

Bond length dependence of cluster expansions of pi-electron energy

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There are two long established methods for representing the delocalized portion of the pi-electron energy of conjugated molecules in a simple local fashion. One, introduced by Hess and Schaad, can be used to provide a very accurate estimate of the energy of acyclic polyenes. Another, introduced originally by Herndon, has been successfully applied to the energy of aromatic ring systems. Both methods can be shown to be forms of cluster expansions, in which the energy of a molecule is expressed exactly as a sum of (successively smaller) contributions from successively larger molecular fragments. As such, it should in principle be possible to combine the methods to provide a consistent description of molecules of almost any structure. However past attempts to do so have yielded physically unreasonable results. It is shown that the key missing ingredient in these attempts is a failure to account for bond stretching and compression. When the energy changes associated with bond length changes are accounted for properly, the combined cluster expansion is quite successful in accounting for molecular pi electron energies in a very compact form.

KEY WORDS: conjugation, aromaticity, pi-electron theory, cluster expansions

1. Introduction

In this paper we propose a resolution of an inconsistency between two standard methods for treating the energetics of pi-electron systems. The methods in question are the Hess and Schaad type method for treating effects of conjugation and the quantitative resonance/conjugated circuits method for treating aromaticity. Both share a common graph-theoretical justification, and thus should provide a consistent picture of pi-electron energies, but past attempts to combine them have been unsuccessful. Here we argue that the key missing ingredient is a proper accounting of energetic effects due to bond length changes. When these are included in the two methods, consistent and physically reasonable results are obtained.

Hess and Schaad [1] were the first to note that when pi-electron energies are evaluated using the Huckel Molecular Orbital (HMO) method there is a great deal of regularity in the results for conjugated acyclic hydrocarbons. To an excellent approximation, the

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π energy of any such molecule can be written as a sum of contributions from each bond, where the energy of a bond depends only on its immediate surroundings. In the original Hess and Schaad method bonds were classified as formally single or double, and by the number of other carbons bonded to each end. This results in nine different bond types, but one appears only in ethylene and there are two linear dependence relations among the other eight, resulting in an effective six-parameter fitting scheme. Jiang et al. [2] later proposed a similar method in which the distinction between single and double bonds is ignored, resulting in six bond types, one of which appears only in ethylene. It has been shown [3] that both of these schemes can be expressed in terms of a cluster expansion, which will be utilized below, and that the Jiang, Tang, and Hoffmann method differs from the Hess and Schaad scheme only by assuming zero contributions from three terms whose values are, in fact, very small.

The other widely applied, graphically based, method for treating π -electron energetics is the Quantitative Resonance Theory (QRT) of Herndon [4], which gives the aromatic stabilization energy of aromatic (and antiaromatic) hydrocarbons directly in terms of contributions from conjugated *rings*. This method has been reformulated by Randić and Trinajstić in a computationally convenient form under the name of conjugated circuit (CC) theory [5]. In this version, the aromatic stabilization energy is given as a sum of contributions from each conjugated cycle appearing in any of the Kekulé structures of the molecule, where a conjugated cycle is a path of alternating single and double bonds around a ring of any size. For aromatic benzenoid hydrocarbons contributions have been determined for cycles of size 6, 10, and 14, and all are stabilizing as expected from the Hückel ($4n + 2$) rule, but of diminishing strength as the cycle size increases. Conjugated circuit theory can also be expressed formally as a cluster expansion, and thus should combine nicely with the Hess and Schaad methods to describe effects due to both conjugation and aromaticity, but as discussed below, this has not proved to be the case.

