Organic Quantum Chemistry. XXVIII. The Bond Order–Bond Length Relationship within the VESCF Method[1,2]

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Abstract: A bond order–bond length relationship has been developed within the VESCF framework and applied to a variety of unsaturated hydrocarbon molecules. A total of 39 different bond lengths have been calculated to within a root-mean-square deviation of ±0.013 Å. It is suggested that the method is comparable in accuracy with the best of such methods previously reported.

That one might be able to predict bond lengths from theoretical calculations on bond orders has been recognized for a long time. Pauling,[4] Penny,[5] and others have applied the so-called Penney–Dirac method to calculate bond orders of alternant hydrocarbons. Coulson[6] similarly used the simple molecular orbital method (Hückel method) at an early date. Much of the earlier work has been summarized and reviewed by Coulson.[7] Subsequent refinements on bond-length determination by the molecular orbital method have appeared from time to time; the best available at the time this work was undertaken is that by Dewar and Gleicher,[8] which was an improvement of an earlier equation by Dewar and Schmeising.[9] Finally, there appeared during the course of this work two papers by Lo and Whitehead[10] in which very good results were reported.

More recent calculations have attempted to take into account in various ways the effect of the σ system in determining bond lengths. Dewar[9] was the first to explicitly point out that sp^2–sp^2 bonds and sp^3–sp^3 bonds may not necessarily follow a bond order–bond length relationship with the same numerical values for the constants, and his equation relating bond order and bond lengths as subsequently[8] modified is

$$r_{ij} = 1.515 - 0.177p_{ij} \tag{1}$$

where r_{ij} is the bond length in Å and p_{ij} is the bond order, which is equal to $(2\Sigma c_i c_j)$.

Salem[11] has given a justification for such relationships. A linear relationship is sufficient to fit the available data; it remains to establish the best values for the constants appearing in the equation, but within the context of Dewar's method, it seems that his equation (1) is close to optimum. Similar equations have been used by a number of investigators.[12–21]

In the case of alternant hydrocarbons, the calculated bond lengths are mostly within 0.01 Å of the experimental values (usually within two times the standard deviation in the experimental values, the amount generally taken to be the experimental error), so the agreement with experiment can be considered excellent. A number of failures are reported of the relationship to give the correct bond length. Examples are azulene,[8,16,21–23] cyclopentadiene, tropilidene, phenanthrene,[8,10,14,16,20] chrysene,[8,10,14,20] triphenylene,[8,10,20] perylene,[10,14,20] quaterrylene,[24] and pyrene.[8,10,16,20] Some of these are nonalternant hydrocarbons, and a few are polynuclear hydrocarbons with unusually long bonds.

We have over the last few years studied the VESCF method of predicting electronic spectra of conjugated systems and have found it superior to the more conventional SCF methods for reasons to which we attach a firm physical interpretation.[25] For these same reasons, it seemed to us that the VESCF method would offer a way to calculate other physical properties more accurately than does the standard SCF method, and this paper explores that possibility. We feel it is especially desirable to have one method which is generally applicable for π-system calculations, rather than tackle each new problem in an *ad hoc* manner, as has often been done in the past. The VESCF method has been shown previously to be applicable to the calculation of electronic spectra and ionization potentials for a wide variety of hydrocarbons, as well as for heterocyclic

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[25] (a) R. D. Brown and M. L. Heffernan, *Aust. J. Chem.*, **12**, 319 (1959); (b) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965).

molecules. This method assumes, as did the earlier methods, that the effect of the σ system need not be explicitly included, but can be handled in terms of the linear bond order–bond length relationship. It may be desirable to include the σ system explicitly in such calculations, and this question has previously been discussed by Coulson[26] and by ourselves.[27] Toward the end of the present investigation, the papers by Lo and Whitehead[10] appeared, in which they used a Morse function to describe the σ part of the C–C multiple bond, and superimposed the σ energy upon the π energy in simple systems, thereby deriving a bond order–bond length relationship (2). This method gives

$$r_{ij} = 1.567 - 0.267p_{ij} \tag{2}$$

rather different bond lengths for bonds of very low bond order, but within the experimentally accessible range the results are almost the same as from eq 1. The overall results of the calculations on many compounds are slightly better by this method than by Dewar's method; however, the difference is small and may result largely from a different choice of experimental data.

