

STRUCTURE OF THE BENZENE MOLECULE ON THE BASIS OF THE THREE-ELECTRON BOND.

Bezverkhniy Volodymyr Dmytrovych.

Ukraine, E-mail: bezvold@ukr.net

Abstract: Using the concept of three-electron bond one can represent the actual electron structure of benzene, explain specificity of the aromatic bond and calculate the delocalization energy. It was shown, that functional relation $y = a + b/x + c/x^2$ fully describes dependence of energy and multiplicity of chemical bond on bond distance. In this article carbon-to-carbon bonds are reviewed. Using these dependences it is possible to calculate chemical bond energy by different bond distance or different multiplicity of chemical bond, that makes possible to calculate delocalization energy of benzene molecule.

Keywords: three-electron bond, interaction through the cycle, spin, delocalization energy, bond energy, bond multiplicity.

INTRODUCTION

Chemical bond has been always a basis of chemistry. Advancement of chemical science can be considered as evolution, development of concepts about chemical bond. Aromatic bond is fundamental basis of organic chemistry. Concept of three-electron bond in benzene molecule enable to explain specificity of aromatic bond. It also becomes apparent, why planar molecules with 6, 10 etc. electrons (according to Hückel rule $4n + 2$) must be aromatic, and planar molecules with 4, 8 etc. electrons cannot be aromatic by definition.

Description of chemical bond, that is given by quantum theory, especially in terms of method of molecular orbitals, is just a mathematical model. This model is an approximate representation of molecules and its bonds, whereas quantum-mechanical calculations of organic molecules require considerable simplifications and are extremely complicated.

Concept of three-electron bond and developed mathematical relations in this work are rather simple, illustrative and give exact results of different values (bond multiplicity, chemical bond energy, delocalization energy of benzene). One must clearly imagine, that three-electron bond is joint interaction of three electrons with relative spins, that results in

new type of chemical bond ($\overset{\uparrow\downarrow\uparrow}{A \bullet \bullet \bullet A}, \overset{\uparrow\downarrow\uparrow}{A \bullet \bullet \bullet B}$). This bond type, three-electron bond, makes possible to describe real molecules of organic and inorganic compounds without invoking virtual structures, which do not exist in real terms.

Using of three-electron bond before description of benzene molecule enables to determine delocalization energy of benzene in an elementary way, understand why multiplicity of C-C bond of benzene is more than 1.5 and to understand the main point of aromatic bond in general, which is appeared to be rather illustrative. Besides, for determination of delocalization energy it is not required to select reference structures. Delocalization energy follows from the concept of aromaticity of benzene and its structure on the basis of three-electron bond.

RESULTS AND DISCUSSION

Supposing that the chemical bond between two atoms can be established by means of three electrons with oppositely oriented spins ($\uparrow\downarrow\uparrow$) the structure of the benzene molecule can be expressed as follows (see figure 1 and figure 2):

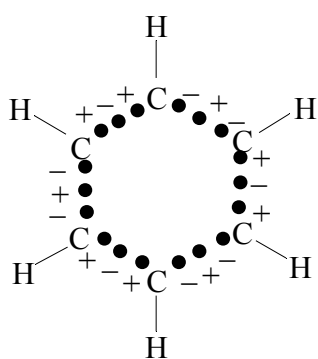


figure 1

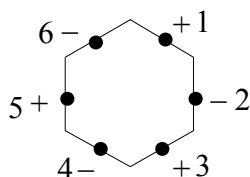
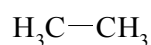


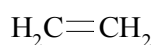
figure 2

"+" - upward spin
 "-" - downward spin

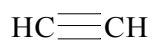
It is interesting to point out that spins of central electrons on opposite sides have an opposite orientation (see figure 2). Now let us consider in detail the interaction of six central electrons between themselves. They will be itemized as shown in figure 2. As the spin of electron 1 and those of electrons 2 and 6 are oppositely oriented (see figure 2) (1 (+), 2 (-), 6 (-)), electron 1 will be attracted to electrons 2 and 6 respectively. Let's indicate that the distance between electrons 1 and 6 or 1 and 2 is equal to 1.210 \AA which can be easily shown taking into account the distance between atoms of carbon in benzene to be 1.397 \AA and the angle between carbon atoms amount to 120 degrees. Let us compare the distance between electrons 1 and 6 and 1 and 2 bond lengths in ethane, ethylene and acetylene [1]:



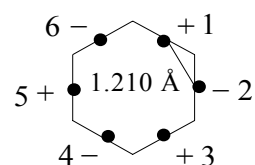
$$L_{\text{C}-\text{C}} = 1.543 \text{ \AA}$$



$$L_{\text{C}=\text{C}} = 1.338 \text{ \AA}$$



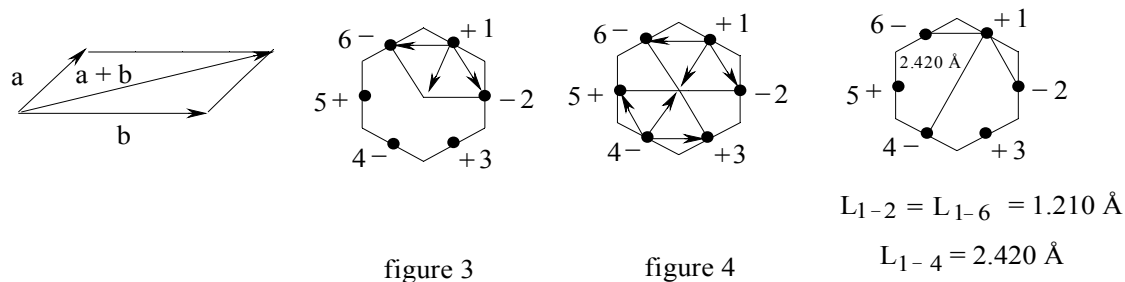
$$L_{\text{C}\equiv\text{C}} = 1.205 \text{ \AA}$$



$$L_{1-2} = 1.210 \text{ \AA}$$

As we observe, the distance between central electrons 1 and 2 and 1 and 6 of the benzene molecule is approximately equal to that between carbon atoms in the acetylene

molecule, therefore, the interaction between electrons 1 (+) and 2 (-) and 1 (+) and 6 (-) has to be rather considerable. Let us express the attraction with arrows. According to summing up vectors the resultant vector will be directed to the centre, which means that electron 1 under the influence of electrons 2 and 6 will move to the centre (figure 3):



If we take a look at electron 4 we see the similar situation with it (figure 4) and it will also move to the centre and, more importantly, its spin and that of electron 1 will be oppositely oriented, i.e. electron 1 (+) and electron 4 (-) will be attracted through the cycle. Electrons 6 (-) and 3 (+) and electrons 2 (-) and 5 (+) will interact similarly. The distance between electrons 1 and 4 in benzene is equal to 2.420 Å. It is interesting, that this distance is twice as much than distance between electrons 1 and 2, or between electrons 1 and 6 ($1.210 \text{ \AA} \cdot 2 = 2.420 \text{ \AA}$). This interaction through the cycle constitutes the essence of the delocalization of electrons, of course together with a three-electron bond. Since besides the three-electron bond in the benzene molecule there is an interaction through the cycle, meaning that the benzene nucleus undergoes a kind of compression it is clear that the c-c bond multiplicity in benzene will exceed 1.5.

