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Are Amide Mode Infrared Frequency Shifts in Crystalline α-Nylon-6 at Low Strains Due to Changes in Nitrogen Pyramidalization?

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In a recent paper,[1] Lee and Gleason (LG) undertook a detailed study of changes in the infrared spectra of thin films of α-nylon-6 subjected to low strains, up to 0.1. By deuteration of the films, which occurs primarily in the (∼50%) amorphous regions, they were able to isolate the effects of spectral changes in the crystalline regions. Dichroic measurements on the NH stretch (s) band, ν(NH), showed that the hydrogen-bonded planes were preferentially aligned parallel to the plane of the film with a random orientation in this plane. When the films were stretched, frequency changes were observed in the NH s and amide II (CN s + NH in-plane bend) modes (the films were too thick to confidently assess shifts in the amide I (C═O s) mode): for a strain of 0.1, ν(NH) of the crystalline regions increased by 4.2 cm^{-1} and ν(II) shifted down by 0.79 cm^{-1}. Moreover, the shifted NH s band exhibited parallel dichroism, indicating that the stress was acting on hydrogen-bonded chains whose axes were essentially perpendicular to the stretching direction, the NH bonds then being parallel to this direction. The authors interpreted these results, quite reasonably, in terms of a weakening of the interchain hydrogen bonds as the separation between these adjacent chains in the crystal increased with stress.

We wish to draw attention to another structural mechanism that can account for the spectroscopic results, viz., a change in the pyramidalization of the N atom as adjacent hydrogen-bonded chains are slightly separated at these small strains. X-ray diffraction determinations of the crystal structure, both the original[2] and slightly corrected[3,4] ones, indicate that the planes of adjacent chains are inclined to the *a*-axis (the hydrogen-bonded plane) by a setting angle of about 3° [4] to 8°.[3] This occurs in order to avoid steric interference between the pentamethylene segments of these chains. The result is that it is not possible to form a linear N−H···O(═C) hydrogen bond between adjacent chains (since the plane of the amide group is parallel to that of the $(CH_2)_5$ group,[2−4,5] despite suggestions to the contrary[6,7]). If the amide group remains totally planar, as is also assumed in all simulations with current molecular mechanics force fields except our SDFF,[8] then a weakened nonlinear hydrogen bond results, which is further weakened as the chains separate under the applied stress.

The hydrogen bond can easily become linear, however, if the N atom is slightly pyramidalized. We have shown[9] that this requires very little energy: for example, in *N*-methylacetamide (NMA) with a planar amide group,[8] an NH out-of plane bend angle, γ, of 10° can be achieved at a cost of ∼0.02 kcal/mol, and γ = 20° costs ∼0.15 kcal/mol.[9] This energy cost is undoubtedly compensated by the formation of a linear, and therefore stronger, hydrogen bond. As the chains become separated by the applied stress, the $(CH_2)_5$ segment steric interferences diminish (which would explain the small decrease in the frequencies of the CH_2 stretching modes seen by LG[1]), the setting angle can decrease, and linear hydrogen bonds with planar N (γ = 0°) become possible.

Table 1. Bond Lengths and Frequencies[a] of an *N*-Methylacetamide−$(H_2O)_2$ System[b] as a Function of Nitrogen Pyramidalization[c]

γ	*r*(NH)	*r*(CN)	*r*(CO)	ν(NH)	ν(I)	ν(II)
0.0	1.0151	1.3541	1.2368	3421.9	1640.2	1590.9
8.7	1.0154	1.3546	1.2366	3418.0	1641.2	1591.4
17.5	1.0157	1.3564	1.2361	3415.2	1642.9	1589.5
26.4	1.0172	1.3596	1.2354	3406.9	1645.8	1588.6

[a] B3LYP/6-31+G* calculation, scaled force constants.[10] Bond lengths in Å, frequencies in cm^{-1}. [b] Linear NH···O(H_2) and C═O···H(OH) hydrogen bonds and planar amide group (nonredundant torsion angle[8]). [c] NH out-of-plane bend angle, γ, in deg.

