  Bull. Chem. Soc. Jpn., 61, 659—666 (1988)

Roles of Kinetic and Potential Energies in Conjugation. I. A Study of Prototypes

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(Received August 3, 1987)

The analysis of the potential and kinetic energy changes between conjugative and nonconjugative structure in vinylamine and nitroethene led to the conclusion that there were two different types of conjugations: the conjugative stability caused by a decrease in the kinetic energy and that given by a decrease in the potential energy. Those two types could be termed conjugations of *kinetic energy origin* and *potential energy origin* respectively. The cojugative stability in vinylamine is produced by an excess decrease in the kinetic energy over the increase in the potential energy (*kinetic energy origin*), which was attributed to a release of the kinetic energy pressure of the lone pair of electrons on nitrogen. On the other hand, the conjugation of nitroethene causes an overwhelming decrease in the potential energy, especially in that belonging to the nitro group (*potential energy origin*).

Conjugation between a substituent and the π system (e.g., the phenyl group) produces a stabilization energy which is referred to as 'conjugation energy.' Conjugation also affects the electron density in a π system to determine the resultant appearance. According to the electronic effect, functional groups have been classified by organic chemists into two groups, i.e., the electron-donating and electron-withdrawing groups. Such an effect of a substituent on the π system is symbolized by using 'arrows' in organic electron theory. This arrow expression has been so widely used that it has come to be one of the basic concepts in organic chemistry. However, one cannot extract any physical meaning from such arrows.

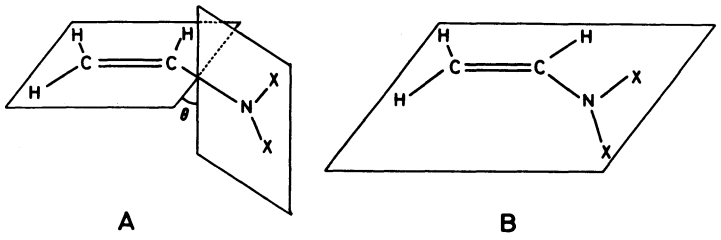
A large number of MO theoretical calculations have been carried out on substituted benzenes,[1] and the conjugation between a substituent and the phenyl group seems to be thoroughly understood. Indeed, an MO calculation reveals the electron density in the system, and the conjugation is usually interpreted in terms of the interaction between the π system and its substituent.[2] However, fundamental questions remain as to why they must interact, why such a conjugation stability is produced, and why a lone pair of electrons delocalizes into the π system. There may be various theoretical approaches. However, as far as organic chemistry is concerned, a theoretical study must contribute to the establishment of a bridge between the basic concepts of organic chemistry and those of physics.

The total energy of any molecular system consists of two fundamental components, the kinetic and potential energies, which are defined according to distinctly different concepts of energy in nature. The interpretation of chemical phenomena through such energy terms is most fundamental and decisive. Recently, we ourselves have shown that the kinetic energy of π electrons plays the decisive role in the stability or instability of an aromatic or antiaromatic system.[3] The physical meaning of aromaticity has been given as the relaxation of the kinetic-energy pressure of π electrons in isolated double-bonds.[4] The kinetic-energy pressure is a different expression of the most fundamental phenomenon and/or concept in modern physics,[5] i.e., Heisenberg's uncertainty principle.[6] Therefore, aromaticity/antiaromaticity, which is also one of the most fundamental concepts in organic chemistry, has been interpreted in terms of the basic principles of nature.

If wave functions are to provide an understanding of the behavior of electrons in a molecule, we must try somehow to extract information on the physically essential features of electronic energies. One of the methods along this line is energy partitioning. The Hamiltonian of a molecular system is composed of operators related to the kinetic energy, the potential energy for an electron in the field of a nuclear charge, and the repulsion energy between electrons. Thus, the electronic energy (E^{el}) is composed of the kinetic energy of electrons (E^T) and the electronic potential energies. The latter is further partitioned into the attractive one-electron potential (E^{V}) and the repulsive two-electron potential energies (E^J).[7] Our strategy in solving the present problems is to identify the roles of these partitioned energies in conjugation.

