CPLT2022

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

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A...Pn-D : The pnicogen (Pn) bond

• Emergent properties of substances/materials at 'bulk' scales are attributes of non-covalent interactions among constituent molecules.

• Pnicogen bonding (A...Pn-D), an analogue of the hydrogen bond, involves an atom of the pnicogen group (Pn) playing the principal electron-acceptor. A: the pnicogen acceptor ; D: the pnicogen donor.

• Localised anisotropy in the molecular electrostatic potential surrounding Pn is the primary facilitator of pnicogen bonds. Polarization of Pn by the atoms to which it is covalently bonded cause the anisotropies. Anisotropies along the extension of Pn-D σ-bond are termed σ-holes while those occurring on π-electron clouds are termed π-holes. Their prominence is directly proportional to the polarizability of Pn and the electronegativity of D.

• Involvement of nitrogen, the smallest of pnicogens, as an electron-acceptor has been elusive to observation, owing to its low polarizability.

• O=N...N pnicogen bonding by nitromethane (NM) and nitrobenzene (NBz) sustaining their heterodimers with ammonia (NM-AM & NB-AM) has been investigated and compared.

Methods

• Pnicogen bonding perturbs the covalent bonds sustaining the geometry of participant molecules.

• These perturbations are captured, as minute shifts in the characteristic normal modes of vibrations of participants, on their respective infrared spectra of enhanced resolution, owed to their isolation within matrixes of Ar and N_2 at 12 K.

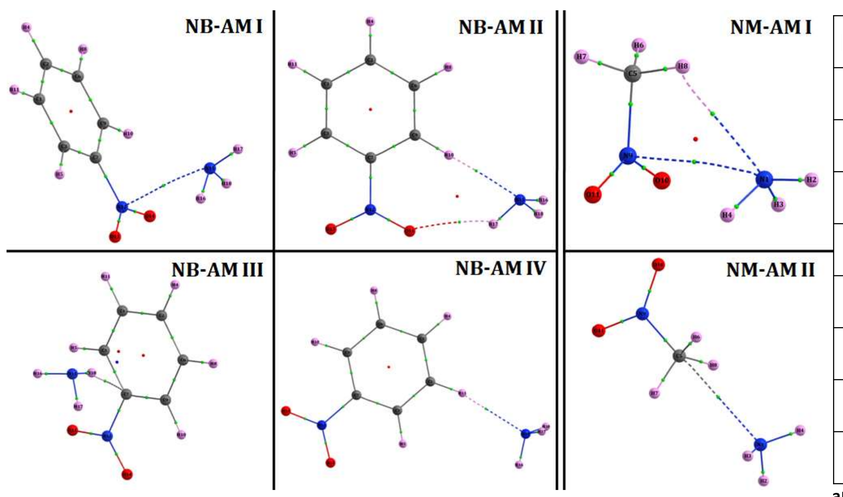
• Matrix isolation also facilitates regulation of the extent of interactions among the molecules of interest.

• Correlation of shifts observed in the said infrared absorptions, with results from harmonic frequency calculations on geometries of NM-AM and NB-AM forms a module of evidence for generation of heterodimers.

• The nature of interactions binding the heterodimers are investigated and interpreted using computational tools: QTAIM, NBO, EDA, ESP mapping and NCI analyses.

• Computational programs/packages used: Gaussian 09, ADF 2016, Multiwfn 3.7, VMD 1.9.3

