A Quantum-mechanical Approach to the Theory of Aromaticity

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The term "aromatic" originated from a characteristic odor which was possessed by certain substances isolated from various natural products such as benzoic acid (e. g. from gum benzoin), benzaldehyde (bitter-almond oil), cymene (carraway oil), toluene (tolu balsam) and the like. Hence this terminology essentially involved much ambiguousness since originally it was not based upon any scientific concept of classification. Recently the term "aromaticity" has attracted anew the attention of many organic chemists[1] since the discovery and the synthesis of multifarious non-benzenoid "aromatic" compounds such as tropolone, sydnone, ferrocene and numerous derivatives of these compounds[2].

A quantum-mechanical attack on the problem of aromaticity was for the first time delivered by Hueckel in regard to benzene, who presented the so-called $4n+2$ rule[3]. According to his theory, a conjugated compound has $4n+2$ π electrons on its ring should exhibit an aromatic character. Although long years have passed since his report, only a very few attempts have been made to approach this problem theoretically. Recent conspicuous developments in the synthetic organic chemistry of non-benzenoid compounds, however, forced pressingly a reexamination of the significance of aromaticity. Craig investigated the compounds containing dπ electrons by simple LCAO MO treatment and defined two types of aromaticity according to the type of $d\pi$ orbital involved[4]. One of them obeys the $4n+2$ rule while the other is of a novel type in which the rule does not hold.

The researchers mentioned above, however, considered only the energy of π electrons and neglected the internuclear repulsion energy. A more dexterous device should accordingly be desired for the elucidation of aromaticity.

The present authors attempted to investigate the aromaticity more minutely from the quantum-chemical point of view. Prior to entering into the main subject it is desirable to define the term "aromaticity". What is meant by aromaticity is of no clear-cut nature and is usually represented by the following characteristics of aromatic compounds.

Aromatic compounds have a plane structure.

Aromatic compounds show a remarkable stability.

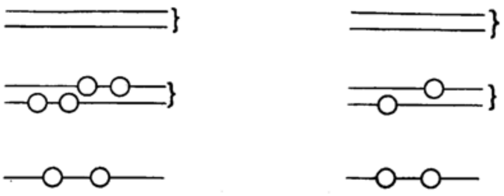
Aromatic compounds have a characteristic reactivity.

Aromatic compounds show a peculiarity in such physical properties as ultraviolet absorption spectra[5], molecular refraction[6], magnetic anisotropy[7], and so forth.

Among these properties some have been already solved and explained satisfactorily, while others have yet been left untouched. The distinguished stability of aromatic compounds aroused the present authors' interest above all other things and is mainly discussed in the present paper.

Energetical Consideration

Classical explanation of the stability of aromatic compounds had been based upon the strain theory, referring to the proposition that a six-membered ring is stable since it undergoes no strain force. However, by means of this theory we can not understand the reason why some five-membered rings such as furan are stable while others such as cyclopentadiene


$4n+2$ electrons

$4n$ electrons

Fig. 1. π-electron configuration of $(4n+2)$- and $(4n)$-membered rings.

The brace } indicates that two levels are degenerate.

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[1] R. Robinson, *Tetrahedron*, 3, 323 (1958); H. C. Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.

[2] W. Baker and W. D. Ollis, *Quart. Revs.* (*London*), 11, 15 (1957); A. W. Johnson, *J. Chem. Soc.*, 1954, 1331; T. Nozoe, "Gendai Kagaku", Vol. 10, Iwanami, Tokyo (1957).

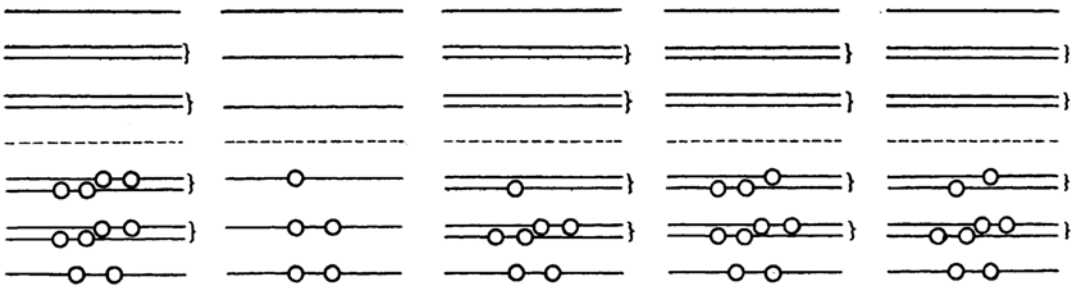
[3] E. Hueckel, *Z. Physik*, 70, 204 (1931).

[4] D. P. Craig, *J. Chem. Soc.*, 1959, 997.