This paper will discuss the cases of vinylamine and nitroethene as prototypes of conjugation between a π system and an electron-donating or an electron-withdrawing substituent. These systems are appropriate for the present study in that the conjugation between the substituent and the ethenyl group can be terminated by making the conformation of the substituent orthogonal to the plane of the ethenyl group. As a sophisticated MO method, we used the 6-311 G** method[8] throughout this work.

It has been indicated that the components of the total energy are very sensitive to the scale factor of the wave function.[9] Since the scale factor applies to the electronic coordinates as well as the nuclear coordinates, the condition or threshold of geometry optimization is considered to affect seriously the



Scheme 1.

components of the total energy. Therefore, the threshold of geometry optimization was set at 0.00003 (maximum) as well as 0.00002 (rms) Hartree/Bohr or radian, which is one tenth of the standard geometry optimization.[10]

Driving Force Which Leads to Conjugation. Vinylamine and nitroethene have near-planar geometries.[11,12] Such a planarity may be maintained by conjugation. If there were no conjugation, the orthogonal structure might be considered to be the most stable geometry because it has the least interatomic repulsions (steric effect), just as ethane favors the staggered conformation. Therefore, we may expect that there are some driving forces that lead to conjugation.

Let us consider how conjugation takes place starting from an orthogonal structure. We suppose that the system follows the minimum-energy path. The orthogonal structure (θ=90° in Scheme 1) and the planar structure (θ=0°) have the maximum-energy and minimum-energy cols; therefore, the torsional forces, $\partial E/\partial\theta$, are zero. Except for these cols, the differential has a positive value. Take any geometry with $0<\theta<90°$, where a certain torsional force is imposed on the C–N bond to lead θ to $\theta-\Delta\theta$. Change in θ is followed by change in all geometrical parameters such as, $R_j \rightarrow R_j+\Delta R_j$ and $\phi_k \rightarrow \phi_k+\Delta\phi_k$, where R_j and ϕ_k are the bond lengths and the bond angles. The cause of the torsion that is put on the C–N bond may be interpreted as the cause of the conjugation.

The total energy is composed of the potential energy (V) and the kinetic energy of electrons (T):

$$E = T + V \tag{1}$$

$$T = E^T \tag{2}$$

$$V = E^V + E^J + E^N \tag{3}$$

where E^N is the nuclear repusion energy.

The differentiation of E with respect to θ gives:

$$\partial E/\partial\theta = \partial T/\partial\theta + \partial V/\partial\theta \tag{4}$$

where $\partial T/\partial\theta$ and $\partial V/\partial\theta$ are the forces due to the kinetic and potential energies, respectively. The

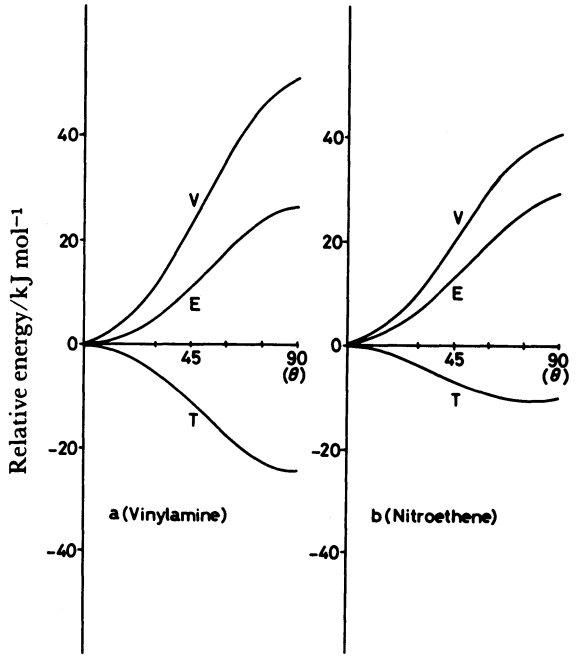


Fig. 1. Plots of the total (E), kinetic (T), and potential (V) energies (kJ mol^{-1}) vs. θ as the conformation changes from A to B through the minimum energy path in vinylamine (a) and nitroethene (b).

positive and negative values represent the increase and the decrease in the corresponding energies as θ increases. At θ=0 or 90°, $\partial E/\partial\theta$ is zero, with $|\partial T/\partial\theta| = |\partial V/\partial\theta|$. When $0°<\theta<90°$, these forces are not balanced. Before an analysis of these forces, let us look at the energy changes in the minimum energy path.

