© 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 3724—3732 (1982) [Vol. 55, No. 12

Cyclic Orbital Interaction and Orbital Phase in Acyclic Conjugation

Satoshi Inagaki,* Hirofumi Kawata, and Yoshio Hirabayashi
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11

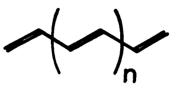
(Received May 7, 1982)

The orbital phase continuity-discontinuity property is shown to control electron delocalization and polarization even in open chain conjugated molecules. Its chemical consequences are discussed.

The π electron delocalization has been one of the central subjects in organic chemistry. There are well-established rules for monocyclic conjugation. The $4n+2$ π electron aromaticity rule[1] is related to the static state of the ground-state molecules at their equilibrium geometries. The stereoselection rule[2–4] is the counterpart for the dynamic process or for the transition state of chemical reactions. Both rules were founded on the identical basis, *i.e.*, the continuity-discontinuity of orbital phase of many composite systems.[5–8] The phase control has been believed to be characteristic of nothing but *cyclic* conjugated molecules. In this paper the orbital phase will be shown to be more fundamental, and to play a significant role in determining electron delocalization even in *acyclic* conjugated molecules.

Theoretical

Delocalization. We are concerned with two types of acyclic conjugation of ethylenic π bonds. In the head-to-tail polyenes (**1**), a π bond interacts at one end (head) with a second bond and at the other end (tail) with a third bond. In the head-to-head polyenes (**2**), a π bond interacts at an end (head) with two neighboring bonds. There is no primary difference between **1** and **2** in the electron delocalization between the adjacent units, which is considered as that in butadiene. The indirect delocalization between two bonds mediated by another should make a characteristic distinction between **1** and **2**. There are two paths for the end-to-end electron delocalization in the triene unit, as is illustrated in Scheme 1.[9]



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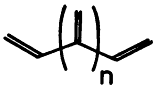

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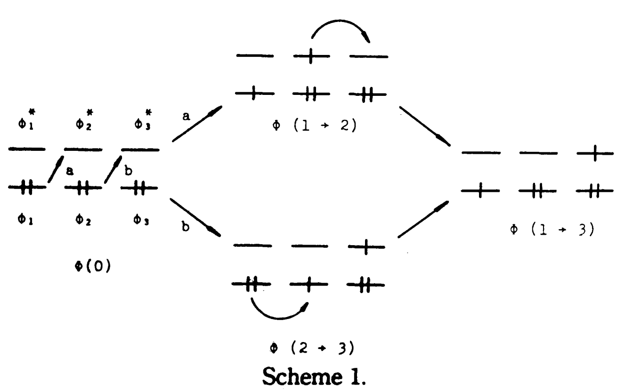


Scheme 1.

An electron in the bonding orbital, ϕ_1, of a terminal bond transfers to the antibonding orbital, ϕ_2^*, of the middle and then to ϕ_3^* of the other terminus (path a). By the other path an electron hole in ϕ_2 resulting from the electron shift from ϕ_2 to ϕ_3^* is supplied with an electron by ϕ_1 (path b). The coefficients, $C_a(1\to3)$ and $C_b(1\to3)$, of the $1\to3$ transferred configuration, $\Phi(1\to3)$, contributed through the paths, a and b, are given by the perturbation theory, respectively:

$$C_a(1\to3) = \frac{\langle\Phi(0)|H'|\Phi(1\to2)\rangle\langle\Phi(1\to2)|H'|\Phi(1\to3)\rangle}{[E(1\to2)-E(0)][E(1\to3)-E(0)]}$$

$$C_b(1\to3) = \frac{\langle\Phi(0)|H'|\Phi(2\to3)\rangle\langle\Phi(2\to3)|H'|\Phi(1\to3)\rangle}{[E(2\to3)-E(0)][E(1\to3)-E(0)]}.$$

When the Hückel approximation is employed, we obtain the following equations:

$$C_a(1\to3) = C_b(1\to3),\ i.e.,\ C(1\to3) = 2C_a(1\to3)$$

for the head-to-tail triene, and

$$C_a(1\to3) = -C_b(1\to3),\ i.e.,\ C(1\to3) = 0$$

for the head-to-head triene. The $1\to3$ delocalization is amplified in the head-to-tail polyenes while cancelled out in the head-to-head polyenes.

The clear-cut difference in the indirect delocalization between the head-to-head and head-to-tail polyenes is ascribed to the cyclic orbital interaction in the acyclic conjugation. The configuration interactions between $\Phi(0)$ and $\Phi(1\to2)$ and between $\Phi(1\to2)$ and $\Phi(1\to3)$ in C_a contain the orbital interactions between ϕ_1 and ϕ_2^* and between ϕ_2^* and ϕ_3^*, respectively. The ϕ_1-ϕ_2^*-ϕ_3^* orbital interaction is involved in the delocalization *via* path a. The corresponding configuration interactions between $\Phi(0)$ and $\Phi(2\to3)$ and between $\Phi(2\to3)$ and $\Phi(1\to3)$ in C_b contain the orbital interactions between ϕ_2 and ϕ_3^* and between ϕ_1 and ϕ_2, respectively. The ϕ_1-ϕ_2-ϕ_3^* orbital interaction is involved in the delocalization *via* path b. These orbital interactions share the ϕ_1 and ϕ_3^* orbitals at either end to form a cyclic orbital interaction like $\overline{\phi_1\text{-}\phi_2\text{-}\phi_3\text{-}\phi_2^*}$. As a result, the extent of the indirect delocalization, *i.e.*, the magnitude of the coefficient of the $1\to3$ electron transferred configuration is dependent on the orbital phase property.