So, the aromatic system is a cyclic system with three-electron bonds where an interaction of central electrons through the cycle is observed. In the benzene molecule there are three interactions through the cycle-pairwise between electrons 1 (+) and 4 (-),

2 (-) and 5 (+), 3 (+) and 6 (-), as shown in figure 5:

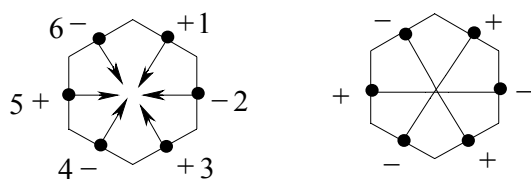
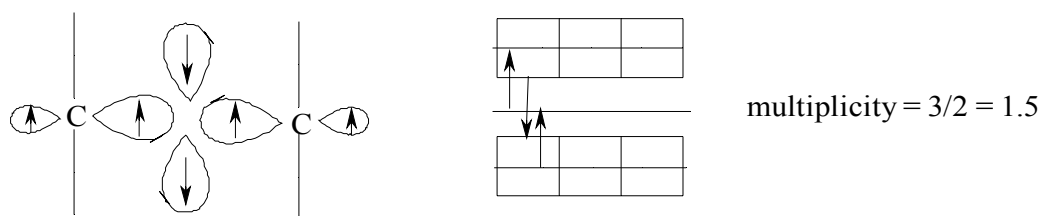
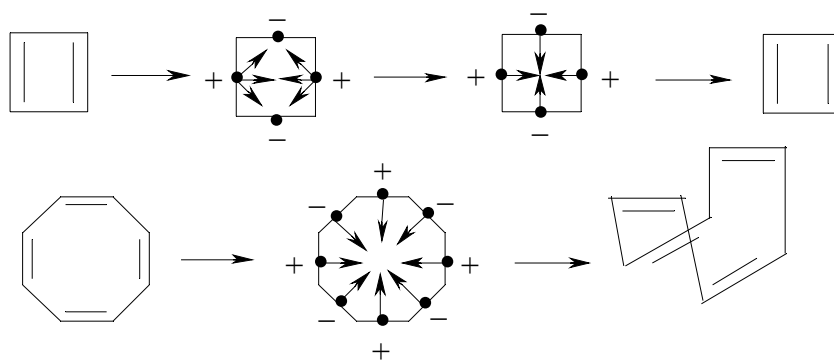


figure 5

Carbon atoms in benzene are sp^2 -hybridized. The three-electron bond between carbon atoms in the benzene molecule can be represented as follows:

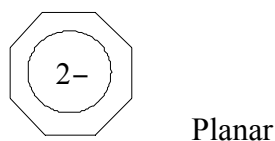


Carbon atoms in benzene have an octet equal to $8 (3 + 3 + 2 = 8)$. It should be pointed out that due to the largest distance from the atoms nuclei the central electrons of the three-electron bond are supposed to be the most mobile compared to other electrons of the three-electron bond. The interaction of central electrons with opposite spins through the cycle can easily explain why cyclobutadiene and cyclooctatetraene are not aromatic compounds:



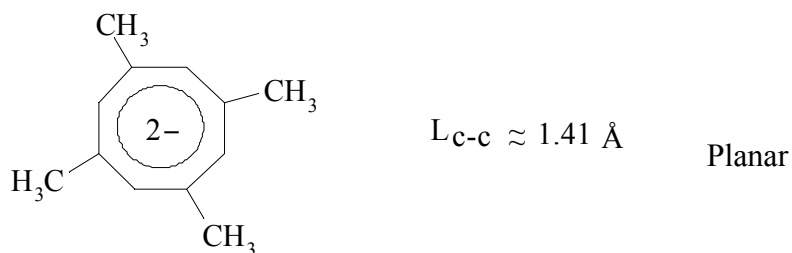
As we see both in cyclobutadiene and cyclooctatetraene, electrons interacting through the cycle have the same spins and, clearly, will be repulsed, therefore there will be no interaction through the cycle and the molecule will not be aromatic. In cyclobutadiene at the expense of small distance it causes the appearance of antiaromatic properties, and in cyclooctatetraene there is a possibility of formation of non-planar molecule, where interaction of central electrons becomes impossible and molecule losing the interaction through the cycle loses also three-electron bonds, that results in a structure, in which single and double bonds alternate.

Explanation, that cyclooctatetraene is non-aromatic, because it is non-planar and does not hold water, insomuch as dianion of cyclooctatetraene is aromatic and has planar structure [2], [3].



X-ray crystal structure analysis determined crystal structure of potassium salt of dianion 1,3,5,7-tetramethylcyclooctatetraene [4], [5].

Octatomic cycle is planar with lengths of C-C bonds nearly 1.41 Å.

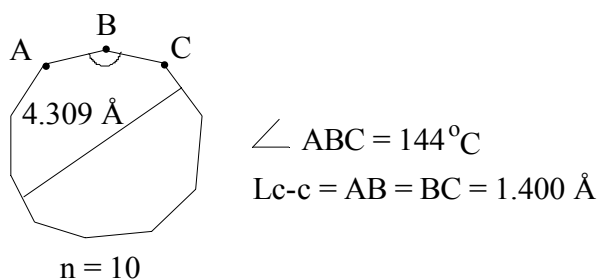
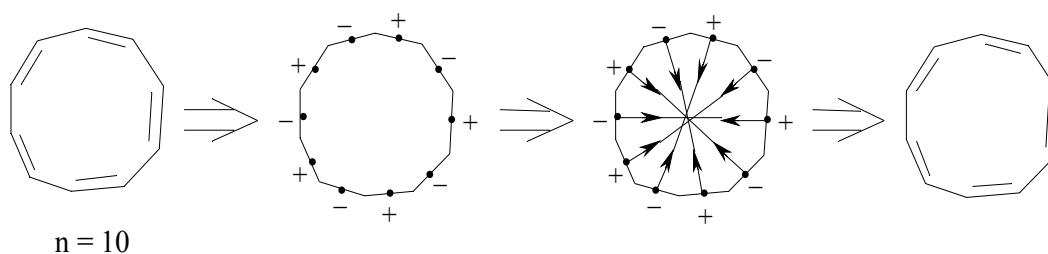


From the mentioned above we can make a conclusion: cyclooctatetraene conforms to the

shape of bath tub not because of high angular pressure (15°) at planar structure, but because by interaction through the cycle central electrons of three-electron bonds have equal spin and will push away. Thus for energy reduction cyclooctatetraene conforms to the shape of bath tub and becomes non-planar, that disables interaction of central electrons.

Cyclobutadiene represents rectangular high reactivity diene [2, p.79].

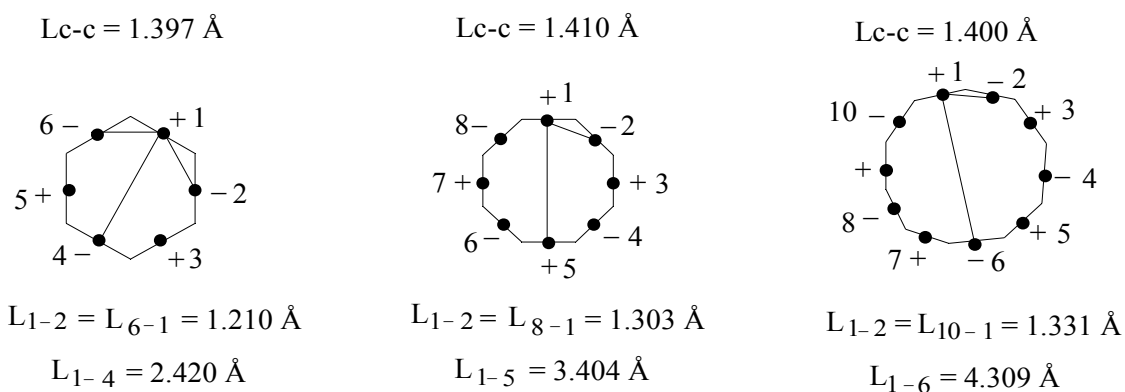
It is also interesting to observe cyclodecapentaene (cis-isomer [10]-annulene).