Pyramidalization of N, i.e., $\gamma \neq 0°$, has sprectroscopic consequences,[10] and the LG results[1] suggest that this kind of change may be happening in the low-strain α-nylon-6 crystals. To determine the magnitude of such frequency shifts, we have extended our previous ab initio calculations[10] to an NMA molecule to which two H_2O molecules are hydrogen bonded, one at the NH group and one at the C═O group. The results are shown in Table 1 for the case of a planar amide group. (This is a reasonable assumption since a torsion about the amide bond is energetically much more costly than an out-of-plane displacement of the NH hydrogen.) We see that for a change from γ = 8.7° to γ = 0°, which is the likely range if the pyramidalization model is applicable, ν(NH) increases by 3.9 cm^{-1} while ν(II) decreases by 0.5 cm^{-1}, of the order of the observed shifts[1] of 4.2 and 0.79 cm^{-1}. While the directions of such shifts are consistent with the expected changes if standard hydrogen-bond weakening were occurring, the predicted downshift in the amide I frequency is not: a weakened hydrogen bond should result in an upshift in what is essentially a C═O s mode. A careful measure of the amide I shift is a definitive test of this pyramidalization proposal. (It is interesting to note that for larger values of γ an increase in ν(II) on NH planarization is expected.)

There is, however, another informative test of this model, viz., the ratio of the two observed shifts, $\Delta\nu$(II)/$\Delta\nu$(NH). In the above NMA−$(H_2O)_2$ system, this ratio is $-0.5/3.9 = -0.13$, and in the α-nylon-6 case this ratio is $-0.79/4.2 = -0.19$. We can ask how this compares with such a ratio in systems in which pyramidalization is unlikely (because of the absence of crystal constraints) and hydrogen-bond weakening is known to occur (for example, as a result of heating the sample). Several such systems have been studied—an amorphous polyamide,[11,12] a partially crystalline nylon-11,[12,13] and a poorly crystalline terpolyamide[12]—and the ratios for these polymers are presented in Table 2. It can be seen that in these polymers, in which the absence of constraints should result in amide groups with planar N, the ratios are similar and significantly larger in magnitude (∼0.6) than that for the strained α-nylon-6, which is of the same order as that associated with the proposed change in N pyramidalization.

Our ab initio studies of ν(NH) in 78 conformers of the alanine dipeptide[10] ($CH_3CONHCH(CH_3)CONHCH_3$) have shown that γ can vary quite significantly (up to 40°)

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Table 2. Ratios of Amide II to NH Stretch Frequency Shifts[a] in Various Polyamide and *N*-Methylacetamide Systems

system	ΔT[b]	$\Delta\nu$(II)	$\Delta\nu$(NH)	$\Delta\nu$(II)/$\Delta\nu$(NH)
amorphous polyamide[c]	180	−11	22	−0.50
nylon-11[d]	180	−20	33	−0.61
terpolyamide[e]	160	−16	22	−0.73
α-nylon-6 [f]		−0.79	4.2	−0.19
NMA−$(H_2O)_2$ [g]		−0.5	3.9	−0.13

[a] In cm^{-1}. [b] In °C. [c] References 11 and 12. [d] References 12 and 13. [e] Reference 12. [f] Reference 1, for a strain of 0.1. [g] This work, for $\gamma = 8.7°$.

even without torsions about the amide bond. Such N pyramidalizations result mostly from nonbonded interactions with the NH hydrogen, but it seems also to occur in one case (the C7eq structure) where pyramidalization would lead to a better (internal) hydrogen bond. We should therefore expect a similar tendency to be operative in polyamide systems.

The strong evidence from the alanine dipeptide structures[10] and the very suggestive evidence from the low-strain studies of crystalline α-nylon-6[1] point up the importance of taking N pyramidalization into account (in addition to possible hydrogen-bond weakening) in correlating frequency shifts of infrared ν(NH) bands with changes in amide hydrogen bond structures and energies.

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