About the aromaticity of $Al_2N_3H_5$ †

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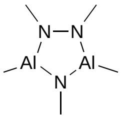
Ab initio quantum-chemical calculations showed that the $Al_2N_3H_5$ ring is not planar, mainly as a result of the repulsion of the neighbouring nitrogen lone pairs. The planar structure, which is a saddle point on the potential energy surface, however, is 1.01 kcal mol^{-1} less stable at the CCSD(T)/6-311 + G(2D)//MP2/6-311 + G(2D) + ZPE level of theory than the minimum-energy structure. According to energy criteria, the aromaticity of the molecule is small, if any. The geometric criteria on the other hand were shown to be useless in the prediction of aromaticity in this case.

In a recent work Wehmschulte and Power[1] reported the synthesis and structural characterization of the first (heavily substituted) Al_2N_3 type ring **1**. Discussing the bond-length distribution and the non-planarity about the two neighbouring nitrogen atoms, they concluded that the delocalization in the ring is negligible. This non-aromatic behaviour, however, could be explained, as noted by the authors,[1] by the steric crowding of the substituents, enforcing a non-planar and thus non-conjugated arrangement.



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The aim of the present work was to investigate the aromaticity of the parent **1**, substituted by hydrogens only, using *ab initio* quantum-chemical calculations. Earlier *ab initio* works on some possibly aromatic six-membered systems containing boron, aluminium, gallium and nitrogen,[2] as well as divalent silicon (silylene) and nitrogen,[3] have shown that such systems have varying extents of aromaticity. Six-membered rings built up from atoms with large electronegativity differences (such as Al and N) were shown to be slightly aromatic, according to different isodesmic reactions.[2] However, the six-membered ring $Al_3N_3H_6$ was found to be planar by quantum-chemical calculations,[2] and the crystal structure of its alkylated derivative was planar as well.[4] In the case of heavy-atom-containing possibly aromatic rings, non-planarity is a quite common phenomenon.[5] On the other hand, there are non-planar rings which have sizeable aromatic character,[6] since the overlap of their 'π' orbitals allows a certain amount of delocalization.

Calculations

Quantum-chemical calculations were carried out by using the GAUSSIAN 94 package[7] at the Hartree-Fock (HF) and Møller-Plesset second-order perturbation (MP2) levels of the theory with 6-31G* as well as 6-311 + G(2D) basis sets. Second-derivative calculations were carried out at the HF/6-311 + G(2D) and MP2/6-31G* levels, on the corresponding optimized structures. For the zero point energy (ZPE) corrections the MP2/6-31G* zero-point energies were considered when investigating the relative stabilities of the planar and non-planar forms, while the HF/6-311 + G(2D) ZPEs were used in the other cases.

Results and Discussion

Geometry optimization on $Al_2N_3H_5$ was first carried out under planarity constraint. The calculation of the second derivatives showed that this structure is a first-order saddle point, characterizable by a i431 cm^{-1} imaginary harmonic frequency at the MP2/6-31G* level (i488 cm^{-1} at the HF/6-311 + G* level). This frequency corresponds to the out-of-plane movement of the hydrogens situated at the two neighbouring nitrogen atoms. Releasing the constraint, the optimization resulted in a structure with C_2 symmetry. The ring atoms themselves remain planar, while the two hydrogens on the neighbouring N atoms have a 63° tilt angle with respect to each other. This structure is a minimum on the MP2/6-31G* and the HF/6-311 + G(2D) potential energy surfaces. Its energy is lower by 1.08 kcal mol^{-1} at the MP2/6-311 + G(2D) + ZPE[2] level than that of the planar form [1.67 kcal mol^{-1} at the HF/6-311 + G(2D) level]. To assess the effect of a higher level of electron correlation, CCSD(T)/6-311 + G(2D)//MP2/6-311 + G(2D) + ZPE calculations were carried out for the planar and non-planar structures, resulting in an energy difference of 1.01 kcal mol^{-1}. Since the level of the theory applied has little effect on the barrier to planarity it is quite safe to assume this value to be 1–1.5 kcal mol^{-1} for the unsubstituted ring. This barrier is significantly smaller than the *ca.* 14 (or 18, see ref. 1) kcal mol^{-1}, which could be derived from the NMR data for the substituted ring.[1] It seems likely that the large difference between the calculated and the observed barriers is due to the steric repulsion of the substituents on the ring, although solvent effects might play some role as well.

