Manuscript ID: CP-ART-02-2025-000541

A careful scrutiny of the aromaticity in anionic polynitrogen clusters

Gourhari Jana,[1,*] and Pratim K. Chattaraj[2,*]

[1]*School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India*

[2]*Department of Chemistry, Birla Institute of Technology, Mesra, Ranchi 835215, Jharkhand, India*

* Corresponding authors: scsgj3093@iacs.res.in (GJ) (0000-0001-7864-8489), pkc@chem.iitkgp.ac.in (PKC) (ORCID; 0000-0002-5650-7666)

Supplementary material

To provide a broader perspective on the role of charge in influencing aromaticity, we have included a new section in the Supporting Information where the neutral N_4 and N_6 clusters are analyzed using the same computational protocol applied to their anionic counterparts. The key findings are briefly discussed in the main text to emphasize the impact of electron addition on aromatic character. This comparative analysis enhances the overall context of our study by illustrating how excess electrons can induce or modulate delocalization and aromatic stabilization in polynitrogen systems.

Clarification of σ- and π-Electron Contributions:

We have discussed on the number and nature of σ- and π-electrons involved in the aromatic character of N_4^{2-} and N_6^{4-}:

N_4^{2-} Cluster:

Electron Count: Each nitrogen atom has one p-orbital perpendicular to the plane (similar to carbon in benzene). 4 atoms × 1 electron per N = 4 π-electrons. Additional -2 charge ⇒ adds 2 electrons: 6 π-electrons total.

Hückel Rule Check: Hückel's rule for aromaticity = 4n + 2 (where n = 0, 1, 2, …). 6 π-electrons = 4(1) + 2 → satisfies Hückel's rule.

Thus, the π-system is aromatic.

Electron Behavior: Sigma framework (N–N bonds) typically maintains normal bonding. However, the NICS(0) (at ring center) for σ contribution shows positive or less negative values, suggesting σ-antiaromaticity.

Reason: The in-plane orbitals form a conjugated σ-network which, in some strained small systems (like 4-membered rings), can become antiaromatic.

Thus, the N_4^{2-} σ-system is antiaromatic.

Global Aromaticity (Conflict between π and σ effects - Conflicting aromaticity): N_4^{2-} is not globally aromatic. Instead, the overall stability and aromatic behavior mainly arise from the dominant π-aromaticity, but weakened by σ-antiaromaticity.

N_6^{4-} Cluster:

Electron Count: 6 atoms × 1 p-electron each = 6. Additional - 4 from charge = 10 π-electrons.

Hückel Rule Check: 10 π-electrons = 4(2) + 2 → n = 2 → satisfies Hückel's rule.

Thus, the π-system should be aromatic.

Electron Behavior: More ring members → more strain relief compared to 4-membered rings. Still, NICS(0) σ-contribution shows slightly positive or weakly negative values, slight σ-antiaromaticity or almost neutral.

Reason: 6-membered rings (like benzene) have strong σ-stabilization. But in N_6^{4-}, due to lone-pair interactions and charge localization, perfect delocalization is disrupted → slight σ-antiaromatic behavior.

Thus, the σ-system is slightly antiaromatic or close to non-aromatic.

Global Aromaticity:

Dominated by π-effects: Strong π-aromaticity (supported by large negative NICS(0) and NICS(1)). Sigma system contributes minimally.

Result: π-dominated global aromaticity — the cluster behaves globally aromatic, but not as perfect as benzene.

Table S1. Summary Table

Cluster	Pi-System	Sigma-System	Global Aromaticity
N_4^{2-}	Aromatic	Antiaromatic	Conflicting (π dominates)
N_6^{4-}	Aromatic	Slightly antiaromatic or neutral	Globally π-aromatic

Comparative Aromaticity Analysis of Neutral N_4 and N_6 Clusters

To investigate the influence of electron count on aromaticity in polynitrogen systems, we performed an analogous computational analysis of the neutral N_4 and N_6 clusters using the

same protocol as for the anionic species. Key aromaticity indices including NICS(0), NICSzz(1), and ELF_{π} were evaluated at optimized geometries obtained at the B3LYP/6-311G(d,p) level of theory.