Figure 1 shows the changes in the total, kinetic, and potential energies as functions of θ, where all the geometrical parameters except θ were optimized with respect to the total energy. It is important to note here that these curves are not pure functions of θ, since geometry optimization is carried out at every θ.

Both total energies increase as θ increases. The difference in total energy between 0 and 90° may correspond to the conjugation energy. It is calculated as 26 and 30 kJ mol^{-1} respectively for vinylamine and nitroethene.[13] Nelander has shown that, if all bond lengths are optimized with respect to the total energy,

the virial theorem ($T=-V/2$) should hold, where angular coordinates have no contribution to the virial ratio.[14,15] The energy profiles of the components in Fig. 1 satisfy this requirement reasonably in vinylamine, but qualitatively in nitroethene. These results imply that the potential energy is always responsible for leading to conjugation, since the sign of the gradient of the potential energy is the same as that of the total energy. This is not true, however, since, as has been mentioned, geometry optimization does not take place at the same time as the change in θ, but *as a result of the change in* θ.

We estimated $\partial E/\partial\theta$, $\partial T/\partial\theta$, and $\partial V/\partial\theta$ by means of the divided differences, $\Delta E/\Delta\theta$, $\Delta T/\Delta\theta$, and $\Delta V/\Delta\theta$, which were obtained as follows. First, the energies were calculated at a θ value with full geometry optimization (except only for θ) to give $E(\theta)$, $T(\theta)$, and $V(\theta)$. Then, θ was increased by $\Delta\theta$ and, *without optimization*, those energies are obtained as $E(\theta+\Delta\theta)$, $T(\theta+\Delta\theta)$, and $V(\theta+\Delta\theta)$. The divided differences were $(E(\theta+\Delta\theta)-E(\theta))/\Delta\theta$, etc. We fixed $\Delta\theta$ at 1°.

The gradients of the curves in Fig. 1 correspond to the divided differences when the geometries at both θ and $\theta+\Delta\theta$ are optimized. In fact, the values at $\theta=45°$, for example in vinylamine, were calculated to be 0.51, −0.73, and 1.24 kJ mol^{-1} deg^{-1} for the total, kinetic, and potential energies respectively; these values correspond to the gradients at 45° in Fig. 1-a.

Table 1 shows the divided differences at $\theta=30$, 45, and 60°. In both vinylamine and nitroethene, $\Delta E/\Delta\theta$ is positive, showing that the systems resist the rotation of the substituent planes; i.e., both systems resist breaking conjugation. The divided differences of the energy components of vinylamine appear to be prominently different from those of nitroethene.

In vinylamine, $\Delta T/\Delta\theta$ is positive, while $\Delta V/\Delta\theta$ is negative, with the former being larger than the latter in quantity. This confirms that the force due to the kinetic energy resists breaking conjugation. The divided difference, $\Delta X/\Delta(-\theta)$ (where $X=E$, T, or V), means the force when the orthogonal conformation becomes the conjugative planar structure. Therefore, it may be deduced that the driving force that leads to conjugation in vinylamine is that by the kinetic energy of electrons.

Nitroethene gave the opposite results: $\Delta V/\Delta\theta$ is positive, while $\Delta T/\Delta\theta$ is negavive. This time, the force due to the potential energy is against the rotation of the functional group, while that due to the kinetic energy helps such a rotation. Since the former exceeds the latter, the planarity is maintained; therefore, it may be concluded that the potential energy is the cause of conjugation in nitroethene.

What Happens to Energy Components by Conjugation. This section will discuss the effect of conjugation on the energy components of the total energy. As has already been stated, if there were no conjugation, the orthogonal structure would be the most stable conformation in both vinylamine and nitroethene. Table 2 shows the geometrical parameters of the optimized orthogonal and planar structures. Considerable differences as to the C–C and C–N bonds can be seen between them. Such geometrical changes are considered to be brought forth by the introduction of conjugation.

