

A Comparative Study of Bond Order and Bond Length Calculations of Some Conjugated Hydrocarbons using Two Different Methods

Manal O. Hamzah

Department of chemistry, college of science of women, University of Baghdad, Jadriah, Baghdad, Iraq

Abstract: In the present work, bond lengths and bond orders of a selected set of benzenoid molecules were calculated. The calculations of bond orders were carried out using two different approaches, Pauling and Coulson. The two versions of Pauling equation of bond length that predicted in 1945 and 1960 were used to calculate the bond lengths. A new set of parameters called R_{new} was used for calculating the bond lengths. The ratio of force constant F in Pauling equation of bond length of the set of molecules was also calculated. At each value of F (0.05, 0.10, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 10.00, and 0.001), 101 values of Pauling bond orders PBOs and relative bond lengths R were calculated. to determine the best value of F . Then the results were compared.

Keywords: bond order, bond length, benzenoid, Pauling, Coulson, Kekuléan.

1. INTRODUCTION

One of the most significant discussions in chemistry is the bond length and bond order calculations. During the 1930s, many attempts by Pauling [1], Lennard Jones [2], Penney [3], Coulson [4] and others were carried out to define the bond order. The first attempt to define the bond order was introduced by Pauling, Brockway and Beach [1] in 1935. It was based on valence bond theory (VBT) [4]. Pauling bond order (PBO) is now the name associated with this definition. Their assumption was that a molecule in the ground state has a wave function represented by a series of canonical structures [4] or Kekulé structures (K). It was also assumed that in a benzenoid the contribution of each of these structures to the π -electron system of carbon-carbon bonds is equal [5]. The bonds in Kekulé structures are specified either as formally double or single. Hence, suitable summation over structures enables a fractional bond order to be defined [4].

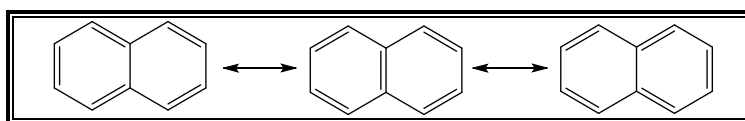


Figure 1. Kekulé structures of naphthalene

In a conjugated molecule, PBO was defined as a ratio between two numbers related to these structures [5].

$$P_{ij}^P = \frac{K_{ij}}{K} \quad (1)$$

where P_{ij}^P refers to Pauling bond order, K is the total number of Kekulé structures in a conjugated molecule, and K_{ij} is the number of Kekulé structures in which the particular chemical bond (ij) exists as a double bond. The formula (1) applies to conjugated systems containing single and double bonds. For π -conjugated systems containing single, double, and triple bonds, the PBO is given as [6]

$$P_{ij}^P = \frac{1}{K} \sum_{k=1}^{K_{ij}} n_{ij}(k) \quad (2)$$

Where

$$n_{ij}(k) = \begin{cases} 1 & \text{for a double bond} \\ 2 & \text{for a triple bond} \end{cases} \quad (3)$$

The PBOs according to formulas (1) and (2) give weights of the π bond on the chemical bond (ij), which are measures of chemical bond (ij) strength [6]. Counting the Kekulé structures of benzenoid hydrocarbons have been described in a large volume of published studies [7]. For single chain condensed aromatic molecules, Cyvin [8] derived some equations to calculate the Kekulé structures of linear chains (polyacenes such as naphthalene) and bent chains (polyphenes such as tetraphene) respectively. The counts are

$$K = Q + 1 \quad (4)$$

$$K = \left\{ \begin{array}{ll} 1 + \frac{1}{4}(Q + 1)^2 & Q = 1, 3, 5, \dots \\ 1 + \frac{1}{4}Q(Q + 2) & Q = 2, 4, 6, \dots \end{array} \right\} \quad (5)$$

Where Q is the number of benzene rings

Another approach of bond order calculations was in 1939, when Coulson derived a definition of bond order based on the molecular orbital theory (MOT) that said "the electrons are allocated to orbitals which spread over the molecule as a whole, subsequently the sharing and delocalization of the electrons are emphasized" [9]. The Coulson bond order CBO was calculated using equation (6).

$$P_{ij}^C = \sum_n g_n c_i^n c_j^n \quad (6)$$

Where g_n is the occupation number of the n th molecular orbital, c_n are the eigenvectors of the adjacency matrix M_{ij} which they defined as [10]

$$c_n = \begin{bmatrix} c_i^n \\ \cdot \\ \cdot \\ \cdot \\ c_N^n \end{bmatrix} \quad (7)$$

Where N is the number of electrons in occupied orbitals.

$$M_{ij} = \begin{cases} 1 & \text{if } i, j \text{ are neighbours} \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

Both definitions of bond order, Pauling and Coulson were used successfully to predict the bond lengths of conjugated systems. In 1930s, Pauling suggested a correlation between bond lengths and bond orders. This empirical correlation included four points with bond orders and bond lengths as ethene (1, 1.34 Å), benzene (0.5, 1.38 Å), graphite (0.75, 1.42 Å), and ethane (0, 1.54 Å). In 1948, the equation that calculating bond lengths which are corresponded to Pauling bond orders was described as [11]

$$R = R_1 - (R_1 - R_2) \frac{FP_{ij}^P}{(F - 1)P_{ij}^P + 1} \quad (9)$$

Where R_1 is the single bond distance and was equal to 1.540 Å, R_2 is the double bond distance and was equal to 1.330 Å and F is the ratio of force constant which was equal to 3. In 1960, the F value was justified to 1.84 and R_1 and R_2 equal to 1.504 and 1.334 Å, respectively. This modification has been given a bond length-bond order correlation with only slight errors from the measured points [5]. The method of Pauling was as effective as molecular orbital (MO) method to predict bond lengths of particular benzenoid hydrocarbons (naphthalene, anthracene, chrysene, quaterrylene and 1,2,8,9-dibenzacridine) [12].

Coulson described the equation of calculation of bond lengths as

$$R = s - \frac{s - d}{1 + \frac{f_s}{f_d} \left(\frac{1 - P_{ij}^C}{P_{ij}^C} \right)} \quad (10)$$

Where s and d are the lengths of pure single and double bond, f_s and f_d are the corresponding force constants [12] and are equal to 2.48×10^5 and 4.90×10^5 dynes/cm, respectively. This correlation was applied to predict the bond lengths in conjugated molecules [4].

