

molecule presumably binds in the half-Met (in-plane) position of the resulting mixed-valence Cu(II)-Cu(I) moiety, in agreement with the proposal of Solomon et al.⁴⁶

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Registry No. I, R = Ph, R' = H, 80734-29-8; I, R = *p*-MeOC₆H₄, R' = H, 80734-30-1; I, R = 2-C₄H₃O, R' = H, 80662-60-8; I, R = Ph, R' = Me, 80662-61-9; I, R = Ph, R' = Ph, 40791-41-1; I, R = H, R' = Me, 67069-47-0; I, R = H, R' = Ph, 80662-62-0; II, 80662-64-2; bis(pyridine-2-thione 1-oxide)copper(II), 14915-37-8; 3,3'-[ethylenebis(nitrilomethylidene)]bis(1-phenyl-2(1*H*)pyridine-thione), 80658-35-1; 1-phenyl-3-formyl-2(1*H*)-pyridinethione, 61856-49-3; ethylenediamine, 107-15-3; NPT, 45529-38-2.

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Cyclic and Noncyclic Electron Delocalization in Cyclic π -Conjugated Molecules. Relative Delocalizabilities of Donor-Acceptor Disposition Isomers

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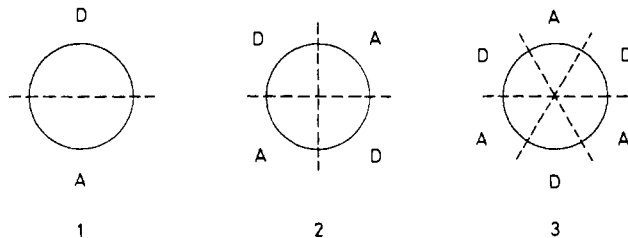
One-electron delocalization energy was defined, calculated, and analyzed to study the *relative* electron delocalizabilities of cyclic π -conjugated isomers where the donor (D)-acceptor (A) components are differently disposed. The present calculation showed that the number of the adjacent D-A pairs is an influential factor in addition to the continuity-discontinuity of both conjugation and orbital phase previously proposed. The continuity-discontinuity properties control *cyclic* delocalizability, and its significance in cyclic polyenes was confirmed. The number of the adjacent D-A pairs primarily determines *noncyclic* delocalizability, to which the delocalizability in both organic and inorganic heterocycles was found to be proportional. This may be the first study to predict the relative delocalizability of the inorganic D-A disposition isomers.

Introduction

The mechanism of electron delocalization has been extensively studied to disclose chemical fundamentals such as the charge-transfer force,¹ the frontier orbital theory,² and so on. However, the theoretical study was limited almost exclusively to the two-system interaction until the three-system interaction theory was developed for the mechanism of catalytic action on the basis of the perturbation theory.³ The theory was shown to reproduce the orbital-phase requirements,⁴ which cover the $4n + 2$ π -electron rule for aromaticity⁵ and the stereoselection rule for chemical reactions via cyclic transition states.^{2c,6} More importantly, the theory gives a clue to studying the mechanism of the electron delocalization in more detail.

Organic chemists have developed the idea of functional group to understand chemical behaviors of innumerable molecules in a unified manner, to predict the property of the molecules in their hands, and to design their target molecules. Molecular orbital methods, widely used for the recent theoretical studies, are not always suitable to the view of functional group but to the gross property of whole molecules. This is a gap of basic terms that chemists have to bridge over in order to advance their own systematic theories. The many-system delocalization theory enables us to take the functional group property into consideration explicitly.

An interesting chemical consequence of the theory is the concept of the continuity-discontinuity of cyclic conjugation.⁷ Cyclic conjugation is classified into continuous and discontinuous conjugations. In the continuously conjugated systems all electron-donating components (D's) are aligned on a part of a cyclic chain with electron-accepting ones (A's) all on the other part, as is illustrated by 1. In the discontinuously



conjugated systems the components are separated into at least four D-A groups as in 2, 3, and so on. We could say that the "frequency of D-A alternation" is 1 in the continuous conjugation and more in the discontinuous conjugation. The orbital-phase property is crucial for electron delocalization in the continuous conjugated molecules, but not in the discontinuously conjugated ones. The requirements for cyclic delocalization^{3,4,7} are as follows: (1) the HOMO and LUMO in phase; (2) the HOMO's out of phase; (3) the LUMO's in phase. The continuous conjugation is subdivided into the electron-delocalizing and electron-localizing conjugations.⁷ The delocalizing molecules satisfy the orbital-phase continuity requirements to be stable due to cyclic delocalization. The Hückel $4n + 2$ π -electron systems are among them. The localizing molecules do not satisfy the requirements and include unstable anti-Hückel $4n$ π -electron systems. The delocalization

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- (3) Fukui, K.; Inagaki, S. *J. Am. Chem. Soc.* **1975**, *97*, 4445.
- (4) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693.
- (5) Hückel, E. *Z. Phys.* **1931**, *70*, 204; **1932**, *76*, 628.
- (6) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395, 2511. (b) Hoffmann, R.; Woodward, R. *Ibid.* **1965**, *87*, 2046.

- (7) (a) Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7418. (b) A perturbation-graph theoretical calculation produced results in agreement with the prediction based on the continuity-discontinuity of cyclic conjugation (Herndon, W. C.; Párkányi, C. *Tetrahedron* **1978**, *34*, 3419).

in the discontinuous conjugation is neither favored by the orbital-phase continuity nor disfavored by the orbital-phase discontinuity. The discontinuously conjugated molecules are nonaromatic $4n + 2$ or nonantiaromatic $4n$ π -electron systems. It was then concluded⁷ that the degree of electron delocalization increases in the order of localizing < discontinuous < delocalizing conjugation.

The continuity-discontinuity of both cyclic conjugation⁷ and orbital phase^{3,4} was derived from the appropriate higher order energy terms of the perturbation theory for many-system interaction. We could understand that the higher order terms are significant in estimating cyclic electron delocalization. The second-order terms estimate only delocalization between the adjacent systems. The delocalization is *noncyclic*. However, the second-order energy is greater in magnitude. Noncyclic delocalization is expected to control the relative delocalizability of some cyclic π -electron systems. The present work was undertaken (1) to define a quantity suitable for estimating the delocalizability of various sorts of cyclic π -electron systems and (2) to examine whether the delocalizability ordering predicted previously is general or conditional.

Another incentive to this work is the inorganic heterocyclic compounds where oxygen, nitrogen, sulfur, etc. with lone-pair electrons are donors, boron being an acceptor. Both $4n$ and $4n + 2$ π -electron heterocycles are known (*vide infra*). Interestingly, they belong almost exclusively to the discontinuous conjugation (Chart I). Does the successful synthesis suggest that the discontinuously conjugated heterocycles are most stable? Did they happen to be synthesized earlier than the continuously conjugated compounds? No existing theories are applicable to these questions. The present work might be the first to study cyclic π -electron inorganic heterocycles in a general way.