Since the non-planarity is characteristic for the N−N fragment of the ring only (*cf.* ref. 1), it is reasonable to consider that the repulsion of the two neighbouring nitrogen lone pairs should be responsible for the folding of the ring. Planarity of hydrazine ($H_2N{-}NH_2$) requires a substantial energy [31.50 and 33.37 kcal mol^{-1} at the MP2/6-311 + G(2D) and HF/6-311 + G(2D) levels, respectively]. For $H_2Al(NHNH_2)$ 16.08 (MP2) and 17.81 kcal mol^{-1} (HF) are needed to make the system planar. On substituting the hydrazine by two AlH_2 groups ($AlH_2{-}NH{-}NH{-}AlH_2$), 4.11 and 5.43 kcal mol^{-1} are required for planarity at the MP2/6-311 + G(2D) and HF/6-311 + G(2D) levels, respectively. Clearly, as the empty p orbital on Al interacts with the nitrogen lone pairs, their mutual repulsive interaction diminishes. Planarity of the four-membered chain ($AlH_2{-}NH{-}NH{-}AlH_2$), however, still requires more energy (by about 3–4 kcal mol^{-1}) than in the case of the five-membered

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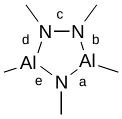
† *Non-SI unit employed*: cal = 4.184 J.

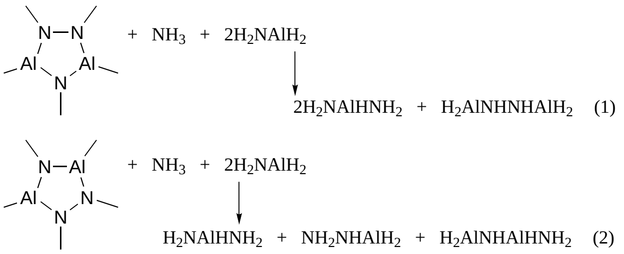
Table 1 Selected structural parameters (in Å), total energies in atomic units and Wiberg bond indices for the planar and non-planar forms of $Al_2N_3H_5$ at different levels of the theory. Bonds are marked a to e as shown

	Non-planar structure, $E_{tot} = -650.900\,770\,4$[a]					Planar structure, $E_{tot} = -650.898\,325\,0$[a]				
	a	b	c	d	e	a	b	c	d	e
HF/1[b]	1.781	1.788	1.442	1.788	1.781	1.783	1.772	1.440	1.772	1.783
MP2/2[c]	1.806	1.811	1.454	1.810	1.807	1.809	1.799	1.447	1.799	1.809
MP2/1[b]	1.801	1.805	1.459	1.805	1.801	1.803	1.793	1.451	1.793	1.803
X-Ray[d]	1.809	1.834	1.443	1.825	1.816	—	—	—	—	—
I_{Wib}[a]	0.529	0.553	1.040	0.553	0.529	0.528	0.575	1.045	0.575	0.528

[a] For the MP2/6-311 + G(2D) geometry using the 6-311 + G(2D) basis. [b] 6-311 + G(2D) basis. [c] 6-31G* basis. [d] For a substituted derivative.[1]

ring. It would be tempting to explain this difference by some small aromatic character of the ring, since a planar ring structure should benefit more from aromaticity than a non-planar one.

To estimate the effect of aromaticity on the non-planar structure an isodesmic reaction, termed semihomodesmic, introduced for five-membered rings[8] was considered. It was shown that the energy of these reactions, which contain delocalized fragments with four π electrons at the right-hand side of the equation, is close to the result obtainable by (super)homodesmic reactions.[8] In the present case two such reactions are (1) and (2). The energy of reaction (1) is −10.44 and −15.31 kcal mol^{-1} at the MP2/6-311 + G(2D) + ZPE and HF/6-311 + G(2D) + ZPE levels, respectively, showing destabilization upon ring formation. In reaction (2) −12.52 (MP2) and −20.06 kcal mol^{-1} (HF) destabilization can be obtained. For the six-membered ring $Al_3N_3H_6$,[3] however, the homodesmic reaction was nearly thermoneutral. Furthermore, this significant destabilization seems to be in contrast with the near-planar structure and with the near 4 kcal mol^{-1} difference in the energies for planarity of the ring and the Al−N−N−Al fragment.



Ring strain may be an important factor in this difference. In the case of the six-membered ring $Al_3N_3H_6$ it was shown[3] that the bond angles are near to 120°. Similarly, near 120° (or even larger) angles can be found in the optimized structures of the fragments used in reactions (1) and (2). Since in the five-membered ring the bond angles are between 103 and 113°, considerable ring strain should be expected, which might account for the destabilization in the semihomodesmic reaction. In the case of the six-membered ring[3] this angle strain should be negligible. To estimate the ring strain, $H_2NAl(H)NH_2$ has been calculated with a 107° N−Al−N angle, which is the value obtained in the ring. The structure optimized under the above constraint is 2.31 kcal mol^{-1} less stable than the minimum and similar destabilization can be expected at each ring atom. This estimate is however an upper bound of the strain, since the repulsion of the in-plane hydrogens in the compressed form should have some effect. A further factor to be considered is the enforcement of the NN fragment to be near planar in the ring. Summing all these contributions for the five ring atoms, an estimated strain of 10 kcal mol^{-1} is reasonable for the Al_2N_3 ring.

