THERMODYNAMIC AND ELECTRONIC FACTORS GOVERNING STABILITY OF CYCLOTRIPHOSPHAZENES

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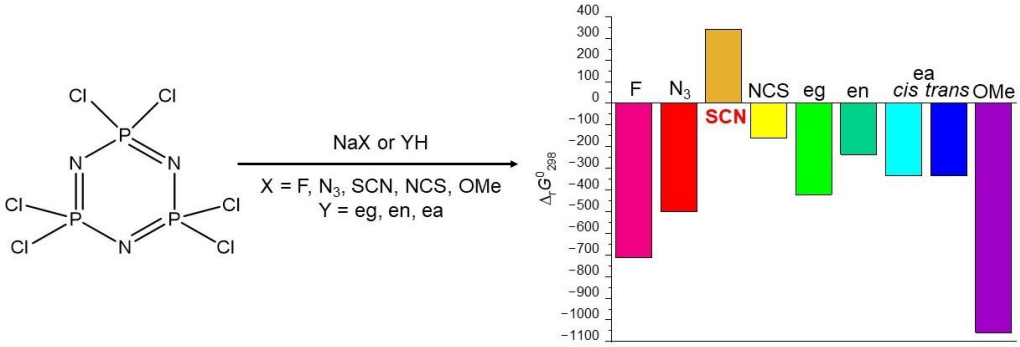
Cyclotriphosphazenes ($N_3P_3X_6$) represent a versatile class of phosphorus–nitrogen heterocycles whose remarkable chemical stability and tunable electronic properties make them promising building blocks for advanced functional materials[1, 2]. However, the fundamental origin of their stability and the role of substituents in controlling their thermodynamic and electronic behavior remain insufficiently understood.

DFT calculations were performed to show that ring formation is strongly exergonic, whereas substitution reactions are enthalpy-controlled and substituent-dependent. Notably, SCN derivatives are thermodynamically unfavorable, while NCS analogues remain stable (see figure).



Thermodynamics of Cyclotriphosphazenes Substitution;
eg is ethylene glycol; en is ethylenediamine; ea is 2-aminoethanol

Despite substituent variation, the P_3N_3 framework remains structurally invariant, with constant P–N bond lengths and polarized closed-shell interactions (QTAIM). In contrast, P–X bonding varies significantly, reflecting substituent-dependent polarity.

Overall, the obtained results establish a thermodynamic framework for understanding and predicting the behavior of cyclotriphosphazenes. The combination of calculated reaction energetics and electronic structure descriptors enables rational assessment of substituent effects on both stability and reactivity. In particular, the revealed polarization-driven stabilization of the P_3N_3 ring provides a unifying explanation for its exceptional robustness and substituent tolerance. These findings demonstrate that targeted modification of substituents can be employed as an effective strategy for tuning thermodynamic properties and guiding the design of phosphazene-based functional materials with predictable performance.

1. C. Gholamrezazadeh et al. J. Mol. Struct. 1312 (2024) 138526.
2. R. F. Weitkamp et al. Chem. Eur. J. 27 (2021) 10807.