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One Metal and Forty Nitrogens. Ab Initio Predictions for Possible New High-Energy Pentazolides

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High-energy nitrogen-rich pentazolides of groups 6 and 13–16 are studied theoretically. Many of them have experimentally known azide analogues. Our highest nitrogen-to-element ratio of 40:1 is achieved in the systems $[M(N_5)_8]^{2-}$ (M = Cr, Mo, W). The thermodynamic and kinetic stability of the studied systems grows with the negative charge on the system and is highest for tetra-pentazolides and hexa-pentazolides of B, Al, and Si. Systems such as $B(N_5)_4^-$ or $Si(N_5)_6^{2-}$ are examples of the most stable candidates for these new species. $N(N_5)_2^-$ is a candidate for a new all-nitrogen system. Neutral and positive systems were less stable. Pentazole derivatives of "dinuclear" C_2H_n and N_2H_n systems were investigated and were found to be of comparable stability as their "mononuclear" analogues. Pentazole derivatives of benzene, the $C_6H_{6-n}(N_5)_n$ ($n = 2, 3, 6$) systems, have a similar stability as the experimentally known phenylpentazole. A borazine analogue, $N_3B_3H_3(N_5)_3$ is predicted to be one of the most stable systems of this family.

Introduction

Since the recent prediction[1] and synthesis[2] of N_5^+, the search for new nitrogen species or nitrogen-rich compounds has received copious attention. Nitrogen-rich systems are potential high energy density materials.

Numerous studies have been done on various all-nitrogen N_n ($n = 2-24$, 48, 60) compounds, such as the N_4 tetrahedrane, N_6 diazide, N_8 cubane, N_{12}, or even the fullerene-like N_{60}.[3] For examples, see refs 4−19. For extensive and systematic studies, see works of Glukhovtsev et al.[5] and Bartlett et al.[19] All-nitrogen systems are generally predicted to be energetically high and kinetically unstable.

Several transition-metal complexes of all-nitrogen planar cyclic ligands were investigated theoretically. Complexes such as $Fe(\eta^5\text{-}N_5)_2$,[20] $Sc(\eta^7\text{-}N_7)$,[21] $M(\eta^6\text{-}N_6)$,[22] and $(\eta^5\text{-}N_5)M(\eta^7\text{-}N_7)$ (M = Ti, Zr, Hf, Th)[23] were found to be energetically lower than the corresponding N_n^q systems. A negative

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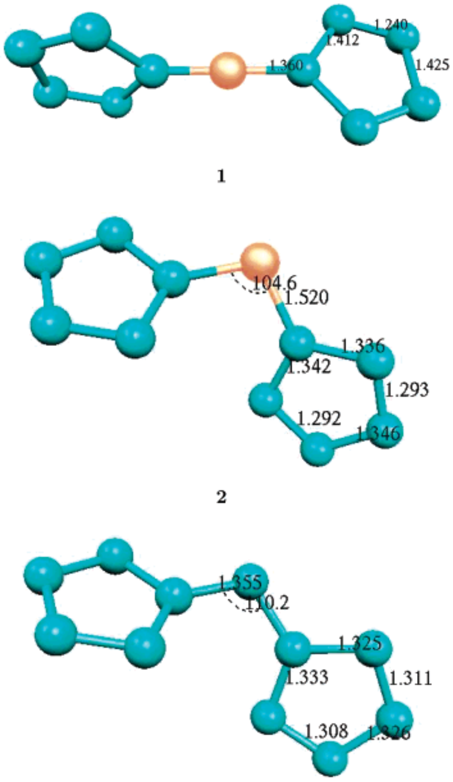

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Figure 1. $A(N_5)_2{}^q$ (A = B, N) pentazolides.

Table 1. Experimental[46] and Calculated Bond Lengths of Phenylpentazole (in Å)

	exptl	calcd
C−N	1.437(0.002)	1.427
$N_\alpha-N_\beta$	1.322(0.002)	1.327
$N_\beta-N_\gamma$	1.307(0.002)	1.292
$N_\gamma-N_\gamma$	1.338(0.002)	1.344

