Lab SE for bipyridine

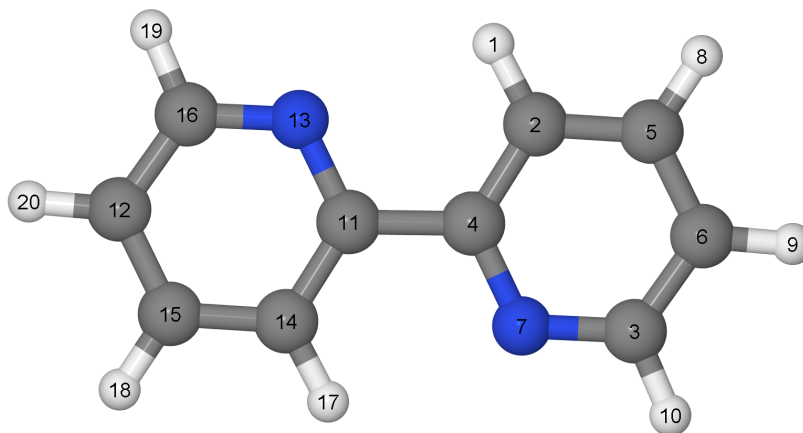Andriy Zhugayevych

November 1, 2016

Figure 1: The lowest energy ground state conformation.

The molecule under the study is 2,2'-bipyridine, chemical formula $C_{10}N_2H_8$. We use semiempirical PM6 method and MOPAC program.

In the ground state the lowest energy conformation is shown in Fig. 1. The molecule is planar with the symmetry C_{2h}. The bridging C–C bond is elongated (1.5 Å) indicative for a single bond, the rings are aromatic (C–C bond lengths are about 1.4 Å).

The MO energies together with their symmetries are shown in Fig. 4. The energy gap is 8.6 eV. The frontier orbitals belong to the π-conjugated system, see HOMO in Fig. 6 and LUMO in Fig. 7. More specifically the six HOMOs and six LUMOs are π-conjugated, except for HOMO-1 and HOMO-2 belonging to nitrogen's lone pairs hybridized with σ-bonds. The four HOMO and four LUMO originate from the doubly degenerate HOMO and LUMO in the archetypal benzene molecule.

In the triplet state the symmetry is lowered to C_h: the molecule is planar but there is no inversion symmetry. A visual inspection of the two unpaired orbitals, see Figs. 8,9, shows that in molecular orbital picture the triplet state corresponds to the right aromatic ring being excited (HOMO to LUMO): the electronic density is depleted on the right ring in Fig. 8 compared to HOMO in Fig. 6, whereas it is localized on the right ring in Fig. 9 in a LUMO pattern shown in Fig. 7. This results in the observed geometrical asymmetry and nonzero dipole moment. The relative energy of the relaxed triplet state is 1.8 eV.

The relaxed PES for the bridging C–C–C–C dihedral is shown in Fig. 2. It is monotonic (DFT calculations show a shallow minimum at $30°$, see Fig. 3). The flipped conformation ($0°$) is unstable due to strong electrostatic and steric repulsion between the two nitrogens and two hydrogens in close contact. This repulsion is much stronger than the attractive effect of the π-conjugation (about 0.1 eV as follows from Fig. 2). The latter is uninfluenced by the flip as can be seen in Figs. 10,11. At $90°$ the π-conjugation between the two rings is broken as well as the σ_h symmetry. As result, in Fig. 5 we observe a hybridization of frontier MOs, initially separated by symmetry.

