Stabilization of the dual-aromatic cyclo-N5— anion by acidic entrapment

Zhang, Lei; Yao, Chuang; Yu, Yi; Jiang, Sheng-Li; Sun, Chang Qing; Chen, Jun

2019

Zhang, L., Yao, C., Yu, Y., Jiang, S.-L., Sun, C. Q., & Chen, J. (2019). Stabilization of the dual-aromatic cyclo-N5— anion by acidic entrapment. *The Journal of Physical Chemistry Letters*, 10(10), 2378-2385. doi:10.1021/acs.jpclett.9b01047

<https://hdl.handle.net/10356/144513>

<https://doi.org/10.1021/acs.jpclett.9b01047>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *The Journal of Physical Chemistry Letters*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.jpclett.9b01047>

Downloaded on 26 Apr 2023 17:48:05 SGT

Stabilization of the dual-aromatic *cyclo*-N₅[−] anion by acidic entrapment

Lei Zhang,^{a,b*} Chuang Yao,^c Sheng-Li Jiang,^a Yi Yu,^a Chang Q Sun,^{c,d} Jun Chen^{b,e†}

^aSoftware Center for High Performance Numerical Simulation, Institute of Applied Physics and Computational Mathematics, Beijing, 100088, China

^bLaboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing, 100088, China

^cEBEAM, Yangtze Normal University, Chongqing, 408100, China

^dNOVITAS, Nanyang Technological University, 639798 Singapore

^eCenter for Applied Physics and Technology, Peking University, Beijing, 100871, China

Abstract: Pentazole anion, the best candidate of full-nitrogen energetic materials, can be isolated only from acidic solution with a puzzled reason that is critical to raising the production yield and energy density of the substance. Herein, we report for the first time the discovery of the dual aromaticity (π and σ) of *cyclo*-N₅[−], which makes the anion unstable in nature but confers additional stability in acidic surroundings. In addition to the usual π -aromaticity, similar to that of the prototypical benzene, five lone pairs are delocalized in the equatorial plane of *cyclo*-N₅[−], forming additional σ -aromaticity. It is the compatible coexistence of the inter-lone-pair repulsion and inter-lone-pair attraction within the σ -aromatic system that makes the naked *cyclo*-N₅[−] highly reactive to electrophiles and easily broken. Only in sufficiently acid solution can the *cyclo*-N₅[−] become unsusceptible to the electrophilic attack and gain extra stability through the formation of hydrogen-bonded complex from surrounding electrophiles; otherwise the *cyclo*-N₅[−] cannot be productively isolated. The dual aromaticity discovered in *cyclo*-N₅[−] is expected to be a universal nature of the pnictogen five-membered ring systems.

Key words: *cyclo*-N₅[−]; dual-aromaticity; stability; reactivity; first-principles studies

TOC

Acidic entrapment of the dual-aromatic energetic cyclo- N_5^-

Annotation: The hydronium ions above the wave patterns represent the acidic aqueous solution. The $cyclo-N_5^- \dots 4H_3O^+$ complex illustrates the optimal dose ratio for the high-yield separation of pentazolate anion. The flame surrounding $cyclo-N_5^-$ has two implications: the high energy storage in its N-N bonds and the second σ -aromatic system derived from the nitrogen lone-pair electrons delocalization.

The concept of aromaticity **has been** conventionally used to define systems with similar characteristics to those of benzene¹ and can be quantified by calculating the structural²⁻⁴, magnetic⁵⁻¹¹, electronic¹²⁻¹⁷, energetic^{8, 18}, and reactivity⁸ indices of the systems using quantum method. For example, Santos *et al.*¹² and Schleyer *et al.*¹⁹ calculated the electron localization function (ELF) and nucleus-independent chemical shifts (NICS) and found that both σ and π molecular orbitals (MO) contribute importantly to the aromaticity of Al_4^{2-} , thereby **confirming** the presence of multiple aromaticity in Al_4^{2-} .^{12, 20-21} All known aromatics, whether singular π -aromatic organic and inorganic compounds or multiple aromatic metallic compounds, share distinct characteristics – they are easily to form, highly stable and non-reactive in addition reactions.^{5, 22}

However, the long pursuit of energy-intensive **material**, the inorganic pentazole anion cyclo-N_5^- , albeit known to be π -aromatic, is surprisingly unstable, difficult to obtain and susceptible to electrophilic attack.^{11, 23-28} The development of a synthetic route to cyclo-N_5^- has a history full of hardships. It started in 1903²⁹ and experienced failure³⁰, misunderstanding³¹, and **dispute**³² in the following decades. In 2002, cyclo-N_5^- was first detected with electrospray ionization mass spectrometry but **existed** only fleetingly in gas³³. From 2003 to 2009, cyclo-N_5^- was proved to be created in a neutral solution using the ^{15}N nuclear magnetic resonance (NMR) techniques, yet with a short lifespan of just a few seconds³⁴⁻³⁵. In 2016, cyclo-N_5^- was demonstrated to be stably **present** in polar THF solution at very low temperatures below $-40\text{ }^\circ\text{C}$ ³⁶. Until 2017, a room temperature stable pentazolate $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal was eventually isolated in a mild acidic solution by introducing *m*-chloroperbenzoic acid (*m*-CPBA) and ferrous bisglycinate $[\text{Fe}(\text{Gly})_2]$.³⁷

However, there are the following three puzzles urgently to be addressed. (i) Why the *cyclo*-N₅[−] anion can be productively separated only from an acidic solution rather than in gaseous phase or in a neutral solution is unclear. The answer is critical to the ligand design, high-yield synthesis and practical application. (ii) The *cyclo*-N₅[−] is known to be basic but prefers unprotonation when confronting several hydronium and ammonium ions in the (N₅)₆(H₃O)₃(NH₄)₄Cl crystal,^{24-25, 37-38} which violates the common sense of acid-base neutralization with an unknown reason. (iii) More importantly, numerous of experimental and theoretical studies^{25, 39-44} show that *cyclo*-N₅[−] can form additional single bonds with H₃O⁺, NH₄⁺, Mn²⁺, Fe²⁺, Co²⁺, Zn²⁺ and other transition-metal ions to stable complex. These studies are declaring the occurrence to *cyclo*-N₅[−] the electrophilic aromatic addition reaction – which consumes the delocalized electrons and diminishes its aromaticity – that is challenging the traditional aromatic premise of none-reactivity to addition reaction. Clarifying these problems will advance the understanding to the structure, stability and reactivity of the *cyclo*-N₅[−] and help devising full-nitrogen substance with higher yield and higher energy density.

