Acidic Stabilization of the Dual-Aromatic Heterocyclic Anions

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Abstract: Recently, we discovered that the delocalization of nitrogen lone-pair electrons (NLPEs) in five-membered nitrogen heterocycles created a second \( \pi \)-aromaticity in addition to the prototypical \( \pi \)-aromaticity. Such dual-aromatic compounds, such as the pentazole anion, were proved to have distinct chemistry in comparison to traditional \( \pi \)-aromatics, such as benzene, and were surprisingly unstable, susceptible to electrophilic attack, and relatively difficult to obtain. The dual-aromatics are basic in nature, but prefer not to be protonated when confronting more than three hydronium/ammonium ions, which violates common sense understanding of acid—base neutralization for a reason that is unclear. Here, we carried out 63 test simulations to explore the stability and reactivity of three basic heterocycle anions (pentazole anion \( \text{N}_5^- \), tetrazole anion \( \text{N}_4\text{C}_2\text{H}_1^- \), and 1,2,4-triazole anion \( \text{N}_2\text{C}_2\text{H}_2^- \)) in four types of solvents (acidic ions, \( \text{H}_3\text{O}^+ \) and \( \text{NH}_4^+ \), polar organics, THF, and neutral organics, benzene) with different acidities and concentrations. By quantum mechanical calculations of the electron density, atomistic structure, interatomic interactions, molecular orbital, magnetic shielding, and energetics, we confirmed the presence of dual aromaticity in the heterocyclic anions, and discovered their reactivity to be a competition between their basicity and dual aromaticity. Interestingly, when the acidic ions \( \text{H}_3\text{O}^+ / \text{NH}_4^+ \) are three times more in number than the basic heterocyclic anions, the anions turn to violate acid—base neutralization and remain unprotonated, and the surrounding acidic ions start to show a significant stabilization effect on the studied heterocyclic anions. This work brings new knowledge to nitrogen aromatics and the finding is expected to be adaptable for other pnictogen five-membered ring systems.

Keywords: acidic stabilization; dual-aromaticity; heterocyclic anions; quantum mechanics calculations

1. Introduction

Nitrogen-rich, high-energy-density materials (HEDMs), in which the nitrogen weight is higher than 50\% [1], are known to generate a large amount of heat when exothermically decomposing into molecular dinitrogen [2]. In addition, a considerable amount of nitrogen-rich HEDMs also show low-shock sensitivity, improved burning rate, and other advanced advantages [3]. Therefore, nitrogen-rich HEDMs are very promising candidates to address the long-standing, high-energy density and low-sensitivity contradiction of HEDMs, and can potentially be utilized to safely conduct space exploration, explore ultra-deep mineral deposits on Earth, and so forth [4–9]. For example, 3-nitro-1,2,4-triazole-5-one (NTO) has a high-energy density (comparable to RDX) and low sensitivity (lower than HMX), and has become a very important ingredient in the polymer-bonded explosive (PBX) formulations for insensitive munitions (IMs) [1,10,11]. Triaminoguanidinium azotetrazolate (TAGzT) can increase the heat generation and burning rates of propellants over a wide pressure range [3]. 5′-hydrazinebistetrazole (HBT) and bis (3,4,5-triamino-1,2,4-triazolium) 5,5′-azotetrazolate (GzZT) contain up to \( \sim \)80% of nitrogen weight and present a relatively high...
combustion heat (−2396 cal/g for HBT and −2775 cal/g for G2ZT) [12]. In particular, the pentazole anion has a nitrogen weight of 100% and its reaction product consists only of molecular dinitrogen. Therefore, the pentazole anion is considered the ultimate in the pursuit of energetic material that is green, non-polluting, and ultra-high energetic [1].

Due to the above satisfactory comprehensive properties, nitrogen-rich HEDMs, such as triazoles, tetrazoles, and pentazoles, are extensively used as building blocks for the design of advanced, new HEDMs [1,13–21]. However, the stabilization mechanism of nitrogen heterocycles, which is essential for the rational design and large-scale production of advanced HEDMs, remains unclear. The problem is mainly focused on the distributions and states of the nitrogen lone-pair electrons (NLPEs), and their influence on the structural stability and chemical reactivity of heterocycles. For example, the valence shell electron pair repulsion (VSEPR) theory suggests that the NLPEs are localized in the vicinity of each separate nitrogen atom. Therefore, the NLPEs in a cyclic system should repel the adjacent C–N bonds and other lone pairs in the ring [22–24], thereby destabilizing the system. However, this derivation contradicts the fact that the presence of nitrogen in the ring can actually impart a higher degree of stability to these molecules compared to their hydrocarbon analogs [22,25]. To interpret this “aza-stabilization” anomaly, some researchers have proposed that the NLPEs are delocalized over the cyclic systems instead of being localized on separate nitrogen atoms [25,26]. However, this proposition is again challenged by the elusive chemistry of the pentazole anion. The pentazole anion has five nitrogen atoms and one π-electron aromatic system, and theoretically, it should be very stable. However, the pentazole anion has been proved to be surprisingly unstable, difficult to obtain, and susceptible to electrophilic attack [26–32]. The pentazole anion is basic in nature, but prefers not to be protonated when facing more than three hydronium/ammonium ions [28,33], which violates the acid–base neutralization rule for reasons that are unclear. Therefore, a better understanding of the stabilization and reactivity of nitrogen heterocyclic species requires new knowledge of nitrogen chemistry.