[5] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley & Sons, Inc., New York (1951); R. Pariser and P. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953).

[6] M. Kotake, "Daiyûkikagaku", Vol. 1, Asakura, Tokyo (1958) p. 204..

[7] L. Pauling, *J. Chem. Phys.*, 4, 673 (1936); F. London, *J. de Physique*, 8, 397 (1937).



Case A Case B Case C Case C Case D

Fig. 2. Electronic configurations which are taken into account in the calculation. The brace } indicates that two levels are degenerate.

are not. Moreover, recent experiments elucidated that some seven-membered conjugated ring compounds such as tropone and tropolone can exist in a stable form. These facts suggest that, in order to answer the question of aromatic stability, other factors than the strain force, e. g. the magnitude of total π electronic energy, should be taken into consideration. For the purpose of attacking this problem, quantum mechanics must obviously be a powerful weapon. Hueckel's $4n+2$ rule was derived by simple LCAO MO treatment3). He showed that the electronic configuration of the compound having $4n+2$ electrons on its ring forms a set of closed shells in MO sense analogous to the atomic structure. In the case of $4n$ electrons the complete closed shell structure is impossible as is seen in Fig. 1.

In Hueckel's $4n+2$ rule, however, the effect of electron-electron repulsion and internuclear repulsion had not been taken into account. Accordingly, this rule is not capable of predicting the number of π electrons which can exist and be stable on a given membered carbon ring. To overcome this difficulty, the π electronic energy is obtained by the formulas utilized by Pople8). In the present method the internuclear and electron-electron repulsion energy are considered explicitly and the antisymmetrized product of Hueckel MO were used for the sake of simplicity. Therefore MO is written as

$$\psi_i=\sum_r C_{ir}\phi_r \tag{1}$$

where ψ_i is the ith MO and ϕ_r represents the AO on the rth carbon atom. Electronic configurations which are taken into account are classified into four cases A, B, C and D and these cases are schematically shown in Fig. 2.

For case A Pople gave the total π electronic energy including nuclear-nuclear repulsion as follows:

$$\begin{aligned}\varepsilon_\pi=&\sum_r P_{rr}\left(U_{rr}+\frac{1}{4}P_{rr}\gamma_{rr}\right)+2\beta\sum_{r<s}{}^{*}P_{rs}\\&+\sum_{r<s}\left\{(P_{rr}-1)(P_{ss}-1)-\frac{1}{2}(P_{rs})^2\right\}\gamma_{rs}\end{aligned} \tag{2}$$

where U_{rr} is a core matrix element, β_{rs} is the resonance integral.

$$\gamma_{rs}=\int\phi_r^*(1)\phi_s^*(2)\frac{e^2}{r_{12}}\phi_r(1)\phi_s(2)\mathrm{d}v_1\mathrm{d}v_2$$

and

$$P_{rs}=2\sum_{i=1}^{n}C_{ir}C_{is} \tag{3}$$

Summation $\sum$ and $\sum^*$ should cover all the atoms and the nearest neighboring atoms, respectively. For the case of regular n-membered ring molecules, U_{rr} and β_{rs} are constant values represented by U and β, respectively. In Eq. 2 the internuclear repulsion energy is included in the following form

$$\varepsilon'=\sum_{r<s}Z_rZ_s\gamma_{rs} \tag{4}$$

and Z_r and Z_s are assumed to be unity. For case B the total π-electronic energy of the non-degenerate system with odd electrons was obtained as follows8):

$$\begin{aligned}\varepsilon_\pi=&\sum_r(P^0_{rr}U+P^\alpha_{rr}P^\beta_{rr}\gamma_{rr})+2\beta\sum_{r<s}{}^{*}P^0_{rs}\\&+\sum_{r<s}\{(P^0_{rr}-1)(P^0_{ss}-1)\\&-[(P^\alpha_{rs})^2+(P^\beta_{rs})^2]\}\gamma_{rs}\end{aligned} \tag{5}$$

where

$$P^\alpha_{rs}=\sum_{i=1}^{n}C_{ir}C_{is},\quad P^\beta_{rs}=\sum_{i=1}^{n-1}C_{ir}C_{is}$$

and $$P^\alpha_{rs}=P^\beta_{rs}+P^\beta_{rs} \tag{6}$$

For case C the total π electronic energy is obtained by only one electronic configuration for regular n-membered ring system, so that the formula for this case is equal to that of case B. For case D the wave functions are chosen as follows.

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8) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); A. Brickstock and J. A. Pople, ibid., **50**, 901 (1954).