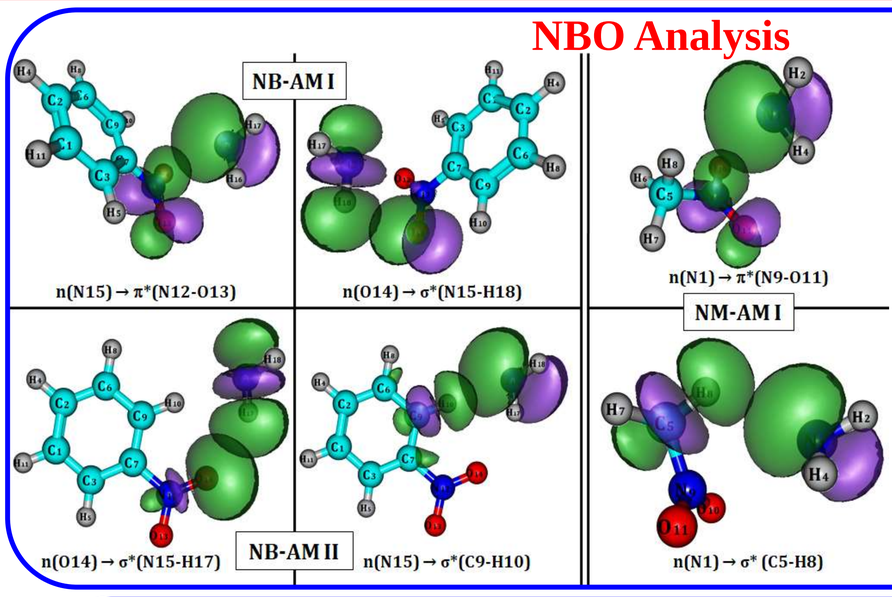
Potential Energy Surface



Heterodimer	[a]ΔE/ B.E.
NM-AM	
NM-AM I	0.0/-5.4
NM-AM II	2.5/-2.9
NB-AM	
NB-AM I	0.0/-2.4
NB-AM II	0.6/-1.8
NB-AM III	1.1/-1.3
NB-AM IV	1.7/-0.7

[a]kcal mol^{-1}

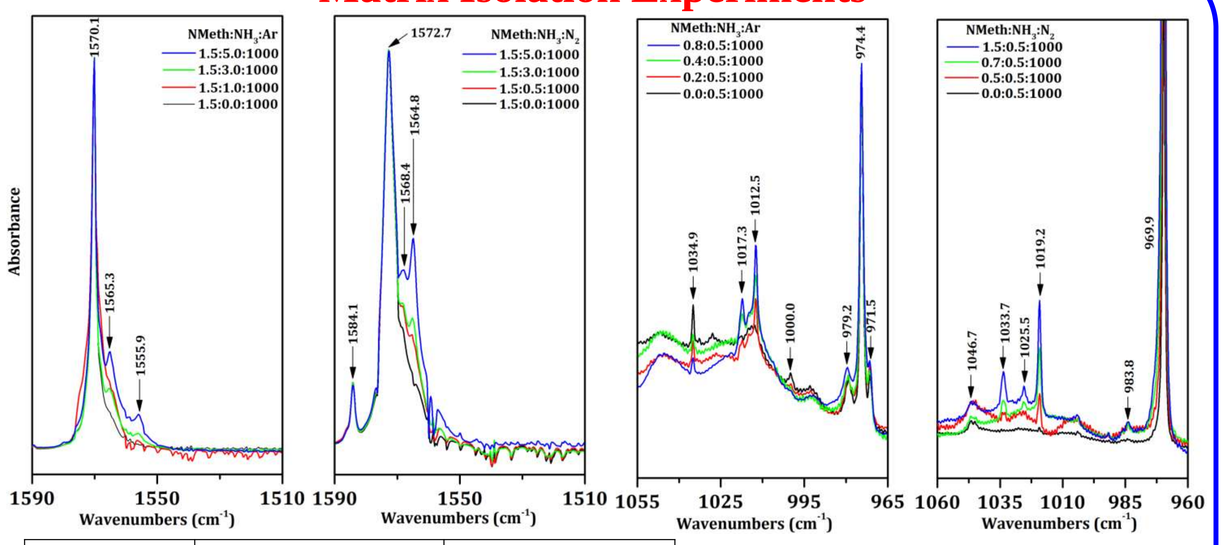
NBO Analysis



Donor-Acceptor	[a]E^2
NB-AM I	
n(N15)→π*(N12-O13)	0.47
n(O14)→σ*(N15-H18)	0.25
NB-AM II	
n(O14)→σ*(N15-H17)	1.25
n(N15)→σ*(C9-H10)	6.06
NM-AM I	
n(N1)→π*(N9-O11)	0.46
n(N1)→σ*(C5-H8)	2.14