Herewith, we have performed a series of quantum calculations on the electron density, molecular orbital, structure, magnetic shielding, energetics and dynamics of the *cyclo*-N₅[−] anion in various acidic surroundings. All the DFT calculations are performed using the HASEM software and confirmed (for non-solid calculations) using Gaussian 09 at the B3LYP/6-311++G(d, p) or higher accuracy level⁴⁵⁻⁴⁸. Nine types of aromaticity criteria, including harmonic oscillator model of aromaticity (HOMA), bird index (BI), NICS, isochemical shielding surface (ICSS), Laplacian distribution of charge density, ELF,

delocalization index (DI), Shannon aromaticity (SA), and the curvature of electron density perpendicular to the ring plane at the ring critical point (RCP ρ curvature), are calculated and the natural bond orbital (NBO) analysis and the quantum theory of atoms in molecule (QTAIM) method are used to probe the contributions to the *cyclo*-N₅⁻ anion's aromaticity solely in terms of π or lone-pair electrons. Please refer to *Supplementary Information* for more detail of the methodology. As supported by all nine aromaticity criteria, we have demonstrated the presence of dual aromaticity (π and σ) in *cyclo*-N₅⁻, which makes the anion intrinsically unstable but confers enhanced stability in acidic solution. The detailed calculations and experimental verifications are shown below.

Discovery of dual aromaticity (π and σ) of the *cyclo*-N₅⁻ anion

Cyclo-N₅⁻ has D_{5h} symmetry, with all of its five nitrogen atoms sp^2 hybridized (Fig. 1A and Fig. 1S). The presence of delocalized bonding in the *cyclo*-N₅⁻ is well visualized by plotting the Laplacian of the calculated electronic charge density in the plane of the ring, as shown in Fig. 1B; the areas of local charge concentration are distributed over all atomic basins. As shown in Table 1 and Fig. 1, the structural measures of HOMA = 1.0 and BI = 100 and the negative magnetic measures of NICS_{zz}(1)_{total} = -43.77, NICS(1)_{total} = -16.38 and NICS(0)_{total} = -17.12 confirm the aromaticity of the *cyclo*-N₅⁻. The highest absolute value of the NICS_{zz} for *cyclo*-N₅⁻ is ~0.6 Å vertically above the RCP, which is the same as P₂N₃⁻ anion¹¹ instead of 1.0 Å for prototypical benzene. In addition, the electronic measures of ELF_{total} = 0.713, SA = 2×10^{-10} and RCP ρ curvature = -0.08 indicate that the overall aromaticity of *cyclo*-N₅⁻ is probably stronger than that of the prototypical benzene, as shown by comparison to the corresponding values for benzene: 0.655, 7×10^{-10} and -0.01,

respectively. This is consistent with a previous review of polynitrogen compounds²³ and the finding that the presence of N-N, N-P, and P-P bonds can increase the aromaticity of five-membered ring systems⁴⁹⁻⁵⁰.

The π -aromaticity of *cyclo*-N₅⁻ is well visualized by the local density of states (LDOS) plotted at the minimum energy level of the π -system in Fig. 1D, which are spread out over the entire molecule above and below the molecular plane. The bifurcation value for the ELF_{min- π} is 0.999922 (Fig. 1D); the DI_{min- π} is calculated to be 0.16 for any two nitrogen atoms (either bonded or non-bonded) in the ring. The two indices further confirm the full delocalization of the electrons at this minimum π orbital. Taking all six π -electrons into account, the bifurcation value for ELF $_{\pi}$ is 0.791 and is lower than the corresponding value for benzene: 0.922, suggesting that *cyclo*-N₅⁻ has a weaker π -aromaticity than benzene.

The lone pairs of nitrogen are commonly known to be localized and basic and to be a reasonably good nucleophile²²; the basicity of *cyclo*-N₅⁻ has also been proven in our previous work to be stronger over NH₃²⁴. However, we discover that the cyclic shape of the five nitrogen atoms allows their lone pairs to be spread out over the whole molecule into a flower shape at the minimum lone-pair σ -MO, as shown in Fig. 1D and Fig. 1S; see the cyclic MO also in Ref.⁴⁰. The bifurcation value for the ELF_{min- σ} is calculated to be 0.999997 (Fig. 1D); the DI_{min- σ} is exactly 0.16 for any two bonded or non-bonded nitrogen atoms in the ring. Both aromaticity criteria indicate that the lone-pair electrons at this orbital are fully delocalized. To summarize the contribution to the aromaticity of *cyclo*-N₅⁻ from all σ electrons, we have also calculated the NICS_{zz}(r) $_{\sigma}$ (Fig. 1C), which is always negative when r varies from 0.0 Å to 5.0 Å vertically above the RPC, while the corresponding curve

for benzene is positive. This comparison indicates the presence of σ -aromaticity in *cyclo-N₅⁻*, whereas benzene lacks such σ -aromaticity. In addition, the values of the aromaticity indices $\text{ELF}_\sigma = 0.797$, $\text{NICS}_{\text{zz}}(1)_\sigma = -18.75$ and $\text{NICS}_{\text{zz}}(0)_\sigma = -8.48$ for *cyclo-N₅⁻* and the corresponding values for benzene (0.686, +7.70 and +29.25, respectively) further support the presence of σ -aromaticity in *cyclo-N₅⁻*.

Comparing $\text{ELF}_\sigma = 0.797$ and $\text{ELF}_\pi = 0.791$, $\text{ELF}_{\text{min-}\sigma} = 0.999997$ and $\text{ELF}_{\text{min-}\pi} = 0.999922$, and $\text{DI}_{\text{min-}\sigma} = 0.16$ and $\text{DI}_{\text{min-}\pi} = 0.16$ shows that the lone-pair σ -electron delocalization in *cyclo-N₅⁻* is as important as the π delocalization, and both contribute considerably to the overall aromaticity⁵¹. As shown in Table 1, although *cyclo-N₅⁻* has weaker π -aromaticity than benzene, its overall aromaticity is stronger due to the presence of additional σ -aromaticity derived from the nitrogen lone-pair electrons delocalization. Such aromaticity reinforcement through the delocalization of σ -electrons was also found in other pnictogen five-membered rings like P_5^- and As_5^- anion⁵²⁻⁵³.

