A Simple and Exact Interpretation of the Bond Lengths and Stacking Distances in Benzene and its Dimers in Terms of Atomic Covalent Radii

(Dedicated to organic chemist, Prof. P.R. Ayyar, I.I.Sc., on the 50th anniversary of his demise)*

Raji Heyrovska[$]

Private Research Scientist, Praha, Czech Republic. Email: rheyrovs@hotmail.com

Abstract

The structure of benzene and the stacking distances in its dimers have long been of interest for scientists. As the various rigorous approaches over the years to understand these have been complicated, the author presents here a new and simple interpretation through the additivity of atomic covalent radii in bond lengths. Considered here are the distances in π-π stacking and T-stacking dimers. The latter appears to be a hydrogen bond between a C atom of one benzene ring and the pi-system of the other.

Keywords. Benzene, pi-pi stacking, T-stacking, additivity of atomic radii, hydrogen bond.

* http://www.jh-inst.cas.cz/~rheyrovs/prayyar.htm

[$]Academy of Sciences of the Czech Republic (former)

1. Introduction

Benzene, a hydrocarbon of formula C_6H_6, was isolated nearly two centuries ago by Michael Faraday in 1825 [1] and its hexagonal structure was determined by x-ray crystallography for the

first time by Kathleen Lonsdale in 1929 [2]. A historical and general introduction to benzene and the Kekule structures can be found in [3]. The structure and bonding in benzene has puzzled many scientists, since the CC bond length (reported values around 1.38 to 1.40 Å) was found to be between that of a covalent single bond (1.54 Å as in diamond and methane [4]) and a covalent double bond (1.34 Å as in ethylene [4]). The present author suggested [5,6] a structure based on the 'additivity of atomic radii in chemical bonds' [7-9]. The latter idea could successfully explain the bond lengths in many small as well large molecules. More recently, it was shown [10] *for the first time* that the 'additivity of atomic radii' can explain the stacking distances graphite. This idea has been extended here to benzene dimers. For an introduction to these dimers, see [11] and for previous work by others, see e.g., [12-14].

2. Present work

2.1. Benzene: The structure of benzene from [5,6] is shown in Figure 1a. It is a planar hexagon with alternate carbon atoms with covalent double bond radii, $R_{d.b.} = d(CC)_{d.b.}/2 = 1.34/2 = 0.67$ Å and resonance bond (as in graphene) radii, $R_{res} = d(CC)_{res.}/2 = 1.42/2 = 0.71$ Å, where $d(CC)_{d.b}$ and $d(CC)_{res.}$ are the respective bond lengths. This makes the sides of the hexagon, $d(CC) = R_{d.b.} + R_{res} = 1.38$ Å. The cavity in the center is of cross section of a circle (marked as dotted circle) of radius, $R_{d.b.}$ (as if a carbon atom of covalent double bond radius has been displaced). This benzene π-cavity attracts other atoms, molecules or ions (like a 'black hole'). A rectangular slab of space occupied by benzene has the dimensions as shown in Figure 1a, with a thickness equal to the diameter, $2R_{res} = D_{Cres} = 1.42$ Å of a carbon atom, C_{res}.

2.2. Benzene dimers: Amongst the dimers of benzene [11], two examples are chosen here: the sandwich π-π stacking (Figure 2, left), where the two benzene planes are parallel to each other and are held by π-π interactions, and the T-shaped stacking (Figure 2, center), where the vertex of one benzene ring is perpendicular to the other benzene ring. The center to center distance in the sandwich dimer is [12] 3.92 Å and that in T-shaped dimer is [12,13] between 4.8 - 5.0 Å. These distances are marked in Figure 1 b) and c).

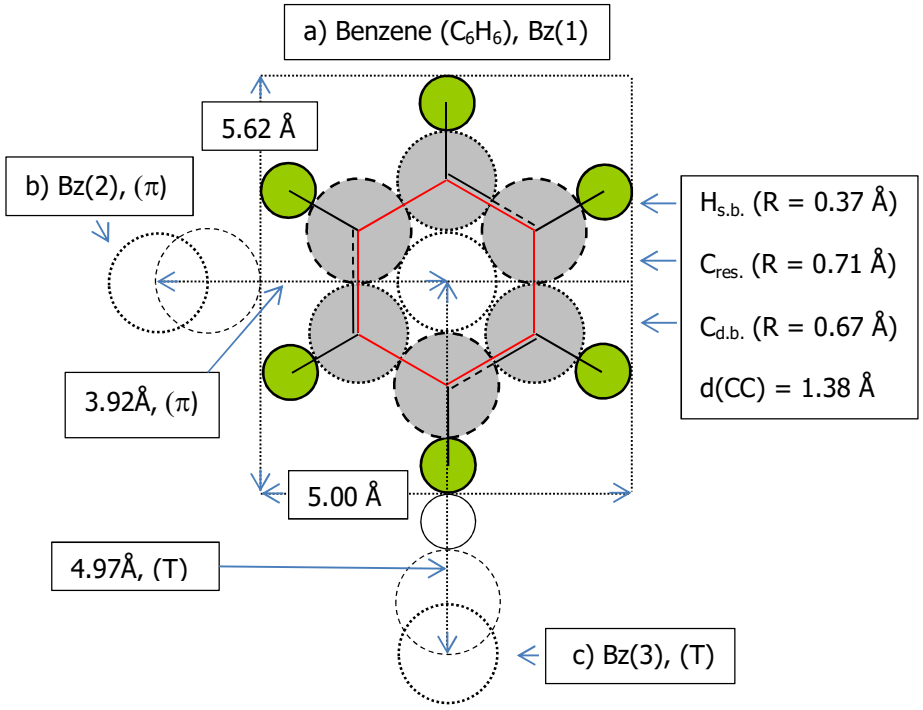

Figure 1. **a)** Benzene, Bz(1), with atomic radii as shown [5,6]. Two kinds of dimers are shown. In **b)** benzene, Bz(2) is bound to Bz(1) by π-π stacking as shown in Fig. 2, with center to center distance of 3.92 Å. **In c)** benzene, Bz(3) is bound to Bz(1) by T-stacking as shown in Fig. 2, with a center to center distance of 4.97Å. In Figs. b) and c) above, only the central cavities of the benzene π-rings are shown and they are out of plane of Bz(1).

