P...N PNICOGEN BONDING INTERACTION IN PHOSPHORYL CHLORIDE...NITROGEN BASES: EVIDENCE FROM MATRIX ISOLATION INFRARED SPCTROSCOPY 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($POCl_3$) prototype with nitrogen-bases such as ammonia (NH_3), aniline (C_6H_7N), and pyridine (C_5H_5N), where phosphorus is predominantly present in pentavalent state.

The basicities of the interacting partner (NH_3,C_6H_7N,C_5H_5N) completely influences the geometrical preference of all these dimers. The $POCl_3$-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 $POCl_3$-C_6H_7N and $POCl_3$-C_5H_5N 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.