Theoretical Considerations

The mechanism of electron delocalization previously proposed^{3,4,7} is illustrated in Figure 1. A conjugated molecule is separated into many parts. A hypothetical electronic structure without interaction between any parts is called the zero (Z) configuration, where each subsystem has the ground-state configuration. Electron delocalization is described by a mixing in of electron-transferred (T) configurations where one electron is shifted from the HOMO of a subsystem to the LUMO of another. The adjacently transferred configurations (T_{adj}) where electron shift occurs between neighboring subsystems mix themselves through the interaction with the Z configuration. The mixing of the distantly transferred (T_{dis}) configurations is caused by the interactions with T_{adj} or another T_{dis} .

In DAAA (Figure 1a), an electron in D shifts to one of the neighboring A's [$Z(DAAA) - T_{adj}(D^+A^-AA)$ interaction] and then to the middle A [$T_{adj}(D^+A^-AA) - T_{dis}(D^+AA^-A)$]. There is a second pathway for the electron in D to reach the middle A via another neighboring A [$Z(DAAA) - T_{adj}(D^+AAA^-) - T_{dis}(D^+AA^-A)$]. It follows that the electron is capable of delocalizing all along the cyclic chain. The D-A disposition is favorable for cyclic delocalization; in other words, the cyclic conjugation is continuous.⁷ The cyclic delocalization involves four configurations, $Z(DAAA)$, $T_{adj}(D^+A^-AA)$, $T_{dis}(D^+AA^-A)$, and $T_{adj}(D^+AAA^-)$. The interrelation of the configurations appears in the fourth-order perturbation energy term, i.e.

$$\frac{(H_{OI} - S_{OI}H_{OO})(H_{IJ} - S_{IJ}H_{OO})(H_{JK} - S_{JK}H_{OO}) \times (H_{KO} - S_{KO}H_{OO})}{(H_{II} - H_{OO})(H_{JJ} - H_{OO})(H_{KK} - H_{OO})}$$

where O = $Z(DAAA)$, I = $T_{adj}(D^+A^-AA)$, J = $T_{dis}(D^+AA^-A)$, and K = $T_{adj}(D^+AAA^-)$, the other notations being the same as were used in ref 3 and 4. From this term the condition of the stabilization due to cyclic delocalization is

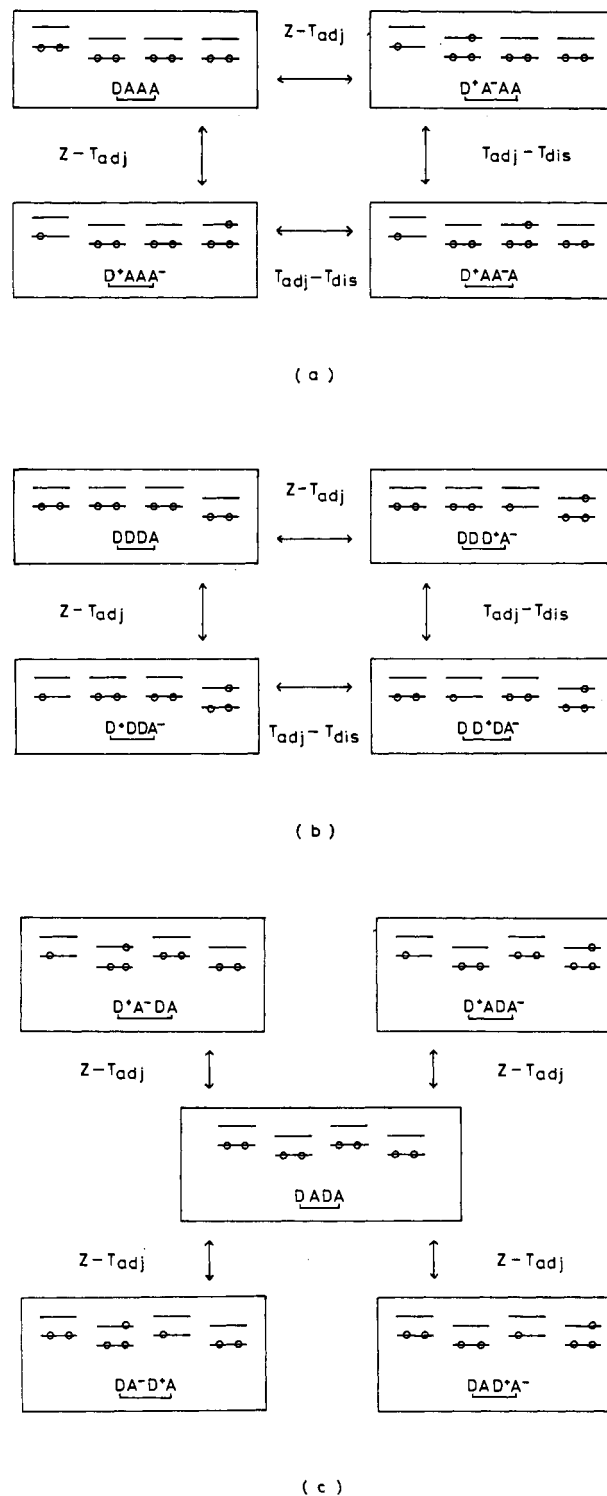


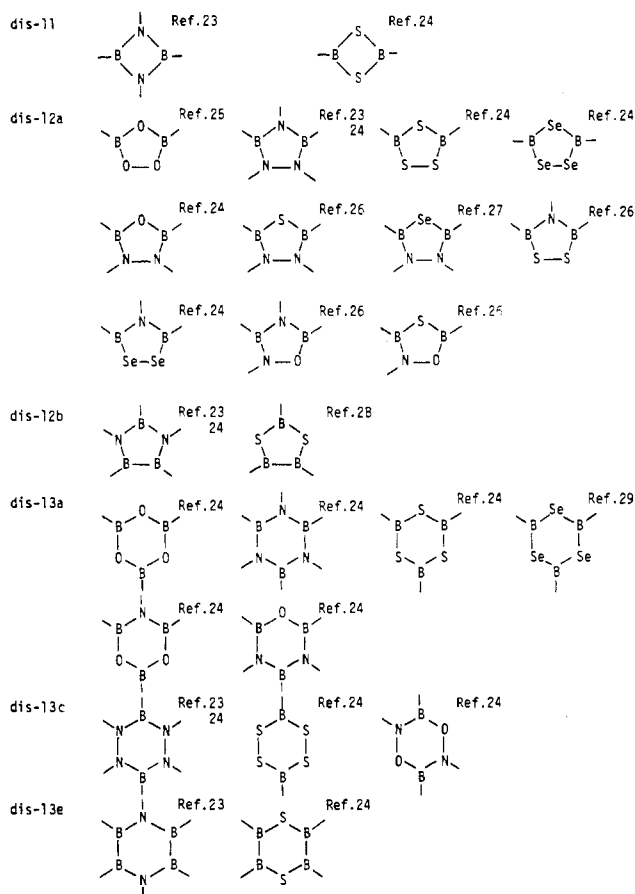
Figure 1. Representative illustrations of cyclic electron delocalization (a) in DAAA and (b) in DDDA and of noncyclic electron delocalization (c) in DADA.

