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Orbital Phase Design of Acyclic Electron Localizing and Delocalizing π-Conjugated Polyions and Related Systems

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Acyclic localization-delocalization of electrons in π-conjugated hydrocarbon polyions was predicted in terms of the continuity-discontinuity of the phase of the component orbitals. Many pairs of electron-localizing and -delocalizing conjugated polyions were designed as the model systems of which the relative stabilities have not been explored so far.

The concept of localization and delocalization of electrons is fundamental in organic chemistry. Among the prominent examples are the $4n+2$ π electron rule for aromaticity[1] and the stereoselection rule for pericyclic reactions.[2] The frontier orbital theory for chemical reactivity[3] emphasizes the delocalization between the molecules or bonds. The charge transfer force for intermolecular complexation of electron donor and acceptor[4] belongs to this category. An introduction of orbital symmetry or phase arguments[2,3] makes substantial progress in the theory of cyclic localization and delocalization. Chemical reactions *via* cyclic transition state are under control of the frontier orbital phase of the reacting molecules or parts of molecules or under the conservation of orbital symmetry.

Recently, mechanism of cyclic delocalization among more than two molecules, molecular fragments, or bonds was examined to derive the orbital phase continuity conditions for cyclic delocalization:[5] (a) The most electron-donating orbitals out of phase; (b) the most electron-accepting orbitals in phase; (c) the most electron-donating and -accepting orbitals in phase. The most electron-donating orbital is the HOMO of molecular systems, a bonding orbital of a bond, or a non-bonding orbital of lone-pair electrons. The most electron-accepting orbital is the LUMO of molecular systems, an anti-bonding orbital of a bond, or a vacant orbital on cationic centers. Electron-delocalizing systems are here defined as those which meet the three orbital phase requirements simultaneously. Otherwise, conjugate systems are classified into electron-localizing ones. The orbital phase conditions were already shown[5,6] to cover the aromaticity rule and the stereoselection rule.

More recently, cyclic orbital interaction was shown to be contained in acyclic conjugation.[7] The orbital phase conditions for cyclic delocalization are also applicable to estimating the degree of acyclic delocalization. Unfortunately, the related chemical phenomena observed so far are limited. In this paper we attempt to explore some new aspects of acyclic conjugation in view of continuity and discontinuity of orbital phase. π-Conjugated hydrocarbon polyions are employed as the model species.

Orbital Phase Design

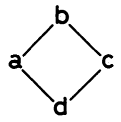
Suppose that four orbitals, a, b, c, and d, interact in a cyclic manner in which the orbital sequence is illustrated in **1**. The interaction is hereafter denoted by the cyclic (a, b, c, d) interaction. The orbitals treated here are limited to occupied (p) and vacant (p*) p-orbitals of ionic centers and bonding (π) and anti-bonding (π*) orbitals of a π-bond. The π and π* orbitals can interact with the others at the same or different atomic orbitals. The former one-centered interaction is denoted by the subscript, 1, the latter two-centered interaction by 2. The other subscripts, s (suprafacial) and a (antarafacial), are introduced to specify whether an orbital takes part in cyclic interaction at the same or opposite side of orbital lobes. For a given set of orbitals, there are many possible modes of cyclic interactions which differ from one another in the orbital sequence, the interacting lobe (s or a) or center (1 or 2). Some interactions are those contained in real molecular systems, the others being not. The orbital interactions are subjected to the orbital phase analysis to predict that the associated molecular systems are electron-localizing or -delocalizing.

We start with cyclic (π_s, p_s, π^*_s, p_s) interactions. The orbital sequence and the interacting lobes are given there. Whether the π and π* orbitals interact at one or two centers makes a difference. There are four modes of interactions: (π_{1s}, p_s, π^*_{1s}, p_s) (**2**), (π_{2s}, p_s, π^*_{2s}, p_s) (**3**), (π_{2s}, p_s, π^*_{1s}, p_s) (**4**), (π_{1s}, p_s, π^*_{2s}, p_s) (**5**) interactions. When we apply the orbital phase condition, we can classify the cyclic orbital interactions into electron-localizing and -delocalizing ones. The p and π orbitals are electron-donating orbitals, and the π* orbital is an electron-accepting orbital.

In **2** all relations between the neighboring orbitals meet the phase requirements: The electron-donating π and p orbitals out of phase, the donating p and accepting π* orbitals in phase. The interaction is electron-delocalizing. The conditions cannot simultaneously be satisfied in **3**, where the dotted line between the p_s and π_{2s} orbitals in phase indicates that the phase relation is opposite to the requirement. The interaction is electron-localizing. Similarly, the remaining interactions, **4** and **5**, are predicted to be delocalizing and localizing, respectively. The cyclic orbital interactions, **2** and **3**, are associated with real acyclic conjugated species, as previously shown[7] and will be briefly described in the following paragraph: The electron-delocalizing interaction **2** with trimethylenemethane (TMM) dianion (**6**) and the localizing interaction **3** with butadiene (BD) dianion (**7**). There are no actual acyclic systems related to the remaining interactions (**4**, **5**).

Dianions of TMM and BD are considered to be composed of two anionic centers and a double bond. The electron delocalization among the three systems is described in terms of the configuration interactions or the orbital interactions as is schematically represented in Fig. 1a.[7] An electron shifts from an anionic center to the double bond through the interaction of the ground-state configuration, G, with the electron-transferred configuration, T_1. The configuration interaction is approximated to be the interaction of the p-orbital of the anionic center with the π^* orbital of the double bond. An electron hole results from the transfer. The hole can be supplied with an electron from the double bond through the interaction of the transferred configuration with the locally-excited configuration, E. The T_1-E configuration interaction corresponds to the p-π orbital interaction. As a result the G-T_1-E configuration interaction or the π-p-π^* orbital interaction is involved in the above process. There is an analogous process starting with an electron shift from the other anionic lone-pair orbital. The process involves the G-T_2-E configuration interaction or the π-p-π^* orbital interaction, where the p orbital is different from that in the aforementioned process. All interactions are suprafacial. Now we realize that the delocalization involves the cyclic (π_s, p_s, π^*_s, p_s) interaction. In the TMM dianion both anionic centers interact with the same carbon of the double bond. The π and π^* orbitals take part in cyclic interaction at one center (π_{1s},π^*_{1s}) as is shown in **2**. In the BD dianion the anionic centers interact with the different carbons of the double bond. The two-centered interactions at the π and π^* orbitals (π_{2s} and π^*_{2s}) are involved in cyclic interaction (**3**).

