



Intuitive and counterintuitive noncovalent interactions of aromatic π regions with the hydrogen and the nitrogen of HCN



Jane S. Murray^{a,b,*}, Zenaida Peralta-Inga Shields^b, Paul G. Seybold^c, Peter Politzer^{a,b}

^a Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA

^b CleveTheoComp, 1951 W. 26th Street, Suite 409, Cleveland, OH 44113, USA

^c Department of Chemistry, Wright State University, Dayton, OH 45435, USA

ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form 31 January 2015

Accepted 2 February 2015

Available online 3 February 2015

Keywords:

Hydrogen cyanide

Noncovalent π -region interactions

Electrostatic potentials

Polarization

Dispersion

ABSTRACT

We have investigated intuitive and counterintuitive complex formation between eight aromatic molecules and HCN. In four of the former, the π regions had negative electrostatic potentials; in the other four, the π regions had positive potentials. Each aromatic molecule was allowed to interact through its π region with both the hydrogen (positive potential) of HCN and also the nitrogen (negative potential). In eight cases, therefore, interaction was intuitively favorable (positive/negative) while in the other eight, attractive interaction would be counterintuitive on the basis of the ground state electrostatic potentials (positive/positive or negative/negative). The intuitive interactions all led to bound complexes, and five of the counterintuitive did as well. The Hellmann–Feynman theorem was invoked to help explain the formation of the five counterintuitive complexes in terms of polarization/dispersion. Very good correlations were obtained, for the intuitive and also the counterintuitive complexes, between the computed interaction energies and values predicted solely on the basis of the most positive and the most negative electrostatic potentials in the π regions and on the HCN.

© 2015 Elsevier B.V. All rights reserved.

1. π Region electrostatic potentials and interactions of unsaturated hydrocarbons

The nuclei and electrons of a molecule (or any other system) create an electrostatic potential $V(\mathbf{r})$ at any point \mathbf{r} in the surrounding space. This is a fundamental property of the molecule [1,2], a physical observable, that can be obtained experimentally by diffraction techniques [3–5] as well as computationally. $V(\mathbf{r})$ is given rigorously by Eq. (1):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

Z_A is the charge on nucleus A, located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the molecule's electronic density. Note that $V(\mathbf{r})$ is determined by the total charge distributions of all of the electrons and nuclei of the molecule. It is positive or negative in any region depending upon whether the contribution of the nuclei or that of the electrons is dominant there.

In analyzing chemical reactive behavior, $V(\mathbf{r})$ is commonly computed on the “surface” of a molecule. As proposed by Bader et al.

[6], we take this to be the 0.001 au (electrons/bohr³) contour of the electronic density $\rho(\mathbf{r})$, which encompasses more than 95% of the molecule's electronic charge. Using a contour of the electronic density to define the surface has the advantage that it reflects specific features such as lone pairs, π electrons, atomic anisotropy and strained bonds. The 0.001 au contour is usually 0.2–0.5 Å beyond the van der Waals radii of the atoms that comprise the molecule [7], so that $V(\mathbf{r})$ computed on this surface – which is labeled $V_S(\mathbf{r})$ – is relevant to the beginnings of noncovalent interactions. The locally most positive and most negative values of $V_S(\mathbf{r})$, of which there may be several, are designated by $V_{S,\max}$ and $V_{S,\min}$, respectively.

In unsaturated hydrocarbons, the electrostatic potentials in regions of high π electron density are typically negative. This can be seen in Fig. 1 for propene, acetylene and naphthalene; the $V_S(\mathbf{r})$ were computed with the density functional M06-2X/6-31+G(d,p) procedure. Many other examples can be found [8–12]. (In older papers, electrostatic potentials are usually presented in planes through or above/below the molecules.)

By means of these negative π region potentials, unsaturated hydrocarbons can interact attractively with positive sites to form noncovalent complexes. Such positive sites include cations, somewhat acidic hydrogens, positive σ -holes [13,14] on covalently-bonded atoms of Groups IV–VII (e.g., halogen bonding) and positive π holes [14,15]. In Fig. 2 complexes between (a)

* Corresponding author at: Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA. Tel.: +1 2023511554.

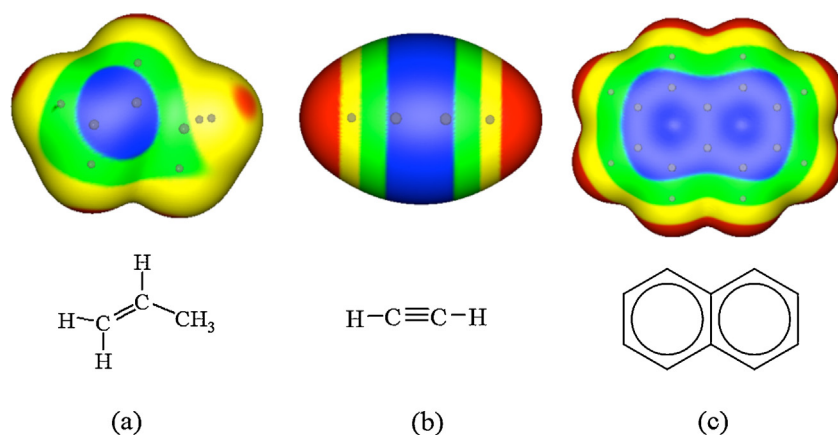


Fig. 1. Computed electrostatic potentials on the 0.001 au molecular surfaces of (a) propene, (b) acetylene, and (c) naphthalene. Color ranges, in kcal/mol, are: red, greater than 10; yellow, from 10 to 0; green, from 0 to -10; blue, more negative than -10. Gray hemispheres denote the positions of the atoms. The most negative regions (blue) are above the double and triple bonds in (a) and (b) and above the rings in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