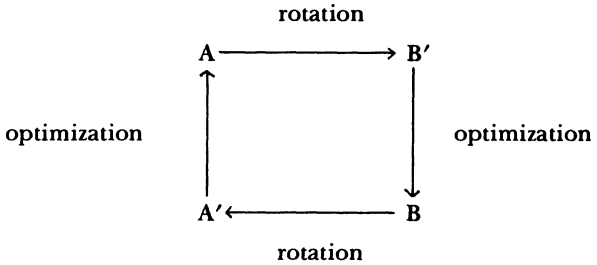
Here let us make the point of the problem clear: it is conjugation that changes the molecular geometries; i.e., a change of geometry occurs following a presentation of conjugation. Thus, we regarded the orthogonal structure (A in Scheme 2) as the reactant structure for conjugation. With a retention of the bond lengths and the bond angles, the substituent was rotated to a planar structure (the intermediate structure: B′), and all the bond lengths and bond angles were optimized with respect to the total energy (the product structure: B). We investigated the energy changes between A, B′, and B: the energy change between A and B′ includes the effect of conjugation, while that between B′and B corresponds to the effect of the geometrical change after conjugation.

There is another way of considering this question. The optimized structure in conjugation (B) may appear to be near-planar. The rotation of the amino or nitro group in B involves an energy barrier which

Table 1. Divided Differences of Total, Kinetic, and Potential Energies with Respect to the Twist Angle θ[a]

	$\Delta E/\Delta\theta$[b]	$\Delta T/\Delta\theta$[b]	$\Delta V/\Delta\theta$[b]
Vinylamine			
30°	0.37	3.59	−3.21
45°	0.51	3.63	−3.12
60°	0.47	3.49	−3.02
Nitroethene			
30°	1.98	−5.78	7.76
45°	2.20	−5.37	7.57
60°	1.81	−3.63	5.45

a) $\Delta\theta$ is set at 1°. b) In kJ mol^{-1} deg^{-1}.

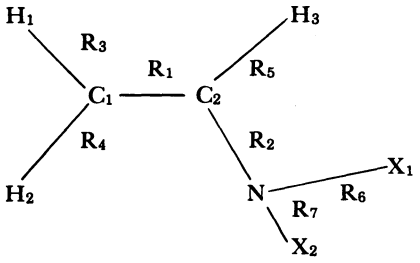


A: geometry-optimized orthogonal structure

B: geometry-optimized planar structure

Scheme 2.

Table 2. Optimized Geometries of A and B Conformations



	Vinylamine (X=H)		Nitroethene (X=O)	
	A	B	A	B
Bond length[a]				
R_1	1.3167	1.3218	1.3057	1.3102
R_2	1.4323	1.3906	1.4665	1.4589
R_3	1.0757	1.0734	1.0740	1.0740
R_4	1.0778	1.0773	1.0748	1.0729
R_5	1.0781	1.0776	1.0720	1.0696
R_6	0.9998	0.9963	1.1843	1.1864
R_7		0.9954		1.1862
Bond angle[b]				
$<C_1C_2N$	125.96	126.76	120.99	120.88
$<H_1C_1C_2$	120.82	120.34	119.98	119.71
$<H_2C_1C_2$	121.89	122.06	121.98	121.32
$<H_3C_2C_1$	119.73	119.75	126.87	127.23
$<X_1NC_2$	111.02	114.56	116.96	118.86
$<X_2NC_2$		114.31		115.56
Twist angle[c]				
$<X_1NC_2C_1$	66.1	16.2	−89.1	0.0
$<X_2NC_2C_1$	−66.1	146.7	89.1	180.0

a) In terms of A. b) In terms of degree. c) Counterclockwise twist angle around the C–N bond to the molecular plane in terms of deg.

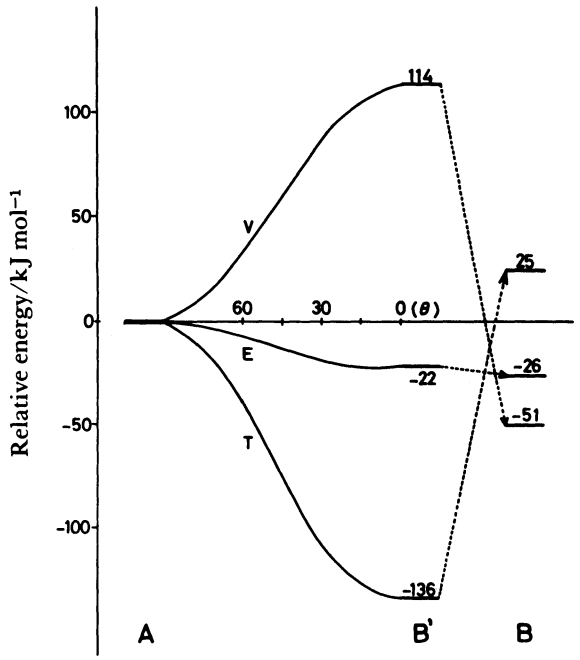


Fig. 2. Plots of the total (E), kinetic (T), and potential (V) energies (kJ mol^{-1}) vs. θ as the conformation changes from A to B′ in vinylamine.