We have examined cyclic (π_s,p_s,π^*_s,p_s) interactions which have been found to include the orbital interactions for the dianions of TMM and BD. We replace p_s by p^*_s to examine the corresponding dications. Similar arguments lead to a (π_{1s}, p^*_s, π^*_{1s}, p^*_s) interaction (**8**) and a (π_{2s}, p^*_s, π^*_{2s}, p^*_s) interaction (**9**) in place of **2** and **3**. The interactions are similarly associated with real systems; those corresponding to **4** and **5** being not. The interaction, **8**, is electron-delocalizing, while **9** is electron-localizing. The delocalizing interaction is contained in the TMM dication (**10**), the localizing one in the BD dication (**11**) as is shown in Fig. 1b. An electron shifts from a double bond to a cationic center through the G-T_1 interaction. The configuration interaction is approximated to the π_s-p^*_s interaction. The transferred electron goes back to the π^* orbital through the T_1-E interaction or through the p^*_s-π^*_s orbital interaction. There is another way of electron delocalization *via* the other cationic center



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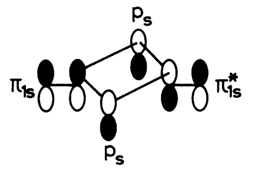

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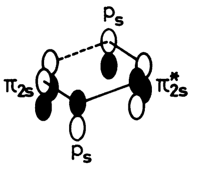

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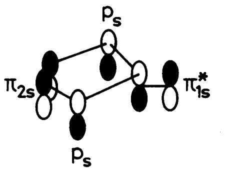

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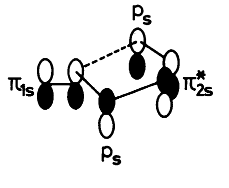

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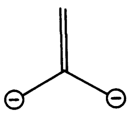

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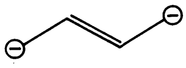

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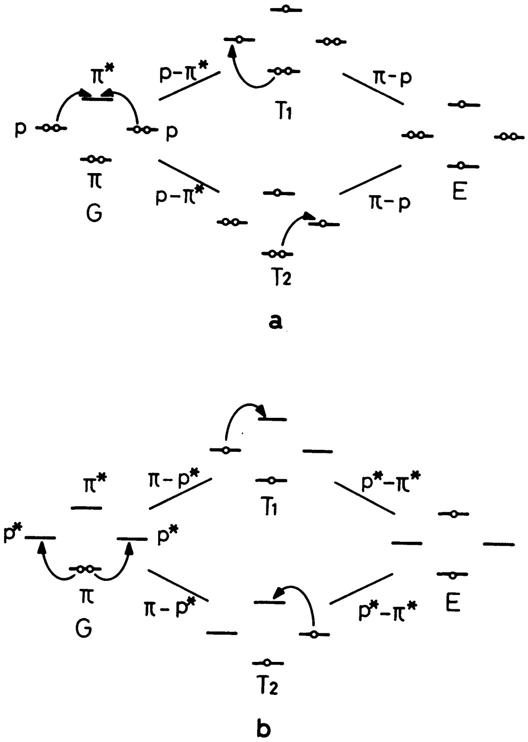
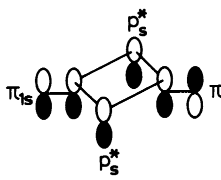


a

b

Fig. 1.



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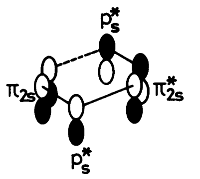

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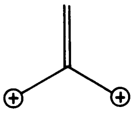

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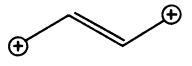

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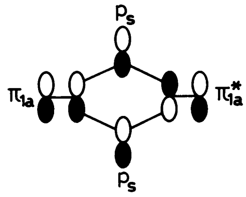
through the G-T$_2$-E interaction or through the π_s-p^*_s-π^*_s interaction. As a result, the delocalization among two cationic centers and a double bond contains the cyclic (π_s, p^*_s, π^*_s, p^*_s) interaction. The delocalizing **8** with one-centered interactions of π and π^* orbitals is associated with the TMM dication, the localizing **9** with the BD dication.

We have described the suprafacial (π_s, $p^{(*)}_s$, π^*_s, $p^{(*)}_s$) interactions and treat here their antarafacial analogues, the (π_a, $p^{(*)}_s$, π^*_a, $p^{(*)}_s$) interactions. The antarafacial counterparts of the suprafacial interactions for the divalent ions of TMM and BD, and these only, are associated with real systems. The electron-delocalizing interaction (**2**) contained in TMM dianion corresponds to the (π_{1a}, p_s, π^*_{1a}, p_s) interaction (**12**). That (**8**) contained in TMM dication corresponds to the (π_{1a}, p^*_s, π^*_{1a}, p^*_s) interaction (**13**). These are related to the antarafacial analogues of the TMM divalent ions, where a double bond interacts with two ionic centers at the same carbon (**14** and **15**). Electron-localizing counterparts are the (π_{2a}, p_s, π^*_{2a}, p_s) and (π_{2a}, p^*_s, π^*_{2a}, p^*_s) interactions (**16** and **17**). The related systemes are the antarafacial analogues of BD divalent ions (**18** and **19**).