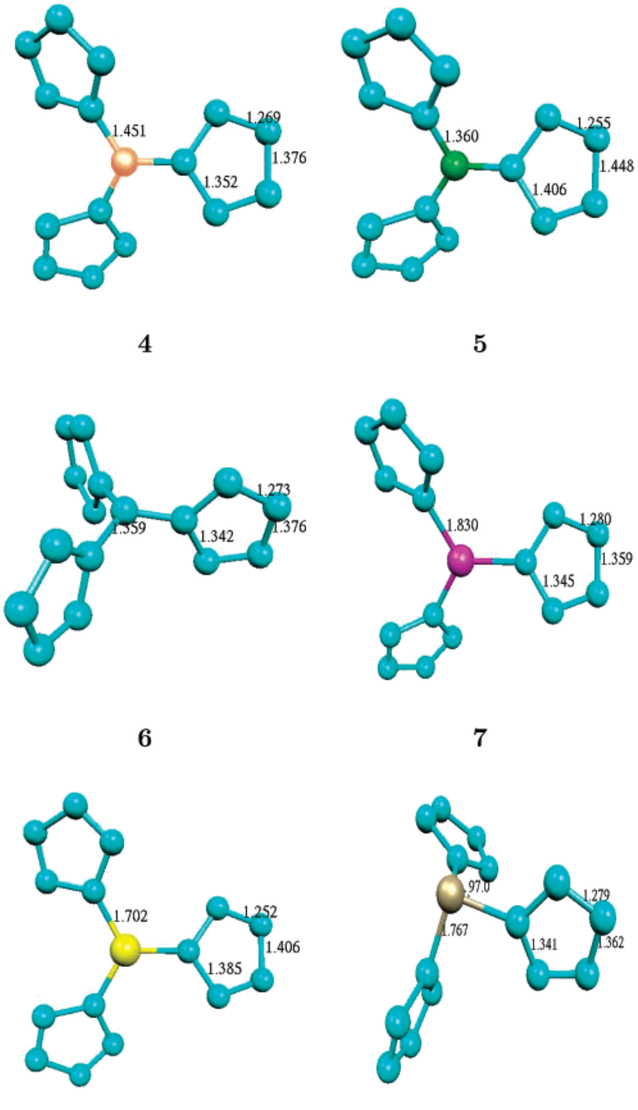

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Figure 2. $A(N_5)_3{}^q$ (A = B, C, N, Al, Si, P) pentazolides.

charge on the nitrogen skeleton together with the multiple bonding between the metal atom and the ring stabilizes the metal-centered species, but they are still above the corresponding metal atom and n N_2.

For the s-elements Na, K, Ca, Mg, and Zn, the η^2-bonding alternative was substantially more stable then the η^1- or η^5-alternatives in the MN_5 and $M(N_5)_2$ systems.[24]

Further alternatives for high-energy density materials can be the nitrogen-rich systems containing hydrogen,[25−27] lithium,[27] or aluminum.[28] The covalently bonded oxygen was found to stabilize planar nitrogen-rings in N_nO_m (n = 4, 6; m = 1, 2, 3)[29] species.

On the experimental side, only a few of the mentioned species are known. The $N_5{}^+$ was made as a cation in bulk compounds in 1999.[2] A metastable N_4[30] and the $(N_6)^{\bullet-}$ diazide chain radical[31] were observed. Pentazole derivatives are known in bulk since 1956.[32] Only aryl pentazoles are known, one possible reason being that the only known synthetic route to pentazole derivatives goes through the diazonium cation, whose existence seems to be limited to aryl derivatives.[33] The bare, gas-phase $N_5{}^-$ anion was observed recently in mass spectra.[34] The accurate CCSD-

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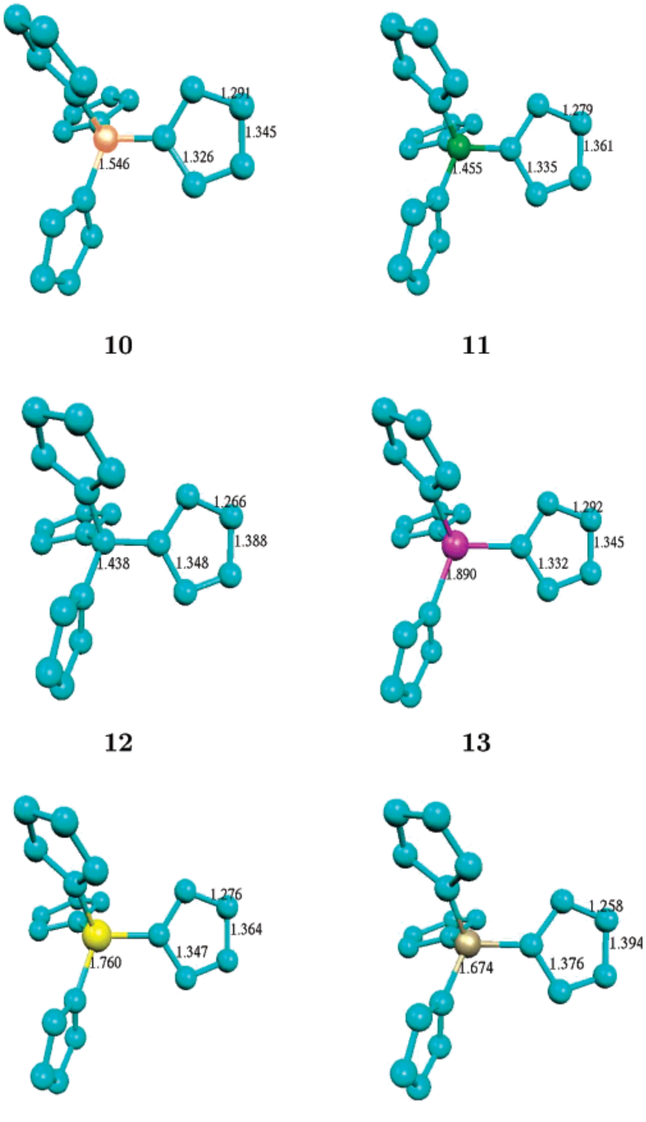

10 **11**

12 **13**

14 **15**

Figure 3. $A(N_5)_4{}^q$ (A = B, C, N, Al, Si, P) pentazolides.

(T)/aug-cc-PVTZ calculations show that the N_5^- anion is a D_{5h} system, lying 14.3 kcal/mol above the $N_3^- + N_2$ with an energy barrier for dissociation of 27.8 kcal/mol.[15] Its preparation may open the route to further pentazole derivatives, as, e.g., the pentazolide species mentioned here. Compared with the azides, which have a rich, well-explored chemistry, with only occasional vacancies,[35] the less stable pentazolides are a greater challenge.