may be caused by a broken conjugation. We also examined the energy change when the substituent at B was rotated to an orthogonal structure (A′), with bond lengths and bond angles being kept at those of B.

Vinylamine. Figure 2 shows the change in the total, kinetic, and potential energies of vinylamine as functions of θ. All the bond lengths and bond angles except for θ were kept the same as those in A. The geometries at θ=90 and 0° are equal to A and B′ respectively. As θ decreases, the total energy decreases by ca. 20 kJ mol^{-1} (at B′). Such a stabilization is produced by conjugation and is a driving energy toward a planar conjugative structure. It is important to note that the potential energy increases, while the kinetic energy decreases, as the geometry is varied from the orthogonal to the planar forms, and that the change in the kinetic energy is larger than that in the potential energy. This simply means that the decrease in kinetic energy is the original conjugation stability.

If all the bond lengths are optimized with respect to the total energy, the virial theorem ($T=-V/2$) should hold where angular coordinates make no contribution.[14-16] Therefore, the energy change between A and B may be supposed to satisfy this relationship:

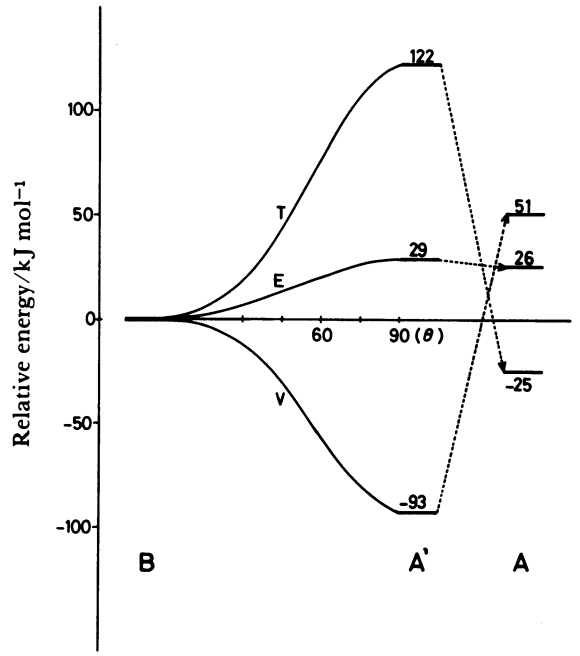


Fig. 3. Plots of the total (E) kinetic (T), and potebtial (V) energies (kJ mol^{-1}) vs. θ as the conformation changes from B to A′ in vinylamine.

$\Delta T=-\Delta V/2$. A comparison between B′ and B shows that the optimization of all geometrical parameters does not produce a large change in the total energy, but does in the potential and kinetic energies. The virial relationship can be seen with a reasonable accuracy.

Figure 3 shows the case when the conjugation between the ethenyl and amino groups is forced to terminate, i.e., the plots of the energy change vs. θ when θ is varied from 0° (B) to 90° (A′) with all the geometrical parameters at B except for θ. The total and kinetic energies increase monotonously as θ increases. At A′, the difference in total energy is around 29 kJ mol^{-1}, and we see that the kinetic energy is the main source of the increase in the total energy. Again, the optimization of all bond lengths and bond angles causes a large change in the potential and kinetic energies to meet the virial theorem, although the lowering of the total energy is less than 5 kJ mol^{-1}. From the results thus obtained, we may conclude that the kinetic energy is the factor in leading to conjugation in vinylamine.

Nitroethene. The nitro group is a representative substituent that withdraws the π electrons of the conjugated π system. Figure 4 shows the changes in the total, potential, and kinetic energies of nitroethene as functions of θ. Again, all the geometrical parameters but θ are kept the same as those in A. Although geometry optimization on B′ does not lower the total energy more than 2 kJ mol^{-1}, its components encounter a considerable change (more than 24 kJ mol^{-1}), much as in the case of vinylamine.