We have described cyclic (π, $p^{(*)}$, π^*, $p^{(*)}$) interactions and found that the orbital interactions (**2**, **3**, **8**, **9**, **12**, **13**, **16**, **17**) are associated with the real molecular systems (**6**, **7**, **10**, **11**, **14**, **15**, **18**, **19**), respectively. Although there are many other possible interactions of four orbitals, none of them are contained in real polyvalent ions. We will here design electron-localizing and -delocalizing species with more electric charges by fusing the cyclic orbital interaction units for the divalent ions singled out above. Charge (positive or negative) does not alter the conclusion with respect to localization and delocalization,[8] as can be seen in the preceding arguments. The following will be confined to polyanions.

We first fuse the suprafacial interaction units, *i.e.*, the delocalizing interaction, **2**, and the localizing interaction, **3**. The fusion of **2** at one of p_s's gives rise to a delocalizing chain of cyclic orbital interaction (**20**). The related system is polyanion where



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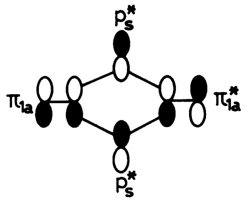

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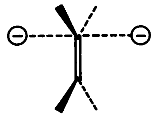

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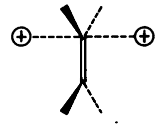

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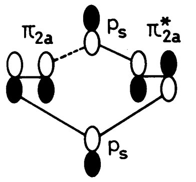

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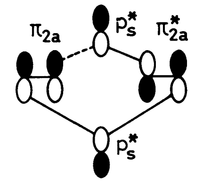

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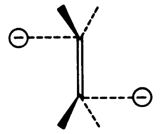

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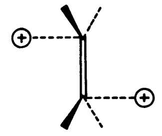

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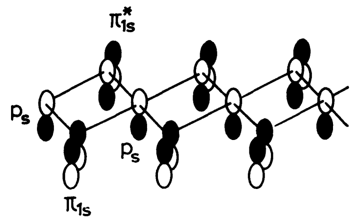
each neighboring pair of TMM dianions share one of anionic centers (**21**). The localizing counterpart (**22**) similarly derives from **3**. The cyclic orbital interaction corresponds to the polyanion (**23**) where anionic centers are shared by BD dianions. The two-site fused interactions (**24** and **25**) are those contained in the delocalizing dianion (**26**) and the localizing dianion (**27**).

Secondly, we fuse the antarafacial interaction units, *i.e.*, the delocalizing interaction (**12**) and the localizing interaction (**16**). Similar arguments lead to the delocalizing (**28**) and localizing (**29**) chains of cyclic orbital interactions in case of one-site fusion. These are associated to ions and double bonds stacked alternately (delocalizing **30** and localizing **31**). The two-site fusion gives rise to the delocalizing (**32**) and localizing (**33**) arrays of orbitals, which are those contained in **34** and **35**, respectively.

We have described the cyclic interactions of two $p^{(*)}$'s, π and π^* orbitals, which have been shown to be contained in the divalent ions of TMM and BD (**6**, **7**, **10**, **11**) and their corresponding antarafacial analogues (**14**, **15**, **18**, **19**) and designed electron-localizing and -delocalizing polyions (**21**, **23**, **26**, **27**, **30**, **31**, **34**, **35**) by fusing them at one and two sites. We will next describe cyclic orbital interactions of one p orbital and three of π or π^* orbitals. The real acyclic systems



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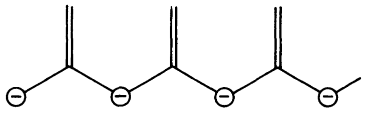

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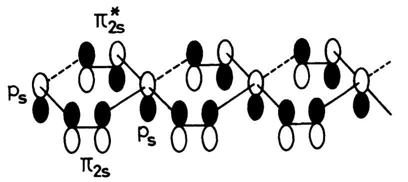

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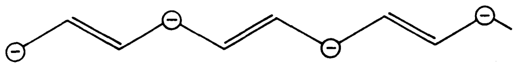

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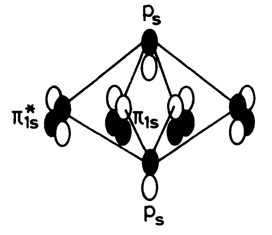

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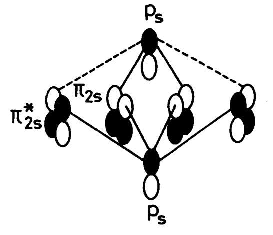

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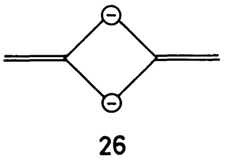

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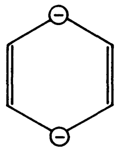

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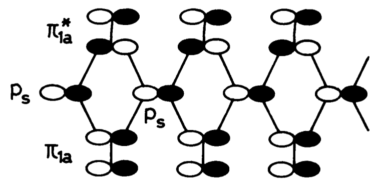
represented by some interactions, *i.e.*, the (p, π^*, π^*, π) interactions (**36**, **38**) and (p, π^*, π, π) interactions (**37** and **39**), are monovalent ion units, *i.e.*, the conjugated anions, **40** and **41**, as will be shown in the following paragraph. We will then design some dianions by fusing the cyclic orbital interaction units in a different manner.