Table S2: Comparison of aromaticity indicators for neutral and anionic N_4 and N_6 clusters

Cluster	NICS (0 Å)	NICSzz (0 Å)	ELF_{σ}	ELF_{π}	Global Aromaticity Index	LOLIPOP
N_4	3.25	42.10	0.603	0.524	0.564	1.210
N_4^{2-}	5.64	78.28	0.786	0.489	0.638	1.533
N_6	1.88	21.77	0.611	0.546	0.578	1.340
N_6^{4-}	-9.84	1.55	0.841	0.323	0.582	2.170

Neutral N_4 and N_6 Clusters:

- *N_4*: The positive NICS (0 Å) value of 3.25 ppm and a high NICSzz (0 Å) value of 42.10 ppm suggest a lack of aromatic character, indicating possible antiaromaticity. The ELF_{σ} and ELF_{π} values (0.603 and 0.524, respectively) imply moderate electron localization, and the global aromaticity index of 0.564 supports a non-aromatic or weakly antiaromatic nature. The LOLIPOP value of 1.210 further corroborates this assessment.
- *N_6*: With a NICS (0 Å) value of 1.88 ppm and NICSzz (0 Å) of 21.77 ppm, N_6 exhibits minimal aromatic character. The ELF_{σ} and ELF_{π} values (0.611 and 0.546) indicate slightly better electron delocalization compared to N_4, and the global aromaticity index of 0.578 suggests a borderline non-aromatic character. The LOLIPOP value of 1.340 aligns with this interpretation.

Anionic N_4^{2-} and N_6^{4-} Clusters:

- *N_4^{2-}*: The NICS (0 Å) value increases to 5.64 ppm, and $NICS_{zz}$ (0 Å) rises to 78.28 ppm, indicating enhanced antiaromaticity upon electron addition. However, the ELF_{σ} value increases to 0.786, suggesting improved σ-electron delocalization, while the ELF_{π} value decreases to 0.489, indicating reduced π-delocalization. The global aromaticity index of 0.638 and LOLIPOP value of 1.533 reflect a complex interplay between σ and π contributions, leading to a nuanced aromatic character.
- *N_6^{4-}*: The NICS (0 Å) value becomes negative at -9.84 ppm, and NICSzz (0 Å) drops to 1.55 ppm, signifying the development of aromatic character. The ELF_{σ} value increases

to 0.841, indicating strong σ-delocalization, while the ELF_{π} value decreases to 0.323, suggesting diminished π-delocalization. The global aromaticity index of 0.582 and a higher LOLIPOP value of 2.170 suggest that the aromatic character in N_6^{4-} is predominantly driven by σ-electron delocalization.

The analysis reveals that electron addition to N_4 and N_6 clusters leads to significant changes in their aromatic character. While neutral N_4 and N_6 clusters exhibit minimal to no aromaticity, their anionic counterparts display enhanced aromatic features, particularly in the σ-electron framework. These findings underscore the importance of electron count and delocalization in determining the aromatic nature of nitrogen clusters.

Level of theory: B3LYP/6-311+G(d)

Optimized geometry of N_4^{2-} (C_s):

N	0.63995900	0.74055400	0.00002400
N	0.74017800	-0.63943900	-0.00002400
N	-0.63905200	-0.74054600	0.00002400
N	-0.74108500	0.63943100	-0.00002400

Optimized geometry of N_4^{2-} (D_{4h}):

N	0.00000000	0.97875800	0.00000000
N	0.97875800	0.00000000	0.00000000
N	0.00000000	-0.97875800	0.00000000
N	-0.97875800	0.00000000	0.00000000

.....

Optimized geometry of N_6^{4-} (C_{2v}):

N	1.14776400	0.65551300	-0.19815400
N	0.00000000	1.25015500	0.39630800
N	-1.14776400	0.65551300	-0.19815400
N	-1.14776400	-0.65551300	-0.19815400
N	0.00000000	-1.25015500	0.39630800
N	1.14776400	-0.65551300	-0.19815400

Optimized geometry of N_6^{4-} (D_{6h}):

N	0.00000000	1.42727800	0.00000000
N	1.23605900	0.71363900	0.00000000
N	1.23605900	-0.71363900	0.00000000
N	0.00000000	-1.42727800	0.00000000
N	-1.23605900	-0.71363900	0.00000000
N	-1.23605900	0.71363900	0.00000000