Large Enhancement of Reactivity of Diels−Alder Reactions on a C(001)−(2×1) Surface: A Hybrid Density-Functional Study

Yasuharu Okamoto[†]

Fundamental Research Laboratories, System Device and Fundamental Research, NEC Corporation, Tsukuba, Ibaraki 305-8501, Japan

Ab initio molecular orbital calculations were used to examine the Diels−Alder reaction of *s-cis*-1,3-butadiene on diamond surface. It was found that the activation energy on the surface is significantly decreased and exothermicity is significantly increased because of the reduced overlap between the p orbitals of the surface C═C dimer. This enhancement of the reactivity on the surface is larger than that produced by chemical substitution of maleic anhydride for ethylene. Calculations show that dienes that contain heteroatoms such as N or S also cause the Diels−Alder reactions easily on the C(001)−(2×1) surface.

Introduction

The Diels−Alder reaction ([4+2] cycloaddition) has been one of the most useful reactions in the field of organic synthesis. Recently, analogous reactions have been intensively studied experimentally[1−4] and theoretically[5−7] by regarding surface dimers on Si, Ge, and C(001)−(2×1) surfaces as a dienophile of the Diels−Alder reactions. Among these studies, Wang et al. first succeeded in the Diels−Alder reaction on a diamond surface.[3] They reported a reaction of 1,3-butadiene with C═C dimers on a C(001)−(2×1) surface. Wang's experiment was done at room temperature, a factor that will be important for the semiconductor industry because it might lead to a breakthrough in the fabrication of diamond films at a low temperature.

The reactivities of Diels−Alder reactions have been studied in terms of the energy level of frontier orbitals, i.e., the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[8] There are three combinations of frontier orbitals of diene and dienophile. Figure 1a shows that the diene reacts with dienophile having a low LUMO energy level. This type of Diels−Alder reaction is called a normal-electron-demand type, in which the energy difference between HOMO(diene) and LUMO(dienophile) governs the reaction rate. Maleic anhydride is a representative dienophile of this type. Figure 1b shows the combination in which the diene reacts with a dienophile such as ethylene, which has neither a low LUMO energy level nor a high HOMO energy level. This type of reaction has a low reactivity and needs a relatively severe condition to cause the Diels−Alder reaction.[8] Figure 1c shows the combination in which the diene reacts with a dienophile having a high HOMO energy level. This type of reaction is called a reverse-electron-demand type, in which the energy difference between HOMO(dienophile) and LUMO(diene) governs the reaction rate. However, this type of reaction is rare compared to a normal-electron-demand type. As a dienophile, ethylene is a counterpart of the C═C dimers on a C(001)−(2×1) surface in an isolated molecular system. However, as stated, the Diels−Alder reaction of ethylene has a low reactivity. Thus, there must be some mechanism of the C(001)−(2×1) surface that enhances the Diels−Alder reaction at room temperature.

In this work, ab initio molecular orbital calculations were done to examine the origin of the enhancement of the reactivity concerning the Diels−Alder reaction of *s-cis*-1,3-butadiene with a C(001)−(2×1) surface. This enhancement is brought about by the decrease of the HOMO−LUMO gap through the reduced overlap between the p orbitals of the surface dimer. The Diels−Alder reaction by dienes that contain a heteroatom such as N or S was also investigated, and it was found that these dienes readily occur with the Diels−Alder reaction on the diamond surface but not with ethylene. Since an efficient n-type doping of diamond is still a challenging problem for the semiconductor industry, Diels−Alder reaction with heterodienes might become useful in this field.

Although it was reported that [2+2] and [4+2] cycloadditions compete on the Si(001)−(2×1) surface,[9] on the C(001)−(2×1) surface, [2+2] cycloaddition was not observed[4] or at most considered to be a minor side product[3] at room temperature thermal reaction. Therefore, the present study only aims at understanding the reactivity of [4+2] cycloaddition. Competition between [4+2] and [2+2] reactions on a C(001)−(2×1) surface, however, is an important topic, and the research in this direction is in preparation.

