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## Hypervalence and Aromaticity

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## 9 Summary

In this thesis, the fundamental chemical concepts of hypervalence and aromaticity have been investigated theoretically by means of Density Functional Theory (DFT) calculations. These two important notions deal with the propensity of a system to localize or delocalize bonds. More precisely, hypervalent and aromatic molecules usually present highly symmetrical structures with equal bonds while the geometries of non-hypervalent and antiaromatic species are asymmetric with alternating short and long bonds. The objective of the work described herein is to develop a transparent physical model that enables us to understand the nature of (non)hypervalence and (non)aromaticity. In other words, we want to understand which feature in the bonding mechanism is essential for determining whether an atom can form a hypervalent structure (or not) or whether a  $\pi$ -conjugated ring adopts an aromatic geometry with delocalized double bonds (or not).

This understanding is obtained from electronic structure theory by developing qualitative physical models based on Molecular Orbital (MO) theory as contained in the Kohn-Sham approach to DFT, which we employ in our DFT computations with the Amsterdam Density Functional (ADF) program.

The first two chapters of this thesis provide an introduction to the concepts of hypervalence and aromaticity and an overview of the theoretical background and DFT as well as *ab initio* methods used in this thesis. The thesis will be further separated into two parts dedicated to hypervalence and aromaticity, respectively.

Part I of this thesis deals with the concept of hypervalence. First, in Chapter 3, the capability of lithium and silicon to form hypervalent structures and the absence of such

capability for hydrogen and carbon have been investigated at the BP86/TZ2P level of density functional theory. The model systems used here to understand this issue are  $\text{Li}_3^-$  and  $\text{SiH}_5^-$  versus  $\text{H}_3^-$  and  $\text{CH}_5^-$  which, although isoelectronic to the former two species, have a distortive, bond-localizing propensity. At first we showed that the hypervalence of Li and Si does not originate from the availability of low-energy  $2p$  and  $3d$  AOs, respectively. Furthermore we showed that all bonding patterns of the valence molecular orbitals present 3-center-4-electron bonds in the axial X–A–X unit and are, therefore, not the key to understand the (non)hypervalence of the various central atoms studied here. Instead, we find that the discriminating factor between carbon and silicon is the smaller effective size of the former atom and the resulting lack of space around it compared to the latter. Interestingly, a similar steric mechanism is responsible for the difference in bonding capabilities between H and the effectively larger Li atom. This is so, despite the fact that the substituents in the corresponding symmetric and linear dicoordinate  $\text{H}_3^-$  and  $\text{Li}_3^-$  are on opposite sides of the central atom.

In Chapter 4, the insights on the (non)hypervalence of carbon and silicon obtained in Chapter 3 have been further developed into the Ball-in-a-Box model that accounts for the (non)hypervalence of  $[\text{Cl-AH}_3\text{-Cl}]^-$  systems with  $\text{A} = \text{C}$  and  $\text{Si}$ . Similarly to  $\text{CH}_5^-$  and  $\text{SiH}_5^-$  respectively,  $[\text{Cl-CH}_3\text{-Cl}]^-$  is labile, with a tendency to localize one of its axial C–Cl bonds and to largely break the other one, while the isostructural and isoelectronic  $[\text{Cl-SiH}_3\text{-Cl}]^-$  forms a stable pentavalent species, with a delocalized structure featuring two equivalent Si–Cl bonds. The Ball-in-a-Box model, based on MO theory and supported by DFT calculations at the BP86/TZ2P level of theory, reveals the key role of steric factors. It further provides a simple way of understanding the above phenomena in terms of different atom sizes. In this model, the five substituents form a cage or "box"  $\text{ClH}_3\text{Cl}^-$  in which they are in mutual steric contact. The central atom A can be viewed as a "ball" in that box. Silicon fits nearly exactly into the box and can bind simultaneously to the top and the bottom. This yields the hypervalent  $\text{ClSiH}_3\text{Cl}^-$  with a trigonal-bipyramidal structure. In opposition, the carbon atom is too small to touch both the top and the bottom and it can thus only bind to one of them. Consequently the carbon-atom ball "drops" onto the bottom of the box leading to a species  $\text{Cl}^- \cdots \text{H}_3\text{CCl}$  with one localized C–Cl bond and one long C–Cl contact. The ball-in-a-box model is furthermore supported by the fact that the  $\text{S}_{\text{N}}2$  central barrier for nucleophilic attack by  $\text{Cl}^-$  decreases monotonically along the substrates  $\text{CH}_3\text{Cl}$ ,  $^{\bullet}\text{CH}_2\text{Cl}$ ,  $^{\bullet\bullet}\text{CHCl}$  and  $^{\bullet\bullet\bullet}\text{CCl}$ . Our findings for  $\text{ClCH}_3\text{Cl}^-$  and  $\text{ClSiH}_3\text{Cl}^-$  are generalized to other group-14 central atoms (Ge, Sn and Pb) and axial substituents (F).