acetylene and the hydrogen of HCN, and (b) propene and the chlorine σ -hole of Cl-CN are shown. The interaction energies ΔE were obtained with Eq. (2):

$$\Delta E = E(\text{complex}) - \sum_{i=1}^2 E(\text{component } i) \quad (2)$$

All of our calculations for this paper were at the M06-2X/6-31+G(d,p) level, using optimized geometries. In an extensive comparison of the effects of various methods and basis sets [16], this procedure has been shown to give good agreement with experimental data for C-H and N-H π complexes, without requiring a correction for basis set superposition.

Table 1 lists the computed interaction energies for noncovalent complexes between a variety of positive sites and the negative π region potentials of several unsaturated hydrocarbons [12,17–21]. The purpose of this table is simply to indicate the ranges of values; since they are from different sources, quantitative comparisons should not be made. Most of the ΔE are between -1 and -5 kcal/mol; striking exceptions are the two for the complexes

involving Mg^{++} and Ca^{++} . The highly positive electrostatic potentials of these cations result in much stronger interactions.

2. π Region electrostatic potentials and interactions of substituted unsaturated hydrocarbons

When one or more of the hydrogens of an unsaturated hydrocarbon are replaced by substituents, the negative potential associated with the π region can be expected to be affected. This can be attributed in part to the electron-withdrawing or -donating tendency of the substituent, but more generally, $V_S(\mathbf{r})$ reflects not only the electronic density at \mathbf{r} but rather the total charge distributions of the electrons and nuclei in the molecule, including those of the substituent [11,22]. Different substituents can make the π region potential of an unsaturated hydrocarbon more negative, less negative or even completely positive. For instance, comparing Fig. 3 with Fig. 1(a) shows that one NO_2 on the saturated carbon (C-3) of propene just weakens the negative π potential, whereas an NO_2 on C-1 eliminates it. In fluoroethylene, the π region has a negative potential but it is less negative than in ethylene, while in nitroethylene, it is entirely positive [23]. On the other hand,

Table 1
Computed interaction energies ΔE of noncovalent complexes involving positive sites (on atoms indicated in bold) and negative π regions of unsaturated hydrocarbons.

Complex	ΔE (kcal/mol)	Method	Reference
FH...acetylene	-3.14	MP2/6-311++G(d,p)	17
FH...ethylene	-3.36	MP2/6-311++G(d,p)	17
FH...cyclopropene	-2.86	MP2/6-311++G(d,p)	17
FH...cyclobutadiene	-3.64	MP2/6-311++G(d,p)	17
NCH...acetylene	-2.53	M06-2X/6-31+G(d,p)	Present work
NCCl...propene	-2.81	M06-2X/6-31+G(d,p)	Present work
ClOH...benzene	-3.93	MP2/6-311++G(2d,2p)	18
HOCl...benzene	-2.04	MP2/6-311++G(2d,2p)	18
IOH...benzene	-4.22	MP2/6-311++G(2d,2p)	18
HOI...benzene	-4.73	MP2/6-311++G(2d,2p)	18
Mg ⁺⁺ ...benzene	-66.87	CCSD(T)/aug-cc-pVDZ	19
Ca ⁺⁺ ...benzene	-60.10	CCSD(T)/aug-cc-pVDZ	19
HCl...benzene	-1.43	CCSD(T)/CBS1	20
HBr...benzene	-2.03	CCSD(T)/CBS1	20
FCl...benzene	-3.03	CCSD(T)/CBS1	20
FBr...benzene	-3.89	CCSD(T)/CBS1	20
NCCl...benzene	-3.35	CCSD(T)/CBS1	20
NCCl...benzene	-4.00	CCSD(T)/CBS1	20
H ₃ Cl...benzene	-2.48	CCSD(T)/CBS	21
F ₃ Cl...benzene	-3.91	CCSD(T)/CBS	21
HC≡CCl...benzene	-2.36	CCSD(T)/CBS	12
HC≡CCl...1,4-dimethylbenzene	-2.82	CCSD(T)/CBS	12
HC≡CCl...hexamethylbenzene	-3.96	CCSD(T)/CBS	12

Download English Version:

<https://daneshyari.com/en/article/430349>

Download Persian Version:

<https://daneshyari.com/article/430349>

[Daneshyari.com](https://daneshyari.com)