Computational Method. In the calculation, the hybrid density-functional theory (B3LYP functional[10]) was used in combination with the appropriate cluster model in order to simulate the Diels−Alder reaction of *s-cis*-1,3-butadiene on a C(001)−(2×1) surface. The 6-31G(d) basis set was used. In the calculation of reaction of 1,3-butadiene with the diamond surface, zero-point vibrational energy (ZPVE) was calculated by using the B3LYP/6-31G(d) model chemistry with C_9H_{12}, $C_{17}H_{20}$, and $C_{32}H_{28}$ cluster models. Since the ZPVE calculation is much too time consuming on the $C_{48}H_{36}$ cluster, the results obtained by the $C_{32}H_{28}$ cluster was used as the ZPVE of the $C_{48}H_{36}$ cluster. On the other hand, in the calculation of the reaction of heterodienes such as pyrrole or thiophene with diamond surface, ZPVEs calculated by the C_9H_{12} cluster model were used in order to save computational time. The reliability of the B3LYP/6-31G(d) model chemistry was assessed by using the G3(MP2)//B3LYP[11−13] model chemistry with a C_9H_{12} cluster. G3(MP2)//B3LYP is now established as a method that provides highly accurate energetics (i.e., reaction energy and
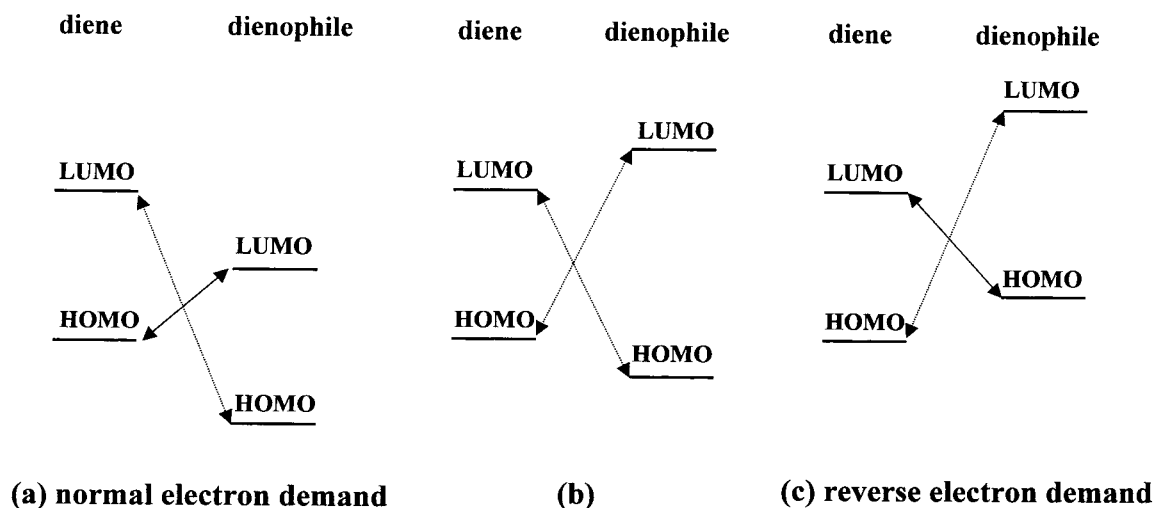
[†] E-mail: y-okamoto@df.jp.nec.com.

