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Structure and stabilities of $(HA1NH)_n$ (n = 2–4)

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Abstract. Ab initio molecular electronic structure methods have been used to study the relative stability of the planar inorganic ring $(HAlNH)_n$ (n = 2–4) during homodesmotic and monomer polymerization reactions. Optimized geometries, frequencies and energies through restricted Hartree-Fock/6-31G* are reported, and energies at the self-consistent field optimized geometries including Möller-Plesset fourth perturbation theory with single, double and quadruple excitation (MP4SDQ) corrections are also reported for both reactions. Homodesmotic reactions with MP4SDQ −28.5 kcal/mol for $(AlN)_2$, 1.9 kcal/mol for $(AlN)_3$ and −0.97 kcal/mol for $(AlN)_4$. On analysing a π-molecular orbitals diagram, only one, three and three strongly bonding π-molecular orbitals exist for the planar four-, six- and eight-membered AlN rings, respectively.

Key words: Stability – Resonance energy – $(HA1NH)_n$ (n = 2–4)

1 Introduction

Aluminium-nitrogen compound chemistry continues to attract great attention. First, in order to understand the structure and reactivity characterization in more detail, there have been many studies about small Al-N molecules [1, 2] and the insertion reaction mechanism of Al atoms into other small molecules [3, 4]. Second, since the discovery of borazine [5], increasing attention has been paid to these exotic species, for example Power [6] has reviewed the theoretical and synthetic studies of some examples. The B_3P_3, Al_3N_3 six-membered ring benzene analogues have been synthesized by Power et al. [7, 8]. NMR evidence together with X-ray crystallography data suggest that they are planar, and there is delocalization of the lone pair from the Group V elements into empty *p*-orbitals of the neighbouring Group III elements. These benzene analogues draw attention to the issue of aromaticity. Thus, Fink and Richards [9] calculated the resonance energies of models of $(HXYH)_3$ (X = B, Al; Y = N, P) according to homodesmotic reactions using electronic energies, and obtained a resonance energy (in kcal/mol) in the order of: C-C(22.1) > B-P(12.7) > B-N(11.1) > Al-N(1.9). The bond orders for $(HXYH)_3$ (X or Y=Zn, B, Al, Ga, C, Si, O, As, P, N, C, Si) were investigated by Matsunaga et al. [10] and the bond energies, and stabilities of isomers by Matsunaga and Gordon [11].

The disubstituted $(AlN)_2$ planar four-membered ring ($[Me_2AlNHDipp]_2$) and mono-substituted $(AlN)_4$ cubic structure ($[MeAlNMes]_4 \cdot 3C_7H_8$) have been synthesized by Waggoner and Power [12], but the syntheses of the mono-substituted planar four- and eight-membered Al-N ring compounds have not yet been reported to our knowledge. Although Power [6] pointed out that the four-membered ring $(RBPR')_2$ is "anti-aromatic", its relative stabilities and whether it obeys Hückel's 4n/4n+2 rule of planar rings $(HAlNH)_n$ (n = 2–4) have not been studied. There is also the question of whether the Al-N bonds in the planar rings of $(HAlNH)_2$ and $(HAlNH)_4$ have strong bond alternation like C-C bonds in cyclobutadiene and cyclooctatetraene. Here we report theoretical studies on $[HAlNH]_n$ (n = 2–4) compounds in comparison with C_4H_4, C_6H_6, and C_8H_8.

2 Computation approach

One of the main characters of the aromaticity is "unusual thermodynamic stability". A homodesmotic reaction was first introduced by George et al. [13, 14] as a measure of aromaticity and was extended to inorganic compounds by Sax and Janoschek in their study of resonance energy in Si_6H_6 using ab initio calculations [15]. The homodesmotic reaction maintains greater similarity of bond types on both sides of the reaction because it requires equal numbers of the same kinds of hybrids. Arising naturally from the constraints of equal numbers of hybrids, the homodesmotic reaction is more sharply focused on the difference in delocalization between adjacent double bonds. Here we use the homodesmotic reactions:

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$$(\mathrm{HAlNH})_n + n\mathrm{H_2Al{=}NH_2} \rightarrow n\mathrm{H_2Al{=}NH\text{-}AlH{=}NH_2}\ (n = 2,\ 3,\ 4),$$

$$(\mathrm{HCCH})_n + n\mathrm{H_2C{=}CH_2} \rightarrow n\mathrm{H_2C{=}CH\text{-}CH{=}CH_2}\ (n = 2,\ 3,\ 4),$$

to calculate their resonance energies by electronic structure energies. Otherwise, as Dewar calculated the ΔH for the trimerization of acetylene to benzene [16], we use the monomer polymerization reactions: nHAlNH → $(\mathrm{HAlNH})_n$ (n = 2, 3, 4) to calculate their reaction energy $\Delta rE(=E_{(\mathrm{HAlNH})_n} - nE_{\mathrm{HAlNH}})$, then to compare their relative stabilities.

