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A Rationalization of Orientation in Nucleophilic Aromatic Photosubstitution[1,2]

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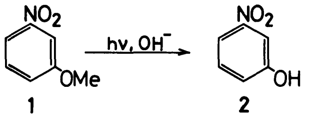
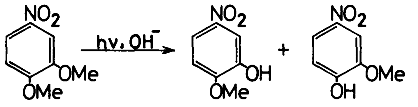
Consideration of the relationship between the mechanisms and orientation effects of the nitro group in nucleophilic photosubstitutions of nitroaromatics leads to the proposal of two rules, making use of frontier molecular orbital theory, for interpreting the regioselectivities and determining the reaction mechanisms. The first rule is a summary of previously proposed interpretations, concerning photoreactions accompanying the direct addition of a nucleophile to an excited nitroaromatic substrate. In this case, the regioselectivity is governed by the HOMO of the substrate. The second rule regards reactions involving photoinduced electron transfer, where regioselectivity is LUMO-controlled. The application of these rules is successfully demonstrated for various types of compounds.

As more examples of photoinduced nucleophilic aromatic substitution accumulate, the effects of several substituents on the regioselectivity have attracted great interest.[3] Among the substituents, the nitro group is probably the most extensively studied because of its unusual *meta*-directing effect. For instance, the irradiation of *m*-nitroanisole (**1**) in aqueous organic solvents containing sodium hydroxide gives *m*-nitrophenol (**2**, Eq. 1),[4,5] and 3,4-dimethoxynitrobenzene (**3**) under similar conditions gives a mixture of 3-hydroxy-4-methoxy- (**4**) and 3-methoxy-4-hydroxynitrobenzene (**5**) with a ratio of 370:1 (Eq. 2)[6]

Compound **1** is not hydrolyzed thermally and **3** undergoes thermal hydrolysis exclusively at C_4, affording **5** as a sole product. Thus, the orientation directing effect of the nitro group in photochemical nucleophilic substitutions is in remarkable contrast to that in corresponding thermal reactions. It is noteworthy that in such photoreactions, the presence of a good leaving group (such as methoxyl) is not a prevailing factor in the determination of the orientation, as shown in Eq. 2.

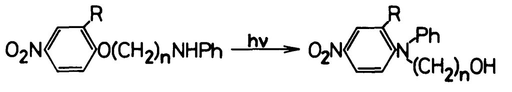


1 **2** (1)

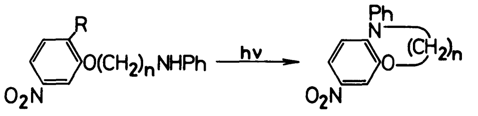


3 **4** **5** (2)

On the other hand, when a homologous series of **6** (Eq. 3, R=H or OMe) is irradiated in acetonitrile or methanol, a corresponding series of rearranged products **7** is obtained.[7,8] In these cases, the directing effect of the nitro group is clearly para, though the nitroaromatic moiety in **6** is essentially the same as in **1** or **3**. A quite similar situation is found in **8** (Eq. 4, R=H or OMe), which gives **9** as the sole isolable product, irrespective of R.[9] Here, again, the nitro group is *para*-directing. These products, **7** and **9**, are also obtained by thermal reactions of **6** and **8** (R=OMe), respectively, catalyzed by a strong base such as sodium hydride or sodium methoxide. Thus, contrary to the cases exemplified in Eqs. 1 and 2, the photoreactions of **6** and **8** show the same regioselectivity as the thermal reactions.



6, R= H or OMe **7** (3)



8, R= H or OMe **9** (4)

Summarizing the data so far reported, it might be concluded that nitro groups exert two apparently contradicting effects, *meta*- and *para*-orientations, in photosubstitution by a nucleophile.

The present paper has three objectives: (1) to rationalize the two distinct regioselectivities observed for the nitro group; (2) to establish orientation rules based on frontier molecular orbital theory; and (3) to assess the validity of our proposed method by testing its applicability to a variety of cases.

Orientation Rules

Attempts to rationalize the *meta*-favoring regioselectivity of a nitro group have been reported by Fleming[10] using frontier molecular orbital theory and by Epiotis[11] with a more sophisticated procedure. Their conclusions regarding on nucleophilic photosubstitutions are the same in that the reactions are presumed to be HOMO-controlled. Havinga, Cornelisse, and their coworkers have also addressed this problem by attempting to correlate a number of experimental data with MO calculations.[6,12–16] Unfortunately, according to the interpretations presented by these researchers, it is impossible to explain why apparently conflicting regioselectivities are observed in practically identical nitroaromatics (Eqs. 1—4).

