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Ab initio Calculations on Octahedral $(CH)_x(NH)_{6-x}$

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Octahedral 38-, 44- and 48-electron systems are closed-shells and could be stable. The latter two systems have a high energy and dissociate via a non-symmetric path. $(NH)_6$ in a chair conformation should be stable.

Key words: Octahedral $(CH)_x(NH)_{6-x}$ – Chair N_6H_6

In recent investigations Hogeveen and Kwant found $(CH)_6^{++}$ to possess C_{5v}-symmetry [1]. One could go one step further and consider $(CH)_6^x$ in octahedral symmetry. In this contribution we study this possibility with *ab initio* calculations. In order to be stable, first-order Jahn-Teller instabilities should not exist, i.e. no partially filled degenerate orbitals are permitted. Consider six NH-fragments, possessing 48 electrons, in octahedral conformation (point group O_h). The 1*s*-orbitals split up to yield one a_{1g}-, one e_g-, and one t_{1u}-orbital. A similar situation holds for the N–H bonds, and the nitrogen lone pairs add the third a_{1g}, e_g, and t_{1u}. The N–H "π"-orbitals combine to form the fourth t_{1u}, and one t_{2g}. However, a calculation of $(NH)_6$ shows an occupation $1\text{–}3a_{1g}$, $1\text{–}3e_g$, $1\text{–}3t_{1u}$, $1t_{2g}$, $1t_{2u}$. The t_{1u}- and e_g-combination of the lone pairs are lying fairly high due to the crowding of these orbitals in the hole of the octahedron. The $4t_{1u}$-orbital is so high in energy that a t_{2u}-orbital will be occupied preferentially. One of the components of the t_{2u}-orbital, triply degenerate, is shown in Fig. 1. It is seen to be antibonding, but interestingly, dissociation of a system in which this orbital is occupied into the corresponding 2+2+2, 3+3, or 4+2 first-row atom monohydrides is symmetry-forbidden. The 44-electron system, in which the high-lying $3e_g$-orbital is now unoccupied, thus exhibits the same features. A calculation on a 38-electron system finally shows the t_{2u}-orbital to be unoccupied. These compounds, closo-$(CH)_2(BH)_4$ are known to be stable [2, 3]. We performed the

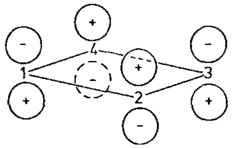

Fig. 1. One of the components of the t_{2u}-orbital

calculations with a minimal STO-3G basis set; in some cases a minimal STO basis set was used. The geometry of all compounds discussed was optimized. We calculated the energies of several 48- and 44-electron systems suggested in the MO-analysis. For the former $(NH)_6$ is suited, for the latter apart from $(CH)_6^{--}$ a partial carbon and nitrogen composition may be acceptable.

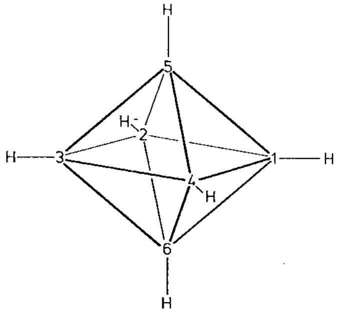

Fig. 2. Octahedral $(XH)_6$

Octahedral $(NH)_6$, having N–N bond lengths of 1.84 Å is calculated 702 kcal/Mole endothermic compared to three molecules *cis*-$(NH)_2$. The highest occupied orbitals, $3e_g$ and $1t_{2u}$, have Ionization Potentials (IP's) of about 4 eV. These orbitals reflect the inability of nitrogen to behave like a pentavalent atom, and must be held responsible for the instability of the system.

Table 1. Compounds discussed and calculated energies at the optimal geometry

Compound		Calculated Energy (a.u.)[a]	
octahedral	$(NH)_6$	STO	−327.7682
chair	$(NH)_6$ H axial	STO	−329.0297
octahedral	$(CH)_6^{--}$	STO	−228.6519
	cis-HNNH	STO	−109.6289
chair	$(NH)_6$ H axial		−325.7795
chair	$(NH)_6$ H equat.		−325.7348
octahedral	$(CH)_2(NH)_4^{++}$ (1,3–C)		−291.6050
octahedral	$(CH)_3(NH)_3^{+}$ (1,2,5–C)		−275.7728
octahedral	$(CH)_4(NH)_2$ (1,3–N)		−259.3944
	cis-HNNH		−108.5453
	trans-HNNH		−108.5570
	cis-HCNH (RHF)		− 92.1752
	$HCNH^+$		− 91.9978
	HCCH		− 75.8562
triplet	NH (RHF)		− 54.2593

[a] 1 a.u. = 27.21 eV = 627.2 kcal/Mole.