Whereas central electrons of three-electron bonds have opposite spins, then interaction through the cycle is possible. But distances between central electrons on opposite sides, which interact through the cycle, are extremely long (4.309 \AA if accept $L_{c-c} = 1.400 \text{ \AA}$ for regular decagon), angular pressure is high (24°) and that's why stabilization at the expense of interaction through the cycle at such long distance will be low and cannot cover energy consumption for creation of planar molecule.

Cyclodecapentaene was received in the form of crystalline substance at -80°C . On spectrums $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ it was determined, that compound is non-planar and is olefin, that is logical on the basis of long distance between central electrons [2, p.84], [6].

Lets draw our attention to the fact that in going from benzene to cyclooctatetraene and to cyclodecapentaene distance increases not only between central electrons on the opposite sides (interaction through the cycle), but also between neighboring central electrons. Lets show it on figure.



As we can see distance between neighboring central electrons 1 and 2 in benzene makes up 1.210 \AA , in regular octagon 1.303 \AA , and in regular decagon 1.331 \AA (almost as distance between carbon atoms in ethene molecule). That is by going from benzene to regular octagon and decagon not only angular pressure (0° , 15° , 24°) and distance between central electrons increase, which are situated on the opposite sides (2.420 \AA ; 3.404 \AA ; 4.309 \AA), as well as distance between neighboring central electrons 1 and 2 (1.210 \AA ; 1.303 \AA ; 1.331 \AA), that causes considerable weakening of interaction through the cycle in regular decagon. That's why regular hexagon (benzene) is ideal aromatic system. As angular pressure is equal to zero, distances between central electrons both neighboring and situated on the opposite sides are minimal (accordingly 1.210 \AA and 2.420 \AA). I.e.

interaction through the cycle will be maximal. By going to regular decagon these advantages will be lost. That's why cyclodecapentaene is olefin.

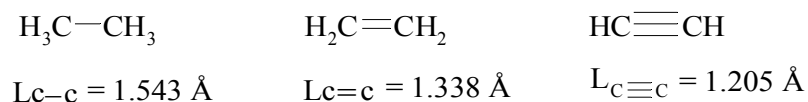
Let us note for comparison that if we take $L_{c-c} = 1.400 \text{ \AA}$ for the planar cyclooctatetraen, we will have $L(1-5) = 3.380 \text{ \AA}$, $L(1-2) = L(8-1) = 1.293 \text{ \AA}$ which vary just slightly from the above mentioned distances between the central electrons at $L_{c-c} = 1.410 \text{ \AA}$.

By means of the interaction through the cycle together with the three-electron bond, three aromaticity of coronen, [18]-annulene, naphthalene and other organic substances can be explained (see conclusion).

Now let's pass to the definition of delocalization energy of benzene. It is easy to show, that relation $\text{multiplicity} = f(L)$ and $E = f(L)$, where multiplicity is multiplicity of bond, L – length of bond in \AA , E – energy of bond in kJ/mole will be described by function $y = a + b/x + c/x^2$ for any types of bond (C-C, C-N, C-O, C-S, N-N, N-O, O-O, C-P).

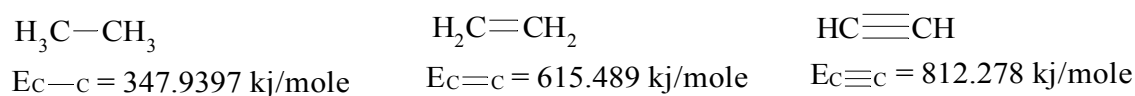
We shall consider ethane, ethylene and acetylene to be initial points for the c-c bond.

For lengths of bonds let us take the data [1]:



As usual, the C-C bond multiplicity in ethane, ethylene and acetylene is taken for 1, 2, 3.

For energies of bonds let us take the data [1, p.116]:



The given bond energies (according to L. Pauling) are bond energy constants expressing the energy that would be spent for an ideal rupture of these bonds without any further rebuilding of the resulting fragments. That is, the above mentioned energies are not bond dissociation energies.

Having performed all necessary calculations we obtain the equation:

$$c-c \text{ bond multiplicity} = -0.06040343 - \frac{5.67787529}{L} + \frac{11.28562201}{L^2} \quad (1)$$

$$E \text{ of } c-c \text{ bonds} = -2221.34518418 + \frac{5065.62912191}{L} - \frac{1699.18638789}{L^2} \quad (2)$$

From these equations we find:

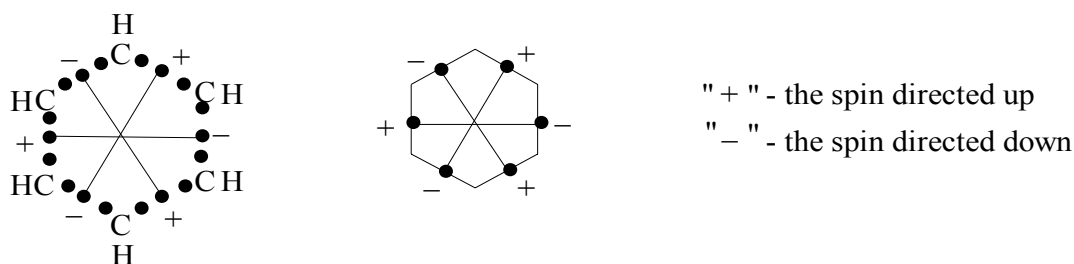
$$c-c \text{ benzene multiplicity } (L = 1.397 \text{ \AA}) = 1.658$$

$$c-c \text{ graphite multiplicity } (L = 1.42 \text{ \AA}) = 1.538 \approx 1.54$$

$$E_{c-c} \text{ benzene } (L = 1.397 \text{ \AA}) = 534.0723 \text{ kJ/mole}$$

$$E_{c-c} \text{ graphite } (L = 1.42 \text{ \AA}) = 503.3161 \text{ kJ/mole}$$

Being aware that the benzene has the three-electron bonds and also the interaction through the cycle, we can calculate the interaction through the cycle energy.



For this purpose we have to determine the energy of the “clean” three-electron bond, that is of the bond with a 1.5 multiplicity and to do that we shall solve the equation:

$$1.5 = -0.06040343 - \frac{5.67787529}{L} + \frac{11.28562201}{L^2} \quad (3)$$

from the equation we find $L = 1.42757236 \text{ \AA}$.

So, if the benzene molecule had a “clean” three-electron bond with a 1.5 multiplicity the c-c bond length would be $L = 1.42757236 \text{ \AA}$.