What actually accelerated this study was the recent experimental study of the astonishingly stable $Si(N_3)_6{}^{2-}$ anion reported by Filippou et al.[36] The compound could be heated to 256 °C without decomposition. Analogous systems of Ge,[37] As,[38] Sn,[39] and Pb[40] are also stable. Granted this extraordinary stability, even if the pentazole anion does lie 14 kcal/mol above $N_3^- + N_2$,[15] one wonders whether analogous species could be produced by replacing the azides by pentazolides. Allowing also carbon atoms, further nitrogen-rich species, containing the pentazole-isoelectronic $CN_4{}^{2-}$ ring, are known experimentally. The tetrazolyl pentazole N_4-CH$-N_5$ was prepared recently,[41] and salts of 5,5′ azotetrazolate $[N_4C{-}N{=}N{-}CN_4]^{2-}$ are known.[42] While this study was in progress, the experimental observation of the pentazolic acid HN_5, pentazole anion N_5^-, and zinc pentazolate salt in solution was reported by Butler, Burke et al.[43]

Table 2. Calculated Relative Energies (kcal/mol per N_2 Unit), Reaction Barriers (kcal/mol), and A$-N_\alpha$ Distances (Å) for the Studied Systems (Energies Calculated from Equation 1, unless Otherwise Mentioned)

structure	system	symmetry	ΔH^a	TS^b	Y$-N_\alpha$
	N_5^-	D_{5h}	9.39	27.1	1.323
	N_5^{-c}	D_{5h}	14.3	27.8	1.334
1	$B(N_5)_2{}^+$	D_{2h}	34.9		1.360
2	$B(N_5)_2{}^-$	C_2	19.3	10.7	1.520
4	$B(N_5)_3$	C_3	35.0	8.9 (3.8^d)	1.451
10	$B(N_5)_4{}^-$	S_4	24.8	19.5	1.546
5	$C(N_5)_3{}^+$	C_3	41.4	1.0	1.360
11	$C(N_5)_4$	S_4	46.7	11.4	1.455
3	$(N_5{-}N{-}N_5)^-$	C_2	25.3	16.1	1.355
6	$N(N_5)_3$	C_{3v}	52.8	8.2	1.359
12	$N(N_5)_4{}^+$	S_4	65.1	2.2	1.438
7	$Al(N_5)_3$	C_3	32.1	12.1	1.830
13	$Al(N_5)_4{}^-$	S_4	23.0	18.4	1.890
16	$Al(N_5)_6{}^{3-}$	S_6	18.4^e	24.2	2.047
8	$Si(N_5)_3{}^+$	C_3	41.3	2.0	1.702
14	$Si(N_5)_4$	S_4	37.5	10.4 (10.0^d)	1.760
17	$Si(N_5)_6{}^{2-}$	S_6	17.0 26.7^e	21.2	1.912
9	$P(N_5)_3$	C_3	42.6	10.4	1.767
15	$P(N_5)_4{}^+$	S_4	48.8	2.1	1.674
18	$P(N_5)_6{}^-$	S_6	31.9 37.8^e	16.3	1.831
19	$S(N_5)_6$	S_6	45.3 51.2^e	8.6	1.807
20	$Cr(N_5)_8{}^{2-}$	S_8	42.1^e		2.106
21	$Mo(N_5)_8{}^{2-}$	S_8	37.8^e		2.182
22	$W(N_5)_8{}^{2-}$	S_8	37.7^e		2.190

[a] In kcal/mol per N_2 unit. [b] Barrier for breaking the N_5 ring. [c] Calculated energies at CCSD(T)/aug-cc PVTZ, geometry at CCSD(T)/6-311+G(d), see ref 15. [d] Barrier for rotation of N_5 ring. [e] Relative to $M(N_3)_n^q$ system, see eq 2.

In this work, we study a series of pentazolide analogues of azides of elements in groups 6 and 13−15. The element-to-nitrogen ratio of 1:40 was achieved in the predicted, closed-shell transition metal complexes $M(N_5)_8{}^{2-}$ (M = Cr, Mo, W). The corresponding octa-azides $Cs_5[Eu(N_3)_8]$[44] and $Cs_6[Ca(N_3)_8]$[45] are known. The possibility of substituting benzene or borazine with more than one pentazole ring is also studied. The phenylpentazole $C_6H_5N_5$ is already experimentally known and crystallographically characterized.[46]