(a) normal electron demand   **(b)**   **(c) reverse electron demand**

Figure 1. Schematically drawn HOMO–LUMO energy levels for three types Diels–Alder reactions.
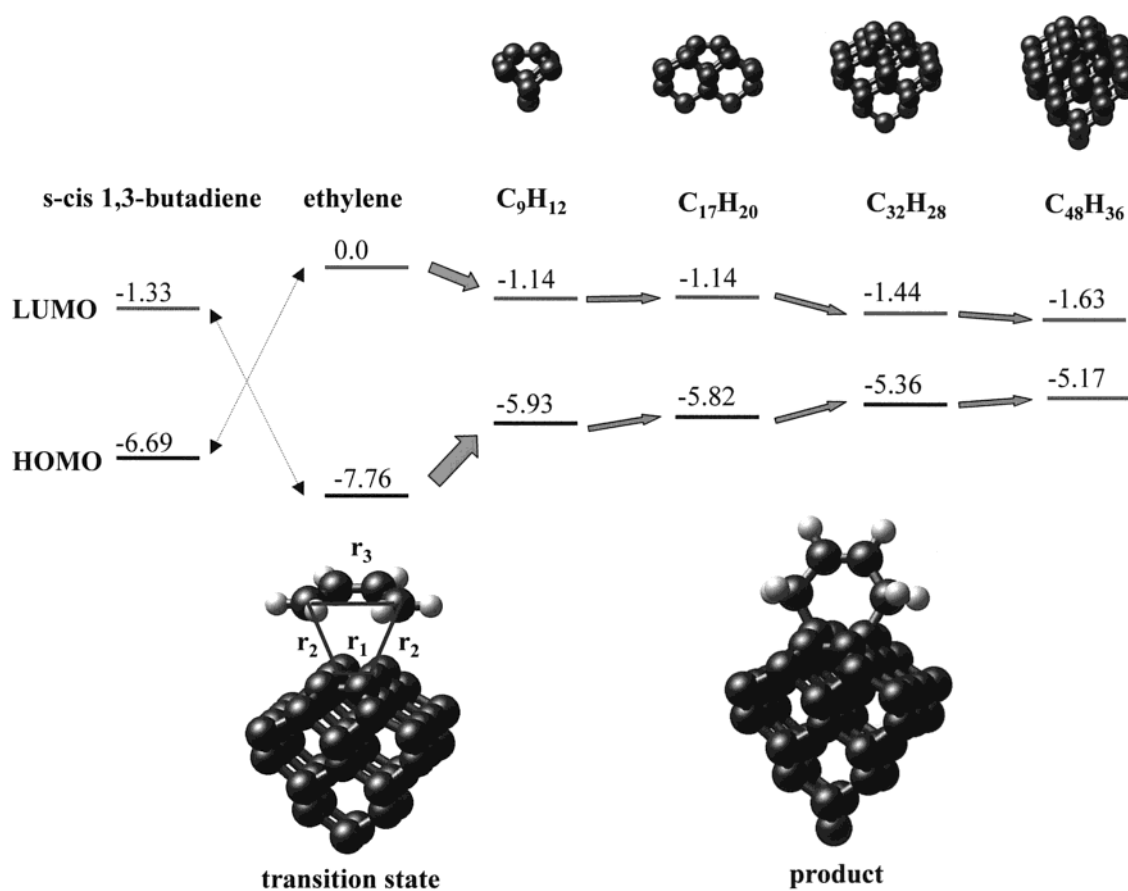

Figure 2. (Top) Four cluster models (C_9H_{12}, $C_{17}H_{20}$, $C_{32}H_{28}$, and $C_{48}H_{36}$) of a C(001)–(2×1) surface and HOMO–LUMO energy levels (eV) of *s-cis*-1,3-butadiene, ethylene, and the above four clusters. (Bottom) Optimized geometries for TS (left) and product (right). Black and white balls, respectively, stand for C and H atoms. Hydrogen atoms used as terminators are not shown for simplicity.

activation energy). The optimized structures of reactant and product were determined by gradient techniques. No geometry constraint was imposed on the clusters. The optimized structure of the transition state (TS) was determined by the following conventional procedure: first, the TS geometry of a reaction was estimated according to chemical intuition; second, the force constants of the estimated geometry were calculated at a low-level model chemistry (e.g. HF/6-31G); third, the estimated TS geometry was relaxed by using a Berny algorithm[14] with the calculated force constants. If the initially estimated TS geometry

is good, this procedure determines a TS. All calculations were done by the Gaussian 98 program.[15]

Results and Discussion

   Cluster Size Effect. A small-cluster calculation may sometimes result in unexpected and unreliable predictions. Thus, the effect of cluster size on the reaction of *s-cis*-1,3-butadiene with the C(001)–(2×1) surface was checked by using four different clusters: C_9H_{12}, $C_{17}H_{20}$, $C_{32}H_{28}$, and $C_{48}H_{36}$ (Figure 2). Clusters C_9H_{12} and $C_{17}H_{20}$ have only a single C=C dimer in the model;

Diels−Alder Reactions on a C(001)−(2×1) Surface

J. Phys. Chem. B, Vol. 105, No. 9, 2001 **1815**

TABLE 1: C=C Dimer Bond Lengths (Å) and Reaction (E_R) and Activation (E_A) Energies (eV) of the Diels−Alder Reaction of *s-cis*-1,3-Butadiene with Ethylene (C_2H_4) or a C(001)−(2×1) Surface Modeled by Four Clusters (C_9H_{12}, $C_{17}H_{20}$, $C_{32}H_{28}$, and $C_{48}H_{36}$)[a]

	dimer bond length	E_R (electronic)	E_R (+ZPVE[b])	E_A (electronic)	E_A (+ZPVE[b])
C_2H_4	1.331	1.789	1.512 (1.505)[c]	0.803	0.918 (0.880)[c]
C_9H_{12}	1.364	3.899	3.653 (3.925)[c]	0.071	0.119 (−0.073)[c]
$C_{17}H_{20}$	1.369	3.941	3.695	0.047	0.096
$C_{32}H_{28}$	1.368	3.860	3.631	0.103	0.142
$C_{48}H_{36}$	1.368[d]	3.934	3.704[e]	0.042	0.081[e]