Now let us determine the energy of the “clean” three-electron bond with a 1.5 multiplicity knowing its length $L = 1.42757236 \text{ \AA}$:

$$E_{c-c} (L = 1.42757236 \text{ \AA}) = - 2221.34518418 + \frac{5065.62912191}{1.42757236} - \frac{1699.18638789}{(1.42757236)^2}$$

$$E_{c-c} (L=1.42757236 \text{ \AA}) = 493.3097 \text{ kJ/mole}$$

Taking into account that the benzene c-c bond energy with a 1.658 multiplicity is equal to $E_{c-c} \text{ benzene} = 534.0723 \text{ kJ/mole}$, the difference will make:

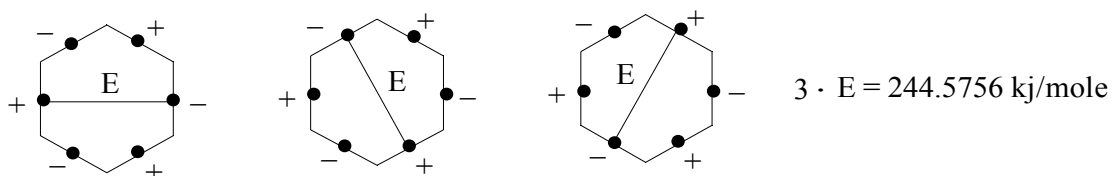
$$\Delta E = 534.0723 \text{ kJ/mole} - 493.3097 \text{ kJ/mole} = 40.7626 \text{ kJ/mole}.$$

40.7626 kJ/mole is the energy of interaction through the cycle per one c-c bond. Therefore, the energy of interaction through the cycle will be two times higher:

$$E_1 = 40.7626 \text{ kJ/mole} \cdot 2 = 81.5252 \text{ kJ/mole} (19.472 \text{ kcal/mole})$$

It is clear that the three interactions through the cycle present precisely the working benzene delocalization energy which is:

$$E = 3E_1 = 3 \cdot 81.5252 \text{ kJ/mole} = 244.5756 \text{ kJ/mole} (58.416 \text{ kcal/mole})$$



It is also possible to calculate the benzene molecule energy gain in comparison with the curved cyclohexatriene (let us assume that energy of C-H bonds in these molecules is similar). For this we calculate the sum of energies of single and double c-c bonds in cyclohexatriene:

$$E_2 = 3E_{c-c} + 3E_{c=c} = 2890.286 \text{ kJ/mole}$$

The energy of six benzene c-c bonds with a 1.658 multiplicity is equal to:

$$E_3 = 6 \cdot 534.0723 \text{ kJ/mole} = 3204.434 \text{ kJ/mole}$$

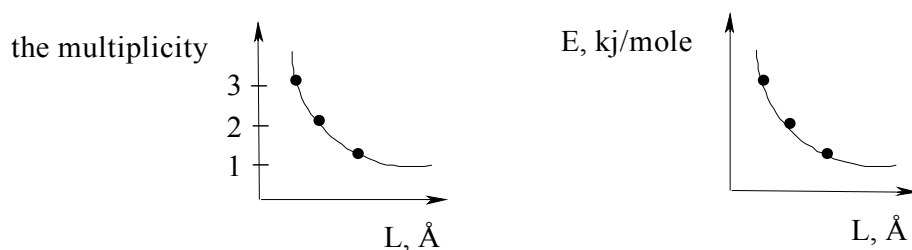
Therefore, the gain energy of benzene compared to cyclohexatriene will amount to:

$$E = E_3 - E_2 = 3204.434 \text{ kJ/mole} - 2890.286 \text{ kJ/mole} = 314.148 \text{ kJ/mole}$$

(75.033 kcal/mole)

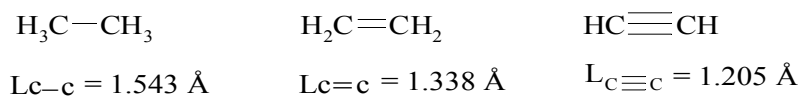
EXPERIMENTAL

Let's show more detailed calculation of ratios for our mathematical relations. Let's consider relation Multiplicity = $f(L)$ and $E = f(L)$ for C-C bonds, where multiplicity is multiplicity of bond, L – length of bond in Å, E – energy of bond in kJ/mole.



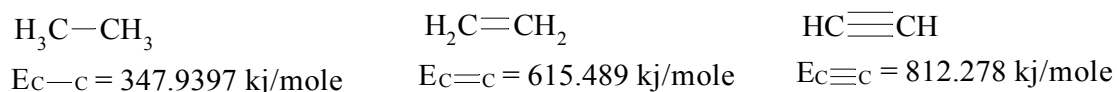
As initial points for the given bonds we will use ethane, ethene and acetylene.

For the length of bonds let us take the findings [1]:



As usual, the C-C bond multiplicity in ethane, ethylene and acetylene is taken for 1, 2, 3.

For the energy of bonds let us take the findings [1, p.116]:



If we have two variants and we received the set of points and we marked them on the plane in the rectangular system of coordinates and if the present points describe the line equation $y = ax + b$ that for choose the coefficients a and b with the least medium-quadratic deflection from the experimental points, it is needed to calculate the coefficients a and b by the formulas:

$$a = \frac{(\sum (x \cdot y) - (\sum x \cdot \sum y) / n)}{(\sum x^2 - (\sum x)^2 / n)} \quad (4)$$

$$b = (\sum y) / n - a (\sum x) / n \quad (5)$$

n -the number of given values x or y .

If we want to know how big is the derivative, it is necessary to state the value of agreement between calculated and evaluated values y characterized by the quantity:

$$r^2 = \frac{[\sum (x \cdot y) - (\sum x \cdot \sum y) / n]^2}{([\sum x^2 - (\sum x)^2 / n][\sum y^2 - (\sum y)^2 / n])} \quad (6)$$

The proximity of r^2 to one means that our linear regression coordinates well with experimental points.

Let us find by the method of selection the function $y = a + b/x + c/x^2$ describing the dependence multiplicity = $f(L)$ and $E = f(L)$ in best way, in general this function describes this dependence for any chemical bonds.

Let us make some transformations for the function $y = a + b/x + c/x^2$, we accept

$$X = 1/x,$$

$$Y = \frac{(y - y_1)}{(1/x - 1/x_1)}, \quad b_1 = b + c/x_1, \quad \text{than we'll receive: } Y = b_1 + cX, \quad \text{that is the simple line}$$

equality, than

$$c = \frac{(\sum (1/x \cdot Y) - (\sum (1/x) \cdot \sum Y)/n)}{((\sum 1/x^2) - (\sum (1/x))^2/n)} \quad (7)$$

$$b_1 = (\sum Y)/n - c(\sum (1/x))/n \quad (8)$$

n—the number of given value Y.

$$\text{Let us find a from the equality: } \sum y = na + b\sum(1/x) + c\sum(1/x^2), \quad (9)$$

when n = 3.

Let us find now multiplicity = f(L) for C–C, C=C, C≡C.

Table 1. Calculation of ratios for relation Multiplicity = f(L).

	1/x	1/x ²	$\frac{(y-y_1)}{(1/x-1/x_1)}$	$\frac{((1/x)(y-y_1))}{(1/x-1/x_1)}$	x (L, Å)	y (multiplicity)
					1.543	1
	0.74738416	0.55858308	10.07089756	7.52682927	1.338	2
	0.82987552	0.68869338	11.00186391	9.13017751	1.205	3
Σ	1.57725967	1.24727645	21.07276147	16.65700678	4.086	6

$$1/x_1 = 0.64808814 \quad x_1 = 1.543 \quad y_1 = 1$$

$$\Sigma(1/x^2) = 1.66729469 \quad \Sigma(1/x) = 2.22534781 \quad \text{when } n = 3$$

$$c = 11.28562201 \quad b = -5.67787529 \quad a = -0.06040343$$

$$\text{Therefore the multiplicity of c-c bonds} = -0.06040343 - \frac{5.67787529}{L} + \frac{11.28562201}{L^2} \quad (1)$$

Let us find from the equation:

Multiplicity C–C (ethane) = 1. Multiplicity C=C (ethylene) = 2.

Multiplicity C≡C (acetylene) = 3.

Multiplicity C–C (graphite) (L = 1.42 Å) = 1.538 ≈ 1.54.

Multiplicity C–C (benzene) ($L = 1.397 \text{ \AA}$) = 1.658

As we can see the multiplicity C–C of benzene bond is 1.658 it is near the bond order of 1.667 calculated by the method MO [2, p.48].

