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A Modification of the Hückel Rule. Effective Discontinuity of Cyclic Conjugation

Satoshi Inagaki* and Yoshio Hirabayashi

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Gifu University, Kakamigahara, Gifu 504, Japan. *Received August 27, 1976*

Abstract: The degree of cyclic electron delocalization is theoretically proposed in an unequivocal manner to be a function of mode of donor (D)-acceptor (A) arrangements of component systems as well as orbital phase continuity requirements. Cyclic conjugation is continuous only for such a D-A arrangement mode as **11**, to which the orbital phase continuity requirements or the Hückel rule contained in them are applicable. Cyclic conjugation is so effectively discontinuous for **12**, **13**, etc., that the orbital phase relation makes no essential sense. There are nondelocalized $4n + 2$ π electron (or nonaromatic) systems and nonlocalized $4n$ π electron (or nonantiaromatic) systems in discontinuously conjugated systems. A novel notion of continuity-discontinuity of cyclic conjugation is exemplified by the experimental results, applied to interesting recent topics, and employed in predicting electronic properties of unknown molecules and in suggesting a device for synthesis of unstable molecules by varying substituents.

"Aromatic" chemistry has long been one of the most fascinating spheres of organic chemistry where both theoreticians and synthesists cooperated with fruitful results.[1,2] Among the theories the Hückel rule[1] is always overwhelmingly important because of its simplicity and wide coverage while other definitions of aromaticity have been proposed in various ways.[2m,n] It is, however, natural that the coverage of the dichotomy based on the number of electrons should be limited. Molecular properties continuously change from one molecule to another in the spectra of which the extremes are $4n + 2$ π electron aromatic and $4n$ π electron antiaromatic systems. It would be interesting to ask whether or not there are any other criteria on which the further detailed nature of cyclic conjugation is predicted or explained.

Essential factors underlying the Hückel rule are disclosed in this paper. Degree of cyclic electron delocalization depends on mode of donor (D)-acceptor (A) arrangements as well as the orbital phase continuity. The condition on which the criterion based on the number of electrons becomes invalid is presented in an unequivocal manner. The theoretical conclusions are exemplified by available experimental results. Application is also made to recent interesting topics, in some cases, together with prediction.

Theoretical Background

The cyclic electron delocalization condition of three interacting systems has been derived from the third-order perturbation energy.[3,4] This is finally expressed in terms of the sign (+ or −) of product of three electron configuration or orbital overlap integrals. The configurations of interest are the initial configuration and the two important transferred configurations inferred from the relative D-A property. The delocalization condition was previously applied to a variety of chemical problems, i.e., catalytic reactions caused by transition metal complexes,[3] a classification of bicyclic compounds with π bonds on each bridge as electron-delocalizing, semi-electron-delocalizing, and electron-localizing systems,[4] etc.

The physical meaning of the formalism and the successful application allow us to suppose that electron delocalization among many (n) systems is formally described by the nth order perturbation energy, or by the sign of product of n configuration overlaps

$$S_{IJ}S_{JK}\ldots S_{ZI} > 0 \tag{1}$$

where the subscript I is the initial configuration, others being important transferred configurations. The similarity of the inequality seems to lead without any proviso to the same orbital phase continuity requirements as those for three-system interaction: (1) the HOMO's of the neighboring systems should be out of phase; (2) the LUMO's of the neighboring systems should be in phase; (3) the HOMO and the LUMO of the neighboring systems should be in phase. It is readily seen that these requirements contain the Hückel rule. However, favorable D-A arrangements are found to be prerequisite to the validity for more than three systems.

