

The Origin of Cis Effect in 1,2-Dihaloethenes: The Quantitative Comparison of Electron Delocalizations and Steric Exchange Repulsions

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The "cis effect" is a phenomenon in which the cis isomer is more stable than the corresponding trans isomer or almost the same stability in some molecules with double bonds. In order to clarify the predominant factor of this cis effect in the 1,2-dihaloethenes (XHC=CHX; **1**: X = F, **2**: Cl, and **3**: Br), the energetic amount of electron delocalizations and steric exchange repulsions were theoretically estimated using the natural bond orbital (NBO) theory at MP2/6-311++G(3df,3pd) level. Two delocalization mechanisms, periplanar hyperconjugations (synperiplanar and antiperiplanar effects) and halogen lone pair delocalizations into the C=C bond antibonding orbitals (LP effect), were found as the cis stabilizing forces, in which the total amount of LP effect was greater than those of periplanar effects, the dominant factor of the cis effect. Moreover, the origin of the cis preference of the LP effect was clearly elucidated with the application of orbital phase theory, i.e., the cyclic orbital interaction was continuous only in the cis isomers of **1**–**3**. The total steric exchange repulsion between two isomers were all trans stabilizing and their energetic gains were 1.26, 16.48, and 23.22 kJ mol^{-1} for **1**, **2**, and **3**, respectively. These steric forces obviously counteract against cis preferable delocalization mechanisms, especially in compounds with larger halogen atoms, but their amounts are apparently less than those of electron delocalizations (29.82, 40.00, and 34.46 kJ mol^{-1} for **1**, **2**, and **3**, respectively). Therefore, electron delocalization, not exchange repulsion, has the largest responsibility for the relative energies of 1,2-dihaloethene systems. The importance of this work is the quantitative elucidation of the dominance of delocalization mechanisms over steric effects on the electronic and energetic view of a simple molecular structure.

The interaction between electronic orbitals has been attracting attention in modern organic chemistry, because of the important roles in molecular structure, stability, and reactivity.[1] Two major quantum models based on orbital–orbital interactions have been advocated to dictate the structural stabilization of molecules; the valence shall electron pair repulsion (VSEPR) theory and electron delocalization.[2] The former is a destabilizing force explained by the Pauli exclusion principle, in which pairs of electrons can not occupy the same space. The latter arises from electron transfer from one occupied orbital to another unoccupied orbital, which leads to stabilization of the molecule. Both of these interactions exist in a molecule and have a significant effect on energetic stability, structure, and reactions, although it is difficult to determine which force is the dominant factor in a molecule. One good example is the ongoing discussion about the origin of rotational barrier of ethane.[3,4] Both orbital interactions could give a reasonable explanation of its rotational barrier, but most textbooks explain that the origin is attributed to exchange repulsion.[5] However, in recent years, some scientists have begun to believe that this rotational barrier comes mostly from the attractive hyperconjugation between the C–H bonds and not from Pauli repulsion.[4] As such, even for simple ethane, the discussion on the dominant factor of rotational barrier still has no concrete conclusion.

1,2-Dihaloethenes (XHC=CHX; **1**: X = F, **2**: Cl, and **3**: Br) are also simple molecules with characteristic energy differences between their two isomers. According to the Pauli exclusion principle, electronically more condensed cis isomers should be less stable than the corresponding trans isomers. However, it was reported that the cis isomers are experimentally more stable than the trans isomers (**1** and **2**) or almost the same stability (**3**).[6] This phenomenon is called "cis effect," and its origin has been discussed over 40 years.[7–9] We thought this phenomenon was the key for understanding of the dominant orbital–orbital interaction in a molecule, and have started to study the energetic origin of the cis effect.[7e,7h]

In the present article, high level ab initio and density functional theory (DFT) calculations with natural bond orbital (NBO) analysis[4c–4e,10] were conducted to estimate the electron delocalizations and steric exchange repulsions in the cis and trans isomers of **1**–**3**, to provide a convincing clue for the origin of cis effect. Orbital phase theory[11] was applied for further understanding of the delocalizations of halogen lone pairs. Our results obviously show that the cis stabilizing delocalizations in the 1,2-dihaloethenes overwhelms the counteracting steric exchange repulsion, giving rise to their cis effect.

Computational Details

All ab initio and DFT calculations including NBO analysis were performed with Gaussian 03 program packages.[12] Geometries for those calculations were edited using Spartan program package.[13] These initial structures were optimized at HF, MP2, B3LYP, and B3PW91 level using 6-311++

Published on the web November 12, 2008; doi:10.1246/bcsj.81.1415

Table 1. Structural Parameters for 1,2-Dihaloethenes **1** (F), **2** (Cl), and **3** (Br)[a)]

		cis					trans				
	Method[b)]	$d_{C=C}$	d_{C-X}	d_{C-H}	θ_{CCH}	θ_{CCX}	$d_{C=C}$	d_{C-X}	d_{C-H}	θ_{CCH}	θ_{CCX}
1	HF	1.305	1.313	1.069	122.27	122.92	1.304	1.318	1.070	124.90	120.50
	MP2	1.327	1.335	1.078	122.27	122.50	1.326	1.341	1.078	125.10	119.92
	B3LYP	1.321	1.339	1.079	122.82	122.62	1.320	1.344	1.079	125.32	120.25
	B3PW91	1.321	1.332	1.081	122.32	122.91	1.320	1.337	1.081	125.09	120.35
	exptl[c),d)]	1.330(11)	1.342(5)	1.099(6)	124.1(4)	122.0(2)					
	exptl[e)]						1.324	1.345(5)	1.089	124	119.6(4)
2	HF	1.309	1.715	1.069	120.07	125.67	1.306	1.723	1.069	123.68	121.80
	MP2	1.334	1.706	1.079	120.03	124.48	1.332	1.715	1.079	123.09	121.39
	B3LYP	1.325	1.721	1.079	120.36	125.37	1.322	1.731	1.078	123.80	121.79
	B3PW91	1.325	1.709	1.081	120.18	125.23	1.323	1.718	1.080	123.51	121.82
	exptl[f)]	1.337(4)	1.717(2)		120(3)	124.0(2)	1.332(8)	1.725(2)		124(3)	120.8(6)
3	HF	1.308	1.874	1.070	120.01	126.59	1.305	1.886	1.068	124.30	121.66
	MP2	1.334	1.865	1.080	120.00	125.30	1.331	1.875	1.079	123.65	121.25
	B3LYP	1.322	1.886	1.079	120.53	126.24	1.319	1.899	1.077	124.77	121.45
	B3PW91	1.323	1.872	1.081	120.45	125.95	1.320	1.883	1.079	124.38	121.56
	exptl[d),g)]	1.36(3)	1.87(2)			124(2)					