TABLE I. THE DELOCALIZATION ENERGY OF FIVE-, SIX- AND SEVEN-MEMBERED RING SYSTEMS

Number of carbon atoms on ring	Number of π electrons	Energy of non-conjugated system, e.V.	Energy of conjugated system, e.V.	Difference e.V.
5	5	5U	5U− 9.80	9.80
	6	6U+10.53	6U− 0.48	11.01
	7	7U+26.78	7U+17.23	9.55
6	4	4U+ 4.90	4U− 6.30	11.20
	5	5U	5U−13.50	13.50
	6	6U	6U−13.88	13.88
	7	7U+10.53	7U− 2.97	13.50
	8	8U+25.96	8U+14.76	11.20
7	5	5U+ 4.38	5U−10.17	14.55
	6	6U	6U−17.32	17.32
	7	7U	7U−14.17	14.17

$$\chi=\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2n!}}\{[\phi_1\overline{\phi}_1\cdots\cdots\phi_n\overline{\phi}_{-n}] - [\phi_1\overline{\phi}_1\cdots\cdots\overline{\phi}_n\phi_{-n}]\} \qquad (7)$$

where ϕ_n and ϕ_{-n} are the molecular orbitals for degenerate levels. In this case we get the total π electronic energy by the same method that Pople used as follows:

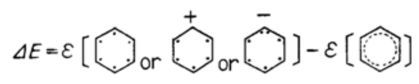
$$\begin{aligned}\varepsilon_\pi=&\sum_r P_{rr}U+\frac{1}{4}\sum_r\{(P_{rr})^2-(C_{nr})^4-(C_{-nr})^4\\&+6(C_{nr})^2(C_{-nr})^2\}\gamma_{rr}+2\beta\sum_{r<s}{}^{*}P_{rs}\\&+\sum_{r<s}\{(P_{rr}-1)(P_{ss}-1)-\frac{1}{2}(P_{rs})^2\\&-\frac{1}{2}(C_{nr}C_{ns})^2-\frac{1}{2}(C_{-nr}C_{-ns})^2\\&+3(C_{nr}C_{ns})(C_{-nr}C_{-ns})\}\gamma_{rs}\end{aligned} \qquad (8)$$

where

$$P_{rs}=2\sum_{j=1}^{n-1}C_{jr}C_{js}+C_{nr}C_{ns}+C_{-nr}C_{-ns} \qquad (9)$$

By using these formulas the total π electronic energy including internuclear repulsion energy is obtained.

Before performance of calculation it is necessary to consider what kind of quantity can be the measure for aromaticity. In many cases the resonance energy was adopted as the measure for aromaticity⁹⁾. Recently, Craig tried to specify the aromatic character by its symmetry of molecular structures and spin functions⁹⁾. This method, however, is inapplicable to the molecule which lacks sufficient symmetry. In this paper, we intend to compare the stability of the systems of regular n-membered ring having m π electrons. Since the calculation is restricted to π electronic energy and the effect of σ bond is neglected, the comparison of stability should be confined to the ring system with the same number of members and variable number of π electrons. We, therefore, adopt the energy difference between conjugated regular n-membered ring molecule and non-conjugated system that has electrons on each atom as the measure for aromaticity as is shown in Eq. 10.



(10)

This measure is nothing but the delocalization energy of the system. The energy of the neutral or ionic non-conjugated system can be given as follows where electron-electron and internuclear repulsions and electron-nuclear attraction are taken into account.

$$\begin{aligned}\varepsilon_{\text{non-conjugated}}=&\sum_{\mu>\nu}(Z_\mu-2)^2\gamma_{\mu\nu}+\sum_{r>s}(Z_r-1)^2\gamma_{rs}\\&+\sum_{r\mu}(Z_\mu-2)(Z_r-1)\gamma_{r\mu}+\sum_{\alpha>\beta}Z_\alpha{}^2\gamma_{\alpha\beta}\\&+\sum_{\alpha,\gamma}Z_\alpha(Z_r-1)\gamma_{\alpha r}+\sum_\alpha\gamma_{\alpha\alpha}+nU\end{aligned} \qquad (11)$$

where r and s denote the carbon atom which has only one electron on it, α and β two electrons, and μ and ν none, respectively, and n is the number of π electrons. For the sake of simplicity the values of Z_r, Z_α and Z_μ are assumed to be unity. Thus the calculated value is the measure of the stability by delocalization of non-conjugated electrons. Therefore the greater the magnitude of delocalization energy is, the more stable the molecule is. Accordingly this measure is expected to be a good index for aromaticity, since the stability of the molecule is the essential character for aromatic compounds. The atomic integral used in calculation is gained by the semiempirical formulas adopted by Pariser and Parr⁵⁾. For brevity, all the C–C bond distances are assumed to be 1.39 Å referring to that of benzene. Thus

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9) D. Ginsburg, "Non-benzenoid Aromatic Compounds", Interscience Publishers Inc., New York (1959).

the obtained results of the delocalization energy are listed in Table I.