Recently, we discovered that the delocalization of NLPEs in five-membered nitrogen heterocycles creates a second σ-aromaticity, in addition to the prototypical π-aromaticity [34,35]. Taking the pentazole anion as an example, it has five nitrogen atoms in a planar ring and all the nitrogen atoms are sp² hybridized. Six electrons at the 2pₓ π molecular orbital (MO) constitute a complete π aromatic system, and ten NLPEs at the 2sp² σ MO give rise to an additional σ aromatic system. The dual-aromatic system features a simultaneous delocalization of the π electrons above/below the plane and the σ lone-pair electrons in the equatorial plane, which is very different from the multi-aromaticity of all-metal systems caused by an electron deficiency. Such dual-aromatic heterocyclic compounds were proved to have distinct chemistry in comparison to traditional π-aromatics, such as benzene. In vacuums, solutions, and crystals, the pentazole anion is protonated when facing less than three H₃O⁺/NH₄⁺ ions, and prefers not to be protonated when the number of H₃O⁺/NH₄⁺ ions is more than three. It is the compatible coexistence of the inter-lone-pair repulsion and inter-lone-pair attraction within the σ-aromatic system that makes the stability and reactivity of these dual-aromatics vary according to their environments [34].

In this work, we designed and conducted a series of quantum mechanical calculations to explore the structural stability and chemical reactivity of three heterocyclic anions in four types of solvents with different acidity and concentrations. Interestingly, when the acidic H₃O⁺/NH₄⁺ ions are three times more in number than the heterocyclic anions, they start to show a stabilization effect on the structural stability of the studied heterocycles. The detailed calculation results and proposed mechanism are shown below.

2. Results and Discussion
2.1. Presence of Dual Aromaticity in the Heterocyclic Anions Studied

From the atomic orbital diagrams in Figure 1, all the carbon and nitrogen atoms in N₅⁻, N₄C₁H₁⁻, and N₃C₂H₂⁻ were sp² hybridized. Taking into account the net foreign electron, which resided at the p orbital, each of the three heterocyclic anions obtained six π electrons,
respectively, forming a complete π-aromatic system. The isosurface of the lowest π MO (MO\textsubscript{min-π}) presented a shape spreading out over the entire molecule above and below each molecular plane. The delocalization index DI\textsubscript{min-π} was calculated to be 0.16 between any two atoms (nearest neighbors and second nearest neighbors) in the ring, thus confirming the full delocalization of the electrons at this minimum π orbital. As shown at the bottom of Figure 1, NICS\textsubscript{zz}(r)\textsubscript{π} was always negative when the vertical distance relative to each ring critical point (r) varied from 0.0 to 5.0 Å, thereby confirming the presence of π-aromaticity in the three heterocyclic anions. By comparing the calculated NICS\textsubscript{zz}(1)\textsubscript{π} of the three anions, the order of their π-aromaticity was N5\textsuperscript{−} (−26.1) > N4C1H1\textsuperscript{−} (−25.8) > N3C2H2\textsuperscript{−} (−25.2). Compared with benzene, which had DI\textsubscript{min-π} = 0.11 and NICS\textsubscript{zz}(1)\textsubscript{π} = −28.96, the three heterocyclic anions presented a higher level of electron delocalization, but a weaker π-aromaticity.

![Figure 1](image-url.com)  
**Figure 1.** Confirmation of presence of dual aromaticity in (A) pentazole anion N5\textsuperscript{−}, (B) tetrazole anion N4C1H1\textsuperscript{−}, and (C) 1,2,4-triazole anion N3C2H2\textsuperscript{−}. For each anion, illustrated from top left to bottom right, are the atomic orbital diagram, top view of isosurface (0.05) of the lowest π MO (MO\textsubscript{min-π}), side view of isosurface (0.05) of the lowest σ MO containing nitrogen lone pairs (MO\textsubscript{min-σ(LP)}), and NICS\textsubscript{zz}(r) (total value and its σ and π orbital components) as a function of the vertical distance relative to each ring critical point.

