

## P...N PNICOGEN BONDING INTERACTION IN PHOSPHORYL CHLORIDE...NITROGEN BASES: EVIDENCE FROM MATRIX ISOLATION INFRARED SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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Pnicogen bonding emerged as an important interaction as ubiquitous hydrogen bonding, the study of interactions of simple molecular model systems involving pnicogen bonding can be a platform to understand the complex mechanisms controlled by these non-covalent interactions. In the present work matrix isolation spectroscopy in combination with quantum chemical computations were used to elucidate the structures of P...N pnicogen bonded dimers of phosphoryl chloride( $\text{POCl}_3$ ) prototype with nitrogen-bases such as ammonia ( $\text{NH}_3$ ), aniline ( $\text{C}_6\text{H}_7\text{N}$ ), and pyridine ( $\text{C}_5\text{H}_5\text{N}$ ), where phosphorus is predominantly present in pentavalent state.

The basicities of the interacting partner ( $\text{NH}_3, \text{C}_6\text{H}_7\text{N}, \text{C}_5\text{H}_5\text{N}$ ) completely influences the geometrical preference of all these dimers. The  $\text{POCl}_3\text{-NH}_3$  dimer is anticipated to have a hydrogen bonded geometry, however with hydrogen bonding, a P...N pnicogen bonding plays a definite and a non-trivial role in their overall stabilization. An interesting paradigm transformation was noticed in  $\text{POCl}_3\text{-C}_6\text{H}_7\text{N}$  and  $\text{POCl}_3\text{-C}_5\text{H}_5\text{N}$  heterodimers, where P...N pnicogen bonding was observed to completely dominate the hydrogen bonding. Furthermore, the characteristic interactions were investigated through electrostatic potential mapping, energy decomposition and non covalent interaction analyses.