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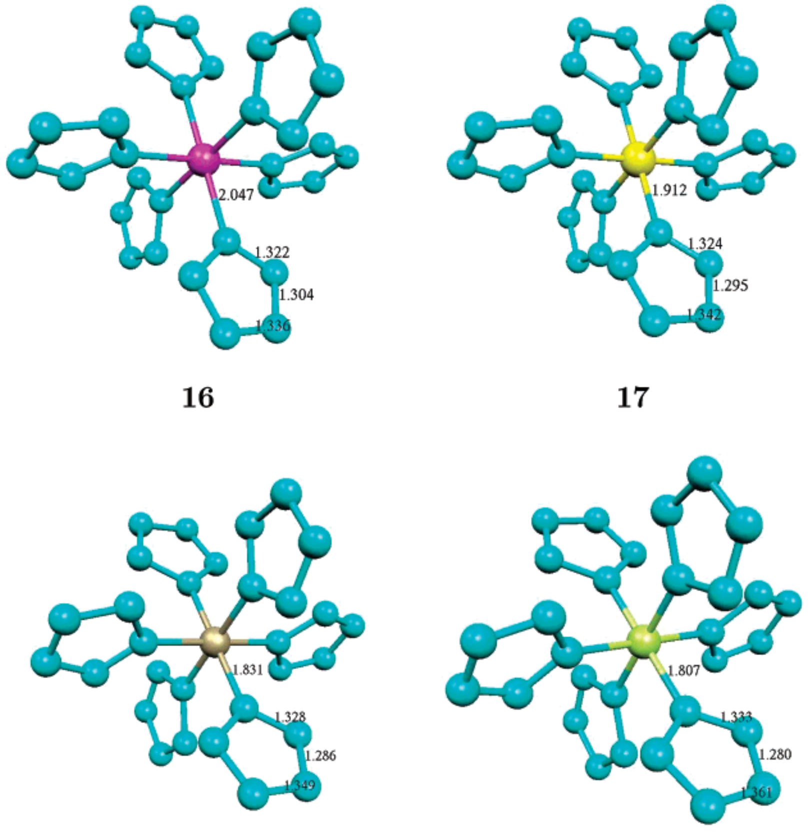

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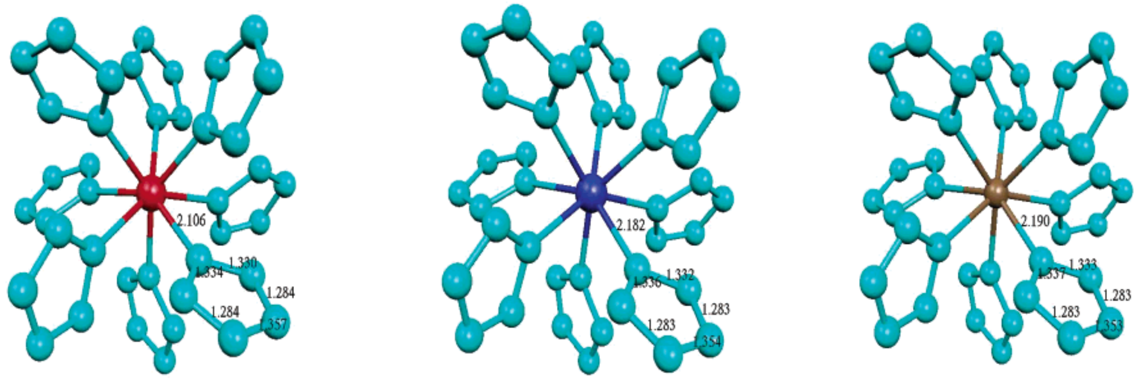
18 **19**

Figure 4. $A(N_5)_6{}^q$ ($A = Al, Si, P, S$) pentazolides.



20 **21** **22**

Figure 5. $M(N_5)_8{}^q$ ($M = Cr, Mo, W$) pentazolides.

Singlet ground states and η^1-type bonding were supposed for all systems. The η^5 ferrocene-like alternatives are not probable for main group elements due to the nonpresence of appropriate d-orbitals. Furthermore, for most of the studied species, steric crowding would not favor the η^5- and also η^2-type bonding. The predicted theoretical systems are new, except the previously proposed $N(N_5)_3$,[15] $(N_5)_2N{-}N(N_5)_2$,[5] $N_5N{=}NN_5$,[47] and the experimentally known phenylpentazole. Structures, relative energies, and energy barriers are predicted using density functional methods.

Results and Discussion

Structures. All the systems mentioned were found to be true minima with no imaginary frequencies. The calculated structure for $C_6H_5N_5$ agrees very well with the experimental X-ray structure, see Table 1. The calculated molecular structures are shown in Figures 1−7. The D_{5h} symmetry of the $N_5{}^-$ anion is broken in the pentazolides. The $N_\alpha{-}N_\beta$ and

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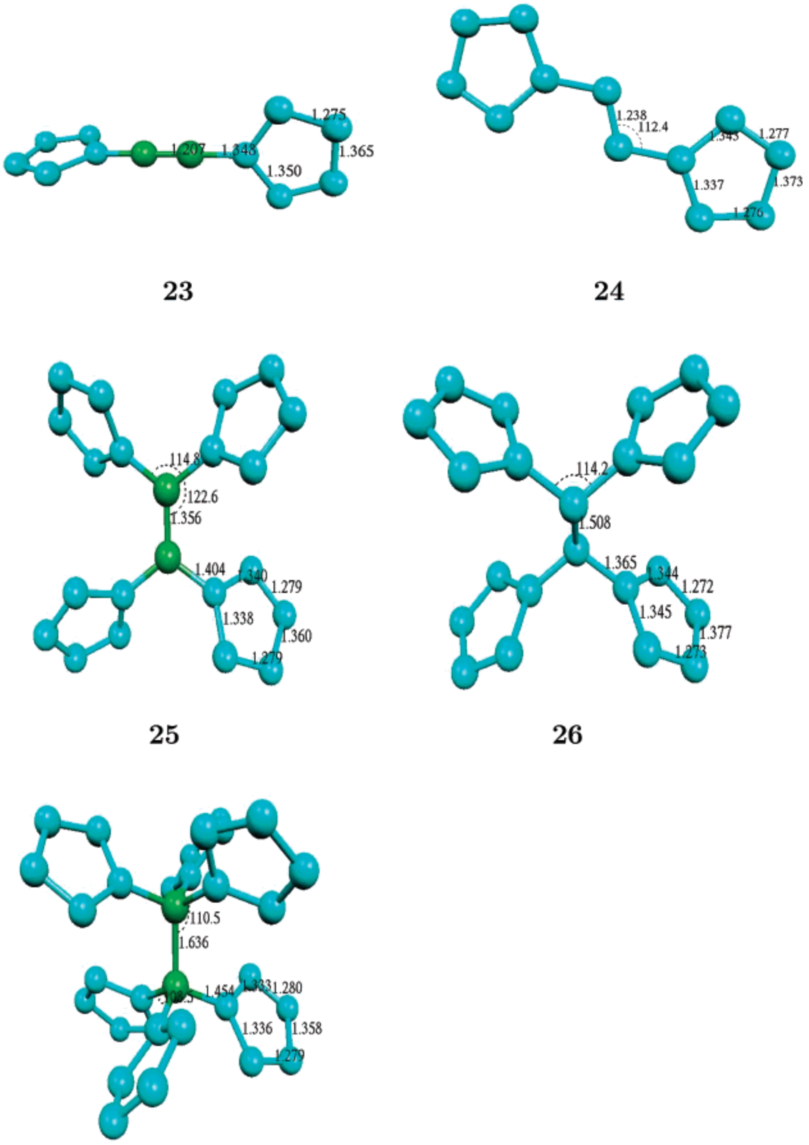