We next turned to the NLPE in the three heterocyclic anions. As shown by the isosurface of MO\textsubscript{min-σ(LP)} at the top of Figure 1, the NLPE presented an obvious delocalization over the rings of N5\textsuperscript{−}, N4C1H1\textsuperscript{−}, and N3C2H2\textsuperscript{−}, and the delocalization region expanded when more nitrogen atoms were present in the ring. Interestingly, the delocalization of the NLPE spreads out over the interior and exterior of the ring (Figure S4 of the Supplementary Materials). In N4C1H1\textsuperscript{−} and N3C2H2\textsuperscript{−}, the presence of the CH bonds destroys the NLPE delocalization in the interior of the ring, but their delocalization in the interior of the ring is not much influenced. In N5\textsuperscript{−}, the NLPE delocalization fulfills both the interior and exterior of the ring. Correspondingly, the DI\textsubscript{min-σ(LP)} values of N5\textsuperscript{−}, N4C1H1\textsuperscript{−}, and N3C2H2\textsuperscript{−} were all calculated to be 0.16, thereby confirming the NLPE delocalization at each minimum σ orbital. As shown at the bottom of Figure 1, the highest absolute value of the NICS\textsubscript{zz}(r)\textsubscript{σ} of N5\textsuperscript{−} was r\textsubscript{extreme} = 0.6 Å vertically above the ring critical point, which is the same as the P₂N₃\textsuperscript{−} anion [27]; for N₄C₁H₁\textsuperscript{−}, r\textsubscript{extreme} = 0.8 Å; for N₃C₂H₂\textsuperscript{−}, r\textsubscript{extreme} shifted to 1.0 Å. As shown in Table 1, the values of NICS\textsubscript{zz}(1)\textsubscript{σ} and NICS\textsubscript{zz}(r\textsubscript{extreme})\textsubscript{σ} were both negative, indicating the presence of an additional σ-aromaticity in the three heterocyclic anions; the order of their σ-aromaticity was N₅\textsuperscript{−} > N₄C₁H₁\textsuperscript{−} > N₃C₂H₂\textsuperscript{−}. The contributions of the NLPE delocalization to σ-aromaticity was also discovered in the (NH)ₙ (n = 3–6) systems [36].
cyclic anion. Therefore, the sequence of their basicity was $N_{5}^- < N_{4}C_{1}H_{1}^- < N_{3}C_{2}H_{2}^-$, which corresponds to a weaker acidity. As shown in Table 2, the calculated values of the proton affinity of pentazole anion $N_{5}^- = 165.0$ kcal/mol and $N_{4}C_{1}H_{1}^- = 204.0$ kcal/mol [39]. We also conducted a $pK_a$ calculation for $H_{2}O$ for further verification. $PA(H_{2}O) = 165.0$ kcal/mol and $PA(NH_{4}^+) = 204.0$ kcal/mol [39]. We also conducted a $PA$ calculation for $H_{2}O$ for further verification. $PA(H_{2}O)$ was calculated to be $396.1$ kcal/mol, which was close to the experimental result of $393.3$ kcal/mol [39]. The $PA(H_{2}O)$ value was between $PA(NH_{4}^+)$ and $PA(benzene)$, which was consistent with the experimental $pK_a$: $9.3$ (NH$_4^+$) $<$ 15.74 (H$_2$O) $<$ 43 (benzene). From the above calculations and for verification, the order of the acidity of the solvents was H$_3$O$^+$ $>$ NH$_4^+$ $>$ H$_2$O $>$

| Indices | $N_{5}^-$ | $N_{4}C_{1}H_{1}^-$ | $N_{3}C_{2}H_{2}^-$ | Benzene |
|---------|----------|-------------------|-------------------|---------|
| Total   | NICS$_{zz}(1)_{total}$ | $-45.16$ | $-40.24$ | $-35.78$ | $-29.07$ |
|         | NICS$_{zz}(r_{extreme})_{total}$ | $-51.81$ | $-43.44$ | $-37.53$ | - |
| $\pi$   | DI$_{min-\pi}$ | 0.16 | 0.16 | 0.16 | 0.11 |
|         | NICS$_{zz}(1)_{\pi}$ | $-26.09$ | $-25.81$ | $-25.23$ | $-28.96$ |
| $\sigma$| DI$_{min-\sigma}$ | 0.16 | 0.16 | 0.16 | - |
|         | NICS$_{zz}(1)_{\sigma}$ | $-19.06$ | $-14.42$ | $-10.55$ | $-0.11$ |
|         | NICS$_{zz}(r_{extreme})_{\sigma}$ | $-19.87$ | $-14.42$ | $-10.55$ | - |

We next evaluated the total aromaticity of the three heterocyclic anions and compared them with the prototypical benzene. As shown in Table 1, the NICS$_{zz}(1)_{total}$ and NICS$_{zz}(r_{extreme})_{total}$ values both showed the order of $N_{5}^- > N_{4}C_{1}H_{1}^- > N_{3}C_{2}H_{2}^-$, and all three heterocyclic anions presented a stronger aromaticity than benzene. Therefore, as more nitrogen atoms are present in the heterocycles, the NLPE are more delocalized, and the $\sigma$-aromaticity and overall aromaticity increases.