We propose here a rationalization composed of two rules which are based on frontier molecular orbital theory and are applicable to a wide variety of nucleophilic aromatic photosubstitutions. Our rules are as follows;

Rule 1. *HOMO-Controlled Regioselectivity* Nucleophilic photosubstitutions which involve one-step formation of a σ-complex *via direct interaction* between an excited aromatic substrate and a nucleophile are HOMO-controlled (Eq. 5)

$$\text{ArH} + \text{:Nu} \xrightarrow{h\nu} \text{ArH}^* + \text{:Nu} \longrightarrow \sigma\text{-complex} \quad (5)$$

Rule 2. *LUMO-Controlled Regioselectivity* Nucleophilic photosubstitutions which involve *electron transfer* from a nucleophile to a nitroaromatic substrate and subsequent recombination of the resultant radical ions are LUMO-controlled (Eq. 6).

$$\text{ArH} + \text{:Nu} \xrightarrow{h\nu} \text{ArH}^* + \text{:Nu}$$
$$\longrightarrow \text{ArH}^{\overline{\cdot}} + \text{Nu}^{+} \longrightarrow \sigma\text{-complex} \quad (6)$$

Rule 1 is a summary[17] of the essential parts of the conclusions obtained by Fleming,[10] Epiotis,[11] and Havinga.[6] It is based on the assumption that the lowest excited state of an aromatic molecule can be approximated by one electronic configuration in which an electron is promoted from the HOMO to the LUMO. Each level is, thus, singly occupied (Fig. 1). When a nucleophile approaches an excited aromatic substrate with two singly occupied MO's, the dominant orbital interaction is expected to be between HOMO (substrate)-HOMO (nucleophile) and not between LUMO (substrate)-HOMO (nucleophile). Thus, the direct attack of a nucleophile on an excited aromatic substrate is the key step in the reaction. As will be discussed below, the reactions shown in Eqs. 1 and 2 fall under this category.

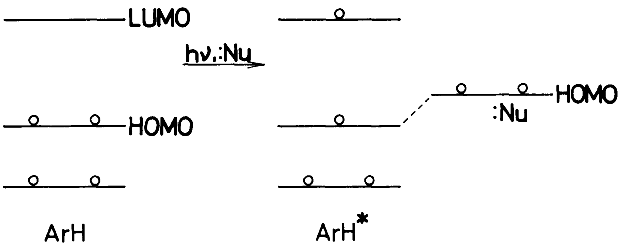


Fig. 1. Schematic illustration of the orientation-determining step, σ-complex formation *via* direct interaction of an excited molecule with a nucleophile. A brokenline denotes the orbital interaction resulting in bond formation. ArH represents an aromatic substrate and Nu a nuleophilic reagent. An asterisk refers to the excited state.

Rule 2 implies an electron-transfer process as a key step in the determination of regioselectivity. This process was originally proposed by Nagakura and Tanaka on the basis of theoretical considerations in 1959[18] regarding the thermal reaction of a nucleophile having a low ionization potential with a substrate having a high electron affinity. The reactions shown in Eqs. 3 and 4 are examples of this category; the formation of a radical ion pair composed of a nitroaryl ether radical anion and an anilino moiety radical cation and the subsequent conversion into a σ-complex (Eq. 6) have been unequivocally confirmed by laser flash photolysis.[9,19,20] As depicted in Fig. 2, in this mechanism, after an initial electron transfer, a strong interaction develops between the singly occupied MO of the nitroaromatic and the singly occupied HOMO of the nucleophile. Since the singly occupied orbital of the aromatic compound corresponds to the LUMO of the ground state, the orientation is LUMO-controlled.