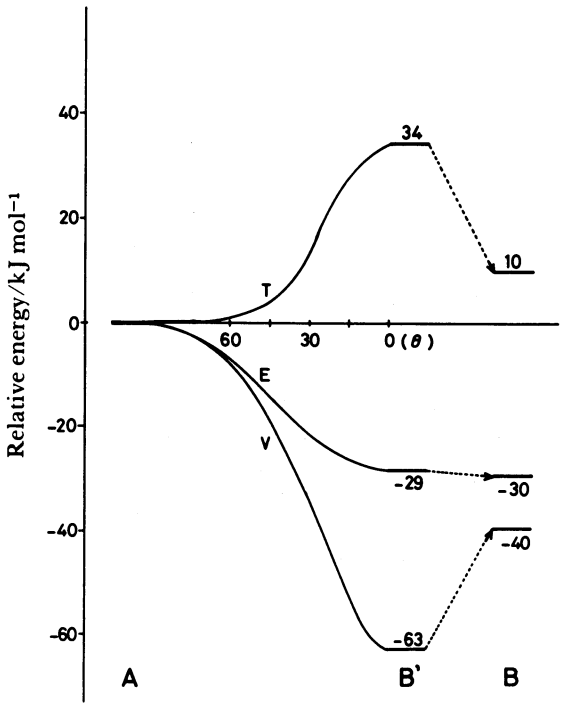


Fig. 4. Plots of the total (E), kinetic (T), and potential (V) energies (kJ mol^{-1}) vs. θ as the conformation changes from A to B′ in nitroethene.

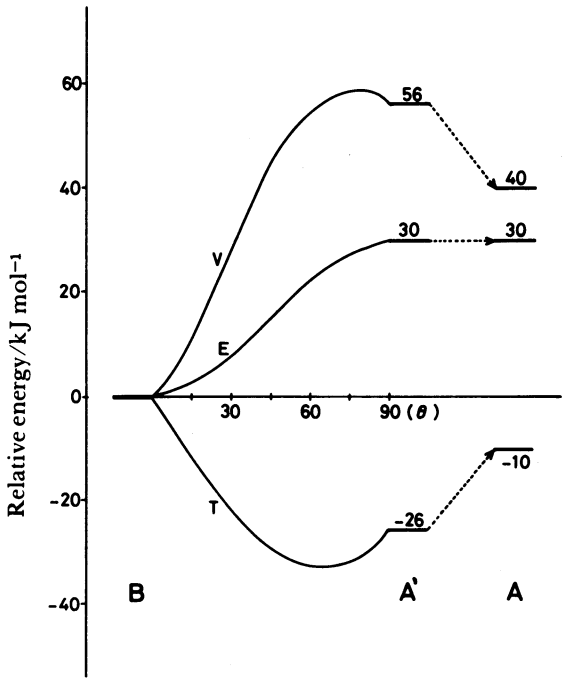


Fig. 5. Plots of the total (E), kinetic (T), and potential (V) energies (kJ mol^{-1}) vs. θ as the conformation changes from B to A′ in nitroethene.

The energy profile in Fig. 4 also seems similar to that in Fig. 2. However, the contents are the exact opposite of those of vinylamine in that as θ decreases, the kinetic energy increases, while the potential

energy decreases, and in that the amount of the decrease is larger than that of the increase. Therefore, it may be said that the conjugation stability is given by a decrease in the potential energy.

The energy profile in Fig. 5 is different from that in Fig. 3: the total and potential energies increase, while the kinetic energy decreases, as θ increases, leading to the conclusion that, contrary to the case of vinylamine, here the increase in the potential energy is the cause of the resistance against the rotation of NO_2. The conclusion in nitroethene is that the potential energy is the factor which leads to conjugation.

Concerning the Virial Theorem. We observed drastic changes in the partitioned energies between Structures A′ and A or between Structures B′ and B. Here we will give the reason.