2.2. Basicity of Heterocyclic Anions and Acidity of Solvents Studied

The $PA$ defined by Equation (1) was employed to evaluate the basicity of the nitrogen heterocyclic anions studied; a higher $PA$ corresponds to a stronger basicity. As shown in Figure 2, the value of the $PA$ increased with the decrease in nitrogen atoms in the heterocyclic anion. Therefore, the sequence of their basicity was $N_{5}^- < N_{4}C_{1}H_{1}^- < N_{3}C_{2}H_{2}^-$, which is consistent with the order obtained from experimental $pH$ tests ($pK_a = 9.1$ for $N_{4}C_{1}H_{1}^-$ and $pK_a = 4.0$ for $N_{3}C_{2}H_{2}^-$) [28,38].

| Indices | $N_{5}^-$ | $N_{4}C_{1}H_{1}^-$ | $N_{3}C_{2}H_{2}^-$ | Benzene |
|---------|----------|-------------------|-------------------|---------|
| $\pi$   | DI$_{min-\pi}$ | 0.16 | 0.16 | 0.16 | 0.11 |
|         | NICS$_{zz}(1)_{\pi}$ | $-26.09$ | $-25.81$ | $-25.23$ | $-28.96$ |
| $\sigma$| DI$_{min-\sigma}$ | 0.16 | 0.16 | 0.16 | - |
|         | NICS$_{zz}(1)_{\sigma}$ | $-19.06$ | $-14.42$ | $-10.55$ | $-0.11$ |
|         | NICS$_{zz}(r_{extreme})_{\sigma}$ | $-19.87$ | $-14.42$ | $-10.55$ | - |

Figure 2. Basicity: proton affinity of pentazole anion $N_{5}^-$, tetrazole anion $N_{4}C_{1}H_{1}^-$, and 1,2,4-triazole anion $N_{3}C_{2}H_{2}^-$. When the $PA$ is used to characterize the acidity of the solvents, a higher $PA$ corresponds to a weaker acidity. As shown in Table 2, the calculated values of the $PA$ were 176.3 kcal/mol for $H_{3}O^+$, 211.9 kcal/mol for $NH_4^+$, 409.7 kcal/mol for THF, and 411.1 kcal/mol for benzene, respectively. Our results were very close to the experimental results of $PA(H_{3}O^+) = 165.0$ kcal/mol and $PA(NH_4^+) = 204.0$ kcal/mol [39]. We also conducted a $PA$ calculation for $H_{2}O$ for further verification. $PA(H_{2}O)$ was calculated to be 396.1 kcal/mol, which was close to the experimental result of 393.3 kcal/mol [39]. The $PA(H_{2}O)$ value was between $PA(NH_4^+)$ and $PA(benzene)$, which was consistent with the experimental $pK_a$: $9.3$ (NH$_4^+$) $<$ 15.74 (H$_2$O) $<$ 43 (benzene). From the above calculations and for verification, the order of the acidity of the solvents was H$_3$O$^+$ $>$ NH$_4^+$ $>$ H$_2$O $>$
benzene > THF, which was consistent with the \( pK_a \) sequence obtained from the experiments: \(-1.74 (\text{H}_3\text{O}^+) < 9.3 (\text{NH}_4^+) < 43\) (benzene) [40].

**Table 2.** Basicity of heterocyclic anions and acidity of solvents studied.

| Type          | Compounds | \( PA \) (kcal/mol) | \(-\log \text{Dissociation Constant} \) |
|---------------|-----------|----------------------|------------------------------------------|
| Heterocyclic anions | \( \text{N}_7^- \)  | 323.2                | -                                        |
|               | \( \text{N}_4\text{C}_1\text{H}_1^- \) | 336.7                | -                                        |
|               | \( \text{N}_3\text{C}_2\text{H}_2^- \) | 344.8                | - \( pK_a = 9.1 \)                      |
| Solvents      | \( \text{H}_3\text{O}^+ \)  | 176.3                | 165.0 [39] \( pK_a = -1.74 \) [40]        |
|               | \( \text{NH}_4^+ \)  | 211.9                | 204.0 [39] \( pK_a = 9.3 \) [40]          |
|               | Benzene    | 409.7                | - \( pK_a = 43 \) [40]                   |
|               | THF        | 411.1                | -                                        |
|               | \( \text{H}_2\text{O} \)  | 396.1                | 390.3 [39] \( pK_a = 15.74 \) [40]        |