a) Structural parameters (d; distance and θ; angle) are given in Å and degree. b) All geometry optimizations were performed with 6-311++G(3df,3pd) basis set. c) Electron diffraction data: A. Spelbos, P. A. G. Huisman, F. C. Mijlhoff, G. H. Renes, *J. Mol. Struct.* **1978**, *44*, 159. d) Experimental errors were derived from the literature (K. Kuchitsu, *Structure Data of Free Polyatomic Molecules*, Springer-Verlag, **1994**) and its appendix. e) Infrared spectra data: N. C. Craig, D. W. Brandon, S. C. Stone, W. J. Lafferty, *J. Phys. Chem.* **1992**, *96*, 1598. f) Electron diffraction data: L. Schäfer, J. D. Ewband, K. Siam, D. W. Paul, D. L. Monts, *J. Mol. Struct.* **1986**, *145*, 135. g) Electron diffraction data: M. I. Davis, H. A. Kappler, D. J. Cowan, *J. Phys. Chem.* **1964**, *68*, 2005.

G(3df,3pd) basis set with 6D option. Following single-point energies were calculated at MP3/6-311++G(3df,3pd), MP4-(STDQ)/6-311++G(3df,3pd), and BP86/6-311++G(3df,3pd) levels on MP2-opmitized structures, to accurately evaluate the influence of electron correlations on the cis–trans energy differences. Furthermore, NBO 2nd-order perturbation analysis[10] as well as natural steric analysis[14] were performed at MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) level to quantitatively determine the energetic contributions of each orbital–orbital interactions. Natural population analysis (NPA) was also calculated at the same level to confirm the dominant factor of the cis effect in terms of the electronic population.[10a,10b]

NBO 2nd-order perturbation energy (E_2), which is often applied to organic molecules,[7e,7f,7h,15] is expressed as the following formula,

$$E_2 = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (1)$$

where q_i is the electron population of the i-th donor orbital, ε_i and ε_j are the energy level of the i-th and j-th orbital, and $F(i,j)$ is the (i, j) element of the Fock matrix which can be approximated in terms of overlapping two corresponding NBOs.

Results and Discussion

Geometries and Single-Point Energies. The geometry optimizations of **1–3** were performed with HF, MP2, B3LYP, and B3PW91 methods using 6-311++G(3df,3pd) basis set and obtained structural parameters are listed in Table 1 (three-dimensional coordinates of all optimized structures are found in the Supporting Information). The available experimental spectral data for **1–3** are also shown in the same Table.

We began our discussion with 1,2-difluoroethenes (**1**) because they are the simplest and widely investigated molecules, in which the cis form of **1** was experimentally determined to be $3.26 \pm 0.17\,\mathrm{kJ\,mol^{-1}}$ more stable than the corresponding trans isomer.[6b] A comparison of these experimental values with HF-optimized geometries is far from satisfaction because all of the bonds of HF structures are exceedingly shorter than those of experiments. On the other hand, the remaining three optimized geometries (B3PW91, B3LYP, and MP2) agreed well with the experiment (Table 1). This result dictates that the electron correlation played a critical role on the molecular structures of **1**. Similarly, in 1,2-dichloroethenes (**2**) and 1,2-dibromoethenes (**3**), the HF methods predicted far shorter $d_{C=C}$ lengths (1.305–1.309 Å) than the experiments (1.332–1.36 Å), while the other methods (B3LYP, B3PW91, and MP2) showed good fit to the experimental structural parameters. This tendency dictates the necessity of post-SCF methods in geometry optimizations of these compounds **1–3**.

Further evaluations of the four theoretical methods used in the structural optimizations were made in terms of their calculated energy differences between the cis and trans isomers of 1,2-dihaloethenes **1–3** (Table 2; the positive number indicates the cis preferable energetic difference). The experimental energy difference in 1,2-difluoroethenes (**1**) is nicely reproduced in the calculated results regardless of the theoretical method used in the optimization (3.18–4.18 $\mathrm{kJ\,mol^{-1}}$), indicating that post-

Table 2. Relative Electronic Energy Differences (Including the ZPE) between *cis*- and *trans*-1,2-Dihaloethenes **1** (F), **2** (Cl), and **3** (Br) ($kJ\,mol^{-1}$)[a)]

Optimized	Single point	**1**	**2**	**3**
HF	HF	3.47	−1.30	−5.36
B3PW91	B3PW91	3.68	1.00	−1.97
B3LYP	B3LYP	3.22	0.38	−2.97
	BP86	3.64	1.55	−1.72
	MP2	4.14	3.18	1.13
	MP3	3.18	1.00	−1.21
	MP4(SDTQ)	3.77	2.26	0.17
MP2	BP86	3.22	1.26	−1.55
	MP2	4.18	3.35	1.17
	MP3	3.18	0.96	−1.59
	MP4(SDTQ)	3.72	2.26	0.17
exptl[b)]		3.26 ± 0.17	1.84 ± 0.38	0.38 ± 1.00

a) All single point energy calculations were performed with 6-311++G(3df,3pd) basis set. b) The difference in electronic energy between the cis–trans isomers; N. C. Craig, L. G. Pipper, V. L. Wheeler, *J. Phys. Chem.* **1971**, *75*, 1453.