There is, of course, a reason to wish to combine the two methods. It has been understood for a long time that one cannot achieve a reasonable energetic measure of “aromaticity” simply by comparing the π energy of aromatic molecules to that of isolated double bonds. Conjugation results in significant energy changes even in noncyclic molecules which are certainly not aromatic. In an aromatic ring the double bonds are conjugated as well as delocalized, and one would like to separate the effects of conjugation from those of aromaticity. The Hess and Schaad method, or any of its variants, gives a straightforward way of doing this. One subtracts from the total π energy the contributions of all acyclic clusters, even those contained within rings, and then identifies the difference as the “aromatic” stabilization energy. These energies should then decompose into ring contributions similar to the empirical conjugated circuit values. It is not difficult to carry this decomposition through using total π energies computed by the HMO method, but the results bear little resemblance to the conjugated circuit values. They show such unphysical results as values which increase with circuit size, or are even of the wrong sign [6]. Why do these methods not match together more smoothly?

One possibility is that the HMO method, which is certainly very approximate, does not give an adequate account of conjugation, aromaticity, or both. To test this possibil-

ity, the Hess and Schaad decomposition of pi-electron energy was carried out for the Hubbard model [7]. The Hubbard model [8] is a two parameter effective pi electron Hamiltonian which combines an electron hopping term of strength t with an on-site electron repulsion term of strength U . When U is equal to zero it reduces exactly to the Huckel model, but as U increases it spans the whole range from independent particle to highly correlated electron–electron interactions. The $U/t \rightarrow \infty$ limit corresponds to the valence bond model in which only covalent configurations contribute to the wave function. In [7] it is shown that the cluster expansion for acyclic energy contributions converges rapidly at all U/t , in a qualitatively similar manner to that for the Huckel model. However, ring contributions calculated from these cluster values and computed total Hubbard energies show the same pathologies as those found from HMO theory [6]. Thus inadequacies of the Huckel model do not appear to be the source of the difficulty.

Examination of the original QRT/CC papers reveals one important difference between the original parameterization of these methods and attempts to extract them from total pi energies. The original papers used aromatic stabilization energies computed by Dewar and DeLano [9] using a version of MNDO theory, which includes sigma as well as pi electrons. All molecules were taken at their minimum energy geometry as computed by this method. Energetic effects due to compression of sigma bonds as pi character varies were thus included from the beginning. Accordingly, we have set out to examine whether coupling of pi energies to bond lengths, with accompanying changes in sigma bond energy, can resolve the discrepancy between Hess and Schaad and conjugated circuit theories. The conclusion below is that it can.

2. Procedure

The analysis is most conveniently carried out using the cluster expansion formalism. A cluster expansion provides a formally exact way of representing a property of a molecule, represented by a graph, as a sum of contributions from subgraphs of the molecular graph. Since the molecule itself is its own largest subgraph, the expansion must necessarily be exact if carried to completion, but often only small subgraphs are found to make significant contributions. We adopt here the cluster expansion introduced in [3,7], in which conjugated hydrocarbons are represented by labeled, hydrogen deleted graphs, with the carbon atoms at the vertices and with the labeling identifying each edge (carbon–carbon bond) as formally double or single. We limit the expansion to connected subgraphs which support a Kekule structure, and order them by diameter, where the diameter d of a graph is the smallest number of edges which must be traversed to connect two maximally separated vertices. Then all of the Hess and Schaad type methods for acyclic hydrocarbons can be derived from the cluster expansion truncated at $d = 5$ [3] which involves only the seven subgraphs shown in figure 1.

For benzenoid aromatics, we also limit the expansion of the acyclic portion of the energy to isometric subgraphs. An isometric subgraph is one which contains at least one shortest path from the parent between any two vertices of the subgraph. Of course,