[a] The B3LYP/6-31G(d) model chemistry was used. [b] ZPVE contributions are added to the electronic energy. [c] The figures in parentheses were calculated by the G3(MP2)//B3LYP method. [d] This value corresponds to the center dimer. The bond lengths of the other two dimers are 1.369 Å. [e] ZPVEs are computed by the $C_{32}H_{28}$ cluster.

on the other hand, $C_{32}H_{28}$ and $C_{48}H_{36}$ clusters, respectively, contain two or three surface C=C dimers. Therefore, the latter clusters are expected to account for the influence of the dimer−dimer interaction on the reaction, while the former clusters are not. The C=C dimer bond length, reaction barrier and reaction energy calculated with these clusters are shown in Table 1. To compare these values with those of a molecular system, the energies of the Diels−Alder reaction of *s-cis*-1,3-butadiene with ethylene are also shown in Table 1. Although the most stable molecular configuration of 1,3-butadiene is s-trans, we used the s-cis configuration in the calculation on the basis of the symmetry consideration of the Diels−Alder reaction. The s-cis configuration has 0.164 eV higher total energy than the s-trans one by B3LYP/6-31G(d) model chemistry with including ZPVE.

The surface Diels−Alder reaction shows a much lower reaction barrier than that of the molecular Diels−Alder reaction (Table 1). Although reaction and activation energies often show a monotonic trend as the cluster size is increased,[16] present calculation is not the case. Moreover, $C_{32}H_{28}$ cluster departs a bit from the trend. This deviation might be due to the boundary effect of cluster model; i.e., no geometry constraint was imposed on the clusters. However, the differences of reaction and activation energies among four clusters are 0.08 and 0.07 eV, respectively, which are sufficiently small to consider the surface Diels−Alder reaction to be insensitive to the size of cluster. This result suggests that the lowering of the reaction barrier was brought about by the single C=C dimer. Thus, the dimer−dimer interaction does not play much part in the surface Diels−Alder reaction. It is worthy of notice that the exothermicity of the surface Diels−Alder reaction is significantly larger than that of the molecular one. The ZPVEs are also insensitive to cluster size (Table 1). The difference between the ZPVE of C_9H_{12} and $C_{32}H_{28}$ is 0.009 eV in the activation energy and 0.017 eV in the reaction energy. Simple analysis of reaction rate by using transition-state theory (using activation energy as Gibbs energy) indicates that the reaction rate on the surface is 10^{12} times larger than in ethylene at 300 K. Thus, the surface Diels−Alder reactions are expected to occur at room temperature, as was observed in the experiments.[3,4] As stated in the Introduction, the reactivity of the Diels−Alder reaction is governed by the HOMO−LUMO energy differences between diene and dienophile and a small energy gap usually means high reaction rate. Figure 2 shows that as the cluster size increases, the energy levels shift only slightly. The large part of the HOMO−LUMO gap reduction of the diamond surface is caused by the smallest cluster model of C_9H_{12} (Figure 2).

The optimized geometries in the transition state and the product are also shown in Figure 2. The 4-center transition state

TABLE 2: Optimized Transition-State Geometry (Å) of the Diels−Alder Reaction of 1,3-Butadiene with Ethylene (C_2H_4) or C(001)−(2×1) Surface Modeled by Four Clusters (C_9H_{12}, $C_{17}H_{20}$, $C_{32}H_{28}$, and $C_{48}H_{36}$)

	r_1	r_2	r_3
C_2H_4	1.386	2.273	2.875
C_9H_{12}	1.388	2.659	2.998
$C_{17}H_{20}$	1.395	2.678	3.001
$C_{32}H_{28}$	1.395	2.649	3.004
$C_{48}H_{36}$	1.395	2.654	2.997

geometries of the four cluster models are found to give much the same geometry (Table 2). The value of r_2 in Table 2 is by about 0.4 Å larger on the surface than in ethylene. Thus, 1,3-butadiene is far away form the surface in the TS of the surface Diels−Alder reaction. This means that the TS resembles the reactant as observed from Figure 2. Therefore, the activation energy becomes small because the difference of the TS and the reactant is expected to be small.

