

配置와 形態에 關한 分子軌道論的 研究 (第 7 報).  
非結合相互作用的 複合파이構造 分析

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MO Studies of Configurations and Conformations (VII).  
Composite  $\pi$  Structure Analysis of Nonbonded Interactions

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**요 약.** 비결합 효과를 기초로 하여 상대적인 이성질체의 안정도를 예측하는 복합파이구조 분석법을 제안하였다. 우선 각 이성질체내의 모든 파이 고리구조를 찾아내고, 이들을  $(n\pi/m)$ 형의 약호로 나타낸 다음 간단한 규칙과 가감율을 사용하여 안정도 순위를 결정한다. 이 분석절차의 예를 여러 가지 들어 해설하였다.

**ABSTRACT.** Composite  $\pi$ -structure analysis has been proposed for predicting relative isomer stabilities based on nonbonded effects: all the possible crowded  $\pi$ -structures are identified for each isomer, and the systems are represented by abbreviated notation of  $(n\pi/m)$ : then using simple rules and additivity of the nonbonded effects, the order of stability can be determined. A number of examples are given in support of this analytical procedure.

The intuitive concept of nonbonded inter-electronic repulsion in organic compounds often fails to predict the relative stability of geometrical or conformational isomers; steric arguments clearly failed in many cases to rationalize structural preferences.<sup>1</sup>

Recently two important one-electron effects that are responsible in determining stereochemical preferences have been MO theoretically identified: (a) "through-space" end-to-end interactions<sup>2</sup> which may be repulsive or attractive,

although in many cases attractive favoring "crowded" forms over sterically preferred "uncrowded" forms; (b) "through-bonds" vicinal-bond-antibond conjugative interactions<sup>3</sup> between two atom pairs oriented in a mutually trans relationship. These two interactions belong to one-electron effects,  $\Delta(2\sum\epsilon_i)$ , contributing to the total Hartree-Fock energy changes,  $\Delta E_T$ , of stereochemical variations;

$$\Delta E_T = \Delta(2\sum\epsilon_i) + \Delta(V_{nn} - V_{ee})$$

where the second term on the right side is a

contribution from steric factors.

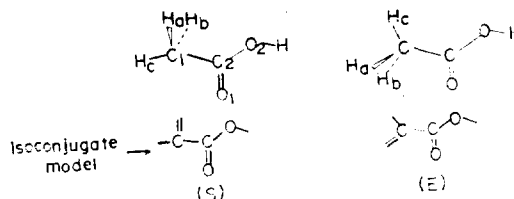
In a previous paper,<sup>4</sup> we have formulated simple rules for predicting "through-space" nonbonded interaction effects based on the frontier orbital (FMO)-perturbational MO (PMO) approaches: (a) nonbonded interactions are significant only in a conjugated (or isoconjugate)  $\pi$  chain with two end atoms in close proximity; (b) the mode and extent of nonbonded interactions are dependent upon number of electrons in the conjugated chain and on the distance between the two end atoms. It was thus shown that: (a) nonbonded interaction is attractive in a decreasing order of  $4N+2$ ,  $4N+1$ , and  $4N-1$  electron systems, while it is repulsive in a  $4N$  electron system; (b) the closer the two end atoms, the stronger is the interaction.

However we often find more than one "crowded" structures within a molecule. These composite  $\pi$  structures in an organic compound are conveniently abbreviated using a notation of  $(n\pi/m)$  representing  $n\pi$  electrons delocalized over  $m$  atoms (or centers) of a conjugated chain forming a crowded structure<sup>4</sup>.

In this paper, we report a further work on the importance of the composite structures in determining conformational preferences. Specifically we shall deal with additivity of nonbonded effects of composite  $\pi$  structures in determining geometry and the isomer stability of a molecule.

The  $\pi$  structure we are interested in is of a planar chain of atoms which contribute one or two  $\pi$  electrons each to the  $\pi$  system. The system may be a true  $\pi$ -conjugated one, but it could be an isoconjugate  $\pi$  structure with methyl groups taking the role of double bonds<sup>5</sup>. Let us take an example to illustrate the use of notation and identifying composite  $\pi$  structures within a molecule. Two forms can be considered for acetic acid depending on the arrange-

ment of methyl group;