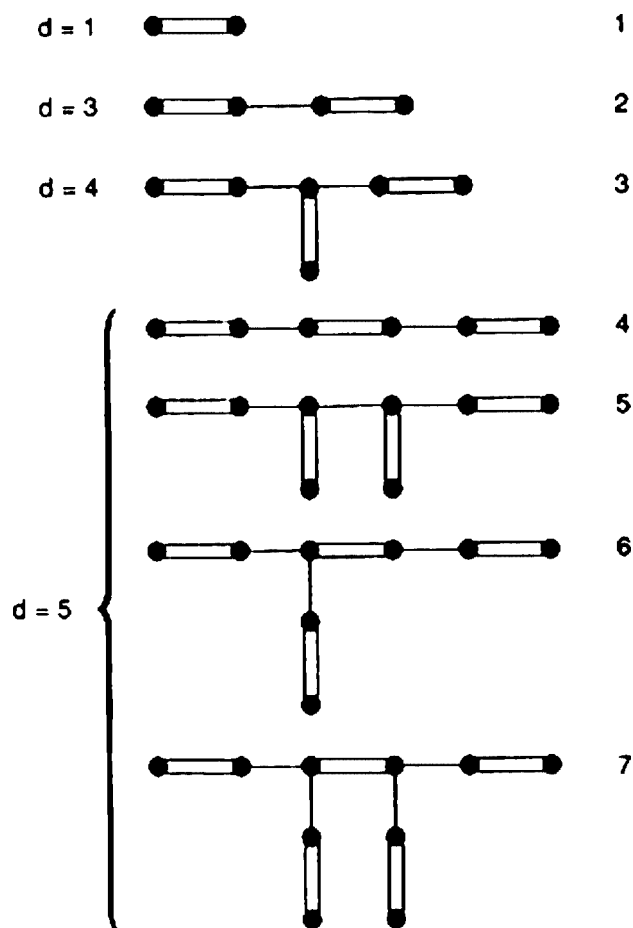


Figure 1. Acyclic molecules and assigned sequence numbers with diameter $d \leq 5$.

the expansion must be carried out for each Kekule structure and averaged for molecules in which there is more than one way to represent the formal placement of single and double bonds. If we exclude “mixed” subgraphs with both cyclic and acyclic portions (the validity of this omission will be checked), we are left with the subgraphs shown in figure 2 to account for aromatic contributions to the energy. They bear an obvious correspondence to conjugated circuits. Truncation at $d = 5$ includes just contributions from conjugated 6- and 10-circuits as in Herndon’s original work [4]. Given the strength of aromatic interactions, it is not surprising that there is good evidence that contributions from 14-circuits ($d = 7$) are not negligible. However, this analysis agrees with [10] that there really should be three distinct 14-circuit contributions while empirically these are generally taken to be equal [5].

A major advantage of formulating these methods as cluster expansions is that cluster expansions can be uniquely solved by inversion if the value of the property under investigation is known for the smallest molecule containing each subgraph [11]. For ex-