Sample Applications

The rules proposed here neglect all other factors, such as leaving groups and the nature of the nucleophiles, and consider only the effective MO's to govern the regioselectivities. Of course, actual

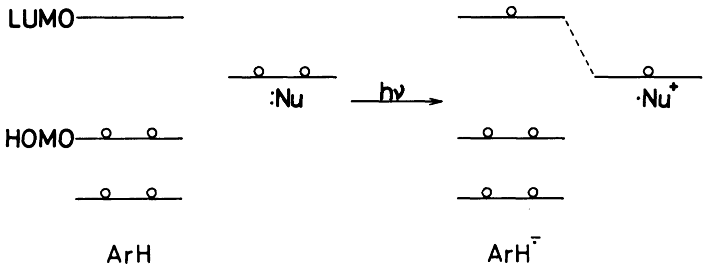


Fig. 2. Schematic illustration of the orientation-determining step, σ-complex formation after photoinduced electron transfer. A broken line denotes the orbital interaction resulting in bond fromation. ArH represents an aromatic substrate and Nu a nucleophilic reagent.

reactions cannot always be interpreted only in terms of frontier MO's; however, the rules are useful in reasoning why specific positions are subject to substitution and in determining whether the reaction mechanism is a "direct attack" or an "electron transfer". Several examples are now discussed.

According to the frontier molecular orbital theory, a nucleophile preferentially attacks the position with the highest frontier electron density (FED) in the corresponding MO's. Here, FED is defined as $\mathrm{FED}_i = n_i c^2_{ir}$, where n_i is the number of electrons occupying the ith MO and c_{ir} the coefficient of rth atomic orbital in the ith MO. The FED shown below is calculated by the CNDO/2 approximation, for the displacement of OR with OH.

m-*Alkoxynitrobenzene.* The FED maps of the HOMO and LUMO of *m*-alkoxynitrobenzene are shown in Fig. 3. The FED's of the HOMO are in the order $C_6 > C_2 > C_3 > C_4$. However, the first two positions are less likely to be attacked by a nucleophile on account of the absence of a good leaving group. Thus, photosubstitutions of *m*-nitroanisole have been observed to occur at C_3 with hydroxide ion[4,5] ammonia,[21] methylamine,[4] and cyanide ion[22,23] In case of the photoamination in liquid ammonia, C_6- and C_2-substituted products are minor side products,[21] consistent with the large FED's of the HOMO on these positions and also with the assumption of preferred substitution at the position with a good leaving group.

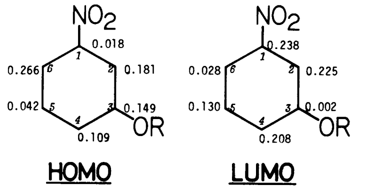
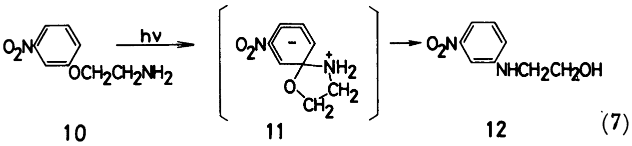


Fig. 3. FED maps of the HOMO and LUMO of *m*-alkoxynitrobenzene.

LUMO-Controlled photosubstitution in *m*-alkoxynitrobenzene analog (**8**, R=H) should occur on either C_2 or C_4 which bear much larger FED's. For steric reason the actual reaction favors the less hindered site C_4 (Eq. 4, R=H).[9] No product suggesting C_3-substitution has been detected.

In connection with the reaction of **8** (R=H), the photochemical behavior of a primary amine analog, 2-(*m*-nitrophenoxy)ethylamine (**10**), studied by Wubbels and his coworkers, is noteworthy (Eq. 7).[24] The structure of the photoproduct (**12**) reveals a *meta*-directing effect of the nitro group, suggesting that the reaction belongs to the category of rule 1, or is HOMO-controlled. Additionally, direct formation of a σ-complex (**11**) from the excited state has unambiguously been confirmed by laser flash photolysis.[25]



10 **11** **12** (7)

The significance of the findings should be emphasized because the key step of a direct attack of a nucleophile, requisite for the HOMO-controlled photosubstitutions, has rarely been confirmed spectroscopically, though the scheme itself is generally accepted. Thus, the photorearrangement of **10** is mechanistically and regioselectively in complete accord with the requirement of rule 1, providing strong supporting evidence for its validity.