First we optimized the planar ring structure parameters of $[\mathrm{HAlNH}]_n$ (n = 2–4). The Al-N bonds are optimized according to both of the strong bond alternations and only one variable at the initial input for $(\mathrm{HAlNH})_2$ and $(\mathrm{HAlNH})_4$, respectively. The structure parameters of the other compounds required for calculation of the reaction energies used as a measure of stability and aromaticity were obtained from Ref. [9]. The butadiene analogue $\mathrm{H_2Al{=}NH\text{-}AlH{=}NH_2}$ was a planar transoid comformer. All optimizations were done by Murtaugh-Sargent (MS) methods [17] at the restricted Hartree-Fock (RHF) level with a 6-31G* basis set.

Vibrational frequencies were obtained on the optimized structure (with the constrained symmetries of D_{2H}, $D_{3\mathrm{H}}$ and D_{4H} for $(\mathrm{HAlNH})_n$ (n = 2–4), respectively). And the electronic energies were calculated by RHF/6-31G*//RHF/6-31G* and Möller-Plesset fourth perturbation theory with single, double and quadruple excitations (MP4SDQ)/6-31G*//RHF/6-31G* methods for optimization structures, respectively. Last we have used the electronic energy of the optimized planar structure to establish the energetic indices of aromaticity for these 4,6,8π-electronic AlN ring systems.

All calculations were done using the Gaussian 92 program on a personal computer.

3 Results and discussion

Table 1 displays the structure parameters of (HAlNH)n where n = 1–4. The Al-N optimized bond lengths are 1.8000/1.8003 Å and 1.7867/1.7870 Å according to strong-bond alternations at the initial input, and the electronic energies are $1.7{*}10^{-6}$ and $4.0{*}10^{-6}$ hartree higher than those obtained in an optimization using one variable of all Al-N bonds at the RHF/6-31G* level for $(\mathrm{HAlNH})_2$ and $(\mathrm{HAlNH})_4$, respectively. So, to a certain extent, these results indicate that strong bond alternations do not exist in AlN 4π- and 8π-electron planar ring systems. This is consistent with the planar ring $(\mathrm{MesBP\text{-}t\text{-}Bu})_2$ of which the BP distances are equivalent to the average value of 1.897 Å from X-ray data [18]. They are obviously different from the C-C 4π- and 8π-electron planar ring systems based upon the alternating C-C bond distance of 1.318/1.568 Å for $\mathrm{C_4H_4}$[19] and 1.323/1.477 Å for $\mathrm{C_8H_8}$[20]. The Al-N bond lengths in the planar ring [HAlNH]n (n = 2–4) are shorter than the single-bond length (2.072–2.350 Å) and longer than the double-bond length (1.78 Å) according to Ref. [2]. These two cases indicate that [HAlNH]n (n = 2–4) compounds may be very weak conjugated systems. The differences between the bond angle Al-N-Al and N-Al-N greatly vary with the size of ring, but the sum of all interior bond angles of one compound obeys the (n–2)180° rule.

Table 2 lists the electronic energies for (HAlNH)n (n = 1–4) and (HCCH)n (n = 2–4) at the RHF/6-31G*//RHF/6-31G* and MP4SDQ/6-31G*//RHF/6-31G* levels. Tables 3 and 4 give the results of reaction energies for homodesmotic and monomer polymerization reactions, respectively. The ΔE_{rxn} for hydrocarbons shows that $\mathrm{C_6H_6}$ (22.1 kcal/mol) is a delocalization system, and $\mathrm{C_4H_4}$ and $\mathrm{C_8H_8}$ are localization compounds because of large negative ΔErxn values (−79.84 and −29.3 kcal/mol, respectively). This is in excellent agreement with the traditional view. But the ΔE_{rxn} (1.9 kcal/

Table 1. $(\mathrm{HAlNH})_n$ n = 2–4 planar optimized geometries at the RHF/6-31G* level (bond length in Å, angles in degrees data in brackets were optimized according to the Al-N strong bond alternation)