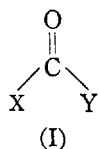


In the (S) form, three  $\pi$ -isoconjugate structures can be identified;  $(5\pi/4)$  system of  $(\text{H}_{ab}\text{C}_1\text{C}_2\text{O}_2)$ ,  $(4\pi/3)$  system of  $(\text{O}_1\text{C}_2\text{O}_2)$  and  $(3\pi/3)$  system of  $(\text{C}_1\text{C}_2\text{O}_1)$ . In the (E) form, there are three  $\pi$ -isoconjugate structures but two of them different from those of the (S) form;  $(4\pi/4)$  system of  $(\text{H}_{ab}\text{C}_1\text{C}_2\text{O}_1)$ ,  $2 \times (4\pi/3)$  systems of  $(\text{C}_1\text{C}_2\text{O}_2)$  and  $(\text{O}_1\text{C}_2\text{O}_2)$ . Common to the two forms is a  $(4\pi/3)$  system of  $(\text{O}_1\text{C}_2\text{O}_2)$  and hence the relative stability should be determined by the remaining two systems. Since  $(5\pi/4)$ , a  $4N+1$  system, and  $(3\pi/3)$ , a  $4N-1$  system, in the (S) form are both end-to-end attractive while  $(4\pi/4)$ , and  $(4\pi/3)$ , both  $4N$  systems, in the (E) form are both end-to-end repulsive<sup>4</sup>, the former should be more stable provided that the composite nonbonded effects are additive. It is indeed found that the former is the preferred form<sup>6</sup>. In the above example we have considered all the possible composite  $\pi$  structures within an isomer, but it is normally sufficient to consider only systems with  $n \geq 4$  and  $m \geq 3$ ; in the above example the  $(3\pi/3)$  system obviously can be safely omitted.

In the following, composite  $\pi$  structure analysis will be demonstrated with a number of illustrations and additivity of nonbonded effects of composite structures will be shown.

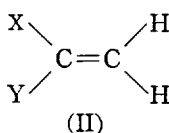
### 1. Molecular Geometry

**Substituted Formaldehydes.** In (I), substituents X and/or Y can be F, Cl, OH,  $\text{NH}_2$ ,  $\text{CH}_3$ ,  $\text{CONH}_2$ , and  $\text{OCH}_3$ . One exemplar in this class is acetic acid for which  $\text{X}=\text{OH}$  and  $\text{Y}=\text{CH}_3$ .

CH<sub>3</sub>.

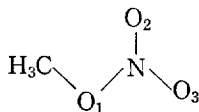
Compounds belonging to this class have two composite  $\pi$ -structures in common; (a)  $(4\pi/3)$  of (OCX) and  $(5\pi/3)$  or  $(5\pi/4)$  of (XCY). The former is a  $4N$  electron system which is nonbonded repulsive, while the latter is a  $4N+1$  electron system which is end-to-end attractive. Therefore we would expect the angle  $\angle OCX$  to be greater than the angle  $\angle XCY$ .<sup>78</sup> Experimental evidence<sup>8,9</sup> supporting this predictions is plentiful; *e.g.*,  $X=Y=F$ ,  $Cl$ ,  $NH_2$ ;  $X=F$ ,  $Y=CH_3$ ;  $X=OH$ ,  $Y=CH_3$ ;  $X=NH_2$ ,  $Y=CONH_2$ ;  $X=F$  or  $Cl$ ,  $Y=OCH_3$ ;  $X=NH_2$ ,  $Y=COCH_3$ , *etc.*

**1,1-Disubstituted Ethylenes.** In a 1,1-disubstituted ethylene, (II), in which both  $X$  and  $Y$  can contribute two  $\pi$  electrons to the system, two composite  $\pi$  structures can be identified;  $(5\pi/3)$  of (XCY) and  $(4\pi/3)$  of (XCC).



Since the former is nonbonded attractive, while the latter is nonbonded repulsive, the angle  $\angle XCC$  is expected to be greater than the angle  $\angle XCY$ . In fact it was found that the angle  $\angle XCY$  is smaller than the angle  $\angle HCH$ ; *e.g.*,  $X=Y=F$ ,  $Cl$ .<sup>2</sup>

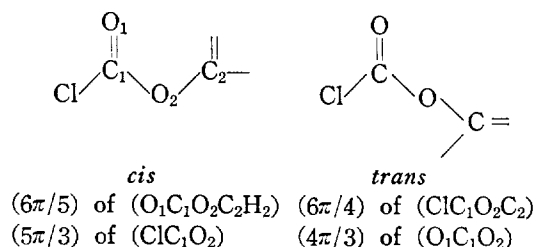
**Methyl Nitrate.** Three composite  $\pi$  systems can be identified in this compound;  $(6\pi/4)$  of  $(O_2NO_1C)$ ,  $(5\pi/3)$  of  $(O_1NO_3)$ , and  $(4\pi/3)$  of  $(O_2NO_3)$ .