It may be helpful to summarize the general results obtained from the previous studies on the three-system interaction.[3,4] (1) Electron delocalization is described in terms of interactions between the initial configuration and transferred configurations and between transferred configurations. (2) The interaction between the initial and the transferred configurations, $D_i \rightarrow A_j$, is effective only when the transferred configuration involves an electron shift between a neighboring D-A pair (**1**). The interaction corresponds to the electron delocalization through the (HOMO)$_D$-(LUMO)$_A$ interaction. (3) The interaction between transferred configurations, say, $D_i \rightarrow A_j$ and $D_k \rightarrow A_l$, is effective only when D_i and D_k are adjacent to each other, A_j and A_l being identical (**2**), or A_j and A_l are adjacent to each other, D_i and D_k being identical (**3**). The interaction between $D_i \rightarrow A_j$ and $D_k \rightarrow A_j$ corresponds to the electron delocalization between D_i and D_k through the (HOMO)$_{D_i}$-(HOMO)$_{D_k}$ interaction. The ($D_i \rightarrow A_j$) – ($D_i \rightarrow A_l$) interaction corresponds to the electron delocalization between A_j and A_l through the (LUMO)$_{A_j}$-(LUMO)$_{A_l}$ interaction.

Let us first consider four modes of D-A arrangement of four interacting systems (**4–7**), and then try to generalize the conclusions obtained. The following arguments are made step by step in order to allow one to imagine the chemical meaning of each step clearly.

In **4** an electron first delocalizes from D_1 to A through the interaction of I with the transferred configuration where an electron is shifted from (HOMO)$_{D_1}$ to (LUMO)$_A$, that is, through the (HOMO)$_{D_1}$-(LUMO)$_A$ interaction. The resulting singly occupied (HOMO)$_{D_1}$ is supplied with an electron by the neighboring (HOMO)$_{D_2}$ through the (HOMO)$_{D_1}$-(HOMO)$_{D_2}$ interaction. The process is represented by the ($D_1 \rightarrow$ A)-($D_2 \rightarrow$ A) interaction. Electron delocalization occurs between D_1 and D_2. Similarly, the resulting singly occupied (HOMO)$_{D_2}$ is in turn supplied with an electron by (HOMO)$_{D_3}$ through the (HOMO)$_{D_2}$-(HOMO)$_{D_3}$ interaction or by the ($D_2 \rightarrow$ A)-($D_3 \rightarrow$ A) interaction, with electron delocalization between D_2 and D_3. Finally, the electron delocalization between D_3 and A occurs through the (HOMO)$_{D_3}$-(LUMO)$_A$ or the I-($D_3 \rightarrow$ A) interaction in order to complete cyclic conjugation. As a result, cyclic [-(LUMO)$_A$-(HOMO)$_{D_1}$-(HOMO)$_{D_2}$-(HOMO)$_{D_3}$-] interaction has an important role.

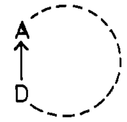
In **5** an electron having first delocalized from D to A_1 through the (HOMO)$_D$-(LUMO)$_{A_1}$ or I-(D $\rightarrow A_1$) interaction is in turn shifted to A_2 through the (LUMO)$_{A_1}$-(LUMO)$_{A_2}$ or (D $\rightarrow A_1$)-(D $\rightarrow A_2$) interaction and further to A_3 through the (LUMO)$_{A_2}$-(LUMO)$_{A_3}$ or (D $\rightarrow A_2$)-(D $\rightarrow A_3$) interaction. The cyclic conjugation is completed by electron delocalization between A_3 and D through the (LUMO)$_{A_3}$-(HOMO)$_D$ or (D $\rightarrow A_3$)-I interaction. It follows that the cyclic [-(HOMO)$_D$-(LUMO)$_{A_1}$-(LUMO)$_{A_2}$-(LUMO)$_{A_3}$-] interaction is important in **5**.

An application of a similar procedure to **6** shows the importance of the cyclic [-(HOMO)$_{D_1}$-(LUMO)$_{A_1}$-(LUMO)$_{A_2}$-(HOMO)$_{D_2}$-] interaction. The same conclusion is obtained whether $D_1 \rightarrow A_2$ or $D_2 \rightarrow A_1$ configuration is chosen as the other significant configuration than I, $D_1 \rightarrow A_1$, and $D_2 \rightarrow A_2$.