derived in the form of the product of the overlap integrals between the configurations:^{3,4,7}

$$S_{OI}S_{IJ}S_{JK}S_{KO} > 0 \quad (1)$$

Importantly, each configuration overlap integral can be reduced to the overlap integral between the orbitals of the adjacent components.⁷ Thus, the overlap integrals, S_{OI} and S_{KO} , between $Z(DAAA)$ and $T_{adj}(D^+A^-AA)$ and between $Z(DAAA)$ and $T_{adj}(D^+AAA^-)$ are both approximated to be the overlap integrals between the HOMO of D and the LUMO of the neighboring A's. Similarly, S_{IJ} and S_{JK} , i.e., those

Chart I. Inorganic Heterocycles Known



between $T_{adj}(D^+A^-AA)$ and $T_{dis}(D^+AA^-A)$ and between $T_{adj}(D^+AAA^-)$ and $T_{dis}(D^+AA^-A)$ are reduced to the overlap integrals between the LUMO's of the neighboring A's. As a result, the stabilization conditions were rewritten in terms of the phase continuity of the HOMO of D and the LUMO's of the A's. DAAA is electron delocalizing when the phase is continuous or electron localizing when the phase is discontinuous.

In another continuously conjugated system, DDDA in Figure 1b, an electron hole goes around in place of an electron. A neighboring D releases an electron to A [$Z(DDDA)-T_{adj}(DDD^+A^-)$]. The resulting electron hole in DDD^+A^- is supplied with an electron by the middle D [$T_{adj}(DDD^+A^-)-T_{dis}(DD^+DA^-)$]. There is another similar pathway [$Z(DDDA)-T_{adj}(D^+DDA^-)-T_{dis}(DD^+DA^-)$] by which an electron hole is generated in the middle D. The electron hole is cyclically delocalizable. The conjugation is continuous. The configurations O, I, J, and K in the perturbation energy term are $Z(DDDA)$, $T_{adj}(DDD^+A^-)$, $T_{dis}^-(DD^+DA^-)$, and $T_{adj}(D^+DDA^-)$, respectively. The overlap of Z with T_{adj} 's, S_{OI} and S_{KO} , are reduced to those between the LUMO of A and the HOMO of the adjacent D's. The overlaps of T_{dis} with T_{adj} 's, S_{IJ} and S_{JK} , are reduced to those between the HOMO's of neighboring D's. Whether DDDA is electron localizing or delocalizing is determined by the phase continuity-discontinuity of the HOMO's of D's and the LUMO of A.

In DADA (Figure 1c), an electron in D shifts to a neighboring A [e.g., $Z(DADA)-T_{adj}(D^+A^-DA)$]. However, further delocalization of neither the electron in A^- nor the electron hole in D^+ is favored by the D-A disposition, because the neighbors of A^- and D^+ are D and A, respectively. The delocalization is limited to the region of the adjacent D-A pairs. This is why such cyclic conjugation was termed "discontinuous". The delocalization is noncyclic. The overlaps

of Z with T_{adj} are approximated to be the HOMO-LUMO overlaps between the neighboring components. However, the overlaps between T_{adj} 's are reduced to the HOMO-HOMO or LUMO-LUMO overlaps of the nonadjacent components. Thus, the overlap integrals of $T_{adj}(D^+A^-DA)$ with $T_{adj}(D^+ADA^-)$ and with $T_{adj}(DA^-D^+A)$ are reduced to those between the LUMO's of A's and between the HOMO's of D's, respectively. The orbital overlapping of the nonadjacent systems is less effective. The orbital-phase restriction makes no primary sense in predicting the delocalizability in such discontinuously conjugated systems.

Ideally, electrons delocalize by the cyclic mechanism in the electron-delocalizing systems while the delocalization is "localized" by the D-A disposition in the discontinuously conjugated systems or by the orbital-phase discontinuity in the electron-localizing systems. The continuity-discontinuity of cyclic conjugation depends on the magnitude of the D-A interaction, which consecutively changes in an actual series of molecules. It is meaningful and necessary to estimate cyclic and noncyclic delocalization separately. Cyclic delocalization demands a mixing in of the most distantly transferred configuration, e.g., $T_{dis}(D^+AA^-A)$ or $T_{dis}(DD^+DA^-)$, or inevitably involves the T-T interactions in addition to the Z-T interaction (Figure 1a and b). On the other hand, the fundamental interaction for noncyclic delocalization is the D-A interaction between the neighboring components or the Z-T interaction (Figure 1c). The Z-T and T-T interaction energies are then used as the measures of noncyclic and cyclic delocalization energies, respectively.

The wave function Ψ is described as a linear combination of electron configurations (LCEC):

$$\Psi = \sum_M C_M \Phi_M \quad (2)$$

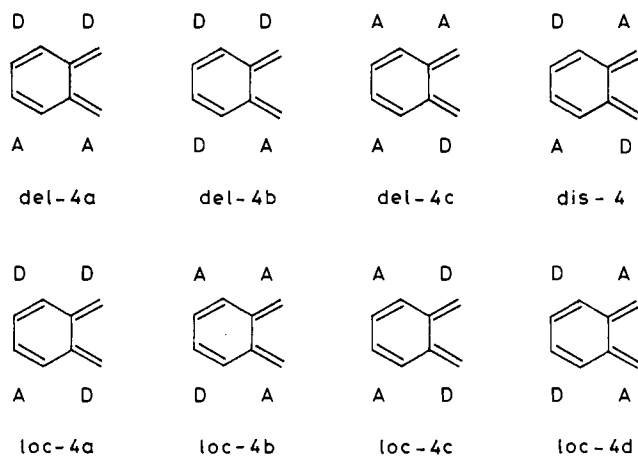
The configurations involved in the calculation are the Z and T configurations. In the present study the conjugated systems are decomposed into as many subsystems as possible, each having zero or two electrons. The total energy E is separated into the three terms

$$E = \sum_M C_M^2 H_{MM} + 2 \sum_{M \neq O} C_O C_M H_{OM} + 2 \sum_{M > N} C_M C_N H_{MN} \quad (3)$$

The first term is the sum of the configuration energies. The second and third terms are the Z-T and T-T interaction energies. One-electron delocalization energy (abbreviated as OEDE) is defined as the sum of the Z-T and T-T interaction energies. Each energy was evaluated as a function of the magnitude of D-A interaction between the components, which was expressed in terms of the transferred configuration energy (TCE). The D-A interaction is enhanced as TCE lowers. The Hückel approximation is employed as the most suitable to the present model calculations as far as we are concerned with the general aspects of cyclic conjugation. The energy gap (2β) between the bonding and antibonding orbitals of an ethylenic unit and the resonance integral (β) of neighboring atomic orbitals are kept constant.