Experimental angles are in accord with the predictions based on these  $\pi$ -systems; the angle  $\angle O_2NO_3$  is greater than the angle  $\angle O_2NO_1$ .<sup>8</sup>

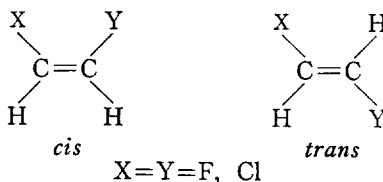
## 2. Isomer Stability

**Methyl Chloroformate.** Two forms are possible, but the *cis* form is found to be more stable experimentally.<sup>9</sup> Composite  $\pi$  structures are given below with the numbering schemes; a common  $\pi$  structure  $(4\pi/3)$  of  $(ClC_1O_1)$  is excluded.



Comparison of the two composite  $\pi$  structures predicts the *cis* form to be the preferred if nonbonded effects are additive; the agreement of the prediction with the experiment thus support the additivity.

**1,2-Dihaloethylenes.** In this compound there will be lone pairs occupying the halogen  $p_z$  orbitals, contributing two  $\pi$  electrons each to the system.

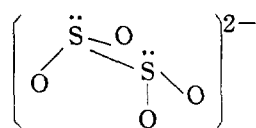


Thus in the case of *cis* form there is a  $(6\pi/4)$  system, while in the *trans* form there are two  $(4\pi/3)$  systems. Hence the two halogen atoms in the *cis* will tend to attract each other while a carbon and a halogen will tend to repel in the *trans* form. Therefore the former is expected to be more stable than the latter, as it was found experimentally.<sup>2</sup>

The same conclusions are reached for mole-

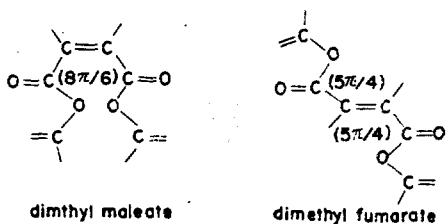
cules in which X or Y, or both are heteroatoms with  $\pi$  lone pairs. Experimental results are available supporting these predictions<sup>2</sup>; *e.g.*, X=CH<sub>3</sub>, Y=OEt; X=CH<sub>3</sub>, Y=OPh; X=CH<sub>3</sub>, Y=Br or Cl, *etc.*

**Dithionite Ion.** This system is known to have eclipsed geometry<sup>10</sup>. Two OSSO frames



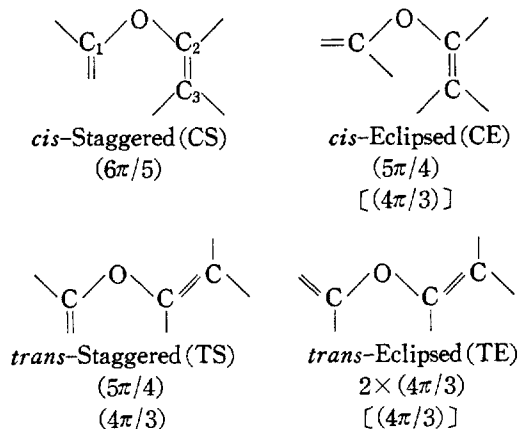
form two  $(6\pi/4)$  systems which are nonbonded attractive between the two vicinal end O atoms when the two have eclipsed arrangement. Any other arrangement, *e.g.*, a staggered, for two S-O bonds will destroy the favorable nonbonded attractions and hence unfavorable.

**Dimethyl Maleate.** It is known experimentally that dimethyl maleate is less stable than its *trans* analogue, dimethyl fumarate.<sup>11</sup> Composite  $\pi$  structures clearly indicate that the former



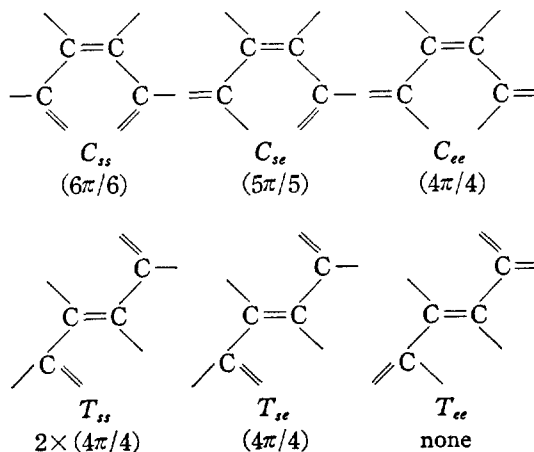
has unfavorable nonbonded effects; the former has a  $(8\pi/6)$  system which is a 4N electron system while the latter has two  $(5\pi/4)$  systems which are nonbonded attractive. There are also common structural features which we have disregarded in our analysis.