There is an essential difference of **7** from **4**, **5**, and **6**. The delocalization between a D-A pair, say, between D_1 and A_1, occurs through I-($D_1 \rightarrow A_1$) or (HOMO)$_{D_1}$-(LUMO)$_{A_1}$ interaction. However, neither is the resulting singly occupied (HOMO)$_{D_1}$ effectively supplied with an electron since the neighboring system is A_2, nor is an electron in the resulting singly occupied (LUMO)$_{A_1}$ effectively shifted since the neighboring system is D_2. Similar conclusions are drawn even if any D-A pair is chosen as the first. As a result, the four systems in **7** are only allowed to enjoy the independent delocalization between the neighboring D-A pairs. Cyclic electron delocalization is essentially interrupted. The cyclic [-(HOMO)$_{D_1}$-(LUMO)$_{A_1}$-(HOMO)$_{D_2}$-(LUMO)$_{A_2}$-] interaction makes no chemical sense but only the independent HOMO-LUMO interactions between the neighboring D-A pairs are significant. One may say that the conjugation is not cyclic in essence.

The cyclic conjugation like **4–6** which is completed by applying the aforementioned step-by-step procedure is hereafter referred to as "continuous", the others like **7** as "discontinuous". The continuity of the cyclic conjugation should be distinguished from that of orbital phase. The orbital phase continuity requirements itemized above and therefore the Hückel rule contained in them are valid for continuous conjugation, but cannot be applicable to discontinuous conjugation. It follows that there may be nonantiaromatic $4n$ π electron systems and nonaromatic $4n + 2$ π electron systems.

It may be useful to present mnemonics by which discontinuous conjugation is differentiated from the continuous one. First, separate component systems into D's and A's. The sequence of D's aligning along the conjugation chain without contaminating A (**8**) is considered to be composed of the type **2** units. The similar sequence of A's (**9**) is considered to be composed of the type **3** units. The conjugations of such D and A groups are continuous in their own regions through the interaction between transferred configurations, i.e., HOMO-HOMO and LUMO-LUMO interactions between the neighboring systems, respectively. The combination **10** of **8** and **9** also allows continuous conjugation among D's and A's. The two conjugation chains of A and D groups need to be connected at either end by the neighboring D-A pair in order to render the cyclic conjugation continuous. As a result, cyclic conjugation is continuous only when the component systems are separated into D and A groups wherein the D's and A's are connected together along the conjugation chain, respectively (**11**). In other systems such as **12**, **13**, etc., cyclic conjugation is discontinuous.



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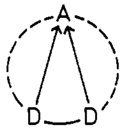

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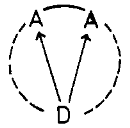

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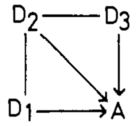

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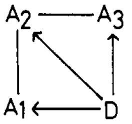

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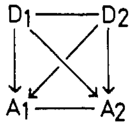

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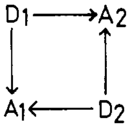

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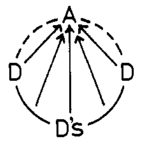

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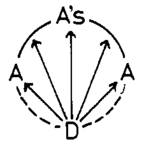

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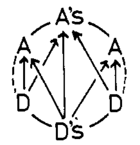

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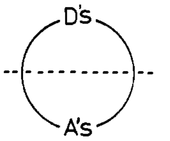

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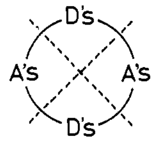

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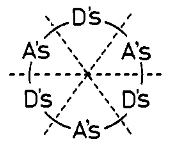

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In concluding the theoretical section it would be meaningful and useful to delineate the categories of cyclic conjugation (see Figure 1). Cyclic conjugation is first classified into continuous and discontinuous by the mode of D-A arrangements of component systems. Electron delocalization degree in discontinuous cyclic conjugation is not significantly affected by the orbital phase relation while the phase relation plays a

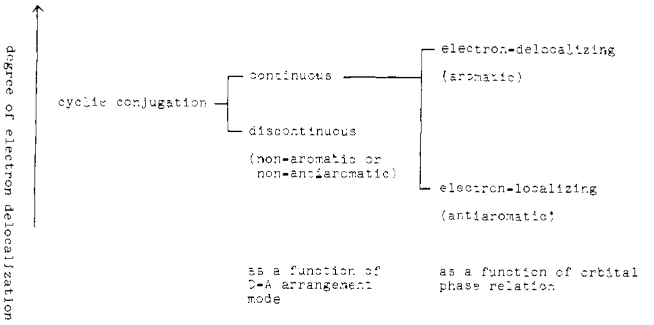


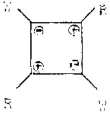
Figure 1. Degree of electron delocalization in cyclic conjugation.

substantial role in continuous conjugation. The continuous conjugation is further classified into electron-delocalizing and -localizing according to the orbital phase continuity requirements.