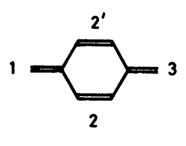
For further understanding of the cyclic property of the orbital interactions involved in the acyclic conjugation, it is preferable to suppose "hypothetical" cyclic systems, **3** and **4**, which have a bonding orbital, ϕ_2, only on the bond 2 and antibonding orbital, ϕ_2^*, only on the bond 2′. There are analogous pathways for the $1\to3$ delocalization. An electron in ϕ_1 transfers to ϕ_2^* of the bond 2′ and then to ϕ_3^* (path c). An electron hole resulting from the electron shift from ϕ_2 of the bond 2 to ϕ_3^* is supplied with an electron by ϕ_1

(path d). The formula for the coefficients of the indirectly transferred configurations contributed from the paths, c and d,

$$C_c(1\to 3) = \frac{\langle \Phi(0)|\mathrm{H}'|\Phi(1\to 2')\rangle\langle \Phi(1\to 2')|\mathrm{H}'|\Phi(1\to 3)\rangle}{[E(1\to 2') - E(0)][E(1\to 3) - E(0)]}$$

$$C_d(1\to 3) = \frac{\langle \Phi(0)|\mathrm{H}'|\Phi(2\to 3)\rangle\langle \Phi(2\to 3)|\mathrm{H}'|\Phi(1\to 3)\rangle}{[\mathrm{E}(2\to 3) - E(0)][E(1\to 3) - E(0)]}$$

are equivalent to C_a and C_b, respectively. In this sense, the acyclic systems, **1** and **2**, have the same features as the cyclic systems, **3** and **4**, with respect to the 1→3 delocalization.



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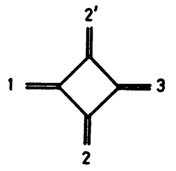

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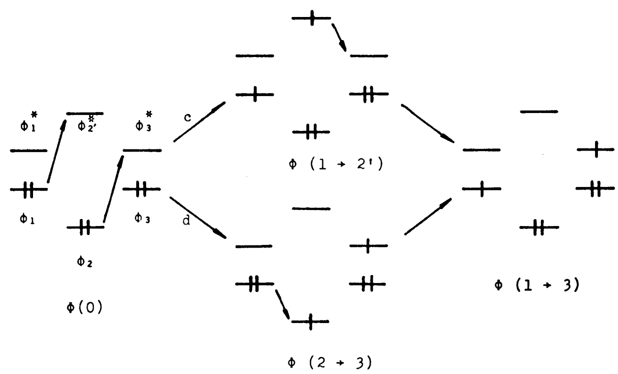
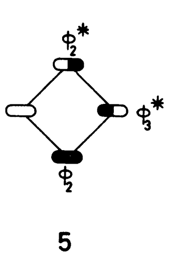


Scheme 2.

The 1→3 delocalization in **3** and **4** is a mode of cyclic delocalization, where the bonds, 1 and 2, are donors, the bonds, 2' and 3, being acceptors. The donors are on one side of the conjugation chain while the acceptors are on the other side. The D-A alternation occurs only twice along the conjugation. Such conjugation is classified into the continuous conjugation.⁶⁾ The delocalization is then subject to the orbital phase continuity-discontinuity property. The orbital phase requirements for many-system interaction are as follows:⁵,⁶⁾ (1) The electron-donating orbitals out of phase, (2) the electron-accepting orbitals in phase, and (3) the donating and accepting orbitals in phase. The requirements are satisfied in **3** (see **5**), but not in **4** (see **6**).¹⁰⁾ The cyclic delocalization is allowed in **3**, but forbidden in **4**. The mathematical equivalence of the 1→3 delocalization in **1** and **2** to the modes of cyclic delocalization in **3** and **4** means that the open-chain conjugated systems share a characteristic with the corresponding cyclic conjugated systems. *Even acyclic conjugation contains cyclic orbital interaction. The delocalizability in acyclic conjugation is also under the influence of the orbital phase property.*

Polarization. Only one-electron transferred configurations were taken into consideration in the preceding section.