Attached are .mop, .out, and .mgf files for the discussed conformers/states marked appropriately: 0, 90, 180 mean the dihedral value, "T" means triplet, "scan" means PES. The scanned relaxed geometries are given in the corresponding xyz-file.
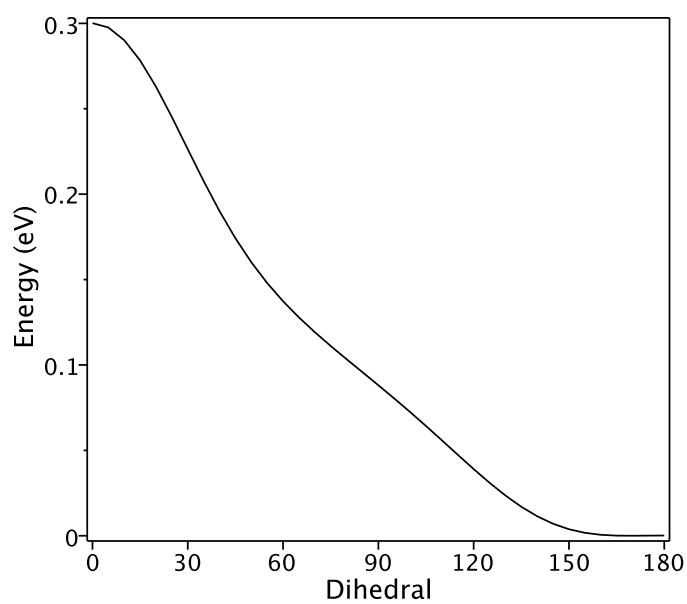
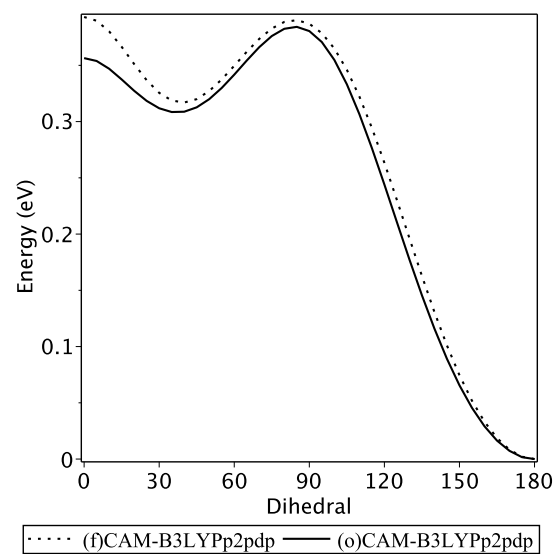Figure 2: PES for the bridging C–C–C–C dihedral.

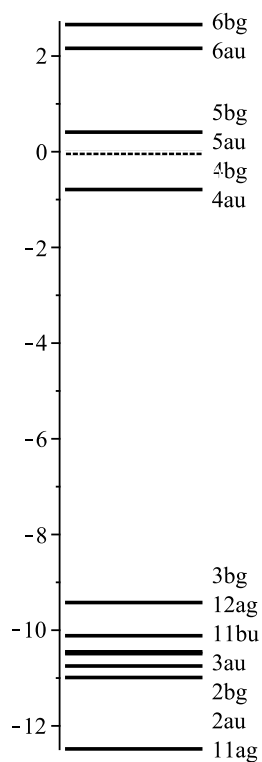Figure 3: Rigid (f) and relaxed (o) PES for the bridging C–C–C–C dihedral by CAM-B3LYP/6-31G**.

Figure 4: MO energies (eV) and symmetries for frontier orbitals.
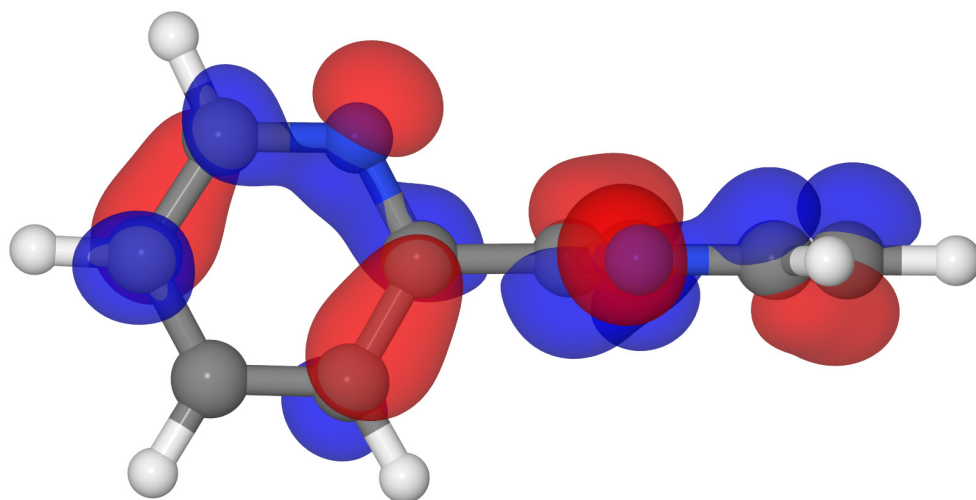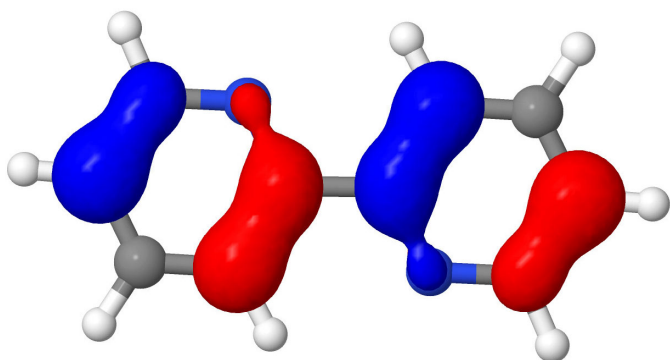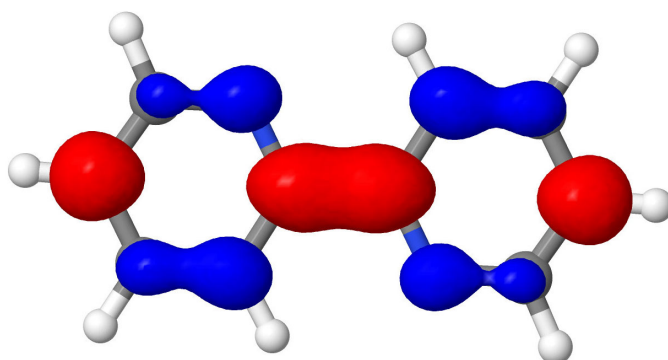