Bond type	HAlNH	$(\mathrm{HAlNH})_2$	$(\mathrm{HAlNH})_3$	$(\mathrm{HAlNH})_4$
r(Al-N)	1.597	1.800 (1.800/1.8003)	1.791	1.7868 (1.7868/1.7867)
r(Al-H)	1.555	1.575 (1.5761/1.5762)	1.583	1.5865 (1.5866/1.5866)
r(N-H)	0.986	0.994 (0.9937/0.9937)	1.003	1.0081 (1.0082/1.0082)
∠(AlNAl)		89.3 (89.28)	125.24	143.92 (143.93)
∠(NAlN)		90.7 (90.72)	114.76	126.08 (126.07)
∠(HAlN)	180.0	134.65 (134.6)	122.62	116.96 (116.94)
∠(HNAl)	180.0	135.35 (135.4)	117.38	108.04 (108.03)

Table 2. Total energies: [a]RHF is restricted Hartree-Fock at 6-31G* basis set level; MP4 is Møller-Plesset fourth perturbation theory with single, double, and quadruple excitations at the 6-31G* basis set level. [b]Taken from Ref [9].

Method[a]	X-Y	HXYH	$(\mathrm{HXYH})_2$	$(\mathrm{HXYH})_3$	$(\mathrm{HXYH})_4$	$\mathrm{X_2Y_2H_6}$[b]	$\mathrm{XYH_4}$[b]
RHF	Al-N	−297.442114	−595.128942	−892.767685	−1190.352552	−596.284850	−298.696091
	C-C		−153.641173	−230.703137	−307.502246	−154.919651	−78.031718
MP4	Al-N	−297.683637	−595.588977	−893.454912	−1191.267335	−596.755411	−298.938198
	C-C		−154.177244	−231.492076	−308.56168 5	−155.462815	−78.310549

mol) for $(HAlNH)_3$ is only slightly bigger than the ΔE_{rxn} (−0.97 kcal/mol) for $(HAlNH)_4$, and this result is in agreement with the conclusion that $\Delta_r E'$ (−84.1 kcal/mol) for $(HAlNH)_3$ is slightly lower than $\Delta_r E'$ (−83.6 kcal/mol) for $(HAlNH)_4$ from the monomer polymerization reactions. And the negative contributions to resonance energy of ΔE_{rxn} for $(HAlNH)_2$ and $(HAlNH)_4$ molecules are greatly lower than those for C_4H_4 and C_8H_8.

Table 3. The results of homodesmotic reaction energies for $(HAlNH)n + nAlH_2{=}NH_2 \rightarrow nAlH_2{=}NHAlH{=}NH_2$ and $(HCCH)n + nCH_2{=}CH_2 \rightarrow nCH_2{=}CHCH{=}CH_2$

Reaction	Ring	ΔE_{rxn} (kcal/mol)	
		RHF/6-31G*// RHF/6-31G*	MP4SDQ/6-31G*// RHF?6-31G*
n = 2	C-C	−84.5	−79.84
	Al-N	−30.5	−28.5
n = 3	C-C	24.7	22.1
	Al-N	0.9	1.9
n = 4	C-C	−30.5	−29.3
	Al-N	−1.59	−0.97

Table 4. Reaction energies for nHAlNH → (HAlNH)n in (kcal/mol)

Reaction	RHF/6-31G*// RHF/6-31G* [a]		MP4SDO/6-31G*// RHF/6-31G*	
	ΔrE^b	$\Delta rE'^c$	ΔrE^b	$\Delta rE'^c$
n = 2	−149.7	−74.9	−139.1	−69.6
n = 3	−270.3	−90.1	−252.3	−84.1
n = 4	−357.6	−89.4	−334.3	−83.6

[a] Corrected by zero-point energy
[b] $\Delta rE = E_{[HAlNH]n} - nE_{[HAlNH]}$
[c] $\Delta rE' = \Delta rE/n$

Table 5 presents the vibrational frequencies scaled by 0.89. Although there are no reported experimental frequencies for comparison, the frequencies calculated could verify that the (HAlNH)n (n = 2–4) are established as true local minima on the surface and exist in theory. For $(HAlNH)_4$, the frequencies 30.1 cm^{-1} (B_{2u}) and 47.9 cm^{-1} (B_{1u}) belong to an out-planar distorted vibration model which consist of four N atoms and four Al atoms, respectively. These two small vibrational frequencies show that the planar AN eight-membered ring is not easy to distort and could be stable enough to exist.