Results and Discussion

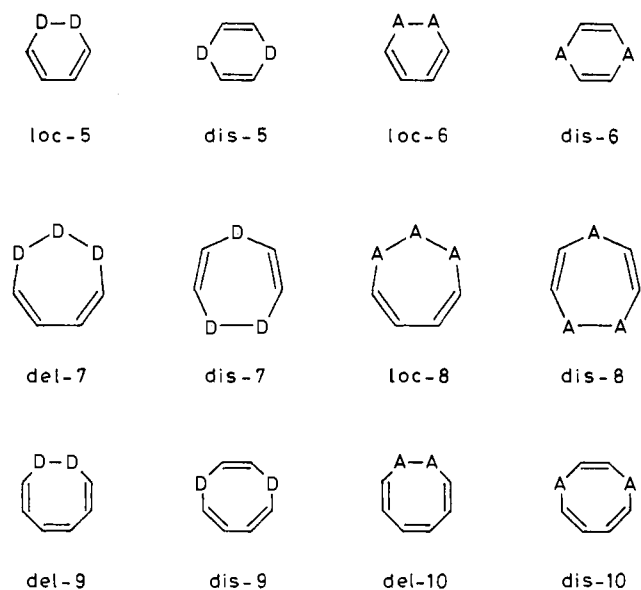
A Representative Example of Polyenes. *o*-Xylylene is composed of four ethylenic double-bond units. Let some units be donors toward the others. Eight "isomers" (4) were classified in the previous paper⁷ and are known to contain all types of conjugations of our present interest. The continuous (localizing and delocalizing) and discontinuous conjugations are denoted by the prefixes like loc-4, del-4, and dis-4, respectively. The calculated OEDE of *o*-xylylene isomers is completely consistent with the previous theoretical prediction⁷ that the relative delocalizability increases in the order of localizing < discontinuous < delocalizing conjugation. The OEDE of the delocalizing (del-4) and localizing (loc-4) isomers relative to the



discontinuous isomer (dis-4) is shown in Figure 2. The ordering is attributed to the difference in the T-T interaction energy (Figure 3). As the donor-acceptor interaction increases, the T-T energy of the delocalizing systems (del-4) increases more than the Z-T energy decreases, and the T-T energy of the localizing systems (loc-4) decreases more than the Z-T energy increases. The result supports the hypothesis that the degree of delocalization is dominated by the T-T interaction or cyclic delocalization.

Some experimental supports are given by the push-pull substituent effects on the stability. Electron-donating substituents on an exocyclic bond and electron-accepting ones on another emphasize all of the delocalization modes, del-4a-c, depress all of the localization modes, loc-4a-d. The powerful substituents were observed to prevent *o*-xylylene from dimerizing.⁸ For more examples, see the previous paper⁷ where the related behaviors of *p*-xylenes and *o*- and *p*-benzoquinone methides were cited.

Organic Heterocycles. This class of molecules examined here is defined as a cyclic combination of ethylenic units and heteroatoms (5-10). The lone-pair electrons on oxygen,



nitrogen, sulfur, etc. work as donors toward the ethylenic units. Otherwise, a vacant p orbital on boron is an acceptor toward the ethylenic units. The delocalizability is lower in the localizing systems (loc-5, -6, -8) than in the discontinuous systems (dis-5, -6, -8) as is shown in Figure 4. This is what was predicted.⁷ However, the ordering of the delocalizing conjugation below the discontinuous one for the weak D-A

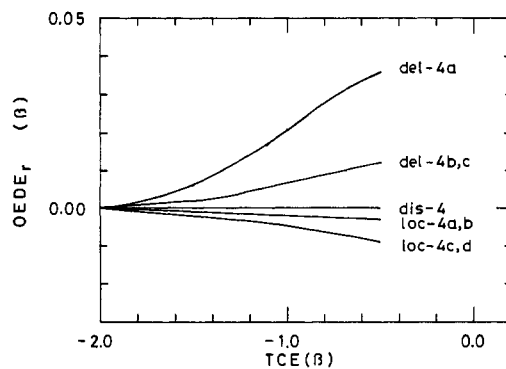


Figure 2. OEDE_r, one-electron delocalization energy of the *o*-xylylene donor-acceptor isomers relative to that of the discontinuous conjugated one, as a function of TCE, the energy of the configuration when an electron is transferred from the bonding orbital of the donors to the antibonding orbital of the acceptors.

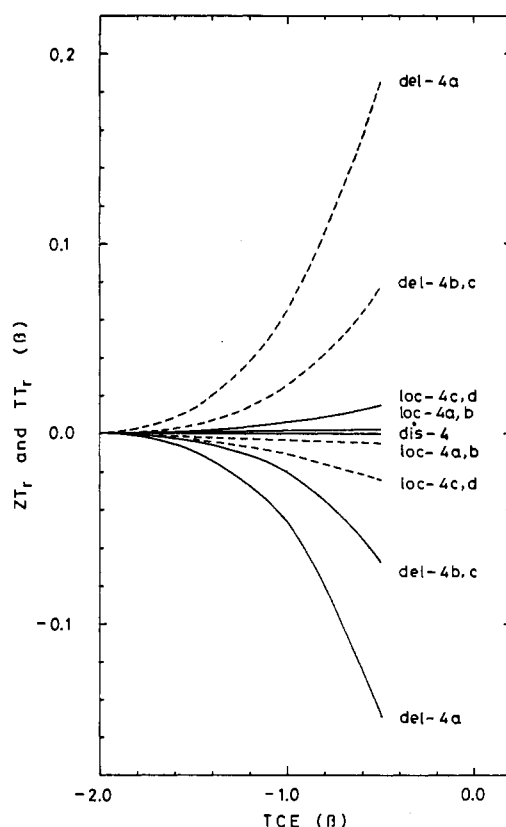


Figure 3. ZT_r (—) and TT_r (---), the Z-T and T-T interaction energies of the *o*-xylylene donor-acceptor isomers relative to that of the discontinuously conjugated isomer, as a function of TCE, the energy of the configuration when an electron is transferred from the bonding orbital of the donors to the antibonding orbital of the acceptors.

interaction is reverse to the prediction (dis- vs. del-7, -9, -10).