It should be noted that the a, b, c coefficients for this $y = a + b/x + c/x^2$ function in case of using three pairs of points (x_1, y_1) , (x_2, y_2) i (x_3, y_3) are defined explicitly; actually, they (the coefficients) are assigned to these points. In that way we find these coefficients for working further with the equation. For making certain that this dependence $y = a + b/x + c/x^2$ describes well the Multiplicity = $f(L)$ and $E = f(L)$ functions it will take only to perform correlation for four or more points. For example, for the dependence Multiplicity = $f(L)$ for C–C bonds we should add a fourth point ($L_{c-c} = 1.397 \text{ \AA}$, Multiplicity = 1.667) and obtain an equation with $r^2 = 0.9923$ and the coefficients $a = -0.55031721$, $b = -4.31859233$, $c = 10.35465915$. As it is difficult, due to objective reason, to define four or more points for the Multiplicity = $f(L)$ and $E = f(L)$ equations for a separate bond type, we will find the a, b, c coefficients using three points (as a rule they are the data for single, double and triple bonds). The dependences obtained in such a way give good results as regards the bond multiplicity and energies.

We'll find the dependence $E = f(L)$ for the C–C bonds

$$y = a + b/x + c/x^2 \quad X = 1/x \quad Y = \frac{(y - y_1)}{(1/x - 1/x_1)}$$

$$b_1 = b + c/x_1 \quad Y = b_1 + cX$$

As usual:

$$c = \frac{(\sum (1/x \cdot Y) - (\sum (1/x) \cdot \sum Y)/n)}{((\sum 1/x^2) - (\sum (1/x))^2/n)} \quad (7)$$

$$b_1 = (\sum Y)/n - c(\sum (1/x))/n \quad (8)$$

n—the number of given value Y.

$$\text{Let us calculate a from the equation } \sum y = na + b\sum(1/x) + c\sum(1/x^2), \quad (9)$$

when n = 3.

Table 2. Calculation of ratios for relation E = f(L).

	1/x	1/x ²	$\frac{(y-y_1)}{(1/x-1/x_1)}$	$\frac{((1/x)(y-y_1))}{(1/x-1/x_1)}$	x (L, Å)	y (E, kj/mole)
					1.543	347.9397
	0.74738416	0.55858308	2694.46159281	2013.79790195	1.338	615.4890
	0.82987552	0.68869338	2554.29339132	2119.74555296	1.205	812.2780
Σ	1.57725967	1.24727645	5248.75498413	4133.54345491	4.086	1775.7067

$$1/x_1 = 0.64808814$$

$$x_1 = 1.543$$

$$y_1 = 347.9397$$

$$\Sigma(1/x^2) = 1.66729469$$

$$\Sigma(1/x) = 2.22534781$$

$$\text{when } n = 3$$

$$c = -1699.18638789$$

$$b = 5065.62912191$$

$$a = -2221.34518418$$

$$E_{c-c} \text{ bonds} = -2221.34518418 + \frac{5065.62912191}{L} - \frac{1699.18638789}{L^2} \quad (2)$$

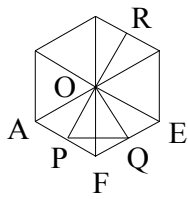
Let us calculate from the equation:

$$E_{c-c} \text{ (ethane)} = 347.9397 \text{ kj/mole} \quad E_{c=c} \text{ (ethylene)} = 615.4890 \text{ kj/mole}$$

$$E_{c\equiv c} \text{ (acetylene)} = 812.2780 \text{ kj/mole}$$

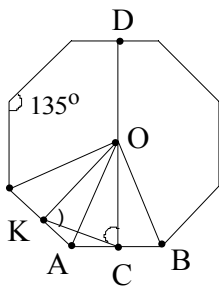
Further we will show determination of distances in regular hexagon, octagon, decagon.

In benzene molecule the carbon atoms are located in the top of regular hexagon (equilateral hexagon), thus



$$\begin{aligned} \angle PAO &= 60^\circ & OA &= AF \\ \angle QPO &= \angle PQR = 60^\circ & \angle AFE &= 120^\circ \\ AF &= 1.397 \text{ \AA} & PQ = OP &= AF \cdot \sin 60^\circ \\ PQ = OP &= AF \cdot \frac{\sqrt{3}}{2} = 1.397 \text{ \AA} \cdot \frac{\sqrt{3}}{2} = 1.210 \text{ \AA} \\ PQ &= 1.210 \text{ \AA} \\ PR &= 2PO = 2 \cdot 1.210 \text{ \AA} = 2.420 \text{ \AA} \end{aligned}$$

For a regular octagon:



$$\begin{aligned} \angle BAO &= 67.5^\circ & AC = CB, Lc-c &= AB = 1.410 \text{ \AA} \\ \operatorname{tg} BAO &= \frac{OC}{AC} & OC &= AC \cdot \operatorname{tg} BAO = \frac{AB}{2} \cdot \operatorname{tg} BAO \\ CD &= 2 \cdot OC = \operatorname{tg} BAO \cdot Lc-c = \operatorname{tg} 67.5^\circ \cdot 1.410 \text{ \AA} = 3.404 \text{ \AA} \\ OK = OC, & \frac{CD}{2} = KO = OC = 1.702 \text{ \AA} \end{aligned}$$

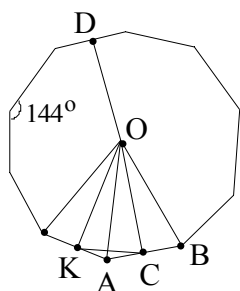
According to cosine theorem.

$$\begin{aligned} KC^2 &= KO^2 + OC^2 - 2 \cdot KO \cdot OC \cdot \cos COK & \angle COK &= 45^\circ \\ KC &= 1.303 \text{ \AA} \end{aligned}$$

If we take $Lc-c = AB = 1.400 \text{ \AA}$ for a regular octagon, then:

$$\begin{aligned} Lc-c &= AB = 1.400 \text{ \AA} \\ CD &= \operatorname{tg} 67.5^\circ \cdot 1.400 \text{ \AA} = 3.380 \text{ \AA} \\ \frac{CD}{2} &= KO = OC = 1.690 \text{ \AA} \\ KC^2 &= KO^2 + OC^2 - 2 \cdot KO \cdot OC \cdot \cos COK & \angle COK &= 45^\circ \\ KC &= 1.293 \text{ \AA} \end{aligned}$$

For a regular decagon:



$$\begin{aligned} \angle BAO &= 72^\circ & AC = CB, L_{c-c} = AB = 1.400 \text{ \AA} \\ \operatorname{tg} BAO &= \frac{OC}{AC} & OC = AC \cdot \operatorname{tg} BAO = \frac{AB}{2} \cdot \operatorname{tg} BAO \\ CD &= 2 \cdot OC = \operatorname{tg} BAO \cdot L_{c-c} = \operatorname{tg} 72^\circ \cdot 1.400 \text{ \AA} = 4.309 \text{ \AA} \\ OK &= OC, \frac{CD}{2} = OC = KO = 2.154 \text{ \AA} \end{aligned}$$

According to cosine theorem.

$$\begin{aligned} KC^2 &= KO^2 + OC^2 - 2 \cdot KO \cdot OC \cdot \cos COK & \angle COK &= 36^\circ \\ KC &= 1.331 \text{ \AA} \end{aligned}$$

CONCLUSION

As we can see, three-electron bond enables to explain aromaticity, find delocalization energy, understand aromatic bond's specificity. Aromatic bond in benzene molecule is simultaneous interaction of three pairs of central electrons with opposite spins through the cycle. But whereas central electrons are the part of three-electron bond, then it is practically interaction of six three-electron bonds between themselves, that is expressed in three interactions through cycle plus six three-electron bonds. We shouldn't forget in this system about important role of six atom nucleuses, around which aromatic system is formed. Properties of nucleuses especially their charge will influence on properties of aromatic system.