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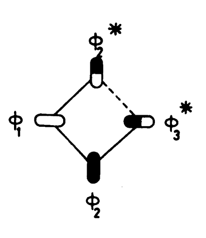

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In general, locally-excited configurations contribute to the electronic structures of interacting systems. Let us study two interacting ethylenic double bonds in butadiene. There are two pathways for electron promotion in a double bond, as is illustrated in Scheme 3.¹¹⁾ An electron in ϕ_1 transfers to ϕ_2^* ande thn back to ϕ_1^* (path e). Otherwise, an electron hole in ϕ_2 resulting from electron shift to ϕ_1^* is supplied with an electron by ϕ_1 (path f). The coefficients of the locally-excited 1→1 configuration, obtained in the same way,

$$C_e(1\to 1) = \frac{\langle \Phi(0)|\mathrm{H}'|\Phi(1\to 2)\rangle\langle \Phi(1\to 2)|\mathrm{H}'|\Phi(1\to 1)\rangle}{[E(1\to 2_j - E(0)][E(1\to 1) - E(0)]}$$

$$C_f(1\to 1) = \frac{\langle \Phi(0)|\mathrm{H}'|\Phi(2\to 1)\rangle\langle \Phi(2\to 1)|\mathrm{H}'|\Phi(1\to 1)\rangle}{[E(2\to 1) - E(0)][E(1\to 1) - E(0)]}$$

have an identical magnitude and the opposite signs:

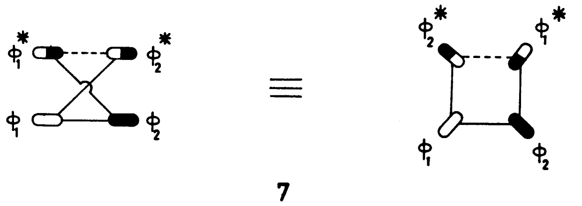
$$C_e(1\to 1) = -C_f(1\to 1).$$

Then

$$C(1\to 1) = 0.$$

The polarization is depressed completely. The result is understood in terms of the cyclic orbital interaction (**7**). The polarization is also controlled by the continuity-discontinuity of orbital phase. The forbidden polarization justifies the neglect of the locally-excited configurations in the preceding arguments about the delocalization in polyenes.

Polarization Effects on Delocalization. The absence of the local excitation in polyenes comes from the



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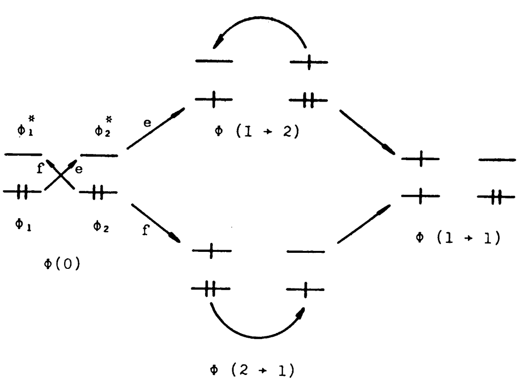
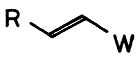


Scheme 3.

peculiar feature of the interaction between the equivalent systems at the equivalent sites like Y–X···X–Y (see C_e and C_f). An ethylenic π bond is usually polarized by the interactions with substituents or attacking reagents. Here, the effects of polarization on delocalization will be examined in terms of orbital phase, using the simple models, *i.e.*, disubstituted ethylenes, **8**—**13**. Electron-releasing (R) and withdrawing (W) substituents are represented by the doubly occupied bonding orbital of ethylene (E) and the vacant anti-bonding orbital, respectively. This model allows the substituted double bond to polarize by eliminating one of the pathways involving the opposite phase mixing of locally-excited configurations.



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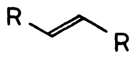

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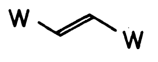

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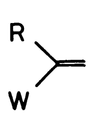

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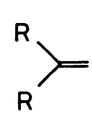

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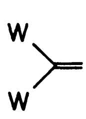

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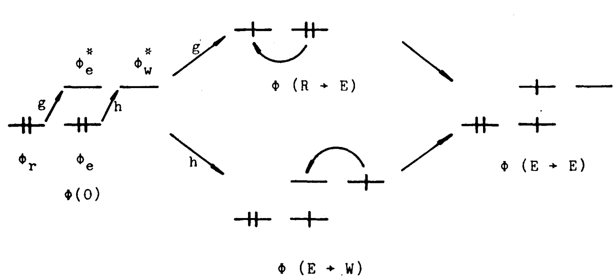
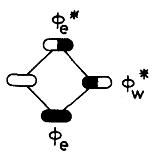
Electron delocalization primarily occurs from R to E and from E to W in R,W-substituted ethylenes, **8** and **9**. The present question is reduced to whether the mixing of the locally-excited configuration, Φ(E→E), can enhance the delocalization or not. There are two pathways for electron promotion in E (Scheme 4). The electron hole in ϕ_r resulting from electron shift $\phi_r \rightarrow \phi_e^*$ is supplied with an electron by ϕ_e (path g). The electron is transferred from ϕ_e to ϕ_w^* and then back to ϕ_e^* (path h). The corresponding cyclic orbital interactions are **14** for **8** and **15** for **9**. The polarization is allowed in the *vic*-R,W-disubstituted ethylene **8** but not in the geminal isomer **9**. The allowed polarization enhances the delocalization due to the interactions of the locally-excited configuration Φ(E→E) with the transferred configurations, Φ(R→E) and Φ(E→W).