In the present work, for a selected set of benzenoids, the calculations of bond lengths and bond orders

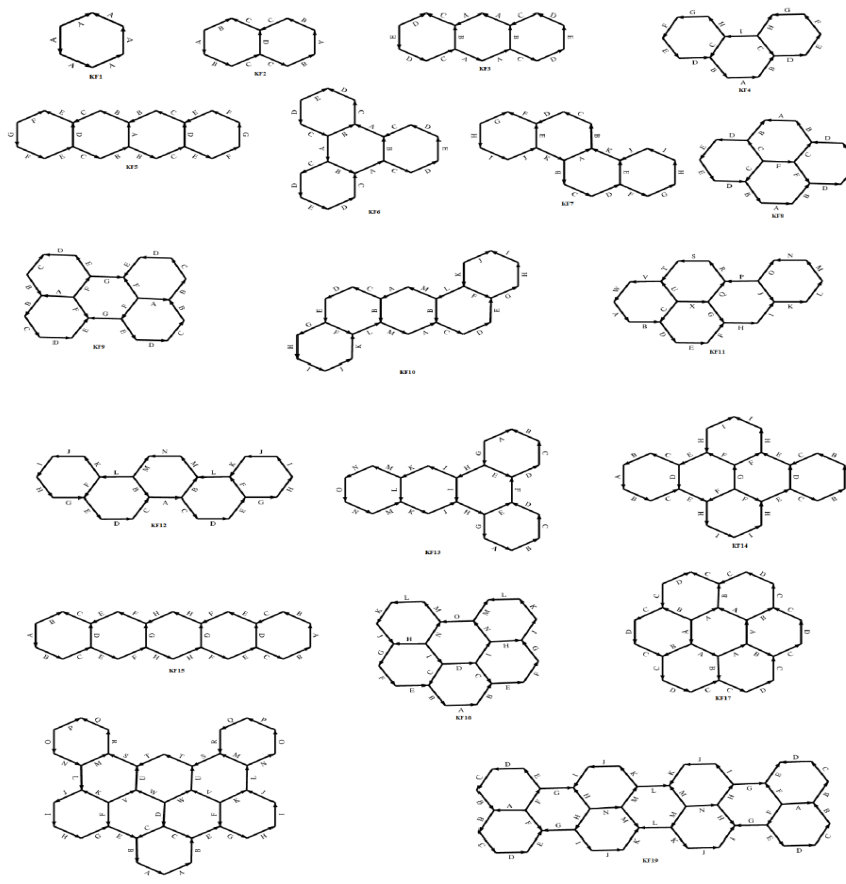
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were carried out using definitions of Pauling and Coulson bond order. This set of polycyclic aromatic hydrocarbons was selected because it considers a good source of data of electronic structure [13].

2. METHODOLOGY

The bond lengths and bond orders calculations of the set of molecules were carried out using two models. This set consists of 27 benzenoids with 309 unique bonds, Fig.2. Many programs were used to predict the bond lengths and bond orders. These programs were written using FORTRAN 77 programming language [14]. Most of these programs were written as scripts (high level language) such as doedge, that plots the molecules with the numbers of edges; doletter, that plots the edges of molecules with letter; do Draw Pauling R, that plots the edges of molecules with the predicted Pauling bond lengths and dotranslate, that plots the edges of molecules with experimental and predicted Pauling bond lengths.

- The Optimal Value of the Ratio of Force Constant F :** to determine the optimal value of F in equation (9) at different F (0.05, 0.10, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 10.00). First, the parameters F , R_1 and R_2 were chosen as 1.84, 1.54 Å and 1.33 Å. Then, at each F , 101 values of bond lengths R and Pauling bond orders PBOs were calculated. Finally, in addition to the experimental correlation of PBOs and R of Pauling bond orders-bond lengths in 1935, the predicted PBOs and R were correlated.
- The Bond Lengths Calculations:** the bond lengths of the set of molecules were predicted using the Pauling equation in 1948 with parameters as ($R_1=1.54$ Å, $R_2=1.33$ Å and $F=3$), the Pauling equation in 1960 with parameters as ($R_1=1.504$ Å, $R_2=1.334$ Å and $F=1.84$) and the Pauling equation with new parameters as ($R_1=1.54$ Å, $R_2=1.33$ Å and $F=1.84$). These equations are called as R_{1948} , R_{1960} and R_{new} , respectively. Finally, theoretical bond lengths R_{theo} , of molecules were calculated using Gaussian 09.
- The Bond Order Calculations:** Pauling bond orders PBOs were predicted using eq. (1). The Coulson bond orders CBOs of the set of benzenoids were calculated using equation (6) and those orders of non Kekuléan conjugated hydrocarbons were calculate using the simple Hückel molecular orbital SHMO program. The Microsoft office excel was used to correlate the results and to explore the connections between bond lengths and bond orders.



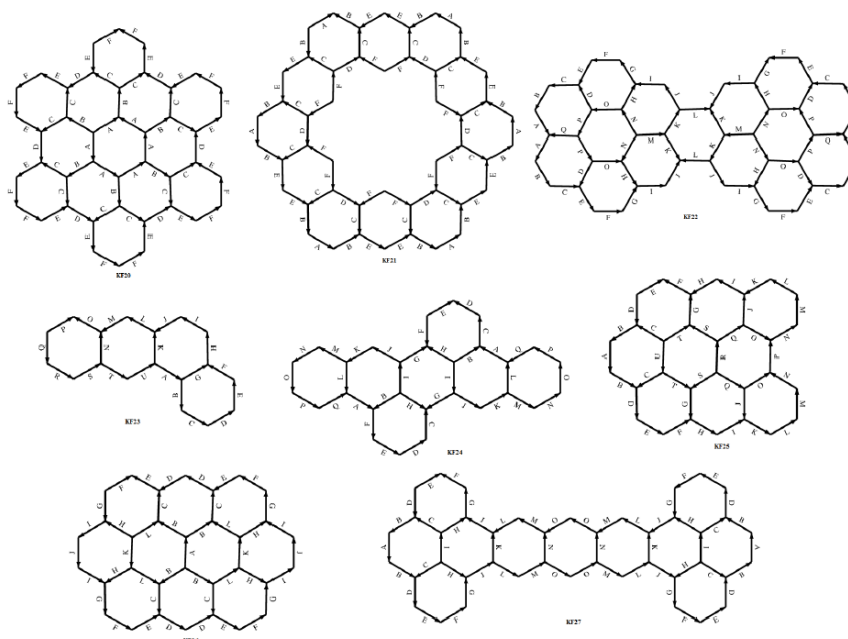


Figure2. The geometric molecular structures of the set of benzenoids

3. RESULTS

- a) The Optimal Force Constant F :** At each value of F (0.05, 0.10, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 10.00, and 0.001), 101 values of Pauling bond orders PBOs and relative bond lengths R were calculated. The calculated PBOs and R were correlated. The correlations have shown that the deviation from the experimental correlation (ethylene, benzene, graphite, and ethane) was too big at F equal to 0.001 and it was too small at F equal to 10.00, but it was identical to experimental correlation when F is equal to 2.5 Fig. 3. This result indicates that the new F of 101 calculated PBOs and R was intermediate between 3 and 1.84, the F of Pauling equation in 1948 and 1960, respectively