The unexpected lowering of the delocalizing systems below the discontinuous systems for the weak D-A interaction is attributed to the predominance of the Z-T interaction (Figure 5) or noncyclic delocalization. Weakening the D-A interactions depresses the first-order mixing in of T_{adj} and, more rapidly, the higher order mixing of T_{dis} to confine the delocalization to the adjacent units, irrespective of the orbital-phase continuity in the delocalizing systems. The magnitude of noncyclic delocalization is expected⁹ to be proportional to the number of the neighboring D-A pairs. There are two pairs

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(9) This expectation is consistent with the result that the continuously conjugated systems, whether localizing or delocalizing, have almost the same relative Z-T energy, which is lower than that of the discontinuously conjugated systems (Figures 5, 7, and 9).

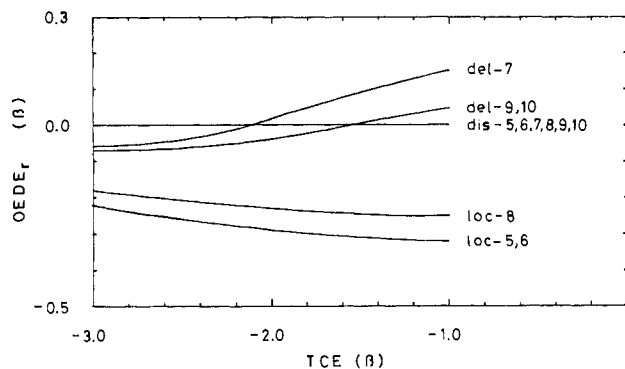


Figure 4. OEDE_r, one-electron delocalization energy of the organic heterocycles relative to that of the corresponding discontinuously conjugated isomers, as a function of TCE, the energy of the configuration where an electron is transferred from the occupied orbital of the donors to the unoccupied orbital of the acceptors.

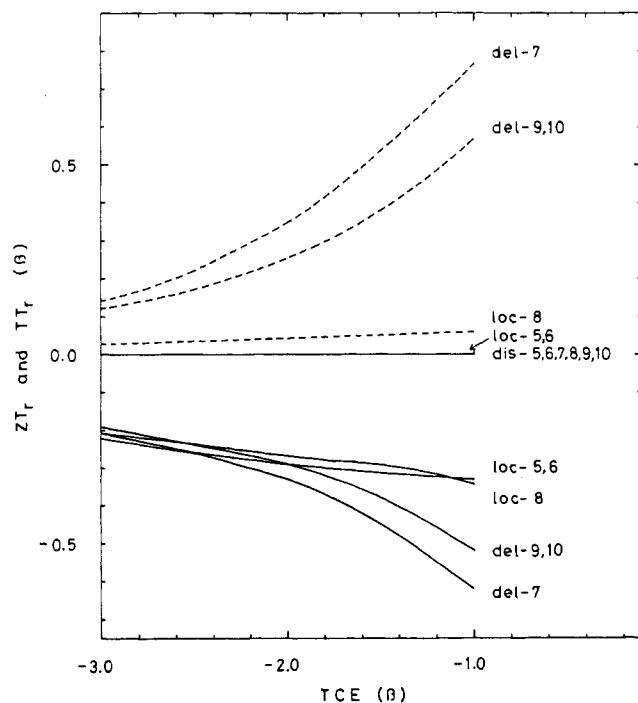


Figure 5. ZT_r (—) and TT_r (---), the Z-T and T-T interaction energies of organic heterocycles relative to those of the corresponding discontinuously conjugated isomers, as a function of TCE, the energy of the configuration where an electron is transferred from the occupied orbital of the donors to the unoccupied orbital of the acceptors.

in the delocalizing systems while there are four in the discontinuous systems. The delocalizability inversion follows.

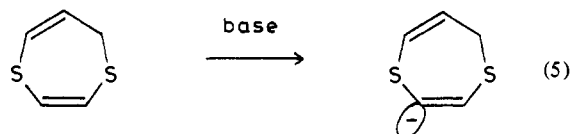
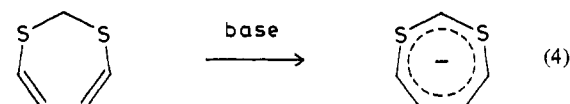
The contrast between the polyenic molecules and the organic heterocycles in the dominating delocalization mechanism results from the intrinsic difference in the nature of the D-A interaction. In the polyenes, the enhanced D-A interaction between the ethylenic units promotes the delocalization from D to A but depresses that from A to D. The systems neither gain nor lose the net noncyclic delocalization. The cyclic delocalization is then more effective. On the other hand, there is no counterbalancing interaction in the organic heterocycles because the heteroatoms do not have both occupied and vacant orbitals. Strengthening the D-A interaction straightforwardly gives rise to the Z-T energy gain without loss. The Z-T interaction is greater than the T-T interaction. Noncyclic delocalization is predominant in determining the relative delocalizability.

At present, there are only a few experimental results suitable for substantiating the prediction, because most of the less

delocalizable isomers have never been synthesized. The relative stability of dithiins is an evidence for the higher delocalizability of the discontinuous conjugation relative to the localizing conjugation. 1,4-Dithiin (dis-5, D = S) was isolated as a thermally stable crystal¹⁰ whereas 1,2-dithiin (loc-5, D = S) readily polymerizes or desulfurizes.¹¹ The reports on other six-membered heterocycles are limited to more stable, discontinuously conjugated molecules such as dioxin (dis-5, D = O),¹² 1,4-dihydropyrazine derivatives (dis-5, D = NR),¹³ and the classical carboranes (dis-6, A = BF, BOCH₃).^{14,15}

No experimental results have ever been reported on the seven-membered heterocycles, whether the heteroatoms are electron donating (7) or accepting (8). The OEDE values suggest that dis-7 is more stable than del-7 for O (TCE ≈ -3.0β) and N (TCE ≈ -2.5β), whereas the delocalizability is opposite for S (TCE ≈ -1.0β).¹⁶ The heterocycle 8 belongs to the discontinuous or localizing conjugation. The localizing systems are the least delocalizing without exception. The synthesis of dis-8 is more promising.