The R→W delocalization in the vicinal isomer corresponds to the 1→3 delocalization in the head-to-tail triene. The cyclic orbital interaction is favored by the orbital phase (**5**). The delocalization is then promoted by the distant delocalization as well. On the other hand, the R→W delocalization in the geminal isomer corresponds to the forbidden 1→3 delocalization in the head-to-head triene (**6**). The delocalization is never enhanced by the R→W delocalization. It is noteworthy that the cyclic orbital interactions, **14** and **15**, for the polarization of the double bond are common to those (**5** and **6**) for the distant R→W delocalization in the R,W-ethylenes. The cyclic orbital interactions have the dual meaning in this sense.



Scheme 4.



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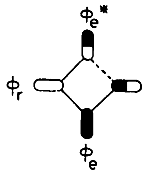

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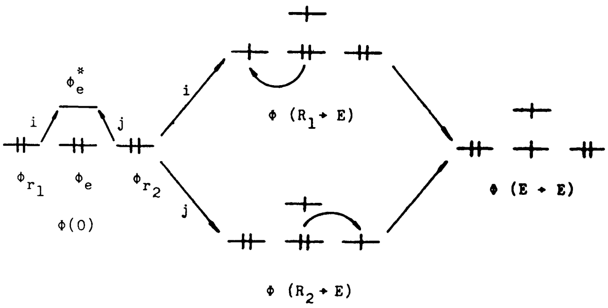
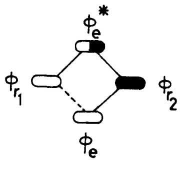
The mechanism of polarization in the R,R-disubstituted ethylenes, **10** and **11**, is illustrated in Scheme 5. An electron in ϕ_{r_1} (ϕ_{r_2}) is transferred to ϕ_2^* by the path i (path j). The resulting electron hole in ϕ_{r_1} (ϕ_{r_2}) is supplied with an electron by ϕ_e. The cyclic orbital interaction meets the phase continuity requirements in the *gem*-R,R-ethylene **11** (see **17**) while not in the vicinal isomer **10** (see **16**). A similar argument is applicable to the polarization in the W,W-ethylenes, **12** and **13**. The cyclic orbital interactions **are** shown in **18** for **12** and in **19** for **13**.

The geminal substituents of the same donor-acceptor property and the vicinal ones of the opposite donor-acceptor property enhance electron delocalization through the polarization. The latter substitution pattern



Scheme 5.



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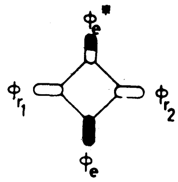

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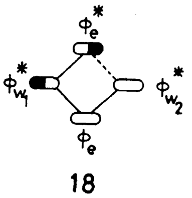

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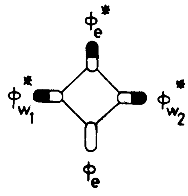

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also promotes the delocalization by the distant R→W delocalization. The other models do not meet the orbital phase continuity requirements. As a result the delocalizability is predicted to increase in the order of *vic*-R,R (**10**), *vic*-W,W (**12**), *gem*-R,W (**9**)<*gem*-R,R (**11**), *gem*-W,W (**13**)<*vic*-R,W (**8**).

Calculation

We carried out calculation by a linear combination of electron configurations at the Hückel level (HMO-LCEC)[12] to examine the preceding theoretical conclusions in a numerical manner. The zero-configuration, $\Phi(0)$, the one-electron locally-excited configuration, $\Phi(n \to n)$, and the one-electron transferred configuration, $\Phi(n_1 \to n_2)$, are involved in the calculation. Figure 1 shows the range of the coefficient ratios, $|C(n_1 \to n_2)/C(0)|$, (see Appendix) of triene through nonaene as the function of the distance ($\Delta n = |n_1 - n_2|$) between the double bonds where an electron transfers. The magnitude of the coefficient ratio reasonably decreases with the distance. There is no significant difference in the adjacent delocalization ($\Delta n = 1$) between the head-to-head and head-to-tail polyenes. Most outstanding is the coefficient ratio of the distantly transferred configurations in the head-to-head polyenes; $|C(\Delta n)/C(0)| = 0$ for $\Delta n \geqq 2$.[13] This is also the case with the locally-excited configurations in both types of polyenes; $C(n \to n)/C(0) = 0$. These results confirm the theoretical prediction. The delocalization is "localized" between the neighboring double bonds in the head-to-head polyenes whereas farther delocalization can take place in the head-to-tail polyenes.