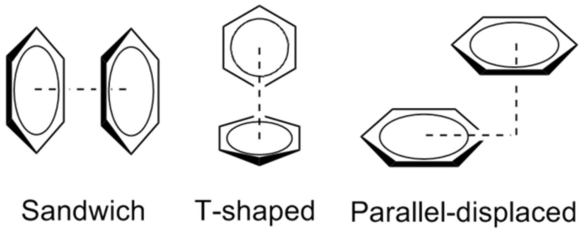

Figure 2. Three possible dimers of benzene, from [11].

2.3. Sandwich dimer: This is shown in Figure 1b, where the two benzene rings, Bz(1) and Bz(2) are separated by π-π interactions with a center to center inter-planar distance, $D_{\pi,\pi}$ = 3.92 Å [9]. It can be seen from the Figure that the distance that separates the two benzene rings is given by,

$$D_{\pi\text{-}\pi} = 2.5 + 1.42 = 3.92 \text{ Å} \quad (1)$$

where 2.5 = 5/2 Å = half the width of the benzene hexagon (which is the span of the Bz(1) molecule about its vertical axis) and 1.42 Å = $2R_{res} = D_{Cres}$, the diameter of one carbon atom, C_{res} and is the thickness of a benzene molecule.

2.4. T- stacking dimer: This is shown in Figure 1c), where Bz(1) and Bz(3) are separated by a center to center distance of $D_{T,\pi}$ = 4.96 Å. From Figure 1c), it follows that this distance is given by the sum,

$$D_{T,\pi} = 2.81 + 2^* 1.08 = 4.97 \text{ Å} \quad (2)$$

where 2.81 = 5.62/2 Å is half the height of the benzene molecule Bz(1) and 2*1.08 = d($C_{res}H$) = 2.16 Å. This seems to imply that Bz(1) and Bz(2) approach each other vertically at the distance of d($C_{res}H$) from each other, but then the H atom of Bz(1) bonds with the π system of Bz(2) ring by hydrogen bonding, which makes Bz(2) turn horizontal. This is different from the other hydrogen bonds discussed in [14].

Conclusion: This article brings *for the first time* a new, simple and precise explanation of the bond lengths and stacking distances in bezene and its dimers in term of atomic covalent radii.

References

1. http://www.rigb.org/our-history/iconic-objects/iconic-objects-list/faraday-benzene

2. Lonsdale, K. The structure of the Benzene ring in hexamethybenzene. *Proc. Roy. Soc*., **123A:** 494, 1929.

3. https://en.wikipedia.org/wiki/Benzene

4. Pauling, L.

5. Heyrovska, R. Atomic Structures of Graphene, Benzene and Methane with Bond Lengths as Sums of the Single, Double and Resonance Bond Radii of carbon. http://arxiv.org/ftp/arxiv/papers/0804/0804.4086.pdf

6. Heyrovska, R. Atomic Structure of Benzene Which Accounts for Resonance Energy http://arxiv.org/ftp/arxiv/papers/0806/0806.4502.pdf

7. Heyrovska, R. The Golden Ratio, Ionic and Atomic Radii and Bond Lengths *Special Issue of Molecular Physics*, 103 (2005) 877 – 882.

8. Heyrovska, R. and Narayan, S. Atomic Structures of Molecules Based on Additivity of Atomic and/or Ionic Radii. a) *AIP Conference Proceedings* 1119 (2009) 216, b) *Nature Precedings* http://precedings.nature.com/documents/3292/version/1 (2009).

9. Heyrovska, R. Bond Lengths as Exact Sums of the Radii of Adjacent Atoms and or Ions in the Structures of Molecules (Lead Lecture). 13th Eurasia Conference on Chemical Sciences, 14-18 December, 2014, I.I.Sc., Bangalore, India. Abstract number 165. http://eurasia13.org/abstract-file/abstract/CTC/IL/1.pdf

10. Heyrovska, R. The Coulombic Nature of the van der Waals Bond Connecting Conducting Graphene Layers in Graphite. http://www.vixra.org/abs/1601.0273 *Graphene*, **5**, 35-38. http://dx.doi.org/10.4236/graphene.2016.52004

11. https://en.wikipedia.org/wiki/Stacking_(chemistry)

12. Bloom, J. W. G., Wheeler, S. E. Taking the Aromaticity out of Aromatic Interactions. *Angew. Chem. Int. Ed*. 2011, 50, 7847 –7849.

13. DiStasio Jr., R.A., von Helden, G., Steele, R. P., Head-Gordon, M. On the T-shaped structures of the benzene dimer. *Chem. Phys. Lett*., 437 (2007) 277–283

14. Heyrovska, R. Dependence of the length of the hydrogen bond on the covalent and cationic radii of hydrogen, and additivity of bonding distances. *Chem. Phys. Lett*. 432 (2006) 348 - 351.