Our conclusions regarding the earlier work may be summarized as follows. A linear bond order–bond length relationship is sufficient to describe, with reasonable accuracy, bond lengths commonly observed in planar conjugated compounds, when the bond orders are determined by a SCF method. A slight improvement appears to be possible when the effect of the σ system is explicitly allowed for. The agreement between theory and experiment is not completely satisfactory, and it is not clear why, but it may be largely due to experimental errors.

Clearly, none of these methods are really adequate when one is studying nonplanar systems, since there will be mixing of the σ and π components, and no treatment of the π part alone is justifiable. Other problems regarding the σ system need to be examined, at least in special cases. For example, it is improbable that the 1–2 bond in 1,2-di-*tert*-butylbenzene will have the same bond length as the corresponding bond in benzene itself. However, no treatment of the π system alone is likely to account for the difference.

Results and Discussion

There are two approaches to the derivation of a bond order–bond length relationship within the MO context. One can either use as a basis a few simple compounds of accurately known structure, or one can use a least-squares fitting of all available data. We have chosen the former approach, using benzene, graphite, ethylene, and butadiene. The first three of these have bond orders of 0.6667, 0.333, and 1.000, respectively, as determined by symmetry. The experimental bond lengths are reported to be 1.397,[28] 1.421,[29] and 1.334.[30]

In the case of butadiene, the bond orders were determined by successive iterations using the VESCF procedure, and adjusting the bond order–bond length parameters to mutual consistency by a least-squares fit of the bond length–bond order data for butadiene, graphite, benzene, and ethylene. The resulting relationship is

$$r_{ij} = 1.525 - 0.191p_{ij} \tag{3}$$

As previously, the bond lengths obtained in the experimentally accessible region are almost the same as those obtained earlier, but the extrapolation point is a little different. This equation fits to the available data on the five bond lengths mentioned with high accuracy (Table I).

Table I. Comparison of the Deviations of the Least-Squares Line from Experimental Bond Lengths for the VESCF Equations

Compd	Exptl bond length, Å	Calcd bond length, Å	Absolute error in calcd bond length
Butadiene	1.343	1.343	0.000
Butadiene	1.467	1.466	0.001
Benzene	1.397	1.398	0.001
Ethylene	1.334	1.334	0.000
Graphite	1.421	1.423	0.002
		Av dev	±0.001

VESCF Method. This method, introduced by Brown,[25a] has been described in detail previously,[25b] and the details will not be given here. It differs from the ordinary SCF method in that the ionization potential of a given atom in the π system is determined by what is attached to the atom; the orbital exponent for the π orbital on that atom is a function of this ionization potential; and both of these quantities vary in response to the electron density at the atom, which is taken into account as the SCF iterations proceed. This modification allows one to deal with atoms which are substituted differently, to obtain a better physical picture as to the environment in the vicinity of each nucleus in the molecule, and to better predict spectra, and presumably other quantities which depend upon electron density and ionization potential. Since bond lengths are among such quantities, it seemed that this method might well be superior to those previously reported for calculating bond lengths from bond orders.

At the time these calculations were carried out (1966–1968), the only computer available to us was an IBM-7074, which was not capable of dealing with a system containing more than 14 orbitals in a practical way, and we therefore were limited to studies of systems of this size or smaller. The molecules examined are all summarized in Table II with respect to calculated and experimental bond lengths.

The results shown in Table II may be briefly discussed as follows. For naphthalene and anthracene,[31,32] the results are good. For hexatriene (assumed planar) the calculated bond lengths are similar to those calculated for butadiene. The experimental bond lengths are rather different, particularly for the abnormally long internal double bond.[33,34] The calcu-

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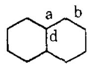
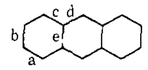
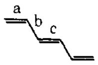
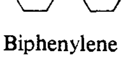
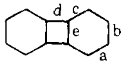
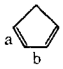
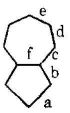
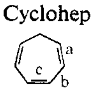
Table II. Summary of Experimental Bond Lengths *vs.* Calculated VESCF Bond Lengths