As is shown in Table I, infive-, six- and seven-membered ring systems the molecule is most stable when it has six π electrons on its ring. In a five-membered ring system this result corresponds to the fact that the five-membered ring molecule with six π electrons such as furan, sydnone exists in stable state. Moreover in the seven-membered ring system the stability of tropone and tropolone corresponds to this result. Accordingly, we can explain and extend Hueckel's $4n+2$ rule on the different physical grounds from Hueckel's and combine the rule with the fact that some five- and seven-membered ring molecules with six π electrons are stable.

In this connection, it may be worth while to add that another approximate method will contribute to the illustration of $4n+2$ rule. This is the method originally presented by Peter[10] in which the resonance energy is approximately obtained by the perturbation method. The wave function of linear polyenes is utilized as a zero order wave function. The intramolecular bonding between the atoms r and s, as is indicated in Fig. 3, is regarded as the perturbation and the stabilization energy due to this bonding is obtained. Result of simple LCAO MO calculation is

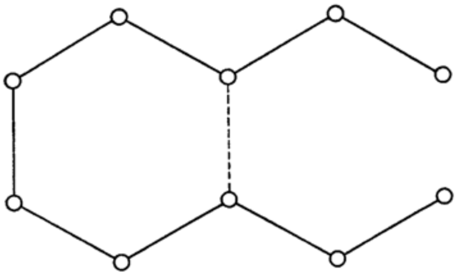


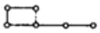
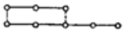
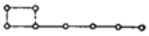
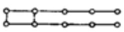
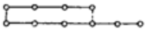
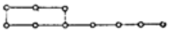
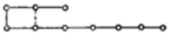
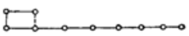
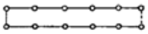
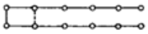
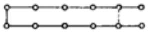
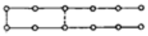
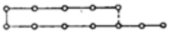
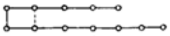
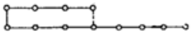
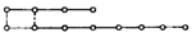
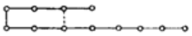
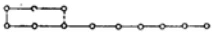
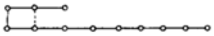
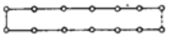
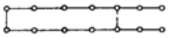
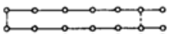
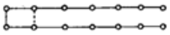
Fig. 3. Scheme for the perturbation method. Dotted line indicates the new bonding engendered.
Circle and line represent the carbon atom and the C-C bond constructing the linear polyene.

$$\delta\varepsilon = 2P_{rs}\delta\beta_{rs} + \Pi_{rs,rs}(\delta\beta_{rs})^2 + \cdots \qquad (12)$$

where $\delta\varepsilon$ is the stabilization energy, P_{rs} and $\Pi_{rs,rs}$ are the order of imaginary bond between the atoms r and s and the selfpolarizability of the imaginary bond $r-s$, respectively, each being of the original polyene, and $\delta\beta_{rs}$ denotes the resonance integral of the bond $r-s$.

A glance at Eq. 4 makes it comprehensible that the magnitude of the stabilization energy predominantly depends on the bond order P_{rs}. Peter obtained the resonance energy of various

TABLE II. THE VALUE OF BOND ORDER OF 4-, 6-, 8-, 10-, 12- AND 14-MEMBERED POLYENES

n	Type of bond formation	Bond order P_{rs}	Number of canonical structure
4		$P_{1.4}=-0.4473$	2
6		$P_{1.6}=\ \ 0.3019$	2
		$P_{2.5}=-0.0866$	1
		$P_{1.4}=-0.3874$	2
8		$P_{1.8}=-0.2293$	2
		$P_{2.7}=-0.3333$	2
		$P_{3.6}=\ \ 0.0340$	1
		$P_{1.6}=\ \ 0.2632$	2
		$P_{1.4}=-0.3673$	2
10		$P_{1.10}=\ \ 0.1855$	2
		$P_{3.8}=\ \ 0.2297$	2
		$P_{2.9}=-0.0170$	1
		$P_{4.7}=-0.1278$	1
		$P_{1.8}=-0.2028$	2
		$P_{3.6}=-0.2293$	2
		$P_{2.7}=\ \ 0.0440$	1
		$P_{1.6}=\ \ 0.2469$	2
		$P_{2.5}=-0.1107$	1
		$P_{1.4}=-0.3576$	2
12		$P_{1.12}=-0.1562$	2
		$P_{3.10}=-0.1798$	2
		$P_{5.8}=-0.2938$	2
		$P_{2.11}=\ \ 0.0100$	1
		$P_{4.9}=\ \ 0.0586$	1
		$P_{1.10}=\ \ 0.1660$	2
		$P_{3.8}=\ \ 0.2146$	2
		$P_{2.9}=-0.0234$	1
		$P_{4.7}=-0.1377$	1
		$P_{1.8}=-0.1896$	2
		$P_{3.6}=-0.3038$	2
		$P_{2.7}=\ \ 0.0485$	2
		$P_{1.6}=\ \ 0.2382$	2
		$P_{2.5}=-0.1142$	1
		$P_{1.4}=-0.3523$	2
14		$P_{1.14}=\ \ 0.1348$	2
		$P_{3.12}=\ \ 0.1491$	2
		$P_{5.10}=\ \ 0.2000$	2
		$P_{2.13}=-0.0063$	1
		$P_{4.11}=-0.0330$	1
		$P_{6.9}=-0.1491$	1