Differences in the regioselectivity observed between **8** (R=H) and **10** are readily explained in terms of the ionization potential (I_p) of the nucleophilic moieties; the I_p of the primary amino group is higher than that of the anilino group (CH_3NH_2 with I_p=9.64 eV[26] and $PhNHCH_3$ with I_p=7.65 eV[27] are approximate models for nucleophilic moieties in **10** and **8**, respectively). Therefore, in **10** with the high Ip nucleophile, photoinduced electron transfer is highly unfavorable and the reaction must proceed *via* a direct addition to the *m*-nitrophenoxyl moiety, resulting in a HOMO-controlled orientation. Consequently, *m*-nitroanisole undergoes HOMO-controlled photosubstitution with methylamine to yield *N*-methyl-*m*-nitroaniline.[4]

p-*Alkoxynitrobenzene.* Nucleophilic photosubstitutions of *p*-nitroanisole reflect the trifunctional nature of this compound; *ipso* (C_1)-substitution has been observed with hydroxide ion and pyridine,[28] C_4-substitution with hydroxide ion[28] and aliphatic amines,[29] and C_3-substitution with cyanide ion[23] and cyanate ion.[30] It is interesting to note that the orientation strongly depends on the natures of the reaction media and the nucleophiles. An examination of the FED's of the HOMO of this molecule (Fig. 4) readily rationalizes the results; that is, the *ipso* carbon (C_1), *meta*-carbon (C_3), and *para*-carbon (C_4) bear fairly large FED's and, therefore, are all able to accept a nucleophile, if appropriate conditions are provided.

In the LUMO (Fig. 4), the FED's on C_1 and C_4 are the largest and the second largest, respectively. Since

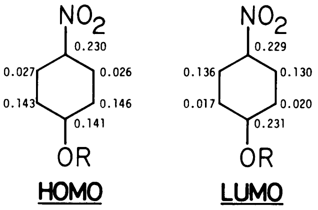


Fig. 4. FED maps of the HOMO and LUMO of *p*-alkoxynitrobenzene.

intramolecular *ipso*-substitution at the NO_2-bearing carbon is sterically inhibited in **6** (R=H), *para*-substitution predominates in its photoreaction (Eq. 3).

3,4-Dialkoxynitrobenzene and Its Isomers. As shown in Fig. 5, the FED's of the HOMO of 3,4-dialkoxynitrobenzene are in the order, $C_3>C_4>C_6>C_1$. As predicted by rule 1, photoreactions with hydroxide ion (Eq. 1),[6] aliphatic amines,[13] and cyanide ion[14] have all been observed predominantly at C_3. These reactions are accompanied by C_4-substituted products,[6,13,16] the formation of which is explained by the high FED as well as the presence of a good leaving group on C_4.

In the LUMO, the FED on the C_4-OR carbon is larger than that on the C_3-OR and photosubstitution has been observed at this position in either **6** (R=OMe)[8] or **8** (R=OMe)[9] (Eqs. 3 and 4).

Furthermore, a good correlation of the FED with experimental results is found in the HOMO-controlled photocyanation of three isomers of dimethoxynitrobenzenes;[31] as shown in Fig. 6, the reaction occurs at the positions with the largest FED in each case.

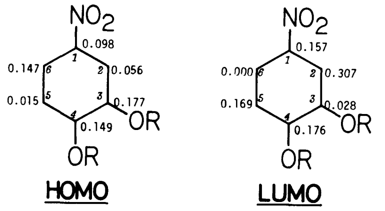


Fig. 5. FED maps of the HOMO and LUMO of 3,4-dialkoxynitrobenzene.

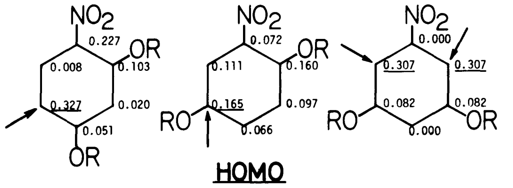
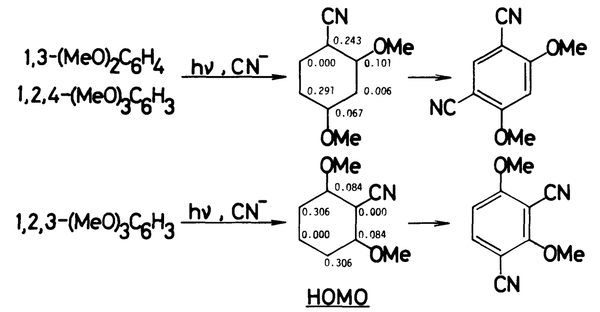


Fig. 6. FED maps of the HOMO of three dialkoxynitrobenzene isomers. The values underlined denote the largest FED's in each ring. Arrows indicate the photocyanated positions.