Discussion, Exemplification, and Prediction

A novel notion of the continuity-discontinuity of cyclic conjugation has been derived from a fundamental theoretical background. Some synthesists seem to have intuitively been "aware" of this principle, and "applied" it to synthesizing their target molecules. Some exemplifications, often together with prediction, are made in this section in order to substantiate the principle, to demonstrate its wide coverage over various chemical phenomena, and to assist creative applications to unknown molecules or their electronic properties. The following discussion is limited to several cases in which the related experimental results are now available. It is tediuos though possible to describe innumerable phenomena, whether known or unknown, in detail.

Cyclobutadienes. Cyclobutadiene is a highly unstable $4n$ π electron system.[5] Roberts' suggestion[6] that "push-pull" substituents might be sufficient in stabilizing cyclobutadiene was substantiated by Gompper and Seybold.[7] According to the present theory cyclic conjugation is effectively discontinuous in cyclobutadienes alternately substituted by electron-releasing (R) and electron-withdrawing (W) groups (**14**), as in **12**, since



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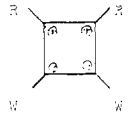

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they are appropriately considered to be composed of carbanionic centers with W and carbocationic centers with R. The "cross-push-pull" cyclobutadiene is special case of **12**.[8] The "parallel-push-pull" cyclobutadiene **15** belongs to a continuous conjugation **11** and consequently is unstable since it obeys the Hückel rule.[8]

Xylylenes, Benzoquinones, and Related Compounds. These species, **16–21**, are composed of four functional groups, two endocyclic and two exocyclic double bonds. All conjugation modes are shown in Figure 2. Conjugation is continuous in some modes and discontinuous in others. Some continuous conjugation modes meet the orbital phase continuity requirements, while the others do not. All modes are expected to contribute in molecules, e.g., *o*- and *p*-xylylenes (**16, 17**), where the four functional groups have similar D–A properties. These features, contrasted with those of a hypothetical molecule, cyclohexatriene, where all modes are continuous and favored by the orbital phase continuity requirements,[4] may be responsible for extreme instability of **16**[9] and **17**[10] relative to benzene.[11] Xylylenes were detected only on matrix at very low temperatures, on trapping as cycloadducts, or postulated as unstable reaction intermediates.

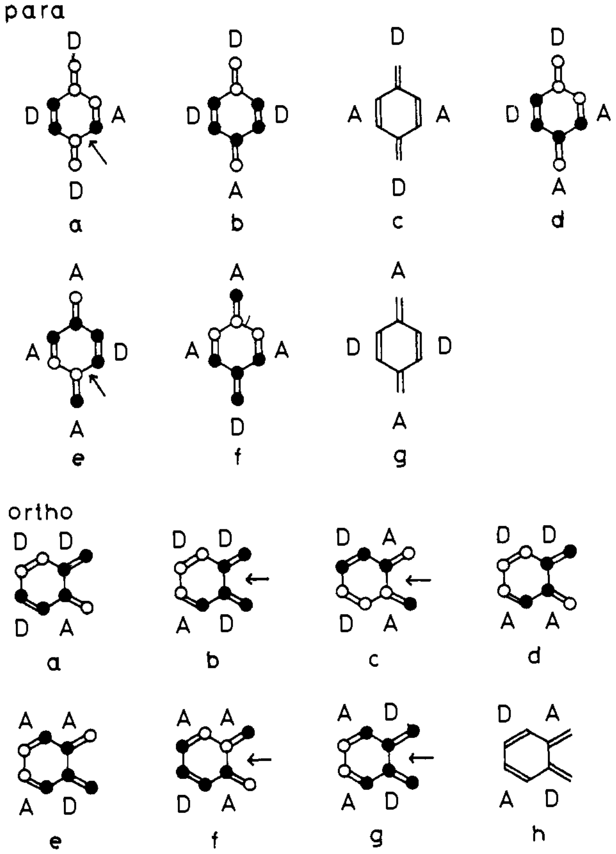
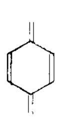