Figure 5: HOMO at 90°.

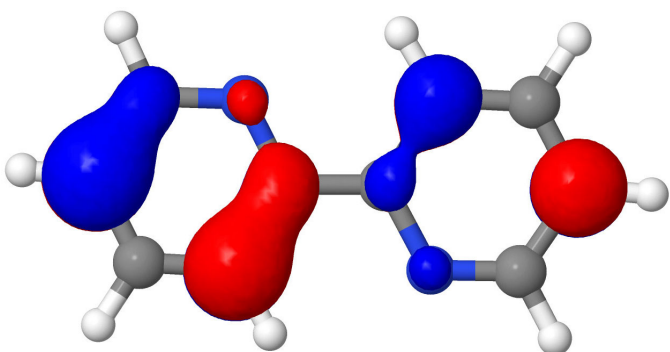Figure 6: HOMO.

Figure 7: LUMO.

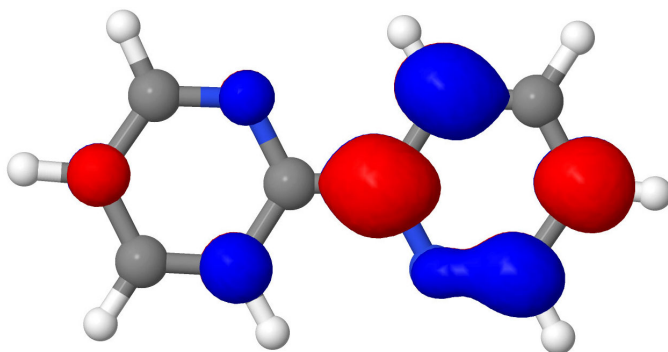Figure 8: Triplet, unpaired MO at -7.8 eV.
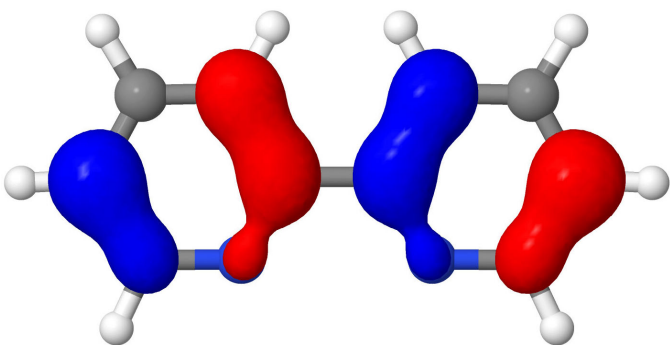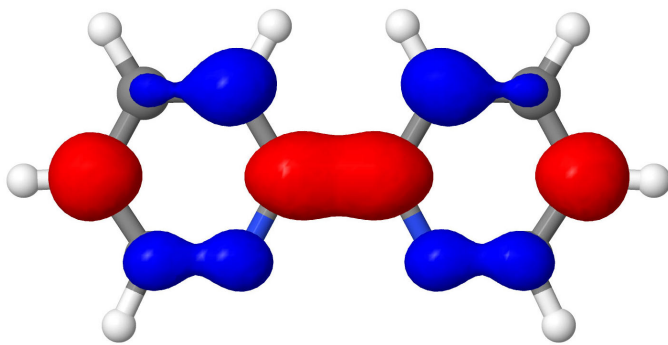

Figure 9: Triplet, unpaired MO at -9.9 eV.

Figure 10: HOMO for flipped dihedral.

Figure 11: LUMO for flipped dihedral.