Finally, postulates of the three-electron bond theory (TBT) can be presented:

1) A chemical bond between two atoms may be established by means of three electrons with oppositely oriented spins ($\uparrow\downarrow\uparrow$).



2) The electron shell of each atom in the stable molecule, ion, radical should have such a number of electrons which corresponds to the octet. A deviation from the octet results in an instability of a particle.

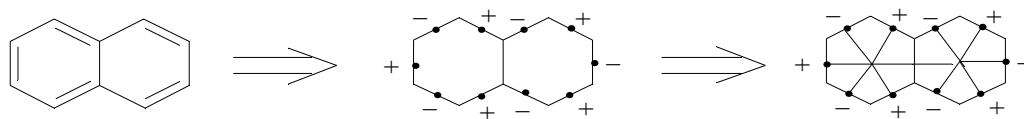
3) The state of the three-electron bond is determined by the octet rule.

4) The number of electrons participating in the chemical bond should be maximal and it's then that the energy of the system will be minimal. Taking into consideration para 5 and 2.

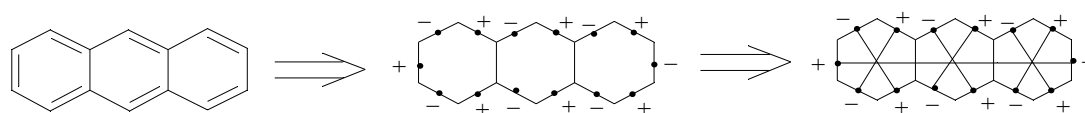
5) In the course of establishing of the chemical bond electrons (their spins) are located in such a way that enables their interaction (attraction) to be maximal.

6) The aromatic bond is a three-electron bond in flat cyclic systems with a specific interaction of electrons through the cycle.

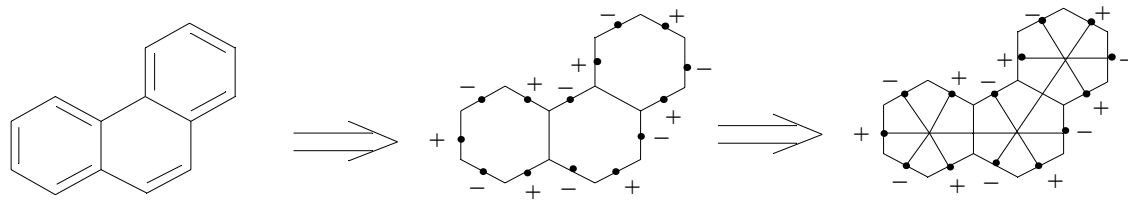
It is easy to show, that using three-electron bond one can explain paramagnetization and structure of oxygen molecule, structure of carboxylate anion, ozone, naphthalene and other organic and non-organic compounds. Let's bring for the example structures of some compounds in terms of three-electron bond.



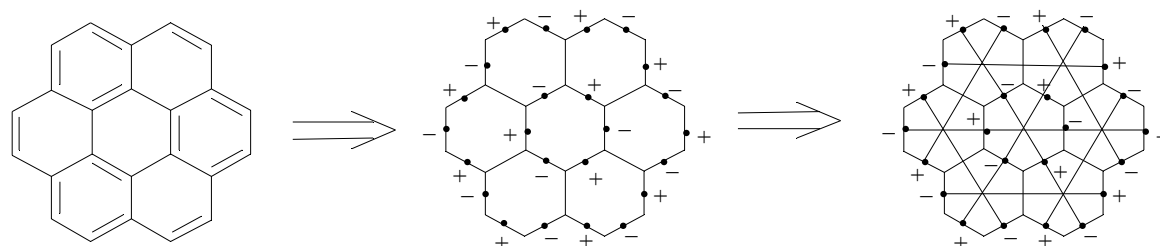
Naphthalene



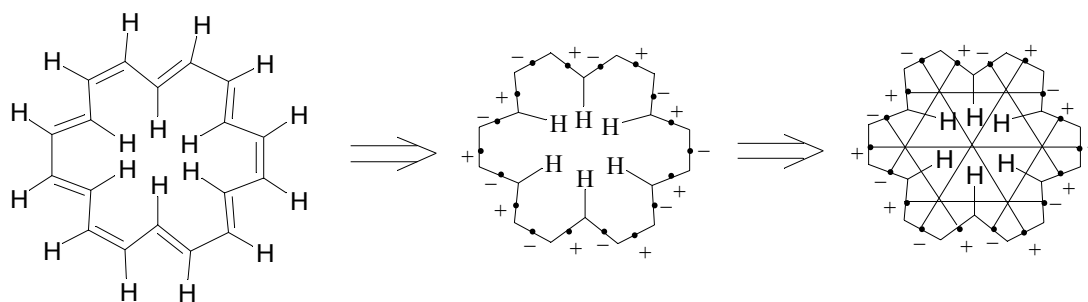
Anthracene



Phenanthrene



Coronene



[18]-Annulene

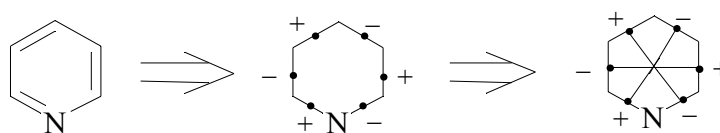
It is interesting to note extreme symmetry of structures of naphthalene, anthracene, coronene and [18]-annulene, that is typical for the majority of aromatic compounds in general.

By the example of [18]-annulene it is possible to illustrate interaction through the cycle of central electrons of three-electron bonds. Interacting through the cycle, it shifts to the centre in the direction of inner atoms of hydrogen thus increasing electron density within the cycle and decreasing outside the cycle. And that's why outside protons (12 H) will give signals in the area of weaker field (reduction of electron density), and inner (6 H) will give signals in the area of stronger field (increase of electron density). Thus this is observed in reality [7]. It also should be noted that inner protons bracing central electrons strengthen interaction through the cycle, and so stabilize aromatic system. But interaction through the cycle is decisive.

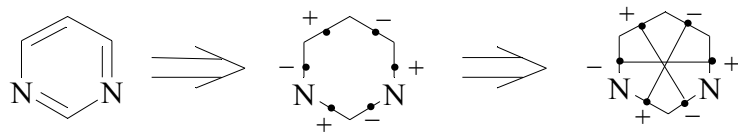
If aromatic system does not have inner protons, then outside protons will give signals in the area of weaker field (one of the features of aromatic compounds).

It is clear that in case of antiaromatic systems when there is no interaction (attraction) through the cycle, because central electrons have similar spins and push away, change in electron density in the centre of the cycle and outside the cycle will be reverse to aromatic systems.

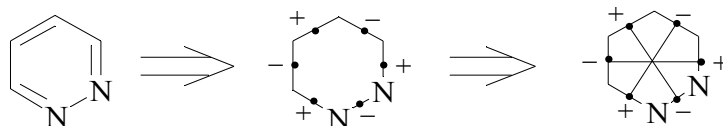
Further we will continue demonstration of construction of organic and inorganic compounds.



