

Deuterium Nuclear Quadrupole Double Resonance  
Studies of Hydrogen Bonding

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The pervasive influence of hydrogen bonding on structure and reactivity, especially in biological systems, is widely recognized. Hydrogen bonds provide the dominant cohesive forces in many organic solids and they play a major role in determining the conformational structures of nucleic acids and proteins. Of central importance to a comprehensive model for the interaction is a description of the rearrangement of charge that occurs when a hydrogen bond forms. The present work was undertaken to investigate details of this charge rearrangement in N-H...O and N-H...N hydrogen bonds via nuclear quadrupole resonance (nqr) spectroscopy. The nqr technique is ideally suited to this task because quadrupolar transition frequencies depend on the distribution of electronic and nuclear charges in the immediate vicinity of the nucleus under observation. Although the lighter quadrupolar nuclei capable of participating in a hydrogen bond, such as  $^2\text{H}$ ,  $^{14}\text{N}$ , and  $^{17}\text{O}$ , give rise to resonances that are too weak for direct detection, their transitions can be observed by applying double resonance methods developed during the last fifteen years [1].

In a previous study, a model was developed relating  $^2\text{H}$  quadrupole coupling constants to hydrogen bond geometry in O-H...O bonds [2,3]. Prior  $^2\text{H}$  nqr investigations of N-H...O systems were limited almost entirely to compounds in which the proton donor is  $-\text{NH}_3^+$  and to a relatively narrow range of N...O distances [4,5]. In developing the current study, attention was given to compiling a body of data that encompasses the range of donor-acceptor distances and variety of N-H donors actually observed for N-H...O and N-H...N hydrogen bonds.

Included in the samples selected for investigation was a series of hydrogen bonded complexes formed from cytosine and derivatives of amino acids. These compounds were chosen because they serve as potential models for nucleic acid-protein interactions and because they afford within each structure several examples of N-H...O hydrogen bonds as well as an  $\text{N}^+\text{-H...O}$  bond. It was possible to make complete assignments of the  $^2\text{H}$  nqr spectra of these complexes by taking advantage of several spectral features including line shapes and intensities, magnetic field effects, and  $^2\text{H}/^{14}\text{N}$  and  $^2\text{H}/^2\text{H}$  double transitions.

The work has led to empirical correlations between  $^2\text{H}$  quadrupole coupling constants and N...O and N...N distances which show that the electric field gradient at a hydrogen bonded deuteron is sensitive to variations in formal charge and bonding configuration at the proton donor as well as to hydrogen bond geometry.

#### References

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