The mechanism of electron delocalization from the anionic center to the distant double bond through the middle bond in **40** and **41** is shown in Fig. 2a. An electron shifts from the anionic center to the middle bond



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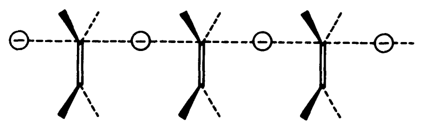

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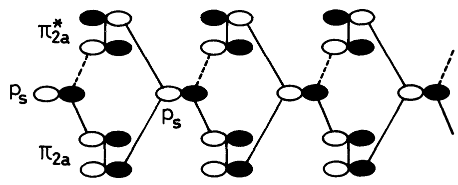

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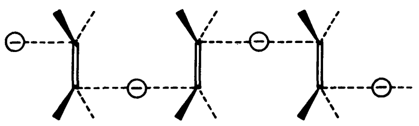

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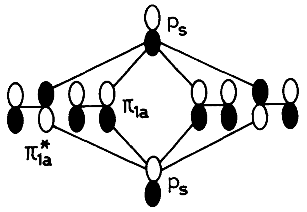

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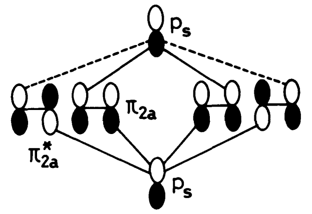

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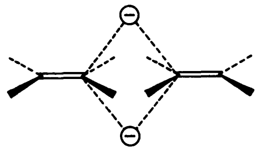

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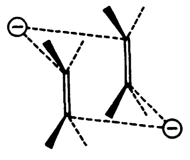

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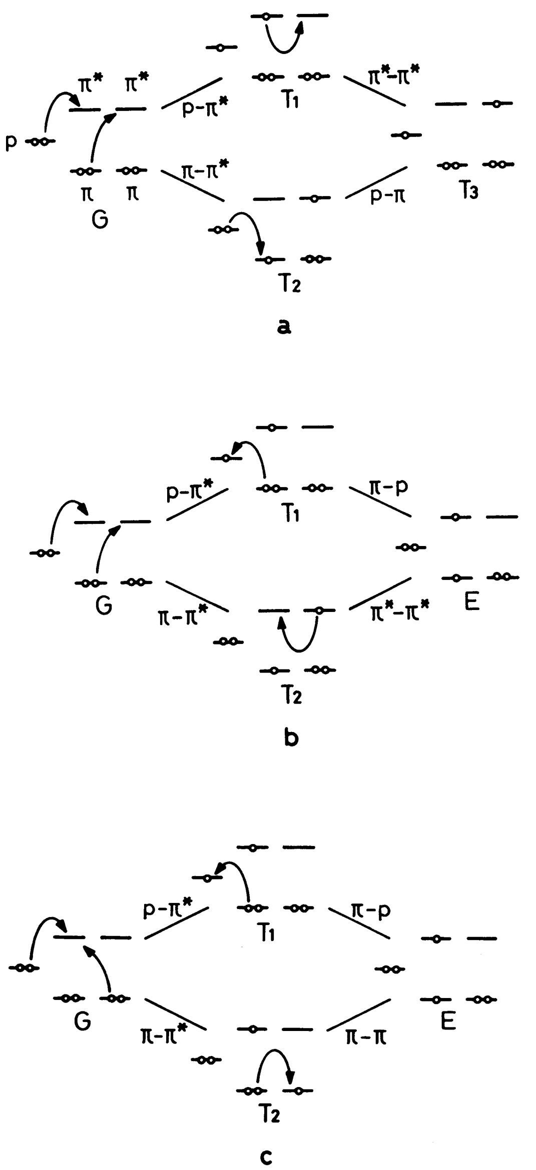
through the G-T$_1$ or p-π^* interaction. The transferred electron shifts farther to the terminal bond through the T$_1$-T$_3$ or π^*-π^* interaction. The process involves the p-π^*-π^* interaction. There is another path for the distant delocalization. An electron shifts from the middle to terminal bond through the G-T$_2$ or π-π^*



a

b

c

Fig. 2.

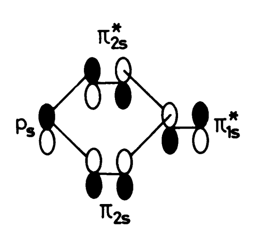
interaction, leaving an electron hole in the middle π bond. The hole then shifts to the anionic center through the T_2-T_3 or p-π interaction. The process involves p-π-π^* interaction. As a result, the distant delocalization *via* the two paths contains the (p_s, π^*_s, π^*_s, π_s) interactions (**36**—**39**).

The cyclic interactions are identical with that involved in a way of polarization of the middle bond (Fig. 2b). The electron shift from the anionic center to the middle bond leaves an electron hole which moves to the latter. The process involves the G-T_1-E or π_s-p_s-π^*_s interaction. In the other path, an electron first shifts from the middle to terminal bond and then back to the former through the G-T_2-E or π_s-π^*_s-π^*_s interaction. As a result, the polarization involves the same (p_s, π^*_s, π^*_s, π_s) interaction as the distant delocalization. The dual property of the cyclic orbital interaction should be noted for forthcoming arguments.

Another polarization path is shown in the bottom half of Fig. 2 c. The electron shift from the terminal to middle bond leaves an electron hole, which moves to the latter through the G-T_2-E or π_s-π_s-π^*_s interaction. This forms a different cyclic (p_s, π_s, π_s, π^*_s) interaction with the π_s-p_s-π^*_s interaction, which has been shown in the preceding paragraph to be involved in the polarization of the middle bond (The top halves of Fig. 2b and 2c represent the identical process).

We have shown that cyclic orbital interactions of one p orbital and three π and π^* orbitals are contained in the conjugated monoanions. The cyclic orbital interaction with the dual nature—the distant delocalization of the lone-pair electrons and the polarization of middle bond—is favored by phase continuity (**36**) in the anion **40**, and disfavored by phase discontinuity (**38**) in the anion **41**. The cyclic orbital interaction for the polarization only is favored by phase continuity (**39**) in **41**, and disfavored by phase discontinuity (**37**) in **40**.