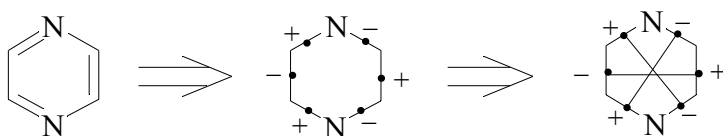
Pyridine



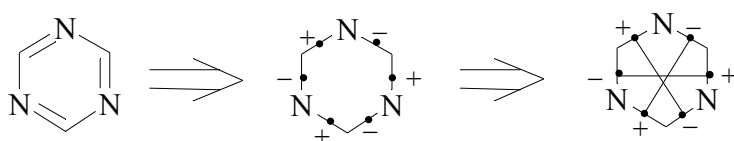
Pyrimidine



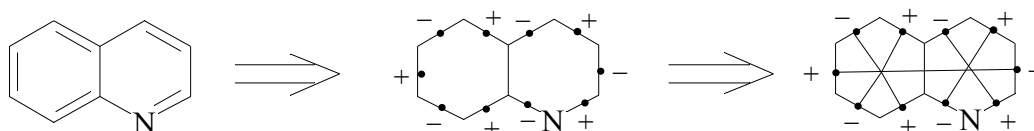
Pyridazine



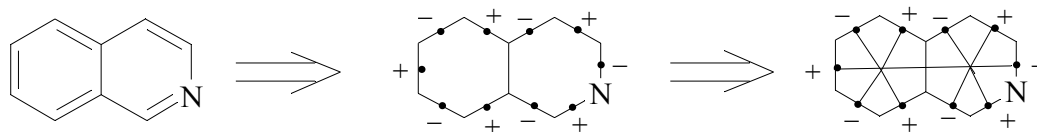
Pyrazine



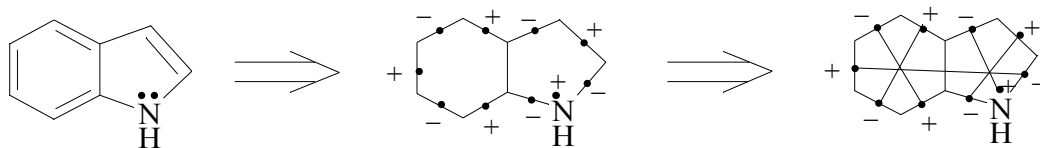
1,3,5-Triazine



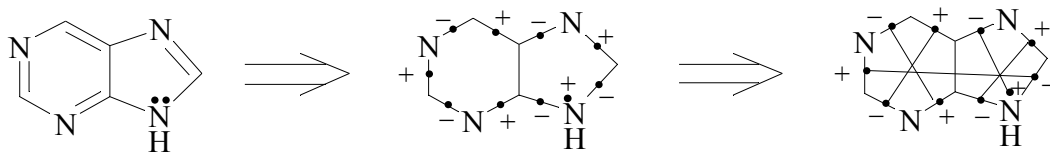
Quinoline



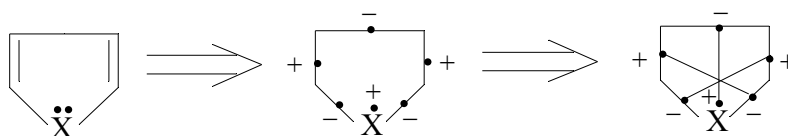
Isoquinoline



Indole

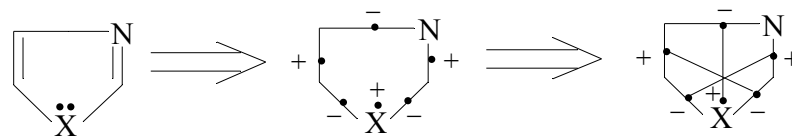


Purine



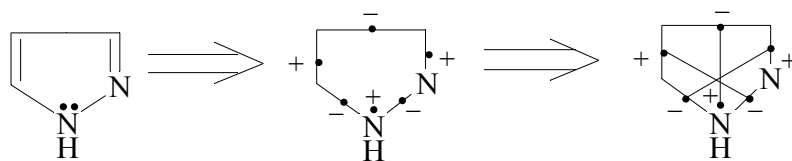
X = O, S, NH

Furan, thiophene, pyrrole

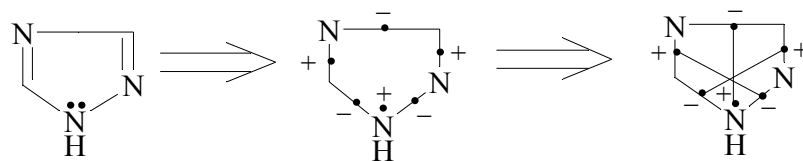


X = O, S, NH

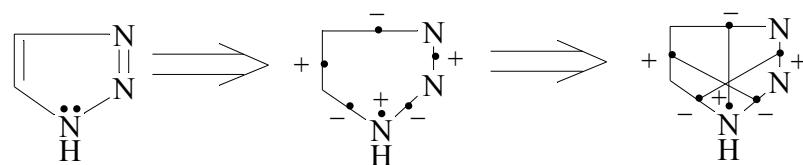
Oxazole, thiazole, imidazole



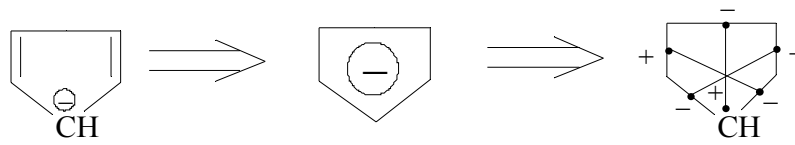
Pyrazole



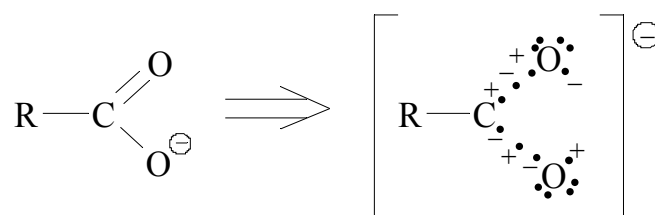
1,2,4-Triazole



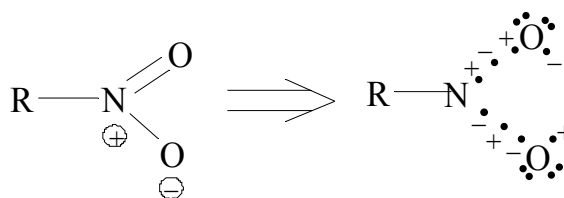
1H-1,2,3-Triazole



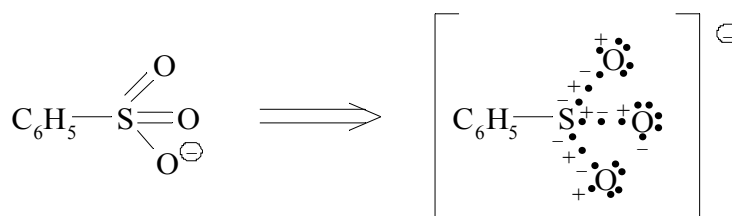
Cyclopentadienyle anion



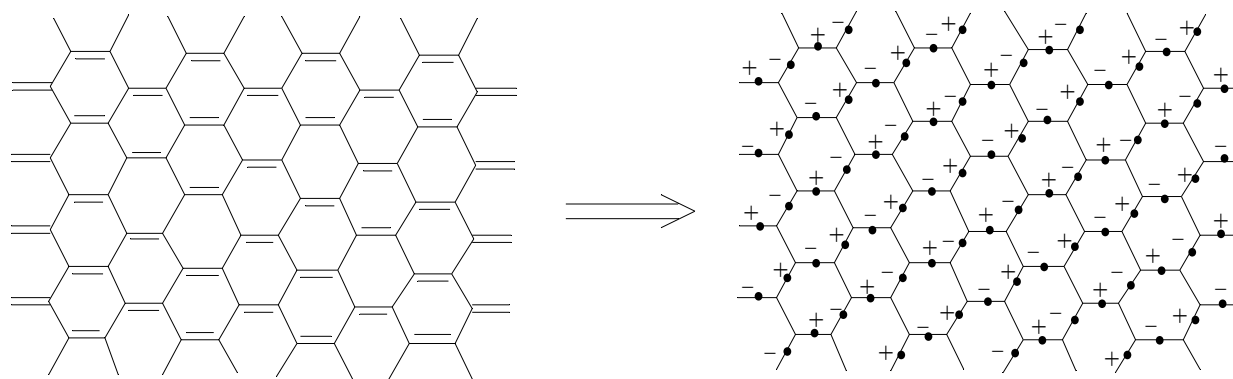
Carboxylate anion



Nitro compounds



Sulfonate anion



Graphite

As we can see with the help of three-electron bond structures of abovementioned molecules and ions are described simply and obviously by one structures, which represents the real distribution of electrons (electron density) in molecules (ions).

