Research paper

Configuration and energy landscape of the benzonitrile anion

Nikita Kirnosov [a], Ludwik Adamowicz [b],*

[a] *Department of Physics, University of Arizona, Tucson, AZ 85721, USA*
[b] *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, USA*

A R T I C L E   I N F O

A B S T R A C T

Quantum chemical calculations are employed to study the configurational isomers of the anion formed by benzene substituted with a cyano group. It is found that an excess electron can form dipole-bound (DB) states with benzonitrile and phenyl-isocyanide isomers. It can also attach to the cyano group, if this group is separated from the benzene ring by some distance, forming a covalent CN^- anion. There are four positions at peripherals of the benzene ring where this anion can localize and form stable complexes with the benzene radical. In these complexes CN^- is connected to the benzene radical via non-covalent interactions.

1. Introduction

Benzonitrile (also called cyanobenzene) is an interesting model system to study formation of stable anions. It is formed by an strong electron-withdrawing group (the cyano radical) and an electron-donating group (the benzene radical). By itself the cyano radical readily attaches an excess electron and forms a very stable anion (CN^-). The combination of an electron-withdrawing group and an electron-donating group causes a significant charge shift in the benzonitrile molecule that results in a sizable dipole moment of the system. As the present calculations show, this dipole moment is around 5 Debye, which is more than sufficient to form a dipole-bound (DB) anion. If the cyano group is rotated by 180°, the resulting system, phenyl isocyanide, is also polar, but its dipole moment is significantly smaller than of benzonitrile (according with the present calculations it is about 3.5 Debye). This is still sufficient to form a dipole-bound anion with an excess electron.

On the experimental side, the determination of the electron affinity of benzonitrile is still a work in progress [1,2]. Even the nature and the structure of the benzonitrile anion is still unclear. In 1992 Burrow et al. [3] performed an electron transmission spectroscopy experiment and concluded that the ground-state anion of benzonitrile was not observable because it was bound by a few tenths of an electron-volt. This finding was consistent with previous experiment which estimated the EA of benzonitrile for about 0.26 eV [1,2].

In 2015 Dixon et al. [4] performed a negative-ion photoelectron imaging study of benzonitrile anion and concluded that an excess electron is bound in this system by 58 ± 5 meV. By an analysis of the photoelectron spectrum which involved Franck-Condon simulation of the spectrum and examination of the photoelectron angular distribution they also concluded that the excess electron in the benzonitrile anion is covalently bound and occupies a π valence state. They also performed some quantum mechanical calculations that seemed to confirm their findings. We have analyzed the approach they used in the calculations, which involved the geometry optimization of the structures of the anion and the neutral system performed at the CCSD/aug-cc-pvdz level of theory and the determination of the vertical detachment energy with the EOM-IP-CCSD method, and concluded that there are some problems with the way the calculations were performed. The major problem is related to their CCSD/aug-cc-pvdz optimization of the anion geometry. As the CCSD/aug-cc-pvdz energies obtained at the equilibrium anion and neutral structures reveal (the energies are shown in the Supplementary Materials in their paper) the anion at that level of theory is unstable with respect to (adiabatic) electron detachment, as its energy is higher than the energy of the neutral. Our test also showed that at the CCSD/aug-cc-pvdz level of theory the anion is unstable with respect to vertical electron detachment. This indicates that the anion, whose structure they obtained in their calculations, is a superficial system where the excess electron is localized on the benzonitrile molecule not because it forms a bound anionic state, but because the basis set used in the calculations did not allow it to detach. If their calculations were done in a basis set that included additional diffuse basis functions (*e.g.*, functions that are capable to describe a DB electron, as it is done in this work) and basis functions representing a free electron, their anion geometry optimization would either converge

* Corresponding author.
   E-mail addresses: kirnosov@gmail.com (N. Kirnosov), ludwik@u.arizona.edu (L. Adamowicz).

to the equilibrium structure of the neutral plus a free electron or to a structure of another anion of benzonitrile (*e.g.* a DB anion), which is stable and can be described in this more extended basis set and with the CCSD method. As the benzonitrile anion described by the 2015 calculations of Dixon et al. is an "unphysical" system, any calculation, where either its optimized geometry or its CCSD/aug-cc-pvdz wave function is used (for example, in the EOM-IP-CCSD calculations), is questionable.

The realization that the dipole-moments of benzonitrile and phenyl isocyanide are sufficiently large to form dipole-bound anions and the realization of the above-described problem with the Dixon et al. calculations prompted us to carry out quantum-mechanical calculations to elucidate the topology of the potential energy surface of the benzonitrile anion. The calculations are performed with the standard it ab initio methods implemented in the Gaussian 09 program package [6].