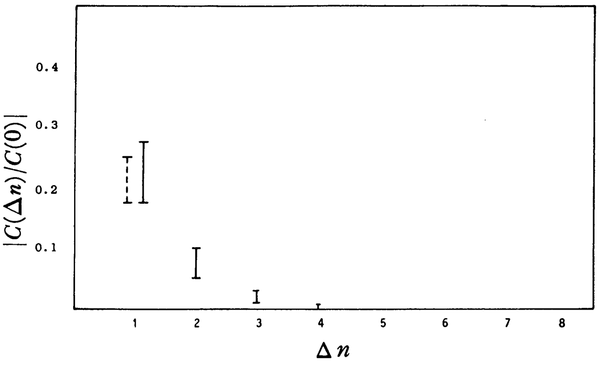


Fig. 1. The coefficient ratio ($C(\Delta n)/C(0)$) of the $n_1 \to n_2$ transferred configurations to the zero-configuration for **1** (I) and **2** (⁞), where $\Delta n = n_1 - n_2$.

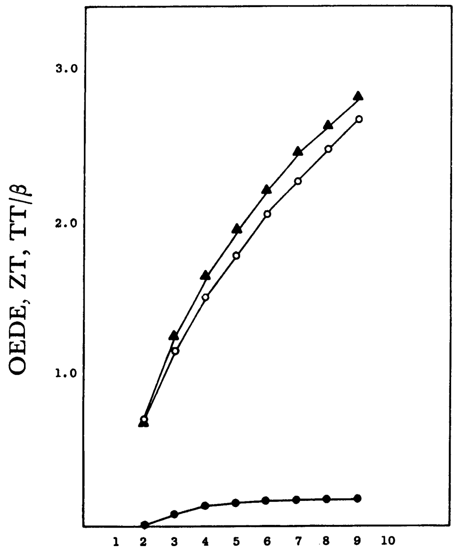


Fig. 2. The one-electron delocalization energies of **1** (▲) and **2** (○), the ZT energies of **1** (○) and **2** (○), and the TT energies of **1** (●) and **2** (zero).

We also calculated one-electron delocalization energy (OEDE),[14] which was recently proposed[8] to be a measure of electron delocalization. The head-to-tail polyenes have greater OEDE than the corresponding head-to-head polyenes (Fig. 2),[15] as is expected. The OEDE is composed of the ZT and TT energies.[8] The ZT energy is due to the interaction between $\Phi(0)$ and $\Phi(n_1 \to n_2)$ or the donor-acceptor interaction between of neighboring bonds. The TT energy is due to the interactions between $\Phi(n_1 \to n_2)$'s, and can be used as a measure of the distant delocalization. The ZT energies of both types of polyenes are found to be identical and equal to be the OEDE of the head-to-head polyenes. The TT energy is appreciable for the head-to-tail polyenes and zero for the head-to-head polyenes. As a result, the difference in OEDE or in electron delocalizability is attributed to the difference in the TT energy or in the distant delocalization. These numerical results argue for the prediction that the 1→3 delocalization is forbidden in the head-to-head polyenes while not in the head-to-tail polyenes.

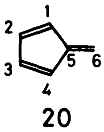
The OEDE was calculated for the model compounds, **8**—**13**. The results are consistent with the prediction. The OEDE of the least delocalizing group including **9**, **10**, and **12** is 0.707β. The intermediately delocalizing **11** and **13** have 0.801β OEDE. The most delocalizing **8** has 0.905β. The OEDE increment from the first to the second group results from the contribution of polarization. Without polarization, the OEDE of both groups is identical (0.707β). The difference between the latter two groups is attributed to the allowed R→W electron delocalization in **8**. Without the transferred configuration, the OEDE is reduced to that of the second group (0.801β).

Discussion

The chemistry of the head-to-head polyenes has been advanced much less than that of the head-to-tail polyenes, presumably due to their instability inferred from the present theory. There are many works on the head-to-tail polyenes. A high polymer of the head-to-tail polyenes, *i.e.*, "polyacetylene," was synthesized more than two decade ago,[16] still attracting attention of chemists because of electrical conductivity of the doped material.[17] Polyacetylene was reported to contain 200—300 ethylenic double bonds.[18] In contrast, there are only a few reports[19] about the head-to-head polyenes limited to their low homologs or up to tetraenes. The present situation is similar for polycarbonyl compounds, an analogous series of the head-to-head polyenes. Only a small number of reports on triones and tetraones are available.[20] No higher homologs were found in the literature.

Independent theoretical calculations make up for the insufficiency of the experimental results. Hess and Schaad[21] obtained the π-single-bond energy, $E^{\pi}_{\mathrm{c-c}}$, of **1** and **2** from the Hückel molecular orbital calculation on the Dewar's assumption[22] that the bond energy is additive: $E^{\pi}_{\mathrm{c-c}}=0.628\beta$ for **1** and 0.396β for **2**. The π-single-bond energy corresponds primarily to the electron delocalization between the double bonds. The conspicuous difference is consistent with our prediction. Del Re[23] calculated the interaction energies between the component systems in some π conjugated molecules. The interaction energy was found to be greater for the head-to-tail coupling than for the head-to-head coupling. Aihara[24] obtained the HMO energy of the unit structure, C=C–C, in cyclic head-to-tail (annulene) and head-to-head (radialene) polyenes, and showed E_{u}(annulene)$>$$E_{\mathrm{u}}$(radialene). Kollmar[25] calculated the resonance energies of 1,3,5-hexatriene (**1**; $n=1$) and 3-methylene-1,4-pentadiene (**2**; $n=1$) as the energy difference between the ab initio SCF energy and the energy expectation value with respect to a model wavefunction in which the SCF π orbitals were replaced by appropriate nonresonating localized π MO's (reference state). The "vertical" and "normalized" resonance energies of the head-to-head triene are smaller by 2.3 and 0.3 kcal/mol than those of the head-to-tail triene.

