# Use of Becke3LYP in the Determination of the Structure of o-Benzyne.

Group 5: "O-Methylation"
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Introduction

The general goal of the following paper, Jiao, H.; Ragué Schleyer, P.; Beno, B.; Houk, K. N.; Warmuth, R. *Angew. Chem. Int. Ed. Eng.* **1996**, *36*, 2761, was the elucidation of the structure of the highly reactive intermediate, o-benzyne. The structures, **1a**, **1b** and **1c**, below, were considered:
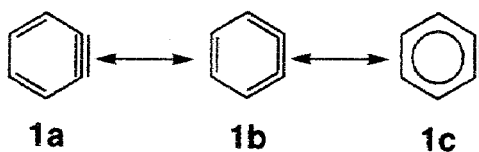
In this study, density functional theory (DFT) using the Becke3LYP and BLYP functionals, and several basis sets with the Gaussian 94 program, were used to optimize the C-C bond lengths of benzyne. The results of the Becke3LYP studies were closest to experimental determinations, and therefore this method was used for further investigation into its structure. The optimized bond lengths for o-benzyne can be seen in Table 1. The structures of 8 related compounds were optimized (Fig. 1.) for comparison of bond lengths and Wiberg bond indices (WBI) to that of benzyne. Analysis of the WBI suggested that the structure of benzyne is most like that of structure **1a**. The experimental and computed NMR shifts were compared, with good correlation (with the exception of C1 and C2.) (Table 2.)

To determine whether the in-plane   -bond affects the aromaticity of o-benzyne, calculations of the criteria of aromaticity, such as Aromatic Stabilization Energy (ASE), magnetic susceptibility ( ), magnetic susceptibility exaltation ( ) and nucleus-independent chemical shifts (NICS) (a simple and efficient means of assessing aromaticity), were carried out. The ASE was calculated using homodesmotic reactions (*e.g.* equations 1 and 2). The ASE,   ,   and NICS are listed in Tables 4 and 5.

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Equation 1   7- butadiene=1

Equation 2   6+8=9+1

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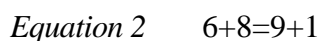
The authors concluded that o-benzyne is aromatic, although the in-plane -bond does induce a small degree of localization, and that o-benzynes large angle strain is responsible for its high reactivity (by comparison of the energies of **7** and **7'**, Fig. 1.)

The computational data section

Table 1. Optimized bond lengths [Å] for **1** at various computational levels.

Level	C1−C2	C2−C3	C3−C4	C4−C5
Becke3LYP/6-31G*	1.251	1.385	1.412	1.408
Becke3LYP/6-311 + G*	1.245	1.383	1.410	1.405
Becke3LYP/6-311G**	1.244	1.382	1.410	1.405
Becke3LYP/6-311 + G**	1.245	1.382	1.410	1.405
BLYP/D95** [12]	1.270	1.401	1.431	1.421
BLYP/6-31G*	1.264	1.394	1.424	1.415
BLYP/6-311 + G**	1.257	1.392	1.422	1.413
CASSCF(8,8)/DZ [8c]	1.274	1.412	1.406	1.432
CASSCF(8,8)/DZP [8a]	1.262	1.406	1.397	1.426
CASSCF(8,8)/cc-pVDZ [8b]	1.262	1.404	1.396	1.424
CASSCF(8,8)/(5s4p2d/3s2p) [8a]	1.251	1.399	1.390	1.420
GVB/6-31G* [7h]	1.260	1.383	1.389	1.404
GVB/6-31G** [7o]	1.260	1.383	1.389	1.404
MP2/6-31G** [7o]	1.268	1.389	1.405	1.410
MP2/DZ + P [7f]	1.275	1.398	1.413	1.417
MP2/TZ + 2P [7e]	1.259	1.385	1.404	1.406
MCSCF(2,2)/6-311G** [7n]	1.255	1.383	1.388	1.404
MCSCF(8,8)/3-21G [7n]	1.260	1.403	1.397	1.422
CCSD(T)/6-31G** [7o]	1.269	1.394	1.411	1.413
exptl [12]	1.24 ± 0.02			