23 **24**

25 **26**

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Figure 6. $A_2(N_5)_2$, $A_2(N_5)_4$ (A = C, N), and $C_2(N_5)_6$ pentazolides.

$N_\gamma{-}N_\gamma$ bond lengths are longer, and the $N_\beta{-}N_\gamma$ bond lengths are shorter as compared to the free anion. The bound η^1 pentazolide corresponds more to the structure with alternating single and double bonds, in contrast to the free N_5^-. The amount of this distortion of the pentazole ring in pentazolides correlates inversely with their kinetic stability; see the Transition States section.

The $A(N_5)_n^q$ pentazolides shown in Figures 1−5 belong to the C_n and C_{nv} ($n = 3$), or S_n ($n = 4, 6, 8$) symmetry groups. Most of the corresponding experimentally or computationally characterized azides possess similar molecular symmetry as compared to their pentazolide analogues. As an example, one can take the S_6 symmetry of $Si(N_3)_6^{2-}$,[36] the S_4 symmetry of $B(N_3)_4^-$,[48] and others. In contrast, the reported $Eu(N_3)_8^{5-}$ posesses a D_{4d} symmetry in the $Cs_5Eu(N_3)_8$ crystal[44] while the predicted $M(N_5)_8^{2-}$ (M = Cr, Mo, W) pentazolides possess the S_8 symmetry, see Figure 5.

The $A{-}N_\alpha$ distances in $A(N_5)_n^q$ pentazolides, Table 2, increase with the negative charge and the number of pentazolide ligands. They are below the sum of the single-bond covalent radii of A and N in di-, tri-, and tetra-pentazolides, a bit longer in hexa-pentazolides, and longest in octa-pentazolides. Consider the Al and Si systems as an example. The sum of the covalent radii of Al and N is $1.25 + 0.70 = 1.95$ Å. The $Al{-}N_\alpha$ bond lengths are 1.83, 1.89, and 2.05 Å for the aluminum tri-, tetra-, and hexa-pentazolide; see the structures **7**, **13**, and **16**, respectively. In the case of silicon, the sum of the covalent radii of Si and N is $1.17 + 0.70 = 1.87$ Å, and the $Si{-}N_\alpha$ distances are 1.70, 1.76, and 1.91 Å for the silicon tri-, tetra-, and hexa-pentazolide; see structures **8**, **14**, and **17**, respectively.

In the “dinuclear” species, Figure 6, the $A{-}N_\alpha$ bonds are shorter as compared to the “mononuclear” ones, and the