2. Calculations

2.1. Dipole-bound anions

The present calculations start with geometry optimizations of the neutral benzonitrile and phenyl isocyanide molecules. The optimizations are performed at the MP2/aug-cc-pvdz level of theory. The geometries of the two structures obtained in the calculations are shown in Fig. 1. The next series of calculations concerns the dipole-bound anions of the two systems. In order to describe the dipole-bound excess electron in these systems the aug-cc-pvdz basis set is augmented with additional basis functions. Our previous studies of dipole-bound molecular anions, particularly those performed using numerical orbitals [7], showed that an adequate basis set for describing a dipole-bound electron should contain at least three additional *sp* shells of single Gaussians with exponents forming a even-tempered $\alpha\beta^n$ series with *n*, in the case of three shells, being 0, 1, and 2, and α and β being optimization parameters. It should also include a *d* shell with the exponent equal to $\alpha\beta$. The optimization of the α and β parameters is performed by the minimizations of the LUMO energy of the neutral system. If the dipole moment of the neutral system is larger than about 2.5 Debye (a practical threshold for the formation of a stable

dipole-bound molecular anion), the LUMO energy should be negative as its absolute value provides, according to the Koopmans theorem, an approximation of the electron affinity of the system. Our previous calculations showed that the β parameter for Gaussian basis functions should be equal to about 3 and the additional Gaussians should be centered at or near the most peripheral atom of the molecule located in the direction of the positive pole of the molecular dipole. Thus, in the present calculations only the α parameter is optimized. The value of this parameter dependents on the magnitude of the dipole moment of the system.

In the present calculations the number of the *sp* and *d* shells added to the standard aug-cc-pvdz basis set to describe a DB electron is 5 and 2, respectively. This basis set is called aug-cc-pvdzX in the discussion that follows. The even-tempered approach is used to optimize the Gaussian exponents of the added shells. The optimization is carried separately for the benzonitrile and phenyl isocyanide, as they have different dipole moments. At the HF/aug-cc-pvdz level these dipole moments are 5.14 and 3.62 Debye, respectively, and the optimal values of the α parameter are 0.0001 and 0.00003, respectively.

The total energies obtained at different levels of theory in the calculations are shown in Table 1. Four sets of results are shown for each system. The first set corresponds to the anion calculated at its equilibrium geometry (A//A), the second set corresponds to the anion calculated at the equilibrium geometry of the neutral molecule (A//N), the third set corresponds to the neutral system calculated at the equilibrium geometry of the anion (N//A), and the fourth set corresponds to the neutral molecule calculated at its equilibrium geometry (N//N). All calculations for a particular system are performed in the aug-cc-pvdzX basis set generated for that system. All anions are assumed to be in doublet states and all neutrals are assumed to be singlets. The comparison of the energies shows that the benzonitrile anion is more stable than the phenyl isocyanide anion. In the table we also show the LUMO energy of the neutral and the HOMO energy of the anion. All this orbital energies are small but negative indicating that the dipole-bound anions of benzonitrile and phenyl isocyanide are stable systems.

The total energies from Table 1 are used to calculate the vertical electron detachment energies (VEDE) of the dipole-bound anions, and the adiabatic electron affinities (AEA) and the vertical electron
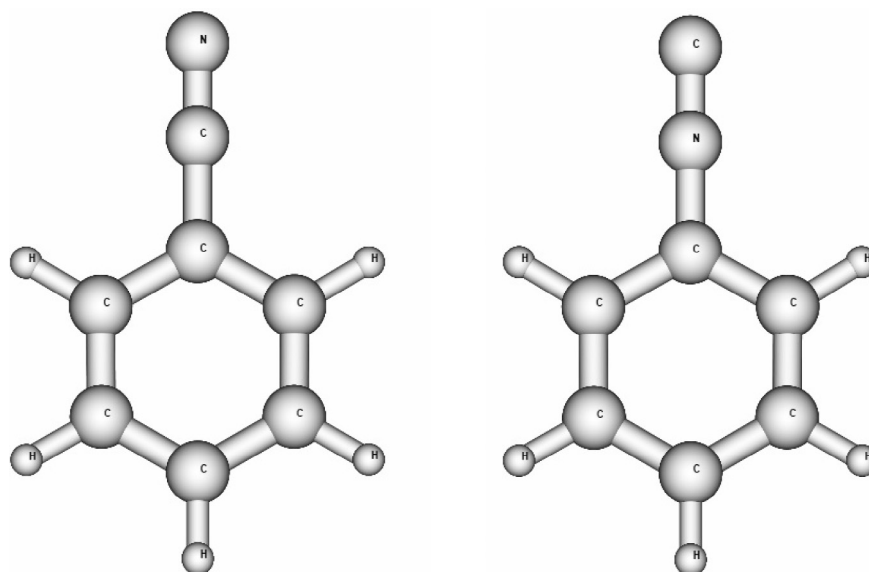

Fig. 1. Benzonitrile and phenyl isocyanide.