There is an elegant evidence for the stability of the delocalizing system (del-7) relative to the discontinuous system (dis-7) at the strong D-A interaction region. That is a clear-cut difference between 1,3- and 1,4-dithiepins in chemical behaviors toward bases (eq 4 and 5). According to the Hückel



rule both are expected to yield 10- π -electron anions, i.e., del-7 and dis-7 (D = 2 S, $\dot{C}H$). Zahradnik^{16b} predicted that both anions are unstable to prepare. In fact, 1,3-dithiepin produces the π anion¹⁷ while 1,4-dithiepin undergoes proton abstraction from an olefinic carbon.¹⁸ The difference was attributed to the continuity-discontinuity of cyclic conjugation.⁷ The conjugation is continuous in the 1,3-dithiepin π anion (del-7). The orbital-phase continuity favors cyclic delocalization. Suppose that the π anion (dis-7, D = 2 S, $\dot{C}H$) is generated from the 1,4-isomer. Cyclic conjugation is discontinuous. There is no advantage of 10 π electrons. The present calculation supports the interpretation. The OEDE increases in the

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- (11) (a) Schroth, W.; Reinhardt, J.; Kränke, K.; Streckenbach, B. *Z. Chem.* **1963**, *3*, 228. (b) Some 3,6-disubstituted derivatives were isolated as crystals (Schroth, W.; Billig, F.; Reinhold, G. *Angew. Chem.* **1967**, *79*, 685).
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- (15) (a) It should be noted that the classical carboranes tend to rearrange into more stable, nonclassical polyhedral isomers.^{15b} The electron-rich substituents on borons work in favor of classical structures. (b) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781.
- (16) (a) Zahradnik^{16b} suggested that dis-7 is more stable even for the sulfur analogue. (b) Zahradnik, R. *Adv. Heterocycl. Chem.* **1965**, *5*, 1 and references cited therein.
- (17) Semmelhack, C. L.; Chiu, I.-C.; Grohmann, K. G. *J. Am. Chem. Soc.* **1976**, *98*, 2005; *Tetrahedron Lett.* **1976**, 1251.
- (18) Murata, I.; Nakasuji, K.; Nakajima, Y. *Tetrahedron Lett.* **1975**, 1895.

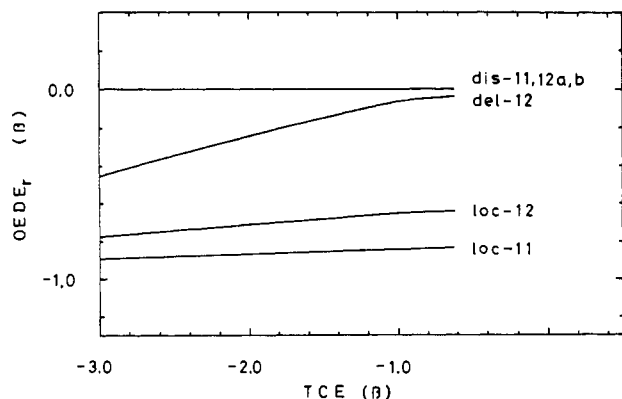


Figure 6. OEDE_r, one-electron delocalization energy of the four- and five-membered inorganic heterocycles relative to that of the corresponding discontinuously conjugated isomers, as a function of TCE, the energy of the configuration where an electron is transferred from the lone-pair electron orbital to the vacant orbital.

order of $\text{dis-7} < \text{del-7}$ for the strong D-A interaction ($\text{TCE} < -2.0\beta$). Both sulfur and carbanion are considered to have ionization potentials low enough ($\text{TCE} \approx -1.0\beta$). Probably, the similar difference could not be observed for the oxygen and nitrogen analogues ($\text{TCE} \approx -2.5\beta, -3.0\beta$).

The eight-membered heterocycles so far synthesized are 1,4-diheterocins (dis-9, D = O, NR, S) only.¹⁹⁻²¹ We cannot compare the experimental results until the 1,2-isomers are prepared. Dioxocin and diazocine (9, D = O, NR) lie on the TCE ($> -1.5\beta$) region where noncyclic delocalization primarily determines the delocalizability. 1,2-Isomers (del-9) are predicted to be less stable. However, dithiocin (9, D = S) is suggested to be subject to cyclic delocalization. 1,2-Dithiocin (del-9) is expected to be more stable than the 1,4-isomer.²² The synthesis of 1,2-dithiocin is most promising of the 1,2-isomers, especially when the ethylenic components have electron-withdrawing substituents.

Inorganic Heterocycles. Cyclic π -electron systems to be examined here have a lone-pair electron orbital on D and a vacant p orbital on A. Electron-donating heteroatoms are O, N, S, etc., and electron-accepting ones include B. We calculated the OEDE of the four- through six-membered ring compounds 11-13. The results show almost the same features as the organic heterocycles. The delocalizability increases in the order of the localizing < delocalizing < discontinuous conjugation (Figures 6 and 8), because of the predominance of the noncyclic over cyclic delocalization (Figures 7 and 9). The delocalizability ordering is similarly suggested to be possibly inverted between the delocalizing and discontinuous conjugation at the strong D-A interaction (see del-13 vs. dis-13b-f around $\text{TCE} \approx -1.0\beta$ in Figure 8).

An interesting implication is that the stability of the inorganic heterocycles increases with the number of the adjacent D-A pairs or with the frequency of D-A alternation. For example, the six-membered heterocycles demonstrate its im-

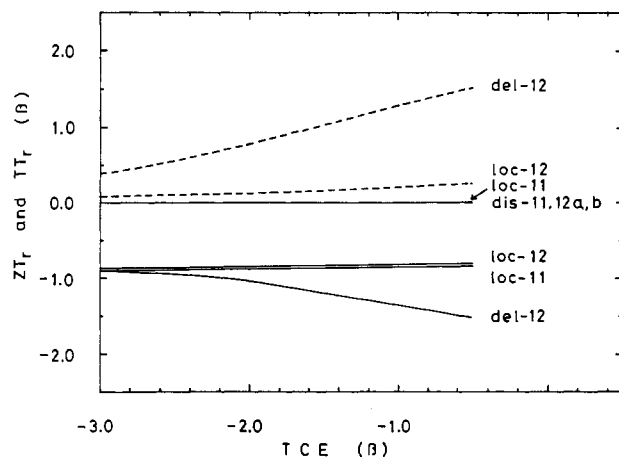


Figure 7. ZT_r (—) and TT_r (---), the Z-T and T-T interaction energies of the four- and five-membered inorganic heterocycles relative to those of the corresponding discontinuously conjugated isomers, as a function of TCE, the energy of the configuration where an electron is transferred from the lone-pair electron orbital to the vacant orbital.

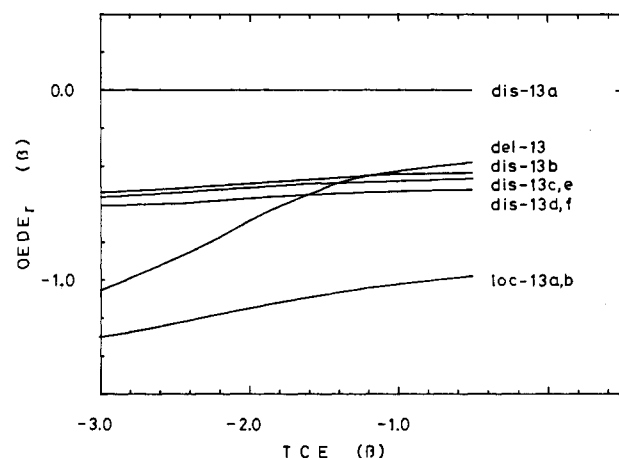


Figure 8. OEDE_r, one-electron delocalization energy of the six-membered inorganic heterocycles relative to that of the most discontinuously conjugated isomer, as a function of TCE, the energy of the configuration where an electron is transferred from the lone-pair electron orbital to the vacant orbital.