SCF method is not significantly important for the cis–trans energy gap in **1**. However, careful selection of the calculation method has to be made in the case of **2** and **3**. The HF level calculation showed that their trans isomers were more stable than the corresponding cis isomers (−1.30 and −5.36 $kJ\,mol^{-1}$ for **2** and **3**, respectively), which is clearly inconsistent with the experimental data (1.84 ± 0.38 and $0.38 \pm 1.00\,kJ\,mol^{-1}$, respectively). Although two DFT results, B3LYP and B3PW91, showed better energy differences than the HF method, they still predicted that the *trans*-1,2-dibromoethene was more stable than its cis counterpart (−2.97 and −1.97 $kJ\,mol^{-1}$, respectively). However, the consideration of electron correlation through the MP2 method provided results closer to the experiment than the DFT calculations. In fact, the MP2-optimized cis form of **3** was found to be 1.17 $kJ\,mol^{-1}$ more stable than its trans form. Accordingly, comparing the three post-SCF methods used in the geometry optimizations from the energetic viewpoint, the MP2-structures were chosen as the best ones. Therefore, single-point energy calculations with several post-SCF methods were performed on the MP2 geometries (Other single-point calculations were performed on B3LYP geometries which showed few differences with those on MP2 structures. See Supporting Information.).

As seen in Table 2, the MP3 energetic differences did not show good agreement with the experiment for 1,2-dibromoethenes (**3**), but the result for 1,2-dichloroethenes (**2**) was improved from that of MP2 calculation. While the very high MP4(SDTQ) level calculations with 6-311++G(3df,3pd) basis set reproduced the experimental values of **1–3** almost perfectly (3.72, 2.26, and 0.17 $kJ\,mol^{-1}$ for **1**, **2**, and **3**, respectively). The good agreement in 1,2-dibromoethenes (**3**) is especially noteworthy because no literature has ever confirmed this subtle cis effect, in which experimental errors exceeded the cis–trans energy difference ($0.38 \pm 1.00\,kJ\,mol^{-1}$). Our results clearly proved that the *cis*-1,2-dibromoethene has almost the same stability as that of the corresponding trans isomer in spite of the repulsive forces between two bromine atoms, and a high level electron correlation method is necessary to reproduce the experimental value.

A comparison of structural data at MP2 level showed three interesting trends (Table 1): First, the CCX angles (θ_{CCX}) of cis isomers (122.5°: **1**, 124.5°: **2**, and 125.3°: **3**, respectively) are greater than those of trans isomers (119.9°: **1**, 121.4°: **2**, and 121.3°: **3**, respectively) in all the 1,2-dihaloethenes. As for the bond lengths, cis isomers (1.327 Å: **1**, 1.334 Å: **2**, and 1.334 Å: **3**, respectively) have longer $d_{C=C}$ than corresponding trans isomers (1.326 Å: **1**, 1.332 Å: **2**, and 1.331 Å: **3**, respectively). Adversely, C–X bond lengths d_{C-X} are longer in trans isomers (1.341 Å: **1**, 1.715 Å: **2**, and 1.875 Å: **3**, respectively) than in cis isomers (1.335 Å: **1**, 1.706 Å: **2**, and 1.865 Å: **3**). In fact, these structural tendencies based on the MP2 structures are also found in all the other geometries including calculated and experimental ones. We thought that these structural trends might imply the origin of the cis effect, and NBO 2nd-order perturbation analysis at MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) level was performed to evaluate their energetic element(s) (Table 3).

Natural Bond Orbital 2nd-Order Perturbation Analysis. According to the results of NBO 2nd-order perturbation analysis, four types of important electron delocalizations, antiperiplanar (AP), synperiplanar (SP), σ-lone pair (σ-LP), and π-lone pair (π-LP) effect, were identified to describe the mechanism of the cis effect in 1,2-dihaloethenes **1–3** (Figure 1). The energy difference of the *i*-th and *j*-th orbital ($\varepsilon_i - \varepsilon_j$) and Fock matrix elements ($F(i, j)$) of two interacting orbitals, both of which were used in the energetic calculation of NBO 2nd-order perturbation analysis, are found in the Tables of Supporting Information.

The first two important delocalizations are antiperiplanar and synperiplanar σ_{CX}–$\sigma_{C'X'}$* (X, X′ = H, F, Cl, or Br) hyperconjugations across the C=C bond (AP and SP effect), in which a doubly occupied orbital of C–X bond (X = H, F, Cl, or Br) interacted with the adjacent unoccupied orbital of a C′–X′ bond (X′ = H′, F′, Cl′, or Br′). The 2nd-order perturbation energies for these periplanar hyperconjugations are given in Table 3 which shows that the magnitudes of each SP effect are uniformly less than 6.0 $kJ\,mol^{-1}$ and much smaller than those of AP effects (6.53–44.14 $kJ\,mol^{-1}$). This predominance of AP effects over SP effects could be explained by the orbital overlaps. As seen in Figure 2, the overlap of the main lobe of the C–H bonding orbital (σ_{CH}) with the antibonding orbital of C′–X′ bond ($\sigma_{C'X'}$*) in the cis isomer (AP effect) is much greater than that in the corresponding trans isomer (SP effect). Due to the electronegativity of fluorine in **1**, σ_{CF} has much lower orbital energy and thus less ability as an electron donor than σ_{CH}, while the $\sigma_{C'F'}$* could be a better electron acceptor than $\sigma_{C'H'}$* for the same reason. Therefore, the most significant combination of occupied and unoccupied orbitals to interact is $\sigma_{CH} \rightarrow \sigma_{C'F'}$*. In fact, the most efficient AP effect in 1,2-difluoroethene (**1**) was $\sigma_{CH} \rightarrow \sigma_{C'F'}$* in the cis isomer (33.18 $kJ\,mol^{-1}$) and the total amount of AP effect made cis isomer 17.76 $kJ\,mol^{-1}$ more stable than the corresponding trans isomer. As the halogen becomes less electronegative, the energetic level of the C–X bonding orbital (σ_{CX}) gets higher while the larger halogen atom provides weaker bonding energy and a longer C–X bond, leading to the smaller energetic gap between the σ_{CX} and $\sigma_{C'X'}$*. Therefore, as halogen atoms