The orbital phase control over the delocalization in acyclic conjugated molecules provides us with an unprecedented insight into a general aspect of cyclic conjugation. Cross-conjugation is an element in the cyclic conjugated hydrocarbons with exocyclic double bonds. The orbital phase discontinuity prohibited electrons from delocalizing from a π bond to another across the exocyclic π bond. The feature clearly distinguishes this class of molecules from cyclic head-to-tail polyenes where the acyclic delocalization is ideally favored by the orbital phase continuity. The orbital phase discontinuity in acyclic delocalization is a key to understanding the extreme instability of cyclic conjugated hydrocarbons with the exocyclic bonds such as fulvene (**20**),[26] heptafulvene (**21**),[26k,27] calicene (**22**),[28] fulvalene (**23**),[29] sesquifulvalene (**24**),[26k,27e,27f,30] heptafulvalene (**25**),[29a,31] 3,4-dimethylenecyclobutene (**26**),[32] 5,6-dimethylene-1,3-cyclohexadiene (**27**),[33] and 3,6-dimethylene-1,4-cyclohexadiene (**28**),[34] irrespective of the number of electrons.



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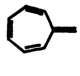
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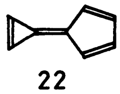
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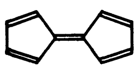
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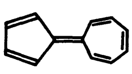
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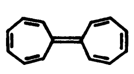
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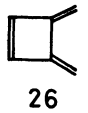
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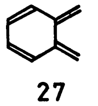
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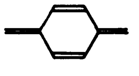
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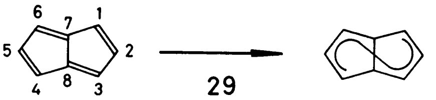
Appreciable stability is gained only when appropriate substituents are attached to the exocyclic bonds. There are usually both cyclically delocalizing and localizing modes of orbital interactions in a π conjugated molecules with exocyclic bonds.[6] The substituents make a delocalizing mode predominate over the localizing modes through the enhanced donor-acceptor power, on one hand. The orbital phase discontinuity for the delocalization across the exocyclic bond is partly due to the identical magnitude of the delocalization through the antibonding orbital of the exocyclic bond (path a) and through the bonding orbital (path b). The substituents prefer a path to the other, and relax the orbital phase discontinuity, on the other hand.

Some theoretical and experimental results argue for the peculiarity of the cross-conjugation in the molecules. Let us see the bond lengths or the bond orders in fulvene. There are two sorts of single bonds, *i.e.*, C_1–C_5 and C_2–C_3 bonds. The C_1–C_5 single bond is an element of the acyclic conjugations, *i.e.*, the head-to-tail C_4=C_3–C_2=C_1–C_5=C_6 and the head-to-head C_2=C_1–C_5(=C_6)–C_4=C_3. On the other hand, the C_2–C_3 bond belongs to the head-to-tail chains, *i.e.*, C_1=C_2–C_3=C_4–C_5=C_6 and C_4=C_3–C_2=C_1–C_5=C_6. Consequently, the delocalization is expected to be low in C_2=$C_1$$\cdots$$C_5$=$C_6$ relative to that in C_1=$C_2$$\cdots$$C_3$=$C_4$. In fact, the bond order[35,36] is smaller between C_1 and C_5 of the head-to-head junction than between C_2 and C_3 of the head-to-tail one. Some molecular orbital calculations[22a,37,38] predicted consistent bond lenghts. The bonds of the head-to-head conjugation are longer than those of the head-to-tail conjugation. This is confirmed by the electron diffraction study of the 6,6-dimethyl derivative.[39] A similar argument is applicable to and confirmed by the theoretical calculations and/or the experiments for **21**,[22a,35–37,40] **22**,[41] **23**,[22a,35–37,40b] **24**,[22a,36,37] **25**,[22a,35–37] **26**,[38,39,41,42] and **27**.[35,41]