The structural characteristics of the planar and non-planar rings are collected in Table 1 at the investigated levels of the theory. The bond lengths of the two structures differ only slightly. This is reasonable, taking the small barrier to planarity into consideration. The four Al−N bond lengths are nearly identical at all the levels investigated here. This bond-length equalization would result in a large Bird aromaticity index,[9] indicating significant aromaticity. A comparison of the Al−N bond lengths of the different fragments used in the isodesmic reactions (1) and (2), however, shows that the lengths vary between 1.777 and 1.788 Å (MP2) only (1.763–1.794 Å at the HF level), thus they cannot be used to judge the aromaticity in the ring. Furthermore, the average Al−N bond length in the ring (1.803 Å at the MP2 level) is somewhat longer than any such length in the fragments, indicating some weakening of the Al−N bonds in the ring. This behaviour can be interpreted by the ring strain and NN lone-pair repulsion as discussed above. It should be noted that H_2AlNH_2 with the nitrogen lone pair fixed in the AlH_2 plane has a bond length of 1.794 Å [HF/6-311 + G(2D)]. This value is just slightly larger than the length in case of the planar minimum (1.773 Å), despite the missing nitrogen lone pair–empty aluminium orbital interaction. Nevertheless, the rotated form is less stable than the planar structure by 9.75 kcal mol^{-1}.

It is widely accepted that aromatic molecules are planar and thus non-planar systems are not aromatic. This behaviour was an important argument used by Wehmschulte and Power[1] when stating that the Al_2N_3 ring is not aromatic. For the AlN rings the planarity criterion, however, is not informative. Owing to the dative π bond formed between the nitrogen lone pair and the empty aluminium p orbital, all fragments investigated here are planar about the Al and N atoms (bonded to aluminium). The calculated second derivatives of planar H_2NNH_2, $H_2AlNHNH_2$ and $H_2AlNHNHAlH_2$ show the flattening effect of aluminium clearly, having three, two and one imaginary frequencies, respectively. (In the case of hydrazine two frequencies correspond to pyramidalization of the two nitrogens and one to the rotation about the N−N bond to avoid the repulsion of the nitrogen lone pairs. For $H_2AlNHNH_2$ one, while for $H_2AlNHNHAlH_2$ both pyramidalization motions became real frequencies.) Thus, all rings with an AlN fragment tend to be planar (*cf.* Al_3N_3 rings[3,5]). So the non-planarity of the five-membered $Al_2N_3H_5$ ring is attributable to the NN lone-pair repulsion only, which cannot be compensated by the energy needed to bend at the Al atoms and the small (if any) aromaticity of the ring.

To investigate the bonding situation in the ring, Wiberg bonding indices[10] were calculated and are collected in Table 1. Their values are very similar for the different Al−N bonds and indicate that the bond has a significant ionic character. Similarly the Wiberg bond index for H_2AlNH_2 is 0.587, indicating the similarity of the bonding in the ring and the 'monomeric' building block (note again the small decrease of the bonding index in the ring). The index of the N−N bond in the ring is just slightly larger than 1. The distribution of the electron density about the Al−N bond is quite asymmetric as shown by the analysis developed by Bader and co-workers.[11] The ellipticity, ε, which is 0 in case of a 'perfect' single bond (as in ethane), is 0.228 in case of the Al–N bonds of the ring. The ellipticity at the N–N bond critical point is 0.051, indicating a very small π interaction between the two nitrogens. The Al–N bond critical point is quite close to the aluminium atom (at 60% of the bond path length) and the laplacian of the density (Δ) is +0.68. Such behaviour is in accordance with ionic bonding.[11] Since $\varepsilon = 0.222$ for H_2NAlH_2, and the density at the critical point is again of similar value (0.093) to that in the ring, it seems that the ring formation has little effect on the electron distribution of the Al–N bond. The aromatic character of the Al_2N_3 ring is small, if any.

Conclusion

The present calculations show that the non-planar arrangement of the heavily substituted Al_2N_3 ring is mainly due to repulsion of the substituents. Nevertheless, $Al_2N_3H_5$ has C_2 and not C_s symmetry, with the two hydrogens on the neighbouring N atoms occupying an out-of-plane position with a 36° H–N–Al–N dihedral angle. The aromaticity of the ring is very small, if any, and cannot overcome the repulsion of the neighbouring nitrogen lone pairs and angle strain of the ring. The use of geometric criteria only in the assessment of aromaticity for AlN rings is misleading, since NAl structures are inherently planar even without aromaticity, and the Al–N bond length varies only slightly in the different chemical environment.

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