Photodicyanation of Polymethoxybenzenes. Another example is photocyanation of polymethoxybenzenes in which dicyanated products are obtained (Eqs. 8 and 9).[32] Since the yields of the dicyano derivatives are lower than those of the concomitant monocyano derivatives and the same dicyanodimethoxybenzene is obtained from 1,2,4-trimethoxybenzene as from 1,3-dimethoxybenzene, it is reasonable to suppose that the photocyanation occurs stepwise, that is, a dicyano derivative is formed by cyanation of the corresponding monocyano derivative. For the first step cyanation, an $S_{R^+N}1$ Ar* mechanism[33] has been proposed,[15,16] but the second step should involve direct attack of cyanide ion because of the strong electron-withdrawing nature of the cyano group. Thus, the HOMO of the predominating monocyano derivatives should determine the position of the subsequent cyanation. As illustrated in Eqs. 8 and 9, the second step takes place at the positions bearing the largest FED in each ring.



(8)

(9)

Chloronitrobenzenes. Generally, it is difficult to tell only from the structures of the starting materials and photoproducts whether a reaction belongs to rule 1 or 2, but sometimes the FED data can give a valuable clue to the reaction mechanism. Photoamination of chloronitrobenzenes is such an example.

Photoamination of the three isomers of chloronitrobenzene was carried out in liquid ammonia at −60 °C.[21] As illustrated in Fig. 7, substitution was observed in all isomers at the *para* position to the nitro group. Since the HOMO's of the *o*- and *m*-isomers show very small FED's at the *para* positions (0.012 and 0.040, respectively) and the corresponding LUMO's show the second largest values (0.246 and 0.244, respectively) at these positions the regioselectivity should be regarded as LUMO-controlled. As for the *p*-isomer, the FED on the *para*-carbon is sufficiently large in both MO's and makes it difficult

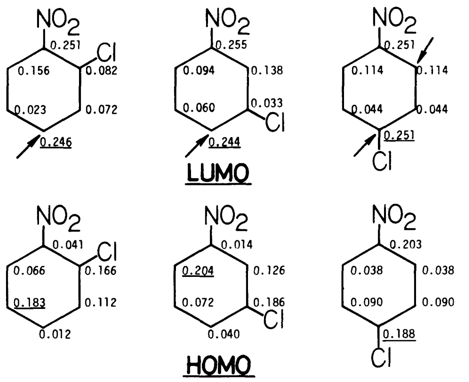


Fig. 7. FED maps of the HOMO and LUMO of chloronitrobenznes. The values underlined show the largest FED in each ring (except C-NO_2 carbons). Arrows denote the positions where photoamination is observed.

to determine which MO dominates the orientation. In this regard, it is noticeable that concurrent *o*-amination is observed as a minor pathway (affording 10% of 2-nitro-5-chloaniline) in contrast to the major pathway (producing *p*-nitroaniline in 45% yield). Examination of the FED maps of *p*-chloronitrobenzene in Fig. 7 suggests that the *o*-amination cannot be HOMO-controlled, because the FED of the HOMO on the *ortho*-carbon (0.038) is too small to allow substitution. Thus, the major part of the photoamination of the *p*-isomer is probably LUMO-controlled, though this conclusion does not completely rule out some concurrent HOMO-controlled process.

In order to obtain further supporting evidence for the electron-transfer mechanism, the key step in the LUMO-controlled reactions, we tried to detect intermediates with the aid of an ESR spectrometer, adopting *p*-chloronitrobenzene as a representative of the isomers. Upon irradiating a solution of this compound in liquid ammonia kept at −70 °C with a high-pressure Hg lamp, a rapid growth of a paramagnetic species was observed. After 10 min of irradiation, a well-defined spectrum with sufficient intensity (Fig. 8) was obtained, which showed slow decay upon cutting off the light. No signal was observed for the solution kept in the dark for the same period. Comparison of the spectral curve obtained with a simulated one, led to an identification of the paramagnetic species as the radical anion of *p*-chloronitrobenzene. Thus, a photoinduced electron transfer was confirmed to take place under similar conditions used for the photoreaction.