[a]kcal mol^{-1}

Matrix Isolation Experiments

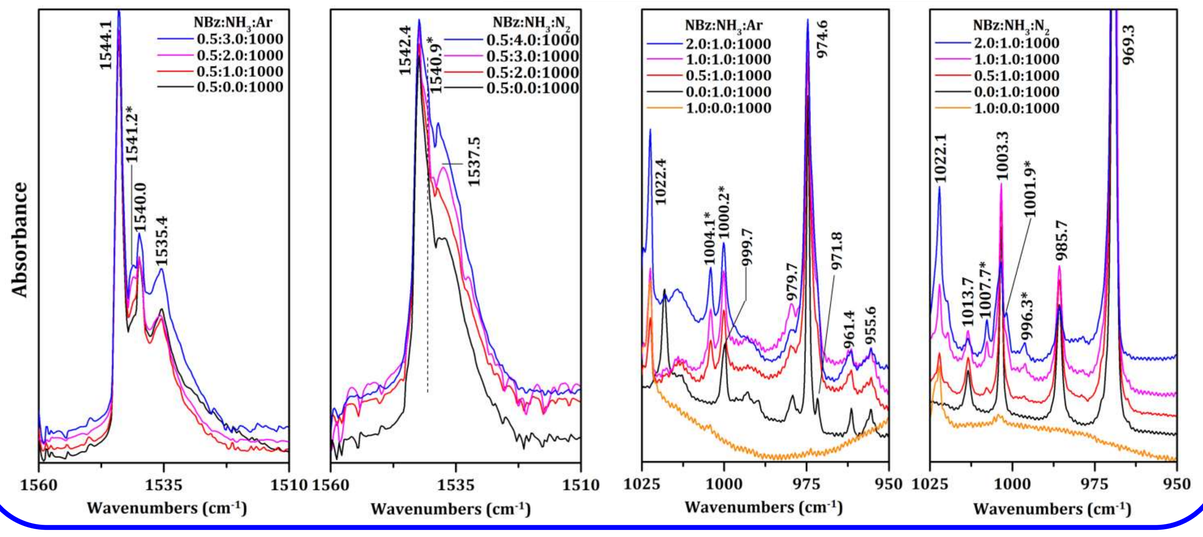


Computed		Experimental				Mode Assignment
		Ar		N_2		
ν	Δν	ν	Δν	ν	Δν	
1100.8 (144)	+58.0	1012.5	+38.1	1019.2	+49.3	N-H bending in NM-AM I
		1017.3	+42.9	1025.5	+55.6	N-H bending in NM-AM I
1756.1(136)	-4.4	1565.3	-4.7	1568.4	-4.3	O=N=O stretch in NM-AM I

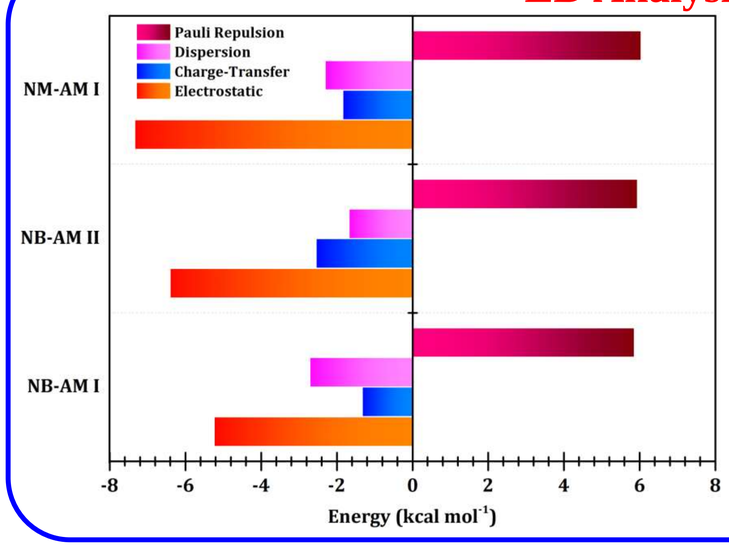
NM – NH_3 co-depositions

NBz – NH_3 co-depositions

Computed		Experimental				Mode Assignment
		Ar		N_2		
ν	Δν	ν	Δν	ν	Δν	
1748.2 (146)	-0.9	1541.2	-2.9	1540.9	-1.5	O=N=O stretching in NB-AM I
1740.6 (94)	-8.5	---	---	---	---	O=N=O stretching in NB-AM II
1078.8 (151)	+36.0	1000.2	+25.6	1001.9	+32.6	N-H bending in NB-AM II
1082.7 (168)	+39.9	1004.1	+29.5	1007.7	+38.4	N-H bending in NB-AM I



