An Improved Two-Parameter Omega Technique (ITPOT) for Molecular Orbital Calculations

Calculation of Bond Lengths from a Modified Coulson's Equation

Dora J. Barbiric, Eduardo A. Castro* y Francisco M. Fernández
INIFTA, Sección de Química Teórica, La Plata, Argentina

ABSTRACT

Bond lengths are calculated for twelve aromatic hydrocarbons by way of the ITPOT and a modified Coulson's equation. Comparisons are made with respect to other theoretical results as well as with available experimental data. The predictive capabilities of the ITPOT and the modified Coulson's equation are pointed out.

SUMARIO

Se calcularon las longitudes de enlace para doce hidrocarburos aromáticos por medio de la técnica omega biparamétrica mejorada (ITPOT) y la ecuación modificada de Coulson. Se hicieron comparaciones con otros resultados teóricos, lo mismo que con datos experimentales disponibles. Se enfatizan las capacidades predictivas de la ITPOT y la ecuación de Coulson.

INTRODUCTION

In spite of the growing existence of computational facilities which make possible to apply sophisticated calculation schemes to determine electronic molecular orbitals (MO), there is still a marked necessity for using semiempirical methods. In fact, it is not really compulsory to be mixed up with the intrincacies of a complete population analysis in order to study certain general trends about chemical reactivity in a set of closely related molecules. Nor it is essential either to perform a complete conformational analysis to estimate equilibrium bond lengths. Although a large number of semiempirical methods for MO calculations has been up to now reported, we deem that there is still room for further improvements. The present time publications of works related to the application of simple semiempirical methods to the study of the chemical phenomena as well as those associated with different lines of formal developments, support our previous statement.

Embodied in this spirit, we have recently presented a new method to calculate the pi-electronic structure of aromatic systems(1) with the purpose of studying, from a theoretical viewpoint, several physicochemical properties. The method is a modification of the procedure given by Mathur et al(2), the so called Two-Parameter Omega-Technique (TPOT), and the formulas for the Hamiltonian matrix elements are

$$H_{rr} = H^{o}_{rr} + (1 - q_r)\, wH^{o}_{rs} - \sum_{\substack{s \text{ bounded} \\ \text{to } r}} (1 - q_s)\, 2w'H^{o}_{rs} \qquad /1/$$

$$H_{rs} = H^{o}_{rs} \exp(0.55\, p_{rs} - 0.366) \qquad /2/$$

w and w' are two omega parameters with the chosen values of 1.4 and -0.6, respectively(2), H^{o}_{rr} is the reference Coulomb integral (the so called alpha integral), H^{o}_{rs} is the reference resonance Integral (the so called beta integral), q_r is the pi-electron density on the r-center, and p_{rs} is the bond order between the r- and s-centers.

Details about the numerical calculation with the TPOT(2) and our ITPOT(1) were given previously, so we remit the interested reader to the original papers.

The applications of the ITPOT performed on neutral, free radical and charged hydrocarbons species to correlate theoretical predictions with experimental data (1,3-4) yielded very good results. In certain cases, our values were better than those determined with more elaborated and sophisticated Self-Consistent-Field methods, such as PPP, CNDO/S2, MINDO and SPO.

The purpose of this communication is to continue with the quality analysis of the ITPOT. For that purpose, we have chosen the calculation of bond lengths between aromatic C-atoms by way of two theoretical formulas presented several years ago. The TPOT method is applied too for the sake of completion and we compare theoretical results with available experimental data.

BOND ORDER - BOND LENGTH FORMULAS

The pi-electron bond order p_{rs} is a measure of the pi-electron probability density in the bond region between atoms r and s (5). Naturally, we expect a relation between the bond order and the bond length R_{rs} for carbon-carbon bonds. The simplest possibility is to assume a linear relationship

$$R_{rs} = a + b\, p_{rs} \qquad /3/$$

where a and b are constants. The usual way of using /3/ is to choose some well-known molecules, where the pi-electron MO coefficients are

determined completely by symmetry, and are independent of any approximation related to whatever particular method.

