

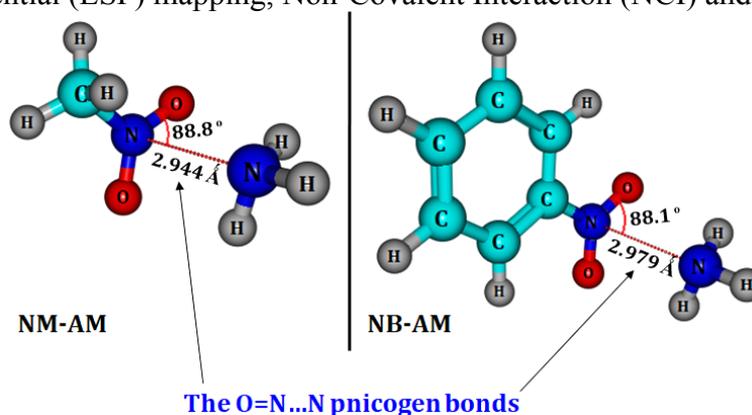
Strengthening of bonding by Ammonia with Nitromethane and Nitrobenzene due to π -hole driven O=N...N pnicoen bonds: Explored using matrix isolation infrared spectroscopy and ab initio computations

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Heterodimers of Nitromethane (NM) and Nitrobenzene (NB) with ammonia (NH₃), NMAM¹ and NBAM respectively, have been isolated within inert gas matrixes (Ar and N₂) at 12 K. Computational elucidation of the geometries of NMAM and NBAM reveal the unambiguous presence of O=N...N pnicoen bonds within both species. The appearance of new absorption features in O=N=O stretching region of the IR spectra of matrix isolated NM/NB as well as in the N-H bending region of NH₃ sub-molecules, is found to be a consequence of the formation of NMAM/NBAM heterodimers. NMAM, bound by O=N...N pnicoen and C-H...N hydrogen bonds, and NBAM, primarily stabilized by O=N...N pnicoen bond, form the most favoured geometries on the respective Potential Energy Surfaces (PESs). Notably, NBAM has two isomers nearly degenerate in terms of energy, one of which is hydrogen bonded and the other, pnicoen bonded. The possibility, of discriminating these isomers by the lifting of degeneracy caused by matrix isolation, is also explored. The electron accepting role of nitrogen in NM and NB, thus hosting a pnicoen bond, is revealed to be a primarily electrostatic phenomenon, by energy decomposition (ED) analysis of NMAM and NBAM. The characteristic perpendicularity of the donor (nitrogen in NH₃) with the O=N=O plane in NM and NB, which is the characteristic directionality of pnicoen bonds manifest, is affirmed to be a consequence of, the π -hole facilitated electrophilicity of nitrogen in NM and NB. A comparative and comprehensive investigation of intermolecular pnicoen bonding hosted by the electron accepting nitrogen, has been performed using the computational tools: Quantum Theory of Atoms in Molecules (QTAIM), Natural Bond Orbital (NBO), Electrostatic Potential (ESP) mapping, Non-Covalent Interaction (NCI) and ED analyses.



¹Chandra, S.; Suryaprasad, B.; Ramanathan, N.; Sundararajan, K. Nitrogen as a pnicoen?: evidence for π -hole driven novel pnicoen bonding interactions in nitromethane-ammonia aggregates using matrix isolation infrared spectroscopy and ab initio computations. *Phys. Chem. Chem. Phys.* **2021**, *23*, 6286-6297.