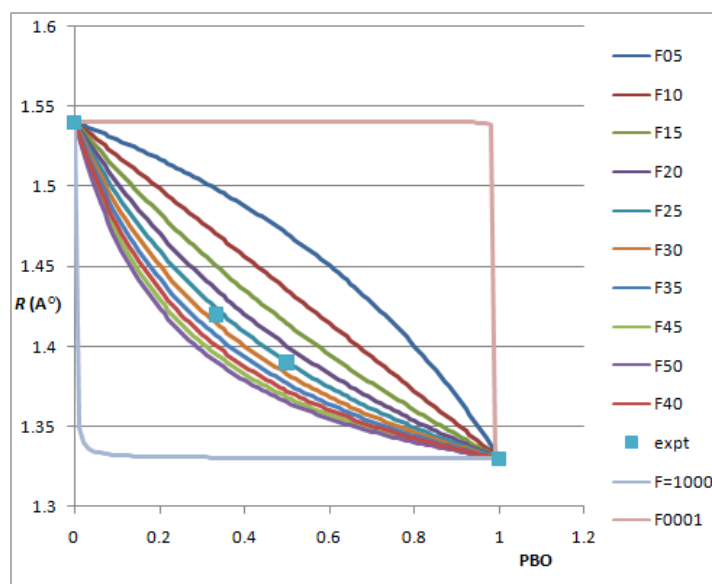


Figure3. The correlation between predicted Pauling bond orders PBO and bond lengths R at different force constant F

- b) The Calculations of Bond Lengths:** the bond lengths of the set of molecules were calculated using Pauling equation in 1948, 1960 and *new*. The calculated lengths are listed in table (1). This table included the set of molecules with their symbols. These symbols refer to the first authors names of the journal article that provided the data of symmetry and measured bond lengths of the unique bonds (unshifted with symmetry operations). In addition it shows the predicted Pauling and Coulson bond orders.

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Many correlations were drawn. Figure4 showed the correlation between R_{1948} and R_{1960} . As shown, the correlation was linearly increased (R^2 equal to 0.9824). This value of R^2 indicated that the two equations in 1948 and 1960 were good to predict R for the set of benzenoids.

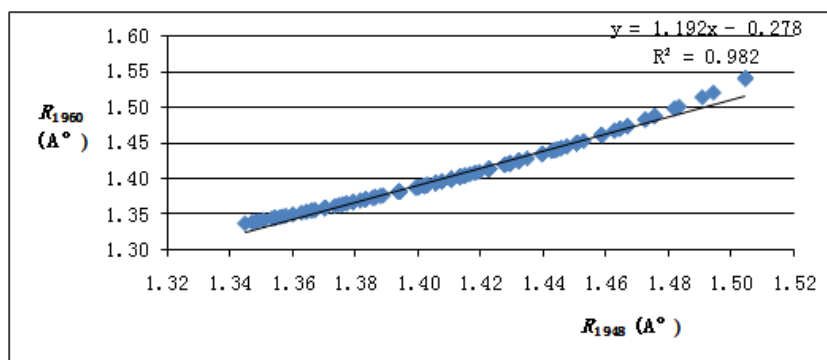


Figure4. The correlation between predicted lengths in 1948 and predicted lengths in 1960

Then, the predicted bond lengths (R_{1948} , R_{1960} and R_{new}) were correlated with experimental R_{exp} to investigate the closeness between predicted and experimental values. As shown in Fig. 5, these correlations were linear (R^2 equal to 0.7477) in 1948 and (equal to 0.7783) in 1960 and R_{new} . These values of R^2 indicated that the R_{1960} and R_{new} were identical and slightly closer to R_{exp} than R_{1948} . Thus, it could conclude that the Pauling equation with the sets of parameters in 1960 and new are more efficient than that equation with the set in 1948.

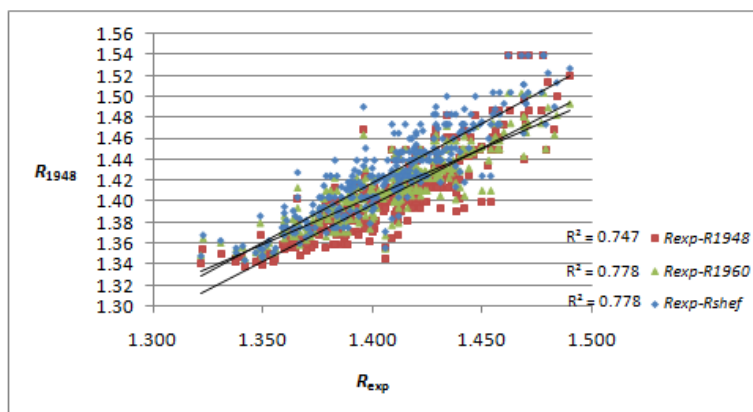


Figure5. The correlation between experimental and predicted bond lengths calculated using Pauling equations in 1948

c) **The Calculations of Bond Order:** The predicted Pauling bond orders PBOs were listed in table 1. Then they correlated with the predicted bond lengths R_{1948} , R_{1960} , R_{new} and R_{exp} , Fig. 6. The figure revealed that for the set of benzenoids, the correlation between bond lengths and bond orders was decreasing and bent. This result confirmed the reverse correlation between bond orders and bond lengths.

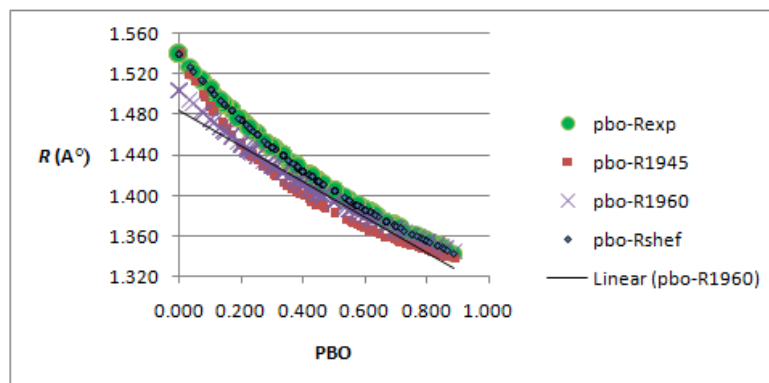


Figure6. The correlation between Pauling bond orders PBO and corresponding bond lengths R (R_{exp} , R_{1948} , R_{1960} and R_{new})

The Coulson bond orders of some non Kekulé conjugated hydrocarbons that calculated using SHMO program were drawn in Fig. 7. As shown, the values of them were zero and negative values.