Figure 2. Cyclic conjugation modes in xylylenes, benzoquinones, and related compounds. Electron-delocalizing: para-b, para-d, para-f, ortho-a, ortho-d, ortho-e. Electron-localizing: para-a, para-e, ortho-b, ortho-c, ortho-f, ortho-g. Discontinuous: para-c, para-g, ortho-h. The arrow shows the point where orbital phase continuity is interrupted.

The delocalization modes, para-b, d, f, suggest a device for synthesizing stable derivatives or analogues of *p*-xylylene. Among them is *p*-benzoquinone methide (4-methylene-2,5-cyclohexadien-1-one, **18**), which corresponds to para-b. However, **18** has not yet been isolated as such because of its high reactivity for self-condensation or cycloaddition reactions with other molecules.[12,13] These facts suggest that a carbonyl group in place of an exocyclic C=C bond is not so strong an acceptor that the para-b mode predominates over other localization modes. A further emphasis of para-b, i.e., substitution of methylene hydrogens by powerful R's, has been found to stabilize derivatives of **18**.[13,14] For example, **22** and **23** are isolated as stable crystals. A similar stabilizing push-pull effect has been also observed in **16** with R's on one methylene and W's on the other (**24, 25**).[15] It is likely that the para-f mode also contributes to the substituent effect.

o-Benzoquinone methide (6-methylene-2,4-cyclohexadien-1-one, **19**) tends to favor a delocalization mode (ortho-a), but the parent molecule and the derivatives with weak substituents cannot be isolated.[16] Thione analogues behave similarly.[17] Such a stabilizing push-pull effect as in para isomers is inferred from the fact that a thione analogue with powerful R's on the methylene moiety (**26**) is so stable that the equilibrium is reached with the dimer at room temperature (eq 2).[18] The push-pull effect was also observed in **17**.[19] The derivative **27a** dimerizes at −10 to −20 °C while **27b** with more distinct D–A relation between the exocyclic double bonds is stable at room temperature.[19] The delocalization modes, ortho-d and -e, may also contribute to the stabilization.

It should be noted that the push-pull effects on cyclobutadiene and on xylylenes come from different origins. For cyclobutadiene the stabilization is gained by changing the con-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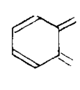
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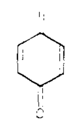
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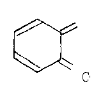
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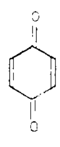
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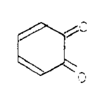
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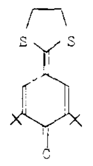
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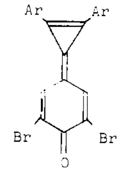
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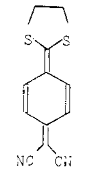
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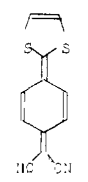
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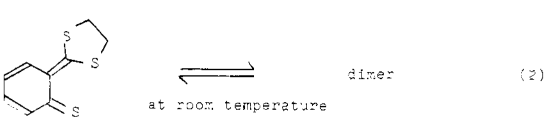

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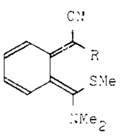
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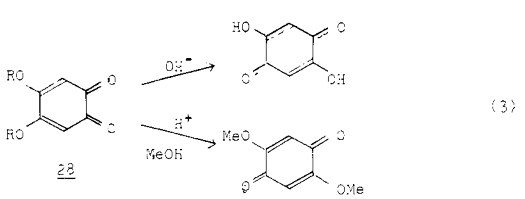
a) R=H
b) R=2,4-dinitrophenyl

tinuous conjugation system, which is not favored by the orbital phase continuity conditions, into a discontinuous conjugation system free from the phase conditions. The substituent effect on xylylenes originates from emphasizing a delocalization mode and depressing localization modes.

