *t*-NMA [1], are small enough for some conformers (0.5–1.0 kcal $mol^{-1}$) such that appreciable amounts of conformers other than the lowest energy one should typically be present; (2) bond lengths between conformers differ by up to about 0.002 Å, generally similar to those for *t*-NMA [1], while bond angles vary by about 1–4° (with an in-plane CCH angle changing by 8.3°), generally larger than the situation for *t*-NMA, about 0.5–2° (with 4.9° for the same CCH angle) [1]; (3) in-plane diagonal force constants generally vary by up to about 2%, the same as for *t*-NMA [1], except for CCN d (15%, vs. 7.4% for *t*-NMA) and CNC d (18%, vs. 13%); (4) out-of-plane diagonal force constants show some larger variations, particularly in NH ob (27%); (5) normal mode frequencies show differences between the conformers that are comparable to that found for *t*-NMA [1], up to about 25 $cm^{-1}$ in some cases (58 $cm^{-1}$ for CNC d). These results emphasize the importance of not neglecting $CH_3$ group conformation in determining the normal modes of a molecule.

In comparing the lowest energy conformers of the *c*-NMA and *t*-NMA isomers, we found the following: (1) longer CN and NH bonds in *c*-NMA and large (5–6°) changes in CCN and OCN angles; (2) some large differences (10–30%) in diagonal force constants, particularly CN s, CCN d, NH ob, and CN

t; (3) significant differences in off-diagonal force constants, both in magnitude and in sign; (4) significant differences, as expected, in amide modes (about 30 $cm^{-1}$ in amide **II**, about 65 $cm^{-1}$ in amide **III**, about 130 $cm^{-1}$ in amide **V**); (5) important differences, in frequency and in composition, of $CH_3$ modes. These results emphasize the importance of having a complete force field in trying to fully interpret the vibrational spectrum of a molecule.

ACKNOWLEDGMENT

This research was supported by National Science Foundation grants DMB-8816756 and DMR-8806975.

REFERENCES

1 N.G. Mirkin and S. Krimm, J. Mol. Struct., 242 (1991) 143.
2 F. Fillaux and C. de Lozé, J. Chim. Phys., 73 (1976) 1004.
3 F. Fillaux and C. de Lozé, J. Chim. Phys., 73 (1976) 1010.
4 S. Ataka, H. Takeuchi and M. Tasumi, J. Mol. Struct., 113 (1984) 147.
5 Y. Wang, R. Purello and T.G. Spiro, J. Am. Chem. Soc., 111 (1989) 8274.
6 S. Song, S.A. Asher, S. Krimm and K.D. Shaw, J. Am. Chem. Soc., 113 (1991) 1155.
7 N.G. Mirkin and S. Krimm, J. Am. Chem. Soc., 112 (1990) 9016.
8 N.G. Mirkin and S. Krimm, J. Am. Chem. Soc., in press.
9 A. Radzicka, L. Pedersen and R. Wolfenden, Biochemistry, 27 (1988) 4538.
10 W.L. Jorgensen and J. Gao, J. Am. Chem. Soc., 110 (1988) 4212.
11 Y. Sugawara, A. Hirakawa, M. Tsuboi, S. Kato and K. Morokuma, Chem. Phys., 62 (1981) 339.
12 T. Miyazawa, J. Mol. Spectrosc., 4 (1960) 155.
13 T.C. Cheam and S. Krimm, Spectrochim. Acta, Part A, 40 (1984) 503.