Table 3. NBO 2nd-Order Perturbation Analysis of *cis*- and *trans*-1,2-Dihaloethenes **1** (F), **2** (Cl), and **3** (Br) (kJ mol^{-1})[a)]

		Periplanar effect				
		AP effect		SP effect		Total[b)]
1	cis	33.18 ($\sigma_{CH} \rightarrow \sigma_{C'F'}^*$)	6.53 ($\sigma_{CF} \rightarrow \sigma_{C'H'}^*$)	0.96 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	0.42 ($\sigma_{CF} \rightarrow \sigma_{C'F'}^*$)	82.18
	trans	19.20 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	11.63 ($\sigma_{CF} \rightarrow \sigma_{C'F'}^*$)	5.98 ($\sigma_{CH} \rightarrow \sigma_{C'F'}^*$)	—[c)] ($\sigma_{CF} \rightarrow \sigma_{C'H'}^*$)	73.62
		Δ_{AP}[d)] = 17.76		Δ_{SP}[d)] = −9.20		$\Delta_{AP\&SP}$[d)] = 8.56
2	cis	40.25 ($\sigma_{CH} \rightarrow \sigma_{C'Cl'}^*$)	13.72 ($\sigma_{CCl} \rightarrow \sigma_{C'H'}^*$)	3.31 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	0.13 ($\sigma_{CCl} \rightarrow \sigma_{C'Cl'}^*$)	114.82
	trans	23.64 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	25.82 ($\sigma_{CCl} \rightarrow \sigma_{C'Cl'}^*$)	2.43 ($\sigma_{CH} \rightarrow \sigma_{C'Cl'}^*$)	0.59 ($\sigma_{CCl} \rightarrow \sigma_{C'H'}^*$)	104.96
		Δ_{AP}[d)] = 9.02		Δ_{SP}[d)] = 0.84		$\Delta_{AP\&SP}$[d)] = 9.86
3	cis	44.14 ($\sigma_{CH} \rightarrow \sigma_{C'Br'}^*$)	16.82 ($\sigma_{CBr} \rightarrow \sigma_{C'H'}^*$)	3.93 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	0.25 ($\sigma_{CBr} \rightarrow \sigma_{C'Br'}^*$)	130.28
	trans	24.48 ($\sigma_{CH} \rightarrow \sigma_{C'H'}^*$)	33.85 ($\sigma_{CBr} \rightarrow \sigma_{C'Br'}^*$)	1.84 ($\sigma_{CH} \rightarrow \sigma_{C'Br'}^*$)	1.55 ($\sigma_{CBr} \rightarrow \sigma_{C'H'}^*$)	123.44
		Δ_{AP}[d)] = 5.26		Δ_{SP}[d)] = 1.58		$\Delta_{AP\&SP}$[d)] = 6.84

		LP effect		
		$n_\sigma \rightarrow \sigma_{CC}^*$	$n_\pi \rightarrow \pi_{CC}^*$	Total[b)]
1	cis	37.20	107.82	290.04
	trans	33.97	100.42	268.78
		6.46	14.80	Δ_{LP}[d)] = 21.26
2	cis	32.89	106.32	278.42
	trans	28.41	95.73	248.28
		8.96	21.18	Δ_{LP}[d)] = 30.14
3	cis	24.98	86.73	223.42
	trans	21.67	76.23	195.80
		6.62	21.00	Δ_{LP}[d)] = 27.62

a) At MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd). AP: antiperiplanar; SP: synperiplanar. b) Total value of periplanar effects or LP effects. The values are doubled because two sets of the same interactions exist. c) — denotes the negligible interactional energy less than 0.08 kJ mol^{-1} (0.02 kcal mol^{-1}). d) Δ_{AP}, Δ_{SP}, and Δ_{LP} denote the cis–trans energy difference in the total value of each interaction.

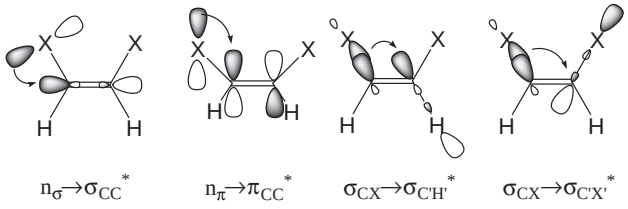

Figure 1. Definitions of the lone pair (n_σ and n_π) delocalization effect (σ- or π-LP effect), the antiperiplanar hyperconjugation effect (the AP effect) and the synperiplanar hyperconjugation effect (the SP effect) within the NBO framework for *cis*-1,2-dihaloethenes (X = F, Cl, or Br).

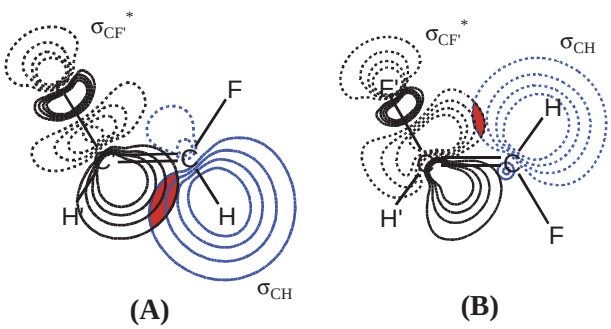

Figure 2. pre-NBO interactions of $\sigma_{CH} \rightarrow \sigma_{C'F'}^*$ hyperconjugation for *cis*- (A) and *trans*-1,2-difluoroethenes (B). The hyperconjugation was antiperiplanar (AP) interaction in the cis isomer whereas the corresponding trans isomer had synperiplanar (SP) interaction. Orbital contours were calculated from the same level for both isomers and the overlap of two orbitals are hatched for clarity.