Benzoquinones (**20** and **21**) are xylylene analogues.[20] The conjugation modes in Figure 2 enable us to compare some properties of **20** and **21**. *p*-Quinone **20** corresponds to a discontinuous conjugation mode, para-g. Cyclic conjugation is not significant. *o*-Quinone **21** corresponds to a continuous conjugation mode, ortho-c, which does not meet the orbital phase continuity requirements. The difference suggests that **20** is more stable than **21**. This theoretical result is substantiated by the following observation. (1) The *p*-quinone **20** has the melting point (115.5 °C) while the *o*-quinone **21** decomposes at 60–70 °C.[21] (2) A nascent *o*-quinone derivative (**28**) was converted in the presence of acid or base to *p*-quinone derivatives rather than the corresponding *o*-quinone derivatives (eq 3).[22] (3) In the oxidation of phenol by peracid, *o*- and *p*-hydroxylations first occur, with the *o*-dihydroxybenzene then being oxidized to hexadienoic acid, presumably via **21**, while the para compound is oxidized to **20** (eq 4).[23] (4) Relative



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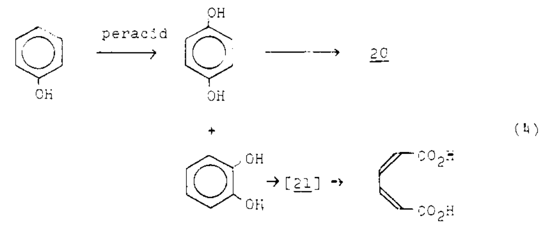
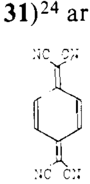


stabilities of *p*-xylylene with W's on both methylene groups (**29**, **30**, and **31**)[24] are attributed to their discontinuous conjugation; the corresponding ortho isomers have not yet been prepared.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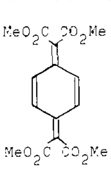
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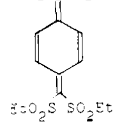
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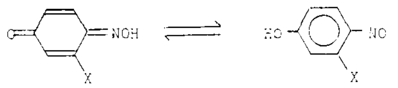
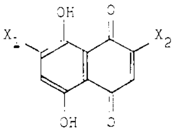
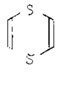
Tautomerism. An interesting substituent effect on tautomeric equilibrium was observed in **32**.[25] **32** with R (X = methyl, halo, or methoxy group) exists predominantly (>95%) in the oxime form (**32a**) whereas **32** with W (X = carbomethoxy) was estimated to be 23% in the nitroso form **32b**. This result is explained as follows: **32a** with R corresponds to a discontinuous conjugation mode, para-g, which is not destabilized. On the other hand, **32a** with W tends to belong to a localization mode, para-e. The oxime form **32a** becomes relatively destabilized to increase the portion of nitroso form **32b**. A similar substituent effect was observed[26] in tautomerization of naphthazarin (formally,[27] 5,8-dihydroxy-1,4-naphthoquinone) systems. The principal tautomer assumes quinoid form on the R-substituted nucleus (**33a**), while that assumes benzenoid form on the W-substituted nucleus (**33b**).


32a 32b


33

a) X_1=H, X_2=C_2H_5, OH, CH_3O, or CH_3CO_2
b) X_1=CH_3CO, X_2=H

Dithiins. 1,4-Dithiin (**34**) is computed to have a negative resonance energy and hence should be antiaromatic.[28] However, it has been synthesized and isolated as a thermally stable molecule with a reactivity widely different from that of aromatic systems.[29] These findings are explained by the present theory. The noninstability in spite of 8 π electrons is considered to come from effective discontinuity of cyclic conjugation;[30] the lone pair electrons on sulfurs as donors and C=C bonds as acceptors are alternately arranged as in **12**. An isomeric 8 π electron system, 1,2-dithiin (**35a**), is predicted to be unstable since cyclic conjugation is continuous and the orbital phase continuity requirements are not satisfied (**35b**).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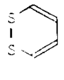
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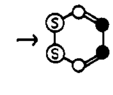
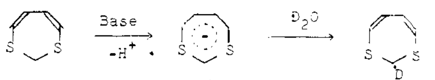