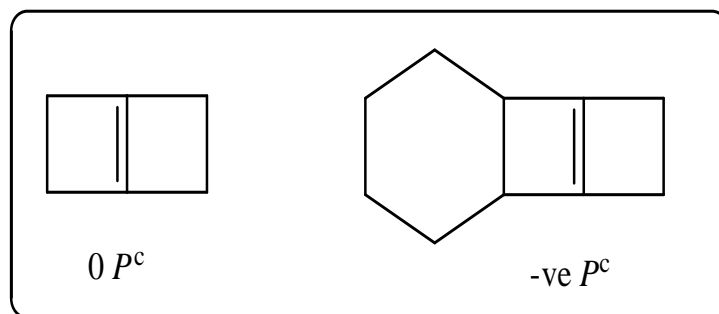


Figure7. The Coulson bond orders of two of non Kekulé conjugated hydrocarbons

The Coulson bond orders CBOs of the set of benzenoids were calculated using the eq. (6). The results were listed in table (1). PBOs and CBOs were correlated with R_{exp} . The figures showed decreased linear correlations. The correlation of PBOs with R_{exp} has R^2 equal to 0.7812 whereas the correlation of CBOs with R_{exp} has R^2 equal to 0.7989. It seems that the later correlation is closer to experiment. These figures also showed that the PBOs are zero for single bonds of bridged ring in perylene KF9, quaterlyene KF19 and dibenzoperylene KF24. But for the same bonds, the CBOs were higher than zero. This result could be due to the nature of calculations of definition of Pauling and Coulson bond order because the former definition depends on the existence of Kekulé structure whereas the later definition depends on the sum of coefficients of the atoms of each bond.

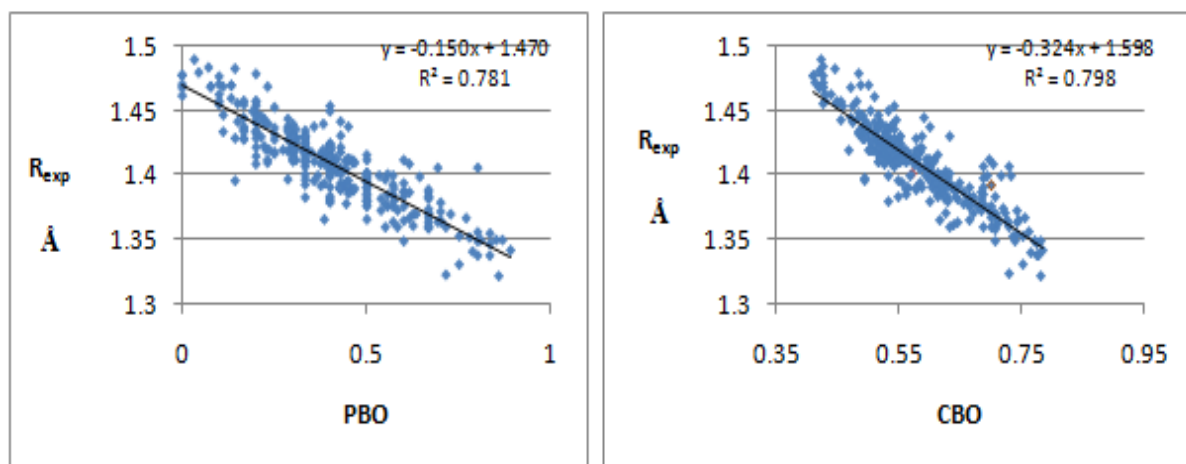


Figure8. (The left side) the correlation between Pauling bond order PBO and experimental bond lengths R_{exp} and (the right side) the correlation between Coulson bond orders CBO and experimental bond lengths R_{exp} .

As shown in Fig. 9, for each molecule, the individual correlations between Pauling bond order and experimental bond lengths (PBO- R_{exp}), Coulson bond order and experimental bond lengths (CBO- R_{exp}), Pauling bond order and theoretical bond lengths (PBO- R_{theo}) and Coulson bond order and theoretical bond lengths (CBO- R_{theo}) are carried out to investigate the differentiation of both types of bond order, Pauling and Coulson. These correlations showed that, for the same molecule KF4 there were two bonds with the same PBO and CBO but different values of R_{exp} . Unlike, for the same molecule KF5 there were two bonds with the same R_{exp} and different PBO but these bonds were with different CBO and different R_{exp} . Kiralj et al. [13] assigned this degeneration in experimental data to the structural variations in the chemical bond, packing forces, unknown experimental errors and other effects. The correlation between PBO and R_{theo} of naphthalene KF2 showed there are two types of bond but the correlation between CBO and R_{theo} of the molecule showed four types of bonds. The same outcome can be noticed in table (1). These results indicate that CBO was more differentiated than PBO. This could be explained as previously according to the nature of Pauling and Coulson definition of bond order. The individual correlations between (CBO and R_{exp}) and (R_{theo} and R_{exp}) give the same number of bonds. This result indicates the similarity between Coulson and *ab initio* definition of bond order. This similarity could be due to the Coulson density matrix which is used in *ab initio* calculations of bond order.

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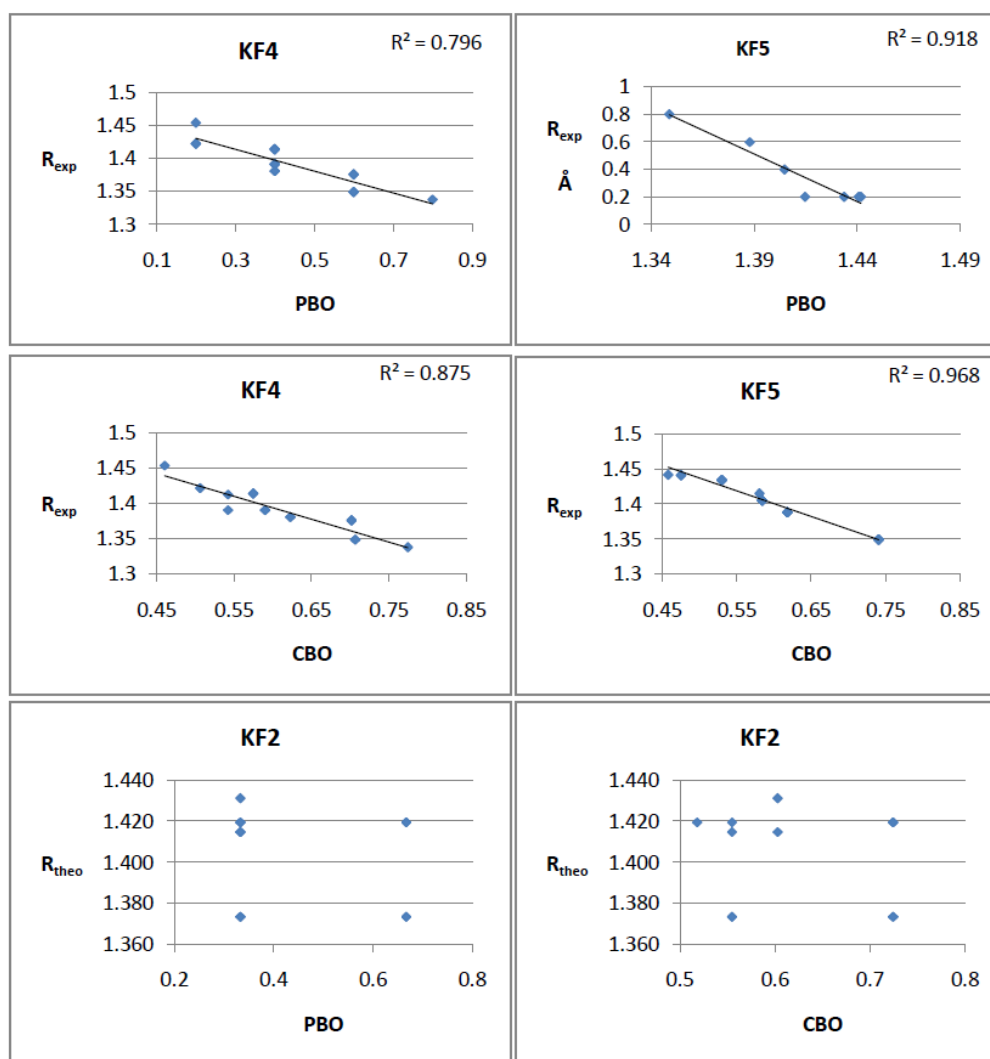