Figure 1 shows the π-molecular orbital diagram for the $(HAlNH)_n$ planar ring and $(HCCH)_n$ (n = 2–4). For $(HAlNH)_2$ and $(HAlNH)_4$, the highest occupied molecular orbitals (HOMOs), which are different from the HOMOs for C_4H_4 and C_8H_8, are only composed of the reverse phase P_z-orbitals of all N atoms and could not form the truly bonding π-molecular orbital. On the other hand, in the second HOMOs, there are the one/two bonding π-molecular orbitals of four-centres/three-centres for $(HAlNH)_2$ and $(HAlNH)_4$, respectively. This is consistent with the planar B_2P_2 ring, where NMR data suggested only one strongly bonding π-molecular orbital is possible [18]. For $(HAlNH)_3$, the HOMOs and second HOMO still could form bonding π-molecular orbitals by the lone pair from N atoms moving into the empty P_z orbital of Al atoms, although the *Pz*-orbital component of Al atoms is small. Thus, there is a little delocalization in $(HAlNH)_3$ which has a resonance energy of 1.9 kcal/mol, and localization for $(HAlNH)_2$ and $(HAlNH)_4$. Since the HOMOs of $(HAlNH)_2$ and $(HAlNH)_4$ are non-bonding π-molecular orbitals, the alternating Al-N bond distance is impossible to form. It is unsuitable to calculate the resonance energy using a homodesmotic reaction for the inorganic ring compounds $(HAlNH)_2$

Table 5. Vibrational frequencies calculated at the RHF/6-31G* (cm^{-1}). All frequencies were scaled by 0.89 [21]

Molecular	Sym.	Freq.	Molecular	Sym.	Freq.	Sym.	Freq.
$(HAlNH)_2$	A_g	454.0			3365.4		3294.6
		786.5		A″	193.2	B_{2g}	129.1
		1832.6			449.6		806.9
		3477.6			588.5		1105.3
	B_{1g}	410.2		E′	228.7		1780.4
	B_{2g}	466.2			535.5	E_g	135.3
	B_{3g}	521.3			709.4		411.8
		625.8			822.6		571.2
		850.8			1013.9	A_{2u}	173.4
	B_{1u}	687.6			1794.3		401.2
		885.7			3366.8		611.1
		1822.5		E″	127.9	B_{1u}	47.9
	B_{2u}	544.9			445.5		479.2
		806.6			527.9	B_{2u}	30.1
		3479.1	$(HAlNH)_4$	A_{1g}	382.6		499.5
	B_{3u}	210.7			475.8	E_u	312.9
		491.1			1793.6		474.0
		565.2			3292.9		683.0
$(HAlNH)_3$	A′	424.2		A_{2g}	603.5		884.3
		565.0			870.2		1081.6
		568.9			1052.3		1784.4
		806.5		B_{1g}	115.8		3293.7
		970.6			551.9		
		1804.3			767.3		