gets heavier, both the electron-donating ability of σ_{CX} and accepting ability of $\sigma_{C'X'}^*$ get larger, and thus the energetic values of $\sigma_{CH} \rightarrow \sigma_{C'X'}^*$ interactions in cis isomers increase (40.25 and 44.14 kJ mol^{-1} for X = Cl and Br, respectively; the energetic differences of two orbitals are available in the Supporting Information). These changes of energy levels in the bonding and antibonding orbitals of C–X bonds also could be confirmed from the energetic values of $\sigma_{CX} \rightarrow \sigma_{C'X'}^*$ in the trans isomers which increased as the halogen atom got larger (11.63, 25.82, and 33.85 kJ mol^{-1} for X = F, Cl, and Br, respectively), leading to the gradually decreasing cis preference energy of AP effect (17.76, 9.02, and 5.26 kJ mol^{-1} for X = F, Cl, and Br, respectively). As a result, the summation of AP and SP effects made cis isomers 8.56, 9.86, and 6.84 kJ mol^{-1} more stable than the trans isomers for **1**, **2**, and **3**, respectively. Accordingly, these periplanar effects were proved to be an important origins of the cis effect.

Second and more importantly are the σ and π halogen lone pair delocalizations into σ and π C=C antibonding orbitals (LP effect). The $n_\sigma \rightarrow \sigma_{CC}^*$ (σ-LP effect) interactions were cis preferable by 6.46, 8.96, and 6.62 kJ mol^{-1} for X = F, Cl, and Br, respectively. The energetic amount of this interaction in 1,2-difluoroethenes (**1**) was the largest among the 1,2-dihaloethenes **1**–**3** (37.20 kJ mol^{-1} for cis and 33.97 kJ mol^{-1} for trans isomer), presumably because of their short C–X bond lengths which led to the largest orbital–orbital overlaps. The influence of the $n_\pi \rightarrow \pi_{CC}^*$ (π-LP effect) interactions were found to be noteworthy, because they stabilized the cis isomers more than the corresponding trans isomers by 14.80, 21.18, and 21.00 kJ mol^{-1}, respectively. Furthermore, the total energetic differences of σ- and π-LP effects (21.26, 30.14, and 27.62 kJ mol^{-1}, respectively) were greater than those of periplanar effects (8.56, 9.86, and 6.84 kJ mol^{-1}, respectively), and thus the LP effect could be treated as the major origin of the cis effect in all the 1,2-dihaloethenes **1**–**3**. Moreover, the total energetic amount of these LP effects (290.04, 268.78, 278.42, 248.28, 223.42, and 195.80 kJ mol^{-1} for *cis*-**1**, *trans*-**1**, *cis*-**2**, *trans*-**2**, *cis*-**3**, and *trans*-**3**, respectively: Table 3) was apparently greater than those of periplanar effects (82.18, 73.62, 114.82, 104.96, 130.28, and 123.44 kJ mol^{-1} for *cis*-**1**, *trans*-**1**, *cis*-**2**, *trans*-**2**, *cis*-**3**, and *trans*-**3**, respectively). The great influence of the LP effect could be seen in the structural parameters, because the LP effect seemed to elongate the C=C bond lengths more and made the C–X bond lengths shorter in the cis isomers. The larger LP effect as well as the greater repulsive forces (dipole–dipole and Pauli repulsions) between two halogen atoms invoked wider CCX angles in the cis isomers than in the trans isomers. In fact, those structural trends could be seen in all the calculated and experimental geometries of **1**–**3** (Table 1). The reason why the σ- and π-LP effects were greater in cis isomers than in trans isomers was clearly elucidated with the orbital phase theory, as explained in the next section. Total summations of periplanar and LP effects of cis isomer exceeded those of trans isomer by 27.82, 40.00, and 34.46 kJ mol^{-1} for **1**, **2**, and **3**, respectively, which suggests that these electron delocalization effects are the incontestable driving forces to produce the cis effect.

Following the NBO 2nd-order perturbation analysis, we performed Natural Population Analysis to estimate the importance of those electron delocalization systems from a different perspective. As we can see in Table 4, all the carbon atoms in the trans isomers had more positive charges than those in the cis isomers. Contrarily, the halogen atoms in the trans isomers were found to be more negative than those in the cis isomers. This observation clearly indicated that the more halogen lone pair electrons moved into carbon atoms in the cis isomers, which could be taken as the obvious evidence of greater LP effect. Moreover, the positive charges of chlorine and bromine atoms in both cis and trans isomers in **2** and **3** might show that those heavy halogen atoms act as good electron donors, supporting the predominance of LP effects.

Table 4. Natural Population Analysis of *cis*- and *trans*-1,2-Dihaloethenes **1** (F), **2** (Cl), and **3** (Br) (au)[a]

	Atom	cis	trans	$\Delta_{cis-trans}$[b]
1	C	0.2204	0.2232	−0.0028
	F	−0.3813	−0.3847	0.0034
	H	0.1609	0.1615	−0.0006
2	C	−0.2193	−0.2089	−0.0104
	Cl	0.0147	0.0051	0.0096
	H	0.2046	0.2038	0.0009
3	C	−0.2973	−0.2839	−0.0134
	Br	0.0873	0.0745	0.0128
	H	0.2100	0.2094	0.0006

a) At MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd). b) $\Delta_{cis-trans}$ denotes differences between cis and trans isomers.

Table 5. Natural Steric Analysis of *cis*- and *trans*-1,2-Dihaloethenes **1** (F), **2** (Cl), and **3** (Br) (kJ mol^{-1})[a]

		Total steric exchange repulsion	Steric repulsion between two lone pairs
1	cis	340.12	3.47
	trans	338.86	2.80
	$\Delta_{cis-trans}$[b]	1.26	0.67
2	cis	323.00	11.92
	trans	306.52	2.89
	$\Delta_{cis-trans}$[b]	16.48	9.03
3	cis	299.45	13.97
	trans	276.23	1.72
	$\Delta_{cis-trans}$[b]	23.22	12.25

a) At MP2/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd). b) $\Delta_{cis-trans}$ denotes differences between cis and trans isomers.