We note that the dual aromaticity in *cyclo-N₅⁻* is very different from that in all-metal aromatic systems, such as Al_4^{2-} dianion. The dual aromaticity of Al_4^{2-} dianion means that two types of electrons (four σ electrons and two π electrons) together form a single aromatic system due to the electron deficiency of the dianion.^{12, 20-21} In contrast, the dual aromaticity of the *cyclo-N₅⁻* anion is derived from two separate aromatic systems, each with a number of $4n+2$ delocalized electrons, where $n = 1$ for the π -system and $n = 2$ for the σ -system. Therefore, the “dual” aromaticity of *cyclo-N₅⁻* has two meanings: (i) two types of electrons and (ii) two aromatic systems.

As shown in Figs. 1D and 1S, the two aromatic systems are independent in real space

but are coupled in energy at the sub-highest occupied molecular orbital of -2.43 eV. The two completely delocalized nonbonding MOs ($2p_z\pi$ for two π electrons and $2sp^2\sigma$ for one electron lone pair) occupy the lowest level among those of the six π electrons and ten lone pair σ electrons and are thereby crucial for the stability of the molecule. Within the aromatic lone-pair σ -system, in addition to the lowest nonbonding state at -5.40 eV, we also discover an anti-bonding state at -2.43 eV, suggesting the presence of electron-electron repulsion as compared to prototypical benzene (Fig. 3S). The former nonbonding state reflects inter-lone-pair attraction, which causes the lone-pair electrons to delocalize to form a cyclic domain and allows the *cyclo*-N₅⁻ anion to be a self-closed system with the characteristics of conventional aromatics – high stability and non-reactivity to electrophilic attack. The latter anti-bonding state, namely, the electron-electron repulsive interaction within the σ -aromatic system, confers instability and basicity on *cyclo*-N₅⁻ anion, making it **easier to** broken and more attractive to electrophiles. Therefore, the competition between the repulsion and attraction components within the two aromatic systems of *cyclo*-N₅⁻ is able to account for the stability mechanism of *cyclo*-N₅⁻.

Anomalous stability and reactivity of dual-aromatic *cyclo*-N₅⁻ anion

We have designed a series of computational simulation tests to explore the stability and reactivity of the *cyclo*-N₅⁻ anion at various levels of acidity ($c = [\text{H}^+]/[\textit{cyclo}\text{-N}_5^-]$).

According to our simulation, when *cyclo*-N₅⁻ is in the presence of one hydronium ion ($c = 1$), the proton quickly transfers from the hydronium ion to the *cyclo*-N₅⁻ anion to form an additional single bond (Figs. 2A and 2B). Dynamic simulation shows that this proton transport is barrierless (Fig. 4S). Simultaneously, the aromaticity of *cyclo*-N₅⁻ as well as its

π and σ components is reduced compared to the naked *cyclo-N₅⁻*, as shown by the decreasing (absolute) values of NICS_{zz}(0.6) (by 5.14, 1.76, and 1.53 for the total and the π and σ components, respectively) and the ELF bifurcation (by 0.028, 0.205, and 0.022 for the total, π , and σ components, respectively) in Table 2 and Figs. 5S and 6S. Meanwhile, this reaction reduces the inter-lone-pair repulsion at the sites of the second adjacent N-N bonds of the protonated nitrogen atom, as marked by the open circles in Fig. 2C, and thus shortens (enhances) these N-N bonds by 0.04 Å (Fig. 7S). From above, at the acidity $c = 1$, the inter-lone-pair repulsion within the σ -aromatic system dominates the chemistry of *cyclo-N₅⁻*, energetically driving the anion to undergo an addition reaction by diminishing the attraction component of two aromatic systems; this process enhances two of the five N-N bonds of the *cyclo-N₅⁻* anion.

When $c = 2$, our calculations show that two nitrogen atoms are alternatively protonated along the ring (Figs. 2A, 2B and Figs. 7S-9S) to relax the interproton $H^+ - H^+$ repulsion at the outer layer of the *cyclo-N₅⁻*. Similar to the situation of $c = 1$, the protonation of nitrogen atoms sacrifices the attractive portion of the dual-aromatic system of *cyclo-N₅⁻*, as shown in Fig. 2D. Quantitatively, the bifurcation value of ELF_{total} is reduced by 4.06% and the absolute value of NICS_{zz}(0.6)_{total} by 16.42% (Table 2). That is, at the acidity $c = 2$, the inter-lone-pair repulsion still pushes *cyclo-N₅⁻* to undergo further addition reaction by continuously diminishing its dual aromaticity. After this reaction, three of the five N-N bonds of *cyclo-N₅⁻* are enhanced.

When $c = 3$, the proton has almost identical interaction strength to that of *cyclo-N₅⁻* (41.92 kcal/mol) and H₂O (44.59 kcal/mol), so we name this case as the critical situation.

Two lone pairs **maintain** at the para-positions of the *cyclo*-N₅[−] ring to secure the cyclic delocalization of the lone-pair electrons and the aromaticity indices of NICS_{zz} and ELF approach minima (Fig. 2D and Table 2). Protonating four or more nitrogen atoms is forbidden because it would not only destroy the dual aromaticity of *cyclo*-N₅[−] (Fig. 10S) but also create additional interproton repulsion, making the *cyclo*-N₅[−] complex even less stable.