Figure9. The individual correlations between Pauling bond orders (1^{st} row) and experimental bond lengths, Coulson and experimental bond lengths (2^{nd} row) and Pauling and Coulson bond orders with theoretical bond lengths calculated by using Gaussian 09, DFT, B3LYP (3^{rd} row)

Table1. The Predicted Pauling bond orders pbo , their relative bond lengths R_{new} , R_{1945} , R_{1960} and Coulson bond orders cbo , of the unique bonds of the set of molecules with their symbolic and symmetries.

Seq	Mol	Name of molecule	Sym	Uniq-uebond	$R_{exp}/\text{\AA}[15]$	Present work				
						R_{new}	R_{1945}	R_{1960}	CBO	PBO
1	KF1	benzene	D_{6h}	A	1.390	1.403	1.382	1.393	0.667	0.500
2	KF2	naphthalene	D_{2h}	C	1.422	1.439	1.414	1.422	0.555	0.333
3				B	1.371	1.375	1.359	1.370	0.725	0.667
4				A	1.407	1.439	1.414	1.422	0.603	0.333
5				D	1.420	1.439	1.414	1.422	0.518	0.333
6	KF3	anthracene	D_{2h}	C	1.428	1.460	1.435	1.439	0.535	0.250
7				A	1.395	1.404	1.382	1.393	0.606	0.500
8				D	1.353	1.362	1.351	1.360	0.737	0.750
9				E	1.418	1.460	1.435	1.439	0.586	0.250
10				B	1.432	1.460	1.435	1.439	0.485	0.250
11	KF4	phenanthrene	C_{2v}	G	1.376	1.386	1.368	1.379	0.702	0.600
12				F	1.381	1.424	1.400	1.410	0.623	0.400
13				E	1.349	1.395	1.368	1.379	0.707	0.600
14				D	1.414	1.424	1.400	1.410	0.575	0.400
15				B	1.422	1.474	1.450	1.450	0.506	0.200
16				A	1.338	1.355	1.346	1.354	0.775	0.800
17				C	1.413	1.424	1.400	1.400	0.542	0.400

18				H	1.391	1.424	1.400	1.410	0.590	0.400
19				I	1.454	1.474	1.450	1.450	0.461	0.200
20	KF5	tetracene	D _{2h}	E	1.434	1.474	1.450	1.450	0.530	0.200
21				C	1.388	1.386	1.368	1.379	0.618	0.600
22				B	1.405	1.424	1.400	1.410	0.584	0.400
23				F	1.349	1.355	1.346	1.354	0.741	0.800
24				G	1.415	1.474	1.450	1.450	0.581	0.200
25				D	1.441	1.474	1.450	1.450	0.475	0.200
26				A	1.442	1.474	1.450	1.450	0.458	0.200
27	KF6	triphenylene	D _{3h}	D	1.385	1.394	1.374	1.385	0.690	0.556
28				C	1.405	1.415	1.391	1.402	0.603	0.444
29				A	1.469	1.501	1.482	1.472	0.428	0.111
30				E	1.390	1.415	1.391	1.402	0.637	0.444
31				B	1.411	1.415	1.391	1.402	0.562	0.444
32	KF7	chrysene	C _{2h}	F	1.415	1.430	1.405	1.414	0.568	0.375
33				D	1.417	1.460	1.435	1.439	0.521	0.250
34				C	1.331	1.362	1.351	1.360	0.754	0.750
35				B	1.437	1.460	1.435	1.439	0.538	0.250
36				K	1.453	1.460	1.435	1.439	0.476	0.250
37				J	1.409	1.430	1.405	1.414	0.583	0.375
38				I	1.370	1.382	1.365	1.375	0.707	0.625
39				H	1.392	1.430	1.405	1.414	0.617	0.375
40				G	1.361	1.382	1.365	1.375	0.712	0.625
41				E	1.417	1.430	1.405	1.414	0.535	0.375
42				A	1.402	1.404	1.382	1.393	0.573	0.500
43	KF8	pyrene	D _{2h}	A	1.347	1.351	1.341	1.350	0.777	0.833
44				B	1.429	1.484	1.461	1.458	0.503	0.167
45				D	1.400	1.404	1.382	1.393	0.594	0.500
46				E	1.380	1.404	1.382	1.393	0.669	0.500
47				C	1.417	1.439	1.414	1.425	0.524	0.333
48				F	1.423	1.439	1.414	1.422	0.536	0.333
49	KF9	perylene	D _{2h}	D	1.393	1.439	1.414	1.422	0.629	0.333
50				G	1.471	1.540	1.540	1.504	0.414	0.000
51				E	1.384	1.375	1.359	1.370	0.644	0.667
52				C	1.359	1.375	1.359	1.370	0.707	0.667
53				B	1.411	1.439	1.411	1.422	0.552	0.333
54				F	1.429	1.439	1.414	1.422	0.529	0.333
55				A	1.426	1.439	1.414	1.422	0.526	0.333
56	KF10	1,2,5,6-dibenzoanthracene	C _{2h}	I	1.403	1.421	1.396	1.409	0.626	0.417
57				H	1.360	1.389	1.370	1.381	0.703	0.583
58				G	1.412	1.421	1.396	1.407	0.579	0.417
59				E	1.436	1.484	1.461	1.458	0.499	0.167
60				D	1.338	1.351	1.343	1.350	0.778	0.833
61				C	1.438	1.484	1.461	1.458	0.501	0.167
62				A	1.391	1.404	1.382	1.393	0.605	0.500
63				M	1.397	1.404	1.382	1.393	0.629	0.500
64				L	1.455	1.484	1.461	1.458	0.451	0.167
65				K	1.406	1.421	1.396	1.407	0.595	0.417
66				J	1.373	1.389	1.370	1.381	0.697	0.583
67				F	1.413	1.421	1.396	1.407	0.544	0.417
68				B	1.426	1.439	1.414	1.422	0.513	0.333
69	KF11	3,4-benzopyrene	C _s	N	1.364	1.375	1.359	1.370	0.710	0.667
70				M	1.397	1.439	1.414	1.422	0.609	0.333
71				L	1.374	1.375	1.359	1.370	0.721	0.667
72				K	1.425	1.439	1.414	1.422	0.552	0.333
73				I	1.419	1.439	1.414	1.422	0.562	0.333
74				H	1.361	1.375	1.359	1.370	0.641	0.667
75				F	1.447	1.501	1.482	1.472	0.493	0.111
76				E	1.342	1.343	1.338	1.344	0.784	0.889