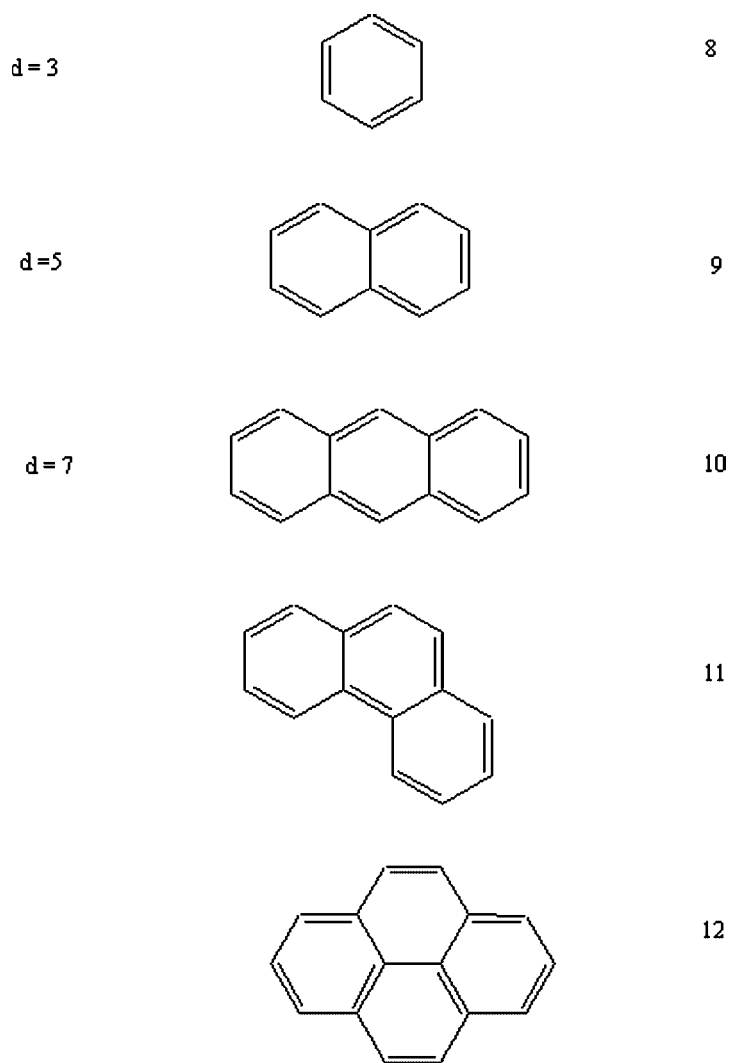


Figure 2. Ring molecules and assigned sequence numbers with diameter $d \leq 7$.

ample, the pi energy of ethylene provides directly the contribution of the first subgraph in figure 1. Butadiene contains the first subgraph twice, so the difference between its energy and twice the contribution of the first subgraph gives the energy contribution of the second subgraph. This process can be continued to derive energy contributions for all remaining subgraphs from calculated energies for the 12 molecules whose graphs are depicted in figures 1 and 2.

We now introduce a model for the energy which includes both the interactions among the pi electrons and the coupling between pi and sigma energies due to bond length changes. The total molecular energy is taken as a sum of a sigma and a pi component. The sigma component represents each bond as a spring with an equilibrium energy

(which need not be known), an equilibrium length, and a quadratic force constant for distortions away from equilibrium. The pi energy here will be calculated from HMO theory, although any other convenient method could be used. The coupling between the two is introduced by assuming a linear bond length–bond order relation, so that each carbon–carbon sigma bond compresses in proportion to the pi bond order placed upon it during the pi energy calculation. We also assume a linear dependence of the Huckel parameter β on bond length, so the calculations must be carried out self consistently until the optimum geometry is found.

The model may be summarized via the equations

$$E = 2 \sum \beta_{rs} p_{rs} + \frac{1}{2} \sum K (R_{rs} - R_e)^2 + \text{constant}, \quad (1)$$

$$\beta_{rs} = \beta_0 (1 + \delta (R_{rs} - R_0)). \quad (2)$$

The two sums in equation (1) represent the bond length dependent pi and sigma contributions to the energy while the constant, which will be ignored, includes the on-site (α) portion of the Huckel energy and the equilibrium single bond energies which do not vary and which do not effect the cluster expansion. R_{rs} , β_{rs} , and p_{rs} are respectively the length, Huckel β value, and pi bond order for bond rs, and the sums in equation (1) extend over all nearest neighbor (bonded) pairs of carbon atoms. The parameter R_0 in equation (2), which is an arbitrary reference point, is taken as 1.399 Å. The model thus depends on four parameters, one of which (β_0) simply determines the energy scale (results will be given in units of β_0), and three (K , R_e , δ) which must be determined from experimental data.

Two of the free parameters in the model can be fixed by comparison to the empirical bond length–bond order relation. There are two relevant molecules whose bond order is completely determined by symmetry (within the HMO approximation), namely ethylene with $p = 1$ and benzene with $p = 2/3$. If one fits these bond orders via a straight line against the experimental bond lengths of these molecules (1.339 Å and 1.399 Å [12]), the resulting relation is