Now we design cyclic orbital interactions for dianions by fusing the delocalizing interaction units derived



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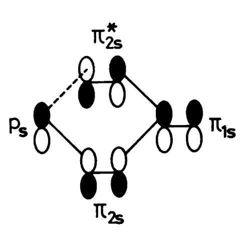

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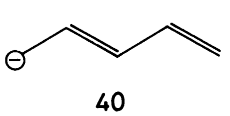
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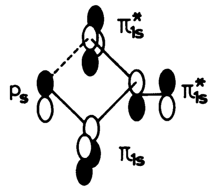

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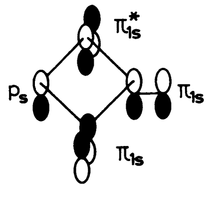

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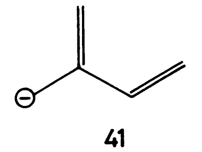
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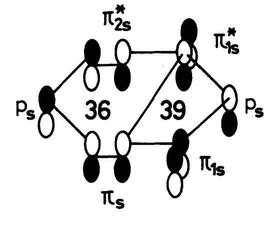
from the monoanions. The interaction (**36**) for the delocalization-polarization in **40** and that (**39**) for the polarization in **41** are combined to share the neighboring pair of π_{2s} and π^*_{1s} in **36** and that of π_{1s} and π^*_{1s} in **39**. The resulting orbital interaction (**42**) is associated with the dianion (**43**) where the diene moieties in the monoanions are superimposed. When the orbital interactions (**36**) for the delocalization-polarization are combined with each other to share the π^*_{1s}-π^*_{2s} pairs, a cyclic interaction (**44**) for the dianion **45** is generated. A combination of the interactions (**39**) for the polarization to share the π_{1s}-π_{1s} pairs leads to a cyclic interaction (**46**) for the dianion (**47**).

Now we predict the relative stabilities of the designed dianions. The cyclic orbital interaction unit (**36**) with the dual nature of delocalization and polarization should contribute to more stabilization than the polarization interaction (**39**). The stability is then expected to increase with the number of the delocalization-polarization interactions involved if there is no extra-stabilization on fusion. In the dianion **45** the cyclic orbital interaction units are both the delocalization-polarization interactions. The dianion **43** contains one, the remaining (**47**) none. The stability then decreases in the order of **45**>**43**>**47**. However, the fusion of orbital interaction units can enhance the effects of each other as significantly as to invert the ordering. A pair of orbitals shared on fusion in **42** is a primary[9] interaction between electron-donating and accepting orbitals. In addition, the cyclic six-orbital (p, π^*, π^*, p, π, π) interaction in **42** satisfies the phase continuity requirements. In contrast, the orbital interactions shared in **44** and **46** are secondary[9] between electron-donating orbitals or between electron-accepting orbitals. The extra-stabilization due to the fusion should be smaller, if any. In addition, the cyclic six-orbital (p, π^*, π^*, p, π, π) interactions do not satisfy the phase continuity requirements.[10] The extra-stabilization on fusion is then expected to be greater in **43**. The stability ordering of **43** and **45** might be inverted.

The conjugate dianions designed in the preceding sections are considered to be vinylogues of TMM and BD dianions. There is a pair of corresponding vinyl-



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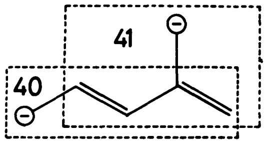

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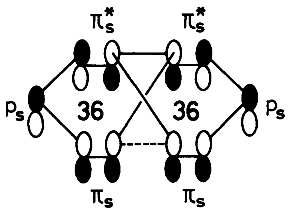

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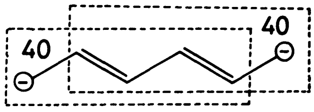

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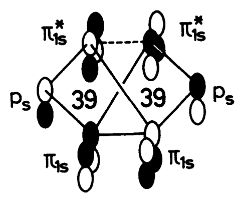

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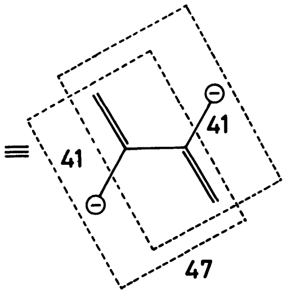

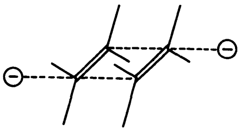

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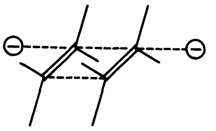

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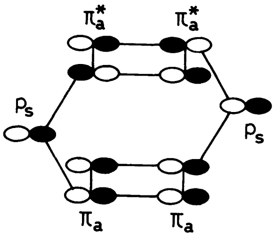

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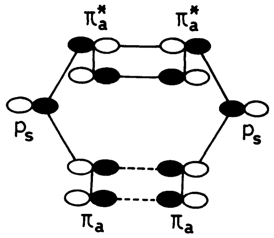

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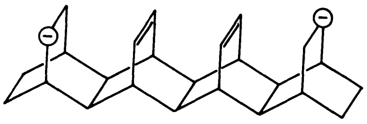

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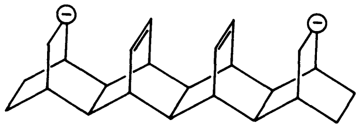

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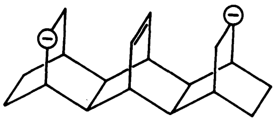

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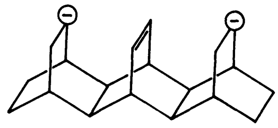

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ogues of the antarafacial analogues (**14** and **18**) of the TMM and BD dianions, where two juxtaposed π-bonds interact with two anionic centers in a different manner as shown in **48** and **49**. The interactions involved are cyclic six-orbital (p_s, π^*_a, π^*_a, p_s, π_a, π_a) interactions, **50** and **51**. The cyclic six-orbital interaction is favored by the phase continuity (**50**) for **48** and disfavored by the phase discontinuity (**51**) for **49**. It follows that **48** is more stable than **49**. The relative stability makes a contrast with the aforementioned stability of the antarafacial analogues (**14**, **18**) of the TMM and BD dianions. We could experimentally examine the prediction by preparing such polycyclic species as **52**—**55**.