35b

Dithiepin Anions. A clear-cut difference between 1,3- and 1,4-dithiepins in the chemical behaviors toward bases most elegantly confirms our theoretical arguments.[31] 1,3-Dithiepin undergoes exchange of the hydrogens on the saturated carbon through delocalized 10 π electron anion **36**, as expected from the Hückel rule (eq 5).[32] 1,4-Dithiepin was surprisingly observed to be substituted on the olefinic carbons via **37** (eq 6).[33]

In the anion **36** electron-donating sulfur lone pair electrons and the carbanionic center existing between them and electron-accepting C=C bonds are aligned to be classified as the type **11**. The cyclic conjugation is continuous. The degree of



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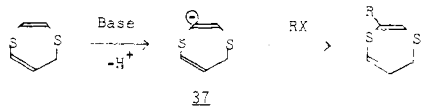

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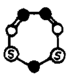
electron delocalization depends on the orbital phase relation. The phase continuity requirements are satisfied in **36** (see **38**),



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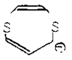

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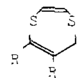

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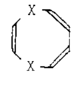
as expected from 10 π electrons. In the anion **39** the cyclic conjugation is discontinuous since the donors and the acceptors are alternately arranged as in **12.** The anion **39** cannot gain the stabilization energy expected from the Hückel rule in spite of 10 π electrons.

The present theory suggestes that appropriately substituted 1,4-dithiepins undergo hydrogen exchange at the saturated carbon as usually expected from the Hückel rule. It is necessary that the continuity of conjugation in **39** should be recovered. For this purpose all components on one side with respect to the sulfur atoms should be acceptors or donors. The most promising model compounds for examining the theoretical prediction are **40** where neither potential reaction site is occupied by the substituents.



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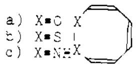

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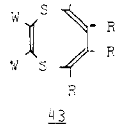

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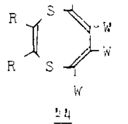

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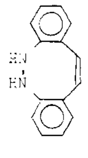

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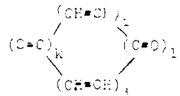
Diheterocins (41, 42). The synthesis and the electronic properties of 1,4-diheterocins **41** recently attracted the attention of organic chemists.[34-36] These compounds have 10 π electrons. The aromatic character is an interesting problem. Suppose that the geometrical structure is planar enough to allow the lone pair electrons on the heteroatoms to contribute appreciably to cyclic conjugation. The cyclic conjugation is then discontinuous since the lone pair electrons as donors and the C=C bonds as acceptors are alternately arranged as in **12.** No extensive delocalization due to $4n + 2$ π electrons is expected. A few experimental results show that **41a**[34] and **41b**[35] have no aromatic character. Further experimental studies on electronic and geometrical structures are required in order to deduce the nature of **42.** There remains a possibility that they are distorted enough to exclude the lone pair electron from the cyclic conjugation to be stable 6 π electron systems.

There is a promising device to synthesize more stable 1,4-diheterocin derivatives. It is recommended to transform the discontinuous conjugation system into any continuous conjugation system. The requirement may be satisfied in **43** and **44.**

In contrast to **41** cyclic conjugation is continuous in **42** since the heteroatoms as donors are adjacent to each other to be classified as the type **11.** Electron delocalization is expected to be extensive in **42** because of 10 π electrons. It is likely that **42** is more stable than **41** if the intrinsic strength of the X-X bond is not so significant. Unfortunately, no information on little perturbed 1,2-diheterocins is available. Only a related experimental result supports the preceding arguments; a yellow crystal **45** is somewhat stabilized compared with the dihydro derivative.[37]