Molecule	Bond	Bond length, Å: Exptl	Calcd	Δ
Naphthalene 	a	1.422 ± 0.004	1.425	−0.003
	b	1.371 ± 0.009	1.379	−0.008
	c	1.412 ± 0.014	1.420	−0.008
	d	1.420 ± 0.007	1.416	0.004
Anthracene 	a	1.375 ± 0.008[a]	1.371	0.004
	b	1.418	1.430	−0.012
	c	1.444	1.437	0.007
	d	1.405	1.405	0.0
	e	1.433	1.426	0.007
Hexatriene 	a	1.337 ± 0.001	1.344	−0.007
	b	1.457 ± 0.002	1.464	−0.007
	c	1.367 ± 0.003	1.353	0.014
Biphenyl 	a	1.398 ± 0.023[a]	1.397	0.001
	b	1.387	1.399	−0.012
	c	1.379	1.404	−0.025
	d	1.497 ± 0.032	1.474	0.023
Biphenylene 	a	1.423 ± 0.003	1.411	0.012
	b	1.385 ± 0.004	1.388	−0.003
	c	1.372 ± 0.002	1.388	−0.016
	d	1.514 ± 0.003	1.491	0.023
	e	1.426 ± 0.003	1.417	0.009
Cyclooctatetraene	a	1.340 ± 0.001	1.340	0.0
	b	1.475 ± 0.001	1.490	−0.015
Cyclopentadiene 	a	1.342 ± 0.003	1.341	0.001
	b	1.469 ± 0.002	1.478	−0.009
Azulene 	a	1.399 ± 0.009	1.400	−0.001
	b	1.418 ± 0.010	1.405	0.013
	c	1.383 ± 0.008	1.408	−0.025
	d	1.406 ± 0.016	1.400	0.006
	e	1.403 ± 0.014	1.402	0.001
	f	1.501 ± 0.005	1.479	0.022
Cycloheptatriene 	a	1.356 ± 0.005	1.340	0.016
	b	1.446 ± 0.007	1.479	−0.033
	c	1.356 ± 0.005	1.344	0.012
Benzene	a	1.397 ± 0.001	1.398	−0.001
Graphite	a	1.421[b]	1.423	−0.002
Ethylene	a	1.334[b]	1.334	0.0
Butadiene	a	1.343 ± 0.012[a]	1.343	0.0
	b	1.467	1.466	0.001

[a] Standard deviation for all bonds not otherwise designated. [b] No standard deviation given.

lated value may be "better" than the experimental value, the latter being perhaps affected by torsional motions to an unusual degree.

For biphenyl it might be expected that the interannular bond, since it is much longer than most of the bonds previously examined, might be difficult to calculate accurately. The deviation of the calculated from the experimental bond length[35] is smaller than the standard deviation in the experimental bond length, so the agreement is satisfactory.

Cyclooctatetraene is alternant, but nonplanar, and the validity of our calculations in this case is suspect. Nonetheless, the agreement between the calculated and experimental values is pretty good, and the same is true for cyclopentadiene.[36] However, the discrepancy between the experimental and calculated values of one bond in each case is more than three times the experimental standard deviation[37] so that agreement cannot be claimed.

For azulene, there is some question concerning the geometry of the molecule. The reported geometry having the smallest standard deviations is that by Bastiansen.[21] The peripheral bonds are all roughly benzenoid in length, and the interannular bond was found to be 1.501 ± 0.005 Å in length,[21,35] markedly different from our calculated value, 1.479. Two crystal structures have been done on azulene, and they tend to be accurate to only about ±0.01 Å in bond length, except that Robertson[38] gives the interannular bond as 1.483 ± 0.004, and Pawley[39] gives this bond length as 1.481. These values are in good agreement with what we have calculated, so that the problem may be with the experimental, rather than with the calculated, value.

For cycloheptatriene,[40] the results are marginal. Finally, the highly strained molecule biphenylene has been examined, and the results do not compare favorably with experimental.[36] The abnormal σ system may play a part here.

Conclusions

For the particular group of compounds studied, which was chosen in a somewhat arbitrary fashion (from among molecules containing not more than 14 π orbitals) so as to illustrate all kinds of structural features on unsubstituted ring systems, we find the following general conclusions can be drawn. The bond order–bond length relationship in eq 3 allows one to calculate bond lengths with an overall accuracy (root-mean-square) of ±0.013 Å from the best available experimental values. The standard deviations in the experimental values over the same set given by the original investigators is ±0.011 Å. A comparison of the root-mean-squares calculated by Lo and Whitehead[10] and by ourselves for those compounds common to both investigations showed no difference in accuracy between the two methods, rms ±0.011 Å.

