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Effect of Bond-Length Alternation on the Aromaticity of Benzene

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Dewar-de Llano PPP-SCF-MO calculations were performed to examine the effect of bond-length alternation on the σ and π frames of benzene. It was confirmed that the equalization of the CC bond lengths in benzene was caused primarily by a high degree of aromaticity. Benzene still is highly aromatic even if it is deformed artificially. Adiabatic and vertical resonance energies were defined for this compound.

There has been controversy in the literature about the origin of the symmetric structure of benzene.[1-7] Hiberty and co-workers recently provided computational evidence that the symmetric hexagonal structure of benzene is caused by the σ frame.[1-4] According to them, the π frame of benzene favors a distorted, localized structure, but this propensity is quenched by the σ frame which strongly resists distortion. They concluded that delocalization of π electrons in benzene is a by-product of a geometric constraint and that it occurs despite the opposite inherent tendency of π electrons.

Distortion of benzene requires energy. The tendency of benzene to remain symmetric and delocalized can be estimated from the energy needed to deform it. This energy may somehow be partitioned between σ and π frames. Hiberty and co-workers compared the energy of symmetric benzene with all CC bond lengths of 1.40 Å with that of distorted benzene with CC bonds of alternating lengths of 1.34 and 1.4627 Å, and showed that the σ energy is better in the symmetric structure by about 17 kcal mol^{-1}, that the π energy is worse by about 11 kcal mol^{-1}, and that overall the symmetric structure is preferred by about 6 kcal mol^{-1}.[1-4]

The length of 1.34 Å chosen by Hiberty and co-workers for shorter CC bonds in distorted benzene is similar to the length for the terminal C=C bonds in butadiene (1.344 Å) and hexatriene (1.337 Å).[1-4] However, it should be noted that all CC bonds in the alternating structure are conjugated from both sides rather than from one.[7] Baird pointed out that the argument by Hiberty and co-workers rests critically on a questionable assumption concerning the bond lengths in the alternating structure and that if more appropriate values are used, their conclusion is reversed and the traditional view that the symmetric structure is due to π electrons is recovered.[7] It is the purpose of this paper to examine arguments from both sides. We design a more realistic alternating structure for benzene, together with its polyene reference, using the Dewar-de Llano bonding model. The non-distortive propensity and aromaticity of benzene is then analyzed in terms of the heat of atomization and Dewar resonance energy.

Theory

As illustrated by Heilbronner,[6] the simple Hückel model (with variable β) may be sufficient for describing the possible propensity of a hexagonal π frame of benzene to distort to an alternating or localized structure. In this paper, the Dewar-de Llano PPP-SCF-MO model, combined with a bond order–bond length relationship,[8,9] is adopted to analyze the electronic structure of benzene and related structures. The energy of the σ frame is estimated by means of a Morse function with parameters established by them. Although this bonding model is semi-empirical in nature, it reproduces very well the experimental heats of atomization for a variety of cyclic and acyclic conjugated hydrocarbons.[8,9]

Heats of atomization and Dewar resonance energies were calculated according to the original Dewar-de Llano definitions.[8-10] As suggested by Hess and Schaad, [11] Dewar resonance energy must be evaluated as the difference between the energy of a given molecule and the energy of the polyene reference with no allowance for differences in nonbonded interactions or ring strain. Fortunately, these troublesome effects are all ignored in the present semi-empirical bonding model.[8,9]

Results and Discussion

Dewar and de Llano demonstrated that the heats of atomization of acyclic polyenes could be quantitatively interpreted in terms of the localized bond model, using a single bond-energy value for all formal C–C bonds and a single bond-energy value for all formal C=C bonds.[8-10] All C–H bonds were also assumed to have the same bond energy.[8,9] Then, the heat of atomization ΔH_a for any acyclic polyene $C_{2n}H_{2n+2}$ is accurately given by the bond-energy sum, namely,

$$\Delta H_a(C_{2n}H_{2n+2}) = n E_{C=C} + (n-1)E_{C-C} + (2n+2)E_{C-H} \quad (1)$$