When $c = 4$, we find that all the intermediate protons are energetically in favour of being H₂O-attached (approximately 1.05 Å) instead of *cyclo*-N₅[−] anion-attached (approximately 1.67 Å) by ~0.41 eV, as shown in Figs. 2B and 8S and Table 1S. The *cyclo*-N₅[−] anion interacts with the surrounding hydronium ions *via* only hydrogen bonding (Fig. 9S) and no protonation occurs to the *cyclo*-N₅[−] anion. Meanwhile, the electron delocalization of the hydrogen bonds⁵⁴ helps the *cyclo*-N₅[−] lone pairs to rebuild the **dual** aromaticity (Fig. 2D), so the absolute value of NICS_{zz}(0.6)_{total} and the bifurcation value of ELF_{total} begin to grow again at $c = 4$ after their minima (around $c = 3$) (Table 2). That is, at $c = 4$, the attraction component of the two aromatic systems of *cyclo*-N₅[−] is **capable** to conquer the inter-lone-pair repulsion and turns *cyclo*-N₅[−] to be unreactive to aromatic addition reaction.

Scheme 1 shows the equilibrium mechanism of the entire N₅[−]⋯4H₃O⁺ complex. In this complex, the *cyclo*-N₅[−] anion serves as a negative charge centre that clusters, reorients, and polarizes the surrounding H₃O⁺ ions. The circumferential H⁺-H⁺ repulsion across the 4H₃O⁺ and the attraction between the lone-pair and the proton balance the entire *cyclo*-N₅[−]⋯4H₃O⁺ complex⁵⁵. These hydronium ions are not free but are clustered around the

cyclo-N₅⁻ anion. The protons of H₃O⁺ stretch the nitrogen lone pair radially away, weakening the circumferential repulsion between the lone pairs of *cyclo*-N₅⁻, and thus enhance all the N-N bonds by approximately 57.16 kcal/mol (Fig. 3A). Therefore, the *cyclo*-N₅⁻⋯4H₃O⁺ complex is the optimal stable structure – with reduced inter-lone-pair repulsion, intact dual-aromaticity and all enhanced N-N bonds – and, in particular, more stable than its naked or protonated counterpart.

Scheme 2 summarizes the stability and reactivity of the *cyclo*-N₅⁻ at various levels of acidity. At low acidity ($c < 3$), the inter-lone-pair repulsion within the σ -aromatic system makes *cyclo*-N₅⁻ highly reactive to electrophiles and only part of the N-N bonds in *cyclo*-N₅⁻ is enhanced. However, as the acidity increases, that repulsion is weakened, and the attraction component of the two aromatic systems becomes dominant. The *cyclo*-N₅⁻ turns to be reluctant to undergo that reaction but will violate acid-basic neutralization rule to form hydrogen-bonded complexes from surrounding electrophiles, making all the five N-N bonds strengthened and thereby giving *cyclo*-N₅⁻ extra stability. In addition, we have proved that replacing hydronium ions with ammonium ions leads to the same result (Fig. 11S and Table 2S).

Experimental verification and practical application of current findings

To verify our findings from an experimental perspective, we have compared the vibrational spectra for the (N₅)₆(H₃O)₃(NH₄)₄Cl crystal³⁷ and the HN₅ molecule in Fig. 3B. The N-H stretching vibration mode featured at 3560 cm⁻¹, which is a sign of the formation of the H-N σ -bond, is not present in (N₅)₆(H₃O)₃(NH₄)₄Cl, suggesting the unprotonated state of *cyclo*-N₅⁻ in the crystal. This vibrational comparison thereby confirms our

theoretical finding that *cyclo*-N₅[−] is non-reactive to electrophiles (hydronium and ammonium ions) when the acidity exceeds three.

Based on our theory, to synthesize *cyclo*-N₅[−] compounds with high yield, the proton concentration should be controlled to remain three times greater (optimally four) than that of *cyclo*-N₅[−] in the solution. As shown in Fig. 2, the required level of acidity **allows** *cyclo*-N₅[−] to form hydrogen bonds with surrounding counterions, making all its five N-N bonds stronger than the C-N bond that links the aryl and pentazole group in 3,5-dimethyl-4-hydroxyphenylpentazole (HPP) by 39.72 kcal/mol (Fig. 3A), thereby allowing the successful separation of *cyclo*-N₅[−] from the solution. This result is experimentally verified by the known yield of *cyclo*-N₅[−] from *m*-CPBA solution, the acidity of which is stabilized by [Fe(Gly)₂].^{37, 40-41, 56-57} If the solution is not sufficiently acidic, as shown in Fig. 3B, some of the N-N bonds of the partially protonated *cyclo*-N₅[−] are weaker than the C-N bond in **the** HPP and will decompose prior to C-N bond cleavage in HPP. This mechanism also explains why the *cyclo*-N₅[−] anion could not be productively isolated in gas or neutral solutions.^{33-34, 36}

Conclusions

To conclude, we have discovered the anomalous dual-aromaticity (π and σ) in the *cyclo*-N₅[−], which makes the anion unstable in nature but confers additional stability in sufficiently acidic surroundings. The long confused stability and reactivity problems of the *cyclo*-N₅[−], such as its instability in the gas phase and in neutral aqueous solution, its enhanced stability in acidic solution, its energetic preference for electrophilic aromatic addition reaction and its violation of acid-base neutralization, can all be addressed from the

competition view between the repulsion and attraction within the two aromatic systems of *cyclo-N₅⁻*.

- (a) The “dual” aromaticity here has double meanings: (i) two types of electrons and (ii) two aromatic systems and is thereby significantly different from the known dual aromaticity of all-metal species.
- (b) The reactivity to electrophilic attack of the *cyclo-N₅⁻* is adaptively dependent on the acidity of its surroundings. At low acidic concentrations, the inter-lone-pair repulsion drives *cyclo-N₅⁻* to undergo electrophilic aromatic addition reactions. In sufficiently acidic condition ($c > 3$), the attraction component of the dual-aromatic system defeats the repulsion component. The *cyclo-N₅⁻* turns to be unsusceptible to that electrophilic attack but will violate acid-basic neutralization rule to form hydrogen-bonded complexes, making all the five N-N bonds strengthened and thereby conferring *cyclo-N₅⁻* additional stability.
- (c) To realize high-yield synthesis of the *cyclo-N₅⁻* compounds, the proton concentration (H_3O^+ or NH_4^+) should be controlled to remain three times greater (optimally four) than that of *cyclo-N₅⁻* in the solution.
- (d) We have informed the key role of the lone pair electrons in distinguishing the chemistry of the nitrogen dual-aromatics from those conventional aromatics. The dual aromaticity discovered in *cyclo-N₅⁻* is expected to be a universal nature of the pnictogen five-membered rings.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

This work is accomplished within JUSMART-D studio. Financial support from the National Natural Science Foundation of China (No. 11604017, 11572053 and U1730244), the Science Challenging Program of China (No. TZ2016001), and the National Supercomputing Center (Shenzhen) and helpful discussions with BC Hu, M Gozin, M Šob, E Hayward, CY Zhang, JG Zhang and HH Zong are gratefully acknowledged.