1 (C_6H_4), C_{2v}

2 (C_4H_6), D_{3d}

3 (C_4H_4), D_{2h}

4 (C_6H_8), C_2

5 (C_6H_6), C_2

6 (C_8H_8), C_2

7 ($C_{10}H_{10}$), C_{2h}

7' ($C_{10}H_{10}$), C_{2h}

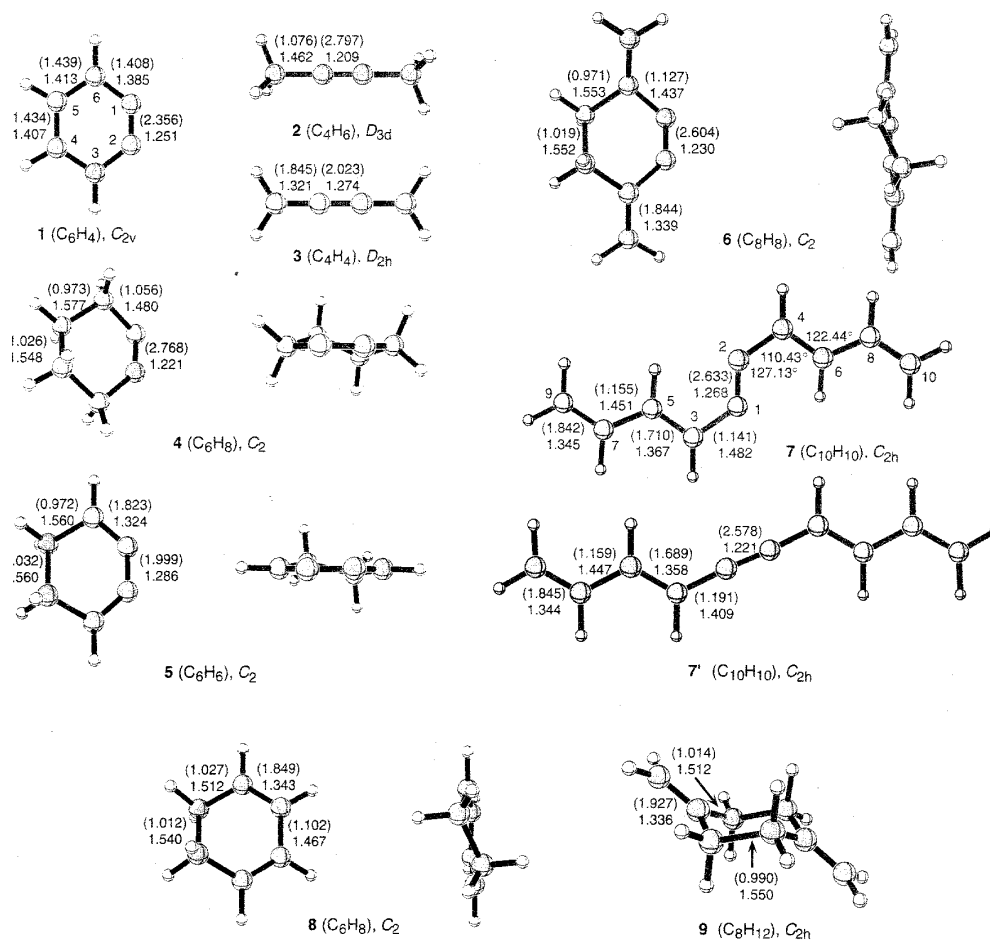**8** (C_6H_8), C_2

9 (C_8H_{12}), C_{2h}

Fig1. Bond lengths and corresponding Wiberg bond indices (in Parentheses) for 1-9 optimized at the Becke3LYP/6-31G* level (7 is partially optimized with bond angles fixed as in 1)

Table 2. ^{1}H and ^{13}C NMR chemical shifts calculated at the SOS-DFPT-PW91/III level and determined experimentally: the differences $\delta_{calcd} - \delta_{exptl} = \Delta\delta$ are given in parentheses.