In Chapter 5, we have studied species that violate this ball-in-a-box behavior: although isostructural and isoelectronic with the above  $[\text{X-CH}_3\text{-X}]^-$  systems, the noble gas–methyl cation complexes  $[\text{Ng-CH}_3\text{-Ng}]^+$  adopt, for  $\text{Ng} = \text{helium}$  and  $\text{neon}$ , a perfectly  $\text{D}_{3\text{h}}$  symmetric structure featuring a stable hypervalent carbon atom with two equivalent C–Ng bonds. Our

analyses show that the carbon atom in  $[\text{Ng-CH}_3\text{-Ng}]^+$  can no longer be considered as a ball in a box of the five substituents because it is much more tightly bound to the equatorial H atoms than to the axial noble-gas substituents. Thus, the  $[\text{Ng-CH}_3\text{-Ng}]^+$  species are better conceived as a "disk between balls". Here, the "disk" is  $\text{CH}_3^+$  and the "balls" are constituted by the two noble-gas atoms.

Finally, we propose to classify the nature of five-coordinate carbon species in terms of a spectrum between the ball-in-a-box situation (nonhypervalent C in Chapter 4) and the disk-between-balls model (hypervalent C in Chapter 5). The position along this spectrum is determined by the ratio (i.e., the relative magnitudes) of the strengths of the carbon–equatorial substituent bond ( $\text{C-H}^{\text{eq}}$ ) versus that of the carbon–axial substituent bond ( $\text{C-X}^{\text{ax}}$ ). Hypervalent species (like  $[\text{He-CH}_3\text{-He}]^+$ ) have large  $\text{C-H}^{\text{eq}}/\text{C-X}^{\text{ax}}$  ratios whereas truly nonhypervalent species (such as  $[\text{Cl-CH}_3\text{-Cl}]^-$ ) have small  $\text{C-H}^{\text{eq}}/\text{C-X}^{\text{ax}}$  ratios. Intermediate or "weakly nonhypervalent" cases (i.e., species with a weak tendency to localize one and to partly break the other axial carbon–substituent bond), such as  $[\text{Ng-CH}_3\text{-Ng}]^+$  complexes with heavy noble-gas atoms, correspond to situations with intermediate  $\text{C-H}^{\text{eq}}/\text{C-X}^{\text{ax}}$  ratios.

Part II of this thesis deals with the concept of aromaticity. First, in Chapter 6, the origin of the regular geometry of benzene as opposed to the localized geometry of 1,3-cyclobutadiene is investigated at the BP86/TZ2P level of density functional theory. Geometry is indeed one of the most direct indicators of aromaticity and antiaromaticity: a regular structure with delocalized double bonds (e.g., benzene) is symptomatic of aromaticity, whereas a distorted geometry with localized double bonds (e.g., 1,3-cyclobutadiene) is characteristic of antiaromaticity. Here, we present a molecular-orbital (MO) model of aromaticity that explains, in terms of simple orbital-overlap arguments, why this is so. Our MO model is based on accurate Kohn–Sham DFT analyses of the bonding in benzene, 1,3-cyclobutadiene and how the bonding mechanism is affected if these molecules undergo geometrical deformations between regular, delocalized ring structures, and distorted ones with localized double bonds. We show that the propensity of the  $\pi$  electrons is always, that is, in both the aromatic and antiaromatic molecules, to localize the double bonds, against the delocalizing force of the  $\sigma$  electrons. More importantly, we show that the  $\pi$  electrons nevertheless decide about the localization or delocalization of the double bonds by showing qualitatively different geometry dependence of the  $\pi$  overlap in benzene and cyclobutadiene. In the aromatic species, the localizing propensity of the  $\pi$  system emerges from a subtle interplay of counteracting overlap effects and is, therefore, too little pronounced to overcome the delocalizing  $\sigma$  system. At variance, in the antiaromatic ring, all  $\pi$ -overlap effects unidirectionally favor localization of the double bonds and can, in this way, overrule the  $\sigma$  system.