References:

1. Schleyer, P. R. v.; Jiao, H., What is aromaticity? *Pure Appl. Chem.* **1996**, *68* (2), 209-218.
2. Kruszewski, J.; Krygowski, T. M., Definition of aromaticity basing on the harmonic oscillator model. *Tetrahedron Lett.* **1972**, *13* (36), 3839-3842.
3. Krygowski, T. M., Crystallographic studies of inter- and intramolecular interactions reflected in aromatic character of π -electron systems. *J. Chem. Inf. Comput. Sci.* **1993**, *33* (1), 70-78.
4. Bird, C. W., A new aromaticity index and its application to five-membered ring heterocycles. *Tetrahedron* **1985**, *41* (7), 1409-1414.
5. Schleyer, P. v. R., Introduction: Aromaticity. *Chem. Rev.* **2001**, *101* (5), 1115-1118.
6. Katritzky, A. R.; Jug, K.; Oniciu, D. C., Quantitative Measures of Aromaticity for Mono-, Bi-, and Tricyclic Penta- and Hexaatomic Heteroaromatic Ring Systems and Their Interrelationships. *Chem. Rev.* **2001**, *101* (5), 1421-1450.
7. Krygowski, T. M.; Cyrański, M. K., Structural Aspects of Aromaticity. *Chem. Rev.* **2001**, *101* (5), 1385-1420.
8. De Proft, F.; Geerlings, P., Conceptual and Computational DFT in the Study of Aromaticity. *Chem. Rev.* **2001**, *101* (5), 1451-1464.
9. Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R., Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* **2005**, *105*, 3842-3888.
10. Hirsch, A.; Chen, Z.; Jiao, H., Spherical Aromaticity in Ih Symmetrical Fullerenes: The $2(N+1)2$ Rule. *Angew. Chem., Int. Ed.* **2000**, *39* (21), 3915-3917.
11. Velian, A.; Cummins, C. C., Synthesis and characterization of $P_2N_3^-$: An aromatic ion composed of phosphorus and nitrogen. *Science* **2015**, *348* (6238), 1001-1004.
12. Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentealba, P., sigma- π separation of the electron localization function and aromaticity. *J. Chem. Phys.* **2004**, *120* (4), 1670-1673.
13. Noorizadeh, S.; Shakerzadeh, E., Shannon entropy as a new measure of aromaticity, Shannon aromaticity. *Phys. Chem. Chem. Phys.* **2010**, *12* (18), 4742-4749.
14. Howard, S. T.; Krygowski, T. M., Benzenoid hydrocarbon aromaticity in terms of charge density descriptors. *Can. J. Chem.* **1997**, *75* (9), 1174-1181.
15. Poater, J.; Fradera, X.; Duran, M.; Solà, M., The Delocalization Index as an Electronic Aromaticity Criterion: Application to a Series of Planar Polycyclic Aromatic Hydrocarbons. *Chem. - Eur. J.* **2003**, *9* (2), 400-406.
16. Matito, E., An electronic aromaticity index for large rings. *Phys. Chem. Chem. Phys.* **2016**, *18* (17),

11839-11846.

17. Matito, E.; Duran, M.; Solà, M., The aromatic fluctuation index (FLU): A new aromaticity index based on electron delocalization. *J. Chem. Phys.* **2004**, *122* (1), 014109.
18. Badri, Z.; Foroutan-Nejad, C., Unification of ground-state aromaticity criteria - structure, electron delocalization, and energy - in light of the quantum chemical topology. *Phys. Chem. Chem. Phys.* **2016**, *18* (17), 11693-11699.
19. Chen, Z.; Corminboeuf, C.; Heine, T.; Bohmann, J.; Schleyer, P. v. R., Do All-Metal Antiaromatic Clusters Exist? *Journal of the American Chemical Society* **2003**, *125* (46), 13930-13931.
20. Li, X.; Kuznetsov, A. E.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L.-S., Observation of All-Metal Aromatic Molecules. *Science* **2001**, *291* (5505), 859-861.
21. Boldyrev, A. I.; Wang, L.-S., All-Metal Aromaticity and Antiaromaticity. *Chem. Rev.* **2005**, *105* (10), 3716-3757.
22. Clayden, J.; Greeves, N.; Warren, S., *Organic Chemistry*. 2 ed.; Oxford University Press: 2000.
23. Nguyen, M. T., Polynitrogen compounds: 1. Structure and stability of N₄ and N₅ systems. *Coord. Chem. Rev.* **2003**, *244* (1), 93-113.
24. Jiang, C.; Zhang, L.; Sun, C.; Zhang, C.; Yang, C.; Chen, J.; Hu, B., Response to Comment on "Synthesis and characterization of the pentazolate anion *cyclo*-N₅⁻ in (N₅)₆(H₃O)₃(NH₄)₄Cl.". *Science* **2018**, *359* (6381), eaas8953.
25. Huang, R.-Y.; Xu, H., Comment on "Synthesis and characterization of the pentazolate anion *cyclo*-N₅⁻ in (N₅)₆(H₃O)₃(NH₄)₄Cl.". *Science* **2018**, *359* (6381), eaao3672.
26. Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F.; Elguéro, J., Can the pentazole anion (N₅⁻) be isolated and/or trapped in metal complexes? *Polyhedron* **1985**, *4* (10), 1721-1726.
27. Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R., Besides N₂, What Is the Most Stable Molecule Composed Only of Nitrogen Atoms? *Inorg. Chem.* **1996**, *35* (24), 7124-7133.
28. Najafpour, J.; Foroutan-Nejad, C.; Shafiee, G. H.; Peykani, M. K., How does electron delocalization affect the electronic energy? A survey of neutral poly-nitrogen clusters. *Comput. Theor. Chem.* **2011**, *974* (1), 86-91.
29. Hantzsch, A., Ueber Diazoniumazide, Ar.N₅. *Ber. Dtsch. Chem. Ges.* **1903**, *36* (2), 2056-2058.
30. Dimroth, O.; Montmollin, G. d., Zur Kenntnis der Diazohydrazide. *Ber. Dtsch. Chem. Ges.* **1910**, *43* (3), 2904-2915.
31. Lifschitz, J., Synthese der Pentazol - Verbindungen. I. *Ber. Dtsch. Chem. Ges.* **1915**, *48* (1), 410-420.
32. Curtius, T.; Darapsky, A.; Müller, E., Die sogenannten Pentazol - Verbindungen von J. Lifschitz. *Ber. Dtsch. Chem. Ges.* **1915**, *48* (2), 1614-1634.
33. Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O., Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion, *cyclo*-N₅⁻. *Angew. Chem., Int. Ed.* **2002**, *41* (16), 3051-3054.
34. Butler, R. N.; Stephens, J. C.; Burke, L. A., First generation of pentazole (HN₅, pentazolic acid), the final azole, and a zinc pentazolate salt in solution: A new N-dearylation of 1-(p-methoxyphenyl) pyrazoles, a 2-(p-methoxyphenyl) tetrazole and application of the methodology to 1-(p-methoxyphenyl) pentazole. *Chem. Commun.* **2003**, *0* (8), 1016-1017.
35. Perera, S. A.; Gregusova, A.; Bartlett, R. J., First calculations of ¹⁵N-¹⁵N J values and new calculations of chemical shifts for high nitrogen systems: a comment on the long search for HN₅ and its pentazole anion. *J Phys Chem A* **2009**, *113* (13), 3197-201.
36. Bazanov, B.; Geiger, U.; Carmieli, R.; Grinstein, D.; Welner, S.; Haas, Y., Detection of *Cyclo*-N₅⁻ in THF Solution. *Angew. Chem., Int. Ed.* **2016**, *55* (42), 13233-13235.