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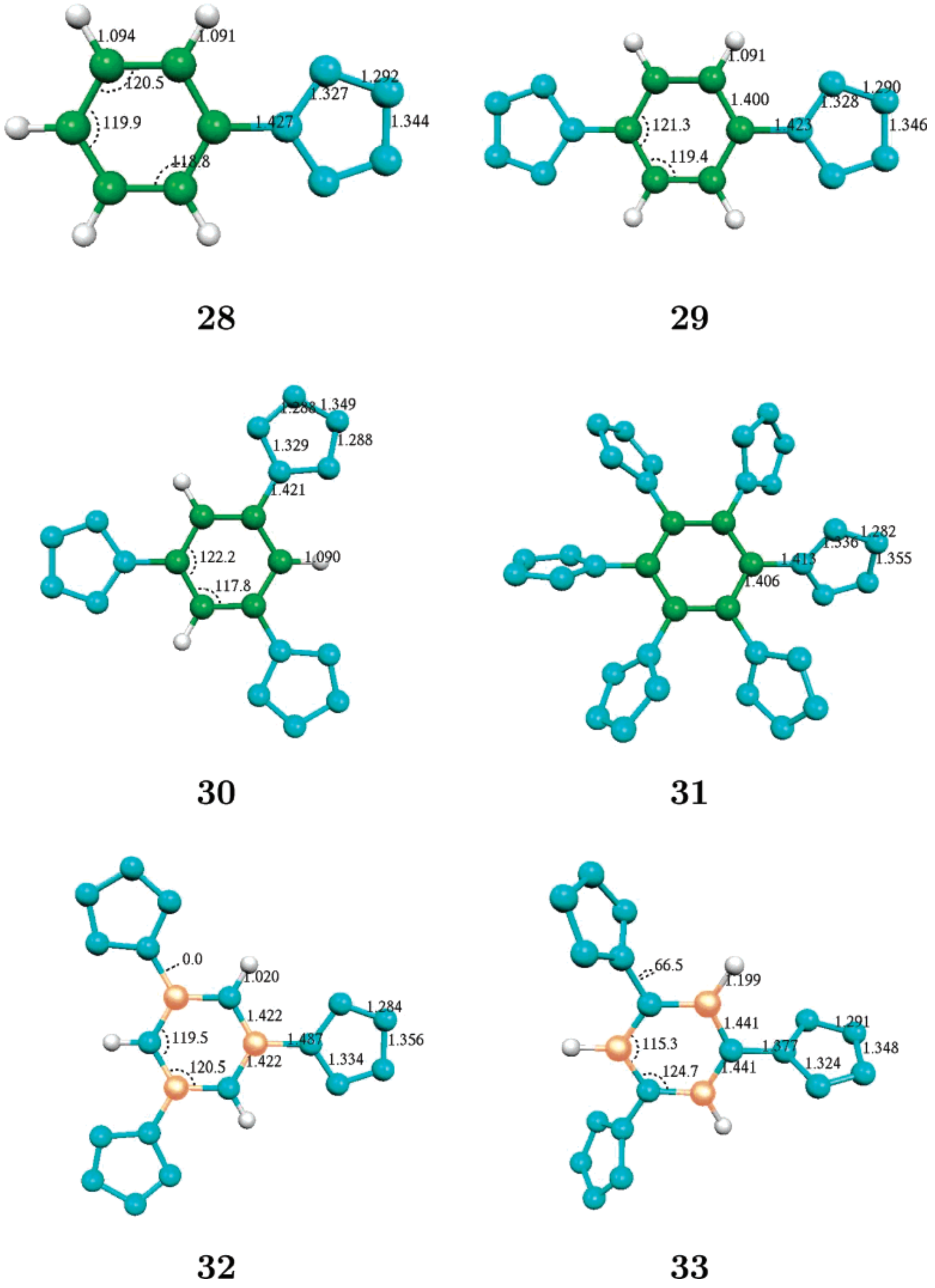


Figure 7. Benzene and borazine pentazolides.

A−A bonds are longer than in the corresponding hydrides. This suggests a delocalization to some extent, in cases where A−A is a multiple bond.

The benzene and borazine pentazolides are mostly planar systems, except for the propellerlike D_3 $C_6(N_5)_6$, structure **31**, and the N−N-bonded C_1 $B_3N_3H_3(N_5)_3$, structure **33**. The C−N$_\alpha$ bond distances remain almost constant for varying number of pentazolide ligands, see Figure 7 or Table 3.

Stability. The energies of the studied systems were calculated relative to a corresponding hydride or azide see eqs 1 and 2.

$$AH_x^q + \frac{x}{2}N_2 \rightarrow \frac{x}{2}H_2 + AN_x^q \qquad (1)$$

$$A(N_3)_x^q + xN_2 \rightarrow A(N_5)_x^q \qquad (2)$$

A zero-point vibrational correction was included in the calculation. To be able to compare systems with a different amount of substituents, we use the "per N_2 unit" energies in the discussion.

The phenylpentazole $C_6H_5N_5$ exists in the bulk at low temperatures[46] and can be considered as marginally stable

Table 3. Calculated Relative Energies (kcal/mol per N_2 Unit), Reaction Barriers (kcal/mol), and A−N_α Distances (Å) for the Studied Systems (Energies Calculated from Equation 1)

structure	system	symmetry	ΔH^a	TS^b	Y−N_α
23	$C_2(N_5)_2$	D_{2d}	45.1	9.7	1.348
25	$C_2(N_5)_4$	C_2	44.5	11.1	1.404
27	$C_2(N_5)_6$	S_6	46.8		1.454
24	$C(N_5)_2$	C_{2h}	48.5	8.8	1.358
26	$C(N_5)_4$	C_{2h}	52.8		1.356
28	$C_6(N_5)_2$	C_{2v}	39.8	19.39 (3.5^c)	1.427
	$O{=}C_6H_5N_5^-$	C_{2v}		23.3 (3.6^c)	1.423
29	p-$C_6H_5(N_5)_2$	D_{2h}	40.4	18.1	1.423
	m-$C_6H_5(N_5)_2$	C_{2v}	40.5	18.1	1.425
30	$C_6H_5(N_5)_3$	D_{3h}	41.1	17.1	1.421
31	$C_6H_5(N_5)_6$	D_3	44.9	12.0	1.413
32	$N_3B_3(N_5)_3$	D_{3h}	30.1	16.1	1.487
33	$B_3N_3(N_5)_3$	C_1	52.2		1.377

[a] In kcal/mol per N_2 unit. [b] Barrier for breaking the N_5 ring. [c] Barrier for rotation of N_5 ring.

species. We can use the calculated thermodynamic parameters of phenylpentazole as limiting criteria for judging the possible existence of the other systems studied, keeping in mind that the calculations are performed only on single, gas-phase molecules. Thus, the crystal forces that influence the systems in the solid phase are not treated at all.

The calculated relative energies (electronic energy + zero-point energy correction) and transition state (TS) barriers for the studied systems are listed in Tables 2 and 3. The transition states are discussed in more detail in the next section; here we discuss the energy barriers.