In order to obtain the steric exchange contribution to the 1,2-dihaloethene systems, natural steric analysis[14] was applied to **1**–**3** (Table 5). In 1,2-difluoroethene (**1**) with the smallest halogen atoms, total amount of steric exchange repulsion in the cis isomer was slightly (1.26 kJ mol^{-1}) greater than that of trans isomer. However, as the halogen atom becomes larger, the cis–trans difference of steric repulsion effect increased steadily (16.48 and 23.22 kJ mol^{-1} for **2** and **3**, respectively), primarily owning to the interatomic repulsion of the two halogen atoms in the cis isomers (3.47, 11.92, and 13.97 kJ mol^{-1} for **1**, **2**, and **3**, respectively). As a consequence, the energetic differences of total steric exchange repulsion were trans stabilizing by 1.26, 16.48, and 23.22 kJ mol^{-1} for **1**, **2**, and **3**, respectively, which obviously counteracts the cis preferable

delocalization mechanisms, especially in the compounds with larger halogen atoms. However, it should be noted that the amount of steric exchange repulsion was apparently smaller than those of delocalizations (29.82, 40.00, and 34.46 kJ mol^{-1} for **1**, **2**, and **3**, respectively), suggesting that the steric repulsion might not be an essential factor of cis–trans energetic differences in the 1,2-dihaloethene systems, but as a mere subordinate mechanism. As a consequence, the summation of the cis–trans energetic differences in the electron delocalizations and steric repulsions were 28.56, 23.52, and 11.24 kJ mol^{-1} for **1**, **2**, and **3**, respectively, which gradually decreased as the halogen atom got larger. Although some other trans stabilizing forces, such as dipole–dipole moment and electrostatic repulsions might be expected, this energetic tendency in the framework of NBO analysis successfully reproduced the experimentally observed cis–trans energetic gaps for **1**–**3** (Table 2).[6b]

The Orbital Phase Continuity–Discontinuity Theory. The cis preference of 1,2-dihaloethenes is also rationalized by the orbital phase continuity–discontinuity theory,[11] which is a basic models in chemistry and has strong influences on stabilities of various systems, i.e., the Hückel rule for aromaticity and frontier orbitals for Diels–Alder reactions. In this effective theory, the orbital phase of cyclic orbital interactions is an important factor in promoting orbital–orbital interactions. The requirements of orbital phase continuity for stabilizing the molecule through effective delocalization are as follows: (a) the electron-donating orbitals (denoted by D–D) are out of phase; (b) the accepting orbitals (denoted by A–A) are in phase; and (c) the donating and accepting orbitals (D–A) are in phase.[11]

In the case of *trans*-1,2-dihaloethenes, the through-bond π cyclic orbital interaction model is given as Figure 3, in which two halogen π lone pairs (p and q) interact with π bonding and antibonding orbitals of the C=C bond (π and π^*). As seen in Figure 3a, the orbitals p, q, and π are occupied with two electrons in the ground configuration G. The process of delocalization from a halogen π lone pair to a π antibonding orbital of a C=C bond ($n_\pi \rightarrow \pi_{CC}{}^*$), in which one electron of p or q moved into a vacant π^* orbital, denoted as p–π^* or q–π^* interactions (T_1 or T_2). As such, from the view point of orbital interactions, delocalizations were achieved via mixing of G with T_1 or T_2 configuration. Moreover, locally excited configuration (E) is yielded when one electron of a π orbital subsequently shifts into a singly occupied p or q orbital of T_1 or T_2, which are denoted as π–p or π–q interactions. Consequently, we could say that cyclic –G–T_1–E–T_2– configuration (or –π–p–π^*–q– interaction) occurs in 1,2-dihaloethenes. The halogen lone pairs (p and q) and π bonding orbital of C=C (π) are clearly electron-donating orbitals (denoted as D) and only the π antibonding orbital of C=C (π^*) could be classified as an acceptor orbital (denoted as A). And so, the stabilization via through-bond electron delocalization is more effective when orbital phases of those donors and acceptors are continuous, but as depicted in Figure 3b, the orbital continuity is not satisfied in this through-bond system.

However, the mechanism in *cis*-1,2-dihaloethenes systems is different because consideration of through-space interactions between two halogen lone pairs should be required. This

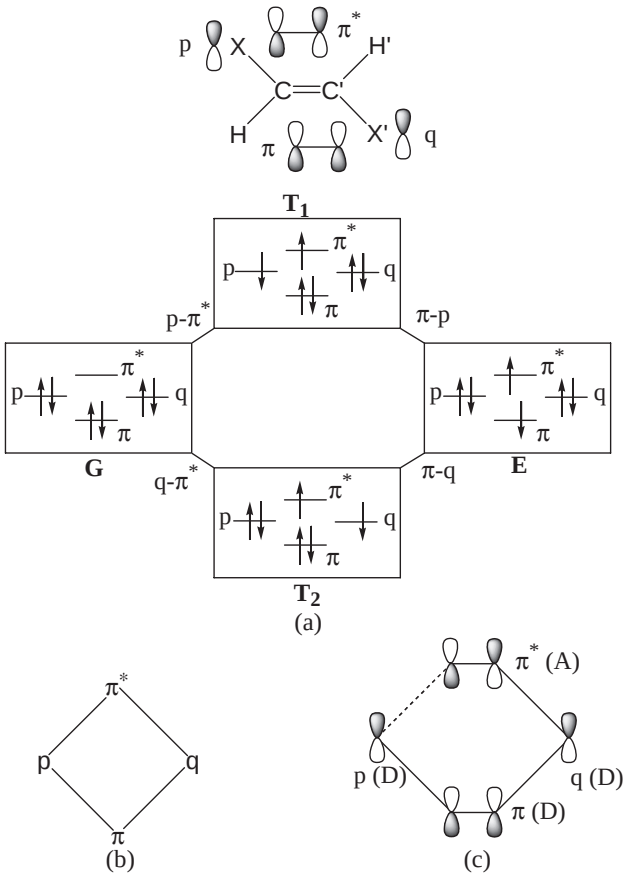

Figure 3. Through-bond interactions in π-LP effect of *trans*-1,2-dihaloethenes. (a) The mechanism of electron delocalizations, (b) the cyclic orbital interaction, (c) the orbital phase discontinuity.