37. Zhang, C.; Sun, C.; Hu, B.; Yu, C.; Lu, M., Synthesis and characterization of the pentazolate anion *cyclo-N₅⁻* in (N₅)₆(H₃O)₃(NH₄)₄Cl. *Science* **2017**, 355 (6323), 374-376.
38. Chen, W.; Liu, Z.; Zhao, Y.; Yi, X.; Chen, Z.; Zheng, A., To Be or Not to Be Protonated: Cyclo-N₅⁻ in Crystal and Solvent. *The Journal of Physical Chemistry Letters* **2018**, 9, 7137-7145.
39. Wang, P.; Xu, Y.; Lin, Q.; Lu, M., Recent advances in the syntheses and properties of polynitrogen pentazolate anion *cyclo-N₅⁻* and its derivatives. *Chem. Soc. Rev.* **2018**, 47, 7522-7538
40. Xu, Y.; Wang, Q.; Shen, C.; Lin, Q.; Wang, P.; Lu, M., A series of energetic metal pentazolate hydrates. *Nature* **2017**, 549 (7670), 78–81.
41. Zhang, C.; Yang, C.; Hu, B.; Yu, C.; Zheng, Z.; Sun, C., A Symmetric Co(N₅)₂(H₂O)₄·4 H₂O High-Nitrogen Compound Formed by Cobalt(II) Cation Trapping of a *Cyclo-N₅⁻* Anion. *Angew. Chem., Int. Ed.* **2017**, 56 (16), 4512-4514.
42. Xu, Y.; Wang, P.; Lin, Q.; Lu, M., A carbon-free inorganic–metal complex consisting of an all-nitrogen pentazole anion, a Zn(ii) cation and H₂O. *Dalton Transactions* **2017**, 46 (41), 14088-14093.
43. Christe, K. O., Polynitrogen chemistry enters the ring. *Science* **2017**, 355 (6323), 351-351.
44. Xu, Y.; Lin, Q.; Wang, P.; Lu, M., Syntheses, Crystal Structures and Properties of a Series of 3D Metal–Inorganic Frameworks Containing Pentazolate Anion. *Chem. - Asian J.* **2018**, 13 (13), 1669-1673.
45. Zhang, L.; Jiang, S.-L.; Yu, Y.; Long, Y.; Zhao, H.-Y.; Peng, L.-J.; Chen, J., Phase Transition in Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) under Static Compression: An Application of the First-Principles Method Specialized for CHNO Solid Explosives. *J. Phys. Chem. B* **2016**, 120 (44), 11510-11522.
46. Chen, J.; Jiang, S.-L.; Zhang, L.; Yu, Y. *HASEM*, 1.0; HASEM 1.0, CAEP-SCNS: 2016.
47. Mo, Z.; Zhang, A.; Cao, X.; Liu, Q.; Xu, X.; An, H.; Pei, W.; Zhu, S., JASMIN: a parallel software infrastructure for scientific computing. *Front. Comput. Sci. China* **2010**, 4 (4), 480–488.
48. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., J. E. P.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, D.01; Gaussian 09, Gaussian, Inc.: Wallingford CT, 2013.
49. Alkorta, I.; Elguero, J., A computational study of azaphospholes: anions and neutral tautomers. *Structural Chemistry* **2016**, 27 (5), 1531-1542.
50. Wang, L.; Wang, H. J.; Dong, W. B.; Ge, Q. Y.; Lin, L., Using three major criteria to evaluate aromaticity of five-member C-containing rings and their Si-, N-, and P-substituted aromatic heterocyclics. *Structural Chemistry* **2007**, 18 (1), 25-31.
51. To provide an intuitive picture of magnetic shielding due to the dual aromaticity of *cyclo-N₅⁻*, we have also presented the ICSS analysis (Supplementary Information Fig. 2S), in which the z-direction external magnetic field is largely shielded in the region above and below the pentazolate anion ring as well as the region of the nitrogen lone pairs, suggesting the presence of dual aromaticity in *cyclo-N₅⁻*.
52. De Proft, F.; Fowler, P. W.; Havenith, R. W. A.; Schleyer, P. v. R.; Van Lier, G.; Geerlings, P., Ring Currents as Probes of the Aromaticity of Inorganic Monocycles : P₅⁻, As₅⁻, S₂N₂, S₃N₃⁻, S₄N₃⁺, S₄N₄²⁺,