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77				D	1.434	1.501	1.482	1.472	0.493	0.111
78				B	1.401	1.394	1.374	1.385	0.604	0.556
79				A	1.378	1.415	1.391	1.402	0.658	0.444
80				W	1.376	1.394	1.374	1.385	0.680	0.556
81				V	1.412	1.415	1.391	1.402	0.580	0.444
82				T	1.441	1.468	1.443	1.445	0.520	0.222
83				S	1.352	1.358	1.348	1.356	0.754	0.778
84				R	1.423	1.468	1.443	1.445	0.539	0.222
85				O	1.419	1.439	1.414	1.422	0.580	0.333
86				J	1.410	1.439	1.414	1.422	0.517	0.333
87				P	1.435	1.439	1.414	1.422	0.489	0.333
88				G	1.444	1.468	1.443	1.445	0.486	0.222
89				Q	1.395	1.415	1.391	1.402	0.556	0.444
90				C	1.414	1.439	1.414	1.422	0.522	0.333
91				U	1.418	1.439	1.414	1.422	0.524	0.333
92				X	1.419	1.439	1.414	1.422	0.538	0.333
93	KF12	picene	C _{2v}	N	1.406	1.371	1.357	1.367	0.732	0.692
94				M	1.430	1.446	1.420	1.427	0.554	0.308
95				L	1.469	1.465	1.440	1.443	0.471	0.231
96				K	1.394	1.428	1.403	1.413	0.586	0.385
97				J	1.409	1.383	1.366	1.377	0.705	0.615
98				I	1.366	1.428	1.403	1.413	0.619	0.385
99				H	1.367	1.383	1.366	1.377	0.710	0.615
100				F	1.414	1.428	1.403	1.413	0.537	0.385
101				G	1.414	1.428	1.403	1.413	0.570	0.385
102				E	1.410	1.465	1.440	1.443	0.517	0.231
103				D	1.367	1.359	1.349	1.357	0.758	0.769
104				B	1.388	1.411	1.388	1.399	0.563	0.462
105				C	1.412	1.465	1.440	1.443	0.532	0.231
106				A	1.429	1.446	1.420	1.427	0.493	0.308
107	KF13	dibenzo [a,c] anthracene	C _{2v}	B	1.389	1.411	1.388	1.399	0.640	0.462
108				C	1.373	1.397	1.376	1.388	0.686	0.538
109				D	1.412	1.411	1.388	1.399	0.607	0.462
110				F	1.469	1.512	1.498	1.481	0.420	0.077
111				A	1.382	1.397	1.376	1.388	0.686	0.538
112				E	1.410	1.411	1.388	1.399	0.564	0.462
113				G	1.410	1.411	1.388	1.399	0.607	0.462
114				H	1.469	1.512	1.498	1.481	0.420	0.077
115				J	1.387	1.383	1.366	1.377	0.658	0.615
116				K	1.409	1.428	1.403	1.413	0.575	0.385
117				M	1.426	1.446	1.420	1.427	0.549	0.308
118				N	1.364	1.371	1.357	1.367	0.727	0.692
119				O	1.412	1.446	1.420	1.427	0.598	0.308
120				L	1.420	1.446	1.420	1.427	0.502	0.308
121				I	1.436	1.446	1.420	1.427	0.513	0.308
122	KF14	dibenzo [fg,op] tetracene	D _{2h}	I	1.383	1.404	1.382	1.393	0.667	0.500
123				H	1.416	1.404	1.382	1.393	0.614	0.500
124				E	1.477	1.504	1.487	1.475	0.428	0.100
125				C	1.438	1.414	1.390	1.401	0.603	0.450
126				B	1.397	1.395	1.375	1.386	0.690	0.550
127				A	1.391	1.414	1.390	1.401	0.637	0.450
128				D	1.386	1.414	1.390	1.401	0.562	0.450
129				F	1.416	1.424	1.400	1.410	0.549	0.400
130				G	1.457	1.474	1.450	1.450	0.482	0.200
131	KF15	pentacene	D _{2h}	C	1.434	1.484	1.461	1.458	0.529	0.167
132				E	1.387	1.375	1.395	1.370	0.622	0.667
133				F	1.412	1.439	1.414	1.422	0.578	0.333