All these facts strongly suggest that the photoamination of all three isomers of chloronitrobenzene proceeds, partly if not wholly, *via* electron transfer, thus conforming to rule 2.

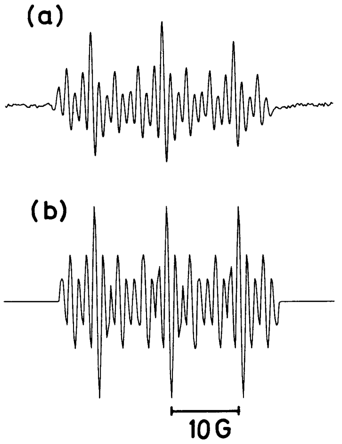


Fig. 8. (a) ESR spectrum of a paramagnetic species formed by irradiation of a solution of *p*-chloronitrobenzene in liquid ammonia. (b) Simulated spectum obtained by employing the following coupling constants; $a_N = 10.4$ G, $a_H(ortho) = 3.40$ G, and $a_H(meta) = 1.20$ G (K. Nakamura, *Bull. Chem. Soc. Jpn.*, **40**, 1 (1967)).

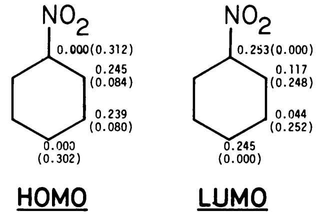


Fig. 9. FED maps of the degenerate HOMO's and LUMO's of nitrobenzene. The values in parentheses belong to nearly degenerate counterparts.

Nitrobenzene. Photoamination of nitrobenzene in liquid ammonia is an example in which the degeneracy of the MO's confuses the assignment of the regio-determining MO. The major reaction takes place at the *para* position to give *p*-nitroaniline in 25% yield.[21] The MO calculation revealed the presence of two pairs of almost degenerate π-MO's, each corresponding to HO and LU levels in energy. Comparison of the FED maps of these MO's (Fig. 9) shows that *p*-amination is explicable either as HOMO- or LUMO-controlled, depending on which HOMO–LUMO pair we choose. Fortunately, it has been reported that the nitrobenzene radical anion is formed upon irradiation of its solution in liquid ammonia,[21] suggesting the occurrence of electron transfer from the solvent to nitrobenzene. Thus, the photoamination of nitrobenzene also proceeds, at least partly, *via* electron transfer.

Concluding Remarks

Although the proposed rules should be regarded as first approximations, they find wide and successful applications to a number of aromatic nucleophilic photosubstitutions. Our present method has, thus, been shown to be useful in interpreting regioselectivities and predicting mechanisms even for polysubstituted aromatics. In addition, the present approach can provide us with a more comprehensive view of photochemical reaction mechanisms than the conventional resonance theory or empirical orientation rules.

It should be noted here that our rules are specifically concerned with the initial stage of nucleophilic photosubstitutions and give no information regarding subsequent reaction pathways. It is also noteworthy that the argument, solely based on MO calculations, does not necessarily identify the reaction mechanism.

Experimental

Calculation. The MO calculations were performed with the CNDO/2 program,[34] adapted by replacing the original two-center electronic repulsion integrals with the Nishimoto-Mataga approximation,[35] on a Mitsubishi MELCOM COSMO 700 III computer at the University of Tokyo. For all benzene derivatives, it was assumed that the aromatic nucleus has the same structure as the unsubstituted parent,[36] regardless of the positions, numbers, or natures of the substituents. The methoxyl group was approximated by a hydroxyl for convenience of calculation. It was found for some simple anisole derivatives that no significant change in the FED distribution pattern occurred along with this treatment.

ESR Spectra. ESR Spectra were recorded on a Varian E-112 spectrometer equipped with an optical transmission cavity and a variable temperature accessory. Saturated solutions of *p*-chloronitrobenzene in liquid ammonia kept at −70 °C were irradiated with a high-pressure Hg lamp (500 W) through a Pyrex water jacket and a focusing lens.

We are grateful to Professor Koichi Ohno of the University of Tokyo for providing us with the computer program, to Dr. Akinori Inoue for his advice and help in calculation, and to Professor G. L. Closs of the University of Chicago for valuable suggestions. This work was supported by the Joint Studies Program (1984) of the Institute for Molecular Science.

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