**Methyl Vinyl Ether.** Four rotamers of interest are shown below with  $\pi$  composite structures; in the CS form, there is only one crowded  $\pi$  structure,  $(6\pi/5)$ , and in the TE form there are two  $(4\pi/3)$   $\pi$  structures of  $(C_1OC_2)$  and  $(OC_2C_3)$ . In the CE and TE forms, we can identify an extra  $(4\pi/3)$  system formed by



a methyl double bond with oxygen  $\pi$  lone pairs. Including these the relative nonbonded stabilization would be in the order, CS>CE $\approx$ TS>TE, based on the composite  $\pi$  structures assuming additivity of the effects of contributing  $\pi$  systems. Ab initio results,<sup>12</sup> however, predicted the order to be CS>CE>TS>TE, based on the total  $\pi$ -overlap populations. This implies that: (1) the  $(4\pi/3)$  system formed by a methyl double bond with oxygen lone pairs has very small contribution to the total effect of composite structures, (2) the additivity of nonbonded effect indeed holds.

**2-Butene.** The six conformations of 2-butene are shown below with composite  $\pi$ -structures. For *trans* isomers, the relative order of stability

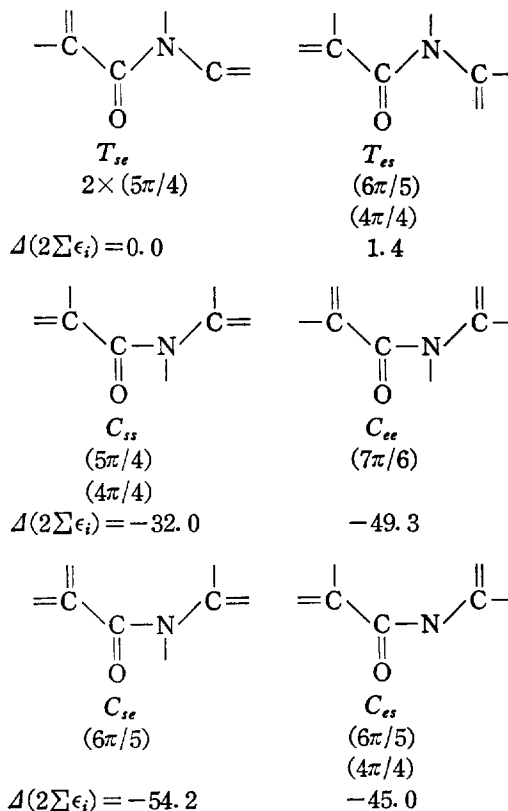
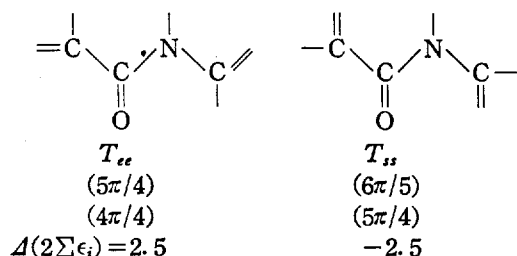


is found to be  $T_{ee} > T_{se} > T_{ss}$  based on the ab initio calculations.<sup>13</sup> This is in excellent agreement with our prediction based on the composite  $\pi$  structure analysis: the  $T_{ss}$  has two repulsive ( $4\pi/4$ ) systems whereas the  $T_{se}$  has one ( $4\pi/4$ ) and the  $T_{ee}$  has no significant crowded  $\pi$  structure. Again the additivity rule holds well.