Other very popular manner of applying /3/ is to perform a least squares fitting over a set of molecules the geometrical parameters of which are experimentally well determined. Although these procedures "work"(1), they are plainly empirical because the starting point is the assumption of the linear relationship /3/. The first attempt to provide a theoretical scheme for deriving a relation between R_{rs} and p_{rs} from "first principles" was given by Coulson(6), and latter, several formulas were presented (7-11).

Coulson's formula is

$$R = 1.515 - \frac{0.18}{1 + K\left\{\frac{1 - p_{rs}}{p_{rs}}\right\}} \qquad /4/$$

and it is based on the MO-LCAO theory(6). K is the quotient between the force constants for a single and double C-C bond, respectively. Although, according to its definition, the proper K value should be 0.45, it leads to absurd theoretical results. So, an empirical value of 1.05 has been widely used in practical applications. To overcome this formal difficulty, Gastmans and Gastmans(12) have derived from the perturbation theory, a modified Coulson's equation, the analytical expression of which is

$$R_{sr} = 1.574 - \frac{0.239}{1 + \frac{0.444\, p_{rs} + 0.0488\, \Pi_{rs,rs}}{0.632\, p_{rs} + 0.0999\, \Pi_{rs,rs}}\left\{\frac{1 - p_{rs}}{p_{rs}}\right\}} \qquad /5/$$

$\Pi_{rs,rs}$ is the standard bond-bond polarizability, and its definition and chemical interpretation can be found elsewhere(13). The application of /5/ to twelve aromatic compounds within the context of a SCF procedure(14) has shown to be clearly superior with respect to /4/(15).

RESULTS AND DISCUSSION

The chosen aromatic molecules are displayed in Figure 1. We applied the TPOT(2) and the ITPOT(1) for determinig the pi-electronic structure. Then, we used the elements of the density matrix p_{rs} and the orbital energies to calculate the bond lengths according to Eqs. /4/ and /5/. In Table I we give the calculated bond lengths, together with the experimental data. The comparison of results shows that, in general, there is a good agreement between predicted and experimental values. To put this comparison on more quantitative grounds, we present in Table II the values for two accuracy estimators d and s, defined as follows:

$$d = \frac{1}{n} \sum_{\text{bonds}}^{n} \left| R_{rs}^{theor} - R_{rs}^{exp} \right| \qquad /6/$$

$$s = nd^2 - n^2 \left[\sum_{\text{bonds}}^{n} \left[R_{rs}^{theor} - R_{rs}^{exp} \right] \right]^2 \qquad /7/$$

n is the number of molecules considered. We see that/5/ within the context of the ITPOT yields the best results. To complement the goodness analysis of the results, we show in Table III a distribution of bonds within certain intervals. Again, we note a satisfactory concordance among the different results, although/5/ produces better results than/4/. This is not the usual case, because within the context of the Huckel MO theory, Coulson's formula/4/ presents a sharp maximum around the interval 1.410-1.420 A(15). Another interesting enough aspect of the comparison is that the larger deviations take place for the larger bond lengths. On the contrary, for intermediate and shorter bond lengths, the error is less. This general behavior, previously noted by Gastemans and Gastemans(15), is clearly shown in Table IV, where again we verify that the modified Coulson's formula gives better values.

In conclusion, the precedent results allow us to confirm the necessity of applying the modified Coulson's equation in order to determine reliable bond lengths in aromatic molecules. Moreover, the ITPOT shows again its excellent capability of producing trustworthy predictions. In order to judge properly this particular test of quality, we deem suitable to insist on the extreme simplicity of computational implementation to perform the calculations with the ITPOT(1), as well as the limited requirements of memory and time in the computer.

TABLE I

CALCULATED AND EXPERIMENTAL BOND LENGTHS (In A)

		Eq. |4|		Eq. |5|		|Exper/tal|
Molecule	Bond	TPOT	ITPOT	TPOT	ITPOT	(*)
Butadiene	a	1.343	1.346	1.342	1.346	1.337
	b	1.466	1.456	1.485	1.477	1.479
Naphtalene	a	1.376	1.381	1.373	1.380	1.367
	b	1.422	1.416	1.424	1.421	1.413
	c	1.425	1.421	1.429	1.429	1.421
	d	1.411	1.418	1.411	1.425	1.419

TABLE I: Continuación.