$$R = 1.519 - 0.180p. \quad (3)$$

This implies a length for a pure single bond between sp^2 hybridized carbon atoms of 1.519 Å, in good agreement with other estimates [9]. We note in passing that equation (3) also predicts the bond length of another “molecule”, graphite, whose bond order of 0.52486... [13,14] is fixed by symmetry, in excellent agreement with the experimental value of 1.421 Å [12]. If we now take equation (1) for the energy of ethylene or benzene and differentiate with respect to bond length we find the condition for the location of the energy minimum to be

$$\frac{dE}{dR} = 2\beta_0\delta p + K(R_{\min} - R_e) = 0 \quad (4)$$

or

$$R_{\min} = R_e - \frac{2\beta_0\delta p}{K}. \quad (5)$$

Table 1
Total pi energy in units of $|\beta_0|$ for molecules in figures 1–2.

Molecule	Fixed β	Variable β
1	-2.000000	-2.454800
2	-4.472136	-5.013978
3	-6.898979	-7.573587
4	-6.987918	-7.576210
5	-9.331737	-10.132863
6	-9.445871	-10.140111
7	-11.924777	-12.709468
8	-8.000000	-8.000000
9	-13.683239	-13.418282
10	-19.313709	-18.766126
11	-19.448251	-18.904900
12	-22.505459	-21.668178

Comparison of equation (5) with equation (3) thus gives $R_e = 1.519 \text{ \AA}$ and $2\beta_0\delta/K = 0.180 \text{ \AA}$.

There are several ways that the remaining free parameter could be fixed, but in this work we simply adjusted δ to give the experimentally observed difference between the double and single bond lengths in butadiene (0.118 \AA [12]). Thus the experimental content of the model is fixed by the bond lengths of the isolated double bond in ethylene, the aromatic double bond in benzene, and the conjugated bonds in butadiene – just the effects which we are trying to model. If we assign β_0 a standard aromatic value of -2.5 eV , this yields the final values $R_e = 1.519 \text{ \AA}$, $K = 105.3 \text{ eV}/(\text{\AA})^2$, and $\delta = -3.79 (\text{\AA})^{-1}$.

The computational procedure for use of the model is to guess bond lengths, compute β values from equation (2), and then to carry out the HMO calculation to generate bond orders. These are used in equation (3) to revise the bond lengths, and the procedure is repeated until the output bond lengths agree with the input to $1 \times 10^{-4} \text{ \AA}$. Finally, the first term of equation (1) is used to evaluate the pi energy in the presence of sigma bond compression. In table 1 we give the total pi energies, in units of β_0 , for the molecules in figures 1 and 2, with and without the adjustment for changing bond length.

3. Results

We first consider the effect of the bond length adjustment on the cluster expansion for the energy of acyclics. Table 2 gives the cluster contribution from fragments generated from the first seven molecules in table 1 via the inversion procedure of references [3,7]. It is clear that bond length variations make the cluster expansion even more rapidly convergent, almost to the point that clusters beyond the first two make negligible contributions to the energy. This result makes good sense since the effect of the bond length adjustment is to strengthen formal double bonds and weaken formal single bonds. In the limit that single bonds become infinitely weak, the molecule would be described

Table 2
Cluster contributions in units of $|\beta_0|$ for acyclic fragments
shown in figure 1.

Cluster	Fixed β	Variable β
1	-2.0000	-2.4548
2	-0.4721	-0.1044
3	0.0453	-0.0004
4	-0.0436	-0.0031
5	-0.0059	0.0003
6	0.0125	-0.0012
7	-0.0024	0.0001

exactly as a collection of noninteracting double bonds, and the cluster expansion would converge after the first term. The other change which stands out is the change of cluster 3, which represents a branch in the carbon chain, from a significantly destabilizing contribution for the uniform beta case to a very small but stabilizing contribution for the bond adjusted expansion. This result appears to be somewhat coincidental because the form of the cluster expansion forces the difference between the contribution of cluster 3 and that of cluster 4 to be equal to the calculated energy difference between molecule 3 and molecule 4. Since bond adjustment makes the energy less sensitive to structural variations, these two cluster values must move closer together. The fact that the cluster 3 value has moved through zero is probably without great significance.