Circle written on the line represents the carbon atom which is a member of linear polyene
Dotted line indicates the new bond to be formed.

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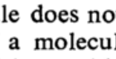
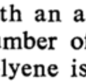
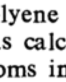
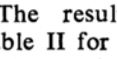
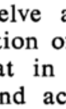
[10] D. Peter, *J. Chem. Soc.*, **1958**, 1023.

compounds by applying this method and the $4n+2$ rule generally, that is, the molecule in the case that the bond formation makes $4n+2$ ring has the largest resonance energy and therefore more stable than that in the case of $4n$ ring.

If we assume that internuclear repulsion energy stated above does not vary so much according to its geometrical structure, so far as the number of the atoms constituting a molecule does not change, the change of total energy of a molecule may approximately be discussed with an aid of Eq. 4. In many cases that the number of carbon atoms constituting the linear polyene is altered, the value of the bond order was calculated between several carbon-carbon atoms in simple LCAO MO treatment.

The result of calculation is collected in Table II for the cases of four, six, eight, ten, twelve and fourteen carbon atoms. Investigation of this table leads to the conclusion that in a polyene molecule the addition of a bond accompanied with the formation of a $4n+2$ ring stabilizes the molecule, while with the formation of a $4n$ ring it becomes unstable. It may be of interest to examine Table II more carefully to find that in the case of the bond formation with a $4n+2$ ring the corresponding value of bond order increases with the number of describable canonical structures which have alternate single and double bonds, while in $4n$ ring formation the relation is reversed. Hence the number of canonical structures can be a measure for the stability of a $4n+2$ ring molecule but no longer so for $4n$ ring molecules.

TABLE III. THE PARALLELISM BETWEEN BOND ORDER AND CONJUGATION ENERGY

Molecule	Conjugation energy per electron, β	Bond order P_{rs}
	1.100	−0.3874
	1.148	−0.0866
	1.165	0.0000
	1.244	0.0000
	1.333	0.3019

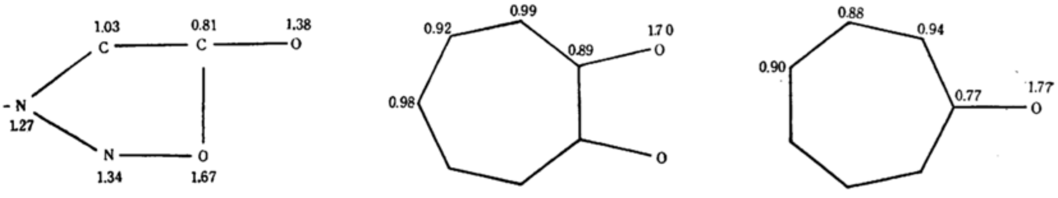
Dotted line indicates the bond formed between atom r and s. β in parenthesis is the resonance integral of carbon-carbon bond for hydrocarbon.

The way of estimating the stabilization energy mentioned above can be replaced by the calculation of conjugation energy per electron in perturbed molecule with simple LCAO MO treatment. The relation between these two methods is shown in Table III, in which a good parallelism is seen.

Electron Distribution

According to the $4n+2$ rule, it is seen that π electron distribution should be correlated closely with the stability of aromatic compounds and molecules with the ring containing $4n+2$ π electrons may be more stable than those with $4n$ π electrons. Therefore the aromatic compound should have the ring which has $4n+2$ π electrons on it. With regard to this rule it is non-benzenoid aromatic compounds with substituents such as sydnone, tropone and so on that attract our interest more strongly.