- S5N5⁺, S42⁺ and Se42⁺. *Chemistry – A European Journal* **2004**, 10 (4), 940-950.
53. Liu, Z.-Z.; Tian, W.-Q.; Feng, J.-K.; Zhang, G.; Li, W.-Q., Theoretical Study on Structures and Aromaticities of P5⁻ Anion, [Ti (η⁵-P5)]⁻ and Sandwich Complex [Ti(η⁵-P5)₂]². *The Journal of Physical Chemistry A* **2005**, 109 (25), 5645-5655.
54. Zhang, Z.; Li, D.; Jiang, W.; Wang, Z., The electron density delocalization of hydrogen bond systems. *Adv. Phys.: X* **2018**, 3 (1), 1428915.
55. Sun, C. Q.; Sun, Y., *The Attribute of Water: Single Notion, Multiple Myths*. Springer-Verlag: 2016; p 494.
56. Zhang, W.; Wang, K.; Li, J.; Lin, Z.; Song, S.; Huang, S.; Liu, Y.; Nie, F.; Zhang, Q., Stabilization of the Pentazolate Anion in a Zeolitic Architecture with Na₂₀N₆₀ and Na₂₄N₆₀ Nanocages. *Angew. Chem., Int. Ed.* **2018**, 57 (10), 2592-2595.
57. Sun, C.; Zhang, C.; Jiang, C.; Yang, C.; Du, Y.; Zhao, Y.; Hu, B.; Zheng, Z.; Christe, K. O., Synthesis of AgN₅ and its extended 3D energetic framework. *Nat. Commun.* **2018**, 9 (1), 1269.
58. 肖鹤鸣; 居学海, *高能体系中的分子间相互作用*. 科学出版社: 2004.
59. The geometries of these complexes are optimized using the HASEM method, the NICS analysis is performed at the B3LYP/6-311++G(d, p) level and the ELF analysis is at the CCSD(T)/6-31G+ level.

Author information

Correspondence and requests for materials should be addressed to L.Z (zhang_lei@iapcm.ac.cn) and J.C. (jun_chen@iapcm.ac.cn).

Supplementary information

The Supplementary Information includes computational methods, eleven figures and two tables.

Computational methods include eight sections: (1) Probing dual aromaticity of *cyclo*-N₅⁻; (2) Geometry optimization; (3) Dynamics simulation; (4) Vibrational spectra; (5) Local density of states (LDOS); (6) Crystal orbital overlap population (COOP); (7) Covalent/hydrogen bond strengths; (8) Proton-affinity.

Figure 1S shows the (L)DOS distribution of the *cyclo*-N₅⁻.

Figure 2S confirms the dual aromaticity of *cyclo*-N₅⁻ by the magnetic shielding index.

Figure 3S confirms the coexistence of inter-lone-pair attraction and inter-lone-pair repulsion within the σ -aromatic system of *cyclo*-N₅⁻ using crystal orbital overlap population.

Figure 4S shows the dynamic simulation results, revealing the completely opposite reactivity of *cyclo*-N₅⁻ in (N₅)₆(H₃O)₃(NH₄)₄Cl crystal (surrounded by two ammonium ions and three hydronium ions) and in the vacuum (with only one hydronium ion).

Figures 5S and 6S show the evolution of the dual aromaticity of *cyclo*-N₅⁻ at various acidities using magnetic index NICS and electron-based index ELF, respectively.

Figure 7S shows the structures of the N₅⁻ complexes, revealing that acidic surroundings weaken the inter-lone-pair repulsion within *cyclo*-N₅⁻ and shorten its N-N bonds.

Figure 8S shows the reactivity of *cyclo*-N₅⁻ as a function of acidity using a combination of structural, energetics and orbital methods.

Figure 9S illustrates the hydrogen bond interaction mechanism using a combination of crystal orbital overlap population and density of states.

Figure 10S compares the aromaticity of *cyclo*-N₅⁻ when it is assumed to be protonated and unprotonated at the optimal acidity $c = 4$.

Figure 11S confirms that ammonium ion can also entrap and stabilize *cyclo*-N₅⁻, similar to that of hydronium ion.

Table 1S and 2S give the lengths and strengths of the N₅⁻-attached bond and the H₃O⁺-attached bond in the *cyclo*-N₅⁻...*c*H₃O⁺ and *cyclo*-N₅⁻...*c*NH₄⁺ complexes. Both demonstrate that as the acidity increases, *cyclo*-N₅⁻ changes from a protonated to an

unprotonated state.

Figures and tables

Fig. 1 Discovery of dual aromaticity in the *cyclo-N₅⁻* anion. (A) Atomic orbital diagram of *cyclo-N₅⁻* anion. (B) The topology of the Laplacian distribution of charge density ρ in the plane of the *cyclo-N₅⁻* anion is shown with regions of charge depletion in solid curves and those of charge concentration in dashed curves. Bond paths, bond and ring critical points, and atomic basin paths are also depicted. (C) NICS_{zz}(r) of the *cyclo-N₅⁻* anion and its σ and π orbital components as a function of the vertical distance relative to the ring critical point; the corresponding curves for benzene are also plotted for comparison. (D) π and lone-pair σ MOs of *cyclo-N₅⁻* anion. Also given are the ELF isosurface (at the bifurcation points) and the LDOS isosurface for the π and lone-pair σ electrons at each minimum energy level. The ELF isosurfaces for all six π electrons and for all ten lone-pair σ electrons are also plotted, respectively, to confirm the presence of the dual aromaticity in *cyclo-N₅⁻*.