2.3. Different Reactivity of Heterocyclic Anions Depending on Solvent Types and Concentrations

Taking the solvent \( \text{NH}_4^+ \) as an example, Figure 3A presents the optimized structures of the \( \text{N}_7\text{C}_2\text{H}_2 \cdots \cdots \text{cNH}_4^+, \text{N}_4\text{C}_1\text{H}_1 \cdots \cdots \text{cNH}_4^+, \) and \( \text{N}_5 \cdots \cdots \text{cNH}_4^+ \) complexes. When \( c < 3 \), the \( \text{NH}_4^+ \) ions turned to be neutral \( \text{NH}_3 \) molecules after the reaction, and the heterocyclic anions were protonated. That is, acid and base underwent a neutralization process. Correspondingly, the \( BE \) values of the three heterocyclic complexes all increased to the maximum when the \( \text{NH}_4^+ \) concentration increased from \( c = 1 \) to \( c = 2 \), as shown in Figure 3B–D. However, when \( c \geq 3 \), the proton would stay near \( \text{NH}_4^+ \), and the heterocyclic anions tended to remain unprotonated, as shown by the interaction strengths (distances) of the proton with the heterocyclic anion and with solvent species in Figures S5 and S6 of the Supplementary Materials. Namely, acid and base would not proceed neutralization. Besides, the \( BE \) value of the complex started to decrease with a further increase in \( c \), as shown in Figure 3B–D.

The effect of the \( \text{H}_3\text{O}^+ \) concentration on the reactivity of the three heterocyclic anions was similar to that of \( \text{NH}_4^+ \), as shown in Figure S1 of the Supplementary Materials. However, the interactions between \( \text{H}_3\text{O}^+ \) and the heterocyclic anion were about 60% stronger than those between \( \text{NH}_4^+ \) and the heterocyclic anion. This resulted in \( \text{H}_3\text{O}^+ \cdots \cdots \) heterocyclic complexes having higher \( BE \) values than the \( \text{NH}_4^+ \cdots \cdots \) heterocyclic complexes by 28–79 kcal/mol. In benzene and THF solvents, when \( c \) varied from 1 to 5, the three heterocyclic anions were never protonated, as shown in Figures S2, S3, S5, and S6 of the Supplementary Materials. The interactions between benzene/THF and the heterocyclic anion were weak hydrogen bonds (HB, <10 kcal/mol), much weaker than the HB connected to \( \text{H}_3\text{O}^+ \) or \( \text{NH}_4^+ \), as shown in Figure S7 of the Supplementary Materials. Correspondingly, the \( BE \) values of the benzene/THF \cdots \cdots \) heterocyclic complexes increased monotonously with the increase in \( c \), but were much lower than the \( BE \) values of the \( \text{H}_3\text{O}^+ / \text{NH}_4^+ \cdots \cdots \) heterocyclic complexes, as shown in Figure 3B–D.

The anomaly of the reactivity of the three heterocyclic anions is that they are basic, but they prefer to be unprotonated when encountering more than three \( \text{H}_3\text{O}^+ \) or \( \text{NH}_4^+ \) ions. This not only violates the common sense of acid–base neutralization, but also leads to an increase in the total energy of the complex, as shown in Figure 3B–D. This increase in energy is caused by the mutual repulsion between the adjacent \( \text{H}_3\text{O}^+ / \text{NH}_4^+ \), because when \( c \geq 3 \), the proton was in the vicinity of \( \text{H}_3\text{O}^+ / \text{NH}_4^+ \) instead of near the heterocyclic anions. It is interesting that these \( \text{H}_3\text{O}^+ / \text{NH}_4^+ \) ions would rather suffer mutual repulsion than diffuse away from the heterocyclic anion center. Although the protonation of \( \text{N}_5^- \), \( \text{N}_4\text{C}_1\text{H}_1^- \), and \( \text{N}_3\text{C}_2\text{H}_2^- \) could eliminate this mutual electrostatic repulsion and convert intermolecular HBs into much lower energy H–N bonds to reduce the total energy of the
complex, this process did not proceed as expected when $c \geq 3$. There must be some unseen incentives to drive mutations in the reactivity of heterocyclic anions.