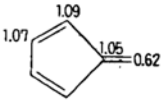
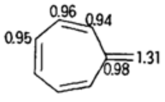
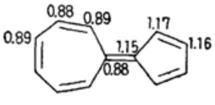
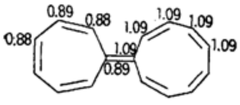
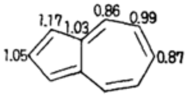
The sum of π electron density on the whole ring was obtained in Fig. 4 in the cases of sydnone, tropone and tropolone. These results suggest that in any cases the aromatic compounds tend to form a ring involving $4n+2$ π electrons. When the sum of π electron density exceeds 6, the 6-membered ring repels electrons to the substituent, and when it is less than 6, the ring attracts electrons to the ring. Further calculation of the electron distribution in some hydrocarbons containing odd-membered ring is done. The result is shown in Table IV, which illustrates that the $(4n+3)$-membered ring repels electrons and $(4n+1)$-membered ring attracts them independently of the ring size. Thus in azulene the seven-membered ring is positively



Sydnone 6.12 Tropolone 6.58 Tropone 6.21

Fig. 4. Total π electron distribution of non-benzenoid aromatic compounds. The value written under the figure is the sum of the π electron density of all member atoms constituting the ring.

TALBE IV. π ELECTRON DISTRIBUTION OF ODD-MEMBERED RING

	Sum of the total π electron density for $(4n+1)$-membered ring	Formal charge of $(4n+1)$-membered ring	Sum of the total π electron density for $(4n+3)$-membered ring	Formal charge of $(4n+3)$-membered ring
	5.37	−0.37	—	—
	—	—	6.68	+0.32
	5.81	−0.81	6.19	+0.81
	9.81	−0.81	6.19	+0.81
	5.45	−0.45	6.63	+0.37

The value written in figures is the total π electron density at each position.

and the five-membered ring negatively charged representing the Fries' rule[11].

The same tendency can also be ascertained by such a perturbation treatmeat as is described above. A $(4n+1)$- or $(4n+3)$-membered ring can be formed as a result of the bond formation between appropriate two atoms in corresponding polyene molecule, as is shown in Fig. 5. This bond formation is considered as a perturbation. The wave function for linear polyene is available as a zero order wave function. The total π electron density at the rth carbon atom, q_r, is represented by

$$q_r = 1 + \Pi_{r,st}\delta\beta_{st} + \cdots\cdots \qquad (13)$$

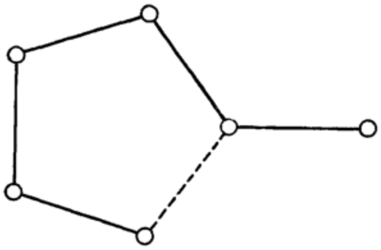


Fig. 5. Adopted model in perturbation method. Circle and line represent the carbon atom and the C–C bond constructing the linear polyene. Dotted line indicates the new bonding engendered.

where $\delta\beta_{st}$ is the resonance integral of the new bond $s-t$ and $\Pi_{r,st}$ is the atom-bond polarizability of the atom r and the bond $s\cdots\cdots t$ of the original polyene given by

$$\Pi_{r,st} = \frac{\partial q_r}{\partial \beta_{st}} = \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{C_{rj}C_{rk}(C_{sj}C_{tk}+C_{tj}C_{sk})}{\varepsilon_j - \varepsilon_k} \qquad (14)$$

TABLE V. THE VALUE OF ATOM-BOND POLARIZABILITY AND THE ENERGY DIFFERENCE BETWEEN THE HIGHEST OCCUPIED ORBITAL OF $(4n+1)$- AND $(4n+3)$-MEMBERED RINGS AND U

$(4n+1)$-membered ring

n	$\Pi_{1,2.4n+2}$ $(1/\beta)$	$\varepsilon_f - U(\beta)$
1	$\Pi_{1,2.6} = -0.4675$	0.6180
2	$\Pi_{1,2.10} = -0.3148$	0.3474
3	$\Pi_{1,2.14} = -0.2383$	0.2408
4	$\Pi_{1,2.18} = -0.1920$	0.1848
5	$\Pi_{1,2.22} = -0.1242$	0.1474

$(4n+3)$-membered ring

n	$\Pi_{1,2.4n+4}$ $(1/\beta)$	$\varepsilon_f - U(\beta)$
1	$\Pi_{1,2.8} = 0.2964$	−1.2468
2	$\Pi_{1,2.12} = 0.2709$	−0.8310
3	$\Pi_{1,2.16} = 0.2127$	−0.6180
4	$\Pi_{1,2.20} = 0.1750$	−0.4914
5	$\Pi_{1,2.24} = 0.1146$	−0.4068

$\Pi_{r,st}$ represents atom-bond polarizability.
ε_f is energy level of highest occupied orbitals of $(4n+1)$- and $(4n+3)$-membered ring.
α and β are Coulomb integral of carbon atom and resonance integral of carbon-carbon bond in polyene, respectively.

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[11] K. Fries, *Ann. Chem.*, **516**, 248 (1935).