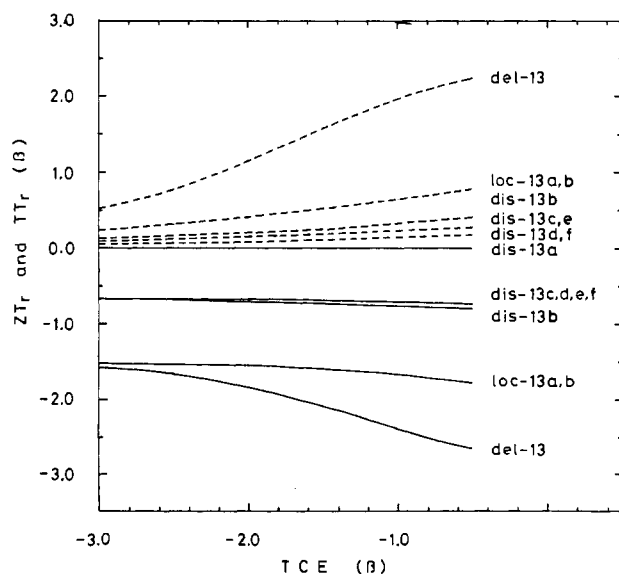
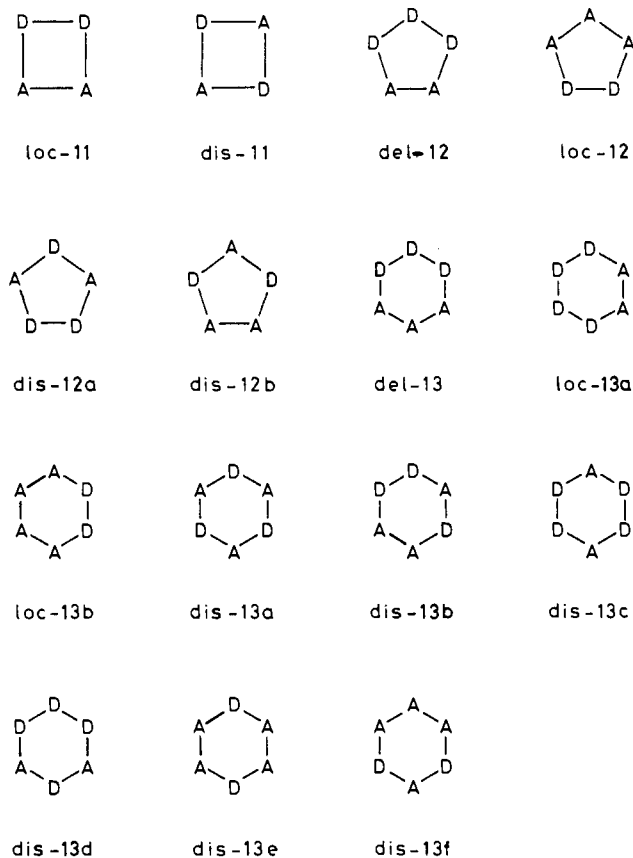


Figure 9. ZT_r (—) and TT_r (---), the Z-T and T-T interaction energies of the six-membered inorganic heterocycles relative to those of the most discontinuously conjugated isomer, as a function of TCE, the energy of the configuration where an electron is transferred from the lone-pair electron orbital to the vacant orbital.

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- (20) For 1,4-dithiocins see: (a) Vogel, E.; Schmidtbauer, E.; Altenbach, H.-J. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 736. (b) Eggelte, H. J.; Bickelhaupt, F. *Ibid.* **1974**, *13*, 345. (c) Eggelte, H. J.; Bickelhaupt, F.; Loopstra, B. O. *Tetrahedron* **1978**, *34*, 3631.
- (21) For 1,4-diazocines see: (a) Prinzbach, H.; Breuninger, M.; Gallenkamp, B.; Schwesinger, R.; Hunkler, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 348. (b) Altenbach, H.-J.; Stegelmeier, H.; Wilhelm, M.; Voss, B.; Lex, J.; Vogel, E. *Ibid.* **1979**, *18*, 962. (c) Breuninger, M.; Gallenkamp, B.; Müller, K.-H.; Fritz, H.; Prinzbach, H.; Daly, J. J.; Schönholzer, P. *Ibid.* **1979**, *18*, 964.
- (22) The reality remains open to question because the TCE is close to the critical point ($\text{TCE} \approx -1.5\beta$) where the ordering is inverted between del-9 and dis-9.



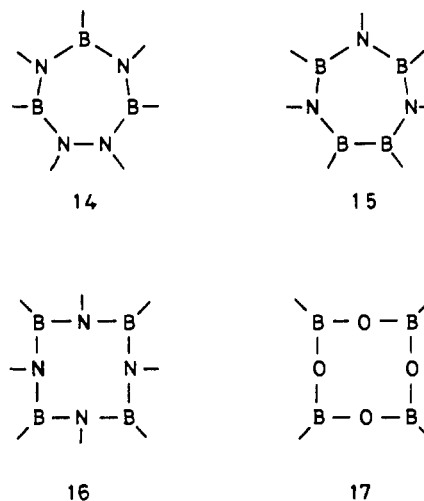
portance. The number of the D-A pairs is 2 in the continuously conjugated systems (loc-13a,b and del-13), 4 in some discontinuously conjugated systems (dis-13b-f), and 6 in the other (dis-13a). In fact, the OEDE is primarily in this order (Figure 8).

Cyclic delocalization is subsidiary. Appreciable OEDE difference between the continuously conjugated del-13 and loc-13 is attributed to cyclic delocalizability because there is no preference of one to the other in noncyclic delocalization (Figure 9). Another outstanding result from cyclic delocalization is that the delocalizing heterocycle del-13 of the lowest OEDE groups may disturb the ordering or go beyond the high-OEDE groups as the D-A interaction is enhanced. The continuity of both conjugation and orbital phase favors cyclic delocalization in del-13, whereas the discontinuity of conjugation or orbital phase restricts the delocalization to the local regions in the rest of the isomers. The cyclic delocalizability in del-13 is sensitive enough to the D-A interaction magnitude to overcome the inferiority in the noncyclic delocalizability to the discontinuously conjugated systems (Figure 8).