2.4. Mechanism of Anomalous Reactivity of Heterocyclic Anions

In the following, we take $\text{N}_4\text{C}_1\text{H}_1^-$ in an $\text{NH}_4^+$ solvent as an example to explore the mechanism of its anomalous reactivity. When $\text{N}_4\text{C}_1\text{H}_1^-$ was protonated at $c = 1$ and $c = 2$, compared with its naked state, the $\text{DI}_{\text{min}-\sigma}(\text{LP})$ in the ring was reduced by 0.08, and the values of $\text{NICS}_{zz}(1)_{\text{total}}$, $\text{NICS}_{zz}(1)_{\pi}$, and $\text{NICS}_{zz}(1)_{\sigma}$ were reduced by 2.72, 1.17, and 1.55 ppm, respectively, as shown by the red curves in Figure 4C,D and Figure S8 of the Supplementary Materials. This implied that the formation of additional single bonds consumed the delocalization of electrons in the heterocycles, thereby reducing their dual aromaticity, whereas the formation of H–N bonds could substantially lower the total energy of the complex, as shown in Figure 3A. Therefore, the basicity of $\text{N}_4\text{C}_1\text{H}_1^-$ dominated the reactivity, and the anion underwent an additional reaction by scarifying the dual aromaticity.
If N$_4$C$_1$H$_1^-$ continued to be protonated by more NH$_4^+$, the dual aromaticity would be further weakened, which provoked N$_4$C$_1$H$_1^-$ to balance the dual aromaticity and its basicity in another way when $c \geq 3$. In order to keep the dual aromaticity intact, N$_4$C$_1$H$_1^-$ started to reduce the bonding states of electrons with nearby protons, tending to remain unprotonated and interact with all NH$_4^+$ through intermolecular HB. In this way, the electron delocalization of HB helped increase the dual aromaticity of N$_4$C$_1$H$_1^-$ [41]. Compared with its protonation state, the DI$_{\text{min-or}}(\text{LP})$ in the N$_4$C$_1$H$_1^- \cdots 3\text{NH}_4^+$ complex increased by 0.03, and the aromaticity indices NICS$_{zz}(1)$$_{\text{total}}$, NICS$_{zz}(1)$$_{\sigma}$, and NICS$_{zz}(1)$$_{\pi}$ increased by 1.01, 0.31, and 0.71, respectively, as shown in Figure 4C,D. Note that at $c = 3$, the interactions of the proton with N$_4$C$_1$H$_1^-$ and NH$_3$ were in a critical state of competition, and \( \sigma \)-aromaticity is apparently the lead in changing the reactivity of N$_4$C$_1$H$_1^-$. When $c = 4$, N$_4$C$_1$H$_1^-$ interacted with the surrounding NH$_4^+$ ions via typical intermolecular HBs, the DI$_{\text{min-or}}(\text{LP})$ in the N$_4$C$_1$H$_1^-$ \( \cdots 4\text{NH}_4^+ \) complex further increased by 0.03, and the aromaticity indices NICS$_{zz}(1)$$_{\text{total}}$, NICS$_{zz}(1)$$_{\sigma}$, and NICS$_{zz}(1)$$_{\pi}$ continued to increase by 0.55, 0.45, and 0.10, respectively, as shown in Figure 4C,D. That is, at $c = 4$, the dual aromaticity of N$_4$C$_1$H$_1^-$ totally defeated its basicity and totally dominated the N$_4$C$_1$H$_1^-$ to violate the acid–base neutralization.

The reaction mechanism of N$_4$C$_1$H$_1^-$ in H$_3$O$^+$ was similar to that in NH$_4^+$. Because H$_3$O$^+$ ($\text{pK}_a = -1.74$ [39]) has a higher acidity than NH$_4^+$ ($\text{pK}_a = 9.3$ [39]), the electron delocalization and aromaticity in N$_4$C$_1$H$_1^- \cdots \text{cH}_3\text{O}^+$ presented larger variations than that in N$_4$C$_1$H$_1^- \cdots \text{cNH}_4^+$ with the increase in $c$, as shown in Figure 4C,D. The proposed mechanism of the anomalous reactivity of N$_4$C$_1$H$_1^-$ is also applicable to N$_5^-$ and N$_3$C$_2$H$_2^-$, as shown in Figure 3A. It is worth mentioning that N$_3$C$_2$H$_2^-$ contains two hydrogen atoms, repelling nearby H$_3$O$^+$/NH$_4^+$ ions. Therefore, this anion could have up to three H$_3$O$^+$/NH$_4^+$ ions in its vicinity, and the fourth H$_3$O$^+$/NH$_4^+$ ion was not allowed to approach thermodynamically.