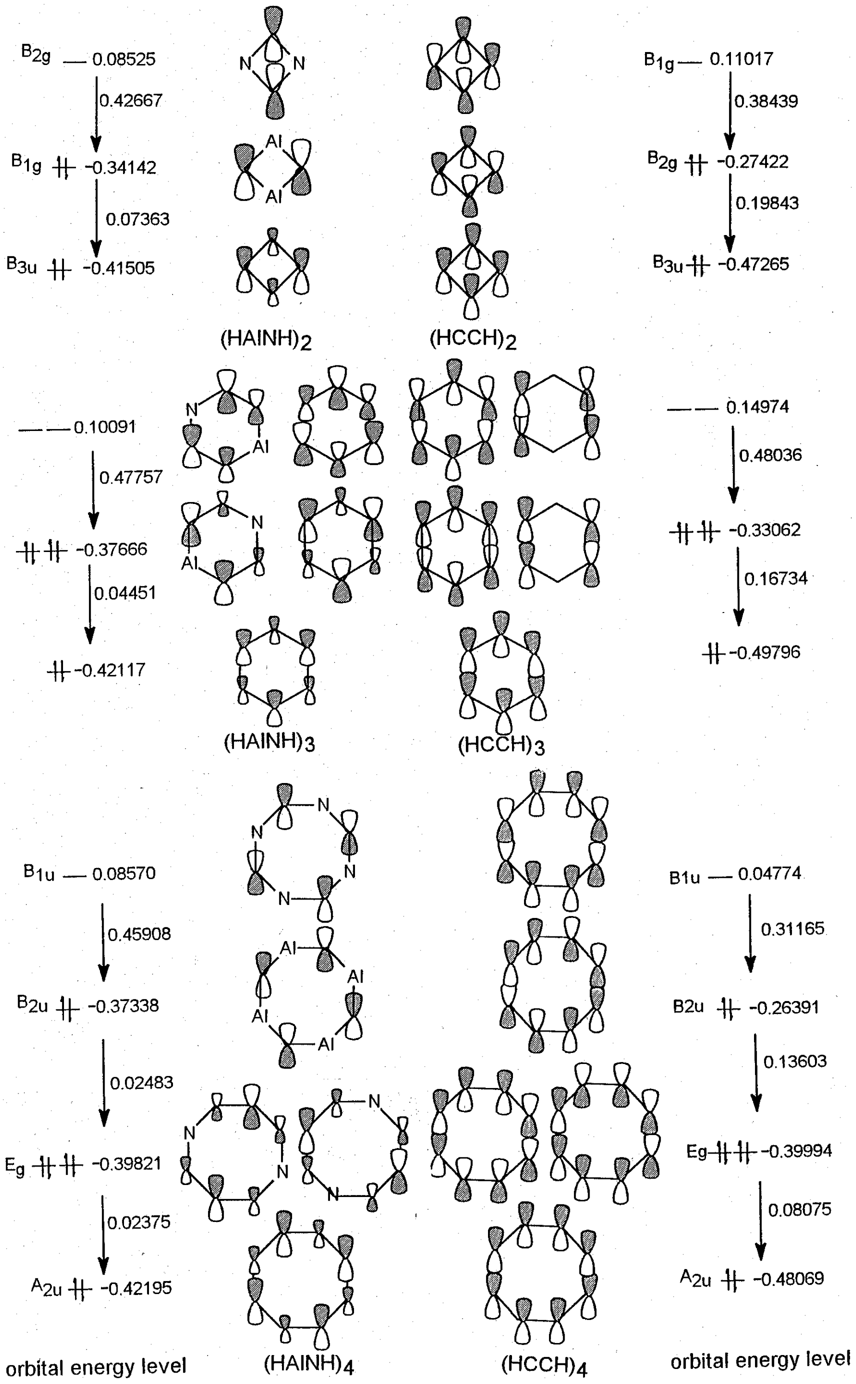

Fig. 1 π-molecular orbital diagram and orbital energy level

and $(HAlNH)_4$ because of the equal numbers of π-bonds on both sides of the reaction.

Figure 1 also displays the π-molecular orbital energy levels. For $(HCCH)_n$ (n = 2–4), the lowest unoccupied molecular orbital (LUMO)-HOMO energy gap index is $E_g(C_6) > E_g(C_4) > E_g(C_8)$, and the energy gap index between the HOMO and second HOMO is $E'_g(C_4) > E'_g(C_6) > E'_g(C_8)$. There are similar energy gap indices for $(HAlNH)_n$ (n = 2–4) with $E_g(Al_3N_3) > E_g(Al_4N_4) > E_g(Al_2N_2)$ and $E'_g(Al_2N_2) > E'_g(Al_3N_3) > E'_g(Al_4N_4)$. But, on comparison with AlN systems, the energy gap values between the HOMO and second HOMO for $(HCCH)_n$ (n = 2–4) are much higher. This indicates that the cyclic hydrocarbons more easily form conjugated second HOMOs.

4 Conclusion

The major conclusions that can be drawn from this work are the following:

1. We did not find the alternate Al-N bond lengths in the compounds $(HAlNH)_n$ (n = 2, 4), to be the same as those in the compounds $(HCCH)_n$ (n = 2, 4).

2. The resonance energies of $(HAlNH)_n$ (n = 2, 3, 4) calculated by the homodesmotic reaction, did not show

that the Hückel rule existed. While the same kind of calculation confirms the Hückel rule for $(HCCH)_n$ ($n = 2, 3, 4$).

3. The π-molecular orbital diagrams show that only the one, three and three strongly bonding π-molecular orbitals could exist for $(HAlNH)_n$ ($n = 2, 3, 4$), respectively. This is obviously different from $(HCCH)_n$ ($n = 2, 3, 4$) which have two, three and four strongly bonding π-molecular orbitals, respectively.

4. Although the planar AlN four- and eight-membered rings have not been synthesized, the frequencies calculated suggest these compounds could be stable and exist in theory.

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