The employed model chemistry was checked. Since thermochemical properties do not much depend on cluster size as clarified above, the B3LYP/6-31G(d) model chemistry was compared to the G3(MP2)//B3LYP model chemistry by using a C_9H_{12} cluster and ethylene as dienophiles and 1,3-butadiene as a diene. The results are shown in Table 1. In the Diels−Alder reaction of *s-cis*-1,3-butadiene with ethylene, the activation and reaction energies given by B3LYP/6-31G(d) agree with those by the G3(MP2)//B3LYP. In the Diels−Alder reaction of *s-cis*-1,3-butadiene with a C_9H_{12} cluster, the reaction energy given by B3LYP/6-31G(d) agrees well with that by the G3-(MP2)//B3LYP. On the other hand, the activation energy becomes a small negative value (−0.073 eV) by the G3(MP2)//B3LYP calculation. The TS geometry might be sensitive to employed electron correlation methods. (The geometry optimized by the B3LYP/6-31G(d) model chemistry is used in G3-(MP2)//B3LYP.) If we consider the s-trans configuration of 1,3-butadiene as the reactant, we obtain a reaction barrier of 0.08 eV by the G3(MP2)//B3LYP calculation. The trend that surface Diels−Alder reaction gives a much smaller reaction barrier is consistent between B3LYP/6-31G(d) and G3(MP2)//B3LYP results. These results confirm that the B3LYP/6-31G(d) model chemistry provides a fairly reliable description of the Diels−Alder reaction on a C(001)−(2×1) surface.

Decrease of the Reaction Barrier on a C(001)−(2×1) Surface. The above arguments strongly suggest that a large decrease of the activation energy of the surface Diels−Alder reaction is due to the single C=C dimer. Since an obvious structural difference between the surface C=C dimer and ethylene is that back-bonds of the C=C dimer are not in a plane as they are in ethylene. Hrovat et al. calculated olefin strain energies and showed that the HOMO−LUMO gap of the C_9H_{12} cluster becomes smaller by 2.48 eV than that of unbridged alkene (C_8H_{12}) by using HF/3-21G model chemistry.[17] Our calculation is consistent with their observation because the HOMO−LUMO gap of the C_9H_{12} cluster become smaller by 2.97 eV than that of ethylene by using B3LYP/6-31G(d) model chemistry (Figure 2). The back-bond bending causes the hybridization of 2p atomic orbitals and reduces the overlap between the p orbitals. This reduction of the overlap accounts for the lengthening of C=C bond from ethylene (1.331 Å) to the surface dimer (1.368 Å) as shown in Table 1. The reduction of the overlap also accounts for the HOMO and LUMO energy levels shown in Figure 2. The HOMO energy level goes up while the LUMO energy level goes down. This results in significant reduction of both the energy gaps of HOMO(diene)−LUMO(dienophile) and HOMO(dienophile)−LUMO(diene) and

TABLE 3: Reaction ($E_R{}^{a,b}$) and Activation ($E_A{}^a$) Energies (eV) of the Diels−Alder Reaction of Heteroatoms Containing Dienes with Ethylene (C_2H_4) or C(001)−(2×1) Surface Modeled by the $C_{32}H_{28}$ Cluster^c

	E_R (ethylene)	E_R (surface)	E_A (ethylene)	E_A (surface)
pyrrole	−0.286	1.305	1.405	0.440
Thiophene	0.051	1.679	1.560	0.615
CH_2=NB=NH	0.077	2.335	1.435	0.366

^{a} ZPVEs are included in the energies. For diamond surface reactions, ZPVEs are calculated with C_9H_{12} cluster. ^{b} A minus sign means the reaction is endothermic. ^{c} The B3LYP/6-31G(d) model chemistry was used.

leads to the large decrease of the reaction barrier. The back-bond bending also explains a large exothermicity observed on the surface the Diels−Alder reaction (Table 1) since the reactant is somewhat unstabilized by the back-bond bending from the desirable planar sp^2 configuration for the three-coordinate carbon atom.