Polycarbonyl Cycloolefins (46). A class of the title compounds (**46,** i = an odd number; $j = 0$; k or $l \neq 0$) are predicted to be delocalized π electron systems. The cyclic conjugation is continuous as in **11;** C=C bonds and carbonyl groups are D's and A's, respectively. The orbital phase is also continuous since the sign is required to be $i - 1$ (an even number) times inverted along the D chain while no sign inversion is required to take place along the A chain. This class includes cyclopropenone (**47**), 3-cyclobutene-1,2-dione (**48**), 4-cyclopentene-1,2,3-trione (**49**), 5-cyclohexene-1,2,3,4-tetraone (**50**), 2,4,6-cycloheptatrien-1-one (tropone, **51**), 3,5,7-cyclooctatriene-1,2-dione (**52**), etc.

Molecules in the second class of **46** (i = an even number; $j = 0$; k or $l \neq 0$) are predicted to be localized π electron systems. The cyclic conjugation is similarly continuous, but the orbital phase continuity requirements are not satisfied since the sign is required to be $i - 1$ (an odd number) times inverted along the D chain. Among this class are 2,4-cyclopentadiene-1-one (**53**), *o*-benzoquinone (**21**), 4,6-cycloheptadiene-1,2,3-trione (**54**), 5,7-cyclooctadiene-1,2,3,4-tetraone (**55**), etc.



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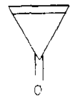

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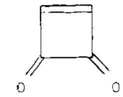

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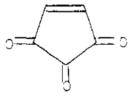

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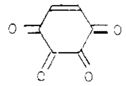

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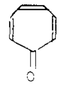

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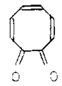

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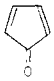

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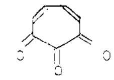

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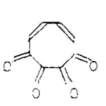

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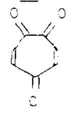

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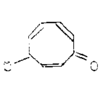

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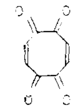

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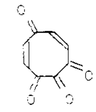

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The cyclic conjugation in the last class of **46** ($i, j, k, l \neq 0$) is discontinuous as in **12** and consequently not significant. They are nondelocalized or nonlocalized π electron systems independent of the orbital phase conditions. This class contains *p*-benzoquinone (**20**), 3,6-cycloheptadiene-1,2,5-trione (**56**), 2,5,7-cyclooctatriene-1,4-dione (**57**), 3,7-cyclooctadiene-1,2,5,6-tetraone (**58**), 4,7-cyclooctadiene-1,2,3,6-tetraone (**59**), etc.

Some of the above predictions are substantiated while others have not yet been examined experimentally. The monoketones, **47**[38] and **51**,[39] are typical nonbenzenoid aromatics. Derivatives of **48**[40] and **49**[41] undergo substitution reactions on the olefinic carbons, a characteristic of aromatic compounds, whereas **53** is highly reactive for Diels-Alder dimerization.[42]

Remarkable differences in chemical properties were recently observed between a localized electron system **54**[43] and a discontinuously conjugated system **56.**[44] (1) **56** was isolated as a crystal although **54** was only spectroscopically detected in solution. (2) **56** was quantitatively yielded by oxidation of 5-hydroxytropolone by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone while 3-hydroxytropolone, submitted to a similar oxidation, afforded a hemiketal of **54** as an isolable product, presumably formed through the reaction of **54** with alcohol as solvent. (3) A hemiketal of **56** easily reverted to **56** on evaporation of solvent while all attempts to liberate alcohol molecule from the hemiketal of **54** were unsuccessful. These facts confirm our prediction that **56** is more stable than **54**.

A discontinuously conjugated system **57** was just recently synthesized and the chemical properties were investigated.[45] The NMR signals of the hydrogens on the diene part of **57** are nearly superimposed on those of the 2,3-dihydro derivative of **57**. It was concluded that **57** is not aromatic. However, **57** is so stable that it decomposes at 500 °C to a slight degree. These experimental results are compatible with the prediction that discontinuously conjugated systems are more stable than continuously conjugated systems with phase discontinuity. It would be interesting to compare **57** with **52** about which any experimental data are, unfortunately, not available now.

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