2.5. Acidic Stabilization of the Dual-Aromatics Studied

It is of interest to take advantage of the discovered anomalous reactivity to catalyze a generating rate and improve the production yield of heterocycles. Taking N$_5^-$ as an example, a successful preparation of N$_5^-$ from the solution is to keep all the N-N bonds intact before the rupture of the C–N bond in 3,5-dimethyl-4-hydroxyphenylpentazole (HPP). Although the synthesis of N$_5^-$ was successfully achieved with the aid of m-chloroperbenzoic...
acetic acid (m-CPBA) and ferrous bisglycinate [Fe(Gly)$_2$] [42], the production yield as well as the generating rate of N$_5^-$ is still to be improved and accelerated.

One of the most important preconditions of the catalysis of these heterocyclic anions is to keep their structure stable in the preparation solution. Because the strength of the C–N and N–N bonds of a heterocycle is one of the most important factors for its structural stability, we calculated all the bond strengths in the rings of N$_5^-$, N$_4$C$_1$H$_1^-$, and N$_3$C$_2$H$_2^-$ under different solvent concentrations. For all three heterocycles in each solvent, the weakest bonds were all N–N bonds, and their strengths were plotted as a function of concentration $c$, as shown in Figure 5 and Figure S9 of the Supplementary Materials. The calculation method of the bond strength is detailed in the Methodology Section.

Figure 5. All bond strengths and weakest bond strengths in the rings of (A,B) N$_5^-$, (C,D) N$_4$C$_1$H$_1^-$, and (E,F) N$_3$C$_2$H$_2^-$ in variant H$_3$O$^+$/NH$_4^+$ concentration. The weakest bond strength in the ring of each naked heterocyclic anion is marked by a dashed line for comparison.

Compared with naked N$_5^-$, N$_4$C$_1$H$_1^-$, and N$_3$C$_2$H$_2^-$, the bonds of heterocycles in H$_3$O$^+$/NH$_4^+$ solvents were significantly enhanced, and this enhancement increased with the increase in H$_3$O$^+$/NH$_4^+$ concentration. For example, the weakest bond in the N$_5^-$···4H$_3$O$^+$ complex was 145.24 kcal/mol, which was improved by 54% than that of the naked N$_5^-$; the weakest bond in N$_5^-$···4NH$_4^+$ was 140.54 kcal/mol and was improved by 48.7%. Similarly, the weakest bonds in the N$_4$C$_1$H$_1^-$···4H$_3$O$^+$ and N$_4$C$_1$H$_1^-$···4NH$_4^+$ were enhanced by 67% and 51%, respectively, compared with that of the naked N$_4$C$_1$H$_1^-$; the weakest bonds in N$_3$C$_2$H$_2^-$···3H$_3$O$^+$ and N$_3$C$_2$H$_2^-$···3NH$_4^+$ were enhanced by 44% and 37%, respectively, compared with the naked N$_3$C$_2$H$_2^-$. In contrast, the presence of benzene and THF surrounding N$_5^-$, N$_4$C$_1$H$_1^-$, and N$_3$C$_2$H$_2^-$ showed little influence on the strength of the bonds in the rings. Their influence on the weakest bond strength was in the range of $-4.0$–$6.6\%$. Therefore, the H$_3$O$^+$/NH$_4^+$ ions showed a significant stabilization effect on the enhancement of the studied heterocyclic structures, in particular at a high concentration of H$_3$O$^+$/NH$_4^+$, implying a potential catalytic effect of the H$_3$O$^+$/NH$_4^+$ ions in the preparation of heterocyclic compounds.

The stabilization effect of the H$_3$O$^+$/NH$_4^+$ ions on the heterocyclic structures was caused by their HB interactions with the NLPE. Such HB interactions stretched the NLPE away from its original position, thereby reducing the inter-lone-pair repulsion within the $\sigma$-aromatic system. In contrast, since the HB interactions between the heterocycles and the benzene/THF were very weak, the location of the NLPE in the heterocycles was almost unaffected. Therefore, the two solvents showed little effect on the structural stability of the heterocycles.
3. Methodology

The heterocyclic anions studied here include the pentazole anion $\text{N}_5^-$, tetrazole anion $\text{N}_4\text{C}_1\text{H}_1^-$, and $1,2,4$-triazole anion $\text{N}_3\text{C}_2\text{H}_2^-$. In order to evaluate the influence of the acidity and concentration of the solvent on the reactivity of heterocyclic anions, we built atomistic models for each heterocyclic anion by traversing the four solvents of $\text{H}_3\text{O}^+$, $\text{NH}_4^+$, benzene, and THF. For each type of solvent, the molar ratio of solvent to heterocyclic anion increased from $c = 1$ to $c = 5$. In addition, one naked anion laid in a vacuum was calculated for comparison. Therefore, 63 atomistic models were used for calculation and evaluation in total.