Geometry Optimization

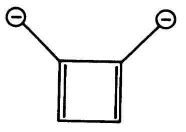
The preceding orbital phase arguments have been limited to the localization-delocalization of π electrons, and have not taken into account the effects of σ electrons and inner-shell electrons. It is necessary to examine whether these effects may modify or alter the orbital phase predictions, and to supplement the qualitative arguments by means of numerical values. Molecular geometries of some ions are optimized by *ab initio* molecular orbital calculations with STO-3G basis set. The geometries fully optimized under given symmetry constraints are shown in Fig. 3. The relative energies of the isomers to be compared are listed in Table 1.

The TMM dianion is estimated to be more stable by 22.5 kcal mol^{-1}[†] than the BD dianion. The relative stability is consistent with the orbital phase prediction[7] and with the experimental observation.[11] The bond lengths also support the preceding arguments. The bond alternation is remarkable in the electron-localizing BD dianion. The small distance (1.35 Å) between the inner carbons suggests a double bond character while the distance between the inner and outer carbons is long (1.47 Å). The carbon–carbon bond length (1.42 Å) in the electron-delocalizing TMM dianion is intermediate between those in the BD dianion.[12] Similar results are obtained for the TMM and BD dications. The energy difference is 18.1 kcal mol^{-1}. The bond lengths are 1.43 Å in the TMM dication, and 1.36 Å and 1.50 Å in the BD dication.

The one-site fusion is found to still retain the delocalization and localization characters of the unit dianions. The fully cross-conjugated C_7H_9 trianion[13] (**21**) is more stable by 7.6 kcal mol^{-1} than the fully linearly conjugated C_7H_9 trianion[14] (**23**). The bond alternation in the linear trianion is similar to that in the BD dianion. The short bond length is 1.35 Å, the long bond lengths being 1.47 Å and 1.48 Å. All the carbon–carbon bond lengths (1.41, 1.43, and 1.47 Å) in the cross trianion range between those in the linear trianion. Noteworthy is that the distance between the fused and central carbons in the TMM dianion unit is close to the larger distance in the linear trianion. The cross trianion tends to shift from the one-site fused pair of TMM dianions to two allyl anions connected with each other at their central carbons by an anionic carbon.

The two-site fusion of the TMM and BD dianion units gives rise to the four and six-membered ring dianions (**26**, **27**). The direct comparison of the thermodynamic stabilities due to π-electron delocalization is hampered by ring strain. The instability of benzene dianion is also a direct result of the Hückel rule. It is more interesting to compare the delocalizing dianion (**26**) with its four-membered ring isomer (**56**). The delocalizing **26** was estimated to be more stable by 29.2 kcal mol^{-1}. The bond lengths range less widely (1.36—1.46 Å). The structure of the 1,3-isomer deviates from formally fused TMM dianions toward a combined system of anionic centers and exocyclic double bonds. The 1,2-isomer tends to obtain a property of linearly-conjugated dianion by lengthning a bond in the ring.

Geometry optimization of C_6H_8 dications shows that the relative stability decreases in the order of **57**>**58**>**59**. The stability of **57** relative to **58** suggests the importance of the extra-stabilization by sharing the primary orbital interaction corresponding to **42** for the dianions. A conspicuous feature in the optimized geometry is a strong tendency toward two allyl cations. The linear dication appreciably alternates



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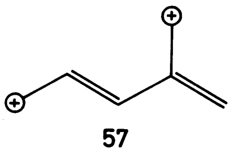

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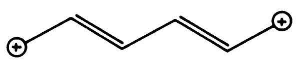

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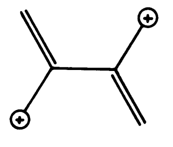

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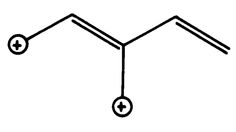

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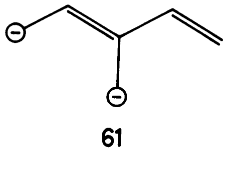

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[†] 1 cal=4.184 J.