cis specific interaction could be denoted as p–q interaction in Figure 4a, in which one electron of doubly occupied p/q orbital moves into singly occupied q/p orbital. The existence of this interaction effects the mechanism of the electron delocalization system and the other cyclic triangle interaction, –G–T_1–T_2– (–π^*–p–q–), is newly provided (Figure 4b). According to Figure 4c, –G–T_1–T_2– configuration is obviously continuous. Because of this speculation, the LP effect ($n_\pi \rightarrow \pi_{CC}{}^*$) in *cis*-1,2-dihaloethenes are predicted to be greater than in trans isomers. Similar models could be provided for a σ-LP effect system.

Conclusion

High level MO calculations were performed to estimate the contribution of electron delocalizations and steric exchange repulsion in the energetic difference of cis and trans isomers of 1,2-dihaloethenes (XHC=CHX; **1**: X = F, **2**: Cl, and **3**: Br). According to the NBO 2nd-order perturbation analysis, two types of delocalization mechanisms were found important: the periplanar effect between C–X bond (X = H, F, Cl, or Br) and C′–X′ bond (X′ = H′, F′, Cl′, or Br′) locating at an anti or syn position across the C=C bond (AP and SP effect); the second and greatest one was the electron delocalizations from halogen lone pairs into σ and π antibonding orbitals of the C=C bond (LP effect). This greater LP effect in the cis isomer

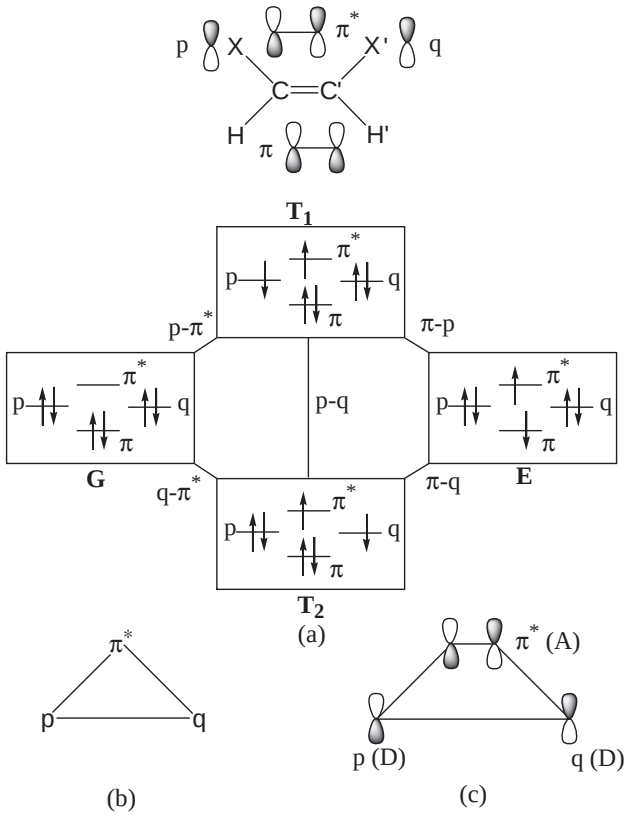

Figure 4. Through-space interactions in π-LP effect of *cis*-1,2-dihaloethenes. (a) The mechanism of electron delocalizations, (b) the cyclic orbital interaction, (c) the orbital phase properties.

was clearly explained with orbital phase theory, i.e., the cyclic orbital interaction was continuous only in the cis isomers of **1**–**3**, while steric exchange repulsion was found as a trans-stabilizing force especially for the 1,2-dihaloethenes with large halogen atoms, based on natural steric analysis. However, the total energetic gain of steric exchange repulsions was apparently less than those of cis preference delocalizations for all the 1,2-dihaloethenes. Therefore, the periplanar and LP effects could be regarded as the origin of cis effect and the latter was predominant. The cis–trans differences in the bond lengths and atomic charges supported the fact. The central point of this article is the electron delocalization, not the exchange repulsion, has the largest responsibility for the energies of 1,2-dihaloethene systems. This energetic concept regarding the orbital–orbital interactions could be a guide to a new aspect of modern organic chemistry to understand diverse molecular phenomena,[16] from the simple ethane rotational barrier[4] to larger and more complex systems, such as polymer rheology and protein foldings.

The Research Center for Computational Science, Okazaki National Research Institutes is greatly acknowledged for the use of SGI Origin 2000, NEC SX-5 and Fujitsu VPP5000. This work is supported by the Japan Society for the Promotion of Science. We express our best appreciation to Prof. Satoshi Inagaki for the discussions about the orbital phase continuity–discontinuity theory.

Supporting Information

The tables of the single point calculations and the three-dimensional coordinates of all optimized structures are provided. Tables 3 and 5 are displayed in kcal mol^{-1} instead of using kJ mol^{-1} as a unit. The energy difference of the *i*-th and *j*-th orbital ($\varepsilon_i - \varepsilon_j$) and Fock matrix elements ($F(i, j)$) of two interacting orbitals which were used in the energetic calculation of NBO 2nd-order perturbation analysis are found. These materials are available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 a) P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry*, Pergamon, Oxford, **1983**. b) P. Deslongchamps, *Tetrahedron* **1975**, *31*, 2463.

2 *Chemical Bonding and Molecular Geometry. From Lewis to Electron Densities*, ed. by R. J. Gillespie, P. L. A. Popelier, Oxford University Press, Oxford, **2001**.