The tendency to avoid the cross-conjugation is also recognized in pentalene (**29**),[43] azulene (**30**),[44] heptalene (**31**).[45] There are two possible ways to reduce the cross-conjugation effects by adjusting the bond distances; *i.e.*, by stretching the fused bond (C_7–C_8 in **29**, C_9–C_{10} in **30**, C_{11}–C_{12} in **31**) and the peripheral bonds (C_1–C_7, C_4–C_8 in **29**, C_1–C_9, C_4–C_{10} in **30**, C_1–C_{11}, C_6–C_{12} in **31**). The fused bond elongation provides the molecules with a quality of the peripheral monocyclic head-to-tail conjugation. With the lengthened peripheral bonds, the molecules acquire a property of acyclic head-to-tail polyenes. Azulene prefers monocyclic conjugation because of 10 π electrons. According to the experimental data,[46] the peripheral bond alternation is small. The deviation of the bond distances fall in the range of 0.03 Å. The fused bond is much longer by 0.07 Å than the longest peripheral bond. The similar theoretical results[37,40b] are available. On the other hand, pentalene and heptalene should choose acyclic conjugation because of 4n π electrons on the periphery. Some calculations[37,40b,47] suggest that the peripheral cross-conjugated bond in pentalene is the weakest, the fused bond being stronger, while the single bonds between the endocyclic double bonds are much stronger than both. The shortening of the fused bond is interpreted as the geometrical deformation to gain the stabilization due to acyclic head-to-tail conjugation.



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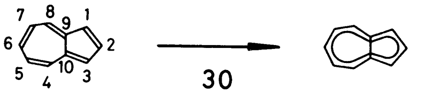

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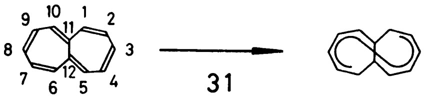

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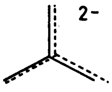
Acyclic Aromaticity. The degree of electron delocalization in trimethylenemethane (**32**) and butadiene (**33**) dianions was shown in a preliminary communication[48] to be determined by the orbital phase properties. Trimethylenemethane dianion is considered to be a π-conjugated molecule where two anion centers interact with an end of the double bond (see **34**). Butadiene dianion has the identical subsystems which, however, lie in the different relative positions (see **35**). The orbital phase aspects of the dianions are the same as those of the R,R-substituted ethylene models. Trimethylenemethane dianion corresponds to *gem*-R,R (**11**) while butadiene dianion corresponds to *vic*-R,R (**10**). The cyclic orbital interaction is favored by the orbital phase continuity in trimethylenemethane dianion (see **17** for **11**), but not in butadiene dianion (see **16** for **10**). This is consistent with the suggestion of "Y-aromaticity,"[49] with the experimental observation of the relative thermodynamical stabilities of the anions,[50] and with the heat of formation of the related species calculated by Schleyer *et al.*[51]



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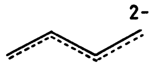

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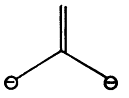
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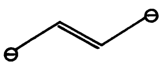
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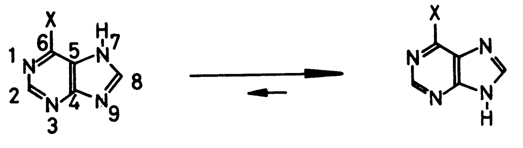
Tautomerim in Purines. A significant polarization effect is found in the protropic tauromerism of biological important bases, purine (**36a**; X=H) and adenine (**36b**; X=NH$_2$).[52] There is no difference in the Kekulé structures of the pyrimidine and imidazole rings between the 7H- and 9H-tautomers. The way of fusion of the heterocyclic rings distinguishes one from the other. The preceding theoretical result has shown that electrons delocalize to the greatest degree when R- and W-substituents are attached to the vicinal carbons of the C=C double bond. In both tautomers, the bond in the pyrimidine ring, vicinal to the electron-donating amino nitrogen in the imidazole ring, is identical, *i.e.*, the imino double bonds. However, the electron accepting power of the C=N moiety is different between C and N. The AO coefficient in the LUMO is larger at C than at N. The imino group is linked at the nitrogen, N$_3$, in the 7H-tautomer and at the carbon, C$_6$, in the 9H-tautomer. As a result the donor-acceptor disposition favors electron delocalization in the 9H-tautomer.



7H-36 9H-36

The calculation supports the prediction. The OEDE is by 0.021β greater for 9H-**36a** than for 7H-**36a**. In order to examine the origin of the difference, we carried out the calculations without the locally-excited configuration of each bond. The OEDE of the 9H-tautomer significantly decreases to be close to the almost unchanged OEDE of 7H-**36a**, when the polarization of the fused C$_4$=C$_5$ bond is excluded. The polarization effect of the other bond was found to be of negligible importance. Another series of calculations confirmed this conclusion. The OEDE difference between 7H- and 9H-**36a** is small ($\approx$0.005β) when only transferred configurations are involved. With the inclusion of the fused bond polarization function, the difference increases up to 0.021β. The polarization of the other bonds makes no considerable change in OEDE. As a result, the relative stability of the purine tautomers is attributed to electron delocalization assisted by the polarization at the fused C$_4$=C$_5$ bond, or to the orbital phase continuity-discontinuity in the acyclic conjugation. A similar result of calculation were obtained for the tautomerism of adenine, *i.e.*, 6-aminopurine (**36b**).

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The calculations were carried out by the HITAC-M200H computer, Institute for Molecular Science and the FACOM M-200 computer, Nagoya University Computer Center. The authors thank Prof. P. von R. Schleyer of Universität Erlangen-Nürnberg for private communication in prior to publication of the results (Ref. 51).