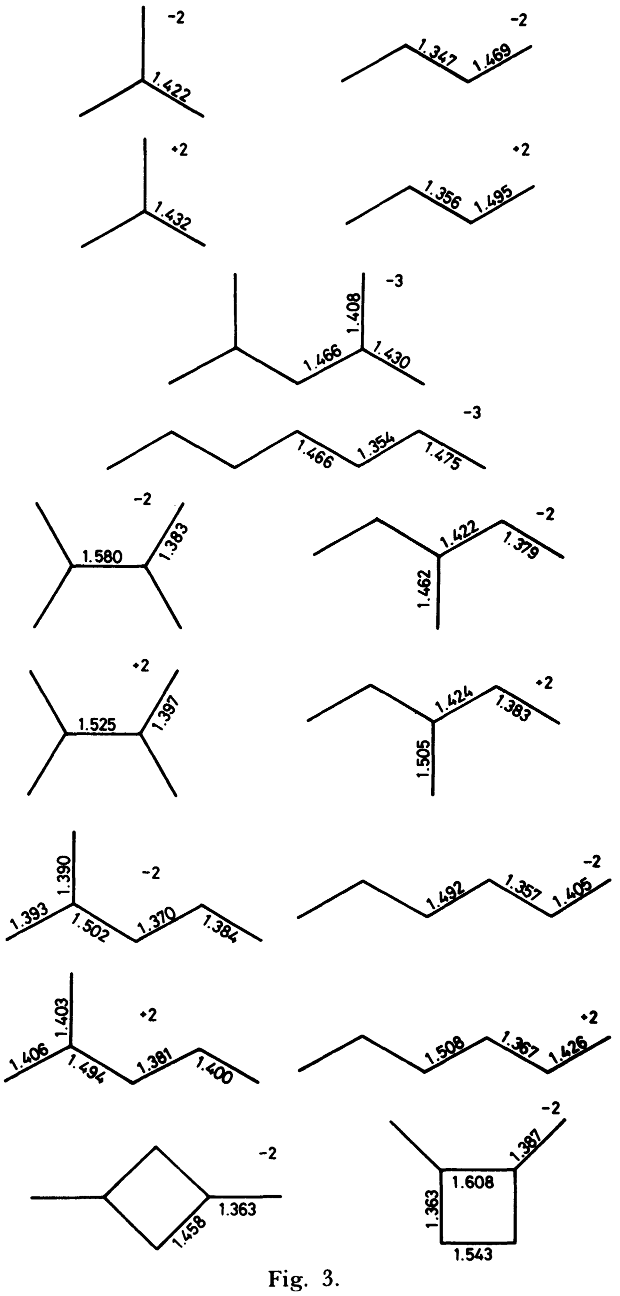

Fig. 3.

TABLE 1. RELATIVE ENERGIES (kcal/mol) AND RESULTS OF CONFIGURATION ANALYSIS[a]

Molecule	Geometry optimization		Configuration analysis[c]			
	Point group	Relative energy[b]	GT	TE	TT	Total
6	D_{3h}	0	0.430	0.139	—	0.569
7	C_{2h}	+22.46	0.286	0	—	0.286
10	D_{3h}	0	0.452	0.144	—	0.596
11	C_{2h}	+18.10	0.257	0	—	0.257
21[d]	C_{2v}	0	0.725	0.208	0.014	0.947
23[d]	C_{2v}	+7.62	0.561	0.001	0.017	0.579
26	D_{2h}	0	0.606	0.136	—	0.742
56	C_{2v}	+29.21	0.490	0.070	0.034	0.594
43	C_s	0	0.586	0.108	0.037	0.731
45	C_{2h}	+1.24	0.534	0.042	0.036	0.612
47	D_{2h}	+17.27	0.586	0.111	0.010	0.707
61	C_{2v}	+53.40	0.590	0.039	0.145	0.774
57	C_s	0	0.626	0.113	0.037	0.776
58	C_{2h}	+1.31	0.524	0.043	0.032	0.598
59	D_{2h}	+12.64	0.658	0.011	0.014	0.683
60	C_{2v}	+53.31	0.601	0.046	0.153	0.800

a) With STO-3G basis set. b) The reference is the total energy of the most stable isomer. c) Each term is defined in the text (Eq. 3). d) Trianion.

the single and double bonds. The remaining isomer of C_6H_8 dications, **60**, which has an electron-localizing BD dication unit, is the least stable. The geometry suggests that the dication is a combination of a pentadienyl cation and a cationic center. These results are almost the same as those of the dianionic analogues[15)] (**43**, **45**, **47**, **61**).

Electron Configuration Analysis for Many System Interaction

The *ab initio* calculations almost completely support the orbital phase predictions on the relative stabilities of the polyions, and give more detailed information of molecular geometries. Here we attempt to look into the relation of these calculated properties with the mechanism of electron delocalization among many bonds, cationic and anionic centers. We are concerned with the delocalization of π-electrons in conjugate polyions, composite systems of double bonds and anionic or cationic centers. The ground-state configuration (G) has two electrons in each bonding orbital of double bonds and in each non-bonding orbital on the anionic centers, and no electron in p-orbitals on the cationic centers. The delocalization is expressed by mixing the electron transferred configurations (T) and locally-excited configurations (E) into G. The ground-state wavefunction is then formulated as

$$W = C_G G + \sum_T C_T T + \sum_E C_E E + \qquad (1)$$

In the transferred configuration an electron is shifted from an occupied orbital of a bond or an anionic center to a vacant orbital of another bond or a cationic center. In the locally-excited configuration an electron is promoted from the bonding orbital to the antibonding orbital in a bond.

In general there are many Kekulé structures for a given molecule. A Kekulé structure corresponds to a ground-state configuration. It is meaningful to analyze how electrons delocalize starting from the main Kekulé structure. The electron configuration analysis for many system interaction (ECAMSI)[16)] is employed to single out the main Kekulé structure. The wavefunction is subjected to ECAMSI for different ground-state configurations or Kekulé structures. The calculations yield the coefficients of G, T, and E configurations. The main Kekulé structure is one with the biggest C_G.

Some quantities are defined to examine the delocalization in a quantitative manner. The integration of the normalized wavefunction (Eq. 1) all over the space leads to the following equation:

$$1 = C_G^2 + \sum_T C_T^2 + \sum_E C_E^2 + \sum_T 2C_G C_T S(G,T) + \sum_{T_1>T_2} 2C_{T_1} C_{T_2} S(T_1,T_2) + \sum_{T,E} 2C_T C_E S(T,E) + \qquad (2)$$

The square terms are the weights of electron configurations. The first cross terms represent the contribution from the G-T configuration interactions. This can be used as a measure of adjacent delocalization through the neighboring occupied and unoccupied orbital interactions. The second cross terms represent the contribution from the T-T configuration interactions. This can be used as a measure of distant delocalization beyond more than one systems through the interactions between the neighboring occupied orbitals and between the neighboring vacant orbitals. The third cross terms represent the contribution from the T-E configuration interactions. This can be used as a measure of polarization of bonds. The coefficients of configurations show the extent of contribution of each configuration to the electronic structure of a molecule. It has been shown that the ratios of coefficients of various configurations to that of the ground state configuration (C/C_G) are more preferable for comparing electronic structures of different molecules.[7b)] We discuss the results of configuration analysis on the basis of the coefficient ratios. The GT, TT, and TE terms of interest are defined as follows:

$$\begin{aligned} GT &= \sum_T 2C_G C_T S(G,T)/C_G^2 \\ TT &= \sum_{T_1>T_2} 2C_{T_1} C_{T_2} S(T_1,T_2)/C_G^2 \\ TE &= \sum_{T,E} 2C_T C_E S(T,E)/C_G^2 \end{aligned} \qquad (3)$$