Nucleus	δ_{exptl} [9]	δ_{calcd} [a] ·	δ_{calcd} [b]	δ_{calcd} [c]
H(C3.C6)	7.6	7.9 (0.3)	7.8 (0.2)	7.9 (0.3)
H(C4.C5)	7.0	7.1 (0.1)	7.0 (0.1)	7.2 (0.2)
C1.C2	182.7	186.4 (3.7)	193.7 (11.0)	195.1 (12.4)
C3.C6	126.9	127.2 (0.3)	129.1 (2.2)	128.7 (1.8)
C4.C5	138.2	142.3 (4.1)	143.3 (5.1)	143.2 (5.0)

[a] With Becke3LYP/6-311 + G** geometry. [b] With CASSCF(8,8)/DZP geometry. [c] With CCSD(T)/6-31G** geometry.

Table 4. Becke3LYP/6-31G* total energies E_{tot} in Hartree. ASE values in kcal mol^{-1}, and χ and Λ values in ppm cgs (at the CSGT-Becke3LYP/6-31G*// Becke3LYP/6-31G* level) for 1 and some important comparison compounds.

	E_{tot}	ASE [a]	χ	Λ [a]
1	− 230.90996 [b]	− 18.6(1), − 18.7(2)	− 46.4	− 23.4(1)
6	309.50726			
7 [c]	− 386.87239		− 45.8	
8	233.41892			
9	− 312.04609			
trans-butadiene	− 155.99216		− 22.8	
all-trans-decapentaene	− 388.21302		− 51.7	
benzene	− 232.24870	− 17.5(3)	− 46.1	− 16.7(3)

[a] The homodesmotic Equation used for calculating the value is given in parentheses. [b] The Becke3LYP/6-311 + G* total energies for the singlet and triplet states of 1 are − 230.96566 and − 230.91499, respectively. [c] The total energy for fully optimized 7' is − 386.95777.

Table 5. The calculated NICS values for **1** and **6** as well as their difference (ΔNICS(1 – 6)) compared with those for benzene at the GIAO-SCF/6-31 + G*// Becke3LYP/6-31G* level.

$R[\text{Å}]$ [a]	NICS(1)	NICS(6) [b]	NICS(1) – NICS(6)	NICS(benzene)
0.0	– 20.8	– 9.5	– 11.3	– 9.7
0.5	– 19.1	– 7.7	– 11.4	– 11.5
1.0	– 14.3	– 4.5	– 9.8	– 11.5
1.5	– 9.1	– 2.1	– 7.0	– 8.4
2.0	– 5.4	– 0.9	– 4.5	– 5.3
2.5	– 3.3	– 0.4	– 2.9	– 3.4
3.0	– 2.1	– 0.2	– 1.9	– 2.2

[a] Distance from the geometrical center and perpendicular to the ring plane.
[b] Computed at the same distance (1.133 Å) as in **1** between the molecule center and the midpoint of the triple bond.

1. Which experimental studies provide information about the structure of o-benzyne? (ICR)

2. What are Wiberg Bond Indices? (SCL)

3. Explain the purpose of calculating bond lengths and Wiberg bond indices for compounds other than benzyne, and list the most important of these in the structural determination of benzyne. (SCL)

4. Using Becke3LYP/6 calculations the paper concludes that **1a** is the best structure. Do the tabulated bond lengths support this? Discuss. (RQD)

5. Do the conclusions drawn support experimental data, particularly in terms of the reactivity of benzyne? (EVL)

Group Dynamics

Emma's thoughts: I have found working in a group very helpful for several reasons. Sharing ideas with others aids in thier understanding substantially, both the act of communicating the idea and listening to someone elses thoughts on the same thing. Sharing the workload with someone else is also a benefit. I have enjoyed getting to know Hongbin better, and working in the same lab has made the experience very convenient.

Hongbin's thoughts: In the process of doing Project #1 we had three group meetings and group dynamics. Our first meeting was choosing the topic. We read four interesting papers from 10 important journals and finally we chosen the topic that we share interest. This meeting was about one hour. After the selection of the paper we decided that both of us read the paper carefully and then each of us raise four questions from different types. We decided the five questions on our second meeting. We not only gave out the questions but also came out with the answers. It took us one hour. On Feb. 15 we had our third meeting. We discussed the every part of the write-ups and finished writing and scanning in three hours. As Emma said it is very helpful to work in a group. I love this game.