Appendix

The wavefunction, Ψ^M, of any electronic state of molecule, M, can be expanded[53] in terms of electron configurations including electron transferred and locally-excited configurations:

$$\Psi^M = C_0^M\Phi_0^M + \sum_K C_K^M\Phi_K^M,$$

where the zero-configuration, $\Phi(0)$ is the wavefunction of the reference state involving neither electron promotion nor shift. The magnitude of the configuration coefficients provides us with the information on the detail of electronic structure. A question comes to our minds when we compare the corresponding parts of electronic structure in different molecules. The number of configurations involved increases with the size of molecules or with the number of subsystems. Then the magnitude of coefficients relatively decreases because of the normalization even if the chemical situation is equivalent. The coefficient ratio C_K/C_0 was, though intuitively, recommended as a preferable measure rather than C_K itself.[7] We present a rigorous meaning of the coefficient ratio.

Suppose an arbitrary molecule, R, as a reference, the wavefunction, Ψ^R, being expanded similarly:

$$\Psi^R = C_0^R \Phi_0^R + \sum_L C_L^R \Phi_L^R.$$

The wavefunction, Ψ^{RM}, of the combined system of R and M, where R and M do not interact with each other at all, is then as follows:

$$\begin{aligned}\Psi^{RM} &= \Psi^R \Psi^M \\ &= C_0^{RM} \Phi_0^R \Phi_0^M + \sum_K C_K^{RM} \Phi_0^R \Phi_K^M + \sum_L C_L^{RM} \Phi_L^R \Phi_0^M \\ &\quad + \sum_{K,L} C_{K,L}^{RM} \Phi_L^R \Phi_K^M,\end{aligned}$$

where

$$\begin{aligned} C_0^{RM} &= C_0^R C_0^M \\ C_K^{RM} &= C_0^R C_K^M \\ C_L^{RM} &= C_L^R C_0^M \\ C_{K,L}^{RM} &= C_L^R C_K^M. \end{aligned}$$

The configuration coefficients of the reference molecule in RM, C_L^{RM}, is dependent on the molecule, M. The coefficient, C_L^{RM}, should be invariable and equal to C_L^R when we study the electronic structure through comparing the configuration coefficients between different molecules. Dividing C_L^{RM} by C_0^M transforms the wavefuction as required:

$$C_L^{RM}/C_0^M = C_L^R.$$

The transformation leads to

$$C_K^{RM}/C_0^M = C_0^R(C_K^M/C_0^M).$$

The coefficient of the reference, C_0^R, can be taken to be a constant, *i.e.*, unity for the present purpose. It follows that C_K^M/C_0^M is a good measure for comparing different molecules.

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9) The mechanism of electron delocalization among many systems in such a form as described in the text has been proposed and successfully applied to various chemical problems;[5-8] see also: J. P. Malrieu, "Localization and Delocalization in Quantum Chemistry," ed by O. Chalvet *et al.*, D. Reidel Publishing Company, Dordrecht-Holland (1975), Vol. 1, p. 335.

10) In the illustrations of the orbital phase relation throughout the paper, the solid and dashed lines denote the orbital pairs between which the phase requirements are satisfied and dissatisfied, respectively. In general, there are an odd number of the orbital pairs dissatisfying the requirements, in the discontinuous orbital phase systems, while an even number of them in the continuous ones. The number can be reduced to one or zero, respectively. The continuity-discontinuity of the orbital phase is a property of a whole molecule but not of specific parts of molecule. However, it is preferable to place the discontinuity between the HOMO's or between the LUMO's in the illustrations if possible since the HOMO–LUMO interaction is more primary.

11) Our attention is confined to the mixing-in of the locally-excited configurations through orbital overlapping though there are the other origins of polarization, *e.g.*, electrostatic interaction.

12) a) The method[8] is a simple extension of the "Molecules in Molecule" approach[b,c] in the sense that the interaction is considered to occur among many systems; b) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); c) J. N. Murrell, *ibid.*, **A68**, 969 (1955).

13) According to the HMO–ECAMSI calculation,[7] C(Δn: odd) has non-zero (negligibly small) value, possibly because the other configurations than are involved in the HMO–LCEC calculations are contained implicitly.

14) The total energy of the HMO–LCEC calculation[8,12a] is decomposed into three terms:

$$E = \sum_M C_M^2 H_{MM} + 2\sum_{M\neq 0} C_0 C_M H_{OM} + 2\sum_{M<N} C_M C_N H_{MN}.$$

The OEDE is defined as a measure of the delocalization to be the sum of the energies of the interactions between $\Phi(0)$ and $\Phi(n_1 \rightarrow n_2)$ (the second terms denoted by the ZT energy) and those between $\Phi(n_1 \rightarrow n_2)$'s (the third terms denoted by the TT energy). The energy of the interaction between $\Phi(n \rightarrow n)$ and $\Phi(n_1 \rightarrow n_2)$ is here contained in the latter terms.

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