Here, $E_{C=C}$, E_{C-C}, and E_{C-H} are the bond energies of the bonds indicated by the subscripts. This kind of energy additivity is reproducible by means of ab initio MO theory.[11]

Table 1. Heats of Atomization for Linear Polyenes with Alternating Bond Lengths

Number of carbon atoms	Heat of atomization/eV[a]			
	σ Component	E_X^σ	π Component	E_X^π
2	21.0064		2.3036	
		16.1411		2.6022
4	37.1475		4.9058	
		16.1475		2.6122
6	53.2950		7.5180	
		16.1494		2.6130
8	69.4444		10.1310	
		16.1498		2.6129
10	85.5942		12.7439	
		16.1499		2.6129
12	101.7441		15.3568	
		16.1500		2.6128
14	117.8941		17.9696	
		16.1500		2.6129
16	134.0441		20.5825	
		16.1499		2.6128
18	150.1940		23.1953	
		16.1500		2.6128
20	166.3440		25.8081	

a) 1 eV=23.060 kcal mol^{-1}=96.484 kJ mol^{-1}.

We calculated heats of atomization for linear polyenes with up to ten C=C bonds (Table 1). Within the framework of the Dewar-de Llano bonding model,[8,9] $\Delta H_a(C_{2n}H_{2n+2})$ can be partitioned exactly between the σ and π frames in the molecule. Contributions of the σ and π frames to ΔH_a will be referred to simply as the σ and π energies, respectively. As the number of carbon atoms is increased by two in the linear polyene series, a -CH=CH- unit (X) is added to the chain. The increments of the σ and π energies due to one additional -CH=CH- unit are denoted by E_X^σ and E_X^π, respectively. It is clear from Table 1 that except for some small polyenes, energy additivity is satisfactory. E_X^σ and E_X^π are almost constant for larger polyenes, i.e.,

$$E_X^\sigma = E_{C=C}^\sigma + E_{C-C}^\sigma + 2E_{C-H} = 16.1500\,\text{eV}, \quad (2)$$

$$E_X^\pi = E_{C=C}^\pi + E_{C-C}^\pi = 2.6128\,\text{eV}. \quad (3)$$

Here, superscripts σ and π stand for the σ and π components of the bond energy, respectively. The overall contribution of X to the heat of atomization of the entire polyene is given as a sum of E_X^σ and E_X^π, namely,

$$E(X) = E_X^\sigma + E_X^\pi = 18.7628\,\text{eV}. \quad (4)$$

We now begin to analyze the energy of benzene. This compound is known to be highly aromatic with a large Dewar resonance energy.[7-10] If benzene loses its entire aromaticity, CC bond lengths in it must be changed to those in nonaromatic linear polyenes and the alternating hexagonal structure results. Structure

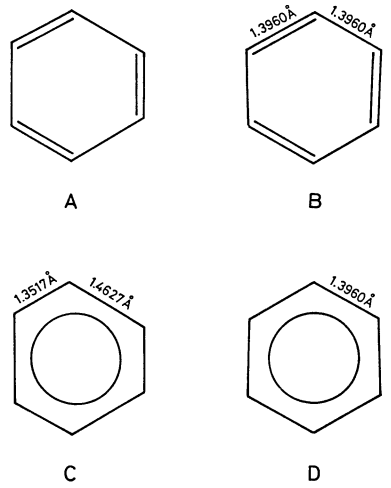

Fig. 1. Benzene and related structures. Alternating polyene-like structure (A), symmetric polyene-like structure (B), distorted aromatic benzene (C), and symmetric aromatic benzene (D).

