Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information:

Evidence of blue-shifting N–H···N hydrogen bonding despite elongation of the N–H bond

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1.

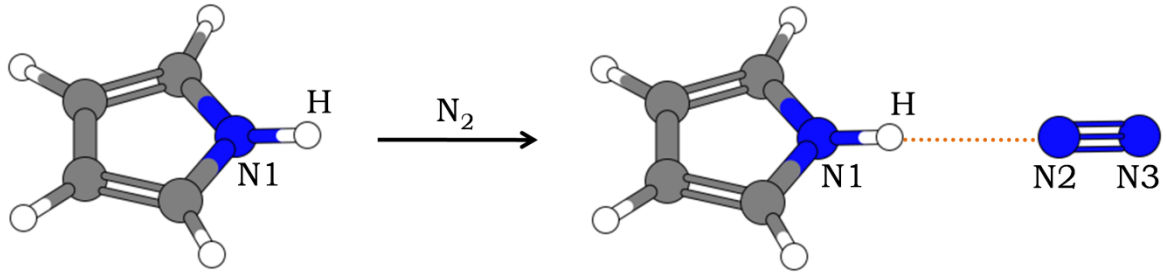

Table S1. Some geometrical parameters of pyrrole and pyrrole···N_2 cluster optimized at MP2/6-31+G(d) level of theory. Relevant atom labels are defined in the above picture.

Geometrical Parameters	Pyrrole	Pyrrole···N_2 cluster
N1–H (Å)	1.0123	1.0130
H···N2 (Å)	-----	2.3673
N1–H–N2 (degree)	-----	179.97
H–N2–N3 (degree)	-----	179.99

2.

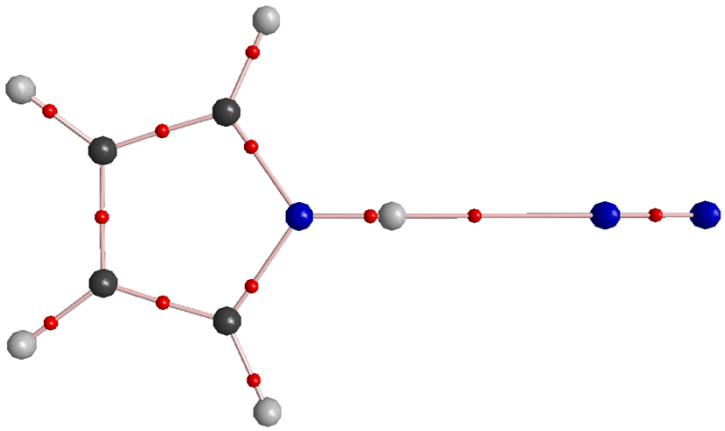

Figure S1. Bond critical points on the optimized geometry (at MP2/6-31+G(d) level of theory) of pyrrole···N_2 cluster, obtained by AIM calculation, are shown as red spheres. Blue, grey and white (shaded) spheres represent N, C and H respectively.

3.

Table S2. Comparison of experimental ν_{N-H} of pyrrole in gas phase with those computed (anharmonic) at various levels of theory

Experimental* (cm^{-1})	MP2/6-31G(d,p) (cm^{-1})	MP2/6-31+G(d) (cm^{-1})	MP2/6-31+G(d,p) (cm^{-1})	MP2/6-311++G(d,p) (cm^{-1})	MP2/aug-cc-pVDZ (cm^{-1})
3531	3615	3532	3597	3557	3538

*Taken from Ref. 36 of the main manuscript.

4.

Table S3. Theoretical predictions for changes of N–H bond length (Δr_{N-H}) and shifts in N–H stretching frequency ($\Delta\nu_{N-H}$) due to pyrrole···N_2 cluster formation.

Computational level	Δr_{N-H} (Å)	$\Delta\nu_{N-H}$ (harmonic)	$\Delta\nu_{N-H}$ (anharmonic)
MP2/6-31G(d,p)	+0.0007	-4 cm^{-1}	-2 cm^{-1}
MP2/6-31+G(d)	+0.0007	+3 cm^{-1}	+8 cm^{-1}
MP2/6-31+G(d,p)	+0.0005	-1 cm^{-1}	+0.3 cm^{-1}
MP2/6-311++G(d,p)	+0.0005	-4 cm^{-1}	-2 cm^{-1}
MP2/aug-cc-pVDZ	+0.0005	-1 cm^{-1}	-2 cm^{-1}