The large change in the partitioned energies may be explained in terms of the scaling error. The virial relationship (i.e., $V=-2T$) may be supposed to hold at an equilibrium geometry. The scaling factor of the wave function for this geometry is unity. At a non-equilibrium geometry, however, the scaling factor must be adjusted in order to satisfy the virial relationship.[17]

If the molecular geometry is expressed by a set of internuclear distances R_j and angular coordinates ϕ_k, the virial theorem for a polyatomic molecule may be written as:[14,16]

$$2T+V+\sum R_j(\partial E/\partial R_j)=0 \tag{5}$$

Suppose that the total energy, geometry, and wave function at a non-equilibrium geometry are expressed by E, $G(R_j,\phi_k)$, and $\psi(\mu_i;R_j,\phi_k)$, where μ_i are the electronic coordinates. Here, we introduce a scaling factor η:

$G(R_j,\phi_k)$	$G(\eta R_j,\phi_k)$
$\psi(\mu_i;R_j,\phi_k)$	$\eta^{(3N/2)}\psi(\eta\mu_i;\eta R_j,\phi_k)$
E	E'
Unscaled system	Scaled system

where N is the number of electrons and E' is the total energy of the scaled wave function.

We can now obtain the normal virial relationship between the scaled potential and kinetic energies, i.e., $V'=-2T'$. Thus, each geometry has its own scaling factor that satisfies the virial relationship. If we consider the scaled wave function, a geometrical change from the one to the other gives rise to a scaling error for the wave function.

Pedersen and Morokuma[9] considered the effect of the scaling of the wave function on the total energy and its components. Introducing a scaling error $\gamma(=\eta-1)$ and expanding the differences between the scaled and unscaled energies in a power series or γ, they obtained these differences in energy:

$$\begin{aligned}\Delta E &= E(\gamma^2+\cdots\cdots)\\ \Delta T &= E(-2\gamma+3\gamma^2+\cdots)\\ \Delta V &= E(2\gamma-2\gamma^2+\cdots)\end{aligned} \tag{6}$$

These expressions clearly show that the kinetic and potential energies change in the first order of γ, while the total energy changes only in the second order. The present problem is a case of just this, since the geometries at A′ and B′ are non-equilibrium.

Here we must make another possibly confusing point clear. E' is always lower than E.[18] A question is, then: "Should we consider the scaled energies (T' and V') instead of the unscaled energies (T and V) at A′ and B′?" The answer is "No!" for the geometry for the scaled wave function is no longer the same as that for the unscaled wave function (namely, the R_j values are multiplied by η in G for the scaled wave function). What we need is the unscaled energy at A′ or B′ where the third term of Eq. 5 is surely far from null.

What Happens to the Substituent upon Conjugation. So far, we have discussed the changes in the partitioned energies in the whole system. In order to see the details of conjugation, this section will now deal with the changes in those energies for atoms in ethenyl and amino or nitro groups as the θ value changes.

Since, in the LCAO MO theory, each MO is expanded by a linear combination of atomic orbitals (AO's), and since, via the Fock matrix, the three- and four-center terms are reduced to two-center terms, the Hartree–Fock equation is formally expressed by the sum of monocentric (E_A) and bicentric (E_{AB}) terms:

$$E=E_A+\sum_{A>B}E_{AB} \tag{7}$$

These terms can be further partitioned as:

$$E_A=E_A{}^T+E_A{}^V+E_A{}^J \tag{8}$$

$$E_{AB}=E_{AB}{}^T+E_{AB}{}^V+E_{AB}{}^J+E_{AB}{}^N \tag{9}$$

where $E_{AB}{}^N$ is the nuclear repulsion energy between atoms A and B; it is, of course, one of the potential energies in the given system. The details of the calculation method have been given elsewhere.[3,7]

Following the method presented in the definition of Mulliken population analysis,[19] the kinetic and potential energies concerning the electrons belonging to a specified atom, X, $T(X)$, and $V(X)$, are defined as;

$$T(X)=E_X{}^T+1/2\sum_{A\neq X}E_{XA}{}^T \tag{10}$$

$$V(X)=E_X{}^V+E_X{}^J+1/2\sum_{A\neq X}(E_{XA}{}^V+E_{XA}{}^J+E_{XA}{}^N) \tag{11}$$

The electronic effect of enamine may be expressed in organic chemistry as follows.[20]

$$\underset{\mathbf{1}}{C_1=C_2-\ddot{N}} \longleftrightarrow \underset{\mathbf{2}}{C_1^- - C_2=N^+}$$