ED Analysis

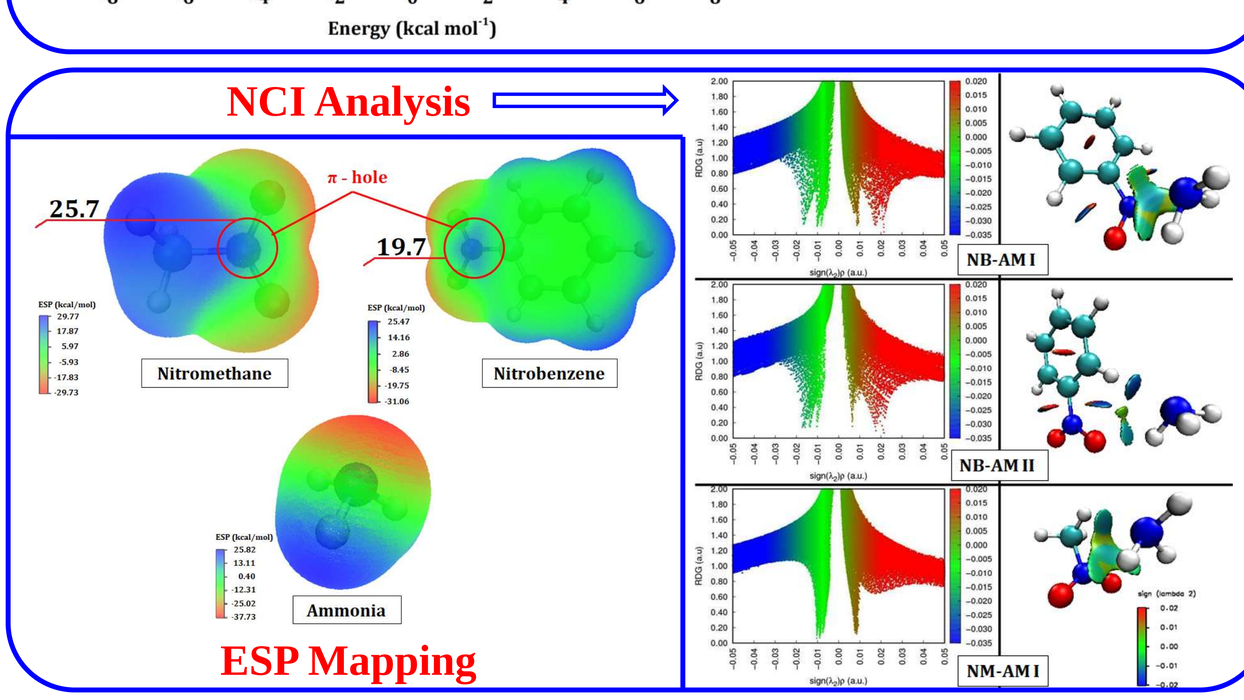


• Contribution from electrostatics decreases in NB-AM I relative to NM-AM I.

• This is in line with the reduced magnitude of ESP at the π-holes of NBz.

• The phenyl moiety of NBz appears to stay 'aloof' in the intermolecular bonding within NB-AM I & II, as indicated by the minimal contribution from dispersion forces.

NCI Analysis



Conclusion

• Strength of the O=N...O pnicogen bond is directly influenced by magnitude of positive ESP at the π-hole over the electron accepting nitrogen: Lower the magnitude, lower is the strength

• The electron withdrawing effect of the NO_2 moiety on the π-electron cloud of the phenyl group is evident from the minimal contribution of dispersion effects in stabilization of NB-AM.

Swaroop Chandra is grateful to the Department of Atomic Energy and the Homi Bhabha National Institute for the grant of research fellowship and the funding for this trip.

This poster was displayed for presentation at CPLT-2022, Hotel Visegrád, Visegrád, Hungary

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