We therefore conclude that the VESCF method enables one to calculate bond lengths with an accuracy competitive with or better than previous methods, with the possible exceptions of "long bonds" such as occur in perylene (which we could not study) and for substituted molecules in which the σ system is highly strained or distorted. However, the VESCF modification was not found to be conspicuously better than the ordinary SCF method, as had been hoped. The calculations give bond lengths which are on the average as good as have been obtained by experimental measurement. (There are specific cases where the discrepancy is several times the reported standard deviation in the experimental values, however.) We suspect at this point that the remaining discrepancy between experiment and calculation for planar compounds where large steric effects are absent is *largely the fault of the experiment*, although until we have a more accurate way for dealing with the σ system, this is only a suspicion.

None of the π-system calculations given here, or

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previously, adequately deal with nonplanar systems or with molecules containing large steric interactions in the σ system. It is possible, of course, to do an all valence electron calculation, but these are in general very lengthy, often prohibitively so, and still of somewhat questionable reliability. A better approach to the problem, the force field approach, will form the subject of a subsequent paper.[41]

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[41] N. L. Allinger and J. T. Sprague, unpublished results.

Calculations on Quinonoid Compounds. I. The Quinododimethides

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Abstract: A series of 31 quinododimethides have been investigated by SCF molecular orbital calculations. No support can be found for earlier predictions that appreciable electron delocalization may be found for such nonbenzenoid systems. The relevance of quinododimethides to certain electrocyclic ring opening reactions is dealt with.

Current theory concerning electronic structure in polyolefinic compounds tends toward the conclusion that a slight, consistent delocalization is operative. Self-consistent field (SCF) calculations on branched polyolefins indicated that the total π energy was a simple sum of the contributing parts.[2,3] While the quinododimethides were not treated in these studies, it is plausible that only limited aromaticity is associated with these species.

Early calculations on the quinododimethides, however, were of the most simple type. These calculations, whether involving a Hückel molecular orbital or valence bond approach, were uniform in their predictions. Thus, Namiot, Dyatkina, and Syrkin determined appreciable resonance energies for 1,2- and 1,4-benzenequinododimethide by both methods.[4] The molecular orbital approach was also applied to the hypothetical 1,3-benzenequinododimethide. While predicted to possess less resonance energy than its two isomers, significant stabilization was claimed.[4] Coulson, Craig, Maccoll, and Pullman obtained results which tended to substantiate the above findings.[5] In the case of 1,4-benzenequinododimethide, a very low separation between the singlet and triplet structures was predicted by molecular orbital theory.[5] Dyatkina and Syrkin also calculated similarly low energy barriers for other quinododimethides, particularly for those systems where only a single classical structure can be drawn.[6]

Experimental findings tend to contradict the prediction of moderate stability for simple quinododimethides. Thus, for example, 1,2-benzenequinododimethide should be obtained from the thermal elimination of sulfur dioxide from 1,3-dihydroisothianaphthene 2,2-dioxide. While the quinododimethide has been trapped as a Diels–Alder adduct with anthracene, it has resisted isolation.[7] A similar failure was noted in the attempts to prepare 1,4-benzenequinododimethide *via* pyrolysis of the *p*-methylbenzyl radical.[8] Even those systems in which the quinododimethide moiety should be stabilized by the annellation of benzene rings have not been isolated at room temperature. Eliminations from various precursors should yield 9,10-anthracenequinododimethide and 9,10-phenanthrenequinododimethide. Both can be trapped only as Diels–Alder adducts.[9,10]

Recent reconsiderations of HMO calculations also would indicate that the earlier results have exaggerated possible electron delocalization in related systems. Hess and Schaad have pointed out that in assigning the π energy of the hypothetical, localized reference structure as 2β/double bond without consideration of the nature of attached groups and, more importantly, by neglecting contributions to the π energy by formal single bonds, the total π energy of these structures may be seriously underestimated.[11] Subsequent recalculations of resonance energies as differences in π energy between those of HMO calculations and those newly determined for the reference state have produced results which nicely parallel the corresponding results of the SCF approach.[11,12] Unfortunately, the quinododimethides were again not considered.

In order to systematically study this class of compounds, we have carried out SCF calculations for the 31 quinododimethides shown in Figure 1. Two variants of the Pople–Pariser–Parr approach were utilized. The first was based upon fixed geometries in which a constant bond length (CBL) of 1.4 Å was employed. The second method allowed for the use of variable bond lengths (VBL) *via* incorporation of a bond order–bond

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