Table 3. Electron Density, Kinetic Energy, and Potential Energy on an Atom in Orthogonal Conformation and Their Differences from the Planar Conformation(B′)

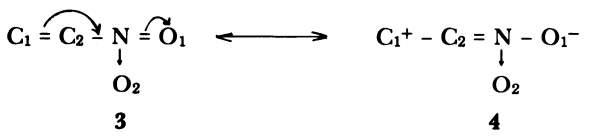
	Electron density		Kinetic energy		Potential energy	
	A	Difference[a]	A	Difference[b]	A	Difference[b]
Vinylamine						
C_1	6.2105	68.0	37.802446	97.2	−76.170861	−488.9
C_2	6.0045	−46.1	37.767568	−77.9	−75.488585	523.1
N	7.5127	−44.0	54.410705	−97.2	−110.686940	402.3
Nitroethene						
C_1	6.1460	−29.6	37.768174	70.9	−76.146852	169.0
C_2	5.9815	44.9	37.839717	4.8	−75.275044	−730.0
N	6.5987	43.7	54.303856	−73.8	−106.642428	964.4
O_1	8.3624	31.5	74.968693	43.8	−151.656224	−696.8
O_2	8.3624	5.9	74.968693	−5.4	−151.656224	33.2

a) $D(B')-D(A)$ in 10^{-3} electron units. b) $X(B')-X(A)$ in kJ mol^{-1}, where X is the kinetic or potential energy.

These expressions indicate that some of the lone-pair electrons on the nitrogen atom flow to the π system and are localized on the β carbon atom.

Table 3 shows the differences, between A and B′, of $T(X)$ and $V(X)$, as well as the total atomic charges of the carbon, nitrogen, and oxygen atoms. Agreeing with the cannonical structure **2**, the conformation change from A to B′, i.e., the introduction of conjugation in vinylamine, reduces the electron densities of N as well as of C_2 and enriches that of C_1.[21] Since the potential energy and kinetic energy of electrons on an atom are essentially proportional to its electron density,[22] a change in electron density involves proportional changes in the kinetic and potential energies, which are agreeingly reproduced, as may be seen in Table 3.

The substituent effect of the nitrogen group on a π system may be symbolized as follows:



3 **4**

which indicates that conjugation makes the electron density of the β carbon atoms low and only one of the oxygen atoms high. The results in Table 3 coincide well with the above symbols. That is, on a conjugative structure, the electron density at the β carbon atom is reduced, while that of O_1 is increased. An increase in the electron density at C_2 is observed. This may be interpreted as C_2 being at the allylic position to O_1 and O_2, which have three or two lone pairs of electrons respectively.

An electron migration takes place because such a migration produces a stabilization energy; the degree of migration is determined by the lowest total energy, which is given by including all the interactions in the system. However, the only structural difference between vinylamine and nitroethene is in the substituent. Therefore, the differences in conjugation thus far discussed should be totally attributed to the nature of the substituent. That is, the sources of conjugation in vinylamine and nitroethene are the kinetic energy of electrons and the potential energy, which are given by the electronic effects of the amino and nitro groups respectively.

Concluding Remarks. In an orthogonal conformation, the movement of mobile electrons in both the ethenyl and substituent groups is restricted by the orthogonalized overlap of the p AO's, while in a planar structure those electrons are allowed to move. This produces two situations: (1) The electrons on the substituent move to the π system or (2) the electrons in the π system are withdrawn by the substituent.

The kinetic energy of an electron reflects the degree of the restriction of electron movement. An orthogonal conformation of vinylamine restricts the movement of the lone pair of electrons within the nitrogen atom, resulting in a high kinetic energy of the electrons, equivocally a high kinetic-energy pressure of the electrons. A planar structure allows the electrons to move. Such a less-restricted movement generally causes a decrease in the kinetic energy, i.e., a relaxation of the kinetic-energy pressure. This concept may be extended to any electron-donating substituent.

In nitroethene, the allowed movement of π electrons causes a localization of the π electrons on one of the oxygen atoms; this is a result of the strong electrostatic potentials of the hetero atom, which produces an increase in the kinetic energy, but also an overwhelming decrease in the potential energy. In this way, the cause of conjugation can be of either *kinetic-energy origin or potential-energy origin.*

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