A in Fig. 1 represents such a polyene-like cyclic structure for benzene. This hypothetical structure was constructed by connecting three olefinic -CH=CH- units in a cyclic manner. However, six π electrons in it must have no freedom of cyclic conjugation. The heat of atomization of this alternating structure is naturally equal to three times the energy given in Eq. 4, namely,

$$\Delta H_a(A) = 3\,E(X) = 55.9032\,\text{eV}. \quad (5)$$

The σ and π components of $\Delta H_a(A)$ are listed in Table 2. Note that the lengths of individual CC bonds in structure A were not given explicitly from the above

Table 2. Heats of Atomization for Benzene and Related Structures

Structure	Heat of atomization/eV[a]		
	σ Component	π Component	Total
A (Polyene-like)	48.4500	7.8384	56.2884
B (Polyene-like)	48.6543	7.2489	55.9032
C (Aromatic)	48.4501	8.5300	56.9801
D (Aromatic)	48.6544	8.5028	57.1571

a) See footnote a in Table 1.

Table 3. Energy Changes Caused by Deformation and/or Aromatization of Some C_6H_6 Species

Structural change	Energy change/kcal mol^{-1}[a]		
	σ Component	π Component	Total
A→B	+4.71	−13.59	−8.88
B→D	0	+28.92	+28.92
A→C	0	+15.95	+15.95
C→D	+4.71	−0.63	+4.08
A→D	+4.71	+15.32	+20.03

a) 1 kcal=4.184 kJ.

discussion.

The bond order-bond length relationship in the Dewar-de Llano bonding model sets all CC bond lengths in aromatic benzene equal to 1.396 Å, which is very close to the best experimental value (1.3965 Å).[12] Benzene with this geometry is denoted by D in Fig. 1. Dewar resonance energy of benzene (20.03 kcal mol^{-1}) represents the energy by which this molecule (D) is more stable than its olefinic reference structure (A) or the sum of the stabilization energy of the σ frame (4.71 kcal mol^{-1}) due to the release from distortion and that of the π frame (15.32 kcal mol^{-1}) due mainly to aromatization. It corresponds to the energy change caused by the structural change A→D in Table 3. It is noteworthy that both the σ and π frames of structure A are stabilized in aromatic benzene.

What lengths can realistically be assigned to the C=C and C–C bonds in structure A ? We inspected many optimized CC bond lengths in long polyenes, and chose 1.4627 Å and 1.3517 Å as the representative lengths of polyene C–C and C=C bonds, respectively. In so doing, a couple of CC bonds near both ends of every polyene were disregarded. Interior CC bonds in linear polyenes must resemble the CC bonds in the nonaromatic alternating structure for benzene, in the sense that they are conjugated from both sides. Consequently, the C=C bond length chosen by us (1.3517 Å) is appreciably larger than that chosen by Hiberty and co-workers (1.34 Å).[1–4] It seems very likely that the longer and shorter CC bond lengths in structure A are close to 1.4627 Å and 1.3517 Å, respectively. In fact, the last digits in these bond lengths were determined somewhat arbitrarily, in such a manner that the constructed alternating structure gives the same σ energy as structure A. Interestingly, our C–C bond length (1.4627 Å) coincides with the value chosen by Hiberty and co-workers.[1–4]

Next, ler us imagine distorted benzene in which longer and shorter CC bond lengths are 1.4627 and 1.3517 Å, respectively. If six π electrons retain a freedom of cyclic conjugation, this alternating structure still must be aromatic. This deformed structure of aromatic benzene is denoted by C in Fig. 1. The heat of atomization for this distorted aromatic benzene was evaluated by applying the Dewar-de Llano bonding model to the fixed geometry of the alternating structure. The obtained σ and π components of the heat of atomization are given in Table 2.

Deformation of aromatic benzene reduces the thermodynamic stability by 4.08 kcal mol^{-1}, which is primarily attributable to the destabilization of the σ frame. Deformation of benzene corresponds to the reverse of the structural change C→D in Table 3. The π frame of benzene is seen to have a faint propensity to distort. Thus, the conclusion drawn by Hiberty and co-workers[1–4] that the delocalization of π electrons is a by-product of a geometric constraint was marginally confirmed. Dewar resonance energy of deformed benzene (C) is given as an energy difference between it and structure A, which amounts to 15.95 kcal mol^{-1}. Deformed benzene retains 80 percent of the resonance energy of symmetric benzene. As emphasized by Baird,[7] the aromaticity of benzene is slightly damped, rather than destroyed completely, when it is forced to adopt CC bond lengths appropriate to polyenes.