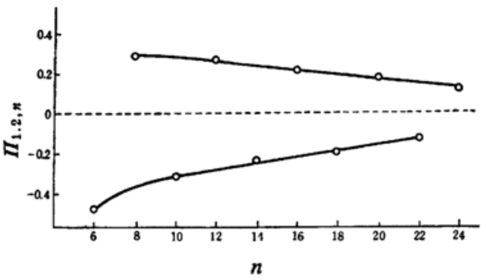


Fig. 6. Atom-bond polarizability and the number of members of linear polyene.

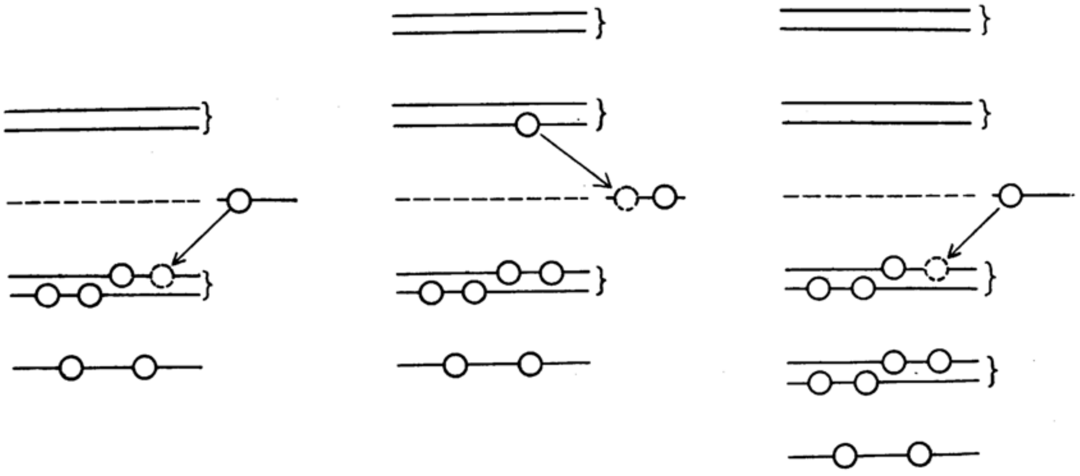
where C_{rj} is the coefficient of the atomic orbital of the rth atom in the jth molecular orbital in the simple LCAO MO treatment, ε_j is the energy of the jth molecular orbital, and subscript 1, 2, 3,……, m and subscript $m+1, m+2$ ……, n denote the occupied and unoccupied molecular orbitals, respectively. The calculated result of $\Pi_{r,st}$ is tabulated in Table V and is also plotted against the number of atoms, n, in Fig. 6. In the series of $(4n+3)$-membered rings the value of $\Pi_{r,st}$ is decreased with n and the sum of π electron density of the whole ring tends to approach to the limiting value, $4n+2$. A quite reverse tendency is seen in the series of $(4n+1)$-membered rings. That is, $\Pi_{r,st}$ is increased with n and the sum of π electron density of the whole ring approaches to the value of $4n+2$. Moreover, it is worth noticing that the absolute value of electronic charge transferred from side chain to ring or in the inverse direction decreases with n in regard to both the $(4n+1)$- and $(4n+3)$-membered rings.

These tendencies may qualitatively be understood from an energetical point of view. The energy levels of $(4n+1)$- and $(4n+3)$-membered rings are given schematically in Fig. 7. In the case of five- and nine-membered rings the charge transfer may occur from side chain to ring and the molecule forms a "closed shell" in a MO sense in order to stabilize itself. On the other hand, in the case of seven-membered ring the direction of the charge transfer is converse.

These circumstances can also be elucidated analytically by using the integral formula for atom-bond polarizability of Coulson[12]. Integral formula for atom-bond polarizability is written as

$$\Pi_{r,st}=(-1)^{s+t}\frac{2}{\pi}\int_{-\infty}^{+\infty}\frac{\Delta_{rt}(iy)\Delta_{st}(iy)}{\{\Delta(iy)\}^2}\,\mathrm{d}y \tag{15}$$

where Δ is the secular determinant for the corresponding linear polyene and Δ_{rt} denotes the secular determinant with row r and column t struck out. Consider a $(4n+1)$-membered ring with a side chain of one carbon atom formed from a $(4n+2)$-membered polyene by a bridging between the 2nd and the $(4n+2)$th atoms of the polyene. The atom-bond polarizability $\Pi_{1,2.4n+2}$ is given by



Five-membered ring with five π electrons

Seven-membered ring with seven π electrons

Nine-membered ring with nine π electrons

Fig. 7. Energy level of odd-membered ring.
The energy written aside represents that of the side-chain carbon.
The dotted line indicates the π electrons transferred and an arrow shows the direction of the electron transfer.