From Tables 2 and 3, we observe several trends. (1) The systems are all endothermic. This is not unexpected, because the N_2 molecule is the most stable form of nitrogen. However, some systems lie even lower on the relative (per N_2 unit) scale than the known phenylpentazole and have higher or closely similar kinetic barriers.

(2) In the "mononuclear" $A(N_5)_n^q$ pentazolides, Figures 1−5 and Table 2, the thermochemical and kinetic stability of systems increases with a negative charge on the system. The negatively charged systems lie energetically low and have energy barriers comparable to that of phenylpentazole. Neutral systems lie higher and have lower energy barriers. The cationic species are not expected to exist because they have almost no energy barriers for disintegration.

(3) The influence of the number of pentazolide ligands on the stability of pentazolides cannot be simply derived, because it is closely connected to the amount of negative charge on the system. For example, the $N(N_5)_2^-$ system with two pentazole rings has a similar relative energy and kinetic barrier as the $Si(N_5)_4^-$ and $B(N_5)_4^-$ systems with four rings, see Table 2. We expect maximum stability for tetra-pentazolide and hexa-pentazolide systems, while the octa-pentazolides may already suffer from steric congestion.

(4) Considering the central atom A in the "mononuclear" pentazolides, the stability increases from the right to the left across the periodic table. For two isoelectronic pentazolides, the one for the atom which is more left in the periodic table will have a larger negative charge and will thus be more stable. Stability also increases when going from row 2 to row 3 of the periodic table, as can be seen by comparing species of B, C, N and Al, Si, P, respectively.

(5) The "dinuclear" pentazolides, see Figure 6 and the top of Table 3, have a similar or worse stability as the corresponding "mononuclear" systems. The possible conjugation does not seem to improve the stability much in systems with a N═N or C═C bond.

(6) The $C_6H_{6-n}(N_5)_n$ ($n = 2, 3, 6$) systems, see Figure 7 and the middle of Table 3, seem to be of similar stability as the phenylpentazole. The relative energy of the systems grows slightly with number of pentazole rings. The kinetic barrier remains almost constant for $n = 1, 2, 3$ and is lower for $n = 6$. The borazine analogue, if substituted on the boron, structure **32**, is less endothermic than the corresponding benzene system and is by far the best candidate for a pentazole system in this family.

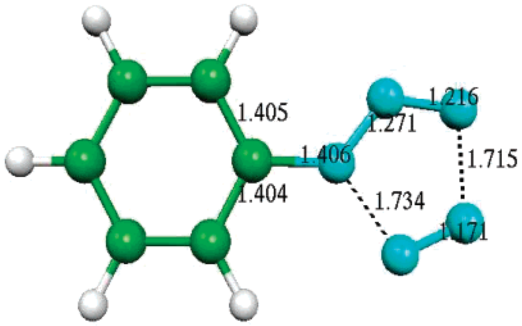
Thus, the best candidates for new species would be the negatively charged systems of B, Al, Si, such as $B(N_5)_4^-$, $Al(N_5)_6^{3-}$, or $Si(N_5)_6^{2-}$. Recall that stable azide analogues of these systems exist.[36,48] Further candidates are the benzene pentazolides. Though energetically higher than main group pentazolides, they are still on same energy scale as experimentally known phenylpentazole and behind energy barriers comparable to the phenylpentazole one. Some neutral "mononuclear" systems might be viable, but they have perhaps too small energy barriers. The $N(N_5)_2^-$ system, **3**, lying low on energy scale and having a high energy barrier, is a candidate for a new all-nitrogen system.

Transition States. Owing to the complexity of the transition state search, one has to use chemical intuition and previous experience when studying transition states for systems of the present complexity. A probable mechanism for the disintegration of the pentazolides is the breaking of the pentazole ring at N_α−N_β and N_γ−N_γ bonds, affording an azide and a N_2 molecule as products. This was observed experimentally for the $X{-}C_6H_4N_5{}^q$ (X = OH, Cl, O) systems,[33,34] and theoretically for the hypothetical N_{12},[17,47] N_{10},[47] N_8,[1] and $N_5^+N_5^-$[16] systems. The TS for breaking the pentazole ring was determined for most of the studied systems; see Tables 2 and 3.

Another disintegration mechanism could be the breaking of the A−N_α bond, affording a pentazolide anion as a product. To our knowledge, this was only observed in the experiment designed specifically to prepare N_5^- from $OC_6H_4N_5^-$ under special conditions.[34] The search of a TS for breaking the A−N_α bond was performed on several systems and remained unsuccessful. The calculations converged either to the minimum, or to the TS for breaking the pentazole ring, or to the TS for a 180° rotation of the pentazolide ligand around the A−N_α bond. The barriers for pentazole rotation were not studied in detail. We were not even able to locate the TS for breaking the C−N_α bond in the $OC_6H_4N_5^-$ molecule, where such a transition state was experimentally found to exist.[34]

The calculated reaction barriers are listed in Tables 2 and 3. A few examples of TS structures are shown in Figure 8.