It is notable that the diamond surface reduces the activation energy much more than chemical activation does, i.e., substitution of an electron attractive functional group for the hydrogen of ethylene. As stated in the Introduction, maleic anhydride is a representative diene of normal-electron-demand type. The energy levels of the HOMO-2[18] and LUMO of maleic anhydride are significantly lower than those of the HOMO and LUMO of ethylene. The calculated activation energy of the Diels−Alder reaction of *s-cis*-1,3-butadiene with maleic anhydride is 0.604 eV by using the B3LYP/6-31G(d) model chemistry and that of *s-cis*-1,3-butadiene with ethylene is 0.918 eV (Table 1). Thus, the activation energy of maleic anhydride is much larger than that of the C(001)−(2×1) surface. It is thus concluded that the diamond surface has a higher reactivity for Diels−Alder reactions.

Dienes that Contain Heteroatoms. Since heteroatoms such as N or S are more electronegative than C atoms, dienes that contain these heteroatoms usually have a low HOMO energy level, which results in lower reactivity of the Diels−Alder reaction. However, as stated, the C(001)−(2×1) surface significantly enhances the reactivity of the Diels−Alder reaction. Therefore even heterodienes may also readily react on the C(001)−(2×1) surface. First, the Diels−Alder reactions of pyrrole (C_5H_5N) and thiophene (C_5H_6S) on the C(001)−(2×1) surface are compared with those in ethylene (Table 3). Since pyrrole and thiophene have an aromatic nature, the reactant is very stable. Thus, the calculated activation energy is larger in heterodienes than that in 1,3-butadiene (Table 1). As expected, the C(001)−(2×1) surface significantly decreases the reaction barrier and increases the exothermicity (Table 3).

Next, the reaction of a hypothetical heterodiene CH_2=NB=NH with C(001)−(2×1) surface was examined. N−B−N is a codopant, that is, a donor−acceptor−donor complex proposed by Yoshida and co-workers, which is a promising candidate for n-type dopant of diamond.[19] The HOMO-1[20] and LUMO energy levels of CH_2=NB=NH are respectively −7.81 and −2.02 eV. In comparison with those in 1,3-butadiene (Figure

2), these energy levels are significantly lower in HOMO and LUMO and become reverse-electron-demand type. This energy level lowering somewhat reduces the reactivity of the Diels−Alder reaction compared to that of 1,3-butadiene, but the reaction still seems to proceed on the C(001)−(2×1) surface easily (Table 3).

Summary

Through ab initio molecular orbital calculations, the mechanism of the large enhancement of the reactivity concerning the Diels−Alder reactions on a C(001)−(2×1) surface was found. This enhancement is brought about by the decrease of the HOMO−LUMO gap through the reduced overlap between the p orbitals of the surface dimer. It was also found that the Diels−Alder reaction by dienes that contain heteroatoms such as N or S occurs with the Diels−Alder reaction on a diamond surface but not in ethylene.

References and Notes

(1) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, *119*, 11100.
(2) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Chem. Phys.* **1998**, *108*, 4599.
(3) Wang, G. T.; Bent, S. F.; Russell, J. N., Jr.; Butler, J. E.; D'Evelyn, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 744.
(4) Hossain, M. Z.; Aruga, T.; Takagi, N.; Tsuno, T.; Fujimori, N.; Ando, T.; Nishijima, M. *Jpn. J. Appl. Phys.* **1999**, *38*, L1496.
(5) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098.
(6) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169.
(7) Choi, H. C.; Gordon, M. S. *J. Am. Chem. Soc.* **2000**, *121*, 11311.
(8) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976; Chapter 4.
(9) Hovis, J. S.; Liu, H.; Hamers, R. *J. Phys. Chem.* **1998**, *102*, 6873.
(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(11) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(12) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
(13) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.
(14) Schlegel, H. B. Geometry Optimization of Potential Energy Surfaces. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific Publishing: Singapore, 1995.
(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(16) Penev, E.; Kratzer, P.; Scheffler, M. *J. Chem. Phys.* **1999**, *110*, 3986.
(17) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.
(18) The HOMO-2 of maleic anhydride corresponds to the HOMO of 1,3-butadiene from the consideration of orbital symmetry. HOMO and HOMO-1 orbitals of maleic anhydride are lone pair orbitals of oxygen.
(19) Nishimatsu, T.; Katayama-Yoshida, H.; Orita, N. *Mater. Sci. Forum.* **1997**, *258−263*, 799.
(20) The HOMO-1 of CH_2=N−B=NH corresponds to the HOMO of 1,3-butadiene from the consideration of orbital symmetry. HOMO orbital of CH_2=N−B=NH is a lone pair orbital of nitrogen.