

# Lab 1 for benzene

Andriy Zhugayevych

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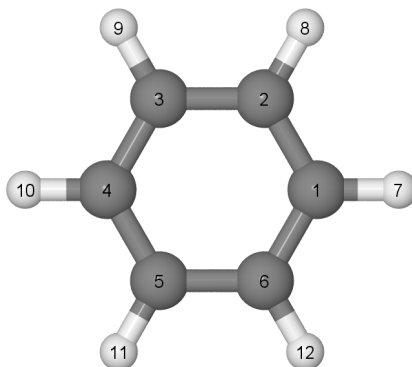


Figure 1: Molecular structure of benzene.

The molecule under the study is benzene, chemical formula  $C_6H_6$ . All calculations are performed in MOPAC 2016 program [1] using semiempirical PM7 method [2]. The geometry is optimized [`molec_PM7_em`] until the gradient norm drops below  $0.01 \text{ kcal/mol/\AA}$ . Then the coordinates are symmetrized by 6/mmm group [`_symmetrize.mw`]. Vibrational frequencies are calculated [`molec_PM7_freq`] to ensure that the energy is minimized: the lowest frequency is  $346 \text{ cm}^{-1}$ .

The optimized geometry is shown in Fig. 1. Computed bond lengths are  $1.394 \text{ \AA}$  for C-C bond and  $1.088 \text{ \AA}$  for C-H bond, in good agreement with experimental values [3] of  $1.397$  and  $1.084 \text{ \AA}$ , respectively. Because the molecule is rigid, no other low energy conformations are expected.

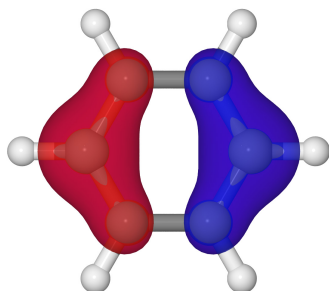


Figure 2: Doubly degenerate HOMO

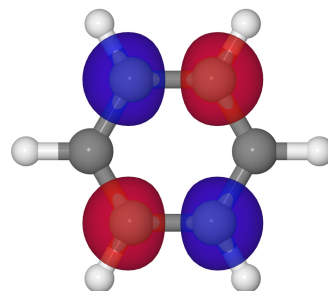
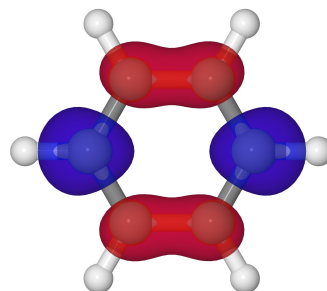
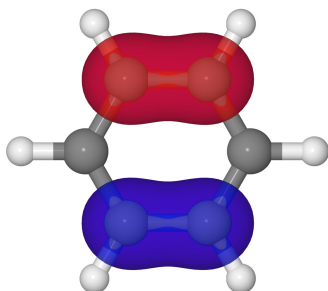


Figure 3: Doubly degenerate LUMO

The frontier orbitals [`molec_PM7_sp`] include doubly degenerate HOMO at  $-9.82 \text{ eV}$  (Fig. 2) and doubly degenerate LUMO at  $0.24 \text{ eV}$  (Fig. 3). The energy separation from other orbitals is about  $2 \text{ eV}$ . The experimental value [3] for vertical IP is  $9.25 \text{ eV}$ , in a reasonable agreement with HOMO energy. The HOMO-LUMO gap is  $10.06 \text{ eV}$ .

Analysis of localized molecular orbitals [`molec_PM7_lmo`] shows presence of  $\sigma$ -bonds at  $-19.94$  and  $-17.56 \text{ eV}$  for C-C and C-H pairs of atoms, respectively. The rest 6 electrons are distributed uniformly among 6  $\pi$ -conjugated  $p$ -orbitals: we cannot localize them due to degeneracy of this  $\pi$ -system, but their subspace is clearly defined by doubly degenerated HOMO and fully symmetric MO at  $-13.43 \text{ eV}$ , forming delocalized (metallic)  $\pi$ -bonding.

In the optimized triplet [`molec_T_PM7_em`] the symmetry is broken to mmm, with bonds C2-C3 and C5-C6 expanded to  $1.482 \text{ \AA}$  and other bonds contracted to  $1.386 \text{ \AA}$ . The lowest vibrational frequency [`molec_T_PM7_freq`] is  $104 \text{ cm}^{-1}$  and the total energy [`molec_T_PM7_sp`] is  $2.34 \text{ eV}$  relative to the ground state (spin gap). The two unpaired orbitals [`molec_T_PM7_sp`] correspond to the right-side HOMO and LUMO in Figs. 2 and 3. This explains the bondlength pattern: the electronic density is transferred from bonding to antibonding orbitals corresponding to C2-C3 and C5-C6 bonds thus loosening them.

## Supporting Information

Attached are input (.mop), output (.out, .mgf) and xyz files, the notations are as follows. States: “P” = cation, “N” = anion, “T” = triplet. Types of calculations: “em” = energy minimization, “sp” = single point, “lmo” = localized molecular orbitals, “freq” = vibrational frequencies.

## References

- [1] J J P Stewart, MOPAC 2016, <http://openmopac.net>
- [2] J J P Stewart, Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters, J Mol Model 19, 1 (2013)
- [3] NIST computational chemistry comparison and benchmark database, <http://cccbdb.nist.gov>