3 a) K. B. Wiberg, D. J. Rush, *J. Org. Chem.* **2002**, *67*, 826. b) O. J. Sovers, C. W. Kern, R. M. Pitzer, M. Karplus, *J. Chem. Phys.* **1968**, *49*, 2592. c) P. A. Christiansen, W. E. Palke, *Chem. Phys. Lett.* **1975**, *31*, 462.

4 a) P. R. Schreiner, *Angew. Chem., Int. Ed.* **2002**, *41*, 3579. b) V. Pophristic, L. Goodman, *Nature* **2001**, *411*, 568. c) L. Goodman, V. Pophristic, F. Weinhold, *Acc. Chem. Res.* **1999**, *32*, 983. d) F. Weinhold, *Nature* **2001**, *411*, 539. e) A. E. Reed, F. Weinhold, *Isr. J. Chem.* **1991**, *31*, 277. f) J. P. Lowe, *J. Am. Chem. Soc.* **1970**, *92*, 3799. g) I. V. Alabugin, T. A. Zeidan, *J. Am. Chem. Soc.* **2002**, *124*, 3175.

5 a) F. A. Corey, *Organic Chemistry*, McGraw Hill, New York, **2000**. b) J. March, *Advanced Organic Chemistry*, John Weily & Sons, New York, **1992**. c) J. E. McMarry, *Organic Chemistry*, Brooks/Cole, Tomson Learning, New York, **1999**.

6 a) K. S. Pitzer, J. L. Hollenberg, *J. Am. Chem. Soc.* **1954**, *76*, 1493. b) N. C. Craig, L. G. Piper, V. L. Wheeler, *J. Phys. Chem.* **1971**, *75*, 1453. c) J. T. Waldron, W. H. Snyder, *J. Am. Chem. Soc.* **1973**, *95*, 5491.

7 a) R. C. Bingham, *J. Am. Chem. Soc.* **1976**, *98*, 535. b) K. B. Wiberg, M. A. Murcko, K. E. Laidig, P. J. MacDougall, *J. Phys. Chem.* **1990**, *94*, 6956. c) K. B. Wiberg, *Acc. Chem. Res.* **1996**, *29*, 229. d) O. Engkvist, G. Karlstrom, P. O. Widmark, *Chem. Phys. Lett.* **1997**, *265*, 19. e) T. Yamamoto, S. Tomoda, *Chem. Lett.* **1997**, 1069. f) I. Novak, *J. Org. Chem.* **2000**, *65*, 5057. g) R. Kanakaraju, K. Senthilkumar, P. Kolandaivel, *THEOCHEM* **2002**, *589–590*, 95. h) T. Yamamoto, D. Kaneno, S. Tomoda, *Chem. Lett.* **2005**, *34*, 1190.

8 a) W. J. Hehre, L. Radom, P. v. R. Schleyer, J. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, Inc., New York, **1986**, Chap. 6, p. 298. b) J. S. Binkley, J. A. Pople, *Chem. Phys. Lett.* **1977**, *45*, 197. c) D. Cremer, *Chem. Phys. Lett.* **1981**, *81*, 481. d) S. R. Gandhi, M. A. Benzel, C. E. Dykstra, T. Fukunaga, *J. Phys. Chem.* **1982**, *86*, 3121. e) D. A. Dixon, T. Fukunaga, B. E. Smart, *J. Am. Chem. Soc.* **1986**, *108*, 1585. f) S. Saebø, H. Sellers, *J. Phys. Chem.* **1988**, *92*, 4266.

9 a) N. D. Epiotis, R. L. Yates, *J. Am. Chem. Soc.* **1976**, *98*, 461. b) F. Bernardi, A. Bottoni, N. D. Epiotis, M. Guerra, *J. Am. Chem. Soc.* **1978**, *100*, 6018.

10 NBO ver. 5.G was used. a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066. b) A. E. Reed, R. B. Weinstock,

F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735. c) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736. d) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899. e) http://www.chem.wisc.edu/~nbo5/.

11 a) K. Fukui, S. Inagaki, *J. Am. Chem. Soc.* **1975**, *97*, 4445. b) S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* **1976**, *98*, 4693. c) S. Inagaki, H. Kawata, Y. Hirabayashi, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724. d) S. Inagaki, K. Iwase, *Nouv. J. Chim.* **1984**, *8*, 73. e) J. Ma, S. Inagaki, *J. Phys. Chem. A* **2000**, *104*, 8989. f) Y. Naruse, J. Ma, S. Inagaki, *Tetrahedron Lett.* **2001**, *42*, 6553. g) J. Ma, A. Hozaki, S. Inagaki, *Inorg. Chem.* **2002**, *41*, 1876. h) J. Ma, A. Hozaki, S. Inagaki, *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1705. i) J. Ma, Y. Ding, K. Hattori, S. Inagaki, *J. Org. Chem.* **2004**, *69*, 4245. j) M. Yasui, Y. Naruse, S. Inagaki, *J. Org. Chem.* **2004**, *69*, 7246. k) Y. Naruse, S. Inagaki, *Chem. Lett.* **2007**, *36*, 820.

12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyenger, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03 (Revision C.02)*, Gaussian, Inc., Wallingford CT, **2004**.

13 *Spartan 4.1.1*, Wavefunction, Inc., **1995**.

14 a) J. K. Badenhoop, F. Weinhold, *J. Chem. Phys.* **1997**, *107*, 5406. b) J. K. Badenhoop, F. Weinhold, *J. Chem. Phys.* **1997**, *107*, 5422. c) J. K. Badenhoop, F. Weinhold, *Int. J. Quantum Chem.* **1999**, *72*, 269.

15 a) A. E. Reed, F. Weinhold, *Isr. J. Chem.* **1991**, *31*, 227. b) P. v. R. Schleyer, M. Kaupp, F. Hampel, M. Bremer, K. Mislow, *J. Am. Chem. Soc.* **1992**, *114*, 6791.

16 a) M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* **2004**, *126*, 5309. b) M. Iwaoka, S. Takemoto, S. Tomoda, *J. Am. Chem. Soc.* **2002**, *124*, 10613.