For *cis* isomers, the order of stability predicted from nonbonded attraction (based on overlap populations<sup>13</sup>) is in agreement with that predicted from our composite  $\pi$  structure analysis; the order of nonbonded attraction predicted being  $C_{ss} > C_{se} > C_{ee}$ . However, due to dominant nuclear-nuclear repulsion which constitutes an index of steric effects, the actual overall order of relative stability is in the reverse order.<sup>13</sup> This is a case of steric effects dominating over one-electron effects. One interesting point here is that the most stable form is the  $T_{ee}$  whereas the least stable form is the  $T_{ss}$  among the above six forms, indicating the importance of additivity of the composite  $\pi$  structures contributing to the stability of the isomers.

**N-Methylacetamide.** The 8 distinct rotamers of interest formed by rotations of two methyl groups in *cis* and *trans* isomers are given below with definitions, composite  $\pi$  structures and the relative (to the  $T_{se}$  form) one-electron energies calculated by the CNDO/2 method.<sup>14</sup>

For the *trans* isomers, composite  $\pi$  structure analysis, taking additivity rule into consideration, predicts the relative order of nonbonded attraction to be  $T_{ss} > T_{se} > T_{ee}$ , which is exactly the relative order of one-electron effects



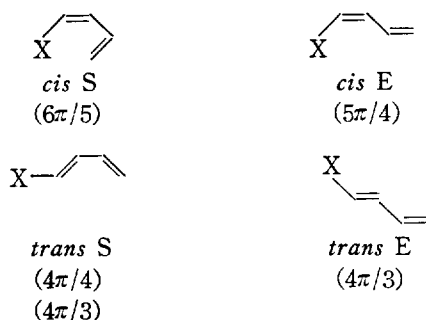
shown; here the rules of  $4N+2$  over  $4N+1$  system, and of additivity are seen to work well.

For *cis* isomers, composite  $\pi$  structure analysis is again consistent with the computed relative order of one-electron effects.

We can conclude from these analysis that one-electron effects in N-methylacetamide are mainly of nonbonded interactions, and that in the *cis* isomers end atoms are much closer than in the *trans* forms since the decreases in one-electron energies are appreciable compared with the *trans* forms.

**1-Substituted Propenes.** Four isomers of interest of 1-substituted propenes,  $XCH=CHCH_3$ , are presented below using isoconjugate models. In this compound the substituent X contributes two  $\pi$  electrons ( $\pi$  lone pairs) to a composite  $\pi$  structure; the systems identified are given below each model.

Composite  $\pi$  structure analysis clearly shows that the general preference for the *cis* over *trans* is the result of attractive nonbonded interactions in the *cis* in contrast to repulsive interactions in the *trans*; experimentally<sup>15</sup> the *cis* was found to be favored over the *trans* for X=F, Cl, Br, OMe, OEt, and OPh.



The expected order of nonbonded attraction according to the composite  $\pi$  structures is *cis* S > *cis* E > *trans* E > *trans* S, which agrees with the CNDO/2 results of Epiotis *et al*<sup>15</sup>; although the *cis* S has greater attractive nonbonded interactions, unfavorable steric factors make it less stable than the *cis* E.

## CONCLUSION

In this paper we attempted to show that effects of nonbonded interactions are additive, and based on this additivity we should be able to predict the relative order of nonbonded attractions by analyzing composite  $\pi$  structures. The analysis presented in this paper is only a qualitative one, but with due considerations on the major determining factors of nonbonded interactions a semi-quantitative type can be formulated; *e.g.*, we can assign certain numbers according to the number of electrons within a  $\pi$  structure recognizing also the importance of effect of distance between the two end atoms of a crowded form. This will be attempted in a forthcoming paper.

## ACKNOWLEDGMENT

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6. In the compounds of the type  $\text{CH}_3\text{COX}$ , where X=H, OH,  $\text{CH}_3$ ,  $\text{NH}_2$  and  $\text{NHCH}_3$  (*trans*), the methyl group has (S) form,<sup>4,5</sup> and the CNDO/2 calculations have shown that the barrier to methyl rotation,  $\Delta E$  for (S)  $\rightarrow$  (E), was a constant value of 0.6 kcal/mol. This value agrees well with the experimental barrier to methyl rotation of 0.5 kcal/mol for acetic acid found by W. J. Tabor, *J. Chem. Phys.*, **27**, 974 (1957).
7. The angle  $\angle\text{OCX}$  is larger and angle  $\angle\text{XCY}$  is smaller than  $120^\circ$ . It should be noted that the angle  $\angle\text{HCH}$  in the unsubstituted formaldehyde, *i.e.*, X=Y=H, is larger than  $120^\circ$ ,<sup>8</sup> which is required by  $\text{sp}^2$  hybrids of carbon atom.
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