Molecule	Bond	TPOT	ITPOT	TPOT	ITPOT	(*)
Biphenylene	a	1.408	1.407	1.408	1.411	1.423
	b	1.388	1.390	1.386	1.390	1.385
	c	1.388	1.390	1.386	1.391	1.372
	d	1.413	1.414	1.414	1.420	1.426
	e	1.485	1.478	1.513	1.516	1.514
Anthracene	a	1.368	1.376	1.366	1.375	1.368
	b	1.432	1.422	1.437	1.431	1.419
	c	1.436	1.428	1.442	1.438	1.436
	d	1.424	1.427	1.427	1.436	1.428
	e	1.403	1.405	1.403	1.408	1.399
Biphenyl	a	1.402	1.404	1.401	1.407	1.397
	b	1.395	1.395	1.394	1.396	1.397
	c	1.398	1.398	1.396	1.401	1.397
	d	1.467	1.459	1.484	1.484	1.507
Pyrene	a	1.397	1.397	1.396	1.398	1.380
	b	1.405	1.407	1.404	1.411	1.420
	c	1.445	1.436	1.453	1.449	1.442
	d	1.362	1.369	1.359	1.368	1.320
	e	1.416	1.420	1.417	1.427	1.417
	f	1.433	1.426	1.438	1.434	1.417
Chrysene	a	1.439	1.435	1.445	1.446	1.380
	b	1.418	1.415	1.420	1.420	1.393
	c	1.389	1.385	1.379	1.385	1.361
	d	1.415	1.411	1.416	1.416	1.427
	e	1.381	1.384	1.378	1.385	1.419
	f	1.419	1.417	1.420	1.423	1.367
	g	1.436	1.430	1.442	1.440	1.425
	h	1.369	1.374	1.366	1.373	1.466
	i	1.434	1.427	1.439	1.436	1.407
	j	1.389	1.406	1.396	1.409	1.407
	k	1.409	1.415	1.409	1.421	1.398
3-4 Benz-phenantrene	a	1.381	1.385	1.379	1.385	1.378
	b	1.416	1.411	1.417	1.416	1.409
	c	1.381	1.385	1.379	1.385	1.378
	d	1.419	1.416	1.421	1.422	1.391
	e	1.436	1.430	1.442	1.440	1.443
	f	1.368	1.373	1.366	1.372	1.352
	g	1.435	1.429	1.441	1.439	1.430

TABLE I: Continuación.

Molecule	Bond	TPOT	ITPOT	TPOT	IPTOP	(*)
	h	1.397	1.406	1.396	1.409	1.412
	i	1.437	1.433	1.444	1.445	1.446
	j	1.418	1.416	1.420	1.422	1.433
	k	1.409	1.415	1.409	1.421	1.431
Tripheny-	a	1.389	1.391	1.387	1.392	1.380
	b	1.406	1.405	1.405	1.408	1.398
lene	c	1.408	1.409	1.408	1.412	1.409
	d	1.454	1.447	1.467	1.465	1.441
	e	1.407	1.411	1.406	1.416	1.411
Perylene	a	1.379	1.384	1.377	1.385	1.370
	b	1.416	1.410	1.418	1.414	1.418
	c	1.386	1.394	1.384	1.395	1.397
	d	1.461	1.452	1.476	1.472	1.471
	e	1.424	1.421	1.428	1.428	1.411
	f	1.412	1.418	1.413	1.424	1.418
	g	1.427	1.424	1.430	1.432	1.425
Tetracene	a	1.365	1.374	1.362	1.373	1.385
	b	1.438	1.425	1.444	1.434	1.479
	c	1.441	1.431	1.449	1.442	1.439
	d	1.393	1.399	1.391	1.402	1.398
	e	1.416	1.413	1.417	1.419	1.409
	f	1.429	1.434	1.433	1.445	1.475
	g	1.432	1.432	1.437	1.442	1.439
Coronene	a	1.373	1.378	1.371	1.377	1.373
	b	1.429	1.425	1.434	1.432	1.429
	c	1.408	1.415	1.408	1.420	1.406
	d	1.429	1.426	1.434	1.434	1.434

(*) Quoted in Ref. 15.