We then estimate the heat of atomization for hypothetically nonaromatic non-distorted benzene or symmetric polyene-like 1,3,5-cyclohexatriene (structure B in Fig. 1). For this purpose, it is necessary to evaluate heats of atomization for a series of linear polyenes with all CC bond lengths fixed at 1.396 Å. Dewar-de Llano MO calculations were carried out for

Table 4. Heats of Atomization for Linear Polyenes with Uniform CC Bond Lengths

Number of carbon atoms	Heat of atomization/kcal mol^{-1}[a)]			
	σ Component	E_Y^σ	π Component	E_Y^π
2	21.4216		1.8005	
		16.2181		2.3715
4	37.6397		4.1720	
		16.2181		2.4056
6	53.8578		6.5776	
		16.2181		2.4130
8	70.0759		8.9906	
		16.2181		2.4153
10	86.2940		11.4059	
		16.2181		2.4159
12	102.5122		13.8218	
		16.2181		2.4163
14	118.7303		16.2381	
		16.2181		2.4163
16	134.9484		18.6544	
		16.2181		2.4163
18	151.1665		21.0707	
		16.2181		2.4163
20	167.3846		23.4870	

a) See footnote a in Table 1.

linear polyenes whose CC bond lengths are all equal to those in real benzene. The results of calculations are listed in Table 4. These hypothetical polyenes are again very additive in energy The increments of the σ and π energies due to one additional -CH=CH- unit are, respectively,

$$E_Y^\sigma = \bar{E}_{C=C}^\sigma + \bar{E}_{C-C}^\sigma + 2E_{C-H} = 16.2181 \text{ eV}, \quad (6)$$

$$E_Y^\pi = \bar{E}_{C=C}^\pi + \bar{E}_{C-C}^\pi = 2.4163 \text{ eV}. \quad (7)$$

Here, Y denotes the -CH=CH- unit in polyenes with equal CC bond lengths; the bar over letter E refers to such polyenes. Then, the overall contribution of Y to the heat of atomization of the entire polyene is

$$E(Y) = E_Y^\sigma + E_Y^\pi = 18.6344 \text{ eV}. \quad (8)$$

Structure B can be constructed by connecting three such -CH=CH- units in a cyclic manner. It must have a heat of atomization given by

$$\Delta H_a(B) = 3\,E(Y) = 55.9032 \text{ eV}. \quad (9)$$

Both structures A and B are polyene-like or nonaromatic by definition. As shown in Table 3, the heat of atomization decreases by 8.88 kcal mol^{-1} on going from A to B. Of the two structures, A has a less stable σ frame and a much more stable π frame. The π energy of structure A is better by 13.59 kcal mol^{-1} than that of structure B. Thus, a polyene-like π frame tends to alternate CC bond lengths. This must be exactly what Hiberty and co-workers wanted to say.[1-4] Paldus and Chin previously noted that for the polyenic systems, the σ energy will oppose the tendency of π electrons to dissipate.[13] As mentioned above, the π frame of benzene (D) is better than that of structure A by 15.32 kcal mol^{-1}. This energy difference represents the sum of the destabilization energy due to symmetrization of the π frame (−13.59 kcal mol^{-1}) and the stabilization energy of the π frame due to aromaticity (+28.92 kcal mol^{-1}).

In principle, there are two types of resonance energies or stabilization energies due to aromaticity. They are adiabatic and vertical ones. Dewar resonance energy is a kind of adiabatic resonance energy, which is defined using the energies of the molecule and the olefinic reference in its optimized geometry.[8,9] Adiabatic resonance energy necessarily consists of contributions not only from the π but also from the σ frame. As has been seen above, when adiabatic resonance energy is sufficiently large, bond-length alternation is not favorable to the molecule. This is the reason why there is no severe bond-length alternation in aromatic molecules.