With the values of the acyclic cluster contributions in hand, we can now extract effective conjugated circuit contributions from the computed energies of molecules 8–12 by expressing the energy of each as the average over Kekule structures of the sum of contributions from all isometric acyclic clusters and all conjugated cycles. The formal expressions are

$$\begin{aligned}
 E_8 &= 3\varepsilon_1 + 3\varepsilon_2 + R_1, \\
 E_9 &= 5\varepsilon_1 + 6\varepsilon_2 + 2\varepsilon_3 + 2\varepsilon_4 + \frac{4}{3R_1} + \frac{2}{3R_2}, \\
 E_{10} &= 7\varepsilon_1 + 9\varepsilon_2 + 4\varepsilon_3 + 4\varepsilon_4 + \frac{3}{2R_1} + R_2 + \frac{1}{2R_3'}, \\
 E_{11} &= 7\varepsilon_1 + 9\varepsilon_2 + 4\varepsilon_3 + \frac{22}{5\varepsilon_4} + \frac{4}{5\varepsilon_5} + \frac{2}{5\varepsilon_6} + 2R_1 + \frac{4}{5R_2} + \frac{2}{5R_3''}, \\
 E_{12} &= 8\varepsilon_1 + 11\varepsilon_2 + \frac{16}{3\varepsilon_3} + 7\varepsilon_4 + \frac{2}{3\varepsilon_5} + \frac{2}{3\varepsilon_6} + 2R_1 + \frac{4}{3R_2} + \frac{2}{3R_3''} + \frac{1}{3R_3'''}
 \end{aligned}$$

where the ε_i 's refer to the contributions of clusters 1–7 and R_1 refers to the contribution of a conjugated 6-cycle, R_2 is that of a conjugated 10-cycle, and R_3' , R_3'' , and R_3''' refer to conjugated 14-cycles around an anthracene, phenanthrene, or pyrene moiety, respectively. Inverting these equations to solve for the R 's gives the results with and without bond length adjustment which are shown in columns two and three of table 3.

Table 3
Ring contributions in units of $|\beta_0|$.

Ring	Fixed β , $d = 5$	Variable β , $d = 5$	Variable β , $d = 3$
R_1	-0.584	-0.322	-0.322
R_2	-0.113	-0.122	-0.132
R_3^c	-0.165	-0.048	-0.055
R_3^d	0.174	-0.061	-0.078
$R_3^{d'}$	-0.149	-0.029	-0.025

The uniform bond results are clearly unreasonable, but the bond adjusted results are well behaved. All $4n + 2$ membered rings make stabilizing contributions, as expected, but of diminishing magnitude as the size of the ring increases. If we choose the standard value -2.50 eV for the energy scale parameter β_0 and average the three types of R_3 , we can get conjugated circuit parameters which can be compared directly to the sets found in the literature, which are highly successful in correlating many chemical properties of benzenoid aromatics [4,5]. We obtain $R_1 = -0.805$ eV, $R_2 = -0.304$ eV, $R_3 = -0.115$ eV compared to Herndon's values of $R_1 = -0.841$ eV, $R_2 = -0.336$ eV, R_3 not included [4], and Randić's values of $R_1 = -0.869$ eV, $R_2 = -0.246$ eV, and $R_3 = -0.100$ eV [5]. Given the limitations of Huckel theory, this level of agreement must be considered quite satisfactory.

There is another requirement which we expect of a successful description of pi-electron energetics besides reasonable values for the R parameters, namely that there should be negligible residual energy contributions from "mixed" clusters containing both acyclic and ring portions. We examine this issue in table 4. The first two molecules, o-xyllylene and p-xyllylene, contain 6-membered rings but are not aromatic because they have only a single Kekule structure in which double bonds are not conjugated around the ring. The remaining molecules have aromatic rings and conjugated chains which are formally noninteracting. We see again that the cluster and ring parameters derived with fixed beta values do not fully account for the fixed-beta pi energies of the molecules, but those derived from the bond-adjusted calculations account almost completely for the bond-adjusted pi energies of the molecules.