Addition of $2s$- and $2p$-polarization functions at the center of mass, representing the influence of a caught small cation, brings the energy firmly down, but can do little for the $3e_g$- and $1t_{2u}$-orbitals, which in a united-atom approach form *d*- and *f*-functions.

$(NH)_6$ is isoelectronic with $(CH_2)_6$, cyclohexane. In a chair form with all nitrogen atoms tetrahedral the STO-3G calculations predict the more stable conformer with axial hydrogen atoms and all $r(N–N) = 1.47$ Å to be 68 kcal/Mole resp. 90 kcal/Mole exothermic with respect to three molecules *trans*-$(NH)_2$ resp. *cis*-$(NH)_2$; the results of the STO-calculations are in complete accordance with this prediction. The corresponding 2+2+2 dissociation is symmetry-forbidden analogous to the symmetry-forbidden dissociation of benzene into three molecules acetylene. Consequently, $(NH)_6$, although experimentally unknown, might be stable.

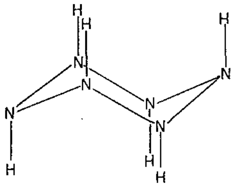

Fig. 3. The stable $(NH)_6$

Generally speaking the stability of the 44-electron systems will be increased with respect to the 48-electron systems as the antibonding $3e_g$-orbital is unoccupied.

The octahedral di-anion of benzene, $(CH)_6^{--}$, may be thought of as built from two cyclopropenyl anions. It is questionable whether this species is stable itself; on combination of two such ions a large (dominant) price in Coulomb-energy has to be paid. Moreover the $1t_{2u}$-orbital lies at nearly +12 eV. This system cannot possibly exist.

Possibly stable 44-electron systems are $(CH)_4(NH)_2$ and $(CH)_3(NH)_3^+$. There is retention of approximate octahedral symmetry for *trans*-$(CH)_4(NH)_2$ (in Fig. 2: 1, 2, 3, 4 = C, 5, 6 = N), as follows from the distances from the origin (center of mass): $r(O–N) = 1.230$ Å, $r(O–C) = 1.147$ Å. Also this retention is clear from the output vectors. Therefore we will keep referring to these structures as octahedral. Some polarization is present: according to a Mulliken population analysis the NH-groups bear 8.0 electrons, the CH-groups bear 7.0 electrons. In point group D_{4h} the occupied t_{2u}-orbital splits into an e_u- and a b_{2u}-orbital, having IP's of 2.8 and −0.9 eV. Even though this last result is surely due to truncation of basis set – a larger basis set will bring this orbital down into the binding region [4] – it forms an indication for the instability of this molecule. This molecule is 509 kcal/Mole endothermic with respect to the 2+2+2 dissociation. $(CH)_4(NH)_2$ (1, 2 = N) is higher in energy and less attractive. On optimizing the geometry of $(CH)_3(NH)_3^+$ (1, 3, 5 = C) this compound is found to dissociate into two fragments and $(CH)_3(NH)^+$. This is a consequence of the fact that the t_{2u}- and the t_{1u}-orbital are no longer distinguishable in this C_{2v}-subgroup: both are converted into an a_1-, b_1- and b_2-orbital.

$(CH)_3(NH)_3^+$ (1, 2, 5=C) is 393 kcal/Mole endothermic with respect to its 2+2+2 dissociation products. The IP's of the $1t_{2u}$-orbital, in C_{3v} the e_u- and a_{2u}-orbitals, are about 12.1 eV. The distortion of octahedral symmetry is somewhat larger for this compound.

Finally non-symmetric distortions were investigated. Several possibilities in which one fragment was shifted into the direction of one or two others were calculated, meanwhile keeping all r(O–C) and r(O–N) constant. For these calculations we chose $(CH)_4(NH)_2$. The octahedral geometry proves to be a saddle point; a very strong preference was found for a distortion for which the symmetry of the system reduces to C_1. We conclude therefore that despite the occupation of the $1t_{2u}$-orbital, which precludes symmetric dissociations, these octahedral compounds cannot possibly be stable.

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