The transition state for the decomposition of the experimentally known phenylpentazole corresponds to the breaking



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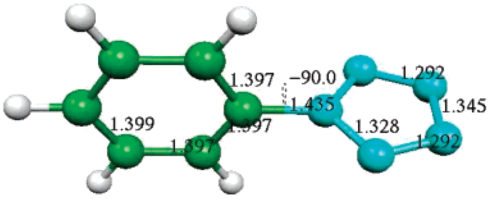

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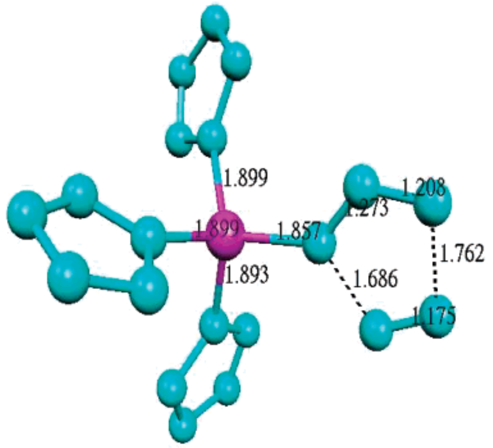

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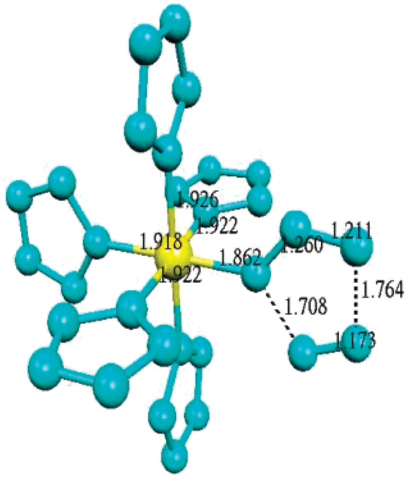

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Figure 8. Selected transition states for pentazolides.

of the pentazole ring, see structure **34**. The calculated barrier of 19.3 kcal/mol is similar to the experimental ones for $XC_6H_5N_5$ (X=Cl, OH, O) systems of at about 20−30 kcal/mol.[33] At the calculated TS, the N_α−N_β and N_γ−N_γ distances lengthen to about 1.7 Å, and the N_β−N_γ distance shortens to 1.17 Å. The structure of TS thus clearly points toward the azide and N_2 products. Similar transition states were observed also for other studied systems. The transition state for the rotation of the pentazole ring around the C−N_α bond, **35**, corresponds to a structure with the pentazole ring rotated 90° from the benzene ring, and it lies 3.6 kcal/mol above the minimum.

Further examples on the calculated transition states are the $Al(N_5)_4^-$ and $Si(N_5)_6^{2-}$ systems, see Figure 8. Again, the N_β−N_γ distances are about 1.17 Å, and the N_α−N_β and N_γ−N_γ distances are about 1.7 Å. We further observe a shortening of the A−N_α distances; in the azide system, the A−N_α distance will be shorter than in the pentazolide system. These trends are common to the other studied systems, too.

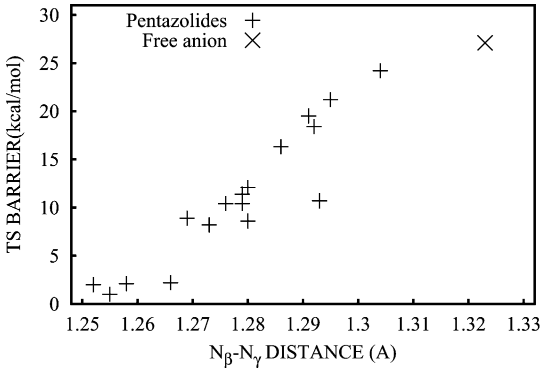

Figure 9. Correlation between TS barriers and the ground-state N_β−N_γ distances in the studied systems.

Finally, we observe a correlation between the height of the transition barrier and the N−N distances in the pentazolides considered. The higher kinetic barrier corresponds to the shorter N_α−N_β, longer N_β−N_γ, and shorter N_γ−N_γ distances. In Figure 9, we plot such correlation for N_β−N_γ distances. It is logical that the more closely the N_β−N_γ distance of the leaving unit already approaches the bond length of an N_2 molecule, the lower is the remaining barrier for disintegration. As pointed out in ref 16, the kinetic stability of negatively charged systems may be reduced by their interaction with the countercations.

Conclusions

Several pentazolides of groups 6 and 13−15 were studied theoretically as possible high-energy-density materials. The structures, relative energies, and energy barriers were calculated. Some of the studied systems show similar, or even higher, thermodynamic and kinetic stability (in the gas-phase) than the experimentally known phenylpentazole, and are hence possible candidates for new species. The stability of the systems increases with the negative charge on the system and is highest for the tetra- and hexa-pentazolides of B, Al, or Si. The neutral and cationic pentazolides are less stable and have lower energy barriers. The higher pentazolides of benzene and borazine have similar stabilities as the parent phenylpentazole and are further candidates for new species. $N(N_5)_2^-$ would be a new all-nitrogen system.

Computational Details

The Turbomole[49] program package was employed in this study. The hybrid density functional B3LYP method[50,51] was used for the calculations. The split-valence polarization (SVP) basis set[52] was used for Cr and the main group elements. For Mo and W, the Stuttgart ECPs and corresponding basis sets were used.[53] Modified basis sets with an additional p function, available in Turbomole as the "def-SV(P)" basis sets, were employed. The method and basis sets chosen correspond to a compromise between reasonable accuracy and affordable resources. The relative energies were calculated with respect to the corresponding hydrides or azides as a sum of the electronic energy and the zero-point energy correction. No positive-energy occupied orbitals were detected in any of the systems.

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