In fact, the cluster expansion for the acyclic clusters with bond adjustment is so rapidly convergent that an even simpler representation of the pi energy is not unreasonable. If we truncate the expansion for the acyclics at $d = 3$ instead of $d = 5$, only two acyclic clusters remain and these are present in equal numbers in all of the Kekule structures of an aromatic. The number of occurrences of cluster 1 is just equal to the number of double bonds and the number of occurrences of cluster 2 is equal to the number of single bonds. This truncation has no effect on the computed value of R_1 but introduces small changes in the values of the other R parameters, shown in the last column of table 3, but without seriously degrading the agreement with the standard literature parameter sets. These parameters are very easy to use and, as shown in the last column of table 4, also give a reasonable description of the "mixed" molecules, although in all cases the longer expansion is more accurate.

Table 4
Residual contributions to the pi-electron energy in units of $|\beta_0|$.

Molecule	Cluster formula	Residual fixed β $d = 5$	Residual variable β $d = 5$	Residual variable β $d = 3$
o-xylylene	$4\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_3$	-0.156	-0.011	-0.012
p-xylylene	$4\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_4$	0.051	-0.007	-0.014
biphenyl	$6\varepsilon_1 + 7\varepsilon_2 + 2\varepsilon_3$ $+ 2\varepsilon_4 + \varepsilon_5 + 2R_1$	0.091	-0.011	-0.018
stilbene	$7\varepsilon_1 + 8\varepsilon_2 + 2\varepsilon_3$ $+ 3\varepsilon_4 + 2R_1$	0.107	-0.015	-0.025
styrene	$4\varepsilon_1 + 4\varepsilon_2 + \varepsilon_3$ $+ \varepsilon_4 + R_1$	0.046	-0.005	-0.009
o-divinylbenzene	$5\varepsilon_1 + 5\varepsilon_2 + 2\varepsilon_3$ $+ 5/2\varepsilon_4 + 1/2\varepsilon_5$ $+ \varepsilon_6 + R_1$	0.089	-0.009	-0.019
m-divinylbenzene	$5\varepsilon_1 + 5\varepsilon_2 + 2\varepsilon_3$ $+ 2\varepsilon_4 + R_1$	0.094	-0.010	-0.017
p-divinylbenzene	$5\varepsilon_1 + 5\varepsilon_2 + 2\varepsilon_3$ $+ 2\varepsilon_4 + R_1$	0.084	-0.012	-0.019

4. Conclusion

We find that the contributions of pi electrons to the electronic energy of conjugated molecules (at least in the absence of heteroatoms) can be accounted for in a simple and consistent way. When expressed as a graphical cluster expansion, the needed terms reproduce both the Hess and Schaad approach to conjugated acyclic chain molecules and the conjugated circuit approach to molecules composed of benzenoid aromatic rings, showing that these methods share a common underlying basis. However, this consistency can only be achieved when the pi energy is calculated by a method which takes proper account of the geometry of the molecules. In this work pi energies were evaluated by the HMO method, and the coupling to geometrical structure was introduced approximately through an empirical bond length/bond order relationship, but it is expected that the same conclusion will be reached for more sophisticated methods of computing the pi electron energy and its dependence on molecular structure. Calculations along these lines are in progress.

The results of the present work show that allowing the pi energy to adjust to the geometry strongly increases the rate of convergence of the cluster expansion of the energy, to the point that it is reasonable to describe the energy of acyclics by just two terms: a contribution from a double bond and a correction for conjugation of a pair of double bonds. Benzenoid aromatic hydrocarbons, in turn, can be described by contributions from conjugated 6-membered cycles, conjugated 10-membered cycles, and conjugated 14-membered cycles, but the contributions of the 14-cycles appear to vary somewhat with the shape of the cycle.

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