Author knowingly did not consider a question about kinds of forces, that make electrons to attract with opposite spins, because it is a subject of a separate consideration. All the more so, because based on famous postulate (attraction of two electrons with opposite spins) concept of localized chemical bond follows. Explaining aromatic bond in benzene molecule, interaction of central electrons is strange on such long distances (2.420 Å). But taking into account, that electrons can show wave-like behaviour and shift to the center of benzene cycle under the influence of neighbouring central electrons, this interaction looks very truly. The fact of the distance between the graphite layers being 3.35 Å (the C-C bond length inside the layer making 1.42 Å) [8] may serve as an indirect confirmation of the possibility of interaction of the electrons through the cycle in benzene. This causes a weak bond between the layers and, as a result, the ability of the layers to shift relative to each other. Since the distance between the central electrons in benzene is less and makes 2.420 Å (in case of an interaction through the cycle), we should expect a stronger

interaction.

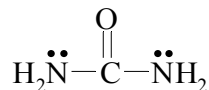
It is clear that, by increasing of cycle, distance between central electrons (both neighboring and through the cycle) will increase, and that's why interaction energy through the cycle will decrease, and by certain distance benefit from aromaticity of system will be lower, than energy consumption for creation of planar equilateral polygon (as in the case of cyclodecapentaene). Therefore existence of large aromatic monocycles will depend on relation of these two values.

With the help of equations $E = a + b/L + c/L^2$ and $\text{multiplicity} = a + b/L + c/L^2$ we can analyze different types of chemical bonds, calculate their multiplicity and energy on the basis of experimental data about bonds distances.

The tables 3 and 4 below show the a, b and c coefficients for these equations for the bonds prevailing in the organic chemistry (C-C, C-O, C-N, C-S, N-N, N-O, O-O). The coefficients have been calculated similarly to the C-C bonds. Using them it is possible to calculate the bonds multiplicity and their energy (bond energy constants) for the most part of organic molecules, both aromatic and non-aromatic ones. It makes it possible to calculate the aromatic compounds delocalization energy.

It is also possible to calculate the real molecules energy gain compared to their classic structures. To do this, it is necessary to subtract the total of the classic structure bond energies from the total of the real structure bond energies (the bond energy is calculated with the $E = a + b/L + c/L^2$ equation). Let us illustrate the above taking the urea molecule as an example (leaving out of consideration the N-H bonds):

Classic structure



Multiplicity C–N = 1

Multiplicity C–O = 2

$$E_{\text{C-N}} = 291.834 \text{ kJ/mole [1, c.116]}$$

$$E_{\text{C-O}} = 728.538 \text{ kJ/mole (for R}_2\text{C=O) [1, c.116]}$$

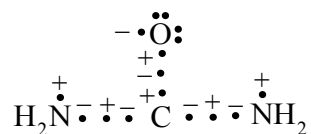
$$E_1 = E_{\text{C-O}} + 2E_{\text{C-N}} = 1312.206 \text{ kJ/mole}$$

$$\Delta E = E_2 - E_1 = 1544.520 \text{ kJ/mole} - 1312.206 \text{ kJ/mole} = 232.314 \text{ kJ/mole}$$

So, the energy gain for a real urea molecule (with three-electron bonds) as compared to the classic structure makes 232.314 kJ/mole (55.487 kcal/mole). Calculations for other molecules may be done in the same way.

This example illustrates why the three-electron bonds appear at all: it proves to be that the three-electron bonds are “more poor” by energy and formation of three-electron bonds is energetically more advantageous. The energetic advantageousness is also the reason of the deviation of the multiplicity of the three-electron bonds from 1.5 which takes place due to either the interaction of the three-electron bonds among themselves (for example, in the benzene molecule) or the interaction of the three-electron bonds with the unpaired electrons located in atoms making the bond (urea molecule). Cases are possible when the bond multiplicity is changed due to the simultaneous influence of the above mentioned

Real structure



$$L_{\text{C-N}} = 1.33 \text{ \AA}, \quad L_{\text{C-O}} = 1.27 \text{ \AA} \quad (8)$$

$$\text{Multiplicity C–N (} L=1.33 \text{ \AA)} = 1.686$$

$$\text{Multiplicity C–O (} L=1.27 \text{ \AA)} = 1.486$$

$$E_{\text{C-N}} (L = 1.33 \text{ \AA}) = 523.790 \text{ kJ/mole}$$

$$E_{\text{C-O}} (L = 1.27 \text{ \AA}) = 496.940 \text{ kJ/mole}$$

$$E_2 = E_{\text{C-O}} + 2E_{\text{C-N}} = 1544.520 \text{ kJ/mole}$$

effects.

It should be also noted that the octet rule holds true in three-electron bond structures. Thus, in the urea molecule the three-electron bond electrons interact partially with the unpaired electrons located in the atoms of oxygen and nitrogen. As a result the three-electron bond electrons do not fully belong to the carbon atom and so the carbon atom octet makes 8 and not 9 (one should not also forget that the electronegativity of the atoms of oxygen (3.5) and nitrogen (3) is higher than the electronegativity of the atom of carbon (2.5)).

Generally, the octet rule defines the state of the three-electron bond, that is, the distribution of the electrons, the energy of their interaction with each other and other unpaired electrons, the fact and the extent of belonging of the three-electron bond electrons to one or another atom.

And finally, here are the values of the a, b, c coefficients in the tables 3 and 4 for the Multiplicity = f(L) and E = f(L) equations.

Table 3. Multiplicity = $a + b/L + c/L^2$ equation coefficients for some types of bonds.

Type of bond	a	b	c
C-C	-0.06040343	-5.67787529	11.28562201
C-O	26.03252883	-72.46498138	52.43899244
C-N	0.63817306	-7.56455294	11.91384503
C-S	55.33256579	-198.81807222	181.87538814
N-N	0.96407492	-6.68791795	9.79339013
N-O	46.00756377	-123.75637485	84.79763896
O-O	23.89786759	-66.85172754	48.79304255
C-P	28.76548555	-109.46128312	107.52805439
Multiplicity - bond multiplicity, L – bond length in Å.			

Table 4. $E = a + b/L + c/L^2$ equation coefficients for some types of bonds.

Type of bond	a	b	c
C-C	-2221.34518418	5065.62912191	-1699.18638789
C-O	11420.81052442	-31359.17576343	22207.04265404
C-N	-2332.69568587	4450.61712191	-866.48412671
C-S	-27772.64385690	90244.55278987	-71414.57485742
N-N	7067.14065437	-20274.81508318	14878.53765631
N-O	-6564.31416262	15895.54907490	-8769.11638979
O-O	10590.40848780	-29935.02909385	21430.93279023

E – bond energy in kJ/mole,
L – bond length in Å.

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(Russian translation from: Structure and mechanism in organic chemistry. Second edition, INGOLD C.K. Cornell University press Ithaca and London, 1969).
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