γ -irradiation of aqueous solutions of proteins than is sometimes supposed.

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N-H Stretching Frequencies of Amines and Amides

Bellamy and Williams¹ found that for primary amines in which both N-H bonds are equivalent and mass and coupling effects negligible, the symmetric (ν_s) and asymmetric (ν_{as}) NH_2 stretching frequencies were related by equation (1) with a standard deviation of 4.8 cm^{-1} and in the more restricted case of *meta* and *para* substituted anilines, Krueger and Thompson² found that equation (2) was obeyed with an average error of less than 1 cm^{-1} .

$$\nu_s = 0.876 \nu_{as} + 345.5 \quad (1)$$

$$\nu_s = 0.682 \nu_{as} + 1,023 \quad (2)$$

For primary amides, Puranik and Ramiah³ deduced the following equation:

$$\nu_s = 1.1214 \nu_{as} - 542.5 \quad (3)$$

Krueger⁴ has recently interpreted the lower slope of the aniline correlation (2) as opposed to the general amine correlation (1) and amide correlation (3) and the fact that the line relating ν_s and ν_{as} given by equation (3) is displaced from equation (2) as evidence for a systematic change of sp^3/sp^2 character of the amino-group in the aniline series as the electron withdrawing or donating power of the substituent alters. However, the displacement of line (3) is probably related to a dipolar field effect on the N-H bond which is *cis* to the carbonyl group⁵. For example, many secondary amides exhibit rotational isomerism and the N-H stretching bands are characteristically different⁶ (*cis* amides, 3,420–3,440 cm^{-1} ; *trans* amides, 3,440–3,460 cm^{-1}). Although steric effects may contribute to this shift in some compounds by a change in planarity and consequent change in resonance effect, this factor is not likely to be large where one of the groups is small. For example, formamide⁷ shows two N-H absorptions separated by 26 cm^{-1} , and for a typical value of ν_{as} (3,500 cm^{-1}) the displacement between ν_s in equations (2) and (3) is 27.6 cm^{-1} . Although the agreement may be to some extent fortuitous, unambiguous evidence⁸ for the non-equivalence of the N-H bonds in primary amides is provided by the spectra of partially deuterated amides which show two N-H stretching bands 20–30 cm^{-1} apart due to the NHD group, arising from the *cis* and *trans* relationship of the N-H bond to the carbonyl group. Steric effects could not account for this difference. A similar *cis-trans* isomerism of NHD

groups has already been shown for intramolecularly hydrogen bonded amines^{5,9}. Part of the change in slope for amides may arise from the variation of this interaction due to changes in polarity of the C=O bond.

The change in sp^2/sp^3 character in substituted anilines which Krueger deduces from the change in slope of equations (1) and (2) is more clearly evident from the N-H stretching frequencies of aliphatic and aromatic amines¹⁰. For example, pyrrole shows an N-H stretching band at 3,490 cm^{-1} and in this case the nitrogen σ -bonds are close to planar (sp^2 hybridized). Secondary aliphatic amines show bands near 3,350 cm^{-1} (in which the nitrogen is almost certainly sp^3 hybridized) and aromatic amines near 3,430 cm^{-1} in which the nitrogen hybridization is intermediate. Similar values are obtained for primary amines if the means of ν_{as} and ν_s are taken¹¹. The large shift in N-H stretching frequency between amines in which the nitrogen atom is sp^2 and sp^3 hybridized (about 140 cm^{-1}) is similar to that observed between the C-H stretching frequencies of saturated and unsaturated hydrocarbons (sp^2 and sp^3 hybridized carbon atoms, about 130 cm^{-1})¹². A systematic change in sp^2/sp^3 character in aniline derivatives cannot alone, therefore, account for the change in slope as the large changes in N-H stretching frequencies in the general amine correlation (1) are already due to a change in sp^2/sp^3 character.

Krueger also suggests that *ortho* substituents involving strong hydrogen bonds appear to lead to planar molecules in which the HNH bond angle may exceed 120°, for example, *ortho*-nitroaniline, 121.7°, and ethylanthranilate, 123.6°. Similar calculations for other hydrogen bonded systems such as 1-aminoanthraquinone⁵ (138.2°) and 1-phenylazo-2-naphthylamine⁹ ($\nu_{as} = 3,478 \text{ cm}^{-1}$, $\nu_s = 3,230 \text{ cm}^{-1}$, HNH bond angle insoluble) leads to the conclusion that the equations of Linnett¹³ are inapplicable where the two N-H bonds are non-equivalent. Little reliance can, therefore, be placed on the calculations of bond angles where intramolecular hydrogen bonding occurs. It has already been shown, however, that good evidence for the planarity or near planarity of the amino group in many intramolecularly hydrogen bonded compounds is provided by the *trans* N-H stretching frequency of the NHD group in the monodeuterated derivative^{5,9}.

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