134				H	1.412	1.404	1.382	1.393	0.596	0.500
135				B	1.355	1.351	1.343	1.350	0.742	0.833
136				A	1.428	1.484	1.461	1.458	0.579	0.167
137				D	1.445	1.484	1.461	1.458	0.472	0.167
138				G	1.458	1.484	1.461	1.458	0.451	0.167
139	KF16	benzo [ghi] perylene	C _{2v}	L	1.394	1.418	1.394	1.405	0.649	0.429
140				K	1.376	1.391	1.371	1.382	0.688	0.571
141				J	1.389	1.418	1.394	1.405	0.579	0.429
142				G	1.430	1.470	1.445	1.447	0.513	0.214
143				F	1.341	1.357	1.374	1.355	0.765	0.786
144				E	1.446	1.470	1.445	1.447	0.519	0.214
145				B	1.396	1.434	1.408	1.418	0.550	0.357
146				A	1.399	1.379	1.362	1.373	0.734	0.643
147				M	1.385	1.391	1.371	1.383	0.627	0.571
148				O	1.484	1.514	1.500	1.482	0.427	0.071
149				H	1.438	1.434	1.408	1.418	0.530	0.357
150				N	1.411	1.434	1.408	1.418	0.537	0.357
151				C	1.406	1.418	1.394	1.405	0.545	0.429
152				I	1.419	1.451	1.425	1.431	0.516	0.286
153				D	1.438	1.451	1.425	1.431	0.519	0.286
154	KF17	coronene	D _{6h}	C	1.414	1.447	1.421	1.429	0.538	0.300
155				D	1.372	1.370	1.356	1.366	0.745	0.700
156				B	1.420	1.424	1.400	1.410	0.538	0.400
157				A	1.424	1.447	1.421	1.429	0.522	0.300
158	KF18	benzo [fg,gi] phenanthro [9,10,1,2,3-pqrst] pentaphene	C _{2v}	Q	1.378	1.395	1.375	1.386	0.689	0.550
159				R	1.396	1.414	1.390	1.401	0.603	0.450
160				S	1.471	1.504	1.487	1.475	0.428	0.100
161				T	1.391	1.404	1.382	1.393	0.621	0.500
162				P	1.392	1.414	1.390	1.401	0.637	0.450
163				O	1.360	1.395	1.375	1.386	0.689	0.550
164				M	1.413	1.414	1.390	1.401	0.561	0.450
165				N	1.413	1.414	1.390	1.401	0.603	0.450
166				L	1.455	1.504	1.487	1.475	0.428	0.100
167				J	1.401	1.404	1.382	1.393	0.615	0.500
168				I	1.366	1.404	1.382	1.393	0.666	0.500
169				H	1.377	1.404	1.382	1.393	0.667	0.500
170				G	1.402	1.404	1.382	1.393	0.613	0.500
171				E	1.463	1.504	1.487	1.475	0.430	0.100
172				B	1.386	1.404	1.382	1.393	0.613	0.500
173				A	1.381	1.404	1.382	1.393	0.667	0.500
174				U	1.408	1.424	1.400	1.410	0.540	0.400
175				K	1.425	1.424	1.400	1.410	0.547	0.400
176				F	1.411	1.424	1.400	1.410	0.548	0.400
177				V	1.449	1.474	1.450	1.450	0.487	0.200
178				C	1.424	1.424	1.400	1.410	0.548	0.400
179				W	1.424	1.424	1.400	1.410	0.546	0.400
180				D	1.433	1.474	1.450	1.450	0.486	0.200
181	KF19	quatrylene	D _{2h}	D	1.401	1.439	1.414	1.422	0.634	0.333
182				C	1.367	1.375	1.359	1.370	0.702	0.667
183				B	1.417	1.439	1.414	1.422	0.552	0.333
184				G	1.468	1.540	1.540	1.504	0.429	0.000
185				E	1.382	1.375	1.359	1.370	0.632	0.667
186				I	1.383	1.375	1.359	1.370	0.616	0.667
187				J	1.383	1.439	1.414	1.422	0.671	0.333
188				L	1.462	1.540	1.540	1.504	0.441	0.000
189				K	1.389	1.375	1.359	1.370	0.612	0.667

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190				A	1.420	1.439	1.414	1.422	0.526	0.333
191				F	1.431	1.439	1.414	1.422	0.529	0.333
192				H	1.431	1.439	1.414	1.422	0.526	0.333
193				M	1.429	1.439	1.414	1.422	0.526	0.333
194				N	1.431	1.439	1.414	1.422	0.535	0.333
195	KF20	hexabenzocoronene [bc,ef,hi,kl,no,gr]	D _{6h}	F	1.376	1.404	1.382	1.393	0.667	0.500
196				E	1.398	1.404	1.382	1.393	0.613	0.500
197				D	1.458	1.504	1.487	1.475	0.431	0.100
198				C	1.417	1.424	1.400	1.410	0.547	0.400
199				B	1.446	1.474	1.450	1.450	0.488	0.200
200				A	1.417	1.424	1.450	1.450	0.542	0.400
201	KF21	kekulene	D _{6h}	B	1.442	1.489	1.467	1.462	0.494	0.150
202				E	1.395	1.404	1.382	1.393	0.612	0.500
203				A	1.350	1.348	1.341	1.348	0.781	0.850
204				C	1.418	1.435	1.410	1.419	0.514	0.350
205				D	1.456	1.489	1.467	1.462	0.450	0.150
206				F	1.386	1.404	1.382	1.393	0.623	0.500
207	KF22	benzo [1,2,3-bc:4,5,6-b,c]dicoronene	D _{2h}	F	1.365	1.370	1.356	1.366	0.748	0.700
208				E	1.419	1.447	1.421	1.429	0.535	0.300
209				C	1.422	1.447	1.421	1.429	0.540	0.300
210				B	1.364	1.370	1.356	1.366	0.743	0.700
211				A	1.417	1.447	1.421	1.429	0.538	0.300
212				G	1.424	1.447	1.421	1.429	0.530	0.300
213				I	1.413	1.447	1.421	1.429	0.561	0.300
214				L	1.478	1.540	1.540	1.504	0.411	0.000
215				J	1.379	1.370	1.356	1.366	0.664	0.700
216				D	1.415	1.424	1.400	1.410	0.535	0.400
217				Q	1.422	1.424	1.421	1.429	0.538	0.400
218				P	1.422	1.447	1.421	1.429	0.521	0.300
219				H	1.412	1.424	1.400	1.410	0.529	0.400
220				O	1.424	1.447	1.421	1.429	0.526	0.300
221				K	1.432	1.447	1.421	1.429	0.512	0.300
222				N	1.421	1.447	1.421	1.429	0.519	0.300
223				M	1.420	1.424	1.400	1.410	0.547	0.400
224	KF23	benz[a]anthracene	C _s	O	1.436	1.451	1.425	1.431	0.542	0.286
225				M	1.431	1.418	1.394	1.405	0.590	0.429
226				L	1.384	1.391	1.371	1.383	0.628	0.571
227				J	1.429	1.491	1.469	1.464	0.494	0.143
228				I	1.322	1.347	1.341	1.348	0.783	0.857
229				H	1.396	1.491	1.469	1.464	0.494	0.143
230				F	1.418	1.418	1.469	1.464	0.581	0.429
231				E	1.393	1.391	1.371	1.382	0.700	0.571
232				D	1.392	1.418	1.394	1.405	0.628	0.429
233				C	1.400	1.391	1.371	1.382	0.695	0.571
234				G	1.442	1.418			0.546	0.429
235				B	1.401	1.418	1.394	1.405	0.597	0.429
236				K	1.434	1.451	1.425	1.431	0.500	0.286
237				A	1.483	1.491	1.469	1.464	0.447	0.143
238				U	1.364	1.391	1.371	1.383	0.646	0.571
239				N	1.397	1.451	1.425	1.431	0.495	0.286
240				T	1.422	1.418	1.394	1.405	0.584	0.429
241				S	1.428	1.451	1.425	1.431	0.545	0.286
242				R	1.360	1.368	1.354	1.364	0.731	0.714
243				P	1.323	1.368	1.425	1.431	0.732	0.714
244				Q	1.444	1.451	1.425	1.431	0.593	0.286