It should be noted here that the number of electrons has only a minor effect on the delocalizability. Unambiguous evidence against the Hückel rule is that the six- π -electron dis-12a and the four- π -electron dis-12b have identical OEDE values. In fact both types of heterocycles are known (see Chart I). We can find the related numerical results on the six-membered heterocycles, dis-13b-f. They have four, six, or eight electrons but similar magnitudes of OEDE, compared with the highest OEDE of the $(4n+2)$ - π -electron dis-13a and with the lowest OEDE of the $4n$ - π -electron loc-13a,b (Figure 8). These findings are not surprising in view of the discontinuity of conjugation.⁷

We realized that the successful syntheses of the discontinuously conjugated inorganic heterocycles are due to the delocalizability primarily controlled by the noncyclic delocalization or the number of the adjacent D-A pairs. The compounds with O, N, S, or Se as D and with B as A prepared

so far all belong to the discontinuous conjugations, as is listed in Chart I.²³⁻²⁹ The homologous seven- and eight-membered ring compounds are also known though limited to the highest D-A alternated isomers, i.e., 14,²³ 15,²³ 16,²³ and 17.²⁴



There is no experimental information on dis-13b,d,f, though they have the same number of adjacent D-A pairs as the already known dis-13c,e. According to the OEDE values (Figure 8) dis-13b (D = O, N, S; A = B) is more feasible than dis-13d,f to synthesize.

Among more challenging molecules are the continuously conjugated heterocycles, i.e., $(4n+2)$ - π -electron molecules (del-12 and -13), and $4n$ - π -electron ones (loc-11, -12, and -13a,b). The synthesis of the delocalizing compounds is unquestionably more promising, especially when the donors with low ionization potentials are employed.

Conclusion and Remarks

We defined one-electron delocalization energy (OEDE) and studied the relative π -electron delocalizability of the D-A disposition isomers. In the previous paper⁷ we proposed the continuity-discontinuity of cyclic conjugation to be important in addition to that of orbital phase and predicted that the delocalizability increases in the order of the localizing < discontinuous < delocalizing conjugation. The ordering was now found to be conditional. The number of the neighboring D-A pairs may play a predominant role. The ordering is then inverted between the discontinuous and delocalizing conjugations. The relative significance of the three factors depends on the type of molecules and the magnitude of the D-A interaction between the components. The continuity properties of conjugation and orbital phase control cyclic delocalization. The number of the neighboring D-A pairs estimates noncyclic delocalization. Cyclic delocalization rules over compounds such as polyenes whereas noncyclic delocalization rules over the heterocyclic molecules.³⁰ Cyclic delocalization is ap-

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preciable for strong D-A interaction even in the heterocycles.

The present calculation substantiated the classification of cyclic conjugation. An interesting chemical consequence is the inapplicability of the Hückel rule to some π -electron systems. The relative delocalizability is not dependent on the number of electrons but proportional to the frequency of the D-A alteration. This is fundamental in the heterocycles.

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Our attention has been centered on the *relative* delocalizability of the D-A disposition isomers but not on the intrinsic delocalizability of each isomer. The possibility cannot be ruled out that noncyclic delocalization may control the relative delocalization of some isomers, of which the other properties may be determined by cyclic delocalizability, and vice versa.

Acknowledgment. The calculations were carried out by the Facom 230-28 computer of Gifu University and the Facom M200 computer of Nagoya University Computer Center.

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Interconversions among Alkoxyfluorophosphoranes: Effect of Differences in Apicophilicity on the Equilibrium Distribution of Substituents on 5-Coordinated Phosphorus

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Fluorine atoms and alkoxy groups (OR = OCH₂CF₃ or OCH₂CCl₃) redistribute readily on the 5-coordinated phosphorus center



resulting in interconversions among the series of alkoxyfluorophosphoranes PhPF_{4-n}(OR)_n. An equilibrium is reached after less than 2 days at room temperature. No phosphorylated species, exchange of phenyl groups, nor conversion to ionic isomers was observed. Quantitative molar distribution data were obtained from ¹H or ¹⁹F NMR spectra of 15 equilibrated samples, prepared in various ways, for R = CH₂CF₃ and of 8 samples for R = CH₂CCl₃. All the mixed species are thermodynamically favored, the dialkoxydifluorophenylphosphoranes so strongly that their disproportionation products were never detected. Within the limits of detection by NMR (ca. 1%), the sorting of fluorine vs. alkoxy groups among equatorial sites and among apical sites can be treated independently and described respectively by $\bar{K}_1 = [\text{PhPF}_4][\text{PhPF}_2(\text{OR})_2]/[\text{PhPF}_3(\text{OR})]^2 = (5.6 \pm 0.5) \times 10^{-2}$ and $\bar{K}_3 = [\text{PhPF}_2(\text{OR})_2][\text{PhP}(\text{OR})_4]/[\text{PhPF}(\text{OR})_3]^2 = (1.7 \pm 0.3) \times 10^{-2}$ (for R = CH₂CF₃). An upper limit was set for $\bar{K}_2 = [\text{PhPF}_3(\text{OR})][\text{PhPF}(\text{OR})_3]/[\text{PhPF}_2(\text{OR})_2]^2 < 10^{-4}$, which expresses a difference of apicophilicity of at least 10 kJ between the two substituents. It is suggested that the measuring of redistribution equilibria could provide a way of establishing the concept of apicophilicity on a thermodynamic basis.

Introduction

Although redistribution reactions are an important feature of phosphorus chemistry,¹ there appears to be no quantitative study yet of a redistribution equilibrium on a 5-coordinated phosphorus atom—nor on any other 5-coordinated trigonal-bipyramidal atom—though the occurrence of the redistribution phenomenon has often been recognized^{2,3} in this fast developing field. The problem is of special interest since there are in the case of a bipyramidal arrangement of the substituents *two sets of distinct sites*—apical and equatorial—to be considered on the *same* central atom and there is no reason why two distinct substituents should distribute randomly between these two sets of sites. In other words, the position of the equilibrium is expected to be strongly dependent on the relative *apicophilicity*⁴ of the exchangeable substituents. Conversely, the

gathering of *equilibrium* data could provide a means of evaluating differences in apicophilicity on a quantitative *thermodynamic* basis.

We have shown previously that alkoxyfluorophosphoranes, although they can be stabilized with respect to their irreversible decomposition into phosphoryl derivatives, nevertheless undergo easy disproportionation reactions which preserve the pentacoordinate character of phosphorus.^{2,5} For example, PhPF₃(OCH₂CCl₃) irreversibly decomposes only by heating above 200 °C, while its disproportionation products PhPF₄ and PhPF₂(OCH₂CCl₃)₂ already appear after 1 h at room temperature. *t*-BuOPF₄ disproportionates at room temperature^{3a} and PF₄(OCH₂CF₃) below room temperature² (which prevents its isolation), while advantage has been taken of redistribution reactions to synthesize various dialkoxyfluorophosphoranes⁶ as well as difluoro(trifluoromethyl)phosphorane (CF₃)₃PF₂.^{3b} These reactions, which lead to interconversions among the series of alkoxyfluorophosphoranes, are often reversible, in which case they can be described in terms of redistribution equilibria, for example, in the case of the series PhPF_{4-n}-

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