All the calculations were performed using a quantum mechanical method based on the density functional theory (DFT). The quantities of electron density, atomistic structure, interatomic interactions, MO, magnetic shielding, and energetics were calculated based on the corresponding optimized structure, which was obtained using Gaussian 09 at the B3LYP/6-31G(d) level [43]. After the optimization of the 63 atomistic models, 55 presented with clustered structures, with 1 heterocyclic anion present in the middle and solvent species distributed nearby, as shown in Figures S1–S3 of the Supplementary Materials. For the other 8 models with $c = [\text{H}_3\text{O}^+ \text{or } \text{NH}_4^+]/[\text{N}_5^-, \text{N}_4\text{C}_1\text{H}_1^-, \text{or } \text{N}_3\text{C}_2\text{H}_2^-] = 5$ and $c = [\text{H}_3\text{O}^+ \text{or } \text{NH}_4^+]/[\text{N}_3\text{C}_2\text{H}_2^-] = 4$, the $\text{H}_3\text{O}^+/\text{NH}_4^+$ ions diffused away from the vicinity of the heterocyclic anions.

The strengths of the relevant interatomic interactions, including bonding interactions, nonbonding interactions, and antibonding interactions, were evaluated by the integrated value of the crystal orbital Hamilton population (COHP) below the Fermi energy, using a recently developed High Accuracy Atomistic Simulation for Energetic Materials (HASEM) package [44,45]. The number of electrons shared between atoms was characterized by the delocalization index (DI); a higher DI value suggests a stronger delocalization of the $\pi$-electrons/lone-pair electrons, using the natural bond orbital (NBO) [48–50] analysis and the quantum theory of atoms in molecules (QTAIM) [51,52] method that was implemented in the Multiwfnn application [53]. The indices with $\pi/\sigma$ subscripts are the components contributed by all the $\pi$-electrons/$\sigma$-electrons, whereas those with min-$\pi$/min-$\sigma$(LP) subscripts are the components contributed by the $\pi$-electrons/lone-pair $\sigma$-electrons at each lowest energy level.

The basicity of the nitrogen heterocyclic anions and the acidity of the solvents studied were evaluated by their proton affinity (PA) [54,55]:

$$PA = E_{\text{protonated}} - E_{\text{unprotonated}}$$  \hspace{1cm} (1)

where $E_{\text{protonated}}$ is the total energy of the protonated species and $E_{\text{unprotonated}}$ is the total energy of the corresponding unprotonated species. The higher the PA, the stronger the base and the weaker the conjugate acid in the gas phase. Therefore, the heterocyclic anion with a higher PA is more basic, and the solvent with a lower PA is more acidic.

The energetics of the heterocyclic anion–solvent complexes were characterized by binding energy (BE):

$$BE = E_{\text{anion}} + \sum c E_{\text{solvent}} - E_{\text{complex}}$$  \hspace{1cm} (2)

where $E_{\text{anion}}$ is the total energy of the naked heterocyclic anion, $E_{\text{solvent}}$ is the total energy of a separate solvent ion or molecule, and $E_{\text{complex}}$ is the total energy of the overall complex. A higher positive BE value implies that the interspecies interactions are more favorable and the complex is energetically more stable. Otherwise, the negative BE value indicates that the structure of the proposed complex is thermodynamically unstable.
4. Conclusions

We performed a series of quantum mechanical calculations to explore the stability and reactivity of the pentazole anion $N_5^-$, tetrazole anion $N_4C_1H_1^-$, and 1,2,4-triazole anion $N_3C_2H_2^-$ in four types of solvents with different acidities and concentrations. The main conclusions are as follows:

(1) Through the analysis of electron density, atomistic structure, interatomic interactions, molecular orbital, magnetic shielding, and energetics, we confirmed the basicity of $N_5^-$, $N_4C_1H_1^-$, and $N_3C_2H_2^-$, and the presence of dual aromaticity in the three heterocyclic anions;
(2) The three heterocyclic anions were found to violate the acid–base neutralization rule when confronting more than three $H_3O^+$/NH$_4^+$ ions. The mechanism of the anomalous reactivity of heterocyclic anions was found to be a competition between their basicity and dual aromaticity;
(3) Due to the stretching effect of hydrogen bonding on the nitrogen lone-pair electrons, the $H_3O^+$/NH$_4^+$ ions showed a significant stabilization effect on the studied heterocyclic structures, in particular at a high concentration of $H_3O^+$/NH$_4^+$. In contrast, benzene and THF presented little influence on the structural stability of heterocyclic anions.

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