Fig. 2 Structures, energetics, LDOS plots and NICS_{zz} indices of the *cyclo*-N₅[−] at various acid concentrations. (A) Optimized structures of the *cyclo*-N₅[−] complex/crystal at various acid concentrations. (B) Energetic landscape of the *cyclo*-N₅[−] complex/crystal as a function of the N-H distance when the proton goes from the *cyclo*-N₅[−] anion-attached to the H₂O-attached location. (C) LDOS at the anti-bonding energy level plotted in the equatorial plane of *cyclo*-N₅[−] under various acidities. (D) NICS_{zz}(0.6)_{total} and NICS_{zz}(0.6)_σ of the *cyclo*-N₅[−] anion under various acidities and the corresponding LDOS isosurfaces plotted for the lowest energy level (nonbonding) of the aromatic π - and σ - systems.

Fig. 3 Experimental verification. (A) N-N bond strengths in the $cyclo-N_5^-$ anion (bars) at various acid concentrations with respect to the C-N bond strength in HPP (dashed line). The $cyclo-N_5^-$ can be productively separated from the solution only when all the N-N bonds in the $cyclo-N_5^-$ anion are stronger than the C-N bond in HPP, namely, when $c > 3$. (B) Vibrational spectra suggest the absence of the H-N σ -bond in the $(N_5)_6(H_3O)_3(NH_4)_4Cl$ crystal and confirm the non-reactivity of $cyclo-N_5^-$ to hydronium and ammonium attack when the acidity is greater than three.

Scheme 1. Equilibrium of the entire $cyclo-N_5^- \cdots 4H_3O^+$ complex at the optimal acidity $c = 4$. The attraction between the lone-pair electrons and the proton shortens and strengthens not only the H-O bond in H_3O^+ but also the N-N bond along the N_5^- ring. The former is realized by hydrogen bond cooperativity. The latter is realized by weakening the inter-lone-pair repulsion. The circumferential interproton repulsion among the four H_3O^+ and the attraction between the lone-pair and the proton balance the entire $cyclo-N_5^- \cdots 4H_3O^+$ complex. (N:H is the nonbonding attraction, with “:” representing the electron lone pair.)

Scheme 2. Various reactivity of cyclo-N_5^- to hydronium/ammonium ions at different acidity ($c = [\text{H}^+]/[\text{cyclo-N}_5^-]$). At low acidity ($c < 3$), the cyclo-N_5^- undergoes electrophilic aromatic addition reactions and have part of its N-N bonds enhanced. When $c > 3$, the cyclo-N_5^- turns to be unsusceptible to the electrophilic attack but will violate acid-basic neutralization rule to form hydrogen-bonded complexes, making all the five N-N bonds strengthened and thereby conferring cyclo-N_5^- additional stability. Introducing a fifth proton into the isolated complex is proved to be impossible due to the inclusion of too strong interproton repulsion but is possible in a crystal with the aid of the balance of the crystal packing force.

Table 1 Confirmation of dual aromaticity in *cyclo*-N₅[−] anion (as compared to prototypical benzene) **using the structural, magnetic, and electronics-based aromaticity indices**⁵⁸. The aromaticity indices with π/σ subscripts are the components contributed by all the π -electrons/lone-pair σ -electrons, whereas those with min- π /min- σ subscripts are the components contributed by the π -electrons/lone-pair σ -electrons at **each** lowest energy level.

Aromaticity indices		<i>Cyclo</i>-N₅[−]	Benzene
Magnetic	NICS _{zz} (1) _{total}	-43.77	-29.07
	NICS _{zz} (1) _{π}	-25.02	-28.96
	NICS _{zz} (1) _{σ}	-18.75	+7.70
	NICS(1) _{total}	-16.38, -16.5 ²³	-10.24, -10.0 ²³
	NICS _{zz} (0) _{total}	-42.71	-14.48
	NICS _{zz} (0) _{π}	-34.22	-35.58
	NICS _{zz} (0) _{σ}	-8.48	+29.25
	NICS(0) _{total}	-17.12	-8.07
Electronic	ELF _{total}	0.713, 0.73 ¹²	0.655, 0.68 ¹²
	ELF _{π}	0.791, 0.78 ¹²	0.922, 0.91 ¹²
	ELF _{σ}	0.797, 0.81 ¹²	0.686, 0.76 ¹²
	ELF _{min-π}	0.999922	0.999984
	ELF _{min-σ}	0.999997	-
	DI _{total} ^{15,(1)}	1.61	1.47
	DI _{min-π} ⁽²⁾	0.16	0.11
	DI _{min-σ} ⁽²⁾	0.16	
	SA ¹³	2×10 ⁻¹⁰	7×10 ⁻¹⁰
	RCP ρ curvature ¹⁴	-0.08	-0.01
Structural	HOMA ²⁻³	1.0	1.0, 1.0 ²
	BI ⁴	100	100

Notes: (1) DI_{total} is calculated for the N-N bond in *cyclo*-N₅[−] and the C-C bond in benzene

in order to show their multiple bonding character. (2) $DI_{\min-\pi}$ and $DI_{\min-\sigma}$ are calculated for any two nitrogen atoms in $cyclo-N_5^-$ ($C_5^2 = 10$ possible combinations). $DI_{\min-\pi} = DI_{\min-\sigma} = 0.16$ for all the ten possible combinations in $cyclo-N_5^-$, thereby confirming the full delocalization of the electrons at the minimum π and σ orbitals and the presence of dual aromaticity of $cyclo-N_5^-$.

Table 2 Probing evolution of the dual aromaticity of the *cyclo*-N₅[−] anion as the acidity increases⁵⁹. Tabulated are the most negative NICS_{zz}(*r*) values (when *r*=0.6 Å above the RPC of the *cyclo*-N₅[−] anion; refer to *Supplementary Information* Fig. 5S) and bifurcation values of ELF (refer to *Supplementary Information* Fig. 6S) of the *cyclo*-N₅[−] anion under various acidities; the corresponding π - and σ -components of each aromaticity index are also given.

Acidity <i>c</i>	NICS _{zz} (0.6)			Bifurcation values of ELF		
	Total	π	σ	total	π	σ
0	-50.45	-31.77	-18.68	0.713	0.791	0.797
1	-45.31	-30.00	-17.15	0.685	0.586	0.775
2	-42.17	-28.72	-15.47	0.684	0.557	0.766
3	-43.44	-33.96	-11.75	0.696	0.536	0.784
4	-44.45	-29.70	-16.26	0.702	0.693	0.795
5	-48.52	-32.34	-18.39	0.713	0.777	0.794