The main Kekulé structures are confirmed to be such forms as drawn. The results of configuration analysis on the optimized geometries are listed in Table 1. The relative stabilities are completely paralleled with the sums of three terms for the dianions of TMM and BD and for the one-site fused trianions. A difference in the electronic structures comes from the double bond polarization. There is no double bond polarization (C_E=0.0 therefore TE=0.0) in the electron-localizing isomers (**7**, **11**, **23**), as has been predicted by the phase discontinuity of the cyclic orbital interaction. In the delocalizing ones the polarization contributes as significantly as the adjacent delocalization. According to perturbation theory the adjacent delocalization should be similar for the localizing and delocalizing pairs. The increment of the GT term in the delocalizing isomers is considered to be induced by the allowed polarization

The GT and TE terms of the delocalizing two-site fused dianion (**26**) are greater than those of the reference species (**56**), as was predicted. The relative stability can be similarly understood to be also due to the allowed bond polarization and the induced increment of the adjacent delocalization.

The most stable C_6H_8 dianion (**43**) has a greater sum of the three terms than the second (**45**). The magnitude of the GT term in **43** is due to the enhanced mixing of the transferred configuration or primary interaction between the π-π^* interaction shared by the fused cyclic orbital interactions as has been described (**42**). The configuration coefficient ratio (0.24) of the transferred configuration is larger than that (0.17) of the corresponding transferred configuration in **45**. A similarly expected difference in polarization is found in the coefficient ratios. The locally-excited configuration ratio (0.32) for the cross-conjugated double bond in **43** is more than twice greater than that (0.13) in **45**.

There is a limit to the parallelism between the simply predicted or calculated stabilities and the results of configuration analysis. The sum of the three terms for the dianions (**47** and **61**) of lower stabilities are greater than that of more stable **43** or **45**. A possible explanation for the lost parallelism might be related with the "multiplicity" of the main Kekulé structure. The main Kekulé structure is uniquely determined "singlet" for **43** and **45** for which the sum of the three terms of configuration analysis is well correlated to the total energy. There is one more equivalent Kekulé structure for **47** and **61**, which are then expressed by the "doublet" Kekulé structures. The multiplicity arises from the discrepancy in symmetry between Kekulé structures and molecular geometries. Lower symmetry of Kekulé structures might enforce "undesirable" electronic rearrangements to recover the symmetry of electronic structures imposed by molecular geometries. The artificial failure inevitably results in overestimation of GT, TT, and TE terms.

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8) a) The pioneering works by Clark, Schleyer and their collaborators have been encountered with greater difficulties in preparing dications[b)] than dianions[c)] of TMM, and they have been tempted to throw doubt on the thermodynamic stability of the dications. The TMM dianion with a phenyl group on each methylene was readily prepared at 20°C, whereas a reasonable synthetic route to the corresponding triphenyl TMM dication leads only to ring closure or intramolecular Friedel-Crafts reaction involving the aromatic moiety. This contrast may be attributable to the kinetic cause: Electrophilic aromatic substitutions are familiar while the substrates of nucleophilic ones are limited. The difficulties have been demonstrated by other attempts, but the origins seem unclear. There may be no well-established grounds for claiming that polycations and polyanions have similar stabilities. The similarities, which allow us to exclude a group of counterparts (polycations) from the arguments in the text, are the relative stabilities of the isomeric ions. Meaningful is the comparison of the TMM dication with the BD dication, but not that of the dication with the dianion; b) K. Schötz, T. Clark, H. Schaller, and P. v. R. Schleyer, *J. Org. Chem.*, **49**, 733 (1984); c) D. Wilhelm, T. Clark, P. v. R. Schleyer, K. Buckl, and G. Boche, *Chem. Ber.*, **116**, 1669 (1983).

9) According to the perturbation theory the interaction between electron-donating and accepting orbitals is contained in the second-order energy terms, whereas those between donating orbitals and between accepting orbitals are contained in higher-order terms.[5)]

10) On fusion there appears another cyclic six-orbital interaction, *i.e.*, (p, π^*, π, p, π^*, π) interaction. The orbital phase is continuous. However, the continuity does not promote electron delocalization because the donating and accepting orbitals are excessively alternated along the chain in the orbital cycle. For more details see the continuity and discontinuity of cyclic conjugation.[6)]

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12) a) Some molecular orbital calculations of more realistic models with coordinated Li atoms have been reported. In the BD "dianion" lithium cations were indicated to bridge the terminal carbons symmetrically and doubly.[b)] The most stable structure of TMM "dianion" has a 1,3- and 1,3′-bridged structure (C_2)[c)], which was, however, found to be different from the X-ray structure of tribenzylidenemethane di(lithium tetramethylethylene diamine (TMEDA))[c)]: one lithium bridges the 1,3 positions of a allyl system while the other bridges the remaining carbons in 1,2-manner. The models for this structure (C_s) and with the highest symmetry (D_{3h}) were calculated to be higher in energy by about 4 kcal mol^{-1}. Anyway, we think that our dianion model is sufficient to compare the relative stabilities of polymetallated hydrocarbon isomers of the same number of carbons and charges but topologically different carbon skeletons; b) P. v. R. Schleyer, *Pure & Appl. Chem.*, **55**, 355 (1983); c) D. Wilhelm, H. Dietrich, T. Clark, W. Mahdi, A. J. Kos, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **106**, 7279 (1984).

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