In Chapter 7, we show that the MO model of (anti)aromaticity that we presented for cyclobutadiene and benzene in Chapter 6 extends also to the corresponding next larger analogs, cyclooctatetraene ( $C_8H_8$ ) and cyclodecapentaene ( $C_{10}H_{10}$ ), respectively. Our MO model accounts for the antiaromaticity of  $C_8H_8$  and the only very weakly aromatic nature of  $C_{10}H_{10}$ . Thus, in none of the cases does the  $\pi$ -electron system favor a symmetric, delocalized ring. The regular, symmetric structure of benzene has the same cause as that of cyclohexane, namely, the  $\sigma$ -electron system. Nevertheless, the  $\pi$  system decides if delocalization occurs by showing qualitatively different geometry-dependence of the  $\pi$  overlap in the aromatic ( $C_6H_6$  and  $C_{10}H_{10}$ ) versus the antiaromatic rings ( $C_4H_4$  and  $C_8H_8$ ). In the latter two, all  $\pi$ -overlap effects unidirectionally favor localization of the double bonds and can, in this way, overrule the  $\sigma$  system. The somewhat more pronounced steric repulsion between vicinal C–H bonds in planar  $C_8H_8$  causes cyclooctatetraene to adopt the nonplanar, tub-shaped equilibrium conformation in which this steric repulsion is reduced around C–C single bonds. In the aromatic species, the localizing propensity of the  $\pi$  system emerges from a subtle interplay of counteracting overlap effects. In benzene, it is therefore too little pronounced to overcome the delocalizing  $\sigma$  system. In cyclodecapentaene, the  $\pi$  system shows a somewhat increased localizing propensity but, in our BP86 calculations, this is still not strong enough to overcome the delocalizing  $\sigma$  system. Therefore, we arrive at a delocalized structure which, however, adopts a nonplanar, saddle-shaped conformation to minimize the steric repulsion between vicinal C–H bonds. Our electronic structure analyses nicely confirm that the  $\pi$ -electron system of cyclodecapentaene causes the aromatic character of this species to be much reduced if compared to benzene.

Finally, we have shown in Chapter 8 that the MO model of aromaticity, recently developed for the archetypal aromatic molecule of benzene, is also valid for *heterocyclic* and *inorganic* benzene analogs, such as *s*-triazine, hexazine, borazine, boroxine, hexasilabenzene and hexaphosphabenzene. At variance to the other model systems studied here, hexazine, hexasilabenzene and hexaphosphabenzene adopt nonplanar equilibrium structures. To facilitate a direct comparison and to enable us to separate  $\sigma$  and  $\pi$  electron bonding consistently along all species, we have included the planar species hexazine, hexasilabenzene and hexaphosphabenzene into our set of model systems. In none of the cases does the  $\pi$ -electron system favor a symmetric, delocalized ring. Instead, the regular, symmetric structure that results for all planar model systems, except hexazine, is caused by the delocalizing force of the  $\sigma$ -electron system. Simple orbital-overlap arguments account for this behavior. In planar hexazine, the delocalizing force of the  $\sigma$ -electron system is less pronounced and is therefore slightly overruled by the localizing orbital interaction in the  $\pi$  system. This causes  $D_{6h}$  symmetric hexazine to be nearly "undecided" but yet with a slight bias towards bond localization which eventually results in barrierless formation of 3  $N_2$  molecules.

As a concluding remark, the work carried out in this thesis allows Molecular Orbital (MO) theory to catch up with Valence Bond (VB) theory regarding the treatment and understanding of the phenomenon of hypervalence and aromaticity. It also nicely shows how the interplay of electronic and steric factors plays a role in the question if an atom has the capability to form stable hypervalent structures with its substituents while the question of whether a species is aromatic or antiaromatic is a purely electronic problem.