Vertical resonance energy is defined as a stabilization energy of a given molecule relative to the polyene reference having the same geometry. Within the present bonding model, vertical resonance energy is totally ascribed to the resonance stabilization of the π frame. For example, vertical resonance energy of symmetric benzene (d) is 28.9 kcal mol^{-1}. In this case, the symmetric polyene structure (B) represent the reference structure. Vertical resonance energy of deformed benzene (C) is 15.95 kcal mol^{-1}, which is an energy difference berween structures C and A, both having the same geometry (Table 3). Vertical

Table 5. Comparative MO Study of the Distortion Energy of Benzene

MO model	Distortion energy[a]/kcal mol^{-1}[b]		
	σ Component	π Component	Total
Dewar-de Llano[c]	+14.6	−9.4	+5.2
STO-3G[d]	+17.1	−11.9	+5.2
6-31G[d]	+16.3	−9.7	+6.6

a) Energy change due to the distortion of benzene with all CC bond lengths chosen as 1.40 Å to a structure with CC bonds of alternating lengths of 1.34 and 1.4627 Å. This way of structural change was adopted by Hiberty and co-workers.[1-4] The positive value of distortion energy represents reluctance to distort. b) See footnote a in Table 3. c) Refs. 8 and 9. d) ab initio MO theory; see Refs. 1—4.

resonance energy of benzene is reduced to 55 percent by the introduction of bond-length alternation. Both Hess-Schaad resonance energy[14] and topological resonance energy [15,16] are kinds of vertical resonance energies.

We have seen in Table 2 that the π energy of symmetric aromatic benzene (D) is really comparable to that of deformed aromatic benzene (C). This phenomenon can be interpreted as follows. As shown in Table 3, the π energy of the symmetric polyene-like species (B) is worse by 13.59 kcal mol^{-1} than that of the deformed polyene-like structure (A). On the other hand, the vertical Dewar resonance energy of symetric benzene (D) is larger by 12.97 kcal mol^{-1} than that of deformed benzene (C). It is worth remarking that both symmetric and deformed benzene molecules have essentially the same π energy. This is because the increase in π energy due to bond-length alternaton almost cancels the decrease in π energy due to diminished aromaticity.

Concluding Remarks

Realistic geometries were presented for the alternating structure of benzene and related structures. We caluculated the energy of symmetric benzene (D) with all CC bond lengths of 1.3960 Å and that of distroted benzene (C) with CC bonds of alternating lengths of 1.3517 and 1.4627 Å, and showed that the σ energy is better in the symmetric structure by 4.71 kcal mol^{-1}, that the π energy is worse by 0.63 kcal mol^{-1}, and that overall the symmetric structure is preferred by 4.08 kcal mol^{-1}. It is true that the π frame of benzene would have a faint propensity to distort without the buttressing effect of the σ frame.[1-4] However, this does not contradict with Baird's conclusion that the main symmetrizing force in benzene originates from the π frame.[7]

Note again that real benzene with a full Dewar resonance energy is symmetric in shape, whereas the polyene reference with no Dewar resonance energy takes an alternating structure. As shown in Table 3, the π frame contributes much more to the Dewar resonance energy than the σ frame. Therefore, benzene would have taken an alternating structure if its Dewar resonance energy were smaller by a certain amount than it is. In this sense, we might say that the regular geometry and special stability of benzene are due primarily to π electrons, which tend to cluster in a symmetric arrangement to form a so-called aromatic sextet.

Finally, one comment must be made on the validity of the Dewar-de Llano bonding model. As can be seen from Table 5, this model reproduced very well the distortion energy of benzene calculated using the ab initio bonding model[7] within an accuracy of a few kcal mol^{-1}. Definitions of the σ and π energies in the former model are different from those in the latter one. Therefore, the σ and π energies reported in this paper cannot be compared directly with those reported by Hiberty and co-workers,[1-4] but the differences in σ and π energy between two related structures can be compared very well. It is the Dewar-de Llano bonding model that Baird used with confidence to discuss the effect of bond-length alternation on benzene.[7]

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