TABLE II

ACCURACY ESTIMATORS s AND d FOR THEORETICAL BOND LENGTHS

	TPOT		ITPOT	
	Eq. | 4|	**Eq. | 5|**	**Eq. | 4|**	**Eq. | 5|**
$d \times 10^3$	14.113	13.958	14.282	13.606
$s \times 10^3$	16.288	16.531	16.445	14.931

TABLE III

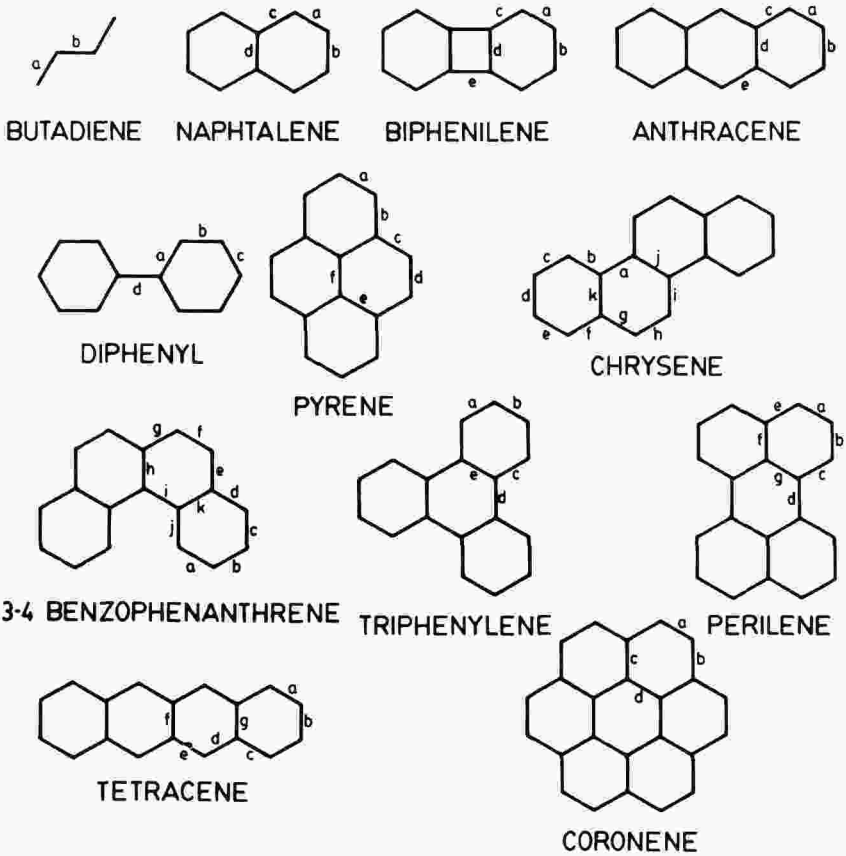
DISTRIBUTION OF BOND LENGTHS

Interval (A)	TPOT		ITPOT		Experimental
	Eq. | 4|	Eq. | 5|	Eq. | 4|	Eq. | 5|	
1.330 - 40	-	-	-	-	1
40 - 50	1	1	1	1	-
50 - 60	-	1	-	-	2
60 - 70	5	4	1	1	3
70 - 80	3	7	5	5	5
80 - 90	8	4	6	6	5
90 - 1.400	6	6	8	6	10
1.400 - 1.410	10	10	8	7	6
10 - 20	12	8	16	8	11
20 - 30	8	8	13	14	9
30 - 40	11	8	8	10	7
40 - 50	2	8	1	8	4
50 - 60	1	1	3	-	-
60 - 70	3	1	-	1	3
70 - 80	-	1	1	2	3
80 - 90	1	2	-	1	-
90 - 1.500	-	-	-	-	-
1.500	-	1	-	1	1

TABLE IV

DEVIATIONS OF CALCULATED BOND LENGTHS

		TPOT		ITPOT	
		Eq. | 4	Eq. | 5|	Eq. | 4|	Eq. | 5|
$s \times 10^3$	R < 1.400 Å	15.130	15.996	14.428	13.423
	1.401 ≤ R ≤ 1.425	8.707	9.934	8.196	7.837
	R > 1.426	21.684	21.508	21.321	20.551
$d \times 10^3$	R < 1.400 Å	14.222	14.111	15.407	15.963
	1.401 ≤ R ≤ 1.425	10.227	12.045	6.773	10.818
	R > 1.426	17.864	15.682	20.409	13.500



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