245	KF24	2,3,8,9-dibenzoperylene	C _{2h}	D	1.387	1.386	1.368	1.379	0.686	0.600
246				C	1.422	1.424	1.400	1.410	0.589	0.400
247				A	1.458	1.474	1.450	1.450	0.456	0.200
248				Q	1.403	1.424	1.400	1.410	0.594	0.400
249				P	1.412	1.386	1.368	1.379	0.698	0.600
250				O	1.399	1.424	1.400	1.410	0.621	0.400
251				N	1.384	1.386	1.368	1.379	0.709	0.600
252				L	1.379	1.424	1.400	1.410	0.533	0.400
253				M	1.413	1.424	1.400	1.410	0.567	0.400
254				K	1.409	1.474	1.450	1.450	0.529	0.200
255				G	1.478	1.540	1.540	1.504	0.411	0.000
256				J	1.406	1.355	1.346	1.354	0.689	0.800
257				F	1.394	1.386	1.368	1.379	0.632	0.600
258				E	1.381	1.424	1.400	1.410	0.647	0.400
259				B	1.384	1.424	1.400	1.410	0.550	0.400
260				I	1.479	1.474	1.450	1.450	0.486	0.200
261				H	1.454	1.424	1.400	1.410	0.544	0.400
262	KF25	1,14-benzobisanthrene	C _{2v}	F	1.470	1.494	1.473	1.466	0.501	0.133
263				H	1.370	1.380	1.363	1.374	0.626	0.633
264				I	1.400	1.432	1.406	1.416	0.570	0.367
265				K	1.430	1.439	1.414	1.422	0.552	0.333
266				L	1.370	1.375	1.359	1.370	0.703	0.667
267				M	1.430	1.439	1.414	1.422	0.633	0.333
268				N	1.360	1.375	1.359	1.370	0.634	0.667
269				P	1.490	1.527	1.520	1.493	0.424	0.033
270				E	1.350	1.346	1.340	1.347	0.772	0.867
271				D	1.460	1.494	1.473	1.466	0.510	0.133
272				B	1.390	1.410	1.387	1.399	0.565	0.467
273				A	1.400	1.398	1.377	1.388	0.717	0.533
274				G	1.440	1.465	1.439	1.442	0.496	0.233
275				J	1.420	1.447	1.421	1.429	0.509	0.300
276				O	1.430	1.447	1.421	1.429	0.532	0.300
277				C	1.420	1.424	1.400	1.410	0.534	0.400
278				T	1.430	1.447	1.421	1.429	0.527	0.300
279				U	1.440	1.447	1.421	1.429	0.522	0.300
280				S	1.410	1.410	1.387	1.399	0.551	0.467
281				Q	1.400	1.424	1.400	1.410	0.535	0.400
282				R	1.470	1.494	1.473	1.466	0.489	0.133
283	KF26	ovalene	C _{2v}	E	1.441	1.474	1.450	1.450	0.511	0.200
284				D	1.400	1.404	1.382	1.393	0.604	0.500
285				F	1.356	1.355	1.346	1.354	0.764	0.800
286				G	1.429	1.474	1.450	1.450	0.519	0.200
287				I	1.413	1.424	1.400	1.410	0.556	0.400
288				J	1.365	1.386	1.368	1.379	0.726	0.600
289				C	1.424	1.447	1.421	1.429	0.508	0.300
290				H	1.450	1.424	1.400	1.410	0.535	0.400
291				L	1.411	1.447	1.421	1.429	0.526	0.300
292				K	1.413	1.447	1.421	1.429	0.521	0.300
293				B	1.415	1.424	1.400	1.410	0.541	0.400
294				A	1.435	1.474	1.450	1.450	0.497	0.200
295	KF27	Tetrabenzo [de,no,st,c,d] heptacene	D _{2h}	F	1.390	1.419	1.394	1.405	0.648	0.427
296				G	1.380	1.391	1.371	1.383	0.629	0.573
297				J	1.480	1.523	1.513	1.490	0.420	0.045
298				L	1.370	1.366	1.353	1.362	0.671	0.727
299				M	1.420	1.454	1.428	1.434	0.553	0.273
300				O	1.380	1.404	1.382	1.393	0.602	0.500

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301				E	1.390	1.391	1.371	1.383	0.688	0.573
302				D	1.390	1.419	1.394	1.405	0.580	0.427
303				B	1.450	1.476	1.452	1.452	0.506	0.191
304				A	1.350	1.354	1.345	1.353	0.774	0.809
305				K	1.440	1.466	1.441	1.444	0.497	0.227
306				N	1.420	1.466	1.441	1.444	0.468	0.227
307				H	1.440	1.428	1.403	1.413	0.540	0.382
308				C	1.420	1.428	1.403	1.413	0.536	0.382
309				I	1.420	1.464	1.438	1.442	0.504	0.236

4. CONCLUSIONS

It is concluded that Pauling definition was important to predict the bond orders for Kekulébenzenoids. The predicted bond orders were positive and in range between zero for single bond, one for double bonds and fractions for intermediate bonds. And the Coulson definition was crucial to predict the bond orders for benzenoids and non benzenoids where the predicted bond orders were positive and negative fractions. The comparison between both definitions showed that Coulson bond order CBO was more bonds differentiated than Pauling bond order PBO since the definition of PBO depends on counting of Kekulé structures of a benzenoid but CBO is a sum of coefficients of atoms for each bond of molecule.

Two versions of Pauling equation that predicted in 1948 and 1960 were used to calculate the bond lengths. The two equations were successful and precise to predict the bond lengths. A deviation of predicted lengths R_{1960} and R_{1948} from experiment was about (0.068) Å and (0.078) Å, respectively. The linear correlations between measured bond lengths and the calculated R in 1948 and 1960 were with R^2 equal to (0.7477) and (0.7783), respectively. The closeness between these equations was also investigated which obviously appeared through the linear correlation with R^2 equal to (0.982).

Pauling equation of bond length with new parameters, called R_{new} was tested. These parameters were (1.54 Å for single bond R_1 , 1.33 Å for double bond R_2 and 1.84 for force constant F). As shown, a deviation of predicted lengths R_{new} from experiment was about (0.094) Å. The measured bond lengths R_{exp} and the lengths that predicted using different versions of Pauling equation (R_{1948} , R_{1960} and R_{new}) were correlated. The correlation showed that the R_{new} had as the same value of R^2 (0.7783) as R_{1960} .

The best value of the ratio of force constant in Pauling equation of bond length of the set of molecules was also determined. Different values of F and 101 values of bond lengths range between (1.33-1.54) Å and 101 bond orders range between (0 and one) were used. The results have been shown that for the set of benzenoids, Pauling equation was fitting to experiment at F equal to (2.5).

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