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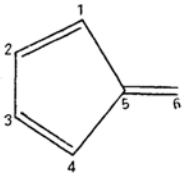
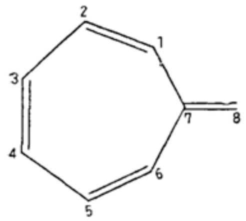
[12] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).

TABLE VI. REACTIVITY INDEXES FOR $(4n+1)$- AND $(4n+3)$-MEMBERED RINGS

Compound	Position	f_r(N)	S_r(N)	q_r
	1	0.246	0.906	1.092
	2	0.156	0.784	1.073
	5	0.073	0.598	1.047
	6	1.124	2.701	0.623

Compound	Position	f_r(E)	S_r(E)	q_r
	1	0.223	2.049	0.942
	2	0.100	1.071	0.962
	3	0.163	1.502	0.953
	7	0.046	0.756	0.976
	8	0.982	4.744	1.311

f_r, S_r and q_r are frontier electron density, superdelocalizability and total π-electron density at position r, respectively. (N) and (E) denote the reactivity indexes for nucleophilic and electrophilic reaction, respectively.

$$\Pi_{1,2.4n+2}=(-1)^{2+4n+2}\frac{2}{\pi}\times\int_{-\infty}^{+\infty}\frac{\Delta_{1,2}(iy)\Delta_{1,4n+2}(iy)}{\{\Delta^{(4n+2)}(iy)\}^2}\,\mathrm{d}y \qquad (16)$$

Following relations are easily proved[12]

$$\Delta_{1,4n+2}(iy)=1, \quad \Delta_{1,2}(iy)=\Delta^{(4n)}(iy)>0$$

$$\text{and} \qquad \Delta^{(4n+2)}(iy)<0 \qquad (17)$$

where $\Delta^{(4n)}$ and $\Delta^{(4n+2)}$ denote the secular determinants for $(4n)$- and $(4n+2)$-membered polyene, respectively. From Eqs. 13 and 16 with the aid of Eq. 17 it follows that

$$\Pi_{1,2.4n+2}>0 \quad \text{and} \quad q_1=1+\Pi_{1,2.4n+2}\delta\beta<1. \qquad (18)$$

Hence the total density at the atom of side chain is less than unity, since $\delta\beta$ is negative. In the case of $(4n+3)$-membered ring originated from a $(4n+4)$-membered polyene the following inequalities are obtained in a similar manner.

$$\Pi_{1,2.4n}<0 \quad \text{and} \quad q_1=1+\Pi_{1,2.4n}\,\delta\beta>1 \qquad (19)$$

Thus the total density becomes larger than unity.

Moreover, a close relation is observed between the atom-bond polarizability of a polyene and the highest occupied levels of $(4n+1)$- and $(4n+3)$-membered rings formed from the polyene. Table V illustrates this relation with regard to the cases of $(4n+1)$-membered ring formed from $(4n+2)$-membered polyene and $(4n+3)$-membered ring formed from a $(4n+4)$-membered polyene. In the table it is clearly observed that the lower the highest occupied level of $(4n+1)$-membered ring is, ······ and also the higher the highest occupied level of $(4n+3)$-membered ring is, the larger the amount of charge transferred from ring to side chain is. This result also coincides with the fact that the absolute value of the charge transferred decreases with n.

Thus a ring in the molecule has a tendency to approach to a $4n+2$ electron ring by the charge transfer to stabilize the molecule. The position to be attacked by a reagent was predicted for azulene in the paper symposium on aromatic character[13]. The attack of reagent was supposed to occur so as to make the ring possess $4n+2$ electrons by the process of reaction. Similarly, from the consideration stated above, it is predicted that the molecule containing a $(4n+1)$-membered ring and a side chain attached to it such as fulvene may be apt to react with a nucleophilic reagent at the side chain carbon. Inversely, in the case of $(4n+3)$-membered ring, an electrophilic reagent is inclined to attack the side chain carbon. Therefore, $4n+2$ rule can be said to govern the orientation of chemical reaction. Further, this rule also suggests a guiding principle in the syntheses of new aromatic compounds. Namely, we should choose an appropriate substituent attached to the ring that makes the ring possess $4n+2$ electrons. If a molecule

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13) D. H. Reid, *Tetrahedron*, 3, 339 (1958).

has excessive electrons on its ring, the substituent to be chosen is electron-attracting, and if it has insufficient electrons, an electron-repelling substituent should be introduced to stabilize it.

This has also been supported by several quantum-mechanical theories of chemical reactivity such as the static method[12] and the frontier electron theory[14]. The reactivity indexes used in these theories have been calculated and tabulated in Table VI, showing that the